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Copper removal from water using a bio-rack system either unplanted or planted with *Phragmites australis*, *Juncus articulatus* and *Phalaris arundinacea*

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ABSTRACT

A bio-rack system was developed for treating Cu-contaminated freshwaters. Each pilot constructed wetland (CW, 110 dm^3) contained 15 perforated vertical pipes filled with a mixture of gravel (diorite; 80%) and perlite (20%) and assembled as a rack. The whole experimental device consisted of 12 CW planted either with *Phragmites australis*, *Phalaris arundinacea* or *Juncus articulatus*, and unplanted as control (in triplicates). All plants were sampled at a Cu-contaminated site. The CWs were filled with a mix of freshwater (30%) from the Jalle d'Eysines River (Bordeaux, France) and tap water (70%). Water was spiked with Cu (2.5 μM, 158.5 $\mu g\,L^{-1}$). Three CW batches were carried out, i.e. in early spring (March, S#1), beginning of the growing season (May, S#2), and peak growing season (June, S#3). The S#3 water was initially acidified to pH 6. For all batches, water was recirculated in the CW during 14 days. Physico-chemical parameters (pH, electrical conductivity, redox potential, BOD_5 and Cu^{2+} concentrations) were measured every three days. Water pH of both S#1 and #2 ranged between 7.8 and 8.5 for all treatments during the experiment. Initial and final total Cu concentrations were analysed for all CWs and batches. Relative Treatment Efficiency Index (RTEI) indicated the plant effect compared to the unplanted CW. Free Cu^{2+} removal was <10% for all S#1 treatments (RTEI ranged between 0 and −1) whereas it increased to 77% (RTEI = 0.1) in S#2 for *P. arundinacea*. In acidic conditions (S#3), Cu^{2+} removal was 99% for all treatments (RTEI = 0). For S#1 and S#2, highest total Cu removal occurred in CW planted with *P. arundinacea* (respectively 52% and 68%, RTEI = 0.1 and 0.2). For S#3, total Cu removal peaked up to 90% in the unplanted CW. The RTEI values suggested no beneficial effect of macrophytes on Cu removal at short term. Conversely, the CW planted with *J. articulatus* generally displayed a lower efficiency. The lowest value for total Cu concentration in water after the 14-day period was 13 $\mu g\,L^{-1}$ in S#3 unplanted and planted with *P. arundinacea*. The role of the biofilm as a key-player of Cu removal in such bio-racks is discussed.

1. Introduction

1.1. Constructed wetlands (CW)

Water quality issues are a major challenge faced by mankind in the 21st Century (Corcoran et al., 2010). Treatment of municipal wastewater streams aims at eliminating nutrients, pathogenic microbes, persistent organic pollutants, xenobiotics derived from the pharmaceutical industry and trace elements (TE) from wastewater streams (Schwartzenbach et al., 2010). In industrialized countries, connection to municipal wastewater treatment plants ranges from 50% to 95%, whereas more than 80% of the municipal wastewaters in low-income countries are discharged without any treatment, polluting rivers, lakes, and coastal sea areas (UNESCO, 2009). As a consequence, pollutants accumulate in aquatic ecosystems in surface waters, groundwater, substrates and plants (Aksoy et al., 2005; Demirezen et al., 2007; Lizama et al., 2011, 2012). In Bordeaux area (France), Cu is one of the major contaminant since soluble formulations of Cu-sulphate and chromated Cu-arsenate (CCA)-type C are used as treatment agents against insects and

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fungal attacks in vineyards and timber harvesting industries (Bes et al., 2013).

Constructed wetlands (CW) planted with macrophytes are an emerging phytotechnology frequently used as an efficient and cost-effective alternative for treating wastewater streams due to its low energy requirements, its convenient operation, and weak maintenance (Marchand et al., 2010; Vymazal, 2010; Hsu et al., 2011; Kuschk et al., 2012; Haarstad et al., 2012; Adams et al., 2012). Five mechanisms affect TE removal in natural and constructed wetlands (Sheoran and Sheoran, 2006; Lesage et al., 2007; Marchand et al., 2010): (1) sorption to fine textured sediments and organic matter, (2) (co)precipitation as insoluble salts, mainly sulphides in reducing conditions and Fe/Mn/Al (oxy)hydroxides in oxidative conditions, (3) carbonate (co)precipitation, (4) absorption and induced changes in biogeochemical cycles by plants and associated micro-organisms (fungi and bacteria of the rhizosphere as well as endophytes), and (5) deposition of suspended solids due to low flow rates. All these reactions lead to metal accumulation in the wetland substrate. The CW efficiency depends on inlet metal concentrations, hydraulic loading, pH, redox conditions and the presence/absence of the consortium plant/bacteria (Kadlec and Wallace, 2009).

1.2. Controversial role of macrophytes

Macrophytes are key-players in CW by driving TE uptake and storage in roots and rhizomes (Caldelas et al., 2012), as well as by TE sorption onto the root plaque (McCabe et al., 2001) and into the substrate by releasing organic metal ligands (Ryan et al., 2001). They also contribute to maintain oxidative conditions in the rhizosphere (Armstrong, 1978; Stottmeister et al., 2003; Cheng et al., 2009) and supply plant-derived organic matter over time which continuously provides sites for metal sorption, as well as carbon sources for bacterial metabolism, thus promoting long-term functioning (Jacob and Otte, 2004; Huang et al., 2012; Leto et al., 2013). Although macrophytes are widely used within CW (Marchand et al., 2010), their role and the effect of different plant species on the CW has been controversial, mainly in terms of TE removal (Lee and Scholz, 2007; Brisson and Chazarenc, 2009; Marchand et al., 2010). Moreover, TE uptake by macrophytes largely depends on the vegetative periodic variations (Bragato et al., 2006; Baldantoni et al., 2009; Wu et al., 2013). In this study, the role of the three macrophytes *Phragmites australis* (Cav.) Trin. ex Steud, *Juncus articulatus* L. and *Phalaris arundinacea* L. in Cu removal from water was assessed across the vegetative season in planted bio-racks filled with substrate.

1.3. Bio-racks

Common classification divides wetlands according to their hydrology: (1) Surface Flow Wetlands (SF), (2) Horizontal Sub-Surface Flow wetlands (HSSF), (3) Vertical Sub-Surface Flow wetlands (VF), and (4) Hybrid Systems (HS) (Arias and Brix, 2003). A new CW design was proposed by Valipour et al. (2009), the so called bio-rack system. Unique feature of this system was the presence of numerous vertical pipes, free of sediment but planted with *P. australis*, assembled as a (bio)rack, which is meant for holding vegetation and support matrix for bacterial growth. Here, bio-racks were filled with substrate to take advantage of both systems, i.e. in the conventional CW the substrate provides adsorption sites for TE, while bio-racks provide maintenance facilities by allowing a rack turnover over time. Such turnover may avoid clogging due to OM accumulation, biofilm development and saturation of sorption sites.

2. Materials and methods

2.1. Pilot plant setup

A pilot plant was built in a greenhouse located at the National Institute for Research in Agronomy (INRA, Villenave d'Ornon, 44°46′50″ N 0°33′57″ W, France) and started its operation in January 2011. Experiments were carried out in twelve independent polyethylene tanks: 32 cm × 56 cm surface opening, 36 cm depth, and containing a 60 dm^3 volume at 34 cm operational water depth (Fig. 1). Each tank was connected to a storage tank (total volume: 60 dm^3, 50 dm^3 at operational water depth). For convenience, we will refer to the polyethylene tanks as "unit A", storage tank as "unit B" and the whole as a pilot constructed wetland (CW) throughout the paper. In December 2010, each unit A was filled with 15 vertical PVC pipes (diameter: 10 cm, depth (H): 35 cm, volume (V): 2.75 dm^3) assembled as a rack termed as "bio-rack". All vertical pipes were perforated every five cm in height and width (hole diameter: 5–10 mm) to enable liquid transport and root development out of the pipe, and – contrary to Valipour et al. (2009) – filled with a homogeneous mix of gravels (diorite, 1–5 mm, 3.9 kg) and perlite (0.035 kg) (respectively 80% (v/v) and 20% (v/v)). Porosity of the substrate made of gravels and perlite was 36%, thus the water volume into each pipe was 1 dm^3. Each bio-rack occupied 41 dm^3 of the unit A and contained 15 dm^3 of water and 26 dm^3 of substrate. The 19 dm^3 remaining in each unit A were occupied by free water. Total water volume in each unit A was thus 34 dm^3. Water volume in each unit B was 50 dm^3. The units A were connected to the units B using lift pumps (Vc400ech, 7500 $dm^3\ h^{-1}$, Leroy Merlin, China) (Fig. 1). Total water volume in each CW was 84 dm^3.

2.1.1. Plants

Plants were collected in 2010, at the beginning of the growing season (April–May), at the La Cornubia site (44°54′26″ N; 0°32′46″ W, Bordeaux, France), a former chemical plant producing Cu sulfate and Cu-based fungicides, dating back to a century and closed in 2004. *P. arundinacea* L. and *J. articulatus* L. were sampled in an abandoned constructed pond colonized by macrophytes, connected to a pipe collecting storm water and effluents from the plant. Total soil Cu and soil pH at this sampling sub-site are respectively 205 mg kg^{-1} DW and 5.7. *P. australis* were sampled on the riversides of a small creek that borders this chemical plant, contaminated by effluents, surface runoff, stormwater, and dust fallout. *P. australis* and *J. articulatus* are rhizomatous geophytes, having shoots borne from buds in the soil and resting buds lying beneath the soil surface as rhizomes. *P. arundinacea* is a hemicryptophyte; it exhibits buds either at or near the soil surface (Raunkiær, 1934). Plants of each population were separately kept in buckets and immediately transported to a greenhouse (INRA – Centre Bordeaux Aquitaine, Villenave d'Ornon, S1). The next day, rhizomes and/or stems bearing buds were cut into small pieces (10–20 cm). They were then individually grown during nine months (May 2010-January 2011) in plastic pots placed in polyethylene vats (volume: 60 cm × 40 cm × 15 cm) containing perlite imbibed with tap water and a quarter Hoagland nutrient solution (HNS, Hoagland and Arnon, 1950): KNO_3 (1.62 mM), $Ca(NO_3)_2$ (0.69 mM), $NH_4H_2PO_4$ (0.25 mM), $MgSO_4$ (0.5 mM), H_3BO_3 (11.5 μM), $MnCl_2$ (2.29 μM), $CuSO_4{\cdot}5H_2O$ (0.08 μM), $(NH_4)_6Mo_7O_{24}$ (0.13 μM), $ZnSO_4$ (0.19 μM), and $Fe^{(II)}SO_4$ (48.6 μM). Water volume was maintained constant by tap water addition and monthly changed to avoid anoxia, with addition of 1 dm^3 of a quarter HNS to avoid nutrient depletion in the growing medium. Water was changed every two months during winter. In January 2011, rhizomes and stems bearing buds were cut again into small pieces (5–10 cm). Three unplanted CW were used as controls. Other CWs were planted (in