

# Treatment of groundwater contaminated with benzene, MTBE and ammonium by constructed wetlands

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# Abstract

Multi-component contamination of groundwater at industrial sites due to chemical processing and transport causes a major hazard to the environment. Depending on toxicity, persistence and mobility, chemicals impair the quality of groundwater and can have adverse effect on ecosystems and human health, e.g. when polluted groundwater discharges into rivers / river floodplains, or if the groundwater is used as drinking water source. Within the last decades several groundwater remediation techniques have been developed, but oftentimes the commonly applied P&T methods are economically not feasible. Constructed wetlands (CWs) are a promising near-natural alternative for a cost-efficient remediation of groundwater.

In the present thesis, different pilot-scale horizontal subsurface-flow CW types (gravel CWs with different filter composition and a hydroponic plant root mat) have been tested for their potential to remediate groundwater contaminated with benzene, the gasoline additive methyl *tert*-butyl ether (MTBE) and ammonium at a field site. The performance evaluation comprised (i) the determination of contaminant specific removal efficiency based on season-dependent concentration decline, (ii) the investigation of the fate of the volatile organic compounds in the different CW types during summer and winter time based on a mass balance approach taking into account the main removal pathways volatilization, plant uptake and microbial degradation, and (iii) the hydraulic characterization of the CWs with regard to wetland type and operational mode.

Overall, it could be shown that contaminant decline is greatly affected by the wetland type, with the hydroponic plant root mat achieving lower outflow concentrations than the planted gravel filter, and is season-dependent with highest concentration decline during spring and summer at temperatures above 15°C, and contaminant-specific with most efficient decline observed for benzene. In contrast, the filter composition (gravel matrix with or without filter additives charcoal or ferric oxide) did not enhance treatment efficiency. The hydroponic plant root mat and the planted gravel CW efficiently improved the water quality as indicated by the achieved concentration decline during summer of  $99 \pm 1 \%$  and  $81 \pm 7 \%$  for benzene,  $82 \pm 4 \%$  and  $17 \pm 7 \%$  for MTBE, and  $41 \pm 7 \%$  and  $54 \pm 17 \%$  for ammonium-N, respectively.

The VOC mass balance confirmed the removal trends regarding seasonality, compound- and system-specificity, yet summer mass removal from the aqueous phase was elevated compared to the mere concentration decline, given that water loss via evapotranspiration was considered (hydroponic plant root mat: benzene:  $606 \pm 51 \text{ mg d}^{-1} \text{ m}^{-2} = 99.9 \pm 8.5 \%$ ; MTBE:  $117 \pm 9 \text{ mg d}^{-1} \text{ m}^{-2} = 96 \pm 8 \%$ ; gravel CW: benzene:  $480 \pm 42 \text{ mg d}^{-1} \text{ m}^{-2} = 96 \pm 8 \%$ ; MTBE:  $85 \pm 13 \text{ mg d}^{-1} \text{ m}^{-2} = 75 \pm 11 \%$ ). Moreover, mass balancing enabled to distinguish between elimination and distribution pathways: for the gravel CW and the hydroponic plant root mat, the main benzene flux during summer was by microbial degradation (76.4%, 82.9%), with minor removal via plant uptake and volatilization. In contrast, MTBE removal via microbial degradation was poor for both treatment systems (gravel CW: 30.9%, hydroponic plant root mat: 13.2%). Furthermore, with regard to treatment reliability mass balancing pointed out that the application potential for the hydroponic plant root mat strongly depends on the contaminant to be treated, given that emission was a minor removal pathway for benzene in both CW types (<5%), but was considerably enhanced for MTBE in the plant root mat (23.6%).

The hydraulic characterization of the CWs revealed lower dispersion indices ( $N = 11.3$ ,  $D_n = 0.04$ ,  $Pe = 23$ ) and on that basis better hydraulic flow behavior for the planted gravel CW in comparison to the resting ( $N = 5.3$ ,  $D_n = 0.09$ ,  $Pe = 11$ ) and floating ( $N = 1.9$ ,  $D_n = 0.26$ ,  $Pe = 4$ ) hydroponic plant root mat. So, the fact that the resting plant root mat showed highest removal efficiency although the flow behavior was less optimal evinced that good hydraulic flow behavior with low dispersion is not the only decisive factor for high contaminant removal, but high actual water-root contact, root density and a sufficient residence time are also important.

To conclude, both CW types represent a promising approach for the remediation of VOC and ammonium contaminated groundwater during spring/summer time. However, VOC removal via volatilization should not be overlooked, especially for the hydroponic system.

# Zusammenfassung

Die großflächige und zugleich heterogene Verunreinigung von Grundwasser an Industriestandorten infolge der Verwendung und des Transports von Chemikalien stellt ein hohes Gefährdungspotential für die Umwelt dar. In Abhängigkeit von Toxizität, Persistenz und Mobilität beeinträchtigen die Schadstoffe nicht nur die Grundwasserqualität. Auch andere Umweltgüter und die menschliche Gesundheit können betroffen sein, wenn kontaminiertes Grundwasser beispielsweise in Oberflächengewässer infiltriert, z.B. in Flüsse oder Flussauen, oder das Grundwasser als Trinkwasserquelle dient. In den letzten Jahren wurde eine Vielzahl von Reinigungsstrategien für kontaminiertes Grundwasser entwickelt, wobei sich die klassischen Pump & Treat - Methoden ökonomisch oft als nicht tragbar erwiesen. Eine vielversprechende und zudem kostengünstige naturnahe Alternative stellt die Anwendung von Pflanzenkläranlagen, engl. *constructed wetlands* (CWs), dar.

In der vorliegenden Dissertation wurden verschiedene horizontal unterhalb der Oberfläche durchflossene CWs (bepflanzte Kiesfilter mit unterschiedlichen Filteradditiven und ein hydroponisches Versuchssystem, eine sogenannte hydroponische Wurzelmatte) im Pilotmaßstab und unter Feldbedingungen auf ihr Potential untersucht, mit Benzol, dem Benzinzusatzstoff Methyl *tert*-butyl Ether (MTBE) und Ammonium kontaminiertes Grundwasser zu reinigen. Die Leistungsbewertung umfasste folgende Schwerpunkte: (i) die Bestimmung schadstoffspezifischer Reinigungsleistung basierend auf der erreichten Konzentrationsverringerung, (ii) die Untersuchung der Verteilung der flüchtigen organischen Schadstoffe (engl. *volatile organic compounds*, VOCs) im System Grundwasser-Boden-Pflanze-Atmosphäre basierend auf der Erstellung von Massenbilanzen, wobei die Prozesse Volatilisierung, Pflanzenaufnahme und mikrobieller Schadstoffabbau als die Haupt-Eliminierungspfade berücksichtigt wurden, und (iii) die hydraulische Charakterisierung der verschiedenen *constructed wetlands*, auch im Hinblick auf ihre Betriebsweise. Die Untersuchungen zeigten, dass die Verringerung der Schadstoffkonzentration systemabhängig und schadstoffspezifisch erfolgte. Die Wurzelmatte erzielte im Vergleich zum bepflanzten Kiesfilter eine deutlich höhere Reinigungsleistung und Benzol wurde effektiver eliminiert als die anderen Schadstoffe. Zudem unterlag die Reinigungseffizienz

saisonalen Schwankungen: Die stärkste Abnahme wurde während der Frühjahrs- und Sommermonate verzeichnet bei Lufttemperaturen über 15°C. Keinen Einfluss auf die Reinigungsleistung hatte die unterschiedliche Zusammensetzung der Kiesfilter (Zusatz der Filteradditive Aktivkohle oder dreiwertiges Eisenoxid). Im Sommer wurden die Schadstoffkonzentrationen durch die Behandlung via Wurzelmatte und bepflanzten Kiesfilter effizient verringert: um  $99 \pm 1 \%$  und  $81 \pm 7 \%$  für Benzol, um  $82 \pm 4 \%$  und  $17 \pm 7 \%$  für MTBE, und um  $41 \pm 7 \%$  und  $54 \pm 17 \%$  für Ammonium-N.

Anhand der VOC-Massenbilanzierung konnten die beschriebenen Trends hinsichtlich Saisonalität sowie Schadstoff- und System-Spezifität bestätigt werden, wobei die Eliminierungseffizienz basierend auf Schadstofffrachten im Vergleich zur Konzentrationsverringerung höher ausfiel (Wurzelmatte: Benzol:  $606 \pm 51 \text{ mg d}^{-1} \text{ m}^{-2} = 99,9 \pm 8,5 \%$ ; MTBE:  $117 \pm 9 \text{ mg d}^{-1} \text{ m}^{-2} = 96 \pm 8 \%$ ; bepflanzter Kiesfilter: Benzol:  $480 \pm 42 \text{ mg d}^{-1} \text{ m}^{-2} = 96 \pm 8 \%$ ; MTBE:  $85 \pm 13 \text{ mg d}^{-1} \text{ m}^{-2} = 75 \pm 11 \%$ ). Darüber hinaus ermöglichte die Massenbilanzierung die Unterscheidung zwischen Transformations- und Umverteilungsprozessen. Die Berechnungen ergaben, dass Benzol im bepflanzten Kiesfilter und in der hydroponischen Wurzelmatte hauptsächlich via mikrobiellen Schadstoffabbau entfernt wurde (76,4% bzw. 82,9%), während pflanzliche Aufnahme und Emission eine untergeordnete Rolle spielten. Im Vergleich dazu fiel für MTBE der Anteil des mikrobiellen Abbaus an der Gesamteliminierung gering aus (bepflanzter Kiesfilter: 30,9%; Wurzelmatte: 13,2%). Die Emissionsmessungen unterstrichen zudem, dass das Anwendungspotential des hydroponischen Systems stark von dem zu behandelnden Schadstoff abhängt. Denn während die Emission von Benzol in beiden CW Systemen nur einen geringen Anteil an der Gesamteliminierung ausmachte (<5%), trug die Emission von MTBE in der Wurzelmatte entscheidend zur Gesamteliminierung bei (23,6%).

Die Erfassung der hydraulischen Charakteristika der CWs zeigte für den bepflanzten Kiesfilter eine geringere Tendenz zur Dispersion ( $N = 11,3$ ;  $D_n = 0,04$ ;  $Pé = 23$ ) und somit ein besseres hydraulisches Fließverhalten im Vergleich zum hydroponischen System - unabhängig davon, ob dieses als auf dem Beckenboden aufsitzende ( $N = 5,3$ ;  $D_n = 0,09$ ;  $Pé = 11$ ) oder als schwimmende ( $N = 1,9$ ;  $D_n = 0,26$ ;  $Pé = 4$ ) Wurzelmatte betrieben wurde. Die Tatsache, dass das unter hydraulischen Gesichtspunkten weniger effiziente hydroponische System (die auf dem Beckenboden aufsitzende Wurzelmatte) die beste Reinigungsleistung erzielte, verdeutlicht, dass für eine hohe Schadstoffeliminierungseffizienz eine gutes hydraulisches Fließverhalten nicht allein entscheidend ist. Faktoren wie ein guter Kontakt zwischen den Schadstoffen im Wasser und den Pflanzenwurzeln, aber auch die Wurzelichte sowie eine genügend lange Verweilzeit



spielen hier eine wichtige Rolle.

Abschließend lässt sich sagen, dass während der Vegetationszeit im Frühling und Sommer beide Arten von constructed wetlands eine vielversprechende Methode darstellen für die Reinigung von mit VOCs und Ammonium belastetem Grundwasser. Dabei sollte insbesondere für das hydroponische System der Eliminierungspfad Volatilisierung nicht außer Acht gelassen werden.



# List of abbreviations and notations

## Abbreviations

AC	Activated carbon
BOD <sub>5</sub>	Five-day biochemical oxygen demand
BTC	Breakthrough curve
BTEX	Group of the aromatic compounds: benzene, toluene, ethylbenzene, xylenes
COD	Chemical oxygen demand
CoTra	Compartment Transfer
CSTR	Continuously stirred tank reactor
CW	Constructed wetland
DAC	Dynamic air chamber
DVGW	German guidelines for drinking water quality
E	Evaporation
Eh	Redox potential
EPA	Environmental Protection Agency
ET	Evapotranspiration
FWS	Free water surface
HF	Horizontal flow
HSSF	Horizontal subsurface flow
IARC	International Agency for Research on Cancer
IC	Inorganic carbon
MCB	Monochlorobenzene
MPN	Most probable number
MTBE	Methyl <i>tert</i> -butyl ether
NA	Natural attenuation
NPL	National Priority List
ÖGP	German: Ökologisches Großprojekt; English: large-scale ecological project

P&T	Pump-and-treat
PAH	Polycyclic aromatic hydrocarbon
PCE	Perchloroethylene
PF	Plug flow
PFR	Plug-flow reactor
PHCs	Petroleum hydrocarbons
RTD	Residence time distribution
SSF	Subsurface flow
T	Transpiration
TBA	<i>tert</i> -butyl alcohol
TCA	1,1,1-trichloroethane
TCE	Trichloroethylene
TEA	Terminal electron acceptor
TN	Total nitrogen
TOC	Total organic carbon
TSCF	Transpiration stream concentration factor
USGS	United States Geological Survey
UV	Ultraviolet
VF	Vertical flow
VOC	Volatile organic compound
WHO	World Health Organization

### Notations

The abbreviations shown in brackets represent the dimensionality of the variable being used: M = mass; L = length; L<sup>3</sup> = volume, t = time.

$A$	Surface area of the wetland [L <sup>2</sup> ]
$A_{in}$	Area perpendicular to the flow direction [L <sup>2</sup> ]
$A_{surf}$	Surface area [L <sup>2</sup> ]
$ACL_{in/out}$	Areal contaminant load for the inflow or outflow [M L <sup>-2</sup> t <sup>-1</sup> ]
$c'(\Phi)$	Normalized concentration [-]
$c_A$	Contaminant concentration in the atmosphere
$c_{CW,average}$	Average contaminant concentration in the water compartment of the CW [M L <sup>-3</sup> ]
$c_{in/out}$	Contaminant concentration at the inflow or outflow [M L <sup>-3</sup> ]

$c_{tracer}$	Fluorescein concentration of the tracer solution [M L <sup>3</sup> ]
$c_W$	Contaminant concentration in the water phase [M L <sup>3</sup> ]
$c_{x,y}$	Contaminant concentration at the sampling position (x,y) [M L <sup>3</sup> ]
$D$	Dispersion coefficient [L <sup>2</sup> t <sup>-1</sup> ]
$D_n$	Dispersion number [-]
$E$	Evaporation [L <sup>3</sup> L <sup>-2</sup> t <sup>-1</sup> ]
$ET$	Evapotranspiration [L <sup>3</sup> L <sup>-2</sup> t <sup>-1</sup> ]
$f_{OC}$	Organic carbon content [%]
$h$	Water table [L]
$H$	Henry coefficient [ <i>Pa m<sup>3</sup> mol<sup>-1</sup></i> ]
$K_{AW}$	Henry constant, air-water partition coefficient [-]
$K_d$	Solid water distribution coefficient [L <sup>3</sup> M <sup>-1</sup> ]
$k_f$	Hydraulic conductivity [L t <sup>-1</sup> ]
$K_{OC}$	Soil organic-carbon partition coefficient [L <sup>3</sup> M <sup>-1</sup> ]
$K_{OW}$	Octanol-water partition coefficient [-]
$L$	Solubility [M L <sup>-3</sup> ]
$L$	Length of the wetland [L]
$L_m$	Contaminant loss via microbial degradation [M L <sup>-2</sup> t <sup>-1</sup> ]
$L_p$	Contaminant loss via plant uptake [M L <sup>-2</sup> t <sup>-1</sup> ]
$L_{photo}$	Contaminant loss via photolysis [M L <sup>-2</sup> t <sup>-1</sup> ]
$L_s$	Contaminant loss via sorption on filter material [M L <sup>-2</sup> t <sup>-1</sup> ]
$L_v$	Contaminant loss via volatilization [M L <sup>-2</sup> t <sup>-1</sup> ]
$L_{v,phyto}$	Contaminant loss via phytovolatilization [M L <sup>-2</sup> t <sup>-1</sup> ]
$L_{v,surface}$	Contaminant loss via surface volatilization [M L <sup>-2</sup> t <sup>-1</sup> ]
$LD_{50}$	Lethal dose, 50% [-]
$m_{air,in/out}$	Contaminant mass detected on the adsorption tubes positioned in the inlet and outlet wind flux of the DACs [M]
$M_{in}$	Total mass of tracer applied [M]
$M_{out}$	Total tracer mass recovered [M]
$n$	Gravel porosity [-]
$N$	Number of continuously stirred tank reactors [-]
$nHRT$	Theoretical hydraulic retention time [t]
$Pé$	Péclet number [-]
$p_i$	Vapor pressure of the component $i$
$P_r$	Pumping rate [L <sup>3</sup> t <sup>-1</sup> ]

$Q$	Flow rate [ $L^3 t^{-1}$ ]
$Q_A$	Flow through the cross section A [ $L^3 t^{-1}$ ]
$q_{et}$	Evapotranspiration rate per surface area [ $L^3 t^{-1}$ or $L t^{-1}$ ]
$q_{in}$	Inflow specific discharge [ $L t^{-1}$ ]
$Q_{in}$	Mean inflow rate [ $L^3 t^{-1}$ ]
$Q_{mean}$	Mean flux [ $L^3 t^{-1}$ ]
$Q_{out}$	Mean outflow rate [ $L^3 t^{-1}$ ]
$\overline{Q}_{\Delta(t),in/out}$	Average inflow or outflow water volume between two consecutive concentration samplings at time $t_i$ and $t_{i+1}$ [ $L^3 t^{-1}$ ]
$R$	Gas constant [ $J K^{-1} mol^{-1}$ ]
$R$	Tracer recovery rate [%]
$R_D$	Retardation factor [-]
$R_W$	Contaminant removal efficiency for the water phase [%]
$S$	Conductivity [ $mS L^{-1}$ ]
$t_{1/2}$	Half-life [t]
$t_{break}$	Tracer breakthrough time [t]
$t_s$	Initial tracer detection [t]
$T$	Temperature [ $K$ ; $^{\circ}C$ ]
$T$	Transpired water volume [ $L^3 L^{-2} t^{-1}$ ]
$T_{air}$	Air temperature [ $K$ ; $^{\circ}C$ ]
$v$	Flow velocity [ $L t^{-1}$ ]
$V_{in}$	Water influx [ $L^3 L^{-2} t^{-1}$ ]
$V_{out}$	Water outflux [ $L^3 L^{-2} t^{-1}$ ]
$V_{out}(t)$	Outflow volume accumulated for the time t [ $L^3 t^{-1}$ ]
$v_p$	Vapor pressure [ $Pa$ ]
$V_{preprecipitation}$	resp. $V_{rain}$ : precipitation flux [ $L^3 L^{-2} t^{-1}$ ]
$V_s$	Sample volume [ $L^3$ ]
$V_{sys}$	Estimated pore volume [ $L^3$ ]
$v_{x,y}$	Flow velocity at the sampling position (x,y) [ $L t^{-1}$ ]
$w$	Width of the wetland [L]
$x$	Flow distance [L]

### Greek symbols

$\alpha_L$	Longitudinal dispersivity [L]
$\delta^{13}C$	Carbon stable isotope ratio [‰]

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$\Delta m$	Overall contaminant loss in the water phase [M]
$\Delta t$	Time interval [t]
$\Phi$	Dimensionless flow-weighted time [-]
$\theta$	Porosity [-]
$\rho$	Density of the gravel/soil matrix [M L <sup>-3</sup> ]
$\sigma^2$	Variance [t <sup>2</sup> ]
$\sigma_{\Theta}^2$	Dimensionless variance [-]
$\tau$	Mean residence time [t]
$\tau_{corr}$	Mean residence time corrected for sorption processes [t]
$\tau_{fit}$	Mean residence time of the analytical fit of the RTD [t]





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# 1 Introduction

## 1.1 Chemically Contaminated Groundwater

### 1.1.1 Sources, Pollutants, and Risks

Spills of chemicals during processing or transport, improper waste management, industrial and agricultural run-off water, as well as leaking underground storage tanks have caused manifold and often multi-component contamination of surface and subsurface soils and waters (EEA, 2000). Volatile organic compounds (VOCs), both chlorinated and non-chlorinated aromatic and aliphatic ones, account for the most frequently detected contaminants, given that they are produced in large volumes and are widely used for industrial purposes (USGS, 2006; ATSDR, 2011). Prominent applications of VOCs are the use as solvents (benzene, dichloromethane), degreasing agents in metal industries (benzene, perchloroethene) or precursors (chlorobenzenes) for the production of pesticides, pharmaceuticals and dyes (WHO, 2003b, 2004b,a). As part of the National Water-Quality Assessment Program of the US Geological Survey (USGS) (1985 - 2002), water samples from groundwater and drinking water wells from all over the USA, including 98 aquifers and 3500 wells, have been analyzed for 60 VOCs (USGS, 2006). In this context, it was found that chloroform, the solvents perchloroethene and trichloroethene, and the gasoline oxygenate methyl tert-butyl ether (MTBE) were the most ubiquitous VOCs in both rural and urban areas. Explicitly, for 12% of the wells VOCs were detected at concentrations of potential concern exceeding the US EPA maximum contaminant levels (Squillace et al., 1999, 2002). Although VOCs, once released into the environment, are subject to volatilization, they may also leach from surface waters and soils into groundwater. Under the prevailing anaerobic conditions in most aquifers, many pollutants are recalcitrant. Depending on their toxicity and persistence they therefore impair the quality of groundwater and can cause adverse effects on ecosystems and human health, if used e.g. as drinking water. The US EPA currently lists about 1300 contaminated sites on the National Priority List (NPL) (EPA, 2012); the number of potentially contaminated sites in Germany and Europe

varies depending on the literature source (Germany: 240.000 (EEA, 2000) - 288.000 (LABO, 2011); Europe: 750.000 (CARACAS, 1998) - 1.400.000 (EEA, 2000)). Even though only about 10-15% of the suspected sites in Germany may actually require remediation (Frauenstein, 2009), these facts point out that contamination of soil and water is a worldwide problem. As a consequence, risk mitigation as well as the timely and cost-effective remediation of contaminated soil and groundwater is of political concern.

### 1.1.2 Groundwater Treatment Options

Groundwater remediation can be realized by a multitude of strategies either in situ or ex situ (Farhadian et al., 2008b). A general classification of the available treatment options is derived from the underlying treatment principle, thus one is distinguishing between physical (e.g. air stripping, adsorption on activated carbon (AC) or zeolites, extraction, electro-kinetic separation), chemical (e.g. oxidation with ozone or hydrogen peroxide, reduction at reactive walls of zero-valent iron, immobilization, combustion, UV radiation, heterogeneous catalysis) and biological (e.g. biostimulation, bioaugmentation) methods.

Commonly, the remediation of groundwater is accomplished by so-called pump-and-treat (P&T) technologies in which groundwater is pumped from the subsurface to ex situ remediation facilities and - after being cleaned to certain concentration limits - is either re-injected into the aquifer or infiltrated into surface waters. The appropriate treatment technique is predetermined by the physico-chemical characteristics of the respective contaminant(s), such as volatility, sorption tendency, or potential for biodegradation. For example, the stripping technique is best applicable for pollutants with a vapour pressure of  $>70 \text{ Pa}$  and a Henry coefficient of  $>70 \text{ Pa m}^3 \text{ mol}^{-1}$  (Bracke and Klümper, 2005). Although P&T technologies effectively reduce pollutant concentration and control plume migration they are technically extensive and costly since they require (i) steady energy input for the continuous pumping of water as well as for the treatment facilities and (ii) constant maintenance work. For sites characterized by low pollutant concentrations, P&T remediation measures may not be technically and economically feasible within a reasonable timeframe (Travis and Doty, 1990), in particular for strongly sorbing compounds e.g. polycyclic aromatic hydrocarbons (PAHs). Applying in situ methods such as funnel and gate technologies or reactive barriers instead avoids complex pumping, but still involves enormous technical effort and site disturbance. Therefore, there is an increased interest in moving away from traditional

remediation approaches towards innovative low-tech in situ bioremediation technologies (Collins et al., 2002), which take advantage of the natural potential of microorganisms for remediating contaminated waters. Prerequisites for the successful application of natural attenuation (NA) are: (i) reasonable biodegradability of the pollutants, (ii) availability of microorganisms capable to metabolize the present pollutants, and (iii) convenient geochemical conditions (e.g. electron donors/acceptors, redox potential (Eh), temperature (T), nutrients) for microbial degradation. One prominent example of a passive in situ bioremediation strategy is represented by the constructed wetland (CW) approach, a phytoremediation technique which combines the remediation potential of both microorganisms and plants (Wissing and Hofmann, 2002). Phytoremediation can be used for the treatment of shallow groundwater and surface waters as well as soils and sediments. Overall, phytoremediation is minimally invasive and entails substantially reduced costs compared with conventional P&T clean-up technologies (EPA, 1998c; van Epps, 2006). Furthermore, it is potentially applicable to a variety of pollutants, including petroleum hydrocarbons, chlorinated solvents, metals, nutrients, and PAHs (e.g. Pivetz, 2001; Collins et al., 2002; Kadlec and Wallace, 2008; Imfeld et al., 2009).

## 1.2 Constructed Wetlands: Principles

Constructed wetlands are composed of aquatic or marsh plants, e.g. common reed (*Phragmites australis*), cattail (*Typha spp.*) or soft rush (*Juncus spp.*), growing on gravel or sediment or in hydroponic solution, but always in waterlogged environments and hence reducing conditions. The macrophytes are adapted to the oxygen deficiency in the root zone by the development of a tubular plant tissue, the aerenchyma, which works as a gas-transport system. Oxygen, either plant-produced or atmospheric, is transported into the rhizosphere, enabling root respiration and also forming oxidative protection layers against phytotoxins (e.g. soluble heavy metals, hydrogen sulfide) (Stottmeister et al., 2003). Overall oxygen transfer rates have been found to cover a broad range of  $0.02 - 12 \text{ g } O_2 \text{ m}^{-2} \text{ d}^{-1}$  for common wetland plants, e.g. common reed, cattail, pondweed, or sea grass (e.g. Armstrong et al., 1990; Brix, 1990; Wu et al., 2001; Tyroller et al., 2010; Lai et al., 2012).

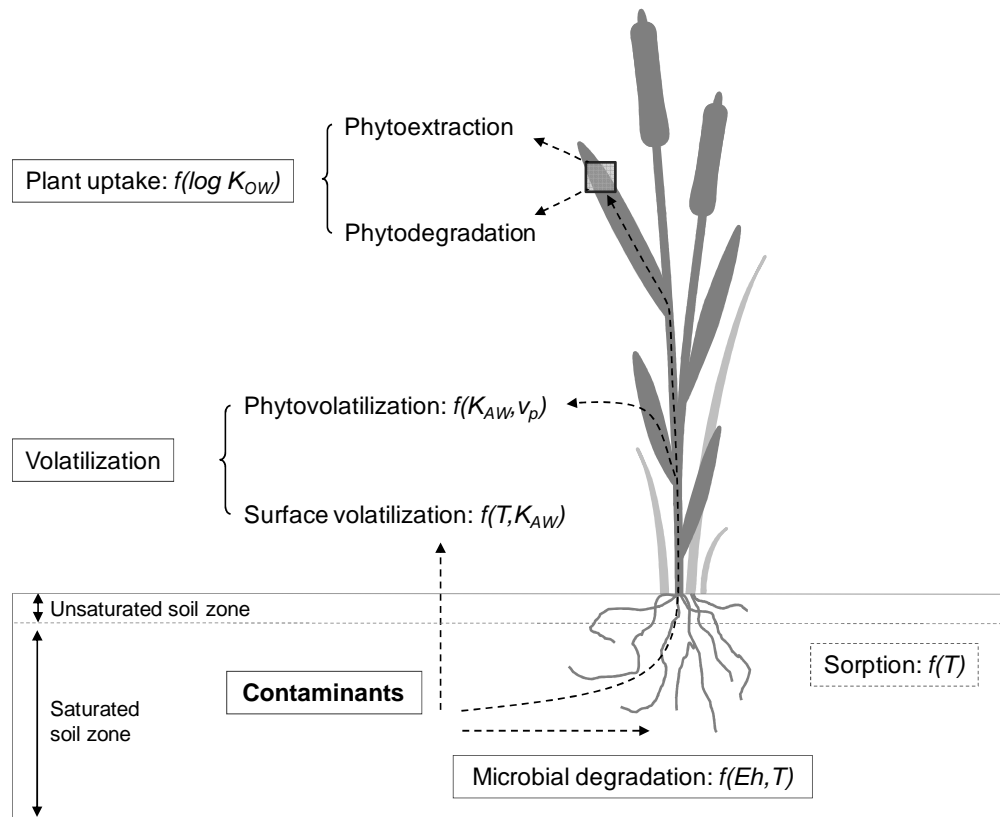
The bioremediation potential of wetlands basically results from the plant associated microorganisms, both rhizospheric and endophytic, which are able to metabolize hazardous substances, using them directly as carbon or energy source to support growth or as secondary substrates in co-metabolic pathways (Kadlec and Wallace, 2008). The plants

influence microbial degradation by providing suitable conditions for the microorganisms and even foster microbial turnover processes in the rhizosphere by emitting root exudates (mostly short chain organic acids, sugars, amino acids, and vitamins), which stimulate the growth of the microbial population, the community diversity and also the enzymatic activity (Pivetz, 2001; Stottmeister et al., 2003). The plant-mediated release of oxygen creates microsites with steep oxygen/Eh gradients at the root surfaces. Given that plant activity changes during the course of the day (Armstrong and Armstrong, 1990), the geochemical conditions in the CW filter also vary on a diurnal scale (Wießner et al., 2005). Consequently, a broad consortium of aerobic and anaerobic microorganisms can exist in adjacent niches, enabling complex contaminant degradation pathways. This stimulation of microbial growth, activity and diversity is referred to as the rhizospheric effect (Williams, 2002).

During the transport of the contaminated water through the CW filter, the fate of the pollutants is governed by a number of competing processes: microbial degradation in the rhizosphere, sorption onto the filter matrix, surface volatilization, and plant uptake with subsequent phyto-degradation, extraction and/or -volatilization (Pivetz, 2001; Pilon-Smits, 2005) (see Figure 1.1). Microbial degradation in the rhizosphere and in planta alone leads to effective mass elimination, the other abiotic pathways - although potentially contributing to a decrease of aqueous contaminant concentration - merely promote the transfer of contaminants from the water phase into adjacent compartments (soil, plants or atmosphere). Overall, the evaluation of CW treatment performance with respect to microbial contaminant turnover, as well as the contribution of abiotic processes to actual load removal is essential for the implementation of CWs as a reliable clean-up technology. In the following each process is discussed briefly, including its determining factors and relevance in CW systems.

### 1.2.1 Microbial degradation

Microbial degradation of pollutants requires the availability of terminal electron acceptors (TEA; e.g.  $O_2$ ,  $NO_3^-$ , Mn(IV), Fe(III),  $SO_4^{2-}$ ,  $CO_2$ ) or electron donors (organic compounds, e.g. short chain organic acids, organic pollutants) - depending on the contaminant degradation mechanism (reductive or oxidative) - in addition to the presence of microorganisms capable of metabolizing the respective chemical at the ambient conditions (Farhadian et al., 2008b). From an energetic point of view, microbial oxidation is most effective when oxygen is used as TEA. However, the amount of oxygen transferred into the rhizosphere is often limited, since the oxygen diffusion from the atmosphere



**Figure 1.1:** Contaminant fate in a CW: microbial degradation in the rhizosphere, sorption, plant uptake, phytotransformation, phytovolatilization, and surface volatilization. Adapted from Reiche (2010).

through the water sediment interface is relatively slow (Imfeld et al., 2009), and the surplus from plant-mediated transfer deducted by root respiration mostly turns out to be relatively small (Dong et al., 2011). In oxygen depleted environments, alternative TEAs yielding less energy may be used instead, following the order nitrate, Mn(IV), Fe(III),  $SO_4^{2-}$ ,  $CO_2$ . Microbial turnover in treatment wetlands has been proven effective for many chemicals and wastewaters, including (ground)water contaminated with organic chemicals such as chlorinated (e.g. Pardue, 2005; Braeckevelt et al., 2011a,b) and non-chlorinated (e.g. Ferro et al., 2002; Moore et al., 2002; Bedessem et al., 2007) VOCs, pesticides (e.g. Haberl et al., 2003) or pharmaceuticals (e.g. Matamoros and Bayona, 2006), or inorganic chemicals such as ammonium, nitrate, sulfide and phosphorus in domestic and agricultural wastewater (e.g. Vymazal, 2007; Konnerup et al., 2009) or landfill leachate (e.g. Bulc, 2006; Yalcuk and Ugurlu, 2009).

### 1.2.2 Sorption

For CWs in the early stage of operation, sorption may constitute a significant contaminant sink, considering the sorption capacity of the previously unexposed filter material. Once sorption-desorption has reached equilibrium and system disturbance by e.g. temperature fluctuations remain small, sorption processes only retard contaminant flow and lower effective contaminant availability (Imfeld et al., 2009), thus indirectly affecting biodegradation rates, but net-loss can be assumed to be negligible. The amount of adsorbed contaminant primarily depends on the soil organic-carbon partition coefficient  $K_{OC}$  of the contaminant, which can be roughly estimated from the octanol-water partition coefficient  $K_{OW}$ , e.g. according to the approximation by Karickhoff (1981) ( $K_{OC} = 0.411 * K_{OW}$ ), as well as the organic carbon content of the filter matrix  $f_{OC}$ . High sorption tendency has been shown for lipophilic compounds, such as PAHs (e.g. Nam et al., 1998; Achten et al., 2011) or chlorinated hydrocarbons (chlorinated benzenes: e.g. Pardue et al. (1993); Lee et al. (2003, 2009b); chlorinated ethenes: e.g. Kassenga et al. (2003)). Nevertheless, many studies provided evidence that adsorbed and even aged contaminants are still bioavailable and can therefore be biodegraded, albeit at reduced rates (e.g. Lee et al., 2003, 2009b; Haritash and Kaushik, 2009). The immobilization of contaminants in the sediment or within the wetland plants following root uptake may account for a considerable mass reduction in the aqueous phase and represent a desired remediation process in particular for persistent substances, such as PAHs (e.g. Fountoulakis et al., 2009) or heavy metals (Cu, Cr, and Ni) (e.g. Liu et al., 2010), but immobilization entails the necessity for post-treatment of sediment and/or plants.

### 1.2.3 Volatilization

The tendency for direct volatilization at the air-water interface can be predicted from the compound specific Henry's Law coefficient  $H$  ( $H = p_i / c_W, Pa m^3 mol^{-1}$ ) or the dimensionless Henry constant  $K_{AW}$  ( $K_{AW} = c_A / c_W = H / RT$ ), both describing the contaminant distribution between water and air under equilibrium conditions for non-dissociated volatile compounds (Kadlec and Wallace, 2008). The actual distribution depends on many factors such as T, pH, salinity, or co-solutes/solvents (Staudinger and Roberts, 2001; Schwarzenbach et al., 2003). For highly water soluble compounds effective water-air transfer might as well result from phytovolatilization rather than from surface emission only. Hence, in order to estimate the volatilization potential of a specific compound, both the Henry coefficient and the water solubility in conjunction



with the water volume transpired by the plants have to be taken into account. In subsurface-flow CW systems soil-borne emission may be restrained by the relatively slow diffusive gas transport through the unsaturated zone to the surrounding atmosphere (Imfeld et al., 2009). Total volatilization (including surface- and phyto-volatilization) in plant-mediated remediation systems was shown to be a relevant removal process for many VOCs, such as benzene, toluene, ethyl-benzene, o/m-xylenes (BTEX) (e.g. Burken and Schnoor, 1998), MTBE (e.g. Hong et al., 2001), gas-condensate C<sub>5</sub>-C<sub>12</sub> hydrocarbons (e.g. Moore et al., 2002), MCB (e.g. Braeckevelt et al., 2011a), and TCE (e.g. Ma and Burken, 2003). In case atmospheric half-lives are reasonably short and hazardous effects towards environmental goods and humans can be assumed to be negligible, volatilization represents a desired removal pathway.

#### 1.2.4 Plant uptake

The plant uptake of organic contaminants can be estimated according to the transpiration stream concept. Plants actively take up water and nutrients via the roots in order to sustain their metabolism; this concomitantly involves the transfer of dissolved contaminants into the plants (Pivetz, 2001). The transpiration stream concentration factor (TSCF) indicates the effectiveness of contaminant translocation and in principle refers to the contaminant concentration as the fraction in the xylem of the plant (the transpiration stream) and the root-external solution (Briggs et al., 1982; Shone and Wood, 1972). The TSCF can also be approximated from the  $K_{OW}$ , either as a Gaussian (Briggs et al., 1982) or sigmoidal relationship (Dettenmaier et al., 2009), of which the latter was found to give a better fit in particular for highly water soluble, low log  $K_{OW}$  compounds such as MTBE, TBA, or sulfolane (Dettenmaier et al., 2009). It is accepted that uptake is most effective for contaminants with intermediate log  $K_{OW}$  values in the range of 0.5 and 3 (Trapp and Karlson, 2001; Stottmeister et al., 2003); compounds with higher or lower log  $K_{OW}$  will be rather retained in or excluded from passing biomembranes (Pilon-Smits, 2005). Notably, the uptake of inorganic compounds represents a biological rather than a physical process and occurs by the help of membrane transporter proteins (Pilon-Smits, 2005). Plant uptake has been investigated for different plant species and pollutants, amongst others for BTEX in Canna (e.g. Boonsaner et al., 2011) and poplar (e.g. Burken and Schnoor, 1998), MTBE in poplar (e.g. Hong et al., 2001), phenanthrene and chlorobenzene in willow and bulrush (e.g. Gomez-Hermosillo et al., 2006), ammonium in bulrush (e.g. Kadlec et al., 2005), and metals such as Cd, Cr, Cu, Ni, Pb, and Zn in reed and wheat (e.g. Tani and

Barrington, 2005; Du Laing et al., 2009; Liu et al., 2010). Once taken up, pollutants are subject to (i) phytoaccumulation, (ii) enzymatic or bacterial phytodegradation, and/or (iii) phytovolatilization. Phytovolatilization turned out to be relevant at high vapor pressure  $v_p$  ( $> 1.01 \text{ kPa}$ ; Burken and Schnoor (1998)) and high  $K_{AW}$  ( $\gg 10^{-5}$ ; Trapp and Karlson (2001)). In comparison to microbial degradation contaminant plant uptake is considered to be of minor importance (Kadlec and Wallace, 2008).

### 1.2.5 Wetland Design

From a technological point, CWs can be classified by many aspects, such as the flow regime (vertical flow (VF), horizontal flow (HF)), the mode of operation (e.g. surface or subsurface flow, up or down flow direction, continuous or discontinuous charging), and the plant growth (submerged, emerged and free floating) (Vymazal, 2007; Vymazal and Kröpfelová, 2008). Widely-used in real-scale application are VF systems, mostly with subsurface feeding, horizontal subsurface flow (HSSF) wetlands and free water surface (FWS) wetlands (Kadlec and Wallace, 2008). The crucial factors in the decision process for choosing the right CW for a wastewater are the systems-specific oxygen transfer rate and the emission potential to such a degree as the amount of oxygen should be high or low enough to allow oxidative or reductive contaminant degradation and the emission potential should be low to prevent pollution of ambient air. Aspects such as energy and areal demand come second. System characteristics and application potential are briefly discussed hereafter.

VF filters are mostly operated in a discontinuous mode. As the water percolates through the filter air refills the void pore space, resulting in increased oxygen input ( $30 - 90 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ; Tyroller et al. (2010)). Therefore, VF CWs show great potential for aerobic degradation, e.g. nitrification of ammonium (Langergraber et al., 2009), but provide less suitable conditions for anaerobic processes, e.g. denitrification to  $\text{N}_2$  (Kadlec and Wallace, 2008). In general, it has to be kept in mind that VF filters use less space, but require higher energy input for the water pumping than HF filters. HSSF CWs are oxygen limited due to the permanent saturation of the filter, and the oxygen input is rather low ( $0.3 - 12 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ; e.g. Armstrong et al. (1990); Tyroller et al. (2010)). However, for treating aerobic and anaerobic degradable contaminants in the same wetland HSSF CWs may be advantageous, since they constitute both aerobic and anaerobic filter zones (Faulwetter et al., 2009). A possibility to increase the oxygen input in HF wetlands is given by modifying the flow regime from continuous feed with stable water level to a tidal flow system, since draining promotes the transport of air

from the unsaturated zone into the filter (Vymazal, 2011). Overall, for HF and VF filters the potential for direct emission of volatile compounds in CWs composed with a vadoze soil zone is low, but phytovolatilization may constitute a considerable removal pathway. FWS wetlands contain open water areas, planted with submerged, emerged or free floating macrophytes. An important advantage of FWS systems is that they have higher time-space-yields and can be operated at variable water depth, which e.g. is relevant for handling storm waters (e.g. Tanner and Headley, 2011). Particularly submerged and emerged vegetated systems are rather aerobic since the direct water-air contact favors  $O_2$  transfer into the wetland. Yet, treating volatile compounds may entail increased emission. Given that in floating systems the water compartment is shielded from direct air contact, these systems are supposed to exhibit reduced emission potential. Overall, in order to treat water containing a complex mixture of aerobic and anaerobic degradable contaminants, a combination of various CW systems in so-called hybrid systems might be appropriate as to exploit the system-specific advantages (Vymazal, 2011).

### 1.2.6 The role of the wetland filter

As the name “constructed wetland” already implies, CWs are designed treatment systems. This allows to improve treatment efficiency to a certain extent by optimizing design parameters that have an impact on contaminant removal effectiveness. The porous filter media influences the treatment potential in various aspects. The filter provides attachment surfaces for microbial biofilm formation, supports plant growth by stabilizing roots/plants and affects the water flow through the CW (Sundberg et al., 2007; Kadlec and Wallace, 2008; Lee et al., 2009a). Roughly speaking, the smaller the grain size the larger the surface area for microbial colonization, but the smaller the hydraulic conductivity  $k_f$  and the higher the chance for clogging of the filter. Balancing the parameters grain size and conductivity with regard to high removal and low hydraulic failure, a grain size of  $>0.06 \text{ mm}$  (up to  $10 \text{ mm}$ ) enabling  $k_f > 10^{-5} \text{ m s}^{-1}$  was found to be favorable (Stottmeister et al., 2003). The roots also function as a surface for microbial growth and loosen the compaction of the porous media, thus preventing the clogging of free pore volume and keeping the filter water permeable (Vymazal and Kröpfelová, 2008).

As treatment efficiency positively correlates with the contact time between contaminants and microorganisms the evaluation of CW flow characteristics is crucial in order to optimize CW design and treatment performance. In the ideal case, water and its

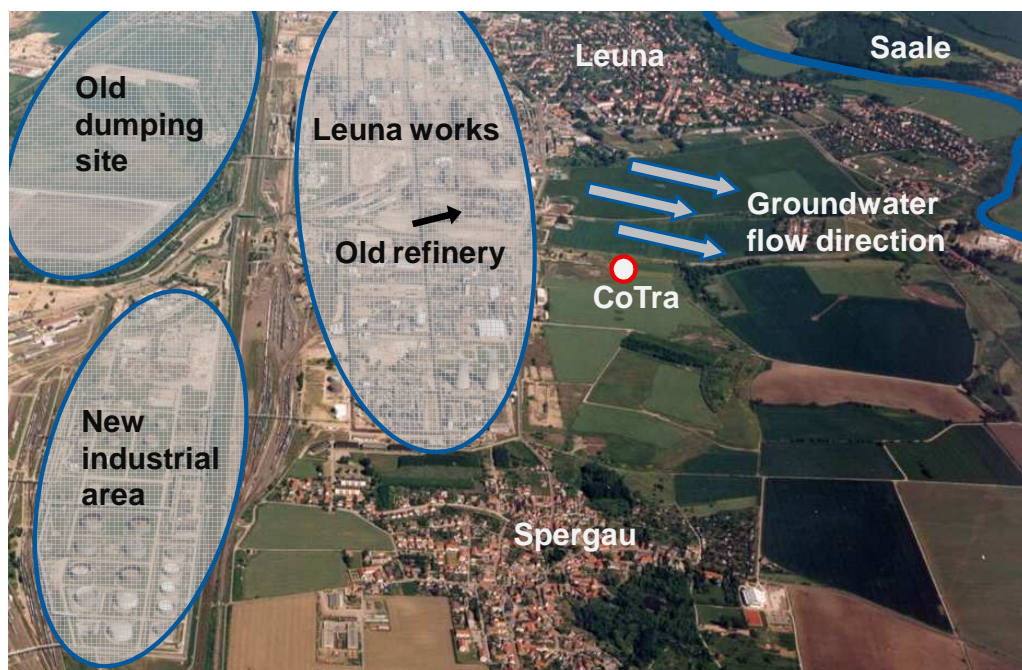
constituents would flow through the filter according to plug flow conditions uniformly utilizing the entire filter volume (Holland et al., 2004). However, in reality, local flow velocities and actual filter residence time are influenced by water loss due to evapotranspiration, the occurrence of different flow paths due to short circuits as well as dead zones and sorption processes. The outcome of this is a distribution of residence times (Werner and Kadlec, 2000). To what extent actual flow deviates from ideal flow and whether or not short circuits and dead zones exist can be assessed by conducting tracer experiments and evaluating the actual residence time distribution by means of the temporal moment concept (e.g. Werner and Kadlec, 1996; Yu et al., 1999; Luo et al., 2006), a statistical approach commonly used to gain information on solute transport mechanisms in soils (e.g. Cirpka and Kitanidis, 2000). For information on how to apply the temporal moment approach in tracer test analysis and what can be concluded from the temporal moments with respect to wetland specific transport parameters see chapter 4.

### 1.3 Industrial site “Leuna”

The industrial site “Leuna” is located in Saxony-Anhalt, Germany, and has been used as a chemical production area since 1916 for the generation of ammonia used as a precursor in nitrogen fertilization and explosives production, the production of ammonium sulfate, and the synthesis of methanol (high pressure synthesis) and synthetic petrol (high pressure hydrogenation of charcoal). As a result of World War II, more than 80% of the facilities were destroyed, which lead to massive local contamination of the saturated and unsaturated zone (Harpke et al., 2006). Between 1949 and 1990, the range of products was expanded, including synthetic rubber, educts for other plastics, e.g. caprolactam for synthesizing the polyamide fiber nylon, and surfactants. Besides, crude oil refinement and the large-scale MTBE production were established (UBA, 2003; LAF, 2009; Schirmer et al., 2012). Given the overall chemical production during that time, accidental spills and leakages from underground storage tanks, and war damage, groundwater and soil at the Leuna site are nowadays heavily contaminated by a diverse chemical mixture: petroleum hydrocarbons (PHCs;  $\sim 1\text{-}10\text{ mg L}^{-1}$ ), BTEX (up to more than  $10\text{ mg L}^{-1}$ ), MTBE (up to  $125\text{ mg L}^{-1}$ ), PAHs (up to more than  $100\text{ }\mu\text{g L}^{-1}$ ), phenols (up to more than  $100\text{ mg L}^{-1}$ ), and ammonium sulfate (UBA, 2003; LAWA, 2004; Niemes and Schirmer, 2010).

An overview of the site-specific geology and hydrogeology is given by Martienssen et al.

(2006). The respective aquifer consists of coarse to fine gravel and has a thickness of 1 - 4 m. The average groundwater table is located 3 - 4 m below the surface, groundwater flow is in southeastern direction, mean hydraulic conductivity was determined as  $k_f = 4 \times 10^{-4} \text{ s}^{-1}$ , and the mean groundwater velocity is 0.3 - 1.0 m d<sup>-1</sup>. Considering the groundwater flow direction, the contaminant plume endangers the nearby river Saale and the drinking water supply plant, which are located 1500 - 2000 m downstream of the mega-site, see Figure 1.2. Minor effects have already been noticed, given that MTBE levels in the Leuna community water system were significantly elevated (712 ng L<sup>-1</sup>) compared to e.g. bank filtered water from Rhine and Main river (<100 ng L<sup>-1</sup>) (Kolb and Püttmann, 2006). Nevertheless, these values are still below the organoleptic/odor threshold of 20 - 40 µg L<sup>-1</sup> (EPA, 1997). As the aquifer has a very low self-cleaning potential for the prevalent pollutants, and in order to prevent further contamination of yet unaffected areas, a impermeable wall (400 m long and 15 m deep) was installed perpendicular to the groundwater flow direction. Furthermore, two clean-up techniques were implemented: (i) an on-site P&T-facility comprising a stripping plant combined with an air purification unit containing activated carbon, (ii) a so-called oxygen-wall,



**Figure 1.2:** Location of the industrial site “Leuna” and the experimental field site CoTra. Adapted from Martiensen et al. (2006). Source of the picture: regional office for contaminated sites “Landesanstalt für Altlastenfreistellung ÖGP Leuna”(LAF, 2012).

used to stimulate the natural remediation potential of the aquifer by oxygen sparging (Niemes and Schirmer, 2010).

Within the framework of the *Compartment Transfer* (CoTra) project, initiated by the Helmholtz Centre for Environmental Research - UFZ, Leipzig, an experimental site was built nearby the Leuna works in 2006/2007 to investigate the potential of alternative near-natural treatment systems for remediating the local groundwater. Based on the principle idea to use flood plains for protecting surface water bodies (e.g. the river Saale) downstream of the plume, the concept of the CoTra project relies on the transfer of the contaminated anaerobic groundwater into more aerobic environments in order to promote microbial contaminant degradation. The treatment plant comprises the following remediation systems at the pilot-scale: HSSF CWs, VF CWs and aerobic ponds (Ruegner et al., 2007).

## 1.4 Main groundwater pollutants at the CoTra plant

Benzene, MTBE and ammonium are the main pollutants in the groundwater used for feeding the CoTra treatment plant. During the first year of plant operation (06/2007-06/2008), the concentrations of benzene, MTBE and ammonium-nitrogen were  $19 \pm 3.7$ ,  $3.8 \pm 0.8$ , and  $45 \pm 4.1 \text{ mg L}^{-1}$ , respectively. Contaminant characteristics, production volumes, sources and emission pathways, and potential degradation pathways are briefly discussed hereafter. The most important physical and chemical characteristics of the organic model compounds are summarized in Table 1.1.

### 1.4.1 Benzene

Benzene ranks in the top 20 of the most abundantly produced petrochemicals in the USA (ATSDR, 2007). Today, its major use is as a feedstock in the production of aromatic intermediates - with ethylbenzene (52%), cumene (20%) and cyclohexane (13%) as the most prominent ones - which are further processed for manufacturing plastics, resins, drugs, dyes, and plant protection agents; the raw compound serves as a solvent, e.g. for ink or glue (RPA, 2000; UBA, 2006; EPA, 2007). Being a natural component of crude oil, benzene is also present in gasoline (EU, 2008b). In 2010 for example the production volume in Germany amounted to 2.1 million  $t a^{-1}$  (VCI, 2011). More than half of the German benzene demand is derived by extractive distillation of naphtha (a product of crude oil distillation which is rich in aromatic compounds, with a benzene content of 31-40 v-%); less important methods to obtain benzene are

isolation from coke oven gas by means of special washing processes, thermal or catalytic toluene dealkylation and toluene disproportionation (Index, 2001).

Classified as a human carcinogen by the IARC (International Agency for Research on Cancer), benzene can cause severe health damage even at short term contact (IARC, 1999a; WHO, 2011). According to a prioritization based on a combination of compound frequency, toxicity, and potential for human exposure, benzene ranks 6<sup>th</sup> on the priority list of hazardous substances (ATSDR, 2011). In order to minimize human health risk, the EU drinking water directive (1998/83/EC) constitutes a threshold of  $1 \mu\text{g L}^{-1}$ , and benzene emission to ambient air is restricted to  $5 \mu\text{g m}^{-3}$  (2008/50/EC). Besides, the maximum content in European gasoline was lowered from 5% to 1% (v/v) since 2000 (Directive 1998/70/EC) (U.S. gasoline standards are even lower since 2011: 0.62% (v/v) (EPA, 2010)), and the overall use as a solvent has decreased due to the implementation of the solvent emission directive 1999/13/EC in 2001 (UBA, 2002).

The release of benzene into the environment occurs from point (e.g. oil refineries, industrial production and processing) and nonpoint sources (e.g. exhaust of motor vehicles, fuel evaporation at automobile service stations, cigarette smoke) (EU, 2008b). Inhalation is the dominant pathway for human exposure, accounting for >99% of the daily intake (ATSDR, 2007). According to Wallace (1996) smokers have an average benzene body burden about 6-10 times that of non smokers, and receive ~90% of their benzene exposure (~2 mg per day) from smoking. Outdoor air concentrations average out at  $<2 \mu\text{g m}^{-3}$  (<1 ppb) (EU, 2008b; EPA, 2008). In case contamination results from fuel hydrocarbons, e.g. by leaking underground storage tanks, benzene occurs concomitantly with other aromatic hydrocarbons such as toluene, ethylbenzene and m-, o- and p-xylene. In groundwater benzene is considered as fairly mobile, given that the  $K_{OC}$  value (predicted from the  $K_{OW}$ ) is not large enough ( $K_{OC} \sim 80$ ) to cause significant retardation (Zogorski et al., 1997) and water solubility is relatively high (see Tab. 1.1). Of course, the mobility of benzene in the subsurface also depends on the organic carbon content ( $f_{OC}$ ) of the respective aquifer. Due to the high volatility, indicated by the Henry constant and the vapor pressure, benzene tends to evaporate from surface soil or water. In the atmosphere benzene is chemically degraded by photooxidation with hydroxyl or nitrogen oxide radicals and ozone, of which the reaction with hydroxyl radicals is fastest and thus most important, resulting in a half-life of several days (5-13) (Zogorski et al., 1997; WHO, 2003a; EPA, 2004; EU, 2008b).

Common in situ benzene treatment technologies involve soil vapor extraction (e.g. Soares et al., 2010) and air sparging (e.g. Reddy et al., 1995; Bass et al., 2000), aiming to enhance volatilization and concomitantly promoting biodegradation; ex

**Table 1.1:** Physical, chemical and biological characteristics and limit values for the organic model compounds benzene and MTBE (at 20-25°C).

		MTBE	Benzol
$v_P$	[kPa]	12.7 <sup>1,5</sup> ; 19.13-19.13 <sup>6</sup>	33.5 <sup>1</sup> ; 32.66-33.55 <sup>7</sup>
$H$	[ $P m^3 mol^{-1}$ ]	557 <sup>1,2</sup>	43.8 <sup>8</sup> ; 60 <sup>1</sup>
$K_{AW}$	[-]	0.22 <sup>5</sup>	0.024-0.12 <sup>7,3</sup>
$L$	[ $g L^{-1}$ ]	1.78 <sup>1,4</sup> ; 1.8 <sup>2</sup>	51.26 <sup>1</sup> ; 43-54.3 <sup>3</sup> ; 42 <sup>8</sup>
$LogK_{OW}$	[-]	2.13 <sup>1,2,3</sup>	1.06 <sup>8</sup> ; 1.2 <sup>1,3,4</sup>
$LogK_{OC}$	[-]	1.92 <sup>1</sup>	1.11 <sup>1</sup> ; 1.04-1.09 <sup>3</sup>
$t_{1/2}$ atmosphere	[d]	5-13 <sup>2,12,14</sup>	3-6 <sup>8</sup>
$LD_{50}$ oral intake***	[ $g kg^{-1}$ ]	1-10 <sup>12</sup>	3.9 <sup>13</sup>
Drinking water limit	[ $\mu g L^{-1}$ ]	1 <sup>**</sup> , <sup>15</sup> ; 10 <sup>10</sup>	20-40 <sup>11</sup>
Air emission limit	[ $\mu g m^{-3}$ ]	5 <sup>9</sup>	n.v.a.*

<sup>1</sup>Arnold et al. (2007); <sup>2</sup>UBA (2006); <sup>3</sup>Zogorski et al. (1997); <sup>4</sup>Schirmer (1999); <sup>5</sup>Howard (1990); <sup>6</sup>Mackay et al. (1992); <sup>7</sup>Mackay et al. (1993); <sup>8</sup>EU (2002); <sup>9</sup>2008/50/EC; <sup>10</sup>WHO (2011); <sup>11</sup>EPA (1997); <sup>12</sup>WHO (2003a); <sup>13</sup>WHO (2005); <sup>14</sup>EU (2008b); <sup>15</sup>DVGW (2001); \*no value available; \*\*limit for German drinking water set by the DVGW (2001); \*\*\*for mice and rats.

situ remediation is for example achieved by air stripping and adsorption on activated carbon (e.g. Wirthensohn et al., 2009). Prominent examples for biological treatment are anaerobic/aerobic bioreactors coupled to air-stripping facilities (e.g. Gusmão et al., 2006; Zein et al., 2006; Farhadian et al., 2008a).

Under aerobic conditions benzene is known to be readily biodegraded by ubiquitous microorganisms (van Agteren et al., 1998; Hunkeler et al., 2001; Liou et al., 2008), the most prominent ones are the *Pseudomonas* species (Coates et al., 2002; Hendrickx et al., 2006; Jean et al., 2008). Although the anaerobic degradation of benzene has been considered to be negligible for a long time (Atlas, 1981), nowadays, benzene oxidation under various terminal-electron-accepting processes has been proven (e.g. Lovley, 2000; Chakraborty and Coates, 2004; Kleinstaubler et al., 2012). In the lab, degradation was shown under nitrate-reducing (e.g. Burland and Edwards, 1999; Coates et al., 2001; Chakraborty et al., 2005), sulfate-reducing (e.g. Phelps et al., 1996; Vogt et al., 2007; Herrmann et al., 2010), iron-reducing (e.g. Lovley et al., 1994; Jahn et al., 2005; Botton and Parsons, 2006), and even under methanogenic (e.g. Kazumi et al., 1997; Weiner and Lovley, 1998; Masumoto et al., 2012) conditions. *Dechloromonas*, *Azoarcus*, *Deltaproteobacteria* and *Clostridia* have recently been identified as organisms involved in anaerobic benzene metabolism (e.g. Chakraborty and Coates, 2004; Cupples, 2011; Meckenstock and Mouttaki, 2011). At field sites, anaerobic benzene degradation was



demonstrated many times (e.g. Lovley et al., 1994; Fischer et al., 2007; Vogt et al., 2007). Besides, the stimulation of in situ biodegradation by injection of nitrate and sulfate was also shown (e.g. Cunningham et al., 2001).

#### 1.4.2 Methyl *tert*-butyl ether

Methyl *tert*-butyl ether (MTBE) has been used as a gasoline additive since the 1970s in order to boost the octane rating and also to improve the combustion process, resulting in lower exhaust emissions (CRS, 2006). It came into widespread use in the 1980s when the toxic octane enhancer tetraethyl lead was phased out (Johnson et al., 2000); the final ban of leaded gasoline became effective in the years 2000 and 1996 in the EU (EU Directive 1998/70/EC) and USA (EPA, 2010), respectively. European gasoline contains ~2% (v/v) MTBE (Effenberger et al., 2001); in the US the addition of MTBE to gasoline was restricted to 0.5% (v/v) (EPA, 2010) from formerly 11-15% (v/v) (EPA, 1998b). In 1997, at the peak consumption of MTBE as a fuel additive, the European production amounted to 3 million  $t a^{-1}$  whereof about 98% was blended with gasoline and only minor amounts were used in the production of isobutylene (1.2%), as a solvent in the pharmaceutical industry (0.3%), or in chemical reactions such as Grignard reactions (EU, 2002; IARC, 1999b). MTBE is manufactured by the chemical reaction of methanol with isobutene over an acidic ion-exchange catalyst (EU, 2002), steamcracking or butane dehydrogenation (Fayolle et al., 2001).

The main source of human exposure to MTBE is likely to occur by inhalation of contaminated air at gas stations and production sites or from automobile exhaust gases. Besides, leaking underground storage tanks and pipelines for petrol storage and distribution, as well as spills during all phases of the petroleum fuel cycle (e.g. production, petrol blending, storage, transport, delivery), resulted in intense contamination of (ground) water and (sub)-surface soils (WHO, 2005; IARC, 1999b), which pose a potential risk for human health as well. According to the IARC MTBE is not classifiable as a carcinogen to humans, though the WHO (2005) and the EPA (1997, 1998b) noted that only very few data exist on the effect of MTBE to humans by inhalation, and no data regarding the oral uptake. Given the very low organoleptic perception level, the US EPA drinking water advisory (EPA, 1997) recommends keeping MTBE levels in the range of 20-40  $\mu g L^{-1}$  or lower for consumer acceptability (CRS, 2006). At these levels MTBE is considered to cause no adverse health effects to humans (EU, 2002).

MTBE is categorized as a low risk chemical, although it is known to be the most mobile and recalcitrant of the gasoline components (Schmidt et al., 2004; WHO, 2011).

Relative to benzene, MTBE exhibits increased water solubility ( $42 \text{ g L}^{-1}$  at  $20^\circ\text{C}$ ; EU (2002)) and decreased tendency for sorption onto soil ( $\log K_{OW} = 1.2$ ; Schirmer (1999)). Therefore, MTBE contamination might spread out over large areas. As indicated by the Henry constant, being one order of magnitude lower than the one of benzene, MTBE is less volatile from water. This also explains why air stripping of MTBE contaminated water is only effective for high air-to-water ratios (200:1), and thus relatively costly. By comparison, an effective air-to-water ratio for benzene is typically about 50:1 (EPA, 1998b). Lifetimes in the atmosphere are in the range of 3-6 days (EU, 2002), and thus similar to those of benzene.

Typically applied physical remediation technologies for MTBE contaminated soil are vapor extraction (in situ) and low-temperature thermal desorption (ex situ) (EPA, 1998a). For contaminated groundwater air sparging (in situ) is used, and given that MTBE does not significantly adsorb to soils and is highly water soluble, also the extraction of groundwater followed by above ground treatment has been shown feasible (e.g. Fayolle et al., 2001; Deeb et al., 2003). Biological treatment includes the use of bioreactors, for example inoculated with material from contaminated aquifers (e.g. Zein et al., 2004, 2006), supplied with oxygen (e.g. Salanitro et al., 2000) or oxygen-release compounds such as  $\text{MgO}_2$  (e.g. Koenigsberg and Sandefur, 1999), or selected microorganisms (e.g. Salanitro et al., 2000) in order to promote biodegradation.

Alkyl ethers such as MTBE are not readily biodegradable (Zogorski et al., 1997; Fayolle et al., 2003). Nevertheless, in recent years biodegradation of MTBE has been shown under oxic (e.g. Schirmer et al., 2003; Volpe et al., 2009; Thornton et al., 2011) and occasionally under anoxic (e.g. Mormile et al., 1994; Bradley et al., 2001; Somsamak et al., 2006) conditions, and also to occur by co-metabolism (e.g. Steffan et al., 1997; Garnier et al., 1999; Liu et al., 2001). For a conclusive overview of biodegradation under various redox conditions and present knowledge of the biodegradability and the degradation pathway see Deeb et al. (2000), Fayolle et al. (2001), and Schmidt et al. (2004). Generally, MTBE metabolism is slow, especially when MTBE is the sole carbon and energy source (Zanardini et al., 2002). Several aerobic degraders that use MTBE as sole C- and energy source have been identified including *Methylobacterium*, *Rhodococcus*, *Arthrobacter* and *Rubrivivax gelatinosus* PM-1 (e.g. Fayolle et al., 2001; Lopes Ferreira et al., 2006). In the field, biostimulation and bioaugmentation by oxygenation and microbial inoculation, respectively, improved MTBE degradation (e.g. Zanardini et al., 2002).

### 1.4.3 Ammonium

The groundwater at the Leuna site is characterized by high ammonium levels accompanied by increased sulfate concentrations. Therefore, the observed ammonium contamination seems to be related to (i) the large scale synthetic production of ammonium sulfate, (ii) the processing of ammonia during nitrogen-fertilizer production, (iii) the coking process and the caprolactam manufacture, during which ammonium sulfate is produced as a by-product, and (iv) the leachate from the near-by dumpsite (UBA, 2003). Ammonium sulfate is known for its use as one of the early nitrogen fertilizers (UNEP, 1998). To a minor extent (~10%) it is used in the chemical industry, in the manufacturing of food additives, and as an ingredient of cleaning products and paints (OECD, 2004). In addition to spillage, anthropogenic emission originates from agricultural activities, e.g. from runoff water containing synthetic fertilizer or animal manure. Naturally, ammonium is produced by the constant microbial mineralization of nitrogen-containing organic matter (ammonification).

Ammonium in the aqueous medium affects the environment in several ways, either directly in the form of ammonium or following microbial oxidation by nitrate and nitrite. In soil systems, ammonium tends to adsorb as an exchangeable ion to positively charged clay surfaces and humic substances (Vymazal, 2007; Lee et al., 2009a), can be taken up and assimilated by plants (OECD, 2004), and furthermore causes acidification of soil and water by nitrification (Kadlec and Wallace, 2008; IFA, 2000). Large amounts of ammonium/nitrate entering pristine aqueous ecosystems (rivers, lakes, oceans), e.g. by agricultural runoff, promote eutrophication (Frink et al., 1999; Ahlgren et al., 2008). Nitrite is known to disrupt multiple physiological functions in aquatic animals and is potentially toxic to infants as it can cause methemoglobinemia (Jensen, 2003). Levels of ammonium in ground/surface waters are usually below  $0.2 \text{ mg L}^{-1}$  (WHO, 2011). Although ammonium does not pose any direct health risk to humans (OECD, 2004), a low limit of  $0.5 \text{ mg L}^{-1}$  is constituted for drinking water in the EU (EU directive 1998/83/EC). This might be related to the fact that ammonium serves as an indicator for contaminated water ( $\text{NH}_4^+$  is formed during microbial decomposition of urea and proteins). Nitrate and nitrite drinking water limits in Europe are  $50 \text{ mg L}^{-1}$  and  $0.5 \text{ mg L}^{-1}$  (EU directive 1998/83/EC).

Various physical-chemical methods can be applied to treat high-strength ammonium wastewaters, including chemical precipitation (e.g. Zhang et al., 2009), air stripping at high pH (e.g. Marttinen et al., 2002; Renou et al., 2008) or ion-exchange using zeolites (e.g. Chang et al., 2009; Widiastuti et al., 2011). For moderate/low-strength ammonium

waters, also the remediation in aerobic-anaerobic bioreactors, such as activated sludge systems (e.g. Carrera et al., 2003), is efficient, proceeding via nitrification-denitrification (e.g. Chan et al., 2009) or partial nitrification-anaerobic ammonium oxidation (e.g. Fux et al., 2002).

Microbial ammonium degradation in CWs occurs via nitrification to nitrate under aerobic conditions, with hydroxylamine and nitrite as intermediates, and, subsequently, via denitrification of nitrate to nitrogen gas (Kadlec and Wallace, 2008). Alternatively, under anaerobic conditions ammonium can be autotrophically converted to  $N_2$  with nitrite as an electron acceptor via the so-called anaerobic ammonium oxidation (anammox) (Lee et al., 2009a). The transformation pathways of the different N species in ecosystems under various environmental conditions are described in the reviews of Paredes et al. (2007) and Lee et al. (2009a).

## 1.5 Current state of research and gaps in wetland phytoremediation of benzene, MTBE and ammonium

Wetland phytoremediation represents a viable treatment technology for lightly to moderately contaminated (ground) water and has attracted increasing interest during the last few years. In most cases, studies investigate CW treatment performance expressed as contaminant removal from the aqueous phase depending on system design and operational mode. Many of them refer to removal efficiency as the mere pollutant concentration decline, and only few report on **areal mass load removal**. The concentration-decline approach is valuable to prove whether effluent water complies with contaminant concentration thresholds and to determine the extent to which design and operational mode affect treatment performance and process indication parameters (e.g. Eh, TEA). However, the assessment of actual mass removal and specifying removal in mass/time/area units is essential to ascertain actual treatment efficiency and to keep results comparable.

For benzene and MTBE, several concentration-decline studies have been published (e.g. Wallace, 2001; Moore et al., 2002; Tang et al., 2009; Rakoczy et al., 2011), while investigations on loads are currently rather rare (e.g. Zhang et al., 2000; Bedessem et al., 2007). Overall, treatment efficiency was found to be (i) site-specific and - for the concentration range investigated - not related to inflow concentrations in particular, and (ii) more efficient for benzene (75-99% concentration decline, e.g. Moore et al. (2002); Tang et al. (2009); Rakoczy et al. (2011)) in comparison to MTBE (<40% concentration

decline, e.g. Keefe et al. (2004); Bedessem et al. (2007)). First evidence on areal load removal showed moderate-to-low efficiency for benzene (e.g. 66% at an inflow load of  $0.18 \text{ g m}^{-2} \text{ d}^{-1}$ ; Bedessem et al. (2007)) and MTBE (e.g. 45% at an inflow load of  $0.67 \text{ g m}^{-2} \text{ d}^{-1}$ ; Zhang et al. (2000)) in comparison to other VOCs (phenol, toluene, TCA, TCE, PCE) for which efficiencies of e.g. 76 - 99% were obtained (at theoretical inflow loadings of  $0.06 - 1.24 \text{ g m}^{-2} \text{ d}^{-1}$ ; Narayanan et al. (1995a,b); James et al. (2009)). The potential for optimizing treatment performance was found promising for subsurface aeration and bioaugmentation, both improving performance by  $\sim 10\text{-}25\%$  (e.g. Zhang et al., 2000; Ferro et al., 2002; Bedessem et al., 2007). Temperature elevation resulted in a similar enhancement (e.g. Eke and Scholz, 2008; Tang et al., 2009).

Regarding ammonium treatment in CWs, many studies address areal load removal, possibly given that for sewage plants this is the common practice. Mostly, data includes total nitrogen (TN) and ammonium-N removal in order to distinguish between transformation and removal. Vymazal (2005) compiled the results of about 100 wetland studies and found average ammonium and TN load removal efficiencies in single-stage HSSF CWs of about 34% and 40% with actual load removal of 133 and  $250 \text{ g N m}^{-2} \text{ a}^{-1}$ , respectively. The performance dependency was investigated for many parameters, including T and season (e.g. Kuschik et al., 2003; Akrotos and Tsihrintzis, 2007), planting (e.g. Zhu and Sikora, 1995; Maltais-Landry et al., 2009), aeration (e.g. Maltais-Landry et al., 2009), fill-and-drain mode (e.g. Vymazal and Masa, 2003), and hybrid systems (e.g. Vymazal, 2005; Tanner et al., 2012). Briefly, high optimization potential was shown for (i) fill-and-drain mode, e.g. ammonium removal was increased by 27% in comparison to non pulsed CWs (Vymazal and Masa, 2003), and (ii) hybrid systems, e.g. for a HF-VF system TN elimination was twice as high compared to the solely HF-treatment (Tanner et al., 2012).

Recent studies on contaminant fate acknowledge the importance of analyzing the role and relevance of different removal pathways. Regarding N fate, studies monitor TN shift and N export in terms of nitrate, ammonium,  $\text{N}_2$  and  $\text{N}_2\text{O}$  to measure biological transformation by nitrification and (in)complete denitrification, and quantify N incorporation in plants and sediment storage. Overall, for various macrophytes plant uptake (with biomass harvesting) accounted for a rather small amount of TN removal ( $<40\%$ ) in comparison to biological transformations (up to 60-84%) (e.g. Tanner et al., 2002; Lee et al., 2009a; Maltais-Landry et al., 2009; Tunçsiper, 2009), and sediment storage was negligible ( $\leq 6\%$  of TN removal) in planted CWs (e.g. Tanner et al., 2002; Reinhardt et al., 2006). For benzene and MTBE, researchers investigated surface- plus phyto-volatilization (e.g. Burken and Schnoor, 1998; Hong et al., 2001; Keefe et al.,

2004), plant uptake (e.g. Burken and Schnoor, 1998; Arnold et al., 2007; Mothes et al., 2010), and rhizo- or endopyhtic degradation (e.g. Trapp et al., 2003; Porteous Moore et al., 2006; Rakoczy et al., 2011). First conclusions can be derived from these studies: (i) benzene and MTBE are taken up by plants, (ii) benzene is susceptible to degradation in planta, but MTBE is not, (iii) phytovolatilization from tree cuttings is high in absence of degradation, e.g. 28% and 18% of the applied mass of MTBE and benzene was phytovolatilized, respectively, (iv) actual mass of benzene and MTBE retained in plant (willow, poplar, reed) tissue is small (<5% of the total removal), and (v) rhizospheric biodegradation may represent the major removal pathway for benzene in pilot-scale CWs, accounting for 85% of the total removal. Unfortunately, either not all potential removal pathways were assessed for one single system or studies were conducted at lab-scale and/or with trees instead of helophytes. Thus, transferability and extrapolation of results to pilot/full-scale CW applications have been limited so far.

However, conclusive insights into the fate of all kinds of contaminants in wetlands are needed to determine and classify actual removal efficiencies and to comprehensively optimize the respective treatment systems. Thereby, it is essential to assess contaminant load removal and to quantify and distinguish between elimination and compartment transfer processes as to proof treatment reliability. This is especially important for the treatment of VOCs, also with regard to legal issues such as emission limits. To date, mass balance studies for benzene and MTBE are rare and were mostly performed at lab-scale, under lab conditions and with tree cuttings. Hence, assessing the fate of VOCs in wetlands using a mass balance approach at a large scale and under field conditions is still missing. Moreover, to conclusively evaluate CW treatment performance and allow for a valid comparison of different treatment systems, the performance evaluation has to include the assessment of system-specific flow behavior.

## 1.6 Aims and outline of the thesis

The overall aim of this thesis was to evaluate the potential of five differently designed pilot-scale constructed wetlands to treat groundwater contaminated with benzene, MTBE and ammonium in a field approach under northern European climate, and to assess contaminant fate and removal pathways on a mass balancing approach following up the gaps of knowledge in wetland phytoremediation described above. Gaining insights regarding these aspects is expected to be crucial for the technological optimization

and implementation of treatment wetlands at a large-scale and to evidence whether CWs constitute a reliable alternative technology for the treatment of VOCs. The HSSF wetlands of investigation were: three planted gravel filters, whereof two contained filter material additives, either charcoal or ferric oxide; one unplanted gravel filter used as a reference; one hydroponic plant root mat.

**The specific objectives of the thesis are to:**

- (i) investigate whether and to which extend the wetland design (gravel filter CW, hydroponic plant root mat) and the filter additives (charcoal, ferric oxide) affect treatment performance,
- (ii) determine the effect of environmental parameters (T, season) on contaminant removal,
- (iii) assess areal load removal efficiencies by taking into account water loss due to evapotranspiration,
- (iv) elucidate the fate of benzene and MTBE by quantifying potential removal pathways, in particular surface- and phytovolatilization, plant uptake and microbial degradation,
- (v) determine the wetland specific flow characteristics and relate these to achieved load removal efficiencies,
- (vi) evaluate the local flow behavior of the gravel wetlands to calculate contaminant loads within the filter.

This doctoral thesis is written in publication format and is based on the following three scientific articles. In addition, the thesis comprises an introductory and summary chapter, embedding the articles into the current state of research in wetland phytoremediation. Paper I and II have been published in **Environmental Pollution** and **Environmental Science & Technology**, respectively, and paper III has been accepted for publication in **Water Research**.

**Paper I** (Chapter 2) is a comparative study, reporting on the effectiveness of the gravel CWs and the hydroponic plant root mat to improve the groundwater quality regarding the concentrations of benzene, MTBE and ammonium, and evaluating how the wetland design and the filter additives affect treatment performance. Positive effects were suggested by (i) increasing pollutant-microorganism contact time due to contaminant sorption processes or (ii) providing additional electron acceptors for microbial contaminant turnover. Besides, for characterizing the CWs and for identifying

processes involved in contaminant removal and to furthermore investigate the potential for microbial degradation of benzene and MTBE in the rhizosphere, seasonal and spatial concentration dynamics of pollutants and environmental parameters (nitrate, nitrite, Fe(II), Eh, O<sub>2</sub>, T) were monitored and most probable number tests and microcosm studies were performed.

**Paper II** (Chapter 3) evaluates contaminant fate and potential removal pathways in wetlands by setting up an integral mass balancing approach. The study aimed to assess actual treatment efficiency on the basis of areal loads and to quantify removal of benzene and MTBE by emission into the air by surface- and phyto-volatilization, plant uptake and biodegradation. In both cases, the dependency on seasonal effects and particularly the wetland design (the comparison of conventional gravel beds with a hydroponic plant root mat system) was of interest. Overall, this study presents the first complete mass balance for VOCs in pilot-scale HSSF CWs.

**Paper III** (Chapter 4) completes the performance evaluation of the CWs by providing a detailed characterization of the system-specific hydraulic flow behavior. Specifically, it aims to investigate the impact of wetland design and operational mode on the flow characteristics, and to examine the relation between the wetland-specific flow characteristics and the achieved removal efficiencies. Aiming to overcome the black box concept often applied to CWs, particular focus was laid on the analysis of local tracer breakthrough curves in order to assess variability of flow velocities within the filters for localizing stagnant zones and for predicting local flow rates and depth-dependent contaminant loads.

Supplementary material of the article published in *Environmental Science & Technology* and of the article accepted for publication in *Water Research* can be found in the Appendix A.1 and A.2, respectively.





## Bioremediation of benzene-, MTBE- and ammonia-contaminated groundwater with pilot-scale constructed wetlands

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### ABSTRACT

In this pilot-scale constructed wetland (CW) study for treating groundwater contaminated with benzene, MTBE, and ammonia-N, the performance of two types of CWs (a wetland with gravel matrix and a plant root mat) was investigated. Hypothesized stimulative effects of filter material additives (charcoal, iron(III)) on pollutant removal were also tested. Increased contaminant loss was found during summer; the best treatment performance was achieved by the plant root mat. Concentration decrease in the planted gravel filter/plant root mat, respectively, amounted to 81/99% for benzene, 17/82% for MTBE, and 54/41% for ammonia-N at calculated inflow loads of 525/603 mg/m<sup>2</sup>/d, 97/112 mg/m<sup>2</sup>/d, and 1167/1342 mg/m<sup>2</sup>/d for benzene, MTBE, and ammonia-N. Filter additives did not improve contaminant depletion, although sorption processes were observed and elevated iron(II) formation indicated iron reduction. Bacterial and stable isotope analysis provided evidence for microbial benzene degradation in the CW, emphasizing the promising potential of this treatment technique.

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### 1. Introduction

Multi-component contamination of groundwater, caused by leakage of storage tanks, improper handling during processing or transport, and disposal at industrial sites (e.g. refineries), causes a major hazard for the environment. In aquifers, anaerobic conditions often prevail; pollutants recalcitrant under these conditions migrate with the groundwater flow and may affect sensitive environments, e.g. surface water or groundwater bodies used as drinking-water resources. Fuel hydrocarbons, BTEX compounds (benzene, toluene, xylenes and ethylbenzene), and fuel oxygenates such as methyl-tert-butyl-ether (MTBE) are among the most commonly found groundwater pollutants (Schmidt et al., 2004); they are all to be found at the investigated site in the Leuna region (Saxony-Anhalt, Germany), accompanied by high levels of ammonia.

For sites contaminated with a broad spectrum of compounds at low concentrations, conventional groundwater remediation techniques such as “pump and treat” methods are often applied. However, these techniques are invasive, cost intensive, and economically inefficient, hence new strategies are needed (Salt et al., 1998; Dietz and Schnoor, 2001). Phytoremediation, with natural or constructed wetlands, is thus a promising near-natural in situ water treatment method, since plants greatly enhance microbial growth

and thereby contaminant degradation by supplying oxygen and root exudates in the rhizosphere (Williams, 2002; Stottmeister et al., 2003; Kadlec and Wallace, 2008). Two principal technical design schemes for constructed wetlands (CWs) can be distinguished: the conventional CW, consisting of a gravel or soil filter matrix on which the wetland plants grow, and the more sophisticated floating/non-floating plant root mat systems, supported by a raft or the densely woven root bed only.

To date, there have been very few pilot- and large-scale field applications involving phytoremediation of chemically contaminated waters with CWs (Ferro et al., 2002; Moore et al., 2002; Singh and Jain, 2003; Wallace and Kadlec, 2005; Bedessem et al., 2007), although application of CWs to clean household waters is very common (Haberl et al., 2003; Vymazal and Kröpfelová, 2008; Vymazal, 2009). In most cases, the CW approach is applied as a secondary treatment step, the so-called polishing technique (Dietz and Schnoor, 2001; Van Epps, 2006). Some studies do report on large-scale applications to treat groundwater containing BTEX and MTBE (Wallace, 2001; Moore et al., 2002; Keefe et al., 2004; Wallace and Kadlec, 2005), but the concentrations treated are rather low. Some strategies to promote contaminant turnover have been tested, but these were limited to bioaugmentation (Mehmannavaz et al., 2002; Nurk et al., 2009), the use of engineered bacteria (Barac et al., 2004), and the aeration of wetlands (Wallace and Kadlec, 2005). In general, the availability of electron acceptors is a crucial aspect in microbial contaminant oxidation (Farhadian et al., 2008).

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In the present study we investigated the treatment potential and effectiveness of different types of horizontal–flow (HF) CWs for remediating groundwater heavily contaminated with benzene, MTBE and ammonia in a field approach. Two types of wetlands, gravel-filter-based systems and a plant root mat system, were examined over a period of 24 months. Furthermore, we aimed to increase removal efficiency using ferric oxide and charcoal as filter material additives in order to promote microbial degradation by either providing additional electron acceptors for contaminant turnover or extending the contact time between pollutant and microorganisms due to contaminant sorption processes. The study focuses on i) the effectiveness of HF CWs with and without soil filter material for the remediation of contaminated groundwater at the pilot-scale, ii) the environmental factors affecting contaminant removal, and iii) the effects of the soil filter material additives (charcoal and ferric oxide) on pollutant removal. Additional efforts were made to assess the microbial contaminant degradation potential of the CWs.

## 2. Materials and methods

### 2.1. Site and project description

In 2007, the pilot-scale treatment plant “Compartment Transfer” (CoTra) was built next to the former refinery and industrial site near the town of Leuna, Saxony-Anhalt, Germany, in order to investigate the potential of near-natural remediation methods for diverse contaminated waters. Horizontal-flow constructed wetlands (HF CWs) represent one of the realized strategies. At the site, large-scale processing of ammonia, used as a precursor for nitrogen fertilizers and explosives since the beginning of the 20th century, and petroleum refinement, starting in the 1970's, led to massive contamination of groundwater and soil (UBA, 2003).

### 2.2. System design

CWs (A, B, C, D and E) were designed to function in horizontal subsurface flow mode; they each consisted of a steel basin (5 m × 1.1 m × 0.6 m). Four wetlands were filled with fine gravel (grain size 2–3.2 mm) up to 0.5 m height. One of these was kept unplanted as a reference (referred to as system D); the others were planted with common reed (*Phragmites australis*) but differed in terms of the filter additive contained (system A: no additive; system B: charcoal (0.1%-wt); system C: ferric oxides (goethite and lepidocrocite: 0.5%-wt)). The water level was set to 40 cm, resulting in a vadose soil zone of 10 cm. System E was designed as a plant root mat without any soil filter material and was operated at a water depth of 15 cm. Inflow water (Table 1) was supplied from a nearby groundwater well. The outflow was controlled by a pump connected to a switch responding to the set water level, and was quantified by flow meters. The filter beds containing gravel were continuously operated under identical conditions since July 2007; the operation of the plant root mat started in April 2008. Table 2 summarizes the wetland characteristics.

**Table 1**

Groundwater inflow characteristics based on samples collected through 2 years of field plant operation (July 2007–July 2009), including values for total organic carbon (TOC), 5-day biological oxygen demand (BOD<sub>5</sub>), total organic carbon (TOC), and inorganic carbon (IC).

Parameter	C <sub>average</sub> (range) [mg/L]	Stdev (σ)	Number of samples (n)
Benzene	20 (13–32)	3.3	72
MTBE	3.7 (1.2–5.9)	0.7	73
NH <sub>4</sub> <sup>+</sup> -N	45 (37–63)	3.4	73
NO <sub>3</sub> <sup>-</sup>	0.1 (0–6.6)	0.78	73
Fe (total)	6.0 (0.6–9.1)	1.3	74
Fe <sup>2+</sup>	5.6 (0.2–9.7)	2.2	73
SO <sub>4</sub> <sup>2-</sup>	8.0 (1.5–27.6)	6.1	74
PO <sub>4</sub> <sup>3-</sup>	1.4 (0.1–2.7)	0.7	72
Dissolved O <sub>2</sub> <sup>a</sup>	0.005 (–)	–	–
Eh <sup>b</sup>	–460 (–)	–	–
COD	114 (79–130)	13	71
BOD <sub>5</sub>	58 (34–93)	14	68
TOC	39 (25–50)	5	65
IC	281 (261–314)	15	27

<sup>a</sup> Oxygen sensor (TriOxmatic<sup>®</sup> 700 IQ, WTW), measured every 15 min.

<sup>b</sup> pH/redox sensor (pH/redox SensoLyte<sup>®</sup> 700 IQ, WTW), measured every 15 min.

**Table 2**  
Constructed wetland characteristics.

System	A	B	C	D	E
Gravel (2–3.2 mm) <sup>a</sup>	×	×	×	×	–
Additive: activated carbon	–	0.1 %-wt	–	–	–
Additive: ferric oxide	–	–	0.5 %-wt	–	–
<i>Phragmites australis</i>	×	×	×	–	×
Inflow rate (Q) [L/h]	6.0	6.0	6.0	6.0	6.9
Water level [cm]	40	40	40	40	15

<sup>a</sup> Height of the gravel filter: 50 cm.

### 2.3. Sampling procedure and pore water analysis

Inflow and outflow water samples were collected at regular intervals, every one to two weeks. Sample preparation and conservation as well as analyses of organic compounds, cations (NH<sub>4</sub><sup>+</sup>, Fe<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>) and anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>) are described briefly hereafter. For determination of the organic compounds, a headspace GC/MS facility (Agilent: auto-sampler with oven 7694, GC 6890, MS 5973) with an HP-1 column (60 m × 0.25 mm × 1 μm) was used and the following temperature program was applied: 35 °C (6 min), 4 °C/min to 120 °C, 20 °C/min to 280 °C (5 min). Prior to analysis, the samples were equilibrated at 70 °C for 60 min. Ammonia and o-phosphate concentrations were measured photometrically (EPOS Analyzer 5060, Eppendorf AG) according to DIN 38406-E5 and DIN 38405-D11-1. For conservation purposes, samples for cation (Fe<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>) measurement were acidified (HNO<sub>3</sub> to pH = 1–2) directly after the sampling procedure. The elemental analyses were performed using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (type: Spectro Ciros, Spectro Analytical Instruments GmbH). Anion concentrations (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>) were analyzed by means of ion chromatography, using a DX500 (Dionex GmbH) and following the EN ISO 10304-2 and DIN 38405-19 protocols.

In addition, pore water was sampled in discrete sampling campaigns. Water from the filter was pumped (peristaltic pump, type: REGLO digital, Ismatec) from nine points distributed along the flow path (0.9 m, 2.5 m, 4.1 m) and the depth of the filter (20 cm, 30 cm, 40 cm). Sample preparation and analysis of organic compounds were performed according to Reiche et al. (2010). Briefly, microbial degradation processes were inhibited by adding NaN<sub>3</sub> (final concentration 0.65 g/L), and bromobenzene-d5 (final concentration 250 μg/L) was used as an internal standard. The samples were analyzed using a headspace GC/MS facility (Agilent: G1888; 7890 GC, 5975MS) equipped with an HP-1MS column (30 m × 0.25 mm × 1 μm), applying the following temperature program: 35 °C (3 min), 5 °C/min to 100 °C, 15 °C/min to 200 °C (5 min). Prior to analysis, samples were equilibrated at 80 °C for 30 min. Concentration analyses of cations (NH<sub>4</sub><sup>+</sup>, Fe<sup>2+</sup>) and anions (NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>) were carried out as described above. The determination of dissolved oxygen and redox potential was performed on-site in a flow-through mode using an optical trace sensor system (polymer optical fibre, sensor spot FTC-PSt6 and instrument FIBOX-3-trace, PreSens) and redox electrodes (Pt/Ag<sup>+</sup>/AgCl/Cl<sup>-</sup> type Sentix ORP, WTW).

### 2.4. Most probable numbers (MPN)

MPN analyses were carried out with R2A mineral medium (Reasoner and Geldreich, 1985) for growth of total aerobic bacteria, with Brunner medium (Vogt et al., 2002) for benzene degraders, and with STNL medium (modified from Rohwerder et al., 2006) containing vitamins and 0.2 mg/L Co<sup>2+</sup> for MTBE-degrading bacteria. MPN testing was performed with pore water and extracted cell solution of gravel. Samples were taken from the groundwater inflow, the planted systems A, B and E, and the unplanted reference (system D), at 4.1 m flow distance and 20 cm depth in August 2009. Cells were extracted from gravel by a method adapted from Riis et al. (1998). 6 g gravel (ww) were transferred into 50 ml centrifuge vials containing 20 ml 0.2% Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> (pH = 8.5, adjusted with HCl). After vortexing (2 min, highest level) and shaking (30 min, room temperature, 200 rpm), the sample was homogenized via ice-cooled sonification (10 min, 50 W, 0.3 s impulses). The supernatant was used for the MPN analysis on 96-well plates. Dilution series (1:10) were carried out for water samples and extracted cell solution to the lowest dilution 10<sup>-8</sup>. Plates were incubated in an air-tight tank at 26 °C together with a filter moistened with 300 μl of the respective sole carbon source, benzene or MTBE, until no further growth was detected by light transmission measurements (Wallace Victor2, 1420 Multilabel Counter, Perkin Elmer).

### 2.5. Microcosm study

In order to investigate the potential of the microorganisms present in the filter systems for degrading benzene under aerobic conditions, microcosm studies were carried out for the planted and unplanted CW in November 2009. Experiments were performed with gravel and plant roots. Samples were taken at 4.1 m flow distance and 15 cm depth. Glass bottles (1.1 L) filled with 300 ml Brunner medium (Vogt et al., 2002), either approx. 27 g gravel (ww) or 7 g of crushed roots (ww), and 50 ml

benzene solution ( $C_{\text{nominal}} = 66 \text{ mg/L}$ ) were incubated at  $20 \text{ }^\circ\text{C}$  (100 rpm). One control and one autoclaved control were set up. Oxygen concentrations in the liquid and headspace were monitored in situ by an optical trace sensor system (see 2.3) and pure oxygen was re-spiked when depletion was detected. Benzene concentration analysis was performed via GC-FID as described elsewhere (Kleinsteuber et al., 2008). The monitoring of the isotopic composition of the residual C-source benzene allowed for verification of microbial benzene degradation. A shift to  $^{13}\text{C}$ -carbon indicates microbial transformation processes of the parent compound. For isotope analysis, 12 ml water sample was mixed with 0.5 ml conc. HCl in 15 ml glass vials with screw cap and septum to stop microbial degradation. 1 ml n-pentane was added in order to extract the benzene, and after vigorous shaking (4 h,  $4 \text{ }^\circ\text{C}$ ) the samples were frozen at  $-18 \text{ }^\circ\text{C}$  to take-off the n-pentane phase. The isotopic composition of the extracted benzene was analysed using a GC-C-IRMS facility (GC: HP 6890, Agilent; IRMS: Finnigan MAT) containing a ZB-1 column ( $60 \text{ m} \times 32 \text{ mm} \times 1 \mu\text{m}$ ) using the following temperature program:  $40 \text{ }^\circ\text{C}$  (5 min),  $3 \text{ }^\circ\text{C}/\text{min}$  to  $60 \text{ }^\circ\text{C}$ ,  $20 \text{ }^\circ\text{C}/\text{min}$  to  $250 \text{ }^\circ\text{C}$  (3 min).

### 3. Results and discussion

#### 3.1. Effectiveness of constructed wetlands

Benzene, MTBE and ammonia concentrations in the effluent water of the different CW types are depicted in Fig. 1. Three main results can be stated: i) pollutant removal changed over the course of the year, ii) treatment in the plant root mat and the planted gravel filter system resulted in higher pollutant concentration decline in comparison to the unplanted reference, with the plant root mat achieving overall best results, and, iii) treatment efficiency was compound-specific, since benzene and ammonia were removed more effectively than MTBE.

High contaminant concentration reduction was observed for both planted CWs during summer at temperatures above  $15 \text{ }^\circ\text{C}$ . In summer 2008 (27/5–26/8/2008,  $n = 9$ ),  $99 \pm 1\%$  (95% C.I.) and  $81 \pm 7\%$  (95% C.I.) decrease of inflow benzene concentration (19.8 mg/L) could be achieved via treatment with the plant root mat and the planted gravel filter respectively, whereas winter removal rates (4/11/2008–31/3/2009,  $n = 11$ ) were considerably lower, with values of  $43 \pm 18\%$  (95% C.I.) and  $18 \pm 15\%$  (95% C.I.). For ammonia, average summer removal efficiencies tended to be lower, giving the observed values of  $41 \pm 7\%$  (95% C.I.) for the plant root mat and  $54 \pm 17\%$  (95% C.I.) for the CW with gravel matrix. In comparison, the unplanted reference achieved only  $15 \pm 7\%$  (95% C.I.) and  $7 \pm 2\%$  (95% C.I.) decline of benzene and ammonia concentration. These findings underline the importance of plant presence for pollutant removal. Minor MTBE concentration decrease during summer was found for the planted and unplanted CWs containing gravel matrix, with values of  $17 \pm 7\%$ ; (95% C.I.) and  $8 \pm 8\%$ ; (95% C.I.), respectively. For the plant root mat, considerably better results ( $82 \pm 4\%$ ; 95% C.I.) were obtained for the same period.

The comparison with other field studies emphasizes the good contaminant removal efficiencies achieved during summer, considering the relatively high inflow concentrations (20 mg/L benzene, 3.7 mg/L MTBE, 45 mg/L  $\text{NH}_4^+\text{-N}$ ). Similar percentage removal results have been reported for a CW pilot system operated at a former BP refinery in Casper, Wyoming, obtaining 63% benzene and 15% MTBE concentration reduction (Haberl et al., 2003), but inflow concentrations there did not exceed 0.6 mg/L benzene and 1.6 mg/L MTBE (Ferro et al., 2002).

##### 3.1.1. Benzene and MTBE

Less pronounced removal of MTBE compared to benzene might be a result of hindered microbial attack due to the compound structure (Schmidt et al., 2004), overall low growth yields of MTBE-utilizing microorganisms (Salanitro et al., 2000), and inhibition of MTBE degradation by BTEX compounds (Deeb et al., 2001). Other field studies on the treatment of petroleum-contaminated groundwater with CWs (Ferro et al., 2002; Bedessem et al., 2007) and

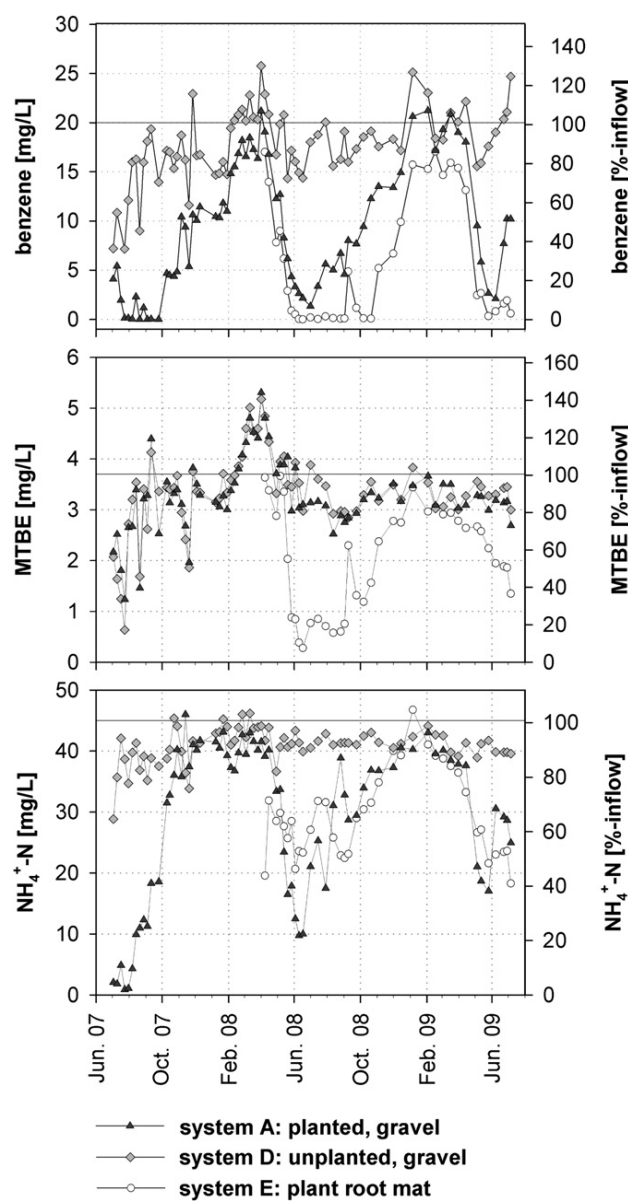


Fig. 1. Benzene, MTBE and ammonia-N concentration in the outflow of the different constructed wetland types: planted gravel filter (system A), unplanted gravel filter (system D), plant root mat (system E). Mean inflow concentrations depicted as horizontal solid line.

aerated trench systems (Jechalke et al., 2010) documented similar results and reported far less MTBE concentration reduction than benzene removal. In contrast, Keefe et al. (2004) found the fate of benzene and MTBE in CWs to be rather similar, ranging within 30–40% for both contaminants, but this might be explained by the low influent contamination concentrations, which were close to detection limits.

However, the good results of the plant root mat in terms of MTBE concentration abatement (82%) during summer could be linked in part to the system properties. The partial open water phase and the lack of a vadose zone presumably promote both atmospheric oxygen diffusion into the water, which leads to enhanced microbial degradation, and volatile organic compound (VOC) emission. Reiche et al. (2010) reported benzene and MTBE volatilization fluxes below 10%

of the total mass removal for the planted HF CWs with gravel matrix at the Leuna site, whereas for an aerated trench system the percentage of mass loss due to emission amounted to 1% for benzene and 53% for MTBE (Jechalke et al., 2010). Given the properties of the different treatment systems, VOC volatilization flux of the plant root mat may be in between the values obtained for the planted gravel system and the aerated trench system. However, volatilization measurements are necessary in order to confirm the good treatment results of the plant root mat, in particular for meeting the legal pollution immission requirements.

VOC emission clearly contributes to MTBE decline but does not completely account for the better performance of the plant root mat, as it does not explain the non-uniform MTBE concentration decrease along the flow path of the plant root mat (Fig. 2). MTBE concentration remained constant in the first part of the flow path, followed by a sudden decrease from 2.94 mg/L (75% residual concentration) at 2.5 m to 1.28 mg/L (33% residual concentration) at 4.1 m, whereby benzene concentration dropped from 3.54 mg/L at 2.5 m to 0.76 mg/L at 4.1 m distance. Therefore, we can assume that after benzene was depleted to values below 3.54 mg/L, MTBE degradation was no longer inhibited by benzene, and as a result, very low outflow MTBE concentrations could be achieved. Suppressed MTBE degradation in the presence of benzene has been reported by Deeb et al. (2001), but in contrast to our study, inhibition lasted until benzene was fully degraded.

### 3.1.2. Ammonia

High  $\text{NH}_4^+$ -N concentration decline during summer and less pronounced removal during winter, as observed in the present study, are consistent with results of He and Mankin (2002). Vymazal (2007) reported total nitrogen removal varying between 40 and 50% in

planted CWs with inflow loadings ranging between 250 and 630 g N/m<sup>2</sup>/a, which are comparable to our wetland loading (416 g N/m<sup>2</sup>/a). Lee et al. (2009) found 30–50% ammonia-N removal efficiency for planted wetlands, whereas a broader range of 15–90% was mentioned by Kadlec et al. (2005) for CWs fed with various waste waters. Microbial transformation (nitrification, denitrification) and plant uptake of ammonia or nitrate are stated to be the main N removal processes in CWs (Huddelston et al., 2000; Lee et al., 2009). According to Molle et al. (2008), who reported N uptake values by *P. australis* during growth of 0.2–0.67 g N/m<sup>2</sup>/d, total nitrogen removal by plant uptake in our CWs ranged between 27 and 78% of the total N removal (0.91 g N/m<sup>2</sup>/d) obtained during summer (27/5–26/8) 2008. The residual amount of N depleted was not recovered as nitrate-N, but this can be explained by nitrification/denitrification taking place simultaneously (Akratos and Tsihrintzis, 2007).

### 3.2. Environmental factors affecting contaminant removal

The presence and activity of plants as well as the temperature affected contaminant depletion to a great extent: the best results were obtained during spring and summer.

Better overall organic chemical removal performance of planted CWs in contrast to unplanted reference systems has been mentioned in the literature many times and is considered to be attributable to the rhizospheric effect (Dietz and Schnoor, 2001; Williams, 2002; Haberl et al., 2003; Gerhardt et al., 2009). Consistent with our findings, Braeckevelt et al. (2008) obtained 33% higher monochlorobenzene removal efficiencies within the first 3 m flow path for the planted filter compared to the unplanted reference.

In northern latitudes, plant activity changes according to season and therefore plant oxygenation and root exudation, both

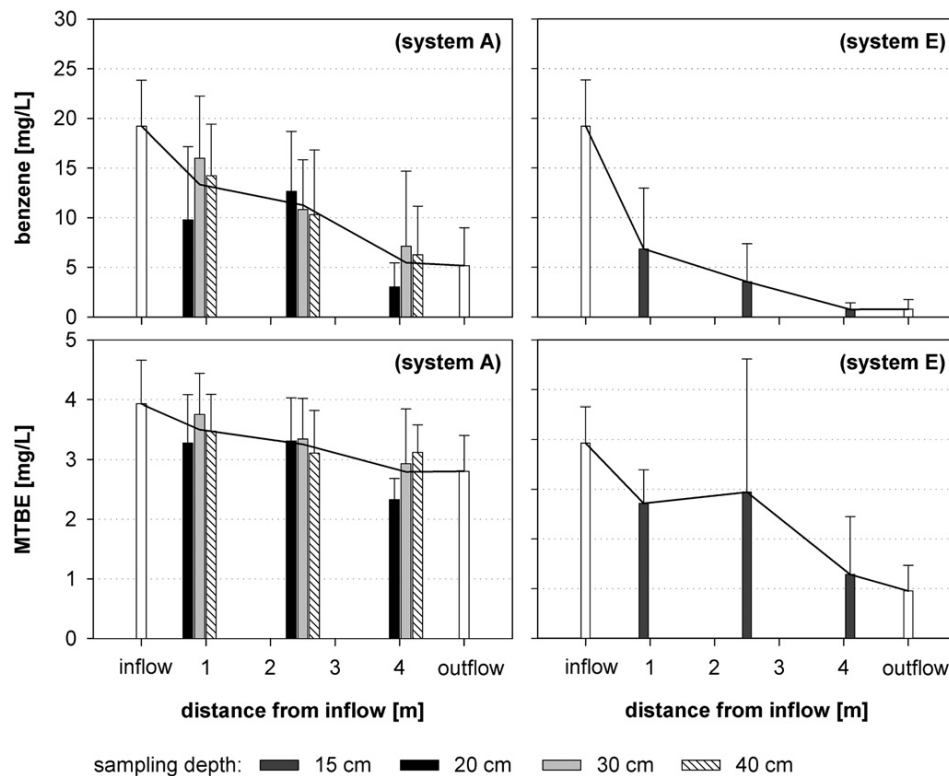


Fig. 2. Benzene and MTBE concentration in the planted CW containing gravel filter matrix (system A) and the plant root mat (system E) depending on flow distance and filter depth during summer 2008. Error bars denote standard deviations of five sampling campaigns (system A: April–July 2008; system B: May–August 2008). Solid black line depicts mean concentration of the different depths.

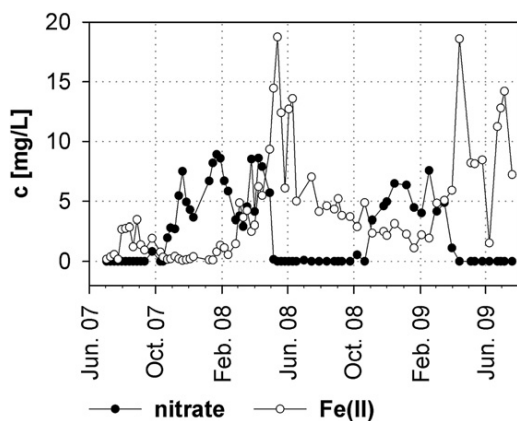


influencing microbial degradation, vary throughout the year. Elevated transpiration rates indicate plant activity and might also affect aqueous contaminant concentration, depending on pollutant uptake via the transpiration stream. In our study, the mean water loss rate during spring and summer 2008 was high for the planted gravel CW ( $70 \pm 2.0$  L/d/CW), clearly exceeding the water loss of the unplanted reference ( $20 \pm 0.9$  L/d/CW) (data not shown). In contrast, both CWs are characterized by similar low winter (2008/2009) water loss rates (planted:  $23 \pm 0.7$  L/d/CW; unplanted:  $18 \pm 0.8$  L/d/CW). Thus, contaminant plant uptake is supposed to be most relevant during summer and negligible during winter. As ammonia is the preferential source for plant nitrogen assimilation, ammonia removal is considered to be highest during spring/summer when plants grow (Vymazal, 2007, in press), as has also been shown in our study.

Elevated temperatures generally favour microbial metabolism (Atlas, 1981; Kadlec and Reddy, 2001). VOC surface volatilization and phytovolatilization are strongly related to the physicochemical properties of the contaminants (vapour pressure, Henry coefficient, log  $K_{OW}$ ) as well as the plants' activity (transpiration rate), which again are temperature-dependent (Atkins, 1996; Imfeld et al., 2009). Our results, implying that contaminant decrease is strongly season-dependent, are consistent with other studies. Tang et al. (2009) reported higher benzene removal efficiency for wetlands in summer than in spring and autumn, and nitrogen removal was found to be most efficient at temperatures above  $15^\circ\text{C}$  (Akratos and Tsihrintzis, 2007), or even at elevated temperatures up to  $20\text{--}25^\circ\text{C}$  (Lee et al., 2009). Better ammonia turnover might be explained by the fact that nitrifying microorganisms are more abundant in spring and summer than in autumn and winter (Kadlec and Wallace, 2008). Vymazal (in press) reported good performance for several CW studies on ammonia removal in northern latitudes, thus microbial adaptation to cold climate is possible in principle, but it may require a longer adaptation time than only one winter season.

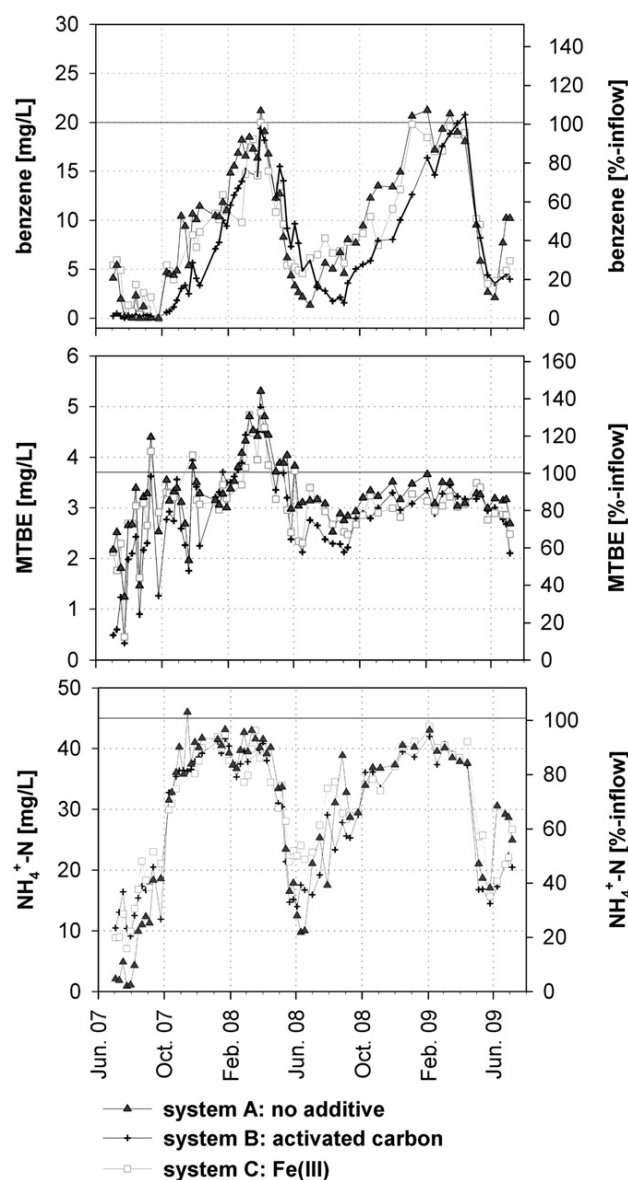
### 3.3. Wetland characteristics

Low maximum oxygen levels of  $0.5$  mg/L obtained along the flow path of the planted CWs characterize the wetlands to be mainly anaerobic. Therefore, oxygen is considered to be one of the limiting factors for contaminant removal throughout the year. A calculation based on oxygen transfer rates for HSSF CWs ( $0.3$  and  $22$  g  $\text{O}_2/\text{m}^2/\text{d}$ ) (Tyroller et al., 2010) would yield theoretical oxygen concentrations of  $>10$  mg/L in our CWs, neglecting oxygen consumption and water loss.



**Fig. 3.** Concentration of redox-relevant species, nitrate and Fe(II), in the outflow of the planted CW containing gravel filter matrix (system A) during sampling period July 2007–July 2009.

Thus, the low measured oxygen concentrations indicate high oxygen consumption and microbial activity in the CWs. Redox potential (Eh) slightly increased after passage of the planted wetlands, with outflow Eh values of  $94$  mV for the system with gravel and  $122$  mV for the plant root mat, whereas the redox potential remained stable at  $\sim 50$  mV for the unplanted reference system. Although Eh values are still within the anaerobic range ( $<300$  mV), this underlines the hypothesis that the planted CWs are more oxidized compared to the unplanted CW and stresses the role of the plants in CW systems. Low levels of nitrite and nitrate in the influent ( $\text{NO}_2\text{-N} = 0.01$  mg/L;  $\text{NO}_3\text{-N} = 0.02$  mg/L) and the outflow of the planted gravel filter ( $\text{NO}_2\text{-N} = 0.007$  mg/L;  $\text{NO}_3\text{-N} = 0.569$  mg/L), the unplanted reference ( $\text{NO}_2\text{-N} = 0.001$  mg/L;  $\text{NO}_3\text{-N} = 0.1$  mg/L) and the plant root mat ( $\text{NO}_2\text{-N} = 0.04$  mg/L;  $\text{NO}_3\text{-N} = 1.17$  mg/L), might be ascribed to limited nitrification capacity of the HF CWs as reported by Faulwetter et al. (2009), but could also be



**Fig. 4.** Benzene, MTBE and ammonia-N concentration in the outflow of the planted gravel filter matrix constructed wetlands depending on the filter material additive: no additive (system A), activated carbon additive (system B), Fe(III) additive (system C). Mean inflow concentrations depicted as horizontal solid line.

a consequence of effective nitrification–denitrification of ammonia-N to gaseous nitrogen. In autumn and winter, considerably higher amounts of nitrate-N were found in pore water samples, with maximum values of 5 mg/L in the plant root mat and 10 mg/L in the planted gravel filter system. This may be caused by i) insignificant uptake of the ammonia nitrification product nitrate by plants during winter, ii) a shift in  $O_2$  consumption from benzene- to ammonia-oxidizing bacteria, considering that the effect of temperature changes on microbial activity is species-dependent, or iii) increased oxygen solubility at lower temperatures. Given the low nitrate level during summer, when ammonia is depleted most effectively and plant oxygenation is supposed to be highest, it can be concluded that nitrification and denitrification took place simultaneously (Akratos and Tsihrintzis, 2007). Seasonal variation of nitrate and Fe(II) concentrations (Fig. 3) give evidence for more aerobic conditions during winter and iron-reducing conditions during spring and summer. This indicates enhanced microbial consumption of the electron acceptors  $O_2$  and Fe(III) during summer and emphasizes how important the availability of appropriate electron acceptors is.

#### 3.4. Effect of filter additives

Contaminant removal efficiencies of the planted CWs containing different filter material additives (no additive vs. charcoal vs. ferrous oxide) did not vary significantly (Fig. 4) in the long run, except for benzene. During the first three months of plant operation (07–09/2007), the mean benzene concentration in the outflow of the system with charcoal (system B) was lower (<0.2 mg/L) than that of the systems without additive (system A) or with Fe(III) additive (system C), which contained 1.3 and 2.3 mg/L, respectively. This effect was presumably due to sorption of benzene to the activated carbon particles. In summer 2008, the highest benzene removal efficiency was achieved two months later than for the other test systems, and considerably lower benzene levels were observed during autumn when temperatures dropped. Both effects might be a response to the temperature dependency of sorption processes. Our initial hypothesis, that sorption results in extended retention time accompanied by increased pollutant degradation, could thus not be proven.

Ferrous iron formation (Fig. 5) was pronounced for the system with ferric iron filter additive in comparison to the system without additive, and may denote enhanced organic carbon oxidation via microbial Fe(III) reduction (Braeckvelt et al., 2008), but did not

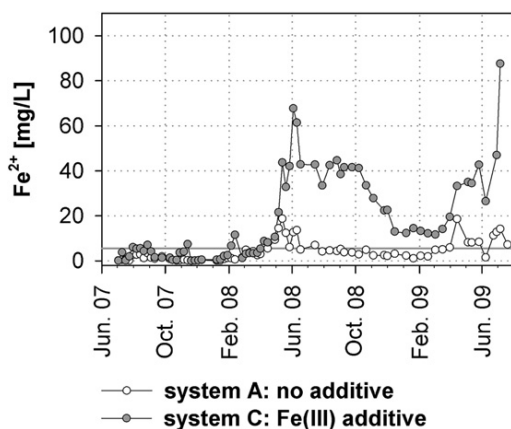


Fig. 5. Fe(II) concentration in the outflow of the planted CW with gravel filter matrix (system A) and the planted CW with gravel/Fe(III) filter matrix (system C) during sampling period July 2007–July 2009. Mean Fe(II) inflow concentration ( $5.6 \pm 0.5$  mg/L; 95% C.I.) depicted as solid line.

Table 3  
MPN (MPN/g water sample, MPN/g gravel (dry weight)) of all aerobic-growing bacteria and of benzene- and MTBE-degrading bacteria in August 2009.

	Aerobes		Benzene degraders		MTBE degraders	
	Water	Gravel	Water	Gravel	Water	Gravel
Inflow	$4.9 \times 10^2$	–	$1.5 \times 10^2$	–	$0.5 \times 10^1$	–
A	$3.3 \times 10^4$	$11 \times 10^5$	$7.8 \times 10^3$	$3.8 \times 10^4$	$0.4 \times 10^2$	$0.8 \times 10^2$
B	$5.5 \times 10^4$	$4.7 \times 10^5$	$3.3 \times 10^3$	$1.6 \times 10^4$	$1.5 \times 10^2$	$0.9 \times 10^2$
D	$1.7 \times 10^4$	$0.8 \times 10^5$	$3.3 \times 10^3$	$0.2 \times 10^4$	$0.8 \times 10^2$	$0.9 \times 10^2$
E	$1.7 \times 10^5$	–	$3.3 \times 10^3$	–	$4.3 \times 10^1$	–

actually result in lower outflow concentrations of the contaminants. Electron-equivalent calculations revealed that even during summer 2008, when high mean Fe(II) levels were detected in the outflow ( $44 \pm 5.5$  mg/L; 95% C.I.), less than 2 mg/L benzene may have been oxidized to  $CO_2$  by microbial ferric iron reduction.

#### 3.5. Indications of microbial degradation

##### 3.5.1. Most probable numbers

MPN cell counts obtained for inflow water were rather low, with values of  $4.9 \times 10^2$ ,  $1.5 \times 10^2$  and  $0.5 \times 10^1$  MPN/g water for aerobic bacteria, benzene degraders and MTBE degraders, respectively. Nevertheless, the inflow can be considered as a continuous source of benzene degraders. Samples taken from the CWs showed 1 to 4 orders of magnitude higher values, following the order aerobic-growing bacteria > benzene degraders > MTBE degraders (Table 3), which points out the beneficial effect of the rhizosphere on microbial growth (Salt et al., 1998; Stottmeister et al., 2003). In turn, MPNs did not depend on the filter material additives.

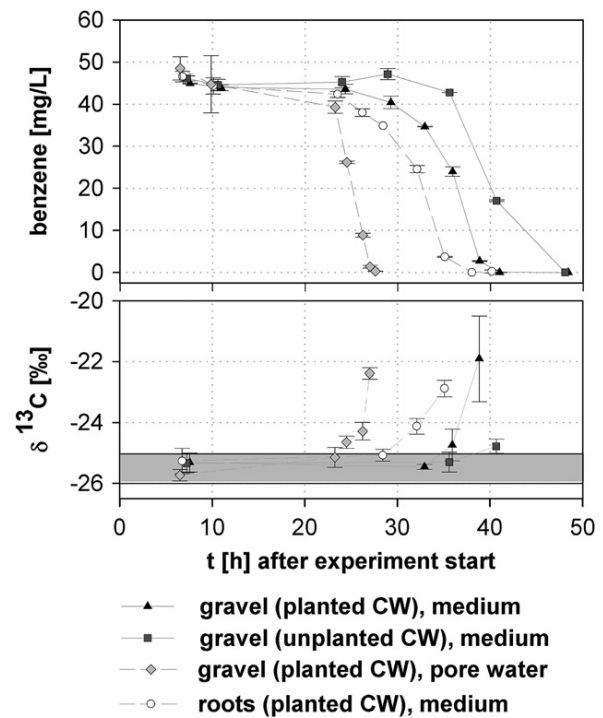


Fig. 6. Microcosm experiment performed with gravel and roots from the planted (system A) and unplanted (system D) constructed wetlands. Mean benzene concentration (top) and respective isotopic signature (bottom) of each microcosm. Error bars denote standard deviation of the means: concentration measurements were performed via duplicate sampling, isotopic composition in triplicate measurement. Gray horizontal bar indicates mean initial benzene isotopic composition ( $-25.53$ ) and standard error ( $\pm 0.5$ ) of all microcosms 7–8 h after experiment start.

According to common acceptance that filter material promotes bacterial biofilm formation (Sundberg et al., 2007), higher bacterial numbers (MPN/g) were obtained for gravel than for water samples. For MPNs performed with the substrate MTBE, only minimal bacterial growth was detected, which may be attributed to residual benzene from the wetland inoculums. MPNs for aerobic benzene degraders ranged from  $3.3 \times 10^3$  to  $7.8 \times 10^3$  MPN/g for water samples and from  $0.2 \times 10^4$  to  $3.8 \times 10^4$  MPN/g for gravel samples. For the water samples, these findings are in agreement with the results of Jechalke et al. (2010), who investigated the treatment performance of aerated trench systems at the Leuna plant.

### 3.5.2. Microbial benzene degradation microcosm experiment

In the aerobic microcosms study, benzene consumption started after a lag phase of 25–35 h and the pollutant was eliminated completely after 35–48 h (Fig. 6). Earliest and fastest turnover was obtained for the microcosm containing gravel from the planted CW and pore water instead of mineral medium. For all microcosms except the one carried out with gravel from the unplanted CW, the decrease of benzene concentration correlated with a significant shift in carbon isotope composition of residual benzene towards heavier isotopes, proving microbial degradation (Fig. 6). The shift of  $\delta^{13}\text{C}$  of about 2.8–3.4‰ demonstrated the benzene degradation potential of the microorganism present in the pore water, on the filter material and on/in the roots of *P. australis*, since a significant increase in  $\delta^{13}\text{C}/^{12}\text{C}$  of the parent compound is generally considered as a proof of microbial contaminant degradation (Hunkeler et al., 2001; Meckenstock et al., 2004).

## 4. Conclusions

The following conclusions can be drawn from this study:

- Treatment performance of HF CWs was highest during spring/summer at temperatures above 15 °C, when plants were growing.
- For the CW with gravel filter, high removal efficiencies were found for benzene (81%) and ammonia (54%), whereas low MTBE depletion (17%) was observed.
- The plant root mat achieved higher organic pollutant concentration decrease than the gravel filter system. Maximum summer removal efficiencies of 99%, 82% and 41% were achieved for benzene, MTBE and ammonia, respectively, showing that the plant root mat is a promising alternative to conventional CWs.
- Oxygen is considered to be one of the limiting factors for contaminant turnover in both wetland types, given low oxygen concentrations (<0.5 mg/L).
- Activated carbon and ferric oxide filter material additives did not promote contaminant removal in the long term, although sorption occurred and elevated ferrous iron formation indicated microbial iron(III) reduction.
- Microbial benzene degradation potential could be proven in an aerobic microcosm study by a shift in carbon isotope fractionation of +2.8–4.3‰, as well as high MPN counts for benzene degraders in water ( $3.3 \times 10^3$  to  $7.8 \times 10^3$  MPN/g) and gravel ( $0.2 \times 10^4$  to  $3.8 \times 10^4$  MPN/g) samples.

The results of the study show HF CWs to be an efficient treatment method for the remediation of chemically contaminated waters and point out that plant root mat systems are a promising alternative to conventional solid filter matrix HF CWs. In order to confirm the good treatment results of the plant root mat and to investigate contaminant fate, emission measurements and mass balance studies for benzene and MTBE in HF CW (with and without gravel

matrix) are currently in progress and will be published hereafter. Since the supply with electron acceptors did not promote contaminant removal, future experiments will deal with the optimization of the removal efficiency with respect to technical approaches, e.g. tidal flow mode as well as coupling of vertical and horizontal filters.

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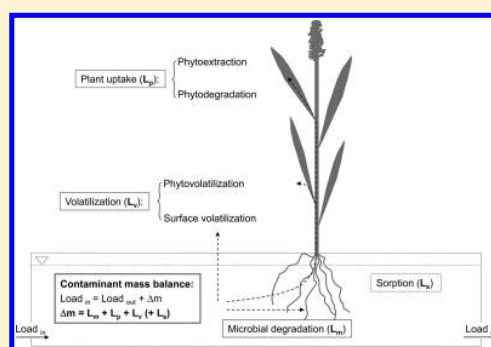
## Performance Evaluation Using a Three Compartment Mass Balance for the Removal of Volatile Organic Compounds in Pilot Scale Constructed Wetlands

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**S** Supporting Information

**ABSTRACT:** To perform a general assessment of treatment efficiency, a mass balance study was undertaken for two types of constructed wetlands (CWs), planted gravel filters and plant root mat systems, for treating VOC (benzene; MTBE) polluted groundwater under field conditions. Contaminant fate was investigated in the respective water, plant, and atmosphere compartments by determining water and atmospheric contaminant loads and calculating contaminant plant uptake, thereby allowing for an extended efficiency assessment of CWs. Highest total VOC removal was achieved during summer, being pronounced for benzene compared to MTBE. According to the experimental results and the calculations generated by the balancing model, degradation in the rhizosphere and plant uptake accounted for the main benzene removal processes, of 76% and 13% for the gravel bed CW and 83% and 11% for the root mat system. Volatilization flux of benzene and MTBE was low (<5%) for the gravel bed CW, while in the root mat system direct contact of aqueous and gaseous phases favored total MTBE volatilization (24%). With this applied approach, we present detailed contaminant mass balances that allow for conclusive quantitative estimation of contaminant elimination and distribution processes (e.g., total, surface, and phytovolatilization, plant uptake, rhizodegradation) in CWs under field conditions.



### 1. INTRODUCTION

Constructed wetlands (CWs) have been stated as a promising example of a simple and cost-effective near-natural technology to effectively treat waters contaminated with volatile organic compounds (VOCs).<sup>1</sup> Recently, several studies report on CW treatment performance and contaminant removal efficiency depending on operational and design parameters.<sup>2–4</sup> In most cases, treatment efficiency is determined for the water compartment either by areal water loadings or observed decline of contaminant concentrations. However, it is essential to investigate the fate of contaminants within wetland compartments (water, atmosphere, and plants), particularly for VOCs. This approach is mandatory in order to evaluate the main removal processes in CWs: biodegradation, volatilization, and plant uptake.<sup>5,6</sup> This allows for actual treatment efficiency in terms of microbial degradation to be assessed.

Studying pollutant removal in the water phase is the first basic step in obtaining evidence concerning CW treatment potential under realistic field conditions. Such investigations show contaminant removal efficiencies based on concentration decrease<sup>3,7–10</sup> or calculations of loads.<sup>4,11</sup> The investigations contributed to transferral of the CW approach from small scale to field scale application.<sup>12,13</sup> Few studies have considered the flux of VOCs into the atmosphere for mass balancing based on experimental data<sup>7,14</sup>

or simulations.<sup>15</sup> Recent wetland research also attempted to examine the role of plant uptake during VOC treatment.<sup>16,17</sup> Although many authors emphasize the importance of assessing contaminant mass balances for CW treatment systems, conclusive studies comprising contaminant biodegradation and other distribution and elimination processes are generally scarce to date. Most of the field studies did not achieve complete mass balances, since certain distribution processes were either not considered at all or only partially, e.g., only surface- or phytovolatilization were investigated instead of total volatilization.

The fate of VOCs in wetlands for groundwater treatment is influenced by a number of processes, namely microbial degradation in the rhizosphere, sorption on filter material, surface volatilization, and plant uptake with subsequent contaminant accumulation, phytodegradation or phytovolatilization.<sup>18</sup> The relative importance of a particular process depends on the physicochemical properties of the contaminant, such as the vapor pressure and the partition coefficients  $K_{AW}$  (air–water partition coefficient) and  $K_{OW}$  (octanol–water partition coefficient), as well as the environmental conditions

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(temperature, redox conditions, and oxygen flux) prevailing in the specific constructed wetland system. For a detailed description of the relationship between the physicochemical characteristics and the fate of contaminants, see Imfeld et al.<sup>6</sup>

Therefore, the objective of our work was to evaluate the performance of different horizontal subsurface flow CWs treating VOC contaminated groundwater under field conditions, utilizing a detailed balancing approach. By this, we were able to subdivide the overall removal efficiencies determined from water loadings into (i) destructive removal via biodegradation in the rhizosphere and (ii) the nondestructive processes VOC-volatilization (surface- and phytovolatilization) and plant uptake. Our approach is based upon three key elements: (i) the monitoring of influent and effluent VOC load, (ii) the determination of total VOC volatilization using dynamic air chambers, and (iii) the calculation of VOC uptake into the plants. Rhizodegradation is assessed as the difference of total removal from water phase and the losses due to plant uptake and volatilization. This evaluation was conducted for two types of CWs, a conventional wetland with a filter matrix (gravel) and a plant root mat system without lithospheric solid state material.

## 2. EXPERIMENTAL SECTION

**2.1. Site Description and Pilot Plant Design.** At the industrial site Leuna (Saxony-Anhalt, Germany), decades of petroleum refinement led to large-scale contamination of the soil and groundwater with the fuel constituents benzene and methyl-*tert*-butyl-ether (MTBE). In 2007, an outdoor pilot plant was built down gradient of the contamination plume at the Leuna site, in order to investigate the remediation efficiency of constructed wetlands (CWs).

The CWs (A and B) were designed to operate in horizontal subsurface flow mode and consisted of steel basins ( $5 \times 1.1 \times 0.6$  m) planted with common reed (*Phragmites australis*). System A was filled with gravel (grain size 2–3.2 mm) up to a height of 50 cm and the water level was set to 40 cm, resulting in a vadose soil zone of 10 cm. System B was designed as a plant root mat (*Phragmites australis*), only supported by the densely woven root bed and was operated at a water depth of 15 cm. An unplanted gravel filter designed and operated like system A was used as a reference. Inflow and outflow connections were installed 5 cm above the bottom of the basins. Inflow water was supplied via a closed nonaerated holding tank ( $nHRT$ : 7 h) from a nearby groundwater well. During the period of investigation (June 2007 to June 2009), the concentrations of the groundwater contaminants benzene and MTBE were  $19 \pm 3.7$  and  $3.8 \pm 0.8$  mg L<sup>-1</sup>, respectively. For other groundwater inflow characteristics see Table S1 in Supporting Information, SI. The hydraulic loading rate was fixed to 6 L h<sup>-1</sup> for system A and 6.9 L h<sup>-1</sup> for system B, respectively. Hydraulic retention times ( $nHRT = V_{\text{sys}}/\text{inflow rate}$ ) were calculated to 5.3 d for system A and to 2.7 d for system B. Water inflow and outflow volumes were quantified by flow meters (15-min interval), allowing for contaminant loading rate to be calculated.

Dynamic air chambers (DACs) were mounted on top of the CWs in order to determine total benzene and MTBE volatilization from the wetlands in an integral approach. The chambers were equipped with wind turbines, so realistic environmental conditions could be simulated within the chambers (air exchange rate > 40 h<sup>-1</sup>). DAC design and construction has been previously described in detail.<sup>19</sup>

**2.2. Sampling Procedure and Analysis of Aqueous and Gaseous Samples.** Inflow and outflow water samples were collected

at regular intervals, every one to two weeks, and were analyzed in duplicate for VOC concentration by a GC–MS system. Sample preparation and conservation, as well as analyses of organic compounds, are described elsewhere.<sup>20</sup> To determine the organic compounds, a headspace GC/MS facility (Agilent: auto sampler with oven 7694, GC 6890, MS 5973) with a HP-1 column (60 m × 0.25 mm × 1 μm) was used and the following temperature program was applied: 35 °C (6 min), 4 °C/min to 120 °C, 20 °C/min to 280 °C (5 min).

The determination of VOC emission rates was performed in discrete 1–2-week sampling campaigns every 2–3 months all around the year, in order to investigate meteorological influence on contaminant volatilization. Atmospheric VOCs were trapped on adsorption tubes, placed in the inlet and outlet tube of the DAC, by means of active gas sampling. After thermal desorption, VOC concentration analysis was performed via a GC–MS system. A detailed description of this process is reported by Reiche et al.<sup>19</sup>

**2.3. Mass Balance and Treatment Removal Efficiency.** Calculation of treatment removal efficiency of the CWs for the water compartment is based upon system-specific influent and effluent loading rates of the contaminants, and thus accounts for the water loss due to evapotranspiration (ET).

The contaminant mass balance in the constructed wetlands is maintained as follows:

$$ACL_{\text{in}} = ACL_{\text{out}} + \Delta m \quad (1)$$

where  $ACL_{\text{in/out}}$  (mg m<sup>-2</sup> d<sup>-1</sup>) is the areal contaminant load for the inflow or outflow, respectively, and  $\Delta m$  is the overall contaminant mass loss in the water phase.  $ACL_{\text{in/out}}$  was obtained as follows:

$$ACL_{\text{in/out}} = A^{-1} \times \sum_{i=1}^n (c_{\text{in/out}}(t_i) \times \bar{Q}_{\Delta t, \text{in/out}}) \quad (2)$$

where  $c$  is the contaminant concentration (mg L<sup>-1</sup>) at the inflow (in) or outflow (out) at a sampling time  $t_i$ ,  $\bar{Q}_{\Delta t, \text{in/out}}$  is the average inflow or outflow water volume (L d<sup>-1</sup>) between two consecutive concentration samplings at time  $t_i$  and  $t_{i+1}$ , and  $A$  is the surface area of the wetland (5.5 m<sup>2</sup>).

The treatment removal efficiency for the water phase  $R_w$  (%) was calculated using eq 3:

Treatment removal efficiency

$$(R_w) = \frac{ACL_{\text{in}} - ACL_{\text{out}}}{ACL_{\text{in}}} \times 100 \quad (3)$$

**2.4. Quantitative Assessment of Elimination and Distribution Processes.** The overall contaminant mass loss  $\Delta m$  (eq 1) can be split up into the losses microbial degradation in the rhizosphere ( $L_m$ ), volatilization ( $L_v$ ), including surface volatilization ( $L_{v, \text{surface}}$ ) and phytovolatilization ( $L_{v, \text{phyto}}$ ), plant uptake ( $L_p$ ), photolysis ( $L_{\text{photo}}$ ), and sorption on filter material ( $L_s$ ), see eq 4:

$$\Delta m = L_m + L_v + L_p + L_{\text{photo}} + L_s \quad (4)$$

As atmospheric halftimes of benzene and MTBE are long, 7 d<sup>21</sup> and 3–6 d,<sup>22</sup> respectively, in comparison to the air exchange rate applied to the DACs (>40 h<sup>-1</sup>), contaminant photolysis is considered to be insignificant in our mass balance approach. In addition, net contaminant loss due to sorption is neglected, since mass calculations

were performed for 1–2-year old CWs and thus overall steady-state conditions for sorption–desorption processes were supposedly reached. Also sorption is considered as a minor removal process for highly water-soluble compounds,<sup>6</sup> such as MTBE and benzene. As a result, the mass balance equation simplifies to the following:

$$\Delta m = L_m + L_v + L_p \quad (5)$$

The contaminant loss resulting from volatilization  $L_v$  ( $\text{mg m}^{-2} \text{d}^{-1}$ ) was obtained as follows:

$$\text{volatilization}(L_v) = \frac{m_{\text{air,in}} - m_{\text{air,out}}}{A \times \Delta t} \quad (6)$$

where  $m_{\text{air,in}}$  and  $m_{\text{air,out}}$  is the contaminant mass (mg) detected on the adsorption tubes positioned in the inlet and outlet wind flux of the DACs,  $A$  is the surface area of the wetland covered by the DAC ( $5.5 \text{ m}^2$ ) and  $\Delta t$  is the sampling duration (1 d).

The contaminant loss due to plant uptake  $L_p$  ( $\text{mg m}^{-2} \text{d}^{-1}$ ) was calculated as follows:

$$L_p = T \times c_{\text{CW,average}} \times \text{TSCF} \quad (7)$$

with the following:

$$c_{\text{CW,average}} = 0.5 \times (c_{\text{in}} + c_{\text{out}}) \quad (8)$$

$$\text{TSCF} = \frac{11}{11 + 2.6^{\log K_{\text{OW}}}} \quad (9)$$

Above,  $T$  ( $\text{L m}^{-2} \text{d}^{-1}$ ) represents the transpired water volume. For the planted CW,  $T$  was estimated as the difference of water loss due to evapotranspiration (ET) and evaporation ( $E$ ) of the unplanted reference. As no  $E$  data was available for an unplanted water basin without gravel matrix, plant uptake for the plant root mat was calculated using ET values instead. ET and  $E$  ( $\text{L m}^{-2} \text{d}^{-1}$ ) are obtained from the water balance of the CWs, i.e., the difference between water influx and precipitation flux ( $V_{\text{in}}$ ,  $V_{\text{precipitation}}$ ) and water outflux ( $V_{\text{out}}$ ; all fluxes in units of  $\text{L m}^{-2} \text{d}^{-1}$ ).  $c_{\text{CW,average}}$  is the average contaminant concentration in the water compartment of the CW, obtained from concentrations at inlet and outlet,  $c_{\text{in}}$  and  $c_{\text{out}}$ . TSCF (dimensionless) is the transpiration stream concentration factor describing contaminant translocation into the shoots and represents how readily a contaminant is taken up by the plants. The TSCF depends on the  $\log K_{\text{OW}}$ , and a nearly sigmoidal relationship between plant uptake and hydrophobicity has been evaluated according to Dettenmaier et al.<sup>23</sup> For the calculation,  $\log K_{\text{OW}}$  values used were 2.13 for benzene and 1.2 for MTBE.<sup>24,25</sup> Equation 7 is in accordance with the calculation of contaminant plant uptake described by Dietz and Schnoor.<sup>26</sup>

With the aim of evaluating CW treatment efficiency in terms of actual contaminant removal via microbial rhizodegradation, two mass balance scenarios are considered, as described hereafter:

- (I) The worst-case scenario states the minimal amount of contaminant subject to biodegradation in the rhizosphere, assuming that VOCs taken up by the plants are not phytovolatilized, and thus atmospheric VOC results from surface volatilization only ( $L_{v,\text{phyto}} = 0$ ,  $L_v = L_{v,\text{surface}}$ ).

$$L_m(\text{worst case scenario}) = \Delta m_w - L_v - L_p \quad (10)$$

- (II) The best-case scenario states the maximal amount of contaminant subject to biodegradation in the rhizosphere,

assuming that atmospheric VOC results from plant uptake with subsequent phytovolatilization only ( $L_v = L_p = L_{v,\text{phyto}}$ ) and surface emission did not occur ( $L_{v,\text{surface}} = 0$ ).

$$L_m(\text{best case scenario}) = \Delta m_w - L_p \quad (11)$$

In case  $L_v$  exceeds maximal possible amount of phytovolatilization subsequent to plant uptake, surface volatilization has to be taken into account as an additional subtrahend.

$$L_m(\text{best case scenario}) = \Delta m_w - L_p - L_{v,\text{surface}} \quad (12)$$

**2.5. Statistical Analysis.** Uncertainties of contaminant loss due to plant uptake, microbial degradation, surface and phytovolatilization, and areal contaminant loadings were determined by Gaussian error propagation. Parameters considered were  $c_{\text{in}}$ ,  $c_{\text{out}}$ ,  $c_w$ ,  $V_{\text{in}}$ ,  $V_{\text{out}}$ ,  $V_{\text{rain}}$ , ET,  $E$ ,  $L_v$ , and the TSCF. The initial error of the parameters comprised the standard error of the mean and the measuring error. The error of the TSCF resulted from the assumption of a 10% variation of the  $\log K_{\text{OW}}$  values of the respective compound.

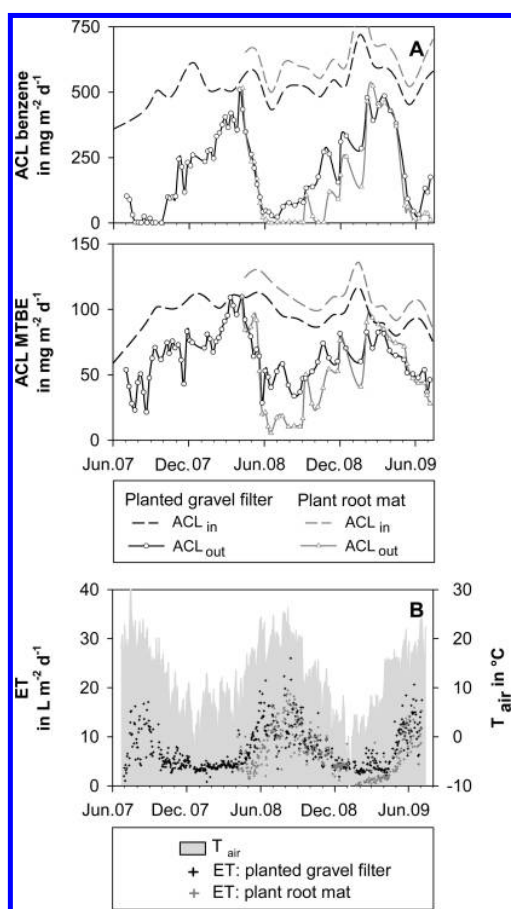
### 3. RESULTS AND DISCUSSION

**3.1. Treatment Efficiency of Constructed Wetlands.** Water quality was improved considerably by being treated with both CW systems tested, the planted gravel filter and the plant root mat. Benzene and MTBE effluent loads showed great seasonal variance, with lowest contaminant loads and highest treatment efficiencies observed during spring and summer (Figure 1A). For summer 2008, the plant root mat revealed maximum removal rates  $R_w$  of  $99.9 \pm 8.5\%$  ( $606 \pm 51 \text{ mg m}^{-2} \text{d}^{-1}$ ) for benzene and  $96 \pm 8\%$  ( $117 \pm 9 \text{ mg m}^{-2} \text{d}^{-1}$ ) for MTBE, whereas the conventional CW including a gravel filter matrix removed only up to  $96 \pm 8\%$  ( $480 \pm 42 \text{ mg m}^{-2} \text{d}^{-1}$ ) and  $75 \pm 11\%$  ( $85 \pm 13 \text{ mg m}^{-2} \text{d}^{-1}$ ), respectively. Notably, the time frame of overall good treatment performance during summer lasted considerably longer for the plant root mat, namely 6 months, than for the gravel filter with only 4 months. Areal contaminant loads of the unplanted reference and outflow concentrations of all systems are presented in Figures S1 and S2 of the SI.

When comparison was made with other CW studies, it was highlighted that our wetlands achieved higher removal efficiencies during summer, especially given the relatively high inflow concentrations. Similarly, high removal efficiencies (80% benzene removal) have been reported by Bedessem et al.<sup>4</sup> for a pilot scale CW fed with petroleum-contaminated groundwater at a benzene loading rate similar to ours, however influent concentrations were low on average and did not exceed  $2 \text{ mg L}^{-1}$ . Contaminant specific removal rates with suppressed removal of MTBE compared to benzene were reported by several authors<sup>12,20</sup> and might result from hindered microbial attack, due to compound structure,<sup>27</sup> overall low growth yields of MTBE utilizing microorganisms,<sup>28</sup> and inhibition of MTBE degradation by BTEX compounds.<sup>29</sup>

In general, the seasonal variation of outflow loadings was found to negatively correlate with the annual variation of ambient air temperature and water loss of the constructed wetlands, due to evapotranspiration (ET; see Figure 1B). High effluent loads were obtained when temperature and ET values were low, and vice versa. This correlation indicated that the excellent summer removal efficiencies achieved resulted from the three fate





**Figure 1.** Areal benzene and MTBE inflow and outflow water load ( $ACL_{in/out}$ ) for the planted gravel filter CW and the plant root mat system (A); evapotranspiration (ET) of the gravel filter CW and the plant root mat system as well as ambient air temperature  $T_{air}$  (daily mean) (B).

pathways of microbial degradation in the rhizosphere, plant uptake, and total volatilization, as discussed hereafter.

Microbial contaminant turnover in the root zone of CWs is known to be greatly affected by the seasonal constitution of the wetland plants. During spring and summer, plants actively transport oxygen and nutrients into the rhizosphere and thereby provide suitable conditions for the prevailing microbes and even enhance microbial growth and diversity.<sup>5,30</sup> As a consequence of this so-called rhizospheric effect, biological contaminant turnover is improved during times when plants are active.<sup>31</sup> In addition, elevated temperatures favor overall microbial metabolism.<sup>32,33</sup>

Contaminant plant uptake via the transpiration stream has to be accounted for as a fate pathway, particularly during times when plant transpiration is high. The water balance of the wetlands revealed transpiration rates of more than  $60 \text{ L CW}^{-1} \text{ d}^{-1}$  ( $>10 \text{ L m}^{-2} \text{ d}^{-1}$ ) during summer 2008, which made up more than 40% of the hydraulic inflow rate. The potential for direct uptake of organic pollutants by plants via the transpiration stream is generally indicated by low to intermediate  $\log K_{OW}$  values ( $0.5 - 3$ ),<sup>18</sup> a characteristic that both benzene ( $\log K_{OW} 2.13$ ) and MTBE ( $\log K_{OW} 1.2$ ) possess.<sup>24,25</sup> The actual amount of contaminant being transported into the plants can be calculated

using the TSCF, a function of the compound-specific characteristic  $\log K_{OW}$ , and, given the TSCF of benzene (0.59) and MTBE (0.78), a relatively large fraction of contaminants will be transferred into the plants. Hence, plant uptake has to be considered as a relevant fate pathway in our CW study, irrespective of the subsequent processes of accumulation in plant material, transformation by endophytic microbes, and phytovolatilization.

Surface volatilization and phytovolatilization are strongly related to the physicochemical properties of the contaminants, which again are temperature dependent. Direct transfer from the water phase into the atmosphere is predicted by Henry's Law coefficient ( $H$ ) and, thus, is related to the vapor pressure ( $v_p$ ),<sup>34</sup> whereas in unsaturated soil zones diffusion transport additionally determines effective atmospheric emissions.<sup>6</sup> Phytovolatilization is most relevant for compounds that are easily translocated into plants ( $\log K_{OW} 0.5 - 3$ ), and are concomitantly characterized by a high vapor pressure ( $v_p > 1.01 \text{ kPa}$ )<sup>35</sup> or Henry's Law constant ( $K_{AW} \gg 10^{-5}$ ).<sup>36</sup> Given the fact that these criteria are fulfilled for benzene ( $K_{AW} = 0.22$ ;  $v_p = 10.13 - 12.66 \text{ kPa}$ )<sup>37,38</sup> and MTBE ( $K_{AW} = 0.024 - 0.12$ ;  $v_p = 32.66 - 33.55 \text{ kPa}$ ),<sup>39</sup> phytovolatilization has to be considered as a potential distribution process in our work. In general, phytovolatilization may be of particular relevance for subsurface-flow (SSF) CWs, since direct volatilization is restrained due to slow diffusion rates through unsaturated soil zones.<sup>6</sup>

Overall, in the case where only the water compartment is considered, both CWs showed high VOC removal efficiencies during summer with the plant root mat performing better than the conventional CW with the gravel matrix.

**3.2. Contaminant Mass Balance.** Contaminant-specific mass balance calculations were performed for distinct summer and winter periods and were based upon benzene and MTBE areal loads of the influent ( $ACL_{in}$ ) and effluent ( $ACL_{out}$ ), as well as the atmospheric load ( $L_v$ ) measured in the dynamic air chambers (Table 1). Contaminant plant uptake and biodegradation in the rhizosphere of the planted CW were calculated according to eqs 7 and 10.

Figure 2 depicts the fate of benzene and MTBE in the constructed wetlands as a fraction of the inflow load ( $ACL_{in}$ ). This approach enabled the overall contaminant removal from the water phase to be split into the losses due to microbial degradation in the rhizosphere ( $L_m$ ), overall plant uptake ( $L_p$ ), phytovolatilization ( $L_{v,phyto}$ ), and surface volatilization ( $L_{v,surface}$ ).

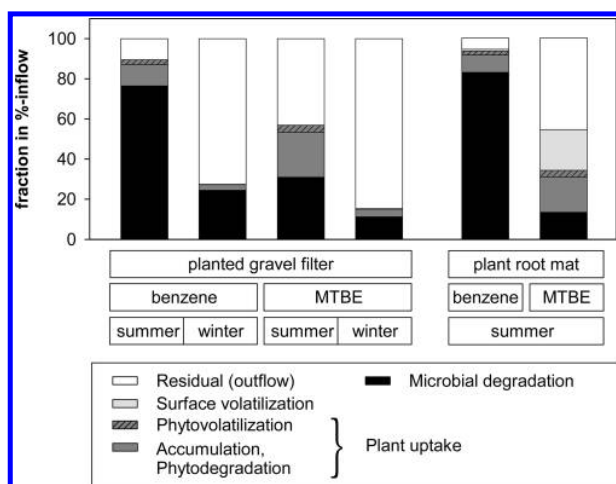
Benzene and MTBE emission rates for the unplanted gravel filter were well below  $0.5 \text{ mg m}^{-2} \text{ d}^{-1}$ , except for MTBE in winter ( $1.9 \text{ mg m}^{-2} \text{ d}^{-1}$ ), (Table S2 of the SI). In all cases, influx and efflux air concentrations were not significantly different from background concentrations,<sup>19</sup> justifying the assumption that surface volatilization was negligible for the planted gravel CW.

Benzene removal efficiency in summer for the CW with the gravel matrix was found mainly to derive from microbial degradation ( $76.4 \pm 10.7\%$ ), whereas plant uptake and phytovolatilization contributed to this to a lower extent, of  $13.0 \pm 2.9\%$  and  $2.3 \pm 0.3\%$ , respectively. During winter, the total percentage of each loss process decreased, but the trend of the distribution remained similar, resulting in  $24.5 \pm 12.2\%$ ,  $2.9 \pm 3.8\%$ , and  $0.1 \pm 0.04\%$  removal with respect to  $L_m$ ,  $L_p$ , and  $L_{v,phyto}$ . The ratio of microbial degradation and plant uptake  $L_m:L_p$  obtained for the summer (6:1) and winter (8:1) periods revealed that even during winter microbial degradation accounted for the major benzene removal capacity. In contrast, for MTBE differences between  $L_m$  and  $L_p$  were less distinct. In summer, removal

**Table 1. Data Used for the Calculation of Contaminant Mass Balances: Areal Contaminant Load (ACL,  $\text{mg m}^{-2} \text{d}^{-1}$ ) of Inflow and Outflow Water, Volatilization Rates ( $L_v$ ,  $\text{mg m}^{-2} \text{d}^{-1}$ ), Average Contaminant Concentration ( $c_{w,average}$ ,  $\text{mg L}^{-1}$ ), and Evapotranspiration and Transpiration Rates (ET,  $T$ ,  $\text{L, CW}^{-1} \text{d}^{-1}$ ) of the Gravel Filter CW and the Plant Root Mat for Summer and Winter Sampling Periods<sup>a</sup>**

	gravel filter CW		plant root mat	
	benzene	MTBE	benzene	MTBE
Summer $ACL_{in}$	493.1 ± 49.9 <sup>b</sup>	99.2 ± 8.6 <sup>b</sup>	565.9 ± 57.1 <sup>d</sup>	104.2 ± 8.5 <sup>d</sup>
$ACL_{out}$	51.9 ± 7.7 <sup>b</sup>	42.8 ± 5.0 <sup>b</sup>	32.0 ± 5.7 <sup>d</sup>	47.6 ± 5.0 <sup>d</sup>
$c_{w,average}$	11.3 ± 0.9 <sup>b</sup>	3.4 ± 0.2 <sup>b</sup>	10.3 ± 0.9 <sup>d</sup>	2.8 ± 0.2 <sup>d</sup>
$L_v$	11.4 ± 1.6 <sup>c</sup>	3.5 ± 0.5 <sup>c</sup>	16.4 ± 0.9 <sup>e</sup>	24.6 ± 2.9 <sup>e</sup>
ET	72.5 ± 7.3 <sup>b</sup>		54.3 ± 8.2 <sup>d</sup>	
T	52.8 ± 10.0 <sup>b</sup>			
Winter $ACL_{in}$	604.5 ± 53.8 <sup>f</sup>	92.2 ± 7.7 <sup>f</sup>	690.3 ± 61.8 <sup>f</sup>	105.3 ± 8.8 <sup>f</sup>
$ACL_{out}$	438.8 ± 45.3 <sup>f</sup>	78.1 ± 7.3 <sup>f</sup>	478.3 ± 49.6 <sup>f</sup>	90.8 ± 8.3 <sup>f</sup>
$c_{w,average}$	21.3 ± 1.3 <sup>f</sup>	3.5 ± 0.2 <sup>f</sup>	19.6 ± 1.2 <sup>f</sup>	3.3 ± 0.2 <sup>f</sup>
$L_v$	0.7 ± 0.3 <sup>g</sup>	0.2 ± 0.04 <sup>g</sup>		
ET	24.4 ± 7.0 <sup>f</sup>		3.1 ± 8.9 <sup>f</sup>	
T	7.7 ± 10.0 <sup>f</sup>			

<sup>a</sup> For measured values the error equals the sum of standard error of the mean and measuring fault. For the parameters  $ACL_{in}$ ,  $ACL_{out}$ ,  $c_{w,average}$ , ET, and T an error analysis was carried according to Gaussian error propagation. Transpiration stream concentrations factors (TSCF) applied for the calculations were 0.59 for benzene and 0.78 for MTBE. <sup>b</sup> Sampling period: 27/5–1/9/2008. <sup>c</sup> Sampling period: 10–20/6 and 5–15/8/2008. <sup>d</sup> Sampling period: 12/5–5/7/2009. <sup>e</sup> Sampling period: 8–12/6/2009. <sup>f</sup> Sampling period: 3/2–16/3/2009. <sup>g</sup> Sampling period: 17–27/2/2009.



**Figure 2.** Contaminant fate in the planted gravel filter and the plant root mat system for summer and winter period. Processes included are microbial degradation, surface volatilization, phytovolatilization, plant uptake, and accumulation/phytodegradation in the reed.

originated from plant uptake and rhizodegradation in similar shares, namely  $26.0 \pm 5.2\%$  and  $30.9 \pm 11.3\%$ . As expected, in winter rhizodegradation was considerably lower ( $11.0 \pm 12.6\%$ ) and plant uptake ( $4.1 \pm 5.4\%$ ) almost negligible.

Given the experimental emission data, MTBE was volatilized to a larger fraction than benzene, accounting for the achieved

figures of  $3.5 \pm 0.6\%$  during summer and  $0.2 \pm 0.04\%$  in winter. For the unplanted reference system, aqueous contaminant removal was considerably lower compared to both planted systems, total/surface volatilization rates were negligible (Table S2 of the SI), and thus contaminant mass balance calculations yielded low but year-round constant microbial contaminant turnover of between  $16 \pm 12\%$  and  $23 \pm 13\%$  with respect to inflow load (Figure S3 of the SI).

Mass balance calculation for the gravel filter clearly illustrated seasonality of all three elimination and distribution processes, but it also showed that the percentage of each process was strongly dependent upon the contaminant properties. Summer–winter action is a controversial issue, as some studies confirm this effect and others do not,<sup>4,9</sup> but commonly it is accepted as a typical CW phenomenon.<sup>5</sup> Complex interactions have been discussed in detail (see Section 3.1) for the contaminants investigated. The contaminant-specific influence became most evident in the plant uptake process. Given the higher TSCF value for MTBE (0.78) in comparison to benzene (0.59), the uptake of MTBE by the wetland plants was calculated to be higher than the uptake of benzene (in relation to inflow loadings).

The mass balance calculations for the plant root mat were based upon the assumption that phytovolatilization of the plant root mat and the planted gravel filter is equal, since surface area covered by plants is the same and plant number per wetland was comparable and summer ET rates were almost alike, amounting to  $13 \pm 1.3 \text{ L m}^{-2} \text{d}^{-1}$  and  $10 \pm 1.5 \text{ L m}^{-2} \text{d}^{-1}$  for the gravel filter (summer 2008) and plant root mat (summer 2009), respectively. Thus, the effective contaminant emission from the plant root mat, which was found to be significantly elevated in comparison to the gravel CW (Tab. 1), could be broken down into emission due to phytovolatilization and surface volatilization. For the plant root mat system, the benzene fate behavior during summer was observed to be similar to the conventional CW, resulting in most pronounced removal via microbial degradation ( $82.9 \pm 10.4\%$ ), followed by plant uptake ( $10.6 \pm 2.1\%$ ), phytovolatilization ( $2.0 \pm 0.3\%$ ) and surface volatilization ( $L_{v,surface}$ ) ( $0.9 \pm 0.3\%$ ), see Figure 2. Contrary to benzene, the total removal of MTBE was different: equally high percentage shares were caused by plant uptake ( $20.9 \pm 3.4\%$ ) and surface volatilization ( $20.3 \pm 2.9\%$ ), whereas rhizodegradation and phytovolatilization accounted only for  $13.2 \pm 10.4\%$  and  $3.4 \pm 0.5\%$ , respectively.

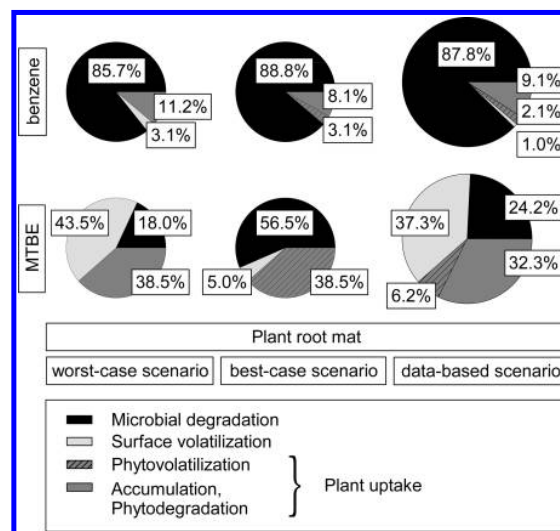
Elevated MTBE flux from the plant root mat into the atmosphere might be induced by the wetland characteristics. Uneven root density leaves parts of the wetland interspersed with open water. This and the lack of a vadose zone might have allowed a more unhindered compartment (water–air) transfer via diffusion compared to the gravel filter CW. In turn, benzene volatilization remained low, possibly impeded by the higher microbial degradation potential of benzene relative to MTBE.<sup>27,28</sup> Given that the plant root mat achieved higher benzene removal via microbial degradation than the conventional gravel filter, it illustrates that direct contact between the atmosphere and water compartment presumably resulted in a better supply of oxygen to the water compartment, and thus favored benzene turnover.<sup>2,40</sup>

The mass balance (Figure 2) displays fractions of benzene and MTBE that were taken up by the plants of the respective wetland types but were not retrieved in the atmosphere, thus indicating phytodegradation or phytoaccumulation of the contaminants. For benzene, the overall low (<5%) experimental emission rates accompanied with high calculated plant uptake possibly resulted from degradation processes within the reed by endophytic

bacteria.<sup>31,41,42</sup> This hypothesis may be confirmed by a study by Mothes et al.<sup>17</sup> investigating the VOC pollutant concentration distribution in *Phragmites australis* plants of our gravel CW. The authors reported a decrease in benzene concentration with plant height, accompanied with low total recovery of benzene ( $15 \text{ mg CW}^{-1}$ ) in the wetland plants. Phytodegradation of benzene is commonly accepted.<sup>9,42</sup> In contrast, for MTBE many studies stated phytovolatilization to be the most relevant process in phytoremediation and that no indication of MTBE metabolism within the plants could be found.<sup>43–45</sup> However, examinations had not been performed with *Phragmites australis* to date. The level of MTBE detected in the plants of the gravel CW was low ( $5 \text{ mg CW}^{-1}$ )<sup>17</sup> compared to the calculated amount taken up by the plants but not phytovolatilized during summer, up to  $\sim 122 \pm 28 \text{ mg d}^{-1} \text{ CW}^{-1}$  for the gravel filter wetland and to  $\sim 101 \pm 20 \text{ mg d}^{-1} \text{ CW}^{-1}$  for the plant root mat. Therefore, the results of the present study suggest microbial turnover of MTBE within the wetland plants. Actual potential of MTBE for phytodegradation is outlined by Newman and Arnold,<sup>46</sup> including studies with alfalfa and hybrid poplars.

The results showed that biodegradation of benzene accounted for the most important removal in the gravel matrix CW and the plant root mat, with significant differences for summer and winter periods. Impacts on the mass balance due to sorption can be regarded as small,<sup>6</sup> and thus would not significantly change the loss due to rhizodegradation. Generally, for the gravel CW benzene and MTBE emission rates were low (<5%), while in the plant root mat direct contact of aqueous and gaseous phases favored surface volatilization of MTBE, amounting to  $20.3 \pm 2.9\%$  of inflow load. Furthermore, high plant uptake of benzene ( $13.0 \pm 2.9\%$ ) and MTBE ( $26.0 \pm 5.2\%$ ) in the gravel CW during summer accompanied with low atmospheric recovery (<5%) gave strong evidence for the degradation of benzene and MTBE by endophytic bacteria either in the rhizosphere or the phyllosphere. For the plant root mat, it has to be pointed out that plant uptake and phytodegradation might be slightly overestimated given that  $L_p$  was calculated using ET rates instead of real transpiration volumes, thus, considering transpiration rates actual removal via rhizodegradation would be even pronounced.

The mass balance approach depicted in Figure 2 was based upon the assumption of realistic conditions ( $L_{v,\text{surface}}$  (planted gravel filter) = 0;  $L_{v,\text{phyto}}$  (planted gravel filter) =  $L_{v,\text{phyto}}$  (plant root mat)). Since our experimental setup did not allow for the measurement of surface- and phytovolatilization for the planted gravel wetland separate from each other, we cannot be sure whether the assumptions set up were completely valid. Therefore, microbial degradation was calculated for a worst-case and best-case scenario to determine the maximal lower and upper limits of microbial degradation in summer (see Section 2.4) as a fraction of contaminant removal from the water phase (Figure 3). For the gravel CW, the estimated percentages for microbial benzene and MTBE degradation were similar for best-case and worst-case conditions (data not shown). These findings are related to the fact that total emission rates were low in general, and thus the origin of atmospheric contaminant hardly affected the calculation of the value for contaminant loss due to microbial degradation. A similar narrow range for upper and lower limit of microbial rhizodegradation was derived for benzene in the plant root mat (Figure 3). In contrast, for MTBE best-case and worst-case scenario calculations covered a broad range of 18.0–56.5%, and the realistic data-based scenario calculations found microbial



**Figure 3.** Comparison of worst-case and best-case removal scenarios with the data-based scenario: Percentage of contaminant removal processes (microbial degradation, surface volatilization, phytovolatilization, plant uptake, accumulation/phytodegradation in the reed) on overall contaminant loss from the water phase of the plant root mat during the summer period.

degradation amounting only to 24.2% of total MTBE mass removal from water phase.

In order to assess the microbial degradation efficiency of the plant root mat, it was essential to know whether or not and to what extent atmospheric contamination resulted from surface- and phytovolatilization. This will be a topic of further research.

A comparison of VOC fate found in this work with that of previous mass balance examinations is possible but would prove very challenging, as the system parameters affecting mass balance results, such as inflow loading, plant species (tree, reed), or experimental setup (lab-, field-scale), were different for each study. Hong et al.<sup>47</sup> performed a lab study with poplars growing in hydroponic solution containing  $^{14}\text{C}$ -MTBE. Mass balancing revealed that the predominant fate pathway was plant uptake and ET from leaves and stems. MTBE removal accounted for 37–67%, whereas around 28% of the total MTBE applied was emitted into the atmosphere. Our work exhibited similarly high MTBE removal efficiencies during summer ( $\sim 56\%$  for both wetland types), and emission of MTBE from the plant root mat system was in the same range (23.6%). However, atmospheric MTBE flux for the gravel CW was found to be considerably lower (<5%). Burken and Schnoor<sup>35</sup> studied the fate of BTEX compounds in poplars in lab experiments and recovered 18% of the benzene applied in the surrounding atmosphere. High total benzene recovery (94%) accompanied with a minor (<1%) fraction of benzene in the plant material indicated that benzene was transferred into the plants and subsequently phytovolatilized. In contrast, in our work, benzene emission from both wetland types did not exceed 5% and a large fraction of benzene taken up into the plants was not retrieved in the atmosphere. Thus, phytovolatilization did not play a major role in contrast to phytodegradation. James et al.<sup>16</sup> performed a mass balance work under controlled field conditions to investigate the phytoremediation of PCE by poplars and reported 100fold lower atmospheric flux ( $<0.1 \mu\text{g m}^{-2} \text{ h}^{-1}$ ) in comparison to our results (benzene/MTBE emission during



summer: gravel CW =  $475 \pm 67/146 \pm 23 \mu\text{g m}^{-2} \text{h}^{-1}$ , plant root mat =  $683 \pm 38/1025 \pm 122 \mu\text{g m}^{-2} \text{h}^{-1}$ ). Conversely to our findings, contaminant loss via transpiration, volatilization, and accumulation in the trees was stated to be of minor relevance compared to overall PCE removal (>99%). Adequate comparison of emission fluxes is highly complicated as inflow concentrations vary between the different studies. Generally, high total hydrocarbon volatilization flux ( $12\,500 \mu\text{g m}^{-2} \text{h}^{-1}$ ) was obtained for high inflow concentrations (BTEX:  $50 \text{ mg L}^{-1}$ ),<sup>7</sup> and low atmospheric flux (benzene:  $0.042 \mu\text{g m}^{-2} \text{h}^{-1}$ , MTBE:  $0.333 \mu\text{g m}^{-2} \text{h}^{-1}$ ) accompanied with low inflow concentrations ( $<0.0002 \text{ mg L}^{-1}$ ).<sup>15</sup> However, our results were in the range stated above. Besides, Moore et al.<sup>7</sup> identified biodegradation and volatilization as being the most important attenuation processes in a wetland treating hydrocarbons, which is in accordance with our findings.

Explicitly, comprehensive evaluation of benzene and MTBE fate in the tested wetland systems clarified the fraction each of the removal processes contribute to the overall removal, and that microbial degradation plays a major role with minor effects by plant uptake and volatilization. This finding may represent a realistic share of removal processes in general. Therefore, the assessment of CW treatment performance should always be based on a mass balance approach that is comprised of a breakdown of the total removal into the various removal processes taking place in a CW.

## ■ ASSOCIATED CONTENT

**S** Supporting Information. Groundwater characteristics, complete mass balance data for the reference system, and contaminant outflow concentrations of all systems. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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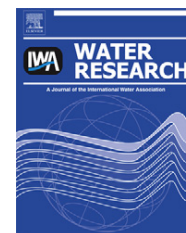
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## Performance evaluation of different horizontal subsurface flow wetland types by characterization of flow behavior, mass removal and depth-dependent contaminant load

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### ABSTRACT

For several pilot-scale constructed wetlands (CWs: a planted and unplanted gravel filter) and a hydroponic plant root mat (operating at two water levels), used for treating groundwater contaminated with BTEX, the fuel additive MTBE and ammonium, the hydrodynamic behavior was evaluated by means of temporal moment analysis of outlet tracer breakthrough curves (BTCs): hydraulic indices were related to contaminant mass removal. Detailed investigation of flow within the model gravel CWs allowed estimation of local flow rates and contaminant loads within the CWs. Best hydraulics were observed for the planted gravel filter (number of continuously stirred tank reactors  $N = 11.3$ , dispersion number = 0.04, Péclet number = 23). The hydroponic plant root mat revealed lower  $N$  and pronounced dispersion tendencies, whereby an elevated water table considerably impaired flow characteristics and treatment efficiencies. Highest mass removals were achieved by the plant root mat at low level: 98% ( $544 \text{ mg m}^{-2} \text{ d}^{-1}$ ), 78% ( $54 \text{ mg m}^{-2} \text{ d}^{-1}$ ) and 74% ( $893 \text{ mg m}^{-2} \text{ d}^{-1}$ ) for benzene, MTBE and ammonium–nitrogen, respectively. Within the CWs the flow behavior was depth-dependent, with the planting and the position of the outlet tube being key factors resulting in elevated flow rate and contaminant flux immediately below the densely rooted porous media zone in the planted CW, and fast bottom flow in the unplanted reference.

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## 1. Introduction

Constructed wetlands (CWs) have proven to be an efficient ecological technology for the treatment of various kinds of contaminated waters (Williams, 2002; Haberl et al., 2003; Kadlec and Wallace, 2008), including domestic and agricultural wastewater (Konnerup et al., 2009; Vymazal and Kröpfelová, 2009), landfill leachate (Bulc, 2006; Yalcuk and Ugurlu, 2009), industrial effluents (Vymazal, 2009) and groundwater

contaminated with organic chemicals (Braeckevelt et al., 2008; Seeger et al., 2011a). The use of CWs has been successfully tested in pilot- (Braeckevelt et al., 2011) and field-scale (Ferro et al., 2002; Moore et al., 2002) applications, providing data on overall contaminant removal efficiency on the basis of either concentrations or loads.

CW treatment efficiency primarily depends on the contact time between the contaminated water and the filter material, including biota, as longer residence times enhance

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contaminant turnover (Werner and Kadlec, 1996). Hence, the characterization of hydraulic flow in CWs is crucial for the evaluation and optimization of system designs and performances (Persson et al., 1999). Moreover, detailed knowledge on flow behavior is essential for the validation and improvement of existing models. The hydraulic characterization of CWs is mostly based on tracer experiments, where the analysis of outlet breakthrough curves (BTCs) using the temporal moment method allows the calculation of the CWs' flow characteristic parameters, such as the mean residence time ( $\tau$ ), porosity ( $\theta$ ), variance ( $\sigma^2$ ), and dispersion parameters. These system-specific parameters may reveal whether the CW is actually operating with ideal flow, short-circuiting, or dead zones, and allow for a comparison between differently designed and operated CWs (Werner and Kadlec, 1996; García et al., 2004; Holland et al., 2004). Since the connection between hydraulic residence time and treatment efficiency has been recognized, many studies have already evaluated the effects of wetland design parameters (e.g. aspect ratio, inlet/outlet configuration, filter medium size, or plant development) and operational modes on the flow behavior or the removal efficiency (García et al., 2005; Kjellin et al., 2007; Ascuntar Ríos et al., 2009; Su et al., 2009; Hijosa-Valsero et al., 2010). Nevertheless, investigations that simultaneously encompass the hydraulic characterization of different CW systems, the change of hydraulic parameters due to operational mode adaptation, and the respective contaminant removal efficiency are rare (Ascuntar Ríos et al., 2009). Most studies evaluate treatment efficiency based on the black box concept, only focusing on overall removal rates. Some studies additionally provide contaminant concentrations of the pore water. However, loads within the wetland have not been described previously, given that actual flow at the sampling points was unknown.

Therefore, the goal of our work was to evaluate the flow characteristics of various pilot-scale horizontal subsurface flow CWs (two conventional wetlands with a gravel filter (planted and unplanted) and a plant root mat system without gravel matrix) and to relate the hydraulic parameters obtained from tracer tests to the achieved treatment efficiencies. For the plant root mat, the effect of low and high water level on both the hydraulic parameters and the pollutant removal was also investigated. Furthermore, local flow rates and local contaminant loads were assessed for the gravel-based CWs in order to identify preferential flow paths and zones with enhanced contaminant flux. The analysis is based upon local tracer BTCs monitored at various sampling points in the porous media.

## 2. Material and methods

### 2.1. Constructed wetland design

The study was carried out at the so-called CoTra (Compartment Transfer) research site in Leuna, Germany, where six pilot-scale horizontal subsurface flow (HSSF) CWs were set up during 2007 in order to evaluate the optimized CW design for the remediation of the local groundwater, which is contaminated with benzene ( $\sim 20 \text{ mg L}^{-1}$ ), methyl tert-butyl ether

(MTBE) ( $\sim 3.7 \text{ mg L}^{-1}$ ) and ammonium ( $57 \text{ mg L}^{-1}$ ) (Seeger et al., 2011a,b). All CWs consisted of steel basins (5 m length  $\times$  1.1 m width  $\times$  0.6 m height). Totally, three CWs were studied. CW A and B were filled with gravel (grain size 2–3.2 mm) to a height of 50 cm, with the water level set to 40 cm. System A was planted with common reed (*Phragmites australis*); system B remained unplanted as a reference. Each wetland was designed with in- and exfiltration zones (0.4 m  $\times$  1.1 m  $\times$  0.6 m) adjacent to the in- and outflow, containing coarse gravel (quartz, grain size 3–8 mm) in order to ensure an even distribution of the inlet stream over the entire wetland cross-section and prevent clogging of the outflow tubes. System C was constructed as a hydroponic plant root mat (*P. australis*), without a gravel matrix except for the in- and exfiltration zone, and was operated at 15 cm (April 2008–September 2009) and 30 cm (since October 2009) water levels. The hydroponic root mat rested on the bottom of the basin at low water level and floated at elevated water level. The groundwater inflow was supplied from a nearby groundwater well; detailed characteristics are provided in Seeger et al. (2011a). Inflow and outflow connections were installed 5 cm above the bottom of the basins; in- and outflow volumes were regulated by pumps. During the time of the tracer test, the hydraulic loading rate was  $12 \text{ L h}^{-1}$  for systems A and B, and  $6.9 \text{ L h}^{-1}$  for system C independent on its water level. At these loading rates the theoretical residence times are similar for CW A, B and C (at low water level) (see Table 1). This is a prerequisite for comparing the treatment efficiency of the CW systems. Inflow and outflow volumes were quantified by flow meters every 15 min, allowing accurate determination of tracer and contaminant loading rates.

**Table 1 – Overview of operational characteristics of the constructed wetland systems (estimated pore volume ( $V_{\text{sys}}$ ), mean inflow rate ( $Q_{\text{in}}$ ), mean flux ( $Q_{\text{mean}}$ ), theoretical hydraulic retention time (nHRT) and experimental settings for the tracer studies conducted (fluorescein concentration of the tracer solution ( $c_{\text{tracer}}$ ), time interval of tracer injection ( $\Delta t$ ), total mass of tracer applied ( $M_{\text{in}}$ )). For the gravel CWs,  $V_{\text{sys}}$  was calculated using a mean gravel porosity ( $n = 0.35$ ). For the hydroponic plant root mat system,  $V_{\text{sys}}$  was derived by means of wetland draining and refilling.**

	Gravel filter		Hydroponic plant root mat	
	Planted	Unplanted	Low water level (15 cm)	High water level (30 cm)
$V_{\text{sys}}$ [L]	770	770	422	1041
$Q_{\text{in}}$ [ $\text{L d}^{-1}$ ]	287	288	167	166
$Q_{\text{mean}}$ [ $\text{L d}^{-1}$ ] = $(Q_{\text{in}} + Q_{\text{out}})/2$	254	274	136	155
nHRT [d] = $V_{\text{sys}}/Q_{\text{mean}}$	3.05	2.81	3.11	6.72
$c_{\text{tracer}}$ [ $\text{mg L}^{-1}$ ]	112	112	153	136
$\Delta t$ [h]	4.12	4.12	3.17	3.45
$M_{\text{in}}$ [g]	5.54	5.54	3.34	3.25

## 2.2. Water sampling and analysis

Inlet and outlet water samples were analyzed every 1–2 weeks. Benzene and MTBE concentrations were determined in duplicates by means of headspace-GC/MS (HP-1 column: 60 m × 0.25 mm × 1 μm, equilibration 70 °C (60 min), temperature program: 35 °C (6 min), 4 °C/min to 120 °C, 20 °C/min to 280 °C (5 min)). Ammonium concentrations were measured photometrically (DIN 38406-E5). In addition, in discrete sampling campaigns water samples were collected from the gravel CW filters at 0.9, 2.5, and 4.1 m flow distance, each at 20, 30, and 40 cm depth using permanently installed stainless-steel lances (0.4 cm outer diameter). A detailed description of the sampling and analysis procedure is provided elsewhere (Reiche et al., 2010; Seeger et al., 2011a). Briefly, duplicate water samples were analyzed for VOC concentration; for ammonium, only one water sample per sampling position was analyzed.

## 2.3. Tracer study

Tracer tests were conducted for the planted and unplanted gravel CWs, and for the plant root mat operating at different water levels (15 cm, 30 cm), by means of a single-shot injection of fluorescein tracer (C<sub>20</sub>H<sub>10</sub>O<sub>5</sub>Na<sub>2</sub>). We choose fluorescein as a tracer since it is (i) detectable at 10<sup>-3</sup> μg L<sup>-1</sup> level (Goldscheider et al., 2008), thus can be applied at low concentrations which precludes the occurrence of density effects, (ii) toxicologically safe unlike e.g. rhodamine (Behrens et al., 2001), (iii) resistant to biodegradation (Bottrell et al., 2010), (iv) not known to be taken up by plants unlike e.g. bromide (Kung, 1990; Xu et al., 2004), (v) frequently used to trace surface- (EPA, 2003) and subsurface waters, e.g. in aquifers (Chua et al., 2007) or wetlands (Netter, 1994), and (vi) its sorption potential was shown to be low in gravel CWs (Netter, 1994) and for gravel/quartz media (Käss, 1992; Magal et al., 2008) even when compared to rhodamine (Kasnavia et al., 1999). Nevertheless, given that it adsorbs on organic matter (Harden et al., 2003) it cannot be considered a conservative tracer *per se*. The tracer solution was prepared using the contaminated groundwater and was introduced into the systems via the inflow tubes at the regular CW flow rates in order to preserve prevailing matrix effects and flow behavior. Table 1 summarizes the characteristics of the CW systems and the settings for each tracer study.

Automatic samplers (VWR international; type TP II – 24) were used to collect outflow water samples at short intervals (≥1.5 h). In order to determine the flow behavior within the gravel-based CWs, local tracer BTCs were monitored by taking pore water samples at the flow distance and filter depths stated above. To keep the flow disturbance minimal, sample volume V<sub>s</sub> per sampling port and pumping rate P<sub>r</sub> were set as small as possible (V<sub>s</sub>: 20 ml, P<sub>r</sub>: 5 ml min<sup>-1</sup>). Samples were stored at 8 °C in the dark until further analysis. Fluorescein concentrations were determined photometrically (λ = 485 nm) utilizing a spectral photometer (CADAS 50; Dr. Lange, Germany, Düsseldorf) with a detection limit of 0.005 mg L<sup>-1</sup>. Samples and blanks (inflow groundwater) were filtrated (0.45 μm polyvinylidene fluoride syringe filters, Roth) prior to analysis.

## 3. Data processing and analysis

### 3.1. Normalized residence time distribution

Transferring time and concentration to the dimensionless flow-weighted time variable  $\phi = V_{\text{out}}(t)/V_{\text{sys}}$  and normalized concentration  $c'(\phi) = c(t_i) V_{\text{sys}}/M_{\text{out}}$ , respectively, displays dimensionless BTCs, which allow the direct visual comparison between differently designed and operated CWs (Holland et al., 2004; Wahl et al., 2010). This procedure also accounts for different tracer mass that might have been applied to the CWs (Werner and Kadlec, 1996; Holland et al., 2004; Headley and Kadlec, 2007).  $\phi$  equals the number of passed theoretical hydraulic retention times (nHRT), i.e. the system water volumes exchanged. For the gravel CWs, the estimated pore volume V<sub>sys</sub> was calculated from the wetland surface area (cm<sup>2</sup>), the water level (cm) and the assumed average gravel porosity (n = 0.35), whereas for the plant root mat V<sub>sys</sub> was derived by emptying and refilling the system. M<sub>out</sub> is the total tracer mass recovered (g).

### 3.2. Hydraulic characteristics

In the tanks-in-series model, the flow behavior of CWs is conceptually described as a transition between a plug-flow reactor (PFR) and a continuously stirred tank reactor (CSTR), where plug flow (PF) is defined via infinite numbers of CSTRs in series. The number N of CSTRs is necessary in order to generate a residence time distribution similar to that obtained for the CW system is given by the inverse of the dimensionless variance ( $\sigma_{\phi}^2 = \sigma^2/\tau^2$ ), Eq. (1). In a single CSTR, all particles entering the reactor are immediately and uniformly distributed, and accordingly, the response curve of a tracer impulse equals an exponential decay function under steady state flow conditions (Headley and Kadlec, 2007). In contrast, for infinite tanks in series, the tracer response curve shows a small degree of dispersion and therefore denotes PF. Thus, the N-index represents a measure of PF behavior.

$$N = \frac{1}{\sigma_{\phi}^2} \quad (1)$$

Given that mixing and dispersion occurs as water flows through the wetland media (Kadlec and Wallace, 2008), flow in CWs may also be evaluated according to the flow in porous media approach. Hence, for a detailed characterization of the flow in treatment wetlands, alternative parameters that display dispersion tendency, such as the dispersion number (D<sub>n</sub> = 1/Pé, dimensionless), the longitudinal dispersivity (α<sub>L</sub> = D/v, m), or the Péclet number (Pé = vL/D, dimensionless), should be calculated from the dispersion coefficient (D = σ<sup>2</sup>v<sup>3</sup>/2L, m<sup>2</sup> d<sup>-1</sup>), where v is the mean flow velocity (v = L/τ, m d<sup>-1</sup>) and L equals the flow distance (m) (here the length of the CW). Regarding CWs, dispersion is accepted to be low for D<sub>n</sub> < 0.025 (U.S. EPA, 2000), indicative of PF, intermediate for D<sub>n</sub> > 0.025 (Kadlec and Wallace, 2008), and high for D<sub>n</sub> > 0.2 (U.S. EPA, 2000), indicative of a high degree of mixing. Overall, Pé is low for dispersion/diffusion-dominated and large for advective-dominated systems (Persson and Wittgren, 2003; Albuquerque et al., 2004).

### 3.3. Flow path integration

A method to estimate the flow-effective pore volume of the basin, accounting for the flow fluctuations implicitly, was derived as follows: consider a parcel of water moving within a – generally non-uniform – flow field. Its residence time will increase over the distance along the motion path. Evapotranspiration in a CW will lead to a linear decrease of flow velocity and flow rate along flow distance  $x$ ; precipitation, *vice versa*, would enhance it. Assuming the water-filled porous medium is homogeneous and fairly conductive, i.e. of constant saturated thickness  $h$ , a 1D scenario in the  $x$ -direction is warranted. To estimate  $\tau$  we use the basic definition of flow velocity  $v = dx/dt$  and re-arrange to  $dt = dx/v$ , which yields the infinitesimal of water residence time.

The water balance along the flow direction in a rectangular wetland undergoing evapotranspiration of flow rate  $q_{et}$  [ $L d^{-1}$ ], i.e. [ $m s^{-1}$ ] at its top area, within the boundary conditions defined by the volumetric fluxes  $Q(0) = Q_{in}$  and  $Q(x = L) = Q_{out}$ , is given by:

$$Q(x) = q_{in}A_{in} - q_{et}A_{surf} = q_{in}hw - q_{et}xw \quad (2)$$

Cancelling the width  $w$ , and replacing  $Q$  by specific discharge  $q = Q/A_{in}$ , being related to water flow velocity  $v$  and effective porosity  $\theta$  by  $v = q/\theta$ , leads to

$$q(x) = q_{in} - \frac{q_{et}x}{h} \quad \text{or} \quad v(x) = v_{in} - \frac{q_{et}x}{\theta h} \quad (3)$$

For  $\tau$  within a single compartment during a time interval of constant flow we obtain the integral:

$$\tau = \int_0^x \frac{dx}{v} = \int_0^x \frac{\theta}{q_{in} - q_{et}x/h} dx \quad (4)$$

The solution is

$$\tau = -\frac{\theta \cdot h}{q_{et}} \cdot \ln \left( 1 - \frac{q_{et}x}{q_{in}h} \right), \quad \text{for } q_{et} \neq 0 \quad \text{and} \quad \tau = \frac{\theta \cdot x}{q_{in}} \quad \text{if } q_{et} = 0 \quad (5)$$

This approach of flow path integration is closely related to particle tracking methods such as described by Pollock (1988). It has no dispersive component, and therefore yields a single breakthrough time representing the center of mass arrival time  $\tau$ . If  $\tau$  is known, solving for  $\theta$  yields flow-effective porosity. The expansion of the method to transient flow conditions is described in the Supporting information.

### 3.4. Evaluation of local BTCs and calculation of local contaminant load

Temporal statistical moments provide a simple and well-established approach for analyzing tracer BTCs (Harvey and Gorelick, 1995; Cirpka and Kitanidis, 2000; Ptak et al., 2004; Shook and Forsmann, 2005). Following up this approach Harvey and Gorelick (1995) developed a method to delineate spatial patterns of solute loads in heterogeneous porous media. This concept has been successfully applied by Englert et al. (2009) to estimate contaminant remediation in heterogeneous aquifers. The concept makes use of the facts that (i) zeroth moment of concentration provides a measure of

accumulated mass having passed a certain location per unit discharge, and (ii) the first moment delivers the required information about the discharge passing the location. More specifically, first over zeroth moment represents the mean tracer arrival time  $\tau$  at the location, which can be linked to flow velocity and thus discharge simply by the spatial coordinate  $x$ :  $q = \theta x/\tau$ . Accordingly, mass per discharge times discharge yields accumulated total mass having passed the zone of interest. In this manner local tracer BTCs can be used to estimate mass flux at each transect.

Mean local tracer breakthrough times  $t_{break}$  within the filter provide information on local flow velocities ( $x/t_{break}$ ), enabling prediction of local flow rates  $Q$  ( $L d^{-1}$ ) if mean filter porosities are assumed. For simplification, the local flow rate was calculated for a distinct horizon of the cross-section around each sampling port normal to flow direction, assuming constant contaminant concentration and flow velocity within. Each horizon was 1.1 m wide (width of the wetland) and 0.1 m high, with the upper and lower edge being 5 cm above and below the respective sampling depth. The local contaminant load was calculated as follows:

$$\text{Load} (mg d^{-1}) = c_{x,y} * \theta * v_{x,y} * A = c_{x,y} * Q_A \quad (6)$$

where  $c_{x,y}$  is the contaminant concentration ( $mg L^{-1}$ ) at the sampling point  $(x,y)$ ,  $v_{x,y}$  is the mean flow velocity ( $m d^{-1}$ ) at the sampling position  $(x,y)$ , accessible by the quotient  $x/t_{break}$ , where  $x$  is the flow distance and  $t_{break}$  is the mean tracer breakthrough time at the respective sampling point  $(x,y)$  derived from the analysis of the local BTC,  $A$  ( $m^{-2}$ ) represents the horizon for which the flow was extrapolated, and  $Q_A$  is the water flow ( $L d^{-1}$ ) through the cross-section  $A$ .

## 4. Results and discussion

The results and discussion part is divided into three sections. The first Section 4.1 addresses the evaluation of the hydraulic flow behavior of the gravel CWs and the hydroponic plant root mat by analyzing outlet tracer BTCs using the temporal moment method. The second part (4.2) is about the relation between the goodness of the hydraulic flow behavior measured by the hydraulic indices and the achieved purification efficiencies. The third paragraph (4.3) presents contaminant loads within the gravel CWs predicted from the temporal moment analysis of local BTCs and the local contaminant concentrations.

### 4.1. CW-specific hydraulic parameters

Generally, the tracer recovery rate  $R$  is used as an indicator for the reliability of the hydraulic parameters calculated from the tracer response curves. For both gravel CWs  $R$  reached  $>80\%$  (Table 2), a threshold stated to be acceptable for the determination of reliable hydraulic indices (Headley and Kadlec, 2007). In contrast, considerably lower recovery rates were observed for the hydroponic plant root mat, which might be an effect of light-induced fluorescein degradation (Käss, 1992) due to the partly open water surface. The contribution of pH-dependent chemical precipitation of the tracer is assumed to be



**Table 2 – Results of the tracer tests including the hydraulic parameters obtained by means of temporal moment analysis of the outlet tracer BTCs: tracer recovery (R, %), initial tracer detection ( $t_s$ , d), mean residence time ( $\tau$ , d), variance ( $\sigma^2$ , d<sup>2</sup>), dimensionless variance ( $\sigma^2 = \sigma^2/\tau^2$ , dimensionless), number of continuously stirred tank reactors (N, dimensionless), dispersion coefficient ( $D = \sigma^2 v^2/(2x)$ , m<sup>2</sup> d<sup>-1</sup>), dispersion number ( $D_n = D/(vx)$ , dimensionless), Péclet number ( $Pé = 1/D_n = v * x/D$ , dimensionless), longitudinal dispersivity ( $\alpha_L = D/v$ , m), and porosity ( $\theta$ , dimensionless). Normalized parameter results are given in brackets (calculation based on the expected system water volume).**

Parameter	Gravel filter		Hydroponic plant root mat	
	Planted <sup>a</sup>	Unplanted <sup>a</sup>	15 cm water level <sup>b</sup>	30 cm water level <sup>c</sup>
R [%]	80	87	53	67
$t_s$ [d]	2.3 (0.66)	2.3 (0.75)	1.5 (0.37)	1.7 (0.24)
$\tau$ [d]	4.6 (1.31)	3.8 (1.26)	7.1 (1.73)	11.9 (1.63)
$\sigma^2$ [d <sup>2</sup> ]	1.9 (0.15)	3.1 (0.34)	9.4 (0.57)	74.4 (1.39)
$\sigma_0^2$ [-]	0.09	0.22	0.19	0.52
N [-]	11.3	4.6	5.3	1.9
D [m <sup>2</sup> d <sup>-1</sup> ]	0.24	0.72	0.34	0.55
$D_n$ [-]	0.04	0.11	0.09	0.26
Pé [-]	23	9	11	4
$\alpha_L$ [m]	0.22	0.54	0.47	1.31
$\theta$ [-]	0.46	0.38	1.08	1.10

a Tracer experiment start: 7/9/2009.

b Tracer experiment start: 3/9/2009.

c Tracer experiment start: 14/10/2009.

negligible, since the pH did not change between in- and outflow (pH:  $7.2 \pm 0.1$  SD), although the actual pH-gradient at root surfaces and thus local chemical precipitation potential remained unknown. However, even at  $R \sim 50\%$  hydraulic parameters were found to be valid (Lin et al., 2003; Dierberg and DeBusk, 2005).

#### 4.1.1. Gravel-based constructed wetlands

Overall, the planting considerably improved the flow behavior in the gravel filter, as indicated by the reduced dispersion tendency and the elevated plug-flow component (see Table 2). The same effect has been reported by Chazarenc et al. (2003) who observed seasonality of Péclet numbers with lower Pé during winter/spring ( $Pé = 7–11$ ) (when plants are in a state of reduced activity) than during summer ( $Pé = 14–16$ ), and by Persson et al. (1999) who simulated the effect of various vegetation styles and found that the number of CSTRs increased from 5.7 to 15 for the base and the fully vegetated case, respectively. In contrast, Hamouri et al. (2007) found almost identical dispersion for planted (*P. australis*:  $D_n = 0.070$ ,  $Pé = 14.29$ ; *Arundo donax*:  $D_n = 0.069$ ,  $Pé = 14.49$ ) and unplanted ( $D_n = 0.072$ ,  $Pé = 13.89$ ) CWs, but did not further discuss these findings.

The hydraulic flow behavior of the planted gravel filter (see Table 1) proved to be good in comparison to other CWs. On average, HSSF CWs achieve an N-index of  $11.0 \pm 1.2$  (Kadlec and Wallace, 2008), with  $N \geq 8$  being indicative for close to PF

behavior (Kadlec et al., 2010): a limit exceeded by the present gravel CW. In order to gauge PF behavior, the dimensionless variance – in theory being zero for PF and unity for a well-mixed system – can be interpreted as the percentage deviation from PF (Kadlec, 1994). Accordingly, the planted and unplanted filter would be 9% and 22% of the way from a PFR to a CSTR, respectively. The dispersion indices obtained for our CWs (Table 1) are similar to those observed for several other HSSF wetlands ( $D$ : 1.18–1.5 mm<sup>2</sup> s<sup>-1</sup> = 0.1–0.13 m<sup>2</sup> d<sup>-1</sup>,  $\alpha$ : 62–67 mm for similar-sized CWs (Grismer et al., 2001);  $D_n$ : 0.017–0.025 for laboratory-scale CWs (Araújo et al., 2008), 0.05–0.18 for pilot-scale CWs (García et al., 2004), 0.001–0.767 for field-scale CWs (Kadlec, 1994; Martinez and Wise, 2003)) and indicate a medium dispersion (U.S. EPA, 2000). This interpretation is supported by the Péclet numbers, which were within the range reported for other CWs ( $Pé = 5–30$ ) (Keefe et al., 2004; Hamouri et al., 2007; Araújo et al., 2008; Ranieri et al., 2011). They were found to be well above the limit at which advection and dispersion processes become significant ( $Pé > 4$ ) (Grismer et al., 2001), but far below the limit representing PF behavior ( $Pé > 100$ ) (Hoehn and Roberts, 1982). Hence, both gravel CWs displayed transitional flow behavior between a PFR and a CSTR.

The large deviation between  $\tau$  and nHRT suggests that the actual porosities of both filters were in fact greater than the assumed gravel porosity, and/or that mean residence times appeared longer due to the presence of stagnant zones or tracer sorption (e.g. by microbial biofilms). The mean actual residence time exceeded nHRT by about 52% and 34% for the planted and unplanted filters, respectively: a trend that has been found for various wetlands (García et al., 2004; Headley et al., 2005). For comparison, mean residence times are typically about 0.91 nHRT for HSSF wetlands, given that the available wetland volume is not fully utilized (Kadlec and Wallace, 2008). Sorption of fluorescein onto gravel is negligible (Käss, 1992); thus, for the unplanted filter, zones of stagnant water may have led to the long RTD tailing, which in turn shifted the centroid to longer residence times. In the planted filter, fluorescein is susceptible to sorption on root surfaces and dead plant material. The retardation factor ( $R_D = 1 + \rho/n * K_d$ ) was calculated according to Käss (1992), where  $\rho$  is the bulk density of the gravel/soil matrix (approximated as  $\rho = 1.7$  g cm<sup>-3</sup> for quartz and a gravel porosity  $n$  of 0.35), and  $K_d (=f_{OC} * K_{OC})$  is the distribution coefficient, with  $K_{OC}$  being the organic carbon water distribution coefficient, and  $f_{OC}$  being the organic carbon content of the porous media (estimated as 5%).  $K_{OC}$  was estimated from the octanol water distribution coefficient ( $K_{OW}$ ;  $\log K_{OW} = -0.39$ ) (Sabatini and Austin, 1991) by means of the regression  $K_{OC} = 0.937 * K_{OW} - 0.006$  (Brown and Flagg, 1981). Calculation yielded a  $R_D$  of 1.103, which indicates a rather weak retardation, suggesting that actual porosity in the planted CW was greater than the assumed gravel porosity.

The calculation of effective filter porosities yielded reasonable porosities of 46% and 38% for the planted and unplanted CW, respectively. Briefly, calculations based on Eq. (5) and its extension in the Supporting information, using the mean residence time corrected for sorption processes ( $\tau_{corr} = 4.2$  d) for the planted CW, and the mean residence time of the analytical fit of the RTD for the unplanted filter,

according to Van Genuchten and Alves (1982) ( $\tau_{\text{Fit}} = 3.0$  d) in order to exclude bias introduced by the long tailing (as discussed in Section 4.3). The difference between actual and theoretical gravel porosity (35%) suggests that growing roots loosened the gravel compaction and opened new pore space. In case of an even coarser gravel material the opposite effect should be expected.

#### 4.1.2. Hydroponic plant root mat

The normalized outlet tracer response curves (Fig. 1) of the hydroponic plant root mat show relatively broad peaks for both water levels, with an onset shortly after tracer injection (far earlier than the ideal theoretical retention time) and extension over up to three system volumes, thus revealing a wider spectrum of residence times compared to the planted gravel CW. These observations are also reflected by the increased RTD spread and dispersion tendency (Table 2).

Raising the water table from 15 to 30 cm considerably impaired the flow behavior of the plant root mat, as demonstrated by the  $N$ -index decreasing from 5.3 to 1.9 while the various measures of dispersion ( $\sigma^2$ ,  $\sigma_{\theta}^2$ ,  $D$ ,  $D_n$ , Péc) increased. Moreover, the water table elevation resulted in an even earlier initial tracer detection and a second tracer peak. Most notably, the RTD at the high level resembled the curve of a CSTR model, with a steep increase accompanied by a long tailing.

The variation in flow properties upon raising the water level may have been due to transformation of the previously resting into a floating root mat system composed of two horizontal compartments: a densely rooted upper zone and a sparsely rooted deeper zone. Thereby, a preferential flow

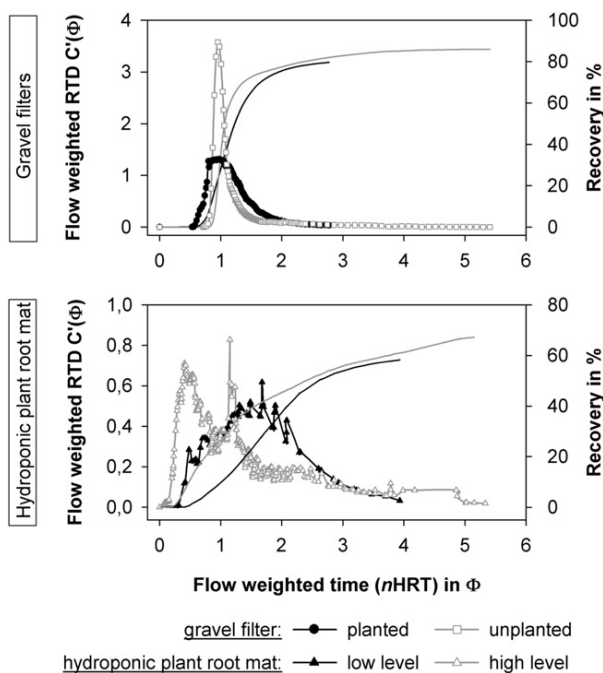
path may have been created in the lower zone at high water level, explaining the short initial detection time. The bimodal shape of the RTD, suggesting the presence of preferential flow paths (Kadlec and Wallace, 2008; Wanko et al., 2009) and/or stagnant zones, and the increased variance ( $\sigma^2 = 74.4$ ) and dispersion at high water level, indicate that the two horizons do not act as discrete layers, but rather that water parcels presumably alternate between the deep and shallow zone while passing the CW.

Overall, our results are in accordance with the findings of Holland et al. (2004), who reported a decrease of  $N$  from 2.1 to 1.4, a 57% increase in RTD spread, and short-circuiting upon a rise of the water table in a 250-m<sup>2</sup> CW. However, detailed comparison of the hydraulic characteristics turned out to be challenging, since very little information is available on the flow behavior of floating plant systems. Comparing a floating plant mat to a free water surface (FWS) wetland ignores the fact that in the latter, flow might be affected by wind friction in the case of sparse vegetation (Lloyd et al., 2003; Kadlec and Wallace, 2008). Nevertheless, dispersion tendency and  $N$ -index of FWS systems ( $D_n = 0.36$  (Kadlec, 2000),  $N = 4.1 \pm 0.4$  (Kadlec and Wallace, 2008)) were similar to our results, at least concerning the low level.

System porosities, as determined by draining and refilling, amounted to 51% and 63% for the low and high level, respectively. In contrast, the flow path integration yielded effective porosities of  $\sim 100\%$  for both water levels. Both approaches are impacted by conceptual errors, given that in the first case the retained water volume is unknown, and in the second case the retardation factor could not be estimated in order to correct  $\tau$  for sorption, since the root mass was unknown. Assuming the adhered water volume to be about 100 L,  $\theta$  calculates to 63% and 69% for the low and high level respectively. These values are reasonable, considering that for dense-emergent-vegetated FWS CWs, porosity values are stated to be 0.65–0.75 (Kadlec and Wallace, 2008).

#### 4.2. Treatment efficiency vs. hydraulic behavior

The planted gravel filter yielded considerably higher benzene, MTBE and ammonium–nitrogen monthly mass removal efficiencies compared to the unplanted reference, upon both a percentage and a mass–load scale (Table 3). Notably, in October and November, when temperatures declined and plant senescence started, the elimination of ammonium sharply decreased for the planted filter, reflecting the stimulating effect of the plants on nitrogen removal (Lee et al., 2009) and the temperature/seasonal dependency of microbial N transformation (Kadlec, 2009). In contrast, the removal of organic compounds was not yet affected by seasonal change. The unplanted reference bed exhibited low but stable removal during the same time period. The treatment efficiency of the hydroponic plant root mat was excellent for the low water level (September), amounting to  $98 \pm 1\%$ ,  $78 \pm 1\%$  and  $74 \pm 1\%$  for benzene, MTBE and ammonium–N, respectively. At the high water level, removal was reduced by 30–44% for all three contaminants. Since seasonal effects can be neglected, at least for the organic pollutants (see Table 3), this trend is probably related to the water table elevation alone. Overall, the CWs can be ranked, regarding absolute contaminant load



**Fig. 1 – Flow-weighted residence time distribution  $C(\Phi)$ : breakthrough curves and tracer mass recovery for the planted gravel CW and the unplanted reference (top) and for the hydroponic plant root mat operated at 15 cm (low) and 30 cm (high) water level (bottom).**

**Table 3 – Contaminant removal (mass load and percentage) and evapotranspiration (ET) for the planted gravel filter, the unplanted reference and the hydroponic plant root mat, for September, October and November 2009. Values give monthly means  $\pm$  standard error; load calculation based on the assumption that contaminant concentrations remained constant between two consecutive samplings (number *N* of sampling campaigns per month: 2–4); ET calculation relates to daily water balances.**

		Benzene removal		MTBE removal		NH <sub>4</sub> <sup>+</sup> -N removal		ET
		[mg m <sup>-2</sup> d <sup>-1</sup> ]	[%]	[mg m <sup>-2</sup> d <sup>-1</sup> ]	[%]	[mg m <sup>-2</sup> d <sup>-1</sup> ]	[%]	[L m <sup>-2</sup> d <sup>-1</sup> ]
Planted gravel filter	Sept	512 $\pm$ 9	53 $\pm$ 1	39 $\pm$ 2	33 $\pm$ 2	819 $\pm$ 27	39 $\pm$ 1	14.3 $\pm$ 0.7
	Oct	527 $\pm$ 29	49 $\pm$ 3	26 $\pm$ 3	22 $\pm$ 2	577 $\pm$ 27	27 $\pm$ 1	10.3 $\pm$ 0.6
	Nov	491 $\pm$ 15	45 $\pm$ 1	36 $\pm$ 3	31 $\pm$ 2	444 $\pm$ 33	21 $\pm$ 2	6.8 $\pm$ 0.6
Unplanted reference	Sept	146 $\pm$ 13	15 $\pm$ 1	17 $\pm$ 3	14 $\pm$ 2	279 $\pm$ 25	13 $\pm$ 1	6.4 $\pm$ 0.2
	Oct	214 $\pm$ 29	20 $\pm$ 3	19 $\pm$ 2	17 $\pm$ 2	281 $\pm$ 23	13 $\pm$ 1	7.1 $\pm$ 0.3
	Nov	321 $\pm$ 20	29 $\pm$ 2	34 $\pm$ 3	29 $\pm$ 2	321 $\pm$ 35	15 $\pm$ 2	5.6 $\pm$ 0.5
Hydroponic plant root mat	Sept	544 $\pm$ 3	98 $\pm$ 1	54 $\pm$ 1	78 $\pm$ 1	893 $\pm$ 17	74 $\pm$ 1	14.0 $\pm$ 0.8
	Oct	420 $\pm$ 20	68 $\pm$ 3	28 $\pm$ 2	42 $\pm$ 3	378 $\pm$ 37	31 $\pm$ 3	8.6 $\pm$ 0.5
	Nov	381 $\pm$ 11	60 $\pm$ 2	28 $\pm$ 2	42 $\pm$ 3	359 $\pm$ 37	30 $\pm$ 3	7.7 $\pm$ 0.4

elimination, as follows: hydroponic plant root mat at low level > planted gravel filter >> hydroponic plant root mat at high level > unplanted gravel filter.

Some recent findings support the observed ranking. The positive effect of low compared to high operational water level on removal efficiency has also been observed for gravel-based SSF CWs concerning chemical oxygen demand (COD), five-day biochemical oxygen demand (BOD<sub>5</sub>) and ammonia (García et al., 2005) as well as ibuprofen (Matamoros et al., 2005). Matamoros et al. (2005) related this fact to more pronounced contact between roots and water in the shallower bed. This might also be the case here, considering that the water table elevation reduced the overall root–water ratio. In this context, Sasser et al. (1991) observed a depth gradient for total nitrogen and phosphorus in a floating marsh, with low concentrations in the mat and high concentrations in the free water below. The elevated treatment potential of the hydroponic plant root mat compared to the gravel CW was previously shown in a long-term performance analysis (Seeger et al., 2011a) and a contaminant mass balance study (Seeger et al., 2011b). Also, the removal of copper and zinc proved to be higher in floating macrophyte systems than for conventional SSF CWs (Tanner and Headley, 2011). Hijosa-Valsero et al. (2010), on the other hand, reported the performance of conventional CWs and soilless systems to be primarily compound-dependent, and the presence of gravel not to be decisive. However, soilless systems such as floating macrophytes revealed good treatment results for wastewaters contaminated with N and P (Nahlik and Mitsch, 2006) as well as veterinary antibiotics (Xian et al., 2010).

Generally, PF is assumed to result in optimum treatment performance (Kadlec, 2000; Headley and Kadlec, 2007; Wahl et al., 2010). The hydraulic indices (Table 1) reflect the deviation from PF, and express the hydraulic performance of the CWs as follows: planted gravel filter > hydroponic plant root mat at low level > unplanted gravel filter > hydroponic plant root mat at high level. Thus, the rankings according to hydraulic performance and removal efficiency did not correlate completely: the CW with the best hydraulic behavior only yielded the second-highest contaminant removal and vice versa. More precisely, although the plant root mat exhibited less ideal flow behavior compared to the planted gravel CW,

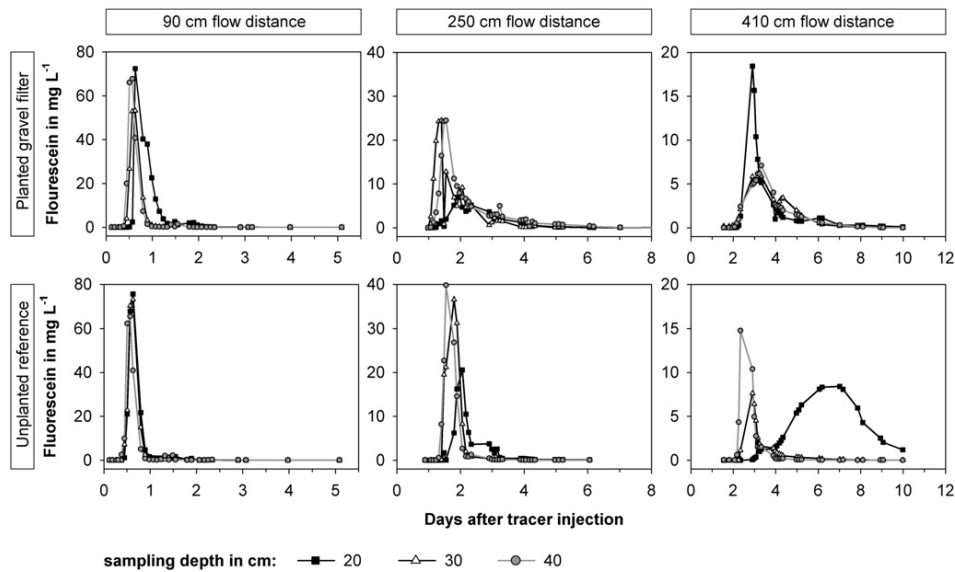
the plant root mat (at low water level) achieved the highest purification efficiency. According to Alcocer et al. (2012), who found that increasing loading rates resulted in increased dispersion, the planted gravel filter might exhibit even better flow indices in case it would be operated at the lower loading rate of the plant root mat. Even though reducing the loading rate would entail increased  $\tau$ , which might result in improved removal performance, previous studies showed that the hydroponic plant root mat still achieved higher percentage removal compared to the gravel CW when both systems were run at similar loading rates (Seeger et al., 2011a,b). Hence, our results indicate, that the key factors for high removal efficiency are the physico-chemical conditions in the rhizosphere, the actual water–root contact and a residence time long enough rather than merely a good flow behavior.

#### 4.3. Local flow and contaminant mass loads

The monitoring of the tracer BTCs at specific positions in the gravel filters enabled: (i) the investigation of local water flow variations, and subsequently (ii) the calculation of local contaminant loads.

Fig. 2 depicts the local BTCs for the gravel CWs. Overall, tracer concentration decreased and peaks became broader with longer flow distance, indicating transversal and longitudinal dispersion processes. The uneven vertical distribution of the tracer at longer flow distance implies non-ideal flow with preferential flow paths, and shows that the three sampling depths interacted with each other. Contrary to our findings, Headley et al. (2005) reported tracer arrival time and concentration to be independent of sampling depth. In the unplanted reference, the tracer response peak at 410 cm flow distance was considerably delayed and much broader for the shallow horizon (20 cm depth) compared to the deeper zones. This suggests a zone of stagnant water at this location (in the following termed 410/20). This would also explain the relatively long tailing of the outlet BTC, given that water from all horizons is mixed at the outlet.

Figure S1 shows mean breakthrough times  $t_{\text{break}}$  of the tracer pulse at the specific sampling positions (*d*, top) and corresponding local flow rates  $Q$  (L d<sup>-1</sup>, bottom). In summary, for the unplanted filter, velocity ( $v = x/t_{\text{break}}$ ) and flow rate



**Fig. 2 – Fluorescein concentration in the planted gravel CW (top) and the unplanted reference (bottom) depending on the flow distance (left: 90 cm; middle: 250 cm; right: 410 cm) and filter depth (20 cm, 30 cm and 40 cm).**

increased with filter depth. The gradient was most pronounced at longer flow distances, e.g. the deviation of  $Q$  between the shallow and deep horizon amounted to  $16 \text{ L d}^{-1}$  and  $37 \text{ L d}^{-1}$  for 250 cm and 410 cm flow distance, respectively. Fast bottom flow has also been observed for a similar-sized planted CW (García et al., 2003). The authors related this fact to the location of the outlet tube at the bottom of the basin. This argument might hold for our CW as well, and we furthermore suggest that this bottom drag might also explain the existence of the zone of stagnant water at the position 410/20. In contrast, for the planted CW, flow velocity and flow rate were higher in the middle horizon ( $v = 1.35 \text{ m d}^{-1}$ ,  $Q = 68 \text{ L d}^{-1}$ ) compared to the shallow ( $v = 0.95 \text{ m d}^{-1}$ ,  $Q = 48 \text{ L d}^{-1}$ ) and deep ( $v = 1.08 \text{ m d}^{-1}$ ,  $Q = 54 \text{ L d}^{-1}$ ) zones (250 cm flow distance). The increased flow rate might be explained by transpiration-induced water drag. This hypothesis is supported by the depth profile taken from an equivalent CW in summer 2009, which showed that the upper 20 cm of the porous media contained 88% of the total root mass (see Table 4). Therefore, most of the transpired water can be assumed to originate from this region: consequently, effective flow in the upper zone is slowed-down and water from the middle zone might be dragged upwards, entailing increased flow in the middle horizon. Notably, close to the outflow the depth gradient of  $Q$  ceased, possibly caused by the interaction of plant-induced upward drag and outflow bottom drag. Although the location of the outlet tube controlled the flow in the unplanted wetland, the differences in the flow patterns of the planted and unplanted CW pointed out that within the planted CW the plant-effect dominated the tube-effect. In summary, our study showed vertical variability of flow rate and velocity, being presumably related to the presence of plants and the position of the outlet tube.

2D contaminant (benzene, MTBE and ammonium-N) load patterns ( $\text{mg d}^{-1}$ ) are presented in Fig. 3; to the best of our knowledge, this is the first time that such patterns have been

assessed for a wetland system. The unplanted filter displayed a depth zonation, which is in accordance with both the contaminant concentration pattern (see Figure S2) and the local flow rates, except for the dead zone (410/20), which is characterized by similar contaminant concentrations as in the lower horizons but considerably reduced flow rate. Contaminant loads in the planted filter decreased with distance from the inlet for all three pollutants, being most pronounced for benzene. MTBE and ammonium-N loads were elevated in the middle horizon, although concentration analysis revealed a depth gradient with highest concentration at lowest sampling depth. Thus, we could demonstrate that 2D removal trends predicted from concentration analysis of the pore water deviated from actual local load changes, and that plant transpiration influences vertical flow rates, leading to

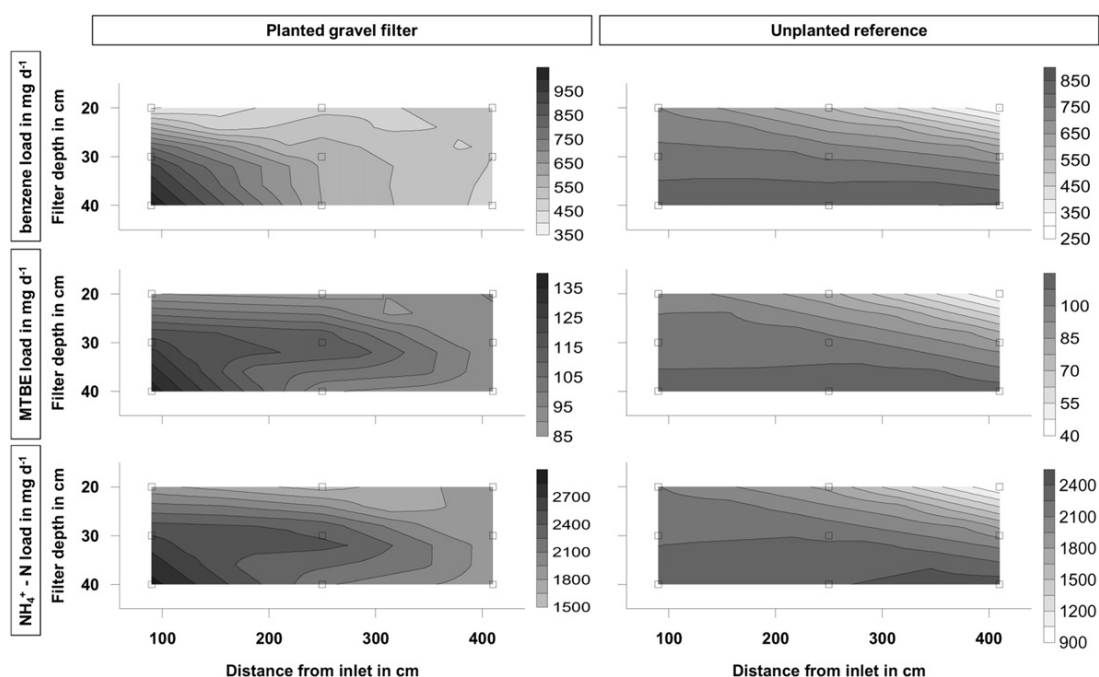
**Table 4 – Vertical profile of the root distribution in an HSSF CW similar to system A. The CW contained gravel with 0.1%-wt charcoal as a filter additive and was planted with *Phragmites australis*. The filter core was taken with a stainless-steel sampling device which was driven into the filter bed using a pneumatic pistol. Gravel compaction may have been affected during the sampling procedure. Therefore, the total core length was divided into 4 equally long sections, considered to represent the four filter depths presented hereafter.**

Filter depth [cm]	Gravel [g]	Fine roots <sup>a</sup> [g]	Medium roots <sup>b</sup> [g]	Rhizome [g]
0–10	283	1.04	0.11	2.67
10–20	212	0.52	0.31	2.00
20–30	237	0.16	0.33	0.00
30–40	283	0.11	0.33	0.00

a Fine roots: <1 mm diameter

b Medium roots: >1 mm diameter.





**Fig. 3 – Benzene (top), MTBE (middle) and ammonium-nitrogen (bottom) load within the planted gravel CW (left) and the unplanted reference (right) calculated for the sampling campaign 17/8/2009. Squares denote the sampling positions in the filters. Counter plot computation based on triangulation and linear interpolation.**

elevated contaminant flux immediately below the densely rooted porous media zone. In our opinion, these findings are transferable to other HSSF–CW systems.

## 5. Conclusion

In the present work we present a detailed evaluation of the hydraulic performance and the load removal efficiency of several HSSF CWs (a planted and unplanted gravel-based CW) and a hydroponic plant root mat system (operated at two water levels) treating gasoline and ammonium contaminated groundwater. We investigated the flow behavior following up the state-of-the-art procedure that comprises the determination of system-specific overall hydraulic indices by analyzing outlet tracer response curves and relating these to the overall contaminant removal efficiency. The analysis of local BTCs (in the filter) reveals vertical variability of flow rate and velocity which allowed for the localization of preferential flow paths as well as stagnant zones and the determination of local contaminant loads within the gravel CWs.

Although conducted at a specific model wetland, the results enabled a complete CW performance analysis and thus the study improves the knowledge on the flow behavior within the CWs in order to overcome the black box concept often applied to CW systems. We also provide implications for improved wetland design and operation. (i) The high contaminant flux in the middle horizon below the densely rooted zone in the planted gravel filter evidenced that water from lower horizons is actively transported into the shallower densely rooted zones, likely induced by plant transpiration.

However, we suggest that CWs should not be designed considerably deeper than the assumed rooting depth, since the zone of influence by transpiration is clearly limited to a certain depth. (ii) The position of the outlet tube at the bottom of the basin affected the flow behavior, resulting in preferential bottom flow and a zone of stagnant water at longest flow distance and shallow filter depth for the unplanted gravel CW. Although this effect was only observed in the unplanted reference filter, it appears to be of advantage to install the outflow at shallower depth. (iii) Since the removal efficiency and the hydraulic performance of the hydroponic plant root mat decreased when the system was transformed from a resting (without free water below the roots) into a floating mat, we recommend that hydroponic plant root mats should be operated in a resting mode in order to ensure optimal contaminant–root contact and avoid short circuits. (iv) Overall, the resting hydroponic plant root mat achieved highest removal efficiency and thus proved to be a promising alternative to conventional soil-based CWs. This would not have been expected from the obtained flow characteristics indicating less ideal flow behavior, presumably a result of increased heterogeneity in root density.

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## Appendix A. Supplementary data

Local  $t_{\text{break}}$  and  $Q$  for the gravel CWs, contaminant pore water concentrations, and supplementary information for the flow path integration approach. This material is available free of charge at <http://dx.doi.org/10.1016/j.watres.2012.10.051>.

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## Glossary

$A_{in}$ : area perpendicular to the flow direction [ $L^2$ ]

$A_{surf}$ : surface area [ $L^2$ ]

$c'(\Phi)$ : normalized concentration [–]

$c_{tracer}$ : fluorescein concentration of the tracer solution [ $M L^3$ ]

$c_{x,y}$ : contaminant concentration at the sampling position (x,y) [ $M L^3$ ]

D: dispersion coefficient [ $L^2 t^{-1}$ ]

$D_n$ : dispersion number [–]

$f_{OC}$ : organic carbon content [%]

h: water table [L]

$K_d$ : solid water distribution coefficient [ $L^3 M^{-1}$ ]

$K_{OC}$ : organic carbon water distribution coefficient [ $L^3 M^{-1}$ ]

$K_{OW}$ : octanol water distribution coefficient [–]

L: length of the wetland [L]

$M_{in}$ : total mass of tracer applied [M]

$M_{out}$ : total tracer mass recovered [M]

N: number of continuously stirred tank reactor [–]

n: gravel porosity [–]

nHRT: theoretical hydraulic retention time [t]

Pé: Péclet number [–]

$P_r$ : pumping rate [ $L^3 t^{-1}$ ]

Q: flow rate [ $L^3 t^{-1}$ ]

$Q_A$ : flow through the cross-section A [ $L^3 t^{-1}$ ]

$q_{et}$ : evapotranspiration rate per surface area [ $L t^{-1}$ ]

$q_{in}$ : inflow specific discharge [ $L t^{-1}$ ]

$Q_{in}$ : mean inflow rate [ $L^3 t^{-1}$ ]

$Q_{mean}$ : mean flux [ $L^3 t^{-1}$ ]

$Q_{out}$ : mean outflow rate [ $L^3 t^{-1}$ ]

R: tracer recovery [%]

$R_D$ : retardation factor [–]

$t_{break}$ : tracer breakthrough time [t]

$t_s$ : initial tracer detection [t]

v: flow velocity [ $L t^{-1}$ ]

$V_{out}(t)$ : outflow volume accumulated for the time t [ $L^3 t^{-1}$ ]

$V_s$ : sample volume [ $L^3$ ]

$V_{sys}$ : estimated pore volume [ $L^3$ ]

$v_{x,y}$ : flow velocity at the sampling position (x,y) [ $L t^{-1}$ ]

w: width of the wetland [L]

x: flow distance [L]

$\Phi$ : dimensionless flow-weighted time [–]

$\Delta t$ : time interval of tracer injection [t]

$\alpha_L$ : longitudinal dispersivity [L]

$\theta$ : porosity [–]

$\rho$ : density of the gravel/soil matrix [ $M L^{-3}$ ]

$\sigma^2$ : variance [ $t^2$ ]

$\sigma_{\theta}^2$ : dimensionless variance [–]

$\tau$ : mean residence time [t]

$\tau_{corr}$ : mean residence time corrected for sorption processes [t]

$\tau_{fit}$ : mean residence time of the analytical fit of the RTD [t]

## 5 Summary, conclusion, and future perspectives

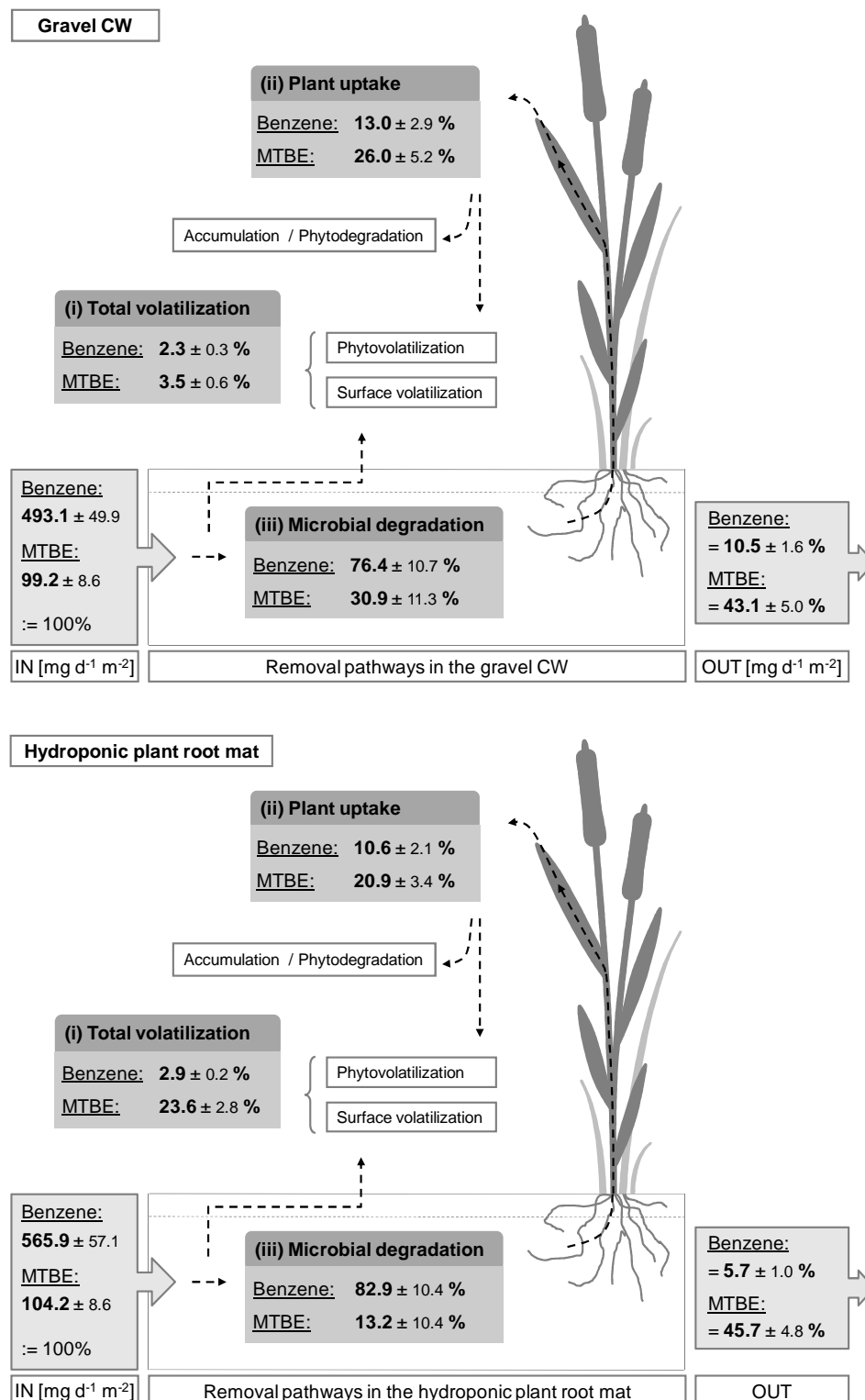
The overall aim of this study was to evaluate the treatment performance of differently designed HSSF CWs at the pilot-scale for the remediation of water contaminated with benzene, MTBE and ammonium. Investigations were carried out at the field site Leuna using the local polluted groundwater for feeding the CWs (gravel CWs with different filter composition, an unplanted gravel filter as a reference system and a hydroponic plant root mat) and were conducted over a period of 30 months. The key objectives were to gain knowledge on (i) contaminant specific treatment efficiency depending on wetland type and filter composition (chapter 2), (ii) the fate of the VOCs in the different CW types taking into account the main elimination pathways volatilization, plant uptake and microbial degradation (chapter 3), and (iii) the hydraulic behavior of the CWs with regard to wetland type and operational mode (chapter 4).

### 5.1 Summary of the results and concluding remarks

In **chapter 2**, the effectiveness of the gravel filter and the hydroponic plant root mat to remove benzene, MTBE and ammonium from groundwater, and also the impact of the filter additives charcoal and ferric oxide, is presented. Overall, the results revealed that the extent of contaminant decline is (i) greatly affected by the wetland type, with the hydroponic plant root mat realizing lower outflow concentrations and longer-lasting high treatment performance than the gravel-based CW, (ii) season-dependent, with increased concentration decline during spring-summer at temperatures above 15°C, when plants were growing, (iii) contaminant-specific with most pronounced decline following the order benzene  $\gg$  ammonium  $>$  MTBE for the planted gravel filter and benzene  $>$  MTBE  $\gg$  ammonium for the hydroponic plant root mat, and (iv) not improved by the filter additives charcoal and ferric oxide in the long term, although sorption processes were observed and elevated ferrous iron formation indicated iron(III)

reduction. Specifically, at average inflow concentrations of  $20 \pm 3.3 \text{ mg L}^{-1}$ ,  $3.7 \pm 0.7 \text{ mg L}^{-1}$  and  $45 \pm 3.4 \text{ mg L}^{-1}$  for benzene, MTBE and ammonium-N, the plant root mat and the planted gravel CW achieved relative concentration decrease during summer (May - Aug. 2008) of about  $99 \pm 1 \%$  and  $81 \pm 7 \%$  for benzene,  $82 \pm 4 \%$  and  $17 \pm 7 \%$  for MTBE, and  $41 \pm 7 \%$  and  $54 \pm 17 \%$  for ammonium-N. Comparison of these results with other wetland studies (HF and VF CWs) emphasizes the excellent treatment performance of the hydroponic plant root mat in particular regarding MTBE, given that concentration decline reported in the literature was less than half of that found in the presented study (e.g. Keefe et al., 2004; Bedessem et al., 2007). For benzene, the results of the present study were in the upper reported range (concentration decline 75-99%; e.g. Wallace et al., 2001; Tang et al., 2009; Rakoczy et al., 2011), whereas ammonium treatment efficiency was lower than the average value reported for 150 HF wetlands (58%; Vymazal (2005)). Based on the determination of milieu parameters, the filters were shown to be mainly anaerobic, as pointed out by the very low dissolved oxygen content ( $<0.5 \text{ mg L}^{-1}$ ), the low redox values of the pore water ( $<122 \text{ mV}$ ) and the observed low levels of nitrate and nitrite (during summer:  $<1.2 \text{ mg L}^{-1}$ ). Therefore, oxygen is considered to be one of the limiting factors for contaminant turnover in both wetland types. Concerning the processes contributing to VOC removal, the potential for microbial degradation could be proven for benzene in an aerobic microcosm study by a shift in carbon isotope fractionation ( $+2.8\text{-}4.3\%$ ) and elevated MPN counts for benzene degraders in water (up to  $7.8 \times 10^3 \text{ MPN g}^{-1}$ ) and gravel (up to  $3.8 \times 10^4 \text{ MPN g}^{-1}$ ) samples taken from the wetlands in comparison with groundwater samples ( $1.5 \times 10^2 \text{ MPN g}^{-1}$ ). Summing up, the results of the comparative study show the principle potential of HF CWs for remediating the present contaminated groundwater and chemically polluted water in general, and furthermore point out that charcoal and ferric oxide do not considerably enhance treatment performance. The key finding, however, is that hydroponic plant root mat systems represent a promising alternative to conventional solid filter matrix HF CWs for treatment of VOC contaminated waters.

The focus of **chapter 3** was on the evaluation of actual treatment efficiency of the gravel CW and the hydroponic plant root mat by investigating contaminant fate and setting up contaminant mass balances in order to quantify and distinguish between elimination and distribution pathways (volatilization, plant uptake, and microbial degradation). The mass balancing was carried out for the compounds benzene and MTBE. For measuring VOC air emission, dynamic air chambers (DAC) were mounted on top of the CWs; the measurement of VOC in the atmosphere for the mass balance calculation



**Figure 5.1:** Benzene and MTBE summer mass balances for the gravel CW (top) and the hydroponic plant root mat (bottom) derived from the monitoring of influent and effluent VOC load, the determination of VOC volatilization using dynamic air chambers, and the calculation of VOC uptake into the plants based on the transpiration stream concentration factor (see chapter 3).

was performed by N. Reiche. First of all, the VOC load removal assessment confirmed the principle trends obtained from the performance evaluation based on contaminant outflow concentrations: Benzene and MTBE effluent loads showed great seasonal variance, with highest removal efficiencies during summer, and the hydroponic plant root mat achieved higher maximum removal (benzene:  $99.9 \pm 8.5 \%$ ,  $606 \pm 51 \text{ mg d}^{-1} \text{ m}^{-2}$ ; MTBE:  $96 \pm 8 \%$ ,  $117 \pm 9 \text{ mg d}^{-1} \text{ m}^{-2}$ ) than the gravel CW (benzene:  $96 \pm 8 \%$ ,  $480 \pm 42 \text{ mg d}^{-1} \text{ m}^{-2}$ ; MTBE:  $75 \pm 11 \%$ ,  $85 \pm 13 \text{ mg d}^{-1} \text{ m}^{-2}$ ). Second, the results and the calculations generated by the balancing model state that (i) not only the overall load removal from the water phase, but also the degree of mass flux via a particular removal pathway is contaminant dependent, and (ii) the wetland's characteristics have a direct impact on emission dimensions. Figure 5.1 gives an overview of the mass fluxes (in % of applied mass) regarding volatilization, plant uptake, and microbial degradation in the rhizosphere for the gravel CW and the hydroponic plant root mat during summer time. Briefly, irrespective of the wetland type benzene was removed to greater extent than MTBE and the main mass flux for benzene was by microbial contaminant degradation (76.4%, 82.9%), while plant uptake and volatilization fluxes amounted to much lower values. During winter the same trend of mass flux was obtained, but the values were lower. By comparison, MTBE mass flux via microbial degradation was relatively poor for both CW types (13.2%, 30.9%). Particular attention should furthermore be paid to the fact that the CW types differed with respect to total volatilization of MTBE, which was enhanced in the hydroponic plant root mat (23.6%) compared to the gravel CW (3.5%). The outcome of this mass balance evaluation can be summarized as follows: The hydroponic plant root mat achieved good treatment results for benzene, with high mass flux via microbial degradation and low emission flux. However, for MTBE removal was much lower and the achieved removal was mainly caused by volatilization, more precisely by surface volatilization presumably resulting from the direct contact between water and atmosphere. Hence, the application potential of the plant root mat strongly depends on the contaminant to be treated, e.g. for VOCs similar to benzene (e.g. volatile but sufficiently fast degradable) it appears to provide a viable and reliable treatment option, whereas for compounds exhibiting high volatility, high water solubility and reduced degradability such as MTBE, emission might arise leading to restricted applicability. In contrast, the gravel CW achieved similar good treatment results for benzene, but volatilization was shown to be negligible (<5%) for both benzene and MTBE. Overall, mass balancing allowed for a conclusive analysis of the reliability of the two CW types, as it enabled estimation of mass flux due to microbial degradation, and the results may serve as a basis for deciding which CW type, a conventional gravel



CW or a hydroponic plant root mat, is appropriate for treatment of a wastewater that contains different VOCs.

**Chapter 4** completes the CW performance analysis by providing a detailed characterization of the wetland-specific flow behavior and relating hydraulic indices to contaminant mass removal in order to investigate to what extent the flow behavior influences and predetermines removal efficiency. Investigations were carried out for the planted gravel CW, the unplanted gravel filter as a reference and the hydroponic plant root mat operated at two water levels. Tracer test results evinced best hydraulic behavior for the planted gravel CW ( $N = 11.3$ ,  $D_n = 0.04$ ,  $Pe = 23$ ), whereas the plant root mat exhibited pronounced dispersion tendencies and thus less optimal flow even when operated at low water table ( $N = 5.3$ ,  $D_n = 0.09$ ,  $Pe = 11$ ). However, highest mass removal for benzene, MTBE and ammonium were achieved by the plant root mat (at low water level). In order to test whether the treatment performance of the plant root mat can still be improved, the resting mat was transformed into a floating system by water table elevation. These changes in operational mode/design impaired both hydraulic flow behavior - as indicated by increased dispersion parameters and the observation of short-circuit flow - and contaminant load removal even though average residence time was increased. The generation of a not yet fully rooted zone below the swimming root mat might have caused this performance decline. Based on the assumption that the water-root/biota contact is essential for contaminant removal, a depth profile of the gravel CW was analysed. Investigations evinced that 80% of the roots were contained in the upper 20 cm of the porous medium. In contrast, the porous media of the resting plant root mat is composed exclusively of roots, hence the plant root mat might provide better water-root/biota contact than the gravel filter at least when operated in a resting mode. Summing up, the aforementioned findings clearly state that high actual water-root contact and root density as well as a long enough residence time - rather than merely a good flow behavior - are decisive factors for high contaminant removal. In order to overcome the black box concept, flow behavior was also investigated within the porous media, exemplarily for the gravel CWs. The analysis of local tracer breakthrough curves allowed the assessment of local variability of flow rate, which could be used for estimation of contaminant loads in the filter and the localization of preferential flow paths and stagnant zones. Summarizing the results, flow in the gravel filter was depth-dependent, with the planting and the position of the effluent tube being key factors. The planting resulted in elevated flow rate and contaminant flux directly underneath the densely rooted porous media zone in the

planted CW, likely induced by transpiration-induced transportation of water from lower into densely rooted shallower horizons. The position of the outlet tube caused fast bottom flow in the unplanted reference. A stagnant zone was only apparent in the unplanted filter, possibly an effect of the fast bottom flow. Overall, investigating CW hydraulics provides implications for improved wetland design and operation, such as (i) CWs should not be designed considerably deeper than the rooting depth, unless anaerobic conditions are desired, (ii) outlet tubes should be installed at shallower depth to prevent fast bottom flow, and (iii) hydroponic plant root mat systems should be operated in a resting mode to realize optimal water-root/biota contact and avoid short-circuit flow.

In order to conclude, the gravel CW and the hydroponic plant root mat achieved good treatment efficiencies for the contaminated groundwater at the Leuna site containing the three main contaminants benzene, MTBE and ammonium, whereas best results were obtained for benzene. However, good treatment performance was seasonally restricted and even during summer time when highest treatment efficiencies were achieved, outflow contaminant concentrations did not comply with the guideline values for drinking water (benzene:  $10 \mu\text{g L}^{-1}$ , MTBE:  $20\text{-}40 \mu\text{g L}^{-1}$ ) or ground/surface waters (ammonium:  $0.5 \text{mg L}^{-1}$ ). Seasonal variations of contaminant concentration decline and load removal outlined in chapter 2 and 3, respectively, underline the importance of assessing annual means to evaluate treatment performance in addition to maximum and minimum removal during summer/winter time. Overall, the resting hydroponic plant root mat proved to be a promising alternative to conventional soil-based CWs, despite the mat exhibited less-ideal flow behavior. According to investigations on investment costs for HSSF CWs the porous media constitutes a high percentage (27-53%) of total costs (Vymazal, 2008). Thus, considerable savings are achievable if plant root mat systems can be applied for the treatment of contaminated waters. However, mass balancing demonstrated the limits of the plant root mat with respect to emission problems, given that considerably elevated emission rates were obtained for MTBE in the hydroponic plant root mat compared to the gravel CW.

Overall, the limiting factor for a successful application of both CW types is the seasonality of the treatment performance. In order to accomplish discharge values throughout the year, the installation of additional treatment subsequent to the CWs for optional use is necessary from a regulatory perspective. In the case of aerobic degradable compounds like benzene and MTBE such a unit could be e.g. an aerobic pond system. Alternatively,

for VOCs in general the adsorption on activated carbon filters or the use of stripping facilities may represent viable options for post-treatment. At sites where enough area for complete remediation is available and affordable, the contaminated water is accessible without extensive pumping, e.g. in case of shallow groundwater discharging into flood plains, or surface waters, and the realization of clean-up is not restricted in terms of time, CWs in combination with low cost post-treatment as back-up systems may be an effective treatment alternative to traditional P&T techniques for remediating contaminated waters.

## 5.2 Outlook and perspective for future research

The experimental results and the concluding remarks presented in the preceding pages underline the potential of CW systems for treating water containing a complex mixture of pollutants. However, some aspects could not be addressed in the present thesis, but should be considered and studied in future work. From a scientific point of view this may be for example:

- (i) the assessment of long-term removal efficiency of the hydroponic plant root mat including the adaptation potential to elevated water level,
- (ii) the measurement of  $N_2O$  and  $N_2$  in addition to ammonium, nitrite and nitrate in order to identify and quantify processes involved in N transformation and find out to whether extent low nitrate/nitrite levels are indicative for limited nitrification or effective denitrification and/or plant uptake,
- (iii) the determination of VOC metabolites both in the wetland filter and the helophytes in order to confirm microbial contaminant degradation,
- (iv) the tracking of isotopically ( $^{13}C$ ,  $^{15}N$ ) labeled contaminants to examine microbial transformation and incorporation, plant uptake and accumulation, phytodegradation and water-plant-air transfer, and
- (v) the experimental differentiation of phytovolatilization and surface volatilization. Relevant for public sanitation systems and application-oriented implementations would furthermore be the evaluation of optimization strategies to promote contaminant removal. In this context investigations should focus on e.g. outflow recirculation, tidal flow mode or the coupling of different CW systems. Testing of different plant species regarding their phytotransformation potential might also be reasonable.



## 6 Bibliography

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# Appendix

## A.1 Supporting Information EST-paper

**Table A.1:** Physico-chemical groundwater inflow characteristics including sum parameters total organic carbon (TOC), chemical oxygen demand (COD), and 5 day biological oxygen demand (BOD<sub>5</sub>). Values represent averages from 24 months with standard deviations ( $\pm \sigma$ ) of 65-74 measurements. Dissolved oxygen, redox potential (Eh), pH, and conductivity ( $S$ ) were measured online every 15 min.

Parameter	Unit	Average $\pm \sigma$
NH <sub>4</sub> <sup>+</sup> -N	$mg L^{-1}$	45 $\pm$ 3
NO <sub>3</sub> <sup>-</sup>	$mg L^{-1}$	0.1 $\pm$ 0.8
Fe(total)	$mg L^{-1}$	6.0 $\pm$ 1.3
Fe <sup>2+</sup>	$mg L^{-1}$	5.6 $\pm$ 2.2
SO <sub>4</sub> <sup>2-</sup>	$mg L^{-1}$	8.0 $\pm$ 6.1
dissolved O <sub>2</sub> <sup>a</sup>	$mg L^{-1}$	< 0.01
Eh <sup>b</sup>	$mV$	-460 $\pm$ 77
pH <sup>b</sup>	-	- 7.1 $\pm$ 0.7
S <sup>c</sup>	$mS cm^{-1}$	2.1 $\pm$ 1.5
TOC	$mg L^{-1}$	39 $\pm$ 5
COD	$mg L^{-1}$	114 $\pm$ 13
BOD <sub>5</sub>	$mg L^{-1}$	58 $\pm$ 13

<sup>a</sup> oxygen sensor (TriOxmatic<sup>®</sup> 700 IQ, WTW)

<sup>b</sup> pH/redox sensor (pH/redox SensoLyt<sup>®</sup> 700 IQ, WTW)

<sup>c</sup> conductivity sensor (LRD 325, WTW)

**Table A.2:** Data used for the calculation of contaminant mass balance for the unplanted reference system: Areal contaminant load (ACL,  $mg\ m^{-2}\ d^{-1}$ ) of inflow and outflow water and volatilization rates ( $L_v$ ,  $mg\ m^{-2}\ d^{-1}$ ) for summer and winter sampling periods. Subtraction of total volatilization ( $L_v$ ) from total removal in water phase ( $\Delta m = ACL_{in} - ACL_{out}$ ) yields contaminant loss via microbial degradation ( $L_m$ ). Evaporation rates (E,  $L\ CW^{-1}\ d^{-1}$ ) of the unplanted reference were used to calculate transpiration rates of the planted gravel CW. For comparison reasons average contaminant concentrations ( $c_{w,average}$ ,  $mg\ L^{-1}$ ) are given. For measured values the error equals the sum of standard error of the mean and measuring fault. For the parameters  $ACL_{in}$ ,  $ACL_{out}$ ,  $c_w$ ,  $L_m$  and E an error analysis was carried out according to Gaussian error propagation.

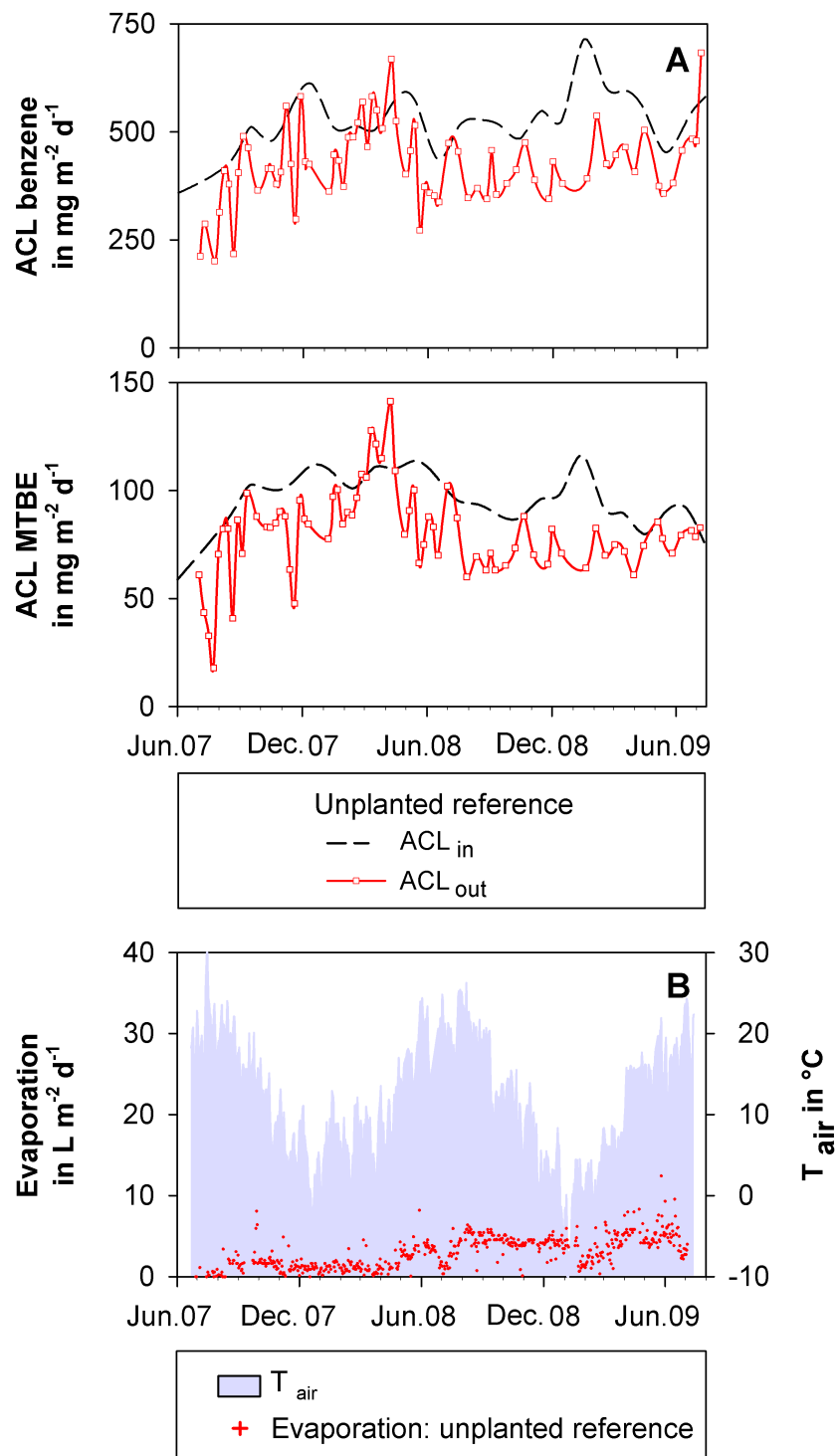
		Unplanted reference	
		benzene	MTBE
Summer	$ACL_{in}$	$498.2 \pm 49.2$ <sup>1)</sup>	$99.2 \pm 8.7$ <sup>1)</sup>
	$ACL_{out}$	$387.1 \pm 43.3$ <sup>1)</sup>	$77.4 \pm 8.1$ <sup>1)</sup>
	$c_{w,average}$	$18.0 \pm 1.2$ <sup>1)</sup>	$3.6 \pm 0.2$ <sup>1)</sup>
	$L_v$	$0.0 \pm 0.00$ <sup>2)</sup>	$0.2 \pm 0.12$ <sup>2)</sup>
	$L_m$	$111.1 \pm 65.5$ <sup>1)</sup>	$21.6 \pm 11.9$ <sup>1)</sup>
	E		$19.7 \pm 6.9$ <sup>1)</sup>
Winter	$ACL_{in}$	$602.7 \pm 53.8$ <sup>3)</sup>	$91.9 \pm 7.7$ <sup>3)</sup>
	$ACL_{out}$	$466.6 \pm 54.9$ <sup>3)</sup>	$75.5 \pm 8.0$ <sup>3)</sup>
	$c_{w,average}$	$21.7 \pm 1.4$ <sup>3)</sup>	$3.4 \pm 0.2$ <sup>3)</sup>
	$L_v$	$0.0 \pm 0.00$ <sup>4)</sup>	$1.9 \pm 0.10$ <sup>4)</sup>
	$L_m$	$136.1 \pm 76.9$ <sup>3)</sup>	$14.5 \pm 11.1$ <sup>3)</sup>
	E		$16.7 \pm 7.2$ <sup>3)</sup>

<sup>1)</sup> sampling period: 27/5-1/9/2008

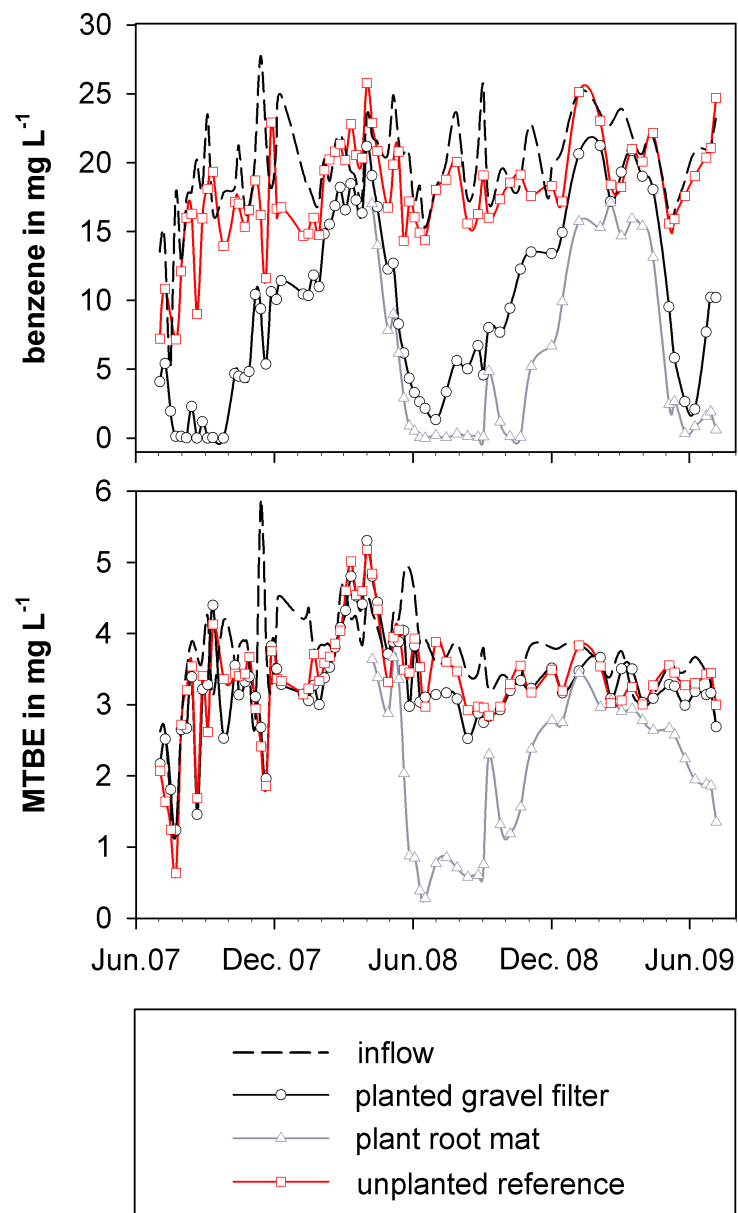
<sup>2)</sup> sampling period: 10-20/6 and 5-15/8/2008

<sup>3)</sup> sampling period: 3/2-16/3/2009

<sup>4)</sup> sampling period: 17-27/2/2009

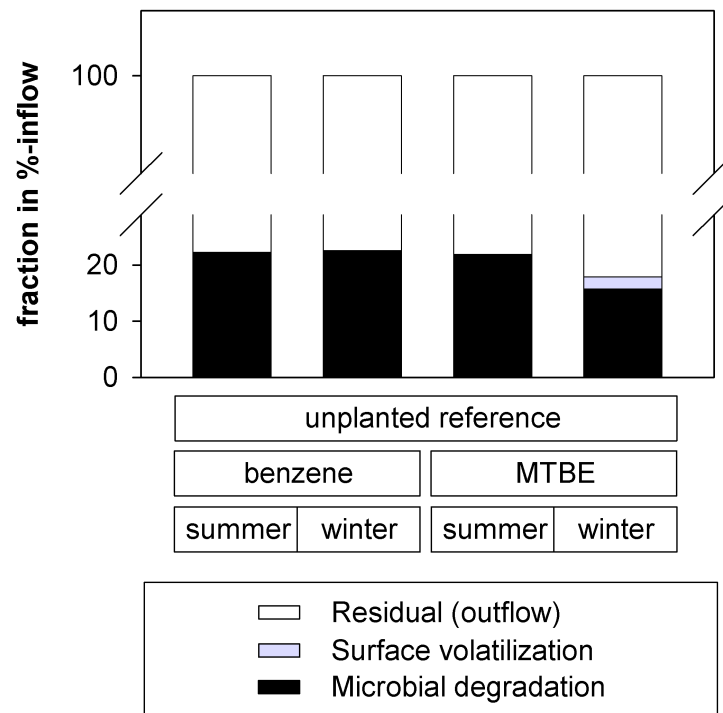


**Figure A.1:** Areal benzene and MTBE inflow and outflow water load ( $ACL_{in/out}$ ) for the unplanted reference system (A); evaporation of the unplanted reference system as well as ambient air temperature  $T_{air}$  (daily mean) (B).



**Figure A.2:** Benzene and MTBE inflow and outflow concentrations for the planted gravel filter, the plant root mat and the unplanted reference system over a time of 24 months.





**Figure A.3:** Contaminant fate in the unplanted reference system for summer and winter period. Processes included are microbial degradation and surface volatilization.

## A.2 Supporting Information WR-paper

subsection Continuitive explanations: the flow path integration approach expanded to transient flow conditions The flow path integration derived in equation 5.1 and 5.2 can be used to compute the travel time  $\tau$  or may simply be re-arranged to calculate the porosity  $\theta$  for a steady-state flow field. If the flow field changes over time, which will be the case if the considered wetland is exposed to weather under real field conditions, the time is divided into small intervals during which flow is assumed constant. Solving eq. 5.1 and 5.2 for travel distance  $x_i$  yields the distance a small particle of water released at time  $t_0$  at the inlet has covered during that time interval  $\tau_i$ :

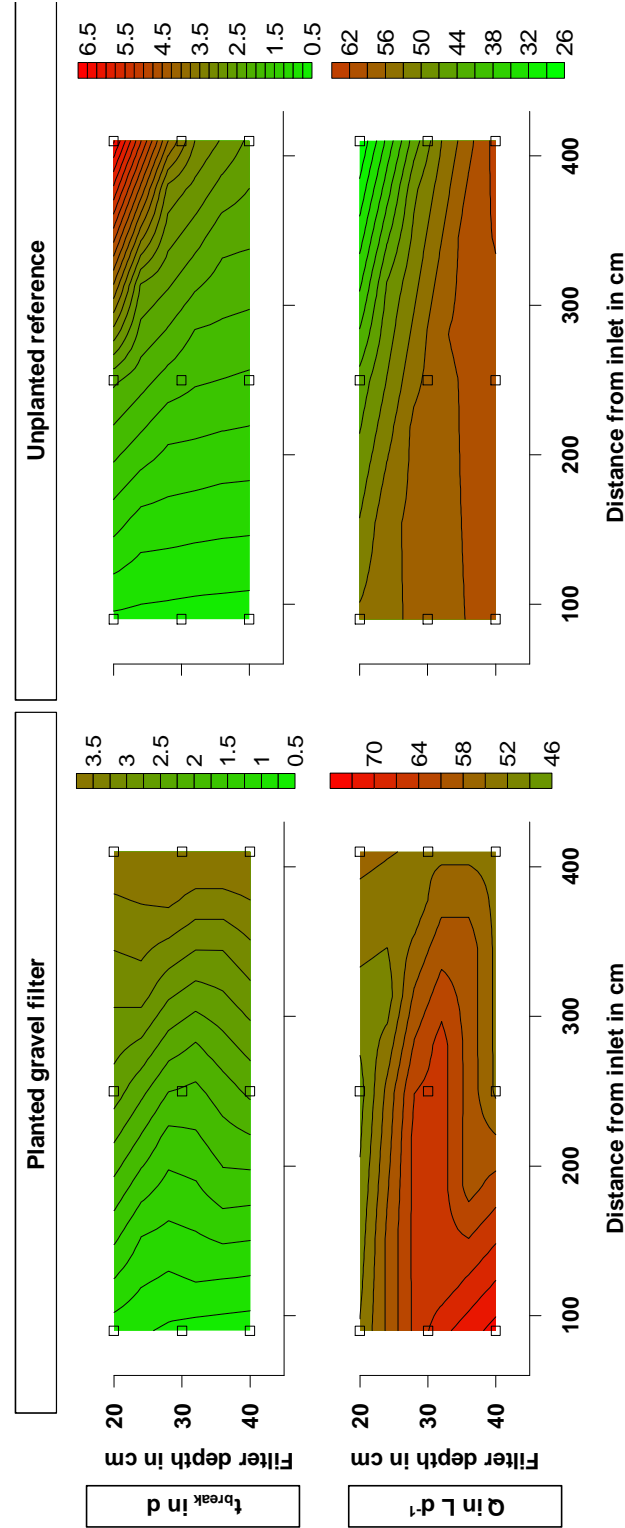
$$x_i = \frac{q_{in} h}{q_{et}} \left(1 - e^{-\frac{q_{et} \tau_i}{\theta h}}\right) \quad \text{for } q_{et} \neq 0 \text{ and} \quad (\text{A.1})$$

$$x_i = \frac{q_{in} \tau_i}{\theta} \quad \text{for } q_{et} = 0 \quad (\text{A.2})$$

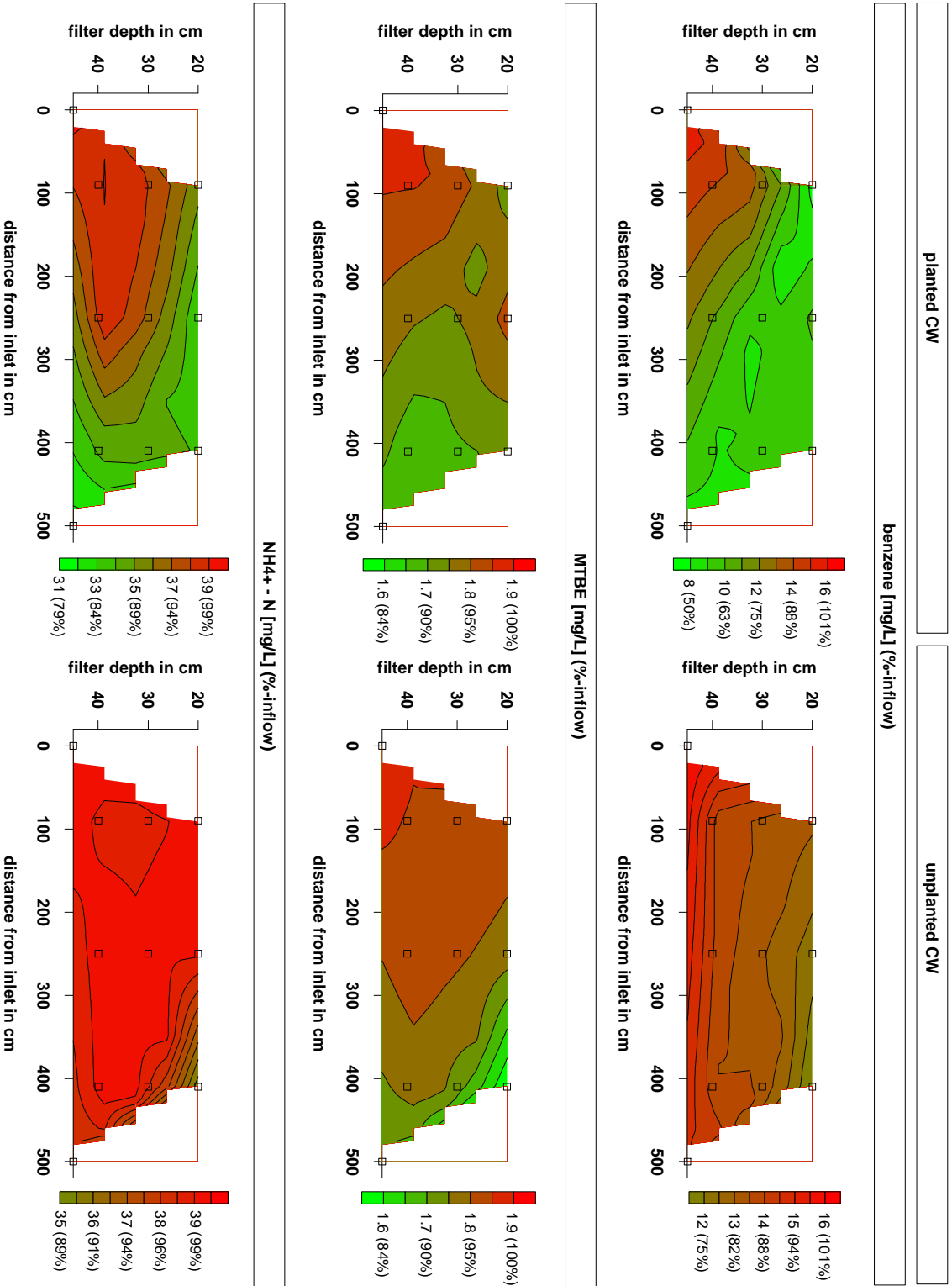
As  $q_{in}$  and  $q_{et}$  vary over time, the travel distance  $x$  may be summed over all the small intervals of constant flow conditions:

$$x_{tot} = \sum x_i \quad (\text{A.3})$$

When outlet distance  $L$  is eventually reached, the total travel time equals the sum over all the time intervals after the particle release time:  $\sum \tau_i$ . If  $L$  is exceeded during an interval, the last time interval has to be stepped back and the residual  $\tau$  required to cover the residual distance is added to the accumulated sum of time intervals, thus yielding the total travel time of the particle. The value of effective porosity  $\theta$  fitting best to the total travel time is picked as representative for the basin. Note that the particle travel time will generally be a function of release time  $t_0$  under transient conditions, thus water residence times will vary over the course of the year. The results were tested with a numerical model, which resolved the geometry exactly in 2-D and yielded very similar results. A problem may arise under steady-state conditions if  $x$  reaches or exceeds  $h q_{in}/q_{et}$ , and travel time becomes infinite as water is completely evaporated and no more flow occurs. Under transient conditions, that problem does not occur: as in the case of stagnant water, the particle will rest at its position until the end of the time interval, and continue its pathway once a later interval introduces new water flow.



**Figure A.4:** Tracer breakthrough times  $t_{break}$  [ $d$ ] (top) and respective flow rates  $Q$  [ $L d^{-1}$ ] (bottom) at the sampling positions (denoted as squares) in the planted gravel CW (left) and the unplanted reference (right). Counter plot computation based on triangulation and linear interpolation.



**Figure A.5:** Contaminant (benzene (top), MTBE (middle), and ammonium-nitrogen (bottom)) concentrations ( $mg L^{-1}$ , %-inflow) within the planted gravel CW (left) and the unplanted reference (right) for the sampling campaign 17/8/2009.

# Selbständigkeitserklärung

Ich erkläre hiermit, dass ich die zur Promotion eingereichte Arbeit mit dem Titel “Treatment of groundwater contaminated with benzene, MTBE and ammonium by constructed wetlands” selbständig verfasst, nur die angegebenen Quellen und Hilfsmittel benutzt und wörtlich oder inhaltlich übernommene Stellen (alternativ: Zitate) als solche gekennzeichnet habe. Ich erkläre, dass die Richtlinien zur Sicherung guter wissenschaftlicher Praxis der Universität Tübingen (Beschluss des Senats vom 25.5.2000) beachtet wurden. Ich versichere an Eides statt, dass diese Angaben wahr sind und dass ich nichts verschwiegen habe. Mir ist bekannt, dass die falsche Abgabe einer Versicherung an Eides statt mit Freiheitsstrafe bis zu drei Jahren oder mit Geldstrafe bestraft wird.

Eva Mareike Seeger



# Curriculum Vitae

## CONTACT INFORMATION

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## WORK EXPERIENCE

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since 08/2012 Helmholtz Centre for Environmental Research - UFZ,  
Leipzig, Germany; Department of Environmental Microbi-  
ology  
Position: Research Assistant

05/2007 – 11/2012 Helmholtz Centre for Environmental Research - UFZ,  
Leipzig, Germany; Department of Environmental Biotech-  
nology  
Position: PhD candidate

## EDUCATION

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since 05/2007 PhD candidate at the Helmholtz Centre for Environmental  
Research -UFZ, Leipzig, Germany supervised by Prof. Dr.  
M. Kästner (UFZ, Department of Environmental Biotechnol-  
ogy) and Prof. Dr. P. Grathwohl (University of Tübingen,  
Center of Applied Geoscience)  
Topic of the PhD project: “Constructed wetlands for the  
treatment of groundwater contaminated by benzene, MTBE  
and ammonium”

05/2007 – 11/2012 Helmholtz Centre for Environmental Research - UFZ,  
Leipzig, Germany; Department of Environmental Biotech-  
nology  
Position: PhD candidate

## EDUCATION

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- |                   |   |
|-------------------|---|
| 03/2007           | Obtaining the Diploma in Chemistry<br>University of Leipzig, Faculty of Chemistry and Mineralogy  |
| 03/2006 – 02/2007 | Diploma thesis at the Helmholtz Centre for Environmental Research - UFZ, Leipzig, Germany; Department Bioremediation<br><br>Title of the thesis: “Constructed wetlands for treating groundwater contaminated by chlorinated VOCs (MCB and PCE)” |
| 10/2004 – 02/2006 | Advanced studies of Chemistry at the University of Leipzig, Faculty of Chemistry and Mineralogy<br>Specialization: Environmental Chemistry, Organic Chemistry, Biosciences  |
| 09/2003 – 09/2004 | Exchange year in Chemistry at the University of Uppsala, Sweden   |
| 10/2000 – 09/2003 | Basic studies of Chemistry at the University of Leipzig, Faculty of Chemistry and Mineralogy  |
| 1987 – 2000       | Elementary school and gymnasium<br>Graduation: Abitur (German high school degree)   |

## RESEARCH STAY

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- |                   |  |
|-------------------|--|
| 11/2008           | Technical University of Pereira (UTP), Colombia; Prof. D. Paredes<br><br>Project: Scientific exchange program regarding wastewater treatment in constructed wetlands within the DAAD-project PROCOL                          |
| 11/2007 – 02/2008 | Technical University Denmark (DTU), Copenhagen; Prof. S. Trapp<br><br>Project: Tree toxicity tests with willow cuttings (benzene, MTBE, TCE, MCB and $TiO_2$ nanoparticles) within the framework of the SAFIRA-project CoTra |
| 3/2003            | University of Southampton, United Kingdom; Prof. M. Hursthouse<br><br>Project: Evaluation of the structures of racemic lithium tartrate hydrates using crystallographic structural   |



LANGUAGE SKILLS

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German	Mother Tongue
English	Fluent in spoken and written
Swedish	Basic knowledge
French	Basic knowledge

ADDITIONAL SKILLS

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Software	Surfer, SigmaPlot, windows applications, basic knowledge of VBA, LaTeX
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# Publications

## Peer-review Articles

SEEGER, E.M.; MAIER, U.; GRATHWOHL, P.; KUSCHK, P.; KAESTNER, M.: Performance evaluation of different horizontal subsurface flow wetland types by characterization of flow behavior, mass removal and depth-dependent contaminant load. *Water Research*, accepted for publication October 2012.

SEEGER, E.M.; REICHE, N.; KUSCHK, P.; BORSODORF, H.; KAESTNER, M.: Performance evaluation using a three compartment mass balance for the removal of volatile organic compounds in pilot scale constructed wetlands. *Environmental Science & Technology* (2011), 45: 8467–8474.

SEEGER, E.M.; KUSCHK, P.; FAZEKAS, H.; GRATHWOHL, P.; KAESTNER, M.: Bioremediation of benzene-, MTBE- and ammonium-contaminated groundwater with pilot-scale constructed wetlands. *Environmental Pollution* (2011), 159: 3769–3776

SEEGER, E.M.; BAUN, A.; KAESTNER, M.; TRAPP, S.: Insignificant acute toxicity of  $TiO_2$  nanoparticles to willow trees. *Journal of Soils and Sediments* (2009), 9: 46–53.

WU, S.; CHEN, Z.; BRAECKEVELT, M.; SEEGER, E.M., DONG, R.; KAESTNER, M.; PASCHKE, H.; HAHN, A.; KAYSER, G.; KUSCHK, P.: Dynamics of Fe(II), sulphur and phosphate in pilot-scale constructed wetlands treating a sulphate-rich chlorinated hydrocarbon contaminated groundwater. *Water Research* (2012), 46(6): 1923–1932.

VOYEVODA, M.; GEYER, W.; MOSIG, P.; SEEGER, E.M.; MOTHEIS, S.: Evaluation of the Effectiveness of different methods for the remediation of contaminated groundwater by determining the petroleum hydrocarbon content. *Clean - Soil, Air, Water* (2012), 40(8): 817–822.

BRAECKEVELT, M.; SEEGER, E.M.; PASCHKE, H.; KUSCHK, P.; KAESTNER, M.:

Adaptation of a constructed wetland to simultaneous treatment of monochlorobenzene and perchlorethene. *International Journal of Phytoremediation* (2011), 13(10): 998–1013.