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A quantitative review and meta-analysis on phytoscreening applied to aquifers contaminated by chlorinated ethenes

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# Science of the Total Environment

## A quantitative review and meta-analysis on phytoscreening applied to aquifers contaminated by chlorinated ethenes

--Manuscript Draft--

<b>Manuscript Number:</b>	STOTEN-D-21-25229R2
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<b>Order of Authors:</b>	Carlotta Leoncini, M.sc. Maria Filippini, Ph.D. Juri Nascimbene, Ph.D. Alessandro Gargini, Ph.D.
<b>Abstract:</b>	<p>Applications and acceptance of phytoscreening, i.e., the use of trees as screening tools for underground contamination, are still limited in many countries due to the lack of awareness of application policies, the intrinsic qualitative nature of the technique, and the paucity of critical analyses on available data. To date, the conditions influencing the effectiveness of the technique have been descriptively discussed, yet rarely quantified. This review will contribute to filling this knowledge gap, shedding light on the most suitable approaches to apply phytoscreening. The focus was placed specifically on chlorinated ethene compounds since they are among the main organic contaminants in groundwater and have been the most studied in the field of phytoscreening. Chlorinated ethenes' behavior and biodegradation potential largely depend on their physicochemical properties as well as the hydrogeological features of the system in which they migrate. Besides, their fate and transport in surface ecosystems are still poorly understood. Here, phytoscreening data from sites contaminated by chlorinated ethenes were extracted from relevant literature to form a global-scale database. Data were statistically analyzed to identify the major drivers of variability in tree-cores concentration. Correlation between tree-core and groundwater concentration was quantified through Spearman's rank coefficients, whilst detectability potential was determined based on tree-cores showing non-detection of contaminants. The influence on such parameters of factors like contaminant properties, hydrogeology, tree features, and sampling/analytical protocols was assessed. Results suggest that factors controlling plant uptake and contaminant phytovolatilization regulate correlation and detectability, respectively. Conditions increasing the correlation (e.g., sites with shallow and permeable aquifers) are recommended for phytoscreening applications aimed at mapping and monitoring contaminant plumes, whereas conditions increasing detectability (e.g., sampling tree-cores near ground level) are recommended to preliminary screen underground contamination in poorly investigated areas.</p>
<b>Response to Reviewers:</b>	<p>To the kind attention of Professor Jay Gan, Co Editor-in-chief, Science of the Total Environment</p> <p>Dear Professor Gan, Please find enclosed the revised manuscript 'A quantitative review and meta-analysis on phytoscreening applied to aquifers contaminated by chlorinated ethenes' submitted by myself on behalf of all co-authors for publication in STOTEN. This is the second revision of the manuscript, after the careful editing from 4 reviewers and your suggestion for English improvements.</p> <p>The paper is now significantly improved grammatically and in the clarity of the</p>

contents.

An account of the changes we made can be found on the “Revised manuscript with changes marked” file.

Thank you for your consideration of this paper, please feel free to contact me for any further information or request concerning this manuscript.

Sincerely,

Carlotta Leoncini

# **A quantitative review and meta-analysis on phytoscreening applied to aquifers contaminated by chlorinated ethenes**

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**To the kind attention of Professor Jay Gan,**  
Co Editor-in-chief, Science of the Total Environment

Dear Professor Gan,

Please find enclosed the revised manuscript '*A quantitative review and meta-analysis on phytoscreening applied to aquifers contaminated by chlorinated ethenes*' submitted by myself on behalf of all co-authors for publication in STOTEN.

This is the second revision of the manuscript, after the careful editing from 4 reviewers and your suggestion on English improvements.

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# A quantitative review and meta-analysis on phytoscreening applied to aquifers contaminated by chlorinated ethenes

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## ABSTRACT

Applications and acceptance of phytoscreening, i.e., the use of trees ~~to screen for~~ as screening tools for underground contamination, are still limited in many countries due to the lack of awareness ~~on~~ of application policies, the intrinsic qualitative nature of the ~~screening method~~ technique, and the ~~lack-paucity~~ of critical analyses on available data. To date, the conditions influencing the effectiveness of the technique have been descriptively discussed, yet rarely quantified. This review will contribute to filling this knowledge gap, shedding light on the most suitable ~~field and intrinsic conditions~~ approaches to apply phytoscreening towards effective use of phytoscreening, with. The ~~a~~ focus was placed specifically on chlorinated ethene compounds ~~contaminants~~ since they are. Chlorinated ethenes ~~are~~ among the main organic contaminants in groundwater and have been the most studied in the field of phytoscreening. Chlorinated ethenes ~~Their~~ behavior and ~~their~~ biodegradation potential largely depend ~~largely on their~~ intrinsic physicochemical properties ~~of the contaminants, but also on as well as~~ the hydrogeological features of the system in which they migrate. Besides, t ~~Their~~ fate and transport in surface ecosystems are still poorly understood. Here, phytoscreening data from sites contaminated by chlorinated ethenes were extracted from relevant literature to form a global-scale database. ~~D~~ The data were statistically analyzed ~~statistically~~ to identify the major ~~factors~~ drivers of the variability in of tree-cores ~~pollutant~~ concentration ~~in tree-cores~~. ~~C~~ Correlation between tree-core and groundwater concentration was quantified through Spearman's rank ~~correlation~~ coefficients, whilst ~~and~~ detectability potential was determined based on tree-cores showing non-detection of contaminants. ~~t~~ The influence on such parameters of factors like ~~a such correlation of~~ contaminant properties, hydrogeology, tree features, and sampling/analytical protocols was assessed. ~~Attention was also given to tree-cores that showed non-detection of contaminants to identify the conditions leading to undetectability~~. Results suggest that

factors ~~influencing-controlling plant~~ uptake and ~~contaminant~~ phytovolatilization ~~processes~~ regulate, respectively, the correlation ~~between tree-core and groundwater concentration~~ and the degree of detectability ~~in tree cores, respectively~~. Conditions ~~favoring higher~~ increasing the correlation (e.g., sites with shallow and permeable aquifers) are ~~optimal~~ recommended for phytoscreening applications aimed at ~~delineating-mapping~~ and monitoring contaminant plumes, whereas ~~the factors-conditions favoring higher~~ increasing detectability (e.g., sampling tree-cores near ground level) are ~~ideal~~ recommended for to preliminary screening of underground contamination in ~~underinvestigated~~ poorly investigated areas.

**KEYWORDS:** groundwater, CEs, trees, quantitative phytoscreening

## 1. INTRODUCTION

Tree roots can carry contaminants dissolved in water through the ~~xylem-trunk~~ up to the ~~leaf sector~~ leaves. This transport is ~~due-based to on~~ direct contact of the roots with water ~~occurring~~ inside the porous medium ~~that of the~~ surrounds the ~~root zone~~ rhizosphere. Water can occur in different energy states: free moving gravity water in the saturated zone of the aquifer, ~~the so-called~~ referred to as groundwater (gw), or retention water (rw) subjected to suction and attached to soil particles as capillary or pellicular water in the unsaturated zone.

The use of plants in environmental hydrogeology has ~~risen~~ gained increasing attention during the last decades in academic research and consultant activity due to stimulating application ~~one~~ perspectives. In ~~conjunction~~ parallel with ~~the removal of~~ contaminants removal by direct uptake and degradation (phytoremediation), Vrobley et al. (1999) demonstrated for the first time that headspace analysis of tree-cores ~~allows to can~~ delineate shallow gw contamination by chlorinated ethenes (CEs) such as trichloroethene (TCE) and cis 1,2-dichloroethene (cDCE). Later, Sorek et al. (2008) termed the technique “phytoscreening” and defined it as a simple, fast, non-invasive, and inexpensive screening for detecting subsurface contamination by volatile organic compounds (VOCs). Since Vrobley et al. (1999), several comparisons between subsurface (soil, soil gas, and gw) and plant contamination were ~~documented~~ conducted, ~~especially-mostly by using~~ with the use of tree-cores but also ~~with-by using~~ leaf and branch samples (e.g., Holm & Rotard, 2011; Wilcox & Johnson, 2016; Gopalakrishnan et al., 2007).

~~Besides~~ Besides screening and monitoring contaminant concentration for plume tracking or natural attenuation evaluation (e.g., Larsen et al., 2008), phytoscreening was used to assess soil vapor intrusions



(e.g., Wilson et al., 2017; Algreen et al. 2015) and ~~to~~ age-date contamination events through dendroecology (Balouet et al., 2007). Phytoscreening potential-applicability was demonstrated for VOCs (e.g., BTEX; Wilson et al., 2013), perchlorate (e.g., Limmer et al., 2014), per- and polyfluoroalkyl substances (PFAS; Gobelius et al., 2017), or inorganic compounds like heavy metals (e.g., Algreen et al., 2014). However, ~~although~~ CEs ~~were~~ are ~~the~~ the most frequently ~~target-encountered~~ target-encountered in reported applications of ~~this technique~~ phytoscreening. This review ~~is focused~~ examines ~~on~~ on phytoscreening applications for CEs in groundwater, ~~for which~~ for which ~~exist literature~~ exists ~~provides~~ provides sufficient literature information ~~for to~~ to conduct a quantitative meta-analysis. These compounds are indeed particularly responsive ~~for to~~ to uptake by plants, being relatively small and moderately hydrophobic (Burken & Schnoor, 1998). In addition to their persistence, ubiquity, and toxicity (Pankow & Cherry, 1996), characterization and monitoring of these plumes require advanced technologies and onerous-high funding, ~~that which~~ which could be ~~alleviated-mitigated~~ alleviated-mitigated by integrating a time-, and cost-effective technique like phytoscreening. The chance to determine the occurrence of subsurface volatile contaminants through trees is also important for evaluating the risks to human health such as potential ingestion and respiration from vapor intrusion into buildings, which are exposure pathways potentially associated with plant uptake. CEs detection in trees is affected by several contaminant-specific loss mechanisms (e.g., volatilization, phytodegradation) which may ~~result in lower~~ reduce concentrations in ~~plant/vegetal~~ plant/vegetal tissues ~~relative as compared~~ relative to gw concentrations. Phytoscreening of contaminated gw was ~~indeed~~ indeed considered ~~an~~ a valuable ecohydrogeological application (Cantonati et al., 2020). However, ~~but, to make the screening technique broadly applicable and accepted,~~ it is necessary to identify the main ~~control~~ control factors that drive the correlation between gw and tree-core contaminant concentration as well as ~~the contaminants'~~ the contaminants' detectability potential in trees in order to make this screening technique widely applicable and accepted, ~~of trees. The~~ The ~~The identification of such factors would allow maximizing the~~ correlation and detection capability can be maximized and would by providing directions ~~on for the the optimization and standardization of sampling, analysis, and data interpretation procedures.~~ Several studies concluded that the technique is only qualitatively reliable due to the poor correlation observed between gw and tree-core concentration (Holm and Rotard, 2011; Larsen et al., 2008; Ottosen et al., 2018). ~~Such poor correlation~~ This was attributed to ~~a variety of multiple~~ a variety of multiple factors that come ~~at~~ into stakeplay when dealing with living organisms (trees) to signal the state of contamination of an

environmental matrix ~~such as (gw.) with which p~~ Plants ~~are indeed involved interact with gw in through a~~  
complex partitioning mechanisms mediated by various chemical, biological, hydrological, and climatic  
factors. ~~Some s~~Synthesis efforts ~~have been were~~ directed to ~~the study investigate of the the limiting~~ factors  
~~that limit the and~~ application opportunities of this technique. ~~For As a general~~ example, Trapp (2007)  
proposed a ~~complex~~ theoretical model for the prediction of chemical uptake in trees ~~, based upon more than~~  
30 parameters, either of hydrogeological or ecological nature, ~~so thus~~ addressing the complexity of  
quantitative phytoscreening.

~~Our work~~This paper provides a systematic review of former literature on the main factors that likely affect:

- a) the correlation between CEs tree-core and gw concentration. Factors ~~conditions that that determine~~  
~~constrain~~ higher correlations ~~can be viewed as are~~ favorable to apply phytoscreening to monitor,  
quantitatively, CEs contamination severity and degradation or natural attenuation processes.
- b) the CEs detectability potential in trees. Factors ~~that determine conditions that constrain~~ a lower  
number of ~~contaminant contaminants undetections non-detections~~ in trees ~~can be viewed as are~~  
favorable to preliminary screen for suspected underground contaminations by CEs in  
~~underinvestigated poorly investigated~~ areas.

Several ~~constraining~~ factors were selected ~~and ,~~ grouped as follows: 1) physicochemical properties of the  
contaminants (molecular weight, water solubility, volatility, partition coefficients); 2) hydrogeology (depth  
to water table, aquifer thickness, hydraulic conductivity); 3) tree identity and anatomy (genus and family,  
xylem structure, tree trunk diameter); 4) sampling and extraction methodology (height above ground of tree-  
core sampling, tree-core length, extraction method of the contaminants).

## 2. MATERIALS AND METHODS

### 2.1 Data source

A systematic search for relevant studies of phytoscreening on CEs was conducted in Scopus in January 2021.

The search string was ~~the following~~:

*TITLE-ABS-KEY (phytoscreening OR (tree AND groundwater AND (trichloroethene OR perchloroethene  
OR dichloroethene OR "chlorinated ethenes"))).*

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110 The first database search yielded 64 references. To form a global-scale database of phytoscreening data on  
 111 CEs, only ~~the~~ references containing datasets of contaminated sites that met the following criteria were  
 112 selected: ~~(1)~~ sampling by tree trunk coring, ~~(2)~~ tree-core analysis of at least one compound among PCE,  
 113 TCE, and cDCE, and ~~(3)~~ spatial proximity between a given tree and a borehole where gw concentration  
 114 analysis showed concentrations above detection limits (the distances between the locations of trees and  
 115 boreholes varied from ~1 to ~10 m, or greater in few cases). When needed, we created contaminant  
 116 concentration contour maps to supplement the reported gw concentration data. A total of 7 articles were  
 117 identified reporting site datasets suitable for this study. The reference lists of these 7 articles were manually  
 118 searched for further studies containing relevant datasets, providing 1 positive result (a technical report).  
 119 Some of the final 8 selected documents contributed with more than one investigated site, providing  
 120 information on a total of 11 sites. A total of 267 tree-core samples (and respective gw samples) were  
 121 compiled in the global database, some of them reporting more than one compound concentration (Table 1).  
 122 The number of tree-core concentration data was 419 (see Supplementary material for the databaset), 118  
 123 being below the analytical detection limit (ND data hereafter). ND data represent a small fraction for most  
 124 sites (below 15%; e.g.e.g., Struckhoff et al., 2005), whereas in a few sites they are almost the majority (e.g.,  
 125 Larsen et al., 2008; Cox, 2002). The observations above detection limits are distributed as follows: PCE - 43  
 126 observations, TCE - 194 observations, cDCE - 124 observations, and the sum of CEs - 58 observations  
 127 ~~relatedpertaining~~ to one study that did not indicate single compound concentrations (Wittlingerova et al.,  
 128 2013). No data were compiled for VC because only Ottosen et al. (2018) were able to detect traces of VC in  
 129 trees ~~in very specific~~under specific environmental conditions. No spatial or temporal average concentrations  
 130 were included in the database except for one site (Nogales site, Arizona; Duncan et al., 2017) ~~where-in which~~  
 131 only ~~an average~~-PCE average gw concentration (2 µg/L) was ~~reported~~provided. ~~It-This site~~ was included in  
 132 the database for its significance in terms of uniqueness ~~in the database~~: cores were sampled and extracted  
 133 with methanol from trees of 4 different families inhabiting in an arid environment with a high-DWTdeep  
 134 aquifer table (9-10 m b.g.l.), ~~cores from trees of 4 different families were sampled and extracted with~~  
 135 ~~methanol~~, showing PCE concentration up to 500 µg/kg.  
 136 Data ~~for on~~ contaminant concentration in tree-core samples and gw samples were reported in two different  
 137 types of units, i.e., mass/mass (typically µg/kg) and mass/volume (typically µg/L), respectively. No

conversion was performed from the mass/mass unit to the mass/volume unit for tree-cores. This was considered acceptable since the focus was on the correlation between the concentration in different matrices along with the detectability potential. The unfeasibility of the conversion is mostly due to the lack of information on sampled tree-core dry weights and volumes. Besides, wood-water partition coefficients of the contaminants would also be needed for a reliable conversion. Very few studies estimated the latter ~~and~~ for a ~~limited-small~~ number of tree species (e.g., poplars in Baduru et al., 2008). The ~~unfeasibility of such~~ lack of conversion hindered the possibility of performing multivariate statistical analyses. Due to this limitation, a meta-analysis of the influence of each factor was performed to analyze the database. It is worth noting that ~~the the~~ results of ~~such-this~~ analysis will be subject to an intrinsic uncertainty associated with processing each factor as independent ~~of one another and singular~~.

Information on the factors influencing the correlation between tree-cores and gw concentration as well as the potential for detectability in trees (i.e., the hydrogeological conditions of the underlying contaminated aquifers, tree identity and anatomy, and sampling and extraction protocols; Table 2) were retrieved from the 8 selected ~~documents-articles~~ and associated to each of the 419 tree-core concentration data.

As for hydrogeological parameters, involving either the permeable porous medium (aquifer) or gw flowing inside it, we retrieved: depth to water table (DWT in m below ground level), intended as the distance between ground level and the surface at water pressure equal to atmospheric pressure (information retrieved for all the 419 tree concentration data); thickness of the saturated portion of the aquifer (b in m) intended as the distance between the water table and the low permeability bottom of the aquifer (retrieved for 235 out of 419 tree concentration); bulk saturated hydraulic conductivity of the aquifer (K in m/s; 373 out of 419 tree concentration). When K values of the aquifers were not specified (25% of the ~~total dataset~~ database), ranges of conductivities were inferred in agreement with the local description of the lithology (Freeze & Cherry, 1979).

With regards to tree identity and anatomy, we retained information on the genus (~~known for~~ 398 out of 419 data) and on the tree diameter at breast height (DBH in cm; ~~for~~ 142 out of 419 ~~tree concentration data~~). ~~From the~~ Based on the genus, we ~~were also able to report-retrieved~~ the correspondent xylem structure, intended as the distribution of pores and vessels among growth rings. ~~The xylem, or sapwood, is the active portion of the trunk where water transport takes place.~~ We considered three ~~main wood-xylem~~ types: coniferous, diffuse-

166 porous, and ring-porous (Panshin & de Zeeuw, 1970). Coniferous xylems are characterized by small cells  
167 used for water transport and structural support. Diffuse-porous xylems additionally contain large vessels that  
168 are randomly distributed throughout the wood, while ring-porous xylems have larger diameter vessels  
169 concentrated in the early-wood. Conifers and diffuse-porous trees tend to have deep functional xylems as  
170 well as low average conductivity due to small and short conduits. In contrast, most of the conductance in  
171 ring-porous species is isolated to the outermost annual growth ring that contains functional vessels (Bush et  
172 al., 2010; Cermak et al., 1992).

173 When available, ~~the~~ sampling and extraction protocols used to prepare tree-cores for analysis were retrieved:  
174 length of tree-core samples (L in cm; 369 out of 419 ~~tree-concentration~~data), sampling height ~~along-on~~ the  
175 trunk (H in cm above ground level; ~~known-for~~ 398 out of 419 ~~tree-concentration~~data), and extraction method  
176 (419 out of 419 ~~tree-concentration~~data) including extraction from dry vials (Cox, 2002; Larsen et al., 2008;  
177 Struckhoff et al., 2005; Vroblesky et al., 1999, 2004), vials containing organic-free water (Wittlingerova et  
178 al., 2013), or methanol solutions (Duncan et al., 2017), Solid Phase Micro-Extraction (SPME; Holm &  
179 Rotard, 2011).

## 180 2.2 Statistical meta-analysis

181 The correlation between gw and tree-core concentration was quantified by Spearman's rank ~~correlation~~  
182 coefficient  $\rho$  (Journel and Deutsch, 1997), a widely used approach for assessing the relationship between  
183 parameters when it is expected to be non-linear, as in highly skewed datasets. Indeed, both tree-core and gw  
184 concentrations represent highly skewed data sets, as ~~normally-regularly~~ found in contaminated sites (Juang et  
185 al., 2001). As an example, tree-core concentrations had a distribution with positive skewness of 3.17, 8.21,  
186 and 6.85 for PCE, TCE, and cDCE, respectively. A useful property of  $\rho$  is that its value is invariant to any  
187 monotonic transformation applied to the data (e.g., logarithmic transformation). Outliers were not removed  
188 from the ~~data~~baseset due to the lack of knowledge about the uncertainty associated with the measurements. It  
189 is worth noting that  $\rho$  is insensitive to outliers, therefore, representing a robust statistic tool ~~in the~~  
190 ~~abovementioned-circumstance for our database~~. The detectability potential of contaminants in trees was  
191 quantified as the percentage of ND (ND%) data to the total number of observations.

192 Spearman's  $\rho$  and ND% were calculated separately for each compound (PCE, TCE, and cDCE) to assess the  
193 influence of contaminant-specific properties such as molecular weight ( $M_w$ ), water solubility ( $S_w$ ), Henry's

constant ( $H_c$ ), and octanol-water partition coefficient ( $\log K_{ow}$ ). In the case of the dataset of Wittlingerova et al. (2013) reporting only sums of CEs (PCE, TCE, cDCE, tDCE, 1,1-DCE, and VC),  $\rho$  and ND% were calculated on the sums.

The factors of in Table 2 were then split/divided into intervals and Spearman's  $\rho$  were derived for the concentration data associated-with/within each interval. For continuous factors (e.g., aquifer properties or tree diameter), we determined discrete intervals based on medians and percentiles associated with each factor to have a similar number of observations within each interval. Only concentration data above detection limits were included-in-the-count/considered. In the case of discrete factors (e.g., tree species, extraction method), only values associated with a minimum of 10 observations were considered in the statistical analysis, except for one single case where only 8 observations were associated with extraction with methanol (Duncan et al., 2017). The ND% was determined within each of the aforementioned intervals to assess the influence of the different factors on detectability. To avoid biases associated with trees that could be growing above more dilute contamination areas, the ND% was calculated only when the concentration in gw was above 11  $\mu\text{g/L}$ . This threshold was determined as the 5<sup>th</sup> percentile of gw concentration data. The final number of ND data was 104 out of 118 ND tree-core data. It is noteworthy that in some cases, such as when processing hydrogeological parameters like b and K, uncertainty-on-the-results may be uncertain should be considered since some/certain parameters do not appreciably vary spatially across a specific site.

Results were interpreted in terms of high or low correlations (determining optimal factors conditions to characterize the contamination) and high or low detectability potential (determining optimal factors conditions to screen gw contamination).

### 3. RESULTS AND DISCUSSION

#### 3.1 Contaminant properties

The correlation between the concentration in tree-cores and gw was statistically meaningful ( $p\text{-value} \leq 0.05$ ) for all four series (PCE, TCE, cDCE, and the sum of CEs).

The  $\rho$  values indicate a low variability among CEs in terms of correlation between tree-core and gw concentration (Figure 1), with slightly lower values for higher chlorinated compounds PCE and TCE ( $\rho$  of 0.37 and 0.34, respectively) compared to the lower chlorinated cDCE ( $\rho$  of 0.41). On the other hand, ND% is widely/greatly different-differed between higher chlorinated compounds PCE and TCE (12 and 23%,

222 respectively) and cDCE (47%) with the first two performing better in terms of detectability potential. It is  
223 noteworthy that the highest correlation coefficient (0.63) and lowest ND% value (0%) were found for the  
224 sum of CEs (reported by Wittlingerova et al., 2013). This could be explained by contaminant transformation  
225 processes taking place either in the rhizosphere or in the xylem (Newman and Reynolds, 2004) that would  
226 negatively affect the correlation of ~~the~~ single compounds. ~~However, (T~~his result is ~~although~~ associated with  
227 only one site.

228 The physicochemical properties of CEs (Table 3) likely influence the behavior of each compound in trees.  
229 Larsen et al. (2008) observed a better correlation for cDCE compared to TCE and PCE which was attributed  
230 to the higher volatility (higher  $H_c$ ) of the latter, possibly causing a higher loss through the bark (Vroblesky et  
231 al., 1999). According to Limmer & Burken (2015), contaminant concentrations decreased with increasing  
232 volatility, due either to volatilization from the roots, bark, or subsurface. Limmer & Burken (2015) reported  
233 a decrease in contaminant concentrations with increasing volatility, attributing it to volatilization from either  
234 the bark, the roots, or the subsurface. The results of oOur study agrees are consistent with these findings,  
235 with PCE and TCE showing a slightly lower  $\rho$  compared to cDCE. ~~In addition, T~~he correlation potential of  
236 PCE and TCE may ~~also~~ be hindered by ~~a~~ their lower tendency ~~for to~~ plant uptake ~~into trees~~ compared to  
237 cDCE, ~~which is~~ driven by their higher  $M_w$  and  $K_{ow}$ , and lower  $S_w$ , and higher  $K_{ow}$ . Uptake from tree roots  
238 was indeed reported to be favored for compounds with low  $M_w$  (~~Baduru et al., 2008~~) due to their higher  
239 tendency to diffuse (~~Baduru et al., 2008~~), whereas higher  $S_w$  would possibly favor contaminant dissolution in  
240 water and consequent tree uptake. Besides,  
241 ~~H~~igh sorption compounds ( $\log K_{ow} > 3$ ) ~~were reported to were shown to have a higher tendency~~ tend to be  
242 absorbed primarily by root surfaces, resulting in less translocation ~~within trees to the xylem~~ (Schnoor et al.,  
243 1995). Similarly, a study by Dettenmaier et al. (2009) indicated that ~~highly high~~-hydrophilic compounds are  
244 most likely ~~to be uptaken~~ absorbed by ~~plant~~ roots and ~~translocated~~ transferred to the xylem. We ~~may can~~ also  
245 ~~assume~~ speculate that once in the ~~tree~~ xylem, higher  $\log K_{ow}$  compounds likely tend to ~~get be absorbed in by~~  
246 ~~the~~ xylem tissues, resulting in a prolonged accumulation in the tree and thus ~~and~~ a higher detectability  
247 potential. ~~PCE and TCE higher log K<sub>ow</sub> can indeed~~ This could ~~explain their the~~ higher detectability potential  
248 of PCE and TCE (lower ND%) compared to cDCE. Besides Moreover, ~~PCE and TCE~~ their higher  $H_c$  can aid  
249 the analytical detection when using headspace methods. Concurrently, the ~~On the other hand, cDCE~~ lower

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log  $K_{ow}$  and ~~lower~~  $M_w$  of cDCE may ~~\_, respectively,~~ hinder accumulation and favor contaminant loss ~~out~~ ~~of~~through the bark ~~despite its low  $H_c$  despite the low  $H_c$~~  (Baduru et al., 2008), resulting in an overall lower detectability potential. The extremely rare detection of VC confirms the role of  $H_c$ ,  $M_w$ , and log  $K_{ow}$  in contaminant detectability in trees.

### 3.2 Hydrogeology and aquifer parameters

Three intervals were considered for DWT:  $DWT < 1$ ,  $1 \leq DWT < 3$ , and  $DWT \geq 3$  m b.g.l.. Concentration data shows a statistically ~~meaningful~~significant correlation value ( $p$ -value  $\leq 0.05$ ; Figure 2) in the three cases. A slightly decreasing correlation with increasing DWT ~~is~~was observed ( $\rho = 0.63$ , 0.54, and 0.52 for  $DWT < 1$ ,  $1 \leq DWT < 3$ , and  $DWT \geq 3$  m b.g.l., respectively). ~~On the other hand, The higher ND% was seen within the~~ shallow interval ~~showed the higher ND% (35%) compared to~~whereas the inferior intervals had significantly ~~lower ND% (16% and 17%, respectively, for the medium and the deep interval for the medium and deep~~ ~~interval, respectively)~~. Duncan & Brusseau (2018) assessed for the first time how DWT could affect the correlation between VOCs concentration in tree tissues and gw (based on 100 measurements). They observed a higher correlation in samples from sites with a  $DWT < 4$  m, concluding that a low thickness of the unsaturated zone significantly affects phytoscreening efficiency. Despite ~~the~~ overall consistency ~~of our~~ ~~results~~ with the ~~cited~~ literature ~~(decreasing  $\rho$  with increasing DWT)~~,  $\rho$  shows small differences among DWT intervals, suggesting a low influence of this factor on the degree of correlation. The difference with Duncan & Brusseau (2018) may lie in the use of different correlation coefficients and interval divisions. In our analysis  $\rho$  was chosen due to the non-linear distribution of the concentration dataset while Duncan & Brusseau (2018) assessed the correlation through Pearson's coefficient ( $r^2$ ) thus assuming linearity of the dataset. Besides, ~~at sites with a more substantial vadose zone, mineralization of CEs can occur before~~ ~~translocation of the contaminant in the tree due to more hypoxic conditions (Bradley & Chapelle, 2011),~~ ~~leading to lower correlation potential for deeper aquifers. Similar findings have been reported by Wilson et~~ ~~al. (2013) for BTEX translocation in trees. At the same time,~~ when DWT is lower, volatilization loss of CEs is promoted at the interface between the saturated and the vadose zone, being the thickness and water content of the latter more subject to atmospheric variations (Pankow & Cherry, 1996). As tree roots are usually located at this interface, the enhanced volatilization of ~~CEs~~CEs could ~~induce a lowering in~~decrease their detectability potential (higher ND% for the shallow interval). ~~At the same time, at sites with a more~~



substantial vadose zone, mineralization of CEs can occur prior to translocation of the contaminant in the tree due to more hypoxic conditions (Bradley & Chapelle, 2011), leading to higher correlation potential for shallower aquifers. Similar findings have been reported by Wilson et al. (2013) for BTEX translocation in trees.

Aquifer thicknesses were ranked-clustered into two intervals:  $b \leq 3.5$  and  $b > 3.5$  m. Data associated with lower aquifer thickness show a very high positive correlation ( $\rho=0.71$ ), whereas those associated with thicker aquifers higher  $b$  have a significantly weaker correlation ( $\rho=0.30$ ). A reason for that This may be because that CEs, in the majority of contaminant events, enter the subsoil as dense non-aqueous phase liquids (DNAPLs), which tend to sink towards deeper sections of the aquifer, thus influencing the shape of dissolved contaminant plumes (e.g., Parker et al., 2003). In particular, the sinking of DNAPLs-CEs could result in an increased distance of the dissolved contaminant plume from the root zone in thicker aquifers. Notably, aquifer thickness appears to have the highest influence on correlation compared to other factors. On the other hand, a lower ND% is associated with the thicker aquifer interval compared to the thinner interval (4% and 19% for  $b > 3.5$  m and 19% for and  $b \leq 3.5$  m, respectively). This result finds poor scientific has poor validations: we can speculate that thin aquifers have a lower geometrical probability of being intercepted by tree roots than thick ones.

Two intervals of  $K$  were considered:  $K < 1 \times 10^{-5}$  and  $K \geq 1 \times 10^{-5}$  m/s. Concentrations referred to higher  $K$  values show a slightly higher correlation ( $\rho=0.73$ ) compared to those referred to lower conductivities ( $\rho=0.66$ ). These results suggest that  $K$  poorly affects the correlation between tree-core and gw concentration. On the other hand, the lower  $K$  interval includes 38% of ND whereas the higher  $K$  interval includes 18%. More permeable aquifers are therefore more suited in terms of detectability potential. A relatively higher permeability can indeed enhance the mobility of contaminants in the subsoil, likely favoring plant uptake, similarly to what happens when extracting gw from wells or soil gas from soil gas probes.

### 3.3 Tree identity and anatomy

The 22 tree genera of our dataset were clustered by divided according to their families and relative-xylem structures (coniferous, diffuse-porous, ring-porous). Results show a significant positive correlation with most families (Figure 3), with  $\rho$  being highest for coniferous, i.e. Pinaceae ( $\rho=0.86$ ) and Cupressaceae ( $\rho=0.66$ ).

305 These conifers also have moderately low ND% (24% and 30%, ~~respectively~~ for Pinaceae and Cupressaceae,  
 306 ~~respectively~~). Consistently with our observations, Trapp et al. (2007) stated that conifers are best suited for  
 307 phytoscreening because they have a broad ~~sapwood-xylem zone~~ (the active portion of the stem), and  
 308 transpire throughout the whole year, resulting in a continuous uptake of gw. Ring-porous Fagaceae  
 309 (primarily *Quercus*) presented a slightly positive correlation ( $\rho=0.39$ ) and a high ND% (57%). The ring-  
 310 porous structure likely promotes volatilization loss through the bark, possibly affecting the observed low  
 311 correlation and detectability potential. Indeed, ~~in ring-porous trees~~, over 90% of water is transported in the  
 312 outermost growth ring ~~in ring-porous trees~~ whereas in diffuse-porous and coniferous trees water flow is more  
 313 equally distributed among rings (Ellmore and Ewers, 1986). Diffuse-porous Nyssaceae and Betulaceae show  
 314 a slightly lower  $\rho$  compared to conifers ~~sous trees~~ (0.74 and 0.65, respectively), and a low ND% (29 and 25%,  
 315 respectively) although results for Nyssaceae must be taken with caution because they refer to one single  
 316 study site (Savannah River Site, USA; Vroblesky et al., 1999) where the aquifer was shallow (DWT<1 m  
 317 b.g.l.). On the other hand, diffuse-porous Salicaceae and Altingiaceae do not show a significant correlation  
 318 ( $p\text{-value}>0.05$ ) and highly fluctuating ND% (very low for Salicaceae – 3% and very high for Altingiaceae –  
 319 64%). The high variability among diffuse-porous families in terms of  $\rho$  and ND% could be associated with  
 320 different arrangements and sizes of the vessels regulating the conductivity of the ~~sapwood~~ xylem, which in  
 321 turn can also vary with age. For example, Salicaceae (*Salix* and *Populus*), widely used in phytoscreening and  
 322 phytoremediation due to their fast growth, high uptake rates, and widespread occurrence in temperate  
 323 climates, showed the ~~highest~~ best detectability potential ~~but-although~~ no correlation between tree-core and gw  
 324 concentration. Besides, Negri et al. (2003) stated that Salicaceae are genetically predisposed to develop roots  
 325 extending to the water table at depths greater than 12 m b.g.l., thereby ~~extending-widening~~ their detectability  
 326 potential to deep aquifers. Altingiaceae (*Liquidambar*, present only in the study of Vroblesky et al., 1999)  
 327 also showed no correlation whilst a low detectability potential. This family was studied by Strycharz and  
 328 Newman (2009) in a greenhouse experiment where also Platanaceae and Salicaceae were involved. ~~R~~The  
 329 ~~results~~ showed that among the 3 families, Altingiaceae was the less recommended for phytoremediation  
 330 activities. Other diffuse-porous, like Betulaceae (*Alnus* and *Betula*), showed instead a correlation and  
 331 detectability ~~potential~~ comparable to conifers. Lewis et al. (2015) calculated that ~~a~~-*Betula pPendula* can  
 332 accumulate similar ~~quantities-amounts~~ of TCE as *Populus* trees due to its lack of heartwood (~~nonfunctioning~~

333 xylem) and homogeneous ~~sapflow-xylem flow~~ (Westhoff et al., 2008), making ~~this species~~ it an ideal  
 334 suitable candidate for phytoremediation and phytoscreening ~~activities-activities~~. Eventually, the low number  
 335 of Platanaceae (diffuse-porous), Ulmaceae (ring-porous), and Rosaceae (diffuse-porous) in the ~~dataset~~  
 336 ~~database~~ (Table 2) ~~made-unfeasible~~ hindered an analysis on these families. Even so, Limmer & Burken  
 337 (2015) showed that the genus *Platanus* (Platanaceae) had a high detectability potential, especially for PCE  
 338 gw contamination, if compared to non-*Platanus* trees. Their result was although associated with *Platanus*  
 339 trees growing ~~primarily~~ in areas with shallow groundwater. ~~Oppositely~~ Conversely, ~~our data~~ data-associated  
 340 with on Platanaceae ~~trees in our dataset~~ showed that 3 out of 4 times this family ~~ese trees~~ did not detect  
 341 ~~contamination-contaminants~~ even with shallow gw (DWT<1 m b.g.l.; Savannah River Site, USA; Vrobletsky  
 342 et al., 1999); ~~although~~ albeit in that particular site aquifer ~~in that specific site (Savannah River Site, USA;~~  
 343 ~~Vrobletsky et al., 1999)~~ K was very low ( $5.3 \times 10^{-6}$  m/s). Yung et al. (2017) pointed out that besides *Populus*  
 344 and *Salix* (Salicaceae, diffuse-porous) and *Betula* (Betulaceae, diffuse-porous), *Quercus* and *Ulmus*  
 345 (Fagaceae and Ulmaceae, both ring-porous) are also efficient biomonitors of PCE and TCE contamination.  
 346 Notwithstanding the contrast with our results on Fagaceae, the 2 Ulmaceae trees in our ~~dataset-database~~  
 347 (Carswell Golf Course, USA; Vrobletsky et al., 2004) showed TCE concentrations above detection limits,  
 348 with DWT at 1 ~~and to~~ 5 m b.g.l. ~~and with an~~ - aquifer K of  $7 \times 10^{-5}$  m/s, and b of 0.9 m. This may suggest that  
 349 even among ring-porous trees a great variability in concentration results is expected.  
 350 Tree size (measured as DBH) in our ~~database-database~~ ranges between 18 and 102 cm and values were split  
 351 into 3 intervals: DBH<25, 25≤DBH<40 ~~cm~~, and DBH≥40 cm. ~~Since~~ data were filled only for 34% of the  
 352 ~~database-database~~ (Table 2), ~~so that~~ results should must be taken considered with caution. The lower interval  
 353 shows a high positive correlation ( $\rho=0.79$ ). The correlation decreases significantly in the medium interval  
 354 ( $\rho=0.47$ ). The higher interval shows no significant correlation ( $p\text{-value}>0.05$ ). ND% is instead comparable  
 355 among DBH intervals (10%, 8%, and 8%, respectively for DBH<25, 25≤DBH<40 cm, and DBH≥40 cm).  
 356 Several studies suggest that tree size has little effect on tree-core concentration (Limmer & Burken, 2015;  
 357 Wahyudi et al., 2012) while other studies demonstrated that diffusional loss in small trees (DBH of 2 cm)  
 358 occurs at a rate 10 times higher than in trees with DBH 15 cm due to their greater surface area to volume  
 359 ratio that more quickly depletes the compound reservoir in the trunk (Schumacher et al., 2004; Struckhoff,  
 360 2003). This could explain the slightly higher ND% of smaller trees. In contrast, our results show that smaller

361 trees have greater efficiency in terms of quantitative analysis of a-gw contamination (high  $\rho$ ). In smaller  
362 trees, we could indeed expect less variability in concentration around and across the trunk due to a less  
363 compartmentalized flow in the ~~sapwood~~xylem. Also, in smaller trees it is highly probable to sample a  
364 consistent thickness of the total ~~sapwood~~xylem, resulting in a concentration that averages the radial  
365 variability. More variability is instead observed in larger trees where sampling direction has a strong  
366 influence on the concentration, thus influencing the correlation.

### 367 3.4 Sampling and analysis protocols

368 In our ~~dataset~~ database tree-core L ranges from 3.8 to 12.5 cm and was ~~clustered~~arranged into two intervals:  
369  $L \leq 6$  and  $L > 6$  cm. Shorter cores do not ~~show a~~ significantly correlation between ~~e-with~~ tree-core and gw  
370 concentration ( $p$ -value $>0.05$ ) whereas longer cores have a high positive correlation ( $\rho=0.71$ ; Figure 6). This  
371 ~~result finds agreement~~agrees with in Ma & Burken (2003) and ~~the the~~ USGS user guide published by  
372 Vroblesky (2008), ~~which suggesting~~ a better correlation when the core samples are longer than  $\sim 7$ -8 cm.  
373 Shorter cores may be ~~also~~ acceptable for ring-porous trees, in which water transport takes place mostly in the  
374 outermost ring (Ellmore and Ewers, 1986). The detectability potential is lower for ~~the longer cores~~the higher  
375 ~~L interval-interval~~ (ND of 11% and 30% ~~for~~  $L \leq 6$  ~~cm and 30% for~~  $L > 6$  cm, respectively), likely  
376 ~~possibly~~ indicating that drilling longer tree-cores ~~could promote diffusional loss out of the sample since~~  
377 ~~sampling employs requires relatively higher longer sampling times~~periods (tree-cores are usually cut in  
378 smaller pieces before being put in the vials) ~~that can possibly promote diffusional loss out of the sample~~.  
379 ~~The s~~Sampling elevation, H from the base of the trunk (~~m a.g.l.~~), ranges between 50 and 900 cm a.g.l. and  
380 was ~~clustered~~split into three intervals:  $H < 99$ ,  $99 < H \leq 120$ , and  $H > 120$  cm a.g.l. The ~~medium~~ interval  
381 ~~99 < H < 120 cm~~ shows a very high correlation between tree-core and gw concentration ( $\rho=0.84$ ; Figure 6),  
382 which decreases ~~above 120 cm a.g.l. for higher H~~ ( $\rho=0.42$ ). ~~Sampling height below 99 cm~~The lower interval  
383 shows no significant correlation ( $p$ -value $>0.05$ ) although the data pertain to only one survey by Holm &  
384 Rotard (2011). The reason for the high  $\rho$  value at medium ~~sampling height~~H is still unknown, ~~but w~~We can  
385 speculate that this is related to the attainment of an equilibrium of the contaminant inside the wood-air-water  
386 partitioning system. On the other hand, a low ~~number of~~ND% data was registered for the ~~lowest~~lower H  
387 interval (7%) whereas the ~~higher~~ intervals ~~99 < H < 120 and H > 120 cm a.g.l.~~ are associated with higher ND%  
388 (24% and 33% ~~for the medium and higher H interval,~~ respectively). This result is consistent with the

389 experiments of Ma & Burken (2003) where a higher TCE loss was observed higher up the trunk. Thus, a  
 390 lower rate of diffusional loss from the bark may be expected for the lower  $\Delta H$  intervals. On the other hand,  
 391 Ottosen et al. (2018) sampled tree-cores just above the ground surface without distinguishing a clear  
 392 advantage from this sampling strategy.

393 Our dataset includes 4 extraction methods used for analysis (dry sample, organic-free water, methanol  
 394 solution, and SPME; Figure 6). The dry and the water extracted samples showed moderately high correlation  
 395 ~~potential~~ ( $p=0.55$  and  $p=0.64$ , ~~for dry and water extraction, respectively for dry and water extraction~~).  
 396 However, data from water extracted samples ~~although~~ <sup>d</sup>pertain to only one survey where concentration data  
 397 ~~corresponds relate~~ to the sum of CEs (Wittlingerova et al., 2013). The high  $p$  could be associated either with  
 398 the extraction method or with the fact that the sum of CEs was considered (see section 3.1). Methanol  
 399 extracted samples, ~~pertaining related~~ <sup>p</sup>to the study cases of Duncan et al. (2017), were collected with  
 400 unfavorable conditions in arid ~~and~~ hot environments (Nogales site, Park-Euclid, and Motorola 52<sup>nd</sup>  
 401 superfund site in Arizona, USA). The small number of tree-cores (8) sampled with this method ~~can be the~~  
 402 ~~reason for its associated in~~ <sup>may explain the observed non-significant correlation value</sup> ( $p\text{-value}>0.05$ ).  
 403 Besides, tree-core concentrations ~~sampled in particularly associated with~~ arid environments ~~are~~ <sup>could be</sup>  
 404 ~~possibly more likely a function of associated with vadose zone~~ vapor phase concentration ~~in the vadose zone~~  
 405 rather than gw concentration since tree-roots would unlikely reach a DWT of 26 m b.g.l. as in the case of the  
 406 Park-Euclid site. ~~In support of this hypothesis, The fact that we also observed that~~ 5 out of 8 tree-core  
 407 ~~methanol~~ concentrations of PCE were higher than 300  $\mu\text{g/kg}$  ~~although despite being~~ associated with very low  
 408 gw concentrations of PCE of 2  $\mu\text{g/L}$  (2  $\mu\text{g/L}$ ; i.e., lower than the gw concentration threshold ~~we~~ defined for  
 409 ~~calculations on ND% calculation; See Section 2.2.)~~ further supports the hypothesis ~~suggesting that trees~~  
 410 ~~were absorbing uptake of~~ contaminants from a matrix ~~different other~~ than gw. This may have further  
 411 hindered correlation with gw ~~in the case of methanol extraction~~. The analysis following SPME, associated  
 412 with only one site (Potsdam-Krampnitz military base, Germany; Holm & Rotard, 2011), ~~also~~ showed no  
 413 significant correlation ( $p\text{-value}>0.05$ ). ~~Even so, the~~ ND% was very low for SPME (7%) ~~and as well as~~  
 414 water extracted samples (0%). ~~However, since these methods were used in single study cases, although~~ these  
 415 results may be ~~associated with~~ <sup>related to</sup> other site-specific conditions or sampling protocols ~~since these~~

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416 ~~methods pertain to single study cases. In terms of ND%, t~~The dry and methanol extraction ~~showed produced~~  
417 comparable results ~~in terms of ND%~~ (34%, and 33% for dry and methanol extraction, respectively).

#### 418 4. SUMMARY AND CONCLUSIONS

419 The ~~efficiency effectiveness~~ of phytoscreening has been ~~tested assessed through via~~ a meta-analysis of  
420 literature data ~~to define determine the potential of trees to~~ (a) ~~the potential of trees to~~ monitor groundwater  
421 plumes of CEs, ~~here~~ expressed as ~~a the~~ degree of correlation between tree-core and gw concentration, and (b)  
422 ~~the potential of trees to~~ detect the occurrence of ~~groundwater gw~~ contamination ~~events~~ by CEs in ~~poorly~~  
423 ~~underinvestigated areas, here~~ expressed as ~~a the percentage rate~~ of tree-cores ~~that showed~~ concentrations  
424 ~~below above the~~ detection limit ~~in significantly contaminated areass in the occurrence of groundwater~~  
425 ~~contamination. To these aims, s~~Several factors ~~possibly likely~~ influencing correlation and detectability were  
426 ~~taken into account considered. These factors included, namely the~~ physicochemical properties of CEs, ~~the~~  
427 hydrogeological conditions of the underlying contaminated aquifers, trees identity and anatomy, and  
428 sampling and extraction protocols.

429 The correlation (~~quantitative quantitative~~ monitoring potential) ~~appears to be is~~ higher when (1) ~~the~~  
430 hydrogeological dynamics favor direct uptake of contaminated water, and (2) ~~the~~ concentration is  
431 homogeneously distributed in the tree and the ~~tree-core~~ sample. ~~Uptake-Direct tree uptake of contaminated~~  
432 ~~gw~~ is favored for the lighter and more soluble cDCE, ~~and in the case of in the case of~~ shallow ~~water tables~~  
433 (DWT<3 m b.g.l.), ~~and in thin~~ (~~b<3.5 m~~), and permeable aquifers (~~b<3.5 m~~;  $K \geq 1 \times 10^{-5}$  m/s). The  
434 homogeneity of concentration in the ~~sapwood xylem~~ is ~~likely~~ higher for Pinaceae and Cupressaceae  
435 (coniferous), due to their non-porous xylem, and ~~in for~~ smaller diameter trees (DBH<25 cm), whereas  
436 homogeneity of concentration in ~~the~~ tree-core is ~~enhanced facilitated in the case when sampling of~~ longer tree-  
437 cores (L>6 cm), ~~and possibly at a sampling height along the stem on the trunk~~ between 99<H≤120 cm a.g.l..

438 The detectability (qualitative screening potential) is higher when factor conditions favor accumulation in the  
439 xylem and hinder volatilization loss through the bark. ~~In these terms, PCE and TCE are more suited~~  
440 ~~compared to cDCE due to This is the case of PCE and TCE thanks to~~ their higher sorption and weight. Low  
441 volatilization loss was also inferred in the case of large-diameter trees (DBH≥40 cm), at ~~a low sampling~~  
442 height ~~on along~~ the trunk (H<99 cm a.g.l.), and for shorter cores ~~due to reduced time of sampling~~ (L≤6 cm)  
443 ~~due to reduced time of sampling~~. In the case of Salicaceae, high uptake rates may compensate for

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444 volatilization losses, thus increasing detectability. ~~Eventually~~Finally, the process of contaminant extraction  
445 ~~has also an effect on detectability that seem~~appears to be maximized when using organic-free water  
446 extraction and SPME.

447 Despite the clarifications provided by our meta-analysis, several factors ~~and processes possibly~~ influencing  
448 phytoscreening effectiveness remain unexplored at a global scale ~~as in the case of 1), among which:~~ climatic  
449 and meteorological conditions ~~influencing~~ affecting uptake and loss from the tree; 2) porosity and volumetric  
450 water content of the unsaturated zone influencing uptake and volatilization loss at the ground surface; 3)  
451 organic content in saturated and unsaturated layers influencing sorption of CEs to the solid matrix; 4)  
452 phytodegradation processes that may hinder correlation with CEs concentration in gw; 5) radial distance to  
453 boreholes likely affecting correlation between tree-core and gw concentration. ~~It is therefore necessary to~~  
454 ~~conduct additional research in these areas to improve the applicability of~~ Further research is needed in order  
455 ~~to fill this lack of knowledge~~the technique.

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## FIGURES CAPTION

**FIGURE 1.** Spearman's  $\rho$  (x-axis) and ND% (y-axis, values in inverse order) of compounds series. Blank symbols refer to as  $p$ -values > 0.05. Solid symbols refer to as  $p$ -values  $\leq$  0.05

**FIGURE 2.** Spearman's  $\rho$  (x-axis) and ND% (y-axis, values in inverse order) of each interval considered for the hydrogeological parameters. Blank symbols refer to as  $p$ -values > 0.05. Solid symbols refer to as  $p$ -values  $\leq$  0.05

**FIGURE 3.** Spearman's  $\rho$  (x-axis) and ND% (y-axis, values in inverse order) of each family and correspondent xylem structure. Blank symbols refer to as  $p$ -values > 0.05. Solid symbols refer to as  $p$ -values  $\leq$  0.05

**FIGURE 4.** Spearman's  $\rho$  (x-axis) and ND% (y-axis, values in inverse order) of each interval considered for tree diameters. Blank symbols refer to as  $p$ -values > 0.05. Solid symbols refer to as  $p$ -values  $\leq$  0.05

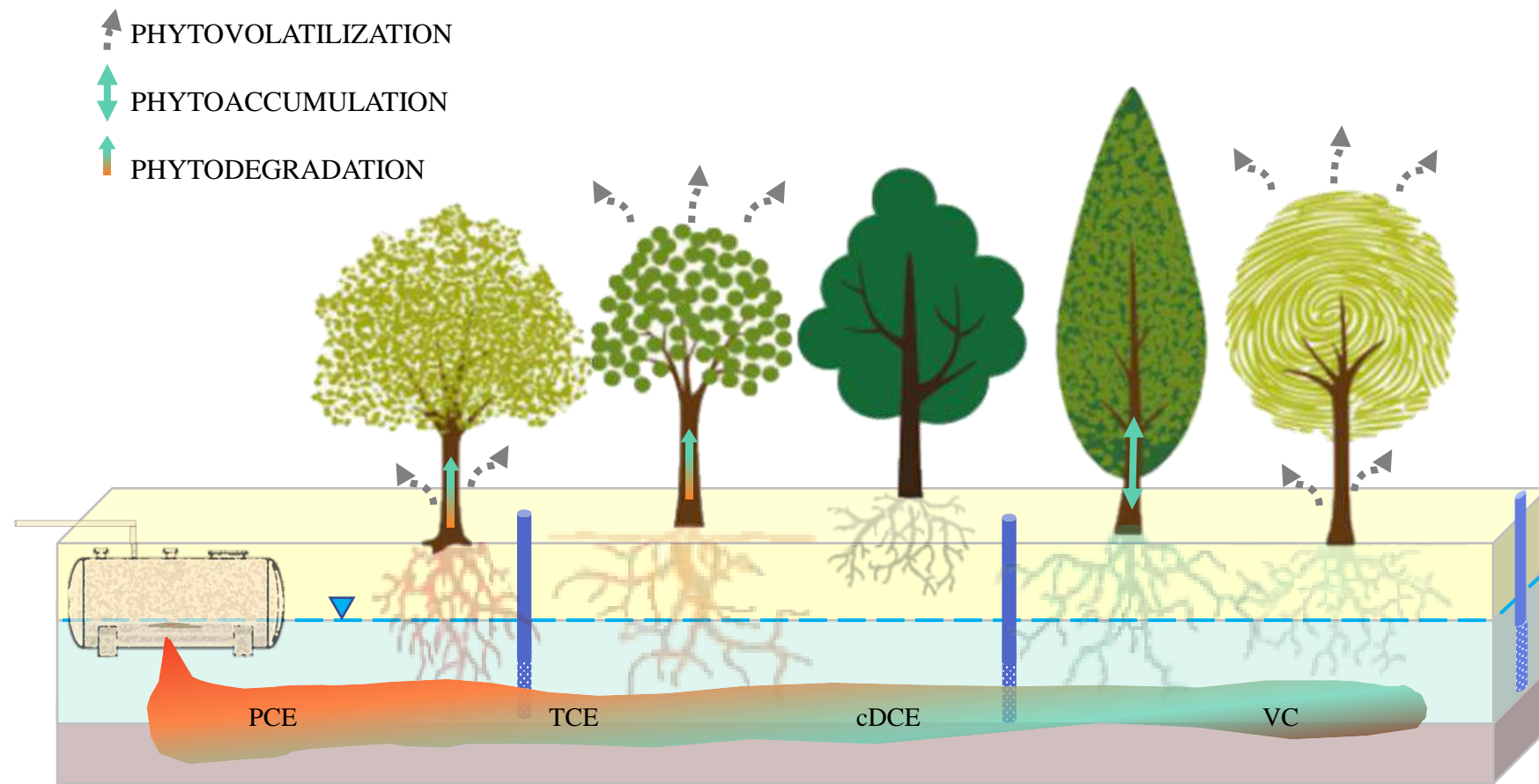
**FIGURE 5.** Spearman's  $\rho$  (x-axis) and ND% (y-axis, values in inverse order) of each interval considered for sampling and analysis protocols. Blank symbols refer to as  $p$ -values > 0.05. Solid symbols refer to as  $p$ -values  $\leq$  0.05

## TABLES CAPTION

**TABLE 1.** References used for statistical analysis of the database: geographical location, number of tree-core samples, and correspondent detected compounds (Above Detection Limit: A.D.L.). Total number of data and Non-Detection% in the last columns.

**TABLE 2.** Factors potentially affecting the effectiveness of phytoscreening of CEs in gw and relative descriptive statistics. Selected intervals, relative number of observations, and relative sites per interval.

**TABLE 3.** Physico-chemical properties of the chlorinated ethenes: molecular weight ( $M_w$ ), water solubility ( $S_w$ ), Henry's constant ( $H_c$ ), octanol-water partition coefficient ( $\log K_{ow}$ ). Derived from Mackay et al. (2006)



## CONTAMINANT QUANTIFICATION POTENTIAL

DETECTABILITY POTENTIAL		
	<p>SORPTION TO TREE TISSUE</p> <p>LOW PHYTOVOLATILIZATION</p>	<p>EFFECTIVE UPTAKE</p> <p>HOMOGENEITY OF COMPOUND DISTRIBUTION IN THE TREE</p>
	<p>INEFFECTIVE UPTAKE</p> <p>PHYTOVOLATILIZATION OR PHYTODEGRADATION</p>	

## HIGHLIGHTS

- Chlorinated ethenes groundwater contamination can be low cost screened by trees;
- Phytoscreening is a quantitative method for shallow, thin, and permeable aquifers;
- Coniferous and diffuse-porous trees show high detectability potential;
- Sampling longer tree-cores at lower heights is preferable.

# **A quantitative review and meta-analysis on phytoscreening applied to aquifers contaminated by chlorinated ethenes**

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## **ABSTRACT**

Applications and acceptance of phytoscreening, i.e., the use of trees as screening tools for underground contamination, are still limited in many countries due to the lack of awareness of application policies, the intrinsic qualitative nature of the technique, and the paucity of critical analyses on available data. To date, the conditions influencing the effectiveness of the technique have been descriptively discussed, yet rarely quantified. This review will contribute to filling this knowledge gap, shedding light on the most suitable approaches to apply phytoscreening. The focus was placed specifically on chlorinated ethene compounds since they are among the main organic contaminants in groundwater and have been the most studied in the field of phytoscreening. Chlorinated ethenes' behavior and biodegradation potential largely depend on their physicochemical properties as well as the hydrogeological features of the system in which they migrate. Besides, their fate and transport in surface ecosystems are still poorly understood. Here, phytoscreening data from sites contaminated by chlorinated ethenes were extracted from relevant literature to form a global-scale database. Data were statistically analyzed to identify the major drivers of variability in tree-cores concentration. Correlation between tree-core and groundwater concentration was quantified through Spearman's rank coefficients, whilst detectability potential was determined based on tree-cores showing non-detection of contaminants. The influence on such parameters of factors like contaminant properties, hydrogeology, tree features, and sampling/analytical protocols was assessed. Results suggest that factors controlling plant uptake and contaminant phytovolatilization regulate correlation and detectability, respectively. Conditions increasing the correlation (e.g., sites with shallow and permeable aquifers) are recommended for phytoscreening applications aimed at mapping and monitoring contaminant plumes, whereas



conditions increasing detectability (e.g., sampling tree-cores near ground level) are recommended to preliminary screen underground contamination in poorly investigated areas.

**KEYWORDS:** groundwater, CEs, trees, quantitative phytoscreening

## 1. INTRODUCTION

Tree roots can carry contaminants dissolved in water through the trunk up to the leaves. This transport is based on direct contact of the roots with water inside the porous medium that surrounds the rhizosphere. Water can occur in different energy states: free moving gravity water in the saturated zone of the aquifer, referred to as groundwater (gw), or retention water (rw) subjected to suction and attached to soil particles as capillary or pellicular water in the unsaturated zone.

The use of plants in environmental hydrogeology has gained increasing attention during the last decades in academic research and consultant activity due to stimulating application perspectives. In parallel with contaminants removal by direct uptake and degradation (phytoremediation), Vroblesky et al. (1999) demonstrated for the first time that headspace analysis of tree-cores allows to delineate shallow gw contamination by chlorinated ethenes (CEs) such as trichloroethene (TCE) and cis 1,2-dichloroethene (cDCE). Later, Sorek et al. (2008) termed the technique “phytoscreening” and defined it as a simple, fast, non-invasive, and inexpensive screening for detecting subsurface contamination by volatile organic compounds (VOCs). Since Vroblesky et al. (1999), several comparisons between subsurface (soil, soil gas, and gw) and plant contamination were conducted, mostly by using tree-cores but also by using leaf and branch samples (e.g., Holm & Rotard, 2011; Wilcox & Johnson, 2016; Gopalakrishnan et al., 2007).

Besides screening and monitoring contaminant concentration for plume tracking or natural attenuation evaluation (e.g., Larsen et al., 2008), phytoscreening was used to assess soil vapor intrusions (e.g., Wilson et al., 2017; Algreen et al. 2015) and age-date contamination events through dendroecology (Balouet et al., 2007). Phytoscreening applicability was demonstrated for VOCs (e.g., BTEX; Wilson et al., 2013), perchlorate (e.g., Limmer et al., 2014), per- and polyfluoroalkyl substances (PFAS; Gobelius et al., 2017), or inorganic compounds like heavy metals (e.g., Algreen et al., 2014). However, CEs were the most frequent target in reported applications of phytoscreening. This review examines phytoscreening applications for CEs in groundwater, for which exist sufficient literature information to conduct a quantitative meta-analysis. These compounds are indeed particularly responsive to uptake by plants, being relatively small and moderately

55 hydrophobic (Burken & Schnoor, 1998). In addition to their persistence, ubiquity, and toxicity (Pankow &  
56 Cherry, 1996), characterization and monitoring of these plumes require advanced technologies and high  
57 funding, which could be mitigated by integrating a time-, and cost-effective technique like phytoscreening.  
58 The chance to determine the occurrence of subsurface volatile contaminants through trees is also important for  
59 evaluating the risks to human health such as potential ingestion and respiration from vapor intrusion into  
60 buildings, which are exposure pathways potentially associated with plant uptake. CEs detection in trees is  
61 affected by several contaminant-specific loss mechanisms (e.g., volatilization, phytodegradation) which may  
62 result in lower concentrations in plant tissues as compared to gw concentrations.

63 Phytoscreening of contaminated gw was considered a valuable ecohydrogeological application (Cantonati et  
64 al., 2020). However, it is necessary to identify the main factors that drive the correlation between gw and tree-  
65 core contaminant concentration as well as contaminants' detectability potential in trees in order to make this  
66 screening technique widely applicable and accepted,. The correlation and detection capability can be  
67 maximized by providing directions on the standardization of sampling procedures. Several studies concluded  
68 that the technique is only qualitatively reliable due to the poor correlation observed between gw and tree-core  
69 concentration (Holm and Rotard, 2011; Larsen et al., 2008; Ottosen et al., 2018). This was attributed to multiple  
70 factors that come into play when dealing with living organisms (trees) to signal the state of contamination of  
71 an environmental matrix such as gw. Plants indeed interact with gw through complex partitioning mechanisms  
72 mediated by various chemical, biological, hydrological, and climatic factors. Synthesis efforts were directed  
73 to investigate the factors that limit the application opportunities of this technique. As a general example, Trapp  
74 (2007) proposed a theoretical model for the prediction of chemical uptake in trees based upon more than 30  
75 parameters, either of hydrogeological or ecological nature, thus addressing the complexity of quantitative  
76 phytoscreening.

77 This paper provides a systematic review of former literature on the main factors that likely affect:

78 a) the correlation between CEs tree-core and gw concentration. Factors that determine higher correlations  
79 are favorable to apply phytoscreening to monitor, quantitatively, CEs contamination severity and  
80 degradation or natural attenuation processes.

b) the CEs detectability potential in trees. Factors that determine a lower number of contaminants non-detections in trees are favorable to preliminary screen for suspected underground contaminations by CEs in poorly investigated areas.

Several factors were selected and grouped as follows: 1) physicochemical properties of the contaminants (molecular weight, water solubility, volatility, partition coefficients); 2) hydrogeology (depth to water table, aquifer thickness, hydraulic conductivity); 3) tree identity and anatomy (genus and family, xylem structure, tree trunk diameter); 4) sampling and extraction methodology (height above ground of tree-core sampling, tree-core length, extraction method of the contaminants).

## 2. MATERIALS AND METHODS

### 2.1 Data source

A systematic search for relevant studies of phytoscreening on CEs was conducted in Scopus in January 2021. The search string was:

*TITLE-ABS-KEY (phytoscreening OR (tree AND groundwater AND (trichloroethene OR perchloroethene OR dichloroethene OR "chlorinated ethenes"))).*

The first database search yielded 64 references. To form a global-scale database of phytoscreening data on CEs, only references containing datasets of contaminated sites that met the following criteria were selected: 1) sampling by tree trunk coring, 2) tree-core analysis of at least one compound among PCE, TCE, and cDCE, and 3) spatial proximity between a given tree and a borehole where gw concentration analysis showed concentrations above detection limits (the distances between the locations of trees and boreholes varied from ~1 to ~10 m, or greater in few cases). When needed, we created contaminant concentration contour maps to supplement the reported gw concentration data. A total of 7 articles were identified reporting site datasets suitable for this study. The reference lists of these 7 articles were manually searched for further studies containing relevant datasets, providing 1 positive result (a technical report). Some of the final 8 selected documents contributed with more than one investigated site, providing information on a total of 11 sites. A total of 267 tree-core samples (and respective gw samples) were compiled in the global database, some of them reporting more than one compound concentration (Table 1). The number of tree-core concentration data was 419 (see Supplementary material for the database), 118 being below the analytical detection limit (ND data

hereafter). ND data represent a small fraction for most sites (below 15%; e.g., Struckhoff et al., 2005), whereas in a few sites they are almost the majority (e.g., Larsen et al., 2008; Cox, 2002). The observations above detection limits are distributed as follows: PCE - 43 observations, TCE - 194 observations, cDCE - 124 observations, and the sum of CEs - 58 observations related to one study that did not indicate single compound concentrations (Wittlingerova et al., 2013). No data were compiled for VC because only Ottosen et al. (2018) were able to detect traces of VC in trees under specific environmental conditions. No spatial or temporal average concentrations were included in the database except for one site (Nogales site, Arizona; Duncan et al., 2017) in which only PCE average gw concentration (2 µg/L) was provided. This site was included in the database for its significance in terms of uniqueness: cores were sampled and extracted with methanol from trees of 4 different families inhabiting an arid environment with a deep aquifer table (9-10 m b.g.l.), showing PCE concentration up to 500 µg/kg.

Data on contaminant concentration in tree-core samples and gw samples were reported in two different types of units, i.e., mass/mass (typically µg/kg) and mass/volume (typically µg/L), respectively. No conversion was performed from the mass/mass unit to the mass/volume unit for tree-cores. This was considered acceptable since the focus was on the correlation between the concentration in different matrices along with the detectability potential. The unfeasibility of the conversion is mostly due to the lack of information on sampled tree-core dry weights and volumes. Besides, wood-water partition coefficients of the contaminants would also be needed for a reliable conversion. Very few studies estimated the latter for a small number of tree species (e.g., poplars in Baduru et al., 2008). The lack of conversion hindered the possibility of performing multivariate statistical analyses. Due to this limitation, a meta-analysis of the influence of each factor was performed to analyze the database. It is worth noting that the results of this analysis will be subject to an intrinsic uncertainty associated with processing each factor as independent of one another.

Information on the factors influencing the correlation between tree-cores and gw concentration as well as the potential for detectability in trees (i.e., the hydrogeological conditions of the underlying contaminated aquifers, tree identity and anatomy, and sampling and extraction protocols; Table 2) were retrieved from the 8 selected articles and associated to each of the 419 tree-core concentration data.

As for hydrogeological parameters, involving either the permeable porous medium (aquifer) or gw flowing inside it, we retrieved: depth to water table (DWT in m below ground level), intended as the distance between

ground level and the surface at water pressure equal to atmospheric pressure (information retrieved for all the 419 tree concentration data); thickness of the saturated portion of the aquifer ( $b$  in m) intended as the distance between the water table and the low permeability bottom of the aquifer (retrieved for 235 out of 419 tree concentration); bulk saturated hydraulic conductivity of the aquifer ( $K$  in m/s; 373 out of 419 tree concentration). When  $K$  values of the aquifers were not specified (25% of the database), ranges of conductivities were inferred in agreement with the local description of the lithology (Freeze & Cherry, 1979). With regards to tree identity and anatomy, we retained information on the genus (398 out of 419 data) and on the tree diameter at breast height (DBH in cm; 142 out of 419 data). Based on the genus, we retrieved the correspondent xylem structure, intended as the distribution of pores and vessels among growth rings. The xylem, or sapwood, is the active portion of the trunk where water transport takes place. We considered three xylem types: coniferous, diffuse-porous, and ring-porous (Panshin & de Zeeuw, 1970). Coniferous xylems are characterized by small cells used for water transport and structural support. Diffuse-porous xylems additionally contain large vessels that are randomly distributed throughout the wood, while ring-porous xylems have larger diameter vessels concentrated in the earlywood. Conifers and diffuse-porous trees tend to have deep functional xylems as well as low average conductivity due to small and short conduits. In contrast, most of the conductance in ring-porous species is isolated to the outermost annual growth ring that contains functional vessels (Bush et al., 2010; Cermak et al., 1992).

When available, sampling and extraction protocols used to prepare tree-cores for analysis were retrieved: length of tree-core samples ( $L$  in cm; 369 out of 419 data), sampling height on the trunk ( $H$  in cm above ground level; 398 out of 419 data), and extraction method (419 out of 419 data) including extraction from dry vials (Cox, 2002; Larsen et al., 2008; Struckhoff et al., 2005; Vroblesky et al., 1999, 2004), vials containing organic-free water (Wittlingerova et al., 2013), or methanol solutions (Duncan et al., 2017), Solid Phase Micro-Extraction (SPME; Holm & Rotard, 2011).

## 2.2 Statistical meta-analysis

The correlation between gw and tree-core concentration was quantified by Spearman's rank coefficient  $\rho$  (Journel and Deutsch, 1997), a widely used approach for assessing the relationship between parameters when it is expected to be non-linear, as in highly skewed datasets. Indeed, both tree-core and gw concentrations represent highly skewed data sets, as regularly found in contaminated sites (Juang et al., 2001). As an example,

tree-core concentrations had a distribution with positive skewness of 3.17, 8.21, and 6.85 for PCE, TCE, and cDCE, respectively. A useful property of  $\rho$  is that its value is invariant to any monotonic transformation applied to the data (e.g., logarithmic transformation). Outliers were not removed from the database due to the lack of knowledge about the uncertainty associated with the measurements. It is worth noting that  $\rho$  is insensitive to outliers, therefore representing a robust statistic tool for our database. The detectability potential of contaminants in trees was quantified as the percentage of ND (ND%) data to the total number of observations. Spearman's  $\rho$  and ND% were calculated separately for each compound (PCE, TCE, and cDCE) to assess the influence of contaminant-specific properties such as molecular weight ( $M_w$ ), water solubility ( $S_w$ ), Henry's constant ( $H_c$ ), and octanol-water partition coefficient ( $\log K_{ow}$ ). In the case of the dataset of Wittlingerova et al. (2013) reporting only sums of CEs (PCE, TCE, cDCE, tDCE, 1,1-DCE, and VC),  $\rho$  and ND% were calculated on the sums.

Factors in Table 2 were then split into intervals and Spearman's  $\rho$  were derived for the concentration data within each interval. For continuous factors (e.g., aquifer properties or tree diameter), we determined discrete intervals based on medians and percentiles associated with each factor to have a similar number of observations within each interval. Only concentration data above detection limits were considered. In the case of discrete factors (e.g., tree species, extraction method), only values associated with a minimum of 10 observations were considered in the statistical analysis, except for one single case where only 8 observations were associated with extraction with methanol (Duncan et al., 2017). The ND% was determined within each of the aforementioned intervals to assess the influence of the different factors on detectability. To avoid biases associated with trees that could be growing above more dilute contamination areas, the ND% was calculated only when the concentration in gw was above 11  $\mu\text{g/L}$ . This threshold was determined as the 5<sup>th</sup> percentile of gw concentration data. The final number of ND data was 104 out of 118 ND tree-core data. It is noteworthy that in some cases, such as when processing hydrogeological parameters like  $b$  and  $K$ , results may be uncertain since some parameters do not vary spatially across a specific site.

Results were interpreted in terms of high or low correlations (determining optimal factors conditions to characterize the contamination) and high or low detectability potential (determining optimal factors conditions to screen gw contamination).

### 3. RESULTS AND DISCUSSION

### 192 3.1 Contaminant properties

193 The correlation between the concentration in tree-cores and gw was statistically meaningful ( $p\text{-value}\leq 0.05$ )  
194 for all four series (PCE, TCE, cDCE, and the sum of CEs).

195 The  $\rho$  values indicate a low variability among CEs in terms of correlation between tree-core and gw  
196 concentration (Figure 1), with slightly lower values for higher chlorinated compounds PCE and TCE ( $\rho$  of 0.37  
197 and 0.34, respectively) compared to the lower chlorinated cDCE ( $\rho$  of 0.41). On the other hand, ND% widely  
198 differed between higher chlorinated compounds PCE and TCE (12 and 23%, respectively) and cDCE (47%)  
199 with the first two performing better in terms of detectability potential. It is noteworthy that the highest  
200 correlation coefficient (0.63) and lowest ND% value (0%) were found for the sum of CEs (reported by  
201 Wittlingerova et al., 2013). This could be explained by contaminant transformation processes taking place  
202 either in the rhizosphere or in the xylem (Newman and Reynolds, 2004) that would negatively affect the  
203 correlation of single compounds. However, this result is associated with only one site.

204 The physicochemical properties of CEs (Table 3) likely influence the behavior of each compound in trees.  
205 Larsen et al. (2008) observed a better correlation for cDCE compared to TCE and PCE which was attributed  
206 to the higher volatility (higher  $H_c$ ) of the latter possibly causing a higher loss through the bark (Vroblesky et  
207 al., 1999). According to Limmer & Burken (2015), contaminant concentrations decreased with increasing  
208 volatility, due either to volatilization from the roots, bark, or subsurface. The results of our study are consistent  
209 with these findings, with PCE and TCE showing a slightly lower  $\rho$  compared to cDCE. In addition, the  
210 correlation potential of PCE and TCE may be hindered by their lower tendency to plant uptake compared to  
211 cDCE, driven by their higher  $M_w$  and  $K_{ow}$ , and lower  $S_w$ . Uptake from tree roots was indeed reported to be  
212 favored for compounds with low  $M_w$  due to their higher tendency to diffuse (Baduru et al., 2008), whereas  
213 higher  $S_w$  would possibly favor contaminant dissolution in water and consequent tree uptake. Besides, high  
214 sorption compounds ( $\log K_{ow}>3$ ) were reported to tend to be absorbed primarily by root surfaces, resulting in  
215 less translocation to the xylem (Schnoor et al., 1995). Similarly, a study by Dettenmaier et al. (2009) indicated  
216 that high-hydrophilic compounds are most likely absorbed by roots and transferred to the xylem. We may also  
217 assume that once in the xylem, higher  $\log K_{ow}$  compounds likely tend to be absorbed by xylem tissues, resulting  
218 in a prolonged accumulation in the tree and thus a higher detectability potential. This could explain the higher  
219 detectability potential of PCE and TCE (lower ND%) compared to cDCE. Moreover, their higher  $H_c$  can aid

the analytical detection when using headspace methods. Concurrently, the lower log  $K_{ow}$  and  $M_w$  of cDCE may hinder accumulation and favor contaminant loss through the bark despite its low  $H_c$  (Baduru et al., 2008), resulting in an overall lower detectability potential. The extremely rare detection of VC confirms the role of  $H_c$ ,  $M_w$ , and log  $K_{ow}$  in contaminant detectability in trees.

### 3.2 Hydrogeology and aquifer parameters

Three intervals were considered for DWT:  $DWT < 1$ ,  $1 \leq DWT < 3$ , and  $DWT \geq 3$  m b.g.l. Concentration data show a statistically significant correlation value ( $p\text{-value} \leq 0.05$ ; Figure 2) in the three cases. A slightly decreasing correlation with increasing DWT was observed ( $\rho = 0.63$ ,  $0.54$ , and  $0.52$  for  $DWT < 1$ ,  $1 \leq DWT < 3$ , and  $DWT \geq 3$  m b.g.l., respectively). On the other hand, the shallow interval showed the higher ND% (35%) whereas the inferior intervals had significantly lower ND% (16% and 17% for the medium and deep interval, respectively). Duncan & Brusseau (2018) assessed for the first time how DWT could affect the correlation between VOCs concentration in tree tissues and gw (based on 100 measurements). They observed a higher correlation in samples from sites with a  $DWT < 4$  m, concluding that a low thickness of the unsaturated zone significantly affects phytoscreening efficiency. Despite the overall consistency of our results with the cited literature (decreasing  $\rho$  with increasing DWT),  $\rho$  shows small differences among DWT intervals, suggesting a low influence of this factor on the degree of correlation. The difference with Duncan & Brusseau (2018) may lie in the use of different correlation coefficients and interval divisions. In our analysis  $\rho$  was chosen due to the non-linear distribution of the concentration dataset while Duncan & Brusseau (2018) assessed the correlation through Pearson's coefficient ( $r^2$ ) thus assuming linearity of the dataset. Besides, at sites with a more substantial vadose zone, mineralization of CEs can occur before translocation of the contaminant in the tree due to more hypoxic conditions (Bradley & Chapelle, 2011), leading to lower correlation potential for deeper aquifers. Similar findings have been reported by Wilson et al. (2013) for BTEX translocation in trees. At the same time, when DWT is lower, volatilization loss of CEs is promoted at the interface between the saturated and the vadose zone, being the thickness and water content of the latter more subject to atmospheric variations (Pankow & Cherry, 1996). As tree roots are usually located at this interface, the enhanced volatilization of CEs could decrease their detectability potential (higher ND% for the shallow interval). Aquifer thicknesses were clustered into two intervals:  $b \leq 3.5$  and  $b > 3.5$  m. Data associated with lower  $b$  show a very high positive correlation ( $\rho = 0.71$ ), whereas those associated with higher  $b$  have a significantly weaker



correlation ( $\rho=0.30$ ). This may be because CEs, in the majority of contaminant events, enter the subsoil as dense non-aqueous phase liquids (DNAPLs), which tend to sink towards deeper sections of the aquifer, thus influencing the shape of dissolved contaminant plumes (e.g., Parker et al., 2003). In particular, the sinking of CEs could result in an increased distance of the dissolved contaminant plume from the root zone in thicker aquifers. Notably, aquifer thickness appears to have the highest influence on correlation compared to other factors. On the other hand, a lower ND% is associated with the thicker aquifer interval compared to the thinner interval (4% and 19% for  $b>3.5$  m and  $b\leq 3.5$  m, respectively). This result has poor validations: we can speculate that thin aquifers have a lower geometrical probability of being intercepted by tree roots than thick ones.

Two intervals of K were considered:  $K<1\times 10^{-5}$  and  $K\geq 1\times 10^{-5}$  m/s. Concentrations referred to higher K values show a slightly higher correlation ( $\rho=0.73$ ) compared to those referred to lower conductivities ( $\rho=0.66$ ). These results suggest that K poorly affects the correlation between tree-core and gw concentration. On the other hand, the lower K interval includes 38% of ND whereas the higher K interval includes 18%. More permeable aquifers are therefore more suited in terms of detectability potential. A relatively higher permeability can indeed enhance the mobility of contaminants in the subsoil, likely favoring plant uptake, similarly to what happens when extracting gw from wells or soil gas from soil gas probes.

### 3.3 Tree identity and anatomy

The 22 tree genera of our database were clustered by families and xylem structures. Results show a significant positive correlation with most families (Figure 3), with  $\rho$  being highest for coniferous, i.e. Pinaceae ( $\rho=0.86$ ) and Cupressaceae ( $\rho=0.66$ ). These conifers also have moderately low ND% (24% and 30%, for Pinaceae and Cupressaceae, respectively). Consistently with our observations, Trapp et al. (2007) stated that conifers are best suited for phytoscreening because they have a broad xylem zone, and transpire throughout the whole year, resulting in a continuous uptake of gw. Ring-porous Fagaceae (primarily *Quercus*) presented a slightly positive correlation ( $\rho=0.39$ ) and a high ND% (57%). The ring-porous structure likely promotes volatilization loss through the bark, possibly affecting the observed low correlation and detectability potential. Indeed, over 90% of water is transported in the outermost growth ring in ring-porous trees whereas in diffuse-porous and coniferous trees water flow is more equally distributed among rings (Ellmore and Ewers, 1986). Diffuse-

275 porous Nyssaceae and Betulaceae show a slightly lower  $\rho$  compared to conifers (0.74 and 0.65, respectively),  
 276 and a low ND% (29 and 25%, respectively) although results for Nyssaceae must be taken with caution because  
 277 they refer to one single study site (Savannah River Site, USA; Vroblesky et al., 1999) where the aquifer was  
 278 shallow (DWT<1 m b.g.l.). On the other hand, diffuse-porous Salicaceae and Altingiaceae do not show a  
 279 significant correlation ( $p$ -value>0.05) and highly fluctuating ND% (very low for Salicaceae – 3% and very  
 280 high for Altingiaceae – 64%). The high variability among diffuse-porous families in terms of  $\rho$  and ND% could  
 281 be associated with different arrangements and sizes of the vessels regulating the conductivity of the xylem,  
 282 which in turn can also vary with age. For example, Salicaceae (*Salix* and *Populus*), widely used in  
 283 phytoscreening and phytoremediation due to their fast growth, high uptake rates, and widespread occurrence  
 284 in temperate climates, showed the highest detectability potential although no correlation between tree-core and  
 285 gw concentration. Besides, Negri et al. (2003) stated that Salicaceae are genetically predisposed to develop  
 286 roots extending to the water table at depths greater than 12 m b.g.l., thereby widening their detectability  
 287 potential to deep aquifers. Altingiaceae (*Liquidambar*; present only in the study of Vroblesky et al., 1999) also  
 288 showed no correlation whilst a low detectability potential. This family was studied by Strycharz and Newman  
 289 (2009) in a greenhouse experiment where also Platanaceae and Salicaceae were involved. Results showed that  
 290 among the 3 families, Altingiaceae was the less recommended for phytoremediation activities. Other diffuse-  
 291 porous, like Betulaceae (*Alnus* and *Betula*), showed instead a correlation and detectability potential comparable  
 292 to conifers. Lewis et al. (2015) calculated that *Betula pendula* can accumulate similar amounts of TCE as  
 293 *Populus* trees due to its lack of heartwood (nonfunctioning xylem) and homogeneous xylem flow (Westhoff  
 294 et al., 2008), making this species a suitable candidate for phytoremediation and phytoscreening activities.  
 295 Eventually, the low number of Platanaceae (diffuse-porous), Ulmaceae (ring-porous), and Rosaceae (diffuse-  
 296 porous) in the database (Table 2) hindered an analysis on these families. Even so, Limmer & Burken (2015)  
 297 showed that the genus *Platanus* (Platanaceae) had a high detectability potential, especially for PCE gw  
 298 contamination, if compared to non-*Platanus* trees. Their result was although associated with *Platanus* trees  
 299 growing in areas with shallow gw. Conversely, our data on Platanaceae showed that 3 out of 4 times this family  
 300 did not detect contaminants even with shallow gw (DWT<1 m b.g.l.; Savannah River Site, USA; Vroblesky et  
 301 al., 1999) albeit in that particular site aquifer K was low ( $5.3 \times 10^{-6}$  m/s). Yung et al. (2017) pointed out that  
 302 besides *Populus* and *Salix* (Salicaceae, diffuse-porous) and *Betula* (Betulaceae, diffuse-porous), *Quercus* and

303 *Ulmus* (Fagaceae and Ulmaceae, both ring-porous) are also efficient biomonitors of PCE and TCE  
304 contamination. Notwithstanding the contrast with our results on Fagaceae, the 2 Ulmaceae trees in our database  
305 (Carswell Golf Course, USA; Vroblesky et al., 2004) showed TCE concentrations above detection limits, with  
306 DWT at 1 to 5 m b.g.l., aquifer K of  $7 \times 10^{-5}$  m/s, and b of 0.9 m. This may suggest that even among ring-porous  
307 trees a great variability in concentration results is expected.

308 Tree size (measured as DBH) in our database ranges between 18 and 102 cm and values were split into 3  
309 intervals:  $DBH < 25$ ,  $25 \leq DBH < 40$ , and  $DBH \geq 40$  cm. Since data were filled only for 34% of the database (Table  
310 2), results must be considered with caution. The lower interval shows a high positive correlation ( $\rho = 0.79$ ). The  
311 correlation decreases significantly in the medium interval ( $\rho = 0.47$ ). The higher interval shows no significant  
312 correlation ( $p\text{-value} > 0.05$ ). ND% is instead comparable among DBH intervals (10%, 8%, and 8%, respectively  
313 for  $DBH < 25$ ,  $25 \leq DBH < 40$  cm, and  $DBH \geq 40$  cm). Several studies suggest that tree size has little effect on  
314 tree-core concentration (Limmer & Burken, 2015; Wahyudi et al., 2012) while other studies demonstrated that  
315 diffusional loss in small trees (DBH of 2 cm) occurs at a rate 10 times higher than in trees with DBH 15 cm  
316 due to their greater surface area to volume ratio that more quickly depletes the compound reservoir in the trunk  
317 (Schumacher et al., 2004; Struckhoff, 2003). This could explain the slightly higher ND% of smaller trees. In  
318 contrast, our results show that smaller trees have greater efficiency in terms of quantitative analysis of gw  
319 contamination (high  $\rho$ ). In smaller trees, we could indeed expect less variability in concentration around and  
320 across the trunk due to a less compartmentalized flow in the xylem. Also, in smaller trees it is highly probable  
321 to sample a consistent thickness of the total xylem, resulting in a concentration that averages the radial  
322 variability. More variability is instead observed in larger trees where sampling direction has a strong influence  
323 on the concentration, thus influencing the correlation.

#### 324 3.4 Sampling and analysis protocols

325 In our database tree-core L ranges from 3.8 to 12.5 cm and was clustered into two intervals:  $L \leq 6$  and  $L > 6$  cm.  
326 Shorter cores do not show a significant correlation between tree-core and gw concentration ( $p\text{-value} > 0.05$ )  
327 whereas longer cores have a high positive correlation ( $\rho = 0.71$ ; Figure 6). This result agrees with Ma & Burken  
328 (2003) and the USGS user guide published by Vroblesky (2008), which suggest a better correlation when the  
329 core samples are longer than  $\sim 7$ -8 cm. Shorter cores may be also acceptable for ring-porous trees, in which  
330 water transport takes place mostly in the outermost ring (Ellmore and Ewers, 1986). The detectability potential

331 is lower for the higher L interval (ND of 11% and 30% for  $L \leq 6$  and  $L > 6$  cm, respectively), likely indicating  
 332 that drilling longer tree-cores could promote diffusional loss out of the sample since sampling requires  
 333 relatively longer periods (tree-cores are usually cut in small pieces before being put in the vials).  
 334 Sampling H from the base of the trunk ranges between 50 and 900 cm a.g.l. and was clustered into three  
 335 intervals:  $H < 99$ ,  $99 < H \leq 120$ , and  $H > 120$  cm a.g.l. The medium interval shows a very high correlation between  
 336 tree-core and gw concentration ( $\rho = 0.84$ ; Figure 6), which decreases for higher H ( $\rho = 0.42$ ). The lower interval  
 337 shows no significant correlation ( $p\text{-value} > 0.05$ ) although the data pertain to only one survey by Holm & Rotard  
 338 (2011). The reason for the high  $\rho$  value at medium H is still unknown. We can speculate that this is related to  
 339 the attainment of an equilibrium of the contaminant inside the wood-air-water partitioning system. On the other  
 340 hand, a low ND% was registered for the lower H interval (7%) whereas the higher intervals are associated with  
 341 higher ND% (24% and 33% for the medium and higher H interval, respectively). This result is consistent with  
 342 the experiments of Ma & Burken (2003) where a higher TCE loss was observed higher up the trunk. Thus, a  
 343 lower rate of diffusional loss from the bark may be expected for the lower H intervals. On the other hand,  
 344 Ottosen et al. (2018) sampled tree-cores just above the ground surface without distinguishing a clear advantage  
 345 from this sampling strategy.  
 346 Our database includes 4 extraction methods used for analysis (dry sample, organic-free water, methanol  
 347 solution, and SPME; Figure 6). The dry and the water extracted samples showed moderately high correlation  
 348 ( $\rho = 0.55$  and  $\rho = 0.64$  for dry and water extraction, respectively). However, data from water extracted samples  
 349 pertain to only one survey where concentration data relate to the sum of CEs (Wittlingerova et al., 2013). The  
 350 high  $\rho$  could be associated either with the extraction method or with the fact that the sum of CEs was considered  
 351 (see section 3.1). Methanol extracted samples, related to the study cases of Duncan et al. (2017), were collected  
 352 with unfavorable conditions in arid-hot environments (Nogales site, Park-Euclid, and Motorola 52<sup>nd</sup> superfund  
 353 site in Arizona, USA). The small number of tree-cores (8) sampled with this method may explain the observed  
 354 non-significant correlation value ( $p\text{-value} > 0.05$ ). Tree-core concentrations associated with arid environments  
 355 are possibly more a function of vadose zone vapor phase concentration than gw concentration since roots  
 356 would unlikely reach DWT of 26 m b.g.l. as in the case of the Park-Euclid site. The fact that 5 out of 8 tree-  
 357 core concentrations were higher than 300  $\mu\text{g/kg}$  despite being associated with low gw concentrations of  
 358 PCE (2  $\mu\text{g/L}$ ; i.e., lower than the gw concentration threshold defined for ND% calculation; See Section 2.2)

359 further supports the hypothesis that trees were absorbing contaminants from a matrix other than gw. This may  
360 have hindered correlation with gw in the case of methanol extraction. The analysis following SPME, associated  
361 with only one site (Potsdam-Krampnitz military base, Germany; Holm & Rotard, 2011), also showed no  
362 significant correlation ( $p$ -value>0.05). Even so, the ND% was very low for SPME (7%) as well as water  
363 extracted samples (0%). However, since these methods were used in single study cases, these results may be  
364 related to other site-specific conditions or sampling protocols. In terms of ND%, the dry and methanol  
365 extraction produced comparable results (34%, and 33% for dry and methanol extraction, respectively).

#### 366 4. SUMMARY AND CONCLUSIONS

367 The effectiveness of phytoscreening has been assessed via a meta-analysis of literature data to determine the  
368 potential of trees to a) monitor groundwater plumes of CEs, expressed as the degree of correlation between  
369 tree-core and gw concentration, and b) detect the occurrence of gw contamination events by CEs in poorly  
370 investigated areas, expressed as the rate of tree-cores that showed concentrations above the detection limit in  
371 significantly contaminated areas. Several factors likely influencing correlation and detectability were  
372 considered. These factors included physicochemical properties of CEs, hydrogeological conditions of the  
373 underlying contaminated aquifers, trees identity and anatomy, and sampling and extraction protocols.

374 The correlation (quantitative monitoring potential) is higher when the hydrogeological dynamics favor direct  
375 uptake of contaminated water and the concentration is homogeneously distributed in the tree and the tree-core  
376 sample. Direct tree uptake is favored for the lighter and more soluble cDCE and in the case of shallow (DWT<3  
377 m b.g.l.), thin ( $b < 3.5$  m), and permeable aquifers ( $K \geq 1 \times 10^{-5}$  m/s). The homogeneity of concentration in the  
378 xylem is higher for Pinaceae and Cupressaceae (conifers), due to their non-porous xylem, and for smaller  
379 diameter trees (DBH<25 cm) whereas homogeneity of concentration in the tree-core is enhanced when  
380 sampling longer tree-cores ( $L > 6$  cm) and at a height on the trunk between  $99 < H \leq 120$  cm a.g.l.

381 The detectability (qualitative screening potential) is higher when factor conditions favor accumulation in the  
382 xylem and hinder volatilization loss through the bark. In these terms, PCE and TCE are more suited compared  
383 to cDCE due to their higher sorption and weight. Low volatilization loss was also inferred in the case of large-  
384 diameter trees (DBH $\geq 40$  cm), at a low height on the trunk ( $H < 99$  cm a.g.l.), and for shorter cores due to reduced  
385 time of sampling ( $L \leq 6$  cm). In the case of Salicaceae, high uptake rates may compensate for volatilization

386 losses, thus increasing detectability. Finally, the process of contaminant extraction appears to be maximized  
387 when using organic-free water extraction and SPME.

388 Despite the clarifications provided by our meta-analysis, several factors influencing phytoscreening  
389 effectiveness remain unexplored at a global scale as in the case of 1) climatic and meteorological conditions  
390 affecting uptake and loss from the tree; 2) porosity and volumetric water content of the unsaturated zone  
391 influencing uptake and volatilization loss at the ground surface; 3) organic content in saturated and unsaturated  
392 layers influencing sorption of CEs to the solid matrix; 4) phytodegradation processes that may hinder  
393 correlation with CEs concentration in gw; 5) radial distance to boreholes likely affecting correlation between  
394 tree-core and gw concentration. It is therefore necessary to conduct additional research in these areas to  
395 improve the applicability of the technique.

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#### 541 FIGURES CAPTION

542 **FIGURE 1.** Spearman's  $\rho$  (x-axis) and ND% (y-axis, values in inverse order) of compounds series. Blank symbols  
 543 refer to as  $p$ -values  $>0.05$ . Solid symbols refer to as  $p$ -values  $\leq 0.05$

544 **FIGURE 2.** Spearman's  $\rho$  (x-axis) and ND% (y-axis, values in inverse order) of each interval considered for the  
 545 hydrogeological parameters. Blank symbols refer to as  $p$ -values  $>0.05$ . Solid symbols refer to as  $p$ -values  $\leq 0.05$

546 **FIGURE 3.** Spearman's  $\rho$  (x-axis) and ND% (y-axis, values in inverse order) of each family and correspondent  
 547 xylem structure. Blank symbols refer to as  $p$ -values  $>0.05$ . Solid symbols refer to as  $p$ -values  $\leq 0.05$

548 **FIGURE 4.** Spearman's  $\rho$  (x-axis) and ND% (y-axis, values in inverse order) of each interval considered for tree  
 549 diameters. Blank symbols refer to as  $p$ -values  $>0.05$ . Solid symbols refer to as  $p$ -values  $\leq 0.05$

550 **FIGURE 5.** Spearman's  $\rho$  (x-axis) and ND% (y-axis, values in inverse order) of each interval considered for  
 551 sampling and analysis protocols. Blank symbols refer to as  $p$ -values  $>0.05$ . Solid symbols refer to as  $p$ -values  $\leq 0.05$

#### 552 TABLES CAPTION

553 **TABLE 1.** References used for statistical analysis of the database: geographical location, number of tree-core samples, and  
 554 correspondent detected compounds (Above Detection Limit: A.D.L.). Total number of data and Non-Detection% in the last  
 555 columns.

556 **TABLE 2.** Factors potentially affecting the effectiveness of phytoscreening of CEs in gw and relative descriptive statistics.  
557 Selected intervals, relative number of observations, and relative sites per interval.  
558 **TABLE 3.** Physico-chemical properties of the chlorinated ethenes: molecular weight ( $M_w$ ), water solubility ( $S_w$ ),  
559 Henry's constant ( $H_c$ ), octanol-water partition coefficient ( $\log K_{ow}$ ). Derived from Mackay et al. (2006)  
560

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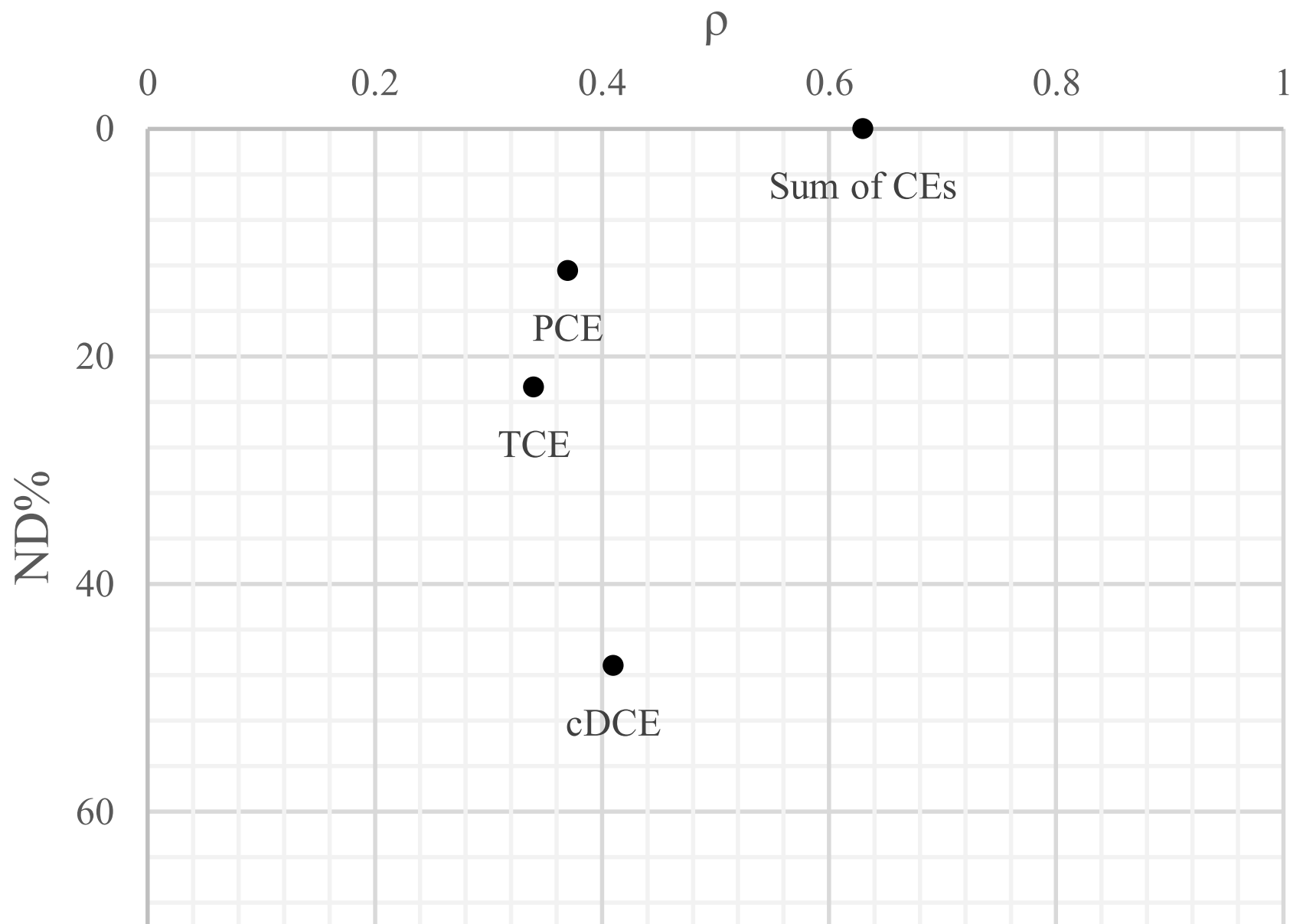
Reference	Location	n° of tree-core samples	Contaminants A.D.L.	n° of data	ND %
Vroblesky et al. (1999)	Savannah River site (South Carolina, USA)	86	TCE, cDCE	179	40
Cox (2002)	Site SS-34N, McChord AFB (Washington, USA)	14	TCE	14	10 0
Vroblesky et al. (2004)	Carswell Golf Course (Texas, USA)	24	TCE	24	4
	Air Force Plant PJKS (Colorado, USA)	9	TCE	9	0
	Naval Weapons Station Charleston (South Carolina, USA)	10	TCE	10	0
Struckhoff & Burken (2005)	Front Street, Riverfront Superfund site (Missouri, USA)	20	PCE	20	15
Larsen et al. (2008)	North Bohemia Carcass Disposal Plant (Czech Republic)	17	PCE, TCE, cDCE	51	47
Holm & Rotard (2011)	Former military base Potsdam-Krampnitz (Germany)	23	TCE, cDCE	46	7
Wittlinglerova et al. (2013)	North Bohemia Carcass Disposal Plant (Czech Republic)	58	Sum of CEs	58	0
Duncan et al. (2017)	Nogales site (Arizona, USA)	4	PCE	4	0
	Park-Euclid (Arizona, USA)	1	PCE, TCE	2	0
	Motorola 52 <sup>nd</sup> Street Superfund site (Arizona, USA)	1	TCE	2	50
8	11	267		419	28

**TABLE 3.** Physico-chemical properties of the chlorinated ethenes: molecular weight ( $M_w$ ), water solubility ( $S_w$ ), Henry’s constant ( $H_c$ ), octanol-water partition coefficient ( $\log K_{ow}$ ). Derived from Mackay et al. (2006)

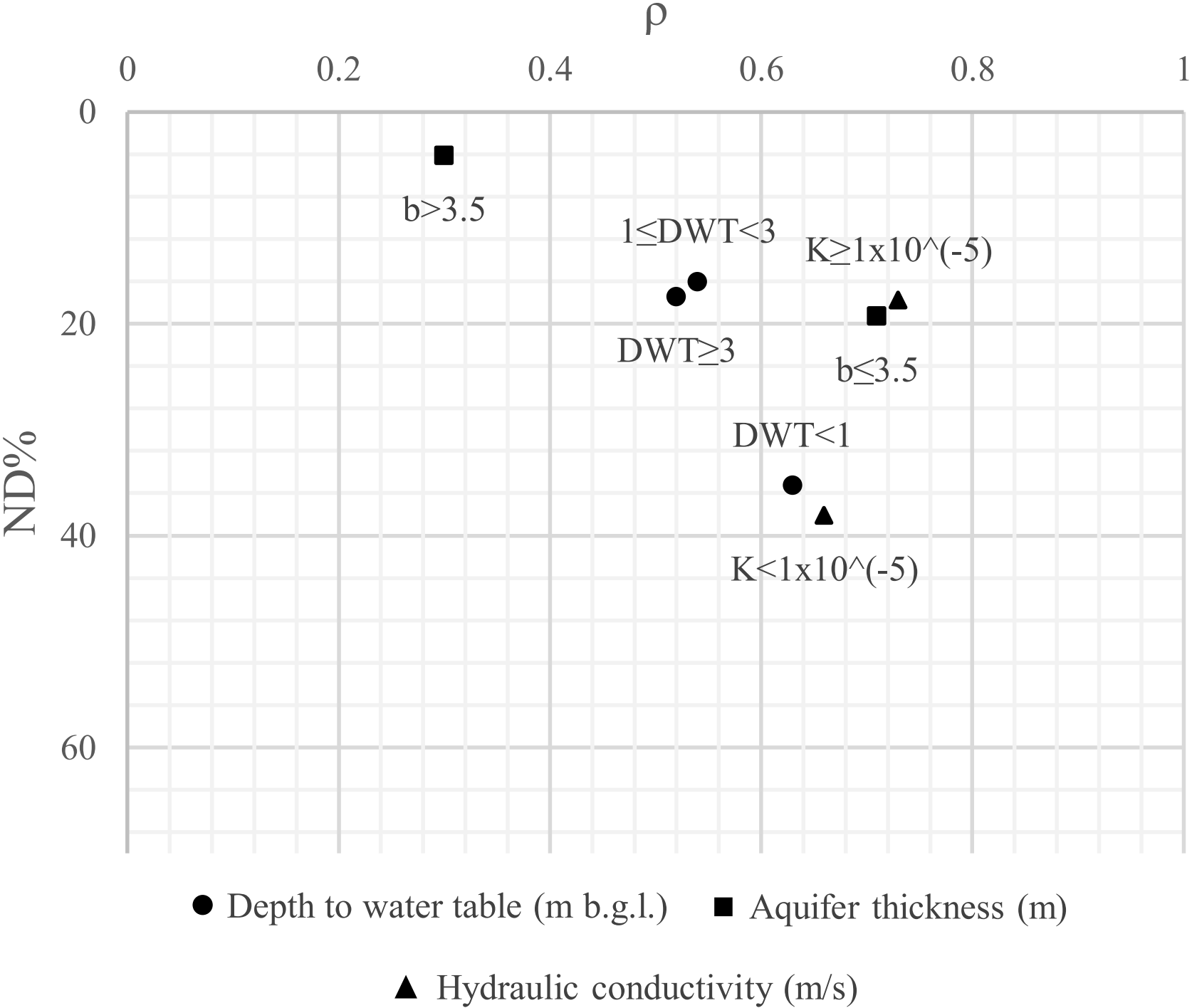
COMPOUND	$M_w$ [g/mol]	$S_w$ at 25°C [mg/L]	$H_c$ [at 17.5°C] [adim.]	$\log K_{ow}$ [adim.]
PCE	165.8	206	0.492	3.40
TCE	131.3	1118	0.265	2.61
cDCE	96.9	3500	0.111	1.86
VC	62.4	2700	0.811	1.46

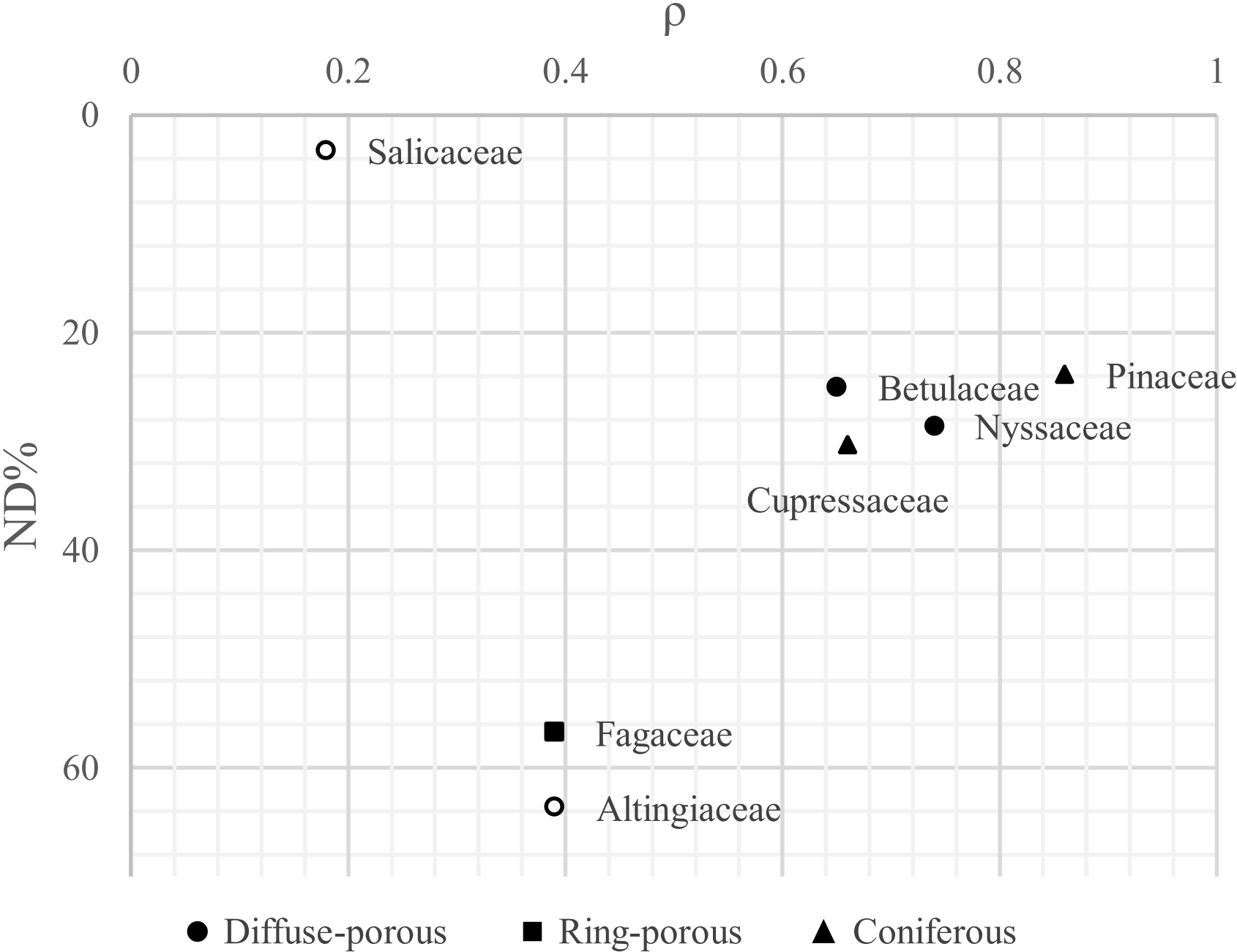
**TABLE 2.** Factors potentially affecting the effectiveness of phytoscreening of CEs in gw

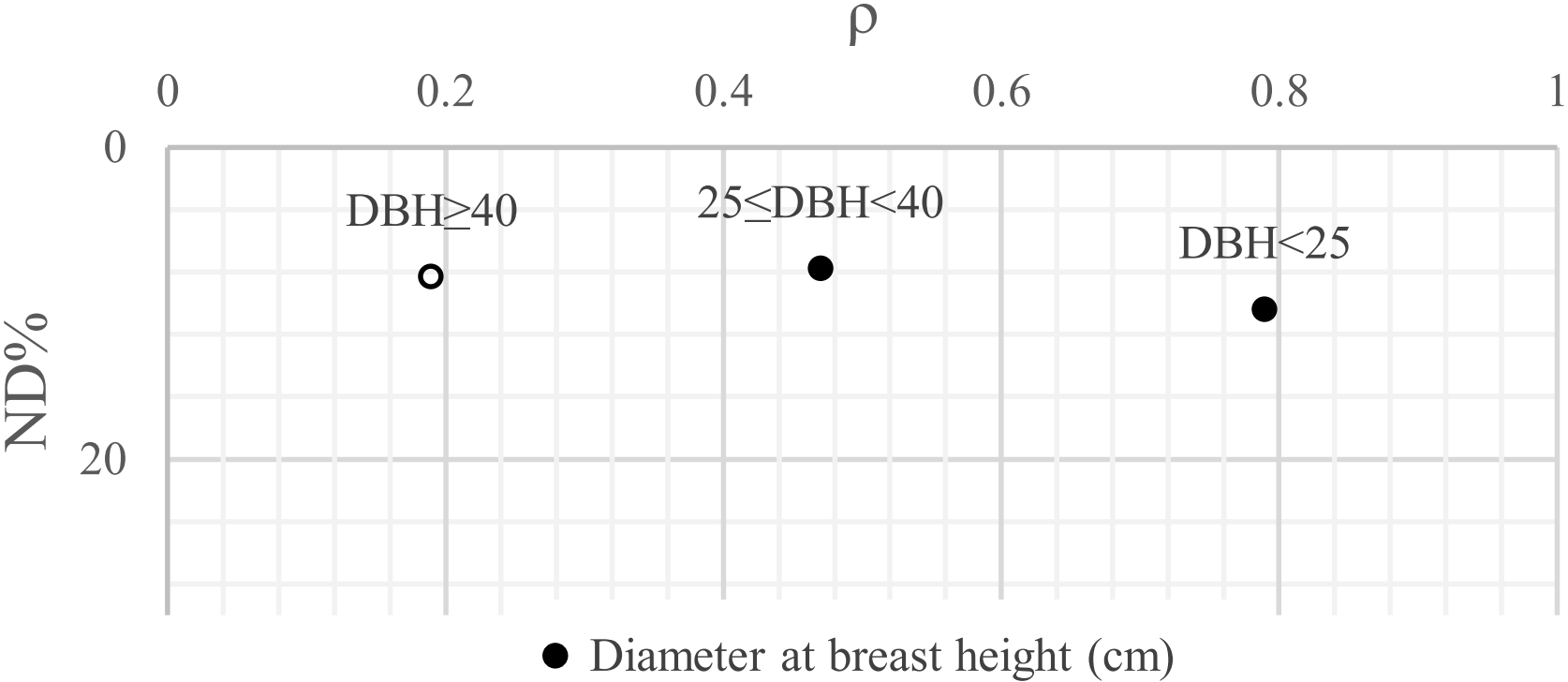
Topic	Factors	Measuring unit	n° of available data (out of 419)	Min.	1st Quartile	Median	Mean	3rd quartile	Max.	Selected intervals	n° of observation per interval	n° of sites per interval
Hydrogeology	Depth to water table (DWT)	m b.g.l. (below ground level)	419	0.35	0.75	1	2.39	2.5	27	DWT<1, 1≤DWT<3, and DWT≥3	204, 138, and 77	3, 5, 9
	Average aquifer thickness (b)	m	235	0.9	3	3	3.29	4	6.6	b≤3.5, b>3.5	157 and 77	5, 4
	Aquifer hydraulic conductivity (K)	m/s	373	4x10 <sup>-6</sup>	1x10 <sup>-5</sup>	1x10 <sup>-5</sup>	9x10 <sup>-5</sup>	1x10 <sup>-4</sup>	1x10 <sup>-3</sup>	K<1x10 <sup>-5</sup> , K≥1x10 <sup>-5</sup>	189 and 184	2, 9
Tree identity and anatomy	Family	e.g., Salicaceae	398							Cupressaceae, Pinaceae, Salicaceae, Nyssaceae, Betulaceae, Altingiaceae, Fagaceae, Platanaceae, Ulmaceae, Rosaceae	112, 71, 62, 14, 68, 18, 45, 4, 3, 2	2, 6, 7, 1, 3, 1, 6, 1, 1, 1
	Xylem structure	e.g., coniferous	398							Coniferous/Diffuse-porous/Ring-porous	183,169, 46	6, 9, 6
	Tree diameter at breast height (DBH)	cm	142	11	24	25	31.96	36	102	DBH<25, 25≤DBH<40 cm, and DBH≥40 cm	51, 66, 24	3, 5, 2
	Trunk drilling length (L)	cm	369	3.8	6	6.8	6.92	6.8	12.5	L≤6 and L>6 cm	123, 245	6, 5
Sampling and extraction methodology	Sampling height (H)	cm a.g.l. (above ground level)	398	50	100	150	129.1	150	900	H<99, 99<H≤120, and H>120 cm a.g.l.	46, 123, 228	1, 3, 7
	Extraction method	e.g., methanol extraction	419							Dry/Water extraction/Methanol extraction/SPME	307, 8, 58, 46	7, 1, 3, 1

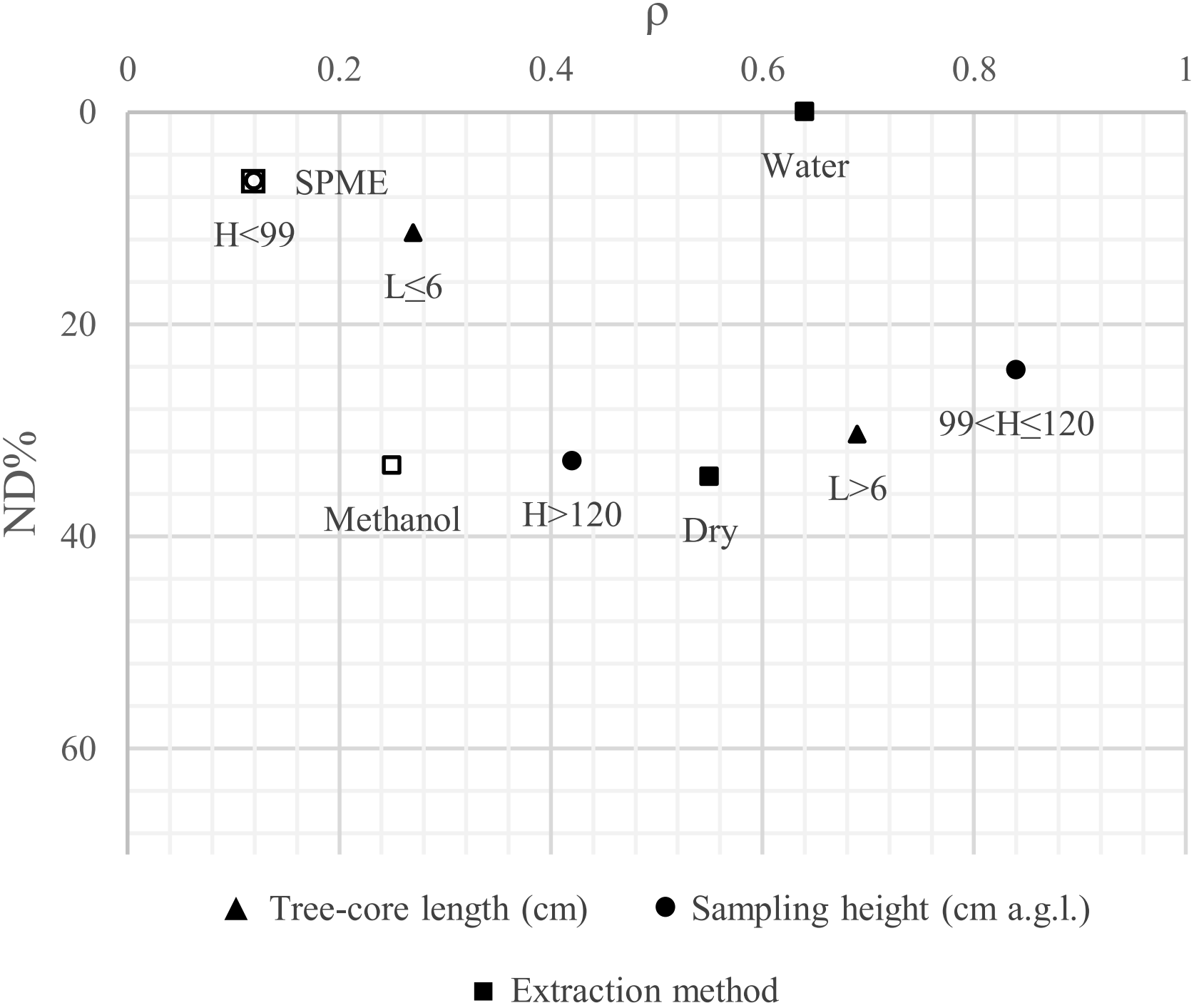


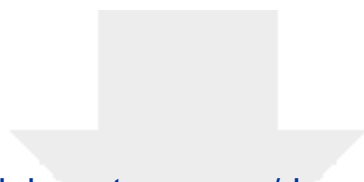






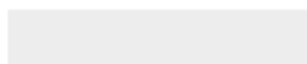






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**Supplementary Material**  
**Supplementary\_Materials.xlsx**



**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:

**CRedit author statement**

**Carlotta Leoncini:** Conceptualization, Methodology, Formal Analysis, Investigation, Writing-Original draft

**Maria Filippini:** Conceptualization, Methodology, Writing-Review & Editing, Supervision

**Juri Nascimbene:** Conceptualization, Methodology, Writing-Review & Editing, Supervision

**Alessandro Gargini:** Conceptualization, Methodology, Writing-Review & Editing, Supervision