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1 Dynamics of chlorinated aliphatic hydrocarbons in the 2 Chalk aquifer of northern France

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11 1. Introduction

12 Chlorinated (aliphatic) hydrocarbons (CHCs) such as the common solvents tetrachloroethene (PCE),
13 trichloroethene (TCE) and 1,1,1-trichloroethane (TCA) are among the most common chemicals that
14 pollute groundwaters worldwide (Clement et al., 2000; Witt et al., 2002; Lenczewski et al., 2003;
15 Arianna et al., 2019; Kawabe and Komai, 2019; La Vigna et al., 2019). They are used as industrial
16 solvents for a broad range of applications in chemical synthesis, degreasing agents of metal parts,
17 cleaning of electronic components, or textile dry-cleaning (Rivett et al., 1990), and are known or
18 suspected to be carcinogenic or mutagenic agents for humans. Natural CHC attenuation occurs under
19 both reducing and oxidizing conditions in groundwater, mainly leading to the formation of less
20 chlorinated compounds such as *cis*-1,2-DCE, 1,1-DCE, 1,2-DCE and 1,1-DCA. Depending on the
21 physico-chemical conditions, these intermediate products can be further degraded to vinyl chloride
22 (VC), ethene and ethane.

23 During reductive dechlorination, chlorine atoms are sequentially removed and replaced with
24 hydrogen; the transformation proceeds from PCE to TCE, to *cis*-dichloroethene (*cis*-1,2-DCE), to vinyl

25 chloride (VC), and from 1,1,1-TCA to 1,1-DCA to chloroethane (CA), and finally to non-toxic
26 ethene/ethane (Vogel et al. 1987, Wiedemeier et al. 1999). Under anaerobic conditions, 1,1,1-TCA
27 may also be degraded abiotically by α -dehaloelimination to 1,1-DCE (Vogel and McCarty, 1987).
28 Commonly, 1,2-DCE and 1,1-DCA accumulate due to incomplete reduction; high concentrations of
29 co-contaminants can also inhibit dechlorinating bacteria (Maymó-Gatell et al., 2001; Kawabe and
30 Komai, 2019). Under oxic conditions, DCE, VC and TCE can be directly mineralized to CO₂ via oxidative
31 pathways (Clement et al. 2000). As dense compounds, CHCs have a tendency for downward
32 migration, transport along fractures, and settling in pools at the base of the aquifer. Less chlorinated
33 daughter products are more mobile in groundwater than PCE or TCE. It has been observed that each
34 of these dechlorination steps is leading to a significant carbon isotope fractionation within the
35 molecules that are involved in the degradation reactions (Hunkeler et al., 1999; Bloom et al., 2000;
36 Sherwood Lollar et al., 2001). Compound- and pathway-specific fractionation factors α (which define
37 the isotopic fractionation between any two compounds) or the enrichment factor ϵ are determined
38 in laboratory batch or column systems with pure or mixed microbial cultures by applying the Rayleigh
39 equation (Braeckevelt et al., 2012).

40 Numerous studies have explored CHC spatial dynamics, mainly focusing on the remediation of
41 contaminated sites with often identified and finite-source pollutions (Clement et al., 2000; Witt et al.,
42 2002; Pooley et al., 2009; Palau et al., 2014; Wanner and Hunkeler, 2015; Arianna et al., 2019). Most
43 studies used classic sampling methods based on pumping at one depth. However, such sampling may
44 be inadequate for characterizing the potential stratification of such pollution. For this purpose,
45 passive diffusion samplers were developed for monitoring CHCs in groundwater (Vroblesky and
46 Campbell, 2001; Divine et al., 2004; Divine and McCray 2004). Such samplers consist of a sealed
47 semipermeable membrane (such as low-density polyethylene (LDPE)) full of pure water, whose
48 concentration increases until equilibrium with the ambient concentrations is reached.

49 In the peri-urban area of southwest Lille (Figure 1), with its mixed agricultural and industrial
50 activities, the Chalk aquifer used for drinking-water production is threatened by the presence of
51 CHCs. Droughts are more frequent and severe in the region since a few years, and the groundwater
52 level has been lowering since 2017. Therefore, the decrease of water *quantity* in the aquifer and the
53 continuing pumping operations cause a decrease in water *quality*. CHC concentrations in
54 groundwater commonly exceed the European water guideline for drinking water ([PCE] + [TCE]
55 $<10 \mu\text{g L}^{-1}$, (RF, 2007)) thus limiting the use of this resource for drinking-water production (40% of the
56 needs of the 1 million inhabitants of the Lille European Metropolis). A good understanding of CHC
57 dynamics and their spatial distribution in the aquifer thus is a key factor, especially in the case of VC,
58 the most toxic and carcinogenic CHC (Lee et al., 1977; Clewell et al., 1995; Giri, 1995) with the most
59 drastic restrictive regulation [VC $<0.5 \mu\text{g L}^{-1}$, (RF, 2007)].

60 To our knowledge, no studies have determined the CHC degradation processes in groundwater over
61 time, and in a large number of multiple well fields. In this paper, sharp investigations of the dynamics
62 and degradation processes of CHCs were performed over a large complex area (2,032 ha) in terms of
63 hydrology, geology and contamination sources at the catchment scale composed of several well
64 fields. Wells were sampled during eight years to evaluate CHC concentrations, using standard one-
65 depth sampling. To assess a possible migration or degradation of the compounds, intensive sampling
66 of some wells along the water column with passive samplers were undertaken as well as compound-
67 specific carbon-isotope analyses. Finally, a detailed hydrochemical definition of the area allows
68 strengthening our conclusions.

69

70 2. Material and methods

71 *2.1. Geological and hydrogeological context*

72 In the study area, the stratigraphic succession of the Paris Basin begins with a highly faulted, more-
73 or-less dolomitic, several-hundred-meters-thick succession of Lower Carboniferous limestone and
74 calcareous shale (Cary et al., 2014). This is overlain by marly Cenomanian Chalk, locally called the
75 “Dièves”, resulting from the Cretaceous transgression. The “Dièves” is followed by a thick deposit of
76 Turonian marly limestone that evolves upward to white and grey flint-bearing Turonian and Senonian
77 Chalk with phosphate beds. The unconformably overlying Tertiary formations comprise the Louvil
78 Clay (Lower Landenian, 9–12 m thick), the Ostricourt Sand (Upper Landenian, 25–30 m thick), and the
79 Flandres Clay (Ypresian, 10–15 m thick). Throughout the Paris-London Basin, the Tertiary formations
80 confine the underlying Chalk aquifer. Quaternary loess (pre-Weichselian and Weichselian) covers
81 practically the entire basin. The uppermost 5 m in the Lille region consist of Quaternary alluvium of
82 the Deûle canal, mainly comprising heterogeneous sandy/clayey deposits.

83 The Dièves marl is the impermeable base of the Chalk aquifer. This is constituted by the Turonian-
84 Senonian Chalk at 10–50 m depth, favoured by the presence of highly permeable horizons with open
85 fissures mainly found at 10–15 m depth. The groundwater of the Chalk aquifer circulates in the fault
86 network, which is highly developed in the valleys where the well fields are sited (Cary et al., 2014).

87 Drinking water for the Lille European Metropolis is pumped from four well fields tapping the Chalk
88 aquifer to the southwest of Lille, the Emmerin (5,346 ha), Houplin-Ancoisne (6,303 ha), Les
89 Ansereuilles (8,298 ha) and Seclin (369 ha) well fields (Figure 1). The Emmerin well field (10 pumping
90 wells) is located at the top of a WNW-ESE anticline. The Houplin-Ancoisne well field (11 pumping
91 wells) lies along the Seclin canal that follows the trajectory of the major NW–SE-trending Seclin Fault;
92 here the Chalk groundwater is locally confined below clayey deposits. The Les Ansereuilles well field
93 (26 pumping wells) is parallel to the highly polluted Deûle canal. The groundwater, which is

94 unconfined southwest of the Deûle, flows northwest to become confined under the alluvial cover
95 that can be 15–20 m thick. In the A12–A15 well area it is locally confined due to the presence of
96 more than 10 m of clay deposited above the Chalk (Cary et al., 2014). The Deûle canal and other
97 small tributaries drain the area, which is affected by quantitative and qualitative pressures of
98 industrial, urban and agricultural origins.

99 Inverse modelling with the MARTHE software has used potentiometric data from the studied well
100 fields (Bessière et al., 2015). The simulation results show the reversed water pathways from selected
101 starting points (pumping wells) to the probable origin (blue lines on Figure 1). Groundwater-
102 drawdown areas are centred around the groups of exploited wells. For example, four groundwater
103 drawdowns are identified in the Les Ansereuilles well field: the northern part centred around A16,
104 the northwestern part around A26, the southwestern part around A18, and the southern part around
105 A21.

106 In all, 363 current and former industrial sites potentially involved in or identified as responsible for
107 CHC pollution are stored in the BASIAS database (<https://www.georisques.gouv.fr/dossiers/basias/>)
108 of French well fields. More than 20% of these sites are metalworking plants (boiler work, automobile
109 factory, sheet-metal manufacture, foundry, etc.) that use PCE, DCE and TCA for metal cleaning.
110 Industrial laundries, chemical plants, and textile and dyeing factories using these CHCs were also
111 identified in the well fields (Figure 1). The difficulties of waste management and recycling in the past
112 caused the storage of CHCs close to groundwater.

113 **Figure 1: Location of the 22 studied wells, geological formations, modelled water pathways and (suspected)**
114 **industrial sources of chlorinated solvents in the four studied well fields (shown by ellipses).**

115 *2.2. Sampling and analyses*

116 Groundwater was sampled by quarterly pumping in 22 wells from 2011 to 2019, to evaluate the
117 chlorinated-solvent concentrations at one depth. Twelve wells were located in Les Ansereuilles (A12,
118 A13, A14, A15, A16, A18, A21, A26, PZ49, PZ55, PZ56, and PZ59), five in Houplin-Ancoisne (H1, H4,

119 H7, H11, and PZ51), four in Emmerin (E5, E7, E8, and PZ61) and one in Seclin (S1) well fields (Figure
120 1).

121 Among the large panel of studied wells, a more detailed analysis has been performed on three wells
122 (PZ56, PZ59, and PZ61) located in three strategic locations of the well fields (northern and southern
123 parts of Les Ansereuilles, Emmerin, respectively). These wells were sampled along the water column
124 with passive samplers (low density polyethylene diffusion bags filled with ultrapure water: 100 μ m
125 thick, 90 cm high, 4 cm large, volume 300 mL), to assess a possible vertical migration of the
126 compounds during a further ten sampling campaigns from 2016 to 2019 during different seasons.
127 The well cross-sections are shown in the Supplementary Information (Fig. SI-1). Deployment of the
128 passive samplers depended on the inflows measured along the water column (PZ56: 6 inflows, 8
129 sampling depths from -19.5 to -52.6 m; PZ59: 3 inflows, 10 sampling depths from -7 to -64.3 m; PZ61:
130 5 inflows, 5 sampling depths from -9 to -23.2 m). Inflows were obtained along vertical profiles using
131 flowmeter measurements (GFTC probe, SEMM logging, France) from the piezometric level to the
132 bottom of the well. Velocity measurements were taken every 0.5 m (Maréchal et al., 2004). During
133 pumped and passive samplings, samples were collected in filled to capacity brown glass bottles,
134 stored in a refrigerated cooler and carried to the laboratory where CHC analyses were made within
135 24 h. The presence of CHC-degradation marker gases (CO_2 , methane, ethane, ethene) was
136 investigated in November 2017. Compound-specific carbon-isotope analysis was used to gain further
137 insight into the intrinsic biodegradation of chlorinated solvents within the aquifer. To this end, three
138 campaigns in 2017, 2019 and 2020 pumped samples from the six observation wells (Fig. 1); some
139 samples were taken at two depths. In addition, a more detailed *in-situ* hydrochemical definition of
140 groundwater studied physico-chemical parameters. Redox potential Eh (whose values are expressed
141 against the SHE electrode) and dissolved oxygen were recorded with a multiparameter probe (EXO 1,
142 YSI Incorporated, Yellow Springs, Ohio, USA).

143 The CHC concentrations in sampled groundwater (PCE, TCE, TCA, *cis*-1,2-DCE, *trans*-1,2-DCE, 1,1-DCE,
144 1,2-DCE, 1,1-DCA, 1,2-DCA and VC) were measured using a HS-GC-MS-MS (Thermoelectron Triplus
145 Duo-Trace GC Ultra-TSQ Quantum XLS) with a quantification limit of 0.2 µg L⁻¹ and an accuracy of 5 to
146 10% depending upon the concentration. Analyses were performed by the Lille European Metropolis
147 laboratory within one day after sampling the groundwater.

148 Gases were analysed by the BRGM laboratory using a Trace GC Ultra Thermo Fisher Scientific gas
149 chromatograph (Thermo Scientific, with FID detector). The gases investigated were CO₂ and C_nH_{2n+2}
150 (n=1 to 2) with injection valves of 25 µL and 250 µL). Detection limits were ±0.0002% for C_nH_{2n+2} and
151 ±0.001% for CO₂. Percentages are volumic.

152 Compound specific isotope analysis (CSIA) is an analytical method that measures the ratio of stable
153 isotopes of a contaminant. Stable carbon-isotope ratios of individual CHC compounds were
154 determined by gas chromatography - combustion – isotope-ratio mass spectrometry (GC-C-IRMS)
155 using a Trace GC Ultra gas chromatograph (Thermo Scientific) equipped with a Rtx-VMS column
156 (60 m x 0.32 mm, 1.8 µm film) connected via a GC IsoLink combustion interface to a Delta V Plus
157 isotope-ratio mass spectrometer (Thermo Scientific). The system was used together with a Combi Pal
158 autosampler where headspace extraction of the water samples was performed by in-tube
159 microextraction (ITEX-2) using a Tenax GR with 80/100 mesh size as sorbent material (ITEX-trap from
160 BGB Analytics); see (Laaks et al., 2010) for further details. Isotopic ratios of each compound are
161 expressed in ‰ difference relative to the VPDB (Vienna Pee Dee Belemnite) international standard
162 using the delta notation given by: $\delta^{13}\text{C} = (R/R_{\text{std}} - 1) \cdot 1000$, where R and R_{std} are the isotope ratios of
163 the sample and the VPDB standard, respectively. Analytical uncertainty (including reproducibility and
164 accuracy) for the given compounds is generally within ±0.5‰. Isotopic measurements were
165 performed in triplicate. The method quantification limit was equal to 5 µg L⁻¹ for TCE and PCE, 15 µg
166 L⁻¹ for *cis*-1,2-DCE and 20 µg L⁻¹ for all other CHCs. Isotope fractionation can be expressed by

167 enrichment factors $\epsilon = \delta^{13}\text{C}_o - \delta^{13}\text{C}_p$, where $\delta^{13}\text{C}_p$ is the carbon isotope ratio of the product and $\delta^{13}\text{C}_o$
168 the carbon isotope ratio of the corresponding precursor (Hunkeler et al., 1999).

169 3. Results

170 The mean concentrations and standard deviations of CHCs from standard sampling (2011 to 2019
171 data) are provided in the Supporting information in Table SI-1. The CHC concentrations from passive
172 sampling in the wells at each depth (2016-2018 data) are presented in the Supporting information in
173 Table SI-3 and summarized with mean-values by depth in Table SI-2.

174 3.1. CHC pollution in the well fields

175 Groundwater in the southwest of the Ansereuilles well field showed the highest average CHC
176 concentrations (PZ59: $185 \mu\text{g L}^{-1}$, PZ56: $150 \mu\text{g L}^{-1}$, A18: $65 \mu\text{g L}^{-1}$, Figure 2-a). To a lesser extent, CHCs
177 were detected in PZ55 and A21 (respectively 30 and $9 \mu\text{g L}^{-1}$). Downstream of the Deûle canal, CHC
178 concentrations decreased from $25 \mu\text{g L}^{-1}$ (A12) to $1.4 \mu\text{g L}^{-1}$ (A14). The Houplin-Ancoisne and
179 Emmerin well fields were less affected by CHC pollution (H7: $9 \mu\text{g L}^{-1}$, E7: $2 \mu\text{g L}^{-1}$, and PZ61: $14 \mu\text{g L}^{-1}$).
180 No CHCs were detected in A26 and H11. In addition, the distribution of the various CHC
181 compounds differed from one well to the next (Figure 2-b). In the southern part of the Ansereuilles
182 well field, either *cis*-1,2-DCE or PCE represented more than 60% of the total concentration (PZ59, A18
183 and PZ49: *cis*-1,2-DCE, A21 and PZ55: PCE). In such highly polluted wells and at these single-depth
184 sampling points, the degradation products were often not detected. However, in the northern half of
185 the Les Ansereuilles almost all CHC compounds were detected, the major compound representing
186 <40% of the total mass concentration. In the Houplin-Ancoisne and Emmerin well fields PCE
187 dominated, followed by TCE and 1,1,1-TCA., except in E8 where TCA was the major compound. In
188 Seclin, TCE was the only compound detected.

189 **Figure 2: (a) Average total CHC concentrations in $\mu\text{g L}^{-1}$ in the studied well fields (data from 2011 to 2019).**
190 **Colours of symbols are shaded according to the CHC concentrations. (b) CHC distribution in percentage (%),**
191 **each colour represents a CHC compound (H11 and A26 not shown because of the absence of CHCs).**

192 *3.2. CHC concentrations along depth and over time*

193 Pearson coefficients were computed to investigate possible correlation between piezometric levels
194 and CHC concentrations at multiple depths between 2016 and 2019. Pearson coefficients are
195 significant if $R_{\text{critical}} > 0.7$ (with $p\text{-value}=0.05$). Results are presented in Table SI-4. In PZ61, pearson
196 coefficients are positive and from 0.73 to 0.97 at -9 m for 1,1-DCE, 1,1,1-TCA, TCE and PCE. For PCE,
197 pearson coefficients are superior to 0.7 and significant at -13 and -19.45m, too. In PZ56, pearson
198 coefficients are positive from 0.72 to 0.99 at -19.5, -25, -31 and -41m for 1,1-DCA, *trans*-1,2-DCE and
199 PCE. At -52.6 m, pearson coefficients are negative from -0.82 to -0.70 for 1,1-DCE, 1,1-DCA, *cis*-1,2-
200 DCE, 1,1,1-TCA, TCE and PCE. In PZ59, pearson coefficient is positive (0.95) for *cis*-1,2-DCE at -10 m
201 and negative (-0.71) for *trans*-1,2-DCE at -53 m. In PZ61 at -15.75m, high concentration of PCE is
202 observed during the high water-level period ($14.0 \mu\text{g L}^{-1}$ in February 2018) while low concentration of
203 PCE is observed during the low water-level period ($8.3 \mu\text{g L}^{-1}$ in September 2018).

204 CHC concentrations in PZ56, PZ59 and PZ61 were sampled with PDB along the water column over ten
205 sampling campaigns from 2016 to 2019. All results are shown in Supporting Information (Table SI-3).
206 In PZ56, all CHC compounds were detected in the water column (from -19.5 to -59 m), except 1,2-
207 DCA that was below the quantification limit ($0.2 \mu\text{g L}^{-1}$). VC was detected at the deepest point of the
208 water column (-59 m, $0.2 \mu\text{g L}^{-1}$). TCE, PCE, *cis*-1,2-DCE, 1,1-DCA and 1,1,1-TCA concentrations
209 decreased with well depth. In PZ59, no CHCs occurred in the first metres of the water column, but
210 were observed from -33.6 to -64.3 m, especially *cis*-1,2-DCE whose concentration decreased with
211 depth (from $160 \mu\text{g L}^{-1}$ at -47 m to $70 \mu\text{g L}^{-1}$ at -64.3 m),. 1,1-DCE and VC were detected, but at low
212 concentrations (respectively $\leq 0.3 \mu\text{g L}^{-1}$ and from 0.2 to $1.1 \mu\text{g L}^{-1}$). Chlorinated ethanes were not
213 detected, except minor 1,1-DCA with concentrations $< 2.9 \mu\text{g L}^{-1}$. In PZ61, only PCE, TCE and TCA were

214 detected along the water column (from -9 to -23.2 m) with a peak at -13 m and a subsequent
215 decrease with depth (PCE: 10.1 to 3.0 $\mu\text{g L}^{-1}$, TCE: 1.2 to 0.5 $\mu\text{g L}^{-1}$, TCA: 0.8 to 0.3 $\mu\text{g L}^{-1}$).

216 Figure 3 shows the evolution of total CHC and of two predominant CHC compounds concentrations
217 over time at multiple depths sampled in PZ56, PZ59 and PZ61. All depths were not sampled for each
218 campaign, the absence of data at some depths in 2016 and 2019 does not mean that the CHCs were
219 under the limit of detection but were not investigated. In PZ56, CHCs were detected from -19.5 m to
220 the bottom (-59 m) and decreased along depth: the average total CHCs concentrations varied from
221 147 $\mu\text{g L}^{-1}$ at -19.5 m to 42 $\mu\text{g L}^{-1}$ at -59 m. In the first part of the well (from -19.5 m to -47m), CHC
222 concentrations increased over time (at -19.5m, from 86 $\mu\text{g L}^{-1}$ in 2017 to 188 $\mu\text{g L}^{-1}$ in 2019) while
223 they were quite stable at the bottom of the well (at -59 m, 51 $\mu\text{g L}^{-1}$ in 2016 to 36 $\mu\text{g L}^{-1}$ in 2018). The
224 piezometric level decreased from -14.03 m in August 2016 to -15.88 m in October 2019, with a peak
225 at -13.70 in June 2018. In PZ59, CHCs were detected from -26 m to the bottom (-64.3 m) and
226 concentrations increased from 0.2 $\mu\text{g L}^{-1}$ at -26.7 m to 180 $\mu\text{g L}^{-1}$ at -67.3 m. The piezometric level
227 decreased from -2.7 m in August 2016 to -5.26 m in October 2019 with a rise at -3.8 in February
228 2018. In PZ61, CHCs were detected from -9 m to -23.2 m. In the first meters of the water column (-9
229 to -15.75 m), CHCs concentrations increased with depth, besides in September 2018 where
230 concentrations decreased along the entire water column. Then from -15.75 m to the bottom of the
231 well, CHCs concentrations decreased along depth from 12.5 $\mu\text{g L}^{-1}$ at -15.75 m to 3.9 $\mu\text{g L}^{-1}$ at -23.2 m.
232 The piezometric level decreased from -5 m in August 2016 to -7.7 m in October 2019, with a rise at -
233 5.4 m in February 2018.

234 **Figure 3 : Sum of CHCs and predominant CHC compounds concentrations along the water column and**
235 **variations of the piezometric level over time (2016-2019) for the wells PZ56, PZ59 and PZ61**

236 *3.3. Physico-chemical conditions in the wells*

237 Carbon dioxide, methane, ethane and ethene gases were analysed as they provide insight into the
238 final degradation products of CHCs. In PZ56 and PZ61, only CO_2 was detected at 1900 $\mu\text{mol.L}^{-1}$ (-

239 19.5 m) and $2000 \mu\text{mol.L}^{-1}$ (-15 m), respectively. In PZ59, at -40 m, CO_2 , methane and ethane were
240 found with 2700, 2.9 and $0.09 \mu\text{mol.L}^{-1}$ at -40 m and 2100, 2.1 and $0.04 \mu\text{mol.L}^{-1}$ at -60 m,
241 respectively.

242 The major inflows and redox potential (Eh) were recorded and analysed along the depth of the three
243 wells. The physico-chemical parameters were recorded during three campaigns (February 2017,
244 November 2017 and February 2018). Only November 2017 data are shown on **Figure 4**, as there were
245 no significant changes between the three campaigns. In PZ56, redox potential increased from 223 mV
246 -20 m to 237 mV at the bottom of the well. In PZ59, redox potential values decreased quickly with
247 increasing depth from 201 mV at -7 m to 84 mV at -30 m and then decreased until 69 mV at the
248 bottom of the well. In PZ61, redox potential values first slightly increased from 241 mV at -10 m to
249 262 mV at -19 m and then decreased until 122 mV at the bottom of the well.

250 **Figure 4: Depth-specific in-situ groundwater physico-chemistry in observation wells PZ56, PZ59 and PZ61.**

251 **Redox potential are presented for November 2017.**

252 ***3.4. Compound-specific isotope compositions***

253 Stable carbon-isotope ratios ($\delta^{13}\text{C}$) of CHC compounds were analysed in wells PZ49, PZ55, PZ56, PZ59
254 and PZ61 in 2017, 2019 and 2020, and in A18 in 2020. The method relies on differences in reaction
255 rates between molecules with light and heavy isotopes during transformation reactions, which
256 causes an enrichment of heavy isotopes (^{13}C) in the residual contaminant fraction. Results are
257 presented in Table 1. Considering the range of analytical uncertainties for these compounds ($\pm 0.5\text{‰}$),
258 most wells showed no variation in $\delta^{13}\text{C}$ -values throughout the duration of the monitoring survey.

259 In PZ49, only *cis*-1,2-DCE was detected with constant $\delta^{13}\text{C}$ values ranging within analytical uncertainty
260 ($\leq \pm 0.5\text{‰}$) from -29.8 to -29.6 ‰, between 2017 and 2020. *Cis*-1,2-DCE concentrations fluctuates
261 from 18.5 to $42 \mu\text{g L}^{-1}$ in 4 years. In PZ56, CHCs and their potential daughter products were detected
262 at the two sampled depths (-19.5 and -47 m). In 2019 at 19.5 m, higher concentrations accompanied

263 more depleted $\delta^{13}\text{C}$ values of PCE, TCE, *cis*-1,2-DCE, 1,1,1-TCA and 1,1-DCE compared to 2017. In
264 2019, relatively homogeneous concentrations along the water column (from -19.5 to -47 m) were
265 observed together with constant carbon-isotope ratios over depth. At -19.5 m, $\delta^{13}\text{C}$ values of PCE,
266 TCE, *cis*-1,2-DCE, 1,1,1-TCA and 1,1-DCE decreased between 2017 and 2019 (respectively -0.1, -2.1, -
267 0.3, -1.1, -0.5‰) (no analysis at -47 m in 2017). 1,1-DCE was not detected at -19.5 m in 2017. In 2020,
268 TCE and PCE were detected at -19.5 m and only TCE at -47 m, with enriched $\delta^{13}\text{C}$ values compared to
269 2017 and 2019.

270 In PZ59, only TCE and *cis*-1,2-DCE were detected at -40, -47 and -60 m. For TCE, the $\delta^{13}\text{C}$ was constant
271 between 2017 and 2019 along the water column at around -24‰ (Table 1). Then, $\delta^{13}\text{C}$ values
272 increased for TCE at -40 m (+1.8‰ between 2019 and 2020) and at -60 m (+0.9‰ between 2017 and
273 2020). For *cis*-1,2-DCE, $\delta^{13}\text{C}$ values were constant between 2017 and 2020 at -40, -47 and -60 m. Only
274 PCE was detected with an enriched $\delta^{13}\text{C}$ value (+2.2‰), accompanied by a strong concentration
275 decrease in PZ55 and a constant value -23.3‰ ($\pm 0.1\%$) in PZ61 between 2017 and 2019. In 2020,
276 CHC concentrations detected in A18 (*cis*-1,2-DCE at $3.6 \mu\text{g L}^{-1}$, and TCE at $0.92 \mu\text{g L}^{-1}$) were below the
277 quantification limit for isotopic analysis.

278 **Table 1: Stable carbon-isotope ratio $\delta^{13}\text{C}$ (in ‰ vs VPDB, $\pm 0.5\%$) and concentrations ($\mu\text{g L}^{-1}$) in the wells**
279 **PZ49, PZ55, PZ56, PZ59 and PZ61 at several depths in 2017, 2019 and 2020.**

280 4. Discussion

281 4.1. *Les Ansereuilles well field*

282 The CHC distribution in the Ansereuilles well field occurred as three separate sectors according to the
283 drawdown areas (Figure 1). The southwestern drawdown, centred around well A18, presented the
284 highest CHC concentrations, from $55.7 \mu\text{g L}^{-1}$ (PZ49) to $185.2 \mu\text{g L}^{-1}$ (PZ59), consisting of mostly *cis*-
285 1,2,-DCE and a small amount of TCE. As showed on Figure 2-a, wells PZ59 and A18 pump
286 groundwater from an industrial area. Two former industrial laundries were located upstream of the

287 wells (red targets on Figure 2-a). The Lille European Metropolis has identified one of these laundries
288 as a high CHC-polluted site. TCE and *cis*-1,2-DCE were found in the soil of this site (0.2 m deep, TCE:
289 $93 \mu\text{g g}^{-1}$, *cis*-1,2-DCE: $2.9 \mu\text{g g}^{-1}$) and high CHC concentrations occur in the directly underlying
290 groundwater (*cis*-1,2-DCE: $430 \mu\text{g L}^{-1}$, TCE: $43 \mu\text{g L}^{-1}$; (Arcadis, 2016)). In PZ59, the $\delta^{13}\text{C}$ values of *cis*-
291 1,2-DCE (-31.9 to -31.6‰) were depleted compared to TCE (-24.3 to -22.4‰). This isotopic pattern is
292 consistent with isotope enrichment ϵ_{TCE} factors being between -18.8 and -6.6‰ (-9.5 to -7.8‰ in
293 PZ59) for reductive dechlorination of TCE (Bloom et al., 2000; Sherwood Lollar et al., 2001; Slater et
294 al., 2001; Aeppli et al., 2009). This may indicate that *cis*-1,2-DCE is a degradation product of TCE
295 (Table 1). In PZ59 (Figure 3), CHCs were found along the water column below -26 m with increasing
296 concentrations for all compounds, suggesting CHC migration without degradation along the well.
297 However VC was found at low concentrations ($<1.2 \mu\text{g L}^{-1}$) and persistent along the water column
298 (Table SI-3). In addition, methane and ethane occurred at -40 and -60 m. The presence of VC, ethane
299 and methane, and the favourable physico-conditions in the well (reducing conditions, Eh <80 mV,
300 Figure 4) suggest reductive dechlorination of a small amount of *cis*-1,2-DCE until methane. But the
301 highly depleted isotopic signatures of *cis*-1,2-DCE from -31.9 to -31.6‰ also indicate that this
302 compound is accumulating and further degradation to VC concerned only a small amount of *cis*-1,2-
303 DCE (Table 2). Furthermore, for TCE, decreasing concentrations at -40 m between 2017 and 2020 (22
304 to $8.6 \mu\text{g L}^{-1}$) and the enrichment of isotopic values in 2020 compared to 2019 (-24.2 to -22.4‰,
305 Table 1) could be the beginning of an active biodegradation as a result of the excavation work of
306 2019 at the polluted site farther upstream (40,000 tonnes of polluted soil excavated). The slightly
307 enriched (compared to PZ59) and steady isotopic signatures of *cis*-1,2-DCE in PZ49 since 2017 suggest
308 the same degradation process in this well as in PZ59 located further upstream. In the well A18
309 located downstream, only very small amounts of CHC have been detected in 2020, compared to
310 relatively high concentrations last measured in 2017, suggesting that the degradation of CHCs is
311 actively ongoing and almost complete within the well. Due to the successful upstream remediation of
312 the source, no further CHCs should be reaching this well.

313 The southern drawdown around well A21 was characterized by major PCE contents ($29 \mu\text{g L}^{-1}$ in PZ55
314 and $8.8 \mu\text{g L}^{-1}$ in A21). Both wells are also located downstream of several industrial laundries, textile
315 factories and dyeing industries (red and blue targets, Figure 2-a). While no PCE-degradation products
316 were found in PZ55, TCE and DCE were detected at low concentrations in A21 (respectively 0.6 and
317 $0.12 \mu\text{g L}^{-1}$). The decreasing concentrations of PCE (29 to $5.1 \mu\text{g L}^{-1}$, Table 1) and the enriched $\delta^{13}\text{C}$
318 values (-28.1 to -25.9% , Table 1) between 2017 and 2020 in PZ55 indicated biodegradation under
319 reducing conditions in this well, resulting in the DCE found in downstream well A21 (Table 1). The
320 assumption of biodegradation reactions is only valid if the two groundwater layers where sampling
321 took place are directly connected. Another hypothesis for the differences in values observed in well
322 Pz55 for the two different depth intervals that are 14 m apart, might be that there are two different
323 sources of PCE contamination.

324 Finally, the northern drawdown around well A16 was characterized by a mix of different CHC
325 compounds at concentrations ranging from $24.5 \mu\text{g L}^{-1}$ (A12) to $1.4 \mu\text{g L}^{-1}$ (A14), including primary
326 products (PCE, TCE, 1,1,1-TCA) and all potential degradation products in variable proportions (*cis*-1,2-
327 DCE, *trans*-1,2-DCE, 1,1-DCE, 1,2-DCE, 1,1-DCA and VC). Well PZ56 was an exception here because of
328 its high CHC concentration ($150 \mu\text{g L}^{-1}$). A former industrial laundry site, potentially the source of this
329 CHC pollution, lies upstream from the well (red target, Figure 2-a). In PZ56 (Figure 3), CHC
330 concentrations decreased along the water column below -19.5 m with, suggesting migration and
331 dilution of the CHCs in the well. VC was mostly below the quantification limit ($0.2 \mu\text{g L}^{-1}$) in the water
332 column (Table SI-3). The isotopic signatures of *cis*-1,2-DCE (-23.2 to -22.9% , Table 1) compared to
333 TCE (-22.6 to -17.7%) also indicate that *cis*-1,2-DCE may be a degradation product of TCE in PZ56.
334 However, the depleted isotopic signatures of PCE (-24.9 to -23.9%) compared to *cis*-1,2-DCE and TCE
335 either suggest that these compounds are not degradation products of PCE, or that the dechlorination
336 reaction of TCE and *cis*-1,2-DCE is ongoing and isotopic enrichment even exceeds the isotopic
337 signature of PCE. This latter hypothesis is supported by Rayleigh enrichment factors for reductive
338 dehalogenation that are smaller for PCE ($\epsilon_{\text{PCE}} -3.6$ to -5.6% ; (Slater et al., 2001; Wiegert et al., 2013;

339 Badin et al., 2014)), and increase for each of the consecutive metabolites (-13.8, -20.4, -22.4 for TCE,
340 *cis*-1,2-DCE and VC, respectively, (Slater et al., 2001)). The depleted isotopic values of 1,1-DCA (-22.1
341 to -21.6‰, Table 1) compared to TCA (-20.2 and -21.3‰ at -19.5 m) indicate that 1,1-DCA is a
342 possible degradation product of TCA. However, no further interpretations are possible, as reported
343 enrichment factors for biodegradation of 1,1,1-TCA to 1,1-DCA can be small (-1.8‰, (Sherwood Lollar
344 et al., 2001)) or quite large (up to -14‰, (Broholm et al., 2014)). Considering the other compounds,
345 an inversion of the TCA isotopic signature at -47 m is noticed (TCA -23‰ at -47 m and enriched to -
346 21.3‰ at -19.5 m in 2019), compared to TCE that has an opposite behaviour (highest value at -47 m,
347 -20.5‰, and depleted at -19.5 m, -22.6‰, in 2019). This inversion suggests potentially different TCA
348 sources at these two depths. A surprising result is the isotopic signature of 1,1-DCE (-18.7 and -
349 17.5‰). These heavy $\delta^{13}\text{C}$ values, compared with the potential primary CHC products (*cis*-1,2-DCE:
350 from 23.2 to 22.9‰, TCE: from -22.6 to -20.5‰, TCA: from -21.3 to -20.2‰), do not allow concluding
351 about a formation of 1,1-DCE by TCE anaerobic biodegradation, nor about an abiotically produced
352 metabolite of 1,1,1-TCA by dehydrochlorination. In addition, the presence of 1,1-DCE as a primary
353 product cannot be excluded due to its use in the plastics industry. In general, the isotopic signature
354 of manufactured solvents is more depleted (<-20‰) (Slater et al., 2001) and the observed $\delta^{13}\text{C}$ value
355 of 1,1-DCE might also be an indicator for ongoing *in-situ* biodegradation in this well. In a study by
356 Hunkeler et al. (2002), 1,1-DCE transformation was very fast compared to other compounds. Isotope-
357 enrichment factors for biodegradation of this compound are between -5.8‰ and -7.3‰ (Hunkeler et
358 al., 2002; Lee et al., 2007), supporting the idea of 1,1-DCE biodegradation in this well. However, as
359 the initial source values are unknown, this shows that the isotope approach has its limitations for an
360 intermediate compound that is simultaneously formed and degraded. With the limited number of
361 monitoring wells and data currently available, we cannot conclude whether TCE was added from
362 additional sources or derives from the dehalogenation of PCE. 1,1-DCE, too, may have been added
363 from another source, or may stem from the dehydrochlorination of 1,1,1-TCA (Table 1).

364 In the Ansereuilles well field, in addition of the importance of the pollution sources, the geology
365 further influences the CHC concentrations in groundwater. The clay deposits at the top of the
366 northern wells (A13 to A15) confine the groundwater, causing reducing conditions. As shown on
367 Figure 5, the wells under reducing conditions (redox potentials from 163 mV in A15 to 236 mV in
368 A13, according to Sigg (2000)) had the lowest CHC concentrations (from 1.4 in A14 to 12.3 $\mu\text{g L}^{-1}$ in
369 A13) with low detection frequency. These low CHC concentrations are consistent with low nitrate
370 concentrations (from below the detection limit in A14 to 8.6 mg L^{-1}) which are an evidence of
371 denitrification processes occurring under reducing conditions, while the wells are located in an
372 agricultural area where high nitrate concentrations can be found in the groundwater under oxidizing
373 conditions (for example, 20-40 mg L^{-1} in A18, Figure 5). On the contrary, the wells under oxidizing
374 conditions (A10, A11, A18 and PZ56, redox potentials from 315 mV in A18 to 436 mV in PZ56) had the
375 highest CHC concentrations with high detection frequency and high nitrate concentrations. The well
376 A12 is located in a transition zone and present moderately reducing condition (redox potential: 300
377 mV), low CHC concentrations with high detection frequency and high nitrate concentrations. Finally,
378 the well PZ59 that is near a major source of TCE presents high CHC concentrations under reducing
379 conditions along with low nitrate concentration.

380 **Figure 5: Redox potential (mV), nitrates (mg L^{-1}) and total CHC concentration ($\mu\text{g L}^{-1}$) according to location**
381 **(Lambert 93 X coordinate) in the Ansereuilles well field**

382 ***4.2. Emmerin, Houplin-Ancoisne and Seclin well fields***

383 The Emmerin well field was separated into two different areas. The first one contains wells E7, E5
384 and PZ61, with low CHC concentrations ranging from 1.7 $\mu\text{g L}^{-1}$ (E7) to 15.8 $\mu\text{g L}^{-1}$ (PZ61). PCE was the
385 most common pollutant in the wells, with lesser amounts of TCA and 1,1-DCE. The second area is
386 around the far western well E8, where TCA dominates followed by TCE, PCE and their degradation
387 products as *cis*-1,2-DCE, 11-DCE and 1,1-DCA. In PZ61, CHC concentrations decreased downward
388 (data in Supporting Information, Table SI-3). The steady isotopic signature of PCE between 2017 and

389 2020 (-23.3 and -23.4‰) suggested that this compound was not further degraded in the well. The
390 isotopic signature of PCE in PZ61 can be compared to initial pure phase $\delta^{13}\text{C}$ values of PCE ranging
391 from -37.2 to -23.3‰ (van Warmerdam et al., 1995). Being at the upper end of reported values
392 either Pz61 represents source values that have never been subject to biodegradation, or as we don't
393 know the initial source of this contamination, we could also assume lower initial values that have
394 been enriched over time, suggesting degradation further upstream before arrival in the well (Table
395 2).

396 **Table 2: Overview of CHCs found in the well fields, their potential origins and degradation processes based**
397 **on the isotopic signatures from 2017 to 2020**

398 The Houplin-Ancoisne and Seclin well fields were the least polluted in CHC. We found a mix of CHCs
399 with low concentrations ranging from 0.2 (S1) to 8.8 $\mu\text{g L}^{-1}$ (H7). Wells PZ51, H7, H4 and H1 were
400 polluted mainly by PCE, TCE and TCA, while only TCE was detected in S1. The low CHCs
401 concentrations can be explained by the minor presence of industrial activities in this area (Figure 1).
402 Then, oxidizing conditions prevail in these well fields, the groundwaters provide conditions for
403 aerobic biodegradation, except for H11 (dissolved oxygen <1 mg/L) where no CHCs were found
404 (Figure 2-a). The absence of TCE- and PCE-degradation products such as *cis*-1,2-DCE suggested that
405 reductive dechlorination does not occur, which is consistent with the observed groundwater
406 geochemistry of these wells. 1,1-DCE could be a primary product from the plastics industry as in
407 PZ56, or a product from previous dehydrochlorination of TCA.

408 ***4.3. Consequences for the further pumping operations***

409 TCE, PCE and VC have regulation standards in the French legislation for their presence in drinking
410 water (RF, 2007). In the studied well fields, the sum of TCE and PCE exceeds the threshold
411 concentration of 10 $\mu\text{g L}^{-1}$ in many wells (A12, A16, A18, A21, E5, E7, H7, PZ56, PZ59, and PZ61). VC
412 exceeds the concentration limit (0.5 $\mu\text{g L}^{-1}$) in only two wells (A18 and PZ59) but is present and
413 persistent in most wells. Our study showed that CHC degradation would be a long process in the well
414 fields, even if this occurs in some part of the Chalk aquifer. In addition, the total amount of CHCs in

415 the surrounding soils probably can never been estimated, preventing a prediction of the time needed
416 for natural attenuation of this complex and diffuse—but also with hot spots—pollution. Currently,
417 drinking-water production uses dilution to reach the regulation CHC standards, but the lowering
418 water table makes this solution unsustainable. In order to continue producing drinking water from
419 the existing well fields, the operators need alternative solutions to reach the regulation CHC
420 standards.

421 The simplest solution would seem to be to adapt the pumping depth in the well. However, our study
422 of CHC concentrations in the PZ56 water column showed that TCE + PCE concentrations decrease
423 with depth, whereas VC shows an inverse trend (Table SI-3). Positioning of the pump is therefore
424 tricky and becomes impractical when the groundwater level lowers due to drought periods, as is
425 already frequently the case in this region. Then, an increase of the piezometric level leads to an
426 increase of CHC concentrations in the wells (for example, in the entire water column of PZ61 and in
427 shallower parts of PZ56 and PZ59 (Table SI-4)). The rise of the piezometric level induced by natural
428 recharge and decrease or stopping of pumping mobilize CHC sources present in surface. In order to
429 limit CHC contamination of the groundwater, as second option the water operators should adopt an
430 individual management of pumping wells in order to maintain the water table in the chalk and not in
431 the upper polluted layers. A third option is to create a protection front by discharging groundwater
432 from selected wells to protect the others from CHC plumes. These solutions require a sharp
433 identification in three dimensions of CHC fluxes in groundwater, but above all it involves wasting a
434 significant amount of water in a context of scarcity. A fourth solution would be to treat the water
435 with methods such as reverse osmosis, combinations of oxidants (e.g. ozone and UV), or
436 volatilization with a waterfall (Love Jr and Eilers, 1982; Foster et al., 1991). Overall, the better
437 understanding of the CHC behaviours described in this paper and the application of some of these
438 recommendations should undoubtedly ameliorate significantly the exploitation of this strategic
439 resource for the Lille Metropolis

440 5. Conclusions

441 Our study contributes to a better knowledge of CHC dynamics in a large strategic well field that
442 supplies drinking water to the Lille European Metropolis. The distribution and concentrations of CHCs
443 in the study area depends on two main factors. The first one is the past and current industrial
444 activities in the area, causing broad CHC plumes in three dimensions that are further accentuated by
445 pumping. The second one is the confined/unconfined nature of groundwater, causing reductive
446 and/or oxidizing conditions that are favourable, or not, for efficient CHC degradation.

447 The strong *cis*-1,2-DCE pollution in the southwest of the Les Ansereuilles well field is due to the
448 release of TCE—and its degradation by reductive dechlorination—from a former industrial laundry
449 upstream of the studied wells. In the same well field, other wells are affected to a lesser extent by
450 the release of PCE from several other industrial laundries, textile factories and dyeing industries,
451 which again was partly degraded by reductive dechlorination. In the northern area of the well field,
452 PCE, TCA, TCE and 1,1-DCE were found as primary products and *cis*-1,2-DCE as a degradation product
453 of TCE by anaerobic biodegradation.

454 The other well fields (Houplin-Ancoisne, Seclin and Emmerin) are less impacted by CHC pollution, and
455 no CHC degradation occurs in the wells as shown by the absence of degradation products, aerobic
456 conditions, and isotopic signature of PCE.

457 The stratification of CHCs along the well-water columns, their steady concentrations over time
458 caused by the large amount of available CHCs, and the little degradation occurring in the wells, all
459 indicate that producing drinking water with a good quality from the well fields will be a major future
460 challenge for water operators, as it is already. As observed in well PZ56, redox conditions and the
461 degree of reductive dechlorination can vary over small distances, showing the importance of high-
462 resolution sampling to demonstrate the attenuation of CHCs. Isotopic investigations combined with
463 long-term monitoring of concentrations, taking into account spatial and in-depth heterogeneity, have
464 proven to be an adequate methodology for identifying further CHC plumes and potential polluters

465 and demonstrating ongoing biodegradation activity within these plumes. The continuation of this
466 monitoring strategy would also make it possible to control the efficiency of the remediation
467 treatment that was recently undertaken.

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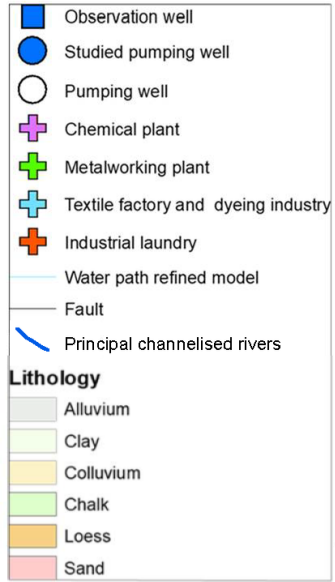
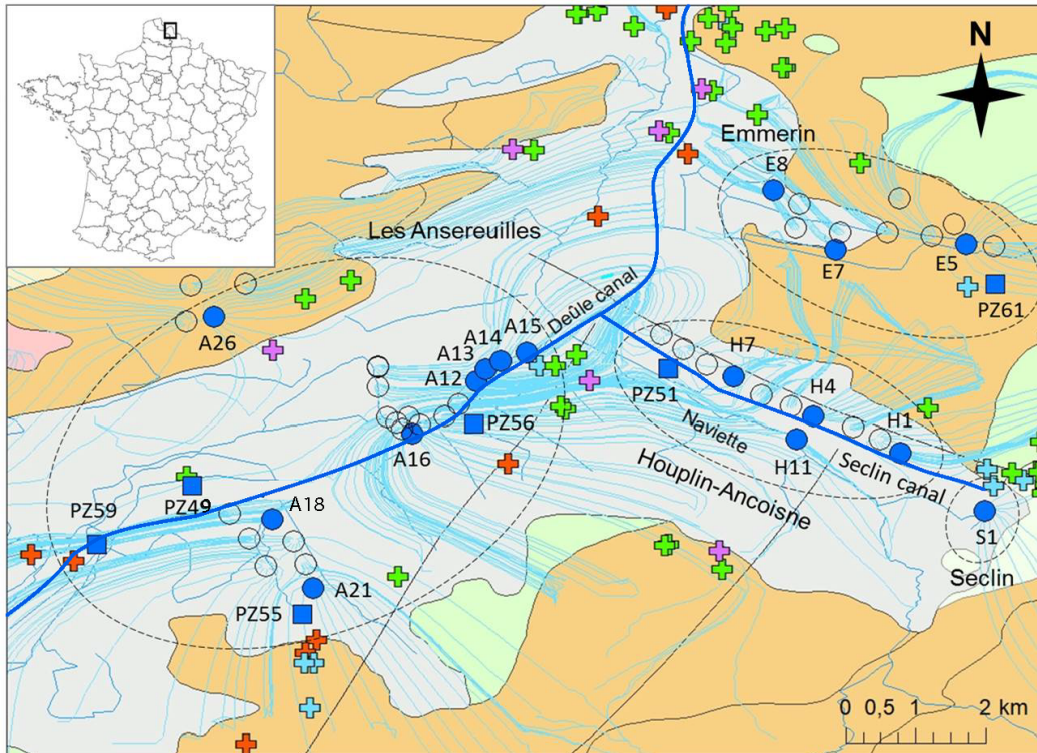
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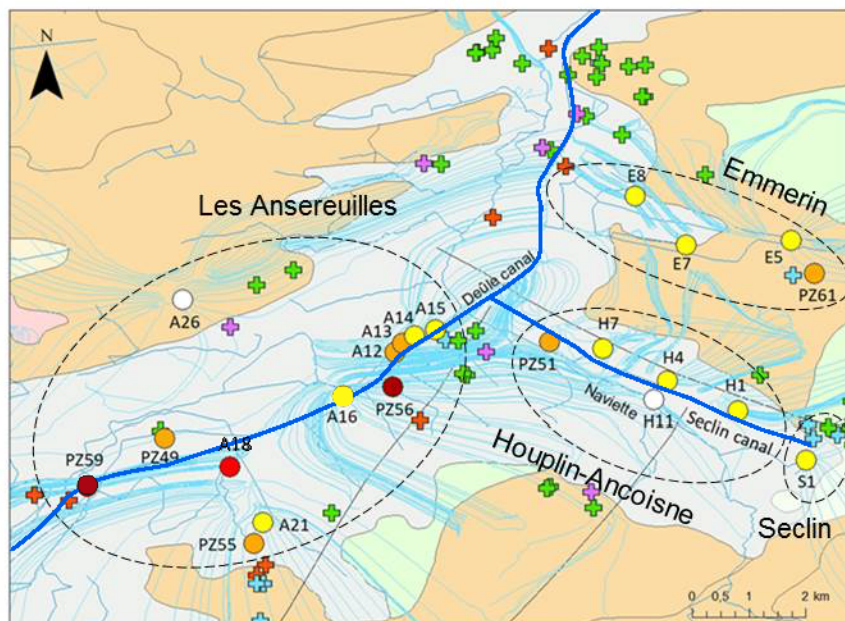
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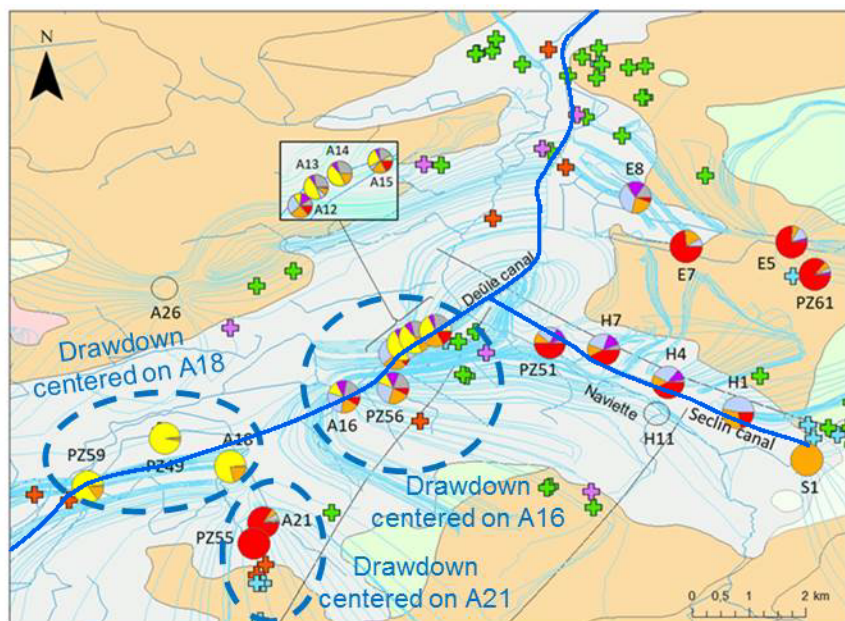
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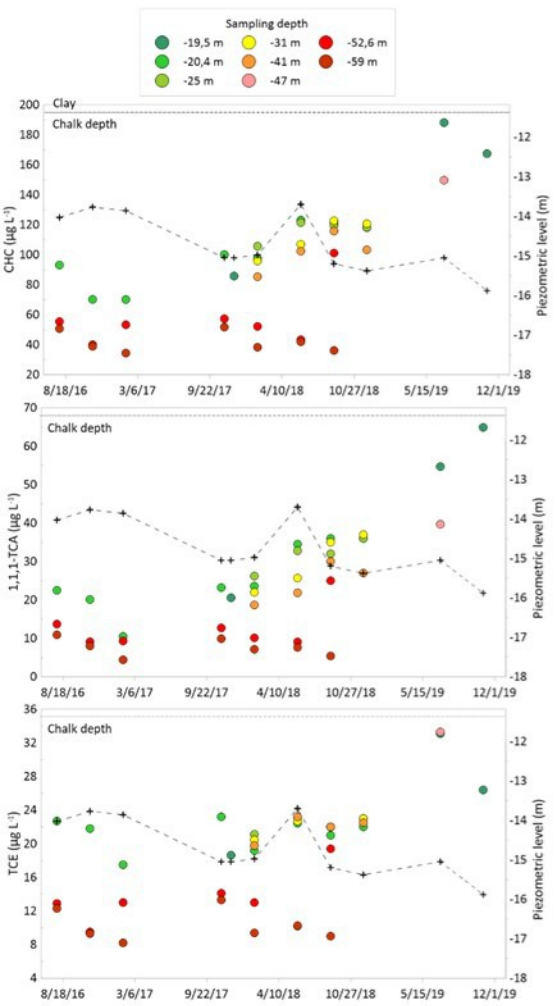
(a)



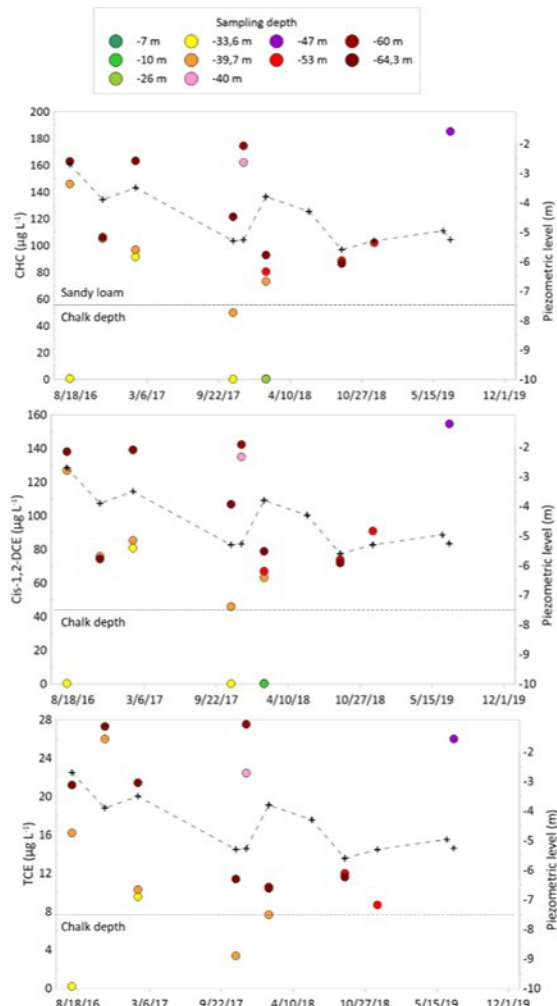
(b)



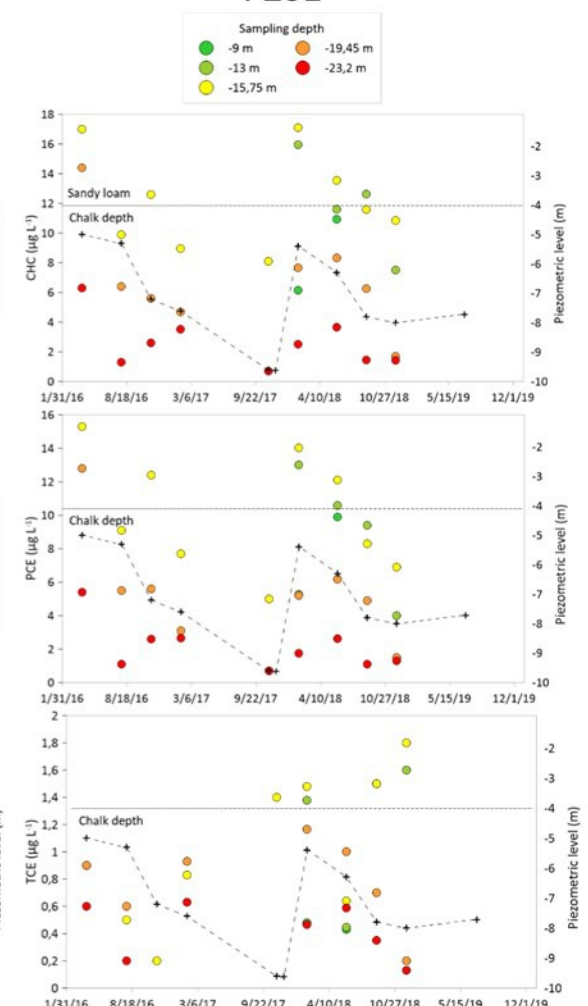
PZ56



PZ59

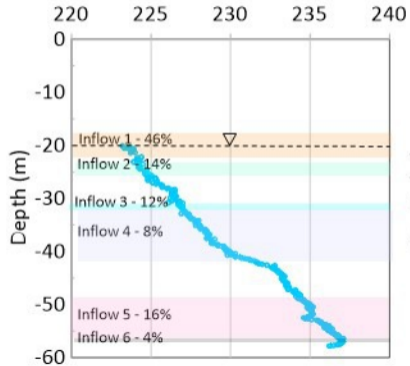


PZ61



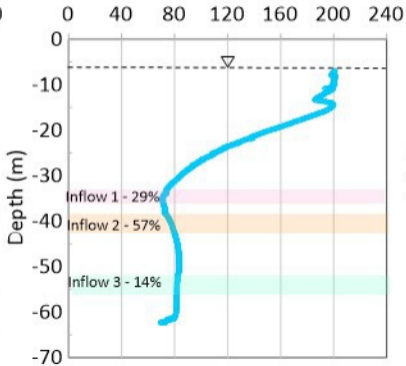
PZ56

Eh (mV)



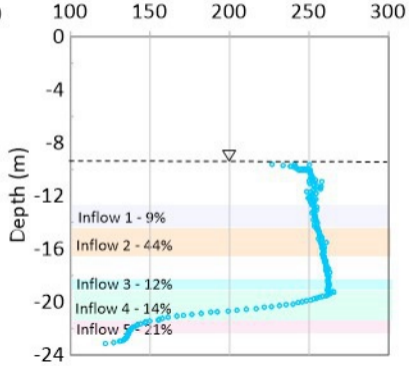
PZ59

Eh (mV)



PZ61

Eh (mV)



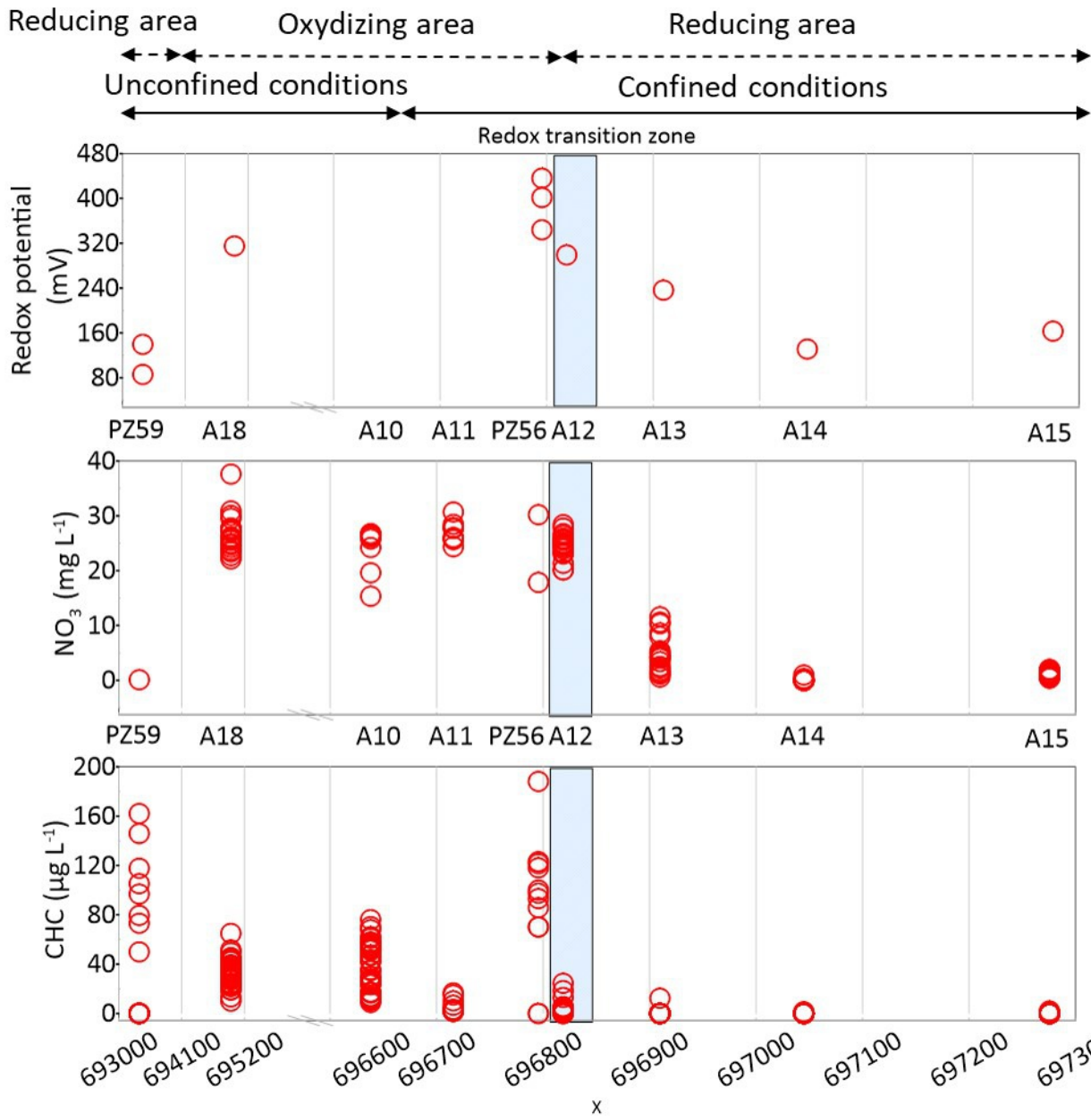


Table 1: Stable carbon-isotope ratio $\delta^{13}\text{C}$ (in ‰ vs VPDB, $\pm 0.5\text{‰}$) and concentrations ($\mu\text{g L}^{-1}$) in the wells PZ49, PZ55, PZ56, PZ59 and PZ61 at several depths in 2017, 2019 and 2020.

Well	Depth (m)	Year of sampling		1,1-DCE	1,1-DCA	Cis-1,2-DCE	1,1,1-TCA	TCE	PCE
PZ49	-52	2017	$\delta^{13}\text{C}$ (‰)	-	-	-29.8	-	-	-
			Concentration ($\mu\text{g L}^{-1}$)	-	-	18.5	-	-	-
	-47	2019	$\delta^{13}\text{C}$ (‰)	-	-	-29.7	-	-	-
			Concentration ($\mu\text{g L}^{-1}$)	-	-	52.8	-	-	-
		2020	$\delta^{13}\text{C}$ (‰)	-	-	-29.6	-	-	-
			Concentration ($\mu\text{g L}^{-1}$)	-	-	42.0	-	-	-
PZ55	-45	2017	$\delta^{13}\text{C}$ (‰)	-	-	-	-	-	-28.1
			Concentration ($\mu\text{g L}^{-1}$)	-	-	-	-	-	29.0
	-31	2019	$\delta^{13}\text{C}$ (‰)	-	-	-	-	-	-25.9
			Concentration ($\mu\text{g L}^{-1}$)	-	-	-	-	-	5.1
		2020	$\delta^{13}\text{C}$ (‰)	-	-	-	-	-	-26.5
			Concentration ($\mu\text{g L}^{-1}$)	-	-	-	-	6.8	
PZ56	-19,5	2017	$\delta^{13}\text{C}$ (‰)	-	-21.6	-22.9	-20.2	-20.5	-24.8
			Concentration ($\mu\text{g L}^{-1}$)	-	15.2	12.8	21	18.6	7.3
		2019	$\delta^{13}\text{C}$ (‰)	-18.7	-22.1	-23.2	-21.3	-22.6	-24.9
			Concentration ($\mu\text{g L}^{-1}$)	30.5	33.3	23.2	54.7	33.1	13.0
	2020	$\delta^{13}\text{C}$ (‰)	-	-	-	-	-19.4	-23.9	
		Concentration ($\mu\text{g L}^{-1}$)	-	-	-	-	17.1	6.5	
	-47	2019	$\delta^{13}\text{C}$ (‰)	-17.5	-22.1	-23.1	-23.0	-20.5	-24.4
			Concentration ($\mu\text{g L}^{-1}$)	19.9	27.8	17.4	39.7	33.3	11.2
2020		$\delta^{13}\text{C}$ (‰)	-	-	-	-	-17.7	-	
		Concentration ($\mu\text{g L}^{-1}$)	-	-	-	-	10.4	-	
PZ59	-40	2017	$\delta^{13}\text{C}$ (‰)	-	-	-31.8	-	-23.8	-
			Concentration ($\mu\text{g L}^{-1}$)	-	-	135.0	-	22.0	-
		2019	$\delta^{13}\text{C}$ (‰)	-	-	-31.6	-	-24.2	-
			Concentration ($\mu\text{g L}^{-1}$)	-	-	104.7	-	10.1	-
	2020	$\delta^{13}\text{C}$ (‰)	-	-	-31.8	-	-22.4	-	
		Concentration ($\mu\text{g L}^{-1}$)	-	-	102.0	-	8.6	-	
	-47	2019	$\delta^{13}\text{C}$ (‰)	-	-	-31.8	-	-24.3	-
			Concentration ($\mu\text{g L}^{-1}$)	-	-	154.7	-	25.9	-
-60	2017	$\delta^{13}\text{C}$ (‰)	-	-	-31.7	-	-23.9	-	
		Concentration ($\mu\text{g L}^{-1}$)	-	-	142.0	-	28.0	-	
	2020	$\delta^{13}\text{C}$ (‰)	-	-	-31.9	-	-23.0	-	
		Concentration ($\mu\text{g L}^{-1}$)	-	-	136	-	19.6	-	
PZ61	-15	2017	$\delta^{13}\text{C}$ (‰)	-	-	-	-	-	-23.3
			Concentration ($\mu\text{g L}^{-1}$)	-	-	-	-	-	8.9
		2019	$\delta^{13}\text{C}$ (‰)	-	-	-	-	-	-23.4
			Concentration ($\mu\text{g L}^{-1}$)	-	-	-	-	-	13.6
		2020	$\delta^{13}\text{C}$ (‰)	-	-	-	-	-	-23.3
Concentration ($\mu\text{g L}^{-1}$)	-		-	-	-	-	12.2		
A18	-41	2020	$\delta^{13}\text{C}$ (‰)	-	-	-	-	-	-
			Concentration ($\mu\text{g L}^{-1}$)	-	-	3.6	0.9	-	-

Table 2: Overview of CHCs found in the well fields, their potential origins and degradation processes based on the isotopic signatures from 2017 to 2020

Well	CHC	Concentrations ($\mu\text{g L}^{-1}$)	Potential origin	$\delta^{13}\text{C}$ (‰)	Suspected degradation process
PZ59	TCE	9-28	Upstream industrial laundry	-24.2 to -22.4	Reductive dechlorination (start in 2020) TCE \rightarrow cDCE
	cDCE	102-155	Reductive dechlorination of TCE	-31.9 to -31.6	Reductive dechlorination (limited, accumulation of cDCE) cDCE \rightarrow VC \rightarrow CH ₄
PZ49	cDCE	19-42	PZ59 ? Reductive dechlorination of TCE	-29.8 to -29.6	No further degradation
PZ55	PCE	5-29	Upstream industrial sites?	-28.1 to -25.9	Reductive dechlorination PCE \rightarrow cDCE
PZ56	1,1-DCE	20-31	From additional source or reductive dechlorination of cDCE or dehydrochlorination of TCA	-18.7 to -17.5	No process evidenced
	1,1-DCA	15-33	Reductive dechlorination of TCA	-22.6 to -22.1	No process evidenced
	cDCE	13-23	Reductive dechlorination of TCE	-23.1 to -22.9	Reductive dechlorination? cDCE \rightarrow 1,1-DCE
	TCA	21-55	No potential source identified	-23.0 to -20.2	Reductive dechlorination TCA \rightarrow 1,1-DCA
	TCE	17-33	From additional source or reductive dechlorination of PCE	-22.6 to -20.5	Reductive dechlorination TCE \rightarrow cDCE
	PCE	7-13	No potential source identified	-24.9 to -24.4	Reductive dechlorination PCE \rightarrow TCE
PZ61	PCE	9-14	No source identified	-23.4 to -23.3	No degradation

