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27 **Abstract**

28 The fate of nine trace organic compounds was evaluated during a 12 month large-  
29 scale laboratory column experiment. The columns were packed with aquifer sediment  
30 and evaluated under natural aerobic and artificial anaerobic geochemical conditions,  
31 to assess the potential for natural attenuation of these compounds during aquifer  
32 passage associated with managed aquifer recharge (MAR). The nine trace organic  
33 compounds were bisphenol A (BPA), 17 $\beta$ -estradiol (E2), 17 $\alpha$ -ethynylestradiol (EE2),  
34 *N*-nitrosodimethylamine (NDMA), *N*-nitrosomorpholine (NMOR), carbamazepine,  
35 oxazepam, iohexol and iodipamide. In the low organic carbon content Spearwood  
36 sediment, all trace organics were non-retarded with retardation coefficients between  
37 1.0 and 1.2, indicating that these compounds would travel at near groundwater  
38 velocities within the aquifer. The natural aerobic geochemical conditions provided a  
39 suitable environment for the rapid degradation for BPA, E2, iohexol (half life <1 day).  
40 Lag-times for the start of degradation of these compounds ranged from <15 to 30  
41 days. While iodipamide was persistent under aerobic conditions, artificial reductive  
42 geochemical conditions promoted via the addition of ethanol, resulted in rapid  
43 degradation (half life <1 days). Pharmaceuticals (carbamazepine and oxazepam) and  
44 disinfection by-products (NDMA and NMOR) did not degrade under either aerobic or  
45 anaerobic aquifer geochemical conditions (half life >50 days). Field-based validation  
46 experiments with carbamazepine and oxazepam also showed no degradation. If  
47 persistent trace organics are present in recycled waters at concentrations in excess of  
48 their intended use, natural attenuation during aquifer passage alone may not result in  
49 extracted water meeting regulatory requirements. Additional pre treatment of the  
50 recycled water would therefore be required.

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## 52 **Introduction**

53           One of the major health concerns associated with the use of recycled water is  
54 the potential presence of low concentrations of a range of trace organics (Díaz-Cruz,  
55 and Barceló, 2008). These trace organics include endocrine disrupting compounds,  
56 hormones, pharmaceuticals, pesticides and disinfection by-products. Recycled water  
57 can be used in many different ways but one mechanism gaining favour in many  
58 countries is recharging the recycled water to aquifers using Managed Aquifer  
59 Recharge (MAR) (Dillon et al. 2006). When recycled water is used for MAR, it may  
60 undergo biogeochemical changes during aquifer storage or aquifer passage resulting  
61 in the natural attenuation of some trace organics. MAR has been shown to reduce  
62 nutrient concentrations and microbial pathogen numbers in recharged water (Dillon et  
63 al. 2006; Toze and Hanna 2002) but less is known about the potential removal of trace  
64 organics during recharge and storage. As the fate of trace organics are determined by  
65 aquifer biological and geochemical conditions (Barber et al. 2009; Carrara et al.  
66 2008), fate assessment results from one aquifer system may not apply to other  
67 systems. To assess the transferability of results between different aquifer systems, fate  
68 assessment comparative data is required for different aquifer systems where MAR  
69 using recycled water is planned.

70           Knowledge of the fate of trace organic compounds in aquifers is essential to  
71 the assessment and design of proposed MAR recycled water treatment strategies. This  
72 fate data can be used to provide design criteria for (i) injection/extraction borehole  
73 spacing or extraction rate to ensure sufficient aquifer residence time for degrading  
74 compounds to be naturally attenuated so that the extraction water meets regulatory  
75 requirements, and (ii) identify if additional pre or post MAR treatment options such  
76 as reverse osmosis, advanced oxidation or UV radiation are required for persistent

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77 trace organic compounds, where sufficient natural attenuation is unlikely to be  
78 achieved during aquifer passage and where significant human exposure to the  
79 recovered water is considered likely.

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80 This paper describes the findings of a 12 month large-scale column experiment  
81 investigating the fate of nine trace organics under natural aerobic aquifer geochemical  
82 conditions and under artificial anaerobic reducing conditions via ethanol addition.  
83 The fate of each trace organic was assessed based on their chemical retardation  
84 coefficient (R) and degradation rate, determined from the experimental data.

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## 86 **Materials and Methods**

87 Nine trace organics were investigated. Bisphenol A (BPA), 17 $\beta$ -estradiol  
88 (E2), 17 $\alpha$ -ethynylestradiol (EE2), carbamazepine (CARB), *N*-nitrosomorpholine  
89 (NMOR) and iohexol (IOX) were all obtained from Sigma-Aldrich (Sydney,  
90 Australia). *N*-nitrosodimethylamine (NDMA) was obtained from Chem Service  
91 (Perth, Australia), iodipamide (IDP) was obtained from Fluka (Sydney, Australia) and  
92 oxazepam (OXAZ) was obtained from the Chemistry Centre of Western Australia.  
93 These trace organics were selected, as all except for IDP have been detected in  
94 effluent water from local wastewater treatment plants (PCRCP, 2009).

## 95 **Aquifer Material**

96 The sediment used in the column experiment was a calcareous medium  
97 grained Spearwood sand low in organic carbon and iron content (see Table 1),  
98 collected from the superficial Tamala aquifer, on the Swan Coastal Plain of Western  
99 Australia. The Spearwood sediment was collected from approximately 1 to 5 m  
100 below the water table (11 to 15 m below the ground surface) by installing a 80 mm  
101 temporary bore casing and using a 65 mm bailer to collect saturated sediment. The

102 bailer, containing the sediment and groundwater, was repeatedly filled then opened  
103 inside the columns, displacing excess groundwater and gradually filling the columns  
104 on-site. Sediment porosities were determined using bromide tracer tests conducted  
105 during the column experiment (Stephens et al., 1998). Hydraulic conductivity ( $K$ ) was  
106 determined based on the Darcy equation and the observed hydraulic head drop along  
107 the column. Other sediment properties were determined on a sediment sub-sample.  
108 Mineralogy of the sediment was determined by X-ray diffraction analysis (XRD)  
109 using a PANalytical X'Pert Pro Multi-purpose diffractometer and quantified using the  
110 commercial package SIROQUANT from Sietronics Pty Ltd. The results were  
111 normalised to 100%, and hence did not include estimates of unidentified or  
112 amorphous materials.

### 113 **Column Setup**

114 Two stainless steel columns were constructed, an experimental column and a  
115 sterilized control column. Each column was 2.0 m in height and 145 mm internal  
116 diameter (i.d.). To avoid sediment migrating into the influent and effluent tubing, a  
117 stainless steel grate with holes 10 mm in diameter and stainless steel mesh was fixed  
118 at the bottom and the top of each column. Nineteen sampling ports were strategically  
119 placed along each column allowing for water samples to be collected from the  
120 columns. Each water sampling port consisted of a 4 mm i.d. stainless steel tube that  
121 protruded 60 mm from the wall of the column into the centre of the column. The inner  
122 end of the tube contained a stainless steel mesh (1 mm diameter) to prevent sediment  
123 entering, while the outer end contained a silicon septum allowing a hypodermic  
124 syringe needle to be inserted for the collection of water samples. The columns were  
125 operated in a saturated up flow mode. The effluent tubing from each column was  
126 passed through a peristaltic pump (ISMATEC Reglo) to regulate column flow at

127 approximately 360 mL d<sup>-1</sup>, giving a linear velocity of approximately 4.7 cm day<sup>-1</sup>,  
128 based on an average porosity of 0.46 estimated from the bromide tracer test for the 2  
129 columns. This gave a water residence time within the columns of 42 days. This linear  
130 velocity is within the range of typical groundwater velocities on the Swan Coastal  
131 Plain (Benker et al., 1997).

132 A silicone polymer mat for the diffusive delivery of ethanol to promote  
133 reducing conditions within the columns (Patterson et al., 2002, Patterson et al., 2004,  
134 Grassi et al., 2007) was installed in each column. The polymer mat was placed  
135 horizontally within the circumference of the column, and orthogonal to the water flow  
136 direction to provide low concentration ethanol delivery via diffusion into the columns.  
137 This type of amendment diffusion delivery enables the ethanol to be introduced  
138 without altering the water flow rate through the column. The polymer mat consisted  
139 of a 100 cm length of silicone tubing (2.0 mm i.d., 3.0 mm o.d.) with a fine stainless  
140 steel spring inserted into the centre of the polymer tubing to provide support and to  
141 prevent twisting or collapsing of the tubing. The polymer tubing was then woven  
142 through a 135 mm diameter flexible plastic support frame that was placed 1.0 m from  
143 the base of the column. To promote the anaerobic conditions, ethanol delivery using  
144 the polymer mat commenced 191 days after delivery of the trace organics  
145 commenced. For ethanol delivery, 5 L of an aqueous ethanol solution (41 ± 3 g L<sup>-1</sup>)  
146 prepared weekly was continuously recycled through each polymer mat, resulting in a  
147 column water ethanol concentration of 700 ± 30 mg L<sup>-1</sup> (360 mg L<sup>-1</sup> C)

148 Column influent water was collected from Subiaco Wastewater Treatment  
149 Plant, Perth Western Australia, subjected to rapid sand filtration and amended with  
150 nitrate (to give 30 mg L<sup>-1</sup>-N). Nitrate was added to ensure consistent nitrate  
151 concentrations throughout the column experiment. The sterile control column was

152 used to differentiate between abiotic and biotic processes. Microbial activity was  
153 suppressed in this column by the addition of the metabolic inhibitor sodium azide  
154 ( $0.65 \text{ g L}^{-1}$ ) to the influent water. A saturated dissolved oxygen concentration of the  
155 influent water for each column was maintained by continuous aeration using a small  
156 air pump discharging into the base of each influent water container. The chemistry of  
157 the recycled water used in the columns is given in Table 1. To reduce the potential for  
158 trace organic degradation prior to injection into the columns, a fresh aqueous stock  
159 solution of the trace organics and bromide (inert tracer) was prepared every two  
160 weeks and stored in a 3 L SKC® Flexfoil Grab Bag. A MCP Standard drive pump  
161 (ISMATEC) injected the stock trace organic solution into a 10-port selection valve  
162 (Valco Instruments model E10-230) which distributed the stock solution semi-  
163 continuously (pulsed in 10 times per day) into each of the column's recycled water  
164 influent lines immediately prior to entering the column. Approximately 30 mL of the  
165 stock trace organic solution was delivered to each column per day. The resultant trace  
166 organic and bromide concentrations of the column influent water are given in Table 2.

167         The microgram per litre concentration range was selected for the influent trace  
168 organic concentrations so low volume column samples could be collected, while still  
169 achieving analytical detection of trace organics, especially if substantial  
170 biodegradation occurred. This enabled discrete sampling from nineteen sampling  
171 ports along each column to provide fine-scale column profile data to assess changes in  
172 the location and rate of biodegradation of the trace organics during the experiment.

173         Throughout the 12 month experiment, influent water and column samples  
174 were collected and analysed to assess trace organic fate. E2, EE2, BPA, CARB and  
175 OXAZ were analysed by direct injection high performance liquid chromatography  
176 tandem mass spectrometry using an Agilent 1200 Series HPLC in conjunction with an



177 Agilent 6410 Series Triple Quad LC/MS System. The column used was a ZORBAX  
178 Eclipse XDB- C18, 4.6 mm i.d. The mobile phase used for E2, EE2 and BPA was a  
179 10 mmol acetonitrile solution at pH 9. For CARB and OXAZ, a 10 mmol ammonium  
180 formate solution at pH 3 along with added methanol was used. Isotopically labelled  
181 standards were not available at the time of analysis to correct for possible matrix  
182 suppression effects. Therefore, quantification of column water samples was performed  
183 using an external calibration solution prepared in non-contaminated column effluent  
184 water and a 1:8 and 1:25 dilution technique (Gros et al., 2006) was used to assess and  
185 account for potential matrix suppression effects including the effects from sodium  
186 azide and the addition of ethanol used during the experiment.

187 IOX and IDP were analysed by direct injection high performance liquid  
188 chromatography tandem mass spectrometry using an Agilent HPLC 1100 Series  
189 coupled with a Micromass Ultima Triple Quadrupole Mass Spectrometer that utilised  
190 an electrospray interface operated in positive mode. Isotopically labelled standards of  
191 IOX and IDP were not commercially available to correct for possible matrix  
192 suppression effects. Therefore, quantification of column water samples was performed  
193 using an external calibration solution prepared in non-contaminated column effluent  
194 water and the standard addition method was used to assess and account for potential  
195 matrix suppression effects including the effects from sodium azide and the addition of  
196 ethanol used during the experiment. The method has previously been described in full  
197 (Busetto et al., 2008) including the standard addition method and validation data for  
198 secondary treated wastewater.

199 For NDMA and NMOR, a liquid-liquid extraction method was used. Water  
200 samples (300  $\mu$ L) were spiked into dichloromethane (2.7 mL) and 20  $\mu$ L surrogate  
201 standard (NDMA-d6, NMOR-d8) was added. Samples were mixed and then dried

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202 with MgSO<sub>4</sub> (s) to remove any water from the solvent. The dried solutions were then  
203 concentrated to ~150 µL at 44 °C under a gentle stream of N<sub>2</sub> gas and 10µL internal  
204 standard (Diphenylamine-d10) added. Extracts were then analysed by gas  
205 chromatography mass spectrometry based on the method of Cheng et al. (2006), using  
206 an Agilent 6890N GC coupled with an Agilent 5975 inert mass spectrometer. A HP-  
207 Innowax wax polyethylene glycol capillary column, 30 mm length and 0.25 mm I.D.,  
208 was used for separation at a flow rate of 1.3 mL min<sup>-1</sup>. The Diphenylamine-d10  
209 internal standard was used to monitor the volume of samples injected into the GC-  
210 MS, while the surrogate standards were used to aid analyte peak identification and  
211 quantification. Quantifying ions (74 m/z, 116 m/z) and qualifying ions (42 m/z, 86  
212 m/z) were selected for NDMA and NMOR respectively. Analytes were quantified via  
213 an external calibration curve spanning 0-1000 µg L<sup>-1</sup>, based on the ratio of analyte to  
214 surrogate standard.

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215 Bromide concentrations were determined by ion chromatography with either  
216 UV or conductivity detection.

### 39 40 217 218 **Field Validation**

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219 A limited field validation experiment was undertaken by assessing the trace  
220 organic plume produced during a managed aquifer recharge (MAR) field experiment  
221 conducted in Perth, Western Australia (Bekele et al., 2006). This field experiment  
222 used the same recycled water source as used in the column experiment without extra  
223 nitrate or trace organic amendments. Also, the aquifer sediment for the column  
224 experiment was collected from this field site. This field experiment involved the  
225 infiltration of the recycled water through the 10 m thick vadose zone at 50 kL day<sup>-1</sup>.  
226 Fifty metres downgradient of the infiltration gallery, groundwater was continuously

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227 extracted (250 kL day<sup>-1</sup>) from bore BH17, screened between 14 and 24 m below  
228 ground surface.

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## 230 **Results and Discussion**

### 231 **Retardation coefficients**

232 Sediment analysis by XRD showed the mineral composition was  
233 predominantly quartz (75 %), with calcite (12 %), microcline/orthoclase (11 %), and  
234 albite/anorthite (2 %). All other minerals were below analytical detection (<1 %).

235 Details of the sediment properties are given in Table 1.

236 Prior to the introduction of the trace organics and bromide, sediment site  
237 groundwater was passed through the column at approximately 360 mL d<sup>-1</sup> for a period  
238 of 2 months to stabilize column water chemistry. After the trace organics and bromide  
239 were introduced into the columns, R values were determined by comparing the  
240 migration rate of the trace organics along each column to the migration rate of the  
241 conservative tracer bromide. Data from the sterile column was used to eliminate the  
242 potential for biodegradation confounding the interpretation of the retardation data.  
243 Trace organic breakthrough profiles after 15 days of trace organic delivery for the  
244 sterile column are shown in Figure 1.

245 R values (assuming linear sorption isotherms) for each trace organic were  
246 determined by (i) initially fitting the bromide data to the convection-dispersion  
247 equation (Parker and van Genuchten 1984) using a nonlinear least squares fitting  
248 routine based on the Levenberg-Marquardt algorithm (Microcal 1995) using Origin®  
249 v7 software, then (ii) fitting the data for each trace organic to the convection-  
250 dispersion equation constrained using the bromide fitted parameters, except R which  
251 was used as the fitting parameter.

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252 For some of the trace organics (e.g. IDP), their travel distance appeared  
253 marginally further than bromide, but this is likely to be a result of sampling/analysis  
254 variability. For these trace organics it was assumed that no sorption to the sediment  
255 occurred and an R value of 1.0 was used. For the non-sterile column, R values of the  
256 non-degrading trace organics (data not shown) were similar to the results from the  
257 sterile column suggesting that the azide solution was not affecting sorption of the  
258 trace organics. Estimated R values and trace organic octanol-water partition  
259 coefficients ( $K_{ow}$ ) are given in Table 2.

260 Sorption of contaminants can occur through hydrophobic attraction between  
261 sediment organic matter and non-polar organic trace organics (hydrophobic  
262 partitioning), or through the attraction of compounds to minerals surfaces by  
263 electrostatic forces (physical sorption). Therefore, the extent to which a trace organic  
264 will sorb is dependent on the structure of the compound and the organic carbon  
265 content of the sediment and/or the minerals present in the sediment. In the low organic  
266 carbon content Spearwood sediment, all trace organics were non-retarded with R  
267 values between 1.0 and 1.2 ( $k_d$  0 to 0.06 L kg<sup>-1</sup>). The low R values of the trace  
268 organics determined for the Spearwood sediment did not correlate with the  $K_{ow}$  values  
269 of the trace organics, and would be consistent with limited hydrophobic partitioning  
270 as a result of the low organic carbon content of the Spearwood sediment (0.02% w/w).  
271 Also, this data suggests there is little physical sorption due to attraction of the trace  
272 organics to mineral surfaces by electrostatic forces. These results are consistent with  
273 the R values calculated from column experiments for benzene (R = 1.1) and  
274 tetrachloroethene (R = 1.1) in similar aquifer material (Patterson et al., 1993).

275 The results for BPA and EE2 are in contrast to the results of Ying et al. (2008)  
276 who conducted sorption batch experiment for BPA and EE2 using Spearwood vadose

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277 zone sediment, rather than aquifer sediment. Ying et al. (2008) found substantially  
278 higher R values for BPA (R = 26) and EE2 (R = 45) than would be expected for the  
279 low organic carbon content sediment used (0.012% w/w) and postulated that the high  
280 sorption results may have been a result of sorption of BPA and EE2 to iron oxide  
281 coatings on the sand grains (Fe = 0.9% w/w). This explanation is consistent with the  
282 data, as the Spearwood aquifer sediment iron content was substantially lower (Fe =  
283 0.13% w/w). Results for CARB (R = 1.0) were marginally lower than results from  
284 Scheytt et al. (2006) who measured an R value of 1.84 ( $k_d = 0.131 \text{ L kg}^{-1}$ ) in a fine-  
285 grained alluvial sand with an organic carbon content (0.13% w/w) via column  
286 experiments for unsaturated conditions. Taking into account the difference in  
287 sediment organic carbon content, the carbon normalized sorption coefficients would  
288 be similar.

289 Gunnison et al. (2000) and Yang et al. (2005) measured sorption coefficients  
290 ( $k_d$ ) of 0.4 to 1.14  $\text{L kg}^{-1}$  and 0.45 to 0.64  $\text{L kg}^{-1}$  respectively for NDMA in batch  
291 experiments on a range of sediments with an organic carbon content between 0.17 and  
292 0.3 % w/w. These  $k_d$  values are higher than the low sorption of NDMA ( $k_d = 0 \text{ L kg}^{-1}$ )  
293 measured in the sterile Spearwood-sediment column experiment, possibly as a result  
294 of the higher organic carbon content.

#### 295 296 **Degradation – Aerobic Conditions**

297 To determine the degradation rate of the trace organics, trace organic  
298 concentration data was plotted against column residence time (Figure 2). To  
299 determine the column residence time, the distance of the sampling ports along the  
300 column was converted to time (days) based on the linear flow velocity of the trace  
301 organic (linear velocity of bromide tracer divided by the trace organic R value). For a  
302 number of trace organics such as BPA and IOX, degradation occurred rapidly over a

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303 narrow zone within the column resulting in insufficient measurement points to  
304 accurately assess the kinetic degradation behaviour. Also, for the slower degrading  
305 trace organics, either zero-order or first-order degradation profiles could be fitted to  
306 the concentration data with similar degrees of confidence. Therefore, both zero-order  
307 and first-order degradation rates were estimated (Table 2). Zero-order degradation  
308 rates for the trace organics were determined by fitting a linear relationship to the  
309 experimental data, while first order half-life degradation rates were determined by  
310 fitting a half-life curve to the experimental data using Origin® v7 software.

311 To determine the maximum degradation rates, concentration data from the last  
312 sampling event (day 330) was used in preference to the earlier sampling events, to  
313 provide an extended time for microbial activity to commence and potentially  
314 overcome any biodegradation lag-time. Earlier and mid-time concentration data was  
315 used to assess the onset of degradation (lag-times). Based on a non-sorbing trace  
316 organic column residence time of approximately 21 days for the aerobic zone of the  
317 column (100 cm from the base of each column), a maximum half-life value of >50  
318 days was determined for non-degrading trace organics. For the day 330 sampling  
319 event (see Figure 2), the sterile control column results were generally lower and more  
320 variable than the non-sterile column results, the non-degrading trace organics OXAZ,  
321 CARB, NDMA, NMOR, and IDP. The difference between these column results could  
322 be associated with analytical artefacts due to matrix suppression effects associated  
323 with the sodium azide in the sterile column and ethanol addition in the treatment  
324 phase of the experiments. The potential influence of matrix suppression for the LC-  
325 MS analytical methods were evaluated in dilution or standard addition experiments.  
326 For the 1:8 and 1:25 dilution technique, OXAZ, CARB data showed responses within  
327 10 %, (after accounting for dilution) suggesting matrix effects were minor under the

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328 sample processing/analytical conditions used. For the standard addition technique  
329 used for IOX and IDP, column water samples spiked with known amounts of IOX and  
330 IDP consistently showed recoveries near 100% demonstrating that the calibration  
331 strategy adopted was efficiently correcting for possible matrix effects. Additionally,  
332 IOX determined by a different analytical technique (GC-MS) not prone to matrix  
333 suppression, also showed similar variability to the other trace organics in the non-  
334 sterile column (Figure 2). Another explanation for the differences between these  
335 column results could be attributed to variability in the effective trace organic dosing  
336 rates between the two columns at this time. This explanation may be more plausible as  
337 all the non-degrading trace organics in the non-sterile column (including IOX)  
338 showed a similar pattern of variability (Figure 2). Note: this variability seemed to be  
339 more evident on the day 330 sapling event compared to earlier sampling events (see  
340 Figure 4A).

341 In the sterile column, no trace organics were observed to degrade, except E2  
342 and BPA. After a lag-time of <15 days, EE2 degraded rapidly with a half-life of <1  
343 day (zero-order degradation rate of  $140 \mu\text{g L}^{-1} \text{day}^{-1}$ ). BPA also showed losses, but  
344 this was more variable. The removal of E2 and BPA was either through abiotic  
345 degradation or the sodium azide concentration ( $0.65 \text{ g L}^{-1}$ ) used was not sufficient to  
346 inhibit all biological activity. Degradation batch experiments by Ying et al. (2008)  
347 showed no substantial BPA and E2 removal in sterilised controls using autoclaved  
348 vadose zone Spearwood sediment. The groundwater used in these batch experiment  
349 controls was filter sterilized and sodium azide was used at an order of magnitude  
350 higher concentration ( $5.0 \text{ g L}^{-1}$ ) than in this study. When ethanol addition commenced  
351 at day 191, successful promotion of denitrification (data not shown) and sulphate  
352 reduction (Figure 3) was observed in the non-sterile sediment column. No

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353 denitrification or sulphate reduction was observed in the sodium azide ( $0.65 \text{ g L}^{-1}$ )  
354 sterilised sediment column. This data suggests that the sodium azide concentration  
355 ( $0.65 \text{ g L}^{-1}$ ) was sufficient to inhibit denitrifying and sulphate reducing bacteria, but  
356 possibly insufficient to inhibit bacteria responsible for BPA and E2 degradation.  
357 Alternatively, BPA and E2 removal may have been through abiotic processes. Sarmah  
358 and Northcott (2008) observed abiotic degradation of BPA, E2 and EE2 in marine  
359 sediment and aquifer material, and postulate a number of explanations including  
360 surface induced abiotic transformation due to catalytic effect with sediment minerals.

361 In the aerobic zone of the non-sterile column, rapid degradation of BPA, E2  
362 and IOX with a half life  $<1$  day (zero-order degradation rate of  $140$  to  $380 \mu\text{g L}^{-1} \text{ day}^{-1}$ )  
363  $^1$ ) was observed. Lag-times were  $<15$  days for BPA and E2, and 30 days for IOX  
364 (Table 2). Other trace organics were not degraded with half-lives  $>50$  days (zero-  
365 order degradation rate of  $<10 \mu\text{g L}^{-1} \text{ day}^{-1}$ ), see Figure 2. As BPA and E2 were also  
366 removed in the sterile Spearwood-sediment column, the mechanism for degradation  
367 (abiotic or biotic) could not be distinguished. Results for BPA and E2 were generally  
368 consistent with aerobic batch experiments using Spearwood vadose zone sediment  
369 undertaken by Ying et al. (2008), which showed degradation half lives of 0.6 and 0.2  
370 days for BPA and E2 using aerobic groundwater and 1.6, and 15 days for BPA and  
371 E2 using aerobic synthetic effluent water. The limited degradation of EE2 (half life  
372  $>50$  days; zero-order degradation rate of  $<10 \mu\text{g L}^{-1} \text{ day}^{-1}$ ) was slower than results  
373 from Ying et al. (2008) who reported half lives of 26 and 15 days for aerobic  
374 groundwater and synthetic effluent water in batch experiments. Ying et al. (2008)  
375 postulated that the presence of a quaternary carbon atom and condensed rings made  
376 EE2 more resistant to microbial degradation than BPA and E2. This may explain why  
377 EE2 was not observed to degrade in this study.



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378           The lag-time for the start of degradation of IOX of approximately 30 days  
379 suggests low numbers of IOX degrading bacteria were initially present in the non-  
380 sterile column. The combination of the approximate 30 day lag-time and then rapidly  
381 increasing degradation rate over a period of approximately 2 months resulted in the  
382 formation of a cut-off plume with the head of the IOX plume not being degraded (as  
383 the bacteria did not have sufficient time to establish on the sediment) and IOX  
384 migrating past the end of the column (between 25 and 125 days, Figure 4). After the  
385 IOX-degrading bacteria had established in sufficient numbers on the sediment, IOX  
386 was rapidly degraded as it entered the column (after approximately 100 days, Figure  
387 4). Another X-ray contrast media compound (iopromide) has also been observed to  
388 degrade under aerobic conditions (Grünheid et al., 2005).

389           IDP was persistent throughout the experiment with a half life of >50 days  
390 (zero-order degradation rate of <math>10 \mu\text{g L}^{-1} \text{ day}^{-1}</math>). Joss et al., (2006) reported partial  
391 removal of IOX in aerobic batch experiments with sewage sludge, while Herberer  
392 (2002) reported that X-ray contrast media was very persistent in the aquatic  
393 environment based on studies on several other iodinated contrast media, but not  
394 specifically IOX.

395           The pharmaceuticals (CARB and OXAZ) and disinfection by-products  
396 (NDMA and NMOR) were also persistent with half lives >50 days (zero-order  
397 degradation rate of <math>10 \mu\text{g L}^{-1} \text{ day}^{-1}</math>). CARB has previously been shown to be  
398 persistent in the environment (Heberer and Adam, 2004; Massmann et al., 2006), and  
399 has been suggested as a potential anthropogenic marker in aquatic environments  
400 (Clara et al., 2004). The results for NDMA are in contrast to the results of Bradley et  
401 al. (2005) and Drewes et al. (2006) who showed NDMA degradation under aerobic  
402 conditions in batch and column studies, respectively. Reasons for this difference may

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403 be attributed either (i) the high NDMA ( $\mu\text{g L}^{-1}$  range compared to  $\text{ng L}^{-1}$  range)  
404 concentrations used in this study, or (ii) low number of NDMA degrading bacteria in  
405 the non-sterile column and insufficient time for acclimation of these bacteria. No  
406 previous literature degradation data was available for OXAZ and NMOR.

407

#### 408 **Degradation – Anaerobic Conditions**

409 In MAR schemes using aerobic aquifers, groundwater becomes anaerobic if  
410 there is sufficient organic carbon, ammonia or reduced iron to consume available  
411 electron acceptors. Gordon and Toze (2003) observed that the rate of bacterial  
412 pathogen inactivation decreased under anaerobic conditions. Ying et al. (2008) noted  
413 that the decay of endocrine disrupting compounds decreased in the absence of oxygen.  
414 Carrara et al. (2008) observed preferential removal of selected pharmaceutical  
415 compounds in aerobic zones of aquifers compared to nitrate reducing zones. Barber et  
416 al. (2009) observed E2 and 4-nonylphenone degradation in an aerobic aquifer.  
417 However, Pavelic et al. (2006) found that chloroform was degraded rapidly under  
418 anaerobic conditions but was persistent under aerobic conditions. Thus it is important  
419 to also understand the potential removal rates of different trace organics under  
420 anaerobic conditions.

421 In this study, ethanol was used to biologically induce anaerobic conditions.  
422 After ethanol delivery commenced 100 cm from the base of each column, no  
423 denitrification, sulphate reduction or ethanol oxidation was observed in the sterile  
424 control column. For the non-sterile column, nitrate concentration decreased from  $\sim 30$   
425  $\text{mg L}^{-1}\text{-N}$  to below detection limits ( $<0.01 \text{ mg L}^{-1}\text{-N}$ ) in the zone of ethanol addition  
426 (data not shown) indicating rapid (half life = 1.9 days) denitrification. Sulphate  
427 concentrations decreased from  $\sim 18 \text{ mg L}^{-1}\text{-S}$  to  $0.5 \text{ mg L}^{-1}\text{-S}$  (Figure 2) indicating

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428 rapid (half life = 2.0 days) sulphate reduction. Some removal of sulphate (Figure 2)  
429 and nitrate (data not shown) upgradient of the ethanol delivery location was also  
430 observed, probably as a combined result of upgradient diffusion of ethanol and the  
431 slow water flow through the column. Also, ethanol concentrations were observed to  
432 decrease from  $700 \pm 30 \text{ mg L}^{-1}$  (based on observed control column concentrations) to  
433 below detection limits ( $<2 \text{ mg L}^{-1}$ ). The production of acetic acid was also observed  
434 initially (up to  $900 \text{ mg L}^{-1}$ ). These rapid denitrification and sulphate reduction rates  
435 are consistent with previous laboratory column (Patterson et al., 2002) and field  
436 experiments (Patterson et al., 2004) using ethanol dosing to promote denitrification.

437         Of the trace organics that were not substantially removed in the aerobic  
438 section of the non-sterile column (first 100 cm from the base of the column), only IDP  
439 (Figure 5) was observed to rapidly degrade with a half life of  $<1$  days (zero-order  
440 degradation rate of  $340 \mu\text{g L}^{-1} \text{ day}^{-1}$ ) in the anaerobic section of the column, with a lag  
441 time of  $<40$  days. IDP was not degraded in the sterile control column (Figure 5). The  
442 mechanism for IDP likely would be via a reductive biodegradation or a co-  
443 metabolism pathway. Previous natural anaerobic column experiments by Patterson et  
444 al. (2010) also showed rapid degradation of IDP.

445         EE2 degradation was not observed (half life  $>50$  days; zero-order degradation  
446 rate of  $<10 \mu\text{g L}^{-1} \text{ day}^{-1}$ ). Ying et al. (2008) also observed that EE2 did not degrade  
447 under anaerobic conditions. Again, the pharmaceuticals (CARB and OXAZ) and  
448 disinfection by-products (NDMA and NMOR) were persistent with half lives  $>50$   
449 days.

#### 450 451 **Field Validation.**

452         Over the length of the MAR site, the aquifer remained aerobic, probably due  
453 to insufficient carbon and nutrients in the recharge water to sufficiently promote

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454 reducing conditions. As a result, no loss of nitrate was observed, however reductions  
455 in phosphate, total organic carbon concentrations and enteric microorganism numbers  
456 were observed (Toze and Bekele 2009). Due to limited sampling at the start of the  
457 field infiltration experiment, trace organic R values could not be determined. To  
458 examine the effectiveness of the MAR scheme to remove trace organics, towards the  
459 end of a 9 month period of relatively stable recycled water infiltration and  
460 downgradient groundwater extraction, data over a 6 week sampling period was used  
461 to determine half-life degradation rates of CARB and OXAZ, assuming no  
462 retardation. Other trace organics were not analysed during this time. Half-life  
463 degradation rates were based on delivery/recovery mass balances studies and relative  
464 changes in groundwater concentrations downgradient from the infiltration gallery.  
465 Based on the groundwater concentrations immediately downgradient (2.3 m) of the  
466 infiltration gallery of  $0.46 \pm 0.05 \mu\text{g L}^{-1}$  ( $n = 4$ ) and  $0.30 \pm 0.11 \mu\text{g L}^{-1}$  ( $n = 4$ ) for  
467 CARB and OXAZ, and an infiltration rate of  $50 \text{ kL day}^{-1}$ , mass delivery rates of  $23 \pm$   
468  $3 \text{ mg day}^{-1}$  and  $15 \pm 6 \text{ mg day}^{-1}$  for CARB and OXAZ were determined. Mass  
469 recovery rates based on extraction bore BH17 concentrations of  $0.088 \pm 0.024 \mu\text{g L}^{-1}$   
470 ( $n = 4$ ) and  $<0.1 \mu\text{g L}^{-1}$  ( $n = 4$ ) for CARB and OXAZ and an extraction rate of  $250 \text{ kL}$   
471  $\text{day}^{-1}$  gave mass recovery rates of  $22 \pm 6 \text{ mg day}^{-1}$  and  $<25 \text{ mg day}^{-1}$  for CARB and  
472 OXAZ. This mass balance data suggests that CARB was not removed during the 70  
473 day aquifer passage, which was consistent with column data that showed a  
474 degradation rate of  $>50$  days. Due to the higher analytical detection limit for OXAZ, a  
475 field assessment of OXAZ degradation based on mass balance data could not be  
476 undertaken.

477 Degradation half-life values for CARB and OXAZ based on changes in trace  
478 organic concentration with distance from the infiltration gallery (Figure 6) were also

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479 investigated. The decreases for both CARB and OXAZ with distance from the  
480 infiltration gallery are likely due to a combination of degradation and/or  
481 dilution/dispersion. As the rates of decrease are similar for both trace organics (similar  
482 ratio of OXAZ to CARB), their degradation rates should also be similar, assuming  
483 that dilution/dispersion is similar for both. Based on this data and CARB mass  
484 balance data, OXAZ degradation half-life is likely to be negligible over the 70 day  
485 aquifer passage. These field-based degradation rates are consistent with column data,  
486 suggesting the column data provides a reliable field-scale estimation of trace organic  
487 degradation rates, at least for persistent trace organics CARB and OXAZ.

488

## 489 **Conclusions**

490 For the Spearwood sediment investigated in this experiment, the low R values  
491 of the trace organics for the sediment suggest these compounds will migrate at similar  
492 velocities to groundwater flow. The natural aerobic geochemical conditions provided  
493 a suitable environment for degradation for the endocrine disrupting compounds (BPA  
494 and E2), and IOH, with bacterial acclimation lag-times ranging from <15 to 30 days.  
495 However, an alternative artificial induced anaerobic geochemical condition would be  
496 required for the removal of IDP. EE2, the pharmaceuticals (CARB and OXAZ) and  
497 disinfection by-products (NDMA and NMOR) were not observed to degrade under  
498 either aerobic or anaerobic aquifer geochemical conditions. However, the lack of  
499 degradation may be a result of insufficient time for bacterial acclimation, especially  
500 for this sediment as it was not previously exposed to trace organic contamination, and  
501 longer-term experiments may be required. Also, increased column residence times  
502 may provide more accurate degradation rate estimations of slowly degrading trace  
503 organics.

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504 The influent trace organic concentrations ( $\mu\text{g L}^{-1}$  range) used in this  
505 experiment were higher than generally detected in environmental water samples (ng  
506  $\text{L}^{-1}$  range). However, low  $\mu\text{g L}^{-1}$  concentrations of pharmaceuticals have been detected  
507 in environmental water samples (Carrara et al., 2008). Recently, toxic effect studies  
508 on the degradation rate of NMOR have been undertaken in long-term experiments  
509 with greater column residence times (Pitoy et al., 2010). Comparable slow NMOR  
510 degradation half-lives were observed at both 200 ng  $\text{L}^{-1}$  and 650  $\mu\text{g L}^{-1}$  NMOR  
511 concentrations, suggesting limited toxic effects up to a concentration of 650  $\mu\text{g L}^{-1}$ .  
512 Based on this toxic effect data, the results from these current column experiments  
513 should provide at least indicative fate data for aquifer systems.

514 While it has been observed that improvements can occur in the nutrient and  
515 microbial quality of recycled water during MAR, there is still the potential for some  
516 trace organics to remain in the recovered water, even if there is a significant residence  
517 time in the aquifer. If persistent trace organics are present in recycled waters at  
518 excessive concentrations for their intended use, natural attenuation during aquifer  
519 passage alone may not result in extracted water meeting regulatory requirements, and  
520 additional pre or post-treatment of the recycled water may therefore be required.

521

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528 facilitating recycling of sewerage and stormwater via managed aquifer recharge.

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**Figure 1. Bromide and trace organic breakthrough data from day 15 used to calculate trace organic retardation coefficients in the sterile sediment column.  $C_o$  (influent concentration) values are given in Table 2**

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**Figure 2. Plots of trace organic concentrations versus time for the sterile and non-sterile columns. The distance of the sampling ports along the column was converted to time (days) based on the linear flow velocity of the trace organic (linear velocity of bromide tracer divided by the trace organic R value). Half-life curves for the non-sterile columns are shown. Results are for the last**

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2 676 sampling (day 330), except for BPA (day 168) due to observed further degradation of BPA in the  
3 677 sterile column at the later monitoring times.

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6 679 Figure 3. Sulphate concentrations as a fraction of influent concentrations for A) the sterile and  
7 680 B) non-sterile sediment columns. Ethanol addition commenced on day 191 at 100 cm along the  
8 681 column. For each column, one pore volume was equivalent to 42 days.

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11 683 Figure 4. IOX concentrations as a fraction of influent concentrations for A) the sterile and B)  
12 684 non-sterile sediment columns. Ethanol addition commenced on day 191 at 100 cm along the  
13 685 column. For each column, one pore volume was equivalent to 42 days.

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16 687 Figure 5. IDP concentrations as a fraction of influent concentrations for A) the sterile and B)  
17 688 non-sterile sediment columns. Ethanol addition commenced on day 191 at 100 cm along the  
18 689 column. For each column, one pore volume was equivalent to 42 days.

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21 691 Figure 6. CARB and OXAZ concentrations along the groundwater flow line between the  
22 692 infiltration gallery and the extraction bore (50 m downgradient) at the MAR field site.

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2 **Table 1. Column sediment properties determined on a sediment sub-sample, and influent water**  
 3 **chemistry. See text for methods used to determine column porosity and hydraulic conductivity.**

Sediment			Influent Water*	
Sediment Organic Matter	0.02% w/w		pH	7.9
(SOM)				
Iron content	0.13% w/w		Na	230 mg L <sup>-1</sup>
Porosity	0.46		K	26 mg L <sup>-1</sup>
Hydraulic conductivity	18 m d <sup>-1</sup>		Mg	10 mg L <sup>-1</sup>
Bulk density	1660 kg m <sup>-3</sup>		Ca	27 mg L <sup>-1</sup>
			Cl	180 mg L <sup>-1</sup>
<b>Mineralogy</b>			HCO <sub>3</sub>	180 mg L <sup>-1</sup>
Quartz	75%		SO <sub>4</sub> -S	18 mg L <sup>-1</sup>
Calcite	12%		NO <sub>3</sub> -N	30 mg L <sup>-1</sup>
Microcline/Orthoclase	11%		Dissolved organic carbon	6.6 mg L <sup>-1</sup>
Albite/Anorthite	2%		Dissolved oxygen	7.8 mg L <sup>-1</sup>

\*Control column influent water also contained 0.65 g L<sup>-1</sup> sodium azide

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1 Table 2. Trace organic column influent concentrations, literature octanol-water partitioning coefficients ( $K_{ow}$ ), and experimental retardation coefficients (R), first-  
 2 order degradation half-lives of trace organics and zero-order degradation rates along with lag-times to the start of degradation, determined from the column  
 3 experiments.

Trace organic	Influent conc. ( $\mu\text{g/L}$ )	Literature $\text{Log } K_{ow}^{\dagger}$	Retardation coefficient R (-)	Sorption coefficient $k_d$ ( $\text{L kg}^{-1}$ )	Aerobic first-order degradation half-life (days)	Aerobic zero-order degradation ( $\mu\text{g L}^{-1} \text{ day}^{-1}$ )	Aerobic lag-time (days)	Anaerobic degradation half-life (days)	Anaerobic zero-order degradation ( $\mu\text{g L}^{-1} \text{ day}^{-1}$ )	Anaerobic lag-time (days)
E2	130	3.9	ND	ND	<1	140	<15	ND	ND	ND
EE2	400	4.1	1.1	0.03	>50	<10	>330	>50	<10	<40
BPA	500	3.6	1.2	0.03	<1	380	<15	ND	ND	ND
OXAZ	400	2.3	1.0	0.00	>50	<10	>330	>50	<10	>140
CARB	680	2.3	1.0	0.00	>50	<10	>330	>50	<10	>140
NDMA	590	-0.64	1.0	0.00	>50	<10	>330	>50	<10	>140
NMOR	650	-0.43	1.0	0.00	>50	<10	>330	>50	<10	>140
IOX	630	-2.8	1.0	0.00	<1	270	30	ND	ND	ND
IDP	700	5.2	1.0	0.00	>50	<10	>330	<1	340	<40
bromide	22 000									

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7 4 ND = not determined, as compound degraded prior to assessment.  
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9 5  $k_d$  estimated using soil porosity and bulk density from Table 1.  
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11 6 <sup>†</sup>SRC (2009)  
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Figure2

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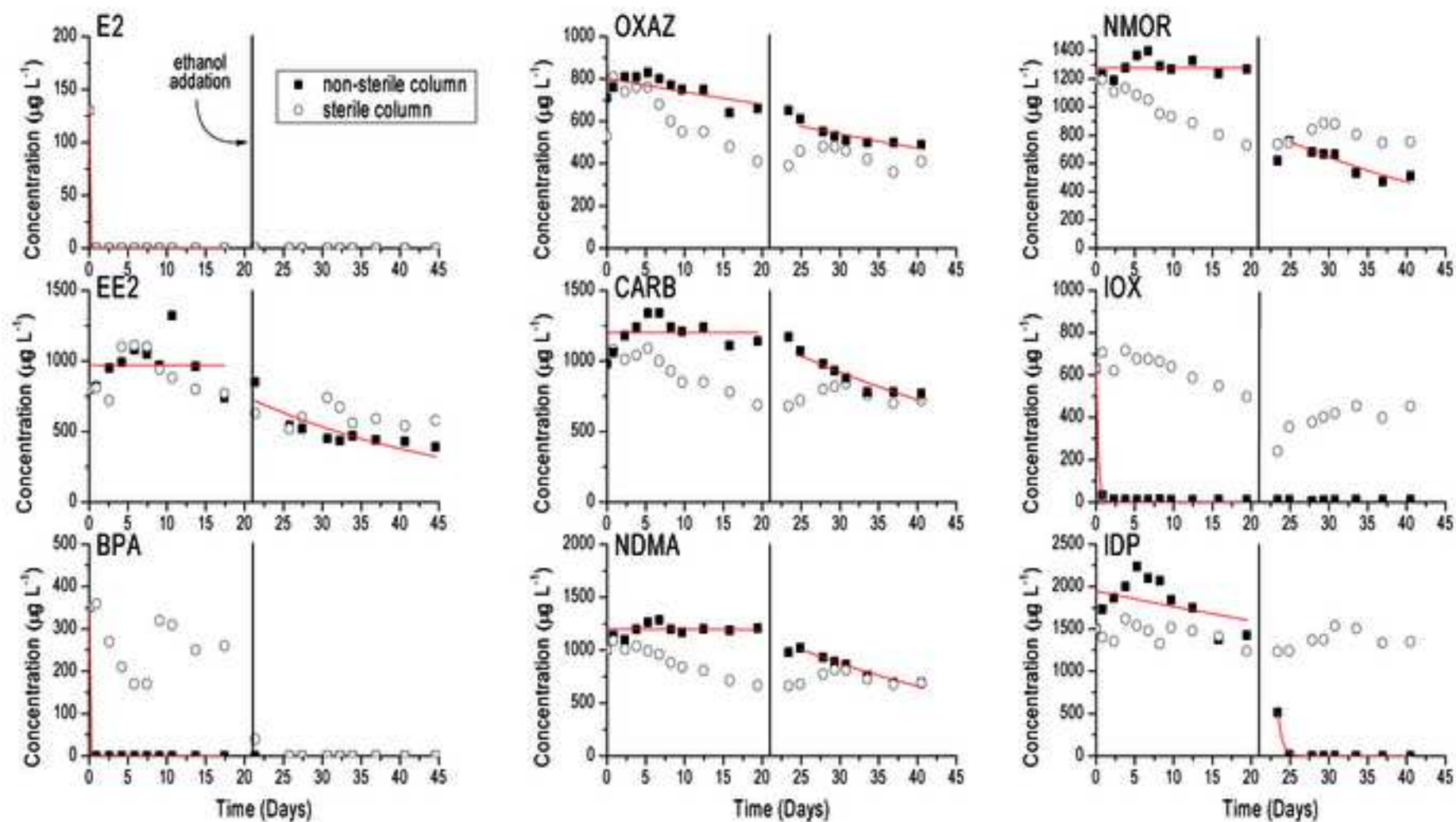


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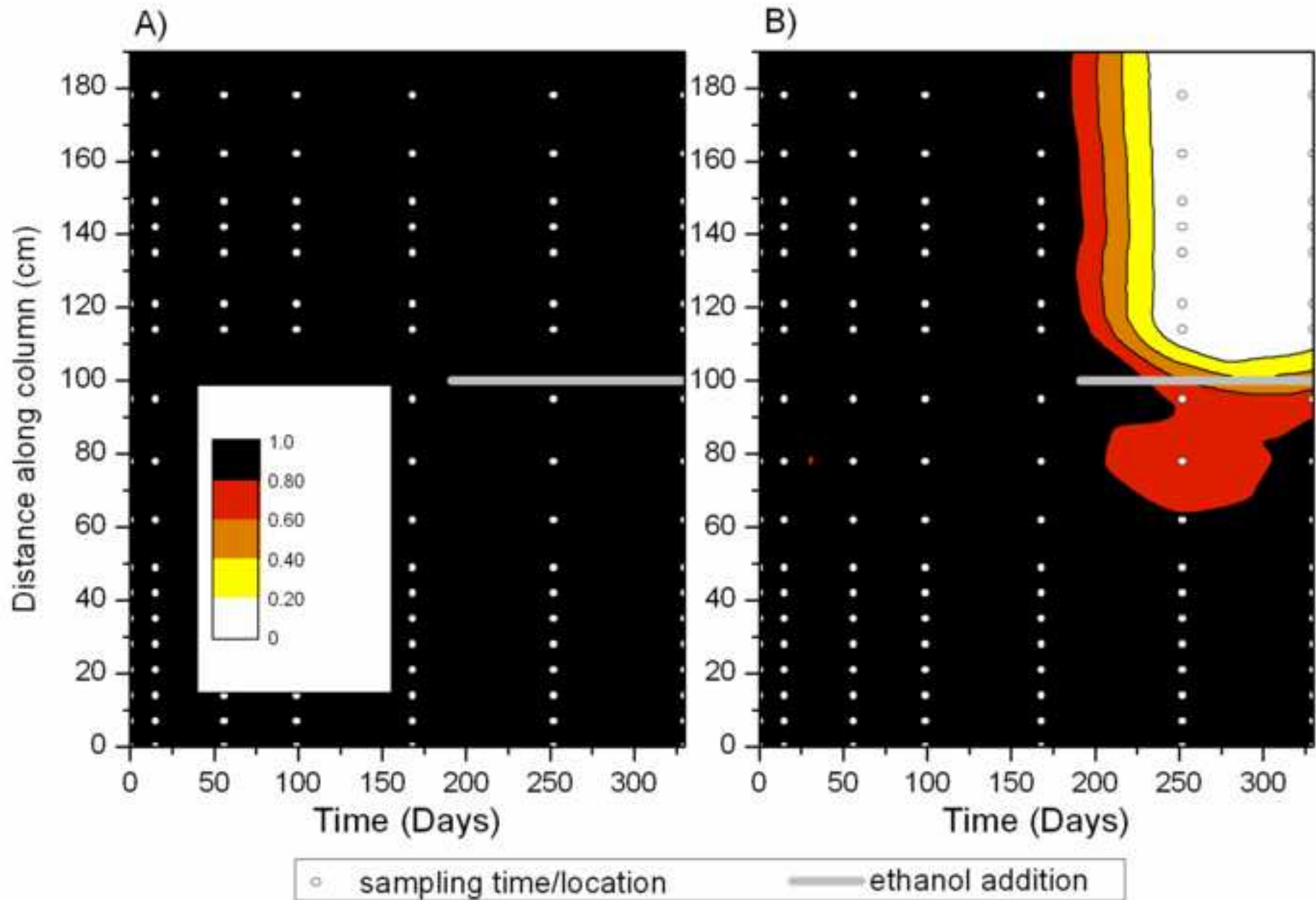


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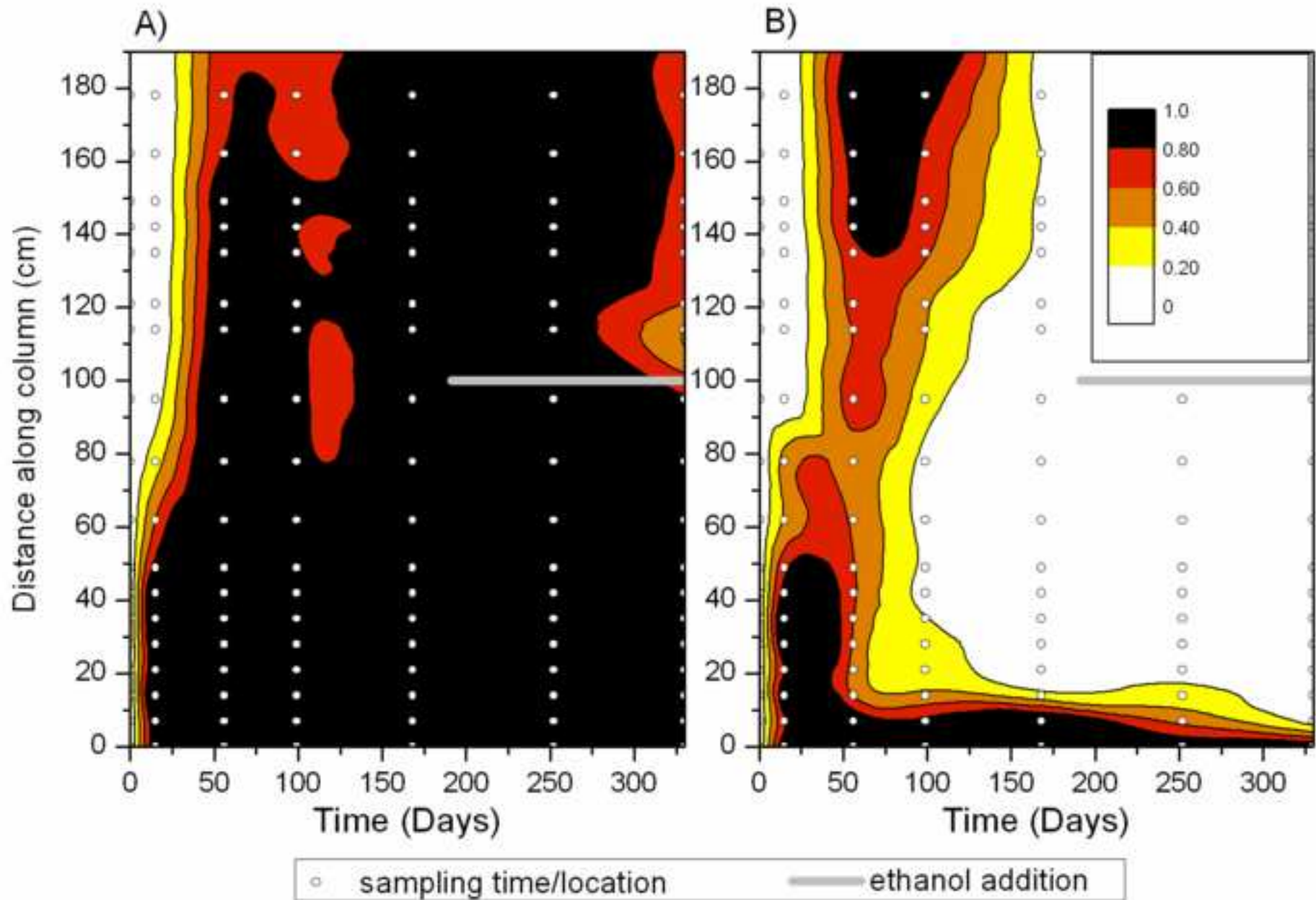


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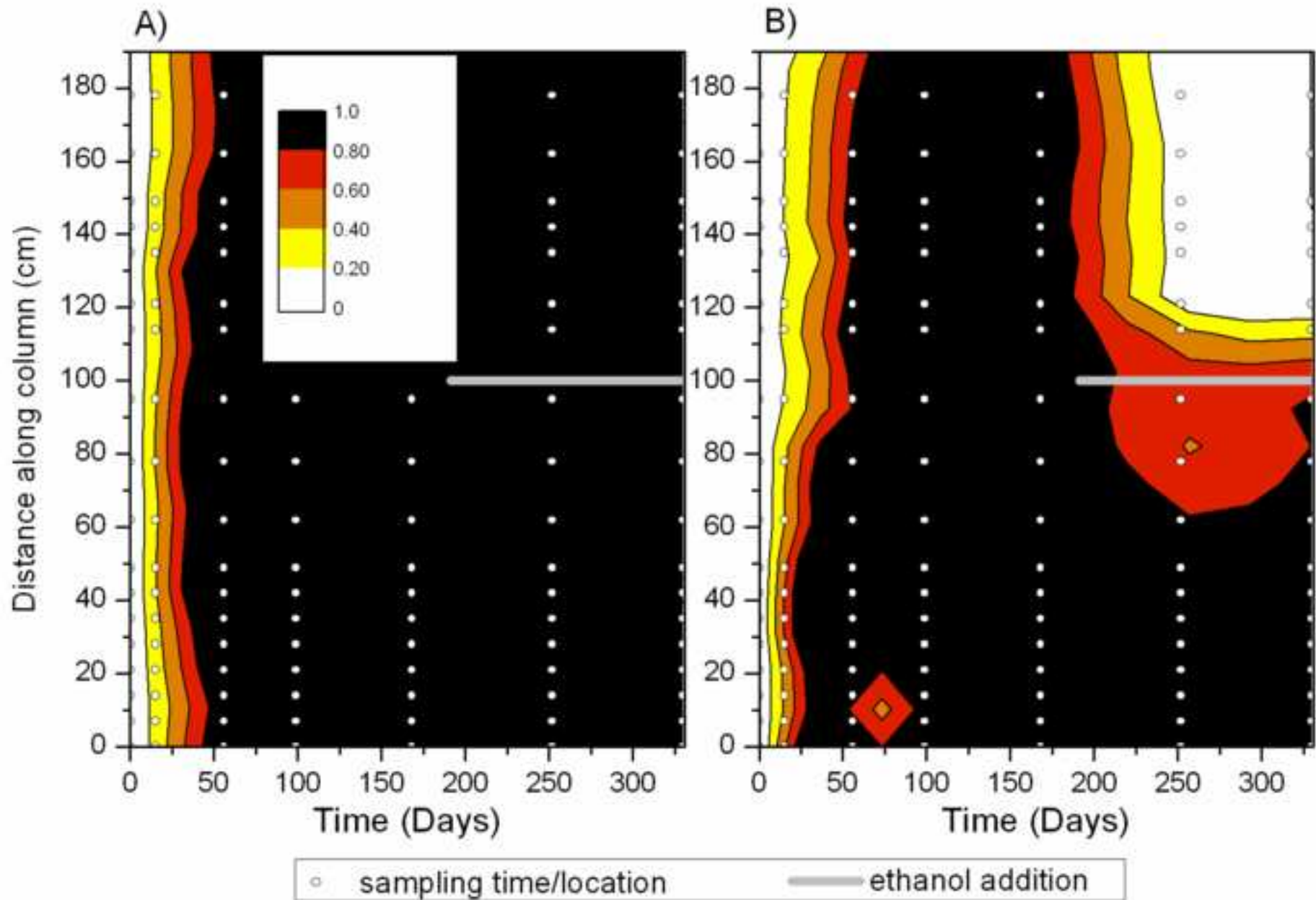




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