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Detecting vinyl chloride by phytoscreening in the shallow critical zone at sites with potential human exposure

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Abstract

Chlorinated ethene (CE) contaminants are widespread in groundwater, and the occurrence of vinyl chloride (VC), among others, is a well-known issue due to its mobility, persistence, and carcinogenicity. Human exposure to VC may occur through inhalation after soil vapor intrusion into buildings at sites with shallow underground contamination. Soil vapor intrusion risk is traditionally assessed through indoor air and sub-slab sampling (direct evidence) or soil gas and groundwater surveys (indirect evidence). Phytoscreening (sampling and analysis of tree trunk matrices) was proven as a cost-effective alternative technique to indirectly detect shallow underground contamination by higher chlorinated ethenes and subsequent vapor intrusion risk. However, the technique has appeared barely capable to screen for the lower chlorinated VC, likely due to its fugacity and aerobic bio-degradability, with only one literature record to date showing successful detection in trees. We applied phytoscreening at two sites with severe CE contamination nearby residential buildings caused by illegal dumping of chlorinated pitches from petrochemical productions. The

two sites show variable amounts of VC in the shallow groundwater ($1\text{e}2$ to $1\text{e}4$ $\mu\text{g/L}$), posing potential sanitary risk issues. Former soil gas surveys did not detect VC in the vadose zone. At both sites, we sampled trunk micro-cores and trunk gas from poplar trees close to contaminated piezometers in different seasons. VC was detected in several instances, disproving the shared literature assumption of the inefficacy of phytoscreening towards this compound. Factors influencing the detectability of VC and other CEs in trees were analyzed through linear regressions. Two different conceptual models were proposed to explain the effective uptake of VC by trees at the two sites, i.e., direct uptake of contaminated groundwater at the first site and uptake of VC from an anoxic vadose zone at the second site. In planta reductive dechlorination of CEs is not expected based on current literature knowledge. Thus, the detection of VC in trunks would indicate its occurrence in the shallow underground, suggesting higher screening effectiveness of phytoscreening compared to soil gas; this has implications for indirect vapor intrusion risk assessment.

Key words

phytoscreening, vinyl chloride, chlorinated ethenes, critical zone, vapor intrusion

1 Introduction

Underground contamination by chlorinated ethenes (“CEs” hereafter) is a well-known global environmental issue. Indeed these contaminants are widespread in most aquifers underlying industrial and urbanized areas, persistent in the underground due to their mobility and poor degradability (Olaniran et al., 2004; Pankow and Cherry, 1996), and toxic/carcinogenic to the human health (e.g., Chen and Wu, 2017). The ability of trees to uptake CEs and thus indirectly reveal their occurrence in the shallow critical zone (here intended as the thickness between the shallowest groundwater and the ground surface) has been known for some decades (Vroblecky et al., 1999). The sampling and analysis of trunk matrices (i.e., wood, gas, or sap) to screen for underground contamination is called phytoscreening (Sorek et al., 2008). Phytoscreening was occasionally proven effective for detecting several inorganic and organic contaminants such as heavy metals (Algreen et al., 2014), BTEX (Wilson et al., 2013), and PFAS (Gobelius et al., 2017).

Nevertheless, the ability of trees to detect CEs was most often studied in the last two decades since these compounds have physicochemical properties optimal for plant uptake (Schöftner et al., 2016). Several factors other than underground contaminant concentration have been shown to affect the migration and accumulation of CEs in tree trunks, among which are the plant species (e.g., Duncan et al., 2017; Yung et al., 2017), seasonal physiological dynamics of the plant, meteo-climatic variables (e.g., Holm and Rotard, 2011; Limmer et al., 2014; Vroblesky, 2008; Wittlingerova et al., 2013), and the depth to water table (Duncan and Brusseau, 2018). The combined effects of such factors cause the variability of contaminant concentration in the trunk either over space (among different trees and radially or azimuthally in the same trunk) or over time. Nevertheless, the literature agrees with the overall conclusion that the technique is effective in screening for underground contamination of the higher chlorinated compounds tetrachloroethene (PCE), trichloroethene (TCE), and dichloroethene isomers (DCE), on a qualitative up to a semi-quantitative level (Leoncini et al., 2022). On the contrary, the detection of the lower chlorinated compound vinyl chloride (VC) in tree trunks has been rarely documented (Ottosen et al., 2018).

The inefficacy of phytoscreening toward VC has been ascribed to its high fugacity and degradability in an aerobic environment (Larsen et al., 2008; Sorek et al., 2008). Moreover, Gas Chromatography coupled with Electron Capture Detection (GC-ECD) was often used to analyze chlorinated ethenes in the phytoscreening literature (e.g., Doucette et al., 2007; Gopalakrishnan et al., 2007; Shetty et al., 2014; Struckhoff et al., 2005; Wilson et al., 2017b), being this technique less effective for VC detection than Gas Chromatography coupled with Mass Spectrometry (GC-MS). An additional cause of VC under-detection in tree trunks may be the scarcity of phytoscreening applications at sites where the compound occurs in significant underground concentration. VC is known to occur in groundwater or the soil gas as the product of reductive dechlorination of higher chlorinated compounds (Bradley and Chapelle, 2010), although dechlorination down to VC only occurs under peculiar bio-geochemical conditions (Yan et al., 2021). As a result, at many sites, VC is found in lower concentrations than its parent compounds. However, when favorable conditions for VC formation and accumulation subsist (e.g., Filippini et al., 2016), its occurrence becomes of

paramount concern being a known carcinogen (Bolt, 2005; Kielhorn et al., 2000) with higher mobility in the water and gas phases compared to other CEs (Mackay et al., 2006). Since VC is a gas at ambient temperature, its main exposure route from underground contamination is through the vapor intrusion pathway (Ma et al., 2020). Several authors presented field or lab evidence of aerobic degradation of VC in the vadose zone of sites contaminated by CEs that would decrease the risk of vapor intrusion (e.g., Kurt et al., 2014; Patterson et al., 2013). On the other hand, Knight and Davis (2013) suggested possible anoxic conditions in the vadose zone below impervious slab structures that may reduce such attenuation capacity. Most vapor intrusion guidance documents recommend a multiple-line-of-evidence approach for evaluating vapor intrusion risk (ITRC, 2007; U.S. EPA, 2015), including direct evidence from indoor air or sub-slab sampling and indirect evidence from groundwater and soil gas (McHugh et al., 2017). The potential of phytoscreening for assessing vapor intrusion risk was previously explored for higher chlorinated compounds PCE and TCE. The application showed some advantages compared to classical soil gas and groundwater screening, being less invasive, less resource-intensive, and able to provide concentrations that buffer the typical temporal and spatial variability associated with soil gas samples (Algreen et al., 2015; Burken et al., 2011; Wilson et al., 2017a; Wilson et al., 2017b). In this article, we verified the effectiveness of phytoscreening for detecting shallow underground contamination by VC in two contaminated sites. In both sites, CE plumes with VC are in migration below residential buildings, potentially causing human exposure through vapor intrusion.

2 Study Sites

The two selected sites, namely the “Caretto site” (Ferrara, Emilia-Romagna Region) and the “Bussi site” (Bussi sul Tirino, Pescara, Abruzzo Region) are in different hydrogeological settings which are described in detail in the following Sections 2.1 and 2.2. In both cases, the primary source of CE contamination is located 20 to 40 m up-gradient residential buildings and consists of former dumping sites where by-products from the production of chloromethanes, known as chlorinated pitches or “heavy ends”, were improperly disposed off between the 1960s and the 1970s. Poplar trees of the same species (*Populus nigra*) occur

nearby the primary sources of the two sites and were selected in this research for phytoscreening, being proved particularly effective for the uptake of organic contaminants (Zalesny Jr et al., 2006).

2.1 Caretti site

The Caretti site is a neighborhood located 0.5 km eastward from the historical walls of the city of Ferrara. The hydrostratigraphy at the site is typical of an alluvial lowland (the Po river plain) with unconsolidated sediments forming metric to decametric horizontal alternations of sandy porous aquifers and silty-clayey aquitards (Regione Emilia-Romagna and ENI-AGIP, 1998). The shallowest aquifer was considered in this study. It has its bottom at about 10 m bgs (below ground surface) and is generally overlain by a metric silty-clayey aquitard, locally enriched in organic matter (Fig. 1). The depth to the water table ranges between 1 and 3 m bgs. Recharge is mostly direct from precipitation (Filippini et al., 2015). The aquifer is contaminated with chloroethenes in concentrations up to the order of 100 mg/L (Filippini et al., 2020). The contamination originates from two dumping sites of chlorinated pitches, known as the “Southern Dump” and the “Northern Dump”, corresponding to dismissed clay quarries up to 5 m deep (Fig. 1). The two dumps share the same history and are underlain by the same hydrostratigraphy, resulting in very similar contamination profiles in the surrounding aquifers (see details in the Supplementary Material – “SM” hereafter). Intense dechlorination activity was observed at the site (Nijenhuis et al., 2013), which appears to be favored by peculiar geological, geochemical, and microbial conditions (Filippini et al., 2016; Ghezzi et al., 2021). As a result, daughter products (mainly cis-1,2 dichloroethene – cDCE and VC) prevail over the parent compounds PCE and TCE, with averaged groundwater concentrations in the source areas in the order of 10 mg/L and 0.1 mg/L for the daughter and the parent compounds, respectively.

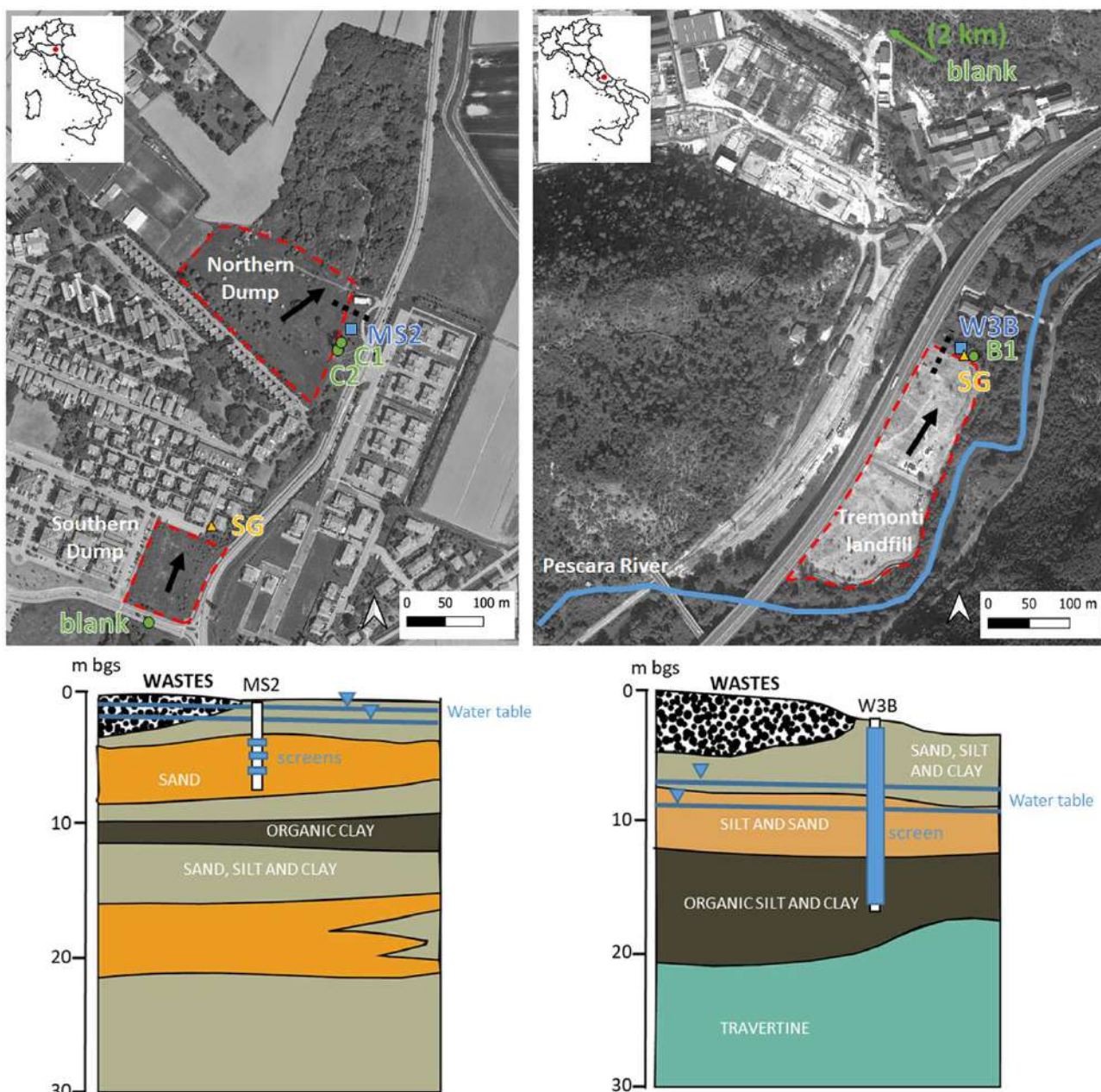


Figure 1. Maps of the Caretti site (left) and Bussi site (right). The primary sources of contamination are bordered with a dashed red line. The black arrows indicate the main groundwater flow direction in the source areas; the green circles indicate sampled trunks; the blue squares indicate groundwater sampling points; the yellow triangles indicate representative soil gas sampling locations (see SM for details on the soil gas surveys). Below each map, a sketch cross-section depicts the hydrostratigraphy of the two sites along the black dotted lines.

2.2 Bussi site

135 The Bussi site is an industrial petrochemical area located near the village of Bussi sul Tirino, 50 km SW from
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136 the city of Pescara, at the upper end of a steep valley incised by the Pescara River, known as the Popoli
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137 gorge. The hydrogeological setting of the valley floor is formed mainly by alluvial macroclastic aquifer
5
138 sediments (gravels and sands) with the local occurrence of fractured/karstified travertine deposits of
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139 lacustrine origin. A non-continuous aquitard cover made of silty-clayey lacustrine deposits overlies the
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140 main aquifer units (Di Curzio et al., 2018; Filippini et al., 2018). The contamination originated from a large
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141 illegal dumping site where chlorinated pitches and other industrial wastes were disposed in the 1970s. The
15
142 dumping site, known as “Tre Monti landfill”, is located along the left bank of the Pescara River (Fig. 1). The
17
143 main hotspot of chloroethene contamination was detected in the NE sector of the landfill, with
20
144 concentrations up to the order of 10 mg/L (Filippini et al., 2018). Here, the shallowest 10 m bgs, of interest
22
145 for this study, are made of a non-continuous silty clayey aquitard layer underlain by a sandy silty aquifer
24
146 unit (Fig. 1). The sandy silty aquifer is recharged directly by precipitation where the aquiclude cover is
27
147 missing, or laterally from the Pescara River. The depth to water table is between 7 and 9 m bgs. Reductive
29
148 dechlorination is less pronounced at the Bussi site compared to the Caretti site due to more oxic conditions.
31
349 Still, concentrations of 1-2 dichloroetene (1,2-DCE) and VC up to 14 mg/L and 2 mg/L, respectively, were
34
350 detected in the NE hotspot of the source area, where a capping was put over the wastes in 2014 as an
36
351 emergency mitigation measure, possibly enhancing geochemical reducing conditions.
38
39

4052

42 3 Methods

44 3.1 Sampling strategy

47 Groundwater and tree trunk samples were collected in the source area of the two sites in three to four
48
49 sampling rounds in different seasonal conditions to analyze the concentration of CEs. One sampling
50
51 location for each site was selected based on (1) the availability of a poplar tree close to an existing
52
53 piezometer and (2) past detection of VC in the shallow groundwater. Blank tree trunk samples were
54
55 collected up-gradient the sources of contamination from trees of the same species (i.e., *Populus nigra*),
56
57 using the same protocols described below for contaminated trunks and following the same temporal
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65

161 schedule. The blank samples were collected before the contaminated ones to avoid cross-contamination of
162 the sampling equipment. The CE concentrations of blank samples were consistently below the detection
163 limit and will not be discussed further.

164 Soil gas samples were also collected at the two sites, in the same location as for the groundwater and tree
165 sampling, or in equivalent locations in terms of hydrostratigraphy and contamination profile.
166 Meteorological factors possibly influencing contaminant uptake and loss from the tree, i.e., air
167 temperature, solar radiation, air humidity, and precipitation, were obtained for the two weeks prior to
168 sampling from the closest available meteorological station. The interval of two weeks prior to sampling was
169 chosen to represent environmental conditions influencing uptake based on previous literature experiences
170 (Ottosen et al., 2018).

172 3.1.1 Caretti site

173 The selected groundwater and tree trunk sampling location is on the eastern fringe of the northern dump.
174 Tree samples were collected in four rounds in May 2019, October 2019, June 2020, and September 2020
175 from two poplar trunks growing a few decimeters apart at the ground level. The two trunks (C1 and C2,
176 hereafter) have a diameter of 59 and 46 cm, respectively, at the sampling height. Following well-
177 established protocols (Trapp et al., 2008; Vroblesky, 2008), duplicate trunk cores of 5 mm in diameter and
178 12 cm long were collected with an increment borer (Haglöf Sweden®) at the height of 1 m above the
179 ground surface (ags) and approximately 10 cm laterally from each other. The duplicate cores were
180 immediately put in 40 mL vials, one filled with 10 mL of methanol and the other with 5 mL of ultrapure
181 water (Milli-Q). The vials were capped with PTFE/Silicone septa and stored at 4°C until analysis. Following
182 Limmer et al. (2013), who analyzed azimuthal variations around tree trunks and observed concentration
183 centroids on the side of the trunk nearest to the most contaminated groundwater, cores were collected
184 from the WNW side of the trunks facing the primary source (i.e., the dump area). In addition to trunk
185 coring, Colorimetric Gas Detector Tubes (“CGDT”; Gastec, AMS® Analytica, model “131L-VC”) were used for
186 expedited field analysis of VC in the trunk gas during the sampling rounds of June and September 2020,

187 following the method UNI EN 1231:1996 (for more details see the “in vivo” sampling method proposed by
1
188 Luchetti and Diligenti, 2014). CGTDs were inserted in the trunk holes immediately after coring, and 100 mL
3
189 of gas were drawn through the tube using a sterile disposable syringe. Two consecutive 50 mL pump
5
190 strokes of 15 s duration were performed, with a resting interval of 45 s between the two. The CGTD
8
191 provides instantaneous colorimetric evidence of VC concentration between 0.2 and 3.0 ppm, assuming a
10
192 total pumping volume of 200 mL. Since only 100 mL were pumped, a correction factor of 2 was applied to
13
193 the observed concentrations.

194 Groundwater samples were collected during the same four sampling rounds of tree coring at 3, 4, and 5 m
17
195 bgs from a multi-screen piezometer a few meters apart from trunks C1 and C2, using a peristaltic pump
20
196 (Model 410, Solinst®). Three 40 mL vials per each depth were filled with groundwater and stored at 4°C
23
197 until analysis. In addition, soil gas data were retrieved from an extensive survey performed at the site
25
198 between 2004 and 2006 (Gargini et al., 2011). Results of the soil gas and groundwater surveys are
28
199 extensively presented in the SM, together with a justification for the choice of soil gas data temporally and
30
200 spatially distant from the primary sampling location.

201 Meteorological data were collected from two stations managed by the Regional Agency for Prevention,
34
202 Environment and Energy (ARPAE), namely “Ferrara Urbana” and “Malborghetto”.

204 3.1.2 Bussi site

205 One poplar tree trunk (“B1” hereafter) of 19 cm diameter, located on the northeastern fringe of the Tre
43
206 Monti landfill, was sampled in three rounds in June 2020, September 2020, and January 2021. Trunk cores
46
207 of 5 mm diameter and 9 cm long were collected at 1 m ags with the same instrumentation of the Caretti
48
208 site in two azimuthal directions around the tree (NE and SW). Cores were put in empty 40 mL vials
50
209 equipped with Headspace Sorbent Pens™ in the cap lid (“HSP” from Entech Instruments; sorbents: Tenax®
53
210 + Carboxen 1000). More precisely, cores were split into three parts of equal length (outer, middle, inner
55
211 section) in the sampling round of June 2020, or two parts (inner and outer section) in September 2020, and
57
212 put in separated vials to assess for radial variability. The core samples were kept frozen until analysis.

213 Additionally, Active Sorbent Pens™ (“ASP” from Entech Instruments; sorbents: Tenax® + Carboxen 1000)
 1
 214 were put in the trunk holes immediately after coring, and trunk gas was sampled by aspiration through the
 3
 215 ASP using a 1 L amber tempered glass bottle equipped with a restrictor valve. The latter acts as a suction
 4
 216 system set at a flow rate of 0.03 L/min (micro-valve and Bottle-Vac™) and can last from 25 to 33 min. After
 5
 217 sampling, the ASPs were placed inside a sleeve to ensure retaining all VOCs and stored at 4°C until lab
 6
 218 analysis. Eventually, GCDTs were used for field detection of VC (as previously described for the Caretti site)
 7
 219 in the sampling rounds of September 2020 and January 2021. Knowing that the occurrence of sap may
 8
 220 decrease the effectiveness of trunk gas analysis, The GCDT sampling was performed on the SW side of the
 9
 221 trunk, which appeared the driest based on previous field evidence. 400 mL of gas were drawn through the
 10
 222 tube using a GV-100 GAS Sampling Pump (Gastech) with four consecutive aspirations of 100 mL each. A
 11
 223 correction factor of 0.5 was applied to refer the observed concentrations to the standard 200 mL volume.
 12
 224 Groundwater was sampled in three rounds in January 2019, June 2020, and September 2020, the last two
 13
 225 being coeval with tree trunk sampling. Samples were collected from a piezometer at 12 m distance from
 14
 226 the tree and screened between 0 and 15 m bgs. Vials of 40 mL volume were filled with a low-flow pump
 15
 227 and stored at 4°C until analysis.
 16
 228 Soil gas was sampled at 10 m distance from the poplar tree during the sampling round of September 2020.
 17
 229 A nesty probe was inserted in the ground down to 2.5 m bgs, and gas was sampled using the same ASP
 18
 230 dispositive used for the trunk gas by applying an incremental sampling through the micro-valve and Bottle-
 19
 231 Vac™ system described above (5 minutes of aspiration and 15of pause) that lasted 2 hours in total. After
 20
 232 sampling, the ASPs were treated as described above for the trunk gas samples.
 21
 233 Results of the soil gas and groundwater surveys are extensively presented in the SM.
 22
 234 Meteorological data were collected from the station “Distretto Chieti” managed by the Regional Agency for
 23
 235 Environmental Protection (ARTA).
 24
 236
 237

3.2 Lab analysis

Compounds PCE, TCE, cDCE, and VC were analyzed in the samples of the Caretti site at the ARPAE lab (district of Ravenna). The trunk samples were analyzed within 24 hours after sampling. Trunk cores in water-filled vials were subject to Purge & Trap extraction (EPA method 5035A, 2002), followed by headspace gas chromatography/mass spectrometry (GC/MS; EPA method 8260C, 2006). When an analyte concentration exceeded the calibration point (0.200 mg/kg), the duplicate core preserved in methanol was analyzed. The extraction in methanol was completed in an ultrasonic bath for 10 min. After diluting 200 µl of extract in 40 ml of ultrapure water, the analysis was carried out by GC/MS. Final concentrations (µg/kg) were reported on a dry wood mass basis. Groundwater samples were analyzed in the same lab following the EPA methods 5030C (2003) and 8260C (2006).

Compounds PCE, TCE, 1,2-DCE, and VC were analyzed in the samples of the Bussi site. Trunk core and gas samples were analyzed by a private certified laboratory within 72 hours after sampling. Trunk cores in HSP vials were subjected to VASE (Vacuum Assisted Sorbent Extraction; EPA method 5021A, 2014) with an extraction cycle of 1 hour up to 35°C. After this, the vial was placed on an aluminum block and chilled in a freezer for 5 min. The analysis was performed with GC/MS (EPA method 8260D, 2018). The use of VASE allowed avoiding solvents for extraction, thus preventing loss of the highly volatile compounds in MS analysis. Final concentrations (µg/kg) were reported on a dry wood mass basis. The ASP gas samples collected from the trunk holes and the soil gas were analyzed with TD-GC/MS following the UNI CEN /TS 13649:2015. Groundwater samples were analyzed at the ARTA lab following the UNI EN ISO 15680:2005 method for VOCs.

3.3 Data analysis

Linear correlation was assessed between tree trunk concentration of CEs and the most plausible influencing factors according to the literature, namely: (1) meteorological factors (precipitation, air temperature, airhumidity, and solar radiation), (2) depth to the water table, and (3) groundwater CE concentration (Vroblesky, 2008). A linear regression model was used to fit the tree concentration of CE versus the above-listed factors, and the coefficient of determination R^2 was calculated when at least three measures were

available. Unfortunately, the statistical significance of the regressions could not be assessed due to the low number of observations (3 to 4). Still, when assuming a linear relationship between the investigated variables, the analysis indicates the type of relationship (direct or inverse) and the relative degree of influence of each factor on trunk concentration trends, with the highest R^2 corresponding to a more prominent influence.

4 Results and Discussion

4.1 Caretti site

4.1.1 Trunk concentration of CEs

CEs were detected in all trunk cores in a total concentration ranging between 545 and 7304 $\mu\text{g}/\text{kg}$ (Tab. 1).

The four analyzed compounds were detected in both trunks, with cDCE showing concentrations 2 to 3 orders of magnitude higher than the others. Cores from trunk C1 provided different CE concentrations than C2 in each sampling round despite both trunks reasonably interact with the same contaminated groundwater. Since the concentration over time of each compound is similar to the total CEs in the same trunk (Fig. 2), only the sum of the four compounds will be discussed hereafter. CEs show similar trends over time in C1 and C2. However, the trend of trunk C2 is more buffered, showing overall lower concentrations and smaller absolute differences between consecutive sampling rounds.

Given that the two trunks are of the same species, are strictly close to each other, and were sampled in the same azimuthal direction facing the source of contamination, the observed dissimilarities may be ascribed to differences in the trunk structure. Starting from the widespread assumption that contaminant transfer up the trunk occurs through active xylem cells following the sap flow pathway, we may speculate that cores collected from trunk C2 contained a higher amount of inactive xylem cells than C1, resulting in lower contaminant concentration in the cores. Differences in the amount of inactive xylem may be due to: (1) natural heterogeneities in the outermost section of the trunk where the sap flow occurs, i.e., the sapwood (e.g., Paudel et al., 2013 observed an irregular distribution of inactive xylem in the sapwood of diffuse-porous trunks), or (2) the smaller diameter of C2 that makes it more likely to reach the innermost sections

of the trunk entirely composed by inactive xylem, i.e., the heartwood, taking into account a constant coring length of 12 cm. Limmer et al. (2014) observed more buffered CE concentration trends in heartwood compared to sapwood. Thus, the higher amount of inactive xylem in cores of C2 may also cause its more buffered trend. Alternatively, the differences between the concentration trends of C1 and C2 may be due to one of the followings: (1) an overall lower transpiration rate in trunk C2 compared to C1, possibly caused by slight differences in exposure to sunlight or a different development of the root systems. Lower transpiration would result in a lower contaminant translocation from the subsurface (e.g., Nietch et al., 1999); (2) soil heterogeneities over a short spatial scale, i.e., the distance between C1 and C2, that may influence the root architecture and the rate of groundwater uptake.

		GW from MLS [ug/L]			Trunk cores [ug/kg]		GCDT [ppm]		Depth to wter table [m bgs]	Air temperature [°C]	Air humidity [%]	Solar radiation [W/m ²]	Rainfall [mm]
		MS2-3	MS2-4	MS2-5	C1	C2	C1	C2					
May 2019	PCE	154.0	13.0	4.4	11.0	3.0			1.6	14.3	76.5	186.3	70.4
	TCE	1129.0	121.0	15.0	74.0	7.0							
	cDCE	23200.0	4500.0	1650.0	5200.0	1160.0							
	VC	7181.0	3550.0	5900.0	33.0	BDL							
	sum of CEs	31664.0	8184.0	7569.4	5318.0	1170.0							
Oct 2019	PCE	23.7	3.3	0.6	9.0	4.0			2.3	17.9	71.1	161.4	28.4
	TCE	284.0	22.0	3.0	62.0	21.0							
	cDCE	3146.0	212.0	28.3	7220.0	1310.0							
	VC	584.0	110.0	1649.0	13.0	3.0							
	sum of CEs	4037.7	347.3	1680.9	7304.0	1338.0							
Jun 2020	PCE	130.0	1.0	0.4	6.5	1.8			1.9	22.1	58.1	291.0	10.6
	TCE	120.0	4.8	1.8	27.9	1.1							
	cDCE	1650.0	96.5	52.5	3150.0	540.0							
	VC	800.0	164.0	2230.0	19.7	1.6	3.0	0.5					
	sum of CEs	2700.0	266.3	2284.7	3204.1	544.5							
Sept 2020	PCE	9.5	4.9	0.7	8.6	4.3			2.3	23.4	60.7	200.6	27.4
	TCE	175.0	28.0	3.3	36.6	7.6							
	cDCE	2116.0	276.0	36.0	5280.0	860.0							
	VC	274.0	119.0	1529.0	BDL	BDL	2.5	1.4					
	sum of CEs	2574.5	427.9	1569.0	5325.2	871.9							

Table 1. CEs concentration and influencing factors at the Caretti site. Concentrations below detection limits are indicated as "BDL". The empty boxes correspond to not performed measurements.

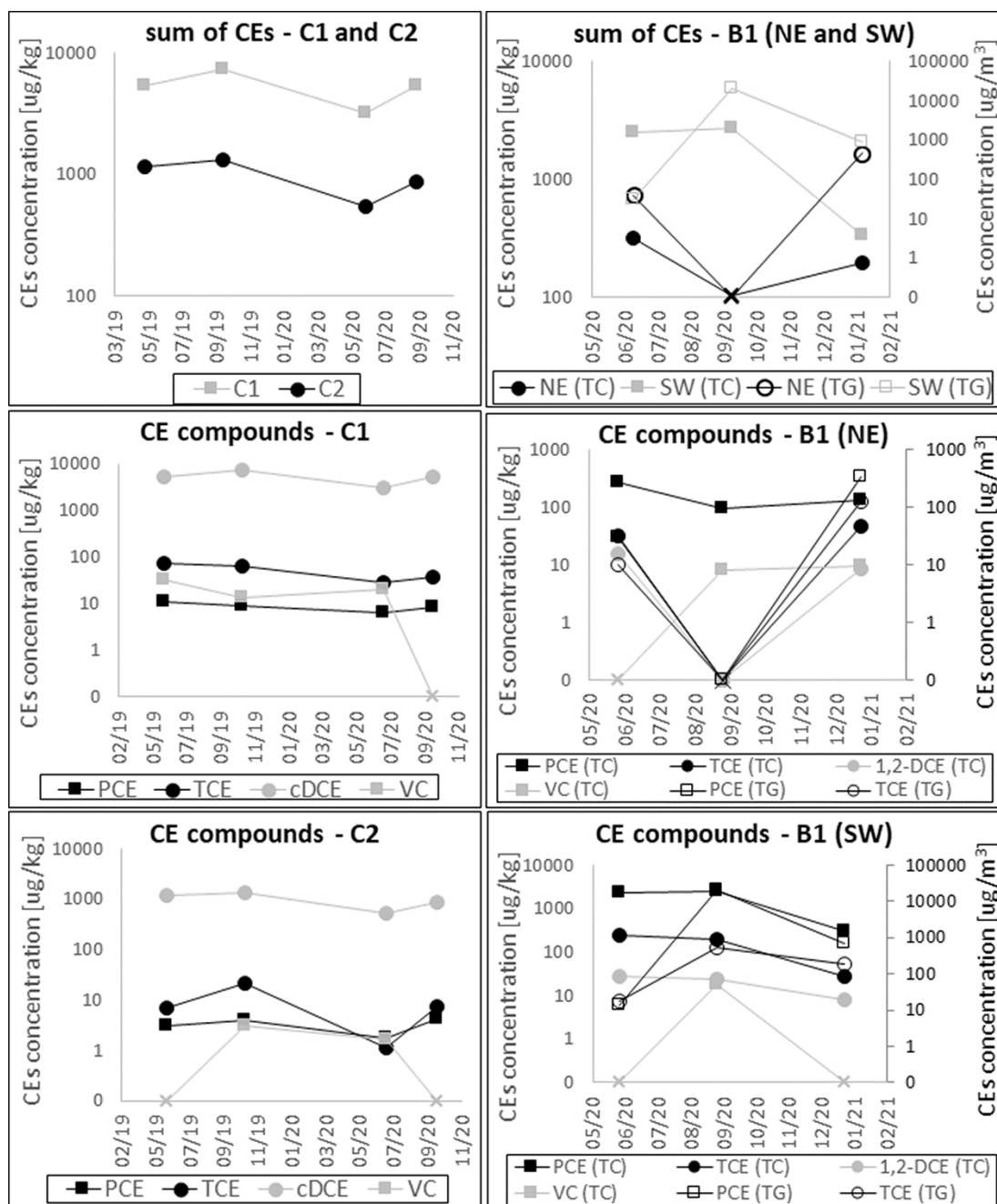


Figure 2. CEs concentration over time in trunks C1 and C2 of the Caretti site (left) and in trunk B1 of the Bussi site both for NE and SW sides (right; “TC” stands for trunk core sample and “TG” stands for trunk gas sample). Concentrations below detection limit are represented with crosses.

4.1.2 Factors influencing CE trunk concentration

4.1.2.1 Meteorological factors and depth to water table

Linear regressions with meteorological factors suggest an inverse relationship between the sum of CEs and solar radiation (R^2 of 0.87 and 0.89 in C1 and C2, respectively; Fig. 3). Such a relationship would be in

contrast with existing literature, e.g., Sorek et al. (2008) and Holm and Rotard (2011), who observed increasing contaminant concentration in higher transpiration periods with transpiration being directly proportional to solar radiation (Pieruschka et al., 2010). The R^2 associated with the single CE compounds is generally lower than 0.6, with few higher values that appear randomly distributed, suggesting that none of the meteorological factors systematically affects the concentration variability in trunks. Of interest is the inverse relationship of VC concentration in trunk C1 with the depth to water table ($R^2 = 1$; Fig. 3), suggesting higher uptake of the compound by tree roots when the water table is shallower, possibly due to decreased effectiveness of aerobic degradation in a thinner unsaturated zone.

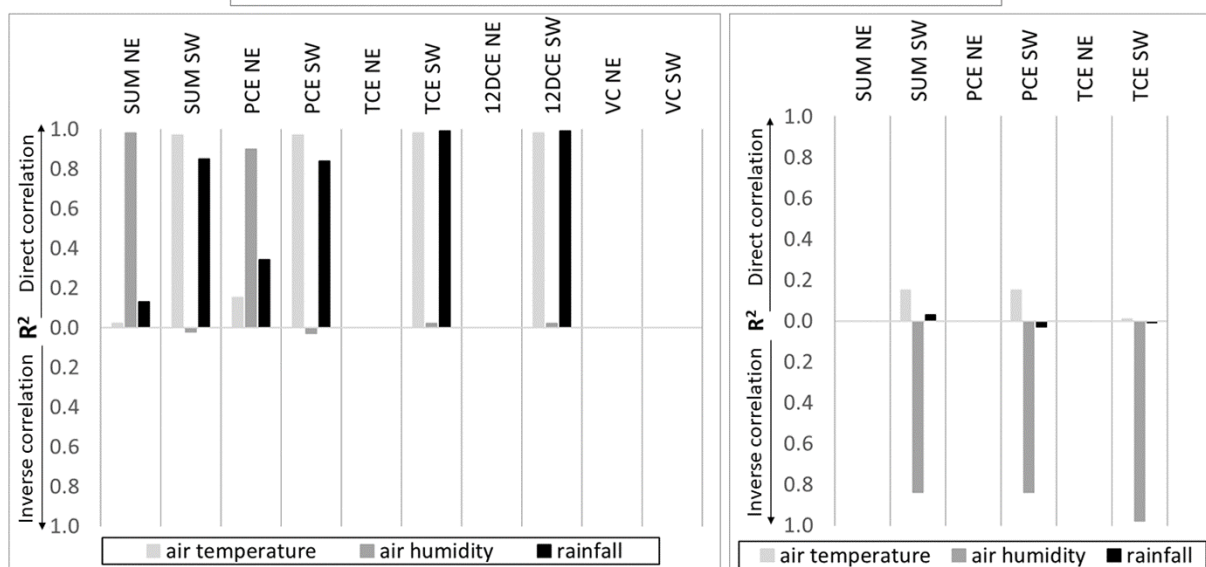
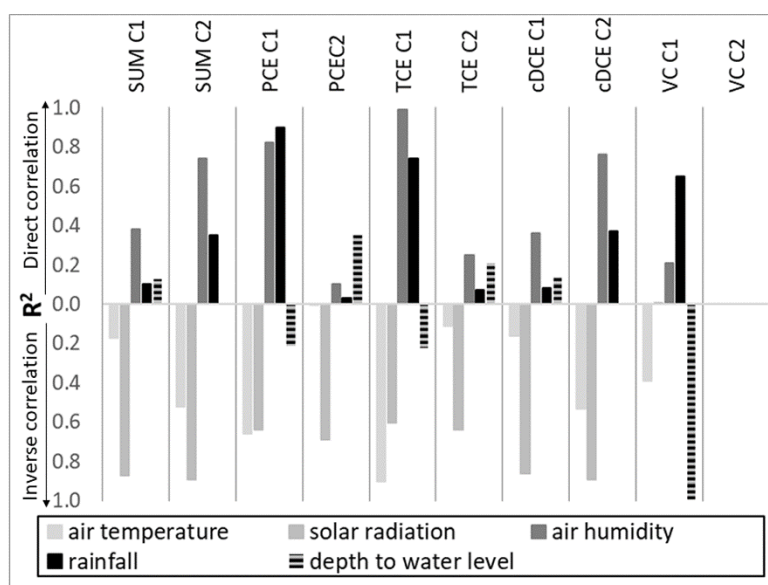


Figure 3. *Coefficients of determination R^2 of CEs concentration in tree trunk vs. influencing factors at the Caretti site (top), at the Bussi site for trunk core samples (bottom left), and at the Bussi site for trunk gas samples (bottom right). The scatter plots used to derive the R^2 are shown in the SM.*

4.1.2.2 CEs concentration in groundwater

Before discussing the linear regressions between the tree trunks and groundwater concentration, it is worth pointing out that the groundwater sampling of May 2019 revealed a significant concentration peak for all CEs, especially in the shallowest sampling screen MC2-3 (see SM). The peak is probably due to heavy rainfalls two weeks before sampling that may have increased dissolution from the residual NAPL phase entrapped in the unsaturated zone. A similar peak was not registered in tree trunks, possibly due to the transpiration of a mix of contaminated groundwater and newly infiltrated water from the heavy precipitations that would have resulted in a dilution of concentration (Vroblesky et al., 2004). For this reason, the sampling of May 2019 was not considered in the linear regression. A direct relationship occurs for the sum of compounds and most of the single compounds, with very similar R^2 in the two trunks (Fig. 4). The R^2 is considerably high in the case of the shallowest groundwater screen MS2-3 (0.94 to 0.99); this may suggest direct uptake of contaminants from the shallow groundwater, which is consistent with the phreatophyte nature of poplars. An exception is an inverse relationship with groundwater PCE from the shallowest screen MS2-3. In this regard, it is worth noting that, differently from all the other groundwater concentration trends, PCE from screen MC2-3 showed an inverse relationship with the depth to water table (see SM): as the water table rises, residual PCE in the unsaturated zone may be intercepted thus increasing the groundwater concentration. The same increase is not seen in trees for one of the following reasons: (1) trees record averaged concentrations both in time and space and may miss the signal of sudden and localized increases in groundwater concentration; (2) the stress induced by groundwater pumping enhances residual PCE remobilization whereas tree roots are not. In the linear regression with shallow groundwater concentration (MC2-3), the CEs show different slopes. Higher slopes suggest higher concentration variability in a tree trunk for a given variability in groundwater

(Fig. 4). Slopes of most compounds are higher in tree C1 than C2, corroborating the above hypothesis of a larger amount of active xylem in the cores or an overall higher transpiration rate (see Section 4.1.1). The highest slopes are that of cDCE. Indeed, the intrinsic properties of the compound make it fit for uptake (relatively high solubility and low molecular weight compared to other CEs; Mackay et al., 2006) and also prone to loss despite its low volatility (low molecular weight and low Kow, which was suggested to be directly related to sorption capacity on wood; Trapp and Miglioranza, 2001) providing high potential for trunk concentration variability. VC was not characterized in terms of R^2 due to data scarcity. The compound has the lowest slopes reflecting an overall attitude to concentration loss in the tree compared to groundwater, likely driven by: (1) high biodegradability in the aerobic unsaturated zone of the site (Patterson et al., 2013), (2) high volatility and low molecular weight that enhance diffusion from the bark (Limmer and Burken, 2016; Ottosen et al., 2018) or loss from the cores during sampling operations.

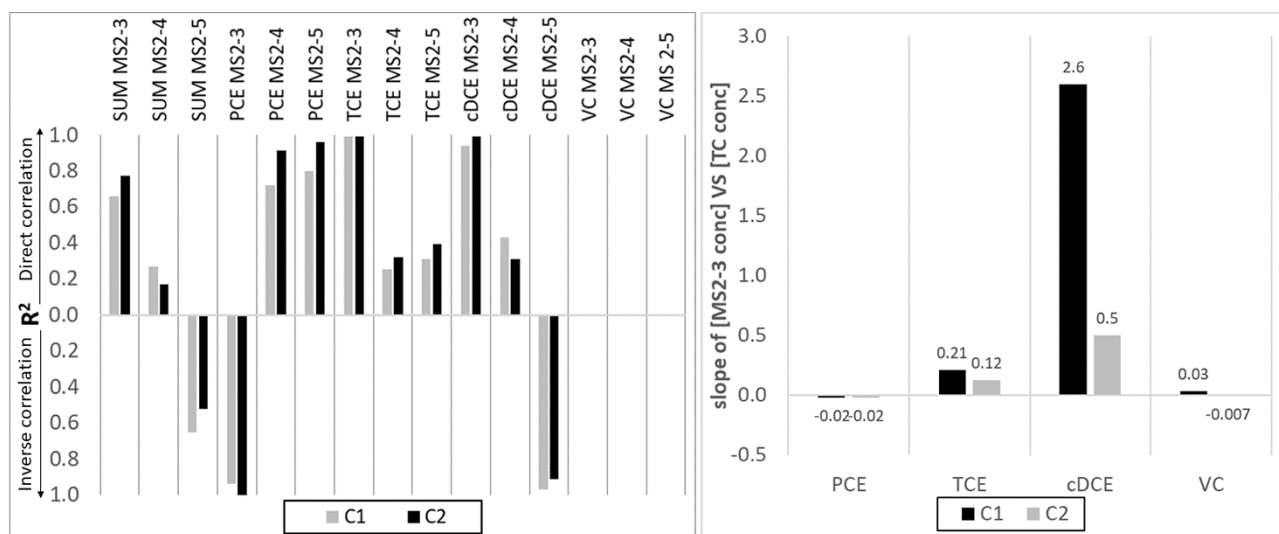


Figure 4. Left: coefficients of correlation R^2 between CEs in tree trunks C1 or C2 of the Caretti site and CEs in groundwater (MS2-3, MS2-4, MS2-5 screened intervals); the scatter plots used to derive the R^2 are shown in the SM. Right: slopes of the linear correlation between CEs concentration in trunks C1 or C2 of the Caretti site and CEs concentration in groundwater from the shallowest screened interval MC2-3.

4.1.3 VC detectability in trunks

VC was detected in 5 out of 8 trunk cores, whereas the other CEs were detected in all cores. The compound was also detected in the four Gas Colorimetric Detector Tubes (sampling of June and September 2020). Overall detectability of VC in trees appears relatively high (63% of core samples and 100% of gas tubes) compared with previous literature reporting sporadic detection only in one case study (Ottosen et al., 2018). High detectability at the Caretti site may be due to: (1) peculiarly high concentration of the compound in shallow groundwater; (2) sampling during the vegetative period (late spring to early autumn) when the highest tree transpiration is expected, whereas no samples were collected during the dormant winter period.

Non-detection in trunk core C2 in May 2019 may be related to the dilution effect of heavy rainfalls preceding the sampling campaign (see SM). In contrast, non-detection in September 2020 in trunks C1 and C2 may be related to the higher depth of the water table, which was inferred to be related to a higher chance of VC degradation before the uptake into trees (see Section 4.1.2.1).

Notably, two GCDT detections (trunks C1 and C2 in September 2020) correspond to non-detections in core samples, suggesting that the expedited field analysis with gas tubes would allow detecting lower VC concentration compared to trunk cores; this may be due to the loss of the volatile compound during sampling, or degradation into the vials, even though the analysis was performed soon after sampling (24 to 72 h). On the other hand, GCDT and trunk core concentration do not always increase or decrease accordingly; this may suggest low quantitative reliability of the CGDT. Further investigations are needed to assess this hypothesis.

4.2 Bussi site

4.2.1 Trunk concentration of CEs

CEs were detected with total concentrations ranging between 103 and 2740 $\mu\text{g}/\text{kg}$ in B1 trunk core samples and between 31 and 20750 $\mu\text{g}/\text{m}^3$ in trunk gas samples (Tab. 2). Higher chlorinated compounds PCE and TCE are the most concentrated in trunks, with averaged concentrations of 928 and 109 $\mu\text{g}/\text{kg}$, respectively,

394 whereas lower chlorinated 1,2-DCE and VC were detected in averaged concentrations of 17 and 12 $\mu\text{g}/\text{kg}$.
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 395 PCE and TCE were also detected in trunk gas samples in averaged concentrations of 4260 and 177 $\mu\text{g}/\text{m}^3$
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 396 whereas 1,2-DCE and VC were never detected, probably due to their relatively low concentration in
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 397 groundwater or due to lower performance of the sorbent materials towards the lower chlorinated
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 398 compounds.
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 399 Within each sampling round, differences were observed in CE concentration from the SW and NE sides of
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 400 the trunk, with systematically higher values in the SW samples, where higher absolute variations between
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 401 sampling rounds were also observed (Fig. 2). Core and gas concentrations show similar temporal trends for
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 402 the same side of the trunk. However, the trends relative to the SW side are not consistent with that of NE,
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 403 with a positive peak in September 2020 at SW that coincides with a negative peak at NE. The dissimilar
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 404 behavior observed in the two azimuthal directions suggests a different response to the variation of
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 405 seasonal factors, likely due to heterogeneities in the root systems feeding the two sides of the trunk.
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 406 Indeed, some tree trunks are characterized by a high sectoriality in xylem transport, meaning that different
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 407 sectors of the root system feed preferentially one side of the trunk due to minimal non-axial flow (Burgess
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 408 and Bleby, 2006). High sectoriality was previously observed in poplars (e.g., Orians et al., 2004). The SW
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 409 side may be preferentially fed by a deeper root system that reaches closer to the contaminated
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 410 groundwater (depth to the water table of 7 to 9 m at this site). Deep roots are expected to be most active
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 411 in dry seasons with high transpiration (McElrone et al., 2004; Pierret et al., 2016), and this would explain
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 412 the higher concentration in summer (June and September 2020 sampling) compared to winter (January
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 413 2021). On the other hand, the NE side may be fed by a shallower root system that is constantly active
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 414 throughout the year but is less effective in collecting deep contaminated groundwater, resulting in lower
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 415 but more stable concentrations over the three sampling rounds.
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 416 Trunk cores collected in June and September 2020 were split radially and analyzed separately, showing
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 417 higher concentrations in the outer and central core sections, except for the SW side in September, which
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 418 provided the highest concentration in the inner cores (Fig. 5). The two different radial trends in the SW side
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 419 during the two sampling rounds could be explained with the model proposed by Limmer et al. (2013)
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suggesting a two steps process of migration of the contaminants inside (“loading” step) and outside (“unloading” step) of the trunk. The first loading step should occur at the beginning of the high transpiration season (sampling round of June), with groundwater contaminants being translocated into the trunk. During this step, the highest concentrations are found in the outer radial sections of the trunk, where most of the axial flow occurs (active xylem cells). Towards the end of the loading step, the contaminants undergo diffusion and partitioning in the trunk tissue (inactive xylem). The second unloading step occurs when transpiration begins to decrease (sampling round of September). In this step, contaminant uptake into the tree is minimized due to the low transpiration; the contaminants are mostly unloaded from the trunk through diffusional loss, causing a decrease in concentration in the outer radial sections closer to the bark. The unloading phase of September is not recorded on the NE side, which shows higher concentrations in the outer trunk sections in both sampling rounds; this is consistent with the abovementioned hypothesis of sectorial xylem transport, with the NE side being fed by shallower roots that are constantly active throughout the year. It is worth noting that 1,2-DCE and VC were almost exclusively detected in the outer core sections irrespectively of trunk side or sampling round, suggesting lower partitioning in the inactive xylem tissue compared to PCE and TCE, the last two being characterized by higher Log K_{ow} (Mackay et al., 2006) that denotes higher aptitude to sorption on wood (Trapp and Miglioranza, 2001).

		GW [ug/L]	Trunk cores [ug/kg]		Trunk gas [ug/m ³]		GCDT [ppm]	Depth to water table [m bgs]	Air temperature [°C]	Air humidity [%]	Rainfall [mm]
		W3B	B1 NE	B1 SW	B1 NE	B1 SW	B1 SW				
Jan 2019	PCE	27640.0						5.6			
	TCE	3922.0									
	12DCE	1492.0									
	VC	241.0									
	sum of CEs	33295.0									
Jun 2020	PCE	10594.0	270.0	2265.0	29.8	13.6		9.2	20.4	69.0	8.3
	TCE	2061.0	31.1	246.4	10.0	17.4					
	12DCE	1274.0	15.2	28.6	BDL	BDL					
	VC	80.1	BDL	BDL	BDL	BDL					
	sum of CEs	14009.1	316.3	2540.0	39.8	31.0					
Sept 2020	PCE	16193.0	94.6	2505.0	BDL	20200.0		9.2	19.1	62.0	7.1
	TCE	2038.0	BDL	192.4	BDL	547.0					
	12DCE	1555.0	BDL	24.0	BDL	BDL					
	VC	197.0	7.9	17.4	BDL	BDL	0.1				
	sum of CEs	19983.0	102.5	2738.7	0.0	20747.0					
Jan 2021	PCE		134.0	297.0	336.1	713.3		9.2	6.8	66.0	4.7
	TCE		47.0	27.5	124.4	185.9					
	12DCE		8.3	8.1	BDL	BDL					
	VC		9.4	BDL	BDL	BDL	0.2				
	sum of CEs		198.7	332.6	460.5	899.2					

Table 2. CEs concentration and influencing factors at the Bussi site. Concentrations below detection limits are indicated as “BDL”. The empty boxes correspond to not performed measurements. Averaged concentrations are reported for trunk cores that where split into multiple subsections (June and September 2020 sampling rounds).

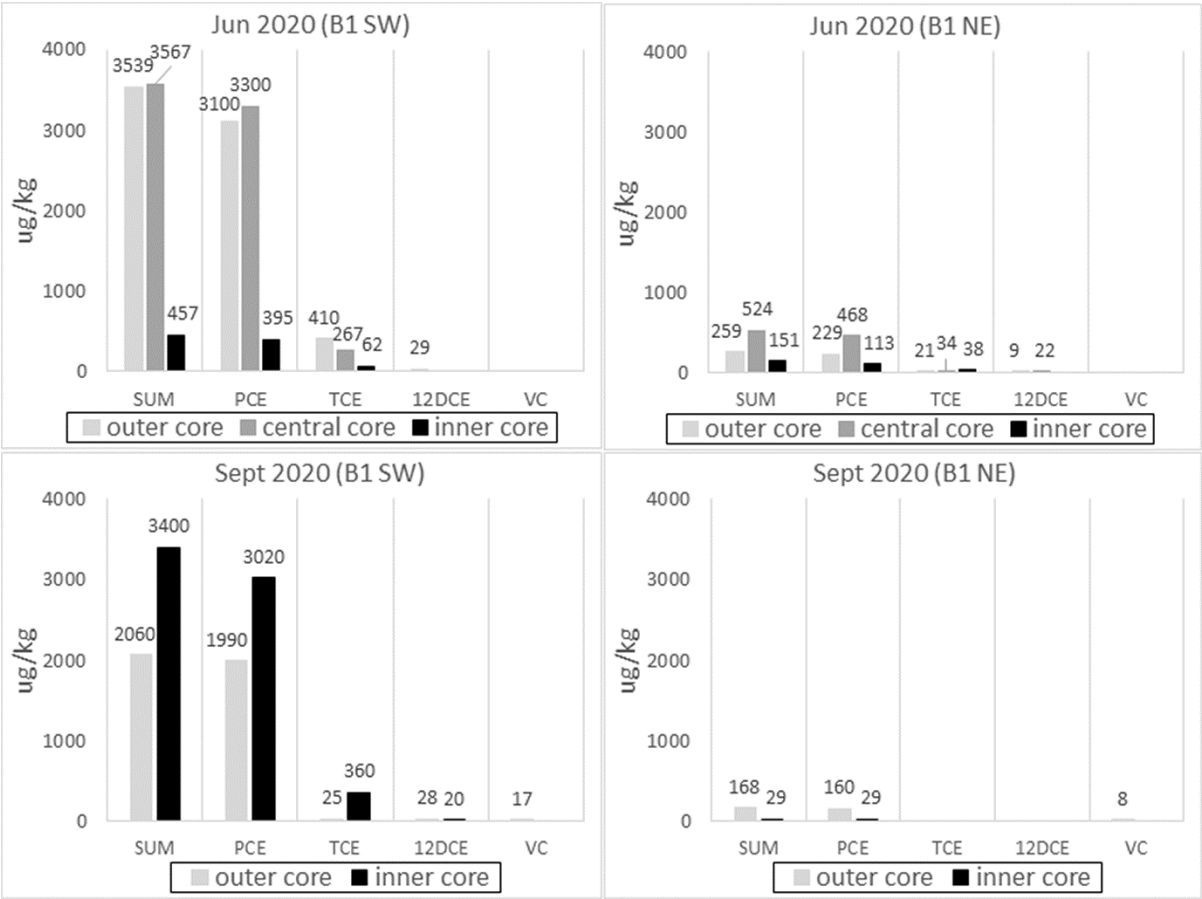


Figure 5. Concentration of CEs in the inner, middle, and outer trunk core sections at the Bussi site.

4.2.2 Factors influencing CE trunk concentration

4.2.2.1 Meteorological factors

The R^2 between trunk concentration and meteorological factors could not be determined in most of the NE side samples due to a paucity of data (less than three observations). Trunk core concentrations from the SW side show the highest R^2 in a direct relationship with air temperature (0.97 to 0.98) and rainfall (0.85 to 0.99), suggesting that at least one of the two factors may drive the concentration variability on this side of

the trunk (Fig. 3). Higher trunk concentration has previously been observed in warmer periods when tree transpiration is higher (Holm and Rotard, 2011; Limmer et al., 2014; Sorek et al., 2008). On the other hand, rainfall events were previously observed to cause a decrease in trunk concentration due to dilution caused by recently infiltrated water in the root zone (Doucette et al., 2003; Vroblesky et al., 2004). Thus, a direct relationship of trunk concentration with air temperature appears the most reasonable. In the case of trunk gas concentration, the highest R^2 is in an inverse relationship with atmospheric air humidity (0.84 to 0.98), most likely reflecting the decreasing performances of the sorbent materials at increasing air water content (e.g., Richter et al., 2020).

4.2.2.2 CEs concentration in groundwater

The R^2 between trunk and groundwater concentrations could not be determined since only two coeval sampling rounds were available. Still, trunk and groundwater concentrations do not always increase or decrease accordingly within the two coeval rounds (Tab. 2), indicating a relatively low influence of groundwater concentration on the trunk; this is expected for a depth of the water table higher than 4 m bgs (i.e., 7 to 9 m bgs at the site) because of decreased interaction between roots and groundwater (Duncan and Brusseau, 2018).

4.2.3 VC detectability in trunks

The detectability of CEs at the Bussi site is comparable to Caretti, with 11 out of 12 samples containing some compounds. On the other hand, VC detectability appears slightly lower, with 3 out of 6 detections in trunk cores (50%) and no detections in trunk gas sampled with ASP. Besides the possible reasons for the low detectability of lower chlorinated compounds mentioned in Section 4.2.1 (i.e., relatively low groundwater concentration and lower performances of ASP), VC availability for uptake may be further decreased due to biodegradation in the 7 to 9 m thick unsaturated zone. On the SW side of the trunk VC was not detected in June 2020, when the temperature was possibly too high prompting loss, and in January 2021, when transpiration was lower due to tree dormancy. Notably, the compound was detected at SW

with GCDT in January 2021, corroborating the hypothesis already advanced at the Caretti site of higher detectability through this expeditious gas analysis. On the NE side, VC was detected in trunk cores in January 2021; this may be because shallow roots, that were inferred to feed this side of the tree, are still active in the low transpiration periods prompting higher trunk concentrations, whereas deep roots feeding the SW side are not. Eventually, VC detection appeared more effective in the outer section of the trunk, likely due to lower sorption capacity on wood compared to other CEs (see Section 4.2.1).

4.3 Conceptual models of VC uptake into trees

VC was detected in tree trunks at both sites despite its absence in the soil gas (see SM). To the best of our knowledge, *in planta* reductive dechlorination of higher chloroethenes down to VC was never observed in the literature. Thus, detecting the compound in trunks implies its uptake from underground contaminated matrices. Two different conceptual models should be considered to explain the tree uptake of VC at the two sites (Fig. 6). At the Caretti site, VC and other CEs were inferred to enter the tree via direct root uptake of shallow contaminated groundwater. For this reason, one cannot draw definitive conclusions on the occurrence and fate of VC in the unsaturated zone based on tree samplings in this setting. Nevertheless, phytoscreening proved more effective than soil gas to screen for the occurrence of the compound in shallow groundwater.

At the Bussi site, uptake of contaminants directly from the groundwater is unlikely due to the higher depth of the water table. Assuming that in such a setting the contaminants may be uptaken by diffusion of gas phase into the roots (Struckhoff et al., 2005), VC would be a good candidate for translocation into trees thanks to its high mobility in aqueous and gas matrices and low molecular weight (Limmer and Burken, 2016), as long as it does not get biodegraded in the unsaturated zone. Indeed, some elements at the sampling site may contribute to decreasing oxygen in the unsaturated zone, thus disfavoring the biodegradation of VC: (1) the occurrence of thin fine-grained organic-rich layers in the shallow critical zone; (2) the likely occurrence of soil contaminated by residual DNAPL (wastes) on the fringe of the landfill; (3) a capping put in place over the wastes in 2014 (Filippini et al., 2018). Thus, the ability of trees to detect VC in

this deep water table setting seems to be related to peculiar anaerobic conditions in the unsaturated zone disfavoring aerobic degradation. The non-detection of VC in the soil gas samples may be due to shallower sampling depth, with soil gases collected at 2.5 m bgs, whereas tree roots can attain higher depths. Moreover, the sorbent pens used for the soil gas sampling may be ineffective in detecting soil gas VC, as it was already inferred when discussing the sampling of the tree cores versus tree gas. In this regard, it is worth noting that VC remained undetected in additional soil gas samples collected with canisters in the surroundings of the B1 tree (see SM).

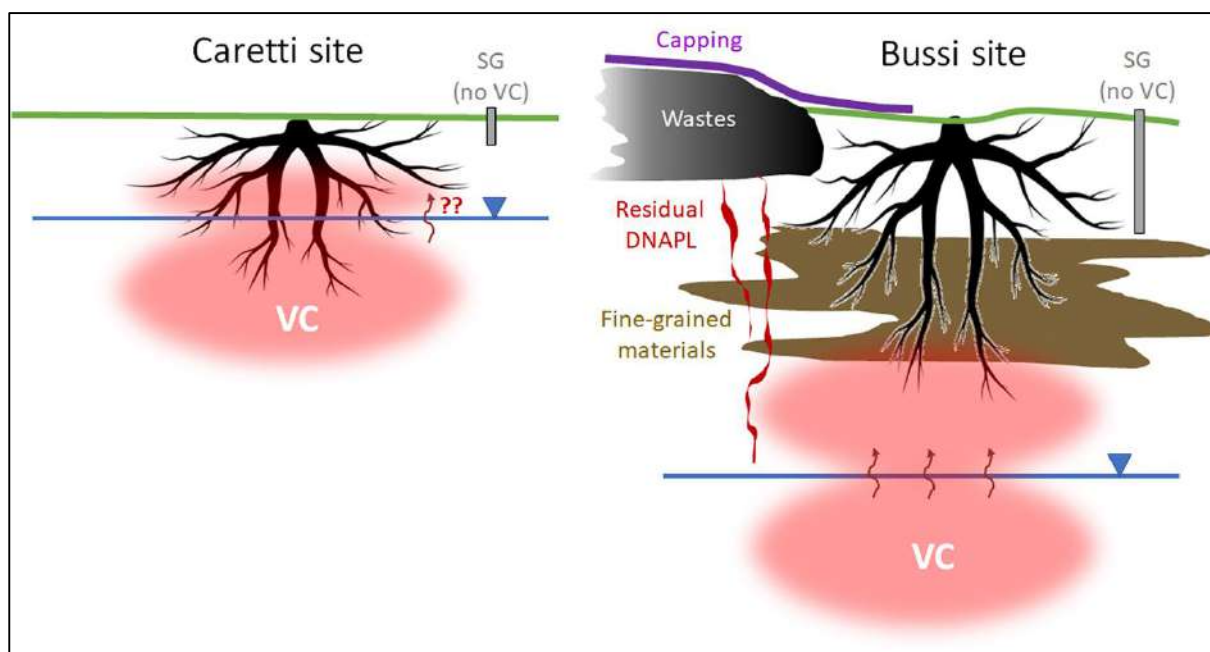


Figure 6. Conceptual models for VC uptake at the Caretti site (left) and the Bussi site (right).

5 Conclusions

The capability of phytoscreening to detect the underground occurrence of VC appears site-specific to some degree and restricted to particular meteorological and tree conditions. Still, poplar trees could screen for the occurrence of VC in the shallow critical zone of two different hydrogeological settings where different trunk sampling and analytical protocols were applied, thus disproving the shared literature assumption of the inefficacy of phytoscreening for detecting the compound.

The new evidence of phytoscreening efficacy towards VC brings implications for assessing vapor intrusion risk. In the two investigated sites, the risk of vapor intrusion in the residential buildings near the contaminant sources was historically excluded based on soil gas screening suggesting the non-occurrence of VC in the unsaturated zone. However, VC detection in soil gas is notoriously troublesome, primarily due to (1) low performances of the sorbent materials toward the compound or (2) spatially and temporally localized losses of soil gas concentration caused e.g. by rain infiltration or changes in barometric pressure (Burken et al., 2011). On the other hand, tree trunks appear to provide a higher “storage capacity” than soil gas for the very volatile VC. Moreover, the broader and deeper sampling area of tree roots compared to that of soil gas sampling rods would ensure buffered concentrations over space and time, as previously observed for higher chlorinated ethenes (e.g., Algreen et al., 2015). Thus, the higher potential of phytoscreening compared to soil gas screening for detecting the occurrence of VC in the shallow critical zone could effectively support preliminary assessments of vapor intrusion risk.

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Detecting vinyl chloride by phytoscreening in the shallow critical zone at sites with potential human exposure

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Abstract

Chlorinated ethene (CE) contaminants are widespread in groundwater, and the occurrence of vinyl chloride (VC), among others, is a well-known issue due to its mobility, persistence, and carcinogenicity. Human exposure to VC may occur through inhalation after soil vapor intrusion into buildings at sites with shallow underground contamination. Soil vapor intrusion risk is traditionally assessed through indoor air and sub-slab sampling (direct evidence), or soil gas and groundwater surveys (indirect evidence). Phytoscreening (sampling and analysis of tree trunk matrices) was proven as an ~~alternative~~ cost-effective ~~alternative~~ technique to indirectly detect shallow underground contamination by higher chlorinated ethenes and subsequent vapor intrusion risk. However, the technique has appeared barely capable to screen for the lower chlorinated VC, likely due to its fugacity and aerobic bio-degradability, with only one literature record to date showing successful detection in trees. We applied phytoscreening at two sites with severe CE contamination nearby residential buildings caused by illegal dumping of chlorinated pitches from

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8 petrochemical productions. The two sites show variable amounts of VC in the shallow groundwater (~~in the~~
9 ~~order of~~ 1e2 to 1e4 µg/L), posing potential sanitary risk issues. Former soil gas surveys ~~at the sites~~ did not
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11 detect VC in the vadose zone. At both sites, we sampled trunk micro-cores and trunk gas from poplar trees
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13 close to contaminated piezometers in different seasons. VC was detected in several instances, disproving
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15 the shared literature assumption of the inefficacy of phytoscreening towards this compound. Factors
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17 influencing the detectability of VC and other CEs in trees were analyzed ~~by means of~~ through linear
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19 regressions. Two different conceptual models were proposed to explain the effective uptake of VC by trees
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21 at the two sites, i.e., direct uptake of contaminated groundwater at the first site, and uptake of VC from an
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23 anoxic vadose zone at the second site. In planta reductive dechlorination of CEs is not expected based on
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25 current literature knowledge. Thus, the detection of VC in trunks would indicate its occurrence in the
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27 shallow underground, suggesting higher screening effectiveness of phytoscreening compared to soil gas-
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29 ~~screening. This~~ has implications for indirect vapor intrusion risk assessment.

30 Key words

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32 phytoscreening, vinyl chloride, chlorinated ethenes, critical zone, vapor intrusion
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35 1 Introduction

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37 Underground contamination by chlorinated ethenes (“CEs” hereafter) is a well-known global environmental
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39 issue. ~~Indeed being~~ these contaminants are widespread in most aquifers underlying industrial and
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41 urbanized areas, persistent in the underground due to their mobility and poor degradability (Olaniran et al.,
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43 2004; Pankow and Cherry, 1996), and toxic/carcinogenic ~~towards to~~ the human health (e.g., Chen and Wu,
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45 2017).

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47 The ability of trees to uptake CEs and thus indirectly reveal their occurrence in the shallow critical zone
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49 (here intended as the thickness between the shallowest groundwater and the ground surface) has been
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51 known for some decades (Vroblesky et al., 1999). The sampling and analysis of trunk matrices (i.e., wood,
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53 gas, or sap) to screen for underground contamination is called phytoscreening (Sorek et al., 2008). ~~Despite~~

Phytoscreening was occasionally proven ~~as an effective tool to detect~~ for detecting several inorganic and organic contaminants such as heavy metals (Algreen et al., 2014), BTEX (Wilson et al., 2013), ~~and~~ PFAS (Gobelius et al., 2017). Nevertheless, the ability of trees to detect CEs was most often studied in the last two decades since these compounds ~~proved to have~~ physicochemical properties ~~that are~~ optimal for plant uptake (Schöftner et al., 2016). Several factors other than underground contaminant concentration have been shown to affect the migration and accumulation of CEs in tree trunks, among which are the plant species (e.g., Duncan et al., 2017; Yung et al., 2017), seasonal physiological dynamics of the plant, ~~and~~ meteorological variables (e.g., Holm and Rotard, 2011; Limmer et al., 2014; Vroblecky, 2008; Wittlingerova et al., 2013), and the depth to water table (Duncan and Brusseau, 2018). The combined effects of such factors cause the variability of contaminant concentration in the trunk either over space (among different trees and radially or azimuthally in the same trunk) or over time. Nevertheless, the literature agrees ~~on~~ with the overall conclusion that the technique is effective ~~to screen~~ in screening for underground contamination of the higher chlorinated compounds tetrachloroethene (PCE), trichloroethene (TCE), and dichloroethene isomers (DCE), on a qualitative up to a semi-quantitative level (Leoncini et al., 2022). On the contrary, the detection of the lower chlorinated compound vinyl chloride (VC) in tree trunks has been rarely documented (Ottosen et al., 2018).

The inefficacy of phytoscreening towards VC has been ascribed to its high fugacity and degradability in an aerobic environment (Larsen et al., 2008; Sorek et al., 2008). Moreover, Gas Chromatography coupled with Electron Capture Detection (GC-ECD) was often used to analyze chlorinated ethenes in the phytoscreening literature (e.g., Doucette et al., 2007; Gopalakrishnan et al., 2007; Shetty et al., 2014; Struckhoff et al., 2005; Wilson et al., 2017b), being this technique less effective for VC detection than Gas Chromatography coupled with Mass Spectrometry (GC-MS). An additional cause of VC under-detection in tree trunks may be the scarcity of phytoscreening applications at sites where the compound occurs in significant underground concentration ~~in the underground~~. VC is known to occur in groundwater ~~and/or in the soil gas~~ as the product of reductive dechlorination of higher chlorinated compounds (Bradley and Chapelle, 2010), although dechlorination down to VC only occurs under peculiar bio-geochemical conditions (Yan et al.,

2021). As a result, at many sites, VC is found in lower concentrations than its parent compounds. However, when favorable conditions for VC formation and accumulation subsist (e.g., Filippini et al., 2016), its occurrence becomes of paramount concern being a known carcinogen (Bolt, 2005; Kielhorn et al., 2000) with higher mobility in the water and gas phases compared to other CEs (Mackay et al., 2006). Since VC is a gas at ambient temperature, its main exposure route from underground contamination is through the vapor intrusion pathway (Ma et al., 2020). Several authors presented field or lab evidence of aerobic degradation of VC in the vadose zone of sites contaminated by CEs that would ~~result in a~~ decrease ~~the~~ risk of vapor intrusion (e.g., Kurt et al., 2014; Patterson et al., 2013). On the other hand, Knight and Davis (2013) suggested possible ~~occurrence of~~ anoxic conditions in the vadose zone below impervious slab structures that may reduce such attenuation capacity. Most vapor intrusion guidance documents recommend a multiple-line-of-evidence approach for evaluating vapor intrusion risk (ITRC, 2007; U.S. EPA, 2015), including direct evidence from indoor air or sub-slab sampling ~~as well as~~ and indirect evidence from groundwater and soil gas (McHugh et al., 2017). The potential of phytoscreening for assessing vapor intrusion risk was previously explored for higher chlorinated compounds PCE and TCE. The application ~~showed~~ showing some advantages ~~with respect~~ compared to classical soil gas and groundwater screening, being less invasive, less resource-intensive, and able to provide concentrations that buffer the typical temporal and spatial variability associated ~~to~~ with soil gas samples (Algreen et al., 2015; Burken et al., 2011; Wilson et al., 2017a; Wilson et al., 2017b).

In this article, we verified the effectiveness of phytoscreening ~~to detect~~ for detecting shallow underground contamination by VC in two contaminated sites. In both sites, CE plumes with VC are in migration below residential buildings, potentially causing human exposure through vapor intrusion. with different hydrogeological settings and depth to the water table. At both sites, namely the “Caretti site” (Ferrara, Emilia-Romagna Region) and the “Bussi site” (Bussi sul Tirino, Pescara, Abruzzo Region), primary sources of CE contamination are located 20 to 40 m up-gradient residential buildings, with plumes in migration below the buildings giving origin to potential human exposure through vapor intrusion. In both cases, the underground contamination originates from former dumping sites where by-products from the production

of chloromethanes, known as chlorinated pitches or “heavy ends”, were improperly disposed between the 1960s and the 1970s. Poplar trees of the same species (*Populus Nigra*) occur nearby the primary sources of contamination of the two sites and were selected in this research for phytoscreening, being proved particularly effective for uptake of organic contaminants (Zalesny Jr et al., 2006). Tree trunk and groundwater samples were collected on a seasonal basis and the concentrations of VC and other CEs were analyzed and compared among different matrices to assess the tree detectability potential. The results of soil-gas surveys performed at the two sites were also considered for discussion.

2 Study Sites

The two selected sites, namely the “Caretti site” (Ferrara, Emilia-Romagna Region) and the “Bussi site” (Bussi sul Tirino, Pescara, Abruzzo Region) are in different hydrogeological settings which are described in detail in the following Sections 2.1 and 2.2. In both cases, the primary source of CE contamination is located 20 to 40 m up-gradient residential buildings and consists of former dumping sites where by-products from the production of chloromethanes, known as chlorinated pitches or “heavy ends”, were improperly disposed off between the 1960s and the 1970s. Poplar trees of the same species (*Populus nigra*) occur nearby the primary sources of the two sites and were selected in this research for phytoscreening, being proved particularly effective for the uptake of organic contaminants (Zalesny Jr et al., 2006).

2.1 Caretti site

The Caretti site is a neighborhood located 0.5 km eastward from the historical walls of the city of Ferrara. The hydrostratigraphy at the site is typical of an alluvial lowland (the Po river plain) with unconsolidated sediments forming metric to decametric horizontal alternations of sandy porous aquifers and silty-clayey aquitards (Regione Emilia-Romagna and ENI-AGIP, 1998). The shallowest aquifer was considered in this study. It has its bottom at about 10 m bgs (below ground surface) and is generally overlain by a metric silty-clayey aquitard, locally enriched in organic matter (Fig. 1). The depth to the water table ranges between 1 and 3 m bgs. Recharge is mostly direct from precipitation (Filippini et al., 2015). The aquifer is

contaminated with chloroethenes in concentrations up to the order of 100 mg/L (Filippini et al., 2020). The contamination originates from two dumping sites of chlorinated pitches, known as the “Southern Dump” and the “Northern Dump”, corresponding to dismissed clay quarries up to 5 m deep (Fig. 1). The two dumps share the same history and are underlain by the same hydrostratigraphy, resulting in very similar contamination profiles in the surrounding aquifers (see [details in the Supplementary Material – “SM” hereafter](#)). Intense dechlorination activity was observed at the site (Nijenhuis et al., 2013), which appears to be favored by peculiar geological, geochemical, and microbial conditions (Filippini et al., 2016; Ghezzi et al., 2021). As a result, daughter products (mainly cis-1,2 dichloroethene – cDCE₇ and VC) prevail over the parent compounds PCE and TCE, with averaged groundwater concentrations in the source areas in the order of 10 mg/L and 0.1 mg/L for the daughter and [the](#) parent compounds, respectively.

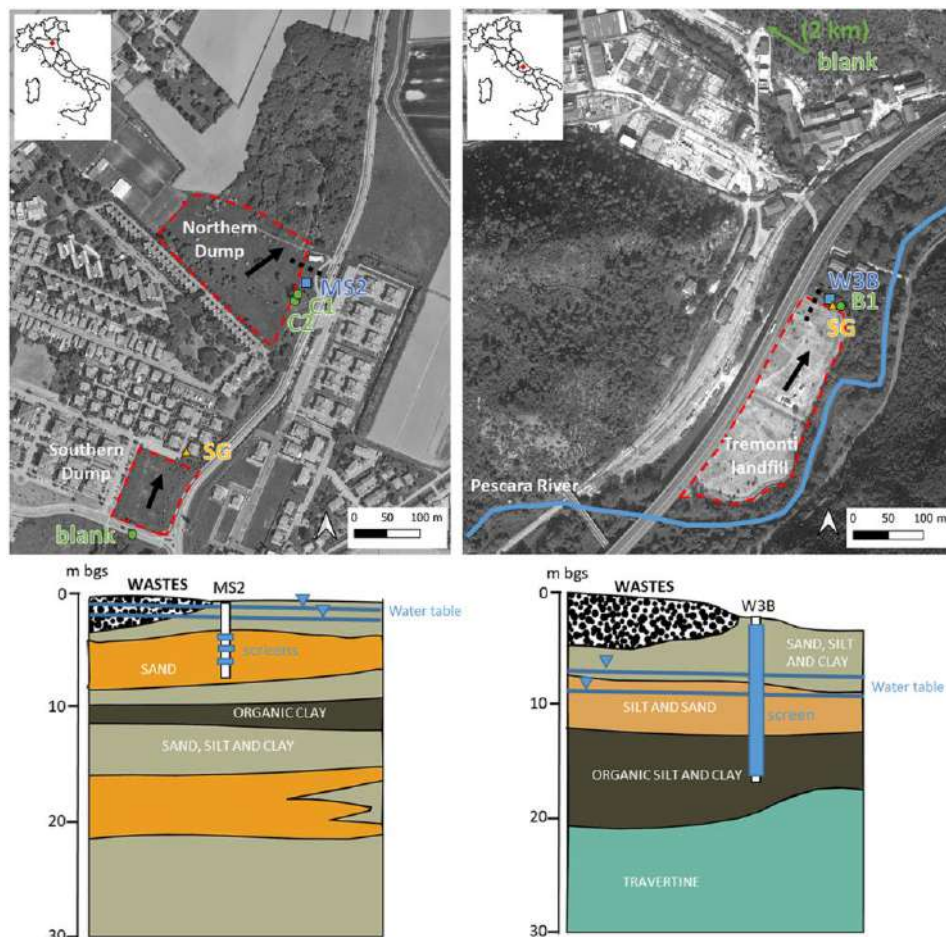


Figure 1. Maps of the Caretti site (left) and Bussi site (right). The primary sources of contamination are bordered with a dashed red line. The black arrows indicate the main groundwater flow direction in the source areas; the green circles indicate sampled trunks; the blue squares indicate groundwater sampling points; the yellow triangles indicate representative soil gas sampling locations (see SM for details on the soil gas surveys). Below each map, a sketch cross-section depicts the hydrostratigraphy ~~at~~ of the two sites along the black dotted lines ~~on the maps~~.

2.2 Bussi site

The Bussi site is an industrial petrochemical area located near the village of Bussi sul Tirino, 50 km SW from the city of Pescara, at the upper end of a steep valley incised by the Pescara River, known as the Popoli gorge. The hydrogeological setting of the valley floor is formed mainly by alluvial macroclastic aquifer sediments (gravels and sands) with the local occurrence of fractured/karstified travertine deposits of lacustrine origin. A non-continuous aquitard cover made of silty-clayey lacustrine deposits overlies the main aquifer units (Di Curzio et al., 2018; Filippini et al., 2018). The contamination originated from a ~~huge~~ large illegal dumping site where chlorinated pitches and other industrial wastes were disposed in the 1970s. The dumping site, known as “Tre Monti landfill”, is located along the left bank of the Pescara River (Fig. 1). ~~A~~The main hotspot of chloroethene contamination was detected in the NE sector of the landfill, with concentrations up to the order of 10 mg/L (Filippini et al., 2018). Here, the shallowest 10 m bgs, of interest for this study, are made of a non-continuous silty clayey aquitard layer underlain by a sandy silty aquifer unit (Fig. 1). The sandy silty aquifer is recharged directly by precipitation where the aquiclude cover is missing, or laterally from the Pescara River. The depth to water table is between 7 and 9 m bgs. Reductive dechlorination is less pronounced at the Bussi site compared to the Caretti site due to more oxic conditions. Still, concentrations of 1,2-dichloroethene (1,2-DCE) and VC up to 14 mg/L and 2 mg/L, respectively, were detected in the NE hotspot of the source area, where a capping was put over the wastes in 2014 as an emergency mitigation measure, ~~possibly may have locally~~ enhanced geochemical reducing conditions.

3 Methods

3.1 Sampling strategy

Groundwater and tree trunk samples were collected in the source area of the two sites in three to four sampling rounds in different seasonal conditions to analyze the concentration of CEs. ~~The One~~ sampling location, ~~one~~ for each site, was selected based on (1) the availability of a poplar tree close to an existing piezometer, and (2) past detection of VC in the shallow groundwater. Blank tree trunk samples were collected up-gradient the sources of contamination from trees of the same species (i.e., *Populus nigra*).

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8 using the same protocols described below for contaminated trunks and following the same temporal
9 schedule. The blank samples were collected before the contaminated ones to avoid cross-contamination of
10 the sampling equipment. The CE concentrations of blank samples were consistently below the detection
11 limit and will not be discussed further.

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15 Soil gas samples were also collected at the two sites, in the same location as for the groundwater and tree
16 sampling, or in ~~in~~ equivalent locations in terms of hydrostratigraphy and contamination profile.

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18 Meteorological factors possibly influencing contaminant uptake and loss from the tree, i.e., air
19 temperature, solar radiation, air humidity, and precipitation, were obtained for the two weeks prior to
20 sampling from the closest available meteorological station. The interval of two weeks prior to sampling was
21 chosen to represent environmental conditions influencing uptake based on previous literature experiences
22 suggesting a residence time of chlorinated compounds of few days to few weeks into the tree trunk
23 (Ottosen et al., 2018).

3.1.1 Caretti site

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32 The selected groundwater and tree trunk sampling location ~~for groundwater and tree trunk sampling~~ is on
33 the eastern fringe of the northern dump. Tree samples were collected in four rounds in May 2019, October
34 2019, June 2020, and September 2020, from two poplar trunks growing a few decimeters apart ~~from each~~
35 ~~other~~ at the ground level. The two trunks (C1 and C2, hereafter) have a diameter of 59 and 46 cm,
36 respectively, at the sampling height. Following well-established protocols (Trapp et al., 2008; Vroblesky,
37 2008), duplicate trunk cores of 5 mm in diameter and 12 cm long were collected with an increment borer
38 (Haglöf Sweden®) at a ~~the~~ height of 1 m above the ground surface (ags) and approximately 10 cm laterally
39 from each other. The duplicate cores were immediately put in 40 mL vials, one filled with 10 mL of
40 methanol and the other ~~one filled~~ with 5 mL of ultrapure water (Milli-Q). The vials were capped with
41 PTFE/Silicone septa and stored at 4°C until analysis. Following Limmer et al. (2013), who analyzed azimuthal
42 variations around tree trunks and observed concentration centroids on the side of the trunk nearest to the
43 most contaminated groundwater, cores were collected from the WNW side of the trunks facing the primary

source (i.e., the dump area). In addition to trunk coring, Colorimetric Gas Detector Tubes ("CGDT"; Gastec, AMS® Analytica, model "131L-VC") were used for ~~an expeditive~~ expedited field analysis of VC in the trunk gas during the sampling rounds of June and September 2020, following the method UNI EN 1231:1996 ~~(for more details see the "in vivo" sampling method proposed by~~ (for more details see the "in vivo" sampling method proposed by Luchetti and Diligenti, 2014). CGDTs were inserted in the trunk ~~drilling~~ holes immediately after coring, and 100 mL of gas were drawn through the tube using a sterile disposable syringe. Two consecutive 50 mL pump strokes of 15 s duration ~~were~~ performed, with a resting interval of 45 s between the two. The CGDT provides instantaneous colorimetric evidence of VC concentration ~~in a range~~ between 0.2 and 3.0 ppm, assuming a total pumping volume of 200 mL. Since only 100 mL were pumped, a correction factor of 2 was applied to the observed concentrations.

Groundwater samples were collected during the same four sampling rounds of tree coring at ~~the depths of~~ 3, 4, and 5 m bgs from a multi-screen piezometer ~~located a few meters apart from trunks C1 and C2, using a~~ presistaltic pump (Model 410, Solinst®). ~~Three 40 mL vials per each depth interval were filled with~~ groundwater and stored at 4°C until analysis. In addition, soil gas data were retrieved from an extensive survey performed at the site between 2004 and 2006 (Gargini et al., 2011). Results of the soil gas and groundwater surveys are extensively presented in the SM, together with a justification for the choice of soil gas data temporally and spatially distant from the primary sampling location.

Meteorological data were collected from two stations managed by the Regional Agency for Prevention, Environment and Energy (ARPAE), namely "Ferrara Urbana" and "Malborghetto".

3.1.2 Bussi site

One poplar tree trunk ("B1" hereafter) of 19 cm diameter, located on the northeastern fringe of the Tre Monti landfill, was sampled in three rounds in June 2020, September 2020, and January 2021. Trunk cores of 5 mm diameter and 9 cm long were collected at 1 m ags with the same instrumentation ~~used at the of~~ the Caretti site, in two azimuthal directions around the tree (NE and SW). Cores were put in empty 40 mL vials equipped with Headspace Sorbent Pens™ in the cap lid ("HSP" from Entech Instruments; sorbents:

Tenax® + Carboxen 1000). More precisely, cores were split into three parts of equal length (outer, middle, inner sections) in the sampling round of June 2020, or in two parts (inner and outer sections) in September 2020, and put in separated vials to assess for radial variability. The ~~vials-core samples~~ were ~~stored-kept at~~ 4°C frozen until analysis.

Additionally, Active Sorbent Pens™ (“ASP” from Entech Instruments; sorbents: Tenax® + Carboxen 1000) were put in the trunk holes immediately after coring, and trunk gas was sampled by aspiration through the ASP using a 1 L amber tempered glass bottle equipped with a restrictor valve. The latter acts as a suction system set at a flow rate of 0.03 L/min (micro-valve and Bottle-Vac™) and can last from 25 to 33 min. After sampling, the ASPs were placed inside a sleeve to ~~assure-ensure~~ retaining of all VOCs, and stored at 4°C until lab analysis. Eventually, GCDTs were used for field detection of VC (as previously described for the Caretti site), in the sampling rounds of September 2020 and January 2021. Knowing that the occurrence of ~~lymph-sap~~ may decrease the effectiveness of trunk gas analysis, The GCDT sampling was performed ~~on~~ the SW side of the trunk, which appeared the ~~most-dry/driest~~ based on previous field evidences. A total of 400 mL of gas were drawn through the tube using a GV-100 GAS Sampling Pump (Gastech) with ~~4-four~~ consecutive aspirations of 100 mL each. A correction factor of 0.5 was applied to ~~bring-back-refer~~ the observed concentrations to the standard 200 mL volume.

Groundwater was sampled in three rounds in January 2019, June 2020, and September 2020, the last two being coeval with tree trunk sampling. Samples were collected from a piezometer ~~located at 12 meters-m~~ ~~apart-distance~~ from the tree and screened ~~from-between~~ 0 to and 15 m bgs. Vials of 40 mL volume were filled with a low-flow pump and stored at 4°C until analysis.

Soil gas was sampled ~~at 10 m distance eters-apart~~ from the poplar tree during the sampling round of September 2020. A nesty probe was inserted in the ground down to 2.5 m bgs, and gas was sampled using the same ASP dispositive used for the trunk gas by applying an incremental sampling through the micro-valve and Bottle-Vac™ system described above (5 minutes of aspiration and 15-of pause) that lasted 2 hours in total. After sampling, the ASPs were treated as described above for the trunk gas samples.

Results of the soil gas and groundwater surveys are extensively presented in the SM.

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258 Meteorological data were collected from the station “Distretto Chieti” managed by the Regional Agency for
259 Environmental Protection (ARTA).
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258 3.2 Lab analysis

259 Compounds PCE, TCE, cDCE, and VC were analyzed in the samples of the Caretti site at the ARPAE lab
260 (district of Ravenna). The trunk samples were analyzed within 24 hours after sampling. Trunk cores in
261 water-filled vials were subject to Purge & Trap extraction (EPA method 5035A, 2002), followed by
262 headspace gas chromatography/mass spectrometry (GC/MS; EPA method 8260C, 2006). When ~~the~~
263 ~~measured concentration of~~ an analyte concentration exceeded the calibration point ~~of calibration~~ (0.200
264 mg/kg), the duplicate core preserved in methanol was analyzed. The extraction in methanol was completed
265 in an ultrasonic bath ~~of for~~ 10 min. After diluting ~~on of~~ 200 µl of extract in 40 ml of ultrapure water, the
266 analysis was carried out by GC/MS. Final concentrations (µg/kg) were reported on a dry wood mass basis.
267 Groundwater samples were analyzed in the same lab following the EPA methods 5030C (2003) and 8260C
268 (2006).
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270 Compounds PCE, TCE, 1,2-DCE, and VC were analyzed in the samples of the Bussi site. Trunk core and gas
271 samples were analyzed by a private certified laboratory within 72 hours after sampling. Trunk cores in
272 HSP vials were subjected to VASE (Vacuum Assisted Sorbent Extraction; EPA method 5021A, 2014) with an
273 extraction cycle of 1 hour up to 35°C. After this, the vial was placed on an aluminum block and chilled in a
274 freezer for 5 min. The analysis was performed with GC/MS (EPA method 8260D, 2018). The use of VASE
275 allowed avoiding solvents for extraction, thus preventing loss of the highly volatile compounds in MS
276 analysis. Final concentrations (µg/kg) were reported on a dry wood mass basis. The ASP gas samples
277 collected from the trunk holes and ~~from~~ the soil gas were analyzed with TD-GC/MS ~~in a private certified~~
278 ~~laboratory~~ following the ~~method~~ UNI CEN /TS 13649:2015. Groundwater samples were analyzed at the
279 ARTA lab following the UNI EN ISO 15680:2005 method for VOCs.
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280 3.3 Data analysis

Linear correlation was assessed between tree trunk concentration of CEs and the most plausible influencing factors according to ~~current the~~ literature, namely: (1) meteorological factors (precipitation, air temperature, ~~air and~~ humidity, ~~and~~ solar radiation), (2) depth to ~~the~~ water table, and (3) groundwater CE concentration (Vroblesky, 2008). A linear regression model was used to fit the tree concentration of CE versus the above-listed factors, and the coefficient of determination R^2 was calculated when at least ~~3~~ ~~three~~ measures were available. ~~Unfortunately, the~~ statistical significance of the regressions could not be assessed due to the low number of observations (3 to 4). Still, when assuming ~~a~~ linear relationship between the investigated variables, the analysis indicates the type of relationship (direct or inverse) and the relative degree of influence of each factor on trunk concentration trends, with the highest R^2 corresponding to ~~a~~ more ~~obvious prominent~~ influence.

4 Results and Discussion

4.1 Caretti site

4.1.1 Trunk concentration of CEs

CEs were detected in all trunk cores in a total concentration ranging between 545 and 7304 $\mu\text{g}/\text{kg}$ (Tab. 1).

The four analyzed compounds were detected in both trunks, with cDCE showing concentration ~~s~~ 2 to 3 orders of magnitude higher than the others. Cores from trunk C1 provided different CE concentration ~~s~~ than C2 in each sampling round despite both trunks reasonably interact with the same contaminated groundwater. Since the concentration ~~trend~~ over time of each compound is similar to ~~that of~~ the total CEs in the same trunk (Fig. 2), only the sum of the four compounds will be discussed hereafter. CEs shows similar trends over time in C1 and C2. However, the trend of trunk C2 is more buffered, showing overall lower concentrations and smaller absolute differences between consecutive sampling rounds.

Given that the two trunks are of the same species, are strictly close to each other, and were sampled in the same azimuthal direction facing the source of contamination, the observed dissimilarities may be ascribed to differences in the trunk structure. Starting from the widespread assumption that contaminant transfer up the trunk occurs through active xylem cells following the sap flow pathway, we may speculate that cores

collected from trunk C2 contained a higher amount of inactive xylem cells ~~compared to~~ than C1, resulting in lower contaminant concentration in the cores. Differences in the amount of inactive xylem may be due to:

(1) natural heterogeneities in the outermost section of the trunk where the sap flow occurs, i.e., the sapwood (e.g., Paudel et al., 2013 observed an irregular distribution of inactive xylem in the sapwood of diffuse-porous trunks), or (2) the smaller diameter of C2 that makes it more likely to reach the innermost sections of the trunk entirely composed by inactive xylem, i.e., the heartwood, taking into account a constant coring length of 12 cm. Limmer et al. (2014) observed more buffered CE concentration trends in heartwood compared to sapwood. Thus, the higher amount of inactive xylem in cores of C2 may also ~~be the~~ cause for cause its more buffered trend. Alternatively, the differences between the concentration trends of C1 and C2 may be due to one of the followings: (1) an overall lower transpiration rate in trunk C2 compared to C1, possibly caused by slight differences in exposure to sunlight or a different development of the root systems. Lower transpiration would result in a lower contaminant translocation from the subsurface (e.g., Nietch et al., 1999); (2) soil heterogeneities over a short spatial scale, i.e., the distance between C1 and C2, that may influence the root architecture and the rate of groundwater uptake.

		GW from MLS [ug/L]			Trunk cores [ug/kg]		GCDT [ppm]		Depth to water table [m bgs]	Air temperature [°C]	Air humidity [%]	Solar radiation [W/m ²]	Rainfall [mm]
		MSZ-3	MSZ-4	MSZ-5	C1	C2	C1	C2					
May 2019	PCE	154.0	13.0	4.4	11.0	3.0			1.6	14.3	76.5	186.3	70.4
	TCE	1129.0	121.0	15.0	74.0	7.0							
	cDCE	23200.0	4500.0	1650.0	5200.0	1160.0							
	VC	7181.0	3550.0	5900.0	33.0	BDL							
	sum of CEs	31664.0	8184.0	7569.4	5318.0	1170.0							
Oct 2019	PCE	23.7	3.3	0.6	9.0	4.0			2.3	17.9	71.1	161.4	28.4
	TCE	284.0	22.0	3.0	62.0	21.0							
	cDCE	3146.0	212.0	28.3	7220.0	1310.0							
	VC	584.0	110.0	1649.0	13.0	3.0							
	sum of CEs	4037.7	347.3	1680.9	7304.0	1338.0							
Jun 2020	PCE	130.0	1.0	0.4	6.5	1.8			1.9	22.1	58.1	291.0	10.6
	TCE	120.0	4.8	1.8	27.9	1.1							
	cDCE	1650.0	96.5	52.5	3150.0	540.0							
	VC	800.0	164.0	2230.0	19.7	1.6	3.0	0.5					
	sum of CEs	2700.0	266.3	2284.7	3204.1	544.5							
Sept 2020	PCE	9.5	4.9	0.7	8.6	4.3			2.3	23.4	60.7	200.6	27.4
	TCE	175.0	28.0	3.3	36.6	7.6							
	cDCE	2116.0	276.0	36.0	5280.0	860.0							
	VC	274.0	119.0	1529.0	BDL	BDL	2.5	1.4					
	sum of CEs	2574.5	427.9	1569.0	5325.2	871.9							

Table 1. CEs concentration and influencing factors at the Caretti site. Concentrations below detection limits are indicated as "BDL". The empty boxes correspond to not performed measurements.

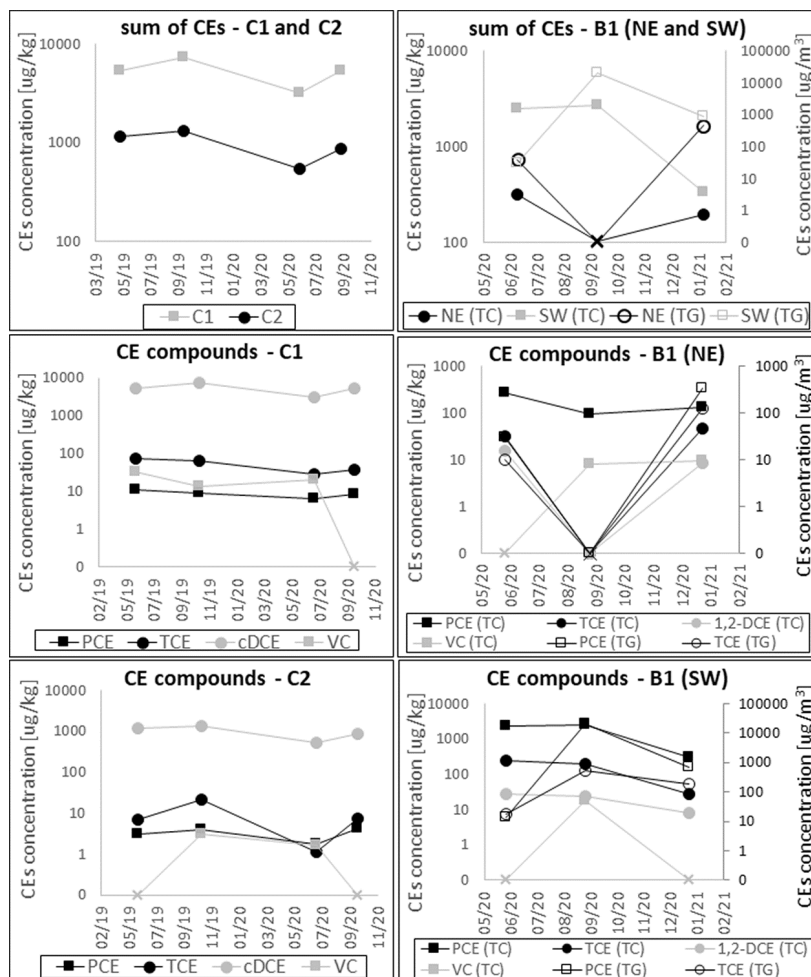


Figure 2. CEs concentration over time in trunks C1 and C2 of the Caretti site (left) and in trunk B1 of the Bussi site both for NE and SW sides (right; "TC" stands for trunk core sample and "TG" stands for trunk gas sample). Concentrations below detection limit are represented with crosses.

4.1.2 Factors influencing CE trunk concentration

4.1.2.1 Meteorological factors and depth to water table

Linear regressions with meteorological factors suggest an inverse relationship between the sum of CEs and solar radiation (R^2 of 0.87 and 0.89 in C1 and C2, respectively; Fig. 3). Such a relationship would be in

contrast with existing literature, e.g., Sorek et al. (2008) and Holm and Rotard (2011), which-who observed increasing contaminant concentration in higher transpiration periods with transpiration being directly proportional to solar radiation (Pieruschka et al., 2010). The R^2 associated with the single CE compounds is generally lower than 0.6, with few higher values that appear randomly distributed, suggesting that none of the meteorological factors systematically affects the concentration variability in trunks.

Of interest is the inverse relationship of VC concentration in trunk C1 with the depth to water table ($R^2 = 1$; Fig. 3), suggesting higher uptake of the compound by tree roots when the water table is shallower, possibly due to decreased effectiveness of aerobic degradation in a thinner unsaturated zone.

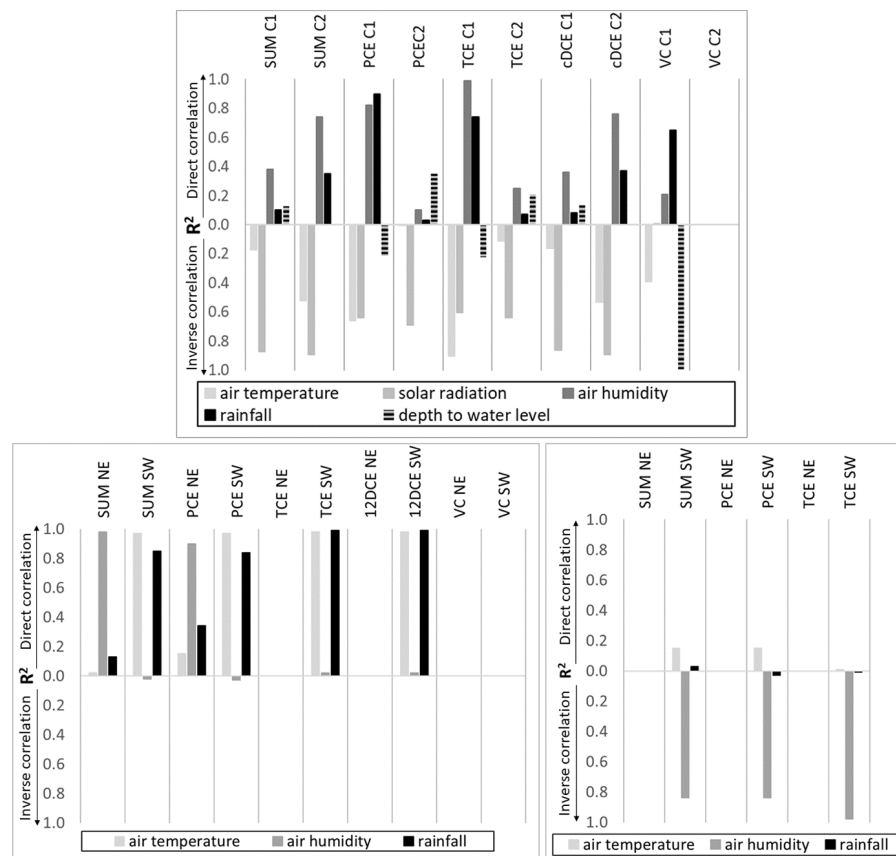


Figure 3. Coefficients of determination R^2 of CEs concentration in tree trunk vs. influencing factors at the Caretti site (top), at the Bussi site for trunk core samples (bottom left), and at the Bussi site for trunk gas samples (bottom right). The scatter plots used to derive the R^2 are shown in the SM. Negative values of R^2 indicate an inverse correlation.

4.1.2.2 CEs concentration in groundwater

Before discussing the linear regressions between the tree trunks and groundwater concentration, it is worth pointing out that the groundwater sampling of May 2019 revealed a significant concentration peak for all CEs, especially in the shallowest sampling screen MC2-3 (see SM). The peak is probably due to heavy rainfalls ~~in the~~ two weeks ~~prior to before~~ sampling that may have increased dissolution from the residual NAPL phase entrapped in the unsaturated zone. A similar peak was not registered in tree trunks, possibly due to the transpiration of a mix of contaminated groundwater and newly infiltrated water from the heavy precipitations that would have resulted in a dilution of concentration (Vroblesky et al., 2004). For this reason, the sampling of May 2019 was not considered in the linear regression. A direct relationship occurs for the sum of compounds and most of the single compounds, with very similar R^2 in the two trunks (Fig. 4). The R^2 is especially considerably high in the case of the shallowest groundwater screen MS2-3 (0.94 to 0.99); this may suggest direct uptake of contaminants from the shallow groundwater, which is consistent with the phreatophyte nature of poplars~~would be consistent with the conclusion of Duncan and Brusseau (2018) of direct groundwater tapping by roots in the case of water tables shallower than 4 m bgs.~~ An exception is the an inverse relationship with groundwater PCE from the shallowest screen MS2-3. In this regard, it is worth noting that, differently from all the other groundwater concentration trends, PCE from screen MC2-3 showed an inverse relationship with the depth to water table (see SM): as the water table rises, residual PCE in the unsaturated zone may be intercepted , resulting in an increase of~~thus increasing~~ the groundwater concentration. The same increase is not seen in trees for one of the following reasons: (1) trees record averaged concentrations both in time and space and may miss the signal of sudden and ~~or~~

localized increases in groundwater concentration; (2) the stress induced by groundwater pumping enhances residual PCE remobilization whereas tree roots are not.

In the linear regression with shallow groundwater concentration (MC2-3), the CEs show different slopes, with higher slopes suggesting higher concentration variability in a tree trunk for a given variability in groundwater (Fig. 4). Slopes of most compounds are higher in tree C1 compared to C2, corroborating the above hypothesis of a larger amount of active xylem in the cores or an overall higher transpiration rate (see Section 4.1.1). The highest slopes are that of cDCE. Indeed, the intrinsic properties of the compound make it fit for uptake (relatively high solubility and low molecular weight compared to other CEs; Mackay et al., 2006) and also prone to loss despite its low volatility (low molecular weight and low Kow, which was suggested to be directly related to sorption capacity on wood; Trapp and Miglioranza, 2001) providing high potential for trunk concentration variability. VC, that was not characterized in terms of R^2 due to data scarcity. The compound has the lowest slopes reflecting an overall attitude to concentration loss in the tree compared to groundwater, likely driven by: (1) high biodegradability in the aerobic unsaturated zone of the site (Patterson et al., 2013), (2) high volatility and low molecular weight that enhance diffusion from the bark (Limmer and Burken, 2016; Ottosen et al., 2018) or loss from the cores during sampling operations.

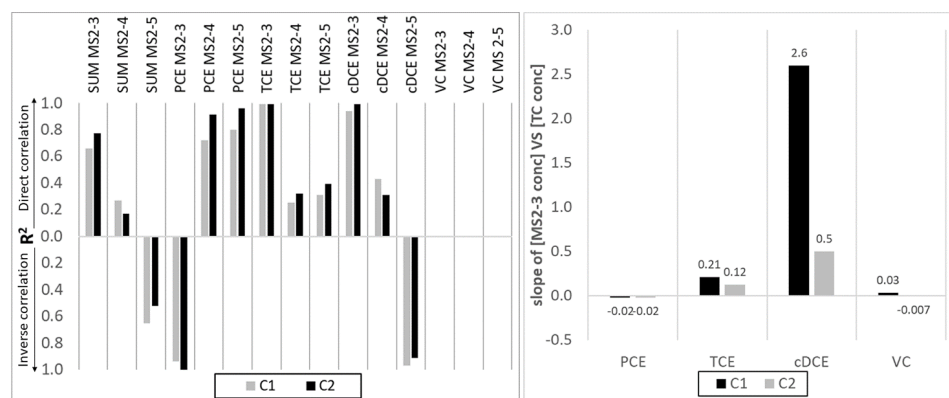


Figure 4. Left: coefficients of correlation R^2 between the sum of CEs in tree trunks C1 or C2 of the Caretti site, and the sum of CEs in groundwater (MS2-3, MS2-4, MS2-5 screened intervals); negative values of R^2

~~indicate an inverse correlation; the scatter plots used to derive the R^2 are shown in the SM. Right: slopes of the linear correlation between CEs concentration in trunks C1 or C2 of the Caretti site and CEs concentration in groundwater from the shallowest screened interval MC2-3.~~

4.1.3 VC detectability in trunks

VC was detected in 5 out of 8 trunk cores, whereas the other CEs were detected in all cores. The compound was also detected in the ~~four~~ 4 gas colorimetric ~~Detector~~ tubes (sampling of June and September 2020). Overall detectability of VC in trees appears ~~quite relatively~~ quite high (63% of core samples and 100% of gas tubes) ~~when~~ compared with previous literature reporting ~~none or very rare sporadic~~ detection only in one case study (Ottosen et al., 2018). High detectability at the Caretti site may be due to: (1) peculiarly high concentration of the compound in shallow groundwater; (2) sampling during the vegetative period (late spring to early autumn) when the highest tree transpiration is expected, whereas no samples were collected during the dormant winter period.

~~It is noteworthy that two GCDT detections (trunks C1 and C2 in September 2020) correspond to non-detections in core samples suggesting that the expeditious field analysis with gas tubes appears to catch lower VC concentration compared to trunk cores. This may be due to the loss of the volatile compound from cores during field sampling or later up to lab analysis.~~

Non-detection in trunk core C2 in May 2019 may be related to the dilution effect of heavy rainfalls preceding the sampling campaign (see SM). ~~In contrast, whereas~~ non-detection in September 2020 in trunks C1 and C2 may be related to the higher depth ~~to of the~~ water table, which was inferred to be related to a higher chance of VC degradation before the uptake into trees (see Section 4.1.2.1).

Notably, two GCDT detections (trunks C1 and C2 in September 2020) correspond to non-detections in core samples, suggesting that the expedited field analysis with gas tubes would allow detecting lower VC concentration compared to trunk cores; this may be due to the loss of the volatile compound during sampling, or degradation into the vials, even though the analysis was performed soon after sampling (24 to 72 h). On the other hand, GCDT and trunk core concentration do not always increase or decrease

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8 accordingly; this may suggest low quantitative reliability of the CGDT. Further investigations are needed to
9 assess this hypothesis.
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13 4.2 Bussi site

14 4.2.1 Trunk concentration of CEs

15 CEs were detected with total concentrations ranging between 103 and 2740 µg/kg in B1 trunk core samples
16 and between 31 and 20750 µg/m³ in trunk gas samples (Tab. 2). Higher chlorinated compounds PCE and
17 TCE are the most concentrated in tree-trunks, with averaged concentrations of 928 and 109 µg/kg,
18 respectively, whereas lower chlorinated 1,2-DCE and VC were detected in averaged concentrations of 17
19 and 12 µg/kg. PCE and TCE were also detected in trunk gas samples in averaged concentrations of 4260 and
20 177 µg/m³ whereas 1,2-DCE and VC were never detected, probably due to their relatively low
21 concentration in groundwater or due to lower performance of the sorbent materials towards the lower
22 chlorinated compounds.
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25 Within each sampling round, differences were observed in CE concentration from the SW and NE sides of
26 the trunk, with systematically higher values in the SW samples, where higher absolute variations between
27 sampling rounds were also observed (Fig. 2). Core and gas concentrations show similar temporal trends for
28 the same side of the trunk. However, the trends relative to the SW side are not consistent with that of NE,
29 with a positive peak in September 2020 at SW that coincides with a negative peak at NE. The dissimilar
30 behavior observed in the two azimuthal directions suggests a different response to the variation of
31 seasonal factors, likely due to heterogeneities in the root systems feeding the two sides of the trunk.
32 Indeed, some tree trunks are characterized by a high sectoriality in xylem transport, meaning that different
33 sectors of the root system feed preferentially one side of the trunk due to minimal non-axial flow (Burgess
34 and Bleby, 2006). High sectoriality was previously observed in poplars (e.g., Orians et al., 2004). The SW
35 side may be preferentially fed by a deeper root system that reaches closer to the contaminated
36 groundwater (depth to the water table of 7 to 9 m at this site). Deep roots are expected to be most active
37 in dry seasons with high transpiration (McElrone et al., 2004; Pierret et al., 2016), and this would explain
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the higher concentration in summer (June and September 2020 sampling) compared to winter (January 2021). On the other hand, the NE side may be fed by a shallower root system that is constantly active throughout the year but is less effective in collecting deep contaminated groundwater, resulting in lower but more stable concentrations over the three sampling rounds.

Trunk cores collected in June and September 2020 were split radially and analyzed separately, showing ~~overall~~ higher concentrations in the outer and central core sections, except for the SW side in September, which provided the highest concentration in the inner cores (Fig. 5). The two different radial trends in the SW side during the two sampling rounds could be explained with the model proposed by Limmer et al. (2013) suggesting a two steps process of migration of the contaminants inside (“loading” step) and outside (“unloading” step) of the trunk. The first loading step should occur at the beginning of the high transpiration season (sampling round of June), with groundwater contaminants being translocated into the trunk. During this step, the highest concentrations are found in the outer radial sections of the trunk, where most of the axial flow occurs (active xylem cells). Towards the end of the loading step, the contaminants undergo diffusion and partitioning in the trunk tissue (inactive xylem). The second unloading step occurs when transpiration begins to decrease (sampling round of September). ~~During In~~ this step, contaminant uptake into the tree is minimized due to the low transpiration ~~and~~, the contaminants are mostly unloaded from the trunk through diffusional loss, causing a decrease in concentration in the outer radial sections ~~that~~ ~~are~~ closer to the bark. The unloading phase of September is not recorded on the NE side, which shows higher concentrations in the outer trunk sections in both sampling rounds. ~~This~~ is consistent with the abovementioned hypothesis of sectorial xylem transport, with the NE side being fed by shallower roots that are constantly active throughout the year. It is worth noting that 1,2-DCE and VC were almost exclusively detected in the outer core sections irrespectively of trunk side or sampling round, suggesting lower partitioning in the inactive xylem tissue compared to PCE and TCE, the last two being characterized by higher Log K_{ow} (Mackay et al., 2006) that denotes higher aptitude to sorption on wood (Trapp and Miglioranza, 2001).

		GW [ug/L]	Trunk cores [ug/kg]		Trunk gas [ug/m ³]		GCDT [ppm]	Depth to water table [m bgs]	Air temperature [°C]	Air humidity [%]	Rainfall [mm]
		W3B	B1 NE	B1 SW	B1 NE	B1 SW	B1 SW				
Jan 2019	PCE	27640.0						5.6			
	TCE	3922.0									
	12DCE	1492.0									
	VC	241.0									
	sum of CEs	33295.0									
Jun 2020	PCE	10594.0	270.0	2265.0	29.8	13.6		9.2	20.4	69.0	8.3
	TCE	2061.0	31.1	246.4	10.0	17.4					
	12DCE	1274.0	15.2	28.6	BDL	BDL					
	VC	80.1	BDL	BDL	BDL	BDL					
	sum of CEs	14009.1	316.3	2540.0	39.8	31.0					
Sept 2020	PCE	16193.0	94.6	2505.0	BDL	20200.0		9.2	19.1	62.0	7.1
	TCE	2038.0	BDL	192.4	BDL	547.0					
	12DCE	1555.0	BDL	24.0	BDL	BDL					
	VC	197.0	7.9	17.4	BDL	BDL	0.1				
	sum of CEs	19983.0	102.5	2738.7	0.0	20747.0					
Jan 2021	PCE		134.0	297.0	336.1	713.3		9.2	6.8	66.0	4.7
	TCE		47.0	27.5	124.4	185.9					
	12DCE		8.3	8.1	BDL	BDL					
	VC		9.4	BDL	BDL	BDL	0.2				
	sum of CEs		198.7	332.6	460.5	899.2					

Table 2. CEs concentration and influencing factors at the Bussi site. Concentrations below detection limits are indicated as "BDL". The empty boxes correspond to not performed measurements. Averaged concentrations are reported for trunk cores that where split into multiple subsections (June and September 2020 sampling rounds).

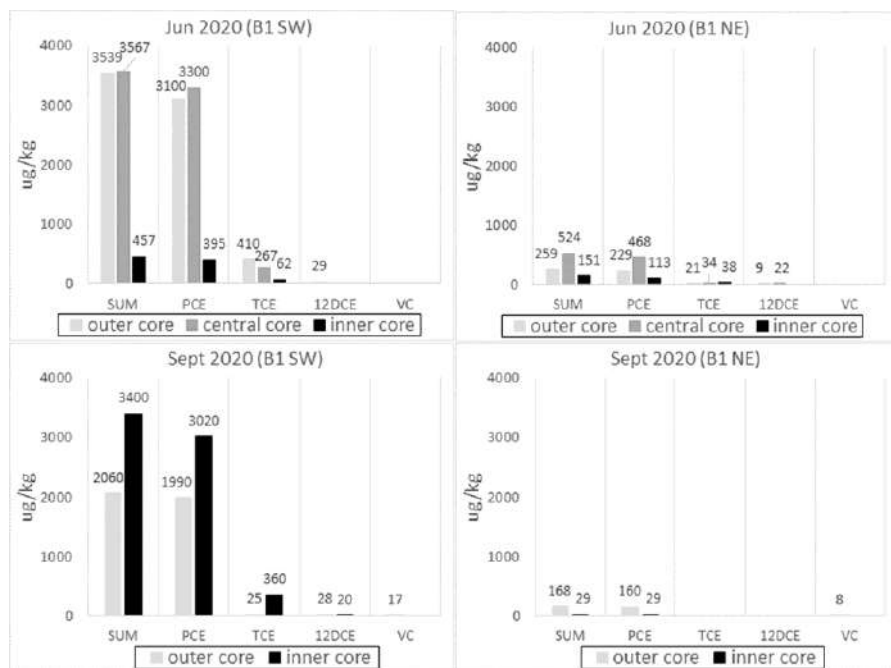


Figure 5. Concentration of CEs in the inner, middle, and outer trunk core sections at the Bussi site.

4.2.2 Factors influencing CE trunk concentration

4.2.2.1 Meteorological factors

The R^2 between trunk concentration and meteorological factors could not be determined in most of the NE side samples due to a paucity of data (less than three observations). Trunk core concentrations from the SW side show the highest R^2 in a direct relationship with air temperature (0.97 to 0.98) and rainfall (0.85 to 0.99), suggesting that at least one of the two factors may drive the concentration variability on this side of the trunk (Fig. 3). Higher trunk concentration has previously been observed in warmer periods when tree transpiration is higher (Holm and Rotard, 2011; Limmer et al., 2014; Sorek et al., 2008). On the other hand, rainfall events were previously observed to cause a decrease in trunk concentration due to dilution caused by recently infiltrated water in the root zone (Doucette et al., 2003; Vroblesky et al., 2004). Thus, a direct relationship of trunk concentration with air temperature appears the most reasonable. In the case of trunk gas concentration, the highest R^2 is in an inverse relationship with atmospheric air humidity (0.84 to 0.98), most likely reflecting the decreasing performances of the sorbent materials at increasing air water content (e.g., Richter et al., 2020).

4.2.2.2 CEs concentration in groundwater

The R^2 between trunk and groundwater concentrations could not be determined since only two coeval sampling rounds were available. Still, within the two coeval rounds, trunk and groundwater concentrations do not always increase or decrease accordingly within the two coeval rounds (Tab. 2), suggesting indicating a rather relatively low influence of groundwater concentration on the trunk, which this is expected in the case of a depth to of the water table higher than 4 m bgs (i.e., 7 to 9 m bgs at the site) due to decreased interaction between roots and groundwater (Duncan and Brusseau, 2018).

4.2.3 VC detectability in trunks

The detectability of CEs at the Bussi site is comparable ~~to that of~~ to Caretti, with 11 out of 12 samples containing some ~~of the~~ compounds. On the other hand, VC detectability appears slightly lower, with 3 out of 6 detections in trunk cores (50%) and no detections in trunk gas sampled with ASP. Besides the possible reasons for the low detectability of lower chlorinated compounds mentioned in Section 4.2.1 (i.e., relatively low groundwater concentration and lower performances of ASP), VC availability for uptake may be further decreased due to biodegradation in the 7 to 9 m thick unsaturated zone. On the SW side of the trunk VC was not detected in June 2020, when the temperature was possibly too high prompting loss, and in January 2021, when transpiration was lower due to tree dormancy. ~~To note that~~ Notably, the compound was detected at SW with GCDT in January 2021, corroborating the hypothesis already advanced at the Caretti site of higher detectability through this expeditious gas analysis. On the NE side, VC was detected in trunk cores in January 2021; ~~it~~ this may be ~~due to the fact that~~ because shallow roots, that were inferred to feed this side of the tree, are still active in the low transpiration periods prompting higher trunk concentrations, whereas deep roots feeding the SW side are not. Eventually, VC detection appeared more effective in the outer section of the trunk, likely due to lower sorption capacity on wood compared to other CEs (see Section 4.2.1).

4.3 Conceptual models of VC uptake into trees

~~At both sites,~~ VC was detected in tree trunks at both sites despite its absence in the soil gas (see SM). To the best of our knowledge, *in planta* reductive dechlorination of higher chloroethenes down to VC was never observed in the literature. Thus, ~~the detection of~~ detecting the compound in trunks implies its uptake from underground contaminated matrices. Two different conceptual models should be considered to explain the tree uptake of VC at the two sites (Fig. 6). At the Caretti site, VC and other CEs were inferred to enter the tree via direct root uptake of shallow contaminated groundwater. For this reason, one cannot draw definitive conclusions on the occurrence and fate of VC in the unsaturated zone based on tree

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8 samplings in this setting. Nevertheless, phytoscreening proved more effective ~~compared to~~than soil gas to
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10 screen for the occurrence of the compound in shallow groundwater.
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12 At the Bussi site, uptake of contaminants directly from the groundwater is unlikely due to the higher depth
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14 ~~to of the~~ water table. Assuming that in such a setting the contaminants may be uptaken by diffusion of gas
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16 phase into the roots (Struckhoff et al., 2005), VC would be a good candidate for translocation into trees
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18 thanks to its high mobility in aqueous and gas matrices and low molecular weight (Limmer and Burken,
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20 2016), as long as it does not~~not~~ get biodegraded in the unsaturated zone. Indeed, ~~Some~~ elements at the
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22 sampling site may contribute to decreasinge oxygen in the unsaturated zone, thus disfavoring the
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24 biodegradation of VC: (1) the occurrence of thin fine-grained organic-rich layers in the shallow critical zone;
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26 (2) the likely occurrence of soil contaminated by residual DNAPL (wastes) on the fringe of the landfill; (3) a
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28 capping put in place over the wastes in 2014 (Filippini et al., 2018). Thus, the ability of trees to detect VC in
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30 this deep water table setting seems to be related to peculiar anaerobic conditions in the unsaturated zone
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32 disfavoring aerobic degradation. The non-detection of VC in the soil gas samples may be due to shallower
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34 sampling depth, with soil gases collected at 2.5 m bgs, whereas tree roots ~~are able to~~can attain higher
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36 depths. Moreover, the sorbent pens used for the soil gas sampling may be ineffective in detecting soil gas
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38 VC, as it was already inferred when discussing the sampling of the tree cores versus tree gas. In this regard,
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40 it is worth noting that VC remained undetected in additional soil gas samples collected with canisters in
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42 the surroundings of the B1 tree (see SM).

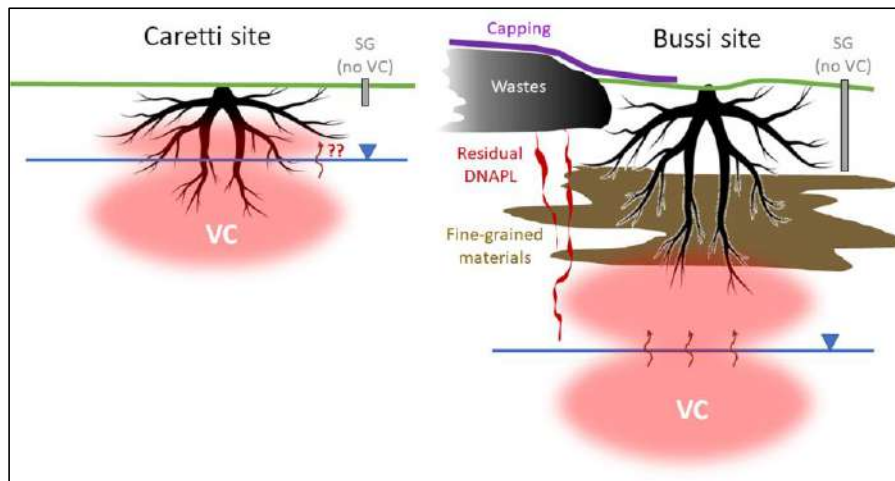


Figure 6. Conceptual models for VC uptake at the Caretti site (left) and at the Bussi site (right).

5 Conclusions

The capability of phytoscreening to detect the underground occurrence of VC appears site-specific to some degree and restricted to particular meteorological and tree conditions. Still, poplar trees ~~were able to~~ could screen for the occurrence of VC in the shallow critical zone of two different hydrogeological settings where different trunk sampling and analytical protocols were applied, thus disproving the shared literature assumption of the inefficacy of phytoscreening for detecting the compound.

The new evidence of phytoscreening efficacy towards VC brings implications for ~~the assessment of~~ assessing vapor intrusion risk. In the two investigated sites, the risk of vapor intrusion in the residential buildings near the contaminant sources was historically excluded based on soil gas screening suggesting the non-occurrence of VC in the unsaturated zone. However, VC detection in soil gas is notoriously troublesome, ~~mostly primarily~~ due to (1) low performances of the sorbent materials toward the compound or (2) spatially and temporally localized losses of soil gas concentration caused e.g. by rain infiltration or changes in barometric pressure (Burken et al., 2011). On the other hand, tree trunks appear to provide a higher “storage capacity” than soil gas for the very volatile VC ~~compared to soil gas~~. Moreover, the broader and deeper sampling area of tree roots compared to that of soil gas sampling rods would ensure buffered

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8 concentrations over space and time, as previously observed for higher chlorinated ethenes (e.g., Algreen et
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10 al., 2015). Thus, the higher potential of phytoscreening compared to soil gas screening for detecting the
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12 occurrence of VC in the shallow critical zone could effectively support preliminary assessments of vapor
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14 intrusion risk.
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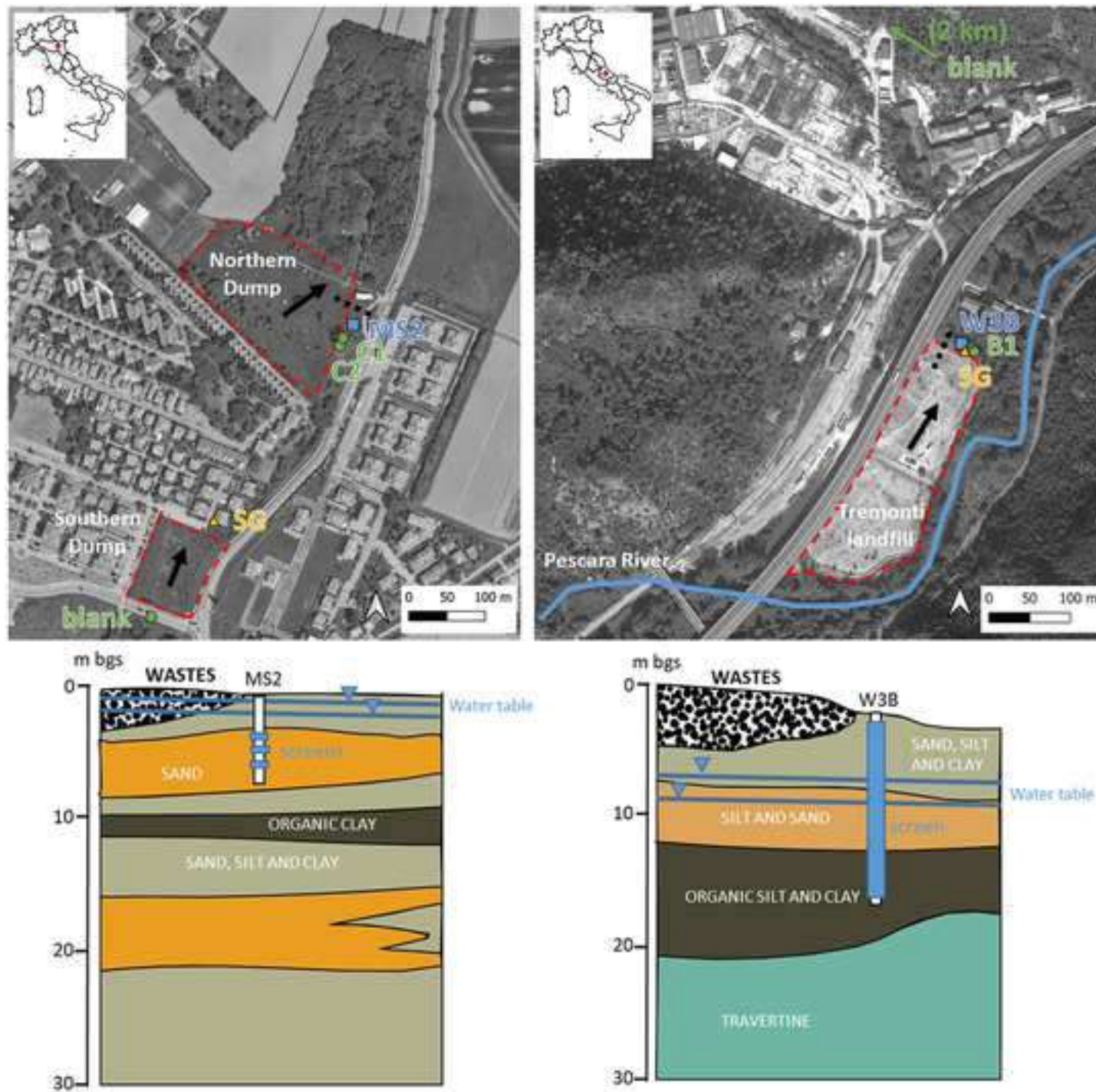
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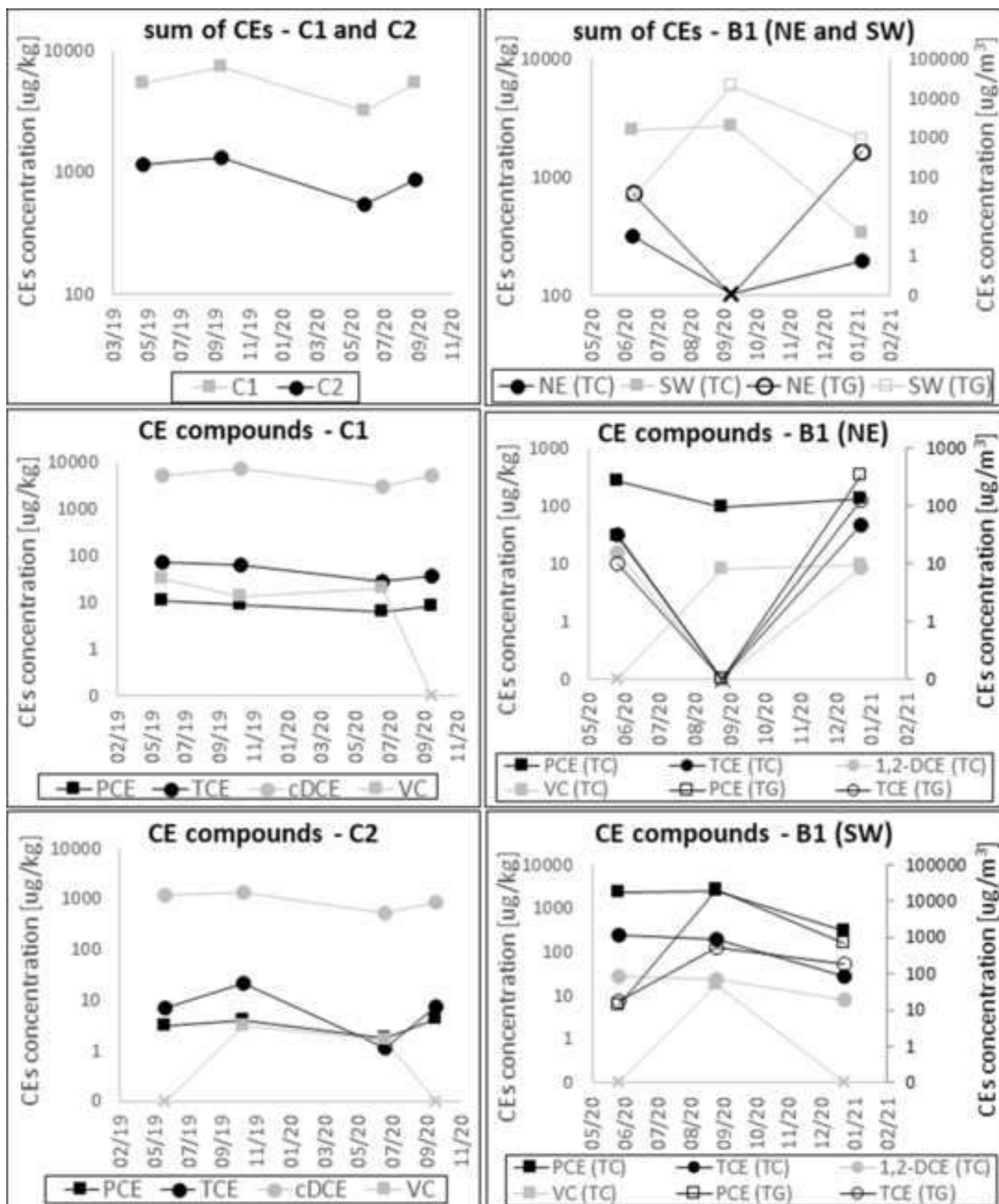
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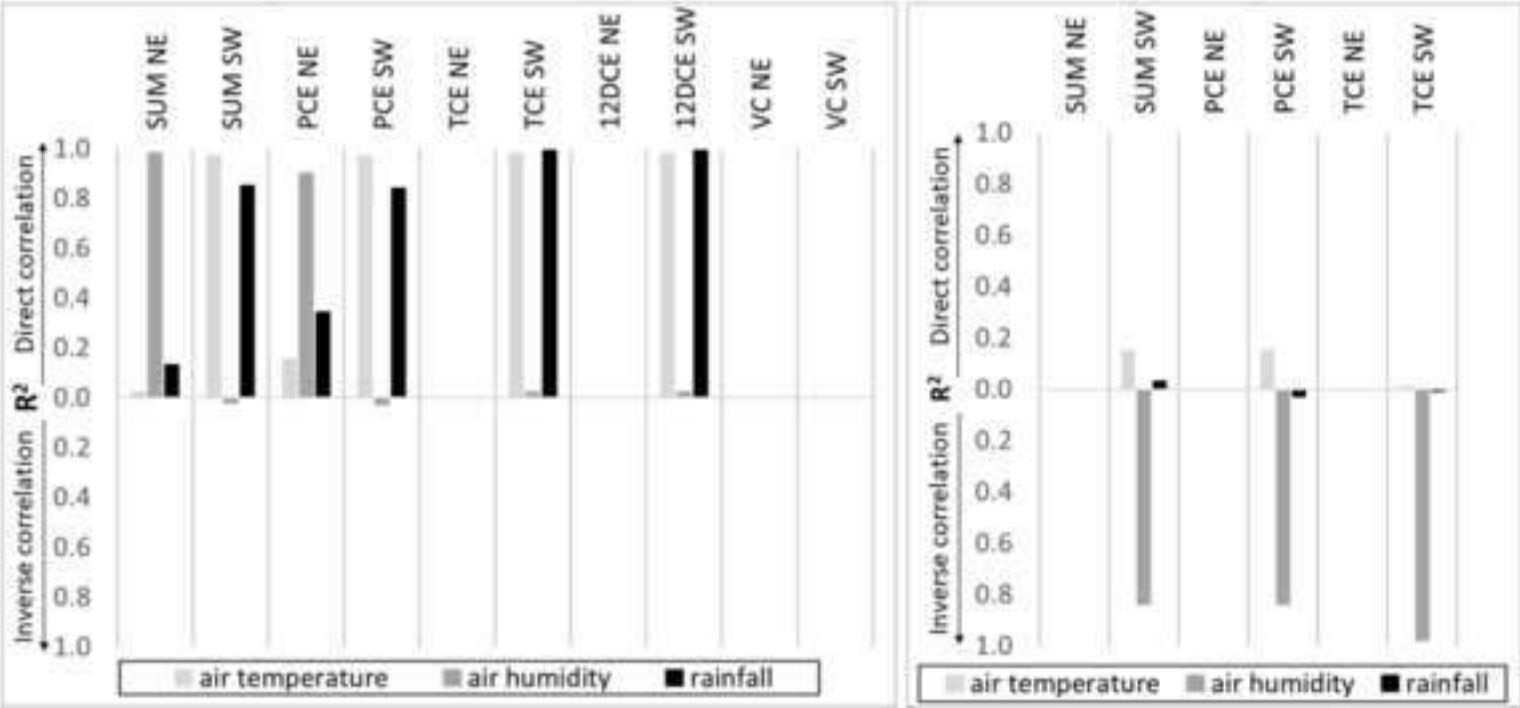
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Figure1







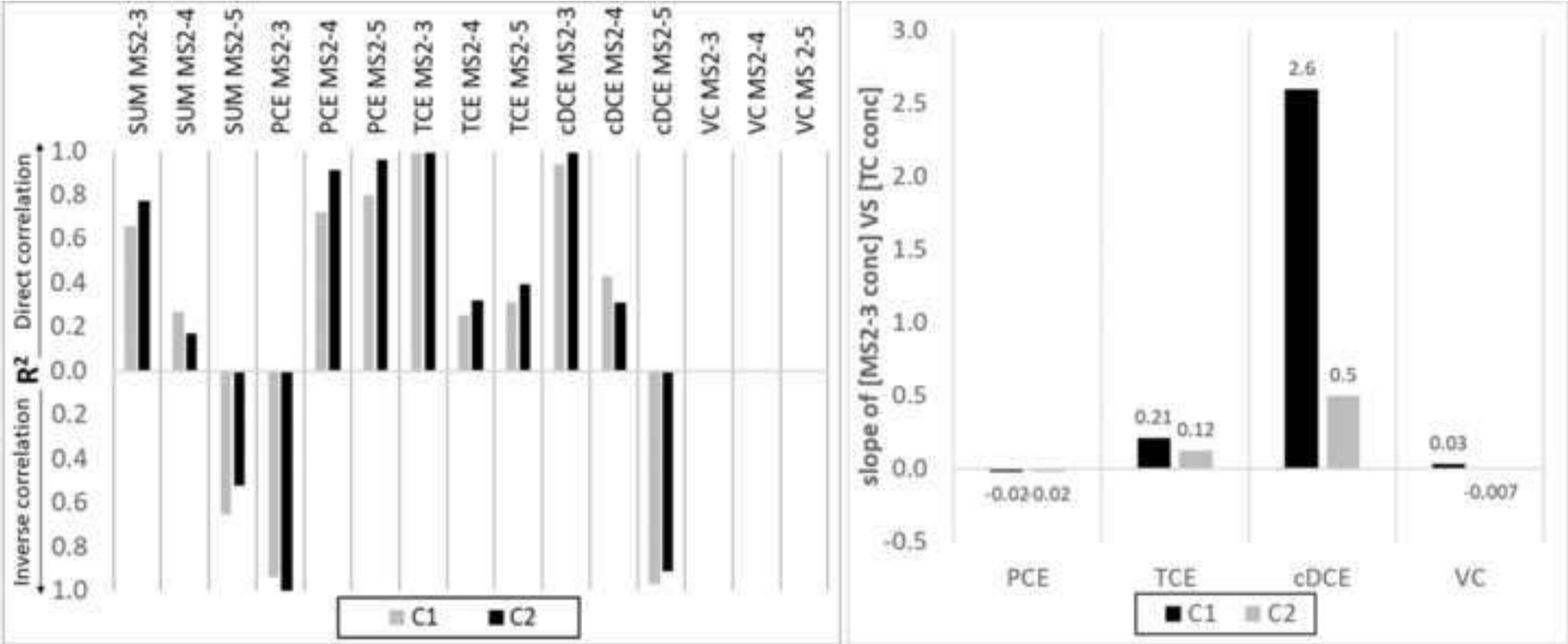
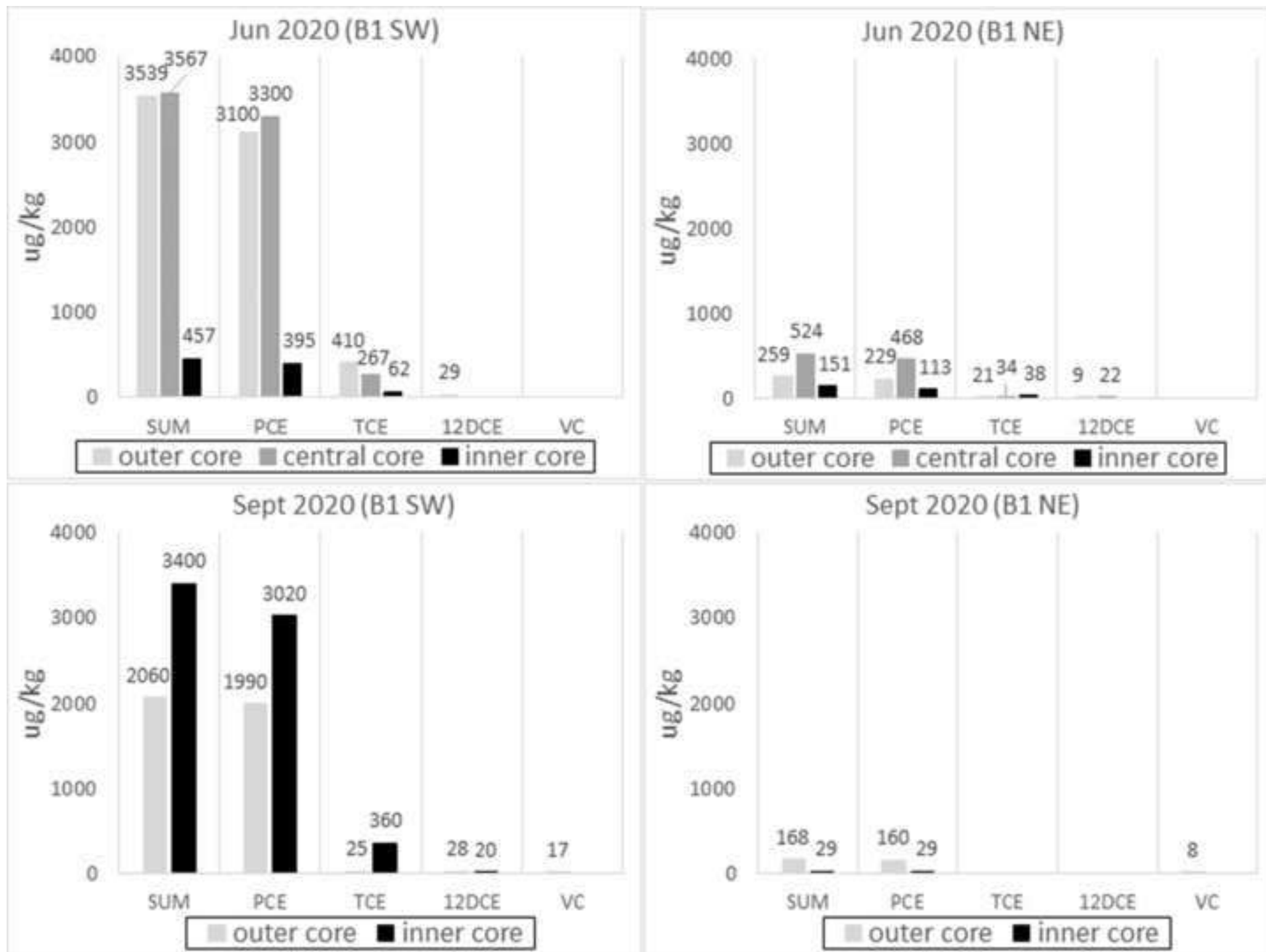


Figure5

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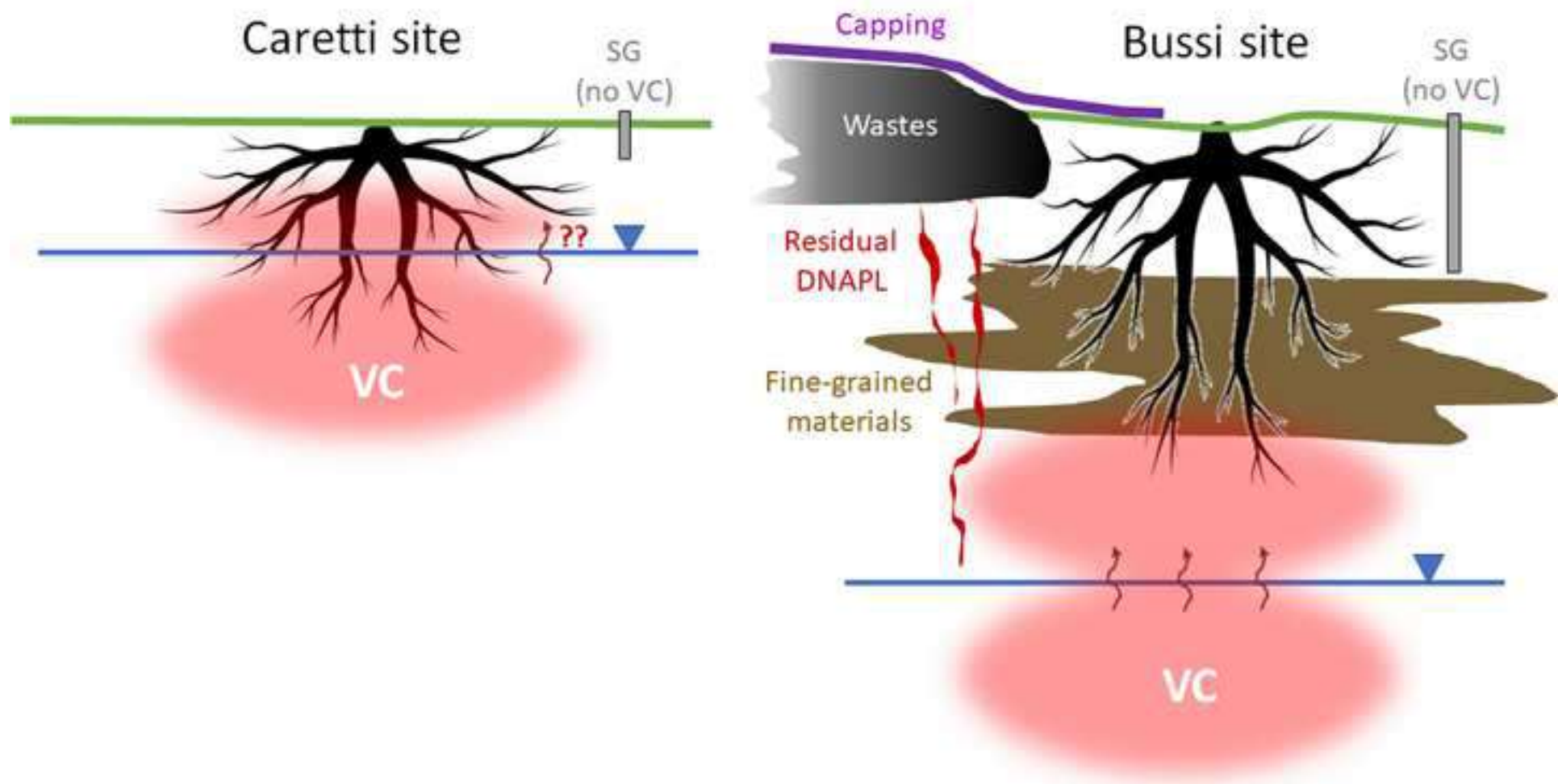


Table1. CEs concentration and influencing factors at the Caretti site. Concentrations below detection limits are indicated as “BDL”. The empty boxes correspond to not performed measurements.

		GW from MLS [ug/L]			Trunk cores [ug/kg]		GCDT [ppm]		Depth to wter table [m bgs]	Air temperature [°C]	Air humidity [%]	Solar radiation [W/m²]	Rainfall [mm]
		MS2-3	MS2-4	MS2-5	C1	C2	C1	C2					
May 2019	PCE	154.0	13.0	4.4	11.0	3.0			1.6	14.3	76.5	186.3	70.4
	TCE	1129.0	121.0	15.0	74.0	7.0							
	cDCE	23200.0	4500.0	1650.0	5200.0	1160.0							
	VC	7181.0	3550.0	5900.0	33.0	BDL							
	sum of CEs	31664.0	8184.0	7569.4	5318.0	1170.0							
Oct 2019	PCE	23.7	3.3	0.6	9.0	4.0			2.3	17.9	71.1	161.4	28.4
	TCE	284.0	22.0	3.0	62.0	21.0							
	cDCE	3146.0	212.0	28.3	7220.0	1310.0							
	VC	584.0	110.0	1649.0	13.0	3.0							
	sum of CEs	4037.7	347.3	1680.9	7304.0	1338.0							
Jun 2020	PCE	130.0	1.0	0.4	6.5	1.8			1.9	22.1	58.1	291.0	10.6
	TCE	120.0	4.8	1.8	27.9	1.1							
	cDCE	1650.0	96.5	52.5	3150.0	540.0							
	VC	800.0	164.0	2230.0	19.7	1.6	3.0	0.5					
	sum of CEs	2700.0	266.3	2284.7	3204.1	544.5							
Sept 2020	PCE	9.5	4.9	0.7	8.6	4.3			2.3	23.4	60.7	200.6	27.4
	TCE	175.0	28.0	3.3	36.6	7.6							
	cDCE	2116.0	276.0	36.0	5280.0	860.0							
	VC	274.0	119.0	1529.0	BDL	BDL	2.5	1.4					
	sum of CEs	2574.5	427.9	1569.0	5325.2	871.9							

Table 2. CEs concentration and influencing factors at the Bussi site. Concentrations below detection limits are indicated as “BDL”. The empty boxes correspond to not performed measurements. Averaged concentrations are reported for trunk cores that where split in multiple subsections (June and September 2020 sampling rounds).

		GW [ug/L]	Trunk cores [ug/kg]		Trunk gas [ug/m ³]		GCDT [ppm]	Depth to water table [m bgs]	Air temperature [°C]	Air humidity [%]	Rainfall [mm]
		W3B	B1 NE	B1 SW	B1 NE	B1 SW	B1 SW				
Jan 2019	PCE	27640.0						5.6			
	TCE	3922.0									
	12DCE	1492.0									
	VC	241.0									
	sum of CEs	33295.0									
Jun 2020	PCE	10594.0	270.0	2265.0	29.8	13.6		9.2	20.4	69.0	8.3
	TCE	2061.0	31.1	246.4	10.0	17.4					
	12DCE	1274.0	15.2	28.6	BDL	BDL					
	VC	80.1	BDL	BDL	BDL	BDL					
	sum of CEs	14009.1	316.3	2540.0	39.8	31.0					
Sept 2020	PCE	16193.0	94.6	2505.0	BDL	20200.0		9.2	19.1	62.0	7.1
	TCE	2038.0	BDL	192.4	BDL	547.0					
	12DCE	1555.0	BDL	24.0	BDL	BDL					
	VC	197.0	7.9	17.4	BDL	BDL	0.1				
	sum of CEs	19983.0	102.5	2738.7	0.0	20747.0					
Jan 2021	PCE		134.0	297.0	336.1	713.3		9.2	6.8	66.0	4.7
	TCE		47.0	27.5	124.4	185.9					
	12DCE		8.3	8.1	BDL	BDL					
	VC		9.4	BDL	BDL	BDL	0.2				
	sum of CEs		198.7	332.6	460.5	899.2					

Detecting vinyl chloride by phytoscreening in the shallow critical zone at sites with potential human exposure

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SUPPLEMENTARY MATERIALS

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Section S3. Scatter plots between tree trunk concentration of CEs and influencing factors

S1 Chloroethenes concentration in groundwater

S1.1 Caretti site

The groundwater sampled at the MS2 multilevel piezometer had averaged concentration over time for the sum of CEs of 10.2, 2.3, and 3.2 mg/L at the three increasing screening depths of 3, 4, and 5 m bgs, respectively (see concentration values in Tab. 1 of the main text).

The highest concentrations were systematically detected in the shallowest sampling screen MS2-3 (3 m bgs; Fig. S1), suggesting vertical leaching from the primary (wastes and chlorinated pitches) and secondary (contaminated soil with NAPL residual phase) sources of contamination located above the water table.

The middle sampling screen (MS2-4; 4 m bgs) had the lowest concentrations, possibly due to a higher permeability of the screened sublayer that would have favored contaminant dilution. A higher permeability is inferable from the higher flowrate provided during sampling compared to screens MS2-3 and MS2-5 (5 m bgs).

CE concentration detected in May 2019 is exceptionally high in all the sampling screens, reaching up to 31.7, 8.2, and 7.6 mg/L in MS2-3, MS2-4 and MS2-5 respectively. This can be explained considering the high precipitation in the two weeks preceding sampling (72 mm, see Tab. 1 of the main text). Such an intense recharge event likely caused remobilization towards the saturated zone of contaminants retained in the waste materials of the Northern Dump, causing the concentration peak.

Excluding the anomalously high results of May 2019, the CE concentration over time is in a direct linear relationship with the depth to water table, suggesting that the contamination in groundwater is less diluted when the saturated zone of the aquifer is thinner (Fig. S2). Few exceptions are represented by PCE in screen MS2-3, cDCE in screen MS2-5 and VC in all the sampling screens. We consider relevant the dynamic for PCE and VC whereas the concentration of cDCE appears too low in the deepest screen and probably affected by its dechlorination rate to VC. The inverse relationship observed for PCE in MS2-3 could be explained assuming the occurrence of residual PCE in the vadose zone in the surroundings of the piezometer at a depth close to the averaged water table; when the water table rises, the residual contamination is intercepted by the groundwater causing the concentration increase. The inverse relationship of VC with the depth to water level in all the three sampling screens suggests a tendency to stripping out in the gas phase with consequent volatilization, possibly followed by aerobic degradation, when the water level is deeper and the vadose zone is thicker.

S1.2 Bussi site

The groundwater concentration of CEs in the long screened piezometer W3B is rather stable over time (Fig. S1). The difference in concentration between year 2019 (33.3 mg/L) and 2020 (17.0 mg/L on average) is attributable to a Pump and Treat system put in place in 2020 in the northern sector of the Tre Monti landfill, with the W3B being one of the pumping points. The effects of pumping are also visible in the variation of hydraulic head of W3B that decreased from 5.6 m bgs in 2019 to 9.2 m bgs in 2020 (see Tab. 2 of the main text).

Figure S1. Total concentration of CEs in groundwater over time at the Caretti site (MS2) and the Bussi site (W3B)

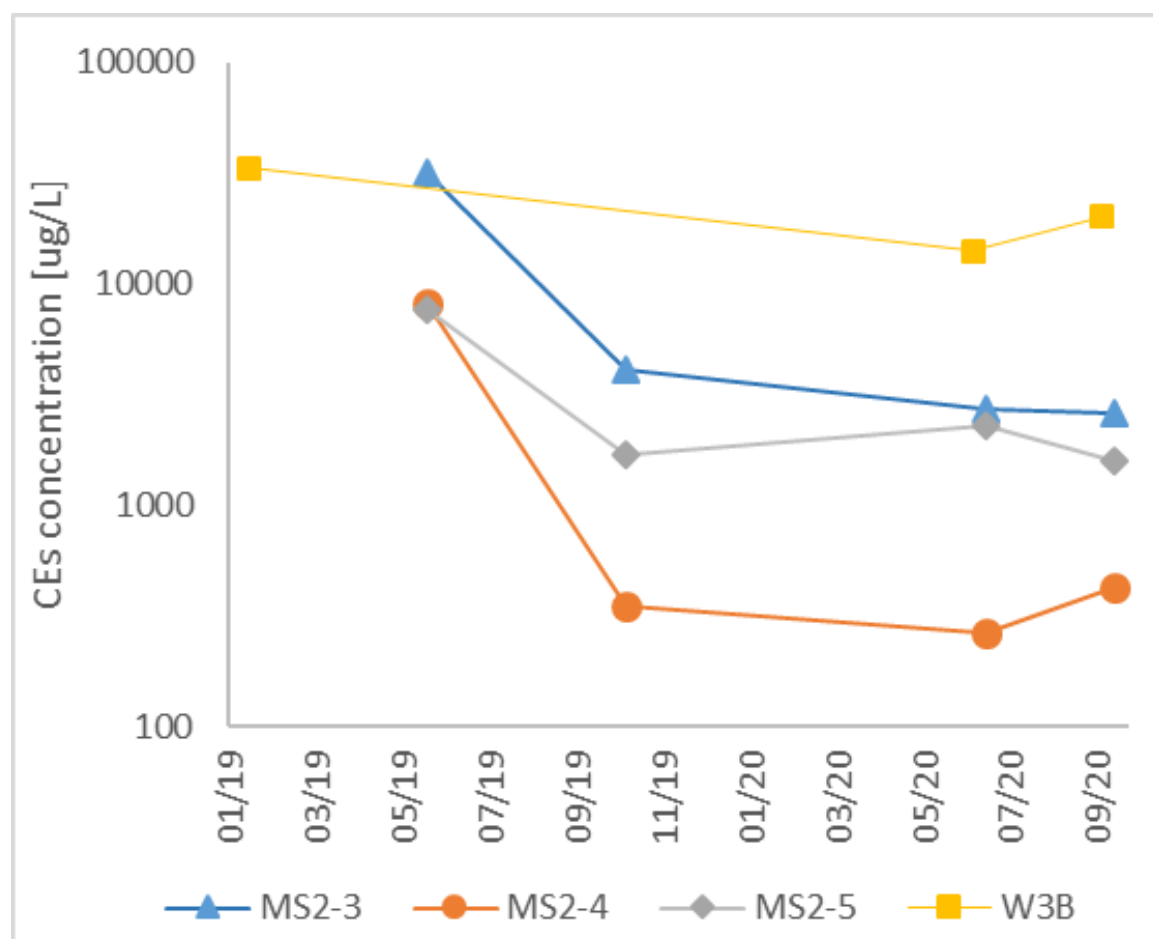
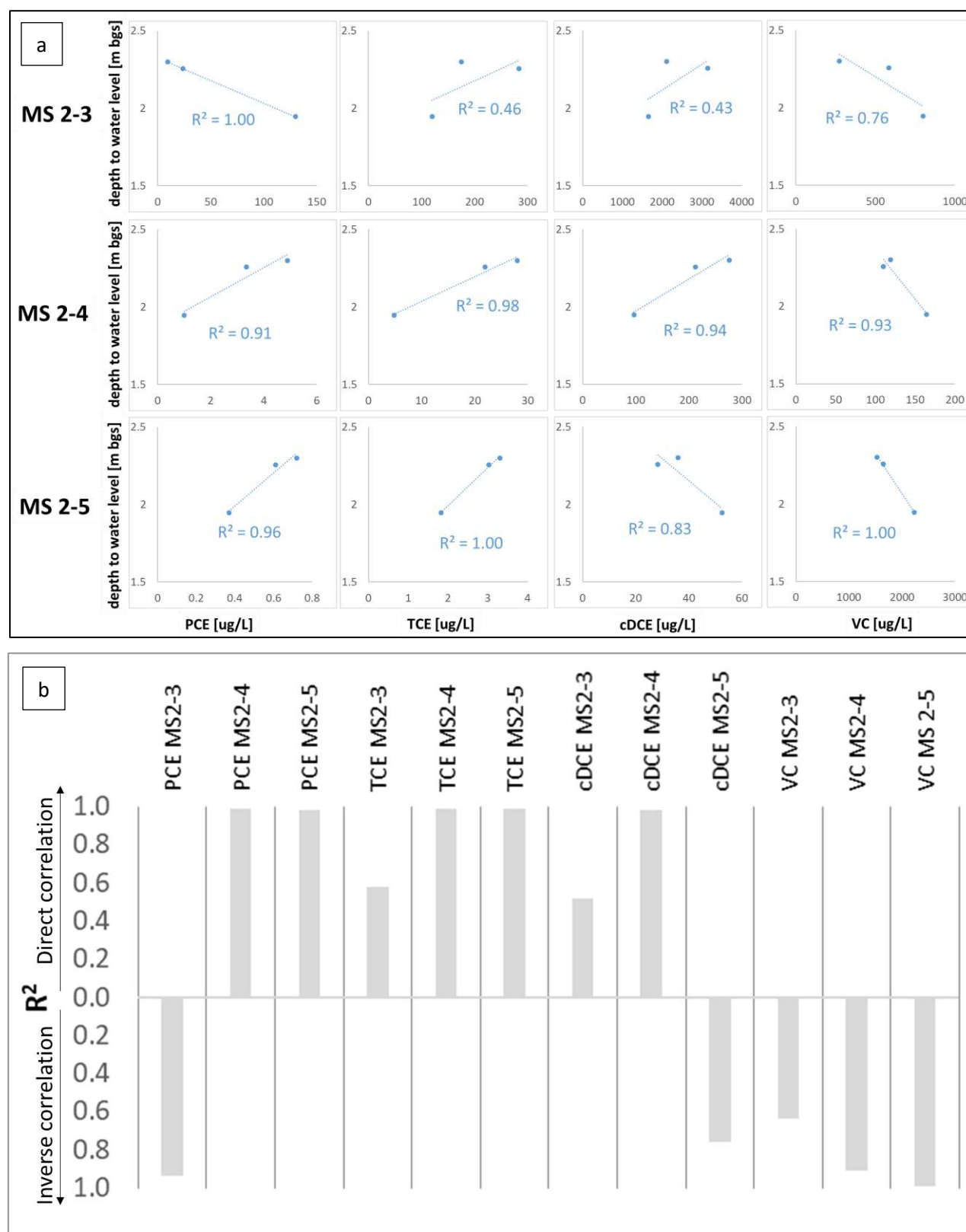


Figure S2. Scatter plots (a) and coefficients of determination R^2 (b) of the linear relationship between CEs concentration in groundwater and depth to water table.



S2 Chloroethenes concentration in the soil gas

S2.1 Caretti site

An extensive soil gas survey was performed at the site between 2004 and 2006. Soil gas was actively sampled in 44 locations at 1 m bgl with activated carbon. Further detail on the survey is provided in Gargini et al. (2011). Soil gas concentrations of the four chloroethenes of concern for this work (PCE, TCE, DCE, VC) are reported in Fig. S3. Unfortunately, none of the 44 points falls close to the sampling location selected for this study. Nevertheless, at least one soil gas sample, collected on a fringe of the southern dump, is a good analog of the current sampling location due to substantial similarity in terms of groundwater contamination (see the comparison in Fig. S4 and Tab. S1) and hydrostratigraphy. The analog sample contained PCE and TCE in a concentration of 1.3 and 9.5 mg/m³, respectively, whereas DCE and VC were not detected despite their occurrence in the shallow groundwater in concentrations up to 33.6 and 14.0 mg/L in the closest piezometer MC4. DCE and VC remained undetected also in the other 43 soil gas sampling points of the site, where VC-enriched plumes are known to occur in the shallow aquifer (Filippini et al., 2016). Moreover, the general contamination levels of by-products in shallow groundwater at the site were more severe in 2004-2006 than today, most likely due to some natural attenuation. Based on the above-presented lines of evidence, it is entirely reasonable to assume that VC wouldn't have been detected in the soil gas of the sampling location selected for this study.

S2.2 Bussi site

A soil gas sampling was carried out in September 2020 at the same time of the trunk and groundwater sampling, in the vicinity of piezometer W3B and tree B1 at a depth of 2.5 m bgs, revealing the occurrence of PCE at 0.2 mg/m³ whereas none of the other CEs of concern were detected in the sample (Tab. S2). The sample was collected with an active approach, using the same active sorbent pens described in the main text for the trunk gas sampling. Two additional soil gas samples (SG3 and SG4) were collected later, in July 2021, close to piezometers D3 and D4, respectively, showing VC contamination in groundwater (Fig. S5), in order to check other instances of soil gas composition close to piezometers where the VC was present in the shallow groundwater. The samples were collected through nesty probes at a depth of 2.5 m bgs, using a canister set at 0.04 L/min flow rate for 2 hours. The canister samples were stored at ambient temperature. The soil gas cannisters were analyzed following the method EPA TO 15 1999 in the laboratory of the Agency for Environmental Protection of the Piemonte Region (ARPA Piemonte). The results show absence of VC in the soil gas despite the compound was present in the groundwater of the corresponding piezometers in concentrations of 3 to 75 µg/L (Tab. S3).

Figure S3. Soil gas survey carried out at the Caretti site between 2004 and 2006 by Gargini et al. (2011). A black arrow indicates the sample selected as an analogue for the soil gas composition in the sampling location of the current study (highlighted in yellow).

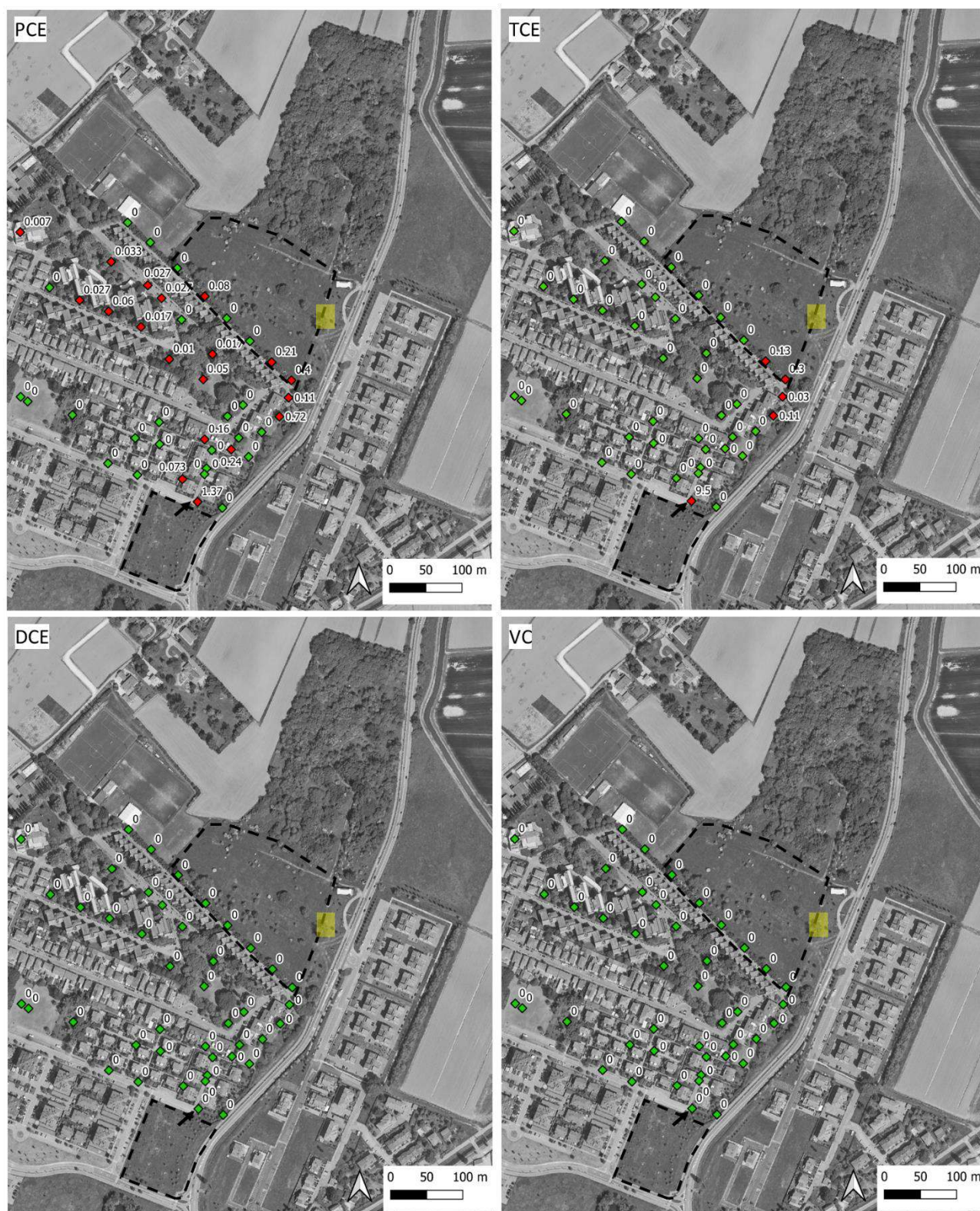


Figure S4. Groundwater contamination and hydrostratigraphy at the Caretti site, in the sampling location of this study (piezometer MS2) and in the analogue location at the southern dump (piezometers MC4 and SN3b). The concentrations in the pie diagrams are temporal and vertical averages of the values of Tab. S1.

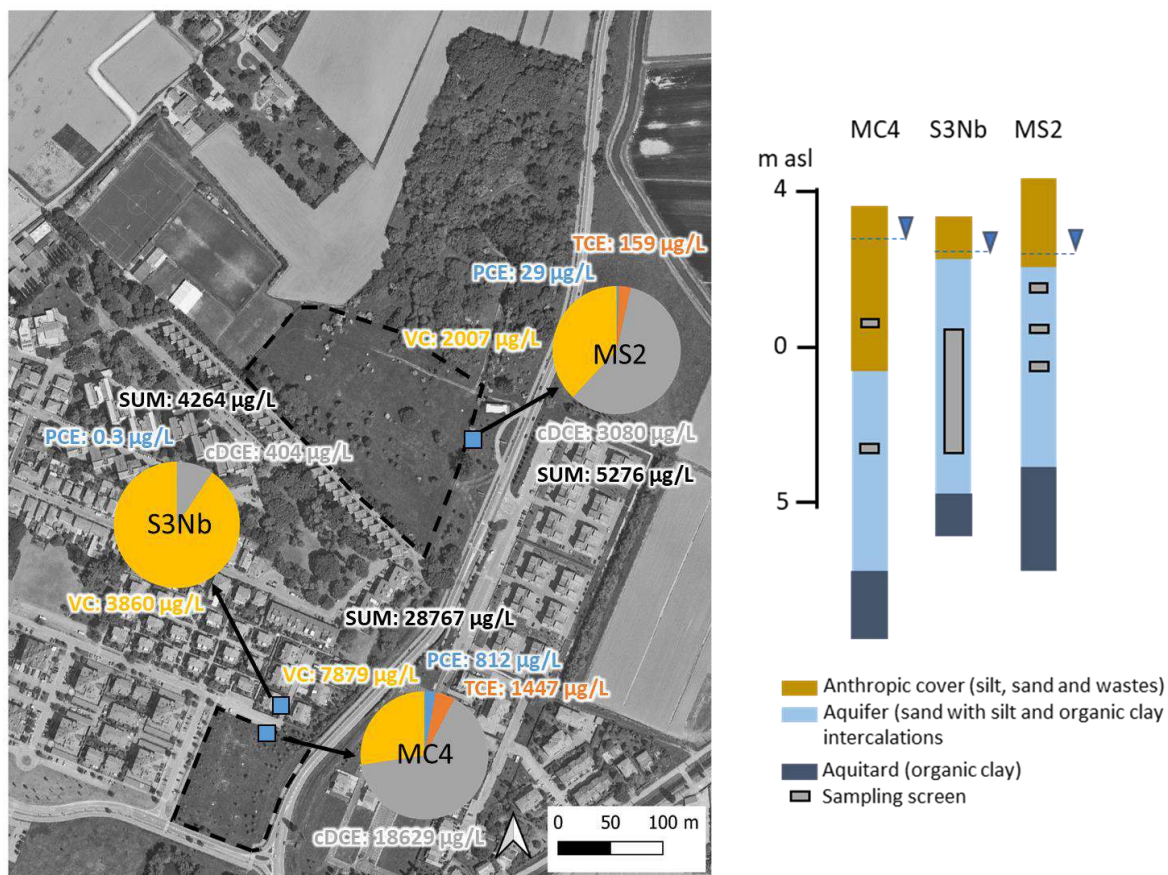


Figure S5. Locations of the soil gas samplings of July 2021 at the Bussi site and the corresponding piezometers.

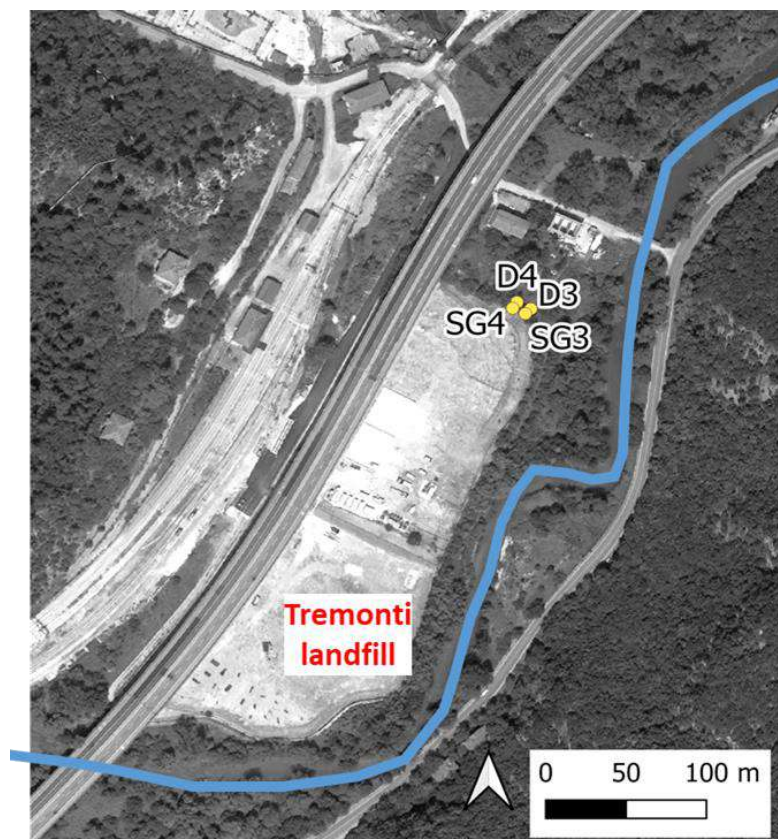


Table S1. *CEs concentration detected in groundwater at multilevel piezometers MS2, MC4 and piezometer SN3b of the Caretti site, and in the analogue soil gas sample highlighted with a black arrow in Fig. S3.*

	PCE	TCE	cDCE	VC	m bgs	year
SG [$\mu\text{g}/\text{m}^3$]	1000	10000	BDL	BDL	<1	2004
SN3b [$\mu\text{g}/\text{L}$]	0.3	BDL	404	3860	3-6	2004
MC4-1 [$\mu\text{g}/\text{L}$]	112	322	3653	1809	3	2013/14
MC4-2 [$\mu\text{g}/\text{L}$]	1512	2573	33615	13950	6	2013/14
MC2-3 [$\mu\text{g}/\text{L}$]	79	427	7528	2210	3	2019/20
MC2-4 [$\mu\text{g}/\text{L}$]	6	44	1271	896	4	2019/20
MC2-5 [$\mu\text{g}/\text{L}$]	2	6	442	2827	5	2019/20

Table S2. *CEs concentration detected in groundwater and in soil gas at the Bussi site in September 2020.*

	PCE	TCE	1,2DCE	VC
SG [$\mu\text{g}/\text{m}^3$]	200	BDL	BDL	BDL
W3B [$\mu\text{g}/\text{L}$]	16193.0	2038.0	1555.0	197.0

Table S3. *CEs concentration detected in groundwater and in soil gas at the Bussi site in July 2021.*

	PCE	TCE	1,2DCE	VC
SG3 [$\mu\text{g}/\text{m}^3$]	517.0	45.5	BDL	BDL
D3 [$\mu\text{g}/\text{L}$]	0.6	1.5	27.1	2.9
SG4 [$\mu\text{g}/\text{m}^3$]	10340.0	3504.0	24.6	BDL
D4 [$\mu\text{g}/\text{L}$]	13.0	196.0	788.0	75.1

S3 Scatter plots between tree trunk concentration and influencing factors

Figures S6 to S9 show the scatter plots used to derive the coefficients of determination R^2 of Figures 3 and 4 in the main text.

Figure S6. Scatter plots between trunk core concentration of CEs and the main meteorological influencing factors at the Caretti site. The values of R^2 are summarized in Figure 3 of the main text.

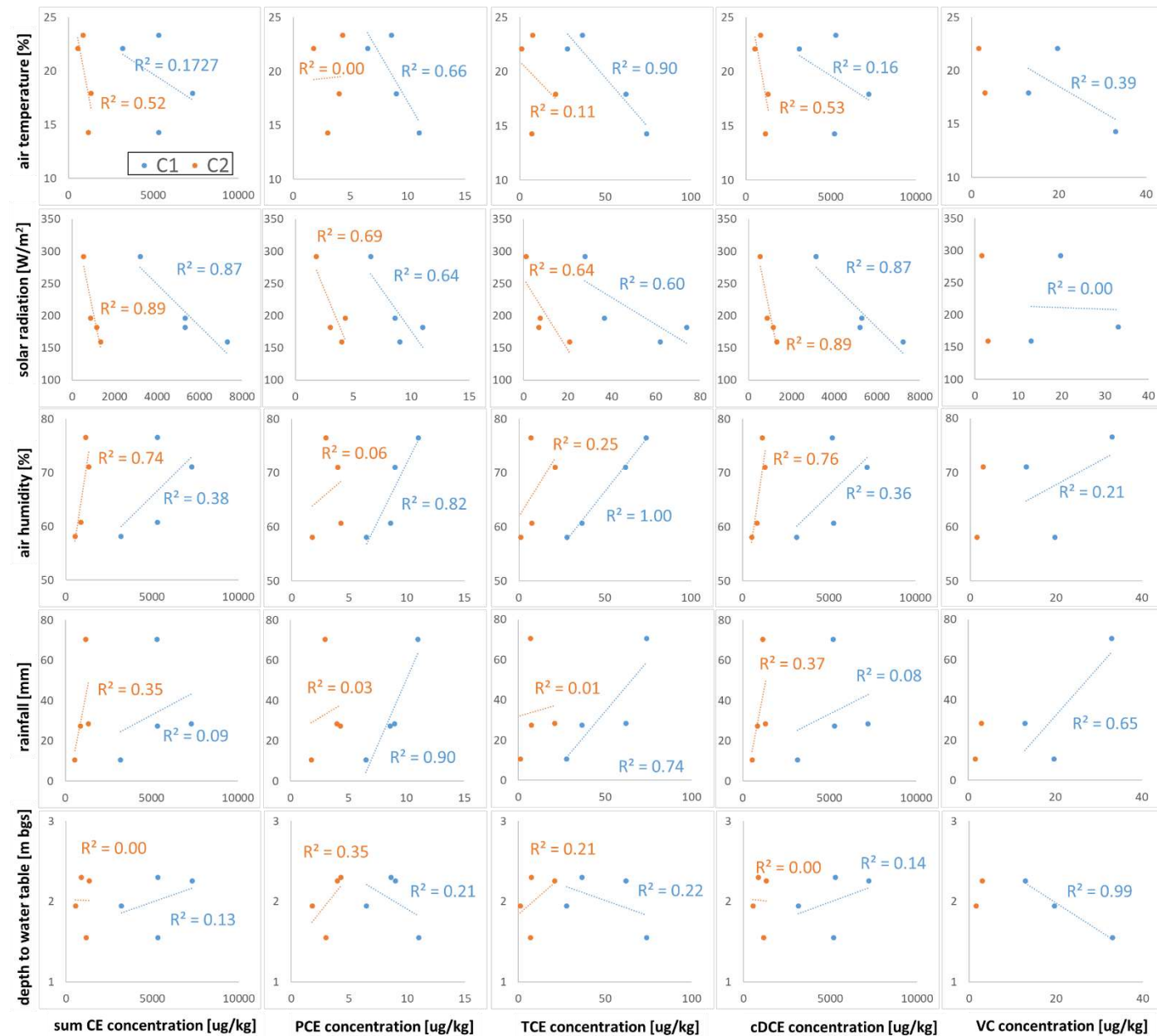


Figure S7. Scatter plots between trunk core concentration of CEs (HSP) and the main meteorological influencing factors at the Bussi site. The values of R^2 are summarized in Figure 3 of the main text.

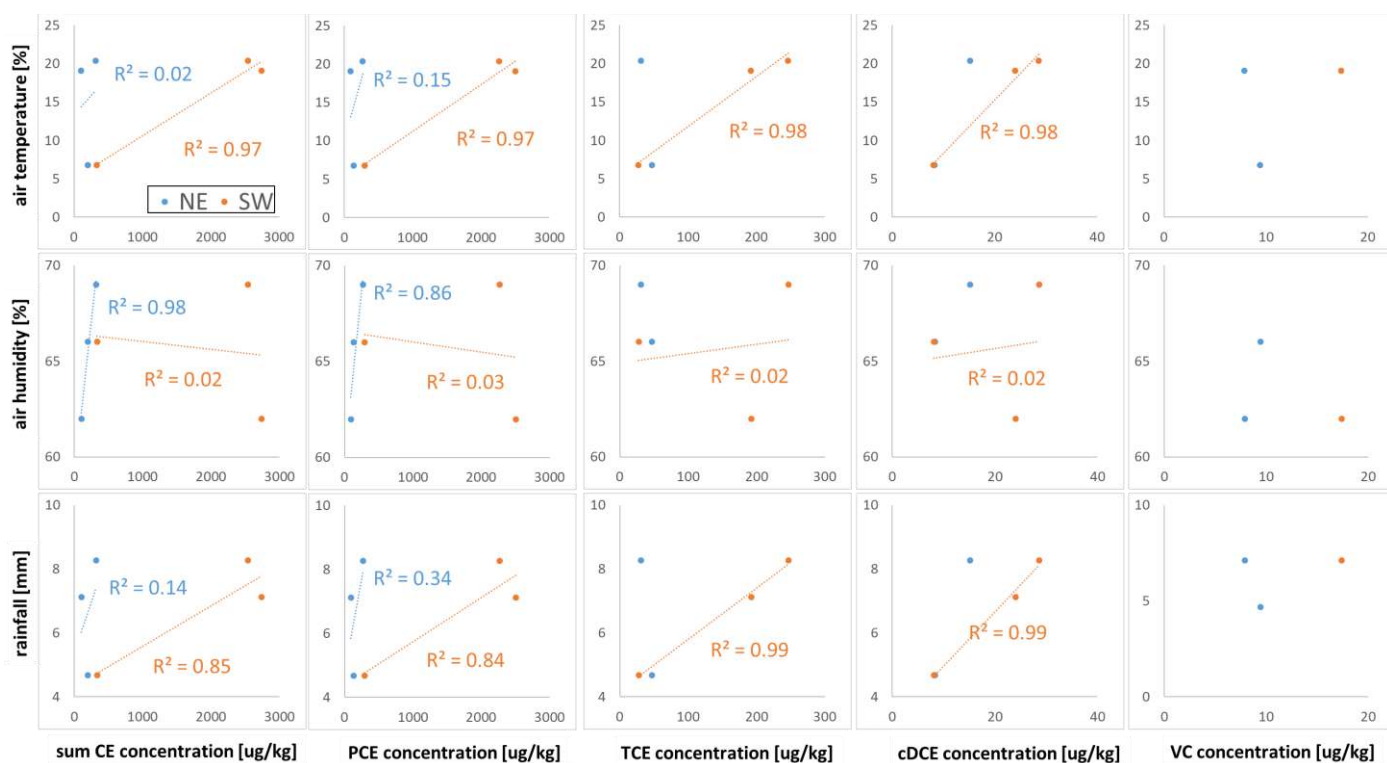


Figure S8. Scatter plots between trunk gas concentration of CEs (ASP) and the main meteorological influencing factors at the Bussi site. The values of R^2 are summarized in Figure 3 of the main text.

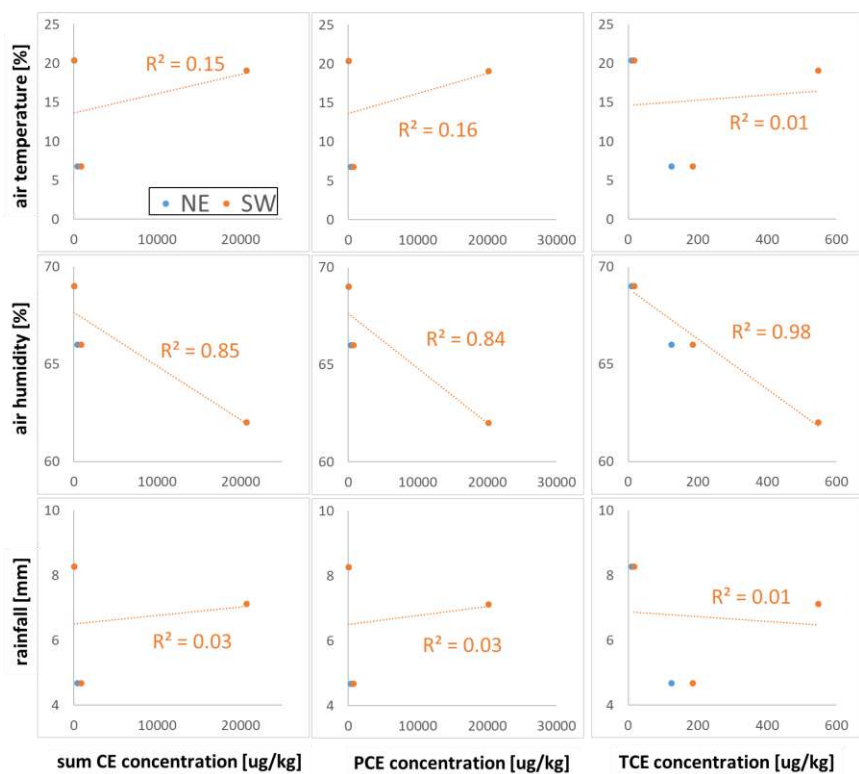
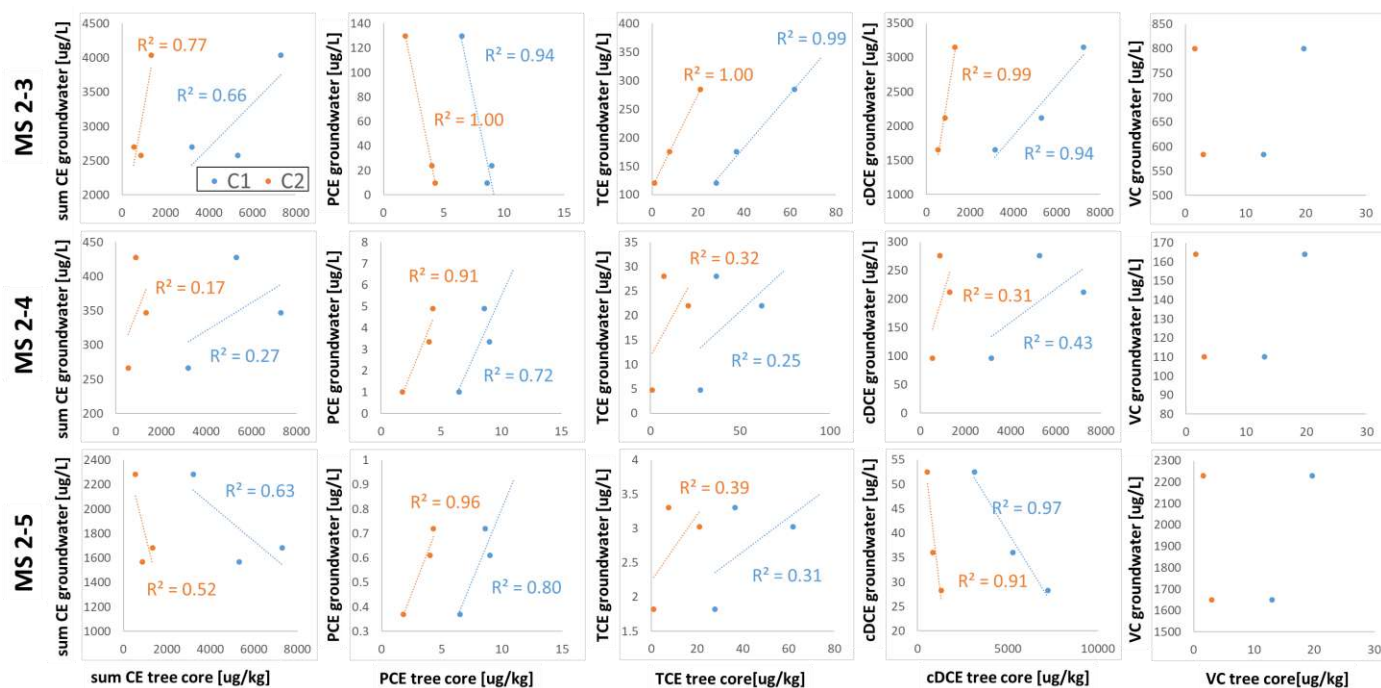


Figure S9. Scatter plots between trunk core and groundwater concentration of CEs at the Caretti site. The values of R^2 are summarized in Figure 4 of the main text.



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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: