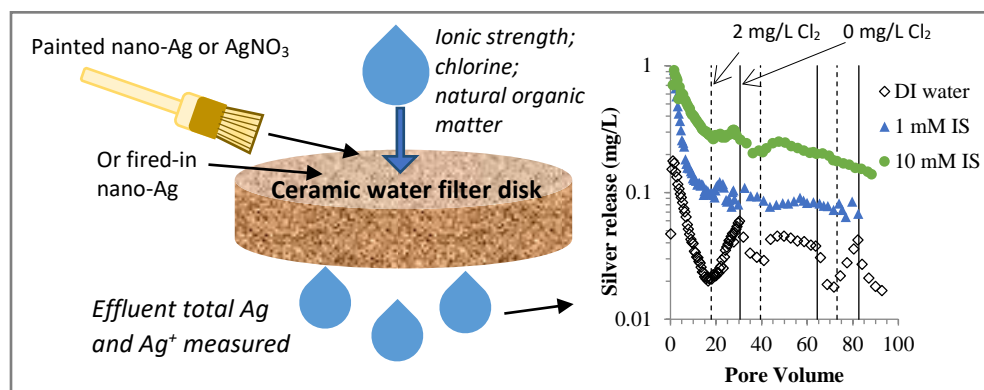


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1 **Impact of Chlorination on Silver Elution from Ceramic Water Filters**

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28 **Abstract**

29 Applying silver nanoparticles (nAg) or silver nitrate (AgNO_3) to ceramic water filters
30 improves microbiological efficacy, reduces biofilm formation, and protects stored water from
31 recontamination. A challenge in ceramic filter production is adding sufficient silver to achieve
32 these goals without exceeding the maximum recommended silver concentration in drinking
33 water. Silver release is affected by silver type, application method, and influent water chemistry.
34 Despite a lack of data, there is an assumption that chlorinated water should not be used as
35 influent water because it may increase silver elution. Thus, the objective of this work was to
36 systematically evaluate the impact of chlorinated water (0-4 mg/L free chlorine residual, FCR)
37 on silver release from ceramic filter disks painted with casein-coated nAg, painted with AgNO_3 ,
38 or containing fired-in nAg over a range of ionic strength ($\text{IS} = 0\text{-}10\text{ mM}$ as NaNO_3) in the
39 presence or absence of natural organic matter (NOM). Influent deionized water containing
40 chlorine increased silver release 2 to 5-fold compared to controls. However, this effect of
41 chlorine was mitigated at higher IS ($\geq 1\text{ mM}$) or in the presence of NOM (3 mg C/L). For filter
42 disks painted with nAg or AgNO_3 , silver release increased with increasing IS (with or without
43 chlorine), and effluent concentrations remained above the World Health Organization (WHO)
44 guideline of 0.1 mg/L even after 30 hr (80 pore volumes, PVs) of flow with a background
45 solution of 10 mM NaNO_3 . Silver speciation (nAg vs. Ag^+) was monitored in effluent samples
46 from painted or fired-in nAg filter disks. Results indicated that in general, greater than 90% of
47 the eluted silver was due to Ag^+ dissolution rather than nAg release. Additionally, a filter disk
48 prepared with fired-in nAg exhibited a lower % released in the nanoparticle form (nAg = 5% of
49 total Ag in effluent) compared to painted on nAg (nAg = 14% of total Ag in effluent). The
50 findings of this study suggest that chlorinated influent water has minimal impact on silver elution

51 from ceramic filters under simulated natural water conditions, and thus, the recommendation to
52 avoid the use of chlorinated water with ceramic filters is not necessary under most conditions.

53 **Keywords:** ceramic water filters, chlorine, household water treatment, silver nanoparticles,
54 silver nitrate, silver dissolution

ACCEPTED MANUSCRIPT

55 1. Introduction

56 Ceramic water filters (CWFs) are household water treatment and safe storage devices
57 manufactured in more than 50 factories worldwide. They are designed to improve the quality of
58 drinking water and reduce the burden of diarrheal disease (Brown et al. 2008, CMWG 2011).
59 CWFs are produced by pressing a mixture of clay and an organic (burnout) material into the
60 filter shape (i.e., ceramic pot) and firing to a ceramic state; silver nanoparticles (nAg) or silver
61 nitrate (AgNO_3) are added to the fired filter via brushing or dipping, or before firing by direct
62 addition to the filter mixture (CMWG 2011). CWFs remove pathogens via pore size exclusion
63 and physio-chemical adsorption, and the bactericidal action of silver improves bacteriological
64 efficacy (Bielefeldt et al. 2009, Oyanedel-Craver and Smith 2008, Rayner et al. 2013b). Silver
65 also reduces biofilm formation and protects filtered water from recontamination. It is currently
66 recommended that factories use nAg rather than AgNO_3 due to concerns over the shorter lifetime
67 of AgNO_3 in the filters; however nAg is more expensive and typically needs to be imported
68 (CMWG 2011, Rayner et al. 2013a). The current recommendation is to apply silver by painting
69 on an nAg suspension; there is no existing recommendation to fire-in nAg due to a lack of
70 research (CMWG 2011, Rayner et al. 2013a). The application of silver by dipping is currently
71 not recommended, because it is difficult to control the amount of silver applied and the actual
72 amount of silver absorbed is unknown (CMWG 2011).

73 A challenge in ceramic filter production is adding sufficient silver to increase efficacy,
74 prevent biofilm growth and protect stored water without adding so much silver that the
75 maximum recommended silver concentration in effluent drinking water is exceeded. The World
76 Health Organization (WHO) guideline value and United States Environmental Protection
77 Agency (US EPA) secondary maximum contaminant level for silver in drinking water is 0.1
78 mg/L (USEPA 2003, WHO 2011). In addition to potential health impacts from silver itself, its

79 release results in silver depletion from the ceramic matrix, thus reducing beneficial effects with
80 time.

81 Water characteristics within a particular region can vary widely over time, particularly in
82 areas with intermittent water treatment and distribution systems, unimproved water sources, and
83 in drought-prone regions (Bielefeldt et al. 2013, Brown and Sobsey 2010, WHO 2011). Previous
84 research has found that influent water chemistry, including pH, ionic strength (IS), organic
85 matter content, and cation species, influences silver release (Mittelman et al. 2015, Rayner et al.
86 2013b, Ren and Smith 2013). For example, Mittelman et al. (2015) observed increased silver
87 elution with increasing IS (1-50 mM NaNO_3), decreasing pH (from pH values of 9-5), and
88 presence of divalent cations (Ca^{2+} and Mg^{2+}) using ceramic filter disks painted with casein-
89 coated nAg or AgNO_3 . In that study, greater than 90% of eluted silver was in the ionic form
90 (Ag^+) rather than the nanoparticle (nAg), and the highest amount of nAg release occurred within
91 the first 5 h (15 pore volumes, PVs) of flushing, and represented less than 1% of the total silver
92 mass released. Current recommendations suggest discarding the first three batches of filtered
93 water (approximately 30 L or 25 PVs for a 10 L capacity filter pot) from CWFs, due in part to
94 this higher initial silver release (CMWG 2011). The laboratory study by Mittelman et al. showed
95 that effluent silver levels did not drop below the WHO/US EPA recommended level of 0.1 mg/L
96 until being flushed with 30-42 PVs of 10 mM NaNO_3 at pH 7 (Mittelman et al. 2015). When the
97 pH was decreased from 7 to 5, in the presence of divalent (Ca^{2+} , Mg^{2+}) cations, or when IS was
98 increased from 10 mM to 50 mM NaNO_3 , effluent silver levels increased to 5-10 times the
99 WHO/US EPA guideline (0.1 mg/L) within 10-20 PVs of flushing.

100 Currently, the recommendation is to not use or clean CWFs with chlorinated water, as it
101 is generally assumed that chlorine will strip silver from the filter (CMWG 2011). This poses

102 concern for recommending CWF use in urban and peri-urban areas that may have intermittent
103 chlorination and microbiologically contaminated drinking water (Kumpel and Nelson 2013,
104 2016) or in areas where household water treatment with chlorine is widely promoted. The
105 recommended free chlorine residual (FCR) concentration in drinking water varies based on
106 distribution system type and place of treatment (WHO 2011) because water quality
107 characteristics can impact chlorination efficacy, which is increased at lower pH and decreased in
108 the presence of natural organic matter (NOM), which exerts chlorine demand (Benjamin and
109 Lawler 2013, WHO 2011). In centrally treated infrastructure (piped) water systems, the WHO
110 recommends an FCR of 0.2-0.5 mg/L at the endpoints (water taps) and stipulates a health-based
111 limit of 5.0 mg/L (WHO 2011). In some systems, water may be intermittently chlorinated, under-
112 or over-treated, or have leaks within or unregulated withdrawals from the system. All of these
113 factors may impact FCR concentrations (Kumpel and Nelson 2013, 2016). For water chlorination
114 at the household level, a chlorine dose of 2.0 mg/L is recommended for clear water (<10
115 nephelometric turbidity units, NTU) to maintain an FCR of 0.2 mg/L, while twice that dose (4.0
116 mg/L as Cl₂) is recommended for turbid waters, >10 NTU (WHO 2011). Thus, CWFs may be
117 used with water containing between 0-5 mg/L FCR, and the chlorine concentration may not be
118 known at any given time.

119 Research on the impact of chlorination on silver elution from CWFs is limited. Bielefeldt
120 et al. (2013) evaluated the impact of chlorine (8.8 mg/L or 525 mg/L; pH 4.5-9.5) on total silver
121 release from nAg-applied ceramic surfaces using a quartz crystal microbalance (QCM), a
122 technique that can be used to rapidly assess small molecule and particle deposition behavior for a
123 range of chemical and flow conditions. The authors used silica-coated quartz sensors because the
124 crystalline SiO₂ material was the closest commercially available QCM sensor material to

125 represent the alumino-silicate surfaces in CWFs (Bielefeldt et al. 2013). Among the parameters
126 evaluated by Bielefeldt and colleagues (pH, IS, chlorine, turbidity, and NOM), chlorine was
127 found to have the greatest impact on silver release; an average of 83% and 86% silver removal
128 after the addition of 8.8 mg/L and 525 mg/L free chlorine, respectively, after less than 3 hours of
129 flow, which was attributed to oxidation reactions and enhanced dissolution of Ag^+ ions
130 (Bielefeldt et al. 2013). This finding suggests that contact between silver-containing CWFs and
131 chlorine could result in decreased disinfection effectiveness over time from the loss of silver and
132 that chlorine solutions should not be used to clean silver-containing CWFs. However, this study
133 was limited by several factors: 1) the fluid dynamics of QCM sensors are not representative of
134 flow through a porous ceramic filter; 2) a ceramic filter could not be used as the surface material;
135 3) chlorine solutions were only prepared in deionized water; 4) effluent silver concentrations
136 were not measured, nor was the form of silver determined (i.e., nAg vs. Ag^+); and 5) the impact
137 of chlorine at recommended drinking water FCR concentrations (0-5 mg/L) was not evaluated.

138 Previous studies have demonstrated that increasing IS can increase silver elution from
139 nAg or AgNO_3 -painted filters (Mittelman et al. 2015). However, to the best of our knowledge,
140 the coupled effect of IS and chlorine on silver release from CWFs has not been investigated.
141 NOM, which is ubiquitous in natural water sources, can also affect the fate and transport of nAg.
142 Past work has demonstrated increased stability and mobility of nAg through porous media in the
143 presence of NOM (Delay et al. 2011, Fabrega et al. 2009, Yang et al. 2014, Zhang et al. 2012).
144 Another important factor in filter performance and effluent water quality is the form of released
145 silver (ionic vs. nanoparticle), because the antimicrobial activity of nAg is thought to result from
146 the dissolution of Ag^+ (Choi et al. 2008, Lok et al. 2007, Xiu et al. 2012).

147 The objectives of this study were to: 1) evaluate silver dissolution and release of silver
148 ions and nanoparticles from ceramic filter disks exposed to intermittently chlorinated water
149 containing 0-4 mg/L FCR; 2) determine the impact of IS (as NaNO_3) on silver dissolution and
150 release from disks; and 3) predict the lifetime of the silver as a function of chlorine and IS. Three
151 different silver application methods were tested: disks painted with nAg, disks painted with
152 AgNO_3 , and disks containing fired-in nAg.

153

154 **2. Materials and Methods**

155 *2.1. Materials*

156 Ceramic filter disks (~10 cm diameter, 1.5 cm thick), manufactured by Advanced
157 Ceramics Manufacturing (ACM, Tucson, AZ) following established protocols, were used for
158 one-dimensional transport experiments. Ceramic disks were used instead of full-sized filters to
159 allow for controlled transport studies and to simplify manufacturing and test methods. Briefly,
160 clay was imported from a Tanzanian factory and pine sawdust (burn-out material) was purchased
161 from Pallet Recyclers (Tucson, AZ). Sawdust was sieved between US no. 30 and no. 60 mesh
162 sieves (0.595 and 0.251 mm openings, respectively) prior to mixing with clay. The mass ratio of
163 sawdust to clay was ~4%, which provided an estimated flow rate equivalent to 2-3 L/h in a full-
164 sized filter. This estimated flow rate was calculated by scaling the surface area of the disks to the
165 surface area (region exposed to fluid) of the full-sized filter (see Supporting Information, SI Text
166 S1), using dimensions of a frustum-shaped full-sized filter (van Halem 2006) and resulting
167 falling-head flow rate tests performed by ACM on the newly manufactured filter disks. The
168 sawdust to clay ratio used in this study corresponds to the lower end of ratios used by factories,
169 who report adding 5-25% by weight to the filter mixture (CMWG 2011). The amount of burn-out

170 material selected for this research was based on several factors, including: clay characteristics,
171 mesh used to screen sawdust, firing temperature, and reported filter mixture recipe from the
172 factory that provided clays.

173 Disks were formed with a hydraulic press and then fired in a furnace. The temperature
174 was gradually increased to 900°C and held for 60 min before cooling. Characterization of the
175 filters (porosity, non-reactive tracer transport, cation exchange capacity) was previously reported
176 (Mittelman et al. 2015). To compare the impact of painting vs. firing-in nAg, an experiment was
177 carried out using one ceramic disk containing a proprietary amount of fired-in nAg. This disk
178 contained the same amount of silver used by some factories in Haiti, Tanzania, and the
179 Dominican Republic, and is similar to the higher end concentration (0.5 mg Ag/g filter)
180 evaluated by Ren and Smith (2013). However, it is important to note that a higher concentration
181 and different type of nAg was used for the fired-in method than for the painted nAg filters (0.03
182 mg Ag/g filter) in the present study. The reason for this difference was the desire to use factory
183 relevant conditions (same silver source and application amount used by the factories that fire-in
184 silver). These filters were prepared by gradually adding a suspension of Silver Nano Powder
185 Type S2-80 (Ames Goldsmith Corp., Glens Falls, NY) to the same type of dry clay and sawdust
186 material mixture used for the filters without nAg prior to firing. The S2-80 nanoparticles, coated
187 with a proprietary surfactant, have an average particle size of 80 nm, as determined by the
188 manufacturer using scanning electron microscopy. Other than the addition of nAg, these filters
189 were manufactured identically to the other disks used in this study.

190 Upon receipt from ACM, disks were reduced to 5 cm in diameter to fit existing holders
191 (Oyanedel-Craver and Smith 2008) using a hole saw and sterilized by heating at 550°C for 30
192 min. The weight of the resulting filters was 45 ± 0.2 g. Casein-coated silver nanoparticles (nAg)

193 were obtained from Argenol Laboratories (Zaragoza, Spain) in powder form (71-75% silver by
194 weight). These nanoparticles have a mean diameter of ~45 nm as determined by transmission
195 electron microscopy (Kallman et al. 2011). Silver nitrate, (AgNO_3 , 99.9+%, metals basis) was
196 obtained from AlfaAesar (Ward Hill, MA). Suwannee River natural organic matter (SRNOM)
197 reverse osmosis (RO) isolate was purchased from the International Humic Substances Society
198 (IHSS, St. Paul, MN). Sodium hypochlorite (~5.25%) for chlorine dosing solutions was obtained
199 from Val Tech Diagnostics, Inc. (Brackenridge, PA).

200

201 *2.2. Silver Dissolution and Release Experiments*

202 A 200 mg/L (as total Ag) silver solution or suspension was prepared using previously
203 described methods (Mittelman et al. 2015). Briefly, AgNO_3 or casein-coated nAg solid was
204 weighed, added to a known volume of DI water and adjusted to $\text{pH } 7.00 \pm 0.05$ using 0.1 M
205 NaOH or 0.1 M HNO_3 . A TeflonTM-coated paint brush (Shur-Line, Mooresville, NC) was used to
206 apply 3 mL to each of the top and bottom surfaces (6 mL total applied), resulting in the
207 recommended silver application of 0.03 mg Ag/g filter proposed by the Ceramic Manufacturing
208 Working Group (CMWG 2011). More recent work has suggested revising this recommendation
209 to 0.3 mg Ag/g for nAg application only, but not for AgNO_3 (Rayner et al. 2013b). The
210 experiments described herein used the current 0.03 mg Ag/g recommendation as a basis for
211 painted nAg and AgNO_3 application, as this is the amount used by the majority of factories.
212 After painting with AgNO_3 or nAg, disks were air-dried for 12 h, placed in modified
213 polycarbonate membrane holders (model 420400, Whatman, UK) (Oyanedel-Craver and Smith
214 2008), and sealed with silicone glue and neoprene O-rings (McMaster-Carr, Elmhurst, IL) at the
215 top and bottom of the disk to prevent the injected solutions from flowing around the disks.

216 A total of nine filter disk experiments were conducted with nine new filters to assess the
217 impact of transient chlorine concentrations, IS, and NOM on silver release and dissolution from
218 filter disks painted with AgNO_3 ($n = 2$) or casein-coated nAg ($n = 6$), or from a filter containing
219 fired-in nAg ($n = 1$), as shown in Table 1. IS was adjusted using 1 or 10 mM NaNO_3 . The Na^+
220 form was selected as a common monovalent cation and to avoid the effect of increased silver
221 release from the presence of divalent cations shown previously by Mittelman et al. (2015). Each
222 silver release experiment began with approximately 20 PVs of flushing (~7 hr, 240 mL) with the
223 corresponding background solution (DI water, 1 mM NaNO_3 , or 10 mM NaNO_3 at pH 7) using a
224 MasterFlex peristaltic pump (Cole Parmer, Vernon Hills, IL) at a flow rate of 0.6 mL/min,
225 followed by the introduction of solutions containing free chlorine (0.2, 2, or 4 mg/L as Cl_2 ,
226 depending on the experiment). Samples were exposed to three cycles of intermittent chlorination
227 (e.g., 0 mg/L as Cl_2 for 20 PVs followed by 2 mg/L as Cl_2 for 20 PVs, then 0, 2, 0, 2, and 0 mg/L
228 as Cl_2 for 10 PVs each). Filter effluent samples were collected in 15 or 50 mL polystyrene
229 centrifuge tubes (VWR International, Radnor, PA) every 10 min for the first 30 PVs (~6 mL or
230 0.5 PVs per sample) and then every 60 min for remainder of the experiment (~36 mL or 3 PVs
231 per sample) using a CF-2 SpectraChrom fraction collector (Spectrum Laboratories, Inc., Rancho
232 Dominguez, CA) and analyzed for total Ag and Ag^+ .

233 The chlorine concentration in the stock solution (Val Tech sodium hypochlorite, ~5.25%)
234 was measured using a digital titrator and Hach Method 8209. Free and total chlorine
235 concentrations in the influent solution and effluent samples were measured using a LaMotte
236 Colorimeter and DPD #1 and #3 Instrument-Grade Tablets (LaMotte Company, Chestertown,
237 MD) to monitor for potential degradation of chlorine and reactions between chlorine and the
238 ceramic material. The influent chlorine solutions were confirmed to contain only free chlorine

239 (i.e., no combined chlorine/chloramines) by analyzing for both free and total chlorine and
240 verifying that free chlorine concentration equaled total chlorine concentration. Chlorine
241 concentrations in the influent solution were stable for the duration of the experiment (e.g., for 2
242 mg/L influent solutions, average \pm standard deviation = 2.04 ± 0.05 mg/L Cl_2), except for the
243 dosing solution containing SRNOM, where a decrease in chlorine concentration over time was
244 expected due to reaction with NOM. In that case, the chlorine concentration was monitored
245 throughout the injection sequence and fresh solutions were prepared for each intermittent
246 chlorine dosing (SI Figure S1).

247

248 *2.4. Analytical Methods*

249 The hydrodynamic diameter and electrophoretic mobility of nAg suspensions were
250 measured with a Malvern ZetaSizer (Malvern, Worcestershire, UK) using dynamic light
251 scattering (DLS) and laser Doppler velocimetry, respectively. These measurements were carried
252 out in triplicate at 25°C using a measurement angle of 173° (backscatter). Electrophoretic
253 mobility measurements were converted into zeta potential values using the Smoluchowski
254 approximation (Smoluchowski 1917). Silver concentrations were determined by inductively
255 coupled plasma-optical emission spectroscopy, ICP-OES (7300 DV, PerkinElmer, Waltham,
256 MA). The detection limit for Ag by ICP-OES was determined to be $9 \mu\text{g/L}$, based on the method
257 of Hubaux and Vos (1970). In a subset of effluent samples, dissolved silver (Ag^+) was separated
258 from nAg by centrifugation at $2,500 \times g$ in ultrafiltration units (Amicon 3k, Millipore, Billerica,
259 MA). The filtrate was then analyzed by ICP-OES to determine the silver speciation (Ag^+ vs. total
260 Ag).

261 The solid-phase silver concentration in unused fired-in nAg disks was measured by
262 microwave-assisted acid digestion (Discover SP-D, CEM Corp., Matthews, NC) with
263 concentrated nitric acid (TraceMetal™ grade, Fisher Scientific, Waltham, MA), followed by
264 analysis for silver by ICP-OES. Three extractions were performed on each solid sample to ensure
265 that all retained silver was extracted (i.e., acid digest removed for analysis, sample rinsed 3×
266 with DI water, fresh nitric acid added, digestion repeated, process repeated until no silver
267 detected in acid digest). On average, the first extraction recovered $79\pm 1\%$ of the total extracted
268 silver, and the first and second extractions together recovered $94\pm 1\%$ of the total extracted silver.

269

270 *2.5. Longevity Analysis*

271 Time to silver depletion was estimated using a constant flow rate of 0.6 mL/min under
272 two general conditions: (1) a worst-case scenario based on the mass of silver remaining after the
273 initial flushing period of 20 PVs (7 hr) and the maximum silver effluent concentration from
274 chlorine addition; and, 2) a more realistic estimate based on the mass of silver remaining and
275 effluent concentration at 85 PVs (30 hr). The water volume to silver depletion in disks was
276 converted to full-sized filter volume (10 L capacity) by scaling the surface area exposed to flow
277 and equating pore volumes (i.e., ~12 mL in disk and ~1.2 L in pot). Water volume was converted
278 to years assuming use of 1 full filter/day. The longevity calculations are based on the methods
279 used by Mittelman et al. (2015) and additional details are provided in SI Text S1.

280

281 **3. Results & Discussion**

282 *3.1. Ceramic Filter and Nanoparticle Characterization*

283 The average pore volume (PVs \pm standard deviation) of ceramic filter disks used in this
284 study was 12.3 ± 0.6 mL. Additional characterization was carried out in previous work using a

285 batch of filters produced with the same materials by the same manufacturer under the same
286 conditions (Mittelman et al. 2015). Filter disk porosity was determined to be $41.9\pm 0.8\%$ using
287 mercury porosimetry, and the filter disks contained a range of pore sizes (approximately 35%
288 pore diameters <20 nm, 10% between 20 nm-1 μm , 45% between 1 μm -30 μm , and 10% >30
289 μm). The average (\pm standard deviation) hydrodynamic diameter of the casein-coated nAg in DI
290 water was 58 ± 7 nm as measured by DLS, and the average (\pm standard deviation) zeta potential
291 was -41.6 ± 3.5 mV. To evaluate the effect of chlorine on silver dissolution and release from
292 ceramic filters, experiments were performed with intermittent chlorination as a function of IS,
293 silver type and application method (painted nAg or AgNO_3 , and fired-in nAg), and in the
294 presence of NOM (Table 1).

295

296 *3.2. Impact of Ionic Strength on Silver Release in Painted-on nAg Disks*

297 An increase in IS from 0 to 10 mM NaNO_3 resulted in increased silver release for
298 ceramic disks painted with nAg (Figure 1). After the initial flush of 20 PVs (7 hr), the effluent
299 silver concentrations were 0.022, 0.096, and 0.27 mg/L for background solutions of DI water, 1
300 mM NaNO_3 , and 10 mM NaNO_3 , respectively. The highest silver release occurred within the
301 first 20 PVs (7 hr), accounting for 1.8-8.7% of the total applied Ag (SI Figure S2). The effluent
302 silver fell below the WHO/US EPA guideline value of 0.1 mg/L after 4.3 PVs (1.5 hr) of DI
303 water flushing (Figure 1a), and 14.6 PVs (5 hr) for 1 mM NaNO_3 (Figure 1b). With a
304 background of 10 mM NaNO_3 and intermittent chlorination exposure, the effluent silver
305 concentration remained above 0.1 mg/L at the completion of the experiment (total Ag = 0.15
306 mg/L at 84 PVs or 29 hr, Figure 1c). In a separate control experiment (10 mM NaNO_3 , no
307 chlorine), the effluent silver concentration fell below 0.1 mg/L after 78.4 PVs (27 h) of flushing

308 with 10 mM NaNO₃ (SI Figure S3). The effluent silver concentrations in the first 180 minutes of
309 flushing painted nAg disks with a 10 mM IS background ranged from 0.17-1.4 mg/L (Figures 1c
310 and S3), which were similar to the effluent levels observed by Ren and Smith (2013) for filter
311 disks painted with Argenol proteinate-coated nAg and exposed to the same flow rate, IS, and
312 time period (effluent concentrations ranged from ~0.2 to 2 mg/L).

313 In selected effluent samples obtained from ceramic disks painted with nAg or containing
314 fired-in nAg, both Ag⁺ and total Ag (nAg + Ag⁺) were measured to determine the silver
315 speciation (Ag⁺ concentrations shown as “+” symbol in Figures 1, 2, 4, and S3). On average, the
316 Ag⁺ comprised 90% of the total eluted Ag (SI Figure S4), suggesting that silver release was
317 predominantly due to dissolution of the silver ion, rather than release of nAg. The lowest release
318 of nAg (highest % Ag⁺) was observed in the fired-in nAg filter disk effluent (Exp. 9, average
319 %Ag⁺/total Ag= 95%), whereas, the highest release of nAg was observed during the first 40 PVs
320 of flushing an nAg-painted filter with a background solution consisting of DI water and 2 mg/L
321 Cl₂ intermittent chlorination (Exp. 1, 48-72% Ag⁺/total Ag). Other than Exp. 1, elution of Ag⁺
322 versus nAg varied throughout each experiment, with no clear relationship between flushing time,
323 chlorination, or water chemistry on the ratio of Ag⁺ versus nAg. The speciation results of the
324 present study are in agreement with previous research that showed primarily Ag⁺ release (>90%)
325 from ceramic filters painted with Argenol casein-coated nAg and exposed to solutions with
326 varying IS (1-50 mM), cations (Na⁺, Mg²⁺, Ca²⁺), and pH 5-9 (Mittelman et al. 2015). However,
327 Ren and Smith (2013) observed the opposite trend in a study investigating the transport of nAg
328 through ceramic filters and release of silver from nAg-impregnated filter disks that were
329 prepared by dipping, painting, or firing-in methods. In that work, the authors reported that Ag⁺
330 comprised less than 1% of the total silver concentration in effluent samples, regardless of the

331 silver application method, suggesting that metallic silver (Ag^0) was the dominant form of silver
332 during transport and release (Ren and Smith 2013). This contrasting result could be due in part to
333 the different type of nanoparticles evaluated in the Ren and Smith study (proteinate-coated and
334 citrate-coated nAg) compared to the casein-coated nAg used for the present work, as well as the
335 different Ag^+ detection method employed (silver/sulfide ion selective electrode vs. ultrafiltration
336 and ICP-OES analysis). Details on the selected effluent sample concentrations or silver ion
337 selective electrode detection limit were not reported in the Ren and Smith (2013) study, but ion
338 selective electrode detection limits are typically higher than those of ICP-OES ($9 \mu\text{g/L}$ for the
339 present study) and may not be appropriate for analyzing low $\mu\text{g/L}$ levels of Ag^+ . A recent study
340 by Meade et al. (2017) showed that a silver ion selective electrode (Hanna HI 98185) with a
341 manufacturer-specified measurement range of 0.11-107,900 mg/L did not accurately measure
342 Ag^+ concentrations below 0.2 mg/L.

343

344 *3.3. Impact of Chlorine on Silver Release in Painted-on nAg Disks*

345 An FCR concentration of 2 mg/L increased silver release 2-5 times for painted nAg disks
346 with a DI water background (Figure 1a). However, even with this increase, effluent silver
347 concentrations remained below the international maximum recommendation of 0.1 mg/L.
348 Application of a lower chlorine dose (0.2 mg/L FCR) had no measurable impact on silver release
349 with the DI water background (SI Figure S5). For disks with a 1 mM or 10 mM NaNO_3
350 background, chlorine had minimal impact on silver release (Figures 1b-c). With a background of
351 1 mM NaNO_3 , the first 2 mg/L chlorine dose resulted in a 0.008-0.025 mg/L (8-26%) increase in
352 silver release, but subsequent chlorine doses showed no measurable impact. Similarly, with the

353 highest IS background solution of 10 mM NaNO₃, the initial chlorine dose resulted in a 0-0.04
354 mg/L (0-15%) increase in silver release.

355 In a previous study that used QCM to evaluate silver nanoparticle detachment from a
356 silica-coated quartz surface, Bielefeldt et al. (2013) observed rapid release of silver following the
357 addition of 8.8 or 525 mg/L free chlorine (83-86% removal within 3 hr). In that study, the
358 chlorine was prepared in DI water, and the findings are in agreement with the DI background
359 results from the current study presented in Figure 1a (Exp. 1). However, as shown in Figure 1b,
360 with a slight increase in IS (1 mM), the impact of chlorine on silver release was minimal.

361 The findings of the present study suggest that IS, rather than chlorine, will influence the
362 silver release from ceramic filters at the chlorine doses that would typically be encountered. In
363 household water treatment applications, source waters are likely to contain some level of
364 background salts. As an example, in a study of 989 drinking water sources across the United
365 States, the US EPA found a median Na⁺ concentration of 16.4 mg/L and maximum value of
366 1,541 mg/L (USEPA 2002). Source water data from countries where CWFs are more commonly
367 used is somewhat limited, but data from the Global Environmental Monitoring System
368 (www.gemstat.org) shows a range of Na⁺ concentrations. For example, median and maximum
369 Na⁺ levels in Tanzania source waters from 1984 were 83 and 143 mg/L, respectively
370 (ICWRGC). For Ghana in 2016, median and maximum Na⁺ concentrations were 18 and 40
371 mg/L, respectively (ICWRGC). Background solutions containing 1 mM and 10 mM NaNO₃
372 correspond to Na⁺ concentrations of 23 mg/L and 230 mg/L, representing average and higher end
373 concentrations in water, respectively.

374

375 *3.4. Influence of Natural Organic Matter on Silver Release from Painted-on nAg Disks*

376 The presence of NOM (3 mg C/L Suwannee River NOM in 1 mM NaNO₃) resulted in
377 slightly decreased silver release from painted nAg disks compared to 1 mM NaNO₃ alone for the
378 initial flushing period of 20 PVs, with effluent silver concentrations dropping below 0.1 mg/L
379 after 4.5 PVs (1.5 h) flushing with 3 mg C/L Suwannee River NOM in 1 mM NaNO₃ (Figure 2,
380 Figure 1b). After the initial flushing period, however, effluent silver levels were similar to those
381 observed for 1 mM NaNO₃ alone (SI Figure S6). The addition of chlorine (4 mg/L as Cl₂) had no
382 measurable impact on silver release in the presence of Suwannee River NOM (Figure 2).

383 Previous work with aqueous suspensions of nAg has shown that humic acid (a model
384 NOM) can decrease the antimicrobial activity of nAg (Fabrega et al. 2009, Zhang et al. 2012),
385 likely due to the NOM coating the nAg surface, which could have implications for filter
386 performance. Rayner et al. (2013b) evaluated the impact of 5 mg/L humic acid solutions on the
387 log reduction values (LRV) of *E. coli* from ceramic filter disks painted with Argenol casein-
388 coated nAg or AgNO₃ (0.003 mg Ag/g filter), and observed no difference in LRV compared to
389 disks exposed to 150 mg/L NaCl or CaCl₂ solutions. This lack of an effect may have been due to
390 the low painted silver concentration, so further experiments are needed to evaluate the coupled
391 impact of NOM on silver release and silver effectiveness in CWFs.

392

393 3.5. Effect of Painted-on Silver Type (AgNO₃ and nAg)

394 While the majority of factories apply nAg, some factories use AgNO₃ due to lower cost
395 and/or local availability (Rayner et al. 2013a), so the effect of painted silver type (nAg vs.
396 AgNO₃) on silver release in the presence of chlorine was evaluated (Exps. 7-8, Table 1). A
397 higher amount of silver release was observed for AgNO₃-painted filter disks compared to those
398 painted with nAg during the first 20 PVs flushing (Figure S7). This is in agreement with

399 previous work by Mittelman et al. (2015), where AgNO_3 -painted disks exhibited greater Ag^+
400 release relative to casein-coated nAg-painted disks flushed with 10 mM NaNO_3 at pH 7. In
401 another study by Rayner and colleagues (2013b), effluent silver concentrations were 3-4.5 times
402 higher in AgNO_3 -painted compared to nAg-painted filter disks after 5 hr of flow (0.03 mg Ag/g
403 filter, pH 7.4, 16.3 mM phosphate buffer solution). However, in the current study, with a
404 background solution of 1 mM NaNO_3 , the effluent concentration from the painted AgNO_3 filter
405 disk continuously decreased, whereas the painted nAg disk effluent silver concentrations
406 exhibited a faster initial decrease but then stabilized (Figure S7a). After 80 PVs (27.5 hr) of
407 flushing with 1 mM NaNO_3 and intermittent 2 mg/L chlorine, the effluent silver concentrations
408 for painted AgNO_3 and painted nAg filter disks were 0.03 mg/L and 0.07 mg/L, respectively.
409 With 10 mM NaNO_3 background, effluent silver concentrations from painted AgNO_3 filter disks
410 were only slightly higher than effluent silver concentrations from painted nAg disks and values
411 were similar after ~40 PVs flushing (Figure S7b). The addition of chlorine did not have a
412 measurable impact on silver release from painted AgNO_3 filters with background solutions of 1
413 mM or 10 mM NaNO_3 ; effluent levels continuously decreased during intermittent chlorination.

414

415 3.6. Fired-in vs. Painted-on Silver Nanoparticles

416 Previous work suggests that adding nAg prior to the firing process (fired-in nAg) results
417 in improved retention of nAg, which could reduce potential exposures to nAg and extend CWF
418 lifetime compared to those prepared by painting on or dipping in an nAg suspension (Ren and
419 Smith 2013). Therefore, an experiment was performed to investigate silver elution following
420 intermittent chlorination of a fired-in nAg filter (Exp. 9, Table 1). The average measured solid
421 phase silver concentration \pm standard deviation ($n=3$) for the fired-in disk before the start of the

422 experiment was 0.34 ± 0.02 mg Ag/g filter. It should be noted that a higher concentration and
423 different nanoparticles were used for fired-in nAg filter disks vs. painted nAg filters (proprietary
424 surfactant-coated nAg vs. casein-coated nAg). The reason for this difference was based on the
425 desire to test factory relevant conditions (same silver source and application amount used by the
426 factories that fire-in silver). Nonetheless, with a background solution of 10 mM NaNO_3 the total
427 silver (nAg + Ag^+) release was similar for the painted-on and fired-in nAg filter disks (Figures 1c
428 and 4). During the initial 30 PVs, the percentage of total silver as Ag^+ in the effluent from the
429 fired-in nAg disk was higher than in the effluent from the painted-on disk (SI Figure S4),
430 suggesting that less silver was released in nAg form from the fired-in nAg disk under the same
431 ionic strength background (10 mM, Exp. 5 vs. 9, SI Figure S8). When 2 mg/L chlorine was
432 added, a slight increase in total silver release was measured in effluent from the fired-in nAg
433 filter (Figure 4), where the effluent Ag increased from 0.22 mg/L to 0.27 mg/L, then steadily
434 decreased back to 0.23 mg/L over 8 PVs or 2.8 hr. Subsequent chlorine addition did not affect
435 silver release, similar to the painted-on nAg and AgNO_3 filter results (Figures 1b-c, 2, 3).

436 Ren and Smith (2013) observed substantially lower silver release from ceramic filters
437 containing fired-in proteinate-coated nAg at 0.05 and 0.5 mg Ag/g filter. In their study, total
438 effluent silver concentrations ranged from 0.002 to 0.02 mg/L over 6 hr of flushing (0.6-1.2
439 mL/min) with a synthetic, moderately hard water (IS = 10 mM) (Ren and Smith 2013), which is
440 10-390 times lower than the effluent concentrations observed for a fired-in nAg disk in this study
441 (Figure 4) over a similar time frame, flow rate, and IS (the first 6 hr of flushing at 0.6 mL/min, IS
442 = 10 mM as NaNO_3). These differences could be due to the nanoparticle coating type
443 (proteinate-coated vs. the proprietary surfactant-coated nAg used in the current work) or silver
444 ion detection method (ion selective probe vs. ultrafiltration/ICP-OES in the present study), but

445 suggest that silver release from fired-in nAg filters should be further evaluated, in particular, the
446 release of nAg versus Ag^+ .

447

448 3.8. Silver Longevity

449 An estimate of the lifetime of the painted or fired-in nAg and painted AgNO_3 in full-sized
450 filters was performed for each condition based on: 1) a worst-case scenario (maximum silver
451 effluent concentration from first chlorine dose); and, 2) a more realistic projection based on the
452 effluent concentration after approximately 85 PVs (30 hr) of flow, shown in Figure 5. These
453 calculations align with the longevity calculation methods used by Mittelman et al. (2015), and
454 additional details are provided in the SI Text S1. The worst-case scenario silver lifetime
455 estimates ranged from 0.08-1.6 years, and estimates based on effluent concentrations after 30 hr
456 of flow ranged from 0.16-2.6 years. For a background solution of DI water with intermittent
457 chlorination at 2 mg/L as Cl_2 , the painted nAg filter lifetime ranged from 0.55 years (worst case
458 scenario) to 1.8 years (based on effluent after 30 hr flow), while the same filter with a
459 background of 10 mM NaNO_3 ranged from 0.10 (worst case scenario) to 0.17 years (based on
460 effluent after 30 hr flow). The filter with the highest silver mass released during the first 20 PVs
461 was observed for the painted AgNO_3 filter disk and a background of 10 mM NaNO_3 , which
462 resulted in lifetime estimates of 0.08-0.16 years. It is important to note that even without silver
463 application, ceramic filters can achieve ≥ 2 log *E.coli* reduction (Brown and Sobsey 2010,
464 Kallman et al. 2011, Oyanedel-Craver and Smith 2008, Rayner et al. 2013b, van Halem et al.
465 2007), and therefore, well-made filters may continue to be effective after the silver coating is
466 depleted.

467

468 4. Conclusions

469 Based on the results presented herein, the following conclusions can be stated.

- 470 • *Ionic Strength and NOM*: Increasing IS (0-10 mM NaNO₃) resulted in increased silver
471 release, which reduces silver lifespan. Presence of NOM (3 mg C/L in 1 mM NaNO₃)
472 resulted in slightly decreased silver release from painted nAg disks during the initial
473 flushing period (20 PVs) compared to filters under the same conditions without NOM.
474 After initial flushing, effluent silver levels remained below 0.1 mg/L and were similar to
475 those of filter disks exposed to 1 mM NaNO₃ alone. Thus, it is advised to maintain the
476 current recommendation of discarding the first three batches of filtered water, which
477 results in flushing approximately 30 L (25 PVs) through a 10 L capacity filter, to reduce
478 effluent silver to below 0.1 mg/L, particularly if using high IS water (IS ≥10 mM).
- 479 • *Chlorine*: Application of chlorine increased silver release in DI water, but measured
480 concentrations did not exceed international guidelines for silver in drinking water (0.1
481 mg/L). The observed increase in silver elution due to chlorine was mitigated when using
482 representative natural waters with IS and NOM. Based on these results, we propose that
483 the recommendation for CWF operation and maintenance be: it is acceptable to use and
484 clean CWFs with chlorinated water at recommended drinking water FCR levels (e.g., 0.2-
485 4 mg/L). However, it is not recommended to clean CWFs with undiluted bleach (50,000-
486 80,000 mg/L as Cl₂) or concentrations greater than drinking water FCR levels (e.g. >5
487 mg/L as Cl₂) until the impacts of cleaning with higher concentrations on silver elution are
488 evaluated.

- 489 • *Silver form (painted-on AgNO₃ versus nAg)*: Higher initial silver release was observed
490 from painted-on AgNO₃ compared to painted-on nAg disks, although this trend did not
491 continue during long-term filter use at the conditions tested in this study.
- 492 • *Silver application (painted-on versus fired-in nAg)*: Total effluent silver concentrations
493 were similar between filter disks prepared with painted-on and fired-in nAg. However,
494 the % of total silver as nAg was lower for the filter disk with fired-in nAg (average = 5%
495 as nAg) versus painted-on nAg (average for all painted-on nAg experiments = 14% as
496 nAg). It is important to note that only one fired-in nAg experiment was performed in this
497 study, with a different type and concentration of silver compared to painted-on nAg.
498 Nevertheless, this finding suggests that the fired-in nAg application method could reduce
499 potential exposure to nAg. Thus, the release of nAg and Ag⁺ from factory manufactured
500 fired-in nAg and nAg-painted filters needs to be further evaluated over a range of
501 anticipated conditions to confirm these results.
- 502 • *Filter Quality*: Consistent with prior research, the experimental results presented herein
503 indicate that the lifetime of silver treatment to filters ranges from a few weeks to almost
504 two years. This work supports the recommendation that silver should not be relied on as
505 the primary mechanism of drinking water treatment in filters, and the pore structure of
506 the CWF must be the primary mechanism of water treatment. It is recommended that
507 filter quality be evaluated by testing for microbial removal prior to silver application.
- 508 • *Limitations*: Limitations of this work are that microbiological efficacy was not assessed
509 and that experiments were not performed in replicate. It is recommended that future work
510 be conducted on silver release and microbiological efficacy, including using waters with
511 NOM, and that replicate tests are carried out when possible.

512

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519

520 **6. References**

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- 597

Table 1. Experimental matrix for ceramic filters coated with painted-on nAg or AgNO₃, or fired-in nAg and flushed with deionized (DI) water, 1 mM NaNO₃, or 10 mM NaNO₃ and intermittent chlorination (0.2, 2, or 4 mg/L as Cl₂ in corresponding background solution). All background solutions were adjusted to pH 7 with 0.1 M HNO₃ or 0.1 M NaOH.

Exp. #	Coating	Background solution	Additives	Chlorine dose sequence (mg/L as Cl ₂)	Results Figure
1	nAg	DI water	--	0, 2, 0, 2, 0, 2, 0	1a
2	nAg	DI water	--	0, 0.2, 0, 0.2, 0, 0.2, 0	S5
3	nAg	1 mM NaNO ₃	--	0, 2, 0, 2, 0, 2, 0	1b
4	nAg	10 mM NaNO ₃	--	0	S3
5	nAg	10 mM NaNO ₃	--	0, 2, 0, 2, 0, 2, 0	1c
6	nAg	1 mM NaNO ₃	3 mg/L (as C) SRNOM	0, 4, 0, 4, 0, 4, 0	2
7	AgNO ₃	1 mM NaNO ₃	--	0, 2, 0, 2, 0, 2, 0	3a
8	AgNO ₃	10 mM NaNO ₃	--	0, 2, 0, 2, 0, 2, 0	3b
9	Fired-in nAg	10 mM NaNO ₃	--	0, 2, 0, 2, 0, 2, 0	4

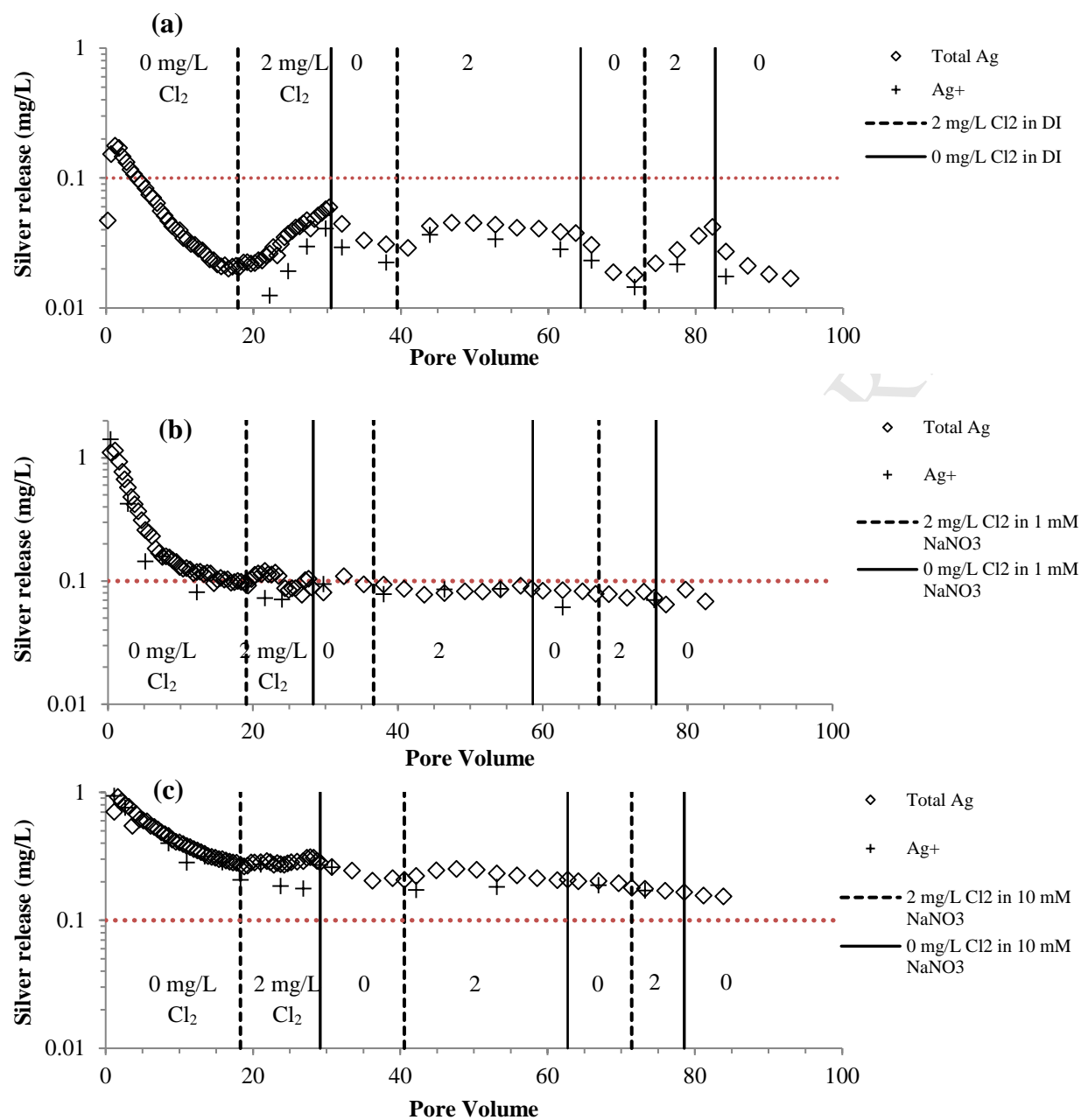


Figure 1. Silver (Ag^+ and total) release from ceramic disks painted with nAg (3 mL of 200 mg/L casein-coated nAg on the top and bottom of each disk) exposed to (a) deionized (DI) water, (b) 1 mM NaNO_3 , (c) 10 mM NaNO_3 and intermittent chlorination (2 mg/L Cl_2). All background solutions were adjusted to pH 7 with 0.1 M NaOH or 0.1 M HNO_3 . Horizontal dashed line represents United States Environmental Protection Agency (US EPA) secondary maximum contaminant level and World Health Organization (WHO) guideline value for silver in drinking water of 0.1 mg/L.

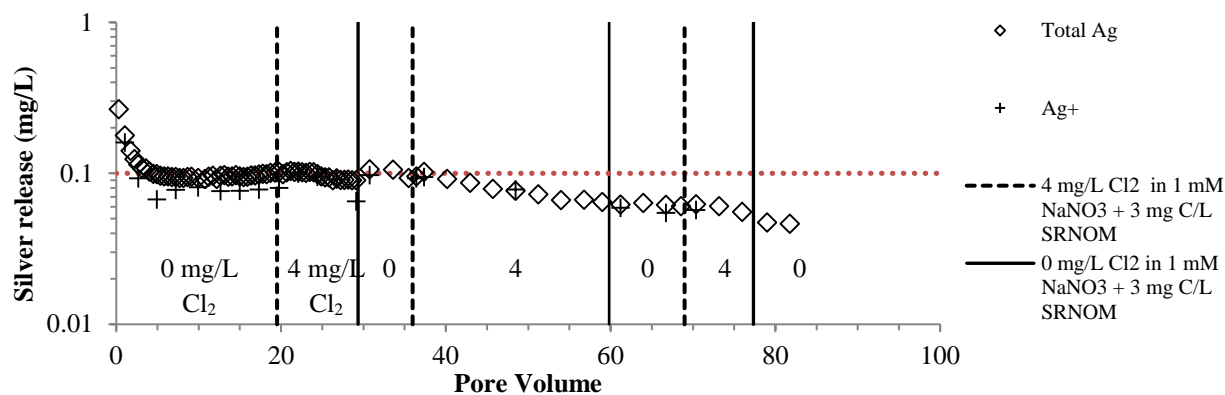


Figure 2. Silver (Ag⁺ and total) release from ceramic disks painted with nAg (3 mL of 200 mg/L casein-coated nAg on the top and bottom of each disk) exposed to 3 mg C/L Suwanee River NOM in 1 mM NaNO₃ and intermittent chlorination (4 mg/L Cl₂). All background solutions were adjusted to pH 7 with 0.1 M NaOH or 0.1 M HNO₃. Horizontal dashed line represents US EPA secondary maximum contaminant level and WHO guideline value for silver in drinking water of 0.1 mg/L.

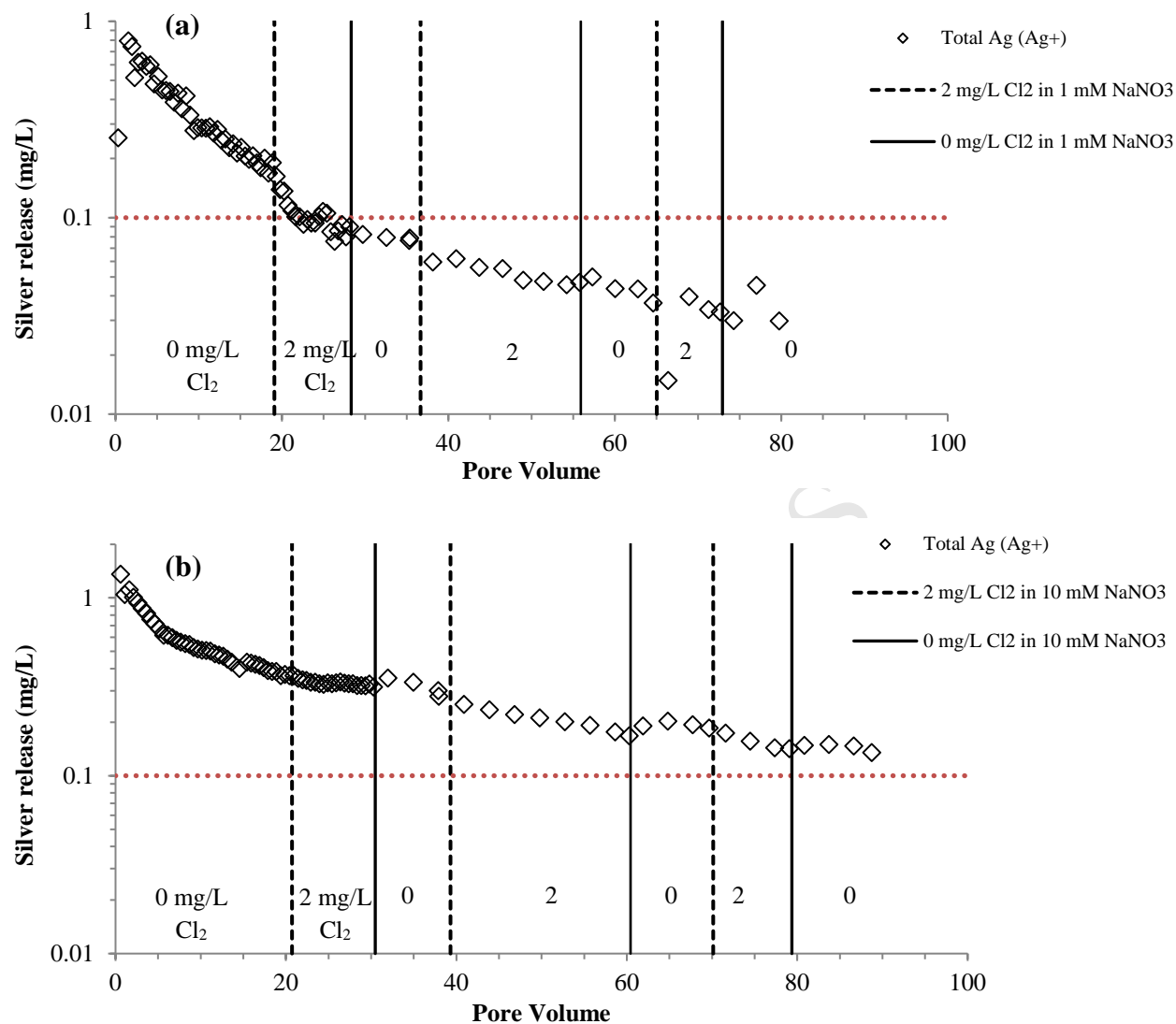


Figure 3. Silver (Ag^+) release from AgNO_3 -painted disk (3 mL of 200 mg/L AgNO_3 on each top and bottom of disk) exposed to (a) 1 mM NaNO_3 or (b) 10 mM NaNO_3 and intermittent chlorination (2 mg/L Cl_2). All background solutions were adjusted to pH 7 with 0.1 M NaOH or 0.1 M HNO_3 . Horizontal dashed line represents US EPA secondary maximum contaminant level and WHO guideline value for silver in drinking water of 0.1 mg/L.

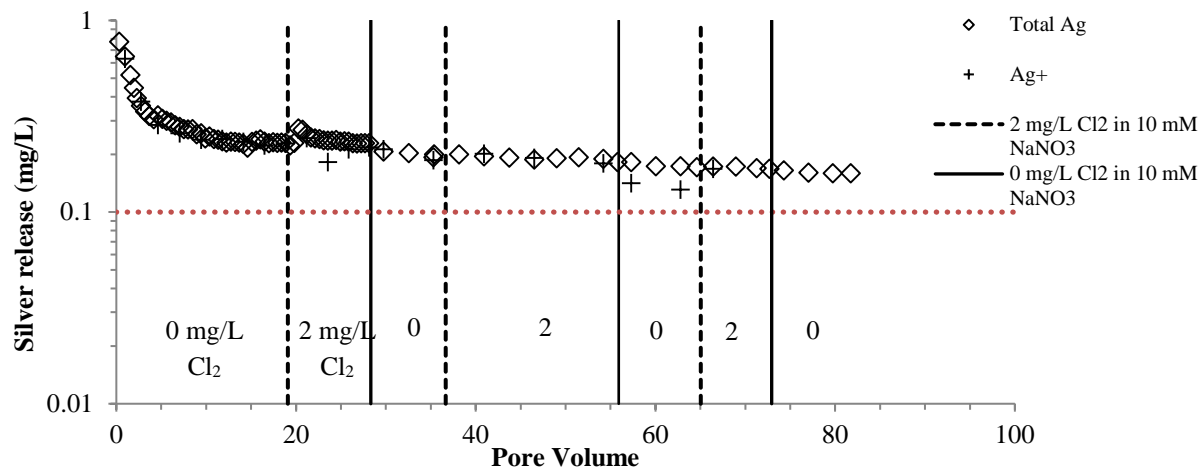


Figure 4. Silver (Ag^+ and total) release from fired-in nAg disk exposed to 10 mM NaNO_3 and intermittent chlorination (2 mg/L Cl_2). All background solutions were adjusted to pH 7. Horizontal dashed line represents US EPA secondary maximum contaminant level and WHO guideline value for silver in drinking water of 0.1 mg/L.

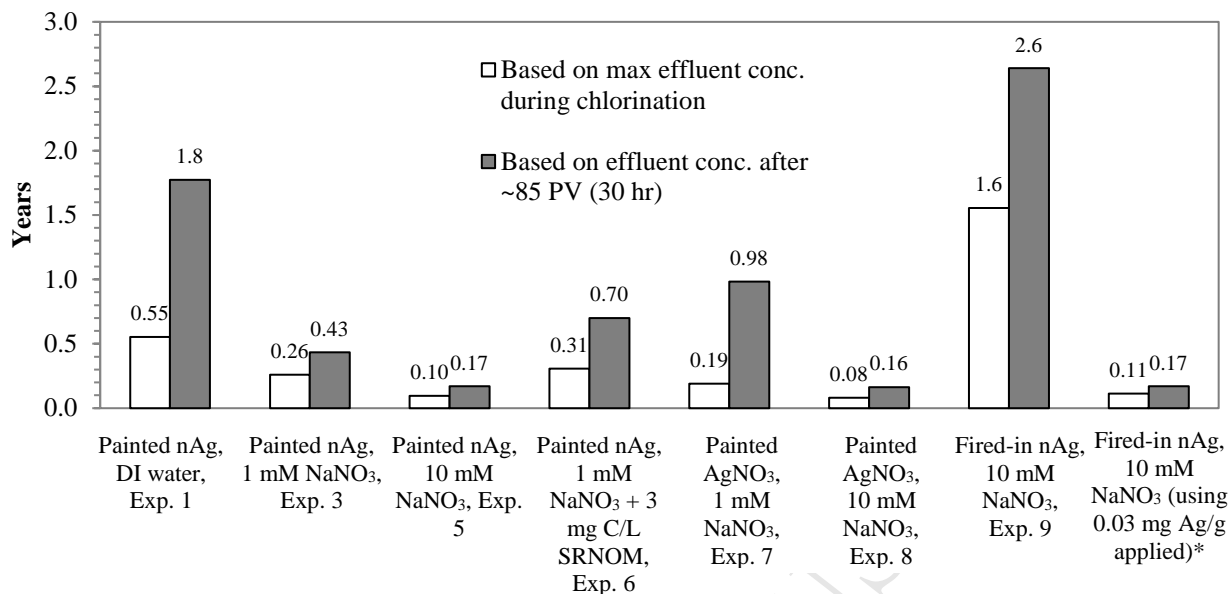


Figure 5. Silver longevity estimates for painted or fired-in nAg and painted AgNO₃ in full-size ceramic filters exposed to varying IS and intermittent chlorination (2 mg/L as Cl₂, except for Exp. 6 with NOM, which used 4 mg/L Cl₂). Values were calculated using the worst-case scenario (maximum effluent silver concentration during chlorination, shown as white bars) or based on the effluent after ~85 PV (30 hr) of flow (grey bars). *The amount of silver measured in the fired-in nAg disks was approximately an order of magnitude higher than that of the painted nAg and AgNO₃ disks (0.34 mg Ag/g filter measured in the fired-in disk compared to 0.03 mg Ag/g for the painted disks), so an additional longevity calculation was performed assuming an initial application of 0.03 mg Ag/g for easier comparison to the other types of silver application.

- Increasing ionic strength (IS) increased silver release from filter disks
- Chlorine increased silver release in DI water, but levels remained below 0.1 mg/L
- Chlorine had no impact on silver release in presence of organic matter or 1-10 mM IS
- Silver eluted primarily in the ionic form (Ag^+), rather than as nanoparticles
- The calculated lifetime of Ag in filters ranged from a few weeks to almost two years