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

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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 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.
Response to Reviewers:	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 for English improvements. The paper is now significantly improved grammatically and in the clarity of the

	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.
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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 analyse~~i~~s 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, sh~~ad~~edding 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~~T~~heir 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 d~~ata were statistically analyzed ~~statistically~~ to identify the major~~ factors~~ drivers of~~ing 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 ~~n 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~~ilst~~ ~~factors~~ conditions ~~favoring higher~~increasing detectability (e.g., sampling tree-cores near ground level) are ~~ideal~~ recommended ~~for~~ to preliminary screen~~ing 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 applicati on~~ve~~ perspectives. In ~~conjunction~~ parallel with ~~the removal of~~ 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~~can~~ delineate shallow gw contamination by chlorinated ethenes (CEs) such as trichloroethene (TCE) and cis 1,2-dichlorethene (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 ~~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 most frequent~~ly~~ target ~~encountered~~ in reported applications of ~~this technique~~phytoscreening. This review ~~is focused~~examines ~~on~~ phytoscreening applications for CEs in groundwater, ~~for which~~for which exist ~~literature provides~~ sufficient literature information ~~for a~~to conduct a quantitative meta-analysis. These compounds are indeed particularly responsive ~~for~~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 could be ~~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~~ tissues ~~relative~~ as compared to gw concentrations.

Phytoscreening of contaminated gw was ~~indeed~~ considered a~~n~~ 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~~ factors that drive the correlation between gw and tree-core contaminant concentration as well as ~~the~~ contaminants' detectability potential in trees in order to make this screening technique widely applicable and accepted~~, of trees~~. The ~~The identification of such factors would allow maximizing the~~ correlation and detection capability can be maximized ~~and would~~by providing~~e~~ 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 factors that come ~~at~~ into ~~stake~~play 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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The first database search yielded 64 references. To form a global-scale database of phytoscreening data on CEs, only ~~the~~ 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 databas~~set~~), 118 being below the analytical detection limit (ND data hereafter). ND data represent a small fraction for most sites (below 15%; ~~e.g.~~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~~pertaining~~ 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 ~~in very specific~~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) ~~where~~ in which only ~~an average~~ PCE average gw concentration (2 µg/L) was ~~reported~~provided. ~~It~~ This site was included in the database for its significance in terms of uniqueness ~~in the database~~: cores were sampled and extracted with methanol from trees of 4 different families inhabiting ~~in~~ an arid environment with a ~~high DWT~~deep aquifer table (9-10 m b.g.l.), ~~cores from trees of 4 different families were sampled and extracted with methanol,~~ showing PCE concentration up to 500 µg/kg.

Data ~~for~~ 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 ~~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-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 early~~-~~wood. 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, ~~the~~ 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 ~~tree concentration~~data), sampling height ~~along~~ on the trunk (H in cm above ground level; ~~known for~~ 398 out of 419 ~~tree concentration~~data), and extraction method (419 out of 419 ~~tree concentration~~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 ~~correlation~~ coefficient ρ (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 ~~normally~~ 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 ρ 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~~set~~ due to the lack of knowledge about the uncertainty associated with the measurements. It is worth noting that ρ is insensitive to outliers, therefore~~,~~ representing a robust statistic tool ~~in the abovementioned circumstance~~ 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 ρ 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), ρ and ND% were calculated on the sums.

F~~The f~~actors ~~of~~ in Table 2 were then split~~divided~~ into intervals and Spearman's ρ 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 µg/L. This threshold was determined as the 5^{th} 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-value≤0.05) for all four series (PCE, TCE, cDCE, and the sum of CEs).

The ρ 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 (ρ of 0.37 and 0.34, respectively) compared to the lower chlorinated cDCE (ρ of 0.41). On the other hand, ND% ~~is~~ widely~~greatly~~ ~~different~~ differed between higher chlorinated compounds PCE and TCE (12 and 23%, respectively) and cDCE (47%) with the first two performing better in terms of detectability potential. It is noteworthy that the highest correlation coefficient (0.63) and lowest ND% value (0%) were found for the sum of CEs (reported by Wittlingerova et al., 2013). This could be explained by contaminant transformation processes taking place either in the rhizosphere or in the xylem (Newman and Reynolds, 2004) that would negatively affect the correlation of ~~the~~ single compounds. However, t~~T~~his result is ~~although~~ associated with only one site.

The physicochemical properties of CEs (Table 3) likely influence the behavior of each compound in trees. Larsen et al. (2008) observed a better correlation for cDCE compared to TCE and PCE which was attributed to the higher volatility (higher H_c) of the latter~~s~~ possibly causing a higher loss through the bark (Vroblesky et al., 1999). According to Limmer & Burken (2015), contaminant concentrations decreased with increasing volatility, due either to volatilization from the roots, bark, or subsurface. ~~Limmer & Burken (2015) reported a decrease in contaminant concentrations with increasing volatility, attributing it to volatilization from either the bark, the roots, or the subsurface.~~ The results of o~~O~~ur study ~~agrees~~ are consistent with these findings, with PCE and TCE showing a slightly lower ρ compared to cDCE. In addition, ~~T~~the correlation potential of PCE and TCE may ~~also~~ be hindered by ~~a~~ their lower tendency ~~for~~ to plant uptake ~~into trees~~ compared to cDCE, ~~which is~~ driven by their higher M_w and K_{ow}, and lower S_w~~, and higher K_{ow}~~. Uptake from tree roots was indeed reported to be favored for compounds with low M_w ~~(Baduru et al., 2008)~~ due to their higher tendency to diffuse (Baduru et al., 2008), whereas higher S_w would possibly favor contaminant dissolution in water and consequent tree uptake. Besides,

~~H~~high sorption compounds (log K_{ow}>3) were reported to ~~were shown to have a higher tendency~~tend to be absorbed primarily by root surfaces, resulting in less translocation ~~within trees~~to the xylem (Schnoor et al., 1995). Similarly, a study by Dettenmaier et al. (2009) indicated that ~~highly~~ high-hydrophilic compounds are most likely ~~to be uptaken~~absorbed by ~~plant~~ roots and ~~translocated~~ transferred to the xylem. We may ~~can~~ also assume~~speculate~~ that once in the ~~tree~~xylem, higher log K_{ow} compounds likely tend to ~~get~~ be absorbed ~~in~~ by ~~the~~ xylem tissues, resulting in a prolonged accumulation in the tree and thus ~~and~~ a higher detectability potential. ~~PCE and TCE higher log K_{ow} can indee~~This could~~d~~ explain ~~their~~ the higher detectability potential of PCE and TCE (lower ND%) compared to cDCE. ~~Besides~~Moreover, ~~PCE and TCE~~their higher H_c can aid 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≤DWT<3, and DWT≥3 m b.g.l.~~.~~ Concentration data show~~s~~ a statistically ~~meaningful~~significant correlation value (p-value≤0.05; Figure 2) in the three cases. A slightly decreasing correlation with increasing DWT ~~is~~ was observed (ρ=0.63, 0.54, and 0.52 for DWT<1, 1≤DWT<3, and DWT≥3 m b.g.l., respectively). On the other hand, ~~The higher ND% was seen within t~~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 ρ with increasing DWT), ρ 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 ρ 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~~b 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~~one~~ (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: $K<1\times10^{-5}$ and $K\geq1\times10^{-5}$ 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~~set~~ were clustered by~~divided according to their~~ families and ~~relative~~ xylem structure~~s (coniferous, diffuse-porous, ring-porous)~~. Results show a significant positive correlation with most families (Figure 3), with ρ 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%, ~~respectively~~ 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 ~~a~~ broad ~~sapwood~~ xylem zone~~zone (the active portion of the stem)~~, and transpire throughout the whole year, resulting in a continuous uptake of gw. Ring-porous Fagaceae (primarily *Quercus)* presented a slightly positive correlation (ρ=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, ~~in ring-porous trees,~~ 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-porous Nyssaceae and Betulaceae show a slightly lower ρ compared to conifers~~ous trees~~ (0.74 and 0.65, respectively), and a low ND% (29 and 25%, respectively) although results for Nyssaceae must be taken with caution because they refer to one single study site (Savannah River Site, USA; Vroblesky et al., 1999) where the aquifer was shallow (DWT<1 m b.g.l.). On the other hand, diffuse-porous Salicaceae and Altingiaceae do not show a significant correlation (p-value>0.05) and highly fluctuating ND% (very low for Salicaceae – 3% and very high for Altingiaceae – 64%). The high variability among diffuse-porous families in terms of ρ and ND% could be associated with different arrangements and sizes of the vessels regulating the conductivity of the ~~sapwood~~xylem, which in turn can also vary with age. For example, Salicaceae (*Salix* and *Populus*), widely used in phytoscreening and phytoremediation due to their fast growth, high uptake rates, and widespread occurrence in temperate climates, showed the highest~~best~~ detectability potential ~~but~~ although no correlation between tree-core and gw concentration. Besides, Negri et al. (2003) stated that Salicaceae are genetically predisposed to develop roots extending to the water table at depths greater than 12 m b.g.l., thereby ~~extending~~ widening their detectability potential to deep aquifers. Altingiaceae (*Liquidambar*; present only in the study of Vroblesky et al., 1999) also showed no correlation whilst a low detectability potential. This family was studied by Strycharz and Newman (2009) in a greenhouse experiment where also Platanaceae and Salicaceae were involved. R~~The r~~esults showed that among the 3 families, Altingiaceae was the less recommended for phytoremediation activities. Other diffuse-porous, like Betulaceae (*Alnus* and *Betula*), showed instead a correlation and detectability potential comparable to conifer~~ou~~s. Lewis et al. (2015) calculated that ~~a~~ *Betula* p~~P~~*endula* can accumulate similar ~~quantities~~ amounts of TCE as *Populus* trees due to its lack of heartwood (nonfunctioning xylem) and homogeneous ~~sapflow~~ xylem flow (Westhoff et al., 2008), making this species~~it~~ ~~an ideal~~a suitable candidate for phytoremediation and phytoscreening activities ~~activities~~. Eventually, the low number of Platanaceae (diffuse-porous), Ulmaceae (ring-porous), and Rosaceae (diffuse-porous) in the ~~dataset~~ database (Table 2) ~~made unfeasible~~hindered an analysis on these families. Even so, Limmer & Burken (2015) showed that the genus *Platanus* (Platanaceae) had a high detectability potential, especially for PCE gw contamination, if compared to non-*Platanus* trees. Their result was although associated with *Platanus* trees growing ~~primarily~~ in areas with shallow gw~~roundwater~~. ~~Oppositely~~Conversely, our data~~data associated with~~ on Platanaceae ~~trees in~~ ~~our dataset~~ showed that 3 out of 4 times this family ~~ese trees~~ did not detect ~~contamination~~ contaminants even with shallow gw (DWT<1 m b.g.l.; Savannah River Site, USA; Vroblesky et al., 1999)~~,~~ ~~although~~ albeit in that particular site aquifer ~~in that specific site (Savannah River Site, USA; Vroblesky et al., 1999)~~ K was ~~very~~ low ($5.3x10^{-6}$ m/s). Yung et al. (2017) pointed out that besides *Populus* and *Salix* (Salicaceae, diffuse-porous) and *Betula* (Betulaceae, diffuse-porous), *Quercus and Ulmus* (Fagaceae and Ulmaceae, both ring-porous) are also efficient biomonitors of PCE and TCE contamination. Notwithstanding the contrast with our results on Fagaceae, the 2 Ulmaceae trees in our ~~dataset~~ database (Carswell Golf Course, USA; Vroblesky et al., 2004) showed TCE concentrations above detection limits, with DWT at 1 ~~and~~ to 5 m b.g.l. ~~and with an~~, aquifer K of $7x10^{-5}$ m/s, and b of 0.9 m. This may suggest that even among ring-porous trees a great variability in concentration results is expected.

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

3.4 Sampling and analysis protocols

In our ~~dataset~~ database tree-core L ranges from 3.8 to 12.5 cm and was clustered~~arranged~~ into two intervals: $L \leq 6$ and $L > 6$ cm. Shorter cores do not show a significant~~ly~~ correlation between ~~e with~~ tree-core and gw concentration (*p*-value>0.05) whereas longer cores have a high positive correlation (ρ=0.71; Figure 6). This result ~~finds agreement~~agrees with ~~in~~ Ma & Burken (2003) and ~~the~~ the USGS user guide published by Vroblesky (2008), which suggest~~ing~~ a better correlation when the core samples are longer than ~7-8 cm. Shorter cores may be also acceptable for ring-porous trees, in which water transport takes place mostly in the outermost ring (Ellmore and Ewers, 1986). The detectability potential is lower for ~~the longer cores~~the higher L interval ~~interval~~ (ND of 11% and 30%~~%~~ for $L \leq 6$ ~~cm and 30% for~~and $L > 6$ cm, respectively), likely ~~possibly~~ indicating that drilling longer tree-cores could promote diffusional loss out of the sample since sampling ~~employs~~ requires relatively ~~higher~~ longer ~~sampling times~~periods (tree-cores are usually cut in small~~er~~ pieces before being put in the vials) ~~that can possibly promote diffusional loss out of the sample~~.

~~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 was clustered~~split~~ into three intervals: $H < 99$, $99 < H \leq 120$, and $H > 120$ cm a.g.l~~.~~. The medium interval ~~$99 < H \leq 120$ cm~~ shows a very high correlation between tree-core and gw concentration (ρ=0.84; Figure 6), which decreases ~~above 120 cm a.g.l.~~for higher H (ρ=0.42). ~~Sampling height below 99 cm~~The lower interval shows no significant correlation (*p*-value>0.05) although the data pertain to only one survey by Holm & Rotard (2011). The reason for the high ρ value at medium ~~sampling height~~H is still unknown. ~~but w~~We can speculate that this is related to the attainment of an equilibrium of the contaminant inside the wood-air-water partitioning system. On the other hand, a low ~~number of~~ ND% ~~data~~ was registered for the ~~lowest~~ lower H interval (7%) whereas the higher intervals ~~$99 < H \leq 120$ and $H > 120$ cm a.g.l.~~ are associated with higher ND% (24% and 33% for the medium and higher H interval,~~,~~ respectively). This result is consistent with the experiments of Ma & Burken (2003) where a higher TCE loss was observed higher up the trunk. Thus, a lower rate of diffusional loss from the bark may be expected for the lower~~s~~ H intervals. On the other hand, Ottosen et al. (2018) sampled tree-cores just above the ground surface without distinguishing a clear advantage from this sampling strategy.

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

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

4. SUMMARY AND CONCLUSIONS

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

The correlation (quantitative ~~quantitative~~ monitoring potential) ~~appears to be~~is higher when ~~(1)~~ the hydrogeological dynamics favor direct uptake of contaminated water~~,~~ and ~~(2)~~ the concentration is homogeneously distributed in the tree and the tree-core sample. ~~Uptake~~ Direct tree uptake ~~of contaminated gw~~ is favored for the lighter and more soluble cDCE ~~,~~ and ~~in the case of~~in the case of shallow ~~water tables~~ (DWT<3 m b.g.l.), ~~and in~~ thin (b<3.5 m), and permeable aquifers (~~b<3.5 m;~~ K≥1x10^{-5} m/s). The homogeneity of concentration in the ~~sapwood~~ xylem is ~~likely~~ higher for Pinaceae and Cupressaceae (conifer~~ou~~s), due to their non-porous xylem, and ~~in~~ for smaller diameter trees (DBH<25 cm)~~,~~ whereas homogeneity of concentration in the tree-core is enhanced~~facilitated~~ ~~in the case~~when sampling ~~of~~ longer tree-cores (L>6 cm) ~~,~~and ~~possibly~~ at a ~~sampling~~ height ~~along the stem~~on the trunk between 99<H≤120 cm a.g.l~~.~~.

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

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

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

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FIGURES CAPTION

FIGURE 1. Spearman's ρ (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≤0.05

FIGURE 2. Spearman's ρ (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≤0.05

FIGURE 3. Spearman's ρ (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≤0.05

FIGURE 4. Spearman's ρ (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≤0.05

FIGURE 5. Spearman's ρ (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≤0.05

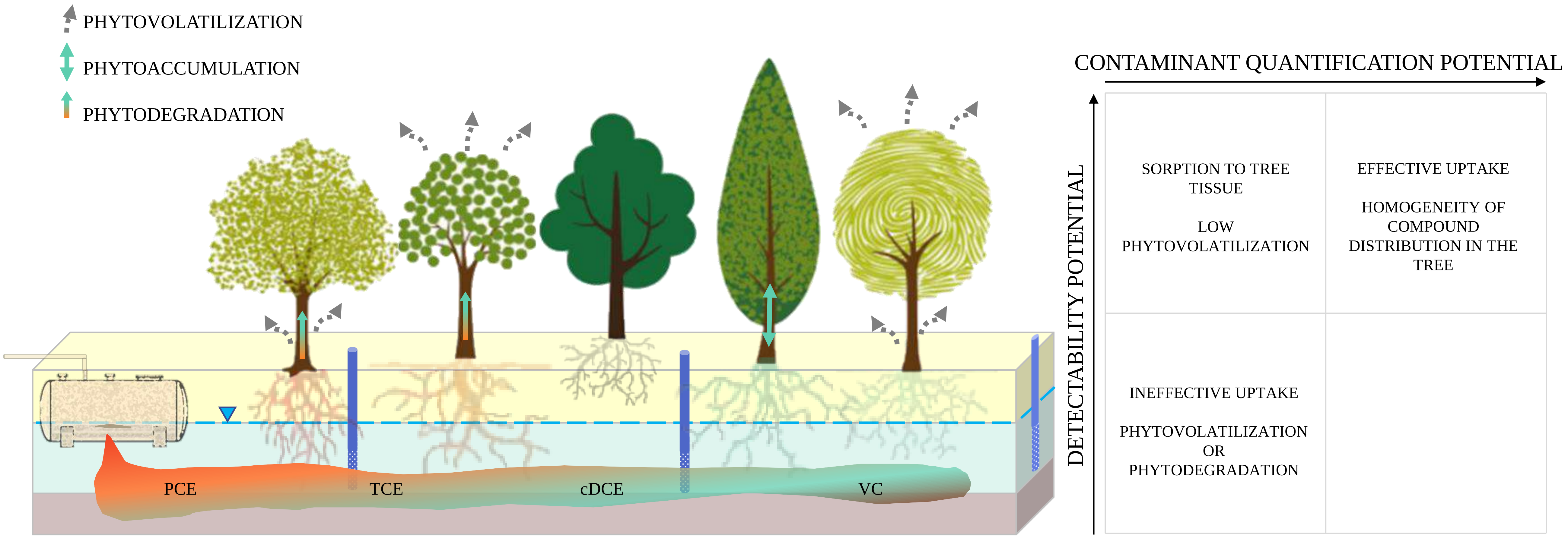
TABLES CAPTION

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)

Graphical Abstract



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-dichlorethene (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 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 high funding, which could be 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 concentrations in plant tissues as compared to gw concentrations.

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

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 that determine higher correlations 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 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 ρ (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 ρ 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 ρ 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 ρ 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), ρ and ND% were calculated on the sums.

Factors in Table 2 were then split into intervals and Spearman's ρ 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 µg/L. This threshold was determined as the 5^{th} 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

3.1 Contaminant properties

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

The ρ 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 (ρ of 0.37 and 0.34, respectively) compared to the lower chlorinated cDCE (ρ of 0.41). On the other hand, ND% widely differed between higher chlorinated compounds PCE and TCE (12 and 23%, respectively) and cDCE (47%) with the first two performing better in terms of detectability potential. It is noteworthy that the highest correlation coefficient (0.63) and lowest ND% value (0%) were found for the sum of CEs (reported by Wittlingerova et al., 2013). This could be explained by contaminant transformation processes taking place either in the rhizosphere or in the xylem (Newman and Reynolds, 2004) that would negatively affect the correlation of single compounds. However, this result is associated with only one site.

The physicochemical properties of CEs (Table 3) likely influence the behavior of each compound in trees. Larsen et al. (2008) observed a better correlation for cDCE compared to TCE and PCE which was attributed to the higher volatility (higher H_c) of the latter possibly causing a higher loss through the bark (Vroblesky et al., 1999). According to Limmer & Burken (2015), contaminant concentrations decreased with increasing volatility, due either to volatilization from the roots, bark, or subsurface. The results of our study are consistent with these findings, with PCE and TCE showing a slightly lower ρ compared to cDCE. In addition, the correlation potential of PCE and TCE may be hindered by their lower tendency to plant uptake compared to cDCE, driven by their higher M_w and K_{ow}, and lower S_w. Uptake from tree roots was indeed reported to be favored for compounds with low M_w due to their higher tendency to diffuse (Baduru et al., 2008), whereas higher S_w would possibly favor contaminant dissolution in water and consequent tree uptake. Besides, high sorption compounds (log K_{ow}>3) were reported to tend to be absorbed primarily by root surfaces, resulting in less translocation to the xylem (Schnoor et al., 1995). Similarly, a study by Dettenmaier et al. (2009) indicated that high-hydrophilic compounds are most likely absorbed by roots and transferred to the xylem. We may also assume that once in the xylem, higher log K_{ow} compounds likely tend to be absorbed by xylem tissues, resulting in a prolonged accumulation in the tree and thus a higher detectability potential. This could explain the higher 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≤DWT<3, and DWT≥3 m b.g.l. Concentration data show a statistically significant correlation value (*p*-value≤0.05; Figure 2) in the three cases. A slightly decreasing correlation with increasing DWT was observed (ρ=0.63, 0.54, and 0.52 for DWT<1, 1≤DWT<3, and DWT≥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 ρ with increasing DWT), ρ 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 ρ 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≤3.5 and b>3.5 m. Data associated with lower b show a very high positive correlation (ρ=0.71), whereas those associated with higher b have a significantly weaker correlation (ρ=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≤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: $K<1x10^{-5}$ and $K\geq1x10^{-5}$ m/s. Concentrations referred to higher K values show a slightly higher correlation (ρ=0.73) compared to those referred to lower conductivities (ρ=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 ρ being highest for coniferous, i.e. Pinaceae (ρ=0.86) and Cupressaceae (ρ=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 (ρ=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-porous Nyssaceae and Betulaceae show a slightly lower ρ compared to conifers (0.74 and 0.65, respectively), and a low ND% (29 and 25%, respectively) although results for Nyssaceae must be taken with caution because they refer to one single study site (Savannah River Site, USA; Vroblesky et al., 1999) where the aquifer was shallow (DWT<1 m b.g.l.). On the other hand, diffuse-porous Salicaceae and Altingiaceae do not show a significant correlation (p-value>0.05) and highly fluctuating ND% (very low for Salicaceae – 3% and very high for Altingiaceae – 64%). The high variability among diffuse-porous families in terms of ρ and ND% could be associated with different arrangements and sizes of the vessels regulating the conductivity of the xylem, which in turn can also vary with age. For example, Salicaceae (*Salix* and *Populus*), widely used in phytoscreening and phytoremediation due to their fast growth, high uptake rates, and widespread occurrence in temperate climates, showed the highest detectability potential although no correlation between tree-core and gw concentration. Besides, Negri et al. (2003) stated that Salicaceae are genetically predisposed to develop roots extending to the water table at depths greater than 12 m b.g.l., thereby widening their detectability potential to deep aquifers. Altingiaceae (*Liquidambar*; present only in the study of Vroblesky et al., 1999) also showed no correlation whilst a low detectability potential. This family was studied by Strycharz and Newman (2009) in a greenhouse experiment where also Platanaceae and Salicaceae were involved. Results showed that among the 3 families, Altingiaceae was the less recommended for phytoremediation activities. Other diffuse-porous, like Betulaceae (*Alnus* and *Betula*), showed instead a correlation and detectability potential comparable to conifers. Lewis et al. (2015) calculated that *Betula pendula* can accumulate similar amounts of TCE as *Populus* trees due to its lack of heartwood (nonfunctioning xylem) and homogeneous xylem flow (Westhoff et al., 2008), making this species a suitable candidate for phytoremediation and phytoscreening activities. Eventually, the low number of Platanaceae (diffuse-porous), Ulmaceae (ring-porous), and Rosaceae (diffuse-porous) in the database (Table 2) hindered an analysis on these families. Even so, Limmer & Burken (2015) showed that the genus *Platanus* (Platanaceae) had a high detectability potential, especially for PCE gw contamination, if compared to non-*Platanus* trees. Their result was although associated with *Platanus* trees growing in areas with shallow gw. Conversely, our data on Platanaceae showed that 3 out of 4 times this family did not detect contaminants even with shallow gw (DWT<1 m b.g.l.; Savannah River Site, USA; Vroblesky et al., 1999) albeit in that particular site aquifer K was low (5.3×10^{-6} m/s). Yung et al. (2017) pointed out that besides *Populus* and *Salix* (Salicaceae, diffuse-porous) and *Betula* (Betulaceae, diffuse-porous), *Quercus and*

Ulmus (Fagaceae and Ulmaceae, both ring-porous) are also efficient biomonitors of PCE and TCE contamination. Notwithstanding the contrast with our results on Fagaceae, the 2 Ulmaceae trees in our database (Carswell Golf Course, USA; Vroblesky et al., 2004) showed TCE concentrations above detection limits, with DWT at 1 to 5 m b.g.l., aquifer K of $7x10^{-5}$ m/s, and b of 0.9 m. This may suggest that even among ring-porous trees a great variability in concentration results is expected.

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

3.4 Sampling and analysis protocols

In our database tree-core L ranges from 3.8 to 12.5 cm and was clustered into two intervals: L≤6 and L>6 cm. Shorter cores do not show a significant correlation between tree-core and gw concentration (*p*-value>0.05) whereas longer cores have a high positive correlation (ρ=0.71; Figure 6). This result agrees with Ma & Burken (2003) and the USGS user guide published by Vroblesky (2008), which suggest a better correlation when the core samples are longer than ~7-8 cm. Shorter cores may be also acceptable for ring-porous trees, in which water transport takes place mostly in the outermost ring (Ellmore and Ewers, 1986). The detectability potential is lower for the higher L interval (ND of 11% and 30% for L≤6 and L>6 cm, respectively), likely indicating that drilling longer tree-cores could promote diffusional loss out of the sample since sampling requires relatively longer periods (tree-cores are usually cut in small pieces before being put in the vials).

Sampling H from the base of the trunk ranges between 50 and 900 cm a.g.l. and was clustered into three intervals: H<99, 99<H≤120, and H>120 cm a.g.l. The medium interval shows a very high correlation between tree-core and gw concentration (ρ=0.84; Figure 6), which decreases for higher H (ρ=0.42). The lower interval shows no significant correlation (*p*-value>0.05) although the data pertain to only one survey by Holm & Rotard (2011). The reason for the high ρ value at medium H is still unknown. We can speculate that this is related to the attainment of an equilibrium of the contaminant inside the wood-air-water partitioning system. On the other hand, a low ND% was registered for the lower H interval (7%) whereas the higher intervals are associated with higher ND% (24% and 33% for the medium and higher H interval, respectively). This result is consistent with the experiments of Ma & Burken (2003) where a higher TCE loss was observed higher up the trunk. Thus, a lower rate of diffusional loss from the bark may be expected for the lower H intervals. On the other hand, Ottosen et al. (2018) sampled tree-cores just above the ground surface without distinguishing a clear advantage from this sampling strategy.

Our database includes 4 extraction methods used for analysis (dry sample, organic-free water, methanol solution, and SPME; Figure 6). The dry and the water extracted samples showed moderately high correlation (ρ=0.55 and ρ=0.64 for dry and water extraction, respectively). However, data from water extracted samples pertain to only one survey where concentration data relate to the sum of CEs (Wittlingerova et al., 2013). The high ρ could be associated either with the extraction method or with the fact that the sum of CEs was considered (see section 3.1). Methanol extracted samples, related to the study cases of Duncan et al. (2017), were collected with unfavorable conditions in arid-hot environments (Nogales site, Park-Euclid, and Motorola 52nd superfund site in Arizona, USA). The small number of tree-cores (8) sampled with this method may explain the observed non-significant correlation value (*p*-value>0.05). Tree-core concentrations associated with arid environments are possibly more a function of vadose zone vapor phase concentration than gw concentration since roots 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-core concentrations of were higher than 300 µg/kg despite being associated with low gw concentrations of PCE (2 µg/L; i.e., lower than the gw concentration threshold defined for ND% calculation; See Section 2.2) further supports the hypothesis that trees were absorbing contaminants from a matrix other than gw. This may have hindered correlation with gw in the case of methanol extraction. The analysis following SPME, associated with only one site (Potsdam-Krampnitz military base, Germany; Holm & Rotard, 2011), also showed no significant correlation (p-value>0.05). Even so, the ND% was very low for SPME (7%) as well as water extracted samples (0%). However, since these methods were used in single study cases, these results may be related to other site-specific conditions or sampling protocols. In terms of ND%, the dry and methanol extraction produced comparable results (34%, and 33% for dry and methanol extraction, respectively).

4. SUMMARY AND CONCLUSIONS

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

The correlation (quantitative monitoring potential) is higher when the hydrogeological dynamics favor direct uptake of contaminated water and the concentration is homogeneously distributed in the tree and the tree-core sample. Direct tree uptake is favored for the lighter and more soluble cDCE and in the case of shallow (DWT<3 m b.g.l.), thin (b<3.5 m), and permeable aquifers ($K \geq 1x10^{-5}$ m/s). The homogeneity of concentration in the xylem is higher for Pinaceae and Cupressaceae (conifers), due to their non-porous xylem, and for smaller diameter trees (DBH<25 cm) whereas homogeneity of concentration in the tree-core is enhanced when sampling longer tree-cores (L>6 cm) and at a height on the trunk between 99<H≤120 cm a.g.l.

The detectability (qualitative screening potential) is higher when factor conditions favor accumulation in the xylem and hinder volatilization loss through the bark. In these terms, PCE and TCE are more suited compared to cDCE due to their higher sorption and weight. Low volatilization loss was also inferred in the case of large-diameter trees (DBH≥40 cm), at a low height on the trunk (H<99 cm a.g.l.), and for shorter cores due to reduced time of sampling (L≤6 cm). In the case of Salicaceae, high uptake rates may compensate for volatilization losses, thus increasing detectability. Finally, the process of contaminant extraction appears to be maximized when using organic-free water extraction and SPME.

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

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FIGURES CAPTION

FIGURE 1. Spearman's ρ (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≤0.05

FIGURE 2. Spearman's ρ (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≤0.05

FIGURE 3. Spearman's ρ (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≤0.05

FIGURE 4. Spearman's ρ (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≤0.05

FIGURE 5. Spearman's ρ (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≤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)

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.

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	100
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 52nd 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	$4x10^{-6}$	$1x10^{-5}$	$1x10^{-5}$	$9x10^{-5}$	$1x10^{-4}$	$1x10^{-3}$	$K<1x10^{-5}$, $K\geq1x10^{-5}$	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
Sampling and extraction methodology	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 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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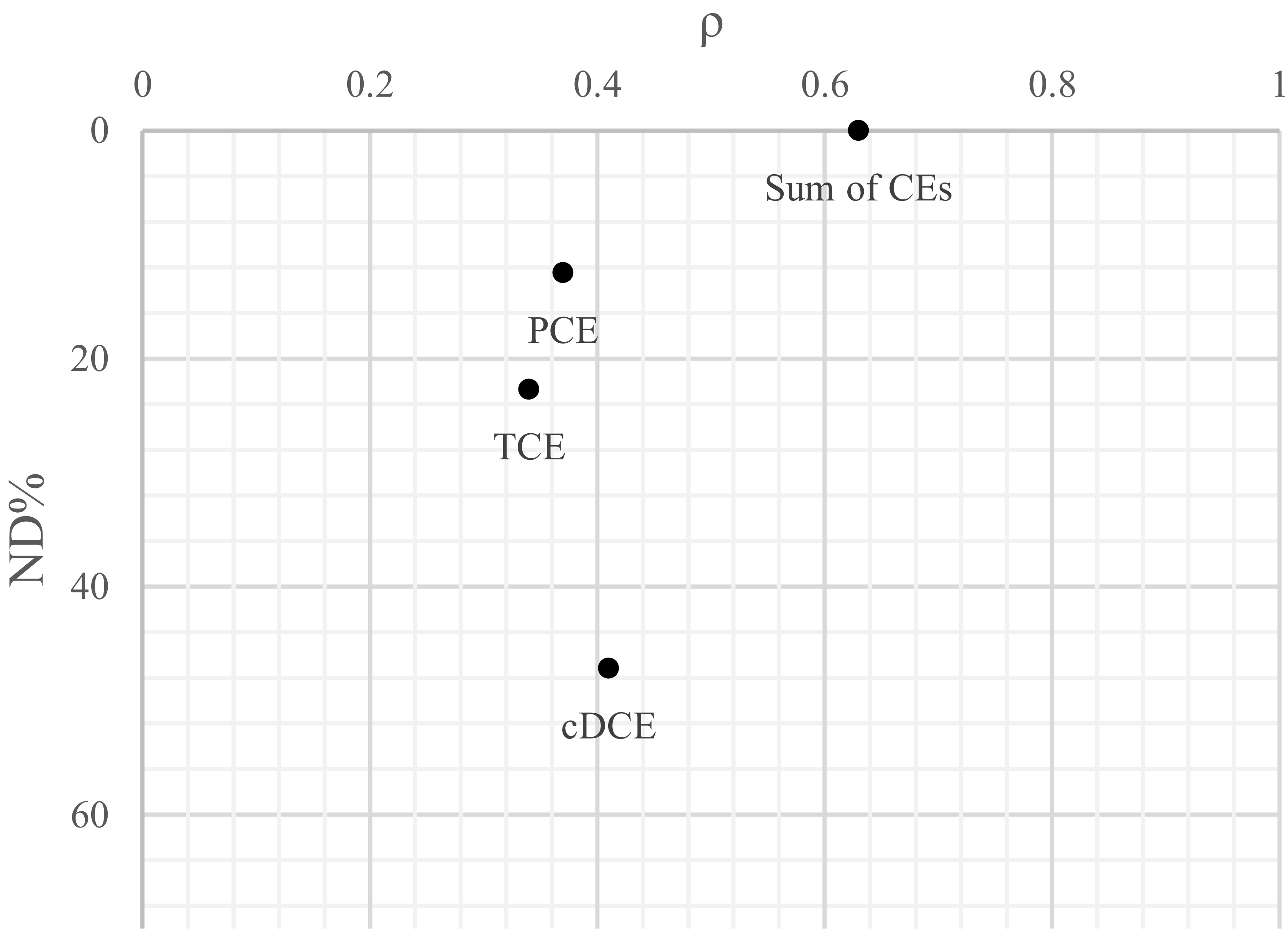

Figure

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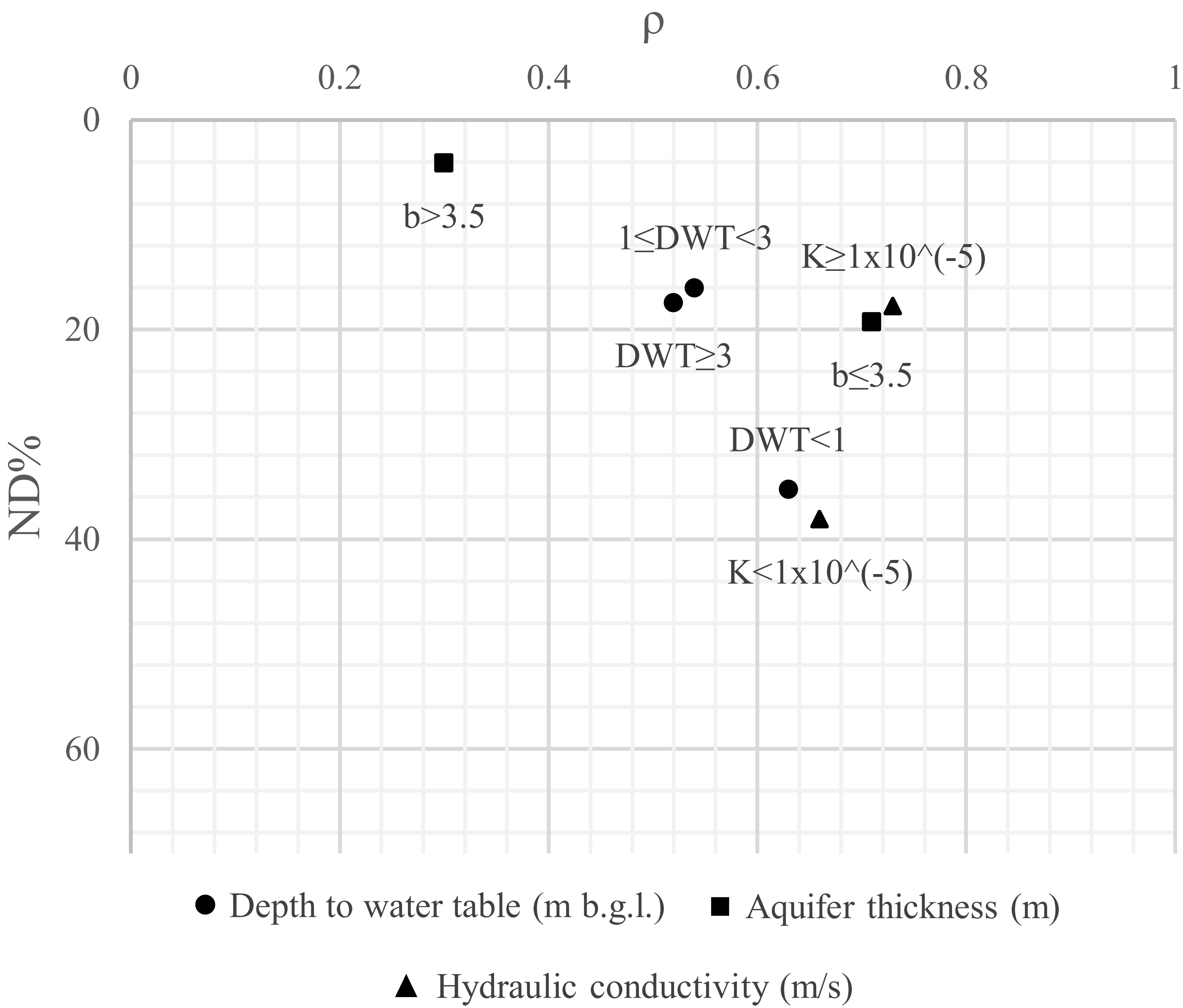

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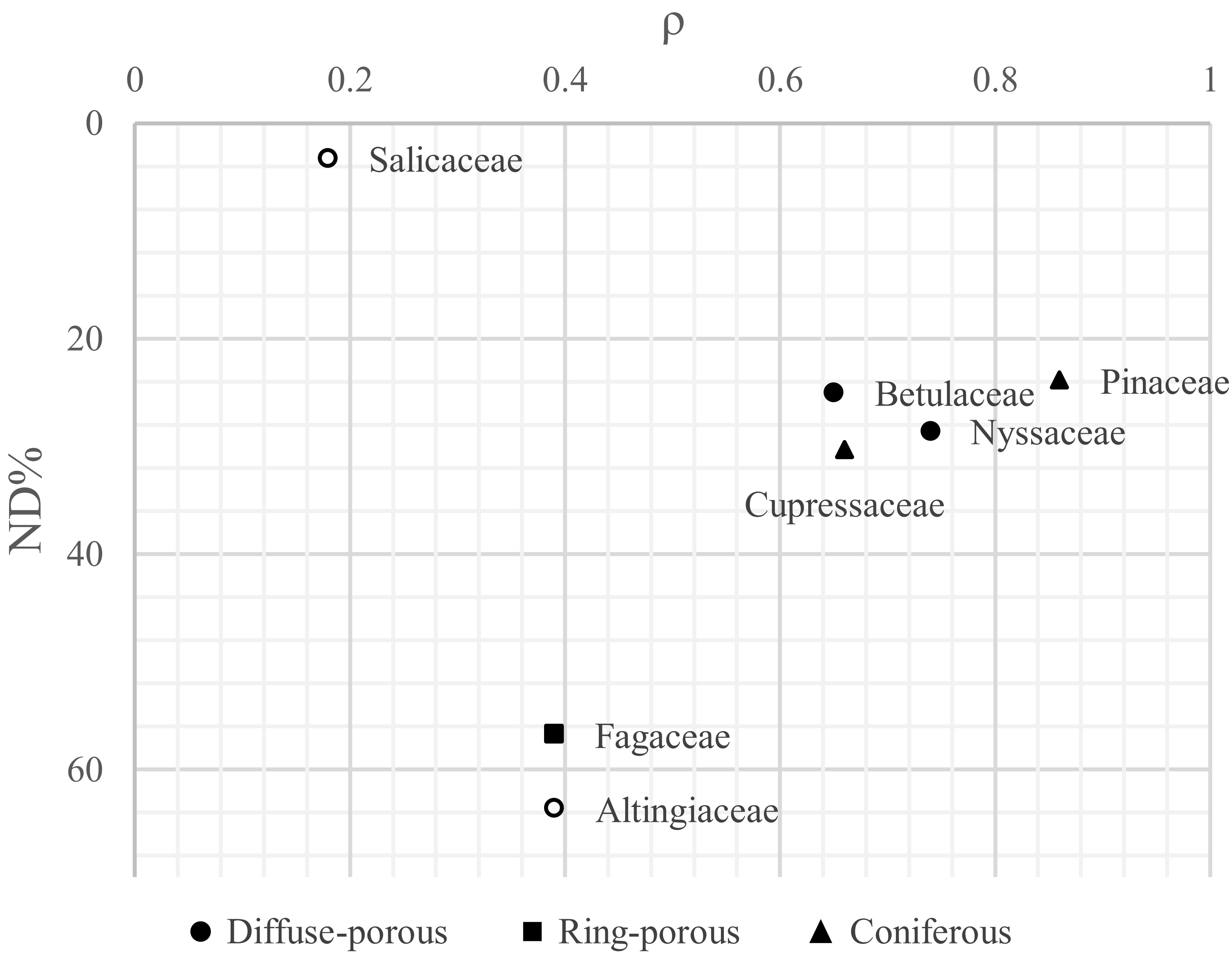
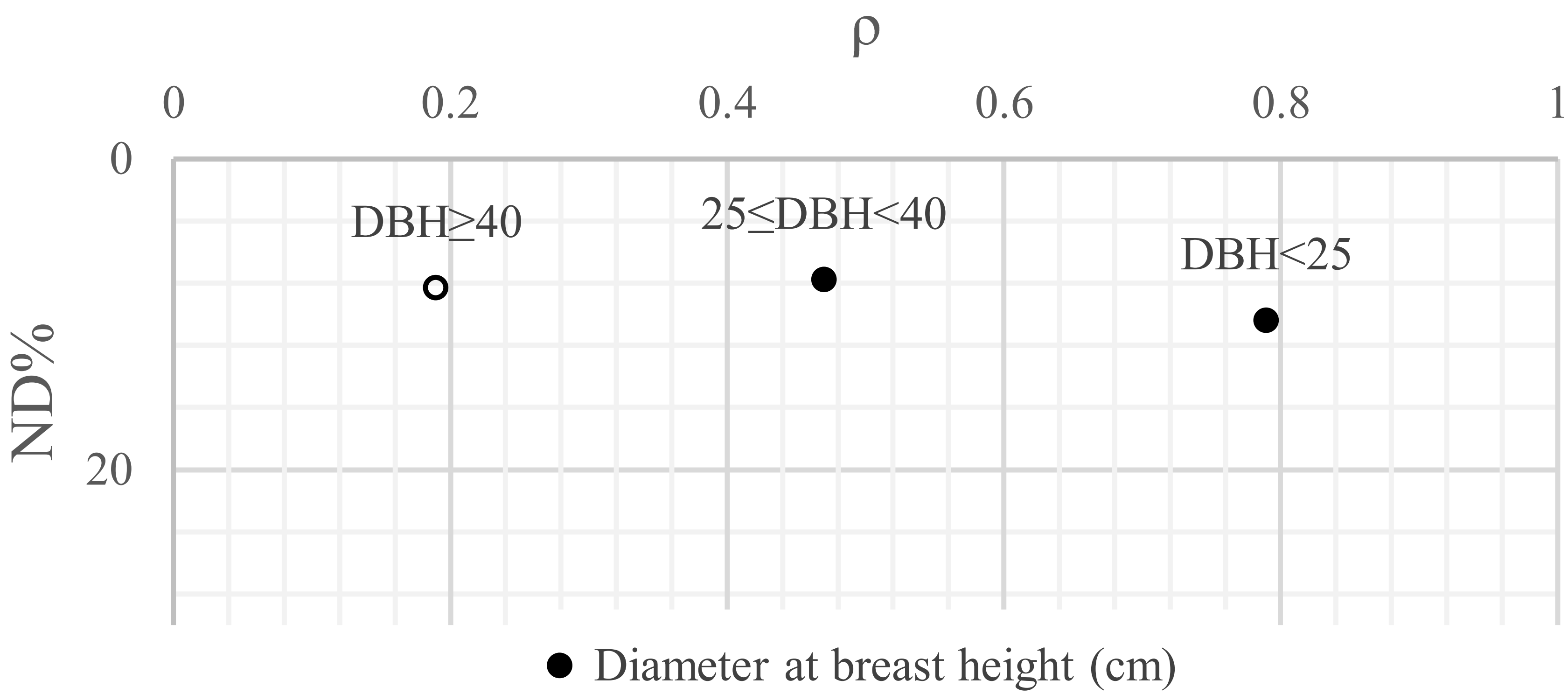
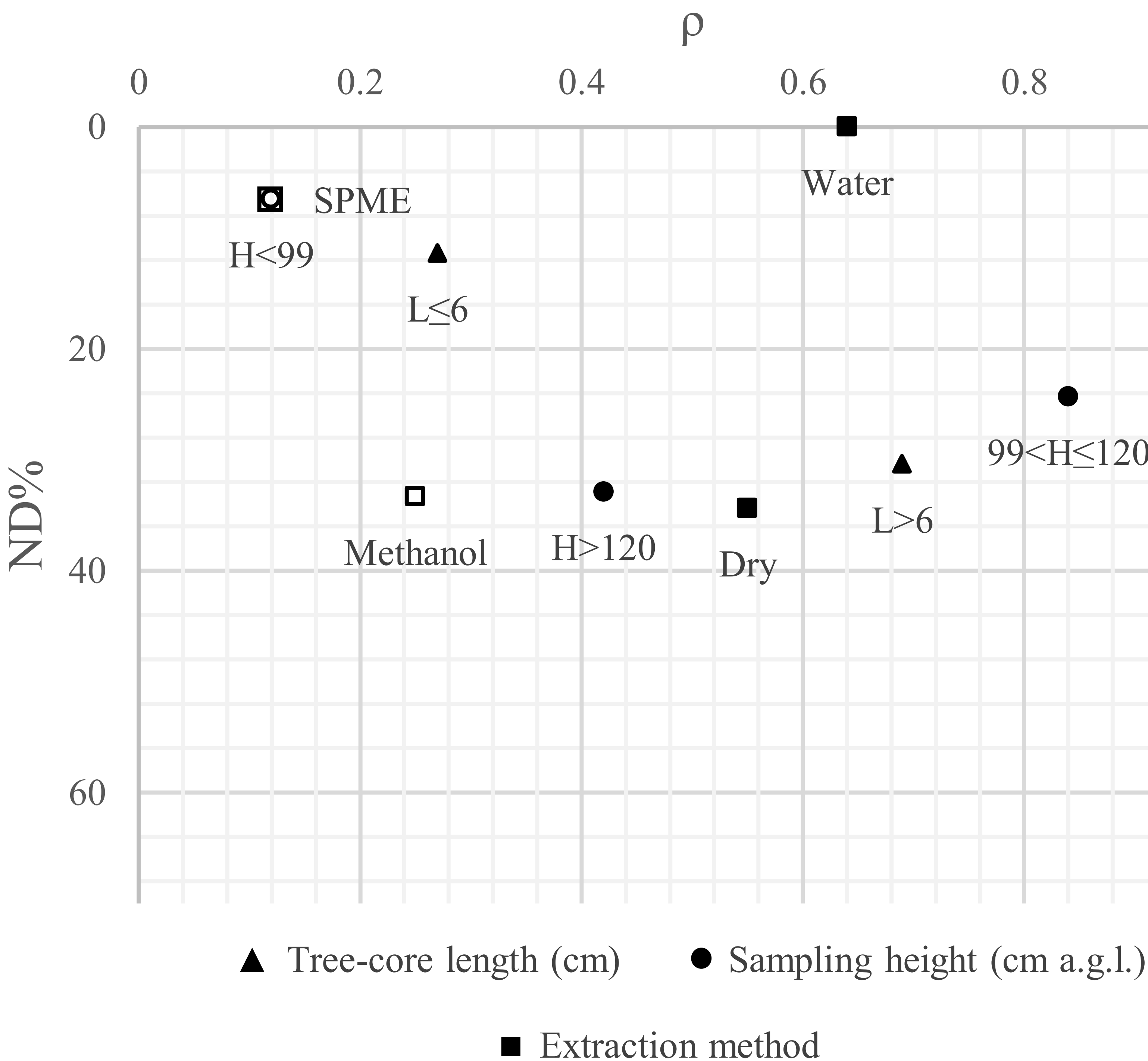



ρ
0
0.2
0.4
0.6
0.8
1
0
20
ND%
DBH≥40
25≤DBH<40
DBH<25
Diameter at breast height (cm)


ρ
0
0.2
0.4
0.6
0.8
1
0
20
40
60
ND%
SPME
Water
H<99
L≤6
99<H≤120
L>6
Methanol
H>120
Dry
Tree-core length (cm)
Sampling height (cm a.g.l.)
Extraction method

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Declaration of interests

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

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

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

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