1   **Behavior of organophosphates and hydrophilic ethers during bank filtration and their**

2   **potential application as organic tracers: A field study from the Oderbruch, Germany.**

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15

16   Abstract

17

18   The behavior of organophosphates and ethers during natural riverbank filtration and

19   groundwater flow was assessed to determine their suitability as organic tracers. Four sampling

20   campaigns were conducted at the Oderbruch polder, Germany to establish the presence of

21   chlorinated flame retardants (TCEP, TCPP, TDCP), non-chlorinated plasticizers (TBEP,

22   TiBP, TnBP), and hydrophilic ethers (1,4-dioxane, monoglyme, diglyme, triglyme,

23   tetraglyme) in the Oder River, bank filtrate, and anoxic aquifer. Selected hydro-chemical

24   parameters were determined in order to characterize the river water and groundwater. The

25   results of the study confirm that organophosphates (OPs) are more readily attenuated during

26   bank filtration than ethers. Both in the river and the groundwater, TCPP was the most

27   abundant OP with concentrations in the bank filtrate ranging between 105-958 ng L^{-1}. 1,4-

28   Dioxane, triglyme, and tetraglyme demonstrated persistent behavior during bank filtration and

29   in the anoxic groundwater. In the bank filtrate concentrations of 1,4-dioxane triglyme, and

30   tetraglyme ranged between 1090-1467 ng L^{-1}, 37-149 ng L^{-1} , and 496-1403 ng L^{-1} ,

31   respectively. A positive correlation was found for the inorganic tracer chloride with 1,4-

32   dioxane and tetraglyme. These results confirm the possible application of these ethers as

33   environmental organic tracers. Both inorganic and organic compounds showed temporal

34   variability in the surface- and groundwater. Discharge of the river water and concentrations of

35 analytes at the time of infiltration were identified as factors influencing the variable amounts

36 of the analytes in the surface- and groundwater. These findings are also of great importance

37 for the production of drinking water via bank filtration and natural and artificial groundwater

38 recharge as the physiochemical properties of ethers create challenges in their removal.

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42

43 1. Introduction

44

45 Natural and artificial processes of riverbank filtration are used in many countries in order to

46 replenish groundwater resources that can be subsequently utilized for drinking water

47 production (Tufenkij, 2002). Yet in many places, surface waters are not sufficiently shielded

48 from numerous point and nonpoint sources of organic contaminants resulting in pollution of

49 adjacent aquifers with compounds that are recalcitrant to attenuation through bank filtration.

50 These compounds can play an important role as indicators of anthropogenic groundwater

51 pollution. Several studies have shown contamination of groundwater with trace organic

52 contaminants including organophosphates (OPs) via bank filtration of surface water or

53 artificial recharge using reclaimed water (Knepper et al., 1999; Fries and Püttmann, 2003;

54 Heberer et al., 2004; Stuyfzand et al., 2007; Hoppe-Jones et al., 2010). The presence of ether

55 compounds in bank filtration or artificial recharge sites has also been reported (Noordsij et al.,

56 1985; Schmidt et al., 2003; Achten et al., 2002; Morgenstern et al., 2003; Stuyfzand et al.,

57 2007; Kuster et al., 2010; Kegel et al., 2010; Wiese et al., 2011).

58 OPs such as the chlorinated flame retardants tris(2-chloroethyl) phosphate (TCEP), tris(2-

59 chloro-1-methylethyl) phosphate (TCPP), and tris(1,3-dichloro-2-propyl) phosphate (TDCP)

60 and; the non-chlorinated plasticizers tris(2-butoxyethyl) phosphate (TBEP), tri-iso-butyl

61 phosphate (TiBP), and tri-n-butyl phosphate (TnBP), are industrial chemicals widely used

62 worldwide. Since the 1940s, OPs have been added to industrial and consumer products as

63 flame retardants and plasticizing agents. Their use increased significantly between 1960 and

64 1980 (Muir, 1984). An estimate, made in 2006 by the European Flame Retardant Association

65 (EFRA) indicated that approximately 91,000 tons of OPs were used annually in the EU. As

66 TCEP, TDCP, and TnBP are classified as category 3 human carcinogens (European chemical

67 substances information system; ECSIS), and as TCPP is considered to be a possible human

68   carcinogen (Reemtsma et al., 2008), concerns about the potential environmental risks of OPs

69   in aquifer systems have arisen.

70   1,4-Dioxane, monoethylene glycol dimethyl ether (monoglyme), diethylene glycol dimethyl

71   ether (diglyme), triethylene glycol dimethyl ether (triglyme), and tetraethylene glycol

72   dimethyl ether (tetraglyme) are solvents used in a wide range of industrial processes. The

73   current production volumes and applications in Europe are not readily available. Until 1995,

74   1,4-dioxane was commonly used as a 1,1,1-trichloroethane stabilizer, which was found to

75   deplete the ozone layer and was consequently regulated under the Montreal Protocol

76   (Doherty, 2000). Currently, the production of 1,4-dioxane in Europe is mainly confined to the

77   BASF AG in Ludwigshafen, Germany. As of 2007, the production volume was estimated to

78   reach 2,000-2,500 tons (ECB, 2002). Moreover, 1,4-dioxane may form as a by-product of the

79   polyester esterification and ethoxylation process in surfactant production (Zenker et al.,

80   2003). Glycol dimethyl ethers (glymes) are generally used as reaction solvents in the area of

81   pharmaceutical production and manufacture of specialty chemicals. According to the

82   Organization for Economic Co-operation and Development and ECSIS, production of

83   monoglyme and diglyme exceeds 1,000 tons per year in at least one member country (ECA,

84   2012a; 2012b). In 2002, the Oxygenated Solvent Producer Association reported the

85   production of triglyme to surpass 1,000 tons (ECA, 2012c). The EU industries have not

86   reported any production numbers for tetraglyme yet.

87   Differences in the physicochemical properties of OPs are caused by specific moieties in the

88   organic ester functional groups. The water solubility of OPs is relatively high, ranging from

89   18.1 mg L^{-1} for TDCP to 7820 mg L^{-1} for TCEP. The values of the n-octanol/water partition

90   coefficients (log P_{ow}) and the solid/water partition coefficients for soils (log P_{oc}) range from

91   1.7 (TCEP) to 4.0 (TnBP) and 2.48 (TCEP) to 5.67 (TBEP), respectively (Verbruggen et al.,

92   2005). The mobility of TCEP and TCPP is reported to be intermediate-to-high in

93   groundwater, whereas the mobility of TDCP and TBEP is quite low (Pitt et al., 1999; World

94   Health Organization, 2000; European Commission, 2006; 2007a; 2007b).Unlike chlorinated

95   OPs, the non-chlorinated OPs are expected to be partially degradable in aquatic environments

96   (Saeger et al., 1979; Kawagoshi et al., 2002). However, the behavior of these compounds in

97   groundwater can vary considerably from that in other aqueous compartments because of

98   differences in redox conditions (Amy and Drewes, 2007). Low water temperatures, marginal

99   dilution effects, and low levels of microbial activity can increase the persistence of trace

100   organic contaminants in groundwater resulting in long residence times (Díaz-Cruz and

101   Barceló, 2008), whereas some biogeochemical redox processes can enhance their

102 transformation processes (Borch et al., 2009). Adsorption, dilution, and biological

103 transformation are the most important processes attenuating OPs in groundwater during bank

104 filtration. These processes have been studied with reference to attenuation of OPs in sewage

105 treatment plants (Bester and Schäfer, 2009; Rauch-Williams et al., 2010) and are only poorly

106 understood in the context of surface water infiltration into groundwater through both artificial

107 and natural processes. Results of previous studies on OP stability, biotransformation, and

108 adsorption in soils and groundwater have been inconsistent (Heberer et al., 2004; Amy and

109 Drewes, 2007; Bester and Schäfer, 2009; Rauch-Williams et al., 2010). Some studies have

110 reported a removal of OPs due to adsorption other due to biodegradation. In the field studies,

111 OPs elimination was highly dependent on the boundary conditions at the field site.

112 The ether compounds selected for this study are highly hydrophilic due to their excellent

113 miscibility in water and low log P_{ow}. The negative log P_{ow} values indicate negligible potential

114 for bioaccumulation and a favored partitioning to the soil moisture (Schwarzenbach et al.,

115 1983). Volatilization from aqueous solutions and soil moisture into the air is negligible due to

116 low Henry's law constants (1.07×10^{-6} to 1.04×10^{-14}). Furthermore, the ether bonds generally

117 show low biodegradability in water under both aerobic and anoxic conditions (Kameya et al.,

118 1995; Grossmann et al., 2001). Anticipated processes of ether attenuation during bank

119 filtration are dilution, dispersion, and possibly biodegradation.

120 Three sampling campaigns were conducted at the Oderbruch polder between October 2009

121 and May 2012. Each time river water, main drainage ditch, and groundwater samples from six

122 shallow and six deep monitoring wells were analyzed to investigate the behavior of OPs and

123 ethers in the aquifer during river water infiltration. The main objectives of this study were a)

124 to establish the transport behavior of OPs in groundwater in comparison to the ethers; b) to

125 discuss possible processes of attenuation of chlorinated and non-chlorinated OPs as well as

126 hydrophilic ethers during bank filtration; and c) to determine if these compounds are suitable

127 for conservative tracer studies.

128

129 2. Materials and Methods

130

131 2.1. Site description

132

133 The Oderbruch polder is located about 60 km east of Berlin and covers an area of more than

134 800 km². The eastern boundary of the German part of the Oderbruch polder is the Oder River,

135 whereas the western boundary is the till plateau of Barnim/Lebus. Large parts of the polder

136   area are intensively used for agriculture, and therefore influenced by significant hydraulic and

137   water management measures. Levee construction, damming, and drainage with ditches and

138   pumping stations enabled intensive land use over recent centuries. The hydrological

139   environment is characterized by permanent bank filtration of Oder River water into the

140   aquifer. The unrestrained hydraulic contact between river and groundwater and the

141   hydraulically permeable river base lead to a constant groundwater movement towards the

142   slightly inclined polder area. The mostly confined groundwater drains into a wide drainage

143   network encompassing the entire region. The hydraulic situation is thought to have been

144   consistent over the last 250 years (Massmann et al., 2004). The aquifer at Oderbruch polder

145   has an average thickness of 25 m and is composed of fine to medium sized sands of

146   Pleistocene glaciofluvial origin. The aquifer is covered by a 0.2–4.0 m thick largely

147   impermeable layer of Holocene alluvial loam (Massmann et al., 2003). The aquifer base is

148   attached to a Saalian till.

149   Even under mean low water conditions Oder River water infiltrates into the bank (flow

150   velocity 0.5–1.5 m d^{-1}), whereas more than 80% of the filtrate discharges several months later

151   into a main drainage ditch running parallel to the river levee situated 100–200 m from the

152   river (Merz et al., 2005). Bank filtrate travel times from the river to the central polder located

153   about 3,500 m from the Oder River are in the order of decades to 120 years (Sültenfuß and

154   Massmann, 2004).

155   Groundwater from a transect comprising of six shallow (7–10 m) and six deep (19–23 m)

156   groundwater monitoring wells was sampled at the Oderbruch polder (Bahnbruecke site) on

157   four occasions between the year 2009 and 2012. Fig. 1 depicts a simplified geological cross

158   section of the sampling site. Each sampling location consists of one deep and one shallow

159   screened well that allows distinguishing spatial differences in the hydrochemistry and the

160   hydraulic conditions of the groundwater system (Sültenfuß and Massmann, 2004). The

161   identification code, grid value, sampling depth, and distance to the Oder River for each

162   monitoring well is shown in Table 1. Field parameters (i.e., pH, temperature, conductivity,

163   dissolved O_2, redox potential) were measured at each well using a flow cell equipped with

164   probes. Sampling of groundwater (1 L) was performed in duplicate after all field parameters

165   had stabilized.

166

167   2.2. Analytical methods

168

169   *Method I:* A detailed description of the analytical method for the determination of OPs using

170   gas chromatography – mass spectrometry (GC-MS) is provided in references Regnery and

171   Püttmann (2009; 2010). Hence, only a brief description is given. This method was also used

172   to analyze triglyme and tetraglyme during the 2011 sampling. Groundwater samples (1 L)

173   were not filtered prior to solid phase extraction (SPE). The samples were extracted using a

174   styrene-divinylbenzene polymeric SPE cartridge (Bond Elute PPL, 1 mL; Varian, Darmstadt,

175   Germany), which was eluted with 1 mL methanol/acetonitrile (1/1 v/v). Quantitative analyses

176   of the target compounds in the sample extracts were performed using a Trace GC Ultra gas

177   chromatograph coupled to a DSQ II mass spectrometer (Thermo Scientific, Dreieich,

178   Germany) operating in full scan mode (50-600 *m/z*). A TR-5MS capillary column (30 m

179   length, 0.25 mm i.d., 0.25 μm film thickness; Thermo Scientific) was used for GC separation

180   with the following temperature program: 80 °C for 1 min, increase to 300 °C at 4 °C min^{-1},

181   final temperature kept for 25 min. Target analytes were quantified using squalane (Sigma

182   Aldrich, Steinheim, Germany) as an internal calibration standard (Regnery and Püttmann,

183   2009). Individual stock solutions (1 μg $μL^{-1}$) of TCEP, TiBP, TnBP, TBEP, tetraglyme

184   (Sigma Aldrich), TCPP, TDCP (Akzo Nobel, Amersfoort, The Netherlands), and triglyme

185   (Alfa Aeser, Karlsruhe, Germany) were prepared in methanol/acetonitrile (1/1 v/v), whereas

186   squalane stock solution (1 μg $μL^{-1}$) was prepared in hexane. Acetonitrile (J. T. Baker,

187   Deventer, The Netherlands) was ultrapure HPLC grade and was used as received. All other

188   solvents (Merck, Darmstadt, Germany) were of analytical grade and were distilled before use.

189   Working standard solutions were obtained by appropriate dilution. All stock and working

190   standard solutions were regularly renewed every 2-4 weeks.

191   *Method II:* The samples acquired during the 2012 sampling were analyzed for 1,4-dioxane,

192   monoglyme, diglyme, triglyme, and tetraglyme with a SPE GC-MS method that has been

193   developed especially for the hydrophilic ether compounds (Stepien and Püttmann, 2013).

194   Coconut charcoal SPE cartridges (Restek, Resprep, 80-120 mesh, approx. 150 μm) were used

195   to extract and enrich the analytes from the water samples. Surrogate (1,4-dioxane-d8, 1 μg $μl^{-1}$

196   ^{1}) was added to each sample resulting in a final concentration of 500 μg L^{-1}. The analytes

197   were eluted with 10 mL of dichloromethane. 10 μL of internal standard 4-

198   chlorotetrahydropyran (12.5 μg L^{-1}) were added to 500 μL extract and the sample vials were

199   placed in the Combi PAL autosampler (CTC Analytics, Switzerland). 2 μL of extract were

200   injected onto the Trace 2000 gas chromatograph coupled to a Voyager mass spectrometer

201   (ThermoQuest Finnigan). The GC was equipped with a DB-624 column (Agilent, Waldbronn,

202   Germany) and the following temperature program applied: 37 °C for 2.5 min, increased to 75

203 °C at 4 °C min^{-1} and 10 °C min^{-1} to the final temperature of 220 °C, kept for 10 min. The

204 standard stock solution (1 µg µL^{-1}) of 1,4-dioxane (Dr. Ehrenstorfer, Ausgburg, Germany),

205 monoglyme (Sigma Aldrich), triglyme, and tetraglyme was prepared in methanol

206 (hypergrade, Merck). The working standards were prepared by appropriate dilution with

207 distilled dichloromethane.

208 The analyses of groundwater hydrochemistry were performed at the Institute of Landscape

209 Hydrology at the Leibniz-Centre for Agricultural Landscape Research (ZALF e.V.). Water

210 samples were analyzed for Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, NO_3^-, NO_2^- and SO_4^{2-} by ion

211 chromatography (DX500, Dionex, Idstein, Germany) using an IonPac column CS12A for the

212 cations and an AS9-HC4 column for the anions. Iron was determined by inductively coupled

213 plasma atomic emission spectroscopy (Jobin Yvon, Unterhaching, Germany), alkalinity was

214 determined by titration and NH_4^+ and PO_4^{2-} were measured by photometry (SPECORD 200,

215 Analytik Jena, Jena, Germany).

216

217 2.3. Quality assurance

218

219 Samples were collected in 1L amber glass bottles, which were thoroughly pre-cleaned prior

220 to sampling to avoid sample contamination. The samples were extracted within 72 hours of

221 collection. As controls for possible contamination during transport and laboratory treatment,

222 blanks of ultrapure water were included and treated identically to the groundwater samples.

223 Concentrations were not corrected in terms of SPE recovery rates. Recoveries of OPs in

224 ultrapure water (n = 6) and natural surface water (n = 3) were in the range of 85–99% and

225 72–99%, respectively, with relative standard deviations (RSD) less than 10%. Triglyme and

226 tetraglyme demonstrated a recovery range of 87-98% in ultrapure water (n = 5) with relative

227 SD less than 7%. Limits of detection (LOD) of 1 ng L^{-1} for TCEP, TCPP, TDCP, TBEP,

228 TnBP, TiBP, and tetraglyme (Method I), and 2 ng L^{-1} for triglyme (Method I) were calculated

229 from seven-point calibration curves of standard mixtures in accordance with DIN 32645

230 (DINTest, University of Heidelberg, $\alpha = 1\%$). For TCEP, TCPP, TiBP, TnBP, triglyme, and

231 tetraglyme the limit of quantification (LOQ) was estimated as three times the LOD, and

232 ranged from 3 ng L^{-1} for TCEP to 5 ng L^{-1} for triglyme. As TDCP (4 ± 6 ng L^{-1}) and TBEP

233 (3 ± 5 ng L^{-1}) were detected in the blanks (n = 8), the LOQ for each compound was calculated

234 as the mean of blank value plus six times the SD of the mean, resulting in LOQs of 40 ng L^{-1}

235 (TDCP) and 33 ng L^{-1} (TBEP). The LOD for the ethers using coconut charcoal SPE

236 extraction and the Voyager GC-MS were calculated by the United States Environmental

237   Protection Agency Chapter 40 part 136, Appendix B of the Federal Register (US EPA, 2011).

238   Eight replicates of the environmental water samples (Main River) were spiked at 40 ng L^{-1},

239   extracted and analyzed in order to calculate the following LODs: Monoglyme, 4 ng L^{-1}; 1,4-

240   dioxane, 16 ng L^{-1}; diglyme, 13 ng L^{-1}; triglyme, 10 ng L^{-1}; and tetraglyme, 12 ng L^{-1}. The

241   LOQs were obtained by multiplying the average SD of the replicate analysis by 10, resulting

242   in LOQs for each compound between 12-52 ng L^{-1}.

243

244   3. Results and Discussion

245

246   3.1. Hydrochemistry

247

248   Geochemical indicators of natural attenuation can help to identify the ongoing processes in

249   the aquifer. A more detailed description of the redox processes in the Oderbruch polder is

250   provided by Massmann et al. (2004). Fig. 2 shows average values for the redox relevant

251   parameters in Oder River water (n = 1; March 2011) and deep groundwater wells (n = 3).

252   Groundwater redox potentials (E_h) varied between samplings but were on average below 100

253   mV. As shown in Fig. 2, both dissolved O_2 and NO_3^- were consumed between the river and

254   the first deep sampling well revealing anoxic conditions in the groundwater. The dissolved

255   organic carbon (DOC) dropped from 7.6 mg L^{-1} (n = 1) to 6.3 mg L^{-1} (n = 3). The decrease in

256   DOC continued until the deep well located 604 m away from the surface water body and

257   slowly increased to 8.4 mg L^{-1} in the last well (3434 m). The pH decreased gradually with

258   distance from the Oder River (pH 7.62 at well 6/99 T to pH 6.89 at well 2144 T). The

259   electrical conductivity of the groundwater decreased together with increasing distance from

260   the river. Sulfate concentration increased in the groundwater flow direction (75.5 to 127 mg

261   L^{-1}). A significant sulfate drop in the last deep groundwater well (49.9 mg L^{-1}; well 2144 T)

262   indicates a sulfate-reducing environment. A continuous increase in dissolved Fe(II) from 0.5

263   mg L^{-1} in the first well (6/99T) to more than 15 mg L^{-1} over a distance of 2980 m (well 3/05

264   T) indicates the occurrence of iron reduction throughout the aquifer (Fig. 2).

265

266   3.2. Infiltration of OPs and ethers into main drainage ditch

267

268   Table 2 summarizes the results of four sampling campaigns carried out between October

269   2009 and May 2012. Concentrations of OPs and ethers detected in the Oder river, the

270   drainage ditch, and seven groundwater sampling wells of the Bahnbruecke transect

271   comprising of three shallow and four deep groundwater wells are listed. Temporal variations

272   of the amount of compounds identified in the river and the bank filtrate were apparent. Except

273   for TnBP, each OP was detected in the Oder River, whereas TBEP and TDCP were not

274   present in the drainage ditch. These two OPs have the highest n-octanol/water partition

275   coefficients and are expected to sorb to soil particles (both log P_{ow} = 3.8) during infiltration.

276   TiBP was the only non-chlorinated plasticizer detected in the ditch and the groundwater,

277   although at low concentrations. Its concentration in the surface water ranged from 4-54 ng L^{-1}

278   and in the main drainage ditch from 4-19 ng L^{-1} . Most abundant OPs in the Oder River were

279   the two chlorinated flame retardants TCEP (7-540 ng L^{-1}) and TCPP (123-2353 ng L^{-1}). In

280   the drainage ditch their concentrations decreased to 9-171 ng L^{-1} and 105-958 ng L^{-1},

281   respectively.

282   Ethers were also readily identified in the collected samples. Triglyme was present in both

283   river and drainage ditch at 20-185 ng L^{-1} and 37-149 ng L^{-1}, respectively. Tetraglyme was

284   detected at high concentrations both in the Oder River (273-1576 ng L^{-1}) and the bank filtrate

285   (496-1403 ng L^{-1}). In the 2012 campaign, water samples were additionally analyzed for

286   monoglyme, diglyme, and 1,4-dioxane with Method II. Monoglyme was not detected in any

287   of the samples. Diglyme was present in the river water at lower concentrations compared to

288   other glymes detected. In the river water its concentration ranged between 65 and 94 ng L^{-1}

289   and in the ditch between 23 and 41 ng L^{-1}. 1,4-Dioxane greatly exceeded in abundance all

290   other analyzed compounds, with concentrations ranging from 1610 to 3290 ng L^{-1} in the Oder

291   River and 1090 to 1467 ng L^{-1} in the ditch.

292   The concentrations of ethers in the river and the main drainage ditch were typically higher

293   in comparison to OPs. The elevated use and poor removal techniques in the wastewater

294   treatment plants might account for their increased presence in the surface water (Vainberg et

295   al., 2006). The high concentrations of ethers (i.e. triglyme, tetraglyme, and 1,4-dioxane)

296   following bank filtration can be related to their vast water solubility and poor sorption to soils

297   (Barker et al., 1990). From the investigated OPs, only TCPP was present at significantly high

298   concentrations (>100 ng L^{-1}) in the bank filtrate. Among the investigated OPs, TCPP and

299   TCEP are expected to be the least affected by the attenuation processes during bank filtration.

300

301   3.3. Occurrence of OPs and ethers in the aquifer

302

303   The groundwater from shallow wells near the Oder River (well 9/99 F and 9536 F) is

304   hydraulically affected by the drainage function of the main ditch (Fig. 1), therefore only

305   groundwater from the six deep monitoring wells (19–23 m deep; Table 1) reaches beyond the

306   ditch and represents undisturbed water transport in the aquifer (Tosaki et al., 2007). The

307   groundwater ages were determined in a previous study using ^{3}H/^{3}He technique and match

308   perfectly the modeled hydraulic ages up to the distance of 1150 m (Massmann et al., 2009a).

309   In the deep wells of the Oderbruch polder TiBP, TCEP, and TCPP have been detected at

310   varying concentrations up to the groundwater age of 5.9 years (well 6/05T, Table 1 and 2). In

311   March 2011, TiBP was not detected above its detection limit in the groundwater. In the 2009

312   and 2012 sampling the concentration of TiBP in the deep groundwater wells increased with

313   water age, indicating a decrease in its use in over past 6 years (Table 2). This decline is

314   confirmed by the lowered river concentration between 2009 and 2012. TCEP and TCPP were

315   present at generally lower concentration during 2011 sampling in the deep groundwater wells

316   (4-20 ng L^{-1} and 14-201 ng L^{-1}) as compared to 2009 and 2012 samplings (9-51 ng L^{-1} and 23-

317   355 ng L^{-1}). In general, concentrations of OPs in the groundwater in May 2012 were higher

318   than in the sampling performed two months earlier, although trends between deep

319   groundwater wells remained similar. In 2009 and 2011, TCEP concentration decreased with

320   groundwater age. In 2012 its concentration was higher in 3 year old groundwater (9560 T)

321   compared to the preceding 6/99 T well (2.1 years), decreasing again in the final well (6/05T)

322   where the compound was detected. These patterns reflect the variability of TCEP

323   concentration in the river during the last decade. The infiltration and transport of TCPP from

324   the river into the aquifer differed compared to other OPs. Its concentration in the aquifer

325   dropped sharply between the groundwater age of 2.1 and 3.0 years, a strong indication for

326   attenuation in the anoxic aquifer.

327   The use of the chlorinated flame retardants TCEP and TCPP did not markedly increase until

328   the 1970s (Muir, 1984). In Germany, both compounds were used in equal proportions in

329   polyurethane foams until the mid 90s, when TCEP was phased out in Europe following a

330   voluntary industry agreement (Leisewitz et al., 2001). Although TCEP is no longer expected

331   to be utilized as flame retardant in the European industry, it is still present in surface waters at

332   fluctuating levels. TCEP has been recently detected in both house dust samples from

333   California, as well as polyurethane foam samples collected from couches in the US (Stapleton

334   et al., 2012; Dodson et al., 2012). These findings document that TCEP still enters the

335   environment via evaporation from flame protected products that are produced outside the EU.

336   Concentration of both glymes decreased with groundwater age during the 2009 and 2011

337   sampling campaigns. In 2012, the concentrations increased with groundwater age. This

338   pattern suggests that glymes were present in 2006 at highest concentrations in the Oder,

considering the residence time of the groundwater in this part of the transect. The anticipated onset of triglyme and tetraglyme might be due to the increasing contribution of treated and/or untreated effluents of industrial origin, but based on their extensive applications the source is difficult to identify at this time. It is clearly visible from the acquired results that triglyme and tetraglyme persist in the anoxic groundwater and are not markedly degraded. Tetraglyme was also detected in the shallow 9561 F well with an estimated groundwater age of 21 years (27-60 ng L^{-1}). 1,4-Dioxane was present at significant concentrations (>200 ng L^{-1}) up to the well 4/05 T with the estimated groundwater age of 34.9 years. In the groundwater between 2.1 and 6 years its concentration exceeded 1000 ng L^{-1}. The drop in the amount of 1,4-dioxane between 6/05 T and 4/05 T can be attributed to lower historical concentration as well as dispersion of groundwater (see section 3.6). The ability to determine 1,4-dioxane in such distant and old groundwater clearly demonstrates its resistance to attenuation by the bank filtration process and the anoxic conditions in the aquifer.

3.4. Factors influencing OP and ether concentrations

In addition to the residence time of the river water and the expected retardation of the particular compound, the highly variable concentrations in the river at the time of infiltration control contaminant dynamics in the groundwater following bank filtration (Noordsij et al., 1985). During winter, many contaminants tend to be diluted by increased natural discharges, such as rain and snow. Whereas during dry season, the river water is expected to have the highest concentrations of contaminants, due to the lesser dilution of effluents coming from the domestic and industrial wastewater treatment (Heberer et al., 2004). Fig. 3 portrays the changing levels and volume rate of water flow (discharge, in m^3 s^{-1}) of the Oder River between January 2006 and May 2012 at Hohensaaten-Finow (river km 664.9), which is located in the proximity to the sampling area (LUGV, 2012). The increased is especially apparent in the winter months. During the sampling in March 2011, the extremely high discharge rates in the Oder River at the end of 2010 and early months of 2011 can explain the low concentrations of some analytes in the river (i.e. TCEP, triglyme, and tetraglyme; Table 2). At that time (discharge, 813 m^3 s^{-1}), concentrations of TCEP, TCPP, triglyme, and tetraglyme in the main drainage ditch exceeded the concentrations in the Oder River. Only the concentration of TCPP remained high in the river during the increased water levels, proposing

372   its entrance with surface runoff from urban areas close to the river (Regnery and Püttmann

373   2009; 2010).

374   In 2009 (discharge, 397 m^3 s^{-1}) concentration of TiBP, TCEP, and TCPP were extremely

375   high compared to the levels observed during successive samplings. Possibly these OPs

376   entered the surface water as a result of the high precipitation in the summer months (seen as a

377   high peak in July-August 2009, Fig.3).

378   In 2012, the concentrations of TiBP, TCEP, TDCP, and TBEP varied with the river water

379   level. In March, during the high river level (discharge, 740 m^3 s^{-1}) concentrations were higher

380   than in May (discharge, 381 m^3 s^{-1}). The opposite is true for TCPP, which almost doubled in

381   May 2012. Glymes were present in the river at similar concentrations during the samplings

382   conducted in 2009 and 2012 and it did not respond to changing water levels. The amount of

383   1,4-dioxane in the river doubled with the decrease in the water level. The abovementioned

384   results suggest that the concentrations of OPs and ethers in the aquifer are generally

385   controlled by the fluctuating input from the Oder River.

386

387   3.5. Attenuation of OPs and ethers during bank filtration

388

389   The results of the study confirm that during bank filtration processes OPs are more readily

390   attenuated compared to ethers. The proportion of analyte removal through bank filtration can

391   only be calculated if the respective surface water concentrations at the time of infiltration are

392   known. Based on the acquired data, attenuation of the studied compounds is discussed.

393   Non-chlorinated OPs are expected to be less stable in an aquifer because of biotransformation

394   processes. Elimination rates of up to 89% have been reported for TnBP and TBEP during

395   bank filtration and in soil infiltration experiments (Schmidt, 2005; Bester and Schäfer, 2009).

396   In the Oderbruch polder, TBEP was removed by the bank filtration processes below detection

397   limit, confirming the biodegradability of this non-chlorinated OP.

398   The attenuation of trace organic compounds during bank filtration is dependent on numerous

399   factors, which include their structure and physical nature, organic carbon content of aquifer

400   material, sorption, biodegradation through microbial activity, rate of infiltration, as well as

401   dilution with older groundwater (Hiscock and Grischek, 2002; Worch et al., 2002). Numerous

402   earlier studies concluded that the microbial degradation of organic matter during bank

403   filtration occurs within the first few meters of infiltration (Jacobs, 1988; Doussan, 1997). The

404   proportion of compound removal following bank filtration can only be calculated if the

405   respective surface water concentrations at the time of infiltration are known. Nevertheless, the

406 processes responsible for attenuation of OPs and ethers in the Oderbruch aquifer are

407 indicated.

408   Based on their physicochemical properties, attenuation of OPs and ethers will likely involve

409 dispersion, dilution, and/or biodegradation. The mixing zone of surface water and subsurface

410 water (the hyporheic zone), in the upper few centimeters of sediments beneath the surface

411 waters of the Oder River, is characterized by intense biogeochemical activity (Massmann et

412 al., 2009b). Adsorption and degradation of organic contaminants during bank filtration are

413 significantly affected by the conditions in the hyporheic zone, which cannot be equated to

414 those in aquifers or soils (Sophocleous, 2002). However, the extent of removal of chlorinated

415 OPs during bank filtration remains controversial (Schmidt, 2005). Non-chlorinated OPs are

416 expected to be less stable in an aquifer because of biotransformation processes. Elimination

417 rates of up to 89% have been reported for TnBP and TBEP during bank filtration and in soil

418 infiltration experiments (Schmidt, 2005; Bester and Schäfer, 2009). Sorption of chlorinated

419 OPs on soils has been reported to be a function of the soil organic carbon content, and

420 sorption to soil components other than organic carbon has been suggested to be insignificant

421 (European Commission, 2007b). Such behavior can also be assumed for the non-chlorinated

422 OPs. According to the modeled Freundlich parameters, TDCP is considerably better adsorbed

423 to organic carbon surfaces than is TCPP or TCEP, which is supported by the absence of

424 TDCP in the bank filtrate (Nowotny et al., 2007). In the riverbank filtration study of Hoppe-

425 Jones et al. (2010) no changes in concentrations of TCEP and TCPP were observed,

426 suggesting their resistance to attenuation during subsurface treatment. Slight seasonal

427 variations were reported for TCEP, with concentrations below 200 ng L^{-1} in the winter and

428 above 200 ng L^{-1} in the summer (Hopee-Jones et al., 2010). The organic carbon composition

429 of the river bed and the hyporheic zone is of major importance in the removal of OPs during

430 river−aquifer interactions. Depending on sedimentation conditions, the concentrations of total

431 organic carbon (TOC) in Oder River sediments varies between 0.2% and 11.0% (Duft et al.,

432 2002). The aquifer at the Oderbruch polder consists of fine-to-medium-sized sands and

433 sediments, and contains less than 0.1% TOC (Massmann et al., 2004). However, high

434 concentrations of organic matter in the top layer of river sediments (i.e. dirt cover, biofilm)

435 and in soils near rivers will enhance the sorption of OPs within the first few centimeters-to-

436 meters during subsurface transport of percolating river water. Sorption of trace organic

437 contaminants, including OPs, can also be influenced by interactions with other compounds

438 present in river water (Li et al., 2007). Nevertheless, adsorption of trace organic pollutants is

439 significantly reduced in the presence of background organic matter (i.e., DOC) (Nowotny et

440 al., 2007). At Oderbruch polder, the DOC value increased from 6.3 mg L^{-1} at site 6/99 T near

441 the Oder River to 8.4 mg L^{-1} in groundwater at well 2144 T, far from the river. Further work

442 will be necessary to clarify whether groundwater contains degradation products (e.g., bi- and

443 mono-alkyl phosphates) of chlorinated and non-chlorinated OPs. Knowledge of the processes

444 of transformation and/or degradation of these analytes in groundwater is rudimentary.

445 Results of this study indicate that ethers are not easily adsorbed or degraded during

446 infiltration. Their high solubility in water and low soil partitioning coefficient prevents them

447 from volatilization and adsorption to aquifer material. As a consequence of the polar

448 characteristics of ethers, these and similar compounds (e.g., methyl *tert*-butyl ether; MTBE)

449 migrate through the aquifer with minimal retardation (Achten et al., 2002; Deeb et al., 2003).

450 Initial degradation studies of MTBE under anaerobic conditions found that it is recalcitrant

451 under sulfate-reducing conditions, and very poorly degraded under nitrate-reducing conditions

452 (Mormille et al., 1994). More recent studies provided evidence of MTBE degradation in

453 anoxic environment under nitrate-reducing, sulfate-reducing, iron-reducing, and

454 methanogenic conditions (Bradley et al., 2001a; Bradley et al., 2001b; Finneran and Lovely,

455 2011). However, a study focusing on the biodegradation of 1,4-dioxane under these hydro-

456 geochemical settings showed no degradation in anaerobic microcosms during more than 400

457 days of incubation (US DOD, 2007). With the help of the acquired hydrochemical data,

458 possible pathways of ether degradation were evaluated. Biodegradation of ethers under

459 methanogenic conditions require very low sulfate concentrations, whereas mineralization of

460 ethers due to denitrification is limited by nitrate availability and only expected to occur in

461 contaminated aquifers. In the Oderbruch aquifer, sulfate reduction occurred in the last

462 sampling well, 3434 m from the river (Fig. 2). No ethers were present in such distant well.

463 According to Fig. 2, denitrification occurred between river and the first deep groundwater

464 well (6/99 T). These two processes are not expected to contribute significantly to the

465 degradation of ethers in the Oderbruch. The high iron (II) concentrations in the groundwater

466 are the result of a reduction of Fe (hydr)-oxides in the sediment of the aquifer (Massmann et

467 al., 2004). Iron reduction is recognized as a biodegradation process that could be responsible

468 for the reduction of organic compounds in the Oderbruch aquifer. Numerous studies focused

469 on establishing 1,4-dioxane decomposition in the presence of iron species in the sludge,

470 wastewater, and contaminated groundwater (Beckett and Hua, 2003; Kiker et al., 2010; So et

471 al., 2009; Shen et al., 2008). In order to observe significant reduction or removal of the

472 compound, strong oxidizing agents in the form of hydrogen peroxide or humic acid had to be

473 supplied. The ex-situ studies suggest the development of anaerobic microbial communities

474 capable of 1,4-dioxane degradation, since Fe (II) is often present in the groundwater

475 contaminated with 1,4-dioxane (Shen et al., 2008). As determination of ether degradation

476 products was not a part of the current study, it cannot be confirmed if iron reduction enhanced

477 the attenuation of 1,4-dioxane in the groundwater. Moreover, Chiang et al. (2008) states that

478 the monitoring of 1,4-dioxane degradation products is difficult in the field. In the last several

479 years numerous studies focused on determining biodegradation of 1,4-dioxane, but relatively

480 few described its possible degradation pathway and applied their results to environmental

481 samples (Shen et al., 2008; Masuda et al., 2012). Kim et al. (2009) isolated a new bacterial

482 strain PH-06 from river sediments able to degrade 1,4-dioxane to 1,4-dioxane-2-ol and

483 ethylene glycol. Vainberg et al. (2006) showed that the terminal product of 1,4-dioxane

484 degradation by the strains tested is 2-hydroxyacetic acid, but was unable to detect it in

485 environmental samples (Steffan, 2007). Based on the concentrations detected and the

486 chemical characteristics of 1,4-dioxane and glymes, only dispersion and dilution will be

487 considered as relevant attenuation processes during riverbank filtration and groundwater flow

488 in the Oderbruch polder. As concluded by Landmeyer et al. (1999) these are possibly the most

489 effective processes in the reduction of trace organic contaminants such as ethers.

490

491 3.6. Organic pollutants as hydrological tracers

492

493 A substance unintentionally released and persistent in the environment can become useful as

494 a hydrological tracer. Ideally such pollutant should move with the water, without sorption to

495 soil and without degradation (Flury et al., 2003). Moreover the chosen tracer should be

496 resistant to changes in pH, alkalinity, or ionic strength and should be easily detected in trace

497 amounts by chemical analysis. The ideal groundwater tracer does not exist, but when different

498 tracers are simultaneously determined, groundwater characteristics can be adequately

499 identified. Chloride (Cl^-) ion is often used as conservative inorganic tracer to study

500 groundwater dynamics (Basberg et al., 1998; Lee et al., 2001; Peters et al., 1998). Cl^- is

501 highly mobile due to its negligible sorption and minor chemical interactions with other

502 materials during bank filtration process (Cox et al., 2007).

503 Persistent pollutants present at significant concentrations in the groundwater can be

504 potentially applied as environmental tracers, therefore only OPs and ethers present at

505 concentrations close to 100 ng L^{-1} were considered. Concentration of TCPP in the 2.1 year old

506 groundwater exceeded 200 ng L^{-1}, but after groundwater residence time of 3 years its

507 concentration decreased by 74-82%. Obviously TCPP is affected by biological and/or

508   chemical processes in the aquifer. Therefore only triglyme, tetraglyme and 1,4-dioxane were

509   evaluated as possible environmental tracers. Consequently, the presence of these compounds

510   was correlated to the inorganic tracer Cl^-. Fig. 4 shows a good correlation of 1,4-dioxane and

511   tetraglyme to Cl^- concentration in the river water and deep groundwater wells. The only

512   points deviating strongly from the linearity occurred in March 2012 in the Oder River for both

513   ethers. The chloride value for this sampling was taken five days prior to the actual sampling

514   for the ether determination (93.8 mg L^{-1}) and may possibly deviate from the actual

515   concentration on the sampling day. Also there are two low correlation points for tetraglyme,

516   when chloride was about 115 mg L^{-1}. These are the amounts detected in the groundwater in

517   2011, which as previously discussed were low for all of the compounds analyzed. Unlike

518   tetraglyme, triglyme concentrations fluctuated greatly in the aquifer as compared to the Cl^-.

519   Such behavior limits the use of triglyme as a tracer; nevertheless its presence in the

520   groundwater can be of great importance when studying the influence of bank filtration on the

521   groundwater contamination.

522   Chloride concentration varied both in the river and the groundwater. Numerous sources

523   affect the presence of Cl^- in the surface water and consequently in the groundwater such as:

524   irrigation runoff, sewage effluents, precipitation, mining, chemical industry, snowmelt, and

525   road salting during the winter (DNR, 2002). Both 1,4-dioxane and Cl^- respond to changes in

526   the discharge rate. Their concentration increased when the discharge was low and fell when

527   the discharge increased. These changes were reflected in the aquifer concentrations

528   considering the residence time of the water. Similarities in the behavior of Cl^- and the organic

529   compounds suggest that 1,4-dioxane and tetraglyme are controlled in the same way by

530   hydraulic process and therefore can be used as additional tracers to study the dynamics of the

531   groundwater system.

532

533   4. Conclusions

534

535   Bank filtration is supposed to be a safety barrier for high concentrations of organic

536   contaminants as well as uncontrolled spills and defects in industrial and domestic wastewater

537   treatment plants (Schmidt et al., 2003). Results presented here clearly demonstrate the great

538   mobility and low degradation potential of hydrophilic ethers during bank filtration and

539   groundwater flow. Under the aquifer conditions described, TCEP, TCPP and triglyme are not

540   suitable as organic tracers in groundwater, although they are good indicators of contamination

541   of groundwater with organic contaminant loaded surface waters. Based on the results herein

542 and the aforementioned studies it can be concluded that the concentration of persistent OPs

543 and ethers in the aquifer following riverbank filtration are controlled by the input from the

544 Oder River. The strong correlation of 1,4-dioxane and tetraglyme with the inorganic tracer Cl⁻

545 suggest that they behave as conservative organic environmental tracers. Therefore, they can

546 play an important in the interpretation of substance flow dynamics in complex groundwater

547 systems. In order to exclude biodegradation of ethers in the aquifer, the formation of

548 degradation products needs to be investigated. Furthermore, the ability to determine both

549 hydrophilic ethers and OPs at low parts per billion concentrations can be of great importance

550 for water works producing drinking water from riverbank filtration and artificial recharge.

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790   Tables and Figures

791

792   Table 1

793   ID codes of the monitoring wells, grid values, sampling depth, distance to Oder River and

794   groundwater age (apparent ^{3}H/^{3}He age) at Oderbruch polder, Germany.

ID	N°	E°	Depth [m]	Distance to river [m]	Apparent age [a] [a]
6/99 T	52°48,7980'	14°13,0820'	19.6	138	2.1
9536 F	52°48,7810'	14°13,0580'	7.0	138	3.3
9560 T	52°48,5420'	14°12,9370'	20.0	604	3.0
9561 F	52°48,5400'	14°12,9380'	7.0	604	21.0
6/05 F	52°48,2320'	14°12,8030'	9.0	1150	41.9
6/05 T	52°48,2320'	14°12,8030'	22.0	1150	5.9
4/05 T	52°47,7820'	14°11,7720'	22.0	2560	34.9
4/05 F	52°47,7820'	14°11,7700'	9.6	2560	36.4
3/05 T	52°47,6960'	14°11,5390'	22.0	2980	36.0
3/05 F	52°47,6960'	14°11,5390'	9.0	2980	34.3
2144 T	52°47,4440'	14°11,0890'	23.0	3434	42.4
2144 F	52°47,4390'	14°11,0930'	9.0	3434	44.4

795   [a] Sültenfuß and Massmann, 2004; Tosaki et al., 2007; Massmann et al., 2009a.

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814   Concentration of OPs and ethers (ng L^{-1}) in the Oder River, adjacent main drainage ditch as

815   well as shallow (F) and deep (T) groundwater sampling wells.

Analyte	Sampling Date	Oder River	Ditch	9536 F	9561 F	6/05 F	6/99 T	9560 T	6/05 T	4/05 T
TiBP	27.10.09	54	19	12			4	6	5	
	10.03.11	4	2	4			BDL	BDL	BDL	
	27.03.12	18	4	7			3	7	6	
	23.05.12	11	10	9			8	12	12	
TCEP	27.10.09	540	171	30			51	20	9	
	10.03.11	7	16	27			20	9	4	
	27.03.12	30	10	18			14	25	12	
	23.05.12	12	9	18			15	28	26	
TCPP	27.10.09	2353	958	261			291	66	31	
	10.03.11	183	198	324			201	36	14	
	27.03.12	123	128	258			206	54	23	
	23.05.12	217	105	406			355	92	55	
TDCP	27.10.09	BDL								
	10.03.11	7								
	27.03.12	7								
	23.05.12	5								
TBEP	27.10.09	BDL								
	10.03.11	43								
	27.03.12	63								
	23.05.12	12								
Triglyme	27.10.09	151	106	245			98	74	19	
	10.03.11	20	37	82			38	35	25	
	27.03.12*	173	100	68			67	104	131	
	23.05.12*	185	149	241			86	125	153	
Tetraglyme	27.10.09	1260	1230	1849	BDL		1230	849	442	
	10.03.11	273	496	803	29		350	369	212	
	27.03.12*	1433	693	547	60		455	520	565	
	23.05.12*	1576	1403	1464	50		496	630	741	
1,4-dioxane*	27.03.12	1610	1467	1440	751	196	1340	1020	1630	208
	23.05.12	3290	1090	740	1040	121	1060	901	1129	219
Diglyme*	27.03.12	94	41	34			31	26		
	23.05.12	65	23	BDL			29	BDL		

* Analyzed by Coconut charcoal SPE and Voyager GC/MS

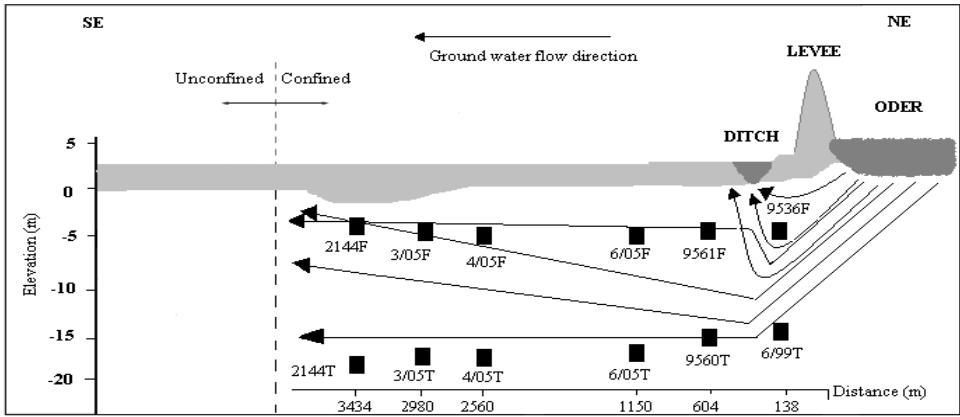816   BDL- below detection limit

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828 Fig.1. Simplified geological cross section of sampling site Bahnbruecke at Oderbruch polder,
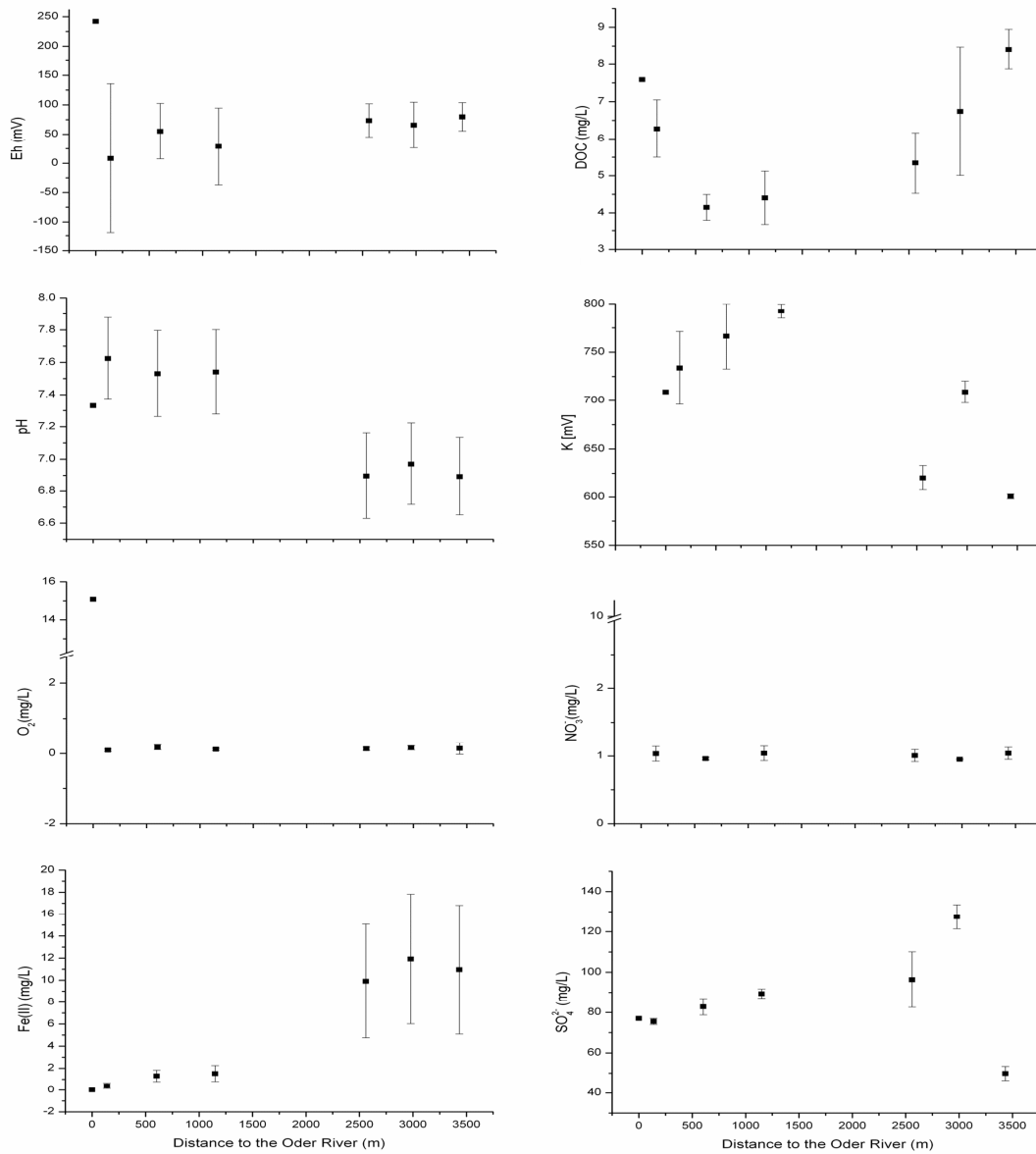
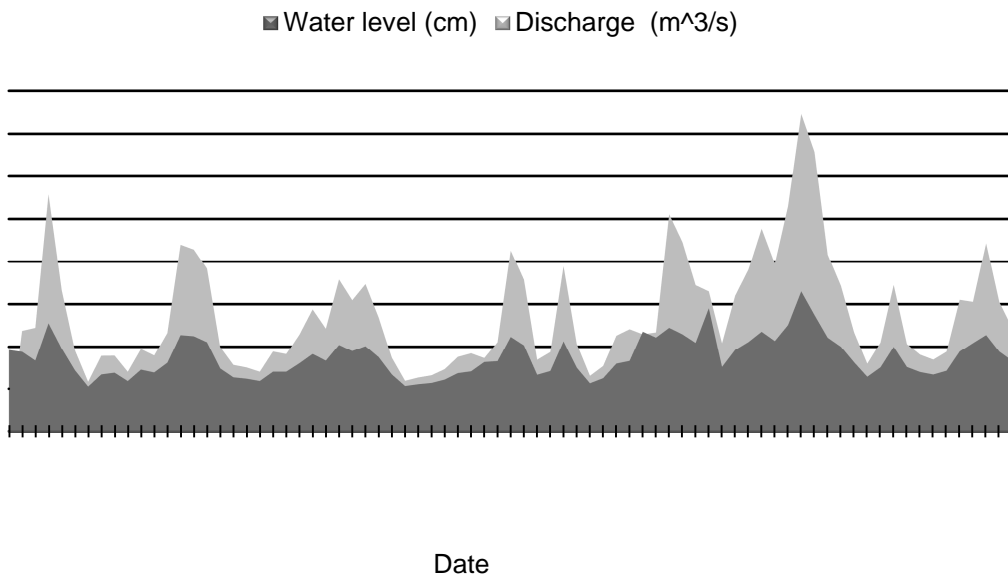829 Germany.

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837　Fig.2. Concentration of redox relevant parameters in the Oder River (n = 1) and six deep

838　groundwater wells (n = 3): redox potential (Eh), dissolved organic carbon (DOC), pH,

839　conductivity (K), oxygen (O_2), nitrate (NO_3^-), ferrous iron (Fe(II)) and sulfate (SO_4^{2-}).

Fig.3. Average monthly water level (cm) and mean flow (discharge, m^3 s^{-1}) of the Oder River
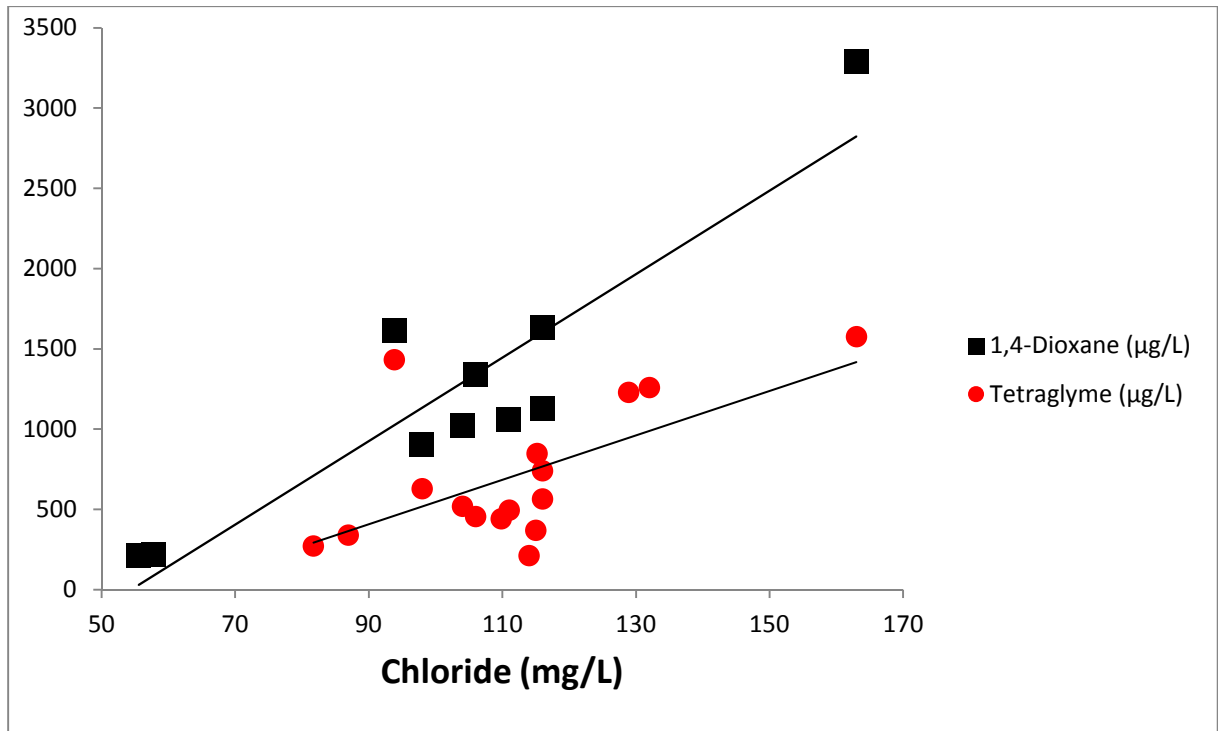
between January 2006 and May 2012 (LUGV, 2011).

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850 Fig.4. Correlation of chloride concentration with 1,4-dioxane and tetraglyme in the Oder

851 River and deep groundwater wells during four sampling campaigns.

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