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5 **The fate of H₂O₂ during managed aquifer recharge: a residual from**
6 **advanced oxidation processes for drinking water production**

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11
12 **ABSTRACT**

13 The fate of H₂O₂ residual from advanced oxidation process (AOP) preceding managed aquifer
14 recharge (MAR) is of concern because H₂O₂ could lead to undesired effects on organisms in the MAR
15 aquatic and soil ecosystem. The objective of this study was to distinguish between factors affecting
16 H₂O₂ decomposition in MAR systems, simulated in batch reactors with synthetic MAR water and slow
17 sand filter sand. The results showed that pure sand and soil organic matter had no considerable effect
18 on H₂O₂ decomposition, whereas naturally occurring inorganic substances on the surface of sand
19 grains and microbial biomass are the two main factors accelerating H₂O₂ decomposition in MAR
20 systems. Additionally, the results showed that the H₂O₂ decompositions with different initial
21 concentrations fitted first-order kinetics in 2-6 hours in a mixture of slow sand filter sand (as a
22 substitute for sand from a MAR system) and synthetic MAR water with high bacterial population. An
23 estimation indicated that low concentrations of H₂O₂ (<3 mg/L) could decompose to the provisional

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24 standard of 0.25 mg/L in the first centimeters of MAR systems with the influent water containing high
25 microbial biomass 38 ng ATP/mL.

26 Keywords: Managed aquifer recharge, Advanced oxidation process, H₂O₂ residual, H₂O₂
27 decomposition factors, Drinking water production

28 **1. Introduction**

29 Managed aquifer recharge (MAR), such as river bank filtration, dune infiltration and artificial recharge,
30 is a natural water treatment process that induces surface water to flow through soil/sediment and into a
31 vertical or horizontal well (Maeng et al., 2011; Tufenkji et al., 2002). This treatment process is robust
32 and cost-effective and is frequently applied in Europe (Van der Hoek et al., 2014). For example, in the
33 Netherlands and Germany, water utilities using MAR as a water treatment process supply drinking
34 water without chlorination as disinfection process (Lekkerkerker, 2012; Maeng, 2010). Previous
35 research demonstrated that the combination of advanced oxidation process (AOP) and subsequent
36 MAR is a potential treatment system to remove various organic micropollutants (OMPs) during
37 drinking water production (Lekkerkerker-Teunissen et al., 2012; Lekkerkerker et al., 2009; Oller et al.,
38 2011). A disadvantage of applying AOP with O₃ is the formation of bromate during oxidation of
39 bromide containing waters. In order to reduce the formation of bromate which has been designated as
40 carcinogenic to humans (Kurokawa et al., 1990), H₂O₂ should be dosed excessively (Knol, 2012; Von
41 Gunten and Oliveras, 1998; Wert et al., 2007). Consequently, the MAR infiltration water may contain
42 residual concentrations of H₂O₂.

43 A number of studies about H₂O₂ decomposition in aquatic ecosystems and soil ecosystems have
44 focused on biotic factors, such as bacteria (Richard et al., 2007; Zappi et al., 2000) and other
45 microorganisms (Cooper and Lean, 1989; Richard et al., 2007) and abiotic factors, such as iron
46 (Moffett and Zafiriou, 1993; Wilson et al., 2000), manganese (Do et al., 2009; Häkkinen et al., 2004;
47 Russo et al., 2013), transition metals (Lousada and Jonsson, 2010; Moreno et al., 2011), lanthanide
48 oxides (Lousada et al., 2013) and iodide (Wong and Zhang, 2008). H₂O₂ decomposition in water also
49 has been reported (Cooper and Lean, 1989; Moffett and Zafiriou, 1993; Richard et al., 2007; Wilson et

50 al., 2000). The results of Schumb (1949) showed that manganese and iron were extremely reactive
51 with concentrated H₂O₂ solutions. Also, H₂O₂ decomposition studies have been conducted in metal- or
52 DOC-rich waters (Chirită, 2009; Wilson et al., 2000). Previous research found that a large fraction of
53 H₂O₂ loss in both a fresh water system and soil was attributable to biotic mechanisms. Richard et al.
54 (2007) found that biologically based reactions (i.e., catalase) were the primary mechanism for H₂O₂
55 decomposition in a shallow fresh water system in New Zealand. It was observed from the literature of
56 Zappi et al. (2000) that the first-order rate constant of biotic reactions was always much higher than
57 that of abiotic reactions for H₂O₂ decomposition in various soils with different calcium, iron,
58 manganese, TOC and phosphorus contents. It is clear that the fate of H₂O₂ in aquatic systems has been
59 investigated comprehensively, and a few studies focused on the reactions of H₂O₂ with natural-
60 occurring constituents in soil (Bissey et al., 2006; Miller and Valentine, 1999). These publications
61 investigated the stability of H₂O₂ as the oxygen source for bioremediation activities in soil, because of
62 several potential interactions of H₂O₂ with various soil constituents and its potentially fast
63 decomposition. Studies of Morgan and Watkinson (1992) and Schumb (1949) reported reaction of
64 H₂O₂ with naturally occurring stabilizers, such as tripolyphosphate, MnO₄⁻ and Cu²⁺ within soils.
65 Bissey et al. (2006) investigated the interactions between catalyzed H₂O₂ propagations and soil organic
66 matter (SOM) within surface soil and reported that the H₂O₂ decomposition rate decreased with the
67 increase of SOM at neutral pH. Miller and Valentine (1999) examined mechanisms and kinetics of
68 abiotic H₂O₂ decomposition in the presence of sand collected from an aquifer and a riverbed. However,
69 more understanding is needed to determine the fate of H₂O₂ in MAR systems specifically. High
70 concentrations of H₂O₂ can cause damage to cell membranes and have deleterious effects on biological
71 systems (Ananthaswamy and Eisenstark, 1976; Collén and Pedersén, 1996; Wong et al., 2003).
72 Schmidt et al. (2006) concluded that H₂O₂ minimum inhibitory concentration (MIC) to the most
73 sensitive bacteria species *Pseudomonas aeruginosa* was 5.1 mg/L. The study of Urfer (1998)
74 demonstrated that the continuous presence of around 1 mg/L H₂O₂ did not lead to a major inhibition of
75 the biological removal of acetate and formate in a lab-scale sand drinking water biofilter. Knol (2012)
76 stated that even very low concentrations of H₂O₂ could lead to undesired destruction of organisms in
77 MAR infiltration ponds and he mentioned a provisional standard of 0.25 mg/L H₂O₂ for MAR

78 infiltration water. Consequently, an improved understanding of the fate of H₂O₂ in MAR systems
79 would be essential to see whether this provisional standard or lower concentrations can be reached.
80 The objective of this study was to distinguish between different factors affecting H₂O₂ decomposition
81 in MAR systems. The general approach in this study was to divide the aquifer environment into two
82 separate physical compartments (water and sand) that contain naturally existing biological and
83 chemical species that might react with H₂O₂. Batch reactor experiments were conducted to determine
84 the reactions of H₂O₂ with biotic (microbial community in water) and abiotic constituents (pure sand
85 particles, inorganic ions in infiltration water, SOM in MAR sand and naturally occurring inorganic
86 substances coating on sand).

87 **2. Materials and methods**

88 **2.1. Materials**

89 The top 0.5-2.0 cm (schmutzdecke) of a slow sand filter (SSF) has diverse microbial communities and
90 greatly contributes to the removal of organic matter by biodegradation processes, so this layer is
91 considered to represent aerobic microbial activity of sand filtration systems (Chekol, 2009; Dizer et al.,
92 2004). The SSF sand in the facilities of drinking water utility Dunea (The Hague, the Netherlands)
93 originated from the dune infiltration area. Consequently, schmutzdecke sand (top of SSF) with natural
94 microbial communities was used in batch reactors as a substitute for the sand in the dune infiltration
95 ponds. As a reference, pure sand (silicon dioxide without any impurities; 1.07711.1000, VWR
96 company) was used. The water for batch reactors was prepared with demineralized water (demi-water)
97 and additive chemicals (33 mg Na₂HPO₄/L, 7.5 mg NaH₂PO₄/L, 22 mg K₂HPO₄/L, 140 mg CaCl₂/L,
98 0.031 mg FeCl₃/L, 0.032 mg NH₄Cl/L, 40.75 mg MgSO₄/L, 17.823 mg NaNO₃/L, 0.00114 mg
99 MnCl₂/L, 82 mg CH₃COONa/L) to simulate the water quality at the MAR site of Dunea. The
100 characteristics are presented in Table 1. Based on preliminary experiments, it was found that
101 CH₃COONa (Merck, Germany) was rapidly consumed as the source of DOC in the batch reactors, so
102 24 mg/L DOC was added in order to have residual DOC in the reactors and avoid bacterial starving
103 conditions. Dosing carbon source to levels exceeding natural MAR systems may lead to higher

104 microbial biomass concentration in batch reactors than in natural MAR systems (Pharand et al., 2014)
 105 and enhance the endurance ability to decompose H₂O₂. Therefore, a short inventory was performed
 106 based on observed adenosine triphosphate (ATP) concentrations in different waters to estimate the
 107 effect of carbon dosage on H₂O₂ decomposition (§ 3.4). The H₂O₂ solutions were prepared from a 30%
 108 standard solution (Merck, Germany). All the solutions used in this study were prepared using water
 109 from a Millipore Milli-Q system. All chemicals were of AR grade.

110 Table 1

111 The quality of MAR influent water in Dunea and synthetic MAR water used in batch reactors.

Parameter	O ₂ (mg/L)	pH	NH ₄ ⁺ -N (mg/L)	NO ₃ ⁻ -N (mg/L)	SO ₄ ²⁻ (mg/L)	Fe ³⁺ (mg/L)	Mn ²⁺ (mg/L)	DOC (mg/L)
MAR influent water	10.4±1.2	7.9±0.2	0.00997	3.7±0.1	48±2	0.0106	0.001	3.9±0.7
Synthetic MAR water	9±1.0	7.8±0.3	0.00847	2.9±0.1	30.6±2	0.0106	0.0005	22±2

112 2.2. Batch experimental setup

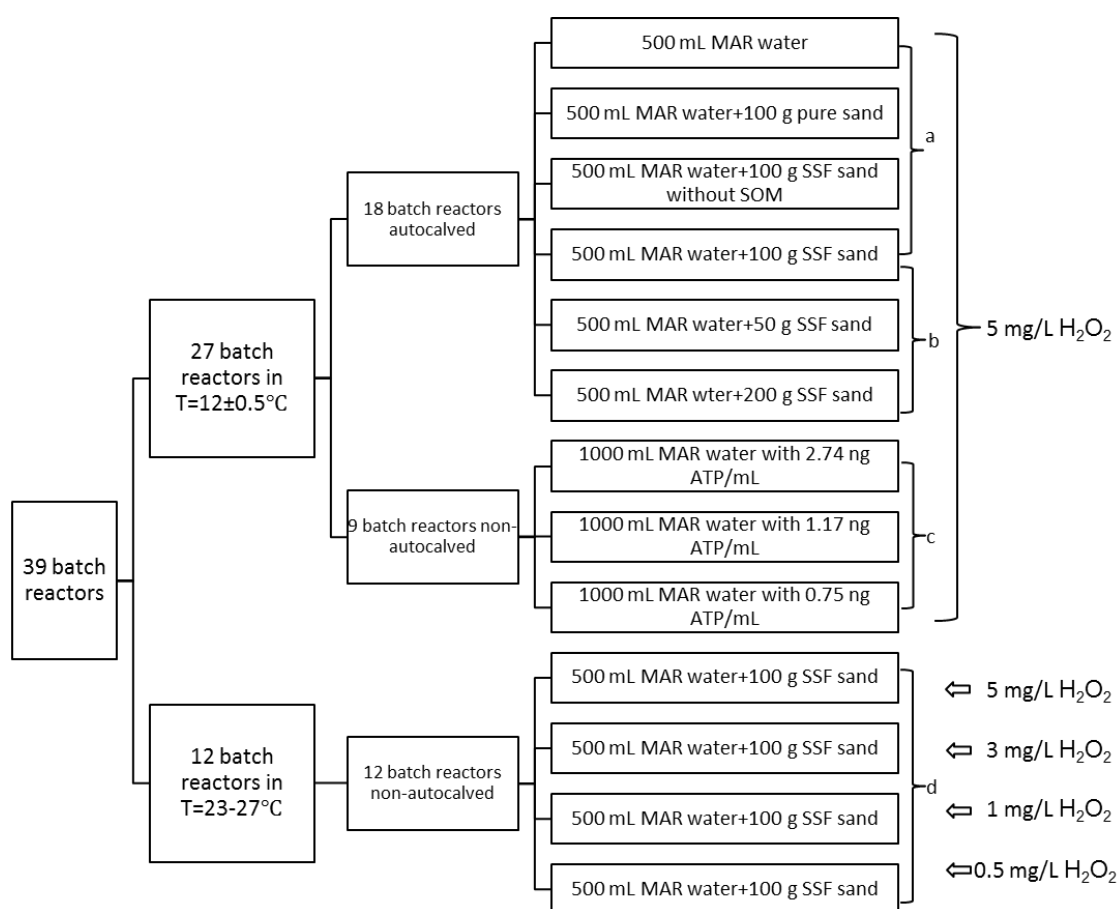
113 Batch experiments were performed with 39 glass batch reactors with a volume of 1 L for around 3
 114 months. Batch reactors were filled with 100 g SSF sand and 500 mL synthetic MAR water to simulate
 115 MAR systems (Lekkerkerker, 2012; Maeng, 2010). In addition, reference batch reactors were prepared
 116 with 100 g pure sand silicon dioxide and 500 mL synthetic MAR water. All batch reactors were placed
 117 in a dark room, either temperature controlled (12±0.5 °C) or ambient temperature (23-27 °C),
 118 depending on the experiment. Batch reactors were uncovered so that air could enter batch reactors to
 119 maintain oxic conditions. To avoid anaerobic conditions, the batch reactors were slightly shaken daily
 120 without disturbing the biofilm that had developed on the sand.

121 2.3. Experiments

122 To divide the aquifer environment into two separate physical compartments (water and sand) that
 123 contain naturally existing biological and chemical species that might react with H₂O₂, this study used
 124 an experimental set-up as shown in Fig. 1, providing an overview of batch reactors' conditions used in

125 the experiments. All batch reactors were prepared and sampled in triplicate. The performed
 126 experiments were divided into:

- 127 a) Abiotic: H_2O_2 decomposition under autoclaved conditions (with/without sand)
 128 b) Effect of sand: H_2O_2 decomposition with 200 g, 100 g, and 50 g autoclaved SSF sand
 129 c) Effect of biomass: H_2O_2 decomposition with microbial biomass, 2.74, 1.17, 0.75 and 0 ng
 130 ATP/mL
 131 d) Effect of initial H_2O_2 concentrations: H_2O_2 decomposition with 5.0, 3.0, 1.0 and 0.5 mg/L



132
 133 Fig. 1. Batch reactors in triplicate with different treatments (non-autoclaved or autoclaved, 23-27 °C or
 134 $12\pm 0.5^\circ C$, 5 mg/L, 3 mg/L, 1 mg/L or 0.5 mg/L dosage).

135 2.3.1. Abiotic experiments

136 To distinguish abiotic reactions from biotic reactions of H_2O_2 in MAR, sand (SSF sand, pure sand) and
 137 synthetic MAR water were autoclaved at 121 °C for 40 minutes to eliminate biological activity. Based

138 on previous study, the enzymatic activity within soil will be completely deactivated by autoclaving
139 (Aggarwal et al., 1991). In this study, ATP was measured in batch autoclaved reactors and was present
140 in the range of 0.04-0.06 ng/mL during the whole experimental process, which indicated that bacteria
141 and enzyme existing in cells and released to water were inactivated by autoclaving. The SOM in SSF
142 sand was removed by heating at 500 °C for 2 hours. To further distinguish between the different
143 abiotic decomposition factors of H₂O₂, 500 mL MAR water, 500 mL MAR water+100 g pure sand,
144 500 mL MAR water+100 g SSF sand without SOM and 500 mL MAR water+100 g SSF sand were
145 put in 12 batch reactors respectively (Fig. 1 series a). 5 mg/L H₂O₂ was dosed into these batch reactors,
146 and H₂O₂ concentration was measured at nine different time points (T=0 h, 1 h, 2 h, 4h, 8 h, 24 h, 48 h,
147 72 h and 144 h). To further investigate to what extent inorganic content (e.g., metal oxides) on SSF
148 sand impacted H₂O₂ decomposition, the experiment was repeated with different amounts of autoclaved
149 SSF sand (50 g, 100 g and 200 g) and 500 mL MAR water (Fig. 1 series b). 5 mg/L H₂O₂ was dosed
150 into these 9 batch reactors. H₂O₂ concentration was measured at six different time points (T=0 h, 2 h, 8
151 h, 24 h, 72 h, 144 h). All 18 abiotic batch reactors were placed in a temperature controlled room
152 (12±0.5 °C).

153 **2.3.2. Biotic experiments**

154 To investigate the relationship of microbial population and H₂O₂ decomposition rate, 5 mg/L H₂O₂
155 was dosed into 9 batch reactors with different initial microbial population (Fig. 1, series c). MAR
156 water with microorganisms was collected from effluent water of a batch reactor with 500 mL MAR
157 water and 100 g SSF sand in ambient temperature 23-27 °C. Batch reactors with 2.74 ng ATP/mL
158 contained the effluent above without dilution. Batch reactors with 1.17 ng ATP/mL and 0.75 ng
159 ATP/mL were prepared by dilution with 500 mL and 725 mL demi-water respectively. H₂O₂
160 concentrations were measured at nine different time points (T=0 h, 4 h, 7 h, 23 h, 30 h, 45 h). The
161 experiments were conducted in a temperature controlled room (12±0.5 °C).

162 **2.3.3. Different concentrations of H₂O₂**

163 12 batch reactors filled with 500 mL MAR water and 100 g SSF sand were placed in ambient
164 temperature (23-27 °C) (Fig. 1, series d). Adaptation of the microbial communities on the SSF to the

165 laboratory conditions was achieved by refreshing water every five days until steady state conditions
166 were reached with respect to DOC removal (Lekkerkerker-Teunissen et al., 2012; Maeng, 2010).
167 Steady state conditions (85% DOC removal) were achieved after two months.

168 After ripening the reactors, H₂O₂ spiking experiments started. To evaluate H₂O₂ fate, different
169 concentrations of H₂O₂ (5 mg/L, 3 mg/L, 1 mg/L, 0.5 mg/L) were dosed to batch reactors one day after
170 water refreshing. The research of Lekkerkerker (2012) and Knol (2012) showed that 6 mg/L H₂O₂
171 dosage was enough to form sufficient OH radicals for oxidation in the AOP, so the residual H₂O₂
172 concentration in effluent water of AOP (being the MAR influent water) will not exceed 6 mg/L. Hence,
173 0.5 mg/L H₂O₂ was dosed into batch reactors in this experiment. H₂O₂ concentrations were measured
174 at five different time points (T=0 h, 1 h, 2 h, 4 h and 6 h).

175 **2.4. Analysis and measurements**

176 DOC was measured with a Shimadzu TOC analyzer. All samples (30 mL) were measured at constant
177 temperature (20 °C) after being filtered through 0.45 µm filters (SPARTANTM, Whatman, Germany)
178 which had been flushed twice with demi-water. Samples were acidified by adding 1.6 mL 2 mol/L
179 HCl (Sigma-Aldrich).

180 ATP is used in all cells as carrier of free energy and phosphate groups to drive many chemical
181 reactions. ATP plays a key role in metabolic processes in the cells and can therefore be used as a
182 measure for biomass. In this study, ATP was measured as total ATP in the supernatant. ATP was
183 measured using a Quench Gone Aqueous test kit and a LB9509 luminometer (both Aqua tools,
184 France).

185 Hydrogen peroxide test kits (1.18789.0001, VWR company) with a detection range of 0.015-6.00
186 mg/L were used for water-phase H₂O₂ measurements because of ease of operation, the rapid
187 decomposition of H₂O₂ and accuracy of results. Since the sand water mixture in this experiment was
188 turbid, 8 mL was pipetted into the reaction cells after being filtered through 0.45 µm filters. After 10
189 minutes, the sample was transferred to a 10/20 mm rectangular cell and measured in a photometer
190 (Spectroquant NOVA 60).

191 Based on X-ray diffraction analysis (Department of Materials Science and Engineering, TU Delft), the
192 inorganic constituents of the SSF sand were determined. Table 2 shows the percentages of important
193 metal oxides in SSF sand.

194 Table 2

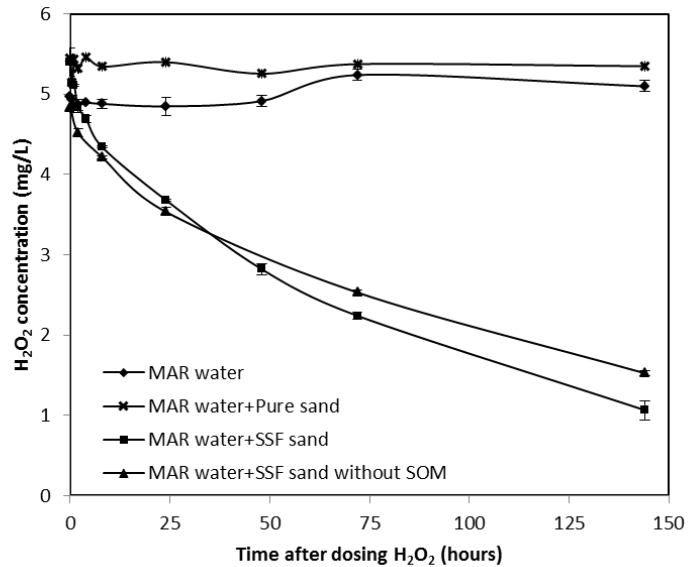
195 The weight percentages of important inorganic constituents other than SiO₂ in SSF sand.

Main inorganic constituents	Weight percentage (%)
Al ₂ O ₃	3.532
Fe ₂ O ₃	0.432
MgO	0.25
TiO ₂	0.037
MnO	0.012
ZnO	0.004

196 **3. Results and Discussion**

197 **3.1 Abiotic decomposition of H₂O₂ in the presence of SSF sand**

198 Fig. 2 shows the abiotic decomposition of H₂O₂ in the autoclaved batch reactors with and without SSF
199 or pure sand. H₂O₂ in autoclaved MAR water did not decompose in 114 hours (6 days). Also, no H₂O₂
200 decomposition was observed in the presence of autoclaved pure sand, which implies that pure sand
201 (silicon dioxide) does not adsorb or react with H₂O₂. However, H₂O₂ decomposed by around 64% in
202 both SSF sand groups with and without SOM. There was no significant difference in the H₂O₂
203 decomposition trend in SSF sand with and without SOM, which indicates that SOM in SSF sand has
204 no effect on H₂O₂ decomposition. These experiments suggest that the reaction of H₂O₂ with naturally
205 occurring inorganic substances on SSF sand (e.g., metal oxides) contributes to H₂O₂ decomposition.



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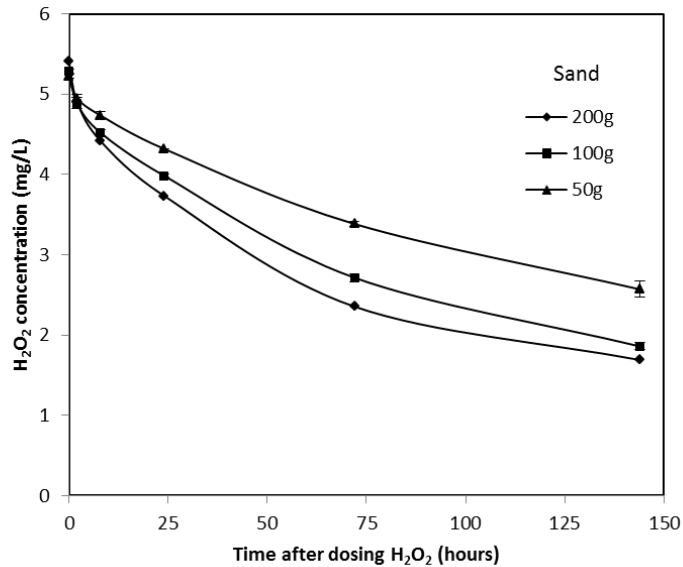
207 Fig. 2. H₂O₂ decomposition under autoclaved batch reactors at T=12±0.5 °C in triplicate (series a Fig.

208

1).

209 In contrast to what would be expected, no H₂O₂ decomposition was observed in MAR water only. It
 210 has long been known that one of the mechanisms of H₂O₂ decomposition is due to catalytic species,
 211 such as Cu²⁺, Fe³⁺ and Mn²⁺, which initiate radical-chain reactions and cause H₂O₂ to decompose more
 212 quickly in alkaline solution than in neutral or acidic media (Galbács and Csányi, 1983). Possible
 213 reasons why H₂O₂ did not decompose in MAR water could be that the low concentrations of metal
 214 ions (0.0106 mg Fe³⁺/L, 0.0005 mg Mn²⁺/L) could not promote H₂O₂ decomposition, the pH in this
 215 experiment was neutral instead of alkaline, and Cl⁻ and SO₄²⁻ might have inhibited H₂O₂
 216 decomposition (De Laat et al., 2004).

217 To further investigate to what extent inorganic content (e.g., metal oxides) within SSF sand impacts
 218 H₂O₂ decomposition, the experiment was repeated with different amounts of autoclaved SSF sand (50
 219 g, 100 g and 200 g). Fig. 3 presents the decomposition of H₂O₂ in 500 mL MAR water and autoclaved
 220 SSF sand, showing an increased removal of H₂O₂ (51%, 64% and 69%) at higher SSF content.



221

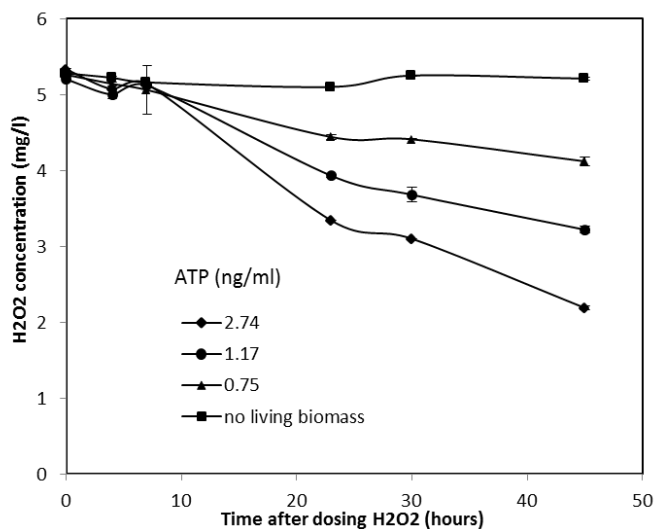
222 Fig. 3. H₂O₂ decomposition with 200 g, 100 g, and 50 g autoclaved SSF sand in 500 mL synthetic
 223 MAR water at T=12±0.5 °C. All batch reactors were in triplicate (series b Fig. 1).

224 This supports the finding that inorganic surfaces on the SSF sand effects H₂O₂ decomposition. Metal
 225 oxides may well be responsible for this observation, as this has also been reported in previous research
 226 (Hiroki and LaVerne, 2005; Lousada et al., 2013; Russo et al., 2013) and metal oxides were present in
 227 the SSF sand (Table 2). This may also explain why in Fig. 2 the H₂O₂ decomposition was slightly
 228 faster without SOM since inorganic content (e.g., metal oxides) coating on SSF without SOM may
 229 have more free surface area. This phenomenon is in agreement with results of Bissey et al. (2006) who
 230 found that H₂O₂ decomposition was faster in sand with 0.2% SOM than with 1.6% SOM at pH 7.
 231 However, the increase of H₂O₂ decomposition with the increase of SSF sand was slow, raising the
 232 question whether abiotic H₂O₂ decomposition by the natural sand will sufficiently contribute
 233 compared to biotic processes.

234 **3.2. Biotic decomposition of H₂O₂ within MAR water**

235 To investigate the effect of microbial biomass (represented as ATP) on H₂O₂ decomposition, 5 mg/L
 236 H₂O₂ was dosed into four synthetic MAR water groups with various levels of microbial biomass,
 237 extracted from SSF sand. Fig. 4 shows the H₂O₂ decomposition in MAR water with different bacterial
 238 populations, without the addition of sand. It was observed that only the group without living biomass

239 did not show H₂O₂ decomposition while H₂O₂ decomposed in the other groups with biomass. The
240 H₂O₂ decomposition rate considerably increased with the increase of microbial biomass.



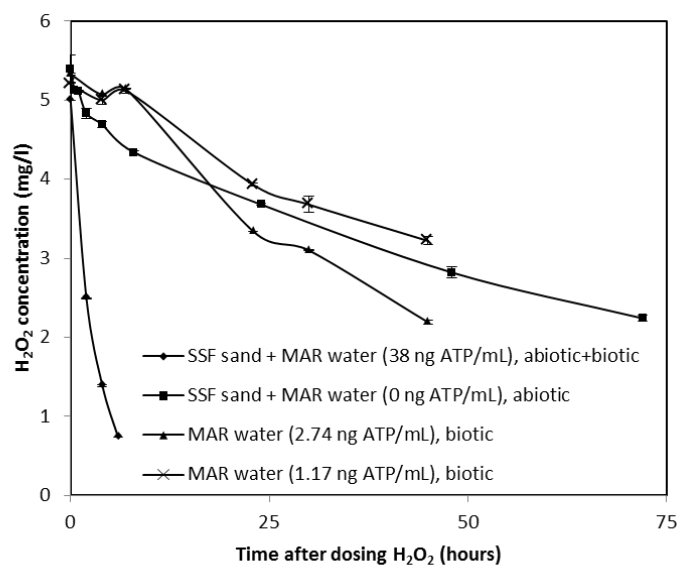
241
242
243 Fig. 4. H₂O₂ decomposition with microbial biomass, 2.74, 1.17, 0.75 and 0 ng ATP/mL at
244 T=12±0.5 °C. All batch reactors were in triplicate (series c Fig. 1).

245 Even low microbial biomass (0.75-2.74 ng ATP/mL) resulted in considerable H₂O₂ decomposition
246 (22-59%) in synthetic MAR water in only 45 hours. Therefore, microbial biomass is another main
247 factor promoting H₂O₂ decomposition in MAR systems. This result is confirmed by previous studies,
248 such as Sarathy et al. (2011) reported that 10 mg/L H₂O₂ was removed quickly by biologically
249 activated carbon filters with high microbial population, Urfer and Huck (1997) reported that the rapid
250 removal of 1 mg/L H₂O₂ in a biological filter may be attributed to its reaction with biomass.

252 3.3. Abiotic vs biotic H₂O₂ decomposition

253 The results above indicated that naturally occurring inorganic substances surfacing on sand grains and
254 living biomass would be the two main factors promoting H₂O₂ decomposition during MAR. To further
255 compare the effects of these two main factors, Fig. 5 shows H₂O₂ decomposition trends under abiotic
256 and biotic conditions, with and without SSF sand. The batch reactors with both non-autoclaved SSF
257 sand and MAR water with 38 ng ATP/mL provided the most rapid H₂O₂ decomposition by achieving
258 almost complete removal in 6 hours. However, the slowest decomposition occurred in both autoclaved

259 MAR water and SSF sand. Comparing the above results, it indicates that the biotic reactions
 260 contributed with a large fraction to H₂O₂ decomposition in the reactors with non-autoclaved SSF sand
 261 and MAR water with 38 ng ATP/mL. Additionally, H₂O₂ decomposition in non-autoclaved MAR
 262 water with 2.74 ng ATP/mL decomposed faster than in the reactors with both autoclaved SSF sand
 263 and MAR water, illustrating that the contribution of biotic reactions, in the presence of 2.74 ng
 264 ATP/mL, to H₂O₂ decomposition in SSF sand is more than abiotic reactions. However, at lower ATP
 265 concentrations (<1.71 ng ATP/mL), abiotic decomposition is faster and should therefore not be
 266 neglected.



267

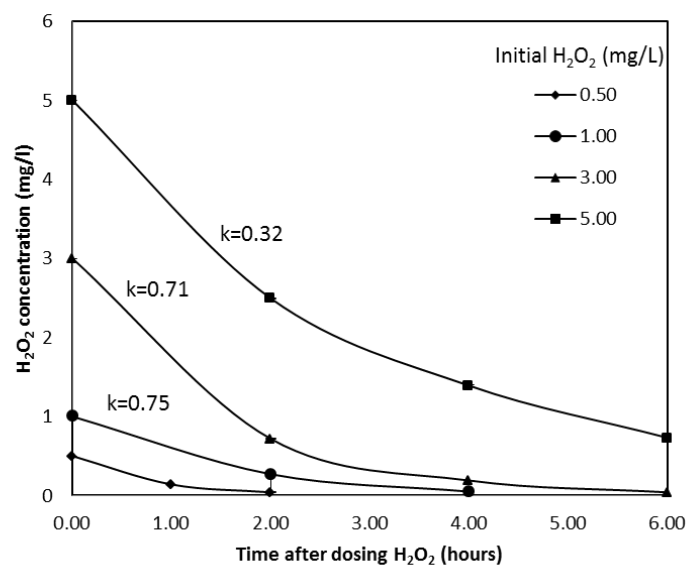
268 Fig. 5. Biotic and abiotic H₂O₂ decomposition. All batch reactors were in triplicate.

269 This result is different from previous studies. As was stated in the introduction, the removal of H₂O₂
 270 was greatly attributed to biotic factors instead of abiotic factors in most cases investigated, such as
 271 biologically active zones in situ (Bajpai et al., 1994) and biologically active filters (Urfer and Huck,
 272 1997) which contain much higher microbial biomass than natural MAR water. Several researchers
 273 investigated the microbial biomass in lakes and rivers, as MAR influent water, and found that ATP
 274 concentration range of 0.1-2 ng/mL (Cavari, 1976; Hamilton-Galat and Galat, 1983; Kramer, 2012;
 275 Noges, 1996; Pridmore et al., 1989). In practice however, especially in the late spring and in the early
 276 summer, ATP increases substantially to values of 2.79 ng/mL in Lake Rotorua (Pridmore et al., 1989)

277 and 2.945 ng/mL in Lake Kinneret (Cavari, 1976). This demonstrates that biotic reactions would be
278 the primary mechanism for H₂O₂ decomposition in MAR systems only when MAR waters contain
279 much higher ATP concentrations than the range of 0-2.74 ng/mL as used in this study.

280 3.4. H₂O₂ decomposition at different initial concentrations

281 So far, previous research has primarily focused on single H₂O₂ concentrations (Häkkinen et al., 2004;
282 Miller and Valentine, 1999; Urfer and Huck, 1997; Zappi et al., 2000), whereas the fate of different
283 H₂O₂ concentrations is important for setting the maximum allowable limit to prevent undesired effects
284 on aquatic and soil ecology. Fig. 6 presents the H₂O₂ decomposition at different initial concentrations
285 in SSF sand and synthetic MAR influent water with a large microorganism content (38 ng ATP/mL).
286 H₂O₂ initial concentrations in the range of 0.5-3 mg/L decomposed to below the detection limit 0.015
287 mg/L in 2-6 hours and 5 mg/L H₂O₂ decomposed to 0.73 mg/L in 6 hours.



288

289 Fig. 6. H₂O₂ decomposition under different initial concentrations, 0.5, 1.0, 3.0 and 5.0 mg/L, in the
290 presence of SSF sand at T=23-27 °C. All batch reactors were in triplicate (series d Fig. 1).

291 As is shown in Fig. 6, H₂O₂ decompositions followed first-order kinetics in the three H₂O₂ spiking
292 groups (5, 3 and 1 mg/L) in the presence of SSF sand. It is in agreement with previous studies (Miller
293 and Valentine, 1999; Zappi et al., 2000). Interestingly, first-order rate coefficients k values increased

294 with the decrease of H₂O₂ initial concentrations. The same phenomenon was reported in the study of
295 Silhacek and Taake (2005).

296 It is noteworthy that to maintain the growth of microorganisms in this experiment, DOC was dosed in
297 concentrations higher than in most MAR influent waters, particularly in winter periods. However, the
298 pre-treatment AOP before MAR can increase the degradable organic matter and lead to increased
299 bacterial population in MAR influent water, probably two to three times higher than MAR systems
300 without the pretreatment AOP (Pharand et al., 2014). Also, natural water may contain higher ATP
301 concentrations by themselves, such as 0.07-18 ng/mL in Lake 227 (Canada), 0.07-7.93 ng/mL in St.
302 Lawrence Estuary, 0.03-11.9 ng/mL in Pyramid Lake (NV) (Hamilton-Galat and Galat, 1983).
303 Therefore, microbial biomass in MAR systems after AOPs may reach 38 ng ATP/ml under specific
304 conditions. Assuming a microbial biomass concentration around 38 ng ATP/mL in MAR influent water
305 and H₂O₂ decomposition rate is steady in the surface of MAR sand, the first-order kinetics were
306 applied to predict the decomposition of residual H₂O₂ in MAR systems. Drinking water utility Dunea
307 operates the MAR with an infiltration velocity of 0.042 m/h (1 m/day). An estimation based on the
308 first-order kinetics is that different initial concentrations (5, 3 and 1 mg/L) of H₂O₂ could decompose
309 to the provisional standard, 0.25 mg/L, stated in the introduction within around 9, 4, and 2 hours
310 corresponding to a depth of 36, 17 and 8 cm. However, in practice the microbial activity may not be
311 steady with depths. Previous studies (Das et al., 2013; Haughton et al., 2001) reported that the highest
312 microbial population exists in the top 0-20 cm of soil and the microbial activity decrease a lot below
313 the depth of 20 cm. It could thus be concluded that low concentration of H₂O₂ (<3 mg/L) may be
314 decomposed to 0.25 mg/L in the first centimeters of dune sand in the presence microbial biomass of 38
315 ng ATP/mL in the MAR infiltration water.

316 **4. Conclusions**

317 This study investigated the fate of H₂O₂ as the residual of AOP during MAR. The main conclusions of
318 this study are:

- 319 • No H₂O₂ decomposition was observed in batch reactors with synthetic MAR water only, nor
320 in reactors containing pure sand. In MAR systems, pure sand and MAR water have no effect
321 on H₂O₂ decomposition.
- 322 • H₂O₂ decomposed slightly faster in batch reactors with SOM than in batch reactors without
323 SOM, but there was no significant difference in H₂O₂ decomposition between the two groups.
- 324 • Naturally occurring inorganic substances on the surface of sand grains and living biomass are
325 the two main factors promoting H₂O₂ decomposition in MAR systems.
- 326 • Low concentration (<3 mg/L) of H₂O₂ in MAR influent water may decompose below 0.25
327 mg/L in the centimeters of MAR systems with water containing high microbial biomass (such
328 as 38 ng ATP/mL).

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