



An assessment of correlations between chlorinated VOC concentrations in tree tissue and groundwater for phytoscreening applications

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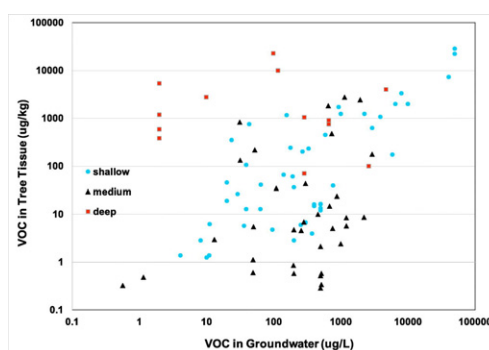
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HIGHLIGHTS

- A meta-analysis is conducted of phytoscreening data collected from several studies.
- We specifically examine correlations between tree-tissue and groundwater VOC concentrations.
- A significant correlation is observed for sites with shallow groundwater.

GRAPHICAL ABSTRACT



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ABSTRACT

The majority of prior phytoscreening applications have employed the method as a tool to qualitatively determine the presence of contamination in the subsurface. Although qualitative data is quite useful, this study explores the potential for using phytoscreening quantitatively. The existence of site-specific and non-site-specific (master) correlations between VOC concentrations in tree tissue and groundwater is investigated using data collected from several phytoscreening studies. The aggregated data comprise 100 measurements collected from 12 sites that span a wide range of site conditions. Significant site-specific correlations are observed between tetrachloroethene (PCE) and trichloroethene (TCE) concentrations measured for tree tissue and those measured in groundwater for three sites. A moderately significant correlation ($r^2 = 0.56$) exists for the entire aggregate data set. Parsing the data by groundwater depth produced a highly significant correlation ($r^2 = 0.88$) for sites with shallow (<4 m) groundwater. Such a significant correlation for data collected by different investigators from multiple sites with a wide range of tree species and subsurface conditions indicates that groundwater concentration is the predominant factor mediating tree-tissue concentrations for these sites. This may be a result of trees likely directly tapping groundwater for these shallow groundwater conditions. This master correlation may provide reasonable order-of-magnitude estimates of VOC concentrations in groundwater for such sites, thereby allowing the use of phytoscreening in a more quantitative mode.

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1. Introduction

It has long been known that vegetation can take up compounds from their surrounding environment through several mechanisms. For example, numerous studies have shown the linkage between contaminated

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soil and uptake of volatile organic compounds (VOCs) by vegetation (Newman et al., 1997; Gordon et al., 1998; Vroblesky et al., 1999; Narayanan et al., 1999; Newman et al., 1999; Ma and Burken, 2002; Ma and Burken, 2003; Vroblesky et al., 2004; Struckhoff et al., 2005; Gopalakrishnan et al., 2007; Sorek et al., 2008; Larsen et al., 2008; Burken et al., 2009; Limmer et al., 2011; Burken et al., 2011; Balouet et al., 2012; Wittlingerova et al., 2013; Rein et al., 2015; Bromilow and Chamberlain, 1995; Nietch et al., 1999). As a result, vegetation (e.g., trees) have been used for both remediation (Newman et al., 1997; Gordon et al., 1998; Newman et al., 1999; Ma and Burken, 2003; Chappell and United States. Environmental Protection Agency. Technology Innovation Office, 1997) and phytoscreening (Narayanan et al., 1999; Ma and Burken, 2002; Gopalakrishnan et al., 2007; Sorek et al., 2008; Larsen et al., 2008; Burken et al., 2009; Burken et al., 2011; Wittlingerova et al., 2013; Rein et al., 2015; Cox, 2002; Landmeyer, 2001; Vroblesky, 2008; Schumacher et al., 2004; Yung et al., 2017; Algreen et al., 2015) applications. Phytoscreening continues to receive attention as a lower-cost, broad-scale screening tool for assessing the occurrence and distribution of VOCs in subsurface environments.

Phytoscreening can provide rapid, lower-cost sampling at high densities in comparison to standard groundwater- and soil-sampling methods. As such, it can be used in a number of ways. First, it can provide an initial screening of a newly identified site in support of an initial risk assessment. Second, to provide screening of poorly characterized regions of existing sites to delineate zones of potential undiscovered contamination. Third, to provide rapid analysis of potential changes in system conditions due to site perturbations, and support dynamic updating of the conceptual site model. Lastly, phytoscreening can be used as a screening method to evaluate potential for vapor intrusion and to complement long-term groundwater monitoring programs.

The majority of prior phytoscreening applications have employed the method as a tool to qualitatively determine the presence of contamination in the subsurface. For example, these applications typically have focused on identifying regions of greater and lesser groundwater or soil contamination based on the tree-tissue data. While such applications have been demonstrated to be useful, a primary question of interest is whether or not phytoscreening can be used more quantitatively, such as for example to estimate or predict groundwater concentrations. The use of phytoscreening in a quantitative mode requires the existence of robust correlations between tree-tissue and groundwater concentrations.

The existence of site-specific correlations would facilitate quantitative application of the method for that particular site. However, the development of such site-specific correlations is relatively costly and time-consuming. The existence of master, site-agnostic correlations would enable broader-scale application of phytoscreening for quantitative assessment without the requirement of conducting site-specific studies. The potential existence of site-specific correlations has been examined in a very small number of studies. Specifically, quantitative correlations have been reported between tree tissue and soil (Struckhoff et al., 2005; Gopalakrishnan et al., 2007; Yung et al., 2017) and groundwater (Struckhoff et al., 2005; Gopalakrishnan et al., 2007; Larsen et al., 2008; Wittlingerova et al., 2013) concentrations. However, the question of master correlations has yet to be addressed.

The uptake of constituents from soil and groundwater by vegetation is expected to be dependent in part upon physiological properties of the specific vegetation involved. Other factors, such as soil/subsurface properties, depth to groundwater, sampling season, and precipitation/evapotranspiration rates, are also anticipated to affect uptake, as noted in many of the studies cited above. The variation of these factors from site to site is anticipated to constrain the robustness of potential master correlations. A critical question is if a few select factors may be of such impact that their use as discriminants may support the development of useful master correlations.

The objective of this research is to examine potential correlations between contaminant concentrations measured for tree tissue and those for groundwater. Field data are compiled from several phytoscreening

studies that span a wide variety of site conditions and plant species, focusing on applications involving chlorinated volatile organic compounds. To the best of our knowledge, this represents the first quantitative meta-analysis of phytoscreening.

2. Materials and methods

The field sites are scattered throughout the United States and Western Europe, and encompass a wide variety of site properties and tree species. The selected constituents of interest are primarily TCE and PCE with one data set comprising 1,1-dichloroethene (DCE). Site locations, depth to ground water, and annual precipitation are reported in Table 1. For each site, data sets were used only for cases wherein there was reasonable and identifiable correspondence between tree and groundwater sampling locations. For some sites, this encompasses most or all of the reported data; for other sites, this resulted in use of only a fraction of the total tree-tissue data set reported.

The sampling and analysis methods were generally consistent among the studies. An increment borer was used with cores placed in a vial and immediately capped. The time used for extraction after collection varied from 24 to 48 h prior to analysis. Cores were heated from 90 to 100 °C for a period of 4–24 h to allow volatilization of the VOCs from the tissue into the headspace. An aliquot of headspace gas was extracted using a micro-liter gas-tight syringe followed by analysis using gas chromatography/mass spectrometry (GCMS).

The raw data reported for contaminant concentrations in tree tissue samples were reported in various units, and therefore conversions were made to produce one set of consistent, mass-based units. Tissue concentrations reported in units of parts per billion by volume of headspace gas were converted using the standard conversion factor (e.g., EPA On-line Tools for Site Assessment Calculation). The VOC concentration in the headspace gas was converted to total VOC in tissue ($\mu\text{g}/\text{kg}$) by assuming that the average core mass is approximately 2 g and that 18 mL of headspace gas is present in a 20-mL vial. As the samples were heated, it is assumed that all VOC initially associated with the tissue samples transfers into the gas phase.

The associated groundwater contaminant concentrations were obtained from analysis of samples collected from nearby monitoring wells. The distances between the locations of the trees and wells varied from ~1 to ~10 m, and in some cases greater. In a few cases, contaminant-concentration contour maps were used to supplement the reported groundwater data. These factors produce some uncertainty in the representativeness of the reported groundwater contaminant concentrations.

3. Results

3.1. Site specific correlations

As previously noted, specific correlations between tree tissue and groundwater VOC concentrations have been reported for a few studies. Larsen et al. (2008) reported a highly significant correlation ($r^2 = 0.98$) between tree-core and groundwater VOC concentrations for a site for which five tree species were sampled. Wittlingerova et al. (2013) reported significant correlations ($r^2 = 0.97$) for long-term average VOC concentrations in tree cores vs groundwater for a different part of the same site studied by Larsen et al. (2008). Gopalakrishnan et al. (2007) reported significant correlations for TCE/PCE in tree branch tissue and those in soil ($r^2 = 0.70$) and groundwater ($r^2 = 0.99$) for two tree species. Our analysis of data reported by Vroblesky et al. (2004) for a site in Texas showed a reasonable correlation for trees sampled in areas with shallow groundwater ($r^2 = 0.65$), in which five species were sampled.

These results indicate that significant site-specific correlations have been observed between tree-tissue concentrations and corresponding groundwater concentrations for some sites. These sites have several factors in common. All sites have relatively shallow groundwater, have climates classified as Group C, temperate/mesothermal according to the

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