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## Accumulation of organic and inorganic micropollutants over time and space in a constructed wetland for urban runoff

J. Roux\*, M. Seidl\*\*, P. Branchu\*\*\*, M.C. Gromaire\*\*, P. Neveu\*\*\*\*, L. Boudahmane\*, E. Caupos\*, V. Alphonse\*, N. Bousserhine\*

\* Laboratoire Eau Environnement et Systèmes Urbains (LEESU), 61 avenue du Général de Gaulle, 94010 Créteil Cedex, FRANCE ([julia.roux@univ-paris-est.fr](mailto:julia.roux@univ-paris-est.fr) ; [bousserhine@u-pec.fr](mailto:bousserhine@u-pec.fr))

\*\* LEESU, 6-8 avenue Blaise Pascal, Cité Descartes, Champs sur Marne, 77 455 Marne-La-Vallée Cedex 2, FRANCE ([martin.seidl@enpc.fr](mailto:martin.seidl@enpc.fr) ; [marie-christine.gromaire@enpc.fr](mailto:marie-christine.gromaire@enpc.fr))

\*\*\*Team Unit, CEREMA, 12 Rue Teisserenc de Bort, 78197 Trappes-en-Yvelines Cedex, FRANCE ([philippe.branchu@cerema.fr](mailto:philippe.branchu@cerema.fr))

\*\*\*\* Direction de la Propreté et de l'Eau (DPE) Ville de Paris, 103 avenue de France, 75013 Paris, FRANCE ([pascale.Neveu@paris.fr](mailto:pascale.Neveu@paris.fr))

### Abstract

To improve the quality of the Seine River, the municipality of Paris (France) has constructed in the framework of the European Life Adsorb project a wetland to treat runoff water of urban roads. This constructed wetland (CW) is separated in two parts with a slightly different composition (addition of an adsorbent substrate for one). The main objectives of the project are to monitor the evolution of the CW efficiency and understand the fate of contaminants within the CW for different substrates. This paper proposes a short balance of the accumulation of metallic and organic micropollutants (MPs) after one year of functioning. The first results show a fast accumulation of MPs in a new sediment layer with also starting retention in the surface sand layer just below. At this stage, the data are not sufficiently consistent to confirm the better retention capacity of the specific adsorbent substrate.

### Keywords

Organic micropollutant, Metallic micropollutant, Constructed wetland, Vertical reed-bed filter, Urban runoff water, Microbial abundance

## INTRODUCTION

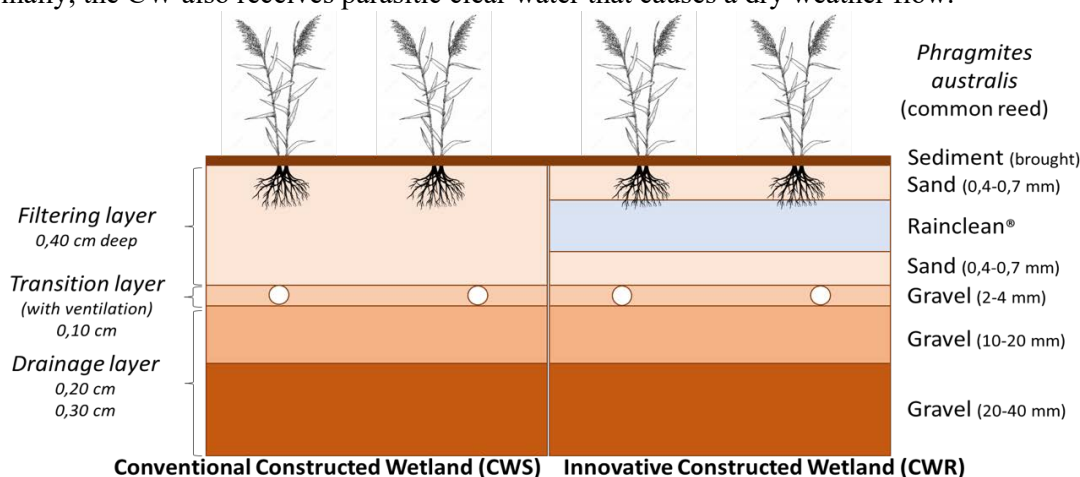
Urban runoff water is known for its contamination with metallic and organic compounds, mainly from road traffic (Markiewicz and al., 2017). This water can contribute to the degradation of the receiving aquatic environments if they are discharged without treatment. To limit these contaminant flows to the Seine River, the European Life Adsorb project has been set up in Paris by the municipality. A vertical flow reed-bed filter, a type of constructed wetland (CW) was built in 2019-2020 to receive and treat road runoff water. This CW is separated in two treatment compartments, with one having a conventional design, and the other having an innovative design for handling dissolved contamination. The innovative system must be able to treat both dissolved and particulate contaminations.

The Life Adsorb project aims to reduce the pollutant loads of Parisian urban runoff waters, but also to better understand the processes involved during the vertical filtration of these waters, like adsorption and biodegradation. Metallic (MMPs) and organic (OMPs) micropollutants (MPs) are particularly studied, as well as microbial communities presents, their evolution and their roles in CWs (very limited studies). In this context, the objective of this study is to compare the evolution in time and space of the two CWs through physicochemical and microbiological parameters and to explain the accumulation of MMPs and OMPs.

## METHODOLOGY

### The constructed wetland

The CW, located in the Bois de Boulogne Park in Paris (France, 48°52'28.6"N 2°15'43.6"E) is subdivided into two CWs of approximately 600 m<sup>2</sup> each and 1 m deep. Their design is similar; from top to bottom there is a filtering layer (40 cm), then a transition layer (10 cm) and finally a drainage layer (50 cm). The difference between these 2 CWs is in the composition of the filtration layer. In the conventional CW (CWS), this layer is composed of 40 cm sand while in the innovative one (CWR), a layer of 20 cm of an industrial adsorbent substrate, the Rainclean® (RC) is inserted between two layers of 10 cm of sand (figure 1). Finally, the CWs are planted with common reeds (*Phragmites australis*), contributing to the hydrological processes and rhizosphere microorganisms support (Wang and al., 2022). Each CW is fed upstream alternatively (monthly frequency) by pumps from a runoff storage reservoir (one feed zone per CW). The output flow is regulated to a maximum of 20 L/s during rain periods. Finally, the CW also receives parasitic clear water that causes a dry weather flow.



**Figure 1.** Vertical profile of the Life Adsorb constructed wetland. The conventional one (CWS, with sand) on the left and the innovative one (CWR, with Rainclean) on the right. Different layers are shown on the left and the nature (substrate with granulometry) of each layer is specified on the right.

### Sampling campaigns and analysis

The CWs began to be fed with contaminated water in February 2021 (almost 2 years of feeding). Three sampling campaigns were carried out, in september 2020 (= T0), september 2021 (= T1) and september 2022 (= T2) to study the space-time evolution of the CWs. During each campaign, core samples were collected from the filtering layer, at the feeding zone (input), the center and the output zone of each CW. The substrates cores were then divided as follows: sediment if present (not at T0), first 10 cm of sand, layer of 10 – 30 cm depth, which is whether sand or RC and deep sand layer of 30 – 40 cm depth. During this conference, results of the T0 and T1 campaigns will be presented.

To physicochemically characterise the CWs, pH, cation exchange capacity (CEC), particle size distribution but also total organic carbon, nitrogen and carbonates content were analysed.

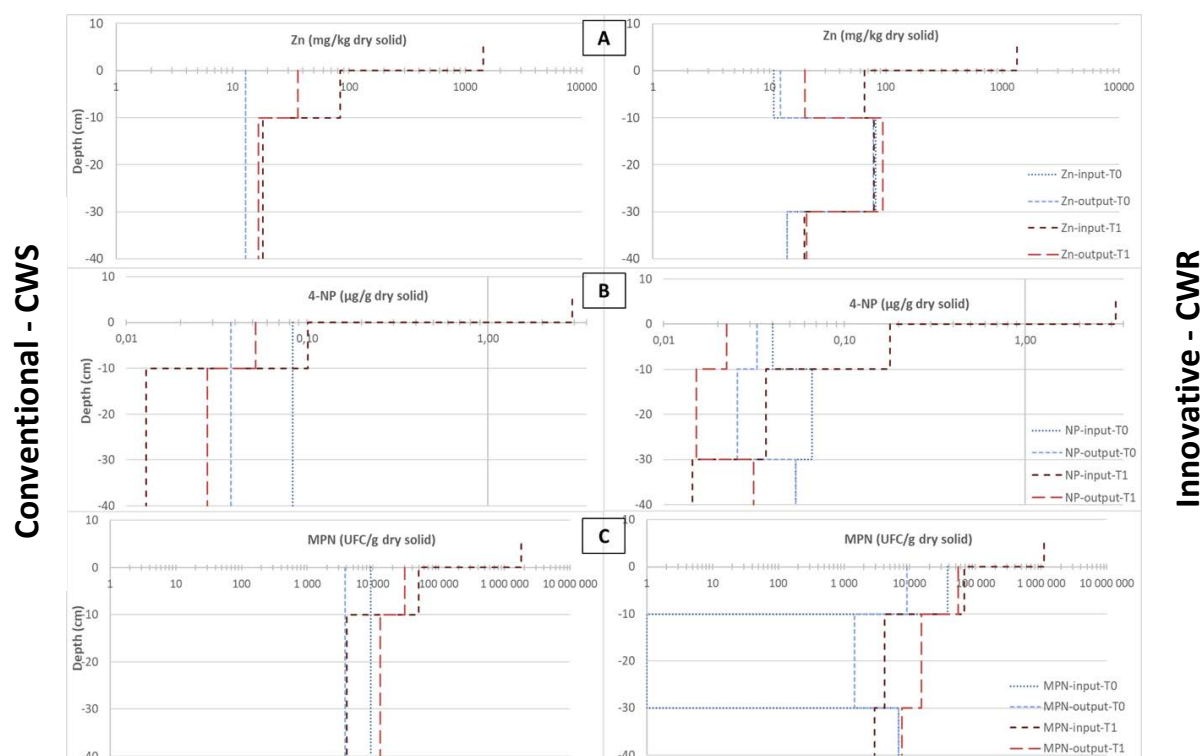
To assess the accumulation of micropollutants (MPs), analyses of their total contents were carried out. Concerning MMPs, 6 metals are studied: Cd, Cr, Cu, Ni, Pb, Zn (extraction with aqua regia and analysis by ICP-AES). In addition, a fine mapping of the surface metal content undertaken by X-ray fluorescence. Concerning OMPs, groups of compounds widely studied in the literature were measured (15 PAH, C10-C40 hydrocarbons), but also emerging compounds such as alkylphenols, phthalates and bisphenol-A (specific solvent extraction then GS-MS or UPLC-MS-MS analyse).

Finally, as the microbial communities present in the CWs are still too little known, three types of microbiological measurements were carried out: abundance of bacteria and fungi (MPN method), genetic diversity (DNA sequencing) and environmental functions (assays of enzymatic activities).

## RESULTS

Results of the physicochemical properties (data not shown) reveal that Rainclean (RC) and sediment are much more organic (around 20 and 150  $g_{oc}/kg$  respectively) than sand (less than 10  $g_{oc}/kg$ ), which implies a higher CEC. On the other hand, the pH of sand and RC are very alkaline (8.6 to 9.2) compared to sediment (7.3 to 7.7). The samples taken in the feeding zone of CWs after one year of operation are richer in organic carbon than the rest of the CWs, due to the water inlet location; runoff organic particulate matter is filtered as soon as it enters the CW. These properties illustrate the physical filtration role of sand (particulate contaminants) and chemical filtration role of RC (dissolved contaminants).

Concerning the horizontal distribution of MMPs in the CWs, results show that the majority is retained in the feeding zone like organic carbon, regardless of the metal (figure 2A, only Zn shown). For example, content of Zn decreases from 65 to 20  $mg/kg$  between input and output zones of the CWR surface sand.



**Figure 2.** Vertical profiles of 3 parameters (logarithmic scale) in the input and output zones of CWS (left) and CWR (right) for T0 and T1 sampling campaigns. A: Zn contents ( $mg/kg_{ds}$ ). B: 4-NP contents ( $\mu g/g_{ds}$ ). C: Bacterial biomass (MPN, CFU/ $g_{ds}$ ).

Regarding the vertical distribution of MMPs, it should first be noted that RC was initially richer in metals than sand (figure 2) and no sediment was present at T0. After one-year of functioning, accumulated sediments show the highest MMPs contents (574 to 656  $mg/kg$  for Cu, 204 to 215  $mg/kg$  for Pb and 1337 to 1418  $mg/kg$  for Zn) and metals contents of the surface sand got close to that of RC (10  $mg/kg$  for Pb in both, 65  $mg/kg$  for Zn in sand against 79  $mg/kg$  for Zn in RC) which seems to indicate that MMPs are essentially retained in the surface sand. This suggest that MMPs associate preferentially with particulate matter contained in water which are then retained by filtration in the sand. Finally, MMPs contents decrease rapidly with depth, with a slight increase in one year. Comparing the MMPs contents found with those measured in another older CW (Walaszek and al., 2018), they are higher for Cu, lower for Zn and in the same concentration range for Pb in sediment and they are lower in the surface of sand layer.

Concerning OMPs (BPA and 2 alkylphenols, 4-OP and 4-NP are discussed), very few accumulations were observed between the two campaigns (figure 2B, only 4-NP shown). Again, sediment show the highest contents (0.6 to 0.7  $\mu g/g$  for BPA, 0.11 to 0.33  $\mu g/g$  for 4-OP and 2.9 to 3.1  $\mu g/g$  for 4-NP).

Concerning the surface sand, few accumulations are observed for 4-OP and 4-NP in the two CWs; for example, in the feeding zone of CWR, values range from 0.007 to 0.023 µg/g between T0 and T1 for 4-OP and from 0.040 to 0.178 µg/g between T0 and T1 for 4-NP. The RC and the lower sand layers were more contaminated at T0 than at T1 for the 3 compounds suggesting losses (biodegradation and/or release). 4-NP is the most present compound, which is consistent with its dominance measured by other authors in urban runoff (Gasperi and al., 2022). As to our knowledge, no study has measured these compounds in CW for runoff treatment, so the values are compared to those measured by Flanagan and al. (2019) in the surface substrates of an infiltration swale of approximately one-year-old. Nor sand nor RC reach levels measured in the swale for any of the OMPs; however, the sediment is 20 times richer in BPA, 2 to 6 times richer in 4-OP and 6 times richer in 4-NP than the swale substrate for the same exposure time.

Finally, regarding the bacterial abundance of CWs (figure 2C), they are essentially present in sediment ( $10^6$  UFC/g) and then in the surface sand layer ( $10^4$  UFC/g). Their abundance is still low in the RC ( $10^3$  UFC/g) although it has increased between the two campaigns.

## CONCLUSION

The results of this study show that runoff MPs accumulate mainly at the feeding zone and on the surface (sediment and surface sand) of both CWs. At this stage, Rainclean has not yet demonstrated all its retention capacities (metallic and organic). The T2 campaign will make it possible to observe whether RC retention efficacy is improved with time. Regarding MMPs, copper seems to be more retained in sand and RC than other metals, which is consistent with their adsorption coefficient. For OMPs, the low accumulation could be explained by the biodegradation of these compounds by the microorganisms present. A contaminant's mass balance of the CWs and specific laboratory biodegradation tests are being carried out to validate these hypotheses.

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