The Fate of MTBE and BTEX in Constructed Wetlands

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Abstract: Hydrocarbon contamination of water resources is a global issue. These compounds are generated and discharged into the environment in industrial areas from chemical and petrochemical plants, oil refineries, power plants, and so forth. Fuel hydrocarbons, namely, BTEX (benzene, toluene, ethylbenzene, and xylenes) and MTBE (methyl *tert*-butyl ether), are commonly found in groundwater, posing environmental and health risks to humans and ecosystems. Nature-based technologies represent an alternative solution, providing high efficiency, an environmentally friendly character, simple operation, and cost efficiency, which are characteristics particularly desired by the international petroleum industry. This article discusses the use of the green technology of constructed wetlands to remediate water polluted with hydrocarbons. Although the number of related international experiences and studies is limited, the article presents the latest developments of wetland technology for the removal of MTBE and benzene-BTEX. The discussion includes the overall efficiency of the different wetland types that have been tested and used, the main transformation and removal processes that regulate the fate of BTEX and MTBE in constructed wetlands, and the potential for future investigations.

Keywords: constructed wetlands; BTEX; benzene; MTBE; industrial wastewater; petroleum industry; hydrocarbons; nature-based solutions

1. Introduction

Hydrocarbons are commonly found water contaminants due to their extensive use. They consist of simple compounds of carbon and hydrogen or complex compounds with varying physicochemical properties and are generally classified into aromatic, alicyclic, and aliphatic hydrocarbons. Light hydrocarbons (i.e., having up to 16 carbon atoms) may have higher volatility and solubility. Some hydrocarbons can be toxic; hence, they pose a risk to the environment [1]. In water, they can be free-floating, dissolved, emulsified, or adsorbed to suspended solids. Larger molecules are typically free, and smaller ones can be emulsified in water. Hydrocarbon contamination typically occurs in areas with industrial activity, for example, close to chemical/petrochemical plants, oil refineries, power plants, manufacturing industries, plastic and steel production facilities, and cooling plants. The continuous demand for oil and gas supply increases the environmental concerns, while accidental spills, partial treatment, and illegal discharge introduce these compounds to the surface and groundwater bodies. Hydrocarbons can also reach surface or groundwater resources through stormwater runoff; spills from roads, tank farms, airport surfaces, and so forth; and transportation [2,3], even near petrol stations. Besides the risks to human health, hydrocarbons can also affect various aquatic ecosystems.

BTEX (benzene, toluene, ethylbenzene, and xylenes) and MTBE (methyl *tert*-butyl ether) are fuel hydrocarbons often detected in water [4,5]. MTBE and BTEX are highly soluble and mobile in water, and both can have toxic effects (i.e., BTEX is related to carcinogenesis); hence, they are regulated contaminants in drinking water (200 and 5 μg/L, respectively [6,7]). Another hydrocarbon compound is phenols, which are found in outflows from oil refineries and petrochemical industries; effluents

from tanneries [8], olive mills [9], and pulp and paper mills [10]; as well as some pesticides and disinfectants [11]. Phenols can also be toxic and a maximum allowable concentration in water has been introduced (0.001 µg/L [12]).

Different physicochemical technologies are applied to remove light hydrocarbons from water, including membranes, porous media adsorption (e.g., on activated carbon and zeolites), advanced oxidation processes (e.g., UV, H_2O_2, and O_3), chemical oxidation, air stripping, and vapor extraction [3,13–15]. These technologies are in general efficient; however, they usually require experienced and skilled personnel, are based on large and sophisticated mechanical equipment, usually demand a high initial investment, have high operation and maintenance costs, and consume large amounts of external energy, which often cannot be covered from the economic and/or technical aspect, particularly in small-scale installations [15]. Hence, the use of alternative and, at the same time, sustainable technologies is a continuously growing need.

Constructed wetlands (CWs) represent an effective green technology with high treatment capacity. CWs can be classified based on the vegetation type and the flow patterns through the system to (a) surface flow constructed wetlands (SF CWs) and (b) subsurface flow constructed wetlands (SSF CWs) [5]. The typical design of SF CW systems consists of a water column (10–50 cm) above a substrate layer (usually soil). SSF CWs are typically gravel beds with vertical flow (VF CW) or horizontal subsurface flow (HSSF). According to the vegetation type, further classification includes emergent macrophyte wetlands and submerged macrophyte wetlands. The most common systems are those with rooted emergent macrophytes [5]. When more than one CW type is combined in one facility, this is called a hybrid wetland system.

CWs generally possess smaller investment requirements and minimal operation and maintenance costs compared with conventional methods [1,5]. CWs are characterized as nature-based systems providing diverse environmental and financial benefits and are widely implemented for domestic and/or municipal wastewater treatment [5]. Their treatment potential is nowadays better realized, which moves the focus towards applications for different industrial wastewater effluents [16]. Particularly, there is the strong potential to use this green technology for petroleum industry effluents that contain various hydrocarbons. The goal of this article is to present the current knowledge and technological status of CWs applied for the removal of light hydrocarbons from water, namely, MTBE and benzene-BTEX.

2. Fate of Benzene in Constructed Wetlands

Benzene (C_6H_6), a BTEX compound generated from gasoline production, is frequently detected in groundwater [17,18]. It has high water solubility (1780 mg/L at 20 °C) and very high mobility [19]. Benzene is the most toxic BTEX compound and can be biologically degraded [20] under oxic [21] or hypoxic environments [22]; however, it is highly recalcitrant under anoxic conditions [23,24].

Different physical, chemical, and biological processes are applied for benzene transformation and/or removal (e.g., sorption, volatilization, and dilution) that change its phase. Plants also assimilate benzene in their tissues and through transpiration transfer and release it to the atmosphere. Microbial degradation is believed to be the most effective process, allowing even for its complete removal. Biodegradation strongly depends on various physicochemical factors (e.g., temperature; oxygen levels; salinity; nutrients; pH; and the chemical composition, physical state, and concentration of the contaminant) and on biological factors, including the composition and adjustability of microorganisms [25].

CWs have also been successfully implemented for the remediation of waters containing benzene. As a nature-based technology, CWs generally remove organic contaminants through different processes initiated by the interactions between plants and microorganisms in the root system [26–29]. CWs create the appropriate environment for the growth of microorganisms that biodegrade organic compounds [30]. Bacteria that degrade volatile organic compounds (e.g., benzene, toluene, ethylbenzene, and p-xylene) have been detected in the plant rhizosphere [31,32]. The most abundant species are those of *Pseudomonas*, representing more than 85% of the degrading bacteria in polluted aquifers [33]. Additionally, isotope studies have revealed that most benzene fractions can be degraded under aerobic conditions [18,34].

The plants in CWs can also uptake compounds such as benzene (phytotransformation), concentrate it in their tissues (phytoextraction), and release it to the atmosphere through their transpiration. Plant uptake is closely related to the compound's lipophilicity; the low octanol–water partition coefficient logKOW of benzene is between 0.5 and 3 (i.e., 2.13), implying plant uptake [35–37]. Benzene can also be released directly from the substrate media surface, while phytovolatilization via plant stems and leaves also occurs. This process relates to substances being rapidly translocated (logKOW < 3.5) and to high vapor pressure (Vp > 1.01 kPa) [38] or high Henry's law constant (KAW > 10–5) [39]. The values for benzene (KAW = 0.22, Vp = 12.7 kPa at 25 °C) [35] imply that phytovolatilization is a possible benzene removal process. Studies have shown that this process is responsible for a major part of both benzene and MTBE emission [40]. It has been found that under a hydraulic residence time exceeding 1 day, the role of volatilization is most important in VF CWs [41], although lower rates (<5%) have also been estimated [42,43]. On the other hand, the contribution of volatilization in benzene removal was assessed at around 1% in HSSF CWs [44].

Table 1 shows studies that can be found in the international literature on benzene removal with different CW types. As can be seen, though all wetland designs have been tested and applied, most of them are with subsurface flow, both horizontal and vertical flow. The reported results clearly indicate the high treatment and removal capacity of CWs for benzene (or BTEX) from water.

Table 1. Studies on constructed wetland (CW) systems treating water contaminated with benzene.

Wetland Type Dimensions (L × W × D; m) [1]	Plant Species	Substrate	Flow (m³/day)	HRT [2] (days)	Influent (mg/L)	Removal Rate (%)	Reference
HSSF [3] CW (6 × 1 × 0.5)	*Phragmites australis*	gravel (67%) sand (25%) lignite (10%)	0.113	6	0.026	93	[34]
HSSF CW (5.9 × 1.1 × 1.2)	*P. australis*	gravel	0.528	10	10.2	72–82	[1]
HSSF CW (5 × 1.1 × 0.6)	*P. australis*	fine gravel, charcoal	0.144		20	81–43 (summer–winter)	[29]
Plant root mat (water depth 0.15 m)	*P. australis*	–	0.166		20	99–18 (summer–winter)	
HSSF CW pilot (7 × 1.7 × 1.1) full scale HSSF + SF CW (1.9 ha, d = 0.9)	*Salix, Phragmites, Schoenoplectus, Juncus, Cornus, Typha angustfolia*	gravel, sand	5.4 and 6000	1	0.17 (benzene) 0.47 (BTEX)	100 (below detection limit)	[45]
HSSF CW (4.8 × 7.2 × 0.6)	*P. australis, Typha latifolia*	clay soil, stones, gravel	1	1.5	0.6	57	[46]
HSSF CW (5 × 1.1 × 0.6)	*P. australis*		0.144		up to 24	1900 mg/day	[47]
HSSF CW (5 × 1.1 × 0.6)	*P. australis*	gravel	0.144	6	13	100 (summer)	[44]
Plant root mat (water depth 0.15)	*P. australis*	–	0.144			100 (summer)	
HSSF CW (7 × 1.7 × 1.1)	*Phragmites, Scirpus, Juncus, Cornus*	washed soil, sand, pea, gravel	5.5		0.395	61–81	[48]
VF CW [4] (H = 0.75, d = 0.1)	*P. australis*	stones, gravel, sand		1	1.3	85–95	[41]
VF CW (0.75, d = 0.1)	*P. australis*	stones, gravel, sand		3.5	1	73–89	[49]
VF CW (2.3 × 1.75 × 1.75)	*Salix alba*	granular media, clay, zeolite	up to 1.9		13.9	100	[43]
SF CW (1 × 0.6 × 0.8)	*Phragmites karka*	gravel, soil		8	66–45	48	[50]
SF CW [5] (4 × 12 × 0.45)	*P. australis T. latifolia*	soil	3		1.573 (benzene) 4.14 (BTEX)	93 92.4	[51]

[1] L × W × D: Length × Width × Depth, [2] HRT = hydraulic residence time, [3] HSSF = horizontal subsurface flow, [4] VF = vertical flow, [5] SF = surface flow.

As Table 1 shows, various benzene influent concentrations have been tested in CWs. High performance is in general achieved, while even complete benzene removal is reported in some systems. Considering that benzene is mainly removed via biodegradation under aerobic conditions, the VF CW design is preferable due to the good aerobic conditions in this wetland type caused by the

feeding method, that is, the wastewater is applied on the gravel surface and then drains vertically with gravity [5]. Aerated ponds and plant root mats are also two systems that have been evaluated [29]. Such natural treatment systems are also efficient, and sometimes the reported efficiency exceeds that of HSSF CWs, reaching almost up to 100% removal for an influent of 20 mg/L [24]. In general, it is reported that only 1% of benzene removal was attributed to volatilization in plant root mats, while benzene removal takes place mostly through aerobic biodegradation.

Seasonal variations also have an effect on benzene removal, with higher removal rates occurring at high temperatures. For values above 15 °C and during the warm season, the performance of both HSSF CWs [1,29,42] and VF CWs [41,52] is enhanced. Benzene removal in VF CWs is reported to be negatively correlated to dissolved oxygen variations and positively correlated to the pH and redox variations related to the season [52]. Considering that oxygen availability is a critical parameter [29], high temperatures favor plant growth and promote the establishment of microbial biofilm, increasing the biodegradation rate. SF CWs have also been found effective, with reported BTEX removal rates exceeding 90% [51].

Plants are another important parameter in benzene removal. Higher removal rates are generally found in planted than unplanted CWs [1,29,42,53–55]. Increased monochlorobenzene removal by 33% was reported in an HSSF CW that was planted with common reeds (*Phragmites australis*) compared with an unplanted unit [27,56]. Another study reported higher benzene removal by 5% in an HSSF CW planted with common reeds than in a *Typha*-planted unit [46], while the efficiency of the planted systems was increased by 23% compared with the unplanted. The same conclusions concerning plants' role have also been reported for SF CWs [50,51]. The positive role of plants is mainly attributed to direct plant uptake and oxygen supply through their root system, which creates favorable conditions for biodegradation in the rhizosphere [5]. Furthermore, a strong reduction of benzene with plant height was also found [46]. On the other hand, the role of plants seems to be less important in VF CWs, since such systems with common reeds showed no significant differences in benzene removal than the unplanted systems [41,52]. The vertical gravitational drainage and the short retention time between water, roots, and the substrate probably limit the extent of many processes, as also reported for VF CWs treating municipal wastewater [57]. Overall, the contribution of plants to benzene removal is mostly indirect, namely, they supply carbon for microbial metabolism and provide attachment areas for microorganisms along the extended roots where oxygen release takes place.

To summarize, various CW types have been found efficient in benzene removal from water. Biodegradation (i.e., microbial degradation) appears to be the main removal process. The VF CW design appears to be the preferable type due to the aerobic environment it provides; however, high removals have also been reported for other CW types. The published literature, though relatively limited, indicates the high treatment capacity; however, more studies are needed in order to adopt design specifications, considering that the performance is strongly affected by the influent load and the season.

3. Fate of MTBE in Constructed Wetlands

MTBE (methyl *tert*-butyl ether; $C_5H_{12}O$) is a fuel oxygenate that is typically used as an alternative to lead additives. MTBE has high water solubility (48 g/L at 25 °C [58]) and volatility (Henry's law coefficient of 0.026 at 25 °C [59]). The global production of MTBE was 21 million t in 1999 [60], but dropped to 12 million tons in 2011 when MTBE was banned in the United States [61]; however, the increasing demand in Asia over the last years is again gradually increasing its global production. Refineries are major release points of MTBE. Significant volumes are discharged into surface water or injected into deep reservoirs [13,62]. Storage tank spills, pipeline leakages, spills from various industrial and fueling facilities, and transportation accidents represent other point sources [13]. Nonpoint pollution sources, such as from urban stormwater and atmospheric deposition [59], are of less importance.

MTBE is highly persistent in the environment [3,13,59] and is frequently found in contaminated groundwaters in Europe and North America [19,63–66]. MTBE affects water taste and odor and may affect human health [13]; therefore, it is classified as a health hazard by the US EPA and has a maximum allowed concentration in drinking water (200 μg/L) in the United States and Germany [44]. Thus, MTBE removal from industrial effluents is required in order to avoid further environmental contamination before it reaches drinking water resources.

MTBE can be removed from water with different abiotic processes [3,13,58]. Activated carbon adsorption is widely used, though other media are also in use, such as resins, diatomite, or silica [66–69]. Although sorption does not produce any harmful by-products, it does not also completely destruct MTBE. Air stripping also shows limited efficiency [66,68], since MTBE has lower volatility than other volatile organic compounds. Membrane technologies are often used to address this limitation [61], while advanced oxidation processes lead to complete MTBE mineralization. However, these processes require expensive reactants and take place under specific conditions, and they may also result in the formation of undesired by-products. In addition, cost efficiency is also an issue for the various abiotic methods [66,68], especially when large volumes are considered for treatment.

Biological processes represent an alternative solution to MTBE removal. Microbial degradation (i.e., biodegradation) has been extensively studied in the laboratory [3,58,70–72], which confirmed its degradation potential under an aerobic environment. However, site-specific parameters affect the occurrence of aerobic MTBE biodegradation [73,74], while only a few microorganisms can utilize MTBE as their sole carbon source [75–77]. Moreover, microbial MTBE degradation is also feasible but slower under anaerobic conditions [58] and production of *tert*-butyl alcohol or other intermediates may take place. Although the number of field studies is smaller, it is generally indicated that in situ biodegradation occurs under aerobic [78] and anaerobic conditions [79]. Nevertheless, anaerobic conditions do not often result in high biodegradation rates, and increased oxygen supply may be required to enhance the process [80–82]. Phytoremediation studies have shown that various plant species, such as poplars [83,84], alfalfa [85], weeping willows [86], or conifers [87], remove MTBE from groundwater through their roots, but no evidence has been provided that MTBE is degraded within plant tissue [84–89]; rather, it is transpired, resulting in potentially harmful emissions. However, no plant toxicity effects have been reported [86].

Considering that aerobic biodegradation is an established removal process, CWs can be a potential treatment option. To date, only a few relevant studies are available in the international literature. Four parallel pilot subsurface flow CWs with upward flow were operated with a hydraulic residence time (HRT) of 1 day for the removal of petroleum hydrocarbons from refinery wastewater [48,89]. The CW units (10 m^2 area, 1 m depth) contained sand; were planted with willows, bulrush, rush, and dogwood; and contained an artificial subsurface aeration system. The pretreated inflow had an MTBE concentration up to 1.5 mg/L and average total hydrocarbons (including BTEX) of 45 mg/L. The MTBE removal was within the range of 15%–30%, lower than for other compounds. Higher removal rates were reported in the units with artificial aeration, while another layer of mature wetland sod improved the performance. Moreover, 40% MTBE removal was measured in systems of 1 ha area treating urban wastewater [90]. However, the MTBE inlet concentration was low (0.1 μg/L) (i.e., approaching the detection limit).

Another study investigated pilot-scale CWs located next to an industrial area with many industrial facilities and an old refinery, where intense groundwater contamination occurred with benzene, MTBE, and ammonium, among other organic compounds [91,92]. The experimental setup included several designs, such as aerated ponds [24], HSSF CWs, and VF CWs. Two VF CWs units were tested [44]: one unplanted with expanded clay as substrate media and one planted with willows (*Salix alba*) containing zeolite. The surface area of each VF CW was 4 m^2 and the depth was 1.75 m. Groundwater was fed every hour and was introduced 15 or 25 cm below the top of the substrate media surface, resulting in an unsaturated downflow. The hydraulic loading rate (HLR) applied was from 60 to 480 L/m^2/day, respectively, resulting in HRTs of a few hours in the control bed and up to 2 days in the

planted bed [28,91,93]. Contaminated groundwater was pumped onsite and fed both beds, with 3 mg MTBE/L, 14 mg benzene/L, and 51 mg ammonium/L on the average in the inflow. The removal of MTBE in the unplanted unit dropped from 97% (lowest HLR) to 75% (highest HLR). On the other hand, the unplanted bed reached a minimum 93% at all HLRs [44]. Higher removal rates were found for benzene (as previously shown).

A study of the flow patterns, transport, and reactions in these CWs and numerical model simulations indicated that the measured MTBE removals occurred mainly due to biodegradation, while emissions due to volatilization were practically insignificant [28,91]. For this, an upper substrate layer in the unsaturated CW was needed to filter the vapor phase of the organic compounds, which was confirmed in the laboratory [94]. Considering the numerical model results, the filter media and the water injection point are important parameters that affect the efficiency of these systems [95].

The pilot HSSF CWs (5 m^2 area, 0.5 m depth) tested in the same experimental facility contained fine gravel, were planted with *P. australis*, and were operated under an HLR of 30 L/m^2/day and 6 days HRT [29]. A plant root mat of the same area was also examined. The inflow concentrations were 4 mg MTBE/L, 20 mg benzene/L, and 45 mg ammonium/L. The CWs performance presented high variations with seasons; the highest values occurred in summer months. The CW containing gravel showed an MTBE removal of 17% in summer, which was slightly higher than the MTBE removal in the unplanted system (8%) but lower compared with benzene and ammonium, without any detected improvement when some media additives were used (charcoal and iron(III)) [29]. On the other hand, the plant root mat reached an MTBE removal rate of 82% for the same period.

The results indicated that volatilization was promoted by wetland plants [40], though it was not a significant contributor to the measured removals in the gravel-based CW beds compared to biodegradation and plant assimilation [41]. In the plant root mat, most of the removal was attributed to volatilization initiated by the direct contact between the aqueous and vapor phases. Other investigations at the same area [42,96] reported similar findings, showing that higher removal of MTBE (up to 33% [96] and 93% [42]) was achieved through microbial community adaptation in the planted gravel bed after 3–4 years of operation. A laboratory-scale CW experiment with the same contaminated source indicated that MTBE removal (as well as benzene and ammonium) is improved through the combination of microbial electrochemical technology with a CW system [97].

Overall, the existing works indicate that MTBE is removed in CWs. Biodegradation appears as the dominant removal process, although with lower degradation rates compared with other petroleum hydrocarbons. The VF CW design seems to be more efficient. However, the number of field studies is relatively low to allow for a complete evaluation of MTBE fate in various CWs.

4. Effect on MTBE and BTEX Fate by Other Compounds

MTBE and BTEX are often present with other compounds in contaminated water. MTBE is often found in groundwater with other gasoline contaminants (e.g., BTEX [98]), which increases the water complexity since various interactions and/or interferences occur between the different contaminants.

Ethylbenzene or xylenes (BTEX compounds) have been found in water containing MTBE, resulting in complete inhibition of MTBE degradation, while partial inhibition could be the result of benzene and toluene's presence [99]. MTBE degradation increased only after the complete elimination of benzene and toluene. Results indicated that MTBE and BTEX degradation occurs via two independent pathways [99]. Another study on biotrickling filters also found that a single BTEX compound or BTEX mixtures partially inhibited the degradation of MTBE [98].

Microbial community composition was found to regulate the simultaneous removal of BTEX and MTBE [71]. MTBE degradation was completely inhibited by BTEX in batch reactors inoculated with MTBE and BTEX enrichment cultures. However, MTBE biodegradation in a semibatch reactor was almost three times higher when BTEX was present, though it occurred at a slower rate than MTBE biodegradation when BITE is not present in the solution. The results of that study indicated that MTBE can be biodegraded when BTEX is present depending on the reactor configuration and the microbial

culture composition [99]. In another study, MTBE degradation was not significantly affected by BTEX in batch conditions [100]. Additionally, MTBE, BTEX, and TBA can also be biodegraded when an appropriate bacterial mixture is utilized [98].

The same has also been reported for CWs used to treat water-containing MTBE and BTEX. Many studies implemented at the experimental facility in Leuna, Germany reported that the presence of BTEX partially inhibits MTBE biodegradation. Lower MTBE removal rates (17%) than benzene (81%) were measured in an HSSF CW with gravel [28], possibly due to hindered microbial activity [58]. Smaller differences were found in an HSSF CW (i.e., 24%–100% for benzene and 16%–93% for MTBE [42]). A higher benzene mass removal rate (98%; 544 mg/m^2/day) compared with MTBE (78%; 54 mg/m^2/day) was also detected in a plant root mat [96]. Volatization of both accounted for less than 10% of the total mass removed in gravel-based, planted HSSF CWs [40], whereas in an aerated trench, system volatilization accounted for 1% and 53% of benzene and MTBE removal, respectively [24]. Additionally, benzene and MTBE were completely eliminated in a two-stage VF CW [44]; the first stage was an unplanted vertical roughing filter followed by a planted vertical flow CW for final polishing, resulting in effluent concentrations of 5 ± 10 and 0.6 ± 0.2 μg/L for MTBE and benzene, respectively (influents were 2970 ± 816 and 13,966 ± 1998 μg/L, respectively). Similar results are reported for CWs [48,89] and aerated trench systems [24] treating groundwater contaminated with petroleum hydrocarbons, whereas MTBE removal was lower than that of benzene. However, similar removal rates were found for benzene and MTBE in other CWs (between 30% and 40%), possibly because the influent concentrations were near the detection limits [90].

The simultaneous fate of benzene, MTBE, as well as phenols (i.e., phenol and m-cresol) has also been studied in HSSF CWs [1]. The two phenolic compounds were completely removed (inflow of 15 and 2 mg/L, respectively) without changing MTBE and benzene removal (20.2 and 334.6 mg/m^2/day, respectively). The planted CW showed a higher removal efficiency, implying the positive contribution of plants. It should also be noted that most of this removal was measured in the first 1/3 part of the CW length, which indicated the potential of the HSSF CW to accept increased influent loads. This was the first study indicating that HSSF CWs are efficient in the removal of different light hydrocarbons simultaneously present in contaminated water.

5. Conclusions

Water contamination by various petroleum hydrocarbons is a global environmental problem. Hydrocarbon contamination is continuously detected in industrial areas such as chemical/petrochemical plants, oil refineries, power plants, and so forth. Fuel hydrocarbons such as BTEX and MTBE are two of the most commonly found groundwater contaminants, and both are considered to be toxic compounds that pose health and environmental risks to humans and ecosystems. Although various treatment technologies have been used for their removal from water sources, the need to identify cost-effective and sustainable treatment technologies keeps rising. CWs, as a nature-based technology, have the required characteristics, namely, high efficiency, ecological, limited environmental footprint, and simple operation, to provide such a solution. Under this framework, they have a high potential for further use in the petroleum industry. This article presented the current information and knowledge on CW technology for the treatment of light hydrocarbons (i.e., MTBE and benzene-BTEX).

Although the application of CWs is rapidly increasing in the industrial sector for the remediation of effluents from various industries, the application of these systems for MTBE and BTEX is still limited, especially for MTBE. Currently published international research indicates that practically all CW types (surface/subsurface flow and horizontal/vertical flow) have been tested for the removal of benzene from contaminated water. The overall results clearly imply that the VF CW type seems to be more effective, mainly due to the better aeration conditions that this type provides. In general, high removal rates are reported in the international literature for various streams and concentrations. Most of the studies indicate that biodegradation is the dominant removal mechanism, while the presence of plants indirectly contributes to the efficiency through their root system. This is in agreement with the general

understanding of wetland processes related to other pollutants as well, where the direct contribution of plants to pollutant removal is usually reported as insignificant. Though less studied than BTEX, the removal of MTBE from water also takes place in CWs, mostly through biodegradation under aerobic conditions, though lower removal rates are, in general, reported compared with benzene. The VF CW type also seems to be preferable for MTBE removal.

Overall, although the international literature includes limited relevant studies, the existing knowledge provides a strong indication of the high removal capacity of constructed wetlands for these light hydrocarbon compounds, particularly the VF CW design. However, further investigation is required in order to adopt design standards, since currently there is no widely accepted or applied design. Additionally, future research should focus on providing a better understanding through not only qualitative but also quantitative analysis of the various involved transformation/removal processes. For example, isotopic fractionation analysis could confirm and/or reveal the biodegradation pathways of light hydrocarbons in CWs, which would also help to acquire new information on the metabolic reaction products and metabolites that may be formed during this process. Moreover, although there are already some first indications of the microorganisms involved in the biodegradation process, further investigation is required to identify the microbial community patterns and composition. Also, the presence of more compounds simultaneously present in water, with diverse properties and behavior in the aquatic environment, is something that needs further study, since the effects on removal performance due to compounds' interactions are not yet clear. Finally, from an engineering point of view, the optimum operating conditions in terms of influent load, residence time, and seasonal variations are yet to be determined for the various systems.

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References

1. Stefanakis, A.I.; Seeger, E.; Dorer, C.; Sinke, A.; Thullner, M. Performance of pilot-scale horizontal subsurface flow constructed wetlands treating groundwater contaminated with phenols and petroleum derivatives. *Ecol. Eng.* **2016**, *95*, 514–526. [CrossRef]

2. Langwaldt, J.H.; Puhakka, J.A. On-site biological remediation of contaminated groundwater: A review. *Environ. Pollut.* **2000**, *107*, 187–197. [CrossRef]

3. Levchuk, I.; Bhatnagar, A.; Sillanpää, M. Overview of technologies for removal of methyl tert-butyl ether (MTBE) from water. *Sci. Total Environ.* **2014**, *476–477*, 415–433. [CrossRef] [PubMed]

4. Wu, Y.; Lerner, D.N.; Banwart, S.A.; Thornton, S.F.; Pickup, R.W. Persistence of fermentative process to phenolic toxicity in groundwater. *J. Environ. Qual.* **2006**, *35*, 2021–2025. [CrossRef]

5. Stefanakis, A.I.; Akratos, C.S.; Tsihrintzis, V.A. *Vertical Flow Constructed Wetlands: Eco-Engineering Systems for Wastewater and Sludge Treatment*, 1st ed.; Elsevier: Amsterdam, The Netherlands, 2014.

6. USEPA. List of Drinking Water Contaminants and MCLs. 2009. Available online: https://www.epa.gov/ground-water-and-drinking-water/table-regulated-drinking-water-contaminants (accessed on 24 November 2019).

7. USEPA. Integrated Risk Information System (IRIS). 2015. Available online: http://www.epa.gov/iris (accessed on 28 November 2019).

8. Costa, C.R.; Botta, C.M.R.; Espindola, E.L.G.; Olivi, P. Electrochemical treatment of tannery wastewater using DSA® electrodes. *J. Hazard. Mater.* **2008**, *153*, 616–627. [CrossRef]

9. Herouvim, E.; Akratos, C.S.; Tekerlekopoulou, A.; Vayenas, D.V. Treatment of olive mill wastewater in pilot-scale vertical flow constructed wetland. *Ecol. Eng.* **2011**, *37*, 931–939. [CrossRef]

10. Abira, M.A.; Van Bruggen, J.J.A.; Denny, P. Potential of a tropical subsurface constructed wetland to remove phenol from pre-treated pulp and paper mill wastewater. *Water Sci. Technol.* **2005**, *51*, 173–176. [CrossRef]

11. Stottmeister, U.; Kuschk, P.; Wiessner, A. Full-scale bioremediation and long-term monitoring of a phenolic wastewater disposal lake. *Pure Appl. Chem.* **2010**, *82*, 161–173. [CrossRef]

12. WHO. *Guidelines for Drinking-Water Quality*, 4th ed.; WHO: Geneva, Switzerland, 2011.

13. Deeb, R.A.; Chu, K.-H.; Shih, T.; Linder, S.; Suffet, I.; Kavanaugh, M.C. MTBE and other oxygenates: Environmental sources, analysis, occurrence, and treatment. *Environ. Eng. Sci.* **2003**, *20*, 433–447. [CrossRef]

14. Hodaifa, G.; Ochando-Pulido, J.M.; Rodriguez-Vives, S.; Nartinez-Ferez, A. Optimization of continuous reactor at pilot scale for olive-oil mill wastewater treatment by Fenton-like process. *Chem. Eng. J.* **2013**, *220*, 117–124. [CrossRef]

15. Stefanakis, A.I.; Thullner, M. Fate of phenolic compounds in Constructed Wetlands treating contaminated water. In *Phytoremediation*, 1st ed.; Abid, A.A., Sarvajeet, S.G., Ritu, G., Guy, R.L., Lee, N., Eds.; Springer: Cham, Switzerland, 2016; Volume 6, pp. 311–325.

16. Stefanakis, A.I. *Constructed Wetlands for Industrial Wastewater Treatment*, 1st ed.; John Wiley & Sons Ltd.: Chichester, UK, 2018.

17. Galbraith, D.; Gross, S.A.; Paustenbach, D. Benzene and human health: A historical review and appraisal of associations with various diseases. *Crit. Rev. Toxicol.* **2010**, *40*, 1–46. [CrossRef] [PubMed]

18. Rakoczy, J.; Remy, B.; Vogy, C.; Richnow, H.H. A bench-scale Constructed Wetland as a model to characterize benzene biodegradation processes in freshwater wetlands. *Environ. Sci. Technol.* **2011**, *45*, 10036–10044. [CrossRef] [PubMed]

19. Squillace, P.J.; Zogorski, J.S.; Wilber, W.G.; Price, C.V. Preliminary assessment of the occurrence and possible sources of MTBE in groundwater in the United States, 1993–1994. *Environ. Sci. Technol.* **1996**, *30*, 1721–1730. [CrossRef]

20. Alexander, M. *Biodegradation and Bioremediation*, 2nd ed.; Academic Press: New York, NY, USA, 1999.

21. Agteren, M.H.V.; Keuning, S.; Janssen, D.B. *Handbook on Biodegradation and Biological Treatment of Hazardous Organic Compounds*, 1st ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1998.

22. Yerushalmi, L.; Lascourreges, J.F.; Guiot, S.R. Kinetics of benzene biotransformation under microaerophilic and oxygen-limited conditions. *Biotechnol. Bioeng.* **2002**, *79*, 347–355. [CrossRef] [PubMed]

23. Foght, J. Anaerobic biodegradation of aromatic hydrocarbons: Pathways and prospects. *J. Mol. Microbiol. Biotechnol.* **2008**, *15*, 93–120. [CrossRef]

24. Jechalke, S.; Vogt, C.; Reich, N.; Franchini, A.G.; Borsdorf, H.; Neu, T.R.; Richnow, H.H. Aerated treatment pond technology with biofilm promoting mats for the bioremediation of benzene, MTBE and ammonium contaminated groundwater. *Water Res.* **2010**, *44*, 1785–1796. [CrossRef]

25. Zhou, E.; Crawford, R.L. Effects of oxygen, nitrogen, and temperature on gasoline biodegradation in soil. *Biodegradation* **1995**, *6*, 127–140. [CrossRef]

26. Imfeld, G.; Braeckevelt, M.; Kuschk, P.; Richnow, H.H. Monitoring and assessing processes of organic chemicals removal in constructed wetlands. *Chemosphere* **2009**, *74*, 349–362. [CrossRef]

27. Braeckevelt, M.; Reiche, N.; Trapp, S.; Wiessner, A.; Paschke, H.; Kuschk, P.; Kaestner, M. Chlorobenzene removal efficiencies and removal processes in a pilot-scale constructed wetland treating contaminated groundwater. *Ecol. Eng.* **2011**, *37*, 903–913. [CrossRef]

28. De Biase, C.; Reger, D.; Schmidt, A.; Jechalke, S.; Reiche, N.; Martinez-Lavanchy, P.M.; Rosell, M.; Van Afferden, M.; Maier, U.; Oswald, S.E.; et al. Treatment of volatile organic contaminants in a vertical flow filter: Relevance of different removal processes. *Ecol. Eng.* **2011**, *37*, 1292–1303. [CrossRef]

29. Seeger, E.; Kuschk, P.; Fazekas, H.; Grathwohl, P.; Kaestner, M. Bioremediation of benzene-, MTBE-and ammonia-contaminated groundwater with pilot-scale constructed wetlands. *Environ. Pollut.* **2011**, *159*, 3769–3776. [CrossRef] [PubMed]

30. Stottmeister, U.; Wießner, A.; Kuschk, P.; Kappelmeyer, U.; Kästner, M.; Bederski, O.; Müller, R.A.; Moormann, H. Effects of plants and microorganisms in Constructed Wetlands for wastewater treatment. *Biotechnol. Adv.* **2003**, *22*, 93–117. [CrossRef] [PubMed]

31. Sugai, S.F.; Lindstrom, J.E.; Braddockm, J.F. Environmental influences on the microbial degradation of Exxon Valdez oil on the shorelines of Prince William Sound, Alaska. *Env. Sci. Technol.* **1997**, *31*, 1564–1572. [CrossRef]

32. Pardue, J.H.; Kassenga, G.; Shinm, W.S. Design approaches for chlorinated VOC treatment wetland. In *Wetlands & Remediation: An International Conference*; Means, J.L., Hinchee, R.E., Eds.; Battelle Press: Columbus, OH, USA, 2000; pp. 301–308.

33. Ridgeway, H.F.; Safarik, J.; Phipps, D.; Carl, P.; Clark, D. Identification and catabolic activity of well-derived gasoline degrading bacteria and a contaminated aquifer. *Appl. Environ. Microbiol.* **1990**, *56*, 3565–3575.

34. Braeckevelt, M.; Rokadia, H.; Imfeld, G.; Stelzer, N.; Paschke, H.; Kuschk, P.; Kaestner, M.; Richnow, H.H.; Weber, S. Assessment of in situ biodegradation of monochlorobenzene in contaminated groundwater treated in a constructed wetland. *Environ. Pollut.* **2007**, *148*, 428–437. [CrossRef] [PubMed]

35. Briggs, G.G.; Bromilow, R.H.; Evans, A.A. Relationships between lipophilicity and root uptake and translocation of non-ionized chemicals by barley. *Pestic. Sci.* **1982**, *13*, 495–504. [CrossRef]

36. Schirmer, M.; Butler, B.J.; Barker, J.F.; Church, C.D.; Schirmer, K. Evaluation of biodegradation and dispersion as natural attenuation processes of MTBE and benzene at the Borden field site. *Phys. Chem. Earth PT B Hydrol. Ocean. Atm.* **1999**, *24*, 557–560. [CrossRef]

37. Pilon-Smits, E. Phytoremediation. *Annu. Rev. Plant Biol.* **2005**, *56*, 15–39. [CrossRef]

38. Burken, J.G.; Schnoor, J.L. Distribution and volatilization of organic compounds following uptake by hybrid poplar trees. *Int. J. Phytoremediat.* **1999**, *1*, 139–151. [CrossRef]

39. Trapp, S.; Karlson, U. Aspects of phytoremediation of organic pollutants. *J. Soils Sediments* **2001**, *1*, 37–43. [CrossRef]

40. Reiche, N.; Lorenz, W.; Borsdorf, H. Development and application of dynamic air chambers for measurement of volatilization fluxes of benzene and MTBE from constructed wetlands planted with common reed. *Chemosphere* **2010**, *79*, 162–168. [CrossRef] [PubMed]

41. Eke, P.E.; Scholz, M. Benzene removal with vertical-flow constructed treatment wetlands. *J. Chem. Technol. Biotechnol.* **2008**, *83*, 55–63. [CrossRef]

42. Chen, Z.; Kuschk, P.; Reiche, N.; Borsdorf, H.; Kaestner, M.; Koeser, H. Comparative evaluation of pilot scale horizontal subsurface-flow constructed wetlands and plant root mats for treating groundwater contaminated with benzene and MTBE. *J. Hazard. Mater.* **2012**, *209–210*, 510–515. [CrossRef] [PubMed]

43. Seeger, E.; Reiche, N.; Kuschk, P.; Borsdorf, H.; Kaestner, M. Performance evaluation using a three compartment mass balance for the removal of volatile organic compounds in pilot scale Constructed Wetlands. *Environ. Sci. Technol.* **2011**, *45*, 8467–8474. [CrossRef]

44. Van Afferden, M.; Rahman, K.Z.; Mosig, P.; De Biase, C.; Thullner, M.; Oswald, S.E.; Mueller, R.A. Remediation of groundwater contaminated with MTBE and benzene: The potential of vertical-flow soil filter systems. *Water Res.* **2011**, *45*, 5063–5074. [CrossRef]

45. Wallace, S.; Kadlec, R. BTEX degradation in a cold-climate wetland system. *Water Sci. Technol.* **2005**, *51*, 165–171. [CrossRef]

46. Ranieri, E.; Gikas, P.; Tchobanoglous, G. BTEX removal in pilot-scale horizontal subsurface flow constructed wetlands. *Desalin. Water Treat.* **2013**, *51*, 3032–3039. [CrossRef]

47. Mothes, F.; Reiche, N.; Fiedler, P.; Moeder, M.; Borsdorf, H. Capability of headspace based sample preparation methods for the determination of methyl tert-butyl ether and benzene in reed (*phragmites australis*) from constructed wetlands. *Chemosphere* **2010**, *80*, 396–403. [CrossRef]

48. Bedessem, M.E.; Ferro, A.; Hiegel, T. Pilot-scale Constructed Wetlands for petroleum-contaminated groundwater. *Water Environ. Res.* **2007**, *79*, 581–586. [CrossRef]

49. Tang, X.; Scholz, M.; Emeka, P.; Huang, S. Nutrient removal as a function of benzene supply within vertical-flow constructed wetlands. *Environ. Technol.* **2010**, *31*, 681–691. [CrossRef]

50. Ballesteros, F., Jr.; Vuong, T.H.; Secondes, M.F.; Tuan, P.D. Removal efficiencies of constructed wetland and efficacy of plant on treating benzene. *Sustain. Environ. Res.* **2016**, *26*, 93–96. [CrossRef]

51. Atif, M.; Azim, M.K.; Raza, Z.; Kori, J.A. BTEX removal in a modified free water surface wetland. *Chem. Eng. J.* **2018**, *333*, 451–455.

52. Tang, X.; Eke, P.; Scholz, M.; Huang, S. Processes impacting on benzene removal in vertical-flow constructed wetlands. *Bioresour. Technol.* **2009**, *100*, 227–234. [CrossRef] [PubMed]

53. Haberl, R.; Grego, S.; Langergraber, G.; Kadlec, R.H.; Cicalini, A.R.; Dias, S.M.; Novais, J.M.; Aubert, S.; Gerth, A.; Thomas, H.; et al. Constructed wetlands for treatment of organic pollutants. *J. Soils Sediments* **2003**, *3*, 109–124. [CrossRef]

54. Gerhardt, K.E.; Huang, X.D.; Glick, B.R. Greenberg BM. Phytoremediation and rhizoremediation of organic soil contaminants: Potential and challenges. *Plant Sci.* **2009**, *176*, 20–30. [CrossRef]

55. Ranieri, E.; Gorgoglione, A.; Montanaro, C.; Iacovelli, A.; Gikas, P. Removal capacity of BTEX and metals of constructed wetlands under the influence of hydraulic conductivity. *Desalin. Water Treat.* **2014**. [CrossRef]

56. Braeckevelt, M.; Mischel, G.; Wiessner, A.; Rueckert, M.; Reiche, N.; Vogt, C.; Schultz, A.; Paschke, H.; Kuschk, P.; Kaestner, M. Treatment of chlorobenzene-contaminated groundwater in a pilot-scale constructed wetland. *Ecol. Eng.* **2008**, *33*, 45–53. [CrossRef]

57. Stefanakis, A.I.; Tsihrintzis, V.A. Effects of loading, resting period, temperature, porous media, vegetation and aeration on performance of pilot-scale Vertical Flow Constructed Wetlands. *Chem. Eng. J.* **2012**, *181–182*, 416–430. [CrossRef]

58. Schmidt, T.C.; Schirmer, M.; Weiss, H.; Haderlein, S.B. Microbial degradation of methyl tert-butyl ether and tert-butyl alcohol in the subsurface. *J. Contam. Hydrol.* **2004**, *70*, 173–203. [CrossRef]

59. Baehr, A.L.; Stackelberg, P.E.; Baker, R.J. Evaluation of the atmosphere as a source of volatile organic compounds in shallow groundwater. *Water Resour. Res.* **1999**, *35*, 127–136. [CrossRef]

60. Von Kraus, K.M.; Harremoes, P. MTBE in petrol as a substitute for lead. In *Late Lessons from Early Warnings: The Precautionary Principle 1896–2000*; Environmental Issue Report, 22; Hearremoes, P., Ed.; Office for Official Publications of the European Communities: Copenhagen, Denmark, 2001.

61. Kujawa, J.; Cerneaux, S.; Kujawski, W. Removal of hazardous volatile organic compounds from water by vacuum pervaporation with hydrophobic ceramic membranes. *J. Membr. Sci.* **2015**, *474*, 11–19. [CrossRef]

62. Johnson, R.; Pankow, J.; Bender, D.; Price, C.; Zogorski, J. MTBE-To what extent will past releases contaminate community water supply wells? *Environ. Sci. Technol.* **2000**, *34*, 210A–217A. [CrossRef] [PubMed]

63. Schmidt, T.C.; Morgenroth, E.; Schirmer, M.; Effenberger, M.; Haderlein, S.B. Use and occurrence of fuel oxygenates in Europe. In *Oxygenates in Gasoline: Environmental Aspects*, 1st ed.; Diaz, A.F., Dorgos, D.L., Eds.; ACS: Washington, DC, USA, 2002; pp. 58–79.

64. Morgenstern, P.; Versteegh, A.F.M.; de Korte, G.A.L.; Hoogerbrugge, R.; Mooibroek, D.; Bannink, A. Survey of the occurrence of residues of methyl tertiary butyl ether (MTBE) in Dutch drinking water sources and drinking water. *J. Environ. Monitor.* **2003**, *5*, 885. [CrossRef] [PubMed]

65. Klinger, J.; Stieler, C.; Sacher, F.; Brauch, H.J. MTBE (methyl tertiary-butyl ether) in groundwaters: Monitoring results from Germany. *J. Environ. Monitor.* **2002**, *4*, 276–279. [CrossRef]

66. Wilhelm, M.J.; Adams, D.; Curtis, J.G.; Middlebrooks, E.J. Carbon adsorption and air-stripping removal of MTBE from river water. *J. Env. Eng. Asce.* **2002**, *128*, 813–823. [CrossRef]

67. Davis, S.W.; Powers, S.E. Alternate sorbents for removing MTBE from gasoline-contaminated ground water. *J. Environ. Eng.* **2000**, *126*, 354–360. [CrossRef]

68. Sutherland, J.; Adams, C.; Kekobad, J. Treatment of MTBE by air stripping, carbon adsorption, and advanced oxidation: Technical and economic comparison for five groundwaters. *Water Res.* **2004**, *38*, 193–205. [CrossRef]

69. Aivalioti, M.; Vamvasakis, I.; Gidarakos, E. BTEX and MTBE adsorption onto raw and thermally modified diatomite. *J. Hazard. Mater.* **2010**, *178*, 136–143. [CrossRef]

70. Deeb, R.A.; Scow, K.M.; Alvarez-Cohen, L. Aerobic MTBE biodegradation: An examination of past studies, current challenges and future research directions. *Biodegradation* **2000**, *11*, 171–186. [CrossRef]

71. Raynal, M.; Pruden, A. Aerobic MTBE biodegradation in the presence of BTEX by two consortia under batch and semi-batch conditions. *Biodegradation* **2008**, *19*, 269–282. [CrossRef]

72. Stocking, A.J.; Deeb, R.A.; Flores, A.E.; Stringfellow, W.; Talley, J.; Brownell, R. Bioremediation of MTBE: A review from a practical perspective. *Biodegradation* **2000**, *11*, 187–201. [CrossRef]

73. Moreels, D.; Bastiaens, L.; Ollevier, F.; Merckx, R.; Diels, L.; Springael, D. Evaluation of the intrinsic methyl tert-butyl ether (MTBE) biodegradation potential of hydrocarbon contaminated subsurface soils in batch microcosm systems. *FEMS Microbiol. Ecol.* **2004**, *49*, 121–128. [CrossRef]

74. Schirmer, M.; Butler, B.J.; Church, C.D.; Barker, J.; Nadarajah, N. Laboratory evidence of MTBE biodegradation in Borden aquifer material. *J. Contam. Hydrol.* **2003**, *60*, 229–249. [CrossRef]

75. Müller, R.H.; Rohwerder, T.; Harms, H. Carbon conversion efficiency and limits of productive bacterial degradation of methyl tert-butyl ether and related compounds. *Appl. Environ. Microbiol.* **2007**, *73*, 1783–1791. [CrossRef]

76. Rohwerder, T.; Muller, R.H.; Weichler, M.T.; Schuster, J.; Hubschmann, T.; Muller, S. Cultivation of *Aquincola tertiaricarbonis* L108 on the fuel oxygenate intermediate tert-butyl alcohol induces aerobic anoxygenic photosynthesis at extremely low feeding rates. *Microbiology* **2013**, *159 Pt 10*, 2180–2190. [CrossRef]

77. Ferreira, N.L.; Malandain, C.; Fayolle-Guichard, F. Enzymes and genes involved in the aerobic biodegradation of methyl tert-butyl ether (MTBE). *Appl. Microbiol. Biotechnol.* **2006**, *72*, 252–262. [CrossRef]

78. Martienssen, M.; Fabritius, H.; Kukla, S.; Balcke, G.U.; Hasselwander, E.; Schirmer, M. Determination of naturally occurring MTBE biodegradation by analysing metabolites and biodegradation by-products. *J. Contam. Hydrol.* **2006**, *87*, 37–53. [CrossRef] [PubMed]

79. Wilson, J.T.; Adair, C.; Kaiser, P.; Kolhatkar, R. Anaerobic biodegradation of MTBE at a gasoline spill site. *Ground Water Monit. Remed.* **2005**, *25*, 103–115. [CrossRef]

80. Salanitro, J.P.; Johnson, P.C.; Spinnler, G.E.; Maner, P.M.; Wisniewski, H.L.; Bruce, C. Field-scale demonstration of enhanced MTBE bioremediation through aquifer bioaugmentation and oxygenation. *Environ. Sci. Technol.* **2000**, *34*, 4152–4162. [CrossRef]

81. Wilson, R.D.; Mackay, D.M.; Scow, K.M. In Situ MTBE biodegradation supported by diffusive oxygen release. *Environ. Sci. Technol.* **2002**, *36*, 190–199. [CrossRef] [PubMed]

82. Smith, A.E.; Hristova, K.; Wood, I.; Mackay, D.M.; Lory, E.; Lorenzan, D. Comparison of biostimulation versus bioaugmentation with bacterial strain PM1 for treatment of groundwater contaminated with Methyl Tertiary Butyl Ether (MTBE). *Environ. Health Persp.* **2005**, *113*, 317–322. [CrossRef] [PubMed]

83. Hong, M.S.; Fermayan, W.F.; Dortch, I.J.; Chiang, C.Y.; McMillan, S.K.; Schnoor, J.L. Phytoremediation of MTBE from a groundwater plume. *Environ. Sci. Technol.* **2001**, *35*, 1231–1239. [CrossRef] [PubMed]

84. Rubin, E.; Ramaswami, A. The potential for phytoremediation of MTBE. *Water Res.* **2001**, *35*, 1348–1353. [CrossRef]

85. Zhang, Q.; Davis, L.C.; Erickson, L.E. Transport of Methyl tert-Butyl Ether through alfalfa plants. *Environ. Sci. Technol.* **2001**, *35*, 725–731. [CrossRef] [PubMed]

86. Yu, X.Z.; Gu, J.D. Uptake, metabolism, and toxicity of methyl tert-butyl ether (MTBE) in weeping willows. *J. Hazard. Mater.* **2006**, *137*, 1417–1423. [CrossRef]

87. Arnold, C.W.; Parfitt, D.G.; Kaltreider, M. Field note phytovolatilization of oxygenated gasoline-impacted groundwater at an underground storage tank site via conifers. *Int. J. Phytoremediation* **2007**, *9*, 53–69. [CrossRef]

88. Trapp, S.; Yu, X.; Mosbaek, H. Persistence of Methyl tertiary butyl ether (MTBE) against metabolism by Danish vegetation. *Environ. Sci. Pollut. Res.* **2006**, *10*, 357–360. [CrossRef]

89. Ferro, A.M.; Kadlec, R.H.; Deschamp, J. Constructed Wetland system to treat wastewater at the BP Amoco former Casper refinery: Pilot scale project. In Proceedings of the 9th International Petroleum Environmental Conference, Albuquerque, NM, USA, 22–25 October 2002.

90. Keefe, S.H.; Barber, L.B.; Runkel, R.L.; Ryan, J.N.; McKnight, D.M.; Wass, R.D. Conservative and reactive solute transport in constructed wetlands. *Water Resour. Res.* **2004**, *40*. [CrossRef]

91. De Biase, C.; Carminati, A.; Oswald, S.E.; Thullner, M. Numerical modeling analysis of VOC removal processes in different aerobic vertical flow systems for groundwater remediation. *J. Contam. Hydrol.* **2013**, *154*, 53–69. [CrossRef]

92. Stefanakis, A.I. Constructed Wetlands case studies for the treatment of water polluted with fuel and oil hydrocarbons. In *Phytoremediation, Management of Environmental Contaminants*, 1st ed.; Ansari, A.A., Gill, S.S., Gill, R., Lanza, G.R., Newman, L., Eds.; Springer: Cham, Switzerland, 2018; Volume 6, pp. 151–167.

93. Reger, D. *Analysis of Contaminant Degradation in Vertical Soil Filter Systems*; Technical University Bergakademie Freiberg: Freiberg, Germany, 2009.

94. Khan, A.M.; Wick, L.Y.; Harms, H.; Thullner, M. Biodegradation of vapor-phase toluene in unsaturated porous media: Column experiments. *Environ. Pollut.* **2016**, *211*, 325–331. [CrossRef]

95. De Biase, C.; Maier, U.; Baeder-Bederski, O.; Bayer, P.; Oswald, S.E.; Thullner, M. Removal of volatile organic compounds in Vertical Flow Filters: Predictions from reactive transport modeling. *Ground Water Monit. Remed.* **2012**, *32*, 106–121. [CrossRef]

96. Seeger, E.M.; Maier, U.; Grathwohl, P.; Kuschk, P.; Kaestner, M. Performance evaluation of different horizontal subsurface flow wetland types by characterization of flow behavior, mass removal and depth-dependent contaminant load. *Water Res.* **2013**, *47*, 769–780. [CrossRef] [PubMed]

97. Wei, M.; Rakoczy, J.; Vogt, C.; Harnisch, F.; Schumann, R.; Richnow, H.H. Enhancement and monitoring of pollutant removal in a constructed wetland by microbial electrochemical technology. *Bioresour. Technol.* **2015**, *196*, 490–499. [CrossRef] [PubMed]

98. Wang, X.; Deshusses, M.A. Biotreatment of groundwater contaminated with MTBE: Interaction of common environmental co-contaminants. *Biodegradation* **2007**, *18*, 37–50. [CrossRef]

99. Deeb, R.A.; Hu, H.Y.; Hanson, J.R.; Scow, K.M.; Alvarez-Cohen, L. Substrate interactions in BTEX and MTBE mixtures by an MTBE-degrading isolate. *Environ. Sci. Technol.* **2001**, *35*, 312–317. [CrossRef]

100. Sedran, M.A.; Pruden, A.; Wilson, G.J.; Suidan, M.T.; Venosa, A.D. Effect of BTEX on degradation of MTBE and TBA by mixed bacterial consortium. *J. Environ. Eng.* **2002**, *128*, 830–835. [CrossRef]