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Behaviour and Fate of Nine Recycled Water Trace Organics during Managed Aquifer Recharge in an Aerobic Aquifer

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Abstract

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

Introduction

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

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

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

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

Materials and Methods

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

Aquifer Material

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

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

Column Setup

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

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

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

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

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

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

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

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

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

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

with $MgSO_4$ (s) to remove any water from the solvent. The dried solutions were then concentrated to ~150 μL at 44 °C under a gentle stream of N_2 gas and 10μL internal standard (Diphenylamine-d10) added. Extracts were then analysed by gas chromatography mass spectrometry based on the method of Cheng et al. (2006), using an Agilent 6890N GC coupled with an Agilent 5975 inert mass spectrometer. A HP-Innowax wax polyethylene glycol capillary column, 30 mm length and 0.25 mm I.D., was used for separation at a flow rate of 1.3 mL min^{-1}. The Diphenylamine-d10 internal standard was used to monitor the volume of samples injected into the GC-MS, while the surrogate standards were used to aid analyte peak identification and quantification. Quantifying ions (74 m/z, 116 m/z) and qualifying ions (42 m/z, 86 m/z) were selected for NDMA and NMOR respectively. Analytes were quantified via an external calibration curve spanning 0-1000 μg L^{-1}, based on the ratio of analyte to surrogate standard.

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

Field Validation

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

extracted (250 kL day^{-1}) from bore BH17, screened between 14 and 24 m below ground surface.

Results and Discussion

Retardation coefficients

Sediment analysis by XRD showed the mineral composition was predominantly quartz (75 %), with calcite (12 %), microcline/orthoclase (11 %), and albite/anorthite (2 %). All other minerals were below analytical detection (<1 %). Details of the sediment properties are given in Table 1.

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

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

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

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

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

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

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

Degradation – Aerobic Conditions

To determine the degradation rate of the trace organics, trace organic concentration data was plotted against column residence time (Figure 2). To determine the column residence time, 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). For a number of trace organics such as BPA and IOX, degradation occurred rapidly over a

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

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

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

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

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

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

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

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

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

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

Degradation – Anaerobic Conditions

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

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

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

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

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

Field Validation.

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

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

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

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

Conclusions

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

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

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

Acknowledgement

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References

Barber, L. B., Keefe, S. H., LeBlanc, D. R., Bradley, P. M., Chapelle, F. H., Meyer, M. T., Loftin, K. A., Kolpin, D. A., Rubio, F. 2009. Fate of sulfamethoxazole, 4-nonylphenol, and 17β-estradiol in groundwater contaminated by wastewater treatment plant effluent. *Environ. Sci. Technol.*, 2009, 43 (13), 4843–4850.

Bekele, E. Toze, S., Rümmler, Hanna, J., Blair, P., and Turner, N. 2006. Improvements in wastewater quality from soil and aquifer passage using infiltration galleries: case study in Western Australia. Proceedings: International Symposium on Management of Aquifer Recharge (ISMAR), 10-16 June 2005, Berlin: 663-668.

Bradley, P. M., Carr, S. A., Baird, R. B., Chapelle, F. H. 2005. Biodegradation of N-nitrosodimethylamine in Soil from a Water Reclamation Facility. Bioremediation Journal, 9 (2), 115 – 120.

Busetti, F., Linge, K.L., Blythe, J.W., Heitz, A. 2008. Rapid analysis of iodinated X-ray contrast media in secondary and tertiary treated wastewater by direct injection liquid chromatography-tandem mass spectrometry. *Journal of Chromatography A*, 1213, 200–208.

Carrara, C., Ptacek, C.J., Robertson, W.D., Blowes, D. W., Moncur, M. C., Sverko, E., and Backus, S. 2008. Fate of pharmaceutical and trace organic compounds in three septic system plumes, Ontario, Canada. *Environ. Sci. Technol.*, 42 (8), 2805–2811.

Cheng, R. C., Hwang, C. J., Andrews-Tate, C., Guo, Y., Carr, S. and Suffet, I. H. 2006. Alternative methods for the analysis of NDMA and other nitrosamines in water. *Journal AWWA*, 98, 82-96.

Clara, M.; Strenn, B.; Kreuzinger, N. 2004. Carbamazepine as a possible anthropogenic marker in the aquatic environment: investigations on the behaviour of Carbamazepine in wastewater treatment and during groundwater infiltration, *Water Res.*, *38*, 947-954.

Díaz-Cruz, M.S., and Barceló, D. 2008. Trace organic chemicals contamination in ground water recharge, *Chemosphere*, 72 (3), 333-342.

Dillon, P., Pavelic, P. and Toze, R., Rinck-Pfeiffer, S., Martin, R., Knapton, A., and Pidsley, D. (2006). Role of aquifer storage in water reuse. *Desalination*, 188 (1-3), 123-134.

Drewes, J. E., Hoppe, C., Jennings, T. 2006. Fate and transport of N-nitrosamines under conditions simulating full-scale groundwater recharge operations. *Water Environment Research*, 78 (13), 2466 – 2473.

Grassi, M. E., Patterson, B.M., Davis, G.B., Robertson, B.S., and McKinley, A. J. 2007. Estimation of ethanol mass delivery to groundwater from silicone polymer mats. *Environmental Science and Technology*, 41, 5453 - 5459.

Gros, M., Petrović, M., Barceló, D. 2006. Development of a multi-residue analytical methodology based on liquid chromatography–tandem mass spectrometry (LC–MS/MS) for screening and trace level determination of pharmaceuticals in surface and wastewaters. Talanta, 70 (4), 678 – 690.

Grünheid, S., Amy, G., and Jekel, M. 2005. Removal of bulk dissolved organic carbon and trace organic compounds by bank filtration and artificial recharge. *Water Research*, *39*, 3219–3228.

Gunnison, D., Zappi, M. E., Teeter, C., Pennington, J. C., Bajpai, R. J. 2000. Attenuation mechanisms of N-nitrosodimethylamine at an operating intercept and treat groundwater remediation system. *Hazard. Mater*. 73, 179-197.

Heberer, T. 2002.Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. *Toxicol. Lett.*, *131*, 5-17.

Heberer, T., and Adam, M. 2004. Transport and attenuation of pharmaceutical residues during artificial groundwater replenishment, *Environ Chem*, 1, 22–25

Microcal™ Software Inc., 1995. *ORIGIN™ User's Manual.* Microcal Software Inc. Northhampton, MA.

Massmann, G., Greskowiak, J., Dünnbier, U., Zuehlke, S., Knappe, A., and Pekdeger, A. 2006. The impact of variable temperatures on the redox conditions and the behaviour of pharmaceutical residues during artificial recharge. *Journal of Hydrology*, *328*, 141–156.

Parker, J.C. and van Genuchten, M.Th., 1984. *Determining Transport Parameters from Laboratory and Field Tracer Experiments*. Bulletin 84-3, Virginia Agricultural Experiment Station, Blacksburg.

Patterson, B.M., Grassi, M.E., Davis, G.B., Robertson, B., and McKinley A.J. 2002. The use of Polymer Mats in Series for Sequential Reactive Barrier Remediation of Ammonium-contaminated Groundwater: Laboratory Column Evaluation. *Environmental Science and Technology*, 2002, 36, 3439-34445.

Patterson, B.M., Grassi, M.E., Robertson, B.S., Davis, G.B., Smith, A.J. and McKinley, A.J. 2004.The use of polymer mats in series for sequential reactive barrier remediation of ammonium-contaminated groundwater: field evaluation. *Environmental Science and Technology*, 38, 6846-6854.

Patterson, B.M., Pribac, F., Barber, C., Davis, G.B. and Gibbs, R., 1993. Biodegradation and retardation of PCE and BTEX compounds in aquifer

material from Western Australia using large-scale columns. *J Contam. Hydrol.*, 14: 261-278.

Patterson, B.M., Shackleton, M., Furness, A. J., Pearce, J., Descourvieres, C. Linge, K. L., Busetti, F., Spadek, T. 2010. Fate of nine recycled water trace organic contaminants and metal(loid)s during managed aquifer recharge into a anaerobic aquifer: Column Studies. *Water Research*, 44, 1471 - 1481.

Pavelic, P., Dillon, P.J., and Nicholson, B.C. 2006. Comparative evaluation of the fate of disinfection by-products at eight aquifer storage and recovery sites. *Environ. Sci. & Technol*., 40, 501-508.

PCRP (2009) Premier¹s Collaborative Research Program (2005-2008) 'Characterising Treated Wastewater For Drinking Purposes Following Reverse Osmosis Treatment'. Technical Report. Water Corporation of Western Australia, Western Australian Department of Health.

Pitoi, M., Patterson, B.M., Furness, A. J., Bastow, T., McKinley, A. J. 2010. Fate of *N*-nitrosomorpholine in an anaerobic aquifer environment used for managed aquifer recharge. Proceeding of Groundwater2010, 31 October – 4 November 2010, Canberra, Australia.

Sarmah, A.; Northcott, G. 2008. Laboratory degradation studies of four endocrine disruptors in two environmental media, *Environ Toxicol Chem.*, 27 (4), 819–827.

Scheytt, T. J.; Mersmann, P.; Heberer, T. 2006. Mobility of pharmaceuticals carbamazepine, diclofenac, ibuprofen, and propyphenazone in miscible-displacement experiments.*J. Contam. Hydrol.*, *83*, 53-69.

SRC, Interactive log Kow, Syracuse Research Corporation, 2009.

Stephens, D.B., Hsu, K., Prieksat, M.A., Ankeny, M.D., Blandford, N., Roth, T.L., Kelsey, J.A., Whitworth, J.R. 1998. A comparison of estimated and calculated effective porosity. *Hydrogeol. J.* 6, 156–165.

Toze, R., and Hanna, J. 2002. The survival potential of enteric pathogens in a reclaimed water ASR project. in: Dillon, P. (ed), Proceeding of the 4th International symposium on artificial recharge of groundwater ISAR-4 - Management of Aquifer Recharge for Sustainability, 22-26 Sept 2002, Adelaide : Balkeme Publishers Australian: 139–142.

Toze, S., and Bekele, E. 2009. Determining requirements for managed aquifer recharge in Western Australia. A report to the Water Foundation. Water for a Healthy Country National Research Flagship CSIRO: Canberra. http://www.clw.csiro.au/publications/waterforahealthycountry/index.html#reports

Yang, W. C., Gan, J., Liu, W. P. and Green, R. 2005. Degradation of N-Nitrosodimethylamine (NDMA) in landscape soils, *J. Environ. Qual.* 34, 336-341.

Ying, G. G., Toze, S., Hanna, J., Yu, X. Y., Dillon, P. J., Kookana, R.S. 2008. Decay of endocrine-disrupting chemicals in aerobic and anoxic groundwater, *Water Research*, 42 (4-5), 1133-1141.

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

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

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

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

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

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

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

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

Sediment		**Influent Water***	
Sediment Organic Matter (SOM)	0.02% w/w	pH	7.9
Iron content	0.13% w/w	Na	230 mg L^{-1}
Porosity	0.46	K	26 mg L^{-1}
Hydraulic conductivity	18 m d^{-1}	Mg	10 mg L^{-1}
Bulk density	1660 kg m^{-3}	Ca	27 mg L^{-1}
		Cl	180 mg L^{-1}
Mineralogy		HCO_3	180 mg L^{-1}
Quartz	75%	SO_4-S	18 mg L^{-1}
Calcite	12%	NO_3-N	30 mg L^{-1}
Microcline/Orthoclase	11%	Dissolved organic carbon	6.6 mg L^{-1}
Albite/Anorthite	2%	Dissolved oxygen	7.8 mg L^{-1}

*Control column influent water also contained 0.65 g L^{-1} sodium azide

Table2

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Table 2. Trace organic column influent concentrations, literature octanol-water partitioning coefficients (K_{ow}), and experimental retardation coefficients (R), first-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 experiments.

Trace organic	Influent conc. (µg/L)	Literature Log K_{ow} [†]	Retardation coefficient R (-)	Sorption coefficient k_d (L kg^{-1})	Aerobic first-order degradation half-life (days)	Aerobic zero-order degradation (µg L^{-1} day^{-1})	Aerobic lag-time (days)	Anaerobic degradation half-life (days)	Anaerobic zero-order degradation (µg L^{-1} 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									

ND = not determined, as compound degraded prior to assessment.

k_d estimated using soil porosity and bulk density from Table 1.

[†]SRC (2009)

Figure1

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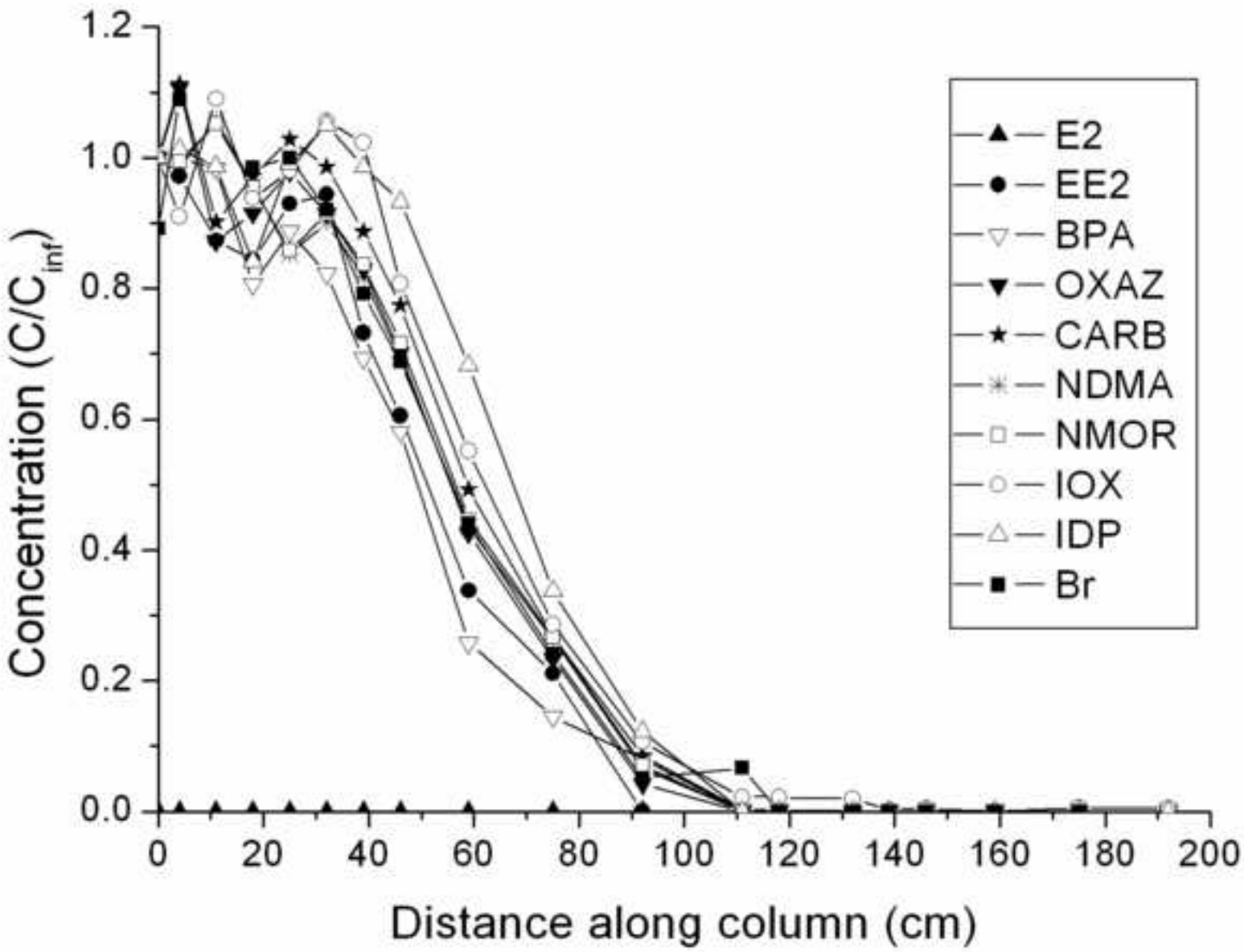

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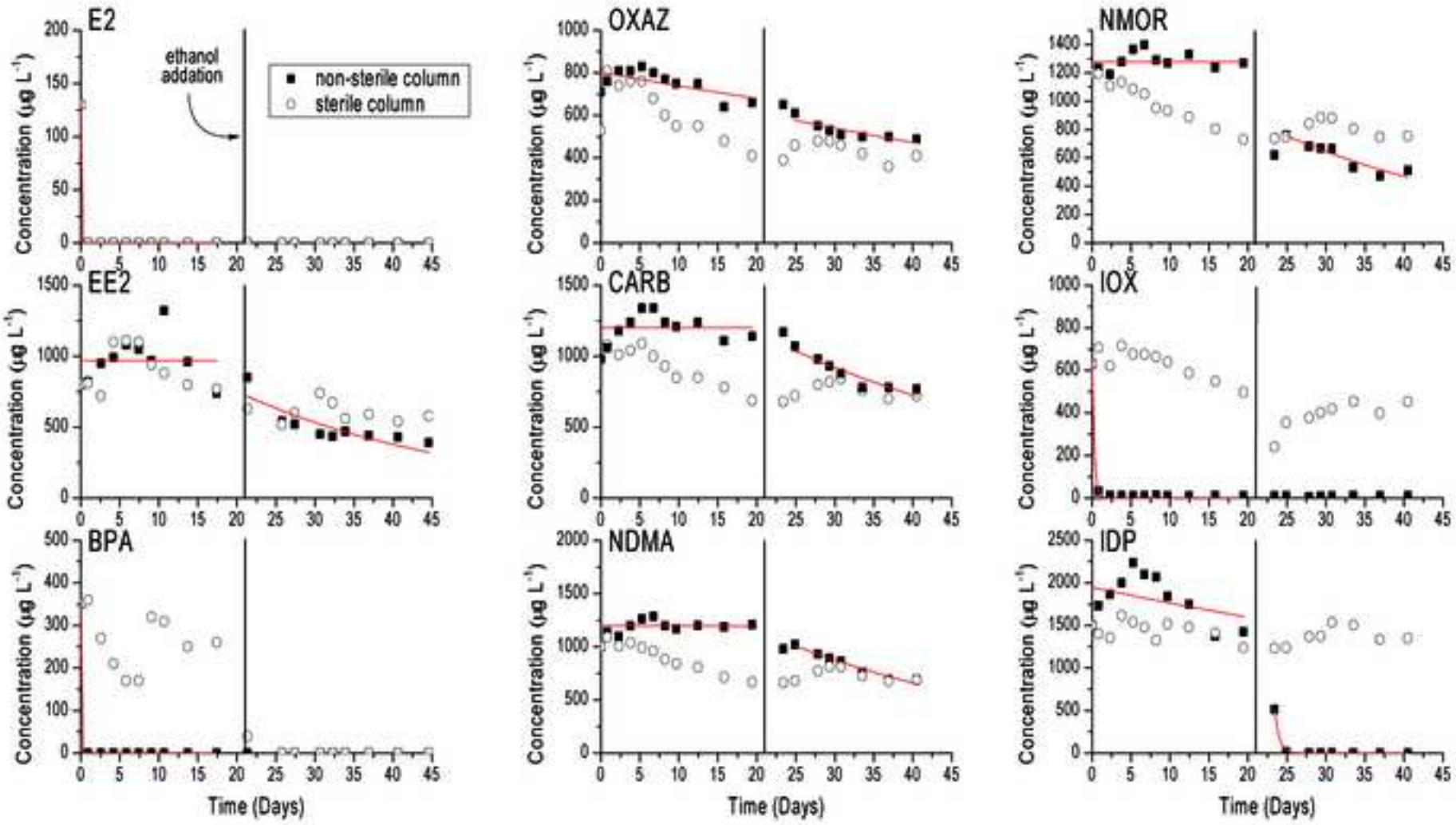

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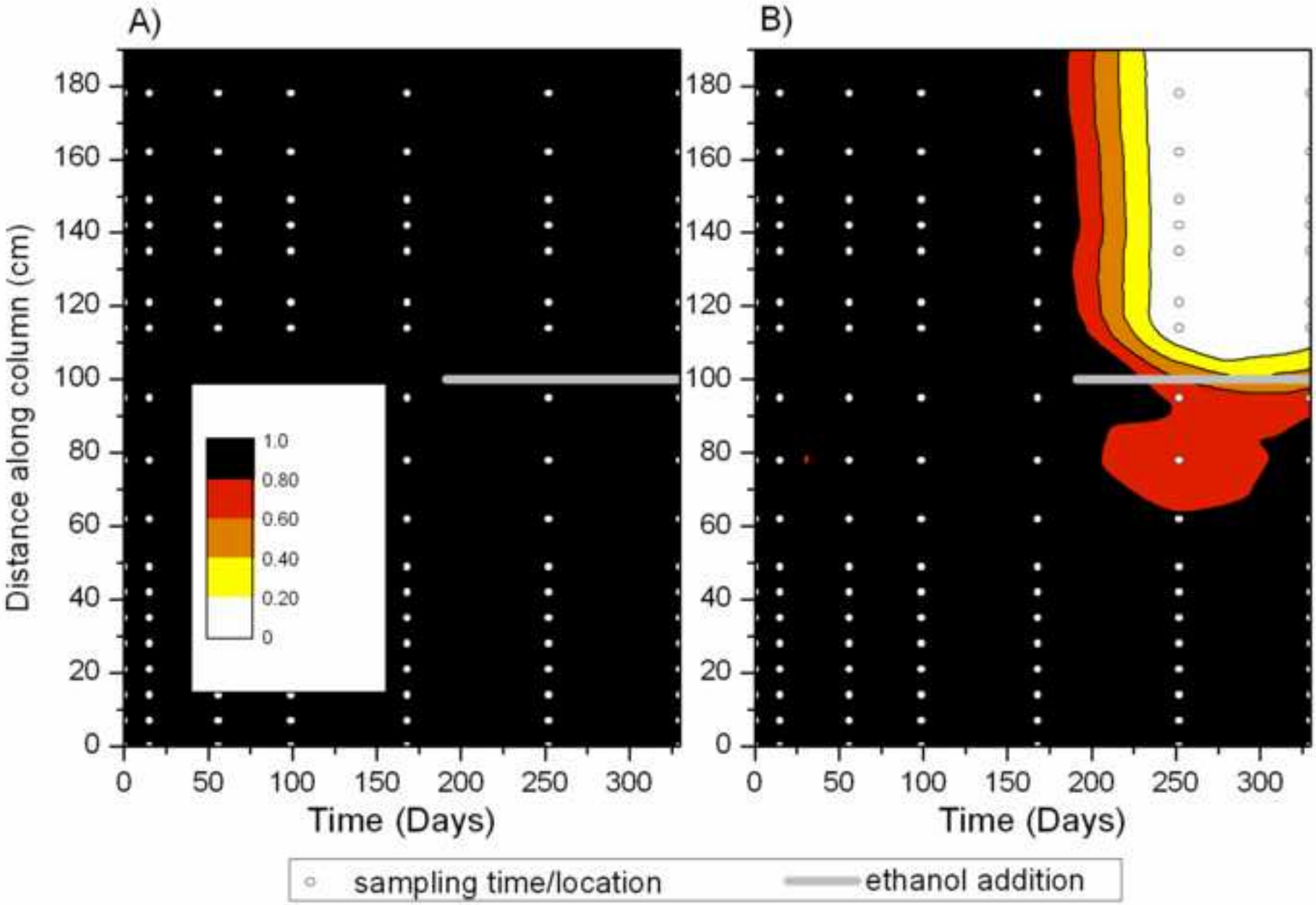

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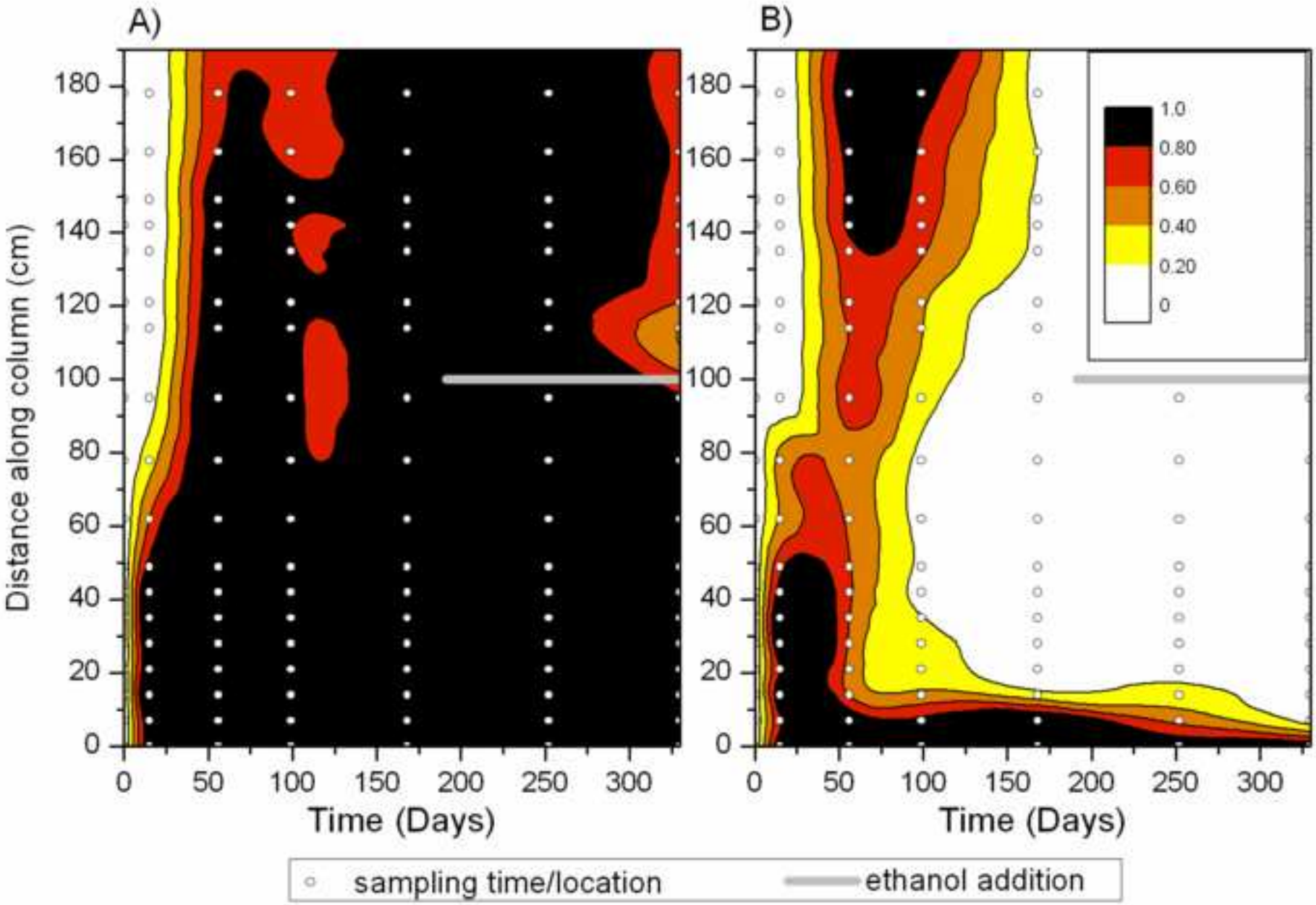

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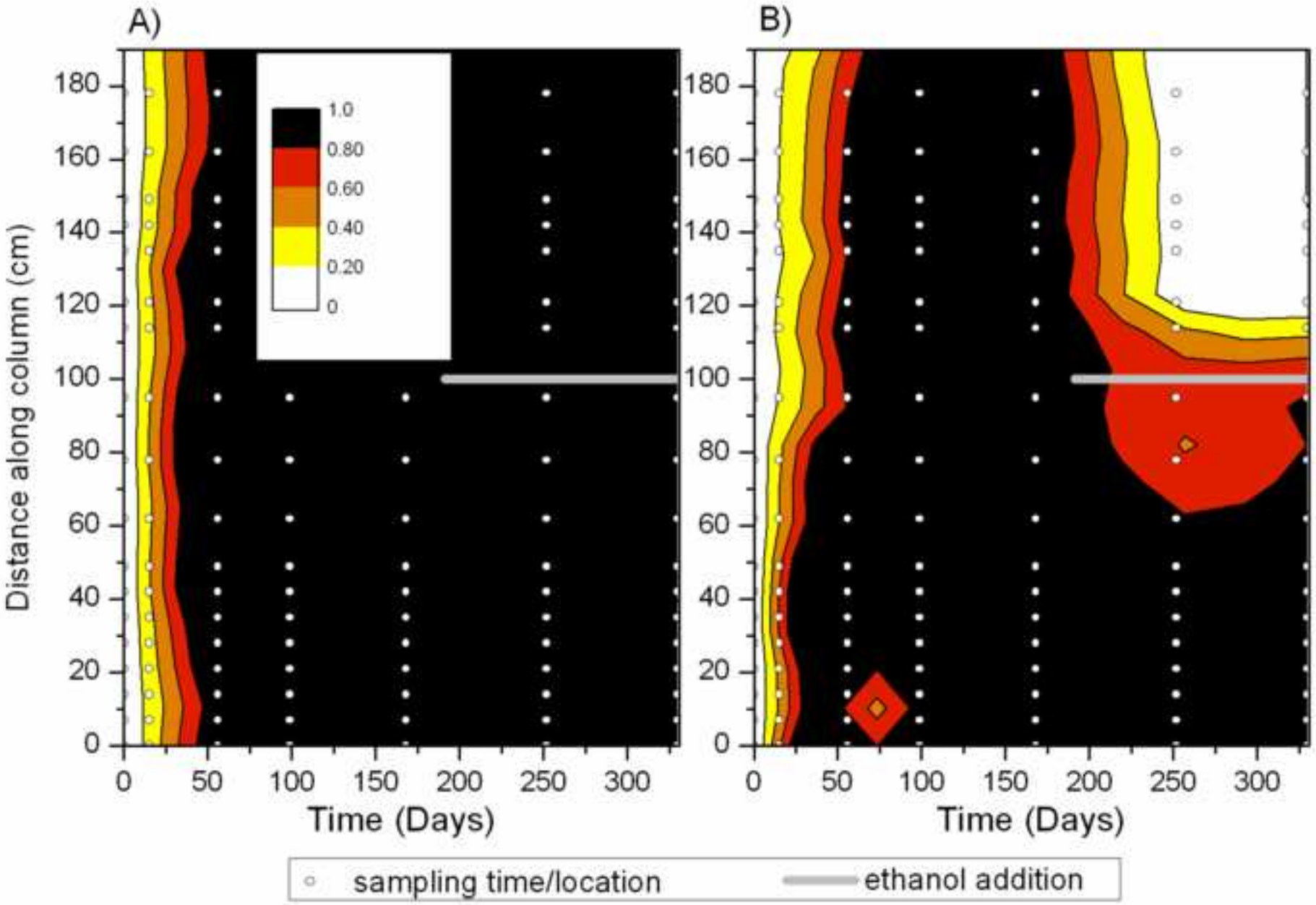

Figure6
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