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Assessing aquitard integrity in a complex aquifer – aquitard system contaminated by chlorinated hydrocarbons

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Abstract

This study investigates for the first time the integrity of multiple stacked aquitards with different degrees of reactivity to contaminant degradation. Aquitard integrity was assessed in a contaminated, multi-layered, alluvial aquifer-aquitard system (Ferrara, northern Italy). The system was contaminated by mixed organic contaminants of industrial origin (mostly chlorinated ethenes) that were illegally disposed in an urban dump four to five decades ago. High spatial resolution profiles of hydraulic head, geochemistry and chlorinated hydrocarbon concentrations were determined through the multi-layered system via discrete interval sampling of continuous cores and multilevel groundwater sampling, at three locations aligned along a transect adjacent to the buried waste to a maximum depth of 53 meters below the water table. The profiles revealed that the two shallow aquitards had low integrity with respect to impeding downward migration of dense non-aqueous phase liquid (DNAPL), and provided little protection to the underlying aquifers against DNAPL contamination due to preferential pathways through imperceptible fractures and/or permeable micro-beds. However, both aquitards inhibited downward DNAPL migration to some extent due to DNAPL retention along its flow paths and accumulation at lower permeability interfaces, with

decreasing peak concentrations at the top of successively deeper aquitard units. Moreover, both aquitards enhanced contaminant biodegradation due to the occurrence of organic rich sub-layers, influencing the contaminant plume composition, mobility and fate in the underlying and overlying aquifers. The deepest aquitard showed evidence of DNAPL accumulation at the top and slow diffusion-dominated transport consistent with 40 years of transport, suggesting higher integrity compared to the two shallower aquitards. However, the occurrence of micro-fractures and/or discontinuities in the aquitard upgradient under the dump (source) is the most likely explanation for contamination of the deepest aquifer. Analytical 1-D simulations of the diffusion profiles in the deepest aquitard revealed that DNAPL contamination down to the top of this aquitard occurred with minimal delay after DNAPL waste disposal began. The results highlight the necessity of high-resolution vertical profiling for assessing the presence of imperceptible features relevant to DNAPL migration and integrity of individual aquitards affecting organic contaminant source zone mass and phase distributions over decades.

KEY WORDS: aquitard integrity, chlorinated ethenes, DNAPL, source zone age and evolution, diffusion mass transfer, fluvial sediments

1 Introduction

The integrity of an aquitard refers to its capability to protect an underlying aquifer against contamination (Cherry et al. 2006, Parker et al. 2004). Until a few decades ago it was assumed that aquitards generally prevent contamination of underlying confined aquifers from surface contamination sources (e.g. Ponzini et al. 1989, U.S. EPA 1987). However, contaminant occurrences in confined aquifers were observed since the 1990's, often involving chlorinated hydrocarbons as dense non-aqueous phase liquids (DNAPL) in the source zones (e.g. PPG Industries 1995, Chapuis 2013, Pedretti et al. 2013, Fjordbøge et al. 2017). This contradicts the assumption that low permeability sediments with hydraulic conductivities less than 10^{-7} cm/s (based on USEPA guidance for compacted clay landfill liners, e.g. Green et al. 1981) generally prevent the migration of contaminants into underlying aquifers. Research at industrial waste disposal sites in the

1990's suggested that deep DNAPL migration can be attributed to pre-existing fractures in natural clay-rich sediments that are imperceptible in bulk hydraulic conductivity testing (Cherry et al. 2006, Wills et al. 1992).

Mathematical modeling and laboratory studies (Jørgensen et al. 1998, O'Hara et al. 2000, Kueper and McWhorter 1991, McWhorter and Kueper 1996) demonstrated that DNAPLs have an exceptional propensity to enter and migrate through very small fractures, even those with hydraulic apertures smaller than 10 μm . These observations were confirmed by several field studies. PPG Industries (1995) reported the migration of tetrachlorethylene (PCE) and trichlorethylene (TCE) DNAPLs through a 50 m thick alluvial clay aquitard to the underlying aquifer at a chemical manufacturing facility, due to root holes and fractures acting as preferential pathways for DNAPL migration. Chapuis (2013) observed high concentrations of chlorinated hydrocarbons in a confined aquifer overlain by a glacial till aquitard, where DNAPL migration through micro-fractures was the most likely explanation. Fjordbøge et al. (2017) characterized a clay till aquitard underlying a PCE and TCE DNAPL source zone, where vertical migration of DNAPL occurred through fractures in a shallow oxidized zone and to a lesser extent through a less fractured reduced zone, reaching the underlying confined limestone aquifer. Beside fractures, unlithified clay-rich aquitards in alluvial settings often enclose thin sand intercalations that can create a stair-step pattern of preferential flow paths for DNAPL flow (e.g. Morrison et al. 1998, Parker 1996). Pedretti et al. (2013) observed lithologic heterogeneities in a shallow clay aquitard while investigating the distribution of chlorinated hydrocarbon contamination (mainly PCE and TCE) at the regional scale in an alluvial multi aquifer-aquitard system, where contaminants breached the clay aquitard at several sites in the region, reaching the underlying confined aquifer. The literature also reports some aquitards capable of preventing DNAPL penetration or allow only partial migration. Morrison et al. (1998) reported partial PCE DNAPL penetration in a thin surficial clayey aquitard at a site where DNAPL was released under controlled conditions. Vertical microfractures allowed DNAPL migration through an upper part, whereas the lower part provided resistance to DNAPL flow. Parker et al. (2004) showed TCE DNAPL accumulation at the bottom of a sandy aquifer overlying a thick aquitard at an industrial property. Diffusion profiles of dissolved contaminants

were observed in the upper part of the aquitard, but with no evidence of DNAPL penetration attributed to lack of fractures given the plasticity of this lacustrine sediment and lack of post-deposition exposure. Adamson et al. (2015a) and Adamson et al. (2015b) advanced the use of diffusion transport contaminant concentration profiles in low permeability clay-rich sediments as a means to assess contaminant source zone history after Parker et al. (1994) and Parker et al. (2004). The source history model proposed by Adamson et al. (2015b) was demonstrated at two industrial sites with chlorinated ethenes and ethanes, showing that after decades most of the contaminant mass occurred in the low permeability aquitard layers due to diffusion enhanced by sorption, with high aquitard integrity with respect to DNAPL penetration, but also how diffusive mass transfer alters the location and phase of contamination. Notwithstanding the existing literature, the parameters that control the integrity of clayey aquitards are not yet clear and often appear to be strongly site-specific requiring careful investigation methods including collection and sampling of minimally disturbed continuous cores. Thus, there is a need for improving the scientific knowledge with respect to different DNAPL source conditions and geologic settings for assessing aquitard integrity. The objective of this paper is to evaluate the integrity of distinct silt and clay-rich, non-indurated (unlithified) aquitards of fluvial origin with different degrees of reactivity to contaminant biodegradation. To the best of our knowledge, the assessment of the integrity of multiple stacked reactive aquitards was never reported in the literature. For this purpose, a site was selected where a 60-m thick multi-layered aquifer-aquitard system of alluvial origin was contaminated by chlorinated aliphatic hydrocarbons, predominantly with chloroethenes, originating from a known mixed DNAPL source. High-resolution hydraulic head, geochemistry and chlorinated hydrocarbon concentration profiles were determined using continuous cores along a transverse cross-section (i.e. transect) adjacent to the contamination source. The investigated multi-layered aquifer-aquitard configuration is representative of many other alluvial systems (e.g. Blum and Törnqvist 2000) so the insights as well as the methods applied are useful for assessment of non-indurated aquitard integrity at other sites.

103

104 **2 Site Description**

105 The selected “Caretti site” is located 1 km east of the historical center of Ferrara in the eastern sector of the
106 Padana plain, about 4 km south of the Po river and covers an area of about 1 km² (Fig. 1). The
107 hydrostratigraphy exhibits an alternation of fine to coarse grained sands of higher hydraulic conductivity
108 (aquifers) and silty–clayey layers of lower hydraulic conductivity (aquitards), to a depth of around 200 m
109 below ground surface (m bgs) (Molinari et al. 2007). Three aquifers are in the upper 60 m bgs indicated as
110 A0, Upper A1, and Lower A1 (Regione Emilia-Romagna and ENI-AGIP 1998), whereby each of them is
111 overlain by a non-indurated aquitard named after the underlying aquifer: Q0, Upper Q1 and Lower Q1 (Fig.
112 2). The A0 aquifer consists of scattered sandy lenses intermingled with fine-grained deposits (Amorosi and
113 Colalongo 2005); the Upper A1 aquifer is characterized by low spatial continuity (i.e. low amalgamation
114 between sandy lenses, that form sandy bodies extended for 10 to 100 m²), whereas the Lower A1 aquifer is
115 a regionally extensive sandy body (on the scale of 10000 m²). The main groundwater flow direction at the
116 Caretti site is NNE in the A0 aquifer, NW in the Upper A1 aquifer and E in the Lower A1 (Nijenhuis et al,
117 2013; Filippini et al. 2016). Two main sources contribute to the recharge of the multi-aquifer system: The
118 Po river (lateral recharge) and the local rainfall (vertical recharge) (Rapti-Caputo and Martinelli 2009). The
119 averaged contribution of vertical recharge decreases from 75% in the A0 down to 26% in the Lower A1
120 whereas the lateral recharge increases with increasing aquifer depth from 25% in the A0 up to 74% in the
121 Lower A1 (Filippini et al. 2015). In the Ferrara region, the confined Lower A1 aquifer is exploited at several
122 locations for irrigation or drinking water supply and the overlying Lower Q1 aquitard is considered capable
123 to protect the quality of this aquifer, as reported in several technical documents (not published). Previous
124 investigations at the Caretti site (Gargini et al. 2011) revealed that the aquifers A0 and Upper A1 are
125 contaminated by chlorinated hydrocarbons, originating from urban waste and chlorinated pitches
126 containing a mixture of chlorinated ethenes and ethanes that were deposited primarily as DNAPL in a clay
127 pit (known as Southern Dump) between the late 1950s and 1970s (Fig. 1). Groundwater contamination by
128 chlorinated hydrocarbons was first detected in 2000 by the local environmental authority, during an
129 investigation for the development of a new residential area. Two chlorinated hydrocarbon plumes were
130 identified in the A0 and Upper A1 aquifers that have migrated about 500 m down-gradient of the Southern

131 Dump (Fig. 1). The plume in the A0 aquifer consists primarily of chloroethenes (PCE; TCE; 1,1-
132 dichloroethene – 11DCE; cis-1,2-dichloroethene – cDCE; trans-1,2-dichloroethene – tDCE; vinyl chloride –
133 VC), and secondarily of chloroethanes (1,1,1,2-tetrachloroethane – 1112TeCA; 1,1,2,2-tetrachloroethane –
134 1122TeCA; 1,1,2-trichloroethane – 112TCA; 1,2-dichloroethane – 12DCA) and chloromethanes (carbon
135 tetrachloride – CT; chloroform – CF; dichloromethane – DCM). Only chloroethenes (PCE, TCE, 11DCE, cDCE,
136 tDCE) and a few chloroethanes and chloromethanes (1122TeCA, 112TCA, CF, DCM) were detected in the
137 plume of the Upper A1 aquifer. The Lower A1 aquifer is considered uncontaminated based on separate
138 characterization efforts by the local authorities.

139

140 **3 Materials and Methods**

141 **3.1 Types of data collected**

142 Stratigraphic, hydraulic head and chemical data were collected along a 60 m wide x 60 m deep cross-
143 section (i.e. transect) located at the northern end of the Southern Dump perpendicular to the groundwater
144 flow direction of the A0 aquifer. The transect consists of two deep profiles (60 m bgs: MC1-2 and MC4-5) at
145 both ends and one shallower profile (30 m bgs: MC3) in the center (Fig. 2), whereby the horizontal distance
146 between the three profiles is 30 m. Data collection and analysis are described in the following sections and
147 further in the Supplementary Material (SM).

148

149 **3.2 Continuous coring and core subsampling**

150 Continuous cores were collected from the three locations in July 2013 using a wireline coring system with
151 triple tube core barrel that provided consistent, high core recovery of 95-98%. For the two deep profiles
152 (MC1-2 and MC4-5) cores were collected at slightly different locations (4-5 m apart) for the shallower (0-30
153 m bgs) and the deeper interval (28 – 60 m bgs) (Fig. 2). Before collecting cores from the deeper interval, the
154 upper 28 m of the borehole was sealed with permanent casing to avoid cross-contamination of the deepest
155 aquifer (Lower A1). Upon retrieval at ground surface, the cores were split longitudinally; one half was used
156 for detailed lithostratigraphic descriptive logging and Pocket penetrometer tests (Eijkelkamp Pocket

157 Penetrometer – Model 06.03) to evaluate sediment consistency, while the other half was used for
158 collection of large sediment samples (~250 g each). The sediment samples were collected at a one meter
159 spacing at locations MC1-2 and MC3 for measurement of grain size distributions in the sandy and silty clay-
160 rich layers. At the MC4-5 location, the other half of the cores was subsampled for measurement of
161 chlorinated hydrocarbon concentrations and for determination of porosity and organic carbon content. The
162 MC4-5 location was selected to perform the sediment core subsampling as it was expected to be the most
163 contaminated profile based on previous site characterization (Gargini et al., 2011; Nijenhuis et al., 2013).
164 Stratigraphic information from the cores was complemented by piezocone penetration tests (CPTU) to 30
165 m depth performed by the municipality of Ferrara 50 m southeastward from the transect (Fig. 1).
166 Core subsampling was conducted following the procedure described by Wanner et al. (2016), Adamson et
167 al. (2015a), Parker et al. (2004) and Parker et al. (2003), targeting a vertical spacing along the core axis of
168 about 10 cm. Three subsamples were collected at each depth (297 sampling depths in total), one for
169 chlorinated hydrocarbon concentration analyses, one for sediment properties (total porosity - ϕ , and
170 organic carbon fraction - f_{oc}), and a third for screening for the presence of DNAPL phase using a
171 hydrophobic dye (Oil-Red-O).

172

173 **3.3 Multilevel systems for hydraulic head and groundwater chemistry profiles**

174 After coring, groundwater multilevel monitoring systems were installed in the five boreholes along the
175 transect (Fig 2). Among the commercially available multilevel systems, the Solinst[®] CMT System (Einarson
176 2006) was selected, because: 1) it is suitable for unconsolidated sediment settings (Einarson and Cherry
177 2002) and 2) it allows selection of screen position and lengths in the field based on borehole-specific
178 lithology distributions from core logging. Each of the five CMT systems was equipped with 7 screens at
179 discrete depths targeting both aquifers and aquitards and avoiding cross-connection across visually distinct
180 permeability zones (Fig. 2).

181 Groundwater from the CMTs was sampled in November 2013 using dedicated 6 mm OD Teflon tubing and a
182 peristaltic pump (Model 410 Peristaltic Pump, Solinst[®]) to perform cation, anion and chlorinated
183 hydrocarbon concentration analyses.

184 Hydraulic heads were manually monitored in the CMTs twice a week between September 9, 2013 and July
185 28, 2014 (321 days) using a 4 mm diameter water level meter (Model 102 narrow diameter cable water
186 level meter, Solinst[®]).

187

188 **3.4 Lab analyses of sediment and groundwater samples**

189 Chlorinated hydrocarbon concentration analyses on core subsamples was performed at the University of
190 Guelph, ON, Canada. The contaminants were extracted from the sediment subsamples as described by
191 Dincutoiu et al. (2003). The analytical technique provides the total chlorinated hydrocarbon analyte mass
192 per mass of wet sediment (C_t) and does not distinguish between the aqueous, sorbed and NAPL phases.
193 Assuming DNAPL-free conditions, the pore water concentration (C_w) and sorbed mass concentration (C_s) in
194 the sediment subsamples can be estimated assuming equilibrium partitioning between dissolved and
195 sorbed phases (e.g. Parker et al. 2004, Adamson et al. 2015a). In addition to direct field screening tests with
196 dye, occurrence of pure phase DNAPL in the sediment samples was verified by comparing the estimated C_w
197 of each compound derived from C_t measurements in sediment samples with their effective solubility based
198 on an estimated analyte mole fraction (provided in SM).

199 Anion concentrations in groundwater were analyzed at the University of Bologna, Italy, by ion exchange
200 high performance liquid chromatography using a Metrohm 883 Basic IC Plus chromatograph. Cations were
201 analyzed in the same lab by Flame Atomic Absorption Spectrometry using a Perkin Elmer AA100
202 spectrometer. Chlorinated hydrocarbon concentrations in groundwater samples were analyzed by a
203 private certified laboratory (Chelab S.r.l., Treviso, Italy), using the analytical methods EPA 5030 C (U.S. EPA
204 2003) and EPA 8260 C (U.S. EPA 2006).

205

206 **3.5 Analytical modeling of diffusive transport in aquitard Lower Q1**

207 The aim of the analytical modeling was to estimate the time of contaminant arrival based on fitting of the
 208 concentration with distance profiles measured in the Lower Q1 aquitard with field and/or literature derived
 209 parameters for the sediment and solute. The PCE and TCE profiles appeared to be diffusion controlled and
 210 PCE and TCE transport in the Lower Q1 aquitard was simulated using a 1D analytical solution of Fick's
 211 Second Law assuming linear, instantaneous sorption (e.g. Parker et al. 2004, Parker 1996, Narasimhan
 212 2004) for a homogeneous, semi-infinite porous medium (e.g. Carslaw and Jaeger 1959):

$$213 \quad C_w = C_0 \operatorname{erfc} (z/(2(tD_e/R)^{1/2})) \quad (1)$$

214 where C_w is the chlorinated hydrocarbon pore water concentration (mg/L), C_0 is the concentration at the
 215 Upper A1-Lower Q1 interface acting as boundary concentration, R is the retardation factor due to sorption
 216 (eq. S9, in th SM), D_e is the effective molecular diffusion coefficient in the porous medium (cm^2/s), z is the
 217 vertical depth (cm), with $z=0$ at the aquitard interface, and t is time (s). Biodegradation of parent
 218 compounds in the Lower Q1 aquitard was assumed to be minor and not included in the simulations, as the
 219 chlorinated hydrocarbon concentration analyses did not show occurrence of the dechlorination product VC,
 220 and relatively low concentrations of cDCE (max 0.6 mg/L) compared to much higher concentrations of the
 221 parent compounds PCE and TCE (max 37 and 10 mg/L, respectively). In the case of PCE, a constant
 222 concentration was fixed at the model interface based on the characteristic shape of the profile with
 223 concentrations declining with distance into the aquitard suggesting relatively steady concentrations at the
 224 interface, and the diffusion time was used as a fitting parameter by varying it until a minimal deviation
 225 between measured and modelled concentrations was obtained. In contrast the TCE profile showed a profile
 226 shape consistent with a declining concentration at the interface, and thus a temporal evolution (step-
 227 decline) of the TCE concentration at the interface was evaluated. This decline was taken into account by
 228 superimposing analytical solutions to simulate a two-step concentration at the interface with C_w calculated
 229 for both steps using eq. S7 (in the SM). In the first step, a high TCE concentration representative of an
 230 earlier contamination stage was fixed at the model interface applying the entire diffusion time obtained
 231 from the PCE modeling. In the second step, a lower TCE concentration was assigned at the interface over a
 232 shorter time period to simulate a second stage when the boundary concentration was clearly lower, and by

233 applying the concept of superposition, these results were subtracted from results of the first step to obtain
234 the combined profile. The diffusion time of the second step and the interface TCE concentrations of both
235 steps were varied until reaching minimal deviation between measured and modeled concentrations.

236 Deviation between measured (m) and modeled (M) concentrations was quantified using the Nash-Sutcliffe
237 model efficiency coefficient (NSE; Nash and Sutcliffe 1970, Legates and McCabe Jr 1999):

$$238 \quad NSE = 1 - \frac{\sum_{i=1}^n (m_i - M_i)^2}{\sum_{i=1}^n (m_i - m_m)^2} \quad (2)$$

239 where m_m is the measured mean. NSE ranges from minus infinity to 1 with higher values indicating better
240 fit.

241 Adamson et al. (2015b) recently provided a source history model for estimating interface concentration
242 history based on measured low-K zone profiles, which was applied as a verification for the analytically
243 simulated profiles, and for refining the concentration history at the interface for the TCE profile. The
244 primary difference for the fits using the source history model is that the total mass concentrations (C_t) are
245 used as primary input whereas the porewater concentration (C_w) are estimated by the model applying
246 average parameter values for bulk density, porosity ϕ , and estimated R factor. The source history
247 simulation results are provided in the SM.

248

249 **4. Results and discussion**

250 **4.1 Contaminant distributions as evidence for aquitard integrity**

251 The thickness of aquitard Q0 at the site is clearly altered due to past excavation for waste disposal. The
252 waste material likely reaches a thickness equal to or higher than the thickness of Q0 in the area of the
253 transect (e.g. in the MC3 profile only 1 m of fine-grained deposits of the Q0 aquitard separate the wastes
254 from the A0 aquifer; Fig. 3). Thus, the integrity of the aquitard Q0 is difficult to assess as the contaminants
255 may have reached the underlying A0 aquifer either due to poor integrity of the Q0 or because the waste
256 dumps penetrated the Q0 due to excavations and contacted the top of the A0 directly. Peaks of
257 chloroethene concentrations were detected into the Q0 aquitard from sediment samples along core MC4-5
258 (mostly cDCE and VC with estimated pore water concentrations, C_w , up to 197 and 16 $\mu\text{g/L}$, respectively)

259 that suggest strong contaminant retention and degradation in the aquitard layer (Fig. 4). Occurrence of
 260 chloroethenes in the Q0 is also confirmed by groundwater concentrations (GW) along profiles MC4-5 and
 261 MC3. The absence of contaminants into this aquitard along profile MC1-2 is more likely justified by the
 262 absence of residual waste above the profile (Fig. 3) rather than locally high Q0 aquitard integrity, since the
 263 profile is positioned at the edge of or beyond the source zone.

264 The cumulative mass distribution per unit area of total VOCs, chloroethenes, chloroethanes and
 265 chloromethanes along the MC4-5 profile suggests accumulation contaminants at the interface between
 266 aquifer A0 and aquitard Upper Q1 (especially PCE, cDCE, 1122TeCA and 112TCA, with peak C_w of 54, 141, 86
 267 and 23 $\mu\text{g/L}$, respectively) and at the interface between aquifer Upper A1 and aquitard Lower Q1 (mostly
 268 PCE and TCE, with max C_w of 37 and 10 $\mu\text{g/L}$, respectively) in a manner consistent with DNAPL migration
 269 and preferential accumulation at those interfaces where capillary pressures were insufficient to invade
 270 sediments with different and smaller pore geometry (Fig. 5). The major mass accumulation zone occurs at
 271 the top of the Upper Q1 aquitard showing strong resistance of DNAPL penetration (i.e. resistance to vertical
 272 flow) and enhanced lateral DNAPL migration in this system, as evidenced by the sudden occurrence of the
 273 chloroethanes, and their absence above this depth. This mass accumulation also corresponds to organic-
 274 rich sublayers in the top meter of the Upper Q1 aquitard (max f_{oc} of 2.6% at 9.5 m bgs; see Fig. 3) where the
 275 organic sediment facilitates contaminant retention by sorption. The same organic-rich sublayers provide a
 276 favorable environment for reductive dechlorination. Filippini et al. (2016) observed reductive
 277 dechlorination of chloroethenes PCE and TCE and accumulation of by-products (mainly cDCE and VC) during
 278 contaminant retention and migration within these fine organic-rich sediments. By analogy, chlorinated
 279 ethanes 112TCA, 12DCA, and methanes DCM, CM that occur exclusively in the shallowest 10-12 m of the
 280 profile are likely by-products from dechlorination of higher chlorinated compounds (e.g. 1112TeCA,
 281 1122TeCA and CF).

282 Despite the high resistance to DNAPL penetration inferred for the Upper Q1 aquitard, the cumulative mass
 283 profiles strongly support some DNAPL invasion through this aquitard given the contamination throughout
 284 the underlying Upper A1 aquifer down to the top of Lower Q1, where the second largest chloroethene

285 mass accumulation was registered. The low contaminant concentrations in the aquifer Upper A1
286 (interposed between the two contaminated aquitards Upper and Lower Q1) at the time of this investigation
287 are explainable due to the active groundwater flow in the aquifer over the last decades and much lower
288 sorption in the sandy sediments compared to fine-grained organic-rich sediments of the underlying and
289 overlying aquitards. Thus, the present day contaminant distributions appear strongly affected by an earlier
290 contamination stage when DNAPL was migrating preferentially downward and laterally along lower K_v
291 aquitard interfaces. Even though field tests with dye provided negative results along the whole profile, the
292 occurrence of pure phase DNAPL could be inferred in at least one sample within the A0 aquifer where
293 estimated PCE pore water concentration most likely exceeded effective solubility limits (see SM). Few other
294 shallow samples (i.e. from Q0 aquitard, A0 aquifer, and Upper Q1 aquitard) showed pore water
295 concentration possibly close to effective solubility for some compounds. This suggests little remaining and
296 highly residualized DNAPL at the time of investigation, but most likely much more mobile DNAPL nearer the
297 time of disposal.

298 The contaminant profiles from MC4-5 cores show evidence of diffusion dominated transport (i.e.
299 characteristic diffusion profiles) at the top of the lower Q1 aquitard with rapid decrease of concentration
300 below the aquifer-aquitard interface (see Fig. 8), suggesting good aquitard integrity preventing deeper
301 DNAPL penetration into and below this zone. However, the aquitard did not prevent migration of some
302 contaminants into the lower A1 aquifer (PCE and TCE concentrations up to 3 mg/L, much lower than in the
303 overlying aquitard), showing evidence of some DNAPL migration pathways to these depths, which might
304 come from breaches in this aquitard upgradient from the core location with horizontal migration by
305 groundwater flow in the Lower A1. Consideration was given to possible cross-contaminant due to drag-
306 down of much higher concentrations and presence of DNAPL shallower in the profile. However, the field
307 methods involved significant steps to reduce this situation, using a separate borehole with a blank casing
308 through the shallower zone for the deep coring locations. This makes the cross-connection explanation
309 unlikely with the more likely scenario that preferential contaminant pathways must have existed at an early
310 stage, when mobile DNAPLs were present. The propensity for deep migration pathways no longer exists

311 once the mobile DNAPL phase dissolves away to the point where the driving force diminishes, which is the
312 condition expected at the drilling locations, but maybe not internal to the dump area. Contaminant
313 concentration profiles at the top of the lower Q1 aquitard are discussed in Section 4.3 providing insights on
314 source history.

315

316 **4.2 Hydraulic head and hydrochemistry profiles as complementary evidence**

317 The strongest vertical hydraulic head variations (Δh_v) of about 0.1 m with depth are localized within the
318 Upper Q1 and Lower Q1 aquitards (Fig. 6). A similar variation is observed in the aquitard below the Lower
319 A1 aquifer, which is beyond the zone of relevance of this paper, but confirms repeated occurrence of head
320 losses in all aquitards. The vertical gradient variability along the thickness of an aquitard layer is caused by
321 heterogeneity of the hydraulic conductivity in the vertical direction (K_v), with steeper gradient in sub-layers
322 of lower K_v (Cherry et al. 2006).

323 From a stratigraphic viewpoint, the main Δh_v in the Upper Q1 aquitard occur inside the organic-rich layer
324 from 8 to 11 m bgs, suggesting this is a sub-layer of lower vertical hydraulic conductivity able to reduce
325 groundwater and DNAPL flow between the aquifers A0 and Upper A1. The vertical distribution of field
326 parameters and ion concentrations shows decreasing trends (increasing in the case of pH) from aquifer A0
327 to aquifer Upper A1 suggesting vertical migration down to the Upper A1 aquifer of dissolved components
328 originating from dump leachate and redox influences by the presence of high VOC concentrations (Fig. 7).
329 An exception was observed for potassium (K) and fluoride (F) where concentrations drop close to zero
330 below the Upper Q1 aquitard, possibly due to adsorption onto clay minerals, oxides and/or hydroxides
331 (Pickering 1985, Mitra and Prakash 1956) which are abundant in the Ferrara aquitards (Amorosi et al.
332 2002). Based on these observations, the Upper Q1 appears to be an ineffective barrier against the vertical
333 migration of dissolved ions and especially ineffective barrier to DNAPL. Otherwise, if the A0 and Upper A1
334 aquifer were effectively insulated by the Upper Q1 aquitard, a change in the vertical trends would have
335 been observed between the two aquifers since they are recharged by different sources (Filippini et al.
336 2015) and have different hydrochemistry at the regional scale (Molinari et al. 2007). The low integrity of the

Upper Q1 aquitard is likely due to the occurrence of imperceptible fractures and coarse-grained sub-layers of higher K_v that facilitate vertical groundwater exchanges between the over- and underlying A0 and Upper A1 aquifers. The higher ion concentration observed in this aquitard and in the overlying and underlying aquifers along MC4-5 and MC3 profiles in comparison to MC1-2 is explained considering that residual waste only remained at the top of the first two profiles (Fig. 3). An exception is SO_4 , which shows the highest concentration in profile MC1-2, while in the more contaminated MC4-5 and MC3 profiles this had likely been depleted as an electron acceptor for reductive biotransformation of chlorinated compounds (Ndon et al. 2000).

The lithostratigraphic features of the Lower Q1 aquitard (uniform grain-size, high clay content of 40%, no visual evidence of fracturing) suggest absence of preferential pathways for contaminant migration and thus, a higher degree of integrity compared to the shallower aquitard units. Hydraulic heads in the Lower Q1 shows the occurrence of a sub-layer of low vertical hydraulic conductivity (main Δh_v) localized in the zone of a markedly clayey section from 28 to 30.5 m bgs, characterized by “hard consistency” from pocket penetrometer tests (see Fig. 3). Such layer is expected to provide an effective insulation between the overlying Upper A1 and underlying Lower A1 aquifers. Despite the absence of visible fractures in the aquitard at the core scale, the pore pressure trend (u ; kPa) obtained from a CPTU performed 50 m southeastward from the transect shows a sudden decrease of u at the same depth of the main Δh_v in the Lower Q1 aquitard (Fig. 6), indicating an over-consolidation of the layer (Chen and Mayne 1996, Mayne et al. 1990, Amorosi and Marchi 1999) and a consequent prone-to-fracturing behavior (“fragility”) with probable occurrence of micro-fractures. Such micro-fractures represent an ideal preferential pathway for the migration of small amounts of DNAPL through the protective clayey layer of the Lower Q1 aquitard. In the context of the southeastern Po river plain, a high consolidation of clays with consequential micro-fracturing is likely attributed to cohesive sediment desiccation during the prolonged phase of subaerial exposure that characterized the area during the last glacial maximum and the first stages of transgression (Amorosi and Marchi 1999, Rizzini 1974). The typical occurrence of fractures and DNAPL migration

362 pathways in natural clay-rich aquitards was also reported by Morrison et al. (1998) and Cherry et al. (2006)
363 especially in clayey aquitards thinner than 15 meters, of fluvial origin and overconsolidated.
364 Hydrochemistry further distinguishes the lower Q1 aquitard conditions compared to the shallower system.
365 Field parameters and ion concentrations show sharp changes of vertical trends below the Lower Q1
366 aquitard suggesting that the Upper and Lower A1 aquifers have dissimilar hydrochemistry with the Lower
367 Q1 aquitard reducing fluxes between the two aquifers (Fig. 7). In particular, the lowest ion concentrations
368 of the entire profiles were observed at the top of the Lower A1 aquifer, suggesting no or much lower
369 influence from the surficial contaminant inputs compared to the two shallower aquifers. This observation
370 confirms that the propensity for deep migration pathways through the deeper aquitard is only effective in
371 the presence of mobile DNAPL phase but not for dissolved components.

372

373 **4.3 Lower Q1 aquitard integrity from diffusion transport**

374 The contaminant distributions of PCE and TCE at the top of the lower Q1 aquitard show concentration
375 profiles characteristic of transient diffusive transport (Fig. 8). The opportunity was taken to use these
376 profiles for assessing the time of first contaminant arrival at the Lower Q1 aquitard. To this aim, the PCE
377 and TCE profiles were reproduced using a mathematical model for 1-D diffusive transport with linear,
378 instantaneous sorption (described in Section 3.5). The shape of the PCE profile shows the peak
379 concentration at the aquifer-aquitard interface with PCE boundary concentration of 37 mg/L, not far from
380 the lower limit of estimated effective solubility (i.e. 54 mg/L; see SM) suggesting possible occurrence of
381 DNAPL over most or nearly all of the contamination history. Based on site history, DNAPL contaminants
382 were disposed in the Southern Dump between the late 1950s and 1970s. Transport time was varied from
383 10 to 60 years to represent the possible time lapse between initial contamination and field characterization
384 in 2013. A best fit between modeled and measured profiles was obtained for 40 years of diffusive migration
385 (Fig. 8) suggesting contamination reached the interface shortly after the waste disposal occurred.
386 The TCE profile in the Lower Q1 aquitard has its peak concentration a few cm below the aquifer-aquitard
387 interface, showing back-diffusion from the Lower Q1 aquitard into the Upper A1 aquifer suggesting a

recent shift to a lower concentration at the boundary over the diffusion time period (Chapman and Parker 2005). Although both PCE and TCE were likely present as DNAPL at this interface, a faster decline of TCE compared to PCE may be best explained by their original composition in the DNAPL and higher effective solubility for TCE, causing a more rapid depletion in TCE at the boundary as a result. In the case of the TCE modeling, the time for 1-D diffusive migration derived from the PCE best-fit time (i.e. 40 years) and the concentration of TCE at the interface was used as the fitting or adjustment parameter. A best fit was determined considering two steps of decreasing TCE at the boundary corresponding to 70 mg/L for the first 12 years and 10 mg/L for the remaining 28 years. The iterative modeling approach described above was corroborated using the source history model developed by Adamson et al. (2015b) with the same boundary concentrations (SM Fig. S4, S5). However, the assumption of a two-stage boundary condition oversimplifies the possibility for strong initial gradients and TCE mass transfer (loss) from the DNAPL source followed by a stage with low concentrations at the boundary and a concentration gradient reversal that would attenuate strongly due to diffusion both in and out of the lower Q1 aquitard. As an alternative scenario, the source history model “tool” was applied assuming an exponentially declining source (SM Fig. S6), also providing a reasonable fit to the measured profile although with slightly larger associated error. This shows the non-unique nature of fits for various assumptions regarding source history conditions. Further to this, DNAPL invasion into the micro-fractures of the Lower Q1 cannot be completely ruled out. Thus, the influence of a single fracture volume of DNAPL invading a typical size fracture in clays, assumed to be 10-50 microns in aperture (e.g. Jørgensen et al. 1998, O'Hara et al. 2000, Hinsby et al. 1996, McKay et al. 1993, Jørgensen et al. 2002, Rudolph et al. 1991), was evaluated. The time of diffusion-based mass transfer of PCE and TCE from DNAPL phase in the fractures causing complete DNAPL dissolution from the fractures was estimated between 38 days and 2.6 years for PCE and between 1 and 32 days for TCE following Parker et al. (1994) (details in the SM). Given such quick disappearance times by a single loading of DNAPL invading these fractures with small apertures, possible dissolution of DNAPL by diffusion from the micro-fractures would have unlikely interfered with the observed diffusion transport characteristics of the profiles, as confirmed by the ability to simulate these PCE and TCE profiles. However, it is also unlikely that

414 a single fracture filling of DNAPL would occur after entry when DNAPL persists at the overlying aquifer-
415 aquitard interface, hence the simplest scenario of no DNAPL entry into the lower Q1 aquitard seems most
416 reasonable and defensible interpretation. Furthermore, it is also expected that DNAPL retention occurs
417 with depth of migration, causing lower volumes of DNAPL at the top of this lower Q1 aquitard interface,
418 making it difficult to overcome entry pressures in deep micro-fractures.

419

420 **5 Conclusions**

421 Three clay-rich non-indurated aquitards in a multi-layered aquifer-aquitard system of alluvial origin did not
422 prevent deep DNAPL migration to lower aquifers likely due to the occurrence of small-scale lithologic
423 heterogeneities and micro-fractures. This observation was made in a setting where, before this study, the
424 aquitards were considered protective of groundwater in the underlying aquifers based on standard
425 methods of site characterization such as lithology descriptions and bulk hydraulic conductivities. Whereas
426 the intermediate aquitard showed low integrity allowing fast advective migration of contaminants towards
427 the underlying aquifer due to occurrence of lithologic heterogeneities, the deepest aquitard showed
428 evidence of DNAPL accumulation at the upper boundary and only diffusive transport (i.e. diffusion profiles)
429 with sorption due to partitioning to solid phase organic carbon without discernable effects of advection,
430 suggesting much higher aquitard integrity. The high-resolution concentration profiles showed that the two
431 shallower aquitard units Q0 and Upper Q1 retained considerable DNAPL mass at/near their upper
432 boundaries and strongly reduced the flux of DNAPL to the lower system, but not completely preventing
433 deep migration. Both aquitards enhanced contaminant biodegradation due to high organic carbon content
434 influencing the contaminant mixtures that reached the underlying aquifers. At the core locations, it appears
435 that DNAPL did not enter the deepest Lower Q1 aquitard as diffusion transport matches the sharp
436 concentration decline with distance from the top of the aquitard over approximately 40 years. However,
437 deeper contamination in the Lower A1 aquifer, although at much lower concentrations, is observed most
438 likely due to some DNAPL penetration of the Lower Q1 aquitard up-gradient from the core locations or
439 aqueous phase transport along flow lines traveling through the DNAPL in the overlying units, making the

integrity assessment of the Lower Q1 aquitard uncertain beyond the local study area. Concentration profiles produced by diffusive transport in this aquitard allowed assessing the approximate timing since initial contaminant arrival at the top of the aquitard, which appears to have occurred with minimal delay from surficial contamination events, suggesting rapid DNAPL migration through the subsurface. The two deeper aquitards impeded DNAPL fluxes to some extent, with accumulation on these units fostering diffusion into aquitards where substantial mass resides as dissolved and sorbed phases, posing a secondary, long term source of contamination to the adjacent aquifers due to slow back-diffusion, even after complete dissolution of the DNAPL or active remediation of the waste zone. Knowing that preferential accumulation occurred at the top of lower K clay-rich units should also guide placement of future monitoring points. The different behavior observed for distinct aquitards of the same multi-layer aquifer-aquitard system highlights the need for high-resolution aquitard-specific investigations for (1) defining the degree of protection provided to the underlying aquifers, and (2) assessing the long-term influence that aquitards might have on contaminant phase re-distribution and transformation. Follow-on studies might enhance the vertical high-resolution information in the lateral directions e.g. by exploring the lateral continuity and geometry of the aquitard-aquifer interfaces by means of lower invasive technologies such as geophysics.

455

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461

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Figure1

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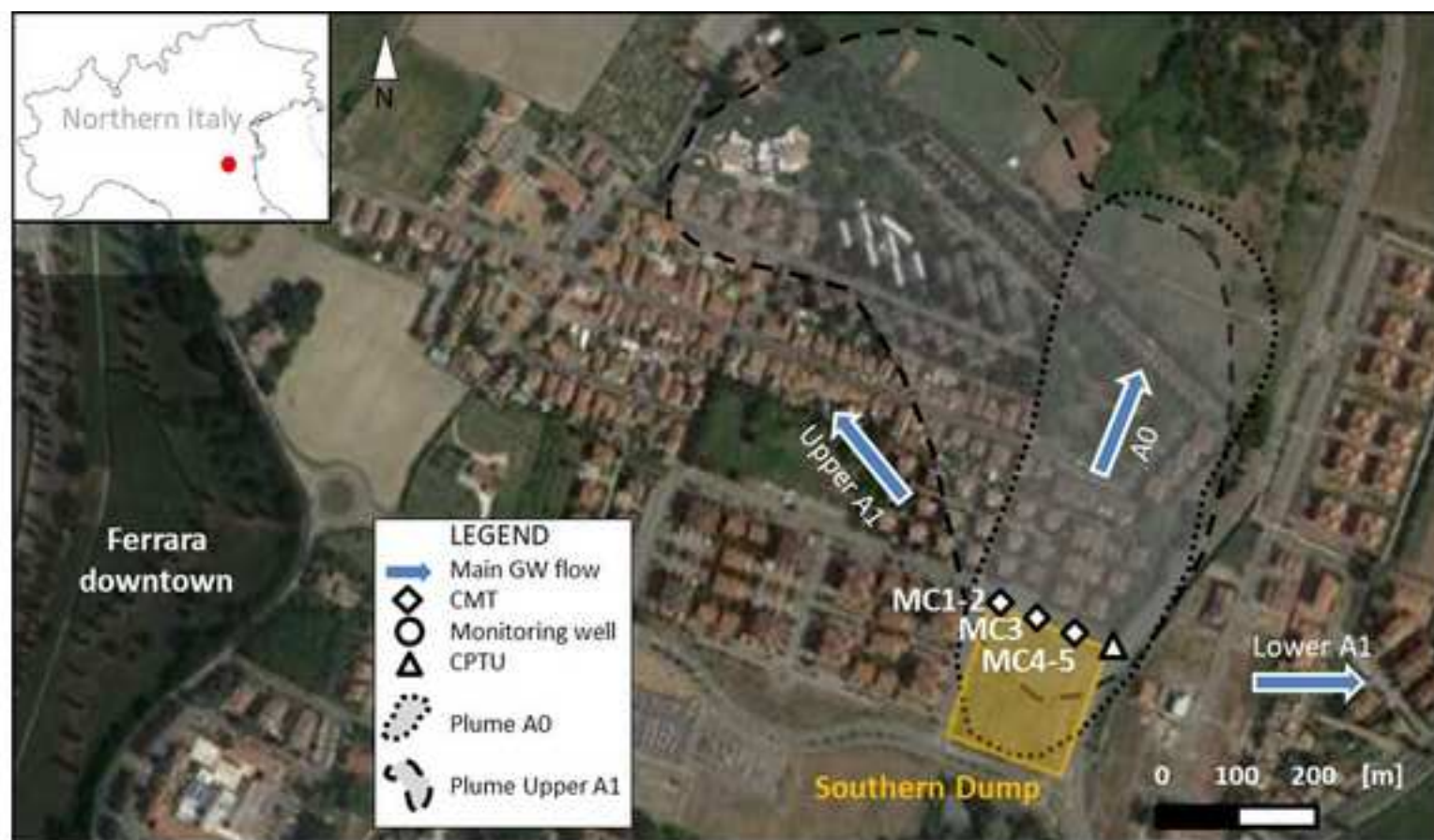


Figure 1: Monitoring network at the Caretti site. The CMT transect ("MC1-2", "MC3", "MC4-5" systems), disposed on an edge of the Southern Dump, is described in detail in Fig. 2. The location of a Cone Penetration Test (CPTU) performed close to the CMT transect is reported on the map (see CPTU results in Fig. 4). The main groundwater flow directions and the mixed contaminant plumes were outlined based on data from Nijenhuis et al. (2013) and Gargini et al. (2011).

Figure2

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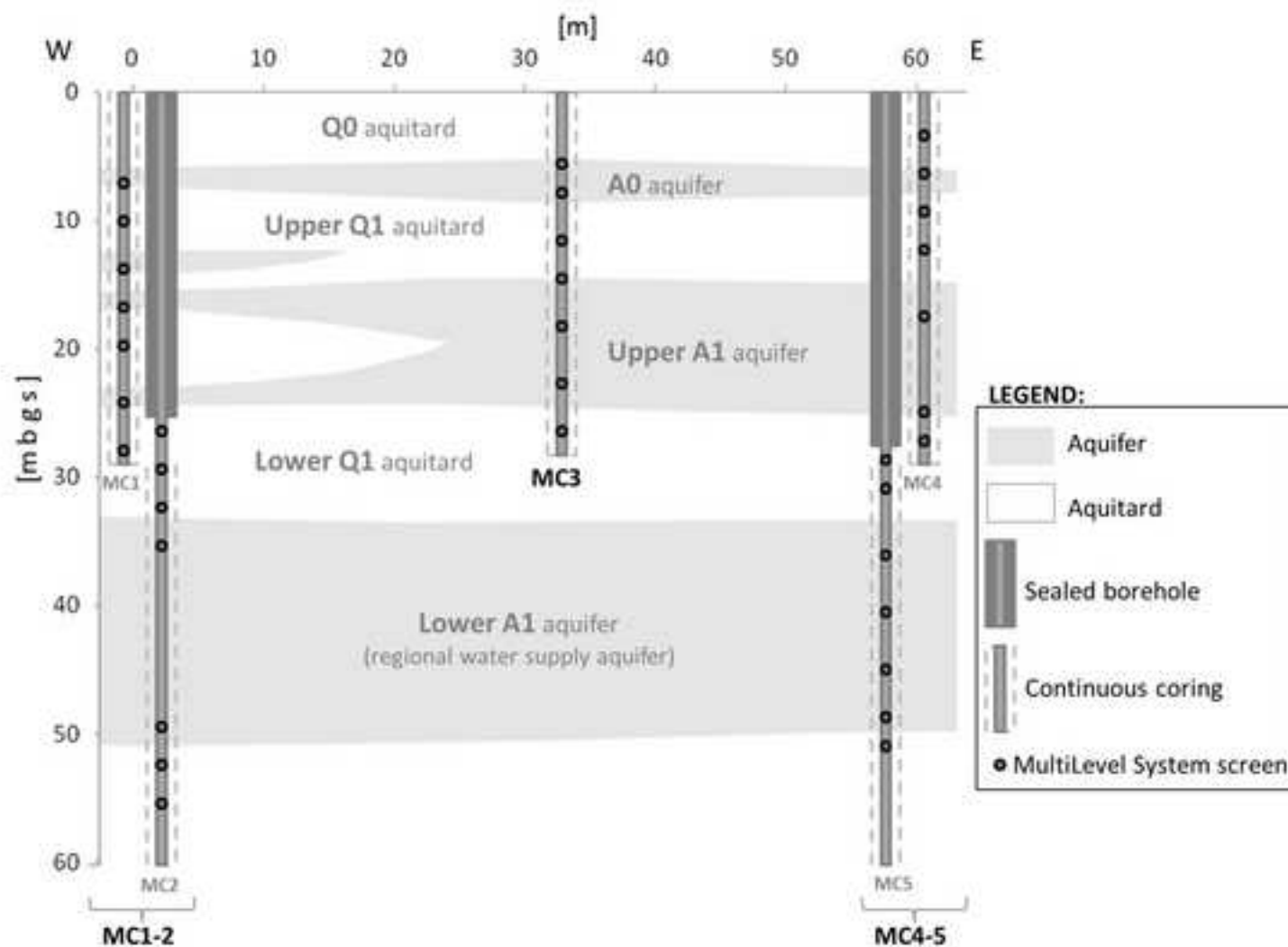


Figure2: Schematic of the CMT transect (see location of the cross-section in Fig. 1). Detailed stratigraphic logs of cores MC1-2, MC3 and MC4-5 are shown in Fig. 3.

Figure3

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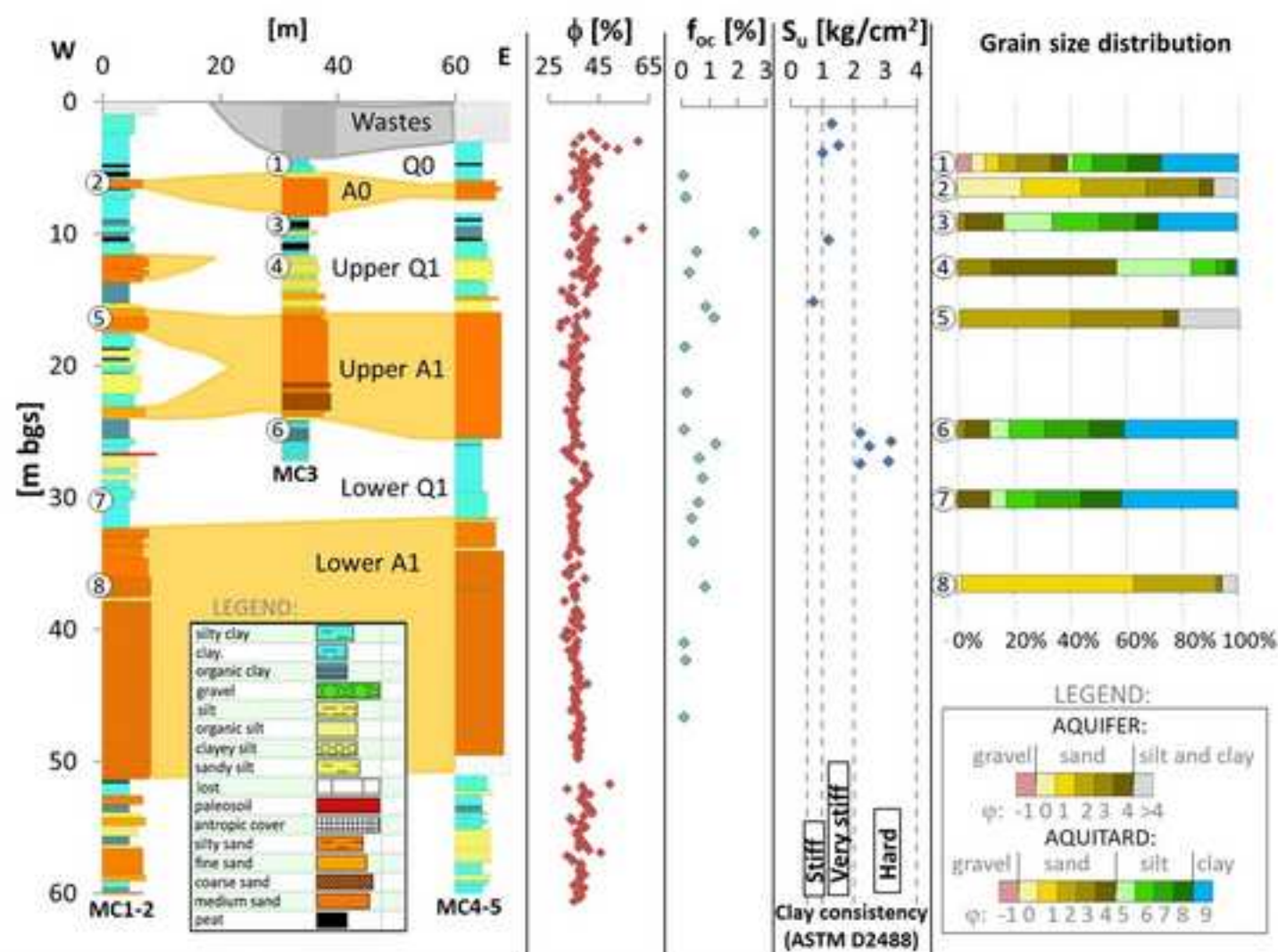


Figure 3: Stratigraphic information collected along the transect. From the left: geologic logs and geometry of aquifers and aquitards; vertical trend of estimated total porosity (ϕ ; from profile MC4-5); vertical trend of organic carbon content (f_{oc} ; from core MC4-5); estimations of undrained cohesion (S_u) on clayey layers via pocket penetrometer tests (from core MC1-2); grain size distribution of aquifers and aquitards (sampling depths indicated with numbers on the MC1-2 and MC3 geologic logs).

Figure4

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Figure 4: Vertical distribution of chloroethenes (a), chloroethanes (b) and chloromethanes (c). From left: concentrations from groundwater samples (GW; Log mg/L - only concentrations > 0.1 mg/L are plotted for graphical reasons (black crosses indicate GW samples with concentration < 0.1 mg/L for all the analyzed compounds); total concentrations in sediment samples along profile MC4-5 (Ct, Log ug/g - only concentrations > 0.1 ug/g are plotted for graphical reasons); estimated pore water concentrations from phase partitioning (Cw; Log mg/L - only concentrations > 0.1 mg/L are plotted for graphical reasons); estimated sorbed mass concentrations from phase partitioning (Cs; Log ug/g - only concentrations > 0.1 ug/g are plotted for graphical reasons). The one sample with estimated pore water concentration of PCE most likely higher than effective solubility is highlighted with a black arrow. The concentration database is in Tables S2 and S3 of the SM.

Figure5

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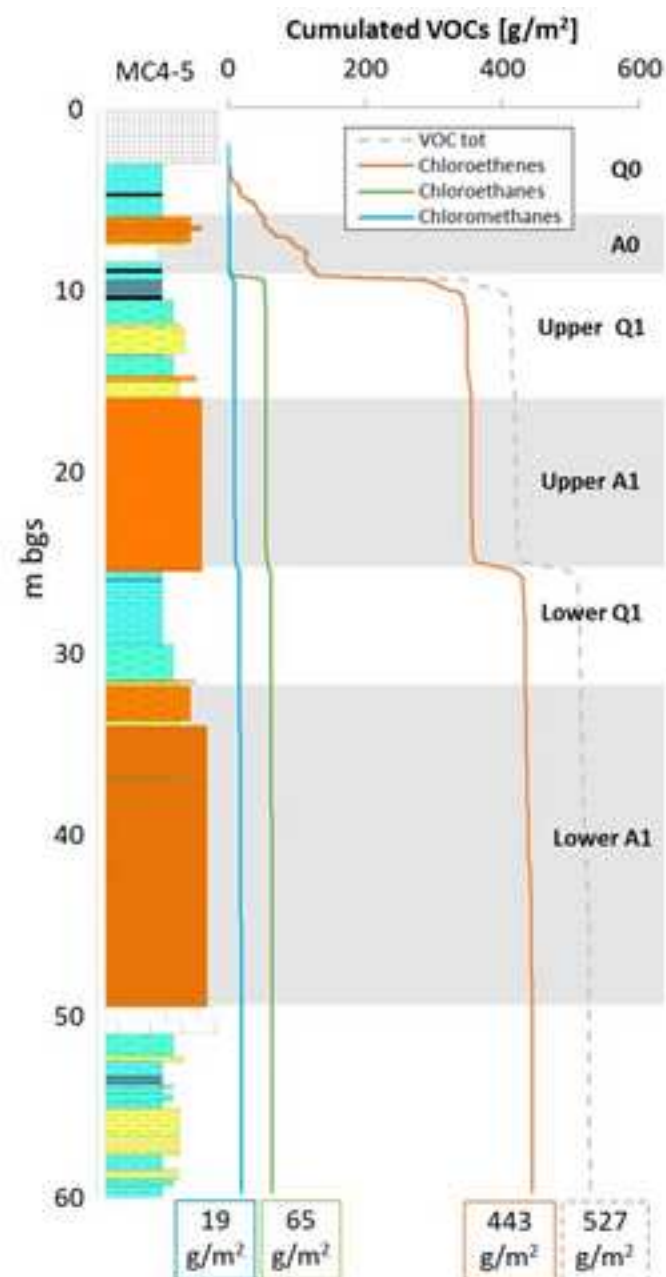


Figure 5: Profiles of cumulative mass per unit area of total VOC, chloroethenes, chloroethanes and chloromethanes at MC4-5 location. Calculations of cumulative mass per unit area are described in the SM.

Figure6

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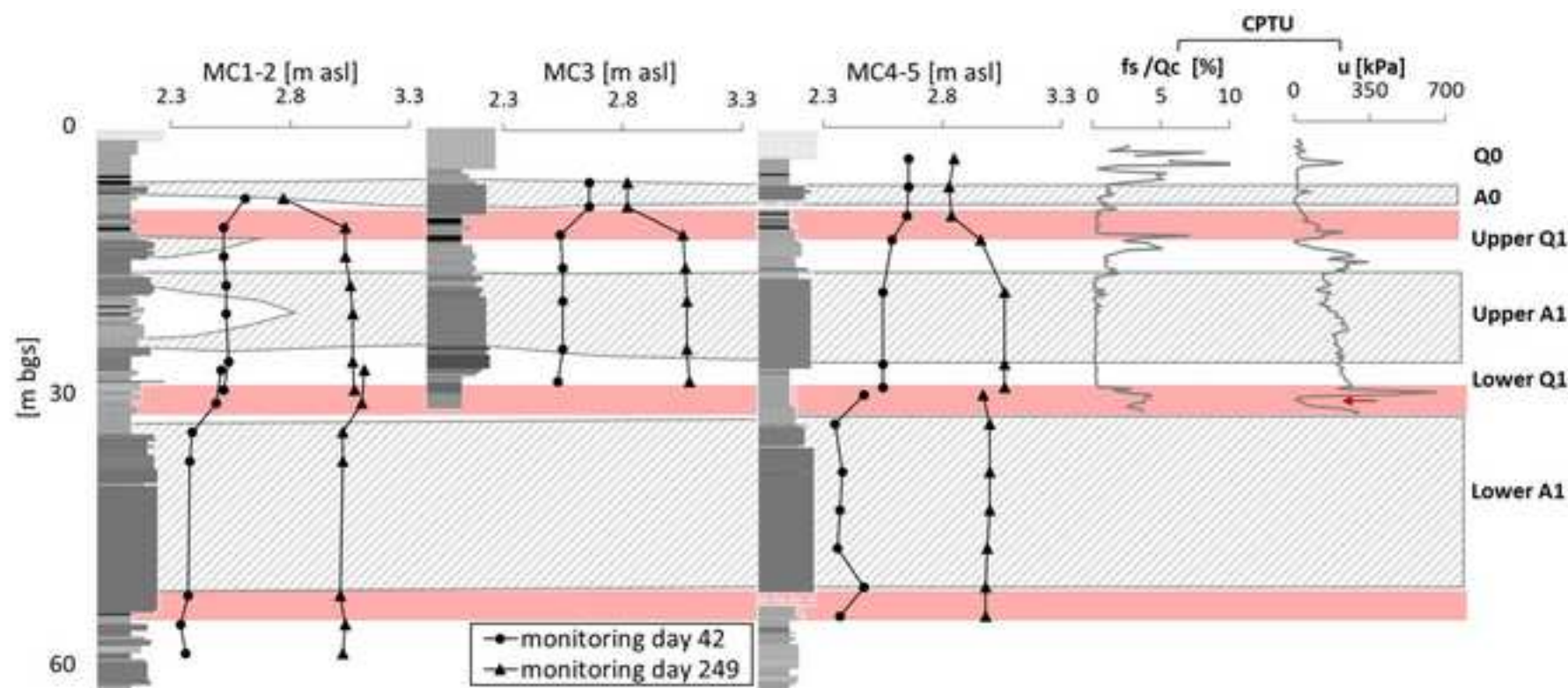


Figure 6: Vertical head distribution along the three profiles of the transect at monitoring days n. 42 and 249. The pink stripes indicate the sections with the steepest hydraulic vertical gradient within in the aquitards. The results of a CPTU test performed 50 m southeastward from the transect are reported beside the head profiles (see CPTU location in Fig. 1). The red arrow highlights a significant decrease of pore pressure (u) that occurs around 30 m bgs in correspondence of the steepest hydraulic vertical gradient in the lower Q1 aquitard.

Figure7

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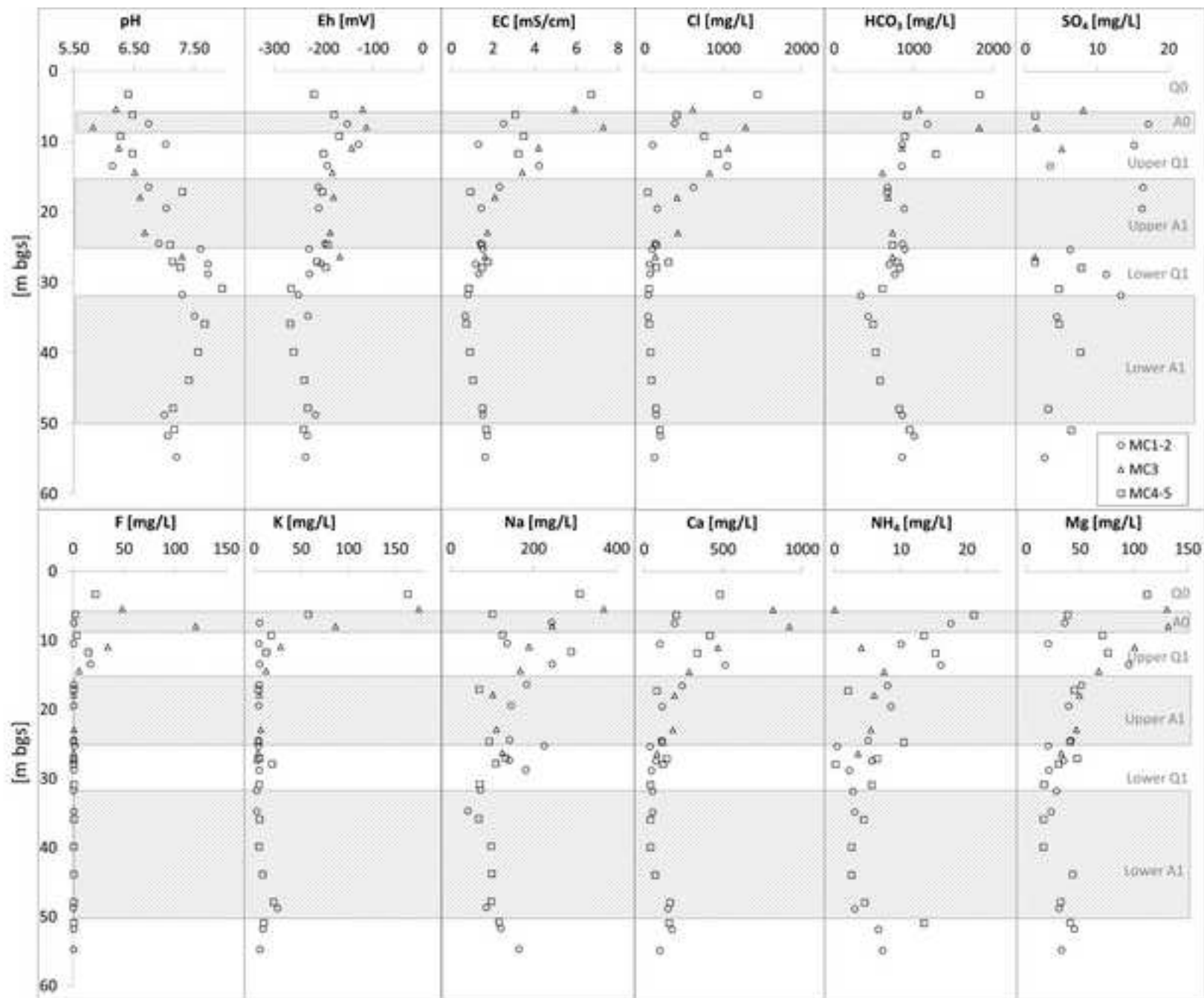


Figure 7: Vertical trends of the main chemical parameters of groundwater and dissolved ions along the three profiles of the transect,

Figure8
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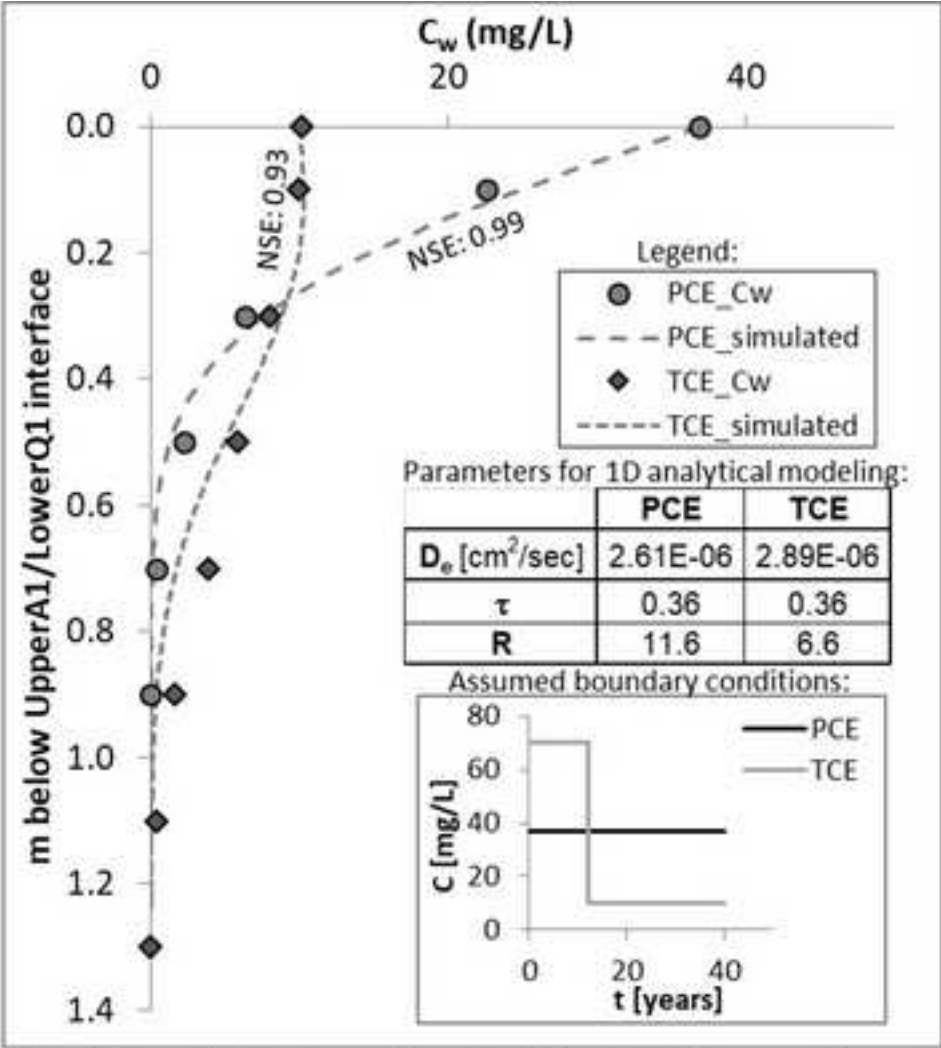


Figure 8: Results of 1D analytical simulation of diffusion profiles of PCE and TCE. The goodness of fit with measured C_w data is reported based on Nash–Sutcliffe model efficiency coefficient (NSE).

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Field parameters and contaminant concentrations

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