

## Comparative evaluation of pilot scale horizontal subsurface-flow constructed wetlands and plant root mats for treating groundwater contaminated with benzene and MTBE

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### ABSTRACT

In order to evaluate technology options for the treatment of groundwater contaminated with benzene and MTBE in constructed wetlands (CWs), a scarcely applied plant root mat system and two horizontal subsurface-flow (HSSF) CWs were investigated. The inflow load of benzene and MTBE were 188–522 and 31–90 mg d<sup>-1</sup> m<sup>-2</sup>, respectively. Higher removal efficiencies were obtained during summer in all systems. The benzene removal efficiencies were 0–33%, 24–100% and 22–100% in the unplanted HSSF-CW, planted HSSF-CW and the plant root mat, respectively; the MTBE removal efficiencies amounted to 0–33%, 16–93% and 8–93% in the unplanted HSSF-CW, planted HSSF-CW and the plant root mat, respectively. The volatilisation rates in the plant root mat amounted to 7.24 and 2.32 mg d<sup>-1</sup> m<sup>-2</sup> for benzene and MTBE, which is equivalent to 3.0% and 15.2% of the total removal. The volatilisation rates in the HSSF-CW reached 2.59 and 1.07 mg d<sup>-1</sup> m<sup>-2</sup>, corresponding to 1.1% and 6.1% of the total removal of benzene and MTBE, respectively. The results indicate that plant root mats are an interesting option for the treatment of waters polluted with benzene and MTBE under moderate temperatures conditions.

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### 1. Introduction

Benzene is a soluble component of gasoline and a common groundwater contaminant, which is of great concern because it can cause leukaemia and has been classified by the IARC as carcinogenic to humans (Group 1) [1]. As a gasoline additive, methyl *tert*-butyl ether (MTBE) has been added to gasoline for over 30 years to improve the engine's performance and make gasoline burn more completely, with the aim to improve air quality. Over time, MTBE has also become a ubiquitous groundwater pollutant, and is known to cause damages to the central nervous system [2]. Furthermore, it is currently listed by the USEPA as a candidate for a maximum contaminant level (MCL) in drinking water [3]. Pollution concentration limits of 200 µg L<sup>-1</sup> and 1 µg L<sup>-1</sup> for MTBE and benzene, respectively, were established by the US EPA for drinking water [3]. Like all volatile organic compounds (VOCs), benzene and MTBE can be removed from water by using different physical and chemical methods, including air stripping, activated carbon adsorption, photocatalytic oxidation, etc. [4]. Moreover, benzene and MTBE can also be removed through biodegradation under both aerobic [5] and

anaerobic conditions [6]. However, compared to the aerobic degradation, the anaerobic MTBE and benzene degradation rates are very low and, thus, of no technological relevance. In natural peat, both aerobic and anaerobic biodegradation of BTEX (benzene, toluene, ethylbenzene, and xylenes) was observed, and about one third of the BTEX loss was attributed to anaerobic degradation [7].

Constructed wetlands (CWs) are a cost-effective technology for wastewater treatment. Here, the plants are generally very important features because they can improve the pollutant removal efficiency mainly due to the enhancement of the microbial density, activity, and diversity in the plant's rhizosphere [8]. A critical review was given about the use of horizontal subsurface-flow (HSSF) CWs for treating various types of wastewater, including municipal, industrial, and agricultural wastewaters, landfill leachate and storm water runoff [9]. However, papers describing the use of CWs for treating groundwater contaminated with VOCs are rare. For instance, in a cold climate (Wyoming, USA) wetland system, the BTEX degradation rate increased in the presence of plants [10]. Moreover, the cumulative mass removal based on one-year operating data approached 80% for benzene and 88% for total BTEX in a study of pilot scale upward vertical flow mode wetlands equipped with subsurface aeration lines [11]. Research investigating benzene removal by vertical flow CWs on a mesocosm scale demonstrated that benzene removal was nearly complete after

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one-day retention time. In this context, the role of volatilisation was discussed but not directly measured [12]. Seasonal variability, i.e. a temperature dependency of benzene removal was found to be significant [13,14]. Pilot scale horizontal subsurface-flow CWs were established for treating groundwater polluted with chlorobenzene [15]. However, no volatilisation of the VOCs was mentioned in these studies. Recently, a dynamic air chamber was established for measuring the volatilisation of benzene and MTBE in pilot-scale CWs, and it was shown that a planted gravel bed has a higher volatilisation compared to an unplanted reference system [16]. Therefore, more pilot and full scale CWs along with different types of VOCs as well as the optimisation of the systems has to be studied.

In the present study, a variant of wetland systems has been established called floating plant root mat. Such floating wetland systems have been used just recently for treating domestic wastewater [17] and storm water [18]. In order to compare floating root mats with traditional soil based CWs, two pilot-scale HSSF-CWs (unplanted and planted), and a pilot-scale floating root mat were investigated for treating groundwater contaminated with benzene and MTBE under temperate climatic conditions. The aims of this study were (1) to compare the treatment efficiency for benzene and MTBE among these three wetlands; (2) to elucidate the volatilisation of benzene and MTBE in the plant root mat and the planted HSSF-CW. With respect to the removal intensification, the influencing removal factors, such as the temperature, the relation between the input of oxygen and the output of rhizodeposition products by the helophyte roots, are discussed.

## 2. Materials and methods

### 2.1. Description of the pilot-scale wetlands

In order to investigate the potential of near-natural remediation approaches for treating contaminated waters, the pilot-scale treatment plant "Compartment Transfer" was built starting in 2007 in Leuna, Saxony-Anhalt, Germany [19]. On this site, the groundwater was contaminated with different gasoline components, the main ones being benzene and MTBE with mean concentrations of  $13 \pm 3 \text{ mg L}^{-1}$  and  $2.2 \pm 0.5 \text{ mg L}^{-1}$ , respectively, during the experiment. The main inflow water composition is shown in Table 1.

Two horizontal subsurface-flow CWs were established, each of them consisting of a basin with a dimension of  $5.0 \text{ m} \times 1.1 \text{ m} \times 0.6 \text{ m}$ . Both basins were filled with gravel each with a height of 0.5 m (with a grain size of 2–4 mm). One basin was planted with common reed (*Phragmites australis*), whereas the second basin was kept unplanted as a control. The planted and unplanted HSSF-CWs have started running in July 2007. The third system was established as a floating plant root mat of common reed (*P. australis*) in a third basin (without gravel) with the same dimension of  $5.0 \text{ m} \times 1.1 \text{ m} \times 0.6 \text{ m}$  in April 2008. Here, the aquatic vegetation is no longer rooted in a solid matrix; but is growing as a

plant root mat, where their roots have direct contact to the water. Such a mat of densely interwoven roots enables the plants for mechanical anchoring with their roots such as in a soil and give the above ground plant parts stability against tilting. The plant roots, such as the soil particles, also provide a high specific surface area to support bacterial attachment and growth. This is beneficial for technological reasons for microbial biomass retention, especially for slow-growing bacteria. Because of buoyancy of these root mats, they can float and are especially suitable for varying water levels. The mean density and height of the plants measured on 9th August 2011, in the HSSF-CW and the plant root mat were 150 and 83 shoots per square meter and 2.0 m and 1.3 m, respectively. All the systems were fed with the same inflow water and the same inflow rate of  $6.0 \text{ L h}^{-1}$ . This corresponded to a theoretical hydraulic retention time of 6 days neglecting the water loss caused by evapotranspiration. The water level in the two gravel wetlands was 0.4 m, and the water level in the basin with the plant root mat was 0.3 m. Both the inflow and outflow were measured using flow meters. Weather data such as precipitation and temperature were collected every day.

### 2.2. Procedures for sampling and analysing pore water

Inflow and outflow water samples were taken along with pore water samples at different distances (1, 2.5 and 4 m) from the inlet and at different depths (20 and 40 cm in the HSSF-CWs, 15 and 30 cm in the plant root mat system) of the system. The temperature and redox potential were measured on-site using a flow-through cell equipped with redox electrodes (Pt/Ag+/AgCl/Cl-type Sentix ORP, WTW, Germany). For measuring organic contaminants, 5 mL of water sample was transferred into 20 mL headspace vials, at the same time added 50  $\mu\text{L}$  bromobenzene- $d_5$  (with a final concentration of  $250 \mu\text{g L}^{-1}$ ) as an internal standard and 5 mL solution of  $\text{NaN}_3$  in deionised water (with a final concentration of  $0.65 \text{ g L}^{-1}$ ) in order to inhibit microbial activity. The samples for the organic analysis were transported to the laboratory using ice bags and stored in a cooling storage room at a temperature of  $4^\circ\text{C}$  until analysis was performed. The VOCs were analysed by means of a Headspace GC-FID (Agilent 6890 Gas Chromatograph) with a capillary column ( $30 \text{ m} \times 0.45 \text{ mm} \times 2.55 \mu\text{m}$ , Agilent DB-MTBE). The following temperature programme was performed:  $35^\circ\text{C}$  (6 min),  $4^\circ\text{C}/\text{min}$  to  $120^\circ\text{C}$ ,  $20^\circ\text{C}/\text{min}$  to  $280^\circ\text{C}$  (5 min). Nitrogen was used as the carrier gas. Prior to the analysis, the samples were equilibrated at  $80^\circ\text{C}$  for 30 min.

The samples for the inorganic analysis were transferred into a 25 mL brown glass bottle and measured in the field laboratory.  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  were measured using a photometer (Spectroquant® Nova 60, Merck) and the Merck quick test (number 1.00683.0001 for  $\text{NH}_4^+$ , 1.09713.0001 for  $\text{NO}_3^-$  and 1.14776 for  $\text{NO}_2^-$ ).

### 2.3. Measurement of organic compounds volatilisation from the wetlands

One-week continuous gas sampling was carried out in early May (mean air temperature of  $13^\circ\text{C}$  during the experimental period) using a dynamic air chamber. Gaseous analyses were trapped onto two replicate sorbent tubes (MARKES, self-packed containing 150 mg Tenax TA and 100 mg Chromosorb 106), analysed directly after arriving at the laboratory, followed by thermal desorption (using a MARKES Unity thermal desorber) and quantification by gas chromatography with mass selective detection. The details of the sampling and analysis procedures are described elsewhere [16].

**Table 1**  
Main inflow water composition of the experimental pilot scale CWs.

Compounds	Average concentration ( $\text{mg L}^{-1}$ ) $\pm$ standard deviation
Benzene	$13 \pm 3$
MTBE	$2.2 \pm 0.5$
$\text{NH}_4^+$	$44.1 \pm 2.8$
$\text{NO}_3^-$	$5.4 \pm 2.9$
$\text{NO}_2^-$	$<0.1$
$\text{Fe}^{2+}$	$6.0 \pm 0.7$
$\text{PO}_4^{3-}$	$1.4 \pm 0.7$
$\text{Cl}^-$	$112.2 \pm 16.9$
TOC	$37.0 \pm 4.0$
COD	$104.0 \pm 8.6$
$\text{BOD}_5$	$56.0 \pm 13.3$

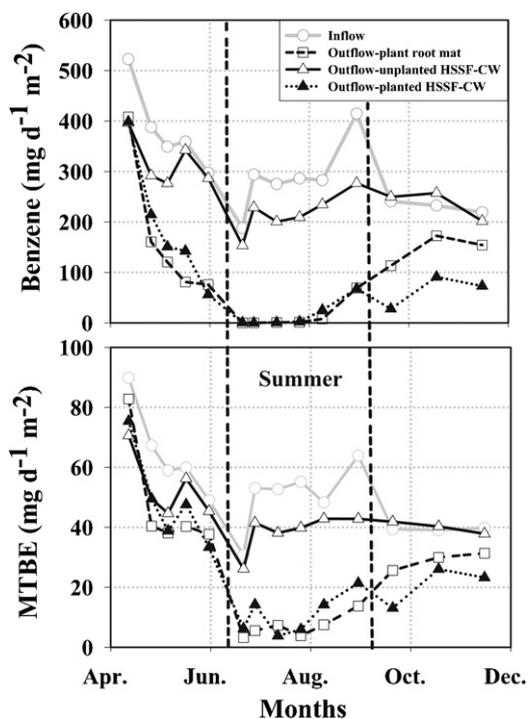


Fig. 1. Inflow and outflow loads of benzene and MTBE in dependence of the year's season of 2010 in three treatment systems (the plant root mat, the planted HSSF-CW and the unplanted HSSF-CW).

#### 2.4. Data analysis

In total, 14 sampling actions were carried out from the 12th of April to the 15th of November 2010. The mean values of two duplicates were used for concentration measurement of MTBE and benzene for each sampling day. The treatment performance was compared using the inflow and outflow loads which were calculated by multiplying the concentration of the pollutants with the water inflow and outflow volume flow rates. The removal percentage by volatilisation was calculated by the mass loss due to volatilisation and the pollutant total mass loss (difference between inflow and outflow mass); detailed way of calculations is described elsewhere [16]. To compare the treatment performance based on the outflow loads between the unplanted HSSF-CW, the planted HSSF-CW and the plant root mat, non-parametric Mann–Whitney *U*-tests [20] were carried out, because a normal distribution could not be assumed after the one-sample Kolmogorov–Smirnov test. In order to explore the treatment process based on the concentration in the systems, non-parametric Mann–Whitney *U*-tests were carried out during summer for different depths, distance and between three treatment systems. The STATISTICA 8.0 programme was used, and the differences were regarded as significant at  $P < 0.05$ .

### 3. Results and discussion

#### 3.1. Treatment performance

The removal performance of benzene and MTBE during the experimental period is summarized in Fig. 1. The results show that both planted systems (the plant root mat and the HSSF-CW) exhibit obviously a better performance than the unplanted HSSF-CW both for benzene and MTBE removal; however, there are no significant differences between both planted systems (the plant root mat and the HSSF-CW). The significant *P* values are presented in Table 2.

The results also indicate that a better removal performance was achieved during summer than in winter both for benzene and

Table 2

Mann–Whitney *U*-test of benzene and MTBE outflow loads in the three treatment systems during the sampling period (April–November 2010; the results are shown for samples taken at 14 different dates, see Fig. 1).

	A–B	A–C	B–C
Benzene	<0.001	<0.001	0.679
MTBE	0.009	0.001	0.854

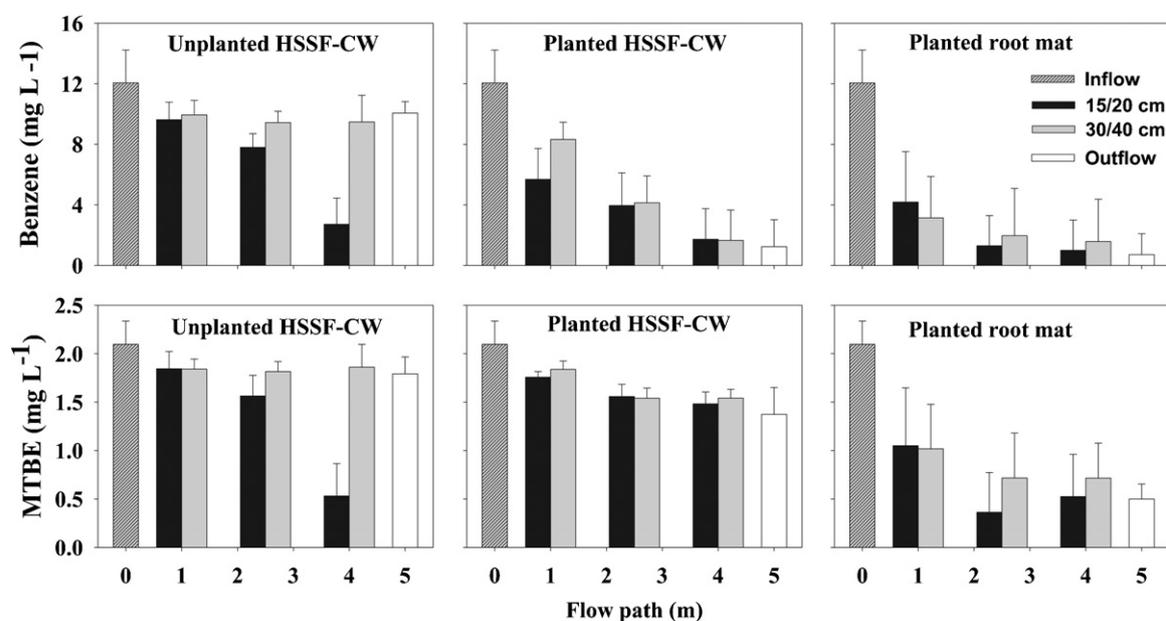
A: unplanted HSSF-CW; B: planted HSSF-CW; C: plant root mat.

MTBE. During the winter period, almost no benzene and MTBE was removed when the unplanted HSSF-CW was used, whereas in summer time, the respective removal rates reached up to  $153 \text{ mg d}^{-1} \text{ m}^{-2}$  and  $24 \text{ mg d}^{-1} \text{ m}^{-2}$  for benzene and MTBE. In the planted HSSF-CW, removal rates of approximately  $140 \text{ mg d}^{-1} \text{ m}^{-2}$  and  $15 \text{ mg d}^{-1} \text{ m}^{-2}$  for benzene and MTBE, respectively, were obtained during winter, and in summer time, the values increased up to approximately  $360 \text{ mg d}^{-1} \text{ m}^{-2}$  and  $48 \text{ mg d}^{-1} \text{ m}^{-2}$ , respectively. In the plant root mat system, the removal rates for benzene and MTBE were  $118 \text{ mg d}^{-1} \text{ m}^{-2}$  and  $8 \text{ mg d}^{-1} \text{ m}^{-2}$  during the winter and  $325 \text{ mg d}^{-1} \text{ m}^{-2}$  and  $51 \text{ mg d}^{-1} \text{ m}^{-2}$  during the summer months. The main reason for these different removal rates might be due to the different mean temperatures during the winter and summer months, as the metabolic activities of microorganisms and plants are strongly linked with the temperature [8].

At the BP Amoco Former Casper Refinery site in Wyoming with relatively low inflow concentrations of  $0.6 \text{ mg L}^{-1}$  benzene and  $1.26 \text{ mg L}^{-1}$  MTBE, a pilot scale vertical flow CW achieved relatively high removal rates of  $94 \text{ g d}^{-1} \text{ m}^{-2}$  for benzene and  $120 \text{ g d}^{-1} \text{ m}^{-2}$  for MTBE. The removal rates even increased up to  $120 \text{ g d}^{-1} \text{ m}^{-2}$  for benzene and  $180 \text{ g d}^{-1} \text{ m}^{-2}$  for MTBE, when aeration was performed [21]. In vertical-flow experimental wetlands operated in batch-flow mode, benzene was removed to about 85% under outdoor conditions (Edinburgh, Scotland) and to about 95% under stable indoor conditions, even at a relatively high benzene inflow concentration of  $1.3 \text{ g L}^{-1}$  [12]. In our study, the respective percentages of benzene and MTBE of 100% and 93% were removed during the summer period, when the HSSF-CW and the plant root mat were used. In another report by Bedessem et al. [11], an upward vertical-flow CW (equipped with subsurface aeration lines and operating with average inflow concentrations of  $0.395 \text{ mg L}^{-1}$  benzene,  $1.38 \text{ mg L}^{-1}$  total BTEX and  $1.2 \text{ mg L}^{-1}$  MTBE) reached a total mass removal in its 1-year operation of about 80% for benzene and 88% for total BTEX, which is comparable with our results for benzene removal. However, Bedessem et al. [11] established only a minimum capability for MTBE removal. While our systems have been operating for three years, we assume that this longer period of time was sufficient for the microorganisms to adapt to the system conditions and become able to degrade MTBE.

The spatial concentration distribution of benzene and MTBE was determined as a function of the distance from the inflow and the depth of the wetland systems during the summer season (Fig. 2). The significant *P* values between depths, distances and treatments are given in Table 3. No significant differences were observed in benzene and MTBE concentrations between the depths in the plant root mat and in the planted HSSF-CW, except for MTBE at one meter in the planted HSSF-CW ( $P = 0.02$ ). Significant differences in benzene and MTBE concentrations were found between depths of 2.5 and 4 m in the unplanted HSSF-CW.

Considering the pollutant concentration changes along the flow distance from the inlet, a significant decrease in benzene and MTBE concentrations was obtained in the unplanted HSSF-CW and in the planted HSSF-CW at distances up to 2.5 m and only up to 1 m in the plant root mat (Table 3). For the three treatment systems, significantly lower benzene concentrations were achieved in the planted HSSF-CW and plant root mat compared to the unplanted HSSF-CW



**Fig. 2.** Concentrations of benzene and MTBE along the flow path and at two depths in the unplanted HSSF-CW, the planted HSSF-CW and the plant root mat system, during summer time (June–September 2010; the results are shown for samples taken at 6 different dates, see Fig. 1).

**Table 3**

Mann–Whitney *U*-test of benzene and MTBE concentrations between depths, distances and three treatment systems (A: unplanted HSSF-CW; B: planted HSSF-CW; C: plant root mat) during summer (June–September 2010; the results are shown for samples taken at 6 different dates, see Fig. 1).

	Depths			Distances <sup>a</sup>			Treatments		
	A	B	C	A	B	C	A–B	A–C	B–C
Benzene									
1 m	0.613	0.088	0.568	0.041	<0.001	<0.001	0.004	<0.001	0.030
2.5 m	0.006	0.802	0.669	0.046	0.015	0.223	<0.001	<0.001	0.095
4 m	<0.001	0.364	0.687	0.001	0.066	0.814	<0.001	0.001	0.757
Outflow	–	–	–	<0.001	0.686	0.622	<0.001	<0.001	0.582
MTBE									
1 m	0.965	0.020	0.916	0.047	0.014	0.001	0.466	0.004	0.005
2.5 m	0.027	0.880	0.191	0.093	<0.001	0.096	0.090	<0.001	<0.001
4 m	<0.001	0.947	0.429	<0.001	0.532	0.738	0.008	0.011	<0.001
Outflow	–	–	–	<0.001	0.272	0.505	0.010	<0.001	<0.001

<sup>a</sup> Comparison of the concentration difference between 1 m with inflow, 2.5 m with 1 m, 4 m with 2.5 m, and outflow with 4 m.

along the flow path (Table 3). Reasons for these observations might be that the plants enhance the microbial activity and phytovolatilisation [16]; but it can be assumed that the plant uptake plays a minor role [22]. In general, the results indicate that in the plant root mat, more favourable conditions for MTBE removal occurred compared to both HSSF-CWs along the flow path (Table 3).

### 3.2. Volatilisation

The volatilisation rates of benzene and MTBE in the planted HSSF-CW and plant root mat are listed in Table 4. The results clearly demonstrate that the plant root mat had higher volatilisation rates than the HSSF-CW for both benzene and MTBE. In this study, the emission rate of MTBE is lower than that of benzene, while a higher MTBE total mass removal was achieved compared

**Table 4**

Volatilisation rates of benzene and MTBE in the planted HSSF-CW and the plant root mat (the values shown are the emission rates ( $\text{mg d}^{-1} \text{m}^{-2}$ ) along with the percentages of mass loss of the total pollutants by volatilisation in brackets).

Pollutants	Plant root mats	Planted HSSF-CW
Benzene	7.24 (3.0%)	2.59 (1.1%)
MTBE	2.32 (15.2%)	1.07 (6.1%)

to benzene in both systems. This can be explained by the higher degree of microbial degradation of benzene compared to MTBE (the total removal efficiency amounted to 65% for benzene and 35% for MTBE during the emission measuring campaign), which, in turn, is accompanied by a relatively lower percentage of benzene remaining in the CWs. The microbial degradation was approved by bacterial and stable isotope analysis performed in former studies at the same site [23]. Moreover, the different behaviour of benzene and MTBE through plant uptake, translocation, metabolism, and phytovolatilisation can also be possible factors for the difference of volatilisation between MTBE and benzene. The physicochemical properties of MTBE and benzene indicate a different volatilisation potential. The Henry's law constants (which characterise the volatilisation of a compound from the dissolved phase to the air) are 0.055 for MTBE and 0.22 for benzene, at 25 °C [4], characterising benzene as being more volatile than MTBE. However, it was found that greater volatilisation fluxes are related to a higher vapour pressure [24]. With a vapour pressure of MTBE (251 mm Hg) being around 3 times higher than that of benzene (86 mm Hg) [4], phytovolatilisation of MTBE is expected to be greater. Furthermore, plant metabolism is also different for benzene and MTBE. Benzene degradation by plants was demonstrated by Collins et al. [25], but MTBE was shown to be persistent against a degradation by plant cells [26]. All these findings are in accordance with our results indicating that

a higher percentage of MTBE compared to benzene was removed by volatilisation. The plant root mat had a higher volatilisation (both for benzene and MTBE) than the planted HSSF-CW in this study, and the volatilisation in the plant root mat was also higher than that in the unplanted HSSF-CW. The concentration of benzene and MTBE measured in the unplanted HSSF-CW was close to the background air concentrations which varied between 1 and  $9 \mu\text{g m}^{-3}$  for benzene and 0.5 and  $28 \mu\text{g m}^{-3}$  for MTBE [16]. The volatilisation in the unplanted HSSF-CW was measured to be less than  $0.5 \text{ mg d}^{-1} \text{ m}^{-2}$  for both benzene and MTBE [16]. The plant root mats with a less developed unsaturated root zone in comparison to the HSSF-CWs with an unsaturated rooted soil zone, which hampers the direct volatilisation, showed higher volatilisation rates probably due to the direct volatilisation of benzene and MTBE from the water to the atmosphere.

### 3.3. Factors affecting the removal of pollutants

Emergent water plants (helophytes) play an important role in the performance of CWs. Also in this study, the planted systems showed a superior performance for the removal of benzene and MTBE than the unplanted system. The reason for this is manifold. Thus, in CWs the roots provide a surface area for the growth of the attached microorganisms [27]. The plants also release organic compounds as root exudates, which together with dead plant material can function as an additional electron donor for microbial anaerobic processes, such as denitrification [21] and dissimilatory sulphate reduction [27]. Furthermore, the helophytes release oxygen from their roots into the rhizosphere [28], which are able to increase the aerobic microbial degradation of organic matter, and nitrification [29]. Meanwhile, the root exudates which contain various compounds might stimulate the activity of microbes [8]. Therefore, in the planted beds the plants improved the microbial activity for benzene and MTBE degradation.

The temperature has also a great influence on the removal of both benzene and MTBE. When the air temperature was above  $10^\circ\text{C}$  from June to September (Figs. 1 and 3), the wetland performance increased. The same effect was also observed in bench-scale vertical flow CWs, which were operated in a fill-and-drain batch mode. Warm temperatures were found to be necessary for improving the treatment performance for benzene removal [30]. However,

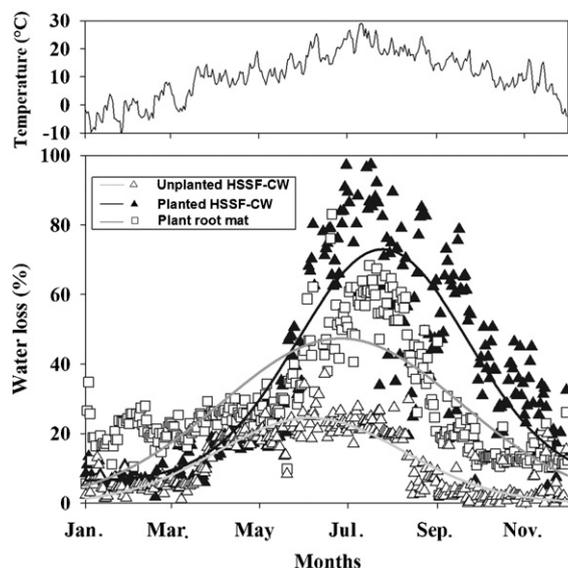


Fig. 3. Temperature and water loss of the plant root mat, the planted HSSF-CW and the unplanted HSSF-CW during the sampling period of the year 2010.

the results of a pilot and full scale subsurface vertical-flow wetland system at the former BP refinery site in Casper, Wyoming, showed little or no temperature effect on the petroleum hydrocarbon degradation rate constants, with a relatively low benzene inflow concentration of  $0.17 \text{ mg L}^{-1}$  [10], indicating that under these conditions other factors would have limited the removal rate.

Water loss includes water evaporation from the water/soil surface and transpiration of plants. It also plays an important role for wastewater treatment in CWs. In this study, both planted systems (the plant root mat and the planted HSSF-CW) indicated a higher water loss than the unplanted HSSF-CW. At the same time, they allowed a better pollutant removal to be obtained. Since September, the water loss in the plant root mat has decreased markedly, as compared to the planted HSSF-CW, and the plant root mat demonstrated a worse performance than the planted HSSF-CW. Thus, plant transpiration is a useful parameter to indicate plant activity and can represent the performance of CWs to some extent.

### 3.4. Redox and electron acceptor conditions

Throughout the year, the redox potential inside all the three pilot-scale treatment systems ranged between 50 and  $125 \text{ mV}$ ; the pH values of the influent and the effluents were between 7.0 and 7.4. The concentration of  $\text{Fe}^{2+}$  was found to be between 2 and  $4 \text{ mg L}^{-1}$  with an inflow concentration of about  $4 \text{ mg L}^{-1}$ . With an inflow concentration of around  $45 \text{ mg L}^{-1}$ , the outflow  $\text{NH}_4^+$  concentration decreased up to 50–100% in the plant root mat and the planted HSSF-CW (in summer time), while no real decrease in the unplanted HSSF-CW has occurred (see Fig. 4). The inflow concentration of  $\text{NO}_3^-$  was  $5.35 \text{ mg L}^{-1}$ , and the outflow concentrations of  $\text{NO}_3^-$  in the plant root mat, the unplanted and planted HSSF-CW amounted to 5.36, 4.18 and  $4.53 \text{ mg L}^{-1}$ , respectively, indicating that no nitrate accumulation and also less denitrification has occurred. The inflowing concentration of  $\text{NO}_2^-$  and the outflow in all the three systems was less than  $0.1 \text{ mg L}^{-1}$ . The redox potential and  $\text{Fe}^{2+}$  concentration data obtained show that all three systems were limited by oxygen (the oxygen concentration was less than  $0.5 \text{ mg L}^{-1}$  in May and less than  $0.15 \text{ mg L}^{-1}$  in July). Ammonium and root exudates were probably competing with benzene and MTBE for electron acceptors (in particular oxygen), thus, it can be assumed that the treatment performance of these three pilot-scale treatment systems was limited by an insufficient oxygen input by the helophyte roots and the surface diffusion into their pore water.

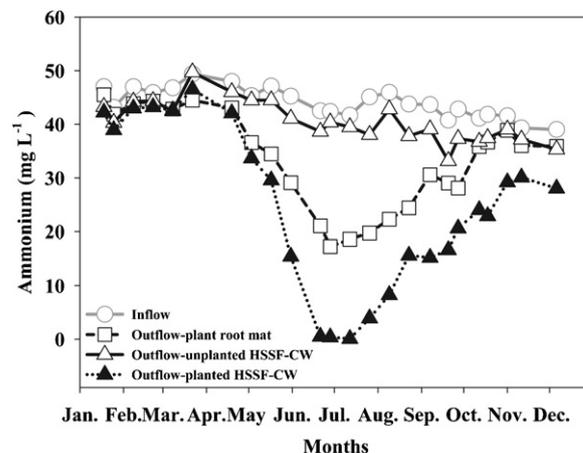


Fig. 4. Outflow concentration of ammonium in three treatment systems (the plant root mat, the planted HSSF-CW and the unplanted HSSF-CW) in dependence on the time.

#### 4. Conclusions

The plant root mat showed a similar treatment efficiency as the planted HSSF-CW for benzene removal and better treatment efficiency for MTBE removal in summer time on a pilot-scale. This confirms that plant root mats as a variant of CWs without a soil matrix could be a cost-competitive variant and alternative for the treatment of distinctively contaminated waters, for example, for the contaminants benzene and MTBE; nevertheless further process optimisation is especially necessary in this case to fulfil national regulations for discharging into nature receiving streams. The removal was very dependent upon the season. Nevertheless, the parameters such as the redox potential and the  $\text{Fe}^{2+}$  concentration showed that in all treatment systems, the oxygen was limited for an optimal microbial degradation of benzene and MTBE. The comparison between the plant root mat and planted and unplanted HSSF-CWs showed that the helophytes stimulated the removal of the contaminants. The relatively low emission of MTBE and benzene compared to the overall removal of these compounds in the HSSF-CW as well as the extremely low biodegradability of benzene and the presumably non-biodegradability of MTBE under strict anaerobic conditions reported in the literature allows to be concluded that the main removal was realised via oxidative microbial degradation.

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