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1 **Evidence of spatio-temporal variations in contaminants discharging to a peri-urban**
2 **stream**

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10

11 **ABSTRACT**

12 Xenobiotic organic compounds can be discharged from contaminated groundwater inflow and may seep
13 into streams from multiple pathways with very different dynamics, some not fully understood. In this study,
14 we investigated the spatio-temporal variation of chlorinated ethenes discharging from a former industrial
15 site (with two main contaminant sources, A and B) into a stream system in a heterogeneous clay till setting
16 in eastern Denmark. The investigated reach and near-stream surroundings are representative of peri-urban
17 settings, with a mix of high channel alteration and more natural stream environment. We therefore
18 propose an approach for risk assessing impacts arising from such complex contamination patterns,
19 accounting for potential spatio-temporal fluctuations and presence of multiple pathways. Our study
20 revealed substantial variations in pathway contributions and overall contaminant mass discharge to the
21 stream. Variable contaminant contributions arising from both groundwater seepage and urban drains were
22 identified in the channelized part of the north stream, primarily from source A. Furthermore, variations in
23 the hyporheic and shallow groundwater flows were found to enhance contaminant transport from source
24 B. These processes result in an increase of the overall mass of contaminant discharged, correlating with the
25 channels' flow. Thus, an in-stream control plane approach was found to be an effective method for
26 integrating multiple and variable discharge contributions quantitatively, although information on specific
27 contaminant sources is lost. This study highlights the complexity and variability of contaminant fluxes
28 occurring at the interface between groundwater and peri-urban streams, and calls for the consideration of
29 these variations when designing monitoring programmes and remedial actions for contaminated sites with
30 the potential to impact streams.

31 **Keywords:** Risk assessment, contaminant mass discharge, chlorinated ethenes, groundwater-surface water
32 interactions, spatio-temporal variation, peri-urban streams

33

34

35 **1 Introduction**

36 The implementation of legislations such as the European Water Framework Directive, which aim to protect
37 water resources and associated ecosystems, are challenged by extensive anthropogenic activities
38 worldwide (McKnight et al. 2012; Vörösmarty et al. 2010). Freshwater resources are particularly sensitive
39 and the related ecosystems exhibit some of the highest decline rates in terms of biodiversity (Strayer and
40 Dudgeon 2010; Sonne et al. 2018). The reasons for such a decline are many and possibly cumulative,
41 including stream flow alteration, habitat degradation, pollution, invasive species and more recently
42 emerging contaminants and climate change (Reid et al. 2018; Sonne et al. 2017).

43 The rapid urbanization observed worldwide has led to a fast and sometimes chaotic development of areas
44 located at the fringe of existing cities or rural and secondary towns. This evolution has contributed to the
45 development of a heterogeneous patchwork of urban, rural and natural areas now defined as peri-urban
46 ‘scapes’ (Eakin, Lerner, and Murtinho 2010; Simon 2008; Allen 2003). These new “landscapes” and resulting
47 mixtures of activities are having profound impacts on the surrounding freshwater, especially for streams
48 and rivers draining these types of catchments. Importantly, stream flow regimes may be modified by the
49 coexistence of mixed catchment response times stemming from the more impervious urban-drained areas
50 and the more rural/natural-drained areas, with possible reductions in evapotranspiration and base flow
51 (Simon 2008; Braud, Fletcher, and Andrieu 2013; Walsh et al. 2016). Furthermore, water quality is often
52 directly affected by the rise of urbanization, with possible increases in water temperature, suspended
53 solids, and enhanced loads of chemical pollutants that may discharge via numerous pathways leading to
54 counterintuitive patterns in contaminant distributions (Walsh et al. 2016; Simon 2008; Paul and Meyer
55 2001; Zoboli et al. 2019).

56 Due to their persistency, ubiquity and low degradation potential, chlorinated aliphatic hydrocarbons (CAH)
57 such as trichloroethene (TCE) remain a major concern regarding legacy contaminants in groundwater for
58 many industrialized countries (Rivett et al. 2012; Freitas et al. 2015; Ellis and Rivett 2007; Conant et al.

2004). Furthermore, the mobility of these compounds and their associated metabolites, such as cis-dichloroethene (cDCE) and vinyl chloride (VC), make them a serious threat to receiving stream waters (McKnight et al. 2010; Freitas et al. 2015; Weatherill et al. 2018; Rønde et al. 2017). Quantification of CAH fluxes in groundwater from former industrialized and contaminated sites can be carried out using the contaminant mass discharge (CMD) approach, where the mass per unit time flowing through a virtual control plane is quantified (Basu et al. 2006; Weatherill et al. 2014). This approach has been successfully applied to the characterization of contaminant plumes in aquifers (Weatherill et al. 2014), although some inherent uncertainty exists (Rønde et al. 2017; Trolborg et al. 2010). This methodology has also been employed to track the fate of contaminants in streams (in-stream CMD), with a simplified approach assuming a full mixing of the contaminants (Rønde et al. 2017; Milosevic et al. 2012; LaSage et al. 2008). Numerous studies have shown the importance of the groundwater pathway for the discharge of CAH to streams (Chapman et al. 2007; Conant et al., 2004; Ellis & Rivett, 2007; Paul & Meyer, 2001; Rasmussen et al., 2016; Roy et al., 2016; Roy and Bickerton, 2012; Shepherd et al., 2006; Sonne et al., 2017). However, the transport pathways for contaminants arising from urban and peri-urban areas may be even more complex and result in variable release dynamics for which little is known (Ellis and Rivett 2007; Braud et al 2013). So although contaminants may reach the stream via groundwater-surface water interactions, there may be more rapid pathways triggered simultaneously from dense underground infrastructures (e.g. pipes or trenches) in more urban-like settings (Kaushal and Belt 2012; Hatt et al. 2004). Notably, a few studies apply the in-stream CMD methodology at several points in time to investigate the groundwater contribution and fate of CAHs (and other dissolved contaminants) in streams (Heejung and Hemond, 1998; LaSage et al., 2008a; Milosevic et al., 2012; Rønde et al., 2017). Quite often, the contaminant mass balance could not be completely closed, indicating the existence of additional pathways for which the dynamics were not quantified at the time of the study.

This lack of knowledge concerning the contaminant dynamics is a shortcoming in the assessment of the chemical status of streams. Monitoring programs traditionally focus on the measurement of stream

84 concentrations for a direct comparison with the relevant Environmental Quality Standards (EQS) at regular
85 time intervals (see, for example, European Commission (2009)). High frequency sampling would be ideal
86 (Brack et al. 2017; Skeffington et al. 2015), but is rarely feasible predominantly due to economic
87 constraints. This focus on specific measurement points in the stream sampled on a regular basis may be
88 misleading and the risk associated to a given pollutant not properly assessed. In a recent study, Zoboli et al.
89 (2019) captured increasing micropollutant concentrations in different Austrian river catchments despite
90 higher stream flows and resulting dilutions. This “counterintuitive” pattern was due to the increased
91 contribution of multiple sources during higher flow regimes, counterbalancing the positive effect of the
92 enhanced dilution. In other words, the dynamic of the sources itself was driving the general trend of the
93 measured concentrations. Thus, improving our understanding of the dynamics of contaminant source
94 releases, associated discharges and dominant pathways would benefit both the design and implementation
95 of monitoring programs, as well as the assessment of chemical status (Sonne et al. 2017).

96 The objectives of this paper are therefore to investigate the spatial variation and discharge dynamics
97 originating from a contaminated site impacting a peri-urban stream in order to (1) quantify the potential
98 temporal variations on contaminant mass discharge to the stream, and resulting stream concentrations; (2)
99 address or identify the key processes and pathways responsible for such variations; and (3) discuss the
100 findings at the site in relation to the development of key legislations, and monitoring strategies. To do so,
101 we applied a discrete in-stream contaminant mass discharge approach at relevant transects along the
102 investigated stretch. We argue that this method allows accounting for the non-fully mixed conditions
103 occurring when multiple contaminant pathways are active, and is crucial when designing suitable
104 monitoring programs capable of capturing the impacts of contaminated sites and resulting chemical status
105 in streams.

106

107 **2 Study site**

108 **2.1 Site description**

109 The study site is a stream reach ca. 500 m long called the *Mølleåen*, located 15 km north of Copenhagen in
110 the town of Raadvad (Fig. 1). Raadvad is the site of a former industrial area, primarily used over the past
111 two centuries for metal manufacturing activities, and is the location for a well-known knife factory that
112 produced domestic metal wares until 1972. In addition to metal works, the site has hosted a number of
113 other factories including a bronze foundry and metal workshop. The site today houses various professions
114 including offices, residential houses and a Nature school offering a variety of activities for children.

115
116 **Figure 1. Overview of the Raadvad site showing land use, stream flow direction and location of the measurement transects. The**
117 **dashed red lines correspond to transect locations where detailed stream water sampling was carried out (5 points per transect);**
118 **solid red lines show the transects used for the in-stream contaminant mass discharge estimation. The dashed black line box**
119 **indicates the location of the north channel presented in more detail in Figure 2.**

120 The annual precipitation in the area is ca. 860 mm (St. 5628; Danish Meteorological Institute, 2017). The
121 stream flows eastwards with a depth ranging from 0.3 to 1.5 m and width from 6 to 12 m along the
122 investigated stretch. The median stream flow is ca. 437 l/s measured at a monitoring station 500 m
123 upstream of the investigated site for the period 2007-2018 (St. 5010; Danmarks Miljøportal, 2018). The
124 urban part of the stream reach consists predominantly of two engineered channels running past the
125 industrial site. The channels flow from an impounded lake through two low-head dams that are rarely
126 operated (i.e. remain in a fixed position), located just west (upstream) of the site. The north channel (the
127 original location of the stream prior to industrialization) is straight and was initially channelized for a water
128 mill used by the industry in the 1900s. It is bounded by a concrete retaining wall on the northern bank in its
129 most upstream section, with a streambed consisting of organic sediments cluttered with rocks. The
130 southern channel flows through a more natural setting and the streambed consists of pebble and stone
131 with patches of organic sediments. These channels then merge to reform the *Mølleåen* downstream of the
132 industrial area and flow through a protected nature area into the Baltic Sea.

133 **2.2 Geology and hydrogeology**

134 The geology in the area of interest is typical for Eastern Denmark. The setting is complex, where gyttja
135 dominates in the vicinity of the streambed, and below this a mixture of layers of sand, gravel and clay till
136 forms a shallow heterogeneous aquifer. Below this shallow aquifer, and separating this layer from a deep
137 Danien limestone aquifer, is another more continuous clay till layer. The terrain is relatively flat at an
138 average elevation of 5 m.a.s.l. (DVR90) with a slight slope from the north side, leading to a shallow
139 groundwater flow towards the stream. It is not known to what extent the shallow aquifer and surface
140 water are hydrologically connected. Previous investigations reported no indication of separate phase
141 mobile CAHs, upward hydraulic gradients from the deep to shallow aquifers, as well as from the shallow
142 aquifer to the stream (Niras 2012). This ruled out contamination (see next section) of the deep aquifer,
143 which is not discussed further in this paper.

144 **2.3 Contamination overview**

145 Previous investigations of the soil (pore air) and groundwater revealed a contamination of the shallow
146 aquifer by CAH (specifically, TCE, cDCE, VC), as well as petroleum hydrocarbons from the leakage of
147 underground and surface storage tanks, urban drains and likely waste deposits placed randomly
148 throughout the site (Niras 2012, Orbicon 2016). Contamination by heavy metals and oil in the topsoil and
149 stream sediments were also detected over most of the industrial site. Figure 2 depicts the locations of the
150 main contaminant source zones for CAH (termed source zone A and B throughout the paper) impacting the
151 shallow groundwater: source zone A is located below the main building on the northern bank of the
152 northern channel, and source zone B is located at the junction of the two channels on the southern bank of
153 the north channel. Finally, a third and comparatively minor source area was also detected in the most
154 upstream part of the south channel, releasing mostly TCE to the stream. However, the concentration levels
155 were not substantial compared to the contribution of the two other sources (Niras 2012; Orbicon 2016;
156 Lemaire 2016), and was therefore not investigated further in this study.

157 Previous investigations by consulting companies revealed CAH concentrations of up to ca. 2500 µg/l in the
158 shallow groundwater, at a monitoring well 1 m from the north bank (see location in Fig. 2). Some of the
159 contamination present in source zone A was further found to be entering the stream, as confirmed by grab
160 samples in the vicinity of the northern bank, and upstream and downstream of the retainment wall (Niras
161 2012, Orbicon 2016). The exact seepage location and contaminant pathways were, however, unknown.
162 Preferential pathways were suspected from former urban drains whose outlets are visible in the retaining
163 wall, as well as through some cracks and fissures made visible by the presence of precipitated iron oxides
164 (see pictures of these features in Fig. 2). Total CAHs of up to 2600 µg/l were measured in the shallow
165 groundwater in source zone B (Niras 2012). However, its potential discharge to the stream had not been
166 estimated prior to this study.

Figure 2: (a) Locations for stream water (blue circles) and streambed (piezometers; open squares) samples used in the estimation of contaminant mass discharge (CMD). Approximate delineation (sum of CAHs concentration > 10 µg/L in shallow groundwater) for the main contaminant source zones A and B are marked with striped red polygons based on previous investigations by a consulting company (Niras 2012). Note that the other transects used for CMD estimation are shown in Fig. 1. (b) Pictures from the site indicate the location of the crack and urban drain in the retainment wall.

175

176 **3 Materials and methods**

177 **3.1 Overview and approach to investigations**

178 A one-year measurement campaign was carried out at the investigated site from June 2016 to May 2017,
179 focusing on the variations of contaminant mass discharge to the stream from the two contaminant sources.
180 The measurements encompassed groundwater, streambed and surface water sampling, flow discharge
181 measurements, as well as groundwater table and stream water level monitoring (10 points) repeated on a
182 monthly basis. A preliminary conceptual model was developed using extra stream water samples (in
183 addition to the first set of measurements collected), which consisted of 5 points along each of the first 5
184 transects (T1 to T5, Fig. 1) in order to document the mixing pattern of the CAHs in the stream water. This
185 was supported by application of a 2D advection-dispersion model of pollutant mixing in streams (Aisopou
186 et al., 2015; Lemaire, 2016) to evaluate the potential location of the discharge to the stream from source
187 zone A (i.e. with respect to chainage, streambed or streambank seepage), and to estimate the CMD and
188 mixing conditions. These results were then used to design all other monitoring campaigns: these consisted
189 of 3 points per transect for transects T1 and T4, and 1 point in transect T6 and T7 where fully mixed
190 conditions (see section 3.5) were achieved (see Fig. 1 for all transect locations). Finally, to better
191 understand some of the variations observed in our dataset, new streambed and stream water samples
192 were collected in June and November 2017 in the north channel, and additional monitoring of the stream
193 water levels within this area including the south channel was performed from October to December 2018.

194 **3.2 Water level monitoring and stream discharge**

195 The stream discharges in the north and south channel were obtained by monthly measurements using an
196 OTT MF pro flow meter and assessed using the mid-section method following the ISO 748 standard. The
197 stream flow measurements were taken at transects T1 and T7 for the north and south channel respectively
198 (Fig. 1 and 2). The flow rate in *Mølleåen* could not always be measured due to the water depth in periods of

199 high flow. Consequently, the flow rate was assumed equal to the summation of the north and south
200 channel flows, i.e. the possible additional groundwater influx was assumed minor over the limited length of
201 the investigated reach.

202 Hydraulic heads in the shallow aquifer and the stream water level were monitored hourly during the entire
203 campaign using mini divers (DI501) from Van Essen. The shallow groundwater was monitored in the
204 existing boreholes in source zone A (screened from 0.5 to 2.5 m.b.s) and B (screened from 1 to 4 m.b.s).
205 The stream water level was monitored approximately 10 m downstream of transect T1.

206

207

208 **3.3 Hyporheic zone (streambed) sampling**

209 Streambed water samples were collected using drive-point piezometers, placed within the hyporheic zone
210 to a depth of 40 cm in the most upstream part of the northern channel. The samples were extracted by use
211 of a peristaltic pump and rigid polyamide tubes, stored in 25 ml glass vials, sealed without air bubbles. The
212 number of drive-points varied across the 12 campaigns in order to enable the best delineation of the
213 contamination entering the stream via the streambed. The measurement locations were chosen based on
214 our conceptual model of the site, inspection of the streambed and ensuing practical constraints (stones,
215 rocks and obstacles in the streambed itself). The piezometers were purged 3 times prior to sampling to
216 ensure a freshwater input without the influence of stagnation. The samples were kept in a cooler on ice
217 during the sampling, and thereafter kept at 4°C prior to chemical analysis. All chemical analyses for CAH
218 were carried out by an independent certified laboratory using P&T/GC-MS method according to ISO 15680.
219 Detection limits for the analyses are 0.02 µg/L.

220 **3.4 Stream water sampling**

221 Stream water grab samples were collected in 25 ml glass vials, sealed without air bubbles. The locations
222 and numbers of samples for each of the measurement transects were previously described in section 3.1).
223 Stream water was sampled from the most downstream point to the most upstream to avoid any sediment
224 disturbance or cross contamination while measuring. They were kept on ice in a cooler on site before being
225 stored at 4°C until sent for analysis. An additional transect, T0, was placed up-gradient of transect T1 in
226 April, June and November 2017 to enable delineation of contamination originating from the urban drainage
227 system (see Fig. 4).

228 **3.5 In-stream contaminant mass discharge**

229 The CAH concentrations measured in the stream are dependent on the stream flow, diluting any
230 contaminants entering the stream. The temporal or spatial variation and fate of the discharged

231 contaminant mass can therefore be evaluated by assessing the mass flowing through different control
232 transects along the stream. Several formulations and simplifications can be used depending on the location
233 of this control transect with respect to the different points of discharge.

234 The in-stream concentration is generally dependent on both the transverse and depth location of the
235 sample within a control transect. For most streams, however, the depth is usually small compared to the
236 width and the vertical mixing occurs over a relatively short distance (Fisher 1979; Aisopou et al. 2015). At a
237 certain distance downstream of the discharge location, the contaminant will therefore be completely mixed
238 in the vertical direction and the contaminant concentration is then only dependent on the transverse
239 location of the sample. Thus the in-stream CMD, J can be evaluated using a discretization of the
240 measurements taken along the in-stream control plane (ITRC 2010):

241

$$J = \sum_{i=1}^n c_i A_i q_i \quad (1)$$

242 where c_i is the pollutant concentration at mid water column in the sub-area i , q_i is the flow velocity in the
243 sub-area of the in-stream control plane of area A_i and n is the number of sub-areas. In our study, $n=3$
244 corresponding to the 3 water samples taken at regularly spaced locations along each of the transects T_i , q_i
245 estimated as the average velocity in this sub-area, and A_i computed using the average depth of the sub-
246 area i and width.

247 A contaminant is considered to be fully mixed when its concentration along a transverse section of the
248 stream remains within 5% of the average concentration (Fisher, 1979). In that case, the concentration is
249 almost constant in the control transects, both in depth and transverse direction. Hence the formula (1)
250 simplifies and can be rewritten as (Rønde et al. 2017):

$$J = c_{mix} * Q_{mix} \quad (2)$$

251 where c_{mix} is the fully mixed concentration and Q_{mix} the stream flow rate at the point of fully mixed
 252 conditions downstream. Equation (2) is hereby applied to estimate the contaminant mass discharge at
 253 transect T6 and T7.

254 Finally, as parent and degradation products have been measured (i.e. TCE, cDCE, VC), the CMD results are
 255 reported using the PCE equivalent unit, defined as:

$$m_{PCE,eq} = M_{PCE,eq} \sum \frac{m_{chl. \ compound}}{M_{chl. \ compound}} \quad (3)$$

256 where m_i is the mass of a given chlorinated compound or metabolite i , and M_i is its corresponding molar
 257 mass.

258 **3.6 Time series and statistical analysis**

259 The investigation of time variations and interactions between the different parameters of interest
 260 (precipitation, hydraulic head, contaminant mass discharge, etc.) was carried out using Spearman rank and
 261 cross-correlation analyses. The cross-correlation analysis was employed to estimate an average lag
 262 between the input driving parameter (i.e. precipitation) and output hydrological responses defined by the
 263 different hydraulic head measurements in the stream and shallow groundwater, following the techniques
 264 described in (Larocque et al.,1998). The discrete cross-correlation function is defined as:

$$\rho_{XY}(k) = \frac{C_{XY}(k)}{\sigma_X \sigma_Y} \quad (4)$$

265

266 with:

$$C_{XY}(k) = \frac{1}{n} \sum_{t=1}^{n-k} (x_t - \bar{x})(y_t - \bar{y}) \quad (5)$$

267

268 where $\bar{x}$ and $\bar{y}$ are the means of time series x and y , σ_x, σ_y are the respective standard deviations and n is
269 the length of the time series.

270 A Spearman rank correlation analysis was then carried out to highlight potential trends between the
271 different time series, especially as these trends are likely to be non-linear and the data not normally
272 distributed. In order to do so, the hourly hydraulic head time series datasets were down-sampled to the
273 measurement frequency (once a month) by averaging over the 4-hr intervals during which the stream
274 water samples were collected. The hourly time series for the precipitation data was down-sampled to the
275 measurement frequency by a cumulative estimate of precipitation between the previously estimated lag
276 (determined by the cross-correlation) and the end of the measurement intervals to account for the time
277 response of the hydrological system.

278

279

280 **4 Results and Discussion**

281 **4.1 Spatial distribution of the contaminants in the stream**

282 The first sampling campaign, carried out in June 2016, revealed a contamination of the stream water by TCE
283 and its degradation products cDCE and VC (Fig. 3). cDCE was the dominant CAH compound in terms of
284 concentration levels along the investigated stream stretch. Specifically, cDCE concentrations of up to ca. 2
285 µg/L were measured in the north channel close to the northern bank in the most upstream transect, T1,
286 where source zone A is discharging. After the junction of the two channels, the concentrations decreased
287 significantly due to dilution resulting from the flow coming from the south channel. Figure 3 furthermore
288 indicates the pattern of mixing across the different transects, where concentration values “flatten out” with
289 distance due to the dispersion and spreading of the contaminants in the transverse direction. However,
290 fully mixed conditions have not been attained even at the most downstream transect location, T5, for this
291 specific campaign based on the criteria defined in section 3.5.

292 Taken altogether, this indicated that the bulk of the contamination originates from the northern channel, is
293 heavily diluted by water inflowing from the south channel, and that the location of fully mixed conditions
294 requires additional measurements further downstream of transect T5.

295

296 **Figure 3. Effects of mixing and dilution of the in-stream contaminant concentrations measured at 5 detailed transects for TCE**
 297 **and detectable degradation products (cDCE and VC) in June 2016. Note that the x-axis corresponds to a normalized stream**
 298 **width, i.e. 0 for the north bank, and 1 for the south bank.**

299 **4.2 Investigating contaminant pathways from source zone A into the stream**

300 Differences in hydraulic head between the streambed piezometers installed in the north channel and the
 301 stream water level were found to vary in time, but always upwards flow (i.e. flow direction from the
 302 streambed to stream) or null at the time of measurements, and on the order of a few mm to a maximum of
 303 4 cm. The corresponding water samples were also variable, revealing a highly heterogeneous overall
 304 contamination pattern, with concentrations of CAHs varying, for example in April 2017, from a few µg/L up
 305 to ca. 2,600 µg/L (PCE eq) over a small confined area close to the retaining wall (Fig. 4a). The

306 measurements taken from the monitoring well in the shallow aquifer revealed concentrations ranging from
 307 ca. 4300 to 7500 $\mu\text{g/L}$ (PCE eq) for all sampling campaigns.

308
 309 **Figure 4. Variations of chlorinated ethene concentrations in the groundwater monitoring well, streambed, and stream in the**
 310 **north channel. a) Spatial variations for a selected period (April 2017) expressed in PCE eq. ; b) Temporal variations of molar**
 311 **ratios for the stream water and streambed water samples at different locations for three selected periods (April, June and**
 312 **November 2017).**

313 Notably, the molar ratios between the different chlorinated compounds were stable in time for both the
314 shallow aquifer and hyporheic zone samples: VC was almost exclusively found under the streambed and
315 mostly cDCE in the shallow aquifer (Fig. 4b). However, significant temporal variations in the molar ratios for
316 cDCE and VC were observed in the stream water samples compared to the relatively stable ratios observed
317 in the shallow aquifer. These temporal variations were especially noticeable directly up- and downstream
318 of the crack in the retaining wall, as well as in the 'temporary' transect (T0), and in the recess and drain (Fig.
319 4b).

320 These observations suggest that the contaminants discharging into the north channel from source zone A
321 occurred via different pathways with variable contributions. VC mostly discharged via the streambed,
322 indicative for a groundwater flow pathway, while the cDCE component entered via different hydrological
323 preferential flow paths from the northern bank (cracks and urban drains). These discharges were extremely
324 dynamic and their respective contribution dependent on the near-surface hydrological flow conditions and
325 hydrogeological properties of the stream bottom. These results are thus reflective of a highly complex
326 system, comprised of natural discharge processes combined with urban flow paths, leading to a highly
327 complicated and heterogeneous contaminant discharge pattern that varies in space and time over a
328 relatively limited area. Nevertheless, all contaminant pathways ultimately converge downstream of this
329 complex discharge zone and add up with the additional CMD from source zone B. Currently the Danish
330 authorities requires an understanding of the total impact from each contaminated site impacting surface
331 waters. From there, the focus of our study shifted from this single source area to determine the overall
332 CMD variation originating from the site.

333 **4.3 Temporal variation of the in-stream contaminant discharge**

334 The temporal variations of the in-stream mass discharge for CAH over 12 months were evaluated at
335 transects T1, T4 and T6 (Fig. 5). When considered individually, significant temporal variations occurred and
336 increased from T1 to T6 with an average yearly discharge of 1.7, 4.7, and 3.7 kg/yr PCE eq (coefficient of

337 variation, CV = 67%, 75% and 96%, respectively). In transect T1, downstream source zone A, the highest
 338 estimate for in-stream contaminant discharge was observed in January and February 2017, while the most
 339 important discharges after the channel junction at transect T4 were found to not coincide with the ones in
 340 T1.
 341

342
 343 **Figure 5: Temporal variations of in-stream contaminant mass discharge for chlorinated compounds (TCE, cDCE and VC) along the**
 344 **north channel (T1) and downstream transects (T4, T6), and in the south channel (T7), expressed as PCE eq. See section 3.5 for**
 345 **calculations.**

At this particular transect, T4, a significant increase in the in-stream CMD was observed for three of the measurement rounds including November 2016 (ranging e.g. from 1.9 in T1 to 13.4 kg/y PCE eq in T4), as well as February and March 2017. These elevated levels in CMD held in “intensity” further downstream to T6 for both November 2016 and March 2017; while continuously increasing in April 2017. This intensification of contaminant mass discharge to the stream was not caused by a sudden discharge from the south channel, considering the relatively low contaminant mass that has been estimated for that point in the same periods (see T7, Fig. 5). Instead, a significant CAH discharge must have been active during these periods and under specific hydrological conditions occurring between transects T1 and T4. The attention was then shifted to assessing the role of source zone B (Fig. 2) and the potential processes governing the increase in CMD.

4.4 Evaluation of governing environmental processes

Spearman rank correlation was used to evaluate the interrelationships between precipitation, monitored hydrological parameters and estimated in-stream CMD in order to investigate the potential drivers for the contaminant dynamics found downstream of the junction at transect T4. Correlations were in fact found to be significant for describing the variation of in-stream CMD with some of the parameters collected on site (see Fig. 6). Specifically, the in-stream CMD, J , for both cDCE and VC exhibited high positive correlation values with the water flow rate, Q , for both the north and south channels ($\rho_s > 0.6$ with $p < 0.05$, Figure 6a). The in-stream CMD at transect T4 varied almost linearly with the measured flow rate in the north channel ($R^2 > 0.8$ for both cDCE and VC, Fig. 6b), and to a certain extent with the measured flow rate in the south channel ($R^2 > 0.3$, with one outlier removed corresponding to an unusually high stream flow in the south channel only).

No significant Spearman rank correlations (Fig. 6a, $\rho_s < 0.6$ and corresponding $p > 0.05$) were observed between the in-stream CMD estimated at transect T4, and drivers/proxies of shallow groundwater flow such as precipitation, N , or the relative water level gradient, Δh , measured between the north channel and

the shallow groundwater monitoring well in source zone A. We therefore speculate that the increase in CAH mass at transect T4 is not caused by a shallow groundwater pathway not accounted for stemming from source zone A. Instead, the interaction between the two channels and source zone B was suspected as the main driver responsible for this mass increase. We also ruled out the possibility of a resuspension of sorbed contaminants, considering the significant increase of CAH between T1 and T4 (ca. 7 times more in November 2016).

Figure 6. (a) Spearman rank correlation, ρ_s , diagonal matrix between in-stream contaminant mass discharge in transect T4 and selected hydrological parameters: precipitation (N), stream flow rates (Q), water table in shallow aquifer (h_{GW}) at source zone A and B, as well as stream water table (h_{SW}) and the hydraulic gradient (Δh). Subscripts A and B refer to source zones A and B, respectively, while subscripts $_N$ and $_S$ refers to the north and south channel, respectively; see Fig. 7 for specific locations. (b) Scatterplot of the in-stream contaminant mass discharge at T4 for cDCE and VC with respect to the stream flow rates in the north and south channel, and associated linear regressions.

Following this analysis, an additional campaign in autumn 2018 was initiated in order to monitor hydraulic heads in the system with a focus on capturing the dynamics associated with source zone B for a two-month period. The hydraulic head is used here as a proxy for the stream flow, the relationship between hydraulic head and stream flow being relatively stable over this limited period of time and at this time of the year.

387 During sustained rain events, an increase in the shallow aquifer water table (head) was observed for the
 388 northern part of the site. In addition, hydraulic heads increased for the north channel compared to the
 389 levels monitored in the shallow aquifer in source zone B and in the south channel (see hydraulic heads in
 390 Fig. 7b: $h(GW_A)$, $h(SW_N)$ compared to $h(GW_B)$ and $h(SW_S)$). These results suggest that sustained rain events
 391 associated with the site topography (with a slight slope from north to south along the investigated area)
 392 could cause a sufficient hydraulic head difference that activates a substantial inter-channel flow. This inter-
 393 channel flow leads to the mobilization and transport of contamination stemming from source zone B, which
 394 is located very close to the bank at the junction of the two channels. This process was only observed for
 395 late times of the year, leading to the hypothesis that vegetation on site may be intercepting and transpiring
 396 a significant part of the precipitation during the summer months and forcing the stream water to flow
 397 towards the shallow groundwater.

399 Figure 7. Variation of hydraulic heads, h , for the shallow groundwater on the north side (GWA), shallow groundwater close to
 400 the junction on the south side (GWB), and stream water level in the north and south channels (SW N/S). a) Monitoring locations;
 401 b) time series for GWA (open red circle), GWB (filled red circle), SWN (filled blue triangle) and SWs (open blue triangle),
 402 displayed as a rolling average over 24 hours. Precipitation levels are displayed on the right-hand y-axis (black solid line)
 403 corresponding to the black lines at the top of the graph. The black arrows indicate sustained rain events corresponding to a
 404 marked increase in GWA; c) Visualization of the water head variations and enhanced hydraulic gradient between the north
 405 channel, south channel and GWB before (Time 1) and after (Time 2) a sustained rain event (as indicated by the dotted lines
 406 labeled Time 1 and 2).

407 5 Practical implications and perspectives

408 Our study investigated the mass discharge of CAH from a former industrial site to a peri-urban stream and
 409 monitored its temporal variations for over a year on a monthly basis. The use of in-stream CMD for the
 410 quantification of the mass discharge through strategically placed control transects appeared to be fruitful.
 411 It allowed us to track and highlight the contribution of different sources to a receiving stream, while
 412 providing valuable insights on the possible contaminant pathways. Furthermore, this approach is valid
 413 without consideration of the full mixing of the contaminant, i.e. independently of any prior knowledge on
 414 the discharge and mixing zone. It is also a convenient way to aggregate the different pathways from a single
 415 source in order to quantify multiple pathway contributions at a larger scale, as carried out with respect to
 416 source zone A in this study. This in-stream approach is limited, however, by practical constraints for the
 417 discretization of an in-stream control plane, and to dissolved contaminants with concentration levels high
 418 enough to be detected after dilution in the stream (Sonne et al. 2018). We observed a substantial increase
 419 in CMD related to increases in stream flow. This is in contrast to, for instance, the study by Rønde et al.
 420 (2017), who observed an almost constant CMD with time in the Grindsted stream (Denmark). The finding in
 421 our study thus implies that the highest concentration in the stream is not necessarily related to the lowest
 422 stream flow (largest dilutions), as intuitively expected from equation (2).

423 Our results highlight the importance of understanding the dynamics associated with the presence of
 424 multiple contaminant discharge pathways emanating from a contaminant source in peri-urban/urban
 425 settings. As expected, shallow groundwater seeping through the streambed played a role, but also key
 426 urban features such as former drains and/or sewer lines which acted as preferential flow paths exhibiting
 427 different temporal dynamics. Such flow paths were also reported by Rønde et al. (2017) identifying

428 drainage culverts as a source of uncertainty in their total CMD calculations. Peri-urban stream systems with
429 such markedly different flow paths can be described as “urban karst”, i.e. comprised of different
430 environmental and engineered compartments as also discussed in Zoboli et al. (2019), and constitute a
431 significant contaminant transport vector for shallow groundwater systems in these settings (Kaushal and
432 Belt, 2012).

433 However, these different pathways were not the main cause for the overall CMD variations documented
434 here, as the largest in-stream CMD downstream did not coincide with the maximum discharge from source
435 zone A. We suggest instead that an inter-channel flow driven by local variations of river stage resulted in a
436 complex contaminant transport from source zone B, located at the junction of two channels, which
437 otherwise seems to be small. Such flow dynamics and resulting contaminant transport is closely related to
438 the meander-driven hyporheic exchange, or transient hydrological conditions at the channel junction scale
439 as described and modelled for example by Boano et al., (2006), Dwivedi et al. (2018) and Han and Endreny
440 (2013). To date, we could not find many other published studies describing point pollutant source dynamics
441 with a source located in the near vicinity of a stream junction (but see Fryar et al (2000) for discussion on
442 the influence of tributary flow and interaction with a contaminant plume). Nevertheless, such a
443 configuration is certainly not unique as many contaminated sites are often historically located in the vicinity
444 of stream waters (Weatherill et al. 2014).

445 The size of the stream and the heterogeneous clayey till setting may also play an important role in the
446 strong CMD variability observed and the resulting variations in concentration levels. Indeed for a given
447 geological setting, small or headwater streams are influenced by local flow systems with high seasonal
448 variations, while higher-order streams and rivers are usually fed by more regional, sustained and steady
449 groundwater components (Winter et al., 1998; Dahl et al., 2007). Furthermore, the low water flow in small
450 stream systems results in a more limited dilution for any contaminant that enters, which in turn has a
451 strong effect on the resulting contaminant concentrations, all CMD variations considered.

452 The outcomes of this study can already be employed to facilitate the design of monitoring plan for the
453 assessment of chemical status of streams affected by contaminated sites. It is clear that for some stream
454 systems, the combination of concentration levels and dilution effects without considering the dynamics of
455 any sources present may be misleading. In Denmark for example, the EPA recommends sampling during
456 low flow periods (where highest contaminant concentrations would be expected) while still acknowledging
457 the possible variations of CMD especially in small stream systems (Miljøstyrelsen (Danish EPA) 2018). This
458 study has shown that such a screening approach is only valid when the discharge of contaminants and
459 stream waters are not strongly correlated, i.e. the CMD variations are negligible compared to the stream
460 flow variation diluting the contaminant. Additionally, the sampling frequency was found to be a key factor
461 to consider when designing monitoring strategies for chemical substances. European legislation, e.g. the
462 Water Framework Directive, for the assessment of chemical status has left it open to its Member States to
463 choose what they think is appropriate, although the seasonal variation should ideally be accounted for
464 (European Commission 2009), especially for contaminants with suspected seasonal patterns (e.g. spraying
465 season of pesticides, or tourist-borne substances such as Personal Care Products).

466 **6 Conclusions**

467 We investigated the temporal and spatial variation of chlorinated ethenes discharging from a contaminated
468 site to a peri-urban stream comprised of two channels. An in-stream CMD approach was applied in order to
469 track these variations at different transects along the investigated stream stretch (ca. 500 m). Our study
470 revealed substantial local variations in concentrations, induced by a highly dynamic contaminant mass
471 discharging to the stream via different pathways comprising a complex system of interlinked environmental
472 and engineered compartments, or urban karst. The in-stream CMD estimates indicated a surprisingly high
473 variation of CMD values, ranging from 1-13 kg/yr depending on the considered transect and measurement
474 period.

475 Variable contributions stemming from the groundwater seepage emanating from the complex geological
476 setting and urban drain features were identified in the channelized part of the stream, originating from
477 source zone A. However, these variations alone could not explain the maximum contaminant discharge
478 estimated further downstream. A cross-correlation between different hydrological parameters and the
479 estimated mass discharge revealed a strong link between these quantities and the flow rates in the two
480 channels. Additional hydraulic head measurements suggested that, in periods of sustained rain, a transient
481 hyporheic flow at the junction scale occurs enhancing contaminant transport from source zone B, a second
482 source located at the confluence. Thus, an in-stream CMD approach was found to be an effective method
483 for quantitatively integrating the multiple and highly variable discharge contributions, even if not fully
484 mixed, although information on specific pathways is lost.

485 This study highlights the complexity and variability of contaminant fluxes occurring at the interface
486 between groundwater and peri-urban streams. Notably, small streams are fed by local water flow systems
487 likely to interact with contaminated sites often located in the near vicinity. Consideration of these temporal
488 variations are therefore essential when designing monitoring programs to determine the potential impact
489 arising from contaminated sites impacting streams (for prioritization purposes). Moreover, spatial aspects
490 related to e.g. the presence of multiple active pathways, possibly dependent on the temporal dynamics,
491 become important when considering remedial actions for prioritized contaminated sites in such peri-
492 urban/urban stream systems.

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<p>Figure 1. Overview of the Raadvad site showing land use, stream flow direction and location of the measurement transects. The dashed red lines correspond to transect locations where detailed stream water sampling was carried out (5 points per transect); solid red lines show the transects used for the in-stream contaminant mass discharge estimation. The dashed black line box indicates the location of the north channel presented in more detail in Figure 2.</p>
<p>Figure 2: (a) Locations for stream water (blue circles) and streambed (piezometers; open squares) samples used in the estimation of contaminant mass discharge (CMD). Approximate delineation (sum of CAHs concentration > 10 µg/L in shallow groundwater) for the main contaminant source zones A and B are marked with striped red polygons based on previous investigations by a consulting company (Niras 2012). Note that the other transects used for CMD estimation are shown in Fig. 1. (b) Pictures from the site indicate the location of the crack and urban drain in the retainment wall.</p>
<p>Figure 3. Effects of mixing and dilution of the in-stream contaminant concentrations measured at 5 detailed transects for TCE and detectable degradation products (cDCE and VC) in June 2016. Note that the x-axis corresponds to a normalized stream width, i.e. 0 for the north bank, and 1 for the south bank.</p>

Figure 4. Variations of chlorinated ethene concentrations in the groundwater monitoring well, streambed, and stream in the north channel. (a) Spatial variations for a selected period (April 2017) expressed in PCE eq. (b) Temporal variations of molar ratios for the stream water and streambed water samples at different locations for three selected periods (April, June and November 2017).

Figure 5: Temporal variations of in-stream contaminant mass discharge for chlorinated compounds (TCE, cDCE and VC) along the north channel (T1) and downstream transects (T4, T6), and in the south channel (T7), expressed as PCE eq. See section 3.5 for calculations.

Figure 6. (a) Spearman rank correlation, ρ_s , diagonal matrix between in-stream contaminant mass discharge in transect T4 and selected hydrological parameters: precipitation (N), stream flow rates (Q), water table in shallow aquifer (hGW) at source zone A and B, as well as stream water table (hSW) and the hydraulic gradient (Δh). Subscripts A and B refer to source zones A and B, respectively, while subscripts N and S refers to the north and south channel, respectively; see Fig. 7 for specific locations. (b) Scatterplot of the in-stream contaminant mass discharge at T4 for cDCE and VC with respect to the stream flow rates in the north and south channel, and associated linear regressions.

Figure 7. Variation of hydraulic heads, h , for the shallow groundwater on the north side (GW_A), shallow groundwater close to the junction on the south side (GW_B), and stream water level in the north and south channels ($SW_{N/S}$). a) Monitoring locations; b) time series for GW_A (open red circle), GW_B (filled red circle), SW_N (filled blue triangle) and SW_S (open blue triangle), displayed as a rolling average over 24 hours. Precipitation levels are displayed on the right-hand y-axis (black solid line) corresponding to the black lines at the top of the graph. The black arrows indicate sustained rain events corresponding to a marked increase in GW_A ; c) Visualization of the water head variations and enhanced hydraulic gradient between the north channel, south channel and GW_B before (Time 1) and after (Time 2) a sustained rain event (as indicated by the dotted lines labeled Time 1 and 2).