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Phytoscreening as an efficient tool to delineate chlorinated solvent sources at a chlor-alkali facility

Loïc Yung [a], Jérôme Lagron [b], David Cazaux [b], Matt Limmer [c], Michel Chalot [a, d, *]

[a] Laboratoire Chrono-Environnement (UMR 6249), Université de Bourgogne Franche-Comté, Pôle Universitaire du Pays de Montbéliard, 4 place Tharradin, BP 71427, 25211 Montbéliard, France
[b] INOVYN France, 39500 Tavaux Cedex, France
[c] University of Delaware, Department of Plant & Soil Sciences, Newark, DE, USA
[d] Université de Lorraine, Faculté des Sciences et Technologies, BP 70239, 54506 Vandoeuvre-les-Nancy, France

HIGHLIGHTS

- CE contamination were delineated at a chlor-alkali facility using tree core data.
- 170 trees were sampled and analyzed for TCE and PCE content using SPME-GC-MS.
- *Populus*, *Quercus*, *Salix* and *Ulmus* species are efficient biomonitors.
- Our tree core dataset was well related to soil gas sampling results.

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ABSTRACT

Chlorinated ethenes (CE) are among the most common volatile organic compounds (VOC) that contaminate groundwater, currently representing a major source of pollution worldwide. Phytoscreening has been developed and employed through different applications at numerous sites, where it was generally useful for detection of subsurface chlorinated solvents. We aimed at delineating subsurface CE contamination at a chlor-alkali facility using tree core data that we compared with soil data. For this investigation a total of 170 trees from experimental zones was sampled and analyzed for perchloroethene (PCE) and trichloroethene (TCE) concentrations, measured by solid phase microextraction gas chromatography coupled to mass spectrometry. Within the panel of tree genera sampled, *Quercus* and *Ulmus* appeared to be efficient biomonitors of subjacent TCE and PCE contamination, in addition to the well known and widely used *Populus* and *Salix* genera. Among the 28 trees located above the dense non-aqueous phase liquid (DNAPL) phase zone, 19 tree cores contained detectable amounts of CE, with concentrations ranging from 3 to 3000 μg L^{-1}. Our tree core dataset was found to be well related to soil gas sampling results, although the tree coring data were more informative. Our data further emphasized the need for choosing the relevant tree species and sampling periods, as well as taking into consideration the nature of the soil and its heterogeneity. Overall, this low-invasive screening method appeared useful to delineate contaminants at a small-scale site impacted by multiple sources of chlorinated solvents.

1. Introduction

Chlorinated ethenes (CE) are hazardous volatile organic compounds (VOC) that contaminate groundwater, currently representing a major source of pollution worldwide (Kueper et al., 2014). Perchloroethene (PCE) and trichloroethene (TCE) are among the most common chlorinated solvents released by production facilities (McGuire et al., 2004). They tend to accumulate at the bottom of aquifers as dense non-aqueous phase liquids (DNAPLs) that serve as reservoirs for long-term solubilization. Indeed, when present in the subsurface, they persist for decades and act as long-term sources of contamination (Johnson and Pankow, 1992). Moreover, chlorinated solvents have the potential to migrate in groundwater and be transported through soil gas (Côme et al., 2008). Additionally, when chlorinated solvents reach the clay confining layers, they

* Corresponding author. Laboratoire Chrono-Environnement (UMR 6249), Université de Bourgogne Franche-Comté, Pôle Universitaire du Pays de Montbéliard, 4 place Tharradin, BP 71427, 25211 Montbéliard, France.
E-mail address: michel.chalot@univ-fcomte.fr (M. Chalot).

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may diffuse into the clay, inducing some heterogeneity in the subsurface contamination (Stroo and Ward, 2010). Because of their complex dispersal, chlorinated solvent contamination is usually particularly heterogeneous, hampering any site remediation effort, as they are difficult to treat and detect.

Site characterization is often time consuming and a financial burden for the site owners, which has raised demand for rapid and inexpensive (pre)screening methods. For this purpose, screening methods based on the potential of the tree to take up compounds through their roots (Vroblesky et al., 1999) or leaves (Odabasi et al., 2015) and to incorporate them into their tissues have emerged. Phytoscreening has been employed and developed through different applications at numerous sites, where it was generally useful for detection of subsurface chlorinated solvents (Rein et al., 2015; Algreen et al., 2015a; Limmer et al., 2013, 2011; Larsen et al., 2008; Sorek et al., 2008; Vroblesky et al., 2004). However, CE concentrations in wood are often site-specific, due to local pedological, groundwater table height and climatic conditions, which is widely accepted by specialists (Algreen, 2015; Limmer et al., 2013; Wittlingerova et al., 2013; Holm and Rotard, 2011).

In order to validate the phytoscreening method, tree core data have been usually compared with groundwater data, resulting, in most cases, in the lack of a straightforward correlation between the two types of dataset (Algreen et al., 2015b; Wahyudi et al., 2012; Limmer et al., 2011; Sorek et al., 2008). This is easily understandable as there may be no direct physical contact between root systems and groundwater. Indeed, release of chlorinated solvents from groundwater and their accumulation and migration in soil is a highly complex process. The semi-quantitative character of phytoscreening is mainly due to factors influencing the behavior of chlorinated solvents in soil, which may limit the application and dissemination of the method. However, recent investigations have tried to establish correlations between CE in soil and CE in tree core, which appeared more relevant (Rein et al., 2015; Algreen et al., 2015b; Gopalakrishnan et al., 2007). More specifically, studies at the Riverfront Superfund Site (New Haven, MO) showed a clear soil-tree core relationship, stronger than that of groundwater PCE to tree core concentrations at the same site. This direct relationship was hypothesized to be caused by diffusion between tree roots and the soil vapor phase in the subsurface (Struckhoff et al., 2005).

Within the research and development project SILPHES (French acronym for Innovative Solutions to Fight Halogenated Compounds in Groundwater), we aimed at delineating subsurface CE contamination at a chlor-alkali facility using phytoscreening. We investigated a total of 170 trees that was sampled and analyzed by solid phase microextraction gas chromatography coupled to mass spectrometry for PCE and TCE concentrations, which are among the most common chlorinated solvents released by chlor-alkali production facilities. Our tree core data were compared with soil data to ascertain correlations between the two datasets, while taking into account variation in biological and pedogeological parameters.

2. Material and methods

2.1. Description of the chlor-alkali facility

The chlor-alkali facility owned by the chemical company INOVYN is located in Tavaux (France) and was first established in 1930. Industrial activities based on the exploitation and processing of salt were developed by a specialization in the manufacture of chlorinated solvents and plastics. On the site, there is a 5–8 m thick confined aquifer made of sands and gravels (hydraulic conductivity ranging from 10^{-3} to 10^{-5} m s^{-1}) recharged by precipitation. It is overlained by a four-meter thick confining clayey and silty alluvial deposit. The lower aquiclude, located at 10–12 m depth below the surface, is a low permeable clay deposit with a hydraulic conductivity less than 10^{-9} m s^{-1}.

At this facility, a leakage from a former landfill was discovered in early 1980s, which resulted in a massive spill of dense non aqueous phase liquids (DNAPLs), located 10 m below the ground surface. The whole area impacted by the DNAPL was investigated using small diameter direct-push core sampling (Geoprobe®) and geophysical methods (self-potential method, high resolution resistivity panels). The investigations revealed an accumulation of pure phase of chlorinated compounds such as hexachlorobutadiene, hexachloroethane and perchloroethylene (PCE) on the top of the aquiclude (Maire et al., 2015) (Supplementary Fig. S1, pink line). From the pure phase, a dissolved plume migrates horizontally and verticaly to the aquifer and consequently to the soil gases of the upper confining layers and topsoil, affecting an area of 30 km^2 downstream. A number of monitoring wells have been set up on the facility. Pumping wells (PW) were installed to contain the source zone, inducing a cone of depression around pumping wells, which lowered the water table from about 2 m below ground surface to 6 m below ground surface. The site map, showing the groundwater flow direction, 10 monitoring wells (MW), and 5 pumping wells (including the PW67 used later) at the facility is presented in Supplementary Fig. S1. Concentrations of total CE at PW68, PW67, MW181 and MW115, near the DNAPLs, were between 3 and 10 mg L^{-1}, whereas most of the surrounding wells did not exceed 100 μg L^{-1}.

The experimental site of around 60 ha contained i) the source area where DNAPL is present, referred to as the DNAPL phase zone, ii) the zone adjacent to the DNAPL phase zone, referred to as the DNAPL adjacent zone, iii) a woody area located downstream from the DNAPL phase zone described above (Supplementary Fig. S1) (referred to as the PW67 zone because of the presence of the pumping well #67). This PW67 zone received contaminants from two potential sources, the DNAPL phase zone and the settling basin, which contained the storage unit of DNAPLs considered to be the original source of contamination. These areas have been naturally colonized by a number of tree genera as described in the next section.

2.2. Soil core, soil gas and tree core sampling

We used semi-quantitative methods for measuring CE in tree and soil cores, as well as in soil gas, as detailed below. For this investigation a total of 170 trees from the PW67 zone, the DNAPL phase zone and the DNAPL adjacent zone was sampled from July 2015 to November 2015 and mapped (Supplementary Table S1). A total of 85 trees that had naturally colonized the PW67 zone of about 2 ha (Supplementary Fig. S1) was sampled in July 2015 and in October 2015. They belong to the tree genera *Betula* (BET), *Carpinus* (CAR), *Fraxinus* (FRA), *Populus* (POP), *Prunus* (PRU), *Quercus* (QRO), *Robinia* (ROB), *Salix* (SAL), *Ulmus* (ULM), *Tilia* (TIL) and *Sorbus* (SOR). Trees present in the DNAPL phase and the DNAPL adjacent zones mostly belong to the *Salicaceous* family. Among them, 83 *Populus* sp. and 2 *Salix* sp. were sampled in November 2015. Tree core sampling protocol was standardized considering recommendations detailed in different methodological guides (Chalot and Balouet, 2015; Holm et al., 2011; Vroblesky, 2008). Briefly, tree cores from healthy and mature trees were collected from July to November 2015 at 1 m above ground surface using a 5 mm diameter increment hammer (Haglof, Sweden), which allowed for collecting tree cores at approximately 2 cm deep. The bark of each core sample was removed to avoid atmospheric influence followed by quick transfer of the remaining wood sample into 20 mL analytical vials and analyzed within the next 48 h. For each tree, a composite sample was made of 3 cores taken within an area of <25 cm^2 to