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Removal capacity of BTEX and metals of constructed wetlands under the influence of hydraulic conductivity

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ABSTRACT

Constructed wetlands are a natural alternative to technical methods of wastewater treatment. They can remove Benzene, Toluene, Ethylbenzene, Xylenes (BTEX), and metals from wastewater, which are commonly encountered pollutants. In this paper, an experimental pilot-scale Horizontal Subsurface Flow Constructed Wetland (HSFCW) located in Lecce (Apulia, South Italy) has been reported. The experiments were carried out in three constructed wetlands. Two of them were planted with two different species of macrophytes and the third was used as a control. The objectives of this study are to compare hydraulic behavior of the CWs with the trend of the model by varying the hydraulic conditions, to evaluate the effect of the clogging and then to assess the efficiency of the different species of macrophytes in removing BTEX and metals. At the beginning of the experience and after 24 months, the results show a good correlation in the hydraulic behavior between model and physical data by modifying input parameters as a consequence of the clogging. The BTEX removal planted fields is higher than the unplanted one, while the three HSFCWs have a similar capacity in removing Cr, Fe, and Pb.

Keywords: BTEX; Constructed wetlands; Hydraulic conductivity; Metals; *Phragmites australis*; *Typha latifolia*

1. Introduction

Constructed wetland systems are widely used in many countries for situations where civil infrastructure is limited and can offer an alternative to large-scale civil engineering interventions through relatively low-cost unitary treatment of wastewater discharge from both domestic and commercial premises. Compared to conventional wastewater treatment technologies, treatment wetlands are

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mechanically simple and have relatively low operation and maintenance requirements [1–3].

Constructed wetlands are artificial wastewater treatment systems consisting of shallow (usually less than 1 m deep) ponds or channels which have been planted with aquatic plants and which rely upon natural microbial, biological, physical, and chemical processes to treat wastewater. They typically have impervious clay or synthetic liners, and engineered structures to control the flow direction, liquid detention time, and water level. Depending on the type of system, they may or may not contain an inert porous media such as rock, gravel, or sand.

Constructed wetlands can also remove metals and volatile organic compounds, like Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX) from wastewater. This topic has been studied increasingly in recent years [4–8]. BTEX frequently occur near petrol stations or where fossil fuels are used, and often contaminate the aquatic environment, while metals are contained in numerous industrial discharges, or also the municipal wastewater into the public sewer can convey these contaminants, which are released from metal surfaces exposed to contact with sewage or rainwater.

Otherwise hydraulic considerations have a significant role in prediction of the actual removal percentages for every contaminant. This study assesses and elaborates the hydraulic performance in the pilot-scale HSFCWs and observes trends over time. Design parameters such as aspect ratio, size of the porous media, and hydraulic loading rate can improve the hydraulic behavior of constructed wetland systems by imparting a hydraulic flow behavior that approaches that of an ideal flow system [9,10]. The experiments were conducted using tracer tests (KBr), which provided the residence time distribution (RTD). Particularly, after 24 months of operating, clogging conditions in experimental HSFCWs result in a lower hydraulic conductivity values.

The objectives of this study are:

- to evaluate the hydraulic behavior of constructed wetlands not planted and planted with different species (*Phragmites australis* and *Typha latifolia*), by varying hydraulic conductivity;
- to assess the correlation of the experimental RTD curves with the curve of the model, as a function on the variation of hydraulic characteristics and clogging;
- to evaluate BTEX and metals removal as a function of the hydraulic residence time (HRT).

2. Materials and methods

2.1. Design of HSFCWs experimental plant

The experimental area includes three constructed wetland fields, two containing different species of plants macrophytes: *P. australis* e *T. latifolia* and the third serving as a control reactor (unplanted). Water is supplied to the fields from four high-density polyethylene (HDPE) tanks; samples are obtained from 18 sampling ports and effluent is stored in two lagoon ponds. Fig. 1 depicts the plan view of the site (Fig. 1(A)) and the longitudinal section of one planted constructed wetland bed (Fig. 1(B)). Each wetland has a planted area equal to 15 m^2 (3 × 5 m), a water depth ranging from 0.6 m to 0.65 m, and a resulting total volume of approximately 9.4 m^3. The constructed wetlands have a bottom slope of 1% to facilitate the outflow of water by gravity. The stability of the side banks is ensured by providing a 45° inclination. Five perforated tubes with 200 mm internal diameter are positioned within each field to permit collection of water samples and control of water levels. The bottom of each reactor is waterproofed with a bentonite liner that is permeable to plant roots but largely impermeable to water. The liner consists of three layers: an upper geotextile 220 g/m^2, a lower geo-textile 110 g/m^2, and sodic powdered bentonite 4,670 g/m^2, containing approximately 90% montmorillonite. The total weight of the geo-composite is 5,000 g/m^2 and its total dry thickness is 6 mm.

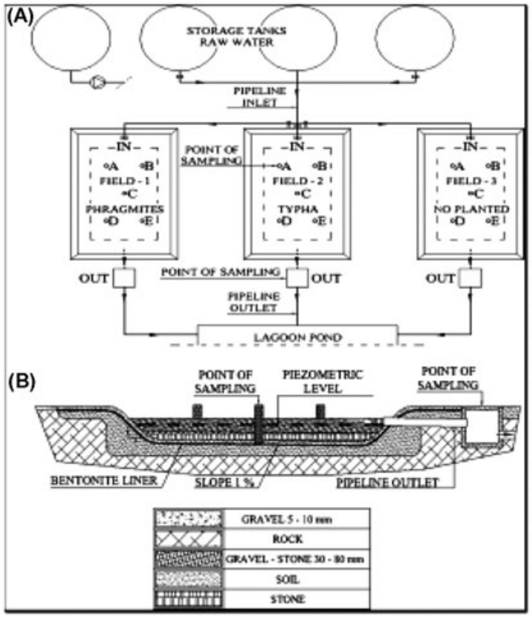

Fig. 1. Constructed wetlands pilot plant at Lecce, Italy: (A) plan view and (B) longitudinal section.

The hydraulic conductivity of the installed liner is $k < 10^{-11}$ m/s.

The hydraulic loading rate is the same for each fields and equal to 66 mm/d. Full-scale CWs hydraulic conductivity measurements were carried out exclusively *in situ* using a constant head permeameter for the direct measurement of hydraulic conductivity of the soil [1–11].

Raw water is supplied at the reactor inlet and passes slowly through the filtration medium under the surface of the bed in a generally horizontal path until it reaches the outlet zone where it is collected and discharged to the lagoon. The filtration medium consists of three layers: 0.1 m of soil, 0.2 m of stones, and 0.30–0.35 m gravel as shown in Fig. 1(B). The mineral composition of the substrate is 59% calcium carbonate, 32% silica, and 9% iron oxide for the rocks and gravel. The soil is a mixture of red clay and organic matter. The unplanted bed served as a control reactor. At no time, during the study was the water depth above the top of the media in any of the reactors, i.e. all flow was subsurface.

The climate at the site is Mediterranean with an average annual temperature and annual accumulated rainfall of 15.6℃ and 530 mm, respectively.

2.2. Tracer injection

2.2.1. Sampling for HRT measurements

The tracer used in the experimental plant was the potassium bromide (KBr), because it is highly soluble, non-degradable, relatively inexpensive, and can be measured quantitatively in very low concentrations. Tracer solution was added in 10 min mixed with wastewater flow in order to reduce sinking effects related to density differences.

Composite samples of the effluent from each constructed wetland were collected in 500 mL amber glass bottles using an auto sampler. Effluent grab samples were taken approximately every 12 h from the morning of day 3 until the evening of day 9. From the morning of day 10 to the morning of day 12, samples were taken every 24 h.

Tests finished on the fourth day after a total sampling period of approximately 330 h. For a time of approximately 300 h, the tracer concentration was not detected and, therefore, a period of time of 300 h was enough to obtain a complete response of the tracer injection.

RTD curves were assessed by introducing 6 kg/m^3 solution of KBr in 10 min along the first cross-section of each wetland unit as a conservative tracer.

2.2.2. BTEX and metals sampling and analysis

BTEX and metals solution was conveyed to the CWs from the supply tanks containing tap water at a constant initial concentration of 0.5 and 2 mg/L, respectively, for each compound, for all tests. Composite samples of the effluent from each constructed wetland were collected in 500 mL amber glass bottles every 6 h using an auto sampler for a time period of 220 d. Samples were collected at inlet and outlet two times per week and were kept refrigerated at 4℃ until analyses. Samples were analyzed according to Standard Methods [12] using an HP 5890 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.

2.3. Plug flow with dispersion reactor model

The RTD curves have been calculated using the plug flow with dispersion reactor (PFDR) model by adjusting the HRT (θ) and the reactor Peclet number to minimize the sum of the squared errors between the experimental bromide concentration data and the analytical solution to the PFDR model given by Levenspiel and Smith [13]:

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

where $\sum_i C_i \Delta t$ is the area under the RTD curve, Pe is Peclet number, and θ is the HRT.

The equation has been modified from its original dimensionless form by multiplying the summation of $C_i \Delta t$, which approximates the area under the RTD curve.

3. Results and discussion

3.1. Effect of clogging

In the pilot HSFCWs, experimental curves have been collected at time $t = 0$ and at time $t = 24$ months to the aim of evaluating the different clogging conditions.

Table 1 reports the hydraulic parameters adopted for the experimental HSFCWs and utilized in the model at the beginning of the experience and after two years for both planted and unplanted fields.

Table 1
Values of parameters that define hydraulic behavior of the tested experimental plants and after 24 months (planted and unplanted)

Parameter symbol	Parameter name	Value (at the beginning)	Value (after 24 months for planted fields)	Value (after 24 months for unplanted field)
K	Hydraulic conductivity	30 (m/d)	25 (m/d)	30 (m/d)
H_{out}	Hydraulic head at the outlet	0.6 (m)	0.6 (m)	0.6 (m)
α_L	Longitudinal dispersion	0.2 (m)	0.35 (m)	0.35 (m)
α_T	Transversal dispersion	0.02 (m)	0.02 (m)	0.02 (m)
D_{KBr}	Diffusion	2.02^{-5} (cm^2/s)	2.02^{-5} (cm^2/s)	2.02^{-5} (cm^2/s)
p	Porosity	0.16	0.16	0.15

Fig. 2(A) shows the comparison between the experimental and the simulated RTD curves, measured at the beginning of the experience in the experimental plant. A good correspondence, $R^2 = 0.98$, according to well-recognized model evaluation techniques [14] between the simulation curve and the tracer test has been found. A less-pronounced plug flow behavior in the Lecce plant is probably due to lower porosity of the substrate. *Phragmites* HSFCWs behavior is quite similar to the *Typha* ones, whereas the unplanted field showing a clearer plug flow behavior. The variation from the ideal plug flow behavior and the coefficient

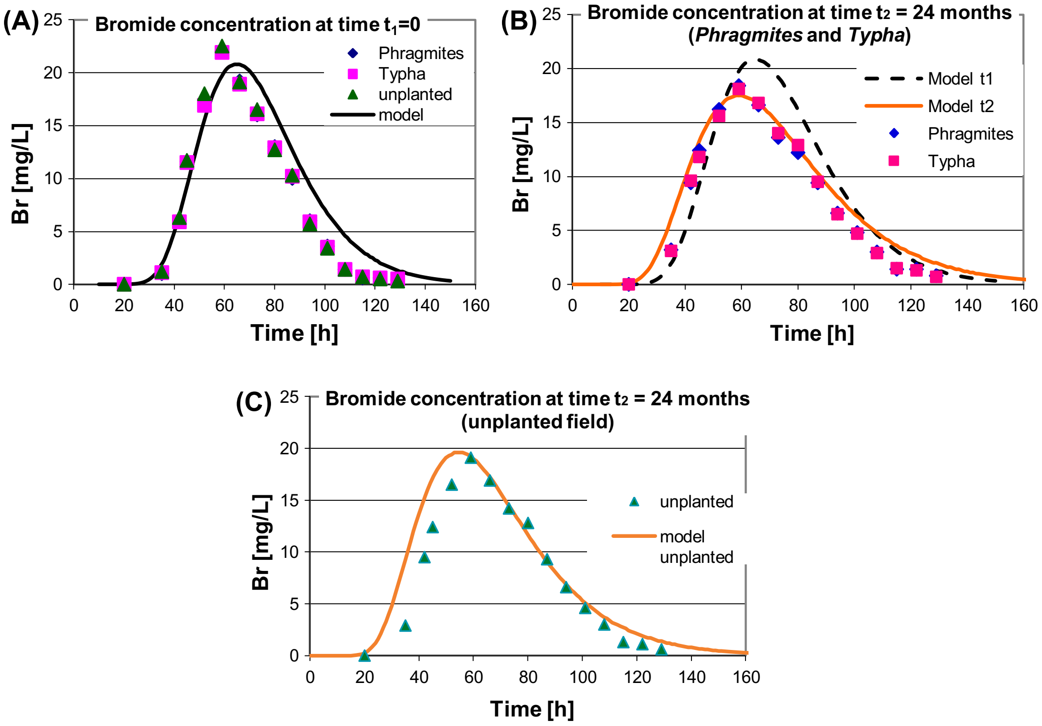

Fig. 2. Bromide concentration trends vs HRT. Comparison between: (A) the experimental (black) and the simulated RTD curves (of *P. australis*, *T. latifolia*, and unplanted field) measured at the beginning of the experience (at time $t = 0$); (B) the experimental curve, the tracer concentration curve and the second simulated RTD curve after two years for *Phragmites* and *Typha* plants; (C) the experimental curve and the second simulated RTD curve after two years in unplanted field.

correlation (R^2) was equal to 0.92 for the unplanted field, 0.87 for the *Phragmites* field and 0.86 for the *Typha* field.

After 24 months, tracer tests were performed and the results are illustrated in Fig. 2(B). The correlation between the model and the experimental data was less evident. In particular, while the unplanted field still maintains a good plug flow behavior, the *Phragmites* and the *Typha* plants show a decrease of the peak with lower concavity of the curve and a higher distance from the model interpolation curve. This is probably due to the lower hydraulic conductivity measured in the field hydraulic conductivity decreasing from 30 to 25 m/d for the *Phragmites* field and 25.2 m/d for the *Typha* field, as reported in previous experiences [9,10].

The RTDs for the unplanted wetland have been assessed after 24 months. Results are shown in Fig. 2(C).

It is observed that the model curve interpolate very well the tracer experimental data in the unplanted field where the hydraulic conductivity still remain equal to 30 m/d and only the porosity decrease from 0.16 to 0.15 as measured in the field.

The RTD curves have been calculated using the PFDR model. All of the PFDR model fits to the tracer data had R^2 values greater than 0.975. The differences between the RTD curves for the planted reactors are probably related to the different root structures of the two species. The roots of *P. australis* penetrate to a depth of approx. 51 cm, while *T. latifolia* roots are not likely to extend beyond about 29 cm, according to previous experience with these species [15]. The differential root penetration depth is likely to be responsible for the slightly different flow regimes in the two wetland beds. Clogging was more significant in the *Phragmites* bed, and this favors the development of preferential flow paths and causes the slightly shorter HRT compared to the *Typha* one bed and the slightly lower Peclet number of 26.7 in contrast to Pe for the *Typha* bed of 29.7. The unplanted bed had a Peclet number of 24.9.

3.2. BTEX removal

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

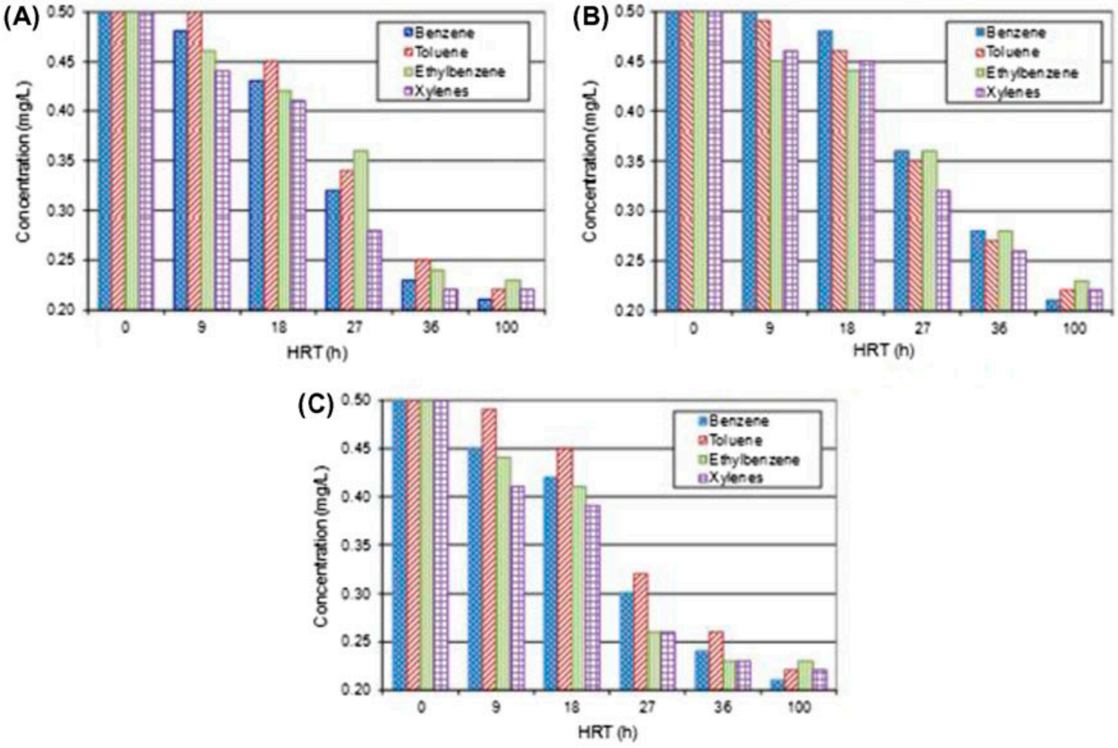

Fig. 3. Benzene, Toluene, Ethylbenzene, and Xylenes vs HRT (A) in the *Phragmites* field; (B) in the *Thypha* field; (C) in the unplanted field.

(Xylenes) nd 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 (Fig. 3(A)–(C)).

The removal efficiencies determined in the present work are lower or similar compared with a similar experimental work [16,17]. 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) [18]. 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 [19]. 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 [20].

3.3. Metals removal

Fig. 4(A)–(C) show the Cr, Fe, and Pb removal in *Phragmites*, *Typha*, and control field, respectively, as a function of HRT (measurements are shown for HRTs equal to 8, 16, 24, 32, and 40 h). All heavy metal concentrations at HRT of 40 h were almost identical with the outlet concentrations (HRT equal to 100 h).

On the basis of the observed data, we can consider that the three HSFCWs fields have a similar capacity in removing the three investigated trace elements. Chromium seems to be more sensible to the medium filtration effect than to the phytoextraction/stabilization process, because of the rapid removal rate along all fields. The chromium removal rate for a short HRT of 8 h (samples from the first piezometer) was higher compared to the removal rates of Fe and Pb in all the fields (ranging from 60% in the control field to 70% in the *Phragmites* field). Cr concentrations at the outlet were quite similar, ranging from 0.23 to 0.25 mg/L and removal of Cr ranged from 86% (control field) to 90% (*Typha* field). Based on the experimental results, it appears that the role of the vegetation is significant as the removal efficiency of the control field was on average 20% lower than that of *Praghmites* and *Typha* fields (Fig. 4), most possibly due to the phenomena of phytoextraction and translocation. No significant variation in heavy metal removal rates was observed among the

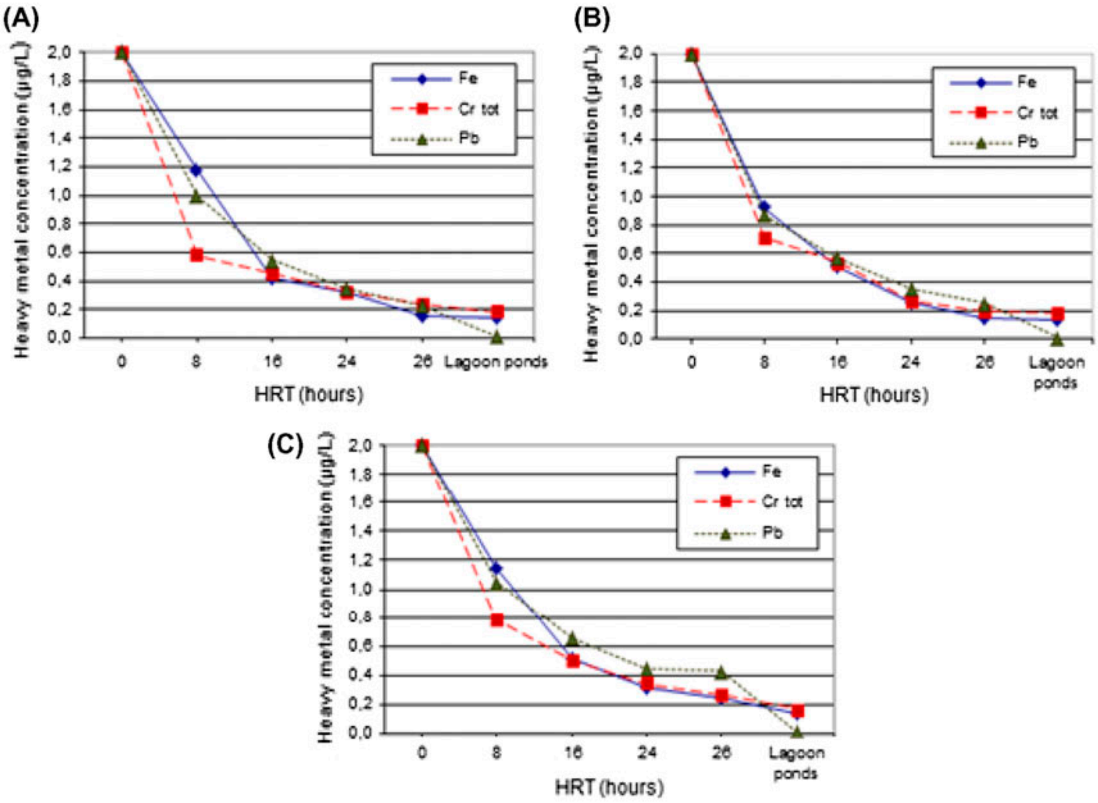

Fig. 4. Metals vs HRT (A) in the *Phragmites* field; (B) in the *Typha* field; (C) in the unplanted field.

two types of vegetation studied (*Praghmites* and *Typha*), thus, both types are considered suitable for the type of phytoremediation studied in the present research [21].

4. Conclusions

HSFCWs are appropriate for removing Fe, Cr, and Pb from wastewater; however, the removal efficiency should be evaluated as a function of the clogging phenomena and the related HRT variations. Heavy metals overall removal by HSFCWs was quite high: Fe removal ranges from 88% (control) to 95% (*Typha*), removal of Cr ranges from 86% (control) to 90% (*Typha*), and removal of Pb ranges from 78% (control) to 88% (*Phragmites*).

Furthermore, 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. 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.

HRT has also been evaluated in constructed wetlands experimental plants. Model shows a good agreement with experimental data for plants. After 24 months, the hydraulic conductivity is varied from 30 m/d to 25 m/d for both *Phragmites* and *Typha* plants in HSFCWs due to clogging and the model curve is capable of interpolating this hydraulic behavior variation. The lack of the vegetation in the unplanted constructed wetland results in a constant value of the hydraulic conductivity after 24 months of operating. In the unplanted field, only a slightly decrease of the porosity has been evidence. This causes a shift of the experimental curve toward lower HRTs. The field measurement of hydraulic conductivity appears to be one crucial parameter useful to predict the actual hydraulic behavior.

Further, large-scale experimental tests should be carried out to validate the results presented in this paper.

The experience of who have measured in the field of constructed wetlands suggests that, despite the definition provides that the treatment processes occurring in the controlled environment, it is impossible that all treatment phases are kept constant within the conditions established. The wet area, in fact, is a complex ecosystem in which sometimes phenomena difficult to predict develop.

Therefore, it is necessary to adapt to nature rather than bend it to our needs, helping her to collaborate with the man in the difficult process of remediation of our environment.

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