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BTEX removal in pilot-scale horizontal subsurface flow constructed wetlands

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ABSTRACT

Benzene, toluene, ethylbenzene, and xylenes (BTEX) are commonly encountered pollutants. The focus of the present work is on the removal of BTEX using pilot-scale constructed wetlands (CWs). Experiment carried out in three similar pilot-scale horizontal sub-surface flow constructed wetlands with an area of 35 m^2 (each), two of which were planted with different macrophytes (*Phragmites australis* and *Typha latifolia*), while an unplanted one was used as control. A number of hydraulic tests were carried out using lithium bromide as tracer, to assess the hydraulic residence time. Residence time distributions for the two CWs indicated that the *Typha* field was characterized by a void volume fraction (porosity) of 0.16 and exhibited more ideal plug flow behavior ($Pe = 29.7$) compared with the *Phragmites* field ($Pe = 26.7$), which had similar porosity. The measured hydraulic residence times in the planted fields were 35.8, 36.7, and 34.1 h for *Typha*, *Phragmites,* and unplanted respectively, at wastewater flow rates equal to 1 m^3/d. The observed percentage removal for BTEX ranged between 46 and 55%. The average removal in the *Phragmites* field was 5% higher than the *Typha* field and 23% higher than the unplanted field. BTEX removal was primarily attributed to volatilization; however, biodegradation also played a significant role.

Keywords: Constructed wetland; Wastewater; Bioremediation; Biodegradation; Benzene; Ethylbenzene; Toluene; Xylene; Hydraulic residence time

1. Introduction

Constructed wetland (CW) processes for the remediation of wastewaters polluted with harmful organic chemicals is an emerging field [1]. Removal of volatile organic compounds, like benzene, toluene, ethylbenzene, and xylenes (BTEX) by CWs has been studied increasingly in recent years [2,3]; however, most of the studies have been carried out in small-scale systems. As part of a program for the restoration of the territory of the Apulian Region (South Italy), the Polytechnic of Bari has promoted the "Cowman Project: constructed wetlands for metals and organics

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removal. Evaluation of full-scale applicability in Apulia" joint research project [4] to evaluate the applicability of constructed wetland treatment process and eventually to extend this practice on a larger scale to serve, in particular, those rural areas which are not currently equipped with centralized wastewater treatment facilities.

The experimental tests during the CWs research project have been focused on BTEX removal because of their impact on the environment and on human health. BTEX frequently occur near petrol stations or where fossil fuels are used, and often contaminate the aquatic environment. However, recalcitrant organics, and particularly BTEX, have been documented to naturally degrade in natural wetland environments [5–7], while diverse sub-surface flow wetlands have been used to treat hydrocarbon-contaminated water in various environmental conditions [8,9].

The focus of the study described in this paper was to investigate the removal of BTEX from wastewater, using large pilot-scale horizontal sub-surface flow constructed wetlands (HSFCWs). Three equal pilot HSFCWs, with area of 35 m^2 each (Fig. 1), planted with different macrophytes (*Phragmites australis* and *Typha latifolia*), have been constructed in Sternatia di Lecce, Italy, while an identical unplanned HSFCW was used as control. The primary goal of the research was to assess the overall removal of BTEX and to investigate the role of the substrate and different macrophytes at Mediterranean conditions.

2. Materials and methods

2.1. Design and construction characteristics of constructed wetlands

The experimental setup comprises three constructed wetland fields, one with *P. australis*, one with *T. latifolia*, and an unplanted one (serving as a control). Wastewater is supplied to the CWs from four high density polyethylene (HDPE) tanks; samples are obtained from 18 sampling ports, while the effluent is stored in two subsequent lagoon ponds. The plan view of the site is depicted in Fig. 1, while the longitudinal section of one CW field is shown in Fig. 2. Each wetland has an area of about 35 m^2 (4.80 × 7.15 m), a planted area equal to 15 m^2 (3 × 5 m), a water depth ranging from 0.6 to 0.65 m and a resulting total volume of approximately 9.4 m^3.

Five 200 mm internal diameter perforated tubes were placed within each field to facilitate the measurement of flow and to control the water level. Wastewater is fed in at a high hydraulic conductivity area of the inlet (to ensure wastewater homogenization at the cross section) and passes slowly through the filtration 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 it is discharged via a level control assembly at the outlet. The medium is composed as following: 0.1 m of clay soil ($D_{50} = 0.05$ mm); 0.2 m of stones ($D_{50} = 5$ mm); and 0.30–0.35 m of gravel ($D_{50} = 1.5$ mm). The constructed wetlands have a bottom slope of 1% to facilitate the flow of water by gravity. The stability of the side banks is ensured by providing 45° inclination. The bottom of each CW is sealed using a HDPE liner, followed by a bentonite liner. The HDPE liner had a thickness of 2 mm, was hot-posed and checked for leaks, while the bentonite liner was 6 mm thick, and had a hydraulic conductivity $k < 10^{-11}$ m/s. The above lining system ensured water tidiness.

The ponds have been connected in a subsequential mode (Fig. 3) and have a total volume of approximately 30 m^3; they are sealed with an HDPE liner followed by a bentonite liner and have a double function: effluent quality enhancement and temporary effluent storage. By considering the effective and most probable hydraulic residence time, the volume of the voids has been calculated in 1.56 m^3 and the relative porosity $n = Vv/Vt = (1.56\,\text{m}^3)/(9.4\,\text{m}^3) = 0.17$ (where Vv is the void volume and Vt is the total volume). The low void fraction (porosity) is due to the nature of clayey soils ("Terra Rossa") that is typical of the Apulian karstic area. Moreover, the porosity of the medium is influenced by biofilms and nondegradable residues.

2.2. Sampling and analysis

BTEX solution was conveyed to the CWs from the supply tanks containing tap water at a constant initial concentration of 0.5 mg/L, for each compound, for all the tests. Composite samples of the effluent from each constructed wetland were collected in 500 mL amber glass bottles every 6 h, using an autosampler (Sigma, Denver, CO, USA) for a time period of 220 days. Samples were collected at inlet and outlet, two times per week, and were kept refrigerated at 4°C until analyses. All analyses were performed within 24 h of sample collection. Samples were analyzed according to Standard Methods [10] using an HP 5,890 series II Gas Chromatograph equipped flame ionization detector and a split/splitless injector. Standard deviation (SD) was calculated for each measurement series and was less than 5% for each compound considered. For all measurements, standard Quality Control (QC) was performed. QC samples consisted of triplicate samples and spiked samples.

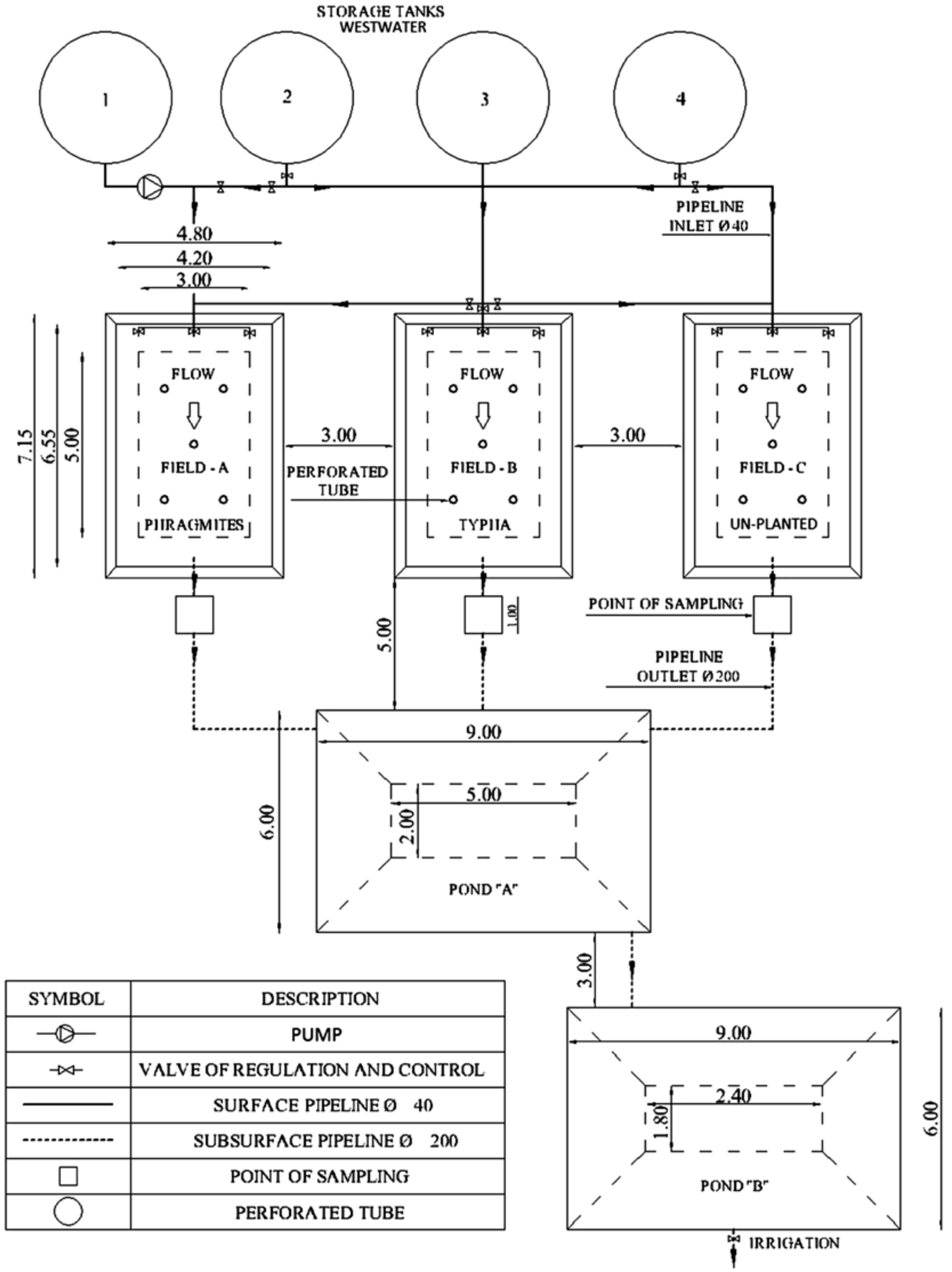

Fig. 1. Constructed wetlands pilot plant at Sternatia di Lecce, Italy—plan view.

Lithium bromide (LiBr) was employed as tracer, to determine residence time distributions (RTD). Measurement of lithium concentrations in the tracer testing were performed by ion chromatography (Dionex DX-600, Sunnyvale, CA, USA) according to the method outlined by Yu-Chen Lin et al. [11]. 30 L of LiBr solution with a concentration of 10 g(Li)/L was released along the first cross-section of the CWs. Samples were collected every 30 min, in each perforated tube and in the sampling points towards the end of the fields.

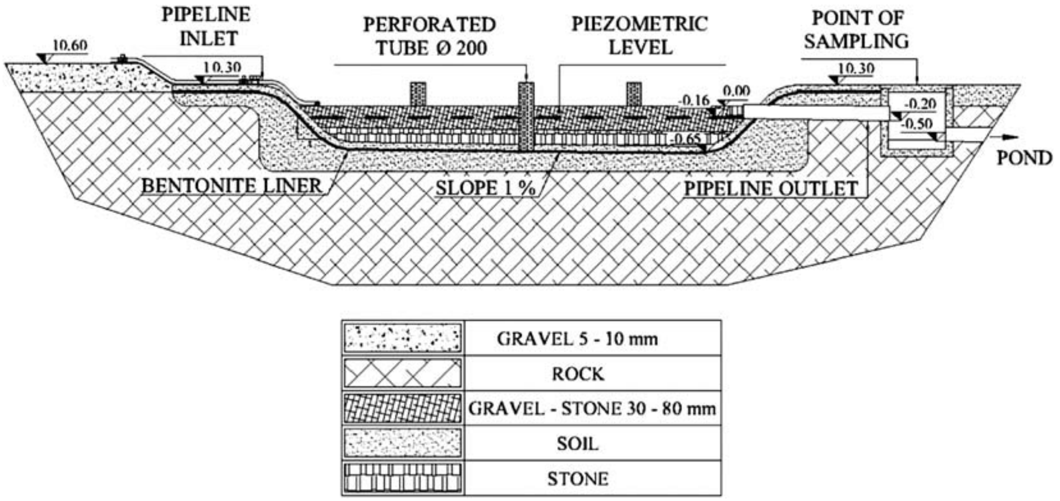

Fig. 2. Longitudinal section of the constructed wetlands at Sternatia di Lecce, Italy.

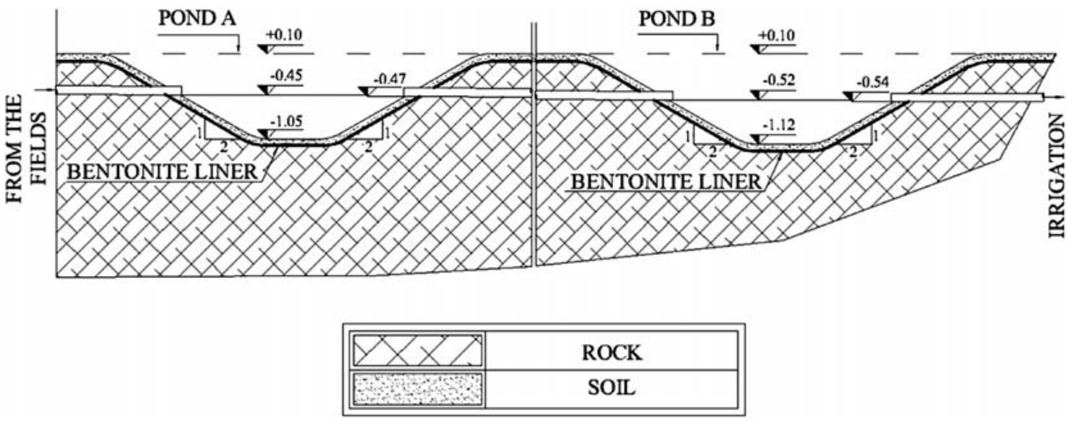

Fig. 3. Longitudinal section of the ponds in Sternatia di Lecce, Italy.

SD was calculated for each measurement series and was ranging from 4% (toluene) to 7% (xylenes). For all measurements, standard QC was performed. QC samples consisted of triplicate samples and spiked samples.

3. Results and discussion

3.1. System hydraulics

The residence time distributions for the two wetland fields planted with *Phragmites* and *Typha* and the unplanted one when operated at $1\,\mathrm{m}^3/\mathrm{d}$ are shown in Fig. 4. The breakthrough curves are also shown in Fig. 4. The latter have been calculated using the plug flow with dispersion reactor (PFDR) model, by adjusting the hydraulic residence time (θ) and the reactor *Peclet number* (Pe) to minimize the sum of the squared errors between the experimental lithium concentration data and the analytical solution to the PFDR model, given by Levenspiel and Smith [12] and Nemade et al. [13] (Eq. (1)):

$$C(t) = \left(\frac{\sum_i C_i \Delta t}{\theta}\right) \frac{e^{\frac{-Pe(1-\theta)^2}{4\theta}}}{\sqrt{4\pi(1Pe)}} \tag{1}$$

The above equation has been modified from its original dimensionless form, by multiplying with the

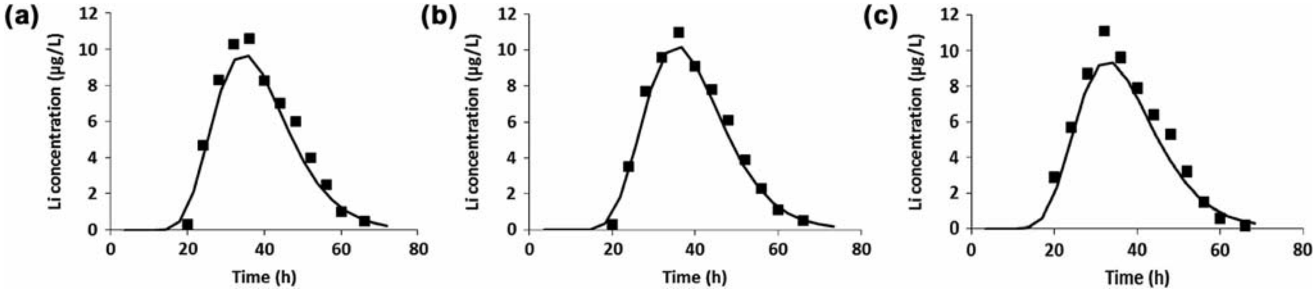

Fig. 4. Lithium concentration in the effluent of the constructed wetlands during the pulse tracer input study for the 1 m^3/d flow rate in the *Phragmites* (a), *Typha* (b), and unplanted (c) fields. Symbols represent experimental data and solid lines show the best fit of the plug flow with dispersion reactor model to the data using Eq. (1).

summation of $C_i\Delta t$ (measured lithium concentration at time = t_i), which approximates the area under the residence time distribution curve. All results from the PFDR model fits, compared to the tracer data, had correlation coefficient (R^2) values greater than 0.975. The differences between the RTD curves for the planted fields are probably related to the different root structures of each species.

The roots of *P. australis* penetrated to a depth of approx. 51 cm while *T. latifolia* roots did not extend beyond about 29 cm, according to previous experience with these species [14]. The differences in root penetration depth are likely to be responsible for the slightly different flow patterns in the two planted wetland fields. Clogging was more pronounced in the *Phragmites* field, which favors the development of preferential flow paths resulting to slightly shorter hydraulic residence time (HRT) of 35.8 h compared to 36.7 h for the *Typha* field, and in slightly lower *Peclet number* of 26.7 in contrast to 29.7 *Pe* for the *Typha* field. The unplanted field had a measured hydraulic residence time of 34.1 h and a *Peclet number* of 24.9. The relatively low HRTs may be attributed to the reduced porosity of the media, as mentioned above.

The effective porosity ($\varepsilon = V_v V_t$) of each reactor was estimated from the hydraulic residence time determined using Eq. (1) as: $\varepsilon = \theta Q/V$ where Q is the volumetric flow rate (1 m^3/d) and V is the total reactor volume (9.4 m^3). The calculated porosities were 0.16 for the two planted CWs and 0.15 for the unplanted CW. The slightly increased HRTs and porosity values of the planted CWs, compared with the unplanted ones, may be attributed to the root systems of the plants, which probably enhanced both the specified parameters.

3.2. BTEX removal

The residual concentrations at the sampling points at the end of the *Phragmites* field ranged between

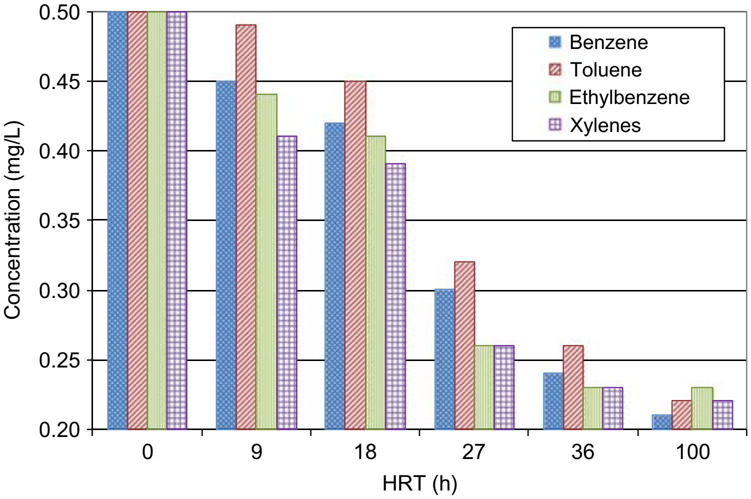

Fig. 5. Benzene, toluene, ethylbenzene, and xylenes vs. HRT in the *Phragmites* field.

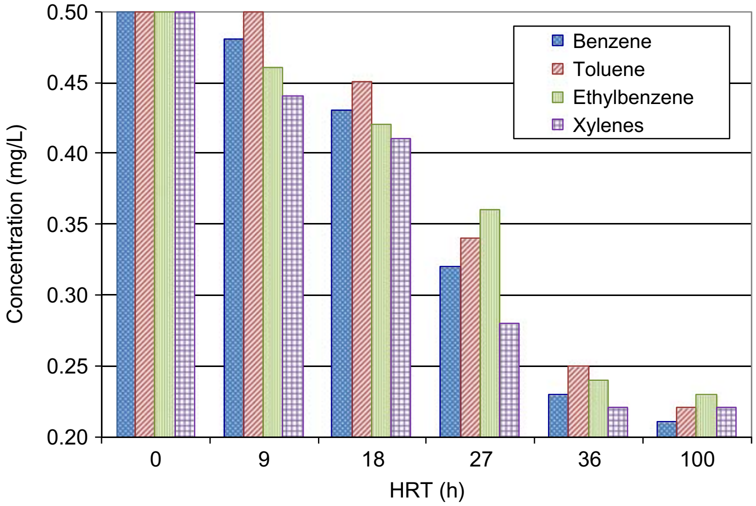

Fig. 6. Benzene, toluene, ethylbenzene, and xylenes vs. HRT in the *Typha* field.

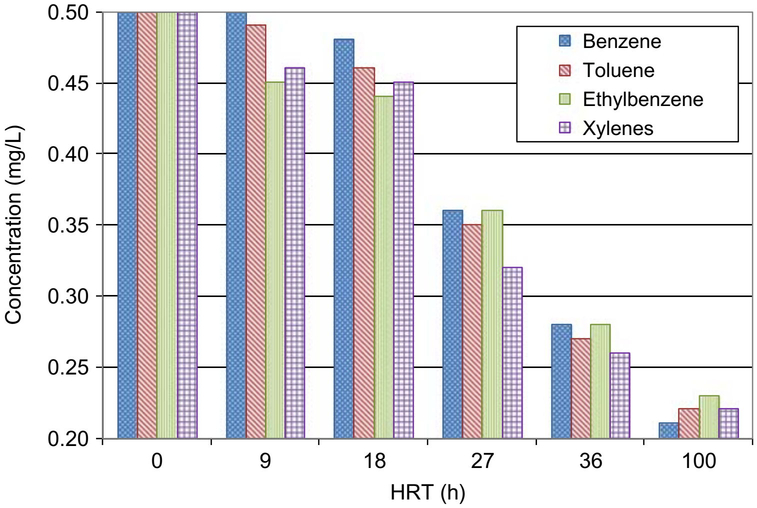

Fig. 7. Benzene, toluene, ethylbenzene, and xylene vs. HRT in the unplanted field.

0.23 mg/L (xylenes and ethylbenzene) and 0.26 mg/L (toluene). The final residual concentrations in the *Typha* field ranged between 0.22 mg/L (xylenes) and 0.26 mg/l (toluene). In the unplanted field, the final residual concentrations ranged between 0.26 mg/L (xylenes) and 0.28 mg/L (benzene). Based on the above, the removal efficiencies ranged from 46% for the unplanted field to 57% for the *Phragmites* field (Figs. 5–7). The removal efficiencies determined in the present work are lower compared with a similar experimental work [15]. The latter may be attributed to the fact that the inflow concentration at the present concentration was lower (0.5 mg/L here, instead of 2 mg/L [15]).

The observed removals in the *Phragmites* field were, on average, 5% higher than the *Typha* field and 23% higher than the unplanted field. However, because of the low affinity of the BTEX compounds with plant tissues, the direct effect of vegetation should be less significant compared with the net effect of sorption [14]. Higher removal is probably due to the microbial communities associated with the plant rhizosphere which create an environment conducive to degradation for many volatile organic compounds [16]. Other reports have attributed a significant role of BTEX removal to volatilization, as the BTEX compounds have a high tendency for volatilization, especially in surface-flow CWs [17], or in systems with forced bed aeration, which enhances the volatilization of BTEX compounds [18].

Despite the volatilization process, which may be the predominant BTEX removal mechanism, some other mechanisms should also contribute in BTEX removal. Microbial degradation is such a mechanism, as BTEX may biodegrade under aerobic or anaerobic conditions [6,19] (the latter are occurring in the deeper layer of the fields). Thus, biodegradation may be responsible for the observed 5–10%, in average, higher removal of toluene as compared to benzene and the other compounds. Also, toluene is less volatile [20], but more biodegradable than benzene [21,22].

Due to the high surface area present in a gravel bed, subsurface-flow wetlands achieve higher biological treatment per unit volume, thus, high strength wastewaters could be successfully treated. In the present study, more than 60% BTEX removal takes place in the first 40% of the wetlands, in each field, slightly less than what other similar studies suggest [18].

3.3. Evaporation measurements

Influent evaporation was particularly noteworthy and ranged from an average of 12 mm/d (unplanted field) to 15 mm/d (*Phragmites* field) to 16 mm/d (*Typha* field) during the six months experimental period (April–October). During the hottest day of July, evaporation reached a peak value of 29 mm/d. Similar values for the same climate conditions have been reported by Papaevangelou et al. [23] and by Ranieri et al. [24–28].

Evapotranspiration was evaluated by monitoring the level of water in the CWs, using the perforated tubes which had been established in the CWs. Climate was typically Mediterranean: average temperatures ranged from 7.9 (January) to 25.4 (July). Rainfalls varied from 19 mm (July) to 83 mm (March).

Evapotranspiration values were compared with the theoretical ones resulting from the application of the Thornthwaite equation for fully vegetated plants (Eq. (1)):

$$ET_P = c \times T^a, \tag{2}$$

where ET_p is the monthly evapotranspiration (cm), T is the monthly average temperature (°C), c and α are Thornthwaite constants depending on I, and I is the Thornthwaite's temperature efficiency index.

Pan measurements were found to be cumulatively equal to 401 mm in July, while Thornthwaite method calculation results in 429 mm for the same month.

4. Conclusions

On the basis of the results and discussion, the following conclusions could be drawn:

- BTEX overall removal by CWs ranges from 46% (unplanted field) to 57% (*Phragmites* field). Removal of toluene (less volatile) was 5–10% higher than other BTEX compounds.
- Although volatilization is the predominant removal mechanism, microbial degradation is also an important removal mechanism as illustrated by comparing the results of the planted fields, particularly in the *Phragmites* field, to the unplanted control.
- Constructed wetlands offer a potential for the removal of more than 60% of BTEX from wastewater at HRT higher than 100 h, however, the latter correlation should be evaluated as a function of inlet concentrations.
- The hydraulic flow pattern in both CWs was well described by the plug flow with dispersion reactor model, with *Peclet numbers* between 24.9 and 29.7, which is consistent with the existence of a limited number of preferential flow paths. The latter may be attributed to deeper root penetration, particularly in the *Phragmites* field.
- Further large-scale experimental tests should be carried out to validate the results presented in this paper.

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