Investigation of phenol and *m*-cresol biodegradation in horizontal subsurface flow Constructed Wetlands

Alexandros Stefanakis[1], Eva Seeger[1], Thomas Hübschmann[1], Susann Müller[1], Anja Sinke[2], Martin Thullner[1]

[1] Department of Environmental Microbiology, Helmholtz Centre for Environmental Research - UFZ, Permoserstraße 15, 04318 Leipzig, Germany

[2] BP International Limited, Sunbury on Thames, Middlesex, TW16 7BP, UK.

Introduction

Constructed Wetlands (CWs) have been proven to be an effective remediation technology for groundwater contaminated with organic pollutants like benzene and MTBE, mainly through aerobic biodegradation. Until today, the applicability of this technology for phenol degradation has hardly been tested and the respective removal processes are not yet fully understood. Moreover, possible physico-chemical interactions between phenols and other contaminants and chemical constituents might limit biodegradation, while other compounds might reduce the available oxygen for phenol degradation. In turn, the presence of phenols might limit the degradation of contaminants like benzene and MTBE. Therefore, the fate of phenols in wetland systems cannot be predicted from existing data and requires tests under in-situ conditions.

Aim of the project

Pilot-scale systems provide an optimal combination of realistic conditions and the ability to observe processes with high accuracy, which allows for the distinction between biodegradation and other removal processes. Therefore, this project focuses on the use of pilot-scale horizontal subsurface flow CWs (HSSF CWs) with three main targets: (a) to investigate the fate and the removal efficiency of two phenolic compounds (phenol and *m*-cresol) in HSSF CWs, (b) to estimate the role of biodegradation and other treatment processes in phenol removal, and (c) to determine the impact of phenol presence on the removal of other contaminants (benzene and MTBE).

Material Methods

Three pilot-scale HSSF CWs (steel basins; L:W:D = 5.9:1.1:1.2 m) are used in the large experimental facility located in Leuna, Germany (Fig. 1). All beds were filled with gravel (2 – 3.2 mm) up to a height of 1 m, whereas the last 1 m length is an open water compartment allowing for direct contact between the water surface and the atmosphere. The water level was set at 95 cm. Two beds (A, C) are planted with common reeds (*Phragmites australis*) and one (B) is left unplanted (Fig. 2). All units are fed with contaminated groundwater (pumped from the local aquifer, containing benzene and MTBE) at an inflow rate of 11 L/h and a HRT of one week. A phenol and *m*-cresol solution is injected to the groundwater loaded to units A and B (inflow concentrations: 14 and 2 mg/L for phenol and *m*-cresol, respectively). The first experimental period lasted for 10 weeks (August-October 2012). The ongoing operation covers the entire growth season (April-October 2013).

Fig. 1. Aerial view of the experimental facility in Leuna, Germany. The black box indicates the HSSF CWs used for this project.

Fig. 2. Pilot CWs (planted/unplanted) during summer and winter operation

Samples are taken from the influent and effluent points of each bed at a bi-weekly scheme. Emphasis is given in the pollutant spatial distribution, in order to obtain a better insight into the removal processes. Thus, samples are taken once a month from three different points along the wetland length (0.5, 1.9, 4.1 m) and three depths (0-5, 30, 80 cm), as shown in Fig 3. All samples are analyzed for the determination of total phenols and *m*-cresol concentrations. Microbial community patterns are observed via flow cytometry.

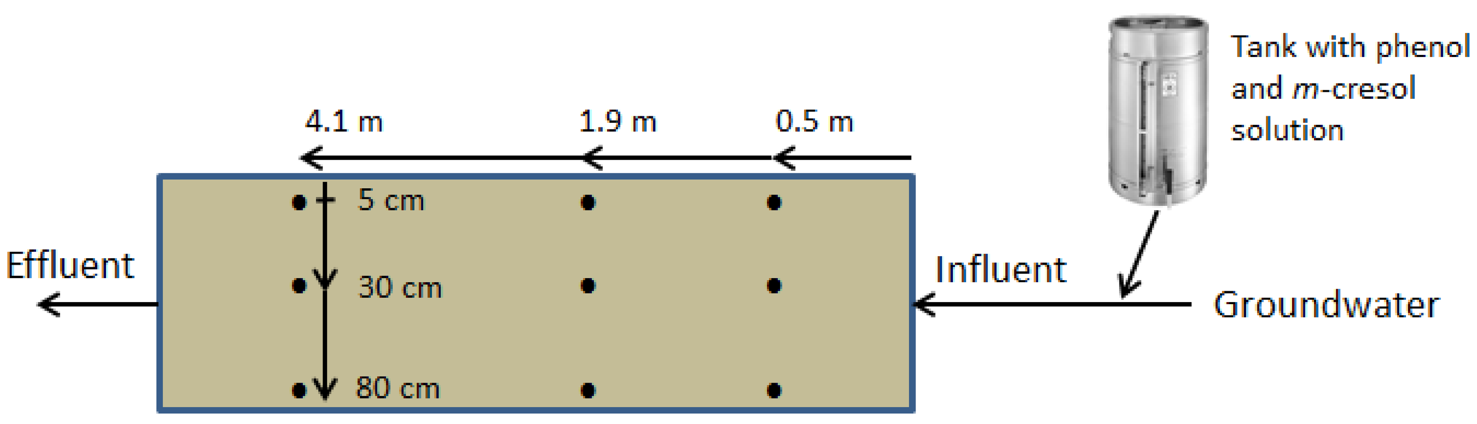

Fig. 3. Side view of a pilot CW bed and sampling points.

Results and Discussion

Results show a complete removal of phenolic compounds in planted bed A with effluent values close to 0 (Fig. 4). The unplanted bed B shows higher mean effluent Total Phenols and *m*-cresol values of 1.8 and 0.4 m/L, respectively. No phenolic compounds were detected in the control unit C. Spatial analysis shows lower concentrations in all sampling points in the planted bed compared to the unplanted one.

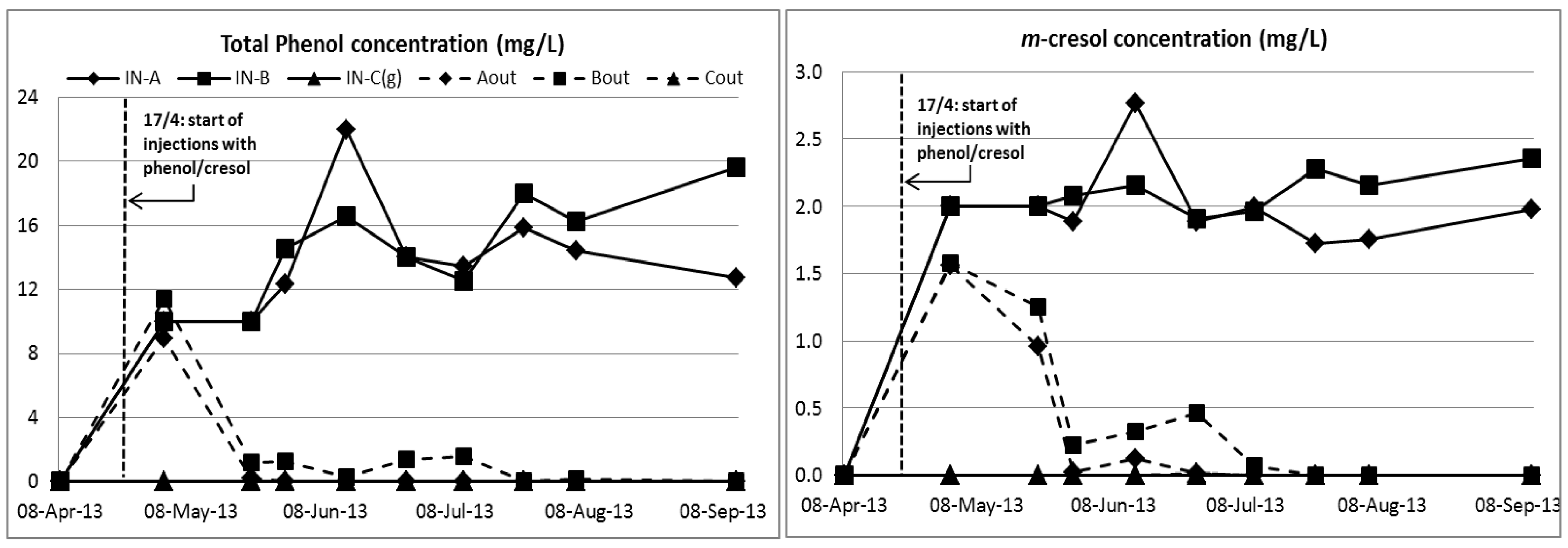

Fig. 4. Phenol and m-cresol influent and effluent concentration variations at various sampling campaigns in 2013 in the three pilot HSSF CWs (A and C planted, B unplanted).

Bottom concentrations are higher in the unplanted bed than in planted bed A, indicating the lack of oxygen in the deeper parts and the positive effect of plant presence in planted bed A. Analyses of the microbial community using flow cytometry show similar patterns for the effluent of all units (Fig. 5). Both beds receiving phenol and *m*-cresol exhibit an increasing shift of the community.

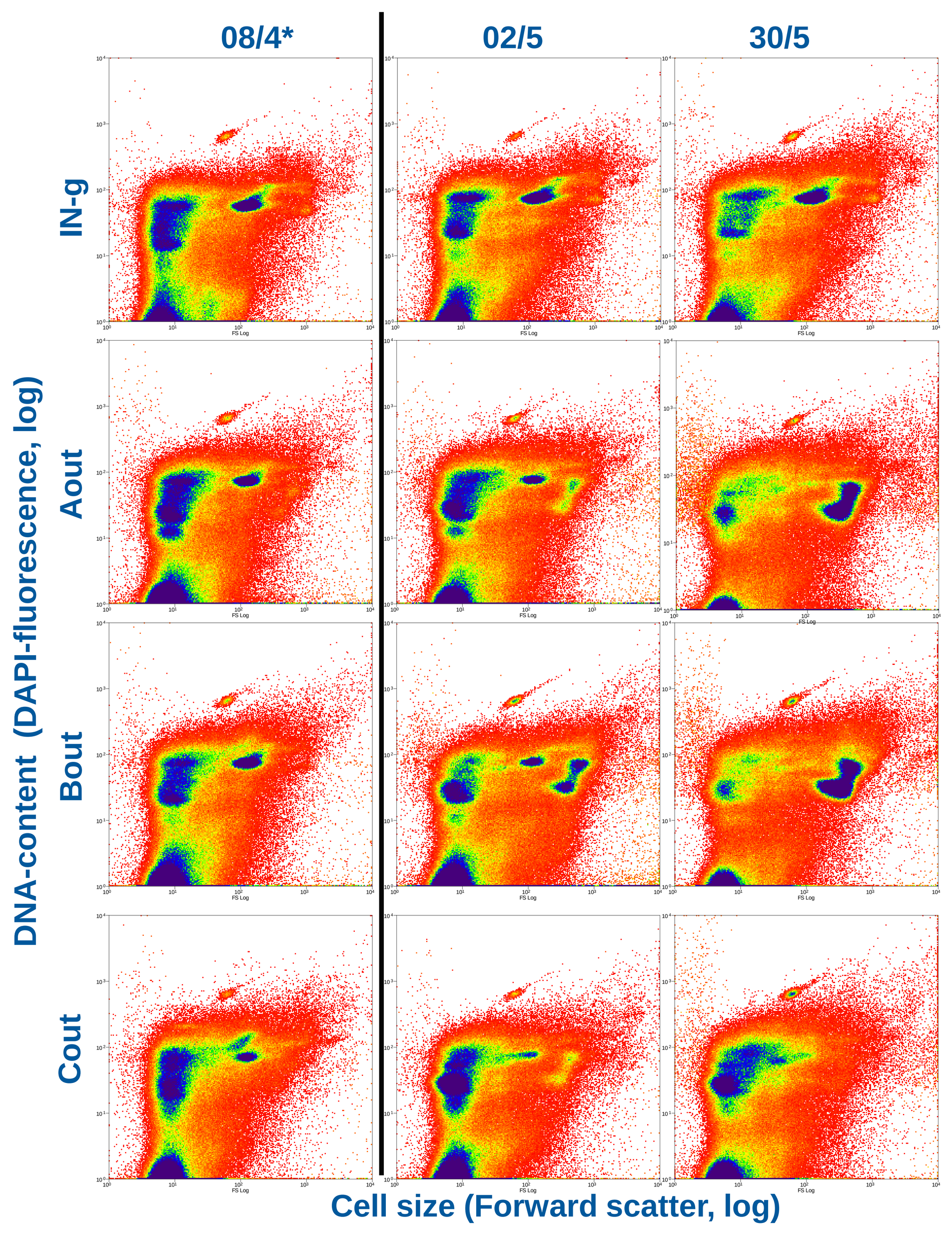

Fig. 5. Alterations of the patterns of microbial communities as observed by flow cytometry

Gradual increase of ambient temperature (from early April to late May) allowed for the growth of microorganisms in the beds, as shown in Fig 5.

Conclusions

Results suggest that HSSF CWs are an appropriate technology for the removal of phenolic compounds from contaminated groundwater. Biodegradation seems to be the dominant removal mechanism. Removal is enhanced by the presence of plants and the respective plant root activity. Vertical concentration profiles show that the lack of oxygen in deeper parts (especially in the unplanted bed) reduces the contaminant removal. This indicates that oxygen input via the CW surface affects the aerobic removal rate, but also anaerobic removal takes place. Flow cytometry analysis implies a shift in the microbial community in the two beds fed with phenol and *m*-cresol, suggesting an adaptation of the community to the added contaminants. The completion of the experiment for the entire growth season and further analyses (flow cytometry, isotope fractionation) will provide significant data towards the determination of the factors affecting these alterations.

Acknowledgements

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Contact: alexandros.stefanakis@ufz.de

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[a] Department of Environmental Microbiology, Helmholtz Centre for Environmental Research – UFZ, Permoserstraße 15, 04318 Leipzig, GERMANY (alexandros.stefanakis@ufz.de)
[b] BP International Limited, Sunbury on Thames, Middlesex, TW16 7BP, UK.

INTRODUCTION

Constructed Wetlands (CWs) have been proven to be effective in the treatment of groundwater contaminated with organic pollutants like benzene and MTBE, promoting their removal mainly via aerobic biodegradation (Seeger et al., 2011). In contrast, CW removal processes for phenols in have not been fully understood, yet. The aim of this project is to investigate the fate of two phenolic compounds (phenol and *m*-cresol) in pilot-scale CWs, to estimate the role of biodegradation and other treatment processes for phenol removal, and to determine the impact of phenol on the removal of other contaminants (benzene and MTBE).

METHODS

Three pilot-scale horizontal subsurface flow CWs (steel basins; L:W:D = 5.9:1.1:1.2 m) are used in the experimental facility located in Leuna, Germany. Two beds (A, C) are planted with common reeds (*Phragmites australis*) and one (B) is left unplanted. All units are fed with contaminated groundwater (pumped from the local aquifer and containing benzene and MTBE) at an inflow rate of 11 L/h and a hydraulic residence time of one week. A solution of phenol and *m*-cresol is injected to the contaminated groundwater loaded to the units A and B (inflow concentrations: 10 and 2 mg/L for phenol and *m*-cresol, respectively). The first experimental period lasted for a 10 weeks period (August-October 2012). The ongoing operation and monitoring covers the entire growth season (April-October 2013).

Samples are taken from the influent and effluent points of each bed at a bi-weekly scheme. Emphasis is given in the pollutant spatial distribution, in order to obtain a better insight into the removal processes. Thus, samples are taken once a month from three different points along the wetland length (0.5, 1.9, 4.1 m) and three depths (0-5, 30, 80 cm). All samples are analysed for the determination of phenol and *m*-cresol concentrations. Microbial community patterns are observed via flow cytometry.

RESULTS AND DISCUSSION

Results from 2012 and first results from 2013 (Figure 1) show an almost complete removal of phenolic compounds in the effluent of the planted unit A after the first 20 operational days (effluent values close to 0.0), while the unplanted bed has a slightly reduced performance. Spatial analysis shows lower concentration values in all sampling points within the planted bed compared to the unplanted one. Concentrations in points closer to the bottom are also higher in the unplanted bed, indicating the lack of oxygen in the deeper parts and the positive effect of plant presence. No phenolic compounds were detected in the control unit C.

First analyses of the microbial community using flow cytometry (Figure 2) show initially similar patterns for the effluent of all units, while during the experiment the units receiving phenol/*m*-cresol exhibit an increasing shift of the community.

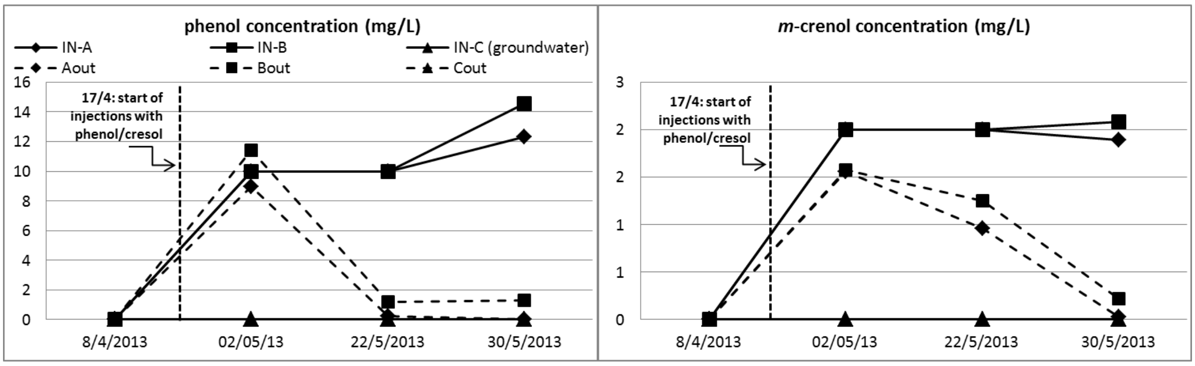

Fig. 1. Phenol and m-cresol influent and effluent concentration variations at various sampling campaigns in 2013.

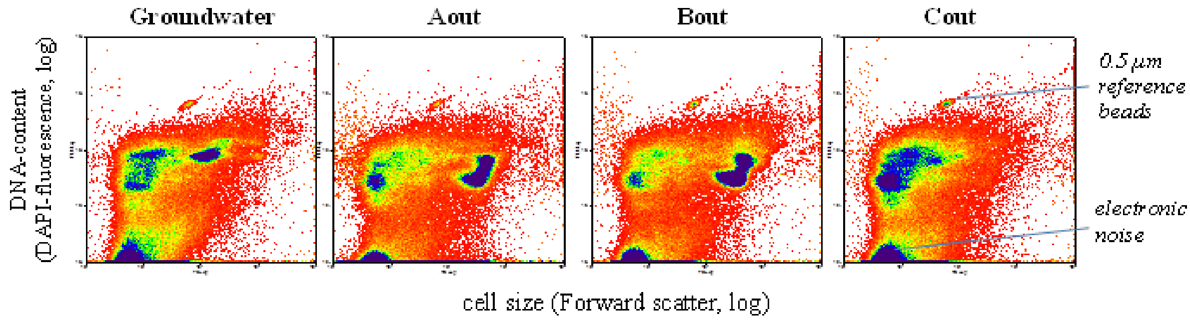

Fig. 2. Microbial community patterns obtained on 13/5/2013 one month after beginning of phenol/*m*-cresol injection.

CONCLUSIONS

The results obtained so far suggest that the investigated horizontal subsurface flow CWs are an appropriate technology for the removal of phenolic compounds from contaminated groundwater. Biodegradation of pollutants seems to be the dominant removal mechanism, while the removal is enhanced by the presence of plants and the respective plant root activity. Vertical concentration profiles in the CW show that in deeper parts the lack of oxygen reduces but does not stop the contaminant removal, especially in the unplanted bed. This indicates that oxygen input via the CW surface affects the aerobic removal rate but also anaerobic removal is taking place. Flow cytometry analysis implies a shift in the microbial community in the two beds which were fed with phenol/*m*-cresol suggesting an adaptation of the community to the additional contaminants. The continuation of the experiment during the entire growth season of this year and respective further analyses will provide significant data in order to determine the factors affecting these alterations.

ACKNOWLEDGEMENTS

This study is funded by BP International. Further funding was provided by the Helmholtz Centre for Environmental Research – UFZ in the scope of the SAFIRA II Research Programme: Revitalization of Contaminated Land and Groundwater at Megasites, project “Compartment Transfer.” The technical support was provided by the UFZ Departments Groundwater Remediation and Isotope Biogeochemistry.

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