

Phytovolatilization of organic contaminants

Baeder-Bederski, O., Kusch, P., Stottmeister, U.
Centre for Environmental Research Leipzig-Halle, Permoserstrasse
15, D-04318 Leipzig, Germany

1. Introduction

Because of economical and ecological advantages and efficiency under specific conditions the treatment of wastewaters and contaminated soils and sludges with the help of macrophytes which stimulate the complex biotic and abiotic rhizosphere processes (phytoremediation) is getting world-wide public.

Nowadays mainly domestic wastewater, agricultural wastewater and mine drainage water are treated in constructed wetlands. The interest in treating landfill leachate, contaminated groundwater, industrial effluents and also the drainage of sludge is still increasing.

The decontamination of soil and sludges by rhizosphere processes is of increasing interest both concerning heavy metals and organic chemicals. Nevertheless the whole technology has yet to be refined with special emphasis on cheap and simple methods for further treatment of the plant biomass which has accumulated these substances.

A further aspect for the application of macrophytes for remediation purposes is based on their water need for transpiration. This can be used for sludge dewatering and for minimizing of rain fall water access to deposits by realizing a planted cover which has a high transpiration rate.

In connection with the increased applicative importance of such systems an intensive technological development has happened during the last years. Although phytoremediation is used widely today a number of basic scientific phenomena are still unknown. In order to further optimise processes and to open up new fields of application broader and more profound basic research in this field is needed.

2. Phytovolatilization - Transfer of organic compounds from the rhizosphere into the phylosphere

The capability of plants to emit phytogenic volatile substances such as terpenes is already well-known and is, under certain circumstances, environmentally relevant ([11], [9]). It is of practical and ecotoxicological interest when macrophytes planted on contaminated soils also enhance their emission of compounds located in the rhizosphere. In contrast to the natural emissions the transport of the contaminant from the soil to the above-ground parts of the plants must be considered in the case of "phytovolatilization" of soil contaminants. This process comprises:

- the transport within the following compartments: soil, root, stem, leaf and atmosphere,
- the sorption equilibrium between the compartments,
- the contaminant metabolism.

When the research started it was not yet known whether plants take up organic substances through the roots on an appreciable scale. In connection with the use of pesticides and herbicides systematic research into uptake and distribution of xenobiotics in plants was conducted ([10], [1], [12]). It was found that the non-dissociated chemicals contained in porewater very often reach the root xylem passively by diffusion and are then transported by the transpiration stream into the above-ground plant parts. However, there is a barrier for the organic contaminants before they reach the xylem. The Caspari-strip, a watertight barrier of lignin and waxy material stops free diffusion in the apparent free space so that all substances at the endodermis have to pass cell membranes. Due to the semipermeable properties of the cell membranes the composition of the xylem sap differs from the composition of the porewater after this passage. SHONE & WOOD [10] introduced the Transpiration Stream Concentration Factor (TSCF), which is calculated from the concentration ratio of organic substances in the xylem sap and the porewater. It describes the transport efficiency of the transpiration stream for organic components. Concentrations of organic non-dissociated components are normally lower than in the porewater ($TSCF < 1$). Only substances with an octanol-water distribution coefficient lgK_{OW} between 1-3 effectively get into the xylem. More lipophilic substances are accumulated in the lipophilic root components, more hydrophilic substances are reflected into the porewater. In order to produce an estimation of the TSCF BRIGGS and coworkers [1] proposed a lgK_{OW} -TSCF-relation. The experimental measurements of the TSCF very often showed a strong correlation with the substance parameters. The TSCF-values measured are only to a small degree plant specific [7]. Nevertheless, an estimation of the TSCF from substance parameters is still not reliable because the exact mechanism of the contaminant transfer from the root epidermis to the xylem is not known. If the substance is already metabolized in the root tissue, the TSCF for each metabolite must be measured or estimated in order to provide an estimation of the contaminant transfer [3].

Many lab experiments in the field of Plant-Enhanced Bioremediation neglect that with an increasing concentration of organic carbon in the soil the concentration of lipophilic substances in the porewater decreases. Because essentially only those contaminants are accessible to the plant that are dissolved in water, the xylem sap concentration in general decreases and due to the sorption in the soil the xylem sap composition changes in favour of hydrophilic substances.

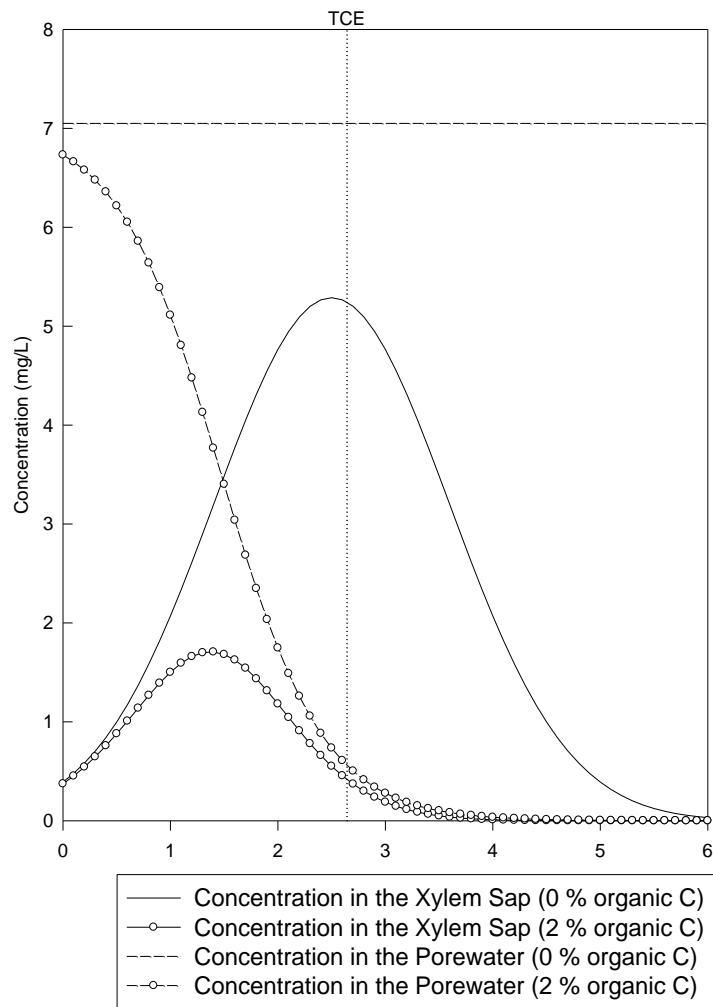


Figure 1: Porewater and xylem sap concentration in dependence on the lipophily and organic carbon content of the soil (contaminant content of 10 mg/kg soil)

So the transfer of such compounds with a high TSCF-value - which could be easily transported in the stem – is limited and only a small portion gets into the xylem.

As an example this has been calculated for the substance parameters of trichlorethylene in a soil with a total porosity of 0.5 and an 0.3 share of pores filled with water. As the plant itself regenerates the organic soil matrix with root exudate and dead root tissue it can be assumed under certain conditions depending on the contaminant load, that this sorption balance is permanently damaged.

DAVIS and coworkers [4] investigated in a long-term experiment both the degradation of phenol and toluene and the contaminant emission of a soil planted with alfalfa (*Medicago sativa*). A nutrient solution was continuously flowing through this soil (about 25 cm under the soil surface) planted with these compounds. The phyllosphere was separated from the

surrounding atmosphere and its air continuously analyzed by FTIR. There could not be detected any traces of both compounds (detection limits: 250 ppb v/v for toluene; 150 ppb v/v for phenol).

While phenol concentration in the porewater decreased drastically, toluene concentration was hardly influenced although the mass balance between entrance and exit of the system showed that microbial decomposition must have taken place. The authors correctly attribute this to different uptake efficiencies of the plant for water and toluene ($TSCF_{\text{water}}=1$; $TSCF_{\text{toluene}} \cong 0.7$, parameter set of [3]) which should result in an increased concentration in the porewater when no microbial decomposition takes place after passage of the root zone. Why is the contaminant concentration in the air reservoir that is sealed to the atmosphere above the plant cover below the detection limit of ca. 960 ng toluene/L? DAVIS and his team [4] estimate that the uptake of organic contaminants by the plant in adapted systems (long-term test!) through the intensive decomposition of associated micro-organisms at the rhizoplane is greatly reduced. This is obviously also the case for toluene although the measurable concentration in the porewater was unchanged and high. There are different opinions about the practical importance of the rhizosphere effect in remediation of contaminated soil ([16], [15]) because it is estimated that the rhizosphere can only constitute app. 3 vol% of the soil [6]. However, if an accelerated decomposition takes place at the rhizoplane this can mean a drastic decrease of the contaminant concentration that is accessible to the plant and the resulting restricted contaminant uptake could lead to a phytovolatilization level that can not be verified. Comparative studies of phytovolatilization of a plant species in different nutrient solutions could be a possibility for quantitative in-situ-measurements of the rhizosphere effect.

Measurements made by GORDON and coworkers [5] have shown that phytovolatilization is also unimportant in the case of very volatile compounds like trichloroethylene (TCE). In lab experiments with poplars growing in contaminated sand (50 ppm TCE) they estimated a TCE emission rate of about 10 $\mu\text{g/h}$ and leaf. But in open air large scale experiment they were unable to measure any significant emissions

The transport of chemicals from leaf to atmosphere is a diffusion process impelled by the concentration gradient between leaf tissue and free atmosphere and is always directed from areas with the higher concentration to areas with the lower concentration. In the case of lipophilic compounds with a sufficient volatility ($>10^{-4}$) it is possible that volatilization from soil is faster than the uptake by plant roots. So the ratio of the concentrations of the contaminants in plant tissue and in the atmosphere is below thermodynamic equilibrium. This means that these

compounds emitted from soil should be absorbed to plant tissue. This question is considered theoretically by TRAPP & MATTHIES [14] for polychlorinated dibenzofuranes and - dioxines and experimentally by SCHROLL and coworkers [8] for different compounds and plant species. The uptake of volatile lipophilic organic chemicals by foliar vegetation should be a further reason to use plants for securing contaminated areas.

Helophytes are planted in constructed wetlands for the treatment of wastewaters. They are well adapted to grow in anoxic flooded soils. Because of their relatively high transpiration rate (maximum of 1.8 - 3.6 mol/m²h for *Phragmites communis*, [2]) it should be tested whether they emit contaminants from the rhizosphere to a greater extent than other plant species.

Experimental Estimations of Emission Rates

For the estimations the following conditions were prepared:

- the measurements were done in closed gas exchange cuvettes - so the plants were excluded from the surrounding atmosphere

- the plants were cultivated in hydroculture in a defined nutrient solution

- the rhizosphere was separated from the phyllosphere by a layer of quartz sand and paraffin

- the inflowing fresh air was catalytically purified (residual hydrocarbon content < 10 ppb v/v)

- gas transport from the rhizosphere into the phyllosphere was prevented by a permanent overpressure in the phyllosphere of the cuvette

- permanent mixing of the atmosphere in the phyllosphere of the cuvette was realized

- the contaminant concentration in the phyllosphere was measured on-line with an automated trap system and GC/MS

Tab. 1: Summary of the experimental conditions

	experiment	
	<i>Mentha aquatica</i>	<i>Iris pseudacorus</i>
surface of the leaves	2028 cm ²	4292 cm ²
height of the plant	90 cm	90 cm
cuvette diameter	12 cm	20 cm
air inflow rate	7.5 L/min	14 L/min
air recirculation (mixing)	9.6 L/min	100 L/min
linear air velocity	0.026 m/s	0.06 m/s
day/night rhythm	15 h/9 h	14 h/10 h
illumination	94 - 304 $\mu\text{mol}/\text{m}^2\text{s}$	94 - 304 $\mu\text{mol}/\text{m}^2\text{s}$
addition of fresh nutrient solution with the contaminant	no	65 mL/min
recirculation rate of the nutrient solution	200 mL/min	200 mL/min
contaminants	2,6-dimethylphenol (26 DMPH)	trichloroethylene (TCE) chlorobenzene (CB) 1,2-dichlorobenzene (1,2DCB)
contaminant concentration	10 mg/l at the beginning	inflow conc. 7 mg/L

Results

In both experiments a clear dependence of contaminant emission from the time of the day and the transpiration rate could be observed. The absolute values of the emission rates were very low and in the range of nmol/h m² foliar surface (see Figure 2 and 3). The emissions of the other compounds (1,2-Dichlorobenzene and Chlorobenzene) were negligible within 70 h time of exposition, but later qualitative measurements showed a detectable emission of these compounds. It was surprising to find the relatively high emission rate of 26DMPH in comparison to the more volatile TCE. Because of the different species of test plants and other experimental conditions it is not possible to compare the values for the emission rates directly. Calculations of the theoretical emission rates without consideration of plant metabolism (model PLANT by TRAPP & MATTHIES [13]) give similar values for TCE and 26DMPH (1100 nmol 26DMPH/h m² and 820 nmol TCE/h m²).

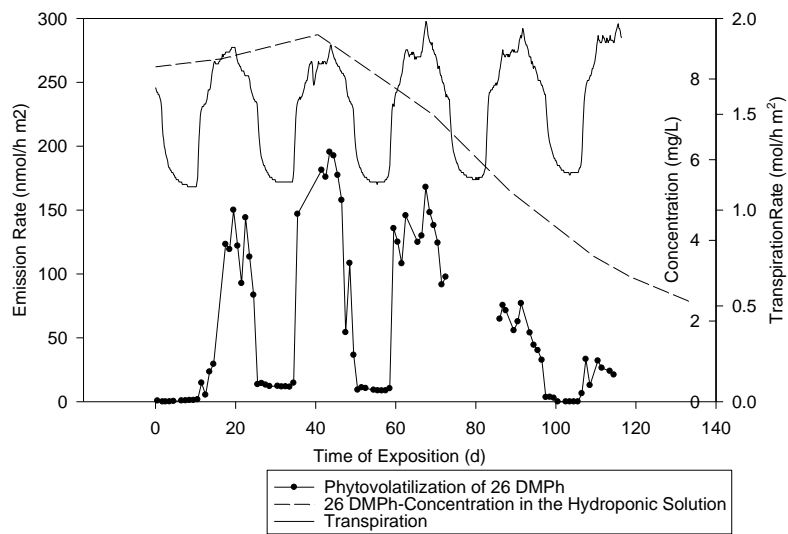


Figure 2: Emission of 2,6-dimethylphenole (26DMPH) by *Mentha aquatica* after exposition of its rhizosphere to 26DMPH

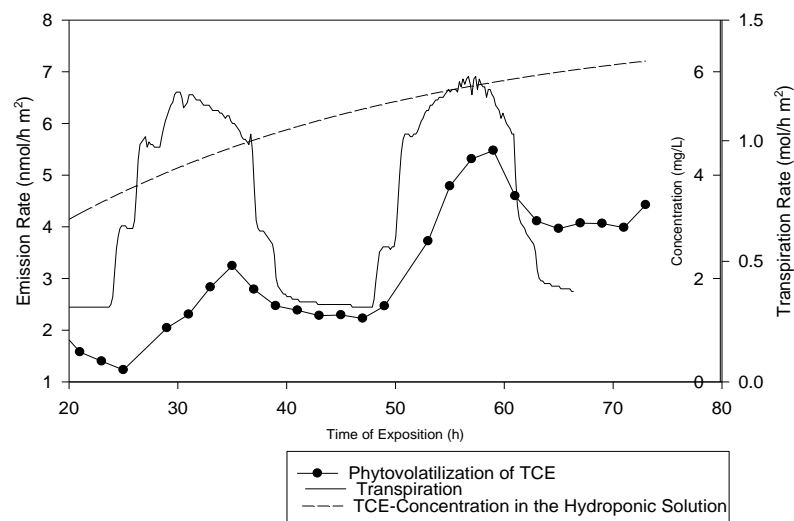


Figure 3: Emission of trichloroethylene (TCE) by *Iris pseudacorus* after exposition of its rhizosphere to TCE

3. Summary and Conclusions

In the past, research on wetlands constructed for wastewater treatment was mainly restricted to technological issues. The role of the plants used in the technologies was more or less overshadowed by the maximization of contaminant removal and the minimisation of the area

needed. Further progress in the application of this technology can only be made when we stop looking at the plant-soil system as a black box and quantitatively study the transport- and conversion processes taking into account the interaction of microorganisms in the soil and the plant. The analysis of the kinetics of phytovolatilization seems to be a viable means for studying the complex transport processes in the undisturbed plant-soil system.

There has been a long-standing scientific discussion about whether contaminants from the rhizosphere are transported unchanged by plants into the phyllosphere and which factors influence this process.

The latest literature and our own results show that the emission rates of volatile organic compounds are very low and relating to practice negligible. Also theoretical modelling of the emission of the highly volatile compound TCE surprisingly resulted in extremely low values. Furthermore, future practical experiments and modelling must consider the possible metabolization both at the rhizoplane and in plant tissue, especially the plant leaf.

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