1   # NOM degradation during river infiltration: Effects of the

2   # climate variables temperature and discharge

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1 Abstract

Most peri-alpine shallow aquifers fed by rivers are oxic and the drinking water derived by riverbank filtration is generally of excellent quality. However, observations during past heat waves suggest that water quality may be affected by climate change due to effects on redox processes such as aerobic respiration, denitrification, reductive dissolution of manganese(III/IV)- and iron(III)(hydr)oxides that occur during river infiltration. To assess the dependence of these redox processes on the climate-related variables temperature and discharge, we performed periodic and targeted (summer and winter) field sampling campaigns at the Thur River, Switzerland, and laboratory column experiments simulating the field conditions. Typical summer and winter field conditions could be successfully simulated by the column experiments. Dissolved organic matter (DOM) was found not to be a major electron donor for aerobic respiration in summer and the DOM consumption did not reveal a significant correlation with temperature and discharge. It is hypothesized that under summer conditions, organic matter associated with the aquifer material (particulate organic matter, POM) is responsible for most of the consumption of dissolved oxygen (DO), which was the most important electron acceptor in both the field and the column system. For typical summer conditions at temperatures >20°C, complete depletion of DO was observed in the column system and in a piezometer located only a few meters from the river. Both in the field system and the column experiments, nitrate acted as a redox buffer preventing the release of manganese(II) and iron(II). For periodic field observations over five years, DO consumption showed a pronounced temperature dependence (correlation coefficient r = 0.74) and therefore a seasonal pattern, which seemed to be mostly explained by the temperature dependence of the calculated POM consumption (r = 0.7). The river discharge was found to be highly and positively correlated with DO consumption (r = 0.85), suggesting an enhanced

52 POM input during flood events. This high correlation could only be observed for the

53 low-temperature range (T<15°C). For temperatures >15°C, DO consumption was

54 already high (almost complete) and the impact of discharge could not be resolved.

55 Based on our results, we estimate the risk for similar river-infiltration systems to

56 release manganese(II) and iron(II) to be low during future average summer

57 conditions. However, long-lasting heat waves might lead to a consumption of the

58 nitrate buffer, inducing a mobilization of manganese and iron.

59

60 Keywords: riverbank filtration; climate change; DOM; POM; groundwater quality;

61 redox conditions

62

2 Introduction

63

64   Riverbank filtration is a widely applied technique to produce drinking water and

65 contributes substantially to the overall drinking water production in several European

66 countries (France ~50%, Germany ~16% (Tufenkji et al., 2002), Switzerland ~25%).

67 Natural attenuation processes during river infiltration efficiently remove particles,

68 bacteria, viruses, parasites and, to a lesser extent, organic contaminants, such as

69 pharmaceuticals (Kuehn and Mueller, 2000; Sacher and Brauch, 2002; Grünheid et

70 al., 2005). During river infiltration, biogeochemical processes can alter the

71 composition of the infiltrating water significantly (Jacobs et al., 1988).

72   The most important biogeochemical process during river infiltration is the

73 biodegradation of natural organic matter (NOM), which occurs within bacterial

74 biofilms in riverbed sediments (Pusch et al., 1998). NOM in river systems originates

75 from both allochthonous (terrestrially-derived) sources and generally more

76 biodegradable autochthonous sources (periphyton) (Pusch et al., 1998; Leenheer

and Croue, 2003). NOM is composed of dissolved organic matter (DOM) and

particulate organic matter (POM), usually quantified as dissolved organic carbon

(DOC) and particulate organic carbon (POC), respectively (Leenheer and Croue,

2003). During infiltration of river water, DOM is transported through the riverbed as a

'mobile substrate', whereas POM is retained in the riverbed sediments as a

'stationary substrate' (Pusch et al., 1998).

The biodegradation of NOM in riverbed sediments leads to a consumption of

dissolved or solid terminal electron acceptors, such as oxygen (O_2), nitrate (NO_3^-),

Mn(III/IV)- and Fe(III)(hydr)oxides and sulfate (SO_4^{2-}). Redox conditions in riverbank-

filtration and artificial-recharge systems were observed to undergo seasonal

variations with the formation of anoxic conditions during summer due to the

temperature dependence of NOM degradation (Greskowiak et al., 2006; Massmann

et al., 2006; Sharma et al., 2012).

In the Swiss context, riverbank filtration is often the only barrier between river

water and drinking water. This is possible because of the usually high dilution of

wastewater effluents in receiving rivers and the generally oxic conditions of shallow

groundwater. However, during the hot summer of 2003, the redox conditions in

several riverbank-filtration systems turned anoxic. Hoehn and Scholtis (2011)

reported a case at the Thur River, where the redox sequence even proceeded to

Mn(IV)- and Fe(III)-reducing conditions. The subsequent re-oxidation of dissolved

Mn(II) and Fe(II) at the pumping station led to clogging of the filter screen and to rusty

water.

Climate models predict an increase in summer air temperatures (4-5 K) and a

decrease in precipitation (25%) inducing lower discharges in rivers during summer

months in northern Switzerland by 2085 (CH2011, 2011; FOEN, 2012). Lower

discharges may give rise to less dilution of wastewater effluents and accordingly to

103 higher DOC concentrations. Combined with higher temperatures, the risk for

104 riverbank-filtration systems to become anoxic or even develop Mn(IV)- or Fe(III)-

105 reducing conditions is likely to increase (Sprenger et al., 2011). To assess this risk

106 more accurately, the dynamics of NOM degradation and its dependence on climate

107 variables need to be better understood (Eckert et al., 2008; Green et al., 2011).

108   Besides the direct influence of temperature and discharge, the biogeochemical

109 processes during river infiltration and hence the redox conditions in the infiltration

110 zone might also be affected by indirect climate-related changes in river water quality.

111 The effect of climate change on river water quality (e.g. dissolved oxygen, nutrients

112 (nitrate, ammonium), DOC and major ions) in relation to hydrologic, terrestrial and

113 resource-use factors has been addressed in many studies (Murdoch et al., 2000;

114 Zwolsman and van Bokhoven, 2007; Park et al., 2010). However, Senhorst and

115 Zwolsman (2005) conclude that the impact of climate change on surface water quality

116 is quite site specific and cannot be generally transferred to other watersheds and

117 hence, should be assessed case by case. Therefore, we focused on the direct effect

118 of the climate-related variables temperature and discharge on NOM degradation and

119 the related consumption of electron acceptors during river infiltration.

120   The objectives of the present study were to assess the contribution of DOM

121 consumption to the overall consumption of electron acceptors and to examine the

122 effects of the climate-related variables temperature and discharge by means of field

123 investigations and column experiments. To capture different temperature ranges, the

124 field investigations consisted of two detailed sampling campaigns performed during

125 typical summer and winter conditions at the peri-alpine Thur River. The column

126 experiments were performed at temperatures that span the range of typical field

127 conditions. Additionally, the data of periodic field samplings that covered a wide

128 range of temperature and discharge conditions over a period of five years were

129 evaluated.

130   Firstly, we assessed the temperature dependence of the consumption of

131 dissolved oxygen (DO) and DOM by comparing the data of the field campaigns with

132 those of column experiments and verified the findings by a correlation analysis of the

133 periodic data. Secondly, we investigated the impact of the discharge conditions on

134 DO and DOM consumption using the periodic field data. Finally, we discuss the

135 implications of our findings on the redox-related groundwater quality at riverbank-

136 filtration systems in a changing climate.

137 **3   Materials and Methods**

138 3.1   Field site

139   The field site of our investigation is located in NE-Switzerland (Niederneunforn)

140 at the peri-alpine Thur River, which drains a catchment of 1700 km^2 (Fig. 1a). As no

141 retention basin is located along the whole course of the river, the discharge behaves

142 very dynamically with a range of 3-1100 m^3/s. During the interdisciplinary RECORD-

143 project (Restored corridor dynamics, http://www.cces.ethz.ch/projects/nature/Record,

144 Schneider et al. (2011), Schirmer (2013)), 80 piezometers were installed (Fig. 1b). To

145 the northern side of the river, the piezometers are arranged in two transects, the

146 forest transect and the pumping station transect. Most of the piezometers are fully

147 screened, covering the full aquifer thickness (5.3±1.2 m). The gravel-and-sand

148 aquifer, which is underlain by lacustrine clay and overlain by 0.5-3 m alluvial fines, is

149 highly conductive with hydraulic conductivities between 4×10^{-3} and 6×10^{-2} m/s. The

150 pumping well at the pumping station transect is operated during a daily period of only

151 3 h extracting a total volume of 36 m^3.

152   A groundwater flow and transport model was set up for low-flow conditions

153   (23 m^3/s) and was calibrated against groundwater heads and experimentally

154   determined travel times (Diem et al., 2012; 2013). According to the resulting

155   groundwater flow field (Fig. 1b, c), river water is naturally infiltrating into the aquifer,

156   both at the forest and the pumping station transect. The low abstraction rate of the

157   pumping well was found not to have any significant effect on the infiltration rate or the

158   groundwater flow field. Groundwater flow velocities were in the order of 5-10 m/d at

159   the pumping station transect and ranged between 20-50 m/d at the forest transect.

160   Neither the pumping station transect nor the forest transect can be considered

161   as a typical riverbank-filtration system with high abstraction rates considerably

162   changing the groundwater flow field. Yet, both transects qualify for studying the

163   microbial degradation processes during river infiltration and their dependencies on

164   the climate-related variables temperature and discharge. Compared to the pumping

165   station transect, the forest transect has the advantage of higher flow velocities and

166   shorter residence times to the closest piezometers, which allows a more detailed

167   assessment of the NOM degradation dynamics. Therefore, in this paper, we focus on

168   results from the forest transect.

169

170   Fig. 1

171

172   3.2   Sampling campaigns and periodic samplings

173   To capture different temperature ranges, we conducted two detailed sampling

174   campaigns during summer and winter 2011. We sampled the river and adjacent

175   groundwater on five days between August 19-26, 2011 (summer campaign) and

176   November 23-29, 2011 (winter campaign). The periodic samplings were carried out

177 during a period of five years (2008-2012) and covered a wide temperature and

178 discharge range (supporting information, Fig. S1). Samples were taken in different

179 piezometers at the forest transect. For better clarity, we only present results from a

180 representative subset of the sampled piezometers (Fig. 1c).

181 The groundwater samples were pumped by a submersible electric pump

182 (Whale®, Bangor, Northern Ireland) with an average pumping rate of 10 L/min.

183 Before taking the in-situ measurements and the samples, we pumped at least 20 L

184 (twice the piezometer volume) and waited until the electrical conductivity (EC) of the

185 pumped groundwater was stable. We measured DO concentrations (LDO10115

186 (optical sensor), Hach Lange GmbH, Berlin, Germany, accuracy ±0.1 mg/L), pH and

187 temperature (PHC10115, Hach Lange GmbH, Berlin, Germany, accuracy pH ±0.1,

188 T±0.3 K) and EC (Cond 340i, WTW GmbH, Weilheim, Germany) in a 10 L bottle,

189 which was constantly flushed with groundwater. The small opening on top of the

190 bottle minimized the gas exchange with the atmosphere and thus guaranteed reliable

191 DO measurements at near-zero concentrations. Groundwater and river water was

192 filled into polypropylene bottles (1 L), filtered within 24 h through a 0.45 µm cellulose

193 nitrate filter (Sartorius AG, Göttingen, Germany) and stored at 4°C until analysis.

194 Concentrations of DOC (to quantify DOM), nitrate, ammonium and major ions were

195 measured in the river water and groundwater samples (for analytical method see

196 section 3.4).

197 DO, as well as temperature and discharge were continuously measured (10-min

198 intervals) in the Thur River at a gauging station of the Federal Office for the

199 Environment (FOEN), which is located in Andelfingen, 10 km downstream of our field

200 site (Fig. 1a). The river DO concentrations in Andelfingen were found to agree well

201 with those at our field site (Hayashi et al., 2012). DO concentrations in the river

202 underwent diurnal fluctuations. Such diurnal DO fluctuations are mainly caused by a

203 combination of photosynthesis of periphyton during daytime and respiration during

204 the night (Hayashi et al., 2012).

205   We calculated the DO consumption that occurred during infiltration by

206 subtracting the measured DO concentration in groundwater from the daily mean DO

207 concentration in the river. The latter was calculated based on the continuous DO time

208 series measured at the gauging station in Andelfingen to minimize the bias in

209 calculated DO consumption due to diurnal DO fluctuations in the river. As the diurnal

210 fluctuations of the DOC concentrations in the river were not significant, we subtracted

211 the measured DOC concentration in groundwater from the DOC concentration in the

212 river to calculate the DOM consumption.

213   Eight grab samples were taken from the riverbed at a depth of 0-20 cm close to

214 the first piezometer R050 (Fig. 1c). The samples were dried and sieved; the riverbed

215 sediment mainly consists of sandy gravel with little silt and clay. To quantify the POM

216 contained in the riverbed sediment, we measured the POC concentrations for three

217 grain-size fractions <0.25 mm. The POC concentration was highest for the fraction

218 <0.063 mm (1.4±0.3% w/w), and lowest for the fraction 0.125-0.25 mm (0.5±0.3%

219 w/w) (for analytical method see section 3.4).

220 3.3 Column experiments

221   A schematic representation of the set-up of the column experiments is shown in

222 Fig. 2. The column casing consisted of a Plexiglas tube (length 30 cm, inner diameter

223 5.2 cm) and was packed with fractionated sand (0.125-0.25 mm grain size) from a

224 gravel bar at the field site close to the forest transect. The sand was dried at room

225 temperature and sieved afterwards before being dry-filled into the column in form of a

226 "sand rain" (von Gunten and Zobrist, 1993). The sand was mainly composed of

227 calcite and quartz (40% and 25%, respectively) and the POC concentration was

228   about 0.3±0.2% (w/w). The sand fraction 0.125-0.250 mm was chosen because it is

229   well defined and represents the available reactive surfaces with a considerable

230   amount of POM.

231   Filtered Thur River water (0.45 µm, cellulose nitrate, Sartorius AG, Göttingen,

232   Germany) was stored in a 2 L tank and was used as feed water for the column. It was

233   pumped from the bottom to the top of the column at a flow rate of 0.4 L/d by means

234   of an HPLC pump (Jasco PU-2080, Jasco Corporation, Tokyo, Japan) (Fig. 2). Every

235   three days, the storage tank was replenished with fresh Thur River water stored at

236   5°C. In case of the experiment at 20°C, Thur River water was allowed to equilibrate

237   for about 6 hours before replenishment. No measurable DOM degradation in the

238   storage tank was observed under these conditions. To assess the hydraulics in the

239   column, a tracer test with a 8.55 mM NaCl solution was conducted and the EC was

240   measured at the end of the column. We estimated an effective porosity of 0.32 and a

241   dispersivity of 0.08 cm by inverse modeling with the software CXTFIT (Toride et al.,

242   1995). The corresponding total pore volume of the column was 0.2 L. Hence, the

243   residence time in the column was 0.5 d at a flow rate of 0.4 L/d.

244   The column was first operated at 20°C in a climatised chamber for 19 days after

245   an equilibration time of about 2 months with Thur River water taken on July 4, 2012

246   (composition 1, Table S1, supporting information). After that, the column was

247   operated at 5°C with the same feed water in an incubator for 26 days including an

248   equilibration time of 20 days. Thereafter, as a control experiment, the column was

249   operated again at 20°C in an incubator for 28 days including an equilibration time of

250   22 days (water composition 2, Table S2, supporting information). This control

251   experiment was conducted to test if any of the column properties relevant for the

252   bacterial degradation processes (sand composition, POM concentration/composition)

253   had changed during the operation period at 5°C.

254   The column featured 15 sampling ports; one at the inlet, 13 along the column

255   and one at the outlet (Fig. 2). DO and temperature were continuously measured at

256   the inlet and at the outlet of the column (LDO101 (optical sensor), Hach Lange GmbH,

257   Berlin, Germany, accuracy ±0.1 mg/L, T±0.3 K), while pH was measured after the

258   column (PHC 301, Hach Lange GmbH, Berlin, Germany, accuracy pH ±0.1) in flow-

259   through cells (Fig. 2). For each of the experiments at different temperatures, we

260   measured three DO concentration profiles after an equilibration time of ≥20 d. DO

261   was measured directly at each sampling port in a flow-through cell. After that, about

262   40 mL of sample volume was taken at the column inlet (SP0) and outlet (SP14) for

263   the DOC and nitrate analyses by connecting a rinsed regenerated 0.45 µm cellulose

264   filter (National Scientific Company, Rockwood, USA) to the port. The sampling

265   procedure was conducted from the outlet to the inlet of the column, following the

266   opposite direction of the water flow.

267   The DO consumption in the column was calculated by subtracting the measured

268   DO concentration at sampling port SP14 from the DO concentration at SP0 0.5 d

269   before. The DOM consumption was determined from the difference of DOC

270   concentrations at SP14 and SP0.

271

272   Fig. 2

273

274   3.4   Analytical methods

275   DOC concentrations were measured with a Shimadzu TOC-V CPH (Shimadzu

276   Corporation, Kyoto, Japan). Nitrate and the other major ions were analyzed by

277   means of a Metrohm 761 Compact IC (Metrohm Schweiz AG, Zofingen, Switzerland).

278   Ammonium was measured with a Spectrophotometer Varian Cary 50 Bio (Varian BV,

279   Middelburg, The Netherlands). The POC concentrations in sediment samples were

280   determined by subtracting the inorganic carbon fraction, measured with a CO_2

281   Coulometer CM5015 (UIC Inc., Joilet, USA), from the total carbon fraction, measured

282   with a CNS analyzer Eurovector EA3000 (Hekatech GmbH, Wegberg, Germany).

283   **4   Results and Discussion**

284   4.1   Hydraulic conditions and concentration profiles of redox-active

285   compounds

286   The winter and the summer sampling campaigns were conducted during low-

287   flow conditions. The daily mean discharge of the Thur River during the field sampling

288   campaigns varied between 13.7 and 24.8 m^3/s in summer and between 5.4 and

289   6.1 m^3/s in winter (Fig. 3). The daily mean temperatures in the river ranged from 20.9

290   to 22.9°C in summer and from 5.9 to 6.7°C in winter (Fig. 3).

291

292   Fig. 3

293

294   The groundwater residence times between the river and the piezometers were

295   estimated based on a groundwater flow model as well as the analysis of EC time

296   series (Diem et al., 2013) and ranged from 0.5 d at the piezometer closest to the river

297   (R050) to 13 d at the piezometer furthest from the river (R023) (Fig. 1c, Fig. 4). As

298   the mean residence time in the column was 0.5 d, the column well represented the

299   situation at piezometer R050. The column experiments additionally allowed resolving

300   the microbially-mediated redox processes on a scale that was not accessible in the

301   field system.

302   The temperature and the concentration profiles of selected redox-active

303   compounds are shown in Fig. 4 for the sampling campaigns and in Fig. 5 for the

304   column experiments. Most of the DO and DOM consumption in the field occurred

305   between the river and the first piezometer (R050), both during summer and winter

306   conditions. This observation indicates that most of the degradation processes took

307   place within the first meters of the infiltration zone and shows that, in agreement with

308   other studies (Bourg and Bertin, 1993; Brugger et al., 2001a; Sobczak and Findlay,

309   2002), the microbial activity was highest in this zone. For the piezometers further

310   away from the river, an additional decrease in DO and DOC was observed in winter.

311   However, considering the longer travel times to these piezometers, the

312   corresponding degradation processes occurred much slower.

313

314   Fig. 4

315

316   The DO concentration profiles for the column experiments revealed that the

317   highest DO consumption rate occurred between the first two sampling ports. This is

318   in accordance with other column experiments, for which the highest DO consumption

319   rate was observed within the first centimeter of the column (von Gunten and Zobrist,

320   1993; von Gunten et al., 1994). At 20°C, the initial decrease of DO was followed by a

321   linear decrease in the column, while at 5°C the DO concentration remained constant

322   after the initial decrease (Fig. 5a). The linear decrease at 20°C suggests a zero-order

323   degradation rate, which means that the DO consumption in the column was not

324   limited by the substrates DO and NOM. The DO profile of the control experiment

325   (performed after the 5°C experiment) was almost identical to the DO profile of the

326   first experiment at 20°C (Fig. S3, supporting information). This indicates that the

327   column properties decisive for the bacterial degradation processes did not change

328   during the operation period at 5°C.

329   We consider aerobic respiration of NOM as the only process responsible for the

330   consumption of DO. Based on measured ammonium concentrations in river water,

331   nitrification (oxidation of ammonium) potentially accounted for ≤2% of the DO

332   consumption in the field campaigns and the column experiments, and can therefore

333   be neglected. The removal of DOM during river infiltration might be attributed to both

334   microbial degradation and abiotic sorption processes (Brugger et al., 2001b).

335   However, the summer and winter field sampling campaigns were conducted during

336   relatively stable temperature and discharge conditions. It is therefore reasonable to

337   assume that the sorption processes were in steady state and did not affect the

338   removal of DOM. The same is true for the column system, which was equilibrated for

339   ≥20 d before the measurements were taken. Therefore, we assume that microbial

340   degradation processes dominated the abiotic sorption processes, which is in

341   agreement with Sobczak and Findlay (2002).

342   The DO consumption between the river and the first piezometer (R050) was

343   larger in summer than in winter and that between the column inlet and column outlet

344   was larger at 20 than at 5°C. This is a clear indication of the temperature

345   dependence of the microbially mediated degradation of NOM by aerobic respiration.

346   In contrast, the consumption of DOM was similar during summer and winter

347   conditions with about 0.7 mg C/L (Fig. 4) during the field sampling campaigns and

348   about 0.3 mg C/L (Fig. 5) in the column experiments. Furthermore, the DOM was not

349   consumed completely, both during the field sampling campaigns and in the column

350   experiments. Only a fraction of about 30-50% of the total DOM was degraded,

351   corresponding to the biodegradable DOM (BDOM). Similar values for the BDOM

352 fraction were reported in several field studies (Sobczak and Findlay, 2002; Sharma et

353 al., 2012). 50-70% of the DOM remained, presumably due to its recalcitrant nature.

354   During summer conditions, DO was nearly completely consumed at the first

355 piezometer R050 (Fig. 4). Similarly, almost anoxic conditions were observed at the

356 column outlet at 20°C (Fig. 5). However, denitrification was not observed either in the

357 field, or in the column. Apparently, under summer conditions, there is enough nitrate

358 available to act as a redox buffer preventing Mn(IV)- and Fe(III)-reducing conditions

359 in the infiltration system.

360

361 Fig. 5

362

363 4.2   Impact of temperature on DO and DOM consumption

364 4.2.1   Sampling campaigns and column experiments

365   To assess the impact of temperature on the aerobic NOM degradation, we

366 compared the DO and DOM consumption between the river and the first piezometer

367 (R050), and between the column inlet and outlet for summer and winter conditions.

368 The resulting mean DO and DOM consumption for the field campaigns and column

369 experiments are shown in Fig. 6. For a simplified version of aerobic respiration, one

370 mole of DO (O_2) is used to oxidize one mole of organic carbon (CH_2O) (Eq. 1):

371

372      $CH_2O + O_2 \rightarrow CO_2 + H_2O$ (1)

373

374   Accordingly, if DOM consumption would explain the entire DO consumption, the

375 corresponding molar consumptions should be equal (bars in Fig. 6). However, during

376 summer conditions (both in the field and in the column), DOM consumption explained

377 only 10-20% of DO consumption (Fig. 6). The remaining 80-90% of the reduction

378 capacity to explain the DO consumption must therefore have been provided by other

379 sources. POM in riverbed sediments and the column sand is an obvious source of

380 additional reduction capacity (Brugger et al., 2001b; Sharma et al., 2012).

381   As mentioned in section 4.1, DO consumption in the field and the column

382 system was much smaller for lower than higher temperatures, while the DOM

383 consumption remained at about the same level (Fig. 6) and did not seem to be

384 significantly affected by temperature. As a result, DOM consumption accounted for

385 larger fractions of 50% and 100% of the DO consumption at lower temperatures in

386 the column and the field, respectively. Furthermore, the different behavior during

387 summer and winter conditions suggests that the variability and temperature

388 dependence of DO consumption are determined by the POM, rather than the DOM

389 consumption.

390

391 Fig. 6

392

393 4.2.2 Periodic samplings

394   To test the dependence of the DO and DOM consumption on temperature more

395 systematically, we compiled the corresponding data of all the samplings taken

396 between 2008 and 2012 at the Thur River and the piezometer R050. We additionally

397 calculated the POM consumption according to Equation (2) assuming that the POM

398 consumption corresponds to the difference between DO and DOM consumption:

399

400      $\Delta POC = \Delta DO - \Delta DOC$ (2)

401

402   Fig. S2 (supporting information) shows the DOM and the calculated POM

403   consumption of all the 45 periodic samplings, including the two sampling campaigns

404   of summer and winter 2011. Fig. 7 shows a plot of the DO consumption, the DOM

405   consumption and the calculated POM consumption as a function of the daily mean

406   river water temperature in scatter plots together with the calculated correlation

407   coefficients. The DO consumption showed a high and significant correlation ($r = 0.74$,

408   Fig. 7a) with the daily mean river water temperature. Thus temperature explained the

409   variation in DO consumption to a high degree. However, DOM consumption was not

410   correlated with river water temperature (Fig. 7b). This result coincides with the data

411   shown in Fig. 6 and is in agreement with findings from Brugger et al. (2001b). Since

412   the calculated POM consumption (Fig. 7c) is based on the difference between one

413   highly-correlated parameter (DO consumption) and one uncorrelated parameter

414   (DOM consumption), it is necessarily the case that POM consumption will also be

415   highly correlated with temperature ($r = 0.7$).

416   This result supports the conjecture that the POM consumption is primarily

417   responsible for the variability and temperature dependence of DO consumption, as

418   stated in section 4.2.1. The divergence between the temperature dependencies

419   observed for DO and DOM consumption also have the consequence that DOM

420   consumption accounts for a larger proportion of DO consumption at lower than at

421   higher temperatures. At lower temperatures ($<10°C$), DOM consumption accounted

422   for 50-100% of DO consumption, while at high temperatures ($>15°C$), DOM

423   consumption accounted for 0-40% of DO consumption (Fig. 7). Correspondingly, the

424   calculated POM consumption makes a more important contribution at high

425   temperatures, suggesting that POM is the most important electron donor under these

426   conditions.

427

428   Fig. 7

429

430   4.2.3   Conceptual explanation

431   The fact that no correlation was observed between DOM consumption and

432   temperature does not mean that this process is not temperature dependent. One

433   conceptual explanation is based on the fact that consumption of the biodegradable

434   fraction of DOM (BDOM) occurs generally at high degradation rates as it is present in

435   a dissolved and bioavailable form. Even though the BDOM degradation rates might

436   be lower at lower temperatures, bacteria most likely were able to completely

437   consume the full BDOM fraction within the residence times of our field and column

438   systems. Accordingly, on our scales of observation, the DOM consumption was

439   limited by the amount of BDOM rather than by temperature-dependent rates. In

440   contrast, POM consumption involves the cleavage of organic macromolecules into

441   soluble monomers by extracellular hydrolytic enzymes (Egli, 1995; Pusch et al.,

442   1998). Therefore, degradation of POM generally occurs at lower rates than

443   degradation of BDOM (Greskowiak et al., 2006; Sharma et al., 2012) and the

444   temperature dependence of POM degradation could be resolved on the timescales of

445   our experimental systems (field, column).

446   This conceptual explanation is based on the assumption that DOM resulting

447   from hydrolysis of POM in bacterial biofilms does not contribute significantly to the

448   DOM pool in the sampled groundwater, and hence did not affect the observed DOM

449   consumption (Fig. 7b). In literature, the hydrolysis of POM is considered to be the

450   rate-limiting step in POM degradation, which implies that the DOM resulting from

451   hydrolysis undergoes fast biodegradation (Valentini et al., 1997; Henze et al., 1999;

452   Vavilin et al., 2008). Furthermore, there is evidence that DOM uptake and

453   transformation by bacteria is very efficient in biofilms (Pusch et al., 1998). Bacterial

454   biofilms in sediments act thus as effective sinks of DOM that originated either from

455   the river (as 'transported/mobile substrate') or from the hydrolysis of POM ('stationary

456   substrate').

457   4.3   Impact of discharge on DO and DOM consumption

458   The temperature dependence of DO consumption might be superimposed by a

459   dependence on hydrologic conditions. High-discharge conditions or flood events are

460   generally not considered to affect the redox conditions in the infiltration zone

461   (Sprenger et al., 2011), but rather to increase the risk of a breakthrough of

462   contaminants or pathogens at the pumping well due to shorter groundwater

463   residence times (Schubert, 2002). However, it is well known that the suspended POM

464   concentration in the river increases with river discharge, as a result of an increased

465   mobilization of allochthonous and autochthonous POM (Meybeck, 1982). The

466   contribution of periphyton (autochthonous POM) to the suspended POM pool in a

467   river was found to positively correlate with discharge, because of the increased

468   abrasive action at the riverbed (Uehlinger, 2006; Akamatsu et al., 2011). Furthermore,

469   it has been observed that the POM import into gravelly riverbed sediments mostly

470   occurred during flood events, which increased the POM concentrations and the

471   microbial respiration rate in the riverbed sediments (Naegeli et al., 1995; Brunke and

472   Gonser, 1997). Hence, the higher POM availability in the riverbed during high-

473   discharge conditions might give rise to an increased DO consumption during river

474   infiltration.

475   The overall correlation between DO consumption and the daily mean discharge

476   (measured in Andelfingen) was small and not significant (Table S3, supporting

477   information). However, DO consumption increased with increasing discharge up to

478   60 m^3/s and leveled off at 200-300 μmol/L beyond this point (Fig. 8). As the data for

479   discharges below 60 m^3/s covered a wide range of temperatures, DO consumption

480   showed only a weak correlation with discharge (r = 0.31). To compensate for the

481   temperature dependence, we defined two temperature ranges, T<15°C (circles) and

482   T>15°C (triangles). Following this separation, we found a significant correlation

483   between DO consumption and discharge for the low-temperature range (r = 0.85).

484   DOM consumption was not correlated with discharge (Table S3, supporting

485   information) suggesting that the increase in DO consumption is probably caused by

486   an enhanced POM consumption, which supports the notion described above.

487   For the high-temperature range, the correlation between DO consumption and

488   discharge was small and not significant. This result can be explained by the fact that

489   DO consumption for the high-temperature range was already high (200-300 μmol/L)

490   and nearly complete at low discharges. Hence, an increase in discharge could not

491   lead to a significant increase in DO consumption.

492   Another process that might explain the increased DO consumption at higher

493   discharges is the leaching of DOM from the soil and vegetation (root zone) at high

494   groundwater tables. At our field site, this effect was found to be restricted to a zone

495   dominated by the pioneer plant *salix viminalis* (willow bush) (Peter et al., 2012). The

496   piezometer R050 was located close to the river, where the gravel-and-sand aquifer is

497   covered by a relatively thin layer of alluvial fines (0.3 m) with no or only little grass

498   vegetation. For this zone, the input of DOM from the soil and vegetation was found to

499   be negligible (Peter et al., 2012).

500

501   Fig. 8

502

503   Low-discharge conditions are expected to promote the DO consumption as a

504   result of increased groundwater residence times and higher loads of DOM in the river

505   due to less dilution of wastewater effluent (Sprenger et al., 2011). In our observations,

506   however, DO consumption did not reveal a significant increasing trend for decreasing

507   discharges, regardless of the considered temperature range (Fig. 8). Furthermore,

508   the DOM consumption did not reveal any significant correlation with discharge, but

509   was positively correlated with DOC concentrations in the river (Table S3, supporting

510   information). However, DOC concentrations in the river increased rather than

511   decreased with discharge; the correlation was weak but significant. This suggests

512   DOM sources other than wastewater treatment plants.

513   4.4   Implications for groundwater quality at riverbank-filtration systems

514   The latest climate change scenarios predict an increase in summer and winter

515   air temperature of 4-5 K for NE-Switzerland by 2085. Furthermore, extreme events,

516   such as summer heat waves, are expected to occur with a higher frequency and

517   intensity (CH2011, 2011). River discharges are expected to decrease in summer and

518   increase in winter. River water temperature, which is decisive for the degradation

519   processes in the riverbed, is likely to increase by the same extent as air temperature,

520   especially during low-flow conditions (FOEN, 2012). During the hot summer of 2003,

521   the mean river water temperature of the Thur River was 22°C for a period of 70-80 d.

522   In the future, we might have to deal more frequently with extreme events of similar or

523   longer duration and even higher mean river water temperatures.

524   According to our results, the calculated POM consumption showed a

525   pronounced temperature dependence and accounted for most of the DO

526   consumption during summer. Consumption of DO was enhanced during high-flow

527   conditions, probably due to an increased import of POM into the riverbed. On our

528 scales of observation, we could not identify any temperature dependence of the DOM

529 consumption, which was rather limited by the fraction of BDOM. Moreover, the

530 expectation that low-discharge conditions would lead to higher DOC concentrations

531 in the river due to less dilution of wastewater effluents, and hence to an increased

532 DOM and DO consumption during river infiltration, is not supported by our data.

533   Sprenger et al. (2011) assessed the vulnerability of riverbank-filtration systems

534 to climate change (drought and flood scenarios) with respect to several water quality

535 parameters (DOM, nutrients, pathogens). The vulnerability of a riverbank-filtration

536 system to climate change with respect to the redox milieu in groundwater might

537 depend on three major factors. (1) The hydraulic connection between the river and

538 groundwater. If infiltration occurs through an unsaturated zone, which is aerated,

539 complete DO depletion is not expected (Huggenberger et al., 1998; Hoehn and

540 Scholtis, 2011). During infiltration in direct hydraulic connection to the groundwater

541 table (saturated), which was the case at our field site, DO is not replenished and

542 might become depleted, as observed during summer. (2) Based on our results, we

543 consider the catchment characteristics as another decisive factor. Rivers in

544 catchments without a retention basin (e.g. a lake) have a more dynamic discharge

545 regime and are likely to have a higher POM load, especially during flood events. (3)

546 The grain-size distribution of the riverbed sediments. In gravelly riverbeds, the import

547 of POM is possible to deeper layers, while in sandy or clogged riverbeds, the import

548 of POM might be physically hindered (Brunke and Gonser, 1997). We therefore

549 anticipate the highest vulnerability to climate change with respect to the redox milieu

550 for riverbank-filtration systems at which infiltration occurs through a gravelly riverbed

551 in direct hydraulic connection to the groundwater table and which are located in

552 catchments without a retention basin.

553   For such riverbank-filtration systems, we consider future summer heat waves to

554   be critical for the redox-related groundwater quality. A substantial increase in river

555   water temperature during future heat waves will enhance the POM turnover, leading

556   to a complete consumption of DO and potentially nitrate. As a consequence, Mn(II)

557   and Fe(II) could be released, as observed during the hot summer 2003 (Hoehn and

558   Scholtis, 2011). An additional POM input into the riverbed during flood events

559   induces a higher consumption of DO and possibly nitrate, which may enhance the

560   risk for Mn(III/IV)-/Fe(III)-reducing conditions in the infiltration zone.

561   The subsequent re-oxidation of Mn(II) and Fe(II) and precipitation of Mn(IV)-

562   and Fe(III)(hydr)oxides can lead to clogging problems and deterioration of the

563   drinking water quality (rusty water) at pumping stations of a drinking water supply.

564   For the removal of dissolved Mn(II) and Fe(II), conventional pump-and-treat

565   techniques can be applied, which are based on physical-chemical or biological

566   processes (Mouchet, 1992). Alternatively, in-situ techniques can be used, in which

567   the oxidation processes take place directly in the aquifer (Mettler et al., 2001).

568   **5   Conclusion**

569   We performed field investigations and laboratory column experiments to

570   investigate the dynamics of redox processes during river infiltration and their

571   dependence on the climate-related variables temperature and discharge. The

572   observations of the summer and winter sampling campaigns in the field could be

573   successfully reproduced by column experiments. Particulate organic matter (POM)

574   was identified as the main electron donor for dissolved oxygen (DO) consumption

575   during summer conditions and both the DO and the calculated POM consumption

576   revealed a pronounced temperature dependence. The DO consumption was

577   enhanced during flood events, presumably due to an additional POM input into the

578   riverbed.

579   In our field and column systems, DO was the most important electron acceptor.

580   In summer (T>20°C), DO concentrations in groundwater were close to zero, but

581   denitrification was not observed. Similarly, most of the Swiss aquifers fed by rivers

582   are (sub)oxic under today's summer conditions and nitrate buffers the redox system

583   before it becomes Mn(III/IV)- and Fe(III)-reducing. Therefore, currently there is no

584   need to implement demanganation and deferisation. However, during future summer

585   heat waves, an enhanced availability of POM as electron donor could lead to a full

586   consumption of DO and nitrate, enabling the release of Mn(II) and Fe(II). As the

587   source, quality and quantity of POM and its input into the riverbed are very difficult to

588   assess, it is nearly impossible to find direct intervention strategies.

589   We recommend long-term monitoring of the redox conditions at riverbank-

590   filtration systems, which are characterized by an infiltration that occurs through a

591   gravelly riverbed in direct hydraulic connection to the groundwater table, and by

592   catchments without a retention basin. Long-term data will allow taking adequate

593   measures in time, while accounting for the site-specific hydrogeological conditions.

594   **6   Acknowledgements**

7   References

609 Akamatsu, F., Kobayashi, S., Amano, K., Nakanishi, S., Oshima, Y., 2011.

610   Longitudinal and seasonal changes in the origin and quality of transported

611   particulate organic matter along a gravel-bed river. Hydrobiologia 669 (1), 183-

612   197.

613 Bourg, A.C.M., Bertin, C., 1993. Biogeochemical Processes during the infiltration of

614   River Water into an Alluvial Aquifer. Environ. Sci. Technol. 27 (4), 661-666.

615 Brugger, A., Reitner, B., Kolar, I., Queric, N., Herndl, G.J., 2001a. Seasonal and

616   spatial distribution of dissolved and particulate organic carbon and bacteria in

617   the bank of an impounding reservoir on the Enns River, Austria. Freshwater

618   Biol. 46 (8), 997-1016.

619 Brugger, A., Wett, B., Kolar, I., Reitner, B., Herndl, G.J., 2001b. Immobilization and

620   bacterial utilization of dissolved organic carbon entering the riparian zone of

621   the alpine Enns River, Austria. Aquat. Microb. Ecol. 24 (2), 129-142.

622 Brunke, M., Gonser, T., 1997. The ecological significance of exchange processes

623   between rivers and groundwater. Freshwater Biol. 37 (1), 1-33.

624 CH2011, 2011. Swiss Climate Change Scenarios CH2011. C2SM, MeteoSwiss, ETH,

625   NCCR Climate and OcCC, Zurich, pp. 88.

626   Diem, S., Renard, P., Schirmer, M., 2012. New methods to estimate 2D water level

627   distributions of dynamic rivers. Ground Water, doi: 10.1111/gwat.12005.

628   Diem, S., Renard, P., Schirmer, M., 2013. Assessing the effect of different river water

629   level interpolation schemes on modeled groundwater residence times.

630   Submitted to Journal of Hydrology.

631   Eckert, P., Lamberts, R., Wagner, C., 2008. The impact of climate change on drinking

632   water supply by riverbank filtration. Water Sci. Technol.: Water Supply 8 (3),

633   319-324.

634   Egli, T., 1995. The ecological and physiological significance of the growth of

635   heterotrophic microorganisms with mixtures of substrates. In: Jones, G.N.

636   (Ed.), Advances in Microbial Ecology. Plenum Press, New York, pp. 305-386.

637   FOEN, 2012. Effects of climate change on water resources and watercourses.

638   Synthesis report on the "Climate Change and Hydrology in Switzerland"

639   (CCHydro) project. Federal Office for the Environment FOEN, Bern, pp. 76.

640   Green, T.R., Taniguchi, M., Kooi, H., Gurdak, J.J., Allen, D.M., Hiscock, K.M., Treidel,

641   H., Aureli, A., 2011. Beneath the surface of global change: Impacts of climate

642   change on groundwater. J. Hydrol. 405 (3-4), 532-560.

643   Greskowiak, J., Prommer, H., Massmann, G., Nützmann, G., 2006. Modeling

644   seasonal redox dynamics and the corresponding fate of the pharmaceutical

645   residue phenazone during artificial recharge of groundwater. Environ. Sci.

646   Technol. 40 (21), 6615-6621.

647   Grünheid, S., Amy, G., Jekel, M., 2005. Removal of bulk dissolved organic carbon

648   (DOC) and trace organic compounds by bank filtration and artificial recharge.

649   Water Res. 39 (14), 3219-3228.

650   Hayashi, M., Vogt, T., Machler, L., Schirmer, M., 2012. Diurnal fluctuations of

651   electrical conductivity in a pre-alpine river: Effects of photosynthesis and

652   groundwater exchange. J. Hydrol. 450, 93-104.

653   Henze, M., Gujer, W., Mino, T., Matsuo, T., Wentzel, M.C., Marais, G.V.R., Van

654   Loosdrecht, M.C.M., 1999. Activated Sludge Model No.2d, ASM2d. Water Sci.

655   Technol. 39 (1), 165-182.

656   Hoehn, E., Scholtis, A., 2011. Exchange between a river and groundwater, assessed

657   with hydrochemical data. Hydrol. Earth Syst. Sc. 15 (3), 983-988.

658   Huggenberger, P., Hoehn, E., Beschta, R., Woessner, W., 1998. Abiotic aspects of

659   channels and floodplains in riparian ecology. Freshwater Biol. 40 (3), 407-425.

660   Jacobs, L.A., Von Gunten, H.R., Keil, R., Kuslys, M., 1988. Geochemical changes

661   along a river-groundwater infiltration flow path: Glattfelden, Switzerland.

662   Geochim. Cosmochim. Ac. 52 (11), 2693-2706.

663   Kuehn, W., Mueller, U., 2000. Riverbank filtration - An overview. J. Am. Water Works

664   Ass. 92 (12), 60-69.

665   Leenheer, J.A., Croue, J.P., 2003. Characterizing aquatic dissolved organic matter.

666   Environ. Sci. Technol. 37 (1), 18A-26A.

667   Massmann, G., Greskowiak, J., Dünnbier, U., Zuehlke, S., Knappe, A., Pekdeger, A.,

668   2006. The impact of variable temperatures on the redox conditions and the

669   behaviour of pharmaceutical residues during artificial recharge. J. Hydrol. 328

670   (1-2), 141-156.

671   Mettler, S., Abdelmoula, M., Hoehn, E., Schoenenberger, R., Weidler, P., von Gunten,

672   U., 2001. Characterization of iron and manganese precipitates from an in situ

673   ground water treatment plant. Ground Water 39 (6), 921-930.

674   Meybeck, M., 1982. Carbon, nitrogen, and phosphorus transport by world rivers. Am.

675   J. Sci. 282 (4), 401-450.

676 Mouchet, P., 1992. From conventional to biological removal of iron and manganese

677   in France. J. Am. Water Works Ass. 84 (4), 158-167.

678 Murdoch, P.S., Baron, J.S., Miller, T.L., 2000. Potential effects of climate change on

679   surface-water quality in North America. J. Am. Water Resour. As. 36 (2), 347-

680   366.

681 Naegeli, M.W., Hartmann, U., Meyer, E.I., Uehlinger, U., 1995. POM-dynamics and

682   community respiration in the sediments of a floodprone prealpine river (Necker,

683   Switzerland). Arch. Hydrobiol. 133 (3), 339-347.

684 Park, J.H., Duan, L., Kim, B., Mitchell, M.J., Shibata, H., 2010. Potential effects of

685   climate change and variability on watershed biogeochemical processes and

686   water quality in Northeast Asia. Environ. Int. 36 (2), 212-225.

687 Peter, S., Koetzsch, S., Traber, J., Bernasconi, S.M., Wehrli, B., Durisch-Kaiser, E.,

688   2012. Intensified organic carbon dynamics in the ground water of a restored

689   riparian zone. Freshwater Biol. 57 (8), 1603-1616.

690 Pusch, M., Fiebig, D., Brettar, I., Eisenmann, H., Ellis, B.K., Kaplan, L.A., Lock, M.A.,

691   Naegeli, M.W., Traunspurger, W., 1998. The role of micro-organisms in the

692   ecological connectivity of running waters. Freshwater Biol. 40 (3), 453-495.

693 Sacher, F., Brauch, H.J., 2002. Experiences on the fate of organic micropollutants

694   during riverbank filtration. In: Ray, C. (Ed.), Riverbank filtration: understanding

695   contaminant biogeochemistry and pathogen removal. Kluwer, Dordrecht, pp.

696   135-151.

697 Schirmer, M., 2013. Das RECORD-Projekt - Flussrevitalisierung, eine ökologische

698   Massnahme in einem komplexen Umfeld. Aqua und Gas 3, 22-28.

699 Schneider, P., Vogt, T., Schirmer, M., Doetsch, J., Linde, N., Pasquale, N., Perona,

700   P., Cirpka, O.A., 2011. Towards improved instrumentation for assessing river-

701   groundwater interactions in a restored river corridor. Hydrol. Earth Syst. Sc. 15

702   (8), 2531-2549.

703 Schubert, J., 2002. Hydraulic aspects of riverbank filtration - Field studies. J. Hydrol.

704   266 (3-4), 145-161.

705 Senhorst, H.A.J., Zwolsman, J.J.G., 2005. Climate change and effects on water

706   quality: a first impression. Water Sci. Technol. 51 (5), 53-59.

707 Sharma, L., Greskowiak, J., Ray, C., Eckert, P., Prommer, H., 2012. Elucidating

708   temperature effects on seasonal variations of biogeochemical turnover rates

709   during riverbank filtration. J. Hydrol. 428, 104-115.

710 Sobczak, W.V., Findlay, S., 2002. Variation in bioavailability of dissolved organic

711   carbon among stream hyporheic flowpaths. Ecology 83 (11), 3194-3209.

712 Sprenger, C., Lorenzen, G., Hulshoff, I., Grutzmacher, G., Ronghang, M., Pekdeger,

713   A., 2011. Vulnerability of bank filtration systems to climate change. Sci. Total

714   Environ. 409 (4), 655-663.

715 Toride, N., Leij, F.J., van Genuchten, M.T., 1995. The CXTFIT Code for Estimating

716   Transport Parameters from Laboratory or Field Tracer Experiments, Version

717   2.0. US Salinity Laboratory, Riverside, CA, pp. 131.

718 Tufenkji, N., Ryan, J.N., Elimelech, M., 2002. The promise of bank filtration. Environ.

719   Sci. Technol. 36 (21), 422A-428A.

720 Uehlinger, U., 2006. Annual cycle and inter-annual variability of gross primary

721   production and ecosystem respiration in a floodprone river during a 15-year

722   period. Freshwater Biol. 51 (5), 938-950.

723 Valentini, A., Garuti, G., Rozzi, A., Tilche, A., 1997. Anaerobic degradation kinetics of

724   particulate organic matter: A new approach. Water Sci. Technol. 36 (6-7), 239-

725   246.

726 Vavilin, V.A., Fernandez, B., Palatsi, J., Flotats, X., 2008. Hydrolysis kinetics in

727   anaerobic degradation of particulate organic material: An overview. Waste

728   Manage. 28 (6), 939-951.

729 von Gunten, H.R., Karametaxas, G., Keil, R., 1994. Chemical Processes in Infiltrated

730   Riverbed Sediments. Environ. Sci. Technol. 28 (12), 2087-2093.

731 von Gunten, U., Zobrist, J., 1993. Biogeochemical changes in groundwater-infiltration

732   systems: Column studies. Geochim. Cosmochim. Ac. 57 (16), 3895-3906.

733 Zwolsman, J.J.G., van Bokhoven, A.J., 2007. Impact of summer droughts on water

734   quality of the Rhine River - a preview of climate change? Water Sci. Technol.

735   56 (4), 45-55.

736

737

738 **8   Figure captions**

739 Fig. 1. (a) Catchment of the Thur River and location of the Niederneunforn field site,

740 NE-Switzerland. (b) Schematic representation of the Niederneunforn field site.

741 Groundwater head isolines (head equidistance 10 cm, light gray) were extracted from

742 a groundwater flow model (Diem et al., 2013). (c) Enlargement of the area indicated

743 by the dashed rectangle in (b), which contains the locations of the piezometers used

744 in this study. The black lines in (c) indicate the advective flow paths from the river to

745 the piezometers according to the resulting flow field of the groundwater flow model.

746

747 Fig. 2. Schematic representation of the set-up of the column experiment with 13

748 sampling ports along the column (SP1-13) and one at the inlet (SP0) and one at the

749 outlet (SP14). River water was pumped from the bottom to the top of the column. DO,

750 temperature (T) and pH were measured in flow-through cells (F).

751

752 Fig. 3. Discharge (black line) and temperature (gray line) time series measured at the

753 FOEN gauging station in Andelfingen covering the two detailed summer and winter

754 sampling campaigns (August 19-26, 2011 and November 23-29, 2011). Each of the

755 sampling days is shown as a dashed vertical line.

756

757 Fig. 4. Temperature and concentration profiles of DO, DOC and nitrate during (a) the

758 summer and (b) the winter campaign. Mean and standard deviations are shown as

759 symbols and error bars, respectively (n=5). Estimated groundwater residence times

760 (τ) between the river and the piezometers are also indicated.

761

762 Fig. 5. Concentration profiles of DO, DOC and nitrate in the column at (a) 20°C and

763 (b) 5°C. Each symbol represents a sampling port. The first data point corresponds to

764 the sampling port at the inlet of the column (SP0), the last data point to the sampling

765 port at the outlet of the column (SP14). Mean and standard deviations are shown as

766 symbols and error bars, respectively (n=3).

767

768 Fig. 6. Comparison of DO and DOM (expressed as DOC) consumption for the

769 summer (20-23°C) and winter (5-7°C) field campaigns and for the column

770 experiments at 20 and 5°C, respectively. The consumption refers to the

771 concentration difference between the Thur River and the piezometer R050 in the field

772 and between column inlet and outlet for the column experiments. Standard deviations

773 are shown as error bars.

774

775 Fig. 7. Scatter plots between (a) DO consumption (ΔDO), (b) DOM consumption

776 (ΔDOC), (c) calculated POM consumption (ΔPOC =ΔDO-ΔDOC) at the piezometer

777   R050, and daily mean river water temperature (T). r is the correlation coefficient

778   between two variables with the significance levels: *** = p<0.001, ** = p<0.01, * =

779   p<0.05, (-) = p>0.05. p is the probability of two variables being uncorrelated.

780

781   Fig. 8. Scatter plot between DO consumption at the piezometer R050 (ΔDO) and

782   daily mean river discharge (Q). r is the correlation coefficient between the two

783   variables with the significance levels: *** = p<0.001, ** = p<0.01, * = p<0.05, (-) =

784   p>0.05. p is the probability of two variables being uncorrelated.

a Field site Niederneunforn
   Andelfingen
   Thur catchment
   Lake Constance
   10 km

c R023
   R059
   R074
   R050
   371.85
   0 15 30   60   90   120 Meters

   Forest transect
b 371.35   371.85   Pumping station transect   372.35
   Thur River

   0 50 100   200   300   400 m

   N

   ○ Piezometer   — Modeling domain   ┼┼┼ Levee
   ☆ Pumping station   — Side channel   ∷ Gravel bar