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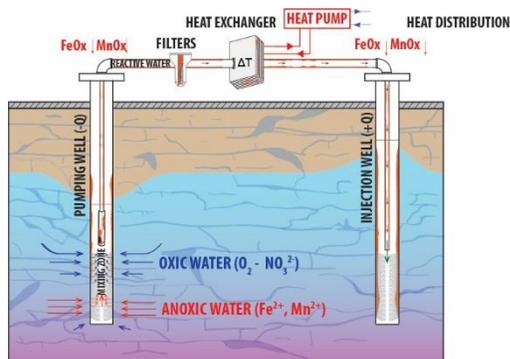
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15 **ABSTRACT**

16 The sustainability of ground-source geothermal systems can be severely impacted by
17 microbially mediated clogging processes. Biofouling of water wells by hydrous ferric oxide is a
18 widespread problem. Although the mechanisms and critical environmental factors associated with
19 clogging development are widely recognized, effects of mixing processes within the wells and
20 time scales for clogging processes are not well characterized. Here we report insights from a joint
21 hydrological, geochemical and metagenomics characterization of a geothermal doublet in which
22 hydrous ferric oxide and hydrous manganese oxide deposits had formed as a consequence of
23 mixing shallow groundwater containing dissolved oxygen and nitrate with deeper, anoxic
24 groundwater containing dissolved iron (Fe^{II}) and manganese (Mn^{II}). Metagenomics identify
25 distinct bacteria consortia in the pumping well oxic and anoxic zones, including autotrophic iron-
26 oxidizing bacteria. Batch mixing experiments and geochemical kinetics modeling of the associated
27 reactions indicate that Fe^{II} and Mn^{II} oxidation are slow compared the residence time of water in
28 the pumping well; however, adsorption of Fe^{II} and Mn^{II} by accumulated hydrous ferric oxide and
29 hydrous manganese oxide in the well bore and pump riser provides “infinite” time for surface-
30 catalyzed oxidation and a convenient source of energy for iron-oxidizing bacteria, which colonize
31 the surfaces and also catalyze oxidation. Thus, rapid clogging is caused by mixing-induced redox
32 reactions and is exacerbated by microbial activity on accumulated hydrous oxide surfaces.



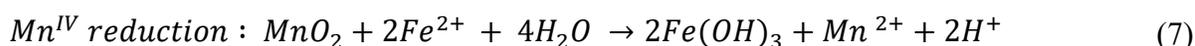
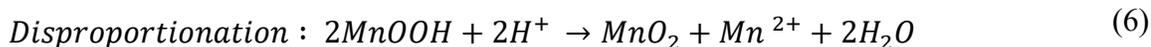
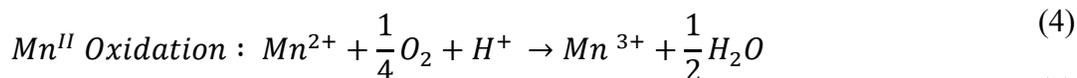
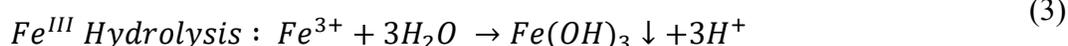
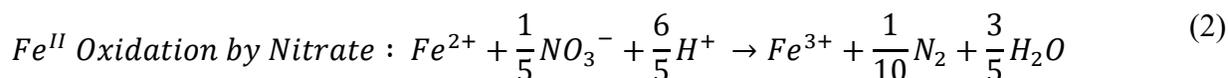
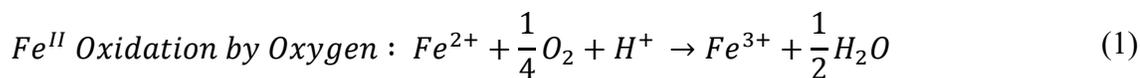
33

Abstract art (4.76 x 8.47 cm)

34 INTRODUCTION

35 Ground-source geothermal heating and cooling technologies can alleviate the use of fossil
36 carbon energy and reduce greenhouse gas emissions to the atmosphere¹. The technology of open-
37 loop systems with direct transfer of energy from groundwater through a heat exchanger between
38 pumping and injection wells (doublets) can be particularly cost-effective for heating and cooling
39 buildings. Yet, the major issue associated with shallow geothermal doublets is the clogging of
40 wells, exchangers, filters and other surface equipment by “biofouling” deposits that consist of
41 mineral²⁻⁵ and microbial⁶⁻⁹ encrustations. Guaranteeing the sustainability of a groundwater heat
42 pump system is challenging because of the rapidity at which such biofouling may appear, during
43 the first year of exploitation in some cases observed by the authors. Clogging issues are also
44 common in other groundwater sectors such as drinking water production¹⁰⁻¹², managed aquifer
45 storage and recovery^{13,14}, and dewatering systems^{15,16}. Although the processes at the origin of
46 biogeochemical clogging have been described¹⁷⁻¹⁹, the critical variables affecting hydrogeological
47 and biogeochemical processes driving well biofouling are poorly characterized²⁰. This is
48 particularly true for unstable field parameters that can vary spatially and temporally with
49 consequent effects on reaction development and rates, especially in the context of geothermal
50 systems where neighboring geothermal doublets may exhibit different sensitivities to clogging, as
51 illustrated in the present study.

52 Physical, chemical and microbiological processes contribute to clogging. Iron and manganese
53 oxide (bio)mineralization is the most common cause of clogging encountered in water systems
54 supplied by groundwater²¹⁻²³. These clogging deposits form when anoxic groundwater containing
55 dissolved iron (Fe^{II}) and manganese (Mn^{II}) mixes with water containing oxygen² or, possibly,
56 nitrate²⁴ (Equations 1-7).



57 Mixing of oxic and anoxic groundwater can occur through different pathways: (1) oxygen-rich
 58 recharge water can infiltrate the aquifer due to pumping and mix with reduced groundwater near
 59 the well bore^{12,25,26}, (2) intermittent pumping can cause fluctuation of the water table and
 60 oxygenation of anoxic groundwater by air entrapment²⁷⁻³¹, (3) mixing of chemically
 61 heterogeneous water bodies in aquifers characterized by localized oxidizing condition (i.e. rich in
 62 O₂, NO₃⁻) and reducing condition (i.e. rich in Fe²⁺, Mn²⁺) at different depths or spatially². Despite
 63 the suspected role of mixing-induced biogeochemical reactions in clogging phenomena, field
 64 evidence demonstrating the impact is sparse³²⁻³⁴. Microbiological communities are known to be
 65 involved in clogging;^{17-19,23,35} however, detailed information on where and when clogging can
 66 occur and potential competition with chemical oxidation is lacking for field conditions^{36,37}. In the
 67 context of geothermal doublets, where fluid residence times in the geothermal loop are brief
 68 (typically few minutes), the mechanisms leading to observed rapid clogging of the system have
 69 not been quantified.

70 Field measurements, batch incubation experiments, and geochemical kinetics modeling were
 71 conducted to provide a quantitative framework for the prediction of clogging of geothermal wells.
 72 An interdisciplinary field campaign was conducted to characterize the key environmental variables

73 involved in mixing induced reactions that cause well clogging, including flow distribution and
74 chemical heterogeneity within the well. A metagenomic study was carried out to investigate
75 microbiological diversity and the potential roles of identified taxa in the chemical reactions. Batch
76 incubation experiments, which included native microbes but excluded previously accumulated
77 sorbent or biofilms, were used to demonstrate rates of change in solution chemistry that result from
78 mixing of water from oxic and anoxic zones in the well. A geochemical kinetics model was then
79 developed to simulate the mixing of the oxic and anoxic waters and observed decreases in
80 dissolved iron and manganese concentrations in the simple batch system (homogeneous kinetics)
81 and in the pumping well system where accumulated precipitate acts as a sorbent (heterogeneous
82 kinetics) within the gravel pack, well bore, and pump. Field observations and modeling results that
83 consider variations in microbial catalysis of Fe^{II} oxidation demonstrate how chemical
84 heterogeneity and biogeochemical reactions promoted by pumping-induced mixing of oxic and
85 anoxic waters can lead to rapid clogging of geothermal loops.

86

87 MATERIALS AND METHODS

88 **Study area.** The field site is a shallow geothermal doublet, DGSY, northeast of the city of
89 Orléans (France) that began operation in October 2011, but eventually failed due to clogging.
90 Technical information on well construction is summarized in **table SI.1** (supporting information).
91 Doublet DGSY extracts groundwater from the limestone aquifer “Calcaire de Pithivier,” which
92 exhibits local karstification. The aquifer is unconfined and vulnerable to contamination as
93 indicated by locally elevated concentrations of volatile organic compounds (1,2-dichloroethene,
94 chloroform, trichloroethylene and methyl *tertiary*-butyl ether) and other unidentified organics that
95 were documented before clogging. Operators report that during the first heating season (winter
96 2011-2012), the heat exchanger was clogged by reddish-brown deposits. Operators tried to

97 maintain the geothermal doublet, however, after multiple rehabilitation efforts, the well pump was
98 removed in May 2016. The pump and the riser pipe were coated by slimy reddish-brown
99 encrustations on the outer surface and underlying hard black deposits on the inner surface (**Figure**
100 **SI.1** in supporting information). The deposits caused a reduction of 20 - 30% of the inner diameter
101 of the riser pipe. Such biofouling was also likely to have accumulated in the well bore and,
102 possibly, in the screen and gravel pack outside the well bore. The same layer of the targeted aquifer
103 is used by another geothermal doublet located 750 m from DGSY. This doublet has been operated
104 since 2008 without clogging issues.

105 In an attempt to understand the striking difference in sensitivity to clogging over a small
106 distance, a series of interdisciplinary field campaigns was conducted during the spring and summer
107 of 2017. In-situ measurements of physical and chemical characteristics were performed during
108 static conditions and while pumped. The latter used a submersible pump (pumping rate of 16 m³/h)
109 placed above the top of the well screen of the pumping well P1 of DGSY to simulate the normal
110 pumping condition.

111

112 **Well logging.** Video camera inspections were performed in each well of DGSY (pumping well
113 P1 and injection well P2), allowing a direct in-situ visualization of clogging deposits. Vertical
114 flowmeter logging was performed during pumping conditions in pumping well P1³⁸. Flowmeter
115 probes measured vertical movement of water in boreholes and allowed estimation of the
116 permeability distribution along the well borehole³⁹. To characterize the groundwater physico-
117 chemical parameters in static and pumping conditions, multiparameter logs (pH, conductivity,
118 dissolved O₂ (DO), Eh and temperature) were performed with a borehole probe in the pumping

119 well P1. Finally, a heat-pulse flowmeter probe was used to detect presence of vertical flows within
120 pumping well P1 in static condition⁴⁰.

121
122 **Chemical and metagenomic analysis.** Water was sampled in pumping well P1 using a
123 submerged well pump. Water was filtered through a 0.2- μm filter on site during sampling. Physico-
124 chemical properties were obtained by using in-situ multiparameter probes placed in a continuous
125 flow cell supplied by the well pump. Concentrations of major cations and anions, trace-element
126 concentrations, dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC)
127 concentrations were analyzed following protocols described in Pédrot et al.⁴¹. Total Fe and Fe^{II}
128 concentrations were measured and showed almost no difference, indicating that Fe is mainly Fe^{II}.
129 An estimate of the relative abundances of all microorganisms was performed in the pumping well
130 P1, by sampling of three replicates of 5 L of groundwater in the top and in the bottom of the well
131 and sequencing of the total DNA by MiSeq run (Illumina INC). Analytical methods are detailed
132 in **supporting information S2**.

133 Moist encrustations were sampled in April 2017 from the P1 pump riser that had been stored in
134 a warehouse since May 2016. A small quantity of deposits was also sampled from the injection
135 well P2. To characterize sampled deposits, scanning electron microscope (SEM) coupled with
136 energy dispersive x-ray and major and trace-element analyses were performed.

137
138 **Estimation of reactivity induced by mixing through batch experiments.** As described in
139 more detail in the Results & Discussion, two productive zones of chemically heterogeneous water
140 (oxic, zone A and anoxic, zone H) were identified in the pumping well P1 during downhole
141 logging. To quantify chemical reactions induced by mixing of the two types of produced water,

142 batch incubation experiments using the oxic and anoxic water were conducted. The batch
143 experiment was designed to evaluate homogeneous oxidation kinetics involving native microbes,
144 but excluding previously accumulated sorbents and biofilms that contribute to heterogeneous
145 oxidation processes. Changes in the chemistry of three sets of water samples were evaluated: (1)
146 oxic water from zone A, (2) anoxic water from zone H, and (3) a 50:50 mixture of the oxic and
147 anoxic water. The water for these batch experiments was collected without atmospheric contact by
148 pumping directly from well P1 at levels A and H into autoclaved glass bottles submerged within
149 water-filled buckets. Ten bottles of each water type and the mixture (obtained by pumping from
150 the oxic and anoxic zones simultaneously) were filled and then sealed with a septum while
151 immersed. The sealed samples were incubated at 20 °C in the laboratory. Over a period of 9 days,
152 one bottle of each series (1 oxic, 1 anoxic and 1 suboxic mixture) was sacrificed daily to measure
153 pH, DO, and concentrations of major ions and trace elements.

154

155 **Geochemical model.** To evaluate potential influences on clogging from various abiotic and
156 biotic kinetic factors, as well as the role of adsorption on the attenuation of Fe^{II} and Mn^{II}, a
157 geochemical model using PHREEQC⁴² was employed. Details of the model construction are given
158 by Cravotta⁴³ and summarized in the **supporting information S1 and S2**. Temperature corrections
159 were automatically applied to constants for aqueous speciation, solubility, and kinetic rate
160 expressions in the geochemical model. The thermodynamic data base, which includes kinetic rate
161 expressions, is available with the model archive file in **supporting information S2**. The model
162 simulates mixing of the oxic water and anoxic water of specified compositions in proportions
163 pumped and considers kinetics of gas exchange and the oxidation of Fe^{II}, Mn^{II}, and organic carbon
164 for three parallel or sequential steps. For the batch oxidation experiment, parallel reactions are

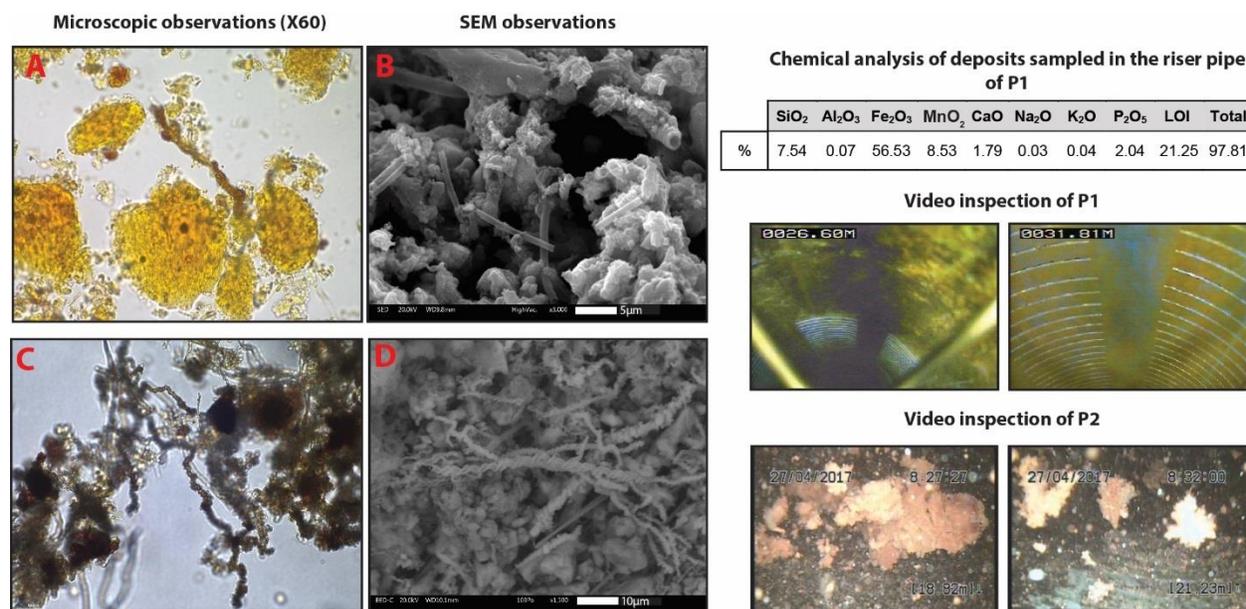
165 simulated for three different water samples: (1) oxic; (2) anoxic; and (3) mixed. The parallel model
166 permits evaluation of the batch experiment as conducted, plus consideration of kinetic variables
167 that may be important for more complex systems. For the more complex well clogging application,
168 sequential steps simulate the generalized flow sequence at pumping well P1 of doublet DGSY: (1)
169 gravel pack in annulus; (2) water column inside the well and screen; and (3) water within the pump
170 and riser pipe to the injection head. Heterogeneous oxidation kinetics are computed for adsorbed
171 Fe^{II} and Mn^{II} . The model computes the neutrophilic iron-oxidizing bacteria (FeOB) contribution
172 to Fe^{II} oxidation as a function of the pH, DO, and adsorbed Fe^{II} .

173

174 **RESULTS & DISCUSSION**

175 **Characteristics of the clogging deposits.** Video revealed clogging deposits covering the inside
176 surface of pumping well P1 from the top down to 33.4 m (6.54 m below the top of the well screen).
177 The clogging deposits are reddish brown and became darker brown upward to the top of the well
178 screen, possibly indicating variations in composition. Below 33.4 m, encrustations were not
179 visible. Pumping tests at P1 showed no significant decrease of the well productivity since the first
180 commissioning (initial values of specific capacity and those obtained during our study are
181 $25 \text{ m}^3/\text{h}/\text{m}$ at $20 \text{ m}^3/\text{h}$ and $48 \text{ m}^3/\text{h}/\text{m}$ at $16 \text{ m}^3/\text{h}$, respectively). The injection well P2 also had
182 extensive deposits on the inner surface of the casing and well screen (**Figure 1**) and strong turbidity
183 in the water column. The video of the injection well showed reddish flocs were easily mobilized
184 from the well surfaces to the water column.

185



186

187 **Figure 1.** Results of microscopic and SEM observations (A - B: deposits from the riser pipe of
 188 pumping well P1, C - D : deposits from the injection well P2), chemical analysis of deposits
 189 sampled in the riser pipe and pictures from the in -situ video inspection of geothermal doublet
 190 DGSY, April 2017.

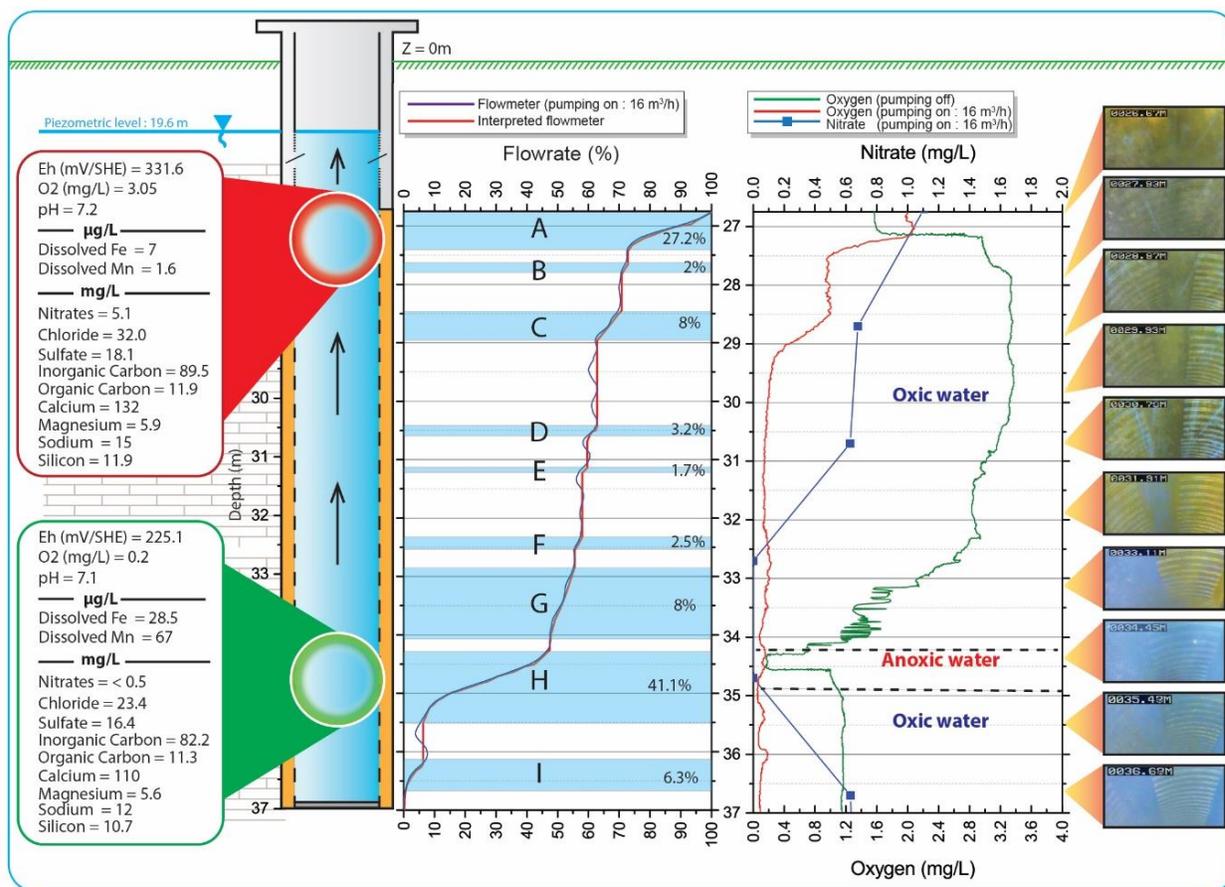
191 The moist deposits in the riser pipe consisted mainly of iron with smaller amounts of silica and
 192 manganese, plus substantial organic carbon and structural water indicated by more than 20 percent
 193 weight loss on ignition (LOI) (**Figure 1**). SEM and microscopic observations indicated the
 194 presence of structures characteristic of FeOB growth (**Figure 1**): Hollow tubes may indicate
 195 *Leptothrix* sp.⁴⁴; twisted stalks may indicate *Gallionella* sp.⁴⁴.

196

197 **Physico-chemical characterization of the groundwater at pumping well P1.** The flowmeter
 198 profile indicated nine productive zones along the well borehole (**Figure 2**). Two major productive
 199 zones, between 26.1 to 27.4 m (zone A) and between 34.2 and 35.5 m (zone H) depth below the
 200 top of the well screen, represented approximately 27.2 % and 41.1 % of the total flux, respectively,

201 during pumping. In static conditions (no pumping), heat-pulse flowmeter logs showed a downward
202 flow (between 0.08 and 0.15 m/min) from the top of the well screen to the bottom of the well
203 (exiting at zone I), indicating that the upper permeable zone has a higher hydraulic head than the
204 lower permeable zone.

205 Dissolved oxygen (DO) profiles indicated significant redox heterogeneity (**Figure 2**). In static
206 conditions, oxic characteristics (DO 1.6 - 3.3 mg/L) predominated above 34.3 m depth, while
207 anoxic characteristics were detected between 34.3 and 34.5 m depth, corresponding to the upper
208 part of zone H. The anoxic conditions coincided with the absence of nitrate (< 0.5 mg/L) between
209 33 and 35 m (**Figure 2**). Hypoxic conditions (DO < 1.2 mg/L) appeared below zone H. During
210 pumping conditions, major inflows of oxygenated water were identified between 26.5 and 27.5 m
211 (zone A) and between 28.5 and 29 m (zone C); however, at greater depths, DO concentrations
212 remained less than 0.2 mg/L.



213

214 **Figure 2.** Vertical profile of dissolved nitrate (mg/L, pumping condition), dissolved oxygen

215 (mg/L, ambient and pumping condition), flow rate (%), video image of the pumping well, and

216 summary of chemical characteristics of the groundwater sampled from productive zones A (oxic)

217 and H (anoxic) in pumping well P1 of doublet DGSY during static conditions, April 2017.

218 Temperature, 12.6°C, is homogeneous along the well borehole.

219 The profiles of measured concentrations of iron and manganese (pumping condition) showed a

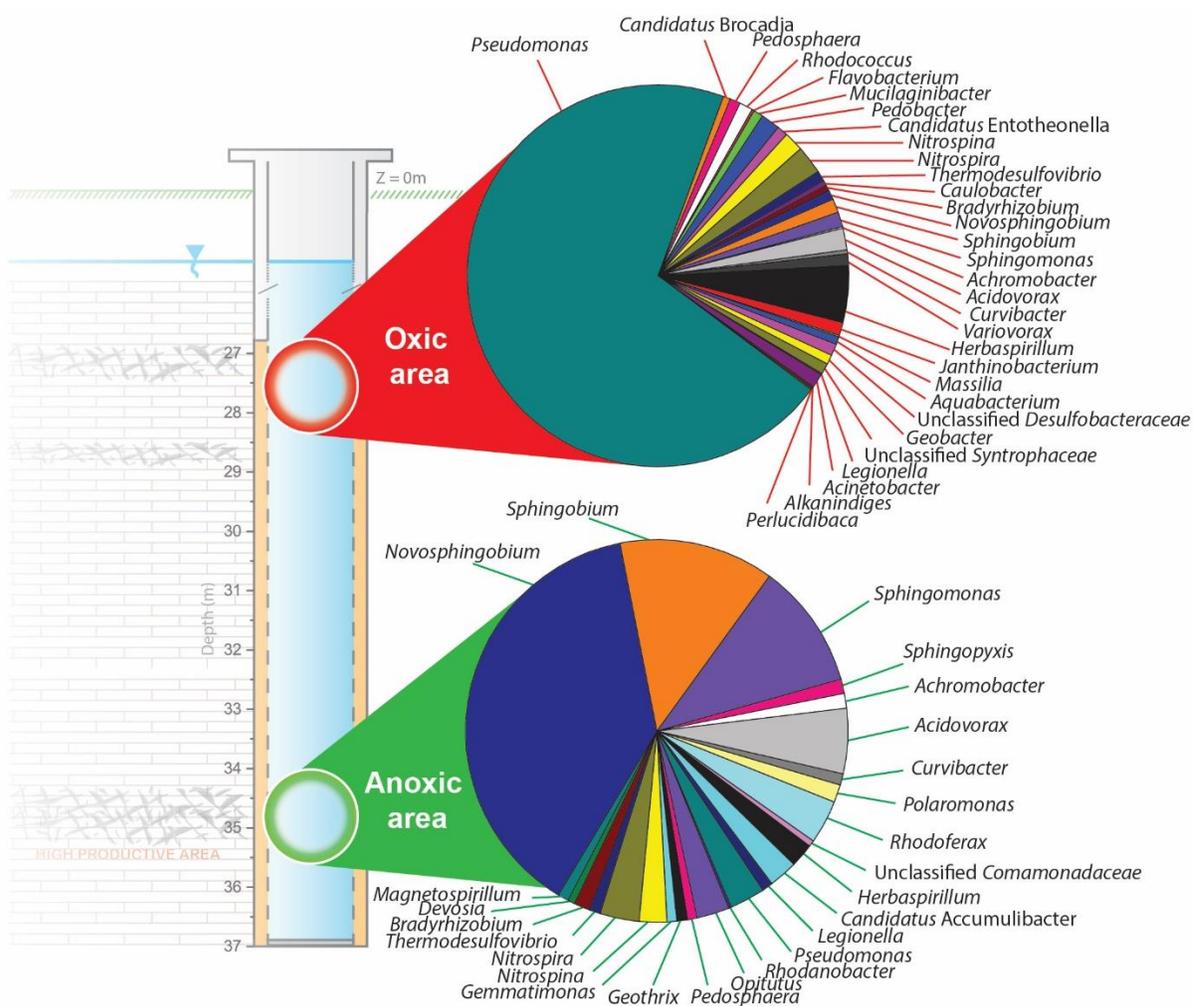
220 maximum near the anoxic zone. Measured concentration of dissolved iron is low compared to

221 previous analysis of total iron performed by the operator at the beginning of the operation

222 (0.1 mg/L in 2011 and 1.1 mg/L in 2014). Measured concentrations of other constituents (dynamic

223 conditions) showed similar vertical heterogeneity along the well screen. Thus, two chemically
224 distinctive waters were identified along the well screens of the pumping well P1 (**Figure 2**).

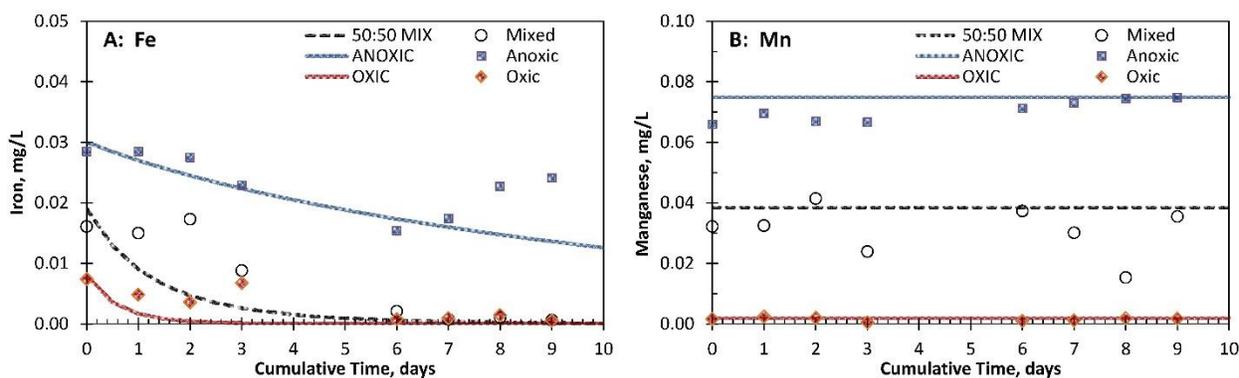
225 **Metagenomic analyses.** The bacteria taxa diversity along the well screen varied vertically
226 (**Figure 3**). Dominant bacteria of the oxic zone are of the *Pseudomonas* genus (e.g., *Pseudomonas*
227 *fluorescens*, *Pseudomonas veronii*) (70.75% of sequences). Globally, the identified bacterial
228 genera in the oxic zone could be involved in manganese oxidation (*Pseudomonas fluorescens*⁴⁵,
229 *Acinetobacter*⁴⁶, *Janthinobacterium*⁴⁷, *Variovorax*⁴⁸, *Caulobacter*⁴⁹, *Flavobacterium*^{47,50,51},
230 *Bradyrhizobium*⁵²) and nitrification (*Nitrospira*, *Nitrospina*). Communities of the anoxic zone
231 (**Figure 3**) are dominated by *Sphingomonadaceae*⁵³ (*Novosphingobium*, *Sphingobium*,
232 *Sphingopyxis* and *Sphingomonas* genera), especially known for degradation of polycyclic aromatic
233 hydrocarbons^{54,55}. Iron reducing bacteria (FeRB) (*Rhodoferrax*, *Geothrix*) are also detected in this
234 zone, as well as *Nitrospira* and *Nitrospina* genera. Moreover, despite the observation by electron
235 microscopy of characteristic structures of the best known FeOB, belonging to the *Gallionellaceae*
236 family (e.g., *Gallionella ferruginea*) and the *Leptothrix* genus (e.g., *Leptothrix ochracea*,
237 *Leptothrix discophora*) in the biofilm, sequences of these bacteria were not found at the two water
238 sampling points in the well. The metagenomics analysis reveals the microbial diversity of the two
239 main water bodies whose mixing induces clogging when operating the geothermal system. While
240 the bacteria involved in clogging process are naturally present in the aquifer, their relative
241 abundance is likely to be modified during the clogging process.



242
 243 **Figure 3.** Relative abundances of bacterial genera present in the groundwater along the well
 244 screens of P1, April 2017.

245
 246

247 **Experimental monitoring of reactive mixing process.** Figures 4 and SI.4 (supporting
248 information) show the observed changes in chemical concentrations of the oxic water, the anoxic
249 water, and the mixed water extracted from pumping well P1 into sealed glass bottles and then
250 monitored daily for 9 days in July 2017. Dissolved manganese concentrations were relatively
251 stable within each series. In contrast, dissolved iron decreased to concentrations below detection
252 and, therefore, is assumed to have been completely oxidized for the mixed water and oxic water.
253 Concentrations of oxygen, nitrate, and dissolved organic carbon decreased in all three samples as
254 shown in Figure SI.4 (supporting information).



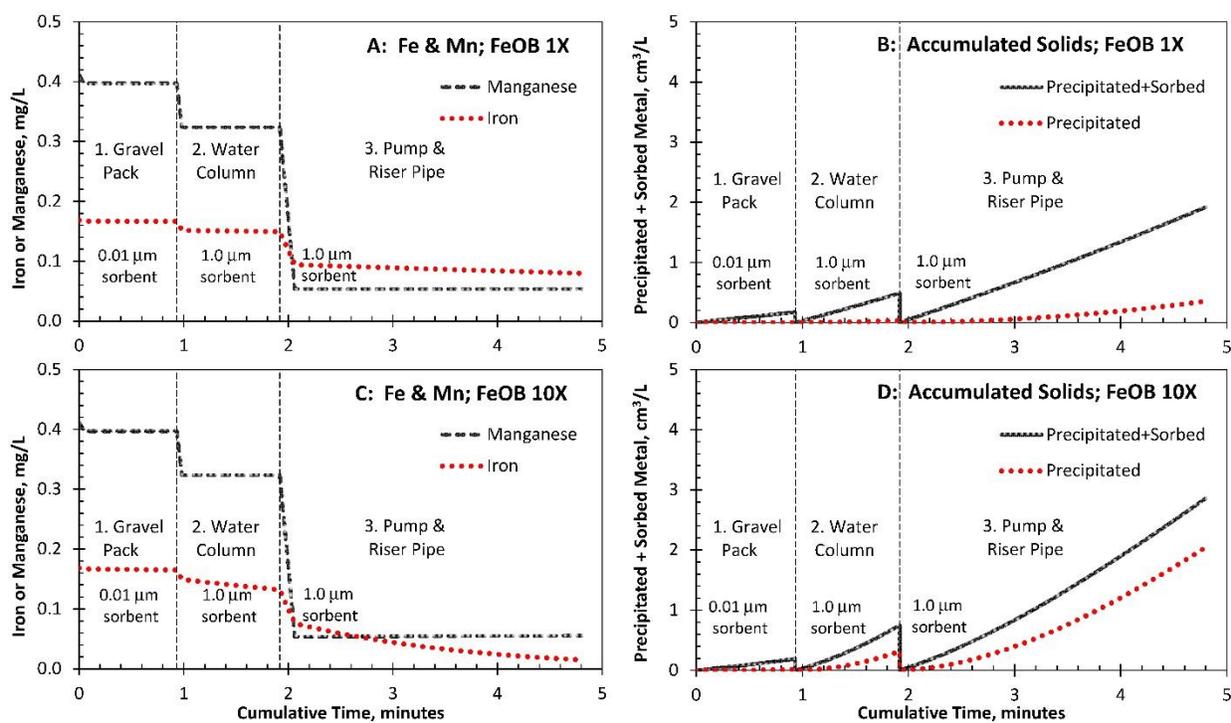
255
256 **Figure 4.** Time series of measured data (points) and PHREEQC simulation (lines) of chemical
257 changes to oxic water, anoxic water, and suboxic water resulting from a 50:50 mixture from
258 pumping well P1 for batch experiment.

259 **Geochemical modeling of reactive mixing process.** Figure 4 shows the model results (curves)
260 compared to the empirical, batch mixing data (points). To simulate the suboxic mixed conditions,
261 the oxic and anoxic waters were mixed in equal proportions (50:50), and the only sorbent
262 considered was that produced by the oxidation and precipitation of initially aqueous Fe^{II} and Mn^{II}
263 (autocatalytic oxidation). The model for the batch experiments demonstrates that the homogeneous
264 Fe^{II} oxidation rate law⁵⁶, with adjustment for organic complexation of dissolved Fe, can account

265 for the observed Fe^{II} oxidation. Organic complexation of aqueous Fe^{II} and Fe^{III} by 1.5 mg/L humate
266 slows down the simulated reaction rate by a factor 0.01, which is consistent with observed rates.
267 Such organic complexation may result from naturally occurring organics, but probably results from
268 locally elevated concentrations of manmade organic compounds (11-12 mg/L of uncharacterized
269 DOC) at doublet DGSY as discussed below.

270 **Figure 5** shows the results for simulations of sequential kinetic reactions within the pumping well
271 system of the geothermal loop that could explain the rapid accumulation of clogging deposits
272 during the 5-minute residence time. For these simulations, the proportion of oxic water and anoxic
273 water was based on flowmeter measurements (respectively 59% and 41%). In contrast to the batch
274 mixing experiment, where the only sorbent considered is that produced by abiotic plus biotic
275 kinetic oxidation of dissolved Fe^{II} and Mn^{II}; the in-situ simulations consider added sorbent and
276 show potential effects on attenuation of Fe^{II} and Mn^{II} by accumulated hydrous ferric oxide (HFO)
277 and hydrous manganese oxide (HMO), plus catalytic activity by FeOB. For both scenarios shown
278 in **Figure 5**, the amount of sorbent in the gravel pack was computed for a thickness of 0.01 μm,
279 whereas that on well and pump was computed for a thickness of 1.0 μm. The accumulations inside
280 the well column and pump were as thick as 0.01 m (**Figure SI.1** in supporting information);
281 however, only a small fraction of that thickness (1.0 μm) is assumed to be in contact with water
282 for surface reactions. Furthermore, the coating on the gravel pack was assumed to be 100% HFO
283 (Fe), whereas that on the well and pump was 97.0% HFO, 2.9% HMO, and 0.1% hydrous
284 aluminum oxide (HAO). Simulation results for the default FeOB oxidation rate (1X) (**Figures.**
285 **5A-5B**) produce the observed “biofouling” with iron-rich solids; increasing the FeOB oxidation
286 rate by a factor of 10 (10X) greatly increases the accumulation of precipitate (**Figures. 5C-5D**).
287 Additional simulation results shown as **Figure SI.5A-5J** (supporting information) demonstrate the

288 effects of different initial coatings (distribution and composition) as well as microbial catalysis
 289 (FeOB rates of 0X, 1X, and 10X) on Fe^{II} and Mn^{II} attenuation.



290
 291 **Figure 5.** PHREEQC simulation of changes in dissolved Fe^{II} and Mn^{II} concentrations in mixed
 292 oxic (59%) and anoxic (41%) water and the consequent volume of precipitated+adsorbed metals
 293 produced by sequential kinetic and equilibrium speciation reactions in gravel pack, water column,
 294 and pump+riser pipe of geothermal loop pumping well P1. Results shown consider previously
 295 accumulated sorbent of varied mass (thickness 0.01 μm in gravel pack and 1.0 μm in well and
 296 pump+riser) and composition (100% HFO in gravel pack, and 97.0% HFO, 2.9% HMO, and 0.1%
 297 HAO in well and pump+riser) plus autocatalytic sorbent: A-B, default (1X) FeOB rate; C-D,
 298 enhanced (10X) FeOB rate.

299
 300 **Biogeochemical processes at the origin of clogging.** Our investigations showed that doublet
 301 DGSY operates within a chemically heterogeneous aquifer (**Figure 2**) with distinct microbial

302 communities in the oxic and anoxic groundwater (**Figure 3**). In the anoxic zone, communities are
303 dominated by *Novosphingobium*, *Sphingobium*, *Sphingomonas* genera, which do not appear in the
304 oxic zones. Such communities are involved in the degradation of polycyclic aromatic
305 hydrocarbons (PAHs)^{24,57,58}. Thus, the anoxic conditions could result from oxygen consumption
306 during bio-oxidation of PAHs that causes the release of dissolved metals from aquifer materials
307 by reductive dissolution. Although no DOC distinction was observed between zone H and other
308 zones, the DOC concentrations were assumed to be remnant of previous oxidation of organic
309 pollutants. SEM analysis and microscopic observations of the deposits from the well pump indicate
310 structures associated with FeOB (iron twisted stalks and iron hollow tubes; **Figure 1**). However,
311 *Gallionella*, *Ferriphaselus* and *Leptothrix* genera were not identified in water samples collected
312 along the well screen. This implies that biological structures in the clogging deposits may result
313 from the activity of different FeOB (i.e. other *Comamonadaceae*⁵⁹ than the known *Leptothrix*
314 bacteria, nitrate-dependent FeOB, or unidentified genera whose genome is not yet referenced), or
315 the water samples may not represent the entire microbial community within biofilms on the well
316 surfaces. Regardless, the positive identification of genera related to iron and manganese oxidation
317 confirms that biological processes are probably involved in clogging processes. Further, once
318 oxidized, Fe^{III} (as HFO) and Mn^{III-IV} (as HMO) may then serve as terminal electron acceptors for
319 FeRB that decompose organic molecules. Sulfate-reducing bacteria (SRB) were observed at a low
320 abundance that may indicate an insignificant contribution to the chemical processes. Although
321 SRB activities have been reported in geothermal wells, redox levels in pumping well P1 were
322 relatively high compared to other geothermal systems.

323

324 **Mass balance of clogging deposits.** The rapid clogging observed during 2011 operations
325 indicates a massive and rapid accumulation of the oxide deposit. We estimated a hypothetical
326 concentration of dissolved iron that could explain the rapid clogging based on the deposit
327 distribution in the water system and the total recorded volume of water pumped since the beginning
328 of operation. Observations of the pump column show a thickness of deposit of about 0.01 m.
329 Assuming a constant thickness along the water system between the submerged well pump of P1
330 and the injection well P2, the estimated volume of clogging deposits is about 0.245 m³. Note that
331 this assumption does not consider the amount of deposits that may have precipitated within the
332 well bore and gravel pack, nor the mobilized deposits that clogged the filter or that had been
333 transported into the injection well P2. Chemical analysis (**Figure 1**) indicates that the dry deposit
334 is composed of 56.5% Fe₂O₃ or 75.7% as Fe(OH)₃. Taking a bulk density of hydrous ferrous
335 oxide⁵⁷ of 1.25 g/cm³, the computed Fe²⁺ concentrations are approximately 0.37 mg/L, which is
336 12 times higher than measured concentrations in 2017 (**Figure 2**), but comparable to the
337 concentrations (0.1 to 1.1 mg/L) reported by the operator at the beginning of operations in 2011.
338 This result indicates that the chemical conditions in the aquifer could have evolved since 2011. In
339 unconfined aquifers, concentrations of chemical species, including redox active species, have
340 seasonal variations linked to recharge or discharge. Evidence of ambient downward vertical flow
341 (infiltration of oxic groundwater from oxic zone to the underlying anoxic zone) was found within
342 the pumping well during static conditions. Since the shutdown of the installation (May 2016), the
343 invasion of oxic water may have caused a progressive oxidation of dissolved iron in the aquifer
344 near the well. Hence, the chemical characteristics of the groundwater extracted from the anoxic
345 zone during our study may differ from the initial conditions of the thermal pump operation in 2011.
346

347 **Location of clogging processes.** Video inspection of the pumping well shows extensive reddish-
348 brown deposits in the upper part of the well and a lack of visible deposits in the anoxic zone. The
349 visible deposits occurred from the piezometric surface at 19.6 m depth to the top of the anoxic
350 zone at 33.4 m depth (**Figure 2**). Thus, clogging deposits appear to develop from the beginning of
351 the geothermal loop where the aqueous Fe^{II} and Mn^{II} in the anoxic water mix with the oxic water
352 during pumping. Presence of this clogging material along the geothermal loop (piping, filter,
353 exchanger and injection well) can be explained by the transport of aqueous and solid forms of Fe
354 and Mn along the flow path, with consequent interactions, explained below.

355
356 **Geochemical modeling of the development of clogging deposits.** The batch mixing
357 experiment demonstrated that mixing of anoxic and oxic waters from the well resulted in more
358 rapid and extensive Fe^{II} oxidation than achieved by solely the anoxic and oxic waters, while little
359 if any Mn^{II} is attenuated (**Figure 4**). For the simulation of the batch experiment, the only sorbent
360 was that formed by the in-situ oxidation of the initial Fe^{II} (0.03 mg/L and 0.008 mg/L) and Mn^{II}
361 (0.075 and 0.002 mg/L) in the anoxic and oxic water, respectively. Complexing by 1.5 mg/L
362 humate was considered to explain the slow rates of Fe^{II} oxidation. A concentration of 1.5 mg/L
363 humate corresponds to approximately 6.5% of the measured, but uncharacterized DOC (11-12
364 mg/L) (**Figure 2**). Humate in the model may be considered a surrogate for natural organic matter
365 (NOM) and manmade organic compounds that have varying capacities to form metal-organic
366 complexes^{60,61}. NOM contains between 40% and 60% C (fulvic acid 40% to 50% and humic acid
367 50% to 60%), whereas organic molecules of manmade origin have wide ranges in concentration
368 of C (tetrachlorethylene 15% C to PAH 90% C). Rose and Waite (2003)⁶⁰ reported that Fe^{II} -NOM
369 complex formation occurs on a similar time scale as Fe^{II} oxidation. Chen and Thompson (2018)⁶¹

370 demonstrated that complexation by natural organic acid substantially retarded Fe^{II} oxidation at 1%
371 O_2 , but had a negligible effect at 21% O_2 . Without the simulated organic complexation of dissolved
372 iron, the model predicted complete Fe^{II} attenuation from the mixed water within 24 hours.

373 The model simulating the mixing and sequential reactions in the pumping well (1) uses an initial
374 concentration of 0.4 mg/L Fe^{II} in the anoxic water, consistent with the mass-balance computations,
375 and (2) indicates that a rapid rate of chemical change, consistent with clogging observations, can
376 take place primarily where previously accumulated HFO and HMO are available for reaction
377 (**Figure 5**). Initial simulations indicate that simple mixing combined with homogeneous
378 (autocatalytic) Fe^{II} oxidation, including microbial catalysis, has a negligible effect on Fe^{II} and Mn^{II}
379 attenuation during the few minutes that water is retained in the well and pumping system (**Figure**
380 **SI.5A-5B**). In this case, the reaction time for kinetic oxidation of Fe^{II} and Mn^{II} increases with
381 distance from the mixing zone, favoring the accumulation of the precipitate further along the flow
382 path between the pumping and injection wells. Such a simulation may mimic the early conditions
383 in doublet DGSY. However, as the clogging deposit accumulated over time, the material began to
384 function as an effective sorbent, catalyst for heterogeneous Fe^{II} and Mn^{II} oxidation, and substrate
385 for microbial growth, all of which facilitated faster and more extensive accumulation of the oxide
386 deposits (**Figures SI.5C-5J**).

387 The simulations show that if a uniform mass of HFO per liter of water is present throughout the
388 gravel pack, well bore, and pump, most of the Fe^{II} and Mn^{II} removal takes place by adsorption
389 processes within the gravel pack, which has a large surface area (**Figures SI.5C-5D**). However,
390 based on our observations, the deposits were more extensive within the upper part of the well,
391 pump, and riser pipe, and the observed materials contained a mixture of HFO and HMO. The
392 simulation results shown in **Figures 5A-5D** (also shown as **Figures SI.5G-5J**) considered a 0.01X

393 smaller mass of sorbent in the gravel pack (0.01 μm thick, where mixing and oxidation are
394 negligible) compared to that within the well and pump (1.0 μm thick, where mixing and oxidation
395 take place), plus variable composition of sorbent (100% HFO in gravel pack; 97.0% HFO, 2.9%
396 HMO, and 0.1% HAO inside well and pump) combined with FeOB activity. Results for the
397 simulations with this heterogeneous sorbent distribution and composition and considering the
398 enhanced (10X) FeOB rate (**Figures 5C-5D** or **SI.5I-5J**) are consistent with the observed
399 biofouling of the pump and riser pipe and demonstrate that accumulated deposits within the upper
400 part of the well system combined with microbial catalysis can have a dramatic effect on attenuation
401 of Fe^{II} and Mn^{II} in that zone. It should be noted that the model default FeOB rate contribution (1X)
402 is an average factor of 20 times the abiotic heterogeneous Fe^{II} oxidation rate under optimum
403 conditions of near-neutral pH (6.5-7.5) and low DO (1.9-2.2 mg L^{-1}), whereas the enhanced rate
404 (10X) modeled is near the maximum FeOB rate reported for those conditions³⁵.

405 Increasing the percentage of HMO in the sorbent increases the attenuation of Mn^{II} . Because the
406 clogging material was heterogeneous, with the black (HMO) deposits overlain by reddish (HFO)
407 deposits, the simulations shown in **Figures 5A-5D** (and **Figures SI.5E-5J**) considered a lesser
408 amount of HMO in the surface layer (97.0% Fe, 2.9% Mn, and 0.1% Al) exposed to the
409 groundwater compared to the content reported for the riser pipe (87.93% Fe, 11.99% Mn, and
410 0.08% Al, expressed as the metals) (**Figure 1**). Simulations for a sorbent with that high HMO
411 content resulted in complete removal of dissolved Mn^{II} , which is inconsistent with observations.

412 The batch incubation experiments and geochemical kinetics models indicate that the rates of
413 homogeneous and heterogeneous Fe^{II} oxidation are relatively slow and inefficient at observed
414 near-neutral pH compared to the short residence time of water in the well bore and gravel pack,
415 even considering microbial catalysis. However, the field observations and modeling of in-situ

416 mixing and oxidation processes indicate that accumulated HFO, HMO, and biofilm on surfaces
417 within the pump and riser pipe, the well bore, and, to a lesser extent, the surrounding gravel pack
418 effectively bind Fe^{II} and Mn^{II} . The adsorbed metals have infinite time for oxidation and provide a
419 convenient source of energy for FeOB that attach to the surfaces. For the modeled conditions
420 within the well, concentrations of dissolved Fe^{II} were low compared to the accumulated HFO
421 sorbent surface area. Despite continuous Fe^{II} adsorption, microbial oxidation of aqueous and
422 (accumulated) adsorbed Fe^{II} replenishes the HFO sorbent. The metagenomics data indicate diverse
423 microbial taxa and heterogeneous conditions in the aquifer; various organisms identified in oxic
424 and anoxic zones could catalyze redox processes. The coupled adsorption and bio-oxidation
425 processes facilitated by mixing of oxic and anoxic waters promote accumulation of $\text{Fe}^{\text{III}}\text{-Mn}^{\text{III-IV}}$
426 precipitate and can thus trigger rapid clogging of pumping wells, despite relatively low
427 concentrations of dissolved oxygen, Fe^{II} and Mn^{II} and short retention times of the groundwater in
428 the well and plumbing system. In addition to restricting flow through the zone of accumulation,
429 scour and transport of precipitated solids could explain rapid clogging of the filter at the heat
430 exchanger within a few hours after a restarting of pumping.

431 The physical and biogeochemical reaction mechanisms described in this study may have a broad
432 relevance for groundwater extraction systems where pumping induces mixing of oxic (O_2/NO_3
433 rich) and anoxic ($\text{Fe}^{\text{II}}/\text{Mn}^{\text{II}}$ rich) groundwaters or introduces oxygenated air into the pumped water.
434 To identify the risk and predict the appearance of clogging processes linked to Fe^{II} and Mn^{II} bio-
435 oxidation, the hydraulic and chemical heterogeneity within the well should be characterized under
436 static and pumping conditions at the start of shallow geothermal projects. In conventional
437 geothermal system design, the feasibility of a geothermal operation is based on the chemical
438 analysis of one water sample obtained at the end of a pumping test. Instead, a depth-oriented

439 sampling strategy, including in-situ water-quality logging, is warranted for identification of
440 potentially oxidizing and reducing conditions along the well screen. In-situ characterization during
441 ambient and dynamic conditions (coupled with flowmeter measurement) is necessary as the
442 chemical signature of the water column inside the well is controlled by natural and induced fluxes.
443 The initial precipitation of HFO and HMO deposits exacerbates additional accumulations, which
444 implies a need for frequent rehabilitation procedures to avoid clogging. The intentional removal
445 of deposits from the pumping well could involve a combination of physical and chemical
446 applications. Adapted preventive methods (automatic back-washing filter, injection well equipped
447 with back-washing pump) could be considered. In situations where clogging risk is significant,
448 closed loop geothermal systems may be considered as an alternative to the open loop doublets.

449

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461

462 **SUPPORTING INFORMATION**

463 Two files of supporting information (Word document and zip file) are offered. SII provides
464 additional details on the characteristics of geothermal doublets DGSY, materials and methods
465 (chemical and metagenomic analyses), and geochemical model development and application.
466 Figures depicting results of geochemical simulations are also included. The model archive is
467 available as a zip file, which includes the executable programs (parallel and sequential models),
468 thermodynamic data base with rate expressions, and Excel files that summarize the simulation
469 results and display the graphics used for figures in the main text and SII.

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