Treatment of waters contaminated by volatile organic compounds (chlorinated hydrocarbons, BTEX aromatics etc.) in constructed wetlands – process characterisation and treatment optimization

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Declaration of Academic Honesty

Hereby, I declare that I have carried out this PhD research project on my own, having used only the listed resources and tools.

Furthermore, I declare that I did not apply for a doctor degree in any other place.

Zhongbing Chen

Leipzig, 13.11. 2012

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Contents

Acknowledgements I
List of abbreviations and symbols V
1 Introduction 1
    1.1 Treatment of water contaminated by volatile organic compounds 1
        1.1.1 Definition of volatile organic compounds 1
        1.1.2 Treatment technologies of volatile organic compounds 1
    1.2 Constructed wetlands for wastewater treatment 2
        1.2.1 General types of constructed wetlands 2
        1.2.2 Removal mechanisms in constructed wetlands 14
    1.3 Constructed wetlands used for treating wastewater polluted by VOCs 18
        1.3.1 Microbial degradation of volatile organic compounds 18
        1.3.2 Volatilization 22
        1.3.3 Plant uptake and plant degradation 23
    1.4 Aim of the work 23
2 Material and methods 25
    2.1 Experimental setup 25
        2.1.1 Pilot-scale experimental system in Leuna 25
        2.1.2 Pilot-scale experimental system in Bitterfeld 26
        2.1.3 Laboratory scale experiments in a planted fixed bed reactor 28
    2.2 Sampling and analytical methods 29
    2.3 Estimation of water loss and contaminant loads 32
    2.4 Data analysis 33
3 Results and discussion 34
    3.1 Results on treating groundwater contaminated by benzene and MTBE in different types of constructed wetlands 34
        3.1.1 Comparison of HSSF CW and FPRM for the removal of benzene and MTBE 34
        3.1.2 Removal of benzene and MTBE by FPRM: effect of water level and root mat age 42
    3.2 Results on the treatment performance of groundwater contaminated by chlorinated hydrocarbons in different types of constructed wetlands 47

Contents

3.2.1 Comparison of HSSF CW and PRMF for the treatment of low-chlorinated benzenes........47

3.2.2 Comparison of HSSF CW and PRMF for the treatment of high-chlorinated ethenes........56

3.2.3 Effect of tidal operation on the HSSF CW performance for treating groundwater contaminated by chlorinated hydrocarbons........64

3.2.4 FPRM for the treatment of chlorinated hydrocarbons: effect of tidal operation........72

3.3 Characterization of MCB and PCE removal in laboratory-scale model wetlands under conditions of different electron acceptors........81

3.3.1 Removal processes of MCB and its derivatives........81

3.3.2 Removal processes of PCE........85

3.3.3 Factors effecting the MCB and PCE removal........85

3.3.4 Influence of nitrate and nitrite on dissimilatory sulphate reduction........88

3.3.5 Conclusions........89

4 Summary........90

5 Outlook........93

6 Reference........95

Appendix........106

Curriculum Vitae........111

List of abbreviations and symbols

List of abbreviations

1,1-DCE	1,1-dichloroethene
1,2-DCB	1,2-dichlorobenzene
1,4-DCB	1,4-dichlorobenzene
Anammox	anaerobic ammonium oxidation
BOD	biochemical oxygen demanding
BOD_5	5 days biochemical oxygen demanding
BTEX	benzene, toluene, ethylbenzenes, xylenes
COD	chemical oxygen demand
cis-1,2-DCE	*cis*-1,2- dichloroethene
CWs	constructed wetlands
DOC	dissolved organic carbon
e.g.	for example
etc.	etcetera
ET	evapotranspiration
FPRM	floating plant root mat
GC-FID	gas chromatography-flame ionization detector
GC-MS	gas chromatography–mass spectrometry
HF	horizontal flow
HSSF	horizontal subsurface flow
HRT	hydraulic retention time
Kow	octanol-water partition coefficient
MTBE	methyl *tert*-butyl ether
MCB	monochlorobenzene
PCE	perchloroethylene
PRMF	plant root mat filter
SSF	subsurface flow
SF	surface flow
TN	total nitrogen
TP	total phosphorus

List of abbreviations and symbols

TOC	total organic carbon
trans-1,2-DCE	*trans*-1,2- dichloroethene
TSS	total suspended solids
TCE	trichloroethene
US EPA	United States Environmental Protection Agency
VC	vinyl chloride
VF	vertical flow
VOCs	volatile organic compounds

List of symbols

cm	centimeter
d	day
°C	degree centigrade
g	gram
h	hour
klx	kilolux
kPa	kilopascals
L	litre
m	meter
µg	microgramme
µm	micron
µmol	micromole
mS	milli Siemens
mg	milligram
mL	milliliter
mm	millimeter
mmol	millimole
mm Hg	millimetre of mercury
mV	millivolt
min	minute
nm	nanometre
%	percentage
m^2	square meter
m^3	cubic meter

1 Introduction

1.1 Treatment of water contaminated by volatile organic compounds

1.1.1 Definition of volatile organic compounds

There is no clear and widely supported definition of volatile organic compounds (VOCs). From a chemistry viewpoint VOCs can mean any organic compound that is volatile (evaporating or vaporizing readily under normal conditions). Definitions vary depending on the particular context. The European Union, states that a VOC is any organic compound having an initial boiling point less than or equal to 250 °C measured at a standard atmospheric pressure of 101.3 kPa and can damage to visual or audible senses. Health Canada classes VOCs as organic compounds that have boiling points roughly in the range of 50 to 250 °C. The emphasis is placed on commonly encountered VOCs which would have an effect on air quality. According to the US EPA's Terms of the Environment, a volatile organic compound is "any organic compound that participates in atmospheric photochemical reactions except those designated by the US EPA as having negligible photochemical reactivity" (http://en.wikipedia.org/wiki/Volatile_organic_compound). Many VOCs are human made chemicals that are used and produced in the manufacture of paints, pharmaceuticals, and refrigerants. VOCs are typically industrial solvents, such as trichloroethylene (TCE); fuel oxygenates, such as methyl *tert*-butyl ether (MTBE); or by-products produced by chlorination in water treatment, such as chloroform.

1.1.2 Treatment technologies of volatile organic compounds

VOCs can be removed by physical, chemical and biological approaches. Soil vapour extraction, bioventing and air sparging are the main physical techniques that rely on physical profile of VOCs, such as vapour pressure for removal. Chemical oxidation is often used when high concentrations of VOCs are present. The main idea for using chemical oxidation approach is to produce the hydroxyl radical, which can increase the oxidative capabilities. Hydrogen peroxide (H_2O_2), ozone (O_3), permanganate (MnO_4^-), persulphate ($S_2O_8^{2-}$) and ultrasound are frequently used oxidants. To date aerobic and anaerobic bioremediation are the main biological approaches for the treatment of VOCs (Moyer & Kostecki, 2003). However, phytoremediation technologies which can form an ecosystem of varying environmental conditions have also been used for the cleaning up of waters contaminated by VOCs.

1.2 Constructed wetlands for wastewater treatment

Highly mechanized and energy intensive technologies are giving way to technologies that utilize solar energy and living organisms in the field of wastewater treatment (Sundaravadivel & Vigneswaran, 2001). The first experiments on the use of wetland plants to treat wastewaters were carried out by Dr. Käthe Seidel in Germany in the early 1950s, and the first full-scale systems were put into operation during the late 1960s. Today, constructed wetlands (CWs) are recognized as a reliable wastewater treatment technology and they represent a suitable solution for the treatment of many types of wastewaters (Vymazal, 2011a).

1.2.1 General types of constructed wetlands

The two main types of CWs are distinguished as: surface flow and subsurface flow CWs (Kadlec & Wallace, 2009). Surface flow (SF) CWs are vegetated systems with open water surface and typically have water depths of less than 0.4 m. In subsurface flow (SSF) CWs, no free water is visible because the water flows through a porous medium planted with emergent water plants (helophytes). SSF CWs are further subdivided into horizontal flow (HF) and vertical flow (VF) systems depending on the direction of water flow through the porous soil (usually sand or gravel). Moreover, hybrid systems which combine different types of CWs are also used (Vymazal et al., 1998). This chapter compares the different variants of CWs.

1.2.1.1 Soil based CWs

Systems with surface flow

SF CWs typically consist of basins or channels, with some sort of subsurface barrier to prevent seepage into groundwater, soil or another suitable materials support the emergent vegetation. Water flows through the unit at a relatively shallow depth. The shallow water depth, low flow velocity, and presence of the plant stalks and litter regulate water flow, especially in long narrow channels in an attempt to reach plug-flow conditions (Reed et al., 1998; Kadlec & Wallace, 2009). These systems function as land-intensive biological treatment systems. Inflow water containing particulate and dissolved pollutants flow and spread out in a large area of shallow water and emergent vegetation. Particles, typically measured as total suspended solids, tend to settle and are trapped due to lowered flow velocities and sheltering from wind. In municipal systems, most of the solids are settled within the first few meters beyond the inlet (Watson et al., 1989).

Attached and suspended microbial growth is responsible for removal of soluble biochemical oxygen demanding (BOD). The major oxygen source for these reactions is re-aeration at the water surface. Nitrogen is mainly removed by nitrification/denitrification. Ammonium is oxidized by nitrifying bacteria in aerobic zones, and nitrate is converted to free nitrogen or nitrous oxide in the anoxic zones by denitrifying bacteria. SF CWs also provide removal of phosphorus, but at relatively slow rates. This removal is caused by adsorption, absorption, complexation and precipitation especially with Al, Fe and Ca ions.

One of the oldest examples of SF CWs has been used in the Netherlands for over 50 years (Greiner & de Jong, 1984). However, most SF CWs are in operation in North America at present (Kadlec & Wallace, 2009).

Systems with horizontal subsurface flow (HSSF)

It is called horizontal flow because the wastewater is fed in at the inlet and flows through the porous medium under the surface of the bed in a more or less horizontal path until it reaches the outlet zone where it is collected before leaving via level control arrangement at the outlet. During this passage the wastewater comes into contact with a network of aerobic, anoxic and anaerobic zones. The aerobic zones occur around roots and rhizomes that leak oxygen into pore water, and at the interface of unsaturated and the top layer of the saturated soil zone. During the passage of the wastewater through these zones the water is exposed to different redox conditions and it is cleaned by microbiological degradation and by physical/chemical processes (García et al., 2010). In Europe, the most common term for HSSF CWs is "Reed Bed Treatment System" coming from the fact that the frequently used plant in these systems is the common reed *(Phragmites australis).* In the Unites States, the term "Vegetated Submerged Bed" has been widely adopted (Cooper et al., 1996).

The first operational HSSF CWs was put into operation in 1974 in Othfresen in Germany and the treatment process was called "Root-Zone Method" (in German “Wurzelraumentsorgung”) (Kickuth, 1977). This first system consisted of a plastic-lined bed containing helophytes (emergent water plants) growing in soil. However, these soil-based systems, as a result of low hydraulic conductivity due to the use of silty soil suffered from surface overflow which prevented the wastewater from coming into contact with the plant roots. The problem of surface runoff was overcome by the use of more porous medium, such as gravel.

Organic compounds are degraded aerobically as well as anaerobically by bacteria attached to plant roots, rhizomes and the surface of the soil particles. The oxygen required for aerobic degradation is supplied directly from the atmosphere by diffusion or oxygen leakage from the helophyte roots and rhizomes in the rhizosphere (Vymazal, 2011b). Numerous investigations have shown that the oxygen transport capacity of the helophytes is insufficient to ensure complete aerobic decomposition in the rhizosphere and that anoxic and anaerobic decomposition play an important role in HSSF CWs (Brix, 1990; Vymazal, 2011b). Settleable and suspended solids that are not removed in the pre-treatment system are effectively removed by filtration and settlement in HSSF CWs(García et al., 2010).

Nitrogen can be removed in HSSF CWs by microbial nitrification/denitrification, volatilization, adsorption and plant uptake. The major removal mechanism of nitrogen in HSSF CWs is nitrification/denitrification. Field measurements have shown that the oxygenation in the rhizosphere of HSSF CWs is insufficient and, therefore, the incomplete nitrification followed by reduction of formed nitrite by organic carbon, hydrogen sulphide or even ammonium (anaerobic ammonium oxidation) seem to play an important role in nitrogen removal. Volatilization, plant uptake and adsorption are usually of less importance (Paredes et al., 2007; Zhu et al., 2010).

Phosphorus is removed from wastewater in HSSF CWs primarily by ligand exchange reactions, where phosphate displaces water or hydroxyls from the surface of Fe and Al hydrous oxides. However, soil used for HSSF CWs (e.g. pea gravel, crushed stones) usually do not contain great quantities of Fe, Al or Ca and therefore, removal of phosphorus is generally low (Kadlec & Wallace, 2009).

Systems with vertical subsurface flow

The significant differences between VF and HSSF CWs can obviously be seen from the flow direction. In addition VF systems often have a distribution system covering the whole surface area. Apart from this the elimination principles are the same for both systems. Usually mechanically pretreated wastewater is piped into the wetland and percolates through the media. The elimination processes take place during this passage.

The earliest VF CWs in Europe were the so-called "infiltration fields" in the Netherlands and the Seidel-System, also known as Krefeld-System or Max Planck Institute Process (Brix, 1994). The infiltration fields have been in operation in Europe for approximately 25 years to treat the wastewater from recreation sites outside the municipal sewer network in the Netherlands (Greiner & de Jong, 1984). The system is typically comprised of a preliminary settling/distribution ditch, four infiltration compartments with soil/sand media, a discharge via drain and an effluent ditch. The infiltration ponds are planted with *Phragmites australis* and are provided with a drainage system 0.55 m beneath ground level. Raw domestic sewage is discharged into the preliminary settling/distribution ditch. After settling the sewage is mixed with surface water from the effluent ditch and fed into one of the infiltration compartments every three to four days. The other three compartments are kept dry for a period of ten to eleven days.

Systems with tidal flow

Several studies have shown the improvement in the performance of a CW by the concept of "tidal flow" (Green et al., 1997; Sun et al., 1999; Vymazal & Masa, 2003). There is an improved removal of BOD_5 achieved through aerobic decomposition and enhanced removal of ammonium through nitrification as maximum media-pollutant contact is established.

During the tidal flow, a cycle of water logged and drained periods in the wetland are created i.e. the soil of the wetland is alternately filled with wastewater and drained. On filling the wetland, air is expelled from the wetland when the level of water rises. When the wetland is drained, the retreating water acts as a passive pump to draw air from the atmosphere into the media. Hence, an unsaturated zone during the draining period is created that will enhance aeration due to higher oxygen transfer. Each volume of effluent drained is displaced by an equal volume of fresh air thus supplying the oxygen required for the nitrification process (Kadlec & Wallace, 2009).

The need for better aerobic or anoxic degradation by providing more oxygen transport into the bed has led to the concept of tidal arrangement also referred to as pulsating water level in HSSF CWs (Vymazal & Masa, 2003). A HSSF CW in Czech Republic was put into tidal operation in order to treat municipal wastewater between September 1999 and September 2000. The results showed a positive effect on the removal of BOD_5 by 53 %, chemical oxygen demand (COD) by 30 % and ammonium by 27 % in comparison to non-tidal beds. But there was also a decrease in removal of suspended solids observed which was probably due to higher outflow velocity of discharged water which could flush out settled particles. There was also no effect of pulsing during the winter months on the treatment efficiency (Vymazal & Masa, 2003).

There was also laboratory research based on tidal flow using vertical soil columns that are typical for VF CWs for treating diluted piggery wastewater (Sun et al., 2005). The removal of ammonium by enhancing oxygen transfer by tidal flow arrangement in the beds was the main objective. Significant removal of organic matter, ammonium and suspended solids was achieved in these columns. Nitrification removal rates were found to be governed by several factors. When dissolved oxygen concentration was lower than 0.5 mg/L, there was no obvious nitrification. Also, significant nitrification did not take place until BOD_5 in wastewater dropped to 200 mg/L or below (Su & Ouyang, 1996; Sun et al., 1998). The contact between pollutants and microorganism is another important aspect for nitrification (Sikora et al., 1995; Reddy & D'Angelo, 1997). All these factors could further govern the efficiency of tidal based CWs.

Hybrid systems

Hybrid systems comprise VF and HF components arranged in a staged manner (Kadlec & Wallace, 2009). Currently there are few of these systems in operation and it is perhaps too early to decide which configuration offers the best arrangement. HF CWs are good for suspended solids removal and will remove some BOD but generally little ammonium. VF CWs are far more aerobic than HF CWs and are good for nitrification as well as BOD removal, yet they are less efficient than HF CWs for suspended solids removal (Kadlec & Wallace, 2009). Systems which are particularly good for removal of phosphorus require a media which will bind the phosphate.

1.2.1.2 Floating plant root mat / non floating plant root mat filter

A new variant of CWs has been developed that employs helophytes, similar to those used in surface and subsurface flow CWs, growing as a floating root mat on the water surface or touching to the rooting proof bottom of the water body where the root mat can function as a biofilter for the contaminated water. However, there is no clear definition of these systems. In general, a floating root mat involves the growth of helophytes, which naturally root into the soil, but in this case are converted into artificially macrophyte root mats floating in a pond or canal. These plants form a dense floating mat of roots and rhizomes, whereby a preferential hydraulic flow in the water zone between the root mat and the non-rooted bottom can be expected. In the case that this root mat occupies the whole water body and touches the bottom of the pond or canal, the water is forced to flow through the root mat which operates as a filter.

Floating plant root mat (FPRM) and non-floating plant root mat filter (PRMF) are hybrids of soil free ponds and conventional soil based CWs containing helophytes. Because of their specific structure, FPRM combines benefits from ponds and CWs, and is therefore used for the removal of different pollutants such as suspended solids, nutrients, metals, and organic contaminants. The interest in them is continuing to grow as observed in Figure 1.2-1 below.

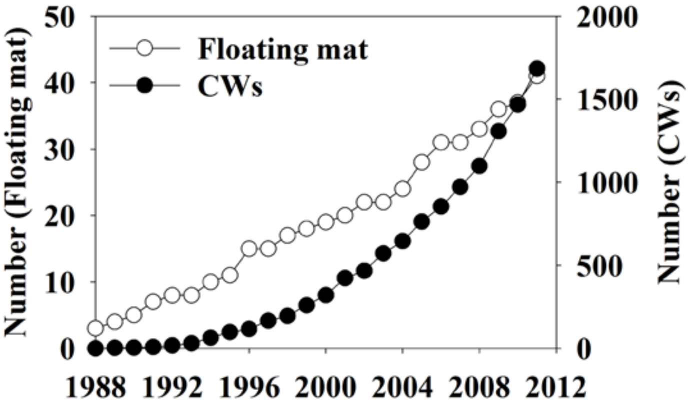

Figure 1.2-1. Accumulated number of publications about floating mat and constructed wetlands per year. The literature search was performed using Thomson ISI research tool and "floating mat" and "constructed wetland" as key words for the title search (The following variables were employed: Doc type: all document type; language: all languages databases: SCI-Expanded, SSCI; Time: 1988-2012). The search was completed on the 7th May, 2012.

Definition of floating root mats

FPRM and PRMF are similar to ponds as they have an open water body, and are also similar to conventional soil based CWs as both of them use helophytes, but ponds are usually dominated by phytoplankton (Kadlec, 2005). Therefore there are a variety of different terms that have been used to describe them. FPRM is often described as "floating islands" (Van Duzer, 2004), "artificial floating islands" (Nakamura et al., 1995), "artificial floating reed beds" (Billore & Prashant, 2008), floating mats (Kalin & Smith, 1992; Li et al., 2009), "floating treatment wetlands" (Van de Moortel et al., 2010; Faulwetter et al., 2011; Headley & Tanner, 2011), or "constructed floating wetlands" (Van de Moortel et al., 2011). Since the root mat is regarded as the most important and representative feature of these systems, and the mat is either floating or non-floating, we termed them as FPRM and PRMF.

History of the development of FPRM and PRMF

Vegetation floating on water bodies is a natural phenomenon. The first written record of floating islands was probably presented by G.C. Munz in 1711 (Van Duzer, 2004). A global bibliography comprising more than 1800 citations of books and articles in twenty languages, including the formation of floating islands, the cause of their buoyancy, their role in the ecology of lakes and wetlands, their flora and fauna, their role in the dispersal of plants and animals, and the methods for controlling and managing them, as well as the use of floating islands for agriculture, wildlife habitat and improvement of water quality was published by

Van Duzer (Van Duzer, 2004). In the field of water treatment, FPRM was probably first used in eutrophicated lakes and rivers, for example, in Germany (Hoeger, 1988) and in Japan (Nakamura et al., 1995). Subsequently, it was also applied in Canada to treat acid mine drainage (Smith & Kalin, 2000), followed by treating storm-water (Revitt et al., 1997; Kerr-Upal et al., 2000; Tanner & Headley, 2008), poultry processing wastewater (Todd et al., 2003), piggery effluent (Hubbard et al., 2004), sewage and domestic wastewater (Ayaz & Saygin, 1996; Hijosa-Valsero et al., 2010b; Van de Moortel et al., 2010; Faulwetter et al., 2011; Cubillos et al., 2011a) and combined sewer overflow (Van de Moortel et al., 2011), as well as eutrophic lake water (Li et al., 2007; 2009a; Song et al., 2009; Wu et al., 2006). Recently, FPRM was used for treating ground waters contaminated by the chemical industry (Seeger et al., 2011b; Chen et al., 2012)

Characterisation and function of FPRM and PRMF

Plant root development

The development of plant roots to form a dense root mat is the most important start up requirement for FPRM and PRMF. A great number of helophyte species have the potential to grow as floating wetlands, where most of them can form self-buoyant floating root mats in nature or grow successfully on rafts with the purpose to improve water quality (Dahl, 1972; Van Duzer, 2004). Water composition and climatic conditions are important factors in determining the plant species. As is the case in media based CWs, the genera *Canna, Carex*, *Cyperus*, *Juncus*, *Phragmites* and *Typha* are frequently used (Kadlec & Wallace, 2009). Species in these genera are typically tall, robust and characterised by the presence of large aerenchyma or air filled cavities in their roots and rhizomes, which enhance their potential for buoyancy. It has to be considered that the phase of plant establishment needs special protection against grazing animals (Tanner et al., 2006). Once established, these mats often become populated by a diverse range of species and can form communities of high species richness (Cherry & Gough, 2006). It can be harmful to the new young plants when under anaerobic conditions H_2S is formed. For big treatment systems, it is possible to transport already well developed root mats from the nursery to the final location.

The root development is influenced by many factors such as plant species, plant age, and nutrient and redox conditions of the water. It is to be expected that a higher root density will result in a higher specific contact area which will be available for an attachment of bacteria to form biofilms. In the case of *Typha latifolia*, the root mass and root density increased with its age (Smith & Kalin, 2000). Average root lengths between 24−48 cm for *Carex dipsacia, Carex virgata, Cyperus ustilatus, Eleocharis acutis* and *Schoenoplectus tabernaemontani* with a maximum of 87 cm for *Juncus edgariae* was reported (Tanner & Headley, 2008). It seems that the development of the roots is especially influenced by the trophic status of the water. So, even a root length of up to 2 m for *T. latifolia* in oligotrophic waters was mentioned (Mueller et al., 1996). On the other hand, the root length of *Phragmites australis*, after a three-year treatment of a groundwater polluted with volatile organic compounds (benzene about 15 mg/L), phosphate (about 3−5 mg/L) and ammonium (about 50 mg/L), using the FPRM in a pilot-scale system, was only around 25 cm (Chen et al., 2012). However, in this case infestation with endophytic moths had a negative effect on the development of the root mat, and plant growth was inhibited (own observation). Beside the root length for technical aspects, the specific root surface area for attached bacteria (biofilms) is of particular importance. To date only limited information about this is available (Smith & Kalin, 2000), see chapter “Suspended solids”).

Water depth

The water level is an important parameter when using FPRM and PRMF. Once a high water level is reached, the plant root mats are floating and a free water zone exists below the mat up to the bottom of the water body. Such a system will mostly be used like a pond for storm-water or waters with a high content of coarse suspended solids for their removal by sedimentation (Headley & Tanner, 2011). When the water level is very low, which prevents the buoyancy of the root mats, this system will function like a filter that is more suitable for the removal of fine particles and dissolved pollutants ensuring a much more direct contact between plant roots, wastewater and microorganisms (Chen et al., 2012). By varying the water level in this way can influence the removal of the contaminants by the FPRM/PRMF. It also should be considered that some wetland plants are quite sensitive to water level fluctuations (Deegan et al., 2007). Nevertheless, species such as *Typha* spp., *Phragmites australis*, *Scirpus* spp., *Juncus* spp. and *Phalaris arundinacea* show a high morphological adaption to water level variations and are therefore applied in stormwater wetlands which are especially characterised by extreme water level fluctuations (Bonilla-Warford & Zedler, 2002; Headley & Tanner, 2011).

The choice of the water level in FPRM/PRMF depends on the treatment purpose and the types of the wastewater. A high water level is needed to treat storm-water. After one year of growth, maximum rooting depths of 57, 62, 68 and 87 cm for *Carex virgata*, *Schoenoplectus tabernaemontani*, *Cyperus ustulatus* and *Juncus edgariae*, respectively were reported when treating an artificial stormwater (Tanner & Headley, 2008). When treating acid mine effluents, the average root length of *Typha angustifolia* was 39 cm after two or more years of growth on floating rafts (Smith & Kalin, 2000).

In general, the reported studies were carried out using different water levels, water compositions and hydraulic retention times, which makes it impossible to summarise the influence of the water depth on the treatment performance. The most recent experiments are focusing on water depths which are much deeper than the roots could be in contact with the wetland/pond bottom (systems with a free water zone below the mat), while the previous surveys were carried out under the conditions of water depths below 0.5 m (Boutwell & Hutchings, 1999; Kyambadde et al., 2005; Tanner & Headley, 2011).

Buoyancy

There are early reports about natural floating islands which are so stable that they could even carry cows (Van Duzer, 2004). However, the reasons of self-buoyancy of these natural floating islands, and in the special case of FPRMs for wastewater treatment, are not yet entirely described. It was reported that entrapped gases under the plant root mats, are composed of methane and nitrogen as final products of anaerobic processes (methanogenesis and denitrification) (Hogg & Wein, 1988a). A further factor for self-buoyancy is the aeration tissue (aerenchyme) in many helophytes, which creates air spaces especially within the rhizomes (Hogg & Wein, 1988b). It can be assumed that this self-buoyancy in natural floating wetlands and FPRMs is affected by several factors, including age, temperature, season and plant species (Hogg & Wein, 1988a; Hogg & Wein, 1988b; Swarzenski et al., 1991; Tomassen et al., 2003).

Several floating materials are used, which function as a solid matrix for supporting plant growth and as a platform structure to fix and support the buoyancy of plants. Floating frames, polyester fibres, individual floaters made of foam or even the use of peat as a matrix have been reported (Smith & Kalin, 2000; Curt et al., 2005; Hu et al., 2010). The use of peat, however, is not recommended because it settled, did not support the plant growth, and caused a high own oxygen demand affecting the plants (Smith & Kalin, 2000).

Influence of the plant root mat on the hydraulic performance

As for all treatment systems, the performance of FPRM and PRMF depends on the hydraulic characteristics. Constructional aspects, such as the relationship between pond length, width and depth, the location of inlets and outlets and their orientation regarding the dominant wind direction as well as the vegetation are critical for obtaining a high hydraulic efficiency (Jenkins & Greenway, 2005). Furthermore, vegetation coverage influences the hydraulic characteristics of the system. With a coverage of 2% of the total treatment area, no change was observed in the retention time and in the effective volume compared to an unplanted pond (Persson, 2000). In contrast, with full plant coverage, the hydraulic efficiency (the ratio of the time of the peak outflow concentration to the nominal detention period) of the system increases twofold (Persson et al., 1999). The free water zone between the roots and the bottom of the system could allow more laminar flow conditions and avoiding re-suspension of settled particles to take place. Nevertheless, since the root density and its depth distribution is usually not ideal or regular, the flow condition in the root mat will not represent an ideal plug flow.

Influence of plant coverage on the water treatment processes

Plant coverage affects the mass transfer of oxygen from the atmosphere to the pore water in SSF CW (Burgoon et al., 1995). More reduced conditions are formed in FPRM, especially below the root mat (Van de Moortel et al., 2010). One of the most cited impacts that plant coverage has on any water body, including that of FPRM and PRMF, is the reduction of light penetration into the water column, which avoids or limits the growth of photosynthetic algae (Zirschky & Reed, 1988; Brix, 1993; Wetzel, 2001; Song et al., 2009; Hubbard, 2010; Li et al., 2010).

Apart from the inhibition of algae growth, plant coverage also has an influence on the nutrient removal. According to three FPRMs used *Carex acutiformis* of different plant coverage (0%, 50% and 100%) for treating combined sewer overflow water (Van de Moortel et al., 2010), the results showed that the removal efficiencies of ammonium, total nitrogen and total phosphorous increased with the increase of plant coverage.

It is assumed that biofilms of non-photosynthetic bacterial communities dominate in FPRM over algae because light penetration is limited by the presence of the covering floating mat (Tanner & Headley, 2008). It can be assumed that differences in the composition of the microbial community may be affected by the spatial dynamics of oxygen and carbon availability throughout the plant root mat biofilm, which may have an effect on the removal processes for different pollutants. It is well known that a significant source of organic matter in wetland systems comes from rhizodeposition products and this is especially important for both microbial denitrification and sulphate reduction of low organic carbon loaded wastewaters (Vanoostrom & Russell, 1994; Smith & Kalin, 2000). The factors determining the magnitude of the carbon flux from the plants or the roots to the water have not yet been fully elucidated. For soil-based plants, however, it has been estimated that approximately 5-10% of the net carbon fixed by photosynthesis is lost by root exudation (Jones et al., 2004), and some experiments performed in hydroponic cultures showed that only between 0.5-1.5%

of fixed carbon is lost (Farrar et al., 2003). In natural floating wetlands (*Typha*) it has been estimated that each year 23% of the shoots, 25% of rhizomes and 30% of dead roots are deposited with the floating mat. For *Glyceria maxima* it was reported that its decaying biomass could contribute electron donors for denitrification at a rate of between 0.5-1 g/m^2/d (Hogg & Wein, 1987; Vanoostrom & Russell, 1994).

Differences between floating root mats, ponds with free floating plants and soil based constructed wetlands

The main characteristics of FPRM system, ponds, ponds with free floating plants, and soil based CW are listed in Appendix 1. Moreover, schematics for different wetland systems are given in Figure 1.2-2. In general, the advantages of FPRM are direct uptake of nutrients from the water through the plant roots, shade preventing algal proliferation, easily coping with varying water levels, root network ensuring physical filtration and providing a large attachment surface for microorganisms and an ecological value/shelter for fauna. Disadvantages are seasonally dependent removal efficiencies and a relatively long start-up period. In contrast to the facultative and aerated ponds, FPRM rely on the presence of macrophytes to achieve an enhanced removal of pollutants. In case of accumulation of too much sediment, the plant root mat can be easily shifted aside to allow its removal.

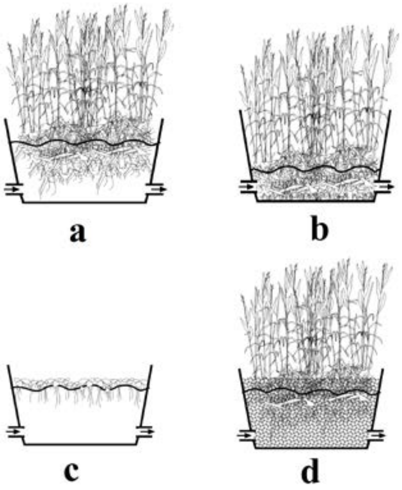

Figure 1.2-2. Schematics of floating plant root mat (a), plant root mat filter (b), free floating plants (c) and horizontal subsurface flow constructed wetland (d)
(drawn by Nancy Hachicho).

The roots in the FPRM provide a high specific surface area for attachment and growth of biofilm-forming bacteria, which allow the development of different removal and transformation processes to be carried out according to the pollutants contained in the wastewater (Kadlec & Wallace, 2009). As is the case in ponds, the hydraulic retention time (HRT) increases when the water level in FPRM is increased. This fact improves the overall removal for some pollutants, however the water volume below the root zone will be higher and will be in less contact with the biofilm formed on the surface of the plant roots. Therefore, the water level has to be optimized according to the removal of specific pollutants and plant species. This is especially the case when the reproductive time of the microorganisms is lower than the hydraulic retention time.

Treatment performance of FPRM

FPRM was used to treat different types of wastewaters. The removal efficiencies are dependent on different factors such as the climatic conditions and the type of water. Examples for the use of floating root mats in the treatment of various types of wastewater are listed in Appendix 2. As the compositions vary with the types of wastewater, only the treatment performances of selected parameters are shown. So far, the most studied pollutants are suspended solids, organic matter, nutrients (nitrogen and phosphorus), and heavy metals.

Principal design of FPRM/PRMF

The main design objectives of FPRM and PRMF for wastewater treatment are the strengthening of the root mat development and optimising the contact between wastewater, the root mat biofilms and the roots themselves. For enhancing the root mat development, vegetation is an important issue. The locally available indigenous aquatic plants are to be preferred, especially with long roots which can form a dense curtain in the water body. In general, species from the genera *Canna*, *Carex*, *Cyperus*, *Juncus*, *Phragmites* and *Typha* are the most commonly used plants to form FPRMs, and they are also commonly used in other types of CWs (Kadlec & Wallace, 2009).

The water level is another important parameter in optimizing the contact between wastewater and the root mat biofilms. The water level should be varied using different target pollutants, for instance, a high water level is necessary for treating water loaded with coarse particles, while a low water level is preferred for treating water with fine particles and dissolved recalcitrant contaminants where a system with attached microbial biomass growth is needed. The dimension of the free water zone below the root mat is adjusted by the water level. The general design features are as follows:

- Floating and fixing structures are necessary to stabilise the buoyancy of the FPRM and helping the plants to resist drifts caused by wind.
- Fencing is necessary, especially during growth of young plants.

- Pre-treatment can be necessary, especially for waters with high concentrations of organic compounds and sulphate to minimise the formation of toxic H_2S.
- A special design is needed for removing sludge from the bottom.

1.2.2 Removal mechanisms in constructed wetlands

CWs are complex systems due to the large number of physical, chemical and biological processes which proceed in parallel and are mutually influence by each other. Therefore, CWs have been considered “black boxes” for a long time and little effort has been made to understand the main processes leading to contaminant removal. Recently, efforts have been made to understand the removal mechanism in CWs in more detail, in order to achieve this target modern tools from environmental microbiology, plant biology, ecology and molecular biology have been used. Generally, the removal processes are taking place between microorganisms and plants as well as the interaction of physical and physico-chemical process in the system.

1.2.2.1 The role of microbes

The resulting process conditions and the usually low flow rates in CWs lead to a high microbial diversity which is generally advantageous for pollutant removal.

The removal of organic carbon in VF CWs with intermittent loading is known to be dominated by aerobic microbiological mineralization. In contrast, the importance and efficiency of different microbiological processes in HSSF CWs is less known. In general, oxygen, nitrite, nitrate, iron(III), many inorganic sulphur compounds with oxidation numbers equal or higher than zero and other compounds may act as electron acceptors for the microbiological mineralization of organic compounds. Otherwise, anaerobic fermentation of organic carbon, including methanogenesis, may be the main processes in limiting electron acceptors for mineralization.

Nitrogen is removed mainly by microbial denitrification which usually depends on previous nitrification (Kadlec & Wallace, 2009). Nitrification affects the generation of nitrite from ammonium via a first oxidation step. In usually oxygen-deficient HSSF CWs, the subsequent transformations remain largely unknown. In theory, nitrite may be further oxidized to nitrate, or direct denitrification of the generated nitrite may be the dominant process. Different reductants may be efficient at reducing nitrite, such as organic compounds from the wastewater, dead plant matter, plant exudates, hydrogen sulphide, iron(II) or ammonium (anaerobic ammonium oxidation – so called “Anammox”) (Paredes et al., 2007).

Phosphorus removal can be explained through a complex of physical, chemical and microbiological processes, although adsorption and precipitation to the soil has usually been considered to be the main removal process (Vymazal & Kröpfelová, 2008; Kadlec & Wallace, 2009); microbiota uptake and plant uptake may also play a role in the removal of phosphorus (Vymazal & Kröpfelová, 2008).

Redox processes of the sulphur cycle, especially dissimilatory sulphate reduction, were found to influence toxicities and removal processes (Wiessner et al., 2008; Faulwetter et al., 2009). Furthermore, simultaneous methanogenesis has been observed in CWs, despite a comparably higher thermodynamic and kinetic potential for sulphidogenesis. Correlations of sulphide generation and methanogenesis as well as the efficiency of re-oxidation of sulphide and methane in the wetlands are important subjects of future research. Moreover, response of biological systems (microorganisms, plants) to sulphide toxicity and the formation and stability of deposited sulphur pools are of special interest (Wiessner et al., 2008)

1.2.2.2 The role of plants

Two major functions have been attributed to plants in CWs: supply of oxygen to the micro-organisms in the rhizosphere and the increase of soil hydraulic conductivity (Brix & Schierup, 1989). Actually, the success or failure of a CW is contingent upon creating and maintaining correct water balance. Water represents 80 to 90% of plants fresh weight, and is involved in all physiological functions, such as photosynthesis, element uptake and plant cooling by leaf evapotranspiration (ET). ET can be an important contributor to water loss on a periodic basis mostly affecting the HRT and pollutant removal efficiency (Kadlec, 2000; Kadlec & Reddy, 2001; Stein et al., 2006; Kadlec & Wallace, 2009). Under hot arid climates, such as in Mediterranean countries, ET losses from CWs can be substantial and result in a loss of water resources and an increase in the salt concentration of the effluent with negative implications for irrigation reuse schemes. ET represents a movement of water from the root zone through the plant and may therefore stimulate mixing within subsurface flow CWs which can affect the treatment efficiency. ET is negatively affected by salt deposition in the root cells and plant defence mechanisms rely on shedding of older leaves (Nilratnisakorn et al., 2007).

Oxygen partial pressure in the rhizosphere is affected by diffusion through the aerenchyma, respiration by roots, root associated microorganisms, root consumption of water and root penetration into the soil creating channels for gas transfer (Armstron, 1971; Philippot et al., 2009), moreover soil oxygen partial pressure is a major factor regulating nitrification, denitrification and methanogenesis and also greenhouse gas emissions. Besides oxygen, organic compounds contained in root tissues can be released into the soil (exudates) (Nguyen, 2003). Plants, by exuding up to 25% of the net carbon fixed during photosynthesis into the rhizosphere, modify the soil-microbe interactions, namely, microbial activity, abundance and community composition (Verkleij et al., 2009). Bacterial coverage of the root surface usually ranges from 5 to 10% and the total number of bacteria within the distance of 1 mm of plant roots is usually 10 times higher than that situated 15-20 mm distance from the root (Vymazal & Kröpfelová, 2008). Bacteria growth is stimulated by carbohydrates, amino acids, phenolics, aliphatic compounds, fatty acids, sterols, enzymes, vitamins, hormones and nucleosides released by secretion, diffusion or cell lysis (Jones et al., 2009; Verkleij et al., 2009). The interaction of plant roots on the oxygen and carbon balance in the soil of SSF CWs have therefore an impact on important pollutant removal processes, especially regarding carbon and nitrogen cycles. In addition, roots are also responsible for mucilages production (exopolysaccharides) that together with exudates affect soil structure and the processes related with water transport (Hinsinger et al., 2009). Detection of exudates have been mostly performed in hydroponic conditions, its production and release in CWs plants rhizosphere and how it affects system performance is not yet clear.

In general, plants play a role in altering the chemical form of the contaminants by changing the environment (e.g., pH, redox potential) around their roots. The microorganisms (bacteria and mycorrhiza) living in the rhizosphere of these plants also have an important role in these processes, they can actively contribute by changing trace element speciation, but they can also assist the plant in overcoming phytotoxicity (Vangronsveld et al., 2009). Plants can be also used to extract pollutants and accumulate them in their tissues, followed by harvesting the above ground plant material. This technique is known as phytoextraction. Uptake of organic chemicals into plant tissue is predominantly affected by the lipophilic nature of organic pollutants, which can be characterized by the octanol water partition coefficient (Kow) (Ryan et al., 1988). Hydrophobic organics with a log Kow > 4 are believed not to be significantly taken up through the plant cell membrane because of significant retention within the root epidermis (Trapp, 1995), but exceptions may occur. Reed and rice plants have been shown to take up highly lipophilic polychlorinated biphenyls (Chu et al., 2006). Only under the condition of significant contaminant uptake by the vegetation, processes like phytovolatilization, phytoaccumulation and plant metabolic transformation have to be considered as potential removal processes for organic contaminants (Imfeld et al., 2009). Rhizo- and phytodegradation of wastewaters contaminated with organic xenobiotics, e.g. pharmaceutical and personal care products, drugs etc., is becoming increasingly popular as a cost-effective remediation strategy (Matamoros et al., 2008; Matamoros et al., 2009; Hijosa-

Valsero et al., 2010a). Plants are equipped with a complex and versatile array of enzymes to defend themselves against xenobiotics (man-made chemicals). The structure and function of many detoxifying enzymes have been reported (Schröder et al., 2007; Carias et al., 2008; Davies et al., 2009).

1.2.2.3 Physical and other processes

The physical and chemical characteristics of the soil used in a CW can greatly influence the overall performance of the CW. Physical properties (such as porosity, hydraulic conductivity, and grain size distribution) influence hydraulic efficiency, which is a critical component of good design. Poor hydraulic efficiency leads to short-circuiting and reduced treatment performance (Kadlec & Wallace, 2009).

Physico-chemical properties of the CW media, such as mineral composition and specific surface area, dictate the adsorption capacity. Irreversible adsorption or precipitation onto the soil surface is a significant removal mechanism for pollutants (Scholz & Xu, 2002; Dordio et al., 2007; Matamoros et al., 2007). Engineered mediums, such as expanded clays and lightweight aggregates have a high specific surface area compared to conventional mediums (such as river gravel) and have been successfully used in CWs to enhance and sustain high levels of treatment performance (Ádám et al., 2007; Vohla et al., 2011). Alternative natural materials (e.g. shell sand) and industrial by-products (e.g. oil shale ash, blast furnace slag, tyre chips) have also been identified as sustainable and cost-effective alternatives to conventional soils (Arias & Brix, 2005; Korkusuz et al., 2005).

Although the use of natural and alternative media in CWs is widespread, the physical and chemical properties of the materials are highly variable, and must be assessed on a case-by-case basis (Hu & Shan, 2009). The selection of media for CWs is largely based on technological considerations, and economic considerations also play a key role. The use of locally available materials can significantly reduce construction costs for CWs (USEPA, 2000).

Poor hydraulic efficiency in CWs often results in reduced treatment efficiency (Knowles et al., 2008; Mena et al., 2008; Rios et al., 2009). Tracer experiments using salts or dyes can be used to characterize the hydrodynamic behaviour of CWs (Grismer et al., 2001; Headley & Kadlec, 2007; Nivala et al., 2012). For HF CWs treating landfill leachate or specific high-salinity industrial wastewaters, density-induced stratification may occur, which can hinder mixing within the system (Breen & Chick, 1995; Rash & Liehr, 1999; Bulc, 2006). Information on how specific design variables and operational practices can affect the hydraulic efficiency of a CW is required for validating existing models and developing more reliable CW design tools.

Clogging is stated as one of the major shortcomings of CW technology (Kadlec and Wallace, 2009). It often reduces the hydraulic conductivity of a CW soil to the extent that it prevents normal operation and often results in surfacing of untreated wastewater. It has been stated to significantly limit the asset lifetime of a CW (Caselles-Osorio et al., 2007). Restorative measures such as renovation or replacement of the porous medium do exist, but they are often costly, and their degree of success is not guaranteed (USEPA, 2000; Wallace & Knight, 2006; Nivala et al., 2012).

1.3 Constructed wetlands used for treating wastewater polluted by VOCs

1.3.1 Microbial degradation of volatile organic compounds

1.3.1.1 Degradation of benzene

Aerobic degradation of benzene

The first step for aerobic benzene degradation is ring cleavage; this is accomplished by a dioxygenase-catalyzed reaction between benzene and molecular oxygen, resulting in production of benzene dihydrodiol (Eaton & Ribbons, 1982). Aromaticity is restored by a dehydrogenase-catalyzed conversion of benzene dihydrodiol to catechol, which is the ring cleavage substrate. The reactions leading to catechol are shown in Figure 1.3-1.

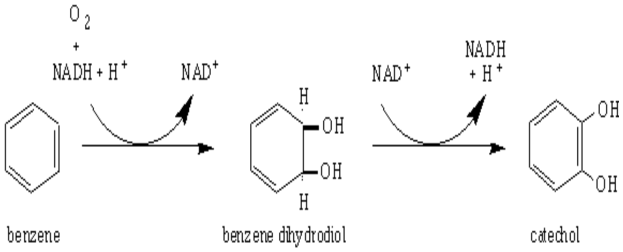

Figure 1.3-1 Microbial oxidation pathways of benzene to catechol

Catechol is catabolized by ring cleavage, in which the aromatic ring is broken. Ring cleavage can occur by either of two pathways: the ortho-cleavage pathway, in which the aromatic ring is split between the two carbon atoms bearing hydroxyl groups, or the meta-cleavage pathway, in which the ring is broken between a hydroxylated carbon atom and an adjacent unsubstituted carbon atom (Feist & Hegeman, 1969). Each of these ring-cleavage reactions is catalyzed by a dioxygenase. The subsequent metabolic pathways are quite different, but they both lead to tricarboxylic acid cycle intermediates (acetate and succinate) or to substrates that can be easily converted to tricarboxylic acid cycle intermediates (Feist & Hegeman, 1969).

Anaerobic degradation of benzene

It has been found that benzene can be anaerobically oxidized with most commonly considered electron acceptors for anaerobic respiration. These include Fe(III), sulphate, nitrate, and possibly humic substances. Benzene can also be converted to methane and carbon dioxide under methanogenic conditions. Evidence from laboratory studies also suggests that benzene may be anaerobically degraded in petroleum contaminated marine sediments under sulphate reducing conditions. But in general, the microbial anaerobic turn over rates are considerably slower in comparison to aerobic pathways (Lovley, 2000).

1.3.1.2 Degradation of MTBE

Aerobic degradation of MTBE

Studies indicate that the ether bond of MTBE is enzymatically cleaved yielding *tert*-butanol and formaldehyde. *tert*-butanol has been shown to be degraded to 2-methyl-2-hydroxy-2-propanol and 2-hydroxy-isobutyric acid. The downstream intermediates include 2-propanol, acetone and hydroxyl acetone (Figure 1.3-2).

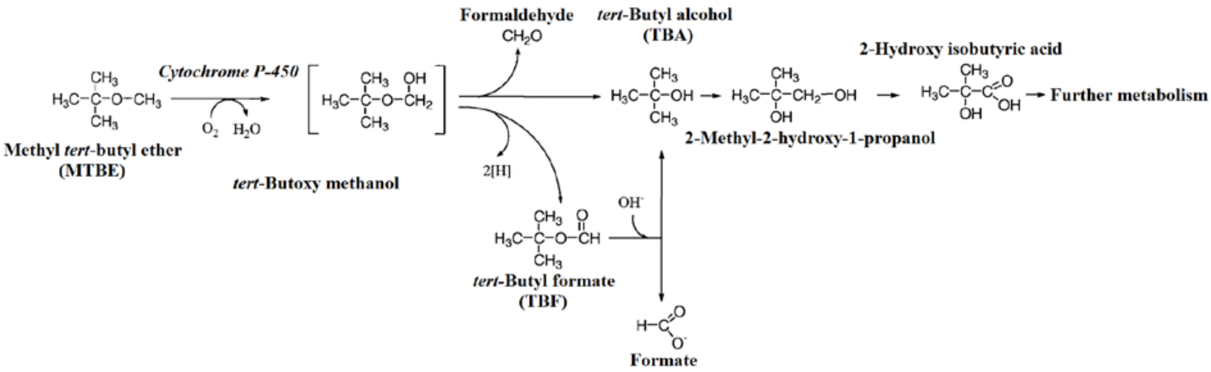

Figure 1.3-2 Degradation pathway of MTBE. Modified from (Fayolle et al., 2001)

Anaerobic degradation of MTBE

There are some evidences for MTBE degradation under denitrifying conditions. The addition of humic substances stimulated the anaerobic degradation of MTBE in aquifer sediments in which Fe(III) was available as an electron acceptor (Finneran & Lovley, 2001). However, the degradation rates were very low. Investigations on MTBE degradation under sulphate reducing and methanogenic conditions indicated that degradation rates were slow or non-existent (Martienssen et al., 2006).

1.3.1.3 Degradation of monochlorobenzene (MCB)

Aerobic degradation of MCB

The microbial aerobic degradation of MCB like the biodegradation of other chlorinated benzenes, starts with a dioxygenase reaction of attacking with an O_2 molecule catalyzed by the enzyme dioxygenase and forming 3-chloro-*cis*-benzene-dihydrodiol. Then the obtained dihydrodiol is dehydrogenated to 3-chlorocatechol. The next step, ring cleavage, is a crucial reaction in the metabolism of haloaromatics (Reineke & Knackmuss, 1984). The 3-chlorocatechol is cleaved by a 1,2-dioxygenase into ortho position, whereby a further O_2 molecule is used. It forms a chlorinated muconic acid. The oxidative dehalogenation process goes further catalyzed by monooxygenase enzyme, where HCl is released (Figure 1.3-3).

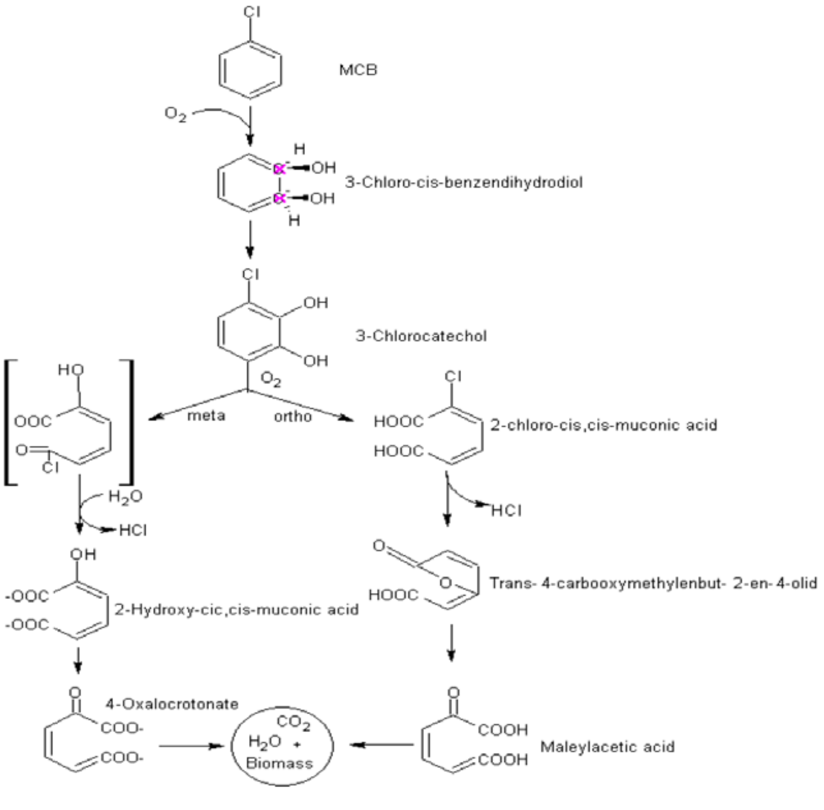

Figure 1.3-3 Aerobic biodegradation pathway of monochlorobenzene (Fetzner, 1998; van Agteren et al., 1998)

Anaerobic degradation of MCB

The anaerobic biodegradation of chlorinated benzene is through a reductive dechlorination process (Nowak et al., 1996). Chlorinated benzene acts as final electron acceptor. The process is called dehalorespiration. Despite the lack of a direct evidence of an anaerobic degradation pathway of MCB, it is hypothesized that the hydrogenolyse process takes place where the chlorine atom is replaced by a hydrogen atom and HCl is produced (Figure 1.3-4). The microbially catalysed dehalogenation pathway follows the redox potential of the various redox couples, i.e., the couples which give rise to the highest energy yield are used preferentially (Dolfing & Harrison, 1993). The electron acceptors with the highest redox potential, generally oxygen, is used first, then nitrate, after that sulphate, and finally carbon dioxide (Zehnder & Stumm, 1988). The redox potential can be used as an indicator to predict the dominant pathway in microbial systems.

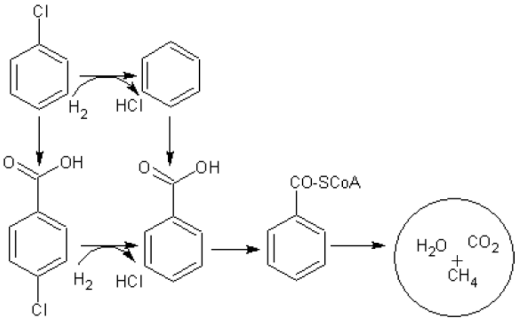

Figure 1.3-4 Simplified hypothetical anaerobic degradation pathway of MCB (Nijenhuis et al., 2005)

1.3.1.4 Degradation of PCE (perchloroethylene)

Chloroethene contaminants were considered recalcitrant to biodegradation before 1980, however, biodegradation become to an essential component of chloroethene plume remediation now (Bradley, 2003). For PCE degradation, anaerobic condition must be formed for the first step of reductive dehalogenation of PCE to TCE and followed by reductive dehalogenation or oxidation of TCE, dichloroethenes (1,1-DCE; 1,2-trans-DCE; 1,2-cis-DCE), VC and ethene in anaerobic and aerobic conditions (Bradley, 2003; Mattes et al., 2010). The dechlorination pathway of PCE was given in Figure 1.3-5.

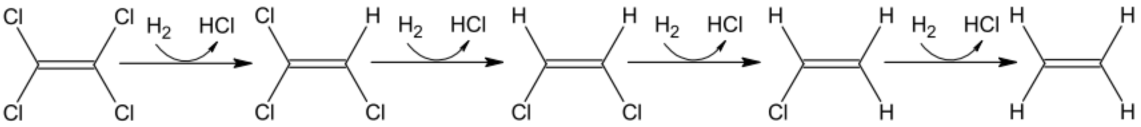

Figure 1.3-5 Complete reductive dechlorination process of PCE to ethene (Vogel & McCarty, 1985).

1.3.2 Volatilization

Volatilization and phytovolatilization are processes to remove VOCs. Volatilization refers to the process that a given compound moves from liquid phase to gas phase. Phytovolatilization is the emission of contaminants from the plant surface to the air by evapotranspiration or diffusion process, and this process depends on system type, plant type, and contaminants.

The Henry coefficient is expected to be a valuable indicator for predicting volatilization behaviour of contaminants. It comprehensively describes the transfer of volatile contaminants from the water phase to the atmosphere. In unsaturated soil zones, additionally the diffusion transport determines effective VOCs emission. A high Henry coefficient is a characteristic of a number of organic contaminant groups frequently treated in CWs such as chlorinated solvents, BTEX compounds (benzene, toluene, ethylbenzenes, xylenes) and MTBE.

Direct volatilization and phytovolatilization are expected to be moderate for hydrophilic compounds such as acetone (Grove & Stein, 2005) and phenol (Polprasert et al., 1996). In contrast, volatilization can be an important removal process for volatile hydrophobic compounds such as lower chlorinated benzenes (Keefe et al., 2004), chlorinated ethenes (Ma & Burken, 2003) and BTEX compounds (Wallace, 2002). In a CW treatment of MTBE, which is characterized by a moderate Henry coefficient, high water solubility and additionally by strong recalcitrance concerning biodegradation under anaerobic conditions (Deeb et al., 2000), various processes can result in the release of the compound to the atmosphere. Uptake by the transpiration stream and subsequent phytovolatilization through the stems and leaves can be a major removal process and significantly contribute to contaminant mass loss; additionally, the vegetation increases the upward movement of water into the unsaturated zone, where enhanced volatilization occurs (Hong et al., 2001; Winnike-McMillan et al., 2003). If the atmospheric half-life of VOCs are reasonably short like three days at 25 °C for MTBE (Winnike-McMillan et al., 2003) and the toxicological risk is assumed to be low, the water-to-atmosphere contaminant transfer occurring in CWs may constitute a possible remediation option. However, volatilization of VOCs can also lead to air pollution and to a dispersal of the contaminant in the environment. This fact and the lack of reliable risk assessment analysis currently discourages regulatory acceptance of volatilization and phytovolatilization as a strategy for VOCs removal (McCutcheon & Rock, 2001).

Phytovolatilization can be of particular relevance in SSF CWs, where direct volatilization is restrained due to slow diffusion rates of contaminants through the unsaturated soil zone as well as laminar flow in water saturated soil zones that may result in relatively low mass transfers. Direct contaminant volatilization is expected to be more pronounced in SF CWs, as water remains in direct contact with the atmosphere (Kadlec & Wallace, 2009).

1.3.3 Plant uptake and plant degradation

Plant uptake of VOCs have a profound relationships with its' chemical and physico-chemical properties (Collins et al., 2002). The compounds can be transported in the transpiration stream when the log $K_{ow} \approx 2$. For compounds with a log K_{ow} 1.0-3.5, metabolism may occur in the leaf and stem tissue and may then be released to the atmosphere through the leaf tissue, additionally 'bound-residue's' can be created in the plants. Those compounds of a log $K_{ow} < 1$ cannot penetrate the lipid containing root epidermis, while those compounds of log $K_{ow} > 2$ become increasing retained by the lipid in the root epidermis and the mucilage surrounding the root as a result of their high hydrophobicity (Collins et al., 2002).

The log K_{ow} for MTBE, benzene, MCB and PCE are 1.24, 2.12, 2.18 and 3.4, respectively. This means that benzene, MCB and PCE have the potential for plant uptake, while MTBE is more consistent with plants. It was reported that MTBE was shown to be persistent against degradation by plant cells (Trapp et al., 2003).

1.4 Aim of the work

At present, the treatment of water contaminated by VOCs (e.g. chlorinated hydrocarbons, benzene, MTBE, etc.) is mainly realised by physico-chemical methods like stripping and adsorption on activated carbon. Therefore, alternative cheaper treatment methods are of high interest for the industry.

Constructed wetlands (CWs) are already applied for the treatment of different kinds of contaminated water, they are proved to be an alternative under distinctive conditions to traditionally applied water treatment technologies especially concerning energy consumption. However, because of the specific characteristics especially the biological recalcitrance and volatility of VOCs, the treatment of such contaminated waters was not in the focus of research and application in CWs till now, and examples were very limited.

In consequence, the objective of this work was to characterize and optimize the treatment process of waters contaminated by VOCs in CWs. For this, known wetland technologies should be tested and new technology variants like soil-free CWs were developed.

Special aspects like sulphide formation and its potential toxicity to aerobic microbes and plants in CWs should be investigated under more stable and well defined conditions in laboratory-scale reactors simulating the conditions of a CW.

The research within this PhD thesis will make a contribution to the application of CWs to new fields and show advantages and limitations of the use of CWs for the treatment of VOC contaminated waters in dependence on the specific technology variants.

Furthermore, with the focus on new variant CWs - floating plant root mat (FPRM) and plant root mat filter (PRMF), investigations were carried out for the treatment of benzene and MTBE in pilot-scale CWs in Leuna and for the treatment of chlorinated hydrocarbons in pilot-scale CWs in Bitterfeld. Moreover, the sulphide effect on the treatment of chlorinated hydrocarbons was investigated in a laboratory-scale planted fixed bed reactor.

In detail, the research was focused on the following aspects:

- Comparing the treatment performance of benzene and MTBE in horizontal subsurface flow constructed wetland (HSSF CW) and floating plant root mat (FPRM)
- Testing the effect of water level and root mat age on the removal of benzene and MTBE in FPRM
- Comparing the treatment performance of low chlorinated benzenes in a HSSF CW and a PRMF
- Comparing the treatment performance of high chlorinated hydrocarbons (PCE and its degradation metabolites) in a HSSF CW and a PRMF
- Testing the effect of tidal operation on the removal of chlorinated hydrocarbons in HSSF CW and FPRM.
- Investigating the removal processes of MCB and PCE in laboratory-scale planted fixed bed reactor.

2 Material and methods

2.1 Experimental setup

2.1.1 Pilot-scale experimental system in Leuna

Within the framework of the UFZ-project CoTra (Compartment Transfer), a pilot-scale experimental site was built near the Leuna industrial site in June 2007. It enabled the investigation of different near-natural groundwater treatment wetland systems, e. g. horizontal subsurface-flow CW, vertical-flow CW, aerobic trench systems, tidal flow CW and floating plant root mat systems, with the focus on optimizing and understanding the removal processes of the main contaminants BTEX, MTBE and ammonium. The experimental plant was equipped with the ability of online measurement for water parameters and a mantle for the determination of emission rates. Regular sampling of the organic contaminants and inorganic compounds was provided by staff and delivered the basic concentration data for the in and out flow. Additionally, sampling campaigns within the systems along the flow path, were also undertaken. A local weather station measured rainfall, ambient temperature and solar radiation.

There were five experimental CWs taken into consideration for this study. The operation conditions of the systems were as follows:

S11 – floating plant root mat (FPRM), established in April 2008 with water level of 15 cm until September 2009 water level at 30 cm

S15 – unplanted horizontal subsurface flow constructed wetland (HSSF CW), established in June 2007; water level at 40 cm

S16 – planted HSSF CW, established in June 2007; water level at 40 cm

S17 – floating plant root mat (FPRM), established in March 2010; water level at 15 cm

S18 – floating plant root mat (FPRM), established in March 2010; water level at 15 cm (2010) and 40 cm (2011)

All the CWs were placed in containers with the dimension of 5 m × 1.1 m × 0.6 m. The HSSF CWs (2 - 3.2 mm) were filled up with gravel to a depth of 50 cm, while the CWs without soil were filled with plant root mats. The contaminated groundwater was pumped from a 15 m depth well at an inflow rate of 6 L/h in each wetland. The theoretical hydraulic retention time (assuming no water loss) was therefore 6.88 days for the soil-based CWs. The concentrations of the major contaminants along with other minor contaminants at the inflow are listed in the Table 2.1-1.

Table 2.1-1 Average concentration of organic and inorganic contaminants of the groundwater used as the wetland's influent in Leuna (2009-2011)

Contaminants	Unit	Mean	Standard deviation
Benzene	mg/L	19.3	3.8
MTBE	mg/L	3.34	1.1
Ammonium	mg/L	57	12
Nitrite	mg/L	0.72	0.28
Nitrate	mg/L	0.49	0.11
Iron(II)	mg/L	4.7	1.5
Chloride	mg/L	117	18
Sulphate	mg/L	8	3
Phosphate	mg/L	1.41	0.35
TOC	mg/L	40	7
COD	mg/L	106	12
BOD_5	mg/L	59	6
pH	-	6.5-7.1	

2.1.2 Pilot-scale experimental system in Bitterfeld

The pilot scale CWs were located at the contaminated site Bitterfeld/Wolfen. This pilot plant was established in December 2002 under the UFZ research project SAFIRA (SAnierungsForschung In Regional kontaminierten Aquiferen), in order to develop and implement in-situ techniques for the remediation of contaminated groundwaters. The base of the CWs was a stainless steel container which had the dimension of 6 m × 2 m × 0.5 m. It was divided into two segments: one was a media based HSSF CW and the other one was a FPRM, both were operated in HF mode and were planted with common reed (*Phragmites australis*). The HSSF CW was established in December 2002, filled with autochthonous quaternary aquifer material consisting predominantly of about 25% sand and about 67% gravel. The soil bulk had a hydraulic conductivity (K value) from 10^{-5} m/s to 10^{-2} m/s and a porosity of 0.28. The iron content was about 0.31-0.65% (Vogt et al., 2002). The soil bulk had the dimension of 5 m × 1 m × 0.5 m. The soil bulk was followed by a free water body with a dimension of 1 m × 1 m × 0.4 m until the outflow. The FPRM was established in March 2010 with well grown root mats. Both systems were continuously supplied with the contaminated groundwater at a flow rate of 5 L/h from a well installed to a depth of 22 m in which accessed the local aquifer. The theoretical HRT was 6 days. The water level was controlled at 0.4 m by float valves in the open water compartments and the outflow volume was recorded by flow meters. All the weather data were collected daily.

Initially, from March 2003 the HSSF CW was ran with only local contaminated groundwater, which the main organic pollutant is low chlorinated hydrocarbons. In order to investigate the performance of CWs treating high chlorinated hydrocarbon, PCE was added in the inflow from May 2006 with a concentration of around 2 mg/L. To fertilize the plants, around 30 mg/L ammonium was added in March 2008 and was increased to 50 mg/L in April 2009. Due to geogenic reason, the groundwater contained high concentration of sulphate (around 850 mg/L). The concentrations of the main contaminants in the inflow are listed in the Table 2.1-2.

Table 2.1-2 Average concentration of organic and inorganic contaminants of the groundwater used as the wetland's influent in Bitterfeld during the experiment 2009-2011, n=45

	Unit	Mean	Standard deviation
PCE	mg/L	1.9	0.4
MCB	mg/L	7.8	2.5
2-Chlorotoluene	mg/L	0.03	0.01
1,2-Dichlorobenzene (1,2-DCB)	mg/L	0.03	0.01
1,4-Dichlorobenzene (1,4-DCB)	mg/L	0.29	0.05
NH_4^+	mg/L	53	11
NO_3^-	mg/L	1.2	0.9
Fe^{2+}	mg/L	0.5	0.2
SO_4^{2-}	mg/L	863	54
S^{2-}	mg/L	0.5	0.6
Cl^-	mg/L	320	89
PO_4^{3-}	mg/L	4.3	2.5
DOC	mg/L	13.6	1.3
Eh	mV	50	87
Electrical conductivity	mS/cm	3.1	0.3
pH	-	6.5-6.7	

The HSSF CW ran with continuous flow till 20th July 2010. From the 21st July 2010, it ran under a 7 day tidal flow cycling regime, which means 2 hours of fast outflow flushing, as a result the water level decreased from 40 cm to 15 cm; the subsequent refilling (5.0 L/h) again to the water level of 40 cm lasted about 34 hours; then there was a further continuous inflow and outflow phase of 132 hours until a new cycle started. From the 13th April 2011, it ran under 2.5 days of cycling, which means 2 hours of fast outflow flushing, by this the water level decreased fast from 40 cm to 15 cm; the subsequent refilling (5.0 L/h) again to the water level of 40 cm lasted about 34 hours; then followed a further continuous inflow and outflow phase of now only 24 hours until a new cycle started.

The FPRM ran continuously until the 12th of April, 2011. From the 13th April 2011, it ran also as a tidal flow system, which means 2 hours of fast outflow flushing, by this the water level decreased from 40 cm to 15 cm. The subsequent refilling (5.0 L/h) again to the water level of 40 cm lasted about 2 weeks; when the water level reached to 40 cm, a fast sampling action (taking pore water samples in different flow distances and depth) started, and subsequently a new cycle started immediately after this sampling.

2.1.3 Laboratory scale experiments in a planted fixed bed reactor

The planted fixed bed reactor comprised of an inflow feeding device in a reactor with an "internal" circulation flow. It consisted of a cylindrical glass vessel (diameter: 30 cm; height: 30 cm) containing a metal basket (diameter: 26 cm; height: 28 cm) filled with 21 kg gravel (2-4 mm) (Figure 2.1-1). The reactor was feed with a constant inflow of Bitterfeld contaminated groundwater provided by a valveless Wobble-piston pump (REGELO-CPF, Ismatec, Switzerland) via a distribution ring in the reactor. The effluent is discharged from the separately pumped internal circulation flow, which was maintained by a peristaltic pump (MCP, Ismatec, Switzerland). The water level and therefore the outflow were controlled by a level control system that comprised of a bottom pressure sensor, which controls the outlet-valve in the internal circulation flow. The reactor was closed with a Teflon lid containing 5 plant openings, which can be sealed with special shims for gas-tight closure of the plants by India rubber resulting in a separated rhizosphere (Kappelmeyer et al., 2002).

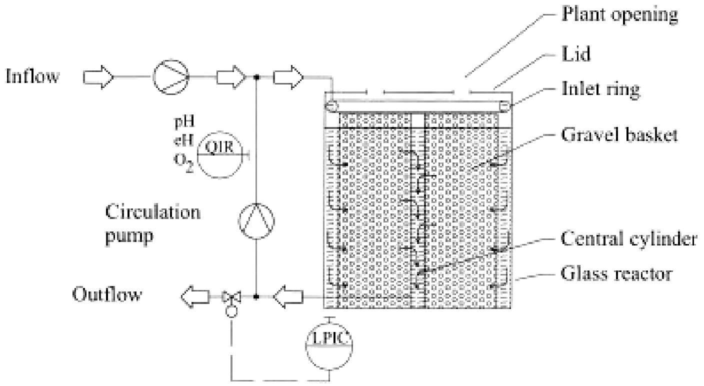

Figure 2.1-1 Diagram of the laboratory-scale reactor (from (Kappelmeyer et al., 2002))

A suction cylinder (diameter: 4 cm; height: 28 cm) was placed in the centre of this basket from which the "internal" circulation flow was pumped by the peristaltic pump and was recirculated into the distribution ring. The distribution ring was located outside the gravel basket and above the surface of the liquid. This internal flow was essential in order to attain a gradient-free flow in the fixed bed. In addition, the pH value (pH-electrode: Jumo/Germany; 2G E-2-G-U-1), the redox potential (Pt-metal redox potential electrode: Jumo/Germany; 2ME-2G-PtK-1), and the dissolved oxygen (membrane electrode, Siemens/France; Spain 34, 7MA3100-8EF) were determined in the circulation flow. The reactor was completely filled with wastewater up to the defined level (Kappelmeyer et al., 2002).

The reactor was placed in a greenhouse and operated under defined environmental conditions to simulate an average summer day in a moderate climate. The temperature set points were 22 °C from 6 am to 9 pm to simulate daytime and 16 °C at night. A lamp (Master SON-PIA 400 W, Phillips, Belgium) was switched on during daytime as an additional artificial light source whenever the natural light fell below 60 klx. This additional illumination provided approximately only 11 klx at the top of the plants (70 cm), 5 klx at the middle of the plants and 3 klx at ground level (Wießner et al., 2005). The operating period started in May 2010 and was continued until December 2011.

2.2 Sampling and analytical methods

Sampling procedure in the pilot-scale plant in Leuna

Inflow and outflow water samples together with pore water samples at different distances (1 m, 2.5 m and 4 m) from inlet and different depths (20 cm and 40 cm) in the CWs were taken. The temperature and redox potential were measured on-site using a flow-through cell equipped with a redox electrode (Pt/Ag+/AgCl/Cl-type Sentix ORP, WTW, Germany). For measuring organic contaminants, 5 mL of water was transferred into 20 mL headspace vials, 50 μL bromobenzene-d_5 (with a final concentration of 250 μg/L) was used as an internal standard, and 5 mL NaN_3 (with a final concentration of 0.65 g/L) were added in order to inhibit microbial activity. These samples were transported to the laboratory using ice bags and stored in a cooling storage room at a temperature of 4 °C before analysis. The samples for inorganic analysis were transferred into 25 mL brown glass bottles and measured in the field laboratory.

One-week continuous gas sampling was carried out in early May 2010 using a dynamic air chamber in two FPRMs (three year old and one year old) and a HSSF CW. Eight one-week continuous gas samplings were carried out from March to October 2011 (every month) in two FPRMs (two years old) with different water levels (15 cm and 40 cm). Gaseous analytes were trapped onto two replicate sorbent tubes (MARKES, self-packed containing 150 mg Tenax

TA and 100 mg Chromosorb 106), analyzed 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 (Reiche et al., 2010).

Sampling procedure in the pilot-scale plant in Bitterfeld

Pore water samples were taken at different distances (0.5, 1, 2, 3 and 4 m) from the inlet and at different depths (0.3, 0.4 and 0.5 m) in the HSSF CW, same distance but only one depth (20 cm) in the PRMF and two depths in the FPRM (20 cm and 40 cm). Outflow was taken in the 0.4 m depth in the open water compartment (a perforated column with a diameter of 20 cm) after a flow path of 5.5 m; inflow was taken directly before it entered both wetlands. A stainless steel lance (3.5 mm inner diameter) was used for taking the samples from different depths, all the water samples were pumped out from the lance through a peristaltic pump with the sampling rate of 78 mL/min. The redox potential was measured in the field using a redox electrode ($Pt/Ag^+/AgCl/Cl^-$ type Sentix ORP, WTW) when taking the samples. The temperature was record by a temperature sensor (PT 1000, PreSens, Regensburg, Germany).

All water samples for inorganic analysis were filtered by 5 µm micro syringe filter to prevent the transfer of suspended particles, and were stored in polyethylene vials without headspace at 4 °C until analysis. For organic analysis, 10 mL water samples were collected in 20 mL glass flasks (Supelco, Bellefonte, USA), sodium azide solution was added into the samples (with a final concentration of 0.65 g/L) to inhibit microbial activity, the bottles were then sealed with Teflon-lined septa.

Sampling procedure in the planted fixed bed reactor

Inflow and outflow water samples were taken twice per week. For inorganic analysis, 20 mL of water was taken with a 20 mL polyethylene vial, and the following parameters NH_4^+, NO_3^-, NO_2^-, SO_4^{2-}, S^{2-} and Fe^{2+} were measured directly after the samples were taken. For organic analysis, 10 mL water samples were collected in 20 mL glass flasks (Supelco, Bellefonte, USA), sodium azide solution was added into the samples (with a final concentration of 0.65 g/L) to inhibit microbial activity and sealed with Teflon-lined septa. The samples were stored in a horizontal position in a cooling storage room at a temperature of -20 °C before analysis.

In order to investigate the volatilization of MCB and PCE, three 24 hours continuous gas sampling campaigns were carried out using a cylindrical flow-through test chamber (ethylene tetrafluoroethylene, internal diameter 34 cm, height 85 cm) which were placed upon the plants over the reactor leaving an air entrance at the bottom of about 5 cm. To determine background concentrations the ambient air was sampled next to the air entrance into test chamber. At the upper funnel-shaped end of the chamber the airflow through the chamber was analysed using a gas sampling device with a flow rate of 60 mL/min for 24 h. Samples were collected on Tenax TA (150 mg) filled into 110 mm × 8 mm glass tubes (SKC, Eighty Four PA, USA). Potential substance breakthrough was monitored by a second tube put in series, but was never observed. Samples were analysed using a Thermo-desorption GC-MS system (EM 640/S, Bruker, Germany) equipped with a DB1 column (30 m × 0.25 mm × 1 µm film). The desorption step was carried out at 250°C (180 seconds) and the following temperature program was applied for GC analysis: 40°C (3 min), 15°C/min to 250°C (1 min). Injection was splitless (120 seconds) with an inlet temperature of 260°C and helium as the carrier gas.

Analytical methods

Oxygen concentration

The determination of the concentration of dissolved oxygen in the influent stream and the soil pore water was measured with an optical trace oxygen sensor (PreSens GmbH) in a specially constructed flow cell made of glass. Care was taken to ensure that oxygen from the atmosphere did not enter into the sample solution. The use of an aluminum foil darkened the flow cell from outside and thus protected the light sensitive oxygen sensor from the influence of external light. The measuring system consisted of a trace oxygen mini sensor (FTC-TOS7) attached in a flow cell, an optical fiber coated fiberglass, a Fibrox-3-Trace single channel fibre-optic trace oxygen meter, a temperature sensor (PT 1000) and a laptop computer with Fibrox-3 software to display and analyze data from the oxygen meter. The calibration of the sensors took place with calibration data supplied by the manufacturer. The system worked with automatic temperature compensation, the measurement of the temperature was done with the help of a temperature sensor.

Organic compounds

The samples for benzene and MBTE determination were analysed by means of a headspace GC-FID (Agilent 6890 GC). The size of the (Agilent DB-MTBE) column was 30 m × 0.45× mm × 2.55 µm, and the following procedures were performed: 35 °C (6 min), 4 °C/min to 120 °C, 20 °C/min to 280 °C (5 min). Nitrogen was used as the carrier gas. Prior to the analysis, the samples were equilibrated at 80 °C for 30 minutes.

The concentrations of the main contaminants MCB and PCE as well as their metabolites were measured by automatic headspace gas chromatography using a HP 6890 gas chromatograph with flame ionization detector (Agilent Technologies, Palo Alto, USA). For headspace analysis a gas volume of 1 ml was injected at an injection temperature of 250 °C with split 1:5 (measurements in duplicates). The chromatographic separation was achieved with an HP-

1 capillary column (Agilent Technologies, Palo Alto, USA) (30 m length × 0.32 mm inner diameter × 5 µm film thickness) with the following oven temperature program: equilibration at 60°C (60 min), GC oven program 45°C (1 min), 20°C/min to 200°C (2.5 min), 65°C/min to 250°C (1 min), and the detector temperature was 280°C. Helium was used as carrier gas with a flow rate of 1.7 ml/min.

Inorganic ions

NH_4^+, NO_3^- and NO_2^- were measured using a photometer (Spectroquant® Nova 60, Merck) and the Merck quick tests (number 1.00683.0001 for NH_4^+, 1.09713.0001 for NO_3^- and 1.14776. for NO_2^-). Sulphate concentration was measured by turbidity of the $BaSO_4$ method at 880 nm after precipitation in acidic gelatine solution. Sulphide was analysed photometrically using the test kit LCW 053 with a measuring range of 0.1-2.0 mg/L (Dr. Bruno Lange GmbH, Düsseldorf, Germany). For the measurement of Fe^{2+}, hydrochloric acid was added and after derivatization with ferrocene, a photometric measurement was performed at 562 nm using a Cadas 100 photometer (Hach Lange, Düsseldorf) (Lovley & Phillips, 1986).

2.3 Estimation of water loss and contaminant loads

Water loss of wetlands through evapotranspiration

In CWs, there can be a considerable amount of water loss due to evaporation of water from the media filter and plant transpiration especially during the warm period. These two processes fall under the term evapotranspiration. The amount of water the plants removed from the systems was calculated by measuring the influent and effluent streams as well as the local rainfall (precipitation). The percentage of water loss ($V_{wl}(\Delta t)$) during a defined period could be calculated by equation (2.3-1). The difference between the influent water volume, precipitation and the effluent water volume results in water loss from the system.

$$V_{wl}(\Delta t) = \frac{V_{in}(\Delta t) + V_{rain}(\Delta t) - V_{out}(\Delta t)}{V_{in}(\Delta t) + V_{rain}(\Delta t)} \times 100 \qquad (2.3\text{-}1)$$

Where, V_{in} (Δt), V_{out}(Δt) and V_{rain}(Δt) are the influent volume, effluent volume and volume of rainfall registered during a time period Δt. The loss of water due to evapotranspiration has to be considered for the calculation of the contaminant loads in the water.

The effect of water loss on actual removal efficiency

The seasonal evolution of concentration decrease shows how important it is to account for water losses and to be able to calculate actual removal efficiencies in terms of load removal (Bojcevska & Tonderski, 2007). Evapotranspiration may have a large impact on the water balance and thereby also on outflow nutrient concentrations and along with that treatment performance. Therefore, mass balance estimations are better than differences between inflow and outflow concentrations, which may lead to underestimation of the treatment performance. The normal efficiency ($E_{\%}$) is calculated by the differences between inflow and outflow concentrations using equation (2.3-2). However, considering the water loss, the efficiency ($E'_{\%}$) can be calculated by equation (2.3-3).

$$E_{\%} = 1 - \frac{C_{out}}{C_{in}} \qquad (2.3\text{-}2)$$

$$E'_{\%} = 1 - \frac{C_{out}}{C_{in}} \times \frac{V_{out}}{V_{in}} \qquad (2.3\text{-}3)$$

The contaminant mass loads were calculated on the basis of water volume flow rates and contaminant concentrations. The decrease of contaminant mass load along the flow path was calculated assuming that the water loss followed a linear change, which means the water flow rate at each calculated distance was recalculated by the linear water loss (see equation 2.3-4).

$$M_{ij} = C_{ij} \times \left[V_{in} - \frac{(V_{in} - V_{out})}{L} \times L_i \right] \qquad (2.3\text{-}4)$$

Here, M_{ij} = contaminant mass at distance i m and depth j cm, mg/d; C_{ij} = contaminant concentration at distance i m and depth j cm, mg/L; V_{in} = inflow volume, L/d; V_{out} = outflow volume, L/d; L_i = distance from inlet at point i, m; L = entire length of the CW, m.

The area specific load was calculated after 4 m from the inlet with the surface area of 4 m^2 in Bitterfeld, whereby in the CWs the mean of the concentration of the different depths was used. As for Leuna, area specific load was calculated with outflow concentration of the whole surface area of 5.5 m^2. The depth related loads were calculated based on the assumption that the concentrations at each depth represented the concentration of the cross section with all the water flow through.

2.4 Data analysis

Mean values of two samples were taken for organic concentrations at one sampling point. T-test analysis was performed based on the loads or concentration to compare the treatment performance between PRMF and HSSF CWs. Non-parametric Mann-Whitney U-tests were carried out when normal distribution could not be assumed according to one sample Kolmogorov-Smirnov tests (Dornelas et al., 2009). All the tests were done by SigmaPlot 11.0 programme, and the differences were regarded as significant at $P < 0.05$.

3 Results and discussion

3.1 Results on treating groundwater contaminated by benzene and MTBE in different types of constructed wetlands

3.1.1 Comparison of HSSF CW and FPRM for the removal of benzene and MTBE

This chapter gives the results of three wetland systems in Leuna (S11, S15 and S16) in 2010, which are the three years old FPRM with a water level of 30 cm, the unplanted HSSF CW and the planted HSSF CW.

3.1.1.1 Treatment performance

The removal performance of benzene and MTBE during the experimental period is summarized in Figure 3.1-1. The results show that both planted systems (the FPRM and the HSSF-CW) exhibited a better performance than the unplanted HSSF-CW both for benzene and MTBE removal; however, there are no significant differences between the two planted systems (the FPRM and the HSSF-CW). The significant P values are presented in Table 3.1-1.

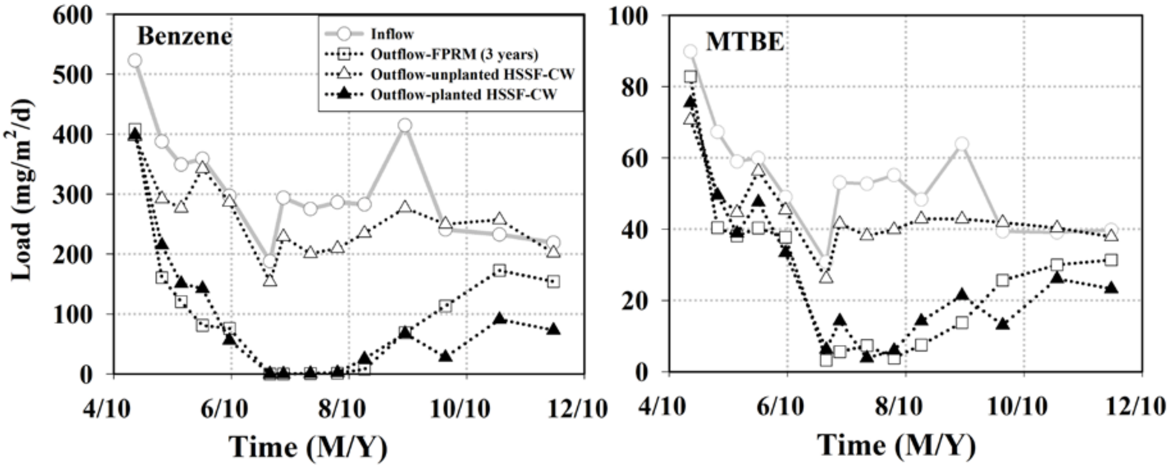

Figure 3.1-1. Inflow and outflow loads of benzene and MTBE during 2010 in three treatment systems (the FPRM, the planted HSSF-CW and the unplanted HSSF-CW)

The results also indicate that a better removal performance was achieved during summer than in winter both for benzene and MTBE. During the winter period, almost no benzene and MTBE was removed when the unplanted HSSF-CW was used, whereas in summer the respective removal rates reached up to 153 and 24 mg/m^2/d for benzene and MTBE. In the planted HSSF-CW, removal rates of around 140 and 15 mg/m^2/d for benzene and MTBE, respectively were obtained during winter and summer, the values increased up to around 360 and 48 mg/m^2/d, respectively. In the FPRM, the removal rates for benzene and MTBE were 118 and 8 mg/m^2/d during the winter and 325 and 51 mg/m^2/d during the summer months. The main reason for these differing 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 (Faulwetter et al., 2009).

Table 3.1-1 Mann-Whitney U-test of benzene and MTBE outflow loads in the unplanted HSSF-CW, FPRM and the planted HSSF-CW, n = 14)

	Unplanted HSSF-CW − FPRM	Unplanted HSSF-CW − Planted HSSF-CW	FPRM−Planted HSSF-CW
Benzene	**<0.001**	**<0.001**	0.679
MTBE	**0.001**	**0.009**	0.854

At the BP Amoco Former Casper Refinery site in Wyoming with relatively low inflow concentrations of 0.6 mg/L benzene and 1.26 mg/L MTBE, a pilot scale vertical flow CW achieved relatively high removal rates of 94 mg/m^2/d for benzene and 120 mg/m^2/d for MTBE. The removal rates even increased up to 120 mg/m^2/d for benzene and 180 mg/m^2/d for MTBE, when aeration was performed (Haberl et al., 2003). In vertical-flow experimental CWs operated in batch-flow mode, benzene was removed to about 85% under outdoor conditions (Edinghburgh, Scotland) and to about 95% under stable indoor conditions, even at a relatively high benzene inflow concentration of 1.3 g/L (Eke & Scholz, 2008). 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 FPRM were used. In another report by Bedessem *et al.*(Bedessem et al., 2007), an upward VF CW (equipped with subsurface aeration lines and operating with average inflow concentrations of 0.4 mg/L benzene, 1.4 mg/L total BTEX and 1.2 mg/L MTBE) reached a total mass removal in its 1st year of operation of about 80% for benzene and 88% for total BTEX, which is comparable with our results for benzene removal. However, Bedessem *et al*. (Bedessem et al., 2007) 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.

3.1.1 Comparison of HSSF CW and FPRM for the removal of benzene and 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 CWs during the summer months (Figure 3.1-2). The significant P values between depths, distances and treatments are given in Table 3.1-2. No significant differences were observed in benzene and MTBE concentrations between the depths in the FPRM 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 meter in the unplanted HSSF-CW.

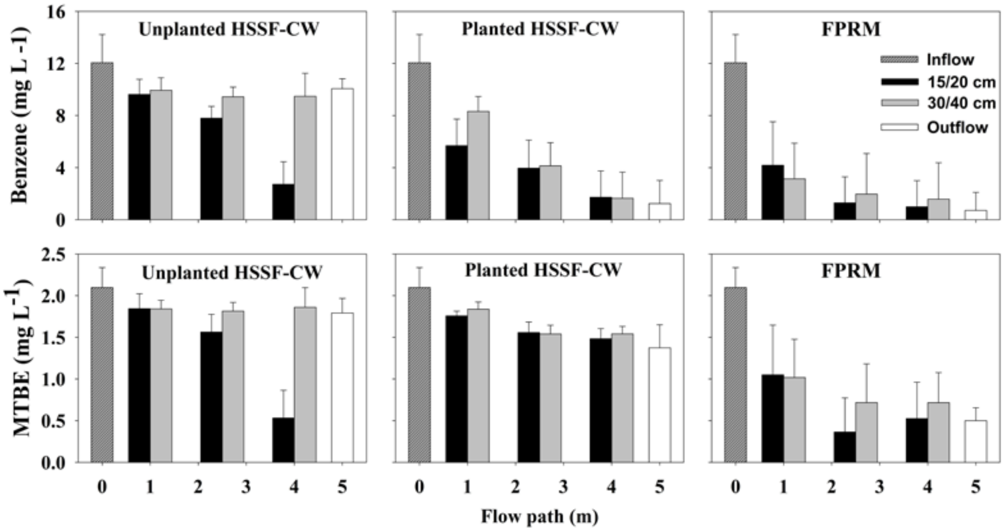

Figure 3.1-2. Measured concentrations of benzene and MTBE along the flow path and at two depths in the unplanted HSSF-CW, the planted HSSF-CW and the FPRM, during summer time (June−September 2010, n = 6)

Table 3.1-2 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: FPRM) during summer (June−September 2010; n = 6)

		Depths			Distances [a]			Treatments		
Benzene		A	B	C	A	B	C	A-B	A-C	B-C
	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**

a: Comparison of the concentration difference between 1m with inflow, 2.5 m with 1 m, 4 m with 2.5m, and outflow with 4 m.

3.1.1 Comparison of HSSF CW and FPRM for the removal of benzene and MTBE

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 meter and only up to 1 meter in the FPRM (Figure 3.1-2, Table 3.1-2). For the three treatment systems, significantly lower benzene concentrations were achieved in the planted HSSF-CW and FPRM compared to the unplanted HSSF-CW along the flow path (Table 3.1-2). Reasons for these observations might be that the plants enhance the microbial activity and phytovolatilization (Reiche et al., 2010); while the plant uptake of benzene and MTBE plays a minor role (Mothes et al., 2010). In general, the results indicate that in the FPRM, more favourable conditions for MTBE removal occurred compared to both HSSF-CWs along the flow path.

3.1.1.2. Volatilization

The volatilization rates of benzene and MTBE in the planted HSSF-CW and the FPRM are listed in Table 3.1-3. The results clearly demonstrate that the FPRM had higher volatilization 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 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 (Seeger et al., 2011a). Moreover, the different behavior of benzene and MTBE through plant uptake, translocation, metabolism, and phytovolatilization can also be possible factors for the difference of volatilization between MTBE and benzene. The physicochemical properties of MTBE and benzene indicate a different volatilization potential. The Henry’s law constants (which characterize the volatilization of a compound from the dissolved phase to the air) are 0.055 for MTBE and 0.22 for benzene, at 25 °C (Moyer & Kostecki, 2003), characterizing benzene as being more volatile than MTBE. However, it was found that greater volatilization fluxes are related to a higher vapour pressure (Burken & Schnoor, 1999). With a vapour pressure of MTBE (251 mm Hg) being around 3 times higher than that of benzene (86 mm Hg) (Moyer & Kostecki, 2003), phytovolatilization 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 (Collins et al., 2002), but MTBE was shown to be persistent against a degradation by plant cells (Trapp et al., 2003). All these findings are in accordance with our results indicating that a higher percentage of MTBE compared to benzene was removed by volatilization. The FPRM had a higher volatilization (both for benzene and MTBE) than the planted HSSF-CW in this study, and the volatilization in the FPRM 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 μg/m^3 for benzene and 0.5 and 28 μg/m^3 for MTBE (Reiche et al., 2010). The volatilization in the unplanted HSSF-CW was measured to be less than 0.5 mg/m^2/d for both benzene and MTBE (Reiche et al., 2010). The FPRM with a less developed unsaturated root zone in comparison to the HSSF-CWs with an unsaturated rooted soil zone, which hampers the direct volatilization, showed higher volatilization rates probably due to the direct volatilization of benzene and MTBE from the water to the atmosphere.

Table 3.1-3 Volatilization rates of benzene and MTBE in the planted HSSF-CW and the FPRM in early May 2010 (the values shown are emission rates (mg/m^2/d) along with the percentages of mass loss of the total pollutants in brackets)

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

3.1.1.3. 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 (Stottmeister et al., 2003). 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 (Haberl et al., 2003) and dissimilatory sulphate reduction (Stottmeister et al., 2003). Furthermore, the helophytes release oxygen from their roots into the rhizosphere (Armstrong & Armstrong, 1990), which increases the aerobic microbial degradation of organic matter, and nitrification (Brix, 1994). Meanwhile, the root exudates which contain various compounds might stimulate the activity of microbes (Faulwetter et al., 2009). Therefore, in the planted CWs 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 °C from June to September (Figure 3.1-1 and 3.1-3), the CW performance increased. The same effect was also observed in bench-scale VF 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 (Eke & Scholz, 2006). However, the results of a pilot and full scale SSF VF 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 mg/L (Wallace & Kadlec, 2005), 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 FPRM and the planted HSSF-CW) indicated a higher water loss than the unplanted HSSF-CW (Figure 3.1-3). At the same time, they allowed a better pollutant removal to be obtained. Since September, the water loss in the FPRM decreased markedly, as compared to the planted HSSF-CW, and the FPRM 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.

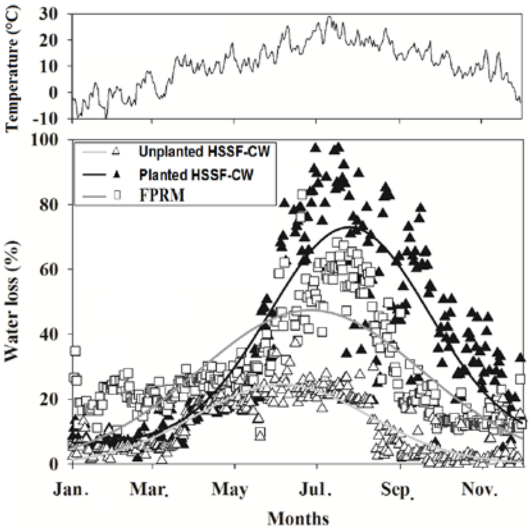

Figure 3.1-3. Air Temperature and evapotranspiration of the FPRM, the planted HSSF-CW and the unplanted HSSF-CW during the sampling period of the year 2010

3.1.1.4 Redox and electron acceptor conditions

Throughout the year, the redox potential inside of all the three pilot-scale CWs ranged between 50 - 125 mV; the pH values of the influent and the effluents were varied from 6.5 to

7.1. The concentration of Fe^{2+} was found to be between 2 - 4 mg/L with an inflow concentration of about 4 mg/L. With an inflow concentration of around 45 mg/L, the outflow NH_4^+ concentration decreased up to 50 - 100% in the FPRM and the planted HSSF-CW (in summer time), while no real decrease in the unplanted HSSF-CW has occurred (Figure 3.1-4). The inflow concentration of NO_3^- was 5.35 mg/L, and the outflow concentrations of NO_3^- in the FPRM, the unplanted and planted HSSF-CW amounted to 5.36, 4.18 and 4.53 mg/L, respectively. The inflowing concentration of NO_2^- and the outflow in all the three CWs was less than 0.1 mg/L. The redox potential and Fe^{2+} concentration data obtained show that all three systems were limited by oxygen (the oxygen concentration was less than 0.5 mg/L in May and less than 0.15 mg/L 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 CWs was limited by an insufficient oxygen input by the helophyte roots and the surface diffusion into their pore water.

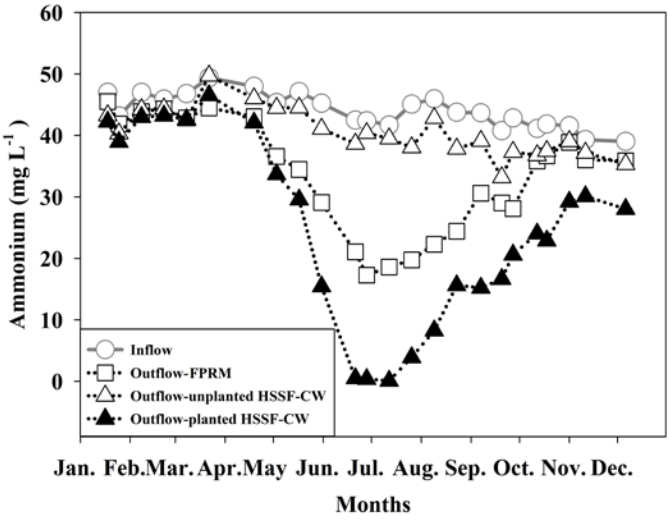

Figure 3.1-4. Outflow concentration of ammonium in three CWs (the FPRM, the planted HSSF-CW and the unplanted HSSF-CW)

3.1.1.5 Conclusions

The FPRM 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 FPRM as a variant of CWs without planting media could be a cost-competitive variant and an alternative for the treatment of distinctively contaminated waters, for example, for the contaminants benzene and MTBE; nevertheless further process optimization is especially necessary in this case to fulfill German national regulations for discharging into natural receiving streams. The removal was very dependent upon the season. Furthermore, the parameters such as the redox potential and the 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 FPRM 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 the conclusion that the main removal was realized via oxidative microbial degradation.

3.1.2 Removal of benzene and MTBE by FPRM: effect of water level and root mat age

This chapter gives the results of three FPRMs in Leuna (S11, S17 and S18) in 2010 and 2011, which are the three years old FPRM with a water level of 30 cm, one year old FPRM with a water level of 15 cm, and one year old FPRM with a water level 15 cm in 2010, and 40 cm in 2011.

3.1.2.1 Effect of water level

Treatment performance

The Figure 3.1-5 shows that both systems have the similar removal behavior for benzene and MTBE removal during the two years operation. However, better removal for both pollutants during the summer time was only found in the first year. This probably due to the effect of worms, which decreased the plant activity with water loss during summer period can reach 40% in 2010 but only 20% in 2011). The results also indicate that the water level had an insignificant influence on the removal of both pollutants (both P > 0.05).

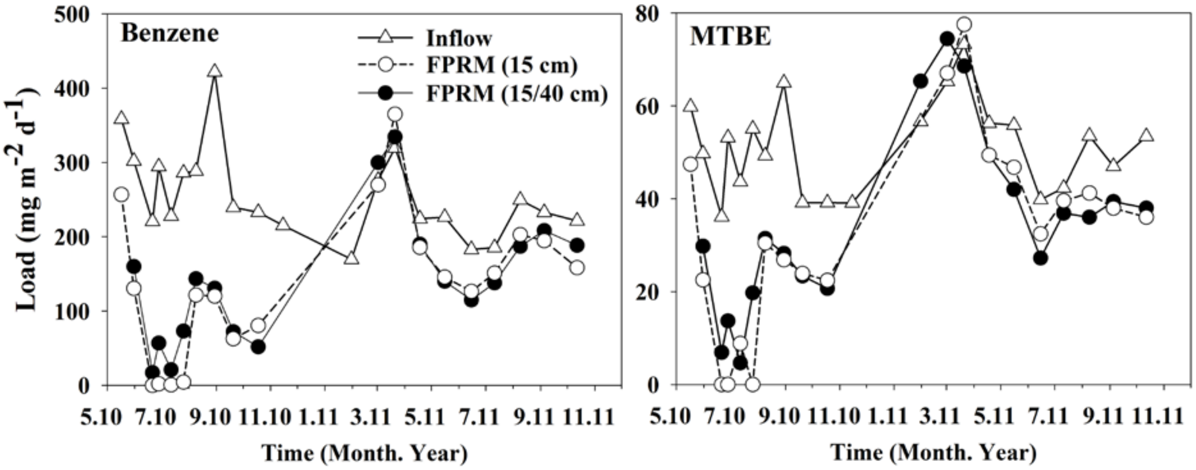

Fig 3.1-5 Inflow and outflow loads of benzene and MTBE in a floating plant root mat with water level of 15 cm, and a floating plant root mat with water level of 15 cm (2010) and 40 cm (2011)

Figure 3.1-6 shows a gradual load decrease of benzene and MTBE along the flow path in 2010 in both systems, while the removal of benzene and MTBE along the flow path in 2011 was less intense than in 2010. It also shows that there was no significant load difference between the different water levels for both benzene and MTBE (all P > 0.05,). In general, the removal efficiency of benzene was higher than that of MTBE (Figure 3.1-6).

3.1.2 Removal of benzene and MTBE by FPRM: effect of water level and root mat age

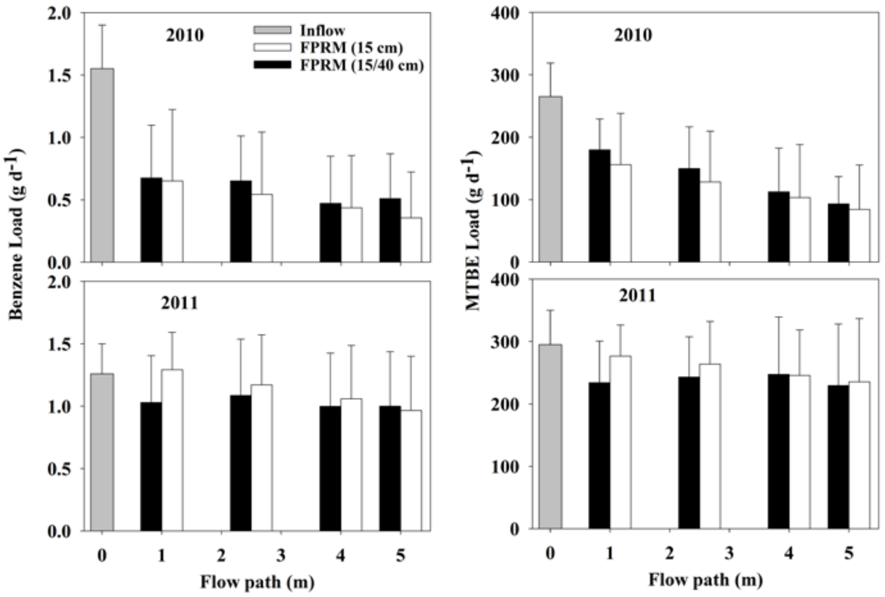

Figure 3.1-6 Loads of benzene and MTBE along the flow path in a floating plant root mats with water level of 15 cm, and a floating plant root mat with water level of 15 cm (2010) and 40 cm (2011), n = 9 in 2010, and n = 10 in 2011

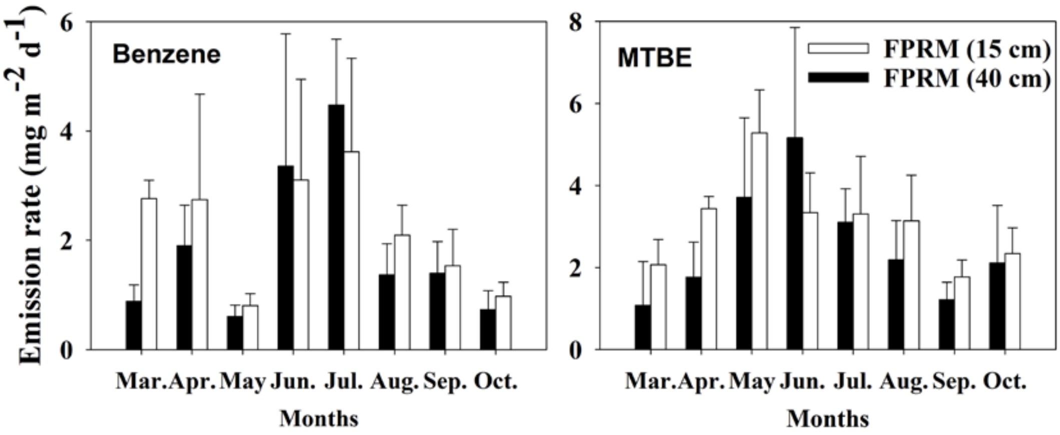

Figure 3.1-7 Emission rate of benzene and MTBE in two floating plant root mats with different water levels (15 and 40 cm) in 2011 (n = 4)

The emission rates of benzene and MTBE were less than 6 and 8 mg/m^2/d, respectively (Figure 3.1-7). This means less than 7% benzene was removed through volatilization (Figure 3.1-8). But the volatilization of MTBE reached up to 60% of the total removal (Figure 3.1-8). The results show that the volatilization potential decreased with the increase of water level. With the similar total removal of benzene and MTBE under different water levels (Figure 3.1-5), the lower volatilization percentage indicates the other pollutant removal processes. The most important process is probably the microbial degradation, as the root mat can be better developed with the increase of water level, which than can offer a higher specific surface area for the attached growth of microbes (biofilms).

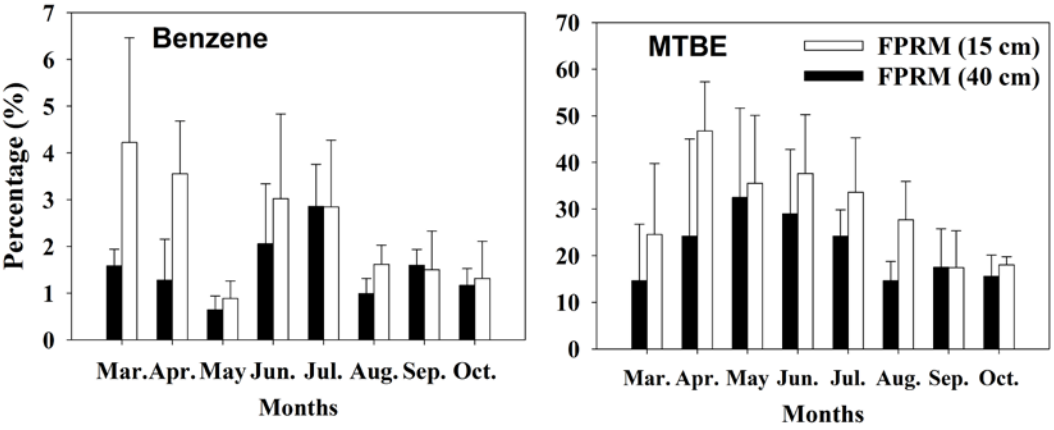

Figure 3.1-8 Percentage of volatilization on the total removal of benzene and MTBE in two floating plant root mats with different water levels (15 and 40 cm) in 2011

3.1.2.1 Effect of the root mat age

It was shown that the four years growth FPRM (water level of 30 cm) got lower outflow load of benzene and MTBE than the two years growth FPRM (water level of 15 cm and 40 cm) (Figure 3.1-9). However, there is no significant load difference of benzene and MTBE between the FPRM with a water level of 30 cm and the FPRM with a water level of 15 cm along the flow path (Table 3.1-4). The increase of treatment performance with the age of the FPRM can be expected by the better root mat development in the FPRM with a water level of 30 cm, where more surface area is supplied for the attachment of biofilms. At the same time, with the higher root density in FPRM with a water level of 30 cm, its porosity should be smaller than the porosity of the FPRM with a water level of 15 cm and the FPRM with a water level of 40 cm. But the hydraulic retention time will be higher than in the FPRM with a water level of 15 cm and lower than in the FPRM with a water level of 40 cm. Overall, the highest reaction time between pollutants and biofilms can be assumed in the FPRM with a water level of 30 cm. Thus, less residual loads were achieved in the FPRM with the water level of 30 cm. The emission rate and percentage of volatilization on total removal of benzene and MTBE are both lower in the old FPRM (water level of 30 cm) in comparison to the younger FPRM (water level of 15 cm) (Figure 3.1-10). This is an important indication that the biodegradation process was enhanced with the age of the root mat and it became the main removal process in the older FPRM.

3.1.2 Removal of benzene and MTBE by FPRM: effect of water level and root mat age

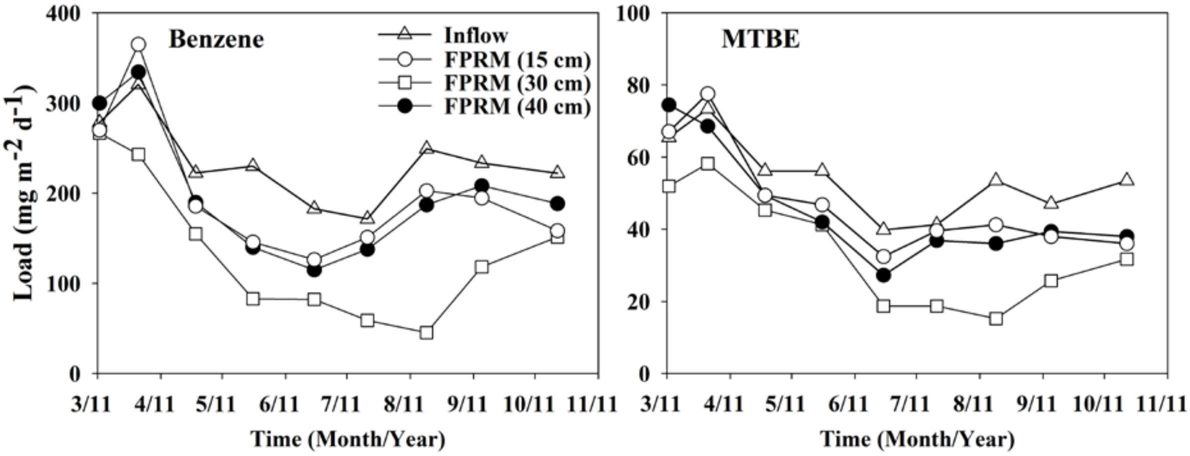

Figure 3.1-9 Inflow and outflow loads of benzene and MTBE in three floating plant room mats with different water levels in 2011

Table 3.1-4 T-test on the concentration difference of benzene and MTBE between depths (15 and 30 cm) in the four years old floating plant root mat with a water level of 30 cm, and load difference between two floating plant root mats (15 and 30 cm) in 2010.

Compounds	Flow path (m)	15 cm vs 30 cm FPRM (30 cm)	FPRM (30 cm) vs FPRM (15 cm)
MTBE	1	0.788	0.932
	2.5	0.060	0.346
	4	0.375	0.951
	5	-	0.912
Benzene	1	1.000	0.705
	2.5	**0.030**	0.120
	4	0.216	0.517
	5	-	0.340

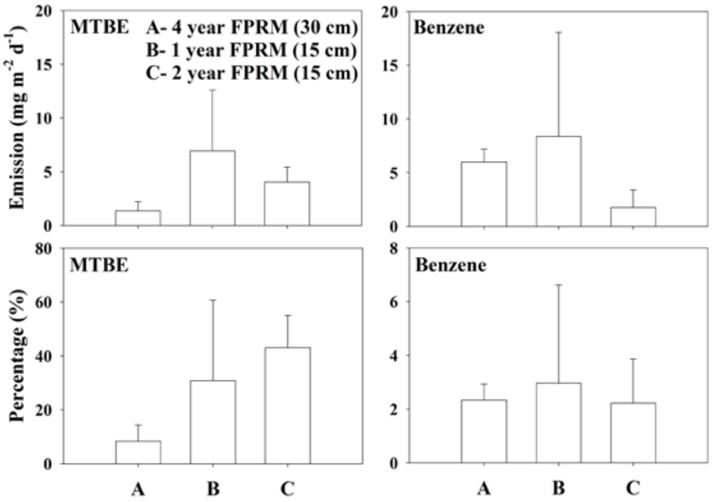

Figure 3.1-10. Volatilization rate and percentage of volatilization of the total removal of MTBE and benzene in different years old floating plant root mats

3.1.2.3 Conclusions

The water level and the root mat age are two important factors which influence the treatment performance of FPRM for benzene and MTBE removal. With increasing age of the root mats, a better root mat development was obtained, which in turn can offer a higher specific surface area for the attachment of the biofilms which therefore, enhances the treatment performance. With the increase of the water level, the total removal efficiency of benzene and MTBE was not significantly affected. Anyhow, the volatilization of benzene and MTBE was decreased with the increase of the water level, which confirmed the improvement of microbial degradation. This is also because of the better root mat development under the condition of the higher water level. Therefore, for better understanding of the treatment processes more research about the root mat development and the water level has to be done in the future.

3.2 Results on the treatment performance of groundwater contaminated by chlorinated hydrocarbons in different types of constructed wetlands

3.2.1 Comparison of HSSF CW and PRMF for the treatment of low-chlorinated benzenes

In this chapter, the results shown are the comparison between HSSF CW and PRMF for low-chlorinated benzenes in 2010. The HSSF CW was ran under two different flow regimes (1) continuous flow from the 11th May, 2010 to 20th July, 2010 and (2) 7 days cycle tidal flow from the 21st July, 2010 to 8th November, 2010.

3.2.1.1 Treatment performance of low-chlorinated benzenes

In general, the load of MCB, 1,2-DCB, 1,4-DCB, and 2-chlorotoluene decreased along the flow path in both the PRMF and the HSSF CW (Figure 3.2-1, Figure 3.2-2, Figure 3.2-3, and Figure 3.2-4). The removal performance of the four low chlorinated benzenes exhibited a similar behavior with 1 m from the inlet of the HSSF CW throughout the year, which means there was no obvious removal of all four organic pollutants within this flow distance (less than 10%, Table 3.2-1). However, a significant load decrease was observed for all four low chlorinated benzenes at 0.5 m from the inlet in the PRMF (all $P < 0.05$), and surprisingly the loads increased at 1 m from the inlet during May to July. The loads of the four organic pollutants gradually decreased along the flow path in the PRMF during August to November. MCB and 1,2-DCB showed a similar load decrease at 3 m and 4 m in both systems (Figure 3.2-1 and Figure 3.2-2), while 1,4-DCB and 2-chlorotoluene had shown a similar load decrease already at the beginning of 2 m in both systems (Figure 3.2-3 and Figure 3.2-4). The differences among the depths in the HSSF CW were recorded from 2 m onward, which means the upper layer (30 cm) exhibited a better removal than the middle (40 cm) and deeper (50 cm) layers along the flow path. However, the differences between 1,4-DCB and 2-chlorotoluene for the depths were less obvious than for MCB and 1,2-DCB.

It seems that the PRMF showed a seasonal dependence for removing MCB (Figure 3.2-5) and the other three low chlorinated benzenes (1,2-DCB, 1,4-DCB and 2-chlorotoluene; data are not shown), which means that a better removal was achieved during the summer months (especially during July and August). However, no clear seasonal dependence during May 11th to November 11th for all four low chlorinated benzenes was found in the HSSF CW (data for MCB see Figure 3.2-5). The PRMF exhibited an extremely high removal for the four organic pollutants within the first 0.5 m from the inlet of the flow path (Table 3.2-1). With the exception at the sampling point of 1 m, where a load increase (with a high standard deviation) during May to July could be observed, the contaminant loads decreased along the flow path after 1 m. This might be either due to the adsorption and/or flow inhomogeneities in the first adaptation phase of the new PRMF established by single mats of 0.5 m^2.

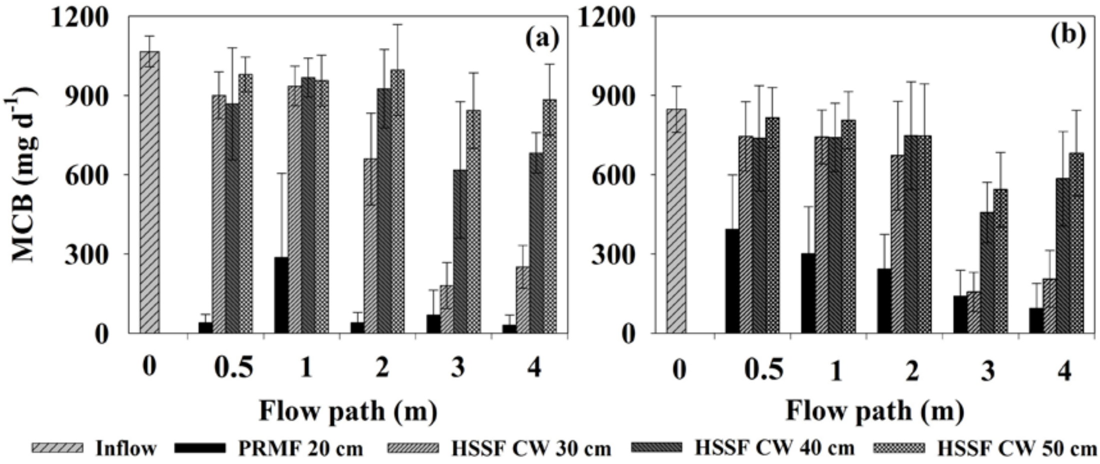

Figure 3.2-1 Loads of MCB (related to the flow distance and depth) in the PRMF and the HSSF CW, operating (a) in a continuous flow mode from May 11th to July 20th, and (b) a 7 days cycle tidal flow mode from August 3rd to November 8th; for each period *n* = 6

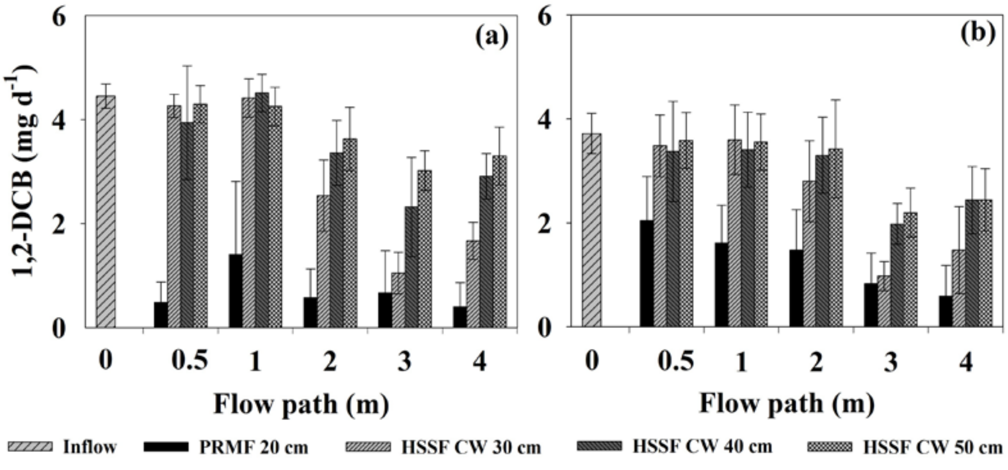

Figure 3.2-2 Loads of 1,2-DCB (related to the flow distance and depth) in the PRMF and the HSSF CW, operating (a) in a continuous flow mode from May 11th to July 20th, and (b) a 7 days cycle tidal flow mode from August 3rd to November 8th; for each period *n* = 6

The HSSF CW showed a less load decrease (< 18%) for all four low chlorinated benzenes within the first 1 m of the flow path in comparison to the PRMF. After a flow path of 3 m, the HSSF CW, like the PRMF, reached similar removal efficiencies for all the four organic pollutants at a depth of 30 cm. Moreover, the mean removal efficiency of all four low chlorinated benzenes did not change significantly (all P > 0.05) after the change in the mode of the HSSF CW to the 7 days cycle tidal flow procedure.

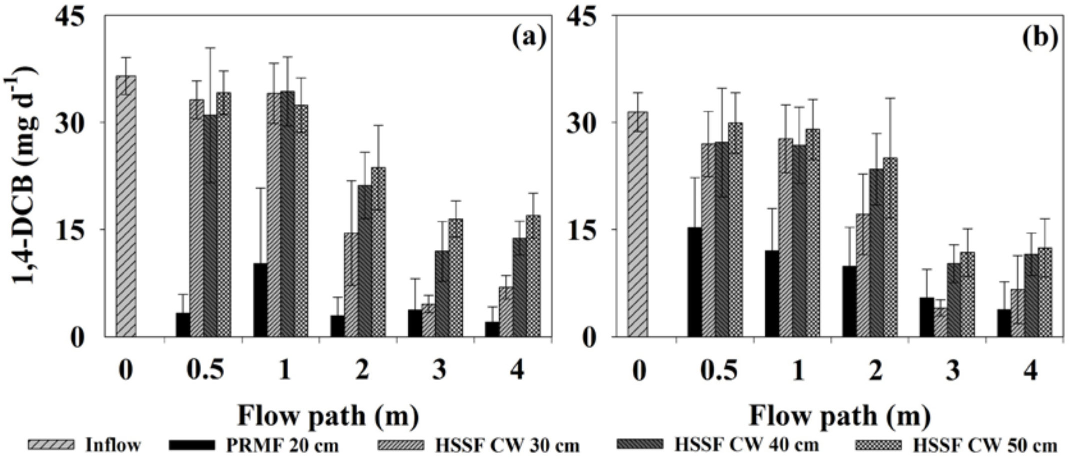

Figure 3.2-3 Loads of 1,4-DCB (related to the flow distance and depth) in the PRMF and the HSSF CW, operating (a) in a continuous flow mode from May 11th to July 20th, and (b) a 7 days cycle tidal flow mode from August 3rd to November 8th; for each period *n* = 6

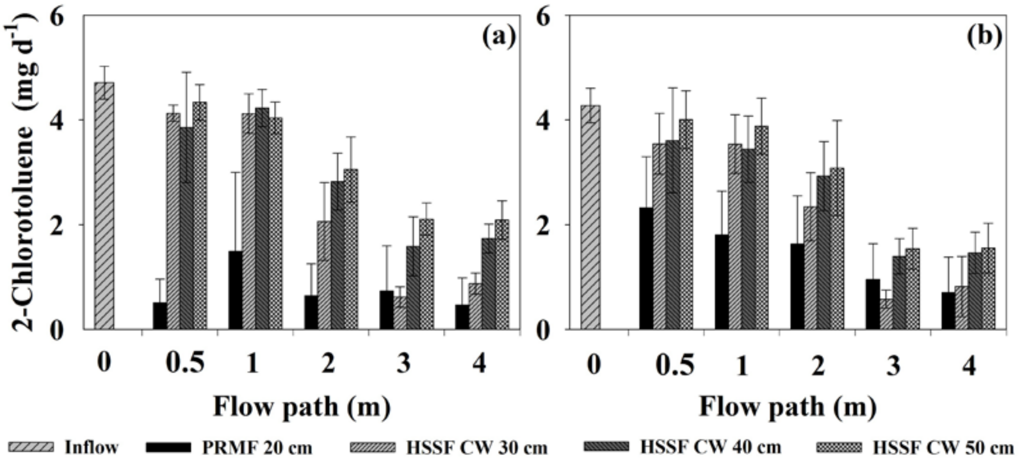

Figure 3.2-4 Loads of 2-chlorotoluene (related to the flow distance and depth) in the PRMF and the HSSF CW, operating (a) in a continuous flow mode from May 11th to July 20th, and (b) a 7 days cycle tidal flow mode from August 3rd to November 8th; for each period *n* = 6

In general, the PRMF showed a significantly higher removal efficiency of all four low chlorinated benzenes than the HSSF CW at every point along the flow path (Table 3.2-1), except at 3 m with a depth of 30 cm (p = 0.263, 0.803, and 1, for MCB, 1,2-DCB, and 1,4-DCB, respectively), and 2-chlorotoluene at 3 m with depths of 30 cm and 40 cm (p = 0.184 and 0.068, respectively), and 4 m with a depth of 30 cm (p = 0.507).

3.2.1 Comparison of HSSF CW and PRMF for the treatment of low-chlorinated benzenes

Table 3.2-1 Mean load removal efficiency along the flow path in the PRMF (n=12) and in the HSSF CW operating in a continuous flow mode from May 11th to July 20th, and a 7 days cycle tidal flow mode from August 3rd to November 8th (in brackets); for each period *n* = 6

Flow path	Depth	MCB	1.2 DCB	1.4 DCB	2-Chlorotoluen
0. 5 m	PRMF 20 cm	70%	61%	66%	62%
	30 cm	15% (12%)	8% (7%)	12% (14%)	17% (17%)
	40 cm	12% (14%)	5% (11%)	8% (10%)	13% (12%)
	50 cm	6% (4%)	1% (4%)	0% (7%)	7% (7%)
1 m	PRMF 20 cm	68%	59%	65%	60%
	30 cm	6% (13%)	-3% (4%)	1% (12%)	10% (17%)
	40 cm	10% (13%)	0% (9%)	5% (12%)	12% (20%)
	50 cm	6% (5%)	-1% (5%)	3% (10%)	10% (9%)
2 m	PRMF 20 cm	83%	71%	79%	71%
	30 cm	34% (22%)	41% (25%)	59% (46%)	55% (46%)
	40 cm	8% (13%)	22% (12%)	40% (23%)	38% (32%)
	50 cm	2% (13%)	16% (9%)	26% (28%)	32% (28%)
3 m	PRMF 20 cm	88%	79%	85%	79%
	30 cm	85% (82%)	80% (74%)	88% (87%)	88% (87%)
	40 cm	41% (46%)	46% (47%)	66% (60%)	65% (67%)
	50 cm	24% (35%)	32% (41%)	57% (59%)	55% (64%)
4 m	PRMF 20 cm	90%	83%	88%	83%
	30 cm	80% (76%)	66% (61%)	83% (79%)	83% (81%)
	40 cm	42% (32%)	39% (35%)	65% (53%)	65% (66%)
	50 cm	22% (20%)	30% (34%)	58% (58%)	58% (64%)

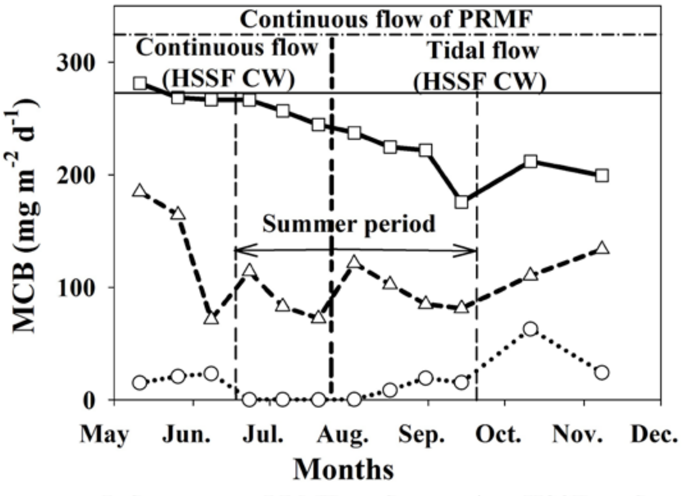

Figure 3.2-5 MCB loads of the inflow and at 4 m in the PRMF and the HSSF CW (operating in a continuous flow mode and 7 days cycle tidal flow mode, respectively) in correlation to the time (from May 11th to November 8th, 2010)

It seems that the age-related adaptation and the nutrient supply (addition of ammonium since 2008) to the CWs with slow growing microorganisms, which can degrade recalcitrant compounds is of importance for their removal efficiency. Hence, a higher removal efficiency was reached in this study in both systems compared to a previous study of the same HSSF CW from November 2004 and October 2005 (Braeckevelt et al., 2011a). While in this study the load removal efficiency with similar inflow loads for MCB, 1,4-DCB, and 1,2-DCB reached up to 90%, 88% and 83% in the PRMF and up to 85%, 88% and 80% in the HSSF CW, in the previous study (period of November 2004 and October 2005) the maximum load removal efficiency was only 65% for MCB, 69% for 1,4-DCB and 42% for 1,2-DCB in the HSSF CW (Braeckevelt et al., 2011a). Furthermore, our results demonstrated that the PRMF also efficiently removed 1,4-DCB at a relatively high inflow concentration (290 µg/L) compared to a full-scale CW with an inflow concentration of 0.74 µg/L (Keefe et al., 2004). However, this full-scale CW obtained a removal efficiency of 63 – 83% for 1,4-DCB (based on concentrations) after running for five years with a surface area of around 1.0×10^4 m^2 (Keefe et al., 2004). 1,2-DCB was not removed both in the planted HSSF CW and the unplanted HSSF CW in a previous investigation (Braeckevelt et al., 2008). However, in our study, the load removal efficiency of 1,2-DCB obtained in the PRMF and the HSSF CW accounted 83% and 80%. This indicates that 1,2-DCB can be removed in the HSSF CW after several years of adaptation and manifestation of the appropriate microorganisms. Furthermore, this is also a proof that the PRMF could remove 1,2-DCB faster than the HSSF CW, as no adaptation phase was needed.

Seasonal variations in the treatment performance of the CWs are affected by many parameters such as temperature, rain, evapotranspiration, as well as inlet concentration (Kadlec & Reddy, 2001). Among these factors, temperature seems to be the most important parameter to influence the treatment performance by especially affecting the microbial degradation. Both systems (the PRMF and the HSSF CW) showed a slightly better removal of the organic pollutants during the summer time compared to spring and autumn. The pore water of the PRMF had a slightly (about 1 - 2 °C) higher temperature in summer and lower temperature in spring and autumn than the HSSF CW (data not shown); however, there was no significant difference ($P > 0.05$). It seems that sulphide formation was also particularly influenced in the PRMF by the season (Figure 3.2-8), which in turn could also influence the activities of the aerobic bacteria.

Volatilization of MCB from the surface of the HSSF CW accounted for less than 4% of the total amount removed (Braeckevelt et al., 2011a). The Henry’s law coefficients for MCB, 1,2-DCB, and 1,4-DCB are 0.00356, 0.0012, and 0.0015 atm m^3/mol, respectively, at 20 °C (USEPA, 2002). This means that 1,2-DCB and 1,4-DCB are less volatile than MCB, which indicates less contribution of volatilization for 1,2-DCB and 1,4-DCB removal in the HSSF CW. However, the volatilization of MCB and 1,4-DCB in a surface flow wetland reached up to 68% and 66%; the volatilization loss of benzene and MTBE was also measured in this surface flow wetland with percentages of 31% and 40%, respectively (Keefe et al., 2004). In the PRMF, the water with a level of 20 cm flowed through the existing three year-old pre-grown root mats with a height of about 30 cm and did not directly reach the top of the mat in this way. Therefore, the volatilization should be lower than in the surface-flow CWs. On the other hand, the PRMF to treat waters contaminated with benzene and MTBE in Leuna found that the mass loss from volatilization was less than 3% for benzene and 15.2% for MTBE, which was slightly higher than in a HSSF CW (1.1% for benzene and 6.1% for MTBE), operated in a parallel way. Thus, we assume that the volatilization for MCB, 1,2-DCB and 1,4-DCB in the PRMF did not contribute in any major aspect to the total removal.

3.2.1.2 Redox conditions and sulphide concentration

The redox potential of the pore water decreased along the flow path in both systems (Figure 3.2-6). The mean redox potential values of the pore water in the PRMF were above zero before 3 m from the inlet, with −5 mV at 4 m. However, in the HSSF CW the mean redox potential values of pore water were below zero in the different depths along the flow path, except in the upper layer (30 cm) at 0.5 m (22 mV). The change of the operation mode (from continuous flow to tidal flow) obviously had a little influence on the general redox pattern. A bigger variation in the redox potential was observed in the PRMF in comparison to the HSSF CW; a lower redox potential was reached during the summer period (data not shown), which correlated with the high sulphide concentrations during this period (see Figure 3.2-8).

The oxygen concentration in the pore water shown for two one-day examples was higher in the PRMF than in the HSSF CW (Figure 3.2-7). On the 26th May 2010, the oxygen concentration in the pore water reached 0.23 mg/L in the upper layer (30 cm) of the HSSF CW at 0.5 m from the inlet, when it was operated in continuous mode. At the same time, in the PRMF, the oxygen concentration in the pore water reached 2.01 mg/L at 0.5 m from the inlet. The oxygen concentration decreased along the flow path from 2.01 mg/L at 0.5 m to 0.16 mg/L at 4 m from the inlet in the PRMF, but was still higher than in the HSSF CW. On the 31st August 2010, when the HSSF CW was operated in a tidal flow mode, the maximum oxygen concentration in the pore water increased up to 0.94 mg/L in the upper layer (30 cm) at 0.5 m from the inlet. In the PRMF, the oxygen concentration in the pore water was relatively low at 1 and 2 m in August (0.74 and 0.37 mg/L), compared to the values measured in May (0.10 and 0.12 mg/L). However, a much higher oxygen concentration was detected at 3 and 4 m in August (1.82 and 1.78 mg/L) than at the same point in May (0.2 and 0.16 mg/L).

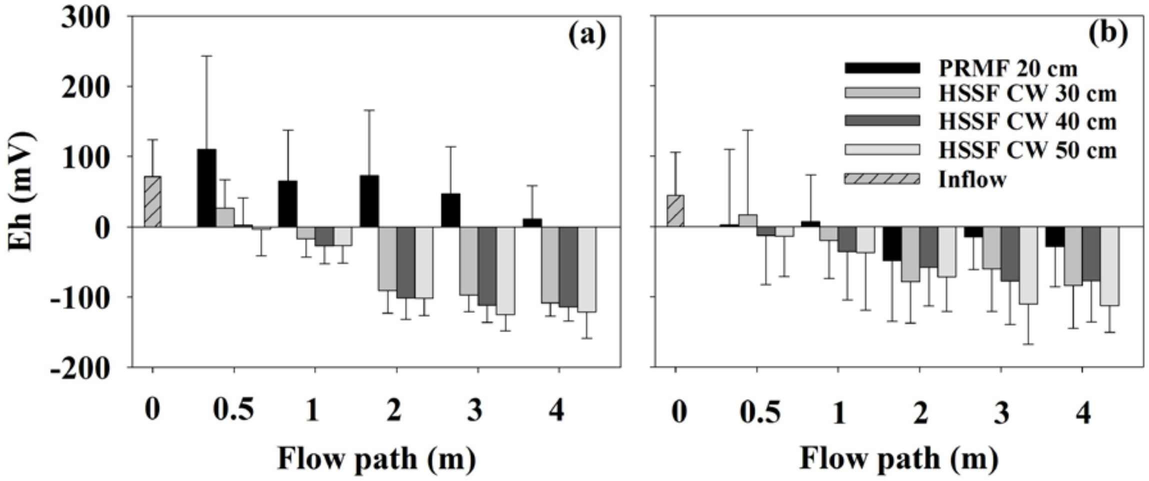

Figure 3.2-6 Redox potential in the pore water along the flow path in the PRMF and in the different depths in the HSSF CW, operating (a) in a continuous flow mode from May 11th to July 20th, and (b) a 7 days cycle tidal flow mode from August 3rd to November 8th; for each period *n* = 6

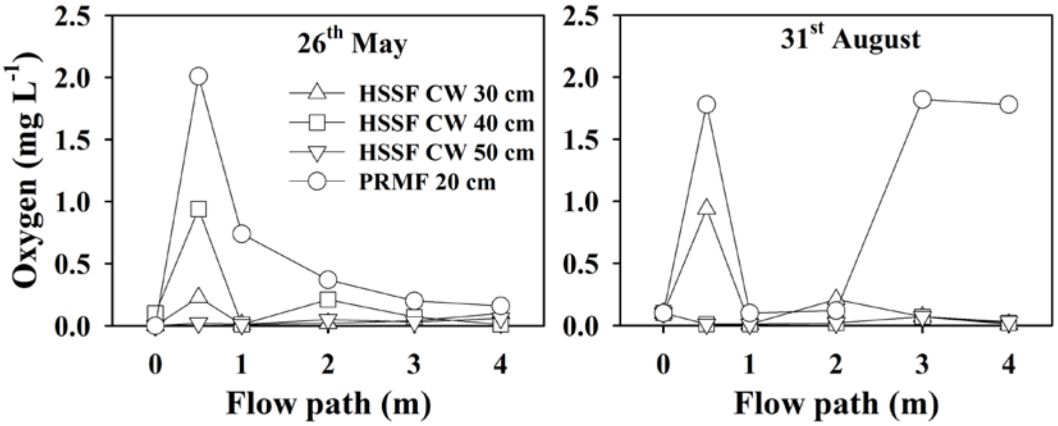

Figure 3.2-7 Measured concentrations of oxygen in the pore water along the flow path and in the PRMF and in different depths in the HSSF CW (operating in a continuous flow mode on May 26th and a 7 days cycle tidal flow mode on August 31st, 2010)

The concentrations of sulphide indicated that sulphate reduction had occurred in both systems simultaneously (Figure 3.2-8). The sulphide concentration was measured in the HSSF CW during the whole period and reached up to 21 mg/L. In the PRMF, sulphide was measured from July, where a concentration of up to 39 mg/L was obtained. Due to the drastic seasonal changes of all four pollutants at 0.5 m from the inlet in the PRMF, Figure 3.2-9 provides a hint to the relationship between MCB removal and different potential impact factors (temperature and sulphide). It shows that MCB removal started to decrease after sulphide concentration had increased. This might be due to the reason that sulphide had a negative effect on MCB removal. It seems that the temperature also had an impact, as the MCB load started to increase when the temperature started to decrease from September.

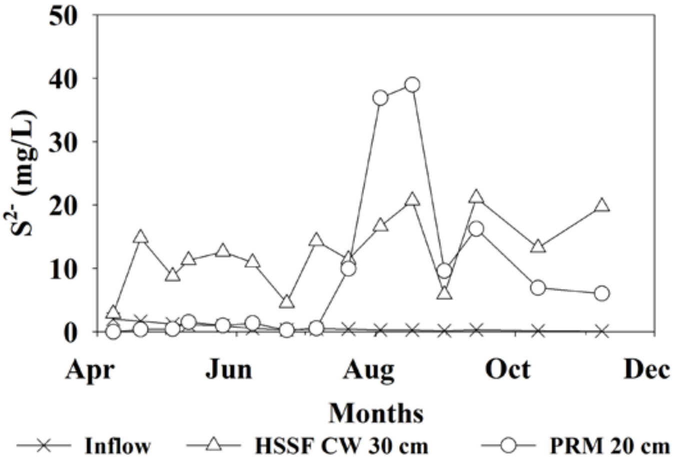

Figure 3.2-8 Measured sulphide concentration in the HSSF CW and the PRMF at 4 m during the investigation period (from May 11th to November 8th, 2010)

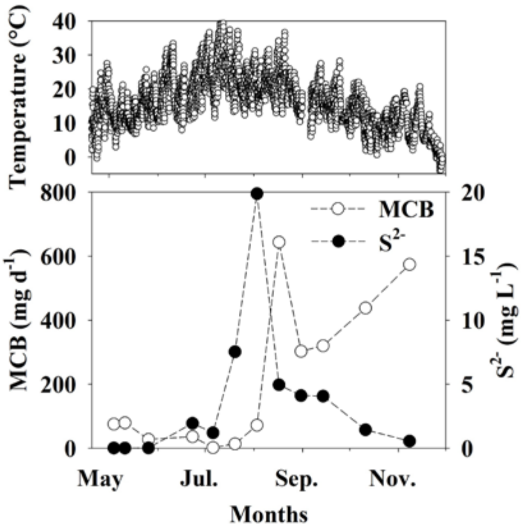

Figure 3.2-9 Air temperatures, MCB load and sulphide concentrations at 0.5 m from the inlet in the PRMF during the investigation period (from May 11th to November 8th, 2010)

The oxygen concentration and redox potential measured in the pore water of the PRMF was higher than the respective values obtained in the HSSF CW. This indicates that the release of oxygen from the roots could stimulate the oxygen consuming reactions within the root mat and the oxygen release from the root mats was higher than in the HSSF CW. A higher oxygen concentration and redox potential was also observed in a floating treatment wetland compared to an open water control system, treating domestic wastewater (Van de Moortel et al., 2010). However, the 7 days cycle tidal flow procedure in the HSSF CW only slightly increased the oxygen concentration in the first half meter of the flow path, and did not improve the removal efficiency of the chlorinated benzenes. Therefore, probably a higher frequency of the tidal flow regime is needed to achieve more oxic conditions which are needed for the aerobic degradation of chlorinated benzenes.

Chlorinated benzenes with four or less chlorine groups are susceptible to the oxidation by aerobic bacteria (Field & Sierra-Alvarez, 2008). The quick concentration decrease of the chlorinated benzenes in the PRMF could be due to the aerobic oxidations in the first half meter from the inlet. A higher removal efficiency for the low-chlorinated benzenes was achieved in the upper zone of the HSSF CW, where the oxygen concentration and redox potential was higher than in the lower zone, which also indicates that aerobic degradation is the dominant removal process for low-chlorinated benzenes. As a result the removal capacity decreased with a decrease in oxygen concentration along the flow path in the PRMF.

3.2.1.3 Conclusions

In conclusion, the PRMF showed a higher potential for the removal of low-chlorinated benzenes (MCB, 1,2-DCB, 1,4-DCB, and 2-chlorotoluene) than the HSSF CW. It seems that the PRMF enables a better oxygen input than the HSSF CW. This could be of interest for the treatment of other types of wastewater, especially those with pollutants which prefer aerobic degradation pathways. Nevertheless, high sulphide concentrations, in particular during the summer months, were also observed and have to be considered. In general, due to no need of a special media with defined porosity, the PRMF could be a cost competitive technology for the HSSF CW, but still long-term observations should be carried out.

The tidal flow procedure (with a cycle period of 7 days) in the HSSF CW was not able to remove the low-chlorinated benzenes more efficiently than the HSSF CW, operating in a continuous flow mode. To enhance the treatment efficiency of low-chlorinated benzenes, a higher frequency of the tidal flow regime is probably needed to achieve more oxic conditions. Whether such a tidal flow procedure could also be an option for improving the treatment efficiency of the PRMF has to be investigated further. The HSSF CW and the tested PRMF provide appropriate habitats for dissimilatory sulphate-reducing bacteria. In the case of high sulphate concentrations and even of low organic carbon load of the wastewater, the organic carbon input by the plant roots can cause high sulphide concentrations which are toxic to the aerobic microorganisms.

3.2.2 Comparison of HSSF CW and PRMF for the treatment of high-chlorinated ethenes

In this chapter, the results shown are the comparison between HSSF CW and PRMF for high-chlorinated ethenes in 2010. The HSSF CW was run under two different flow regimes (1) continuous flow during 11th May 2010 to 20th July 2010 and (2) 7 days cycle tidal flow from 21st July 2010 to 8th November 2010.

3.2.2.1 Performance of PCE removal in the PRMF and the HSSF CW

PCE was removed completely after a flow path of 4 m during the recorded period in the HSSF CW (Figure 3.2-10). However, a similar PCE removal performance was only reached during the summer period (21st June to 21st September) in the PRMF (Figure 3.2-10). This could be due to the temperature effect on the microbial activity, as the soil free PRMF seems to be more sensitive to temperature changes than the media based HSSF CW (date not shown, around 1°C higher in the PRMF during summer, and 1°C lower in the PRMF during winter). On the other hand, as the plant activity was stable during the summer period (represented by water loss, Figure 3.2-11); it can be assumed that during this period plants release more organic carbon (rhizodeposition products) than during the colder seasons which is needed for the anaerobic dechlorination process.

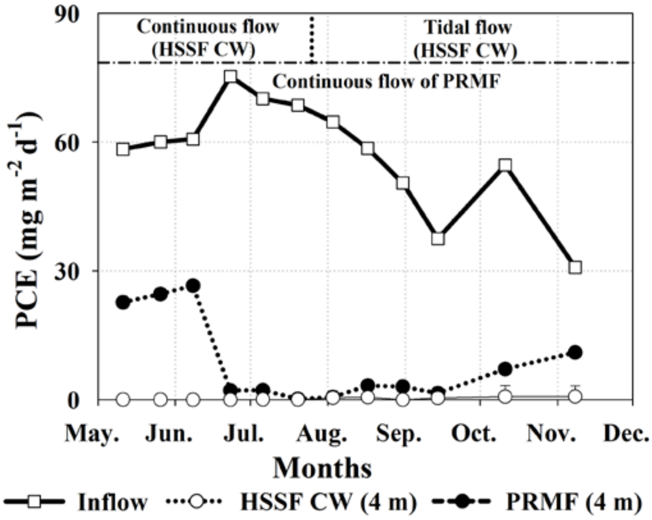

Figure 3.2-10 Mean loads of PCE in inflow and at 4 m in the PRMF and the HSSF CW (with continuous flow n=3, and 7 days cycle tidal flow n=15) in correlation to the time (May 11th to November 8th, 2010)

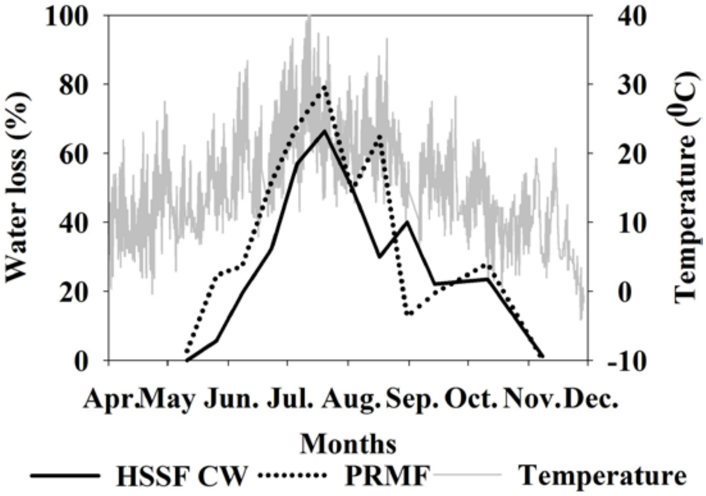

Figure 3.2-11 Air temperature and water loss in the PRMF and the HSSF CW during the investigation period (April-November, 2010)

Significant differences of the PCE load along the flow path was found between the HSSF CW and the PRMF (Table 3.2-2), which means lower residual PCE load was found in the HSSF CW in comparison to the PRMF (Figure 3.2-12 and Figure 3.2-13). The HSSF CW showed robust PCE removal capacity, as all PCE was removed after 0.5 m from the inlet in the HSSF CW (Figure 3.2-12 and Figure 3.2-13). The PCE load decreased gradually along the flow path in the PRMF (Figure 3.2-12 and Figure 3.2-13). These observations can be explained by the lower redox potential and the lower oxygen concentration (data not shown) in the pore water of the HSSF CW in comparison to the PRMF (Figure 3.2-14). In principal, the optimal range for anaerobic PCE dechlorination is between -220 mV to -50 mV (Bouwer, 1994). The redox potential in the HSSF CW was within this range, while the redox potential in the PRMF was between -80 mV to 250 mV (Figure 3.2-14). The redox potential decreased along the flow path in both systems (Figure 3.2-14). Previous results showed that PCE was also removed after 2 m flow path after the first addition of PCE in the HSSF CW within few weeks (Braeckevelt et al., 2011b). However, the PRMF did not remove all PCE after a flow path of 4 m (with the exception during summer) even after nine months of operation.

The difference of PCE concentration in three depths in the HSSF CW was only found at 0.5 m between the 30 cm with 50 cm and 40 cm with 50 cm (Table 3.2-2). The tidal flow mode (7 days cycle) in the HSSF CW in the later summer season had insignificant influence on the PCE removal (Table 3.2-2). The mean redox value was a bit higher than before, but with even a higher standard deviation (Figure 3.2-14), which can be explained by the oxygen input during the outflow flushing.

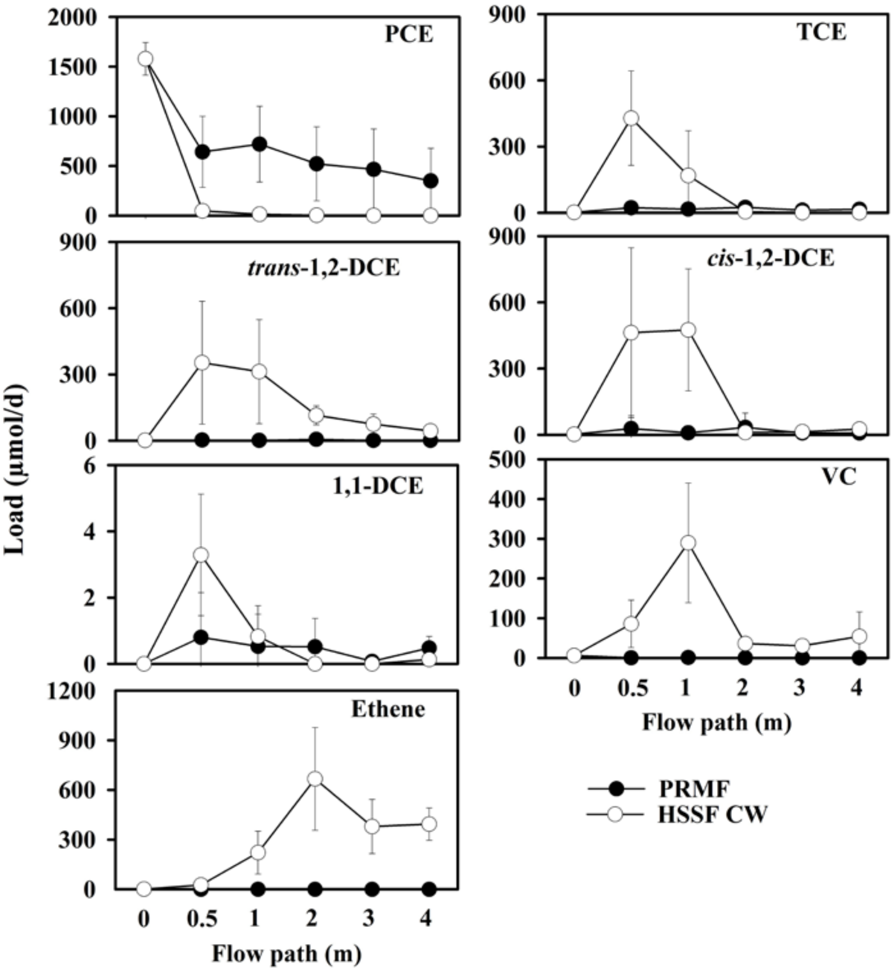

Figure 3.2-12 Loads of PCE and its metabolites along the flow path in the PRMF and the HSSF CW (mean concentration of three depths) run with continuous flow (May 11th to July 20th, 2010).

3.2.2.2 PCE metabolites in the PRMF and the HSSF CW

All PCE dechlorination metabolites were detected in the HSSF CW (Figure 3.2-12), while only some of them were found in the PRMF (Figure 3.2-13). The HSSF CW showed a significant higher accumulation of TCE and *cis*-1,2-DCE than in the PRMF within 1 m from the inlet, also a significant higher accumulation of *trans*-1,2-DCE, VC and ethene in the HSSF CW than in the PFRMF were found (Figure 3.2-12, Table 3.2-2). Only trace amounts of TCE and 1,1-DCE were detected in the PRMF before July (Figure 3.2-12), while more TCE and *cis*-1,2-DCE was detected after August in the PRMF (Figure 3.2-13). Significantly more TCE and *cis*-1,2-DCE were detected in the PRMF than in the HSSF CW after 2 m from the inlet since August (Figure 3.2-13). This indicates that the dechlorination process intensified in the PRMF by time.

3.2.2 Comparison of HSSF CW and PRMF for the treatment of high-chlorinated ethenes

Table 3.2-2 Mann-Whitney Rank Sum Test of concentration differences in three depths in the HSSF CW and load differences between the PRMF (20 cm) and the HSSF CW (mean of three depths) along the flow path, *n*=6

Compounds	Flow path (m)	continuous flow in HSSF CW				7 days cycle tidal flow in HSSF			
		30 cm vs 40 cm	30 cm vs 50 cm	40 cm vs 50 cm	PRMF vs HSSF	30 cm vs 40 cm	30 cm vs 50 cm	40 cm vs 50 cm	PRMF vs HSSF
PCE	0.5	0.394	**0.009**	**0.041**	**0.002**	0.180	**0.026**	**0.041**	**0.002**
	1	0.589	0.699	0.485	**0.002**	0.589	0.818	0.180	**0.002**
	2	0.093	0.132	0.937	**0.002**	0.394	1.000	0.394	**0.002**
	3	0.394	0.310	0.937	**0.002**	1.000	1.000	1.000	**0.002**
	4	1.000	0.589	0.310	**0.002**	1.000	1.000	1.000	**0.002**
TCE	0.5	0.937	0.699	0.937	**0.002**	0.310	0.132	0.093	**0.041**
	1	0.937	0.180	0.485	**0.041**	0.699	**0.015**	**0.026**	**0.015**
	2	0.093	**0.041**	0.180	0.065	0.310	0.818	0.589	**0.002**
	3	0.589	0.699	0.818	**0.004**	0.699	0.699	0.937	**0.002**
	4	0.699	0.937	0.589	**0.002**	0.699	0.818	0.937	**0.002**
cis-1,2-DCE	0.5	1.000	0.699	0.937	**0.004**	0.041	0.132	0.240	**0.002**
	1	0.818	0.589	1.000	**0.002**	**0.009**	**0.002**	**0.004**	**0.002**
	2	0.394	0.394	1.000	0.699	0.589	0.310	0.818	**0.002**
	3	0.937	0.937	1.000	0.310	0.699	0.485	0.240	**0.002**
	4	0.589	0.485	0.818	0.310	0.132	0.818	0.132	**0.002**
trans-1,2-DCE	0.5	0.310	**0.041**	0.180	**0.002**	0.485	**0.004**	0.132	**0.002**
	1	0.699	0.699	0.818	**0.002**	0.937	0.699	0.485	**0.002**
	2	0.026	0.093	0.310	**0.002**	0.394	0.310	0.937	**0.002**
	3	0.180	**0.004**	0.132	**0.002**	0.004	**0.004**	0.394	**0.002**
	4	**0.026**	**0.015**	0.310	**0.002**	0.065	0.065	0.093	**0.002**
1,1-DCE	0.5	0.818	0.818	0.818	**0.041**	0.240	**0.015**	0.394	**0.015**
	1	0.699	0.589	0.485	0.485	0.394	0.065	0.132	0.699
	2	1.000	1.000	1.000	0.394	1.000	1.000	1.000	0.394
	3	1.000	1.000	1.000	0.699	1.000	1.000	1.000	1.000
	4	0.699	0.937	0.818	0.065	1.000	1.000	1.000	0.180
VC	0.5	0.394	**0.026**	0.132	**0.002**	0.132	**0.026**	0.093	**0.002**
	1	0.699	**0.041**	0.240	**0.002**	0.589	**0.002**	**0.002**	**0.002**
	2	0.818	0.937	0.485	**0.002**	1.000	1.000	0.937	**0.009**
	3	**0.026**	**0.026**	0.818	**0.002**	0.394	0.132	1.000	**0.002**
	4	0.132	0.240	0.589	**0.002**	0.310	0.065	0.699	**0.002**
Ethene	0.5	0.394	**0.026**	**0.041**	**0.002**	**0.026**	**0.002**	0.240	**0.002**
	1	0.699	**0.041**	0.132	**0.002**	**0.015**	**0.002**	**0.002**	**0.002**
	2	0.589	0.589	0.937	**0.002**	0.485	0.485	1.000	**0.002**
	3	0.093	**0.041**	1.000	**0.002**	**0.002**	**0.002**	0.394	**0.002**
	4	0.065	0.093	0.818	**0.002**	**0.041**	0.065	0.699	**0.002**

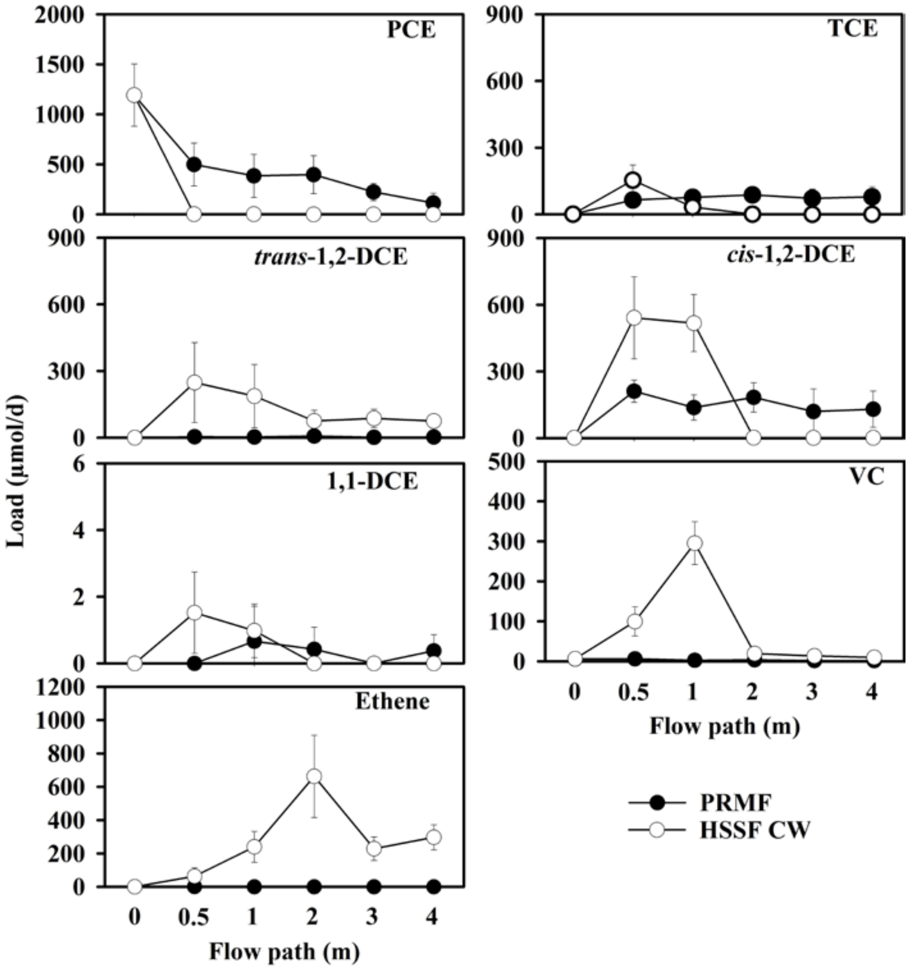

Figure 3.2-13 Loads of PCE and its metabolites along the flow path in the PRMF and the HSSF CW (mean concentration of three depths) run with 7 days cycle tidal flow (July 21st to November 8th, 2010)

At the same time, the lower redox potential in the PRMF (Figure 3.2-14) also gives a hint that this condition was more suitable for dechlorination. The characterization of PCE's metabolites behavior in the PRMF is similar to that of the HSSF CW when PCE was first added (Braeckevelt et al., 2011b), which means that the dechlorination process intensified with time. The accumulation of VC and ethene was found in the HSSF CW after one year operation (Braeckevelt et al., 2011b), therefore, there is a requirement for the long term investigation of metabolite removal processes in PRMF systems.

The 7 days tidal cycle operation in the HSSF CW influenced the TCE accumulation before 1 m (Figure 3.2-12 and Figure 3.2-13), which means less TCE was accumulated at 0.5 m under tidal flow compared to continuous flow. The tidal operation also decreased the accumulation of *trans*-1,2-DCE and 1,1-DCE at 0.5 m in the HSSF CW (Figure 3.2-12 and Figure 3.2-13).

These observations could be explained by the increased oxygen input during tidal operation at 0.5 m in the HSSF CW. Therefore, oxidation processes can be assumed for the removal of TCE, *trans*-1,2-DCE and 1,1-DCE under tidal flow operation. Anyhow, the redox potential in the HSSF CW shows that oxygen was still limited even after the change to tidal operation (Figure 3.2-14).

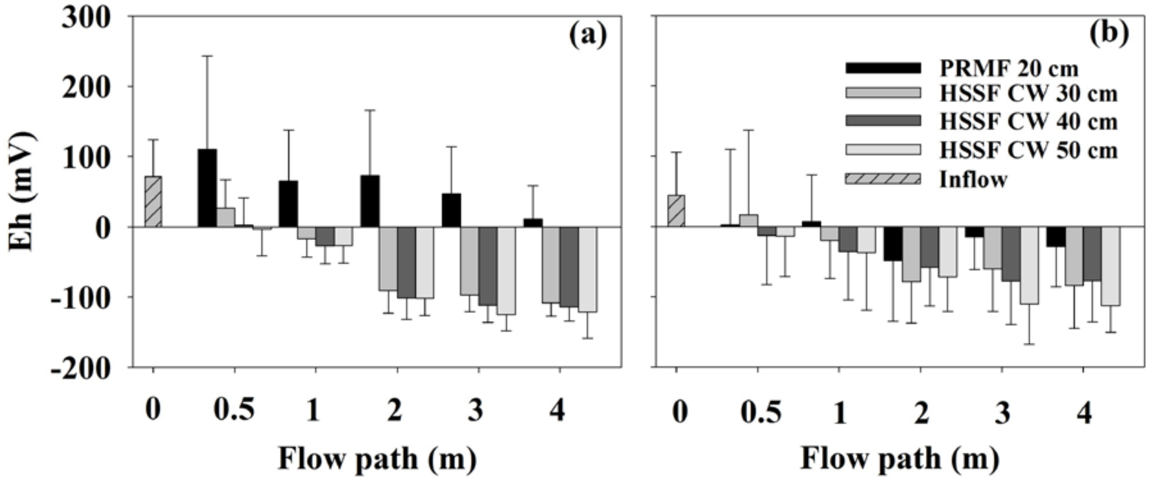

Figure 3.2-14 Redox potential in the pore water along the flow path in the PRMF and in the different depths in the HSSF CW; (a) May 11th – July 20th, continuous flow in the HSSF CW and (b) August 3rd – November 8th, 7 days cycle tidal flow; for each period *n*=6

Volatilization could be a potential removal process for the removal of PCE and its' metabolites, in particular in the PRMF. In a PRMF system in Leuna which was used to treat waters contaminated with benzene and MTBE the mass loss by volatilization was less than 3% for benzene and 15.2% for MTBE which was slightly higher than in a HSSF CW (1.1% for benzene and 6.1% for MTBE), operated in a parallel way. Volatilization fluxes were found to increase with the increase of vapour pressure (Burken & Schnoor, 1999). The vapour pressure of PCE, TCE, *cis*-1,2-DCE, benzene and MTBE are 18.47, 57.8, 373, 86, and 251 mm Hg, respectively. Therefore, we can assume that volatilization of PCE and TCE will be less than 3% (lower than benzene), while the volatilization of *cis*-1,2-DCE would be more than 15% (higher than MTBE).

3.2.2.3 Redox conditions and electron acceptors

The redox potential in the pore water decreased in both systems along the flow path (Figure 3.2-14). In general, the redox potential values of the pore water in the PRMF were higher than in the HSSF CW. The tidal flow operation mode did not obviously influence the general redox pattern. A bigger variation of redox potential was observed in the PRMF in comparison to the HSSF CW; a lower redox potential was reached during the summer period which correlated with the high sulphide concentration during this period (Figure 3.2-15).

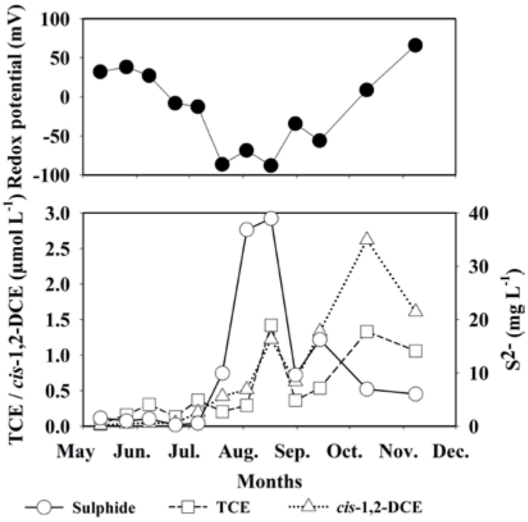

Figure 3.2-15 Mean concentrations (measured) of TCE, *cis*-1,2-DCE, sulphide and redox potential in the pore water of the PRMF at 4 m during the investigation period (May 11th to November 8th, 2010)

The oxygen concentration in the pore water of the PRMF was higher than in the HSSF CW based on two one-day examples (data not shown). In the PRMF, on 26th May 2010, the oxygen concentration in the pore water reached 2.01 mg/L at 0.5 m from the inlet and decreased along the flow path to 0.16 mg/L at 4 m and was still higher than in the HSSF CW. On 31st August 2010, when the HSSF CW ran with tidal flow operation mode, the maximum oxygen concentration in the pore water increased up to 0.94 mg/L in the upper layer (30 cm) at 0.5 m from the inlet, which was higher than 0.23 mg/L measured before tidal flow operation. This gives an indication that the lower TCE and *trans*-1,2-DCE load found at 0.5 m in the HSSF CW (Figure 3.2-13) might be caused due to the more intense oxidation of TCE during this second experimental phase (tidal flow operation mode respectively summer/autumn season).

Sulphide concentrations higher than the inflow (0.68 mg/L) were observed in the PRMF since 20th July 2010 and the concentration reached up to 39 mg/L (Figure 3.2-15). Elevated sulphide concentrations (higher than that of the inflow) were also observed in the HSSF CW during the evaluation period (May 11th to November 8th, 2010) and reached up to 21 mg/L (data not shown). In the PRMF, the concentration of TCE and *cis*-1,2-DCE increased dramatically since the sulphide concentration increased over the level of the inflow. This might be a clue that the dissimilatory sulphate reduction stimulated the dechlorination process. However, due to the high concentration of sulphide in the pore water, toxic effects to the plants and also to the aerobic microorganism can be expected. For instance, the removal of ammonium was inhibited, which means ammonium removal efficiency was decreased from 75% in 2009 to 42% in 2010 in the HSSF CW (Wu et al., 2012).

3.2.2.4 Conclusions

The investigated HSSF CW exhibited complete removal of PCE after a short flow path of 0.5 m during the investigated period from May to November and independent of the change of operation mode from continuous to tidal flow. Also the pattern of the formed dechlorination products like TCE, the three isomers of DCE, VC and ethene within the flow path did not change much. It should be noted that some of these formed dechlorination products have a higher toxicity than the PCE itself. But at the investigated running conditions after a flow path of 4 m with the exception of ethene and VC all other dechlorination metabolites were mainly removed. However, a higher cycle frequency of the tidal flow mode could cause a more profound influence on the redox conditions in HSSF CWs.

The PRMF showed lower removal efficiency for PCE than the HSSF CW. Nevertheless, during the summer period PCE was also completely removed like in the HSSF CW. In comparison to the HSSF CW, not all dechlorination products could be detected, especially VC and ethene, which are preferably metabolized by microorganisms via an aerobic pathway. This is in accordance with the higher redox conditions found in the PRMF in comparison to the HSSF CW. The PRMF seems to be more suitable for the removal of contaminants which need oxic condition like low chlorinated hydrocarbons as VC, mono- and dichlorobenzenes, etc. for their microbial degradation, while HSSF CW provide better conditions for microbial anaerobic processes like the dechlorination of highly chlorinated hydrocarbons as PCE. Nevertheless in both systems even at low concentrations of bioavailable organic contaminants the microbial formation of sulphide in case of high sulphate concentration in the water has to be considered. The carbon input by the plants (rhizodeposition products) is likely to supply the needed electron donors for this reaction.

3.2.3 Effect of tidal operation on the HSSF CW performance for treating groundwater contaminated by chlorinated hydrocarbons

In this chapter, an investigation covering three growing seasons (from April 2009 to December 2011) was carried out in the HSSF CWs to treat sulphate rich groundwater contaminated with MCB and PCE. The system was run under three different flow regimes: regime I: continuous flow during 20th April, 2009 to 20th July, 2010; regime II: 7 days cycle tidal flow from 21st July, 2010 to 12th April, 2011; regime III: 2.5 days cycle tidal flow during 13th April, 2011 to 6th December, 2011.

3.2.3.1 Tidal effect on MCB removal

First of all, plants showed a similar activity (water loss) during the investigation period (Figure 3.2-16) regardless of the tidal effect. In general, the MCB removal load decreased with the decrease of inflow load (Figure 3.2-17). Both tidal flow regimes (7 days and 2.5 days cycle) showed an insignificant difference in MCB load removal efficiency after 4 m compared with the continuous flow regime (Figure 3.2-17, Table 3.2-3). Furthermore, 7 days cycle tidal flow regime even decreased the MCB removal significantly before 2 m from the inlet (Figure 3.2-18, Table 3.2-4). However, intensification of the tidal regime to a 2.5 days cycle tidal flow regime enhanced MCB removal significantly compared with the continuous flow (before 1 m) and the 7 days cycle tidal flow regime (before 2 m) (Figure 3.2-18, Table 3.2-4). This is a proof that intensification of the tidal flow regime can cause benefits for the removal of MCB. The improvement of MCB removal only happened within 2 m from the inlet and gives an indication of an oxygen limitation in the first part of the system.

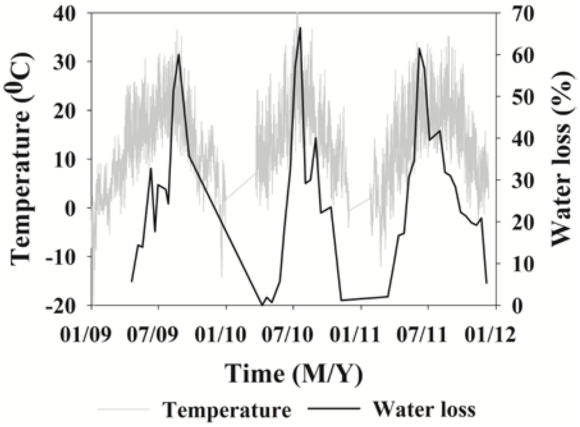

Figure 3.2-16 Air Temperature and water loss during the investigation period

3.2.3 Effect of tidal operation on the HSSF CW performance for treating groundwater contaminated by chlorinated hydrocarbons

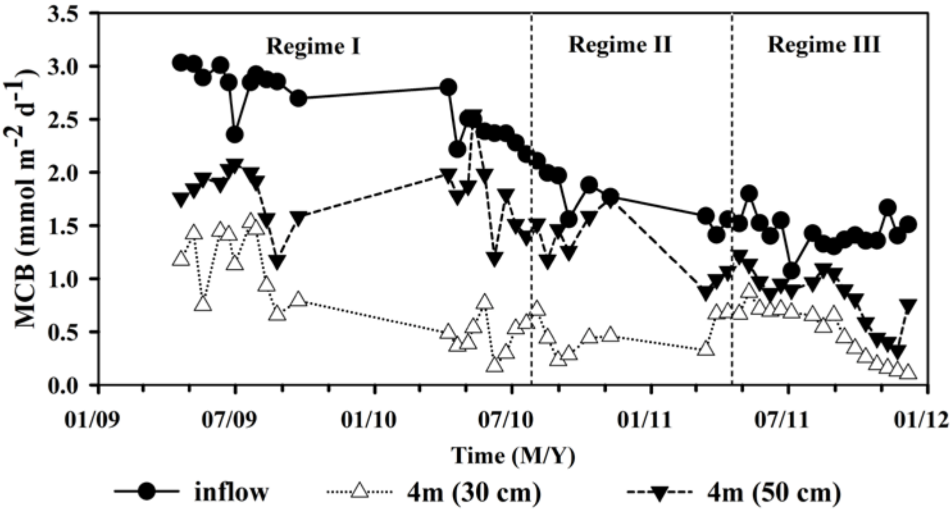

Figure 3.2-17 Inflow and removed loads of MCB after 4 m (30 cm and 50 cm in depth) under different flow regimes (2009-2011)

The vertical profile shows that a better MCB removal performance was reached in the upper layer (30 cm) than in the deeper layer (50 cm) (Figure 3.2-17). Significant difference in MCB concentrations between two depths was found under continuous flow conditions after 2 m from the inlet (Table 3.2-4). MCB concentration differed between the two depths and was found even at 0.5 m when the system ran under the 2.5 days tidal flow regime ($p<0.001$). The 2.5 days cycle tidal flow regime did increase the MCB removal efficiency (mean of depths), but it especially increased the MCB removal in the deeper layer (50 cm) (Figure 3.2-17). This might be explained by the microbial adaption, which means more oxic condition preferring microorganisms were established by the more frequent tidal regime, in particular in the deeper layer (50 cm).

3.2.3.2 Effect of the tidal regime on the removal of PCE and its' metabolites

PCE was completely and steadily removed in the HSSF CW after 1 m under all three different flow regimes (Figure 3.2-18). The PCE removal was significantly enhanced at 0.5 m from the inlet by the 2.5 days cycle tidal flow regime ($p=0.047$). The PCE concentration between the two depths (30 cm and 50 cm) was insignificant along the flow path (Table 3.2-4) except at 0.5 m ($p<0.001$) and 2 m ($p=0.016$) under flow regime I, where a higher PCE concentration was observed at 50 cm and 1 m under flow regime III ($p=0.003$), where a higher PCE concentration was observed at 30 cm.

3.2.3 Effect of tidal operation on the HSSF CW performance for treating groundwater contaminated by chlorinated hydrocarbons

Table 3.2-3 Mann-Whitney Rank Sum Test of the MCB and PCE load removal efficiency, mean mass accumulation of ethene, DCEs and VC, as well as the mean concentration of sulphide under the three different flow regimes.

Compounds	0.5 m			1 m			2 m			3 m			4 m		
	I-II	I-III	II-III	I-II	I-III	II-III	I-II	I-III	II-III	I-II	I-III	II-III	I-II	I-III	II-III
MCB	0.311	**0.032**	**0.016**	0.229	**0.005**	**0.019**	**0.015**	0.115	**0.007**	0.981	0.622	0.977	0.869	0.937	0.887
PCE	0.689	**0.047**	0.350	0.280	0.062	0.533	0.072	0.083	0.121	0.382	0.101	0.505	0.256	0.058	0.062
TCE	0.085	0.787	0.183	0.358	0.083	0.671	0.554	**0.050**	0.202	0.754	0.081	0.180	0.580	**0.024**	0.033
cis-1,2-DCE	0.085	**<0.001**	**0.019**	**0.013**	**<0.001**	**0.003**	0.654	**0.011**	0.295	0.944	**0.006**	0.095	0.869	**0.019**	0.107
trans-1,2-DCE	0.383	**<0.001**	**<0.001**	0.437	**0.016**	**0.002**	0.150	**<0.001**	**<0.001**	0.370	**<0.001**	**<0.001**	0.233	**0.004**	**<0.001**
VC	0.724	**0.037**	0.515	**0.025**	**<0.001**	**0.002**	0.944	0.364	0.932	0.334	0.364	0.977	0.437	0.245	0.932
Ethene	**0.025**	0.454	0.165	0.104	**<0.001**	**<0.001**	0.077	0.738	0.843	0.383	0.644	0.977	0.944	0.220	0.224
Sulphide	0.525	**<0.001**	**0.010**	0.138	**0.004**	**0.004**	0.906	**0.004**	**0.006**	0.311	**0.004**	**0.006**	0.494	**0.004**	**0.006**

Table 3.2-4 Mann-Whitney Rank Sum Test of contaminants concentration difference on two depths (30 cm and 50 cm) under the three different flow regimes

Flow path	Flow regimes	MCB	PCE	TCE	*cis*-1,2-DCE	*trans*-1,2-DCE	VC	Ethene	Sulphide
0.5 m	I	0.49	**<0.001**	0.776	**0.009**	**<0.001**	**<0.001**	0.062	0.239
	II	0.48	0.212	0.596	0.331	0.093	**0.017**	**0.001**	0.401
	III	**<0.001**	0.118	0.161	0.441	**0.002**	0.185	**0.021**	0.953
1 m	I	0.081	0.218	**0.002**	0.120	0.072	**0.005**	**<0.001**	0.298
	II	0.48	0.857	0.377	**<0.001**	0.480	0.052	**<0.001**	0.133
	III	0.836	**0.003**	**<0.001**	0.073	0.925	**0.002**	0.534	0.418
2 m	I	**<0.001**	**0.016**	**0.028**	0.860	0.350	0.675	**0.005**	0.218
	II	0.185	1.000	0.716	0.585	0.077	0.791	0.427	0.216
	III	**0.008**	0.868	0.638	**0.006**	0.057	0.127	0.462	0.638
3 m	I	**<0.001**	0.213	0.817	0.322	0.818	0.473	**<0.001**	0.323
	II	**<0.001**	1.000	0.916	0.422	0.093	0.216	**0.027**	1.000
	III	**0.001**	1.000	0.617	**0.010**	**<0.001**	0.149	0.109	0.286
4 m	I	**<0.001**	0.976	0.499	0.291	0.095	0.060	**<0.001**	**0.022**
	II	**<0.001**	0.856	0.850	1.000	**0.006**	0.158	0.112	0.659
	III	**0.004**	1.000	0.980	0.109	0.220	0.440	0.250	**0.012**

3.2.3 Effect of tidal operation on the HSSF CW performance for treating groundwater contaminated by chlorinated hydrocarbons

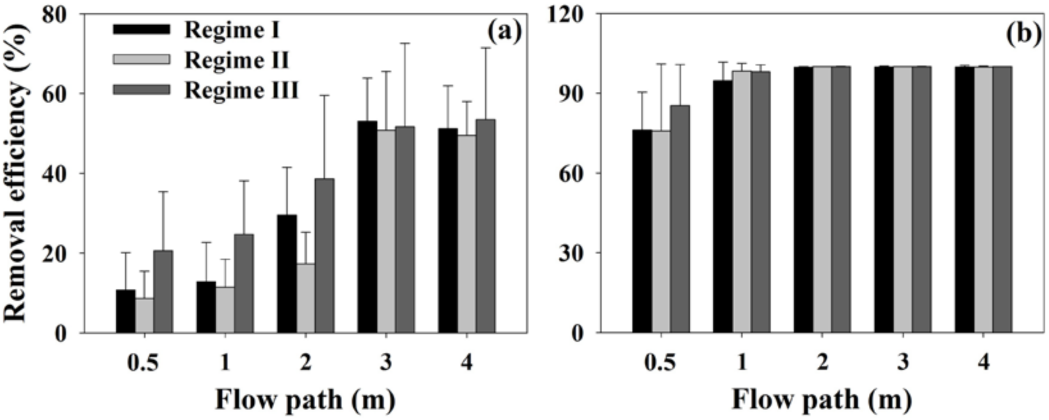

Figure 3.2-18 Load removal efficiencies (mean of depths) of MCB (a) and PCE (b) along the flow path under three different flow regimes.

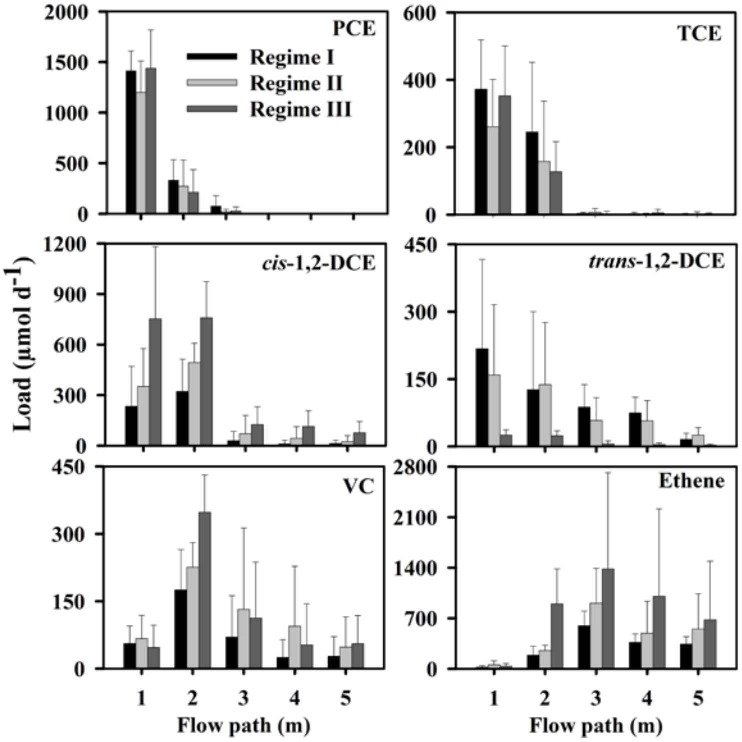

Figure 3.2-19 Loads (mean of depths) of PCE and its metabolites along the flow path in the HSSF CW under the three flow regimes (n=20, 9, 16 for regime I, II, III).

TCE was accumulated before 1 m but after 2 m completely and steadily removed in the HSSF CW under all the different flow regimes (Figure 3.2-19). The tidal operations had an apparently insufficient effect on the accumulation and removal of TCE (Figure 3.2-19, Table 3.2-3), with only slight influence at 2 m (p=0.05) and 4 m (p=0.024) under the 2.5 days cycle tidal regime. The difference of TCE concentrations were insignificant between the two depths except at 1 m (p=0.02) and 2 m (p=0.028) under the continuous flow regime and at 1 m under the 2.5 days cycle tidal regime (p<0.001).

Accumulation of *cis*-1,2-DCE was profound before the 1 m mark under the three different flow regimes, while decreased sharply after 2 m (Figure 3.2-19). However, it accumulated significantly under regime II and III. More *cis*-1,2-DCE was accumulated before 1 m under 7 days cycle regime compared with the continuous flow mode (Table 3.2-3) especially significant accumulation of *cis*-1,2-DCE was found along the whole flow path under the 2.5 days cycle regime conditions compared with the continuous flow conditions (all p<0.05, Table 3.2-3). The *cis*-1,2-DCE concentration difference between two depths was only found at 0.5 m under continuous flow conditions (p=0.009), at 1 m under 7 days cycle regime (p<0.001), at 2 m and 3 m under 2.5 days cycle regime (p=0.006 and p=0.01) where higher concentrations of *cis*-1,2-DCE were found in the upper layer (30 cm). This gives a suggestion that oxygen limitation in the deeper layer caused more anaerobic condition for the dechlorination of *cis*-1,2-DCE.

Maximum accumulation of *trans*-1,2-DCE was observed at 0.5 m in the system under all the three different running conditions and then decreased later along the flow path (Figure 3.2-19). Both tidal operations decreased the accumulation of *trans*-1,2-DCE significantly compared with the continuous flow regime. The 2.5 days cycle regime even more significantly decreased the accumulation of *trans*-1,2-DCE compared to the 7 days cycle regime (all p<0.05). Similarly the *cis*-1,2-DCE, *trans*-1,2-DCE also accumulated more in the upper layer than in the deeper layer.

Maximum accumulation of VC was observed at 1 m in the system under all three running regimes and started to decrease later along the flow path (Figure 3.2-19). Both tidal flow regimes (regime II and III) increased the accumulation of VC significantly compared with the continuous flow (regime I), for instance, at the peak point at 1 m (both p<0.05). The 7 days cycle regime also increased the accumulation of VC at 1 m compared with the continuous flow regime (p=0.25). The difference of the VC concentration between the two depths was found to be significant at 0.5 m under the continuous flow regime (p<0.001), at 0.5 m and 1 m (p=0.017) under 7 days cycle regime (p=0.005), where more VC was accumulated in the upper layer (30 cm). However, VC concentration difference between the two depths (30 cm and 50 cm) was found significant at 1 m under the 2.5 days cycle regime (p=0.002), but more VC was accumulated in the deep layer (50 cm). This may be an indication that VC was removed through oxidation in the upper layer (30 cm).

The tidal operation enhanced the accumulation of ethene (Figure 3.2-19). Significant more ethene accumulation was observed at 0.5 m flow distance under the 7 days cycle regime compared to the continuous flow regime($p=0.025$) and at 1 m under the 2.5 days cycle regime compared to continuous flow regime ($p<0.001$) and the 7 days cycle regime ($p<0.001$). Ethene concentrations show significant differences between the two depths along the flow path under the continuous flow regime, except at the 0.5 m flow distance (Table 3.2-4), where only trace ethene concentration were observed at 0.5 m (Figure 3.2-19). Ethene concentrations also show significant differences between depths before 3 m (except 2 m) under the 7 days cycle regime (Table 3.2-4). Ethene concentration differences between depths were only found at 0.5 m under the 2.5 days cycle regime ($p=0.021$).

3.2.3.3 Tidal effect on sulphide accumulation

Due to the high sulphate concentrations in the inflow water, dissimilatory sulphate reduction intensified year by year in the HSSF CW with the uptake of ferric iron (Wu et al., 2012). With the 7 days cycle tidal flow regime, dissimilatory sulphate reduction was refrained to some extent before 2 m flow path, while even more sulphide was accumulated at 3 m and 4 m but not significantly (Figure 3.2-20, Table 3.2-3). The sulphide concentration in pore water reached up to 23 mg/L during the summer. However, with intensification of the tidal flow (2.5 days cycle regime), the sulphide concentration in pore water reduced significantly (Figure 3.2-20, Table 3.2-3). This can be explained by the increased oxygen input through the tidal operation into the CW (Figure 3.2-21), where the oxygen was a competing electron acceptor with sulphate, and also the sulphide could be oxidized by oxygen. Therefore, lower sulphide concentrations were observed under the 2.5 days cycle regime. Significant differences between the sulphide concentrations in the different depths were only observed at 4 m under continuous flow ($p=0.022$) and 2.5 days cycle regime ($p=0.012$).

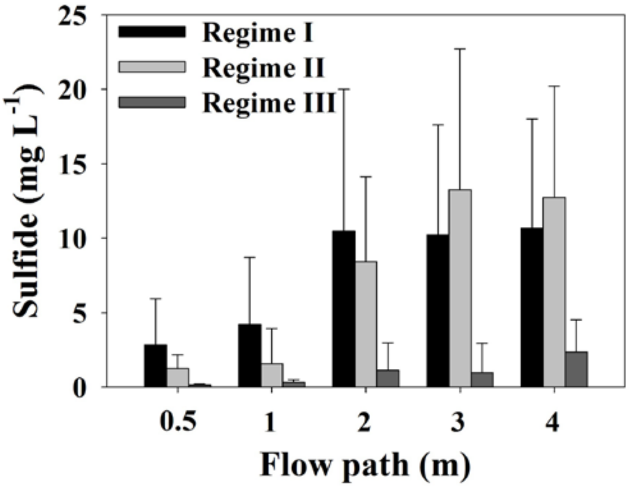

Figure 3.2-20 Measured sulphide concentrations ((mean of depths)) in pore water along the flow path in the HSSF CW run under three flow regimes (n=20, 9, 16 for I, II, III).

3.2.3.4 Oxygen concentration

In general, a HSSF CW is an oxygen limited system. The oxygen concentration in pore water of this investigated CW was less than 0.2 mg/L under the normal continuous flow regime (Figure 3.2-21). However, with the operation of the 7 days cycle tidal flow regime, the oxygen concentration in pore water increased to 0.97 mg/L at 0.5 m in the upper layer (Figure 3.2-21). Furthermore, a higher oxygen concentration was found in pore water both at 30 cm (2.1 mg/L) and at 50 cm (0.5 mg/L) under the operation of 2.5 days cycle tidal flow regime (Figure 3.2-21). This confirms that a more frequent tidal procedure can increase the oxygen input into the HSSF CW.

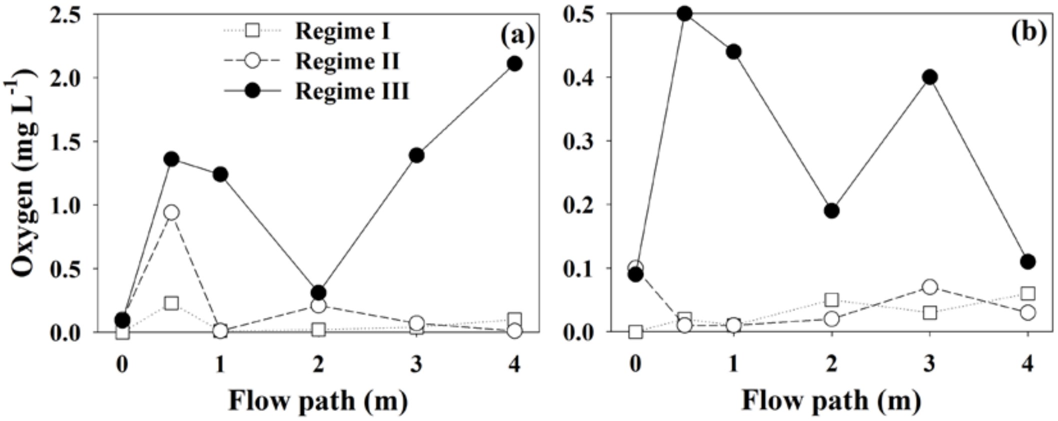

Figure 3.2-21 Oxygen concentrations (measured) in pore water at two depths (a: 30 cm, b: 50 cm) along the flow path in the HSSF CW run under three different flow regimes

With the better oxygen input achieved by the 2.5 days cycle tidal flow regime, the removal efficiency of MCB was enhanced significantly, especially in the flow path before 1 m (Table 3.2-3), where a higher oxygen concentration was observed (Figure 3.2-21). The increased oxygen concentration at 50 cm also gives the probable explanation for the better MCB removal at 50 cm (Figure 3.2-17).

Oxygen is often the most preferred electron acceptor for many biochemical reactions. With the conspicuous increase of oxygen concentration under the 2.5 days cycle tidal flow regime, dissimilatory sulphate reduction was confined to a lower extent (Figure 3.2-20). In these conditions also small amounts of element sulfur were detected (less than 2 mg/L, data not shown). This proves that the intensification of the tidal mode (2.5 days cycle regime) can inhibit the accumulation of sulphide and so reduce the toxic stress for plants and aerobic microorganisms.

3.2.3.5 Conclusions

The intensification of the tidal operation (2.5 days cycle regime) increased the oxygen concentration in pore water, thus, it enhanced the MCB removal efficiency in the HSSF CW significantly before 2 m of the flow path from the inlet and increased the removal efficiency of PCE within the flow path of 0.5 m. The contaminant removal process can be influenced by the tidal flow operation regime (especially under the 2.5 days cycle regime) because of a significant accumulation of *cis*-1,2-DCE, VC and ethene under tidal flow operation. The more intensive tidal operation also inhibited the dissimilatory sulphate reduction and the sulphide concentration decreased in the pore water. Therefore, the intensification of the tidal flow operation is a useful option to increase the removal efficiency of chlorinated hydrocarbons in the HSSF CW, and also to inhibit sulphide toxicity to plants and many aerobic microorganisms when a high amount of sulphate is available for the dissimilatory sulphate reduction.

3.2.4 FPRM for the treatment of chlorinated hydrocarbons: effect of tidal operation

In this chapter, the results from the investigations covering two growing seasons (from April 2010 to December 2011) are described which were carried out in a PRMF (in 2010) under continuous flow with a water level of 20 cm and after modification to a FPRM (in 2011) under tidal flow regime with a varying water level from 15 cm to 40 cm. The tidal flow regime started on the 13th April 2011 with the fast outflow flushing lasted only 2 hours; due to this the water level decreased quickly from 40 cm to 15 cm. The subsequent refilling (5.0 L/h) to the water level of 40 cm lasted about 2 weeks. When the water level again reached 40 cm, water samples were taken and again a new cycle started (fast outflow flushing of only 2 hours and refilling over a period of about 2 weeks).

3.2.4.1 Effect of tidal flow regime on the removal of low chlorinated benzenes

Water quality parameters of the inflow and after 4 m of flow path under continuous flow and tidal flow regime are shown in Table 3.3-5. In general, the outflow concentration of both low chlorinated and high chlorinated hydrocarbons have decreased dramatically.

Figure 3.2-22 shows that MCB was removed more efficiently after 4 meters under the tidal flow regime than during the continuous flow regime. The same phenomenon was observed for the other low chlorinated benzenes (1,2-DCB, 1,4-DCB and 2-chlorotoluene) and benzene (data not shown). This can be explained by a better oxygen input into the root mat by tidal flow operation.

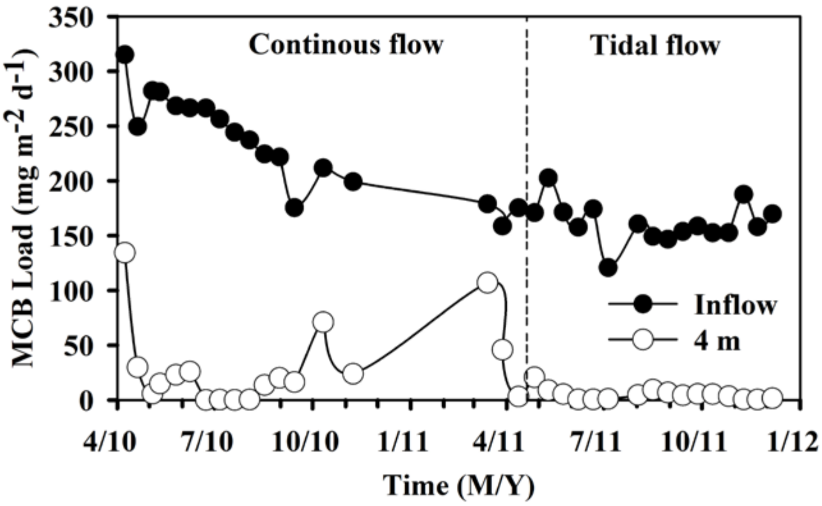

Figure 3.2-22 Inflow and 4 m loads of MCB in a PRMF under continuous flow (water level 20 cm) and after modification in the FPRM under tidal flow condition (water level from 15 - 40 cm)

3.2.4 FPRM for the treatment of chlorinated hydrocarbons: effect of tidal operation

Table 3.3-5 Influent and pore water quality parameters in the plant root mat filter/floating plant root mat after 5.5 m flow path under continuous flow and with tidal flow regime

Compounds	Unit	Continuous flow (water level of 20 cm)		Tidal flow (water level of 15 – 40 cm)	
		Influent	5.5 m flow path	Influent	5.5 m flow path
MCB	mg/L	7.80 ± 1.46	1.11 ± 1.34	5.40 ± 0.61	0.19 ± 0.22
1,2-DCB	mg/L	0.034 ± 0.005	0.008 ± 0.007	0.025 ± 0.003	0.002 ± 0.001
1,4-DCB	mg/L	0.282 ± 0.039	0.048 ± 0.050	0.254 ± 0.035	0.009 ± 0.007
2-chlorotoluene	mg/L	0.037 ± 0.004	0.009 ± 0.007	0.040 ± 0.007	0.002 ± 0.002
PCE	mg/L	1.84 ± 0.42	0.44 ± 0.38	1.99 ± 0.52	0.04 ± 0.06
TCE	mg/L	0.001 ± 0.002	0.055 ± 0.058	0.004 ± 0.003	0.016 ± 0.018
cis-1,2-DCE	mg/L	0.002 ± 0.001	0.053 ± 0.070	0.007 ± 0.006	0.063 ± 0.037
trans-1,2-DCE	mg/L	0.001 ± 0.001	0.001 ± 0.002	0.001 ± 0.002	0 ± 0
1,1-DCE	mg/L	0 ± 0	0.001 ± 0.002	0 ± 0	0.001 ± 0.002
VC	mg/L	0.005 ± 0.004	0.001 ± 0.002	0.019 ± 0.003	0.001 ± 0.001
Ethene	mg/L	1.28 ± 2.21	0.36 ± 0.89	4.67 ± 1.43	0.85 ± 0.62
SO_4^{2-}	mg/L	854 ± 35	1148 ± 566	887 ± 71	925 ± 90
S^{2-}	mg/L	0.57 ± 0.59	7.53 ± 11.94	0.07 ± 0.09	10.34 ± 11.44
NH_4^+	mg/L	55 ± 9	31 ± 20	55 ± 14	45 ± 17
PO_4^{3-}	mg/L	3.98 ± 1.33	4.42 ± 3.94	4.24 ± 1.74	6.00 ± 1.87
Cl^-	mg/L	315 ± 40	440 ± 238	246 ± 57	278 ± 41
pH	-	6.4-6.6	6.3-6.8	6.4-6.6	6.5-7.1
Redox	mV	56 ± 58	-3 ± 56	115 ± 73	-24 ± 83
Conductivity	ms/cm	3.20 ± 0.22	3.88 ± 1.90	2.99 ± 0.29	3.15 ± 0.31

Figure 3.2-23 shows that MCB load decreased gradually along the flow path, and the lower residual MCB load was obtained under the tidal flow condition. Significant differences were found between continuous flow and tidal flow at 1 m ($p=0.01$) and 4 m flow path ($p=0.022$). The similar phenomenon (significant removal efficiency difference between continuous flow and tidal flow) was also found for the removal of 1,2-DCB, 1,4-DCB and 2-chlorotoluene (Table 3.3-6). There is a slight concentration difference between the two sampling depths under the conditions of tidal flow operation (Table 3.3-7), especially at 0.5 m and 2 m.

3.2.4 FPRM for the treatment of chlorinated hydrocarbons: effect of tidal operation

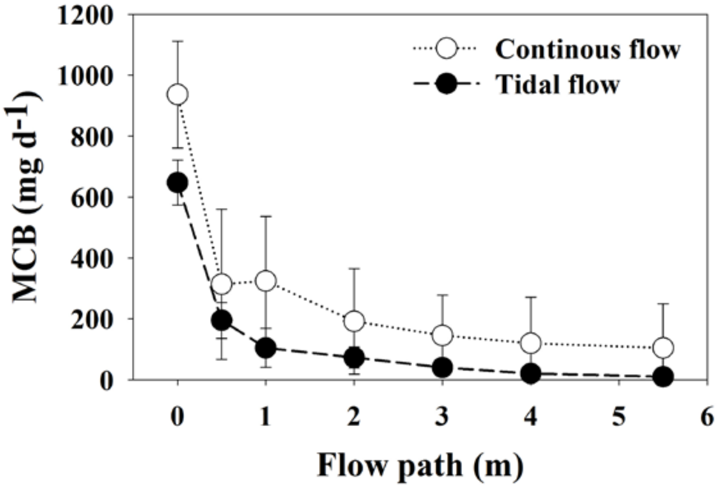

Figure 3.2-23 MCB load along the flow path in a PRMF under continuous flow (water level 20 cm, n=18) and after modifications in the FPRM under tidal flow (water level from 15- 40 cm, n=16)

Table 3.3-6 Mann-Whitney Rank Sum Test of the load removal efficiency of MCB, 1,2-DCB, 1,4-DCB, 2-chlorotoluene, benzene and PCE, mean mass accumulation of DCEs and sulphide concentrations in the plant root mat filter under continuous flow (water level 20 cm) and after modifications in the floating plant root mat under tidal flow condition (water level change from 15 cm to 40 cm) along the flow path.

Compounds	0.5 m	1 m	2 m	3 m	4 m	5.5 m
MCB	0.523	**0.010**	0.692	0.109	0.088	**0.022**
1,2-DCB	0.309	**0.007**	**0.007**	**0.020**	**0.045**	0.068
1,4-DCB	0.458	**0.006**	**0.040**	**0.022**	**0.010**	**0.007**
2-chlorotoluene	0.293	**0.006**	**0.005**	**0.009**	**0.004**	**0.008**
PCE	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**0.003**
TCE	0.196	0.523	0.309	0.352	**0.007**	**0.002**
cis-1,2-DCE	**<0.001**	**<0.001**	**0.009**	**0.002**	0.109	**0.011**
trans-1,2-DCE	0.145	0.711	0.438	0.164	0.287	0.057
1,1-DCE	**<0.001**	**<0.001**	**0.022**	0.205	**0.028**	**0.022**
VC	-	-	-	-	-	-
Ethene	-	-	-	-	-	-
Sulphide	**0.004**	**0.028**	**0.022**	0.101	0.501	0.523

- No accumulation of VC and ethene was observed.

Table 3.3-7 Mann-Whitney Rank Sum test on concentration difference between the two depths (20 cm and 40 cm) along the flow path in the floating plant root mat under the condition of tidal flow operation

Compounds	0.5 m	1 m	2 m	3 m	4 m
MCB	**0.037**	0.086	**0.019**	0.194	0.585
1,2-DCB	**0.014**	0.109	**0.034**	0.778	0.693
1,4-DCB	**0.035**	0.086	**0.020**	0.318	0.003
2-chlorotoluene	0.056	0.101	**0.047**	0.328	0.593
PCE	0.235	0.152	0.142	0.748	0.582
TCE	0.181	0.113	0.092	0.418	0.532
cis-1,2-DCE	0.150	0.418	0.250	0.521	0.662
trans-1,2-DCE	0.474	0.488	0.322	0.698	0.164
1,1 DCE	0.298	0.045	0.222	0.354	0.576
VC	0.278	0.638	0.068	0.929	0.953
Ethene	0.559	0.777	0.137	0.838	0.299
Sulphide	0.836	0.895	0.910	0.462	0.559

3.2.4.2 Effect of the tidal flow regime on the removal of PCE (high chlorinated hydrocarbon)

Figure 3.2-24 shows that low and steady PCE load at 4 m was achieved after the change from continuous flow to tidal flow operation. The PCE load difference at 4 m was significant between continuous and tidal flow operation ($P<0.001$). Significant differences of PCE removal efficiency along the flow path were found between the both running conditions of continuous flow and tidal flow operation regime (Table 3.3-6). However, there were no significant differences in the concentrations of the PCE and its metabolites between the two depths under the condition of tidal flow operation (Table 3.3-7).

The PCE load decreased along the flow path after the change in the conditions of tidal flow operation (Figure 3.2-25). The PCE metabolites TCE, *cis*-1,2-DCE and *trans*-1,2-DCE were detected and peaked at 0.5 m along the flow path under the condition of tidal flow operation, where PCE was removed drastically. However, no VC and ethene were detected in the PRMF independent of the operation conditions (continuous or tidal flow). TCE accumulation was reduced after tidal flow operation in comparison to the continuous flow mode, while more *cis*-1,2-DCE was accumulated under the condition of tidal flow mode (Figure 3.2-25). Anyhow, in comparison to the continuous flow operation all the accumulated metabolites were removed after 5.5 m flow path under tidal flow mode.

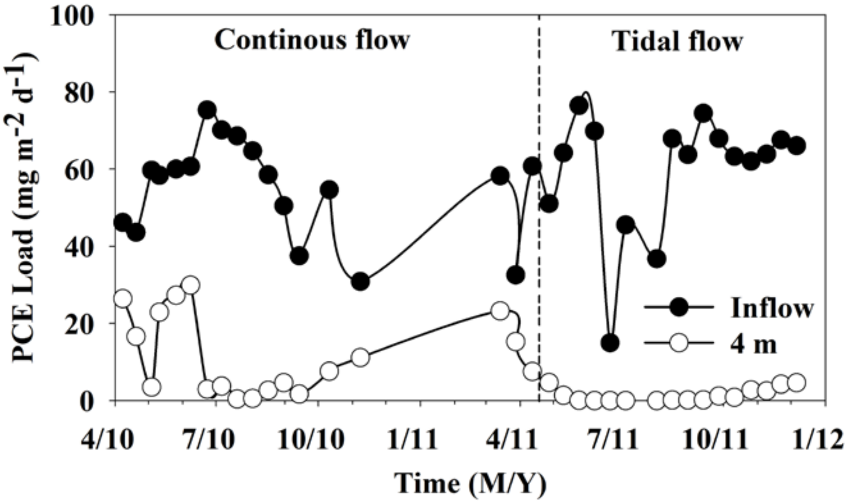

Figure 3.2-24 Inflow and 4 m loads of PCE in a PRMF under continuous flow (water level 20 cm) and after modification in the FPRM under tidal flow condition (water level from 15 - 40 cm)

There were no significant differences of the PCE and its’ metabolites concentrations between the two depths (20 and 40 cm) under the condition of tidal operation (Table 3.3-7). This indicates that the tidal flow operation and the increase of the water level had an insignificant effect for PCE and its’ metabolites removal also concerning the sampling depths.

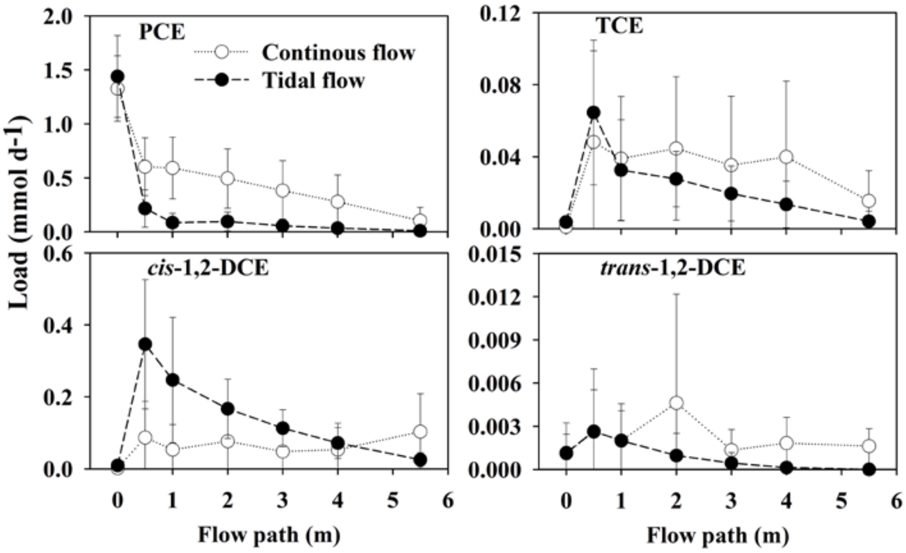

Figure 3.2-25 Loads of PCE and its’ metabolites along the flow path in a PRMF under continuous flow (water level 20 cm) and after modification in the FPRM under tidal flow condition (water level 15 -40 cm)

All in all, the tidal flow operation in the FPRM had a benefit for the removal of PCE; there was also a less accumulation of TCE and *cis*-1,2-DCE, and also no accumulation of the more toxic metabolite VC. The reason for this is that probably more anaerobic conditions were performed during the tidal operation as the water level was increased to 40 cm and the redox potential was more anaerobic than in the case under continuous flow condition (Figure 3.2-28).

3.2.4.3 Effect of the tidal flow regime on the sulphide concentration

The change from continuous flow to tidal flow mode in combination with the increase of the water level from 20 cm to 40 cm had a significant influence on the sulphide accumulation (Table 3.3-6). Figure 3.2-26 shows intensified sulphide accumulation after the change of operation mode. The high standard deviation was caused by the seasonal change of sulphide production, with higher concentrations during the summer period, which reached up to 72 mg/L. This could be due to the high plant activity increase the carbon release which can stimulate the sulphate reduction during the summer period (Faulwetter et al., 2009). The higher sulphide accumulation after the change of operation mode was because of better conditions for dissimilatory sulphate reduction and as result less re-oxidation of the formed sulphide. One explanation could be that more anaerobic conditions were performed with the increase of water level from 20 cm to 40 cm. The other one could be that more organic carbon was provided when more parts of the root mat were emerged into the water body with the increase of the water level.

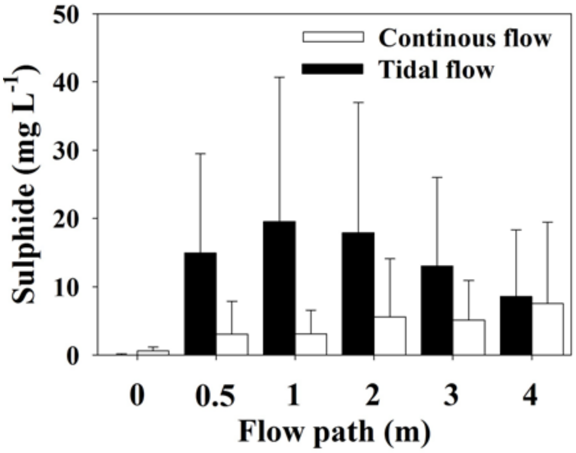

Figure 3.2-26 Sulphide concentration (measured) in the pore water along the flow path in a PRMF under continuous flow (water level 20 cm) and after modification in the FPRM under tidal flow condition (water level from 15 - 40 cm)

3.2.4.4 Factors influencing the chlorinated hydrocarbons removal in the floating plant root mats

PCE removal was enhanced significantly since the PRMF with a continuous flow mode and a water level of 20 cm was changed to a FPRM with a higher water level (40 cm) working in tidal flow mode (Figure 3.2-24). At the same time an increase of sulphide concentration was observed (Figure 3.2-26). Figure 3.2-27 shows that the sulphide accumulation obviously had a negative effect on the PCE concentration which means PCE concentration decreased with the increase of sulphide concentration. This indicates that the dissimilatory sulphate reduction process probably can stimulate the dechlorination of PCE. However, in the presence of sulfate, PCE dechlorination decreased because of interspecific competition, probably between the H_2 oxydizing sulphate reducing bacteria in batch conditions (Cabirol et al., 1998). While no effect of sulphate on PCE dechlorination process was found in semi-continuous fixed bed reactors, which is because of the existence of microbial biofilm (Cabirol et al., 1998). The system was run with continuous inflow, and more biofilm can be formed on the soil surface and root mats which can buffer the effect of sulphate. However, there was no clear correlation between sulphide accumulation and MCB removal.

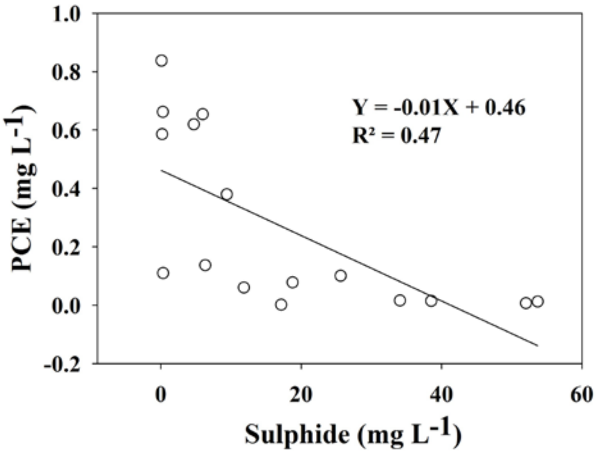

Figure 3.2-27 Relationship between PCE concentration and sulphide concentration (measured) at a flow path of 0.5 m in the FPRM (40 cm) under tidal flow mode

The redox potential seems to be a very important factor for the removal of PCE. After the change to tidal flow operation and the increase in water level from 20 cm to 40 cm the FPRM became more anaerobic (Figure 3.2-28). Interestingly, neglecting the high standard deviation, it seems that under the conditions of continuous flow mode the redox potential decreased along the flow path, while it increased along the flow path under tidal flow mode. The decrease of redox potential could be a result of a higher organic carbon input from the root mats and/or a decreased oxygen input under the condition of a higher water level of 40 cm even under the condition of tidal flow operation. As a result, better conditions for dissimilatory sulphate reduction were created which stimulated the PCE dechlorination directly or indirectly (Ndon et al., 2000; Aulenta et al., 2007).

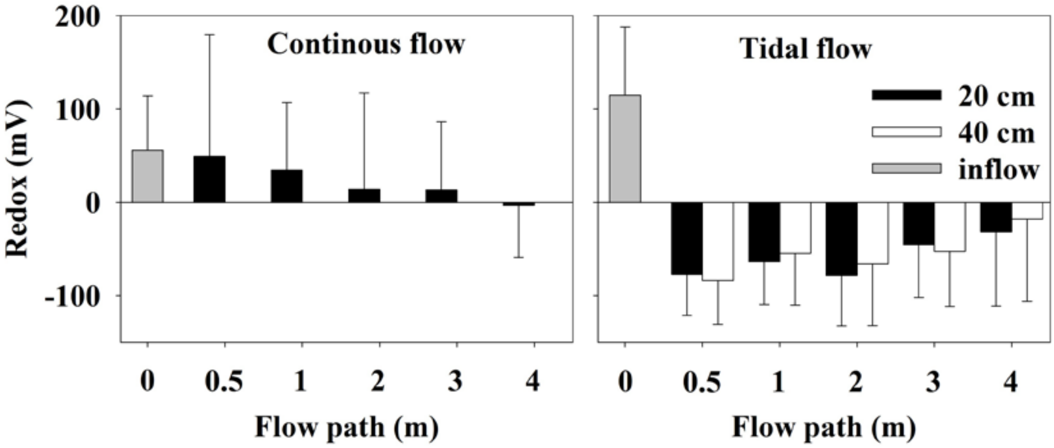

Figure 3.2-28 Redox potential along the flow path in the PRMF (water level 20 cm) with continuous flow and after its modification to the FPRM with tidal flow mode (water level from 15 cm - 40 cm)

The MCB removal was also improved to some extent (Table 3.3-5), but not so significantly like the PCE removal (Table 3.3-6). As MCB is a compound which prefers aerobic degradation, more oxygen input during the fast emptying phase under the tidal flow operation could be a reason for this improvement in MCB removal. On the other hand, the oxygen input by plants could have been inhibited as the water loss (which under distinctive conditions represents the plant activity) under tidal flow operation decreased (Figure 3.2-29). The inhibited plant activity was probably due to sulphide toxicity impacts on the plants, as the sulphide concentration reached up to 72 mg/L, which is relatively high for the health of plants. As it was reported that low sulphide concentrations of 1.6 mg/L are already toxic to the freshwater macrophyte Nitella flexilis (van der Welle et al., 2006)

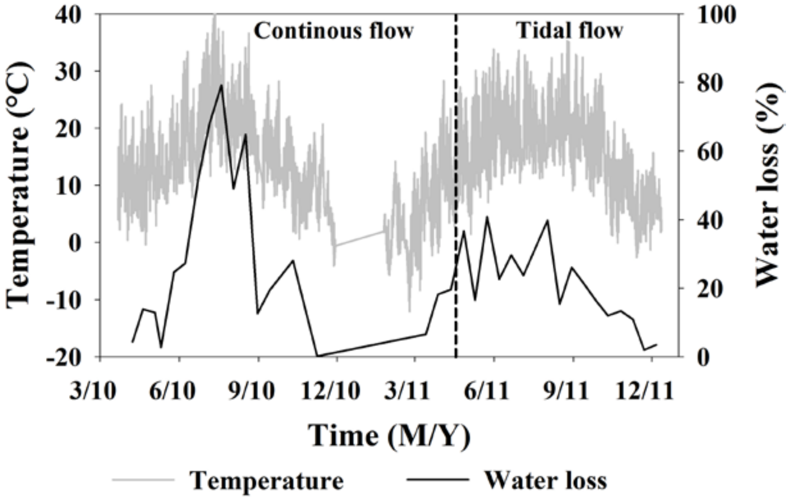

Figure 3.2-29 Air temperature and water loss in the PRMF (water level 20 cm) under continuous flow and after its modification to the FPRM under tidal flow condition (water level from 15 cm - 40 cm)

3.2.4.5 Conclusions

The change from the PRMF with a water level of 20 cm and continuous flow to a FPRM with a higher water level and tidal flow operation increased the PCE dechlorination process significantly and it also improved the removal of MCB to some extent. TCE and *cis*-1,2-DCE were detected under both conditions, but they were almost completely removed after 4 m of the flow path only after the change to a higher water level and to the tidal flow operation. Furthermore, no VC and ethene were detected under the conditions of FPRM with a higher water level and tidal flow operation. Either a higher carbon input by plants into the water of the system or a less re-oxidation of already formed sulphide after the change to tidal flow operation (with increased water level) intensified the dissimilatory sulphate reduction respectively resulted in an increased sulphide accumulation, especially during the summer time. Plant activity (water loss) was seemingly inhibited due to the profound sulphide accumulation. However, it seems that the dissimilatory sulphate reduction stimulated the PCE dechlorination process. But the toxicity of sulphide on plant activity must be considering for future research.

3.3 Characterization of MCB and PCE removal in laboratory-scale model wetlands under conditions of different electron acceptors

In order to better understand the removal processes of different chlorinated hydrocarbons, laboratory-scale experiments were done in a planted fixed bed reactor. The reactor was fed with the same inflow water as in the pilot-scale CWs in Bitterfeld.

Because of the high sulphate content of the water in these laboratory-scale experiments like in the pilot-scale CWs in Bitterfeld an intense sulphide accumulation was anticipated. The aim of the further experiments was to characterize how changes in running conditions influence the sulphide formation/accumulation. So, in a sequential approach different further electron acceptors like nitrite and nitrate and their combinations were added. Due to the high sulphate content and probable reasons like sufficient available carbon input by the plants as in the pilot-scale CW in Bitterfeld an intense sulphide accumulation in the variant A (with no further additions) was observed (Figure 3.3-1) and the plants transpiration (water loss) was seemingly inhibited due to the high accumulation of the toxic sulphide (Figure 3.3-1). Therefore, afterwards this “phase A” nitrite and nitrate were added as electron acceptors to compete with sulphate (phase B: 5-50 mg/L NO_3^- and 10 – 160 mg/L NO_2^-, phase C: 160 mg/L NO_2^-, phase D: 160 mg/L NO_3^-). The plants did not recover from the sulphide toxic effects with the addition of nitrite and nitrate (Figure 3.3-1). Subsequently, the unplanted phases D^-,C^-, and A^- were run with the corresponding additions of nitrite and nitrate. Finally, two further planted phases (D: 160 mg/L NO_3^- and A: without any additions) were run to repeat the phenomena of sulphide effect on the treatment performance.

The variant A at the second plant phase can be divided into four periods (a1, a2, a3, a4) due to the different affections of sulphide on MCB and PCE removal (a1- before sulphide accumulation; a2- sulphide accumulation start with effect on both MCB and PCE removal; a3- sulphide accumulation continue with effect on MCB removal; a4- sulphide accumulation stop), the time division are list in Table 3.3-1.

3.3.1 Removal processes of MCB and its derivatives

Highest MCB removal efficiency (>98%) was achieved under the whole unplanted phases (D^-, C^-, A^-) and the second planted phases when the plants were still healthy (D and a1, before sulphide accumulation started again) (Figure 3.3-2). The similar behavior for the removal of

1,2-DCB, 1,4-DCB, 2-chlorotoluene and benzene was also observed at the same situation (Table 3.3-1).

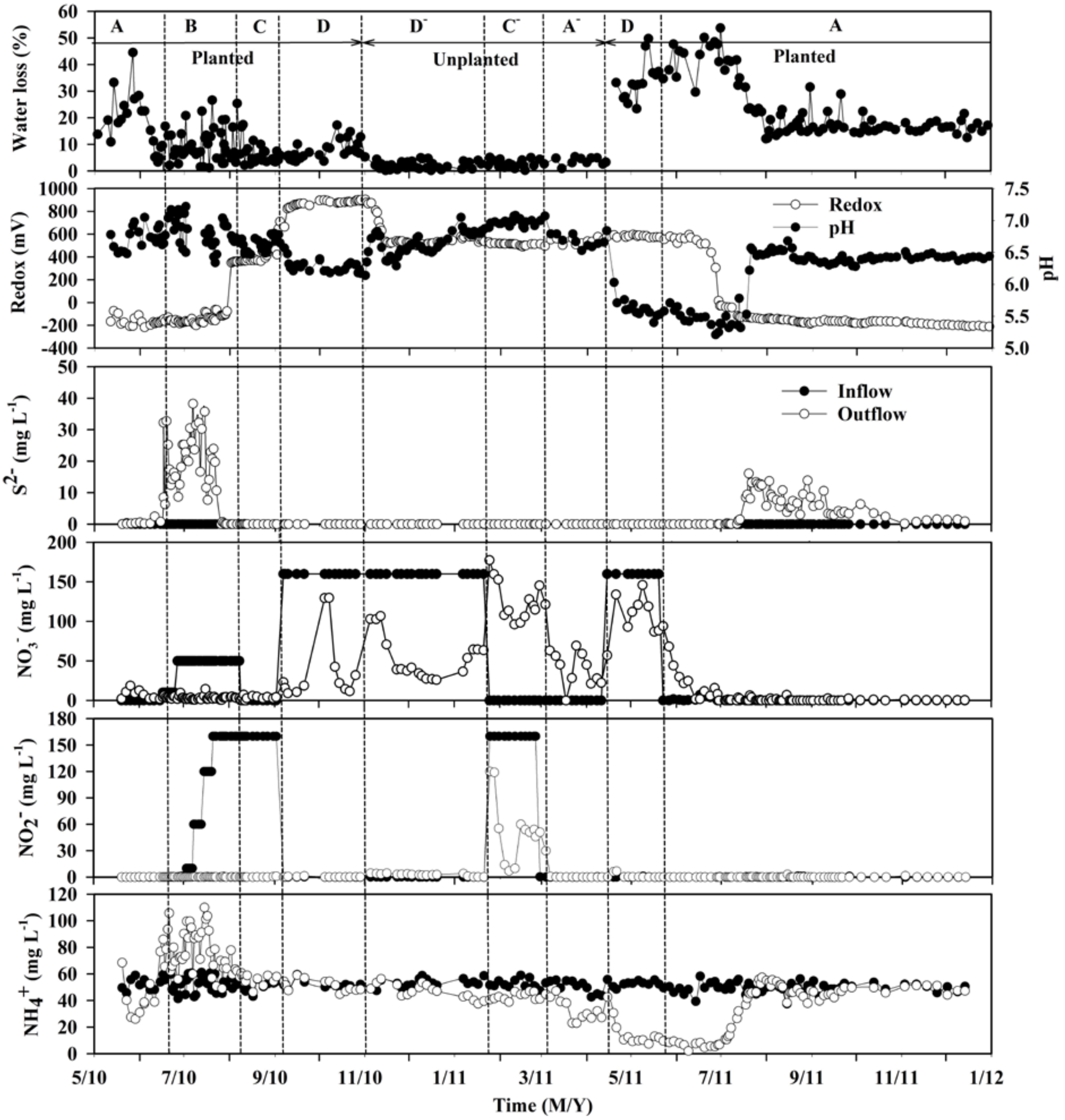

Figure 3.3-1 Water loss and further water parameter in the reactor during the investigation with following additions to the inflow water (all variants had a constant NH_4^+ concentration of 50 mg/L): A - no, B - 5-50 mg/L NO_3^- and 10 – 160 mg/L NO_2^-, C - 160 mg/L NO_2^-, D - 160 mg/L NO_3^-; the variants A^-, B^- and C^- were the corresponding unplanted variants

3.3 Characterization of MCB and PCE removal in laboratory-scale model wetlands under conditions of different electron acceptors

Table 3.3-1 Removal efficiency (%) of PCE, MCB, 1,2-DCB, 1,4-DCB, 2-chlorotulene, benzene under the different phases.

	A	B	C	D	D^-	C^-	A^-	D	A			
									a1	a2	a3	a4
Number of sampling	11	15	8	15	27	16	15	15	17	22	23	18
Period (D/M/Y)	10/5/10-17/6/10	18/6/10-5/8/10	6/8/10-7/9/10	8/9/10-31/10/10	1/11/10-24/1/11	25/1/11-4/3/11	5/3/11-15/4/11	16/4/11-27/5/11	28/5/11-12/7/11	13/7/11-30/8/11	31/8/11-31/10/11	1/11/11-1/1/12
Duration (d)	38	48	32	44	85	38	41	41	45	48	61	61
PCE	81 ± 7	81 ± 13	97 ± 3	72 ± 5	69 ± 8	82 ± 2	85 ± 4	85 ± 3	84 ± 4	71 ± 5	97 ± 5	100 ± 0
MCB	77 ± 7	73 ± 18	75 ± 6	82 ± 2	99 ± 3	99 ± 3	100 ± 0	99 ± 1	98 ± 3	71 ± 6	72 ± 9	80 ± 6
1,2-DCB	85 ± 5	80 ± 14	75 ± 4	71 ± 3	93 ± 9	95 ± 6	97 ± 6	96 ± 4	94 ± 4	74 ± 4	71 ± 7	71 ± 6
1,4-DCB	86 ± 4	79 ± 14	82 ± 3	79 ± 2	86 ± 8	95 ± 2	95 ± 2	96 ± 1	94 ± 2	79 ± 4	81 ± 6	83 ± 4
2-chlorotoluene	82 ± 5	72 ± 19	78 ± 4	72 ± 2	92 ± 8	94 ± 5	99 ± 2	98 ± 2	95 ± 4	74 ± 5	77 ± 5	75 ± 5
Benzene	72 ± 8	69 ± 23	69 ± 8	78 ± 4	99 ± 3	98 ± 4	100 ± 0	100 ± 1	97 ± 4	66 ± 7	66 ± 8	73 ± 6

a1- before sulphide accumulation; a2- sulphide accumulation start (with effect on both MCB and PCE removal);
a3- sulphide accumulation start (with effect on MCB removal); a4- sulphide accumulation stop

3.3 Characterization of MCB and PCE removal in laboratory-scale model wetlands under conditions of different electron acceptors

The emission rate of MCB under the different phases and treatments is shown in Figure 3.3-2. Highest MCB volatilization was found when the reactor was unplanted and without the addition of nitrite and nitrate (A$^-$); the emission rate was less than 0.6 µmol/d, which means less than 1% of the input MCB. This indicates that other more profound removal processes took place, especially the aerobic microbial oxidation, as plant uptake only take small part (< 0.3 %) for chlorobenzenes removal (Wang & Jones, 1994a; Wang & Jones, 1994b).

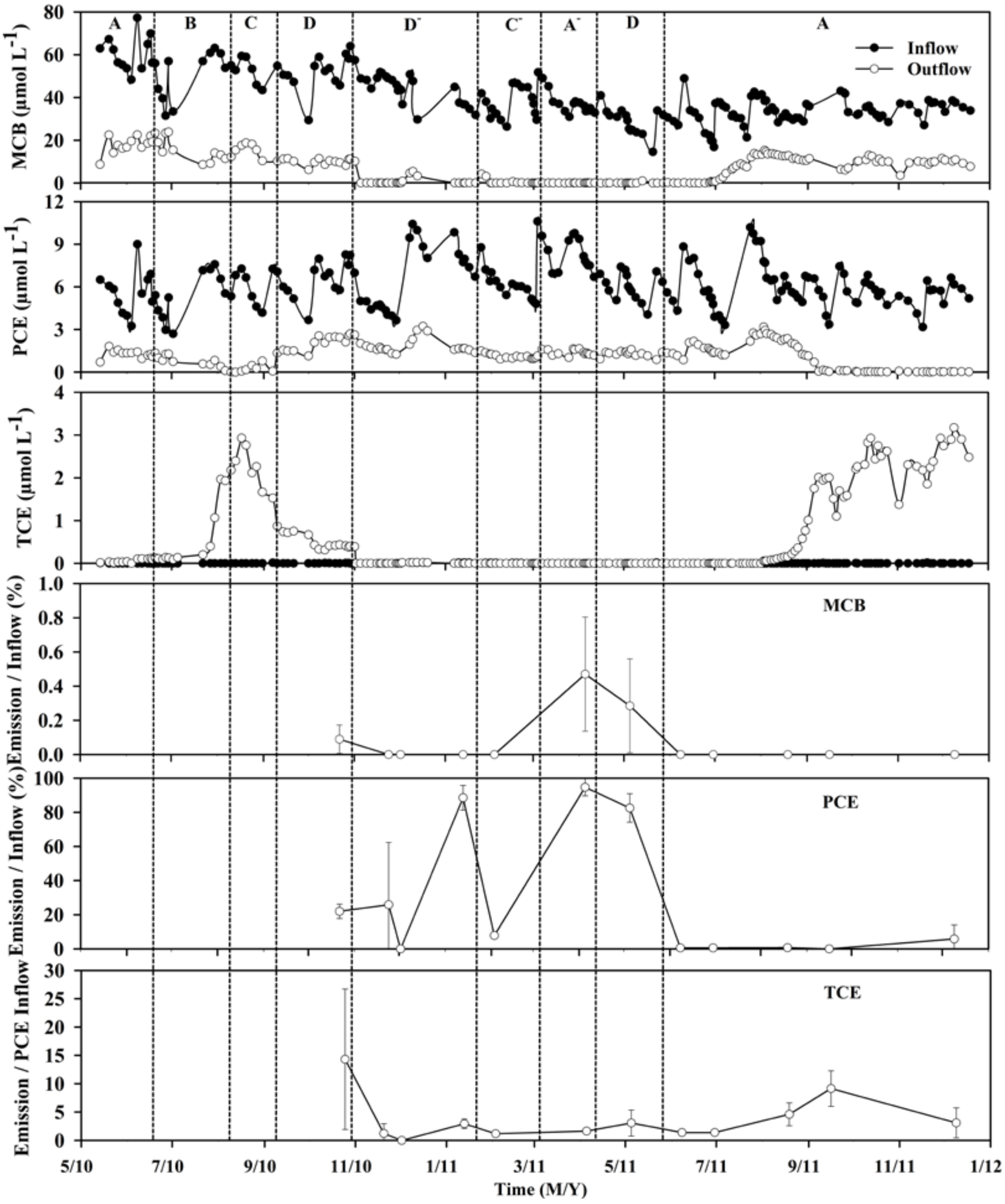

Figure 3.3-2 Inflow and outflow concentration of MCB, PCE, TCE, as well as the percentage of emission compared to the inflow load of MCB and PCE during the investigation with following additions to the inflow water (all variants had a constant NH_4^+ concentration of 50 mg/L): A - no, B - 5-50 mg/L NO_3^- and 10 – 160 mg/L NO_2^-, C - 160 mg/L NO_2^-, D - 160 mg/L NO_3^-; the variants A$^-$, B$^-$ and C$^-$ were the corresponding unplanted variants.

3.3.2 Removal processes of PCE

PCE was effectively removed (>97%) under the treatment conditions of phase C, and second planted phase A (a3 and a4) (Table 3.3-1, Figure 3.3-2). These three treatment conditions are characterized by the presence of plants. This indicates that plants may have enhanced the transformation/removal of PCE. The PCE transformation was confirmed by detection of the dechlorination metabolite TCE (Figure 3.3-2). Normally, dechlorination of PCE prefers more anaerobic condition, the optimal range for anaerobic PCE dechlorination is between -220 mV to -50 mV (Bouwer, 1994). But, the treatment C was under denitrification condition (Figure 3.3-1). Volatilization of PCE varied from the different treatment conditions (Figure 3.3-2). Relatively high volatilization was observed under the treatment conditions of the phases D^-, A^- and D (second planted phase). Volatilization played the main role on the removal of PCE at these three treatment conditions, which reached up to 95% of the total PCE input. After the plants were adapted to the reactor and the redox values decreased again (Figure 3.3-1), PCE volatilization was less than 1% (Figure 3.3-2). This testifies that healthy plants with their influence on microbial anaerobic processes and redox conditions can reduce the volatilization of PCE significantly. Volatilization (up to 15 % of the inflow mass) was also observed for TCE. A relatively high amount of TCE was removed by volatilization under phase D, when TCE was still detectable in the pore water. However, when the TCE concentration in the pore water was even under the detection limit (1 µg/L), some volatilization of TCE was still observed (Figure 3.2-2). When PCE was well dechlorinated to TCE under the conditions of the later second planted phase (a3 and a4), at least up to 60% of the PCE was converted to TCE; the volatilization of TCE was less than 10%. No DCEs were detected either in the gas phase or in the pore water. This confirms that TCE might be removed by oxidation processes under these conditions (a3 and a4).

3.3.3 Factors effecting the MCB and PCE removal

Volatilization of MCB amounted less than 1% of the total MCB removal. This indicates that MCB was removed in the pore water of the wetland system, which can be assumed dominated by microbial degradation. Furthermore, redox potential showed to be an important parameter for the removal of MCB. It was shown that redox potential can be used to correctly predict the major dechlorination pathway of chlorobenzenes in anaerobic microbial ecosystems, which the organisms that use the electron acceptor with the highest redox potential have potentially a clear energetic advantage over organisms that use an electron acceptor with a lower redox potential (Dolfing & Keith Harrison, 1993). Highest MCB removal efficiency was reached when the redox potential was around 500 mV in our model wetland system (Figure 3.3-1), regardless of the presence of plants. This means that plants do not have a direct influence on the removal of MCB. There was also no difference with the addition of electron acceptors (nitrite and nitrate). MCB biodegradation has shown a decrease with decreasing pH in microcosm experiment from 6.7 to 3.8 in mineral medium with low hydrogen carbonate, while pH decrease slowly from 6.7 to 5.8 in groundwater (Balcke et al., 2004). In our model wetland system pH is varied from 7.1 to 5.2 when the highest removal efficiency for MCB was obtained (Figure 3.3-1) and MCB removal even decreased with the increase of pH (second planted phase A). This means the microorganisms for the degradation of MCB were not sensitive within this pH range.

Sulphide accumulation inhibited the MCB removal efficiency (Figure 3.3-3). When the sulphide concentration accumulated to 14 mg/L, MCB removal efficiency decreased sharply (from 100% to 62%). This might be due to the sulphide toxicity on the microorganisms which degrade MCB. Alternatively, the sulphide toxicity on the plants may also effect the removal of MCB indirectly. Because the plant activity (water loss by transpiration) was also inhibited by the sulphide accumulation, subsequently, the release of oxygen by the plants also may have been affected, thus, the MCB removal efficiency probably was also detrimentally influenced.

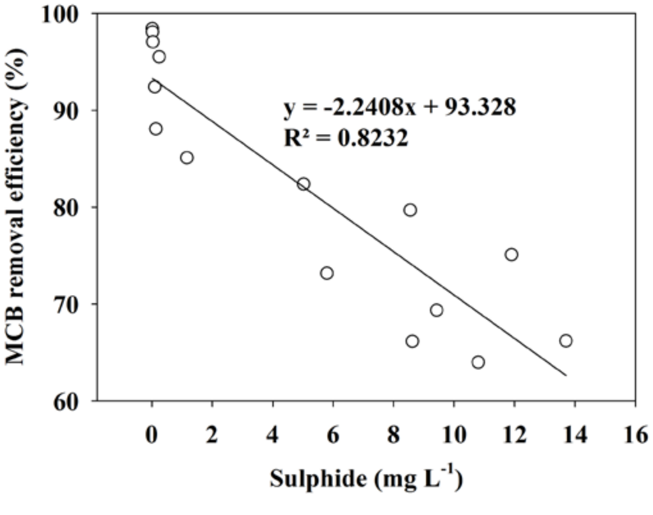

Figure 3.3-3 Relationship between sulphide concentration (measured) and MCB removal efficiency (from 29th June to 12th August, 2011)

Redox potential seemed not to be a crucial parameter for PCE removal, as complete removal of PCE was observed under two very different conditions in our model wetland (around 400 mV and -200 mV). Normally, dechlorination of PCE prefers more anaerobic conditions with the optimal range for anaerobic PCE dechlorination between -220 mV to -50 mV (Bouwer, 1994). However, a theoretical maximum redox potential for the transformation of PCE to TCE was reported at around 580 mV (Vogel et al., 1987). Therefore, the model wetland demonstrated effective conditions for PCE dechlorination under a varied range of redox potential.

It seems that pH might not be an very important parameter on influencing of PCE dechlorination, as similar PCE removal efficiencies were obtained on big range of pH (5.5-7.0) (Table 3.3-1, Figure 3.3-1). Anyhow, the highest PCE removal (TCE detected) was obtained in a very narrow range (around 6.5). Laboratory studies have demonstrated that the optimal pH range for anaerobic microbes is from 6.5 to 7.5, and maximum PCE dechlorination was found at pH 6.8 (Zhuang & Pavlostathis, 1995). All these observations confirm our results.

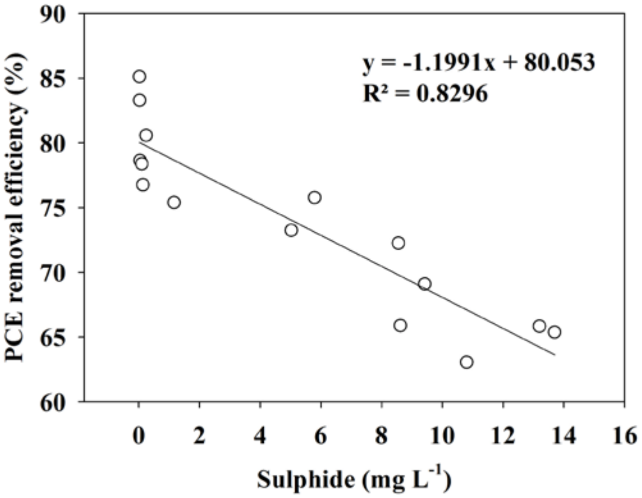

Figure 3.3-4 Relationship between sulphide concentration (measured) and PCE removal efficiency in a laboratory-scale model wetland (from 29th June to 12th August, 2011)

Sulphide has two-sided effects on PCE removal. On one side, sulphide has negative effect on the dechlorination process (Ismail & Pavlostathis, 2010). In our model wetland, when sulphide concentration increased from 0 mg/L to 14 mg/L, the removal efficiency of PCE decreased sharply from 85% to 63% (Table 3.3-1, a1 to a2; Figure 3.3-4). On the other hand, when sulphide concentration decreased from 14 mg/L to almost 0 mg/L PCE removal efficiency increased from 63% to 100% under the middle of the second planted phase A (Table 3.3-1, a3). This indicates that the microbial dissimilatory sulphate reduction even can stimulate PCE dechlorination. Meanwhile, we can assume that dissimilatory sulphate reduction and PCE dechloriantion are competing for electron donors, as chlorinated compounds are stronger oxidants than nitrate and on the basis of thermodynamic considerations, chlorinated hydrocarbons have been shown to act as terminal electron acceptors in a respiratory process (Bhatt et al., 2006). In our model wetland system, electron donating was mainly provided by the released organic carbon from the plants. At the beginning of the experiment, dissimilatory sulphate reduction was probably stimulated and intensified by the high plant activity. It did, however, go down when the plant activity was inhibited by the accumulated toxic sulphide. Afterwards, it can be assumed that due to the lack of carbon source, the dissimilatory sulphate reduction was stopped. While PCE dechlorination continued at the later phase of the second planted phase A (a3 and a4).

3.3.4 Influence of nitrate and nitrite on dissimilatory sulphate reduction

Both nitrate and nitrite out competed dissimilatory sulphate reduction successfully (Figure 3.3-1) and there was no difference in the addition of nitrate and nitrite on the influence of sulphate reduction. A similar observation was found in an activated sludge immobilized agar gel film, with the addition of 1000 µM nitrite (46 mg/L) and nitrate (62 mg/L); in this experiment the sulphide concentration decreased from 12 mg/L to zero (Okabe et al., 2003). However, this study shows that sulphide concentration decreases might be from the direct oxidation by nitrite and nitrate, while in our system, nitrite and nitrate are competing with sulphate for electron donors.

Sulphide accumulation already at relatively low concentrations can inhibit ammonium removal very quickly; 0.5 mg/L sulphide already observed to be toxic for microbial ammonium oxidation in laboratory-scale CW treating artificial wastewater (Wiessner et al., 2008). At the experimental phase A, when the dissimilatory sulphate reduction started, the ammonium removal was inhibited immediately (Figure 3.3-1). The elevated ammonium concentration (up to 110 mg/L) in the outflow probably came from the plant organic nitrogen (ammonification from plant roots). This confirms the sulphide toxicity on the plants, which resulted in the decrease in the water loss (Figure 3.3-1) under the conditions of experimental phase B. Sensitivity of sulphide accumulation on ammonium removal was also observed clearly in the phase a1, it shows a close sigmoidal (Chapman 3-parameter) curve by the regression analyses (Figure 3.3-5). The ammonium removal efficiency can decrease from 95% to 0% (Figure 3.3-1), which is more intense than previous result (75% to 35%) (Wiessner et al., 2005).

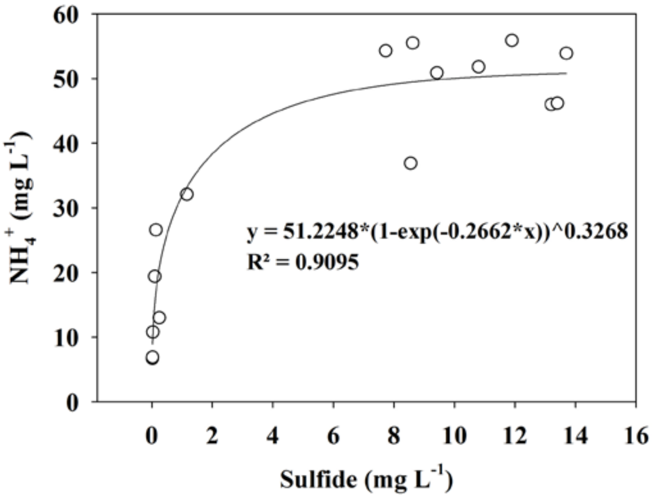

Figure 3.3-5 Relationship between sulphide concentration and ammonium concentration (measured) in a laboratory-scale wetland (29th June to 12th August, 2011)

3.3.5 Conclusions

Both highly chlorinated and low chlorinated hydrocarbons can be removed by CWs (planted fixed reactor) under appropriate conditions. Volatilization of MCB seems to be negligible (less than 1%) regardless of the presence of plants, but volatilization may play an important role in the removal of PCE (up to 95% without plants). Plants can prevent the volatilization of PCE significant, a relatively low PCE volatilization (less than 1%) can be reached after the adaption of plants. Dechlorination of PCE to TCE could only be detected in the presence of plants, which confirms that plants release an organic carbon source for dechlorination. PCE dechlorination was detected under both denitrification and dissimilatory sulphate reduction conditions. Volatilization seems to be the main process for the removal of TCE in the absence of plants and when the plants are under stress by sulphide toxicity.

Plants can stimulate dissimilatory sulphate reduction by the release of organic carbon from their roots. However, the accumulation of sulphide, as the result of microbial dissimilatory sulphate reduction, stimulated by the released organic carbon from the plants, is toxic to plants. This also inhibits ammonium, MCB and PCE removal. It should be noted that PCE dechlorination was not effected when the sulphide concentration was less than 4 mg/L. Maybe more precise parameter are needed to describe the effect of sulphate reduction on the dechlorination process (Ismail & Pavlostathis, 2010).

4 Summary

There is a high interest to find alternative strategies to the usually relatively expensive physico-chemical processes used for the treatment of waters contaminated by VOCs. Because of their volatility and recalcitrance to biological degradation, usually waters contaminated by VOCs were not treated by constructed wetland (CW) technology. Nevertheless, the task of this PhD work was to check the possibility to treat such waters in CWs and find out the specific conditions and limitations.

The results show that CWs are able to treat waters contaminated by several chlorinated hydrocarbons, benzene and MTBE in principle. The detailed conclusions concerning the special conditions and limitations are described below.

Benzene and MTBE removal in the different types of constructed wetlands

Floating plant root mat (FPRM) showed significant higher removal efficiency for benzene and MTBE than unplanted horizontal subsurface flow (HSSF) CW, and the FPRM produced similar treatment efficiencies as the planted HSSF CW for benzene removal but better treatment efficiency for MTBE removal. However, the removal was very dependent upon seasonality. Furthermore, oxygen was limited for an optimal microbial degradation of benzene and MTBE both in FPRM and HSSF CW.

The main removal process for benzene and MTBE via oxidative microbial degradation is speculative due to 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. However, volatilization plays an important role in MTBE removal in the new established FPRM. It can be assumed that the volatilization rate decreases with the age of the root mat, which is due to the better root mat development (root density and height) which enhances the biodegradation.

With the increase of water level, the total removal efficiency of benzene and MTBE was not significantly affected in FPRM. The volatilization of benzene and MTBE was decreased with the increase of water level, which confirmed the improvement of microbial degradation. This is also because of the better root mat development under the higher water level.

4 Summary

Behaviour of low chlorinated benzenes in the different types of constructed wetlands
Plant root mat filter (PRMF) showed a higher potential for the removal of low-chlorinated benzenes (MCB, 1,2-DCB, 1,4-DCB, and 2-chlorotoluene) than HSSF CW. This probably due to the more oxic conditions in the PRMF than in the HSSF CW.

The tidal flow mode with a cycle period of 7 days had no influence on the removal efficiency of low-chlorinated benzenes in the HSSF CW. Intensified tidal operation with 2.5 days cycle regime increased the oxygen concentration in the pore water, thus, it enhanced the MCB removal efficiency in the HSSF CW significantly especially within the first 2 m from the inlet. This higher tidal mode frequency also improved the removal of MCB to some extent in the FPRM.

The volatilization of MCB was negligible (less than 1%) regardless of the presence of plants in laboratory-scale model wetlands.

Behaviour of PCE in the different types of constructed wetlands
The HSSF CW exhibited robust capability in the removal of PCE; complete removal of PCE was achieved after a short flow path of 0.5 m. There were significant changes of operation mode from continuous to tidal flow on PCE removal in the HSSF CW. Complete PCE dechlorination was shown in the HSSF CW by the detection of ethene. VC accumulated and decreased again during the flow path of 4 m.

The PRMF showed less removal efficiency for PCE than the HSSF CW. Nevertheless, during the summer period PCE was also completely removed as was the case in the HSSF CW. In comparison to the HSSF CW, not all dechlorination products could be detected in the PRMF, especially VC and ethene which probably were preferably metabolized by microorganisms via an aerobic pathway. This can be assumed due to the higher redox conditions found in the PRMF in comparison to the HSSF CW. The PRMF seems to be more suitable for the removal of contaminants which need oxic conditions like low chlorinated hydrocarbons as VC, mono- and dichlorobenzenes, etc. for their microbial degradation, while the HSSF CW seems to provide better conditions for microbial anaerobic processes like the dechlorination of highly chlorinated hydrocarbons as PCE.

Tidal flow mode with 2.5 days cycle regime increased the removal of PCE and its metabolites significantly in the FPRM, and it also achieved better removal in the HSSF CW. TCE and *cis*-1,2-DCE were detected as well as in the PRMF and the FPRM during continuous flow conditions even after a flow path of 4 m, but during tidal flow operation both compounds were almost completely removed after the flow path of 4 m. Furthermore, no VC and ethene were detected in the PRMF and FPRM.

Volatilization can play a major role in the removal of PCE (up to 95%) in model wetlands. However, plant can prevent the volatilization of PCE to some extent, with the adaption of plants, volatilization only plays a minor role for PCE removal (less than 1%) when the dechlorination of PCE to TCE is predominant. PCE dechlorination was detected under both denitrification and dissimilatory sulphate reduction conditions. Volatilization seems to be the main process for the removal of TCE in the absence of plants and when the plants are under stress by sulphide toxicity.

Formation of sulphide and its effects in the different types of constructed wetlands

Plants can stimulate the microbial dissimilatory sulphate reduction by release of organic carbon (rhizodeposition products); this was validated in laboratory- and pilot-scale CWs. The sulphide accumulation can reach a toxic level to plants, which was confirmed by the decrease of plant activity (water loss). It also decreased the treatment performance for the removal of ammonium, MCB and PCE. Anyhow, dechlorination seemingly was stimulated by dissimilatory sulphate reduction when sulphide concentration was less than 4 mg/L. A more intense tidal operation (with 2.5 days cycle regime) has shown to be a useful approach to decrease dissimilatory sulphate reduction activity.

In conclusion, PRMF and FPRM as variant of CW without any media could be a cost-competitive variant and alternative for the treatment of distinctively contaminated waters, for example, even for the volatile contaminants benzene, MTBE and chlorinated hydrocarbons. Nevertheless, further process optimization is necessary especially in this case to fulfill national regulations for discharging the wetland effluent into nature receiving streams.

5 Outlook

There is a high interest in low-cost technologies for the treatment of contaminated waters. Methanogenic fermentation of effluents highly loaded with organic compounds, treatment ponds coupled with the production of duckweed for fodder are some approaches to reduce overall treatment costs. Despite of their high land area need, constructed wetlands (CWs) gain also an increasing interest for water treatment. Dependent on their magnitude they bear the potential of using their plant biomass for several purposes.

In this PhD work it could be shown that CWs are also an alternative option to other technologies for the treatment of selected VOCs – compounds characterized by their volatility and often also by their recalcitrance to biodegradation. But because of their inherent mosaic multi-redox gradient principle combined with microbial biomass retention, CWs bear a high potential also to remove recalcitrant compounds.

By this work it could be shown that the CW technology even after some decades of research and application bears potentials for treatment process intensification and reduction of treatment costs.

The most important operational variables that can be used to influence the treatment performance in CWs are water level, flow rate, media type, and plant species. Water level affects the HRT, the atmospheric oxygen diffusion and the plant diversity. So far, no sufficient research has been carried out to determine the complex effects of water level, flow rate and loading when using floating plant root mat (FPRM) and plant root mat filter (PRMF). Therefore, the effects of these operating parameters on the removal of further different pollutants in these both soil free systems have to be characterised.

Much more research is needed with focus on the non-floating PRMF. The specific surface area of the root mat is an important parameter for the biofilms. The more specific surface area the root mats have, the more microorganisms are able to attach. Also the diversity of the microbial community will be influenced by the ratio of the root mat surface to the total water body. The root mat can be a filter in the system when the root mats touch the water body bottom. In this special case with no short-cut flow of the water, the plants could be more affected by toxic pollutants. A better understanding of the structure of the root mats will assist the understanding and optimization of the contaminant removal processes in the root mats.

5 Outlook

Higher ambient temperature can cause a higher water loss (evapotranspiration) in the FPRM/PRMF, as no better temperature insulating soil in the system is available to keep the temperature more steady. Gas exchange is performed seemingly more directly in FPRM/PRMF without the presence of soil particles, gas diffusion rates from the water phase to the atmosphere are higher. This may enhance the removal performance for volatile compounds, however, the volatilization rates of such compounds and their potential transformation within the root mats have to be investigated in more detail.

Currently, there is no detailed and validated design basis available for the FPRM and especially for the PRMF to achieve desired pollutant removal objectives. As a result, more research is needed to understand the removal process and dynamics of different pollutants and clarify the relationships between the water level, the loading rate per unit surface area, hydraulic residence time, the removal rates and achievable effluent quality.

Due to the fact that CW, FPRM and PRMF can be potential habitats for pest mosquitos further work needs to be completed to investigate this issue.

By improving knowledge in these above mentioned aspects it will be in future possible to broaden the application fields of CWs and give better advices to engineers in which special cases CWs can be an advantageous treatment option in comparison to the numerous other available technologies.

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Appendix

Appendix 1: Main characteristics of floating plant root mats treatment systems, ponds, ponds with free floating plants and constructed wetlands

	FPRMs	Facultative ponds	Ponds with free floating plants	HSSF CWs
Plant species	helophytes such as in soil based CWs (*Phragmites*, *Typha*, etc.)	No but algae	*Eichhornia crassipes*, *Lemna* spp., etc.	Emergent water plants (*Phragmites*, *Typha*, etc.)
Importance of plants for the treatment process	High (varies with the water level)	No	Moderate	High (varies with the water logged soil depth)
Planting medium	No	No	No	Yes
Water level (m)[a], (Kadlec & Knight, 1996)	0.3−2.5	1.5−5	0.4−1.2 (*Eichhornia*) 1.2−1.8 (*Lemna*)	Equal or less than the soil bed depth
Hydraulic retention time (days)[a]	Several days	30−180	30-60	Several days
Removal of sludge	Easy/moderate	Easy	Easy	Problematic
Water storage capacity of the system	> 50%	Almost 100%	Almost 100%	< 50%
Costs (Kadlec & Wallace, 2009)	Low	Low	Moderate	High

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[a] USEPA, http://www.epa.gov/nrmrl/pubs/625r00008/html/tfs7.htm (Accessed 17th October 2011)

Appendix

Appendix 2: Examples of treatment performances of floating plant root mats (FPRMs)

Water types (Country)	Parameters	Concentration (mg/L)		Load ($g/m^2/d$)			Efficiency (%)	Scale (length×width×depth)	Remarks	Reference
		In	Out	In	Out	Removed				
Nitrified meat processing effluent (New Zealand)	TN	197	101	11.2	5.9	5.3	47	Pilot scale (2.4 m×1.2 m×0.4m) 1.15 m^3/d	Mean of 23 samples, temperature: 9.7 - 21°C, hydraulic loading rate: 5.7 cm/d, HRT: 7 d	(Van Oostrom, 1995)
	NH_4^+–N	60	39	3.4	2.2	1.2	35			
	COD	405	133	23.5	8	15.5	66			
	BOD_5	38	24	2.2	1.4	0.8	36			
	TSS	321	13	18.4	0.8	17.6	96			
Secondary effluent (Turkey) *Canna*	NH_4^+–N	110	64.5			0.0770	41.7	Lab scale (1.2 m×0.8 m×0.2 m)	two kinds of plants: *Canna* and *Cyperus*	(Ayaz & Saygin, 1996)
	NO_3^-	1.8	2.1			-0.0005	-16.7			
	NO_2^-	1.6	-			-	-			
	PO_4^{3-}	14.4	6.7			0.0128	53.5			
	SO_4^{2-}	12.9	21.2			-0.0138	-64.3			
Cyperus	NH_4^+–N	110	74.3			0.0607	32.9			
	NO_3^-	1.8	16.6			-0.0247	-822.2			
	NO_2^-	1.6	4.4			-0.0047	-175			
	PO_4^{3-}	14.4	12.5			0.0032	13.2			
	SO_4^{2-}	12.9	21.5			-0.0143	-66.7			
Stabilisation anaerobic pond (Uganda)	TP	3.5	0.88			0.12	74.9	Lab scale (0.0962 m^2 ×0.3 m)	40 L buckets, operated in a vertical flow mode	(Sekiranda & Kiwanuka, 1997)
	PO_4^{3-}	1.2	0.44			0.04	63.3			
	NH_4^+–N	62.1	1.31			2.90	97.9			
	NO_3^-	1.9	0.85			0.05	55.3			

Appendix

Motel effluent (Australia)	TN	99	6					Lab scale 20 L No depth mentioned	Surface area 0.04 m^2, 4 d , start volume 14 L, end volume 9.6 L	(Hart et al., 2003)
	TP	10	1							
	NH_4^+–N	93	1							
	TN	52	6.5					Lab scale 240 L No depth mentioned	14 d, start volume 165 L, end volume 111 L	
	TP	21.8	19.3							
	NH_4^+–N	60	6							
	TN	46	22			3.75		Lab scale 20 L/min No depth mentioned	8 d, start volume 1110 L, end volume 981 L	
	TP	5.9	4.1			0.28				
	NH_4^+–N	48	11							
	COD	248	76							
Swine lagoon wastewater (USA)	TN	160				1.16		Pilot scale (Diameter: 1.65 m, height: 0.91 m)	Every two weeks, half of the liquid in each tank was replaced with new wastewater	(Hubbard et al., 2004)
	TP	30				0.17				
Effluent from stabilization ponds (Uganda)	NH_4^+–N	19.1	7.6	2.2	0.69	1.51	68.6	Pilot scale (3 m×2.5 m×0.2 m; 3 m×2.5 m×0.35 m)	Hydraulic loading rate: 11.5 cm/d, HRT: 2.7 d	(Kyambadde et al., 2005)
	NO_3^-–N	0.04	0.04	0.005	0.004	0.001	20.0			
	NO_2^-–N	0.41	0.60	0.054	0.047	0.007	13.0			
	TN	31.0	10.3	3.57	0.93	2.64	73.9			
	PO_4^{3-}	19.0	6.4	2.19	0.58	1.61	73.5			
	TP	23.8	9.1	2.74	0.83	1.91	69.7			
	BOD	320	54	37.0	5.0	32	86.5			

Appendix

Nitrate-rich agricultural runoff (China)	COD	41.8	34.8			1.26	17	Lab scale (2 m×1 m×0.6 m)	HRT: 3 d	(Yang et al., 2008)
	NH_4^+–N	0.93	1.19			-	-			
	TN	3.76	2.59			0.21	31			
	TP	1.25	1.17			0.01	8			
	COD	53	40.2			3.47	24		HRT: 2 d	
	NH_4^+–N	0.91	1.31			-	-			
	TN	4.57	2.95			0.44	35			
	TP	1.35	1.16			0.06	15			
	COD	69	36.7			17.46	47		HRT: 1 d	
	NH_4^+–N	1.38	0.54			0.45	60			
	TN	7.94	2.86			2.74	64			
	TP	1.54	1.34			0.11	13			
Polluted river water (China)	TN	8.71	4.32			0.91	50.4	Lab scale (1.2 m×0.8 m×0.5 m)	Water volume: 0.48 m^3	(Sun et al., 2009)
	NH_4^+–N	2.75	0.00			0.57	100			
	NO_3^-–N	2.46	1.91			0.11	22.4			
	NO_2^-–N	0.76	0.72			0.01	5.3			
	COD	38.1	22.9			3.17	39.9			
Domestic wastewater (Belgium)	TN	21.8	13.1				42.3	Lab scale (1.5 m×0.8 m×0.9 m)		(Van de Moortel et al., 2010)
	NH_4^+–N	16.1	10.8				34.9			
	NO_3^-–N	0.37	0.20				-			
	TP	2.16	1.77				22.1			
	COD	81.3	46.6				52.9			

Appendix

Urban sewage (Spain)	COD (winter)	500	80			21.1	COD (winter)	Mesocosm-scale (1.3 m×0.8 m×0.3 m)		(Hijosa-Valsero et al., 2010)
	COD (summer)	100	20			4.2	COD (summer)			
	BOD (winter)	200	35			8.7	BOD (winter)			
	BOD (summer)	80	8			3.2	BOD (summer)			
	TSS (winter)	300	25			23.8	TSS (winter)			
	TSS (summer)	60	6			2.8	TSS (summer)			
Domestic wastewater Campus University (Colombia)	TSS	114	8.44			7.33	92.6	Pilot scale (3.0 m×0.65 m×0.5 m)	HRT: 4 d	(Cubillos et al., 2011a)
	NH_4^+–N	75	47.10			2.2	37.2			
	NO_3^- –N	9	4.01			0.38	55.5			
	TN	77	43.51			2.39	43.5			
	BOD	111	16.65			6.45	85.0			
	COD	272	68.54			14.16	74.8			

NH_4^+–N, ammonium nitrogen; NO_3^-–N, nitrate nitrogen; NO_2^-–N, nitrite nitrogen

Curriculum Vitae

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Conferences and workshop

Oral presentations

The 9th International conference on Phytotechnologies, 2012, 11-14 Sep, Hasselt, Belgium.
"Evaluation of floating plant root mat for the treatment of groundwater contaminated by benzene and MTBE."

The 6th IWA International Conference for Young Water Professionals, 10-13 July 2012, Budapest, Hungary. **As the best platform presenter of the IWA-1st Danube - Black Sea Regional Conference**

The 8th UFZ DocConference, 2012, 26 March, Leipzig, Germany. “Catch the recalcitrant organic contaminants: sit down or swimming”

The 4th Annual CITE (Chemicals in the Environment) Conference, 2012, 27 March, Leipzig, Germany. “Floating root mat for the treatment of water contaminated by volatile organic compounds”

Joint Meeting of Society of Wetland Scientists, Wetpol and Wetland Biochemistry Symposium, 2011, 3-8 July, Prague, Czech Republic. “Evaluation of plant root mat and horizontal subsurface-flow constructed wetlands for treating groundwater contaminated with benzene and MTBE”

IWA-1st Danube - Black Sea Regional Young Water Professionals Conference, 2011, 14-15 June, Bucharest, Romania. “Comparsion between plant root mats and horizontal subsurface-flow constructed wetlands for treating groundwater contaminated with Benzene and MTBE”

Poster presentation

Pan-American Conference on Wetland Systems for water quality improvement, management and treatment**.** 2012, 26 Feb. – 1 Mar. Pereira, Colombia. “Comparison of plant root mat filter and horizontal subsurface flow constructed wetland for treating groundwater contaminated with monochlorobenzene”

The 7th International conference on Phytotechnologies, 2010, 26-29 Sep, Parma, Italy. “Treatment of groundwater contaminated by volatile organic compounds in pilot scale constructed wetlands – concept and first results of PhD work”

Workshop

Career and Leadership Course, 19-21 September, 2012, Hofgeismar, Germany

Research Management Training Workshop, 12 - 13 September, 2011, Hamburg, Germany