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# Phytovolatilization of Organic Contaminants

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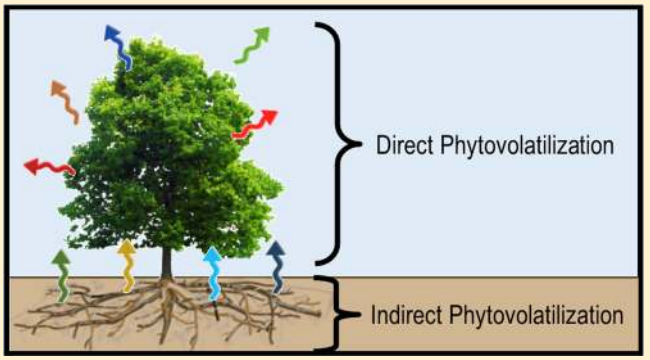
**ABSTRACT:** Plants can interact with a variety of organic compounds, and thereby affect the fate and transport of many environmental contaminants. Volatile organic compounds may be volatilized from stems or leaves (direct phytovolatilization) or from soil due to plant root activities (indirect phytovolatilization). Fluxes of contaminants volatilizing from plants are important across scales ranging from local contaminant spills to global fluxes of methane emanating from ecosystems biochemically reducing organic carbon. In this article past studies are reviewed to clearly differentiate between direct- and indirect-phytovolatilization and we discuss the plant physiology driving phytovolatilization in different ecosystems. Current measurement techniques are also described, including common difficulties in experimental design. We also discuss reports of phytovolatilization in the literature, finding that compounds with low octanol-air partitioning coefficients are more likely to be phytovolatilized (log $K_{OA}$ < 5). Reports of direct phytovolatilization at field sites compare favorably to model predictions. Finally, future research needs are presented that could better quantify phytovolatilization fluxes at field scale.




## INTRODUCTION

Plants interact with the surrounding soil, water, and air, extracting and releasing chemicals throughout their life cycle. Plant systems of membranes and vascular transport evolved to manage water and nutrient uptake and transport, but also allow many unintended compounds to traverse through the plant. The ability of some xenobiotics to enter plant tissues may present a risk to consumers of plants, but also has been used to human advantage for some time in the form of pesticides and herbicides to improve crop yields. The fate of these compounds in plants has been an area of interest for decades and was an early area of interest for studying plant uptake and translocation of xenobiotics. More recently, plants have been used as a sustainable remedial strategy for contaminated soil and groundwater (i.e., phytoremediation), the study of which has furthered our knowledge of plant-contaminant interactions. Perhaps of most interest currently are food crop interactions with emerging contaminants, which represent an unintentional form of phytoremediation, potentially providing an exposure pathway when edible plants interact with contaminated groundwater, soil, or irrigation water.

Once inside a plant, contaminants may be subject to (phyto)degradation, (phyto)excretion or (phyto)volatilization. Contaminants not removed will increase in concentration, possibly leading to toxicity, unless growth dilution is sufficiently fast to control contaminant concentrations. Degradation (or metabolism) includes transformation, compartmentalization and/or sequestration of the contaminant.[1,2] Excretion has been less studied, but may be an important loss mechanism in some plants for hydrophilic and ionized species, where these compounds can be excreted from the leaf through aqueous pores.[3] Volatilization is the partitioning of the contaminant into the air spaces within a plant and subsequent diffusion into the ambient air, under the assumption that ambient air is less contaminated. For volatile and semi volatile organic compounds (VOCs), volatilization from the plant, or phytovolatilization, can represent a major loss mechanism. Phytovolatilization is often considered beneficial, as phytovolatilization of the contaminant generally results in substantial dilution and photochemical decay in the atmosphere. Conversely, phytovolatilization may be viewed as a risk in urban areas, where exposure potential exists and air quality is degraded, such as nonattainment areas, although minimal evidence related to this concern is present in current literature.

Phytovolatilization has been widely observed for a number of contaminants, both inorganic and organic. Volatile forms of several inorganic compounds can be volatilized from plants, including Se,[4] As,[5−7] and Hg.[8] Additionally, phytovolatilization of tritiated water has been reported,[9−11] although this is more properly described simply as transpiration and will not be

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further discussed here. Instead, this review focuses on phytovolatilization of organic compounds and presents existing and developing measurement methods, laboratory and field reports, and modeling approaches. The review also presents the physicochemical domain where organic compound phytovolatilization has been observed and provides topics where additional research is required to advance current knowledge.

## PHYTOVOLATILIZATION PROCESSES

Prior to discussing measurements and reports of phytovolatilization, the terminology must be clarified. Phytovolatilization can exist in two different forms: direct and indirect phytovolatilization (Figure 1). Direct phytovolatilization is the more intuitive and better-studied form, resulting from plant uptake and translocation of contaminants, eventually leading to volatilization of the compound from the stem/trunk and leaves. Historically, this process is simply called "phytovolatilization" or the contaminant is said to be "transpired", as this pathway resembles the transpiration vascular pathway of water. However, the direct phytovolatilization pathway often differs from transpiration, as many compounds that are phytovolatilized are moderately hydrophobic, able to diffuse across hydrophobic barriers such as cutin in the epidermis or suberin in woody dermal tissues. Direct phytovolatilization requires the plant to uptake, translocate and volatilize the compound, so volatilization of compounds produced or transformed by the plant are not considered to be directly phytovolatilized. Compounds not considered to be directly phytovolatilized include the vast quantity and diversity of VOCs produced and emitted by plants[12,13] and transformation products, such as phytotransformation of selenite to the more volatile dimethyl selenide.[4]

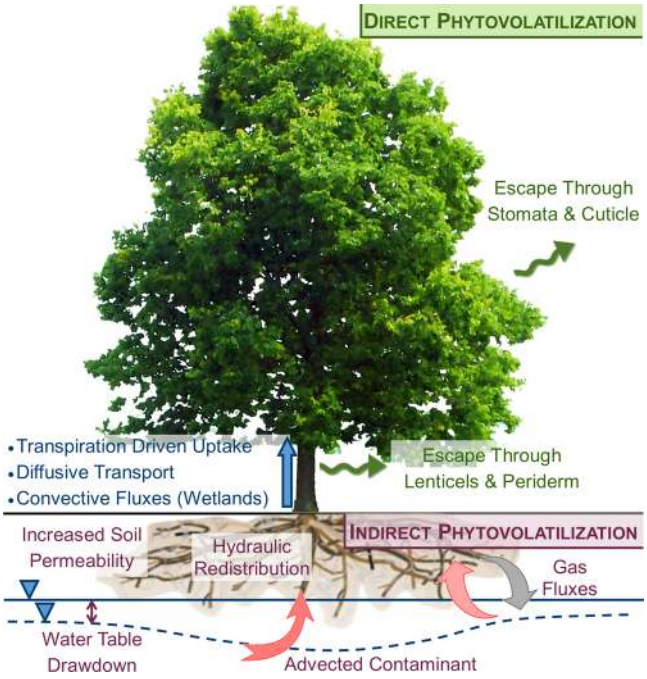


**Figure 1.** Direct and indirect phytovolatilization processes.

Indirect phytovolatilization is the increase in volatile contaminant flux from the subsurface resulting from plant root activities. Plants move vast quantities of water (globally ~62 000 $km^3/yr$)[14] and concurrently explore large volumes of soil. These processes cause profound changes in subsurface chemical fate and transport. The activities of plant roots can increase the flux of volatile contaminants from the subsurface through the following mechanisms:

- Lowering the water table
- Advection with gas fluxes caused by diel water table fluctuations
- Increased soil permeability
- Chemical transport via hydraulic redistribution
- Advection with water toward the surface
- Interception of rainfall that would otherwise infiltrate to dilute and advect VOCs away from surface

Perhaps the most well studied of the above mechanisms is plant removal of subsurface water and subsequent lowering of the water table, thereby increasing the thickness of the vadose zone over weekly/monthly time scales. Volatile contaminants diffuse through air more quickly than through water, so volatile contaminant fluxes may increase due to plant removal of water, particularly if the source area becomes exposed to the vadose zone. Alternatively, the source may be located deeper in the saturated zone, where diffusion to the capillary fringe often limits mass transfer. Lowering the water table reduces the thickness of the saturated zone, reducing distances for diffusion and increasing flux. In a similar phenomenon, the diel fluctuations in plant removal of water also result in diel fluctuations in groundwater elevation, particularly in fine-grained soils.[15,16] These fluctuations can increase vapor fluxes to the subsurface, which has been demonstrated for influx of oxygen and increased rhizodegradation,[17,18] and may also increase efflux of volatile contaminants from the vadose zone by advection.

Contaminant transport in the subsurface can be affected by root activities as they modify soil texture at macro and micro scales during growth and senescence. Root turnover can lead to the creation of low-tortuosity pathways that enhance contaminant volatilization. Meanwhile, living roots can redistribute water throughout the subsurface as water uptake and translocation occurs passively in roots, resulting in the phenomenon of hydraulic redistribution (also called hydraulic lift). Hydraulic redistribution (HR) allows water to move from saturated areas of the subsurface to drier areas via root conduits during periods of limited transpiration.[19,20] Whether this phenomenon also results in the subsurface redistribution of contaminants remains unknown; however, the dissolved constituents likely follow the carrier solvent in many cases. Moving volatile contaminants closer to the surface via HR would increase volatilization rates, provided the vertical fluxes via HR exceed those of diffusion through the soil. Most organic contaminants cross the root membrane passively and have transpiration stream concentration factors (TSCFs) (i.e., the ratio of the chemical concentration in the transpiration stream to the chemical concentration in the porewater or hydroponic solution) less than one,[21−23] indicating HR of contaminants is possible, but also demonstrating that water is moved more efficiently than the contaminant. Finally, phytoremediation systems intercept large amounts of rainfall, which would otherwise enter the vadose zone, absorbing and advecting VOCs downward.[24,25] The reduced infiltration water also decreases soil moisture content, resulting in greater effective diffusion coefficients in the vadose zone.[24−26]


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## TRANSPORT OF GASES IN PLANTS

Plants have evolved to manage transfer of a variety of necessary gases, including carbon dioxide, water vapor, oxygen, ethylene, and some signaling molecules. Upon entering the plant,[21,22,27] VOCs are similarly transported throughout the plant via processes dependent on plant physiology and contaminant properties (Figure 1). For many plants and VOCs, advection with the transpiration stream carries the contaminant to aboveground tissues.[28,29] In these systems, direct phytovolatilization fluxes are correlated to transpiration rate, resulting in periods of low direct phytovolatilization during nighttime and dormancy.

Transport to aboveground plant tissues can also occur by diffusion, as VOCs diffuse through water and air spaces in plant stems and trunks. Diffusion dominates VOC transport in some plant-contaminant combinations such as highly volatile species in wetland plants.[30] Many plants living in water-logged conditions develop aerenchyma tissue in roots and stems to aid oxygen transport to subsurface tissues.[31] The aerenchyma tissue arises from the death of cortex parenchyma cells, leaving behind low tortuosity, air-filled channels from roots to shoots. Additionally, some wetland plants also exhibit internal convective gas flows resulting from pressurization (>50 Pa) of subsurface tissues.[32−35] These convective flows are thought to be driven by differences in humidity between the humid plant interior and the relatively dry atmosphere. With flows exceeding 1 mL/min during these convective events, advective flux of VOCs in these plants may significantly contribute to direct phytovolatilization flux.

In herbaceous plants, during transport of VOCs to aboveground tissues these compounds can escape from primary tissues such as stems and leaves. The plant epidermis is covered by a cuticle, which consists of hydrophobic waxes and cutin to limit water loss. The cuticle is occasionally interrupted by stomata, which open and close to regulate gas exchange. Thus, transport of VOCs through the epidermis occurs through two parallel pathways: diffusion through open stomata and diffusion across the cuticle. Permeability of the cuticle is enhanced for molecules that strongly partition into the cuticle and have small molar volumes.[36,37] Permeability of the cuticle is also strongly plant and temperature dependent,[36,37] and various regression models have been developed to predict permeability of plant cuticles.[37−39]

In woody species, direct phytovolatilization from tree trunks and branches involves the diffusion of VOCs through secondary xylem, secondary phloem and periderm, eventually reaching the atmosphere where activity of the VOC is assumed lower than in the tree. The outermost layer of the periderm, the phellem, consists of dead cells filled with suberin and waxes to regulate water loss from the trunk. However, the phellem must allow some exchange of gases to support the respiration of living cells in the trunk. To allow gas exchange, the phellem is interrupted by lenticels, which are more permeable to oxygen and water vapor than the surrounding tissue,[40] although the permeance of lenticels to $H_2O$ and $O_2$ has been measured at ∼1 order of magnitude lower than stomata.[40] Interestingly, lenticels appear to open and close seasonally, reducing the trunk's permeability during the winter.[41] A study with evergreen species found no seasonal change in lenticel morphology, while deciduous species exhibited seasonal changes in lenticel morphology.[42] Further complicating gas transport in trees, some trees growing in waterlogged conditions develop aerenchymatous phellem (secondary aerenchyma) to aid in oxygen transport to the roots.[43−45] The prevalence of aerenchymatous phellem and its effect on VOC transport in wood remains uncertain; however, increasing the transport of $O_2$ will certainly increase transport of other volatile molecules. Plants growing in flooded conditions can also develop hypertrophied lenticels,[46] which are enlarged lenticels that form on flooded roots up to immediately above the water table. These inflated lenticels aid in gas exchange and desiccate after flooding ceases. Collectively, the transport of VOCs in wood is not well quantified due to uncertainty in the phellem physiology. In studies involving $CO_2$, the phellem's resistance to diffusion, and therefore the flux, is variable, even for clones.[47,48]

## MEASURING PHYTOVOLATILIZATION

Direct phytovolatilization has been measured both in laboratory and field studies. In laboratory studies, plants are often dosed with contaminants, generally radiolabeled, in soil mesocosms or grown hydroponically. After a prescribed amount of time, plant parts are typically analyzed to perform a mass balance on the contaminant. The amount phytovolatilized may be directly measured by analysis of air passed through a sorbent trap in a closed system (preferable) or calculated from the amount of contaminant mass that remains unaccounted for in an open system. Note that the latter may be an overestimate due to incorporation of other loss mechanisms, such as phytodegradation. Additionally, if contaminant mass is captured on a sorbent trap, the phytovolatilization rate can be compared to elapsed time or to transpiration rate.

At field sites, measurement of direct phytovolatilization from entire trees and other large plants is technically challenging and costly, so typically only individual leaves[49] or, more commonly, branches are assessed. The leaves/branches are usually enclosed in a plastic bag, such as polyethylene,[50] Tedlar[51] or Teflon-lined plastic,[52] or in a sealed solid plastic[53] or glass chamber.[54] The enclosure must not be permeable to the analyte of interest. To reduce humidity and to prevent the enclosed tissue from overheating, clean air is generally passed through the bag or chamber. The exiting gas is passed through a sorbent tube to capture the volatile analytes. Alternatively, a static system can be used that employs a cold trap or condenser to reduce humidity and can be sampled using a Summa canister.[51] To measure the flux of VOCs emanating from tree trunks, a flux chamber is often used.[55,56] These chambers are sealed to the tree trunk and operate similarly to the bags that capture VOCs from leaves and branches. Clean air is passed into the chamber and contaminants are captured from the exit stream via a sorbent tube. An alternative technology for monitoring direct phytovolatilization is open path Fourier transform infrared spectroscopy (op-FTIR), a method that can detect VOCs in the air adjacent to the tree canopy. While FTIR has been attempted to monitor TCE volatilizing from a phytoremediation plot, the method was not sensitive enough to detect any TCE phytovolatilizing,[49] although the method has been successfully used in laboratory experiments.[57]

Phytovolatilization experiments with organic contaminants are not trivial to perform due to the volatility of the analytes of interest. Numerous problems with experimental setups have been encountered and discussed in the literature, both in laboratory and field setups.[58,59] See refs 35 and 60 for a discussion of challenges in monitoring biogenic VOC phytovolatilization. Perhaps most problematic is the need to seal the plant in a chamber while ensuring the plant undergoes


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natural photosynthesis and respiration. Artificial and natural light will heat the enclosed space while transpired water vapor will increase the humidity surrounding the leaves. The former can damage the leaf tissues while the latter can slow transpiration. To offset these effects, clean air is usually passed through the chamber at high flow rates to ensure humidity and temperature remain at acceptable levels. All the gas exiting the chamber must pass through a sorbent to collect volatile compounds. The sorbent must have high affinity for the targeted VOCs and low affinity for water. For many VOCs, Tenax meets these requirements. If VOCs are allowed to accumulate to high concentrations in the chamber, the concentration gradient across the plant boundary will lessen, likely resulting in lower diffusive fluxes and an underestimation of phytovolatilization. Additional difficulties often arise in sealing the experimental setup to prevent unmonitored release of VOCs. A particularly difficult region to seal is around the plant tissue. Stems are often sealed using closed cell foam, acrylic caulk, or paraffin wax. In laboratory experiments, the tightness of system should be checked using wooden dowel rod or dead stem controls. However, a well-sealed experimental setup can also limit supply of necessary gases, such as oxygen to the roots, which may result in stress and increased root permeability. Care should be taken in plant selection, particularly when small tissue volumes are sampled. Stress or damage can cause stomatal closure and potentially affect both evapotranspiration and volatilization rates. Additionally, the dermal tissue of first-year wood (whips or branches) will not have the secondary dermal features present in older wood. Extrapolation of phytovolatilization rates from young woody plants to older woody plants is not recommended.

Regardless of the system chosen, a suitable experimental setup must control temperature, relative humidity, and VOC concentrations inside the chamber, ensuring these values remain near ambient. If these values are not well controlled, substantial measurement error is likely. The specific flows of gases and other system parameters will depend on the plant, contaminant, and experimental system under study, so caution must be exercised when adapting systems from literature.

## REPORTS OF PHYTOVOLATILIZATION

**Laboratory Experiments.** Research regarding direct phytovolatilization has largely focused on the common groundwater contaminants, trichloroethylene (TCE) and tetrachloroethylene (PCE), using traditional phytoremediation plants such as willow (*Salix* sp.) and hybrid poplar (*Populus* sp. × *P.* sp.). These volatile contaminants are frequently reported to undergo phytovolatilization, although the degree of phytovolatilization varies substantially. In a closed system with hybrid poplars, Gordon et al.[61] detected $^{14}$C-TCE in the transpired gases after 7 days of exposure. The fraction of transpired TCE to the TCE taken up by the plant was 70−90%. However, when a controlled field study was conducted, a minimal amount of TCE was phytovolatilized, as much of the TCE was dechlorinated in the subsurface. In another closed system experiment with poplar and willow cuttings dosed with $^{14}$C-PCE or $^{14}$C-TCE, 75% of the contaminant mass taken up by the plant was phytovolatilized (range: 27−96%, $n$ = 6), although experimental details are scarce.[62] In flow-through reactors designed to provide a constant supply of contaminants, nutrients and oxygen, <0.1% of the TCE dosed to hybrid poplars was recovered in foliar traps, even under oxygen limited conditions and higher concentrations of TCE (67 mg/L).[58] However, of the limited TCE mass taken up by the plants, 58% was phytovolatilized (range: 11−96%, $n$ = 6).

Other plants have been examined for their ability to directly phytovolatilize chlorinated solvents. In an experiment with TCE and 1,1,1-trichloroethane (TCA), Narayanan et al.[57] measured uptake and phytovolatilization by alfalfa (*Medicago sativa*) in soil mesocosms. Similar and notable fractions of TCE and TCA were volatilized, although it is unclear from the experiment setup whether the volatilized VOCs resulted from direct phytovolatilization, indirect phytovolatilization or volatilization from the soil. In mesocosm experiments with baldcypress (*Taxodium distichum*) planted in a gravel/sand substrate, Nietch et al.[28] observed fluctuations in TCE fluxes. TCE removal was correlated to transpiration on both seasonal and daily scales, with TCE fluxes from the reactor ∼4× greater during summer as compared to winter, suggesting TCE advected with the transpiration stream.

In addition to chlorinated solvents, several studies have investigated plant uptake and subsequent volatilization of methyl *tert*-butyl ether (MTBE). Hydroponic hybrid poplars dosed with $^{14}$C-MTBE for 10 days were able to directly phytovolatilize 17% of the total MTBE. This amount of phytovolatilization represents 96% of the total MTBE translocated by the trees.[63] In another experiment with poplar cuttings, 54% of the total MTBE had phytovolatilized after 7 days of exposure.[64] Concentrations of MTBE in the shoots were below the detection limit, indicating a majority of translocated MTBE was transpired. When MTBE was dosed to weeping willows (*Salix babylonica*) in sealed reactors, 94% of the total MTBE mass was phytovolatilized after 120 h.[65] Of the MTBE mass taken up by the plants, 99% was transpired. In one of the few experiments to measure phytovolatilization solely from stems, the mass of TCE and MTBE captured by diffusion traps was proportional to dosing concentration and duration of exposure.[29,66]

Phytovolatilization of other VOCs has been explored to a lesser degree. In an experiment with alfalfa, most of the applied benzene volatilized directly from the sandy soil, preventing estimates of direct phytovolatilization.[67] A hydroponic study with eight different plants showed 10−40% of the applied $^{14}$C-nitrobenzene phytovolatilized over 3 days, although this was not directly measured, while only 5−25% was recovered in plants.[68] In a mass balance study using poplars and 11 different contaminants, the fraction of the contaminant phytovolatilized was correlated to the contaminant's vapor pressure.[69] In an experiment with *Phragmites australis*, the plants were able to phytovolatilize 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, and γ-hexachlorocyclohexane. The amount of contaminant phytovolatilized was correlated to the contaminant's vapor pressure.[70]

**Synthesis of Laboratory Experimental Data.** From the reported measurements of direct phytovolatilization in laboratory studies (see previous section), the fraction of contaminant phytovolatilized was compared against a variety of physicochemical predictors. Direct phytovolatilization was described as a ratio between contaminant mass phytovolatilized and total contaminant mass translocated.

$$\%\text{directly phytovolatilized} = \frac{\text{mass phytovolatilized}}{\text{mass phytovolatilized} + \text{mass in above ground tissues}}$$

The percent of a contaminant directly phytovolatilized is likely a function of plant species and the amount of water



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transpired, but many of the reports described here are similarly short exposures (1−2 weeks) using poplar cuttings. As previously suggested, the percent directly phytovolatilized was a function of VOC vapor pressure, but was also correlated with log $K_{OW}$. A more appealing descriptor is octanol-air partitioning, which incorporates volatility and hydrophobicity. The data in Figure 2 suggest that a log octanol-air partitioning

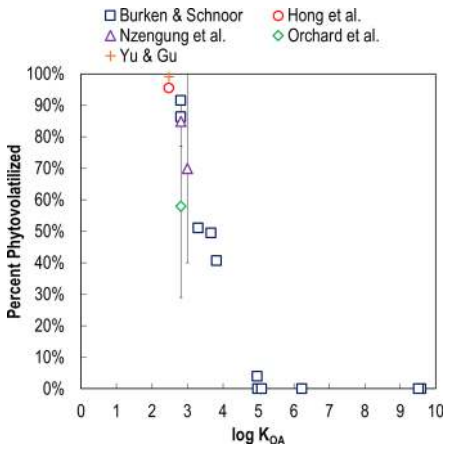


**Figure 2.** Direct phytovolatilization reports from laboratory experiments show a low octanol-air ($K_{OA}$) partitioning coefficient favors phytovolatilization. Error bars represent the standard deviation when available. Log $K_{OA}$ calculated from log $K_{OW}$ values[112,122] and Henry's constant.[112] Figure references: Burken and Schnoor (1,2,4-trichlorobenzene, aniline, atrazine, benzene, ethylbenzene, *m*-xylene, nitrobenzene, pentachlorophenol, phenol, TCE, and toluene),[69] Hong et al. (MTBE),[63] Nzengung et al. (PCE and TCE),[62] Orchard et al. (TCE),[58] Yu and Gu (MTBE).[65]

coefficient (log $K_{OA}$) of less than five is needed for substantial phytovolatilization. Higher values of log $K_{OA}$ favor partitioning of the molecule into the hydrophobic plant tissues over the air, minimizing the likelihood of phytovolatilization. However, uncertainty estimates are missing from many of the data, thus a log $K_{OA}$ greater than five may not preclude phytovolatilization. Additionally, substantial uncertainty exists within and across studies, likely resulting from the difficulty in measuring contaminant fluxes from and concentrations in plants. Furthermore, sufficient experimental details are missing from many studies to ensure the accuracy of the reported values (see section "Measuring Phytovolatilization").

**Field Sites: Phytoremediation Plots.** Measurements of direct phytovolatilization at field sites are less frequent, but provide valuable insight into the magnitude of phytovolatilization fluxes occurring under realistic conditions. While Hirsh et al.[51] found limited direct phytovolatilization from hybrid poplars growing above groundwater contaminated with TCE and 1,1,2,2-tetrachloroethane, many others have measured fluxes of chlorinated solvents emanating from phytoremediation plots. Several authors report fluxes of common contaminants including PCE, TCE, MTBE, and carbon tetrachloride (CT) from leaves, trunks and occasionally soil at phytoremediation sites (Table 1). In addition to these reports, Doucette et al.[54] measured phytovolatilization of TCE from poplar, Russian olive (*Elaeagnaceae angustifolia*) and willow trees. At the site, trees growing near a contaminated seep emitted 1.1 ± 0.97 mg TCE per liter of transpired water, while trees at another location onsite emitted 0.2 ± 0.15 mg TCE per liter of transpired water (mean ± standard deviation,

**Table 1. Fluxes of VOCs from Phytoremediation Field Sites**[a]

| tree | contaminant | media | flux (μmol/m²/d)[b] | reference |
|---|---|---|---|---|
| eucalpytus | TCE | leaves | 0.97 (0.45) | Doucette. et al.[56] |
| eucalpytus | TCE | trunk | 0.06 (0.03) | |
| eucalpytus | TCE | soil | 1.37 (1.00) | |
| poplar | TCE | leaves | 0.13 (0.07) | |
| poplar | TCE | trunk | 0.04 (0.02) | |
| poplar | TCE | soil | 0.1 (0.05) | |
| poplar | CT | trunks | 332 (155)[b] | Wang et al.[55] |
| poplar | PCE | leaves | 0.04 (0.02)[c] | James et al.[113] |
| poplar | PCE | trunk | 1.08 (0.24)[c] | |
| poplar | PCE | soil | 0.29 (0.16)[c] | |
| poplar | TCE | leaves | 0.09 (0.03)[c] | |
| poplar | TCE | trunk | 2.88 (0.48)[c] | |
| poplar | TCE | soil | 9.6 (3.12)[c] | |
| poplar | TCE | leaves | 12 | Newman et al.[49] |
| pine | MTBE | leaves | 2.2 (1.8)[d] | Arnold et al.[53] |
| pine | MTBE | leaves | 23.7 (17.3)[d] | |
| pine | MTBE | leaves | 178 (123)[d] | |
| pine | MTBE | leaves | 18.8 (13.6)[d] | |
| pine | MTBE | leaves | 12.5 (8.49)[d] | |
| poplar | naphthalene | soil | 2.8 (summer) | Marr et al.[72] |
| poplar | naphthalene | soil | 0.56 (winter) | |

[a]See Table 2 and the associated references for additional experimental details. [b]Value in parentheses is the standard deviation. [c]Value in parentheses is the standard error. [d]Value in parentheses is the 95% confidence interval.

$n$ = 3). Reports of other contaminants directly phytovolatilizing from phytoremediation sites are lacking, although indirect evidence of phytovolatilization exists in some cases. For example, 1,4-dioxane was applied to a phytoremediation test plot, but only 18% could be recovered compared to 86% recovery of a bromide tracer.[71] The loss of 1,4-dioxane was attributed to phytovolatilization, although no direct evidence was provided. Note that direct phytovolatilization rates are not directly comparable, as many factors affect the rate of phytovolatilization. These factors are addressed through a modeling approach described in the "Modelling Phytovolatilization" section.

Studies focusing on indirect phytovolatilization are less frequent. At a hybrid poplar phytoremediation site, Marr et al.[72] measured seasonal variations in naphthalene volatilization fluxes from the soil. Fluxes were highest in the late summer and fall, and the fluxes appeared correlated with some meteorological processes, such as changes in atmospheric pressure. The large fluxes in the summer were attributed to the lowering of the water table due to tree transpiration, resulting in a thinner saturated zone. At this site, a source area was located 2.4−3.7 m below ground surface, so reducing the saturated zone thickness substantially decreased the distance over which naphthalene diffused to the vadose zone, thereby increasing flux. Laboratory column studies and a 2-compartment model supported the field flux measurements.[73] At two phytoremediation sites, Doucette et al.[56] measured TCE soil flux from both inside and outside of phytoremediation plots. At one site, significant indirect phytovolatilization was observed,


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with TCE fluxes of 126 ± 92 g/yr inside the phytoremediation plot and 4.6 ± 3.4 g/yr outside the phytoremediation plot. At a second site, TCE volatilization from the soil within the phytoremediation plot (0.7 ± 0.5 g/yr) was lower than outside the phytoremediation plot (1.1 ± 0.8 g/yr). The variability in these initial studies indicate that additional studies are needed to understand the variables that drive indirect phytovolatilization.

**Wetlands.** Phytovolatilization is of interest not only in soil and groundwater phytoremediation systems, but also in natural and constructed treatment wetlands, which can be used to treat industrial waste or groundwater that contains VOCs. Direct and indirect phytovolatilization from constructed wetlands differs from that of phytoremediation systems in two important features. First, direct phytovolatilization is likely to occur at greater rates due to adaptations of wetland plants. Many of these plants develop specialized tissues to encourage oxygen transport to tissues growing in waterlogged conditions (see Transport of Gases in Plants section). Second, indirect phytovolatilization fluxes can differ because of differences in the volatilization pathway. The volatilization pathway depends on wetland construction, primarily whether the wetland is surface- or subsurface-flow, with surface-flow wetlands thought to result in higher VOC fluxes as the contaminants have direct access to the atmosphere.[74]

In a field experiment with subsurface-flow wetlands constructed of a planted gravel filter or a planted root mat, Seeger et al.[75] attempted to separate direct and indirect phytovolatilization for both benzene and MTBE, but only measured total phytovolatilization. No volatilization was observed in an unplanted gravel filter wetland, so indirect phytovolatilization was neglected in the planted analogs. Given this assumption, direct phytovolatilization of benzene and MTBE during the summer was 2.3 ± 0.3% and 3.5 ± 0.6%, respectively. In the winter, this value dropped to 0.1% and 0.2% for benzene and MTBE, respectively. After assuming the rates of direct phytovolatilization in the planted gravel filter and the planted root mat were equal, indirect phytovolatilization was calculated for the plant root mat constructed wetland. Indirect phytovolatilization in the summer for benzene and MTBE were 0.9 ± 0.3% and 20.3 ± 2.9%, respectively. While the data require some assumptions, they demonstrate the importance of seasonality and wetland construction on phytovolatilization, implying transport of these contaminants is dominated by advection with the transpiration stream. When considering all removal mechanisms, these data indicate total phytovolatilization is responsible for ∼3% of benzene removal and 43% of MTBE removal. In subsurface flow constructed wetlands, Chen et al.[76] found >90% removal of chloroform, although only ∼1.5% of the removal resulted from phytovolatilization. The authors suspected much of the chloroform was degraded prior to phytovolatilization, but fate was not conclusively determined. Reid and Jaffé[77] explored direct phytovolatilization of sulfur hexafluoride ($SF_6$) in *Typha latifolia* and *Scirpus acutus*, finding daily fluctuations in the phytovolatilization rate. These fluctuations were correlated to temperature, photosynthetically active radiation (PAR) and vapor pressure deficit (VPD), which affected air−water partitioning, diffusivity, and transpiration of this volatile compound. The correlation between VPD and phytovolatilization rate in *Typha* was thought to result from pressurized internal gas flows.[32] Similar findings have been reported for methane direct phytovolatilization from *Phragmites australis* and *Scirpus lacustris* in constructed wetlands.[78] *Phragmites* exhibited diel fluctuations in direct phytovolatilization, characterized by advective transpirative transport during the day and diffusive transport at night. Diel fluctuations in *Scirpus* were much less, implicating diffusive transport dominated, while transpiration-based fluxes were minimal. Direct phytovolatilization of methane from herbaceous plants in wetlands is relatively well studied (see reviews[79,80]), as methane phytovolatilization can exceed methane volatilization from unplanted wetlands by an order of magnitude.[79]

Direct phytovolatilization of methane from tree trunks has been measured less frequently than from herbaceous plants. Gauci et al.[81] report methane fluxes of 6.1 ± 1.2 $\mu$mol/m$^2$/d in May, 97 ± 88 $\mu$mol/m$^2$/d in June and 151 ± 33 $\mu$mol/m$^2$/d in October from wetland alder (*Alnus glutinosa*) trees (tree diameter 0.18−0.3 m; values are average ± standard deviation, $n$ = 3). The large fluxes of methane in May and June coincide with the tree in full leaf. Conversely, Terazawa et al.[82] report relatively constant methane fluxes from *Fraxinus mandshurica* over five sampling events. Fluxes were measured at 263 $\mu$mol/m$^2$/d at 15 cm above ground surface, decreasing to 145 $\mu$mol/m$^2$/d at 70 cm above ground surface, although this difference was not statistically significant ($p$ = 0.071). Pangala et al.[83] measured methane fluxes of 25−277 $\mu$mol/m$^2$/d in seven of eight tropical trees species. A multiple regression model could explain methane fluxes using stem diameter, wood specific density and porewater−methane concentrations ($R^2$ = 0.808, $p$ < 0.0001), with stem diameter and wood specific density negatively correlated with methane fluxes. Methane fluxes also significantly decreased with height above ground surface ($p$ < 0.0001). These field studies suggest that the methane emissions resulted solely from subsurface translocation, a hypothesis supported by an experiment that correlated methane and nitrous oxide fluxes from stems to subsurface concentrations.[84] The study used 3-year-old black alder (*Alnus glutinosa*) seedlings to demonstrate temporal variability in VOC emissions following flooding and decreasing methane and nitrous oxide ($N_2O$) fluxes with height above ground surface.

Similar to methane, wetland plants can translocate and directly phytovolatilize nitrous oxide. In a laboratory experiment with beech seedlings (*Fagus sylvatica*), Pihlatie et al.[85] demonstrated $N_2O$ emissions that were relatively constant over time. Direct exposure to $N_2O$ in the dosing solution confirmed transport of $N_2O$, rather than plant production of $N_2O$ from $NO_3^-$. Direct phytovolatilization of $N_2O$ has also been observed in crop plants,[86−88] although these measurements may include plant produced $N_2O$ from $NO_3^-$.[89] The importance and magnitude of $N_2O$ direct phytovolatilization remains uncertain at the field scale.[90]

**Indirect Evidence at Field Sites.** Direct phytovolatilization from tree trunks has also been examined through the sampling of tree tissues for VOCs. Decreasing VOC concentrations with sample height indicate a loss mechanism, which has traditionally been assumed to be direct phytovolatilization. Decreasing TCE and PCE concentrations with increasing sample height have been observed both in the lab[91,92] and in the field.[29,93,94] Similar concentrations changes with sample height have also been reported for MTBE in tree trunks[66] and in *Phragmites australis* stems.[95] However, there are some reports where VOC concentrations or fluxes do not change with height.[54,55] The source of these discrepancies remains unclear, although additional dynamic processes have been shown to affect tree VOC concentrations, such as transpiration rate and precipitation.[28,96,97] Concentrations of


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Table 2. Model Parameters Used to Predict VOC Fluxes at Field Sites[a]

| reference | | Doucette[56] | Wang[55] | | James[113] | | Newman[49] | Arnold[53] |
|---|---|---|---|---|---|---|---|---|
| tree | | poplar | eucalyptus | poplar | poplar | poplar | poplar | pine |
| contaminant | | TCE | TCE | CT | PCE | TCE | TCE | MTBE |
| site | $C_0$ (mg/L) | 0.1 | 1 | 12 | 10 | 5 | 16 | 140 |
| | fraction of groundwater used | 0.25[b] | 0.25[b] | 0.8 | 0.8 | 0.8 | 0.8 | 0.70 |
| tree properties | radius (m) | 0.054 | 0.060 | 0.15[c] | 0.035 | 0.035 | 0.094 | 0.24 |
| | trunk sample height (m) | 1[b] | 1[b] | 1[b] | 1 | 1 | – | – |
| | tree height (m) | 9 | 10 | – | 7 | 7 | 7 | 11.5 |
| | sapwood thickness (m) | 0.027[d] | 0.030[d] | 0.075[d] | 0.018[d] | 0.018[d] | 0.075[e] | 0.12[d] |
| | bark thickness (m) | 0.01[f] | 0.01[f] | 0.01[f] | 0.01[f] | 0.01[f] | 0.01[f] | 0.01[f] |
| | sap velocity (m/d) | 40[f] | 40[f] | 40[f] | 40[f] | 40[f] | 40[f] | 40[f] |
| | leaf area ($m^2$) | 34[g] | 31[h] | – | 27 | 27 | 18 | 78 |
| | water content (L/kg) | 0.38[f] | 0.38[f] | 0.38[f] | 0.38[f] | 0.38[f] | 0.38[f] | 0.38[f] |
| | gas content (L/kg) | 0.2[f] | 0.2[f] | 0.2[f] | 0.2[f] | 0.2[f] | 0.2[f] | 0.2[f] |

[a]–, Not needed for model. [b]Estimated. [c]Estimated growth of trees after Newman et al.[49] study. [d]Estimated as 50% of trunk radius. [e]Estimated as 80% of trunk radius for young trees. [f]Default model value. [g]Estimated from allometric relationship (average of *P. alba* and *P. nigra*)[120] [h]Estimated from allometric relationship for *E. globulus* (model 15)[121]

VOCs can also vary substantially around the circumference of a tree, presenting another source of noise.[92] Importantly, any phytodegradation of these contaminants in the tree trunks would also result in decreasing VOC concentrations with height; although for the contaminants discussed above, phytodegradation is generally thought to be minimal.[50,98]

## MODELING PHYTOVOLATILIZATION

Modeling direct phytovolatilization has received attention in the effort to build predictive fate models for the plethora of potential organic contaminants and to predict phytoremediation system performance. Important parameters related to phytovolatilization in these models generally include uptake rates of the contaminant, retardation of the contaminant in the plant, contaminant phytodegradation, and diffusion rates. Perhaps the most uncertain parameter in models is the effective diffusion coefficient, particularly in wood. Effective diffusivities for small VOCs in wood are typically on the order of $10^{-7}$ $cm^2/s$, but variability exists between studies.[99−102] Trapp et al.[103] developed an effective diffusivity by combining a tortuosity factor, the fraction of the contaminant in the water and air phases, and the diffusion coefficient in water and air. This approach uncovers two important sources of variability in effective diffusivities in wood. As VOC diffusivities in air are ∼4 orders of magnitude larger than VOC diffusivities in water, the amount of air in the wood strongly affects effective VOC diffusivities.[104] Gas content in wood depends on tree species, season and time of day.[105] Tortuosity in wood is also relatively uncertain, with estimates ranging from $10^{-1}$ to $10^{-2}$ in the radial/transverse direction and ∼0.5 in the axial/longitudinal direction.[101]

Several advection-diffusion transport models have been developed to explain direct phytovolatilization of organic contaminants from aboveground biomass. Models generally consider the plant stem/trunk as a cylinder with azimuthal symmetry, allowing the problem to be reduced to two dimensions. Advection is considered only to occur in the axial direction and only in the xylem. Note that the models often make assumptions specific to the plant-contaminant system of interest, making use of the model inappropriate for some other plant-contaminant systems.

Zhang et al.[106] developed a model of MTBE phytovolatilization in alfalfa stems. The 2-D model considers advection in the axial direction and diffusion in the radial direction. Because MTBE is relatively hydrophilic and recalcitrant, sorption and degradation were assumed negligible. From experimental data, the model estimated the effective diffusion coefficient at $1.23 \pm 0.39 \times 10^{-7}$ $cm^2/s$, which was a factor of 5 less than experimental measurements.

Ma and Burken[107] developed a model to explain phytovolatilization from large trees that contain both sapwood and heartwood. The model considers advection in the axial direction and diffusion in the radial direction, while another version of the model also considers axial diffusion.[108] Importantly, this model considers advection to only occur in the sapwood, hence the name "donut ring model." The decline of tree TCE concentrations with height was well fit by the model.

Phytovolatilization in wetland plants requires a different set of assumptions due to the unique plant physiology. In a model[109] modified Reid and Jaffé,[77] both transpiration driven uptake and axial diffusion through aerenchyma were considered as influx mechanisms for VOCs. Note that pressurized convective flows, present in some wetland plants, were not considered. Transpiration-driven uptake required estimation of the TSCF,[21,23] although for highly volatile compounds such as methane and $SF_6$, diffusive uptake exceeded transpirative uptake. Additionally, phytovolatilization was the only loss mechanism considered and storage was neglected, so phytovolatilization rates were considered equal to plant uptake rates.

In contrast to the specialized models discussed above, Trapp[110] (also see ref 111) developed a comprehensive and generic plant uptake model consisting of five compartments: fine roots, thick roots, stem, leaves, and fruit. Advective flows with the transpiration stream carry the contaminant up the plant and a variety of first-order loss mechanisms are considered. The model requires estimation of a number of plant-contaminant-environment parameters, but does not require the input of the TSCF. Phytovolatilization is considered as Fickian diffusion out of the stem and leaves. In the stem, the contaminant must diffuse through wood and an unstirred



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boundary layer in series. For leaves, diffusion occurs in parallel between the stomatal pathway and the cuticle.

To assess the ability of the Trapp model to predict direct phytovolatilization fluxes, the model was parametrized and the results were compared to the field data in Table 1. Model parameters are shown in Table 2, generally taken from the publication, while contaminant properties were taken from literature.[112] Note that many parameters in Table 2 were estimated, as the necessary data were not reported. Perhaps the most important estimated parameters are tree sap velocity and tree gas content, which are rarely measured and fluctuate substantially. Using the parameters in Table 2, the model was calculated at steady state following the procedure outlined by Trapp.[110] No loss mechanisms were considered in the subsurface, so the resulting xylem concentration entering the base of the trunk was the groundwater concentration ($C_0$) multiplied by the fraction of groundwater used by the tree. Note that this latter quantity is relatively uncertain, particularly at field sites. To calculate direct phytovolatilization from leaves, the trunk was considered to end at $^2/_3$ of the tree height where the leaves began. No loss mechanisms other than phytovolatilization were considered for the leaves, so at steady state the flux of contaminants entering the leaves equaled the phytovolatilization flux from the leaves.

The predicted and measured direct phytovolatilization data are shown in Figure 3 for both trunk and leaf data. In all but

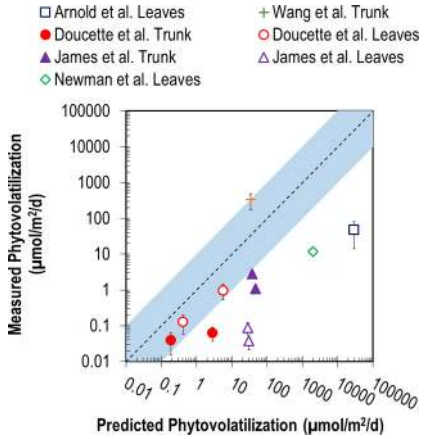


**Figure 3.** A comparison of modeled and measured direct phytovolatilization fluxes. The shaded region indicates ±1 order of magnitude deviation from the 1:1 line. Figure references: Arnold et al.,[53] Doucette et al.,[56] James et al.,[113] Newman et al.,[49] Wang et al.[55] Error bars correspond to the errors provided in Table 1.

one case the model over predicts the measured phytovolatilization rate. This should be expected, as no other loss mechanisms were considered. For example, several of the field trials report reductive dechlorination occurring the subsurface,[32,38,58] which would decrease the quantity of contaminant available for phytovolatilization. Additionally, fluxes would be lower than predicted if the system has yet to reach steady state. Note that the trunk measurement by Wang et al.[55] and James et al.[113] used the same experimental setup, so differences in model agreement with experimental data likely result from input parameters or model structure. In general, trunk data appear to be better predicted by the model, which is expected given the simple geometry of the trunk. The trunk to leaf transition is complex and variable, progressing to increasingly smaller diameter branches before terminating at leaves. These smaller diameter branches present a shorter diffusion path, which increases flux from the tree. This process is not well captured by the model.

Many of the aforementioned phytovolatilization models demonstrate exponentially decreasing trunk VOC concentrations with sample height.[106,107,110] The rate of the exponential decay is related to the phytovolatilization rate and can be described in terms of the half-distance, which is the distance up or along a stem at which the VOC concentration is half the concentration at the base of the stem. The half-distance ($x_{1/2}$) can be calculated from plant and chemical variables.[99]

$$x_{1/2} = \frac{\ln 2 \cdot r \cdot \Delta x \cdot u_w \cdot f_w}{2D_{r,\mathrm{eff}}}$$

Where $r$ is the radius of the stem, $\Delta x$ is the diffusion distance, $u_w$ is the transpiration stream velocity, $f_w$ is the fraction of the contaminant in the water and $D_{r,\mathrm{eff}}$ is the effective radial diffusivity. $f_w$ can be calculated from the fraction of water in the stem divided by the partitioning of the contaminant between the stem and water. Half distances can vary greatly, depending on the diffusivity of the chemical and the diameter of the plant stem/trunk.

## RESEARCH NEEDS

Research into phytovolatilization of contaminants has elucidated the pathways through which many contaminants volatilize from plants. However, the relative importance of many of these removal pathways remains uncertain, especially for compounds that are minimally studied. Figure 4 summarizes studies of direct phytovolatilization and presents the region of physicochemical space where direct phytovolatilization is most likely. Compounds with a log $K_{OW}$ exceeding 5 are unlikely to be translocated in plants due to their strong partitioning to organic matter.[27] Less hydrophobic compounds are more likely

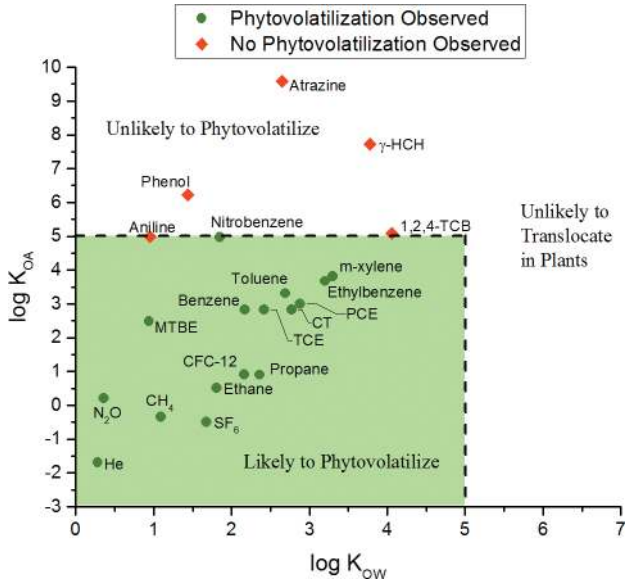


**Figure 4.** Physicochemical domains favoring direct phytovolatilization. Log $K_{OW}$ values from databases[112,122] and log $K_{OA}$ calculated from Henry's Constant (obtained from,[112] except $N_2O$ and $SF_6$, which were obtained from[123]). Contaminants are those shown in Figure 2 and Table 1 with the addition of $CH_4$ and $N_2O$, along with the tracers[30] $SF_6$, He, CFC-12, ethane, and propane.



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to be translocated by plants, although factors such as molecular weight and hydrogen bonding also play a role in compound translocatability.[22] Studies reviewed here indicate that a log $K_{OA}$ around 5 divides compounds able to phytovolatilized from those with minimal tendency to phytovolatilize. Many of the studied compounds have log $K_{OA}$ values between 2 and 3, while the more volatile methane and $SF_6$ have log $K_{OA}$ below zero. Studies with these more volatile compounds suggest that diffusive transport plays an increasingly significant role in transport as log $K_{OA}$ decreases. However, more studies are needed with a wider variety of chemicals. Additionally, compounds unable to translocate in plants due to their hydrophobicity may still be observed in aboveground plant tissues via particle deposition or partitioning from the air.[114−116] Therefore, care must be exercised in experimental design to ensure aboveground biomass contamination indeed resulted from translocation.

Additional understanding is needed in the mechanistic dynamics that govern transport of gases in tree trunks. Lenticel permeability, aerenchyma formation and trunk gas content vary along several time scales. Studies are needed to assess these factors over the life of the plant, and across seasonal and daily time scales. Measuring these fundamental variables allows prediction of diffusivities for a vast number of contaminants, and is therefore more powerful than simply measuring fluxes of a particular contaminant over time.

Measurements of indirect phytovolatilization are lacking, particularly at field scale. Careful measurements are needed to distinguish indirect phytovolatilization from direct soil volatilization. Such belowground processes are difficult to discern and are expected to be site-specific. However, indirect phytovolatilization may represent a substantial removal process, not currently accounted for, in phytoremediation systems.

Individual indirect phytovolatilization processes also need to be studied, such as contaminant hydraulic redistribution. As most of the organic contaminants are passively transported across roots, diffusion from shallow roots into the vadose zone may provide a meaningful loss pathway. Likewise, convective fluxes in some wetland plants likely move measurable quantities of highly volatile contaminants, although the magnitude and modeling of these effects are unknown.

Direct phytovolatilization of VOCs also requires further study in wetland and waterlogged sites. Fluxes of methane from herbaceous and woody plants are likely significant, although the magnitude of nitrous oxide fluxes are less certain.[80] Fluxes of VOCs from plants growing on landfills with vegetative covers are also minimally studied.[117] Many phytoremediation sites operate in areas subject to flooding, where the use of flood-tolerant species may improve VOC removal rates while also improving plant survival.

Phytovolatilization is an important area of study not only for traditional organic contaminants, but also for other compounds naturally present in the subsurface and in plant roots. Some have suggested that phytovolatilization may be important for ammonia.[118] Another volatile organic compound, ethylene, is an important plant signaling molecule.[119] Ethylene's high volatility, small size and minimal hydrophobicity indicate this molecule is highly mobile in the subsurface and in plants. As discussed above, phytovolatilization of greenhouse gases such as methane may be important processes for these volatile compounds.

In summary, phytovolatilization plays an important role in the environmental fate of both anthropogenic and naturally occurring volatile molecules. As such, the magnitude of VOC fluxes through plants requires additional study. Learnings can be applied to alter fate in beneficial manners either to enhance transport in remediation of subsurface settings or to limit transport if undesired. Increasing our knowledge of plant-mediated transport will help us to better understand the connectivity between the atmosphere and the obscure subsurface.

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### Notes

The authors declare no competing financial interest.

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