Chemosphere 282 (2021) 131045

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Effect of ZnO nanoparticles on Zn, Cu, and Pb dissolution in a green bioretention system for urban stormwater remediation

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ARTICLE INFO

Handling Editor: T Cutright

Keywords:
Stormwater runoff
Heavy metals
Nature-based solutions
Phytoremediation
Wastewater
Water pollution

ABSTRACT

Stormwater runoff from urban and suburban areas can carry hazardous pollutants directly into aquatic ecosystems. These pollutants, such as metals, nutrients, aromatic hydrocarbons, pesticides, and pharmaceuticals, are very toxic to aquatic organisms. Recently, significant amounts of zinc oxide engineered nanoparticles (ZnO-NPs) have been detected in urban stormwater and its bioretention systems. This raises concerns about a potential increase of stormwater toxicity and reduced performance of the treatment infrastructures. To tackle these issues, we developed a simple, low-cost bioretention system to remediate stormwater and retain ZnO-NPs. This system retained up to 73% Zn, 66% Cu, and >99% Pb. However, the removal efficiency for Pb was lower after adding ZnO-NPs to the system, possibly due to the remobilization of Pb phosphates. The effect of ZnO-NPs on stormwater toxicity and metal accumulation in wetland plants was also evaluated.

1. Introduction

The steady growth of urban and suburban areas has led to a global increase in impervious surfaces. Stormwater runoff flows on the hard surfaces of roads, parking lots, and roofs, transporting pollutants directly into aquatic environments. Pollutants commonly found in urban stormwater include heavy metals, inorganic salts such as nitrates, organic compounds like aromatic hydrocarbons, oils, pesticides and pharmaceuticals, suspended solids, and faecal microorganisms (Bakr et al., 2020; Brudler et al., 2019; Masoner et al., 2019; Hou et al., 2018). These pollutants decrease water quality and accumulate in the sediments of water bodies (Sharley et al., 2017), with severe consequences for aquatic organisms (Young et al., 2018; Snodgrass et al., 1987; Grapentine et al., 2008). On site remediation by means of bioretention systems is a very effective and low-cost approach to prevent the negative impacts of urban stormwater on environmental health.

Bioretention systems, also called biofilters, consist of a solid substrate planted with vegetation suitable to the local conditions. As stormwater permeates through the bioretention system, the substrate, microorganisms, and plants remove the pollutants and regulate the flow, improving water quality and decreasing the risk of flooding (Bratieres et al., 2008). Water quality improves through a complex combination of natural processes that take place in biofilters including adsorption, precipitation, biodegradation by microorganisms, photodegradation, volatilization, uptake by plants, etc (Liu et al., 2014). Biofilters are very effective and have many advantages: they are low cost, have small dimensions, are low in maintenance, are adaptable to changing conditions, and increase biodiversity (Sharma and Malaviya, 2021). The most suitable plant species for biofilters are native plants well adapted to the local conditions that have fine and extensive root systems and high biomass production (Payne et al., 2018). In the Mediterranean region, few local species have been tested for their performance in biofilters. In other regions, several species of the genus *Carex* sp. and *Scirpus* sp. have shown good performance (Barron et al., 2020; Singh et al., 2021; Pritchard et al., 2018; Yan et al., 2018; Buhmann and Papenbrock, 2013; Tangahu et al., 2013). From these genera, we selected the native sedges *C. vulpina* and *S. holoschoenus*, which show the preferred traits (dense root systems, fast growth, high nutrient and metal uptake) (Guittonny-Philippe et al., 2014). The shrub *Vitex agnus-castus*, which is native to the Mediterranean, has a good capacity to extract metals (Chowdhury et al., 2018), while its flowers add aesthetic value and attract butterflies. Finally, *Ammophila arenaria* is a beachgrass that can tolerate sandy substrates, periods of drought, and temporary submersion in salty water (Chergui et al., 2018; Ievinsh and Andersone, 2020).

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https://doi.org/10.1016/j.chemosphere.2021.131045
Received 7 March 2021; Received in revised form 12 May 2021; Accepted 26 May 2021
Available online 29 May 2021

The growing use of nanoparticles has raised concerns about their impact on aquatic ecosystems and bioretention systems. Zinc oxide engineered nanoparticles (ZnO-NPs) are used extensively as a vulcanizing agent in the manufacture of tyres and are the most abundant nanoparticles in tyre dust (Adachi and Tainosho, 2004). Besides, ZnO-NPs are present in fuels, lubricants, paints, and other sources of urban metal pollution related to traffic (Sahoo et al., 2008; Fiori et al., 2017; Khatri et al., 2019). Although the composition of road dust is site-specific, a recent review has shown that Zn is one of the most dominant metals in the PM0.1 fraction across locations (Rabajczyk et al., 2020). During storms, road dust is washed off into aquatic ecosystems and bioretention systems. Significant levels of NPs have been reported in stormwater, in water samples from stormwater ponds, and in the soils of stormwater bioretention systems (Baalousha et al., 2016, 2020; Wang et al., 2020). This is worrying because ZnO-NPs are toxic to aquatic organisms, both as a source of Zn^{2+} and through specific nanotoxic effects (Ye et al., 2018). Therefore, preventing ZnO-NPs in stormwater from reaching aquatic ecosystems is crucial for environmental health. However, it is still unclear whether bioretention systems are effective in retaining ZnO-NPs and whether the presence of nanomaterials reduces their remediation performance for other substances.

In aqueous solutions, ZnO-NPs tend to agglomerate and sediment (Liu et al., 2018). Consequently, they accumulate in the sediment of bioretention systems (Baalousha et al., 2016) where they might interact with other pollutants like metals. The ZnO-NPs show good capacity to remove Pb, Cu, and other metals from wastewater via physical adsorption and photocatalytic oxidation/reduction (Le et al., 2019). Their capacity to remove metals from the sediment, however, is largely unexplored. Our hypothesis is that releasing ZnO-NPs into the environment might remobilise historic Pb, Cu, or Zn deposits from sediments. Hence, the main objective of this study was to determine the effect of ZnO nanoparticles in Pb, Cu, and Zn dissolution in a bioretention system for urban stormwater remediation. Additionally, we aimed to assess the effect of ZnO-NPs on stormwater toxicity and metal uptake for three native Mediterranean plants suitable as biofilters. Finally, our goal was to develop a simple, low-cost bioretention system based on plants and coarse gravel to remediate stormwater and retain ZnO-NPs.

2. Materials and methods

2.1. Experimental design

The experiment was carried out in the Urban River Lab (41°32′31"N, 2°14′9"E), an outdoor laboratory built in the premises of the Wastewater Treatment Plant (WWTP) of Montornès del Vallès (Barcelona, Spain) (Fig. S1). This is a low altitude (116 m) coastal area (~10 Km from the sea) with Mediterranean climate. During the study period (May 2017 to June 2018), the mean daily temperature was 16.4 ± 1.8 °C, ranging 6.6–25.2 °C, and there were 28 days with freezing temperatures. The mean daily relative humidity was 41.4 ± 1.4%, ranging 57–78%. In this period there were 112 rainy days, and the total rainfall was 659.5 mm. The mean daily solar radiation was 17.5 ± 1.9 MJ m^{-2}, ranging 7.0–26.1 MJ m^{-2}. Meteorological data were provided by the Meteorological Service of Catalonia (www.meteo.cat) from the station of Parets del Vallès, 3.1 km from the experimental site.

The experimental set up consisted of three concrete modules (Fig. S2), to make three independent replicates. Each of the modules was divided into 8 separate cubic compartments or boxes of 0.6 m each side. Each box was lined with butyl rubber, filled with coarse granitic gravel of average particle size 40 mm, and equipped with a piezometer to collect water samples. Granitic materials have a very slow dissolution rate and do not greatly affect the pH of the solution (Van Noort et al., 2018; Bray et al., 2015). Next, each box was planted with nine individuals of one of the following wetland plant species: *Scirpoides holoschoenus* (L.) Soják, *Carex vulpina* L., *Vitex agnus-castus* L., and *Ammophyla arenaria* (L.) Link. Each experimental module had two boxes per species, one control and one treated with synthetic runoff water. The distribution of the plant species and treatments across the compartments of each module was completely randomized. Nine plants were distributed symmetrically in 3 rows and 3 columns within each box. Plants were purchased from a local cooperative specialized in autochthone species (Viver Tres Turons, Barcelona, Spain).

The experiment lasted 9 months (16/05/2017–25/06/2018) and was carried out in three phases. The first phase lasted 12 weeks (16/05/2017–09/08/2017). In phase 1 we let the plants adapt to growing in a bioretention system, which is a challenging environment (gravel soil, flooding, etc.) and recorded their survival. Each box was filled with 40 L of effluent from the wastewater treatment plant (WWTP) to provide nutrition to plants and microorganisms in the biofilter. The composition of this effluent has been published elsewhere (Ribot et al., 2017) and is summarized in Table S1. When needed to compensate for evaporation, the boxes were refilled with WWTP effluent. We checked plant survival weekly. One of the species, *A. arenaria*, did not survive beyond the first two weeks. Boxes planted with *A. arenaria* were cleaned of plant remains and left as controls. The second phase of the experiment lasted 40 weeks (09/08/2017–15/05/2018). In phase 2 we introduced the stormwater and evaluated the performance of the selected species and the bioretention system in removing the metals. The boxes were emptied of WWTP effluent with a pump and refilled with either tap water (control) or synthetic stormwater (treated). The characteristics of the synthetic stormwater are summarized on Table S2 and were based on a literature review of 17 references (Anderson et al., 2016; Barałkiewicz et al., 2014; Boogaard et al., 2014; Egemose et al., 2015; Faucette et al., 2013; Fronczyk et al., 2016; Göbel et al., 2007; Kim et al., 2007; Leroy et al., 2016; Li and Davis, 2014; Okochi and McMartin, 2011, 2012; Prabhukumar et al., 2015; Reddy et al., 2014; Schiff et al., 2016; Sonstrom et al., 2002; Xiao and McPherson, 2011; LeFevre et al., 2015). The pH of the solution was adjusted to 7.4 by adding 1 N HCl Tritipur (109,060 Merck). Until February 2018, plants received supplementary watering with tap water to compensate for evaporation loss. From then on, the experiment was just rain fed. The third phase of the experiment lasted 6 weeks (15/05/2018–25/06/2018). In phase 3 we introduced the ZnO-NP with two goals: i) to evaluate if ZnO-NP could remobilise the metals retained in the previous phase, and ii) to assess ZnO-NP effects on plant growth and metal accumulation. This phase started once we were certain that plants had survived the winter. To each box containing synthetic stormwater, 5 g of ZnO as nanopowder <100 nm particle size (544,906 Aldrich, ≈80%) were added. The NPs were directly added as powder through the piezometers and water was pumped up and down a few times to ensure even distribution. No attempts were made to prevent agglomeration. Nanoparticles naturally agglomerate and sediment in aqueous solutions depending on the pH and ionic strength of the solution (Domingos et al., 2013; Bian et al., 2011). Previously it has been determined that dispersing the NPs in a solution followed by sonication does not prevent the formation of aggregates once the NP are mixed with water (Liu et al., 2018; Keller et al., 2010).

Throughout the experiment, plants and water samples were collected on three occasions: at the end of the first growth season (21/09/2017); at the end of the winter pause, right before the spring growth (12/03/2018); and at the end of spring (25/06/2018). Water samples (~15 mL) were collected from the piezometers in each experimental box using a 6 mm Ø silicone tube, a syringe filter of pore size 0.2 μm (Corning, New York, USA), and a 50 mL syringe. About 300 μL of concentrated HNO_3 (30% Suprapur, 1.07298.1000 Merck) was added to each 15 mL sample tube to prevent precipitation during transport. Once in the lab, samples were frozen/refrigerated until analysis. Three plants per box were collected during each sampling, one per each column and row. Roots were thoroughly washed on site to remove any substrate, then rinsed four times in tap water and once in distilled water. Roots and shoots were measured, weighed, dried at 60 °C for 48 h, and weighed again.

2.2. Chemical analyses and modelling

Plant samples were finely ground for 2 min in a Retzch MM400 mixer mill at a frequency of 20 revolutions per second. Then 0.1 g of each ground sample was digested overnight in an oven at 90 °C in a mixture of 2 mL HNO_3 and 0.5 mL H_2O_2 (30% Suprapur, 1.07298.1000 Merck) in acid-washed Teflon® beakers. Next, 50 μL of HF (40% reagent grade, AC10511000 Scharlab) were added to each sample and digested for 2 h more at 90 °C. Digests were diluted in 30 mL MilliQ water (18.2 Ω) before analysis. Per every 10 samples, 1 blank and 1 aliquot of the BCR-60 reference material (*Lagarosiphon major*, Community Bureau of Reference, Brussels, Belgium) were digested using the same protocol. We obtained 288 ± 3 (n = 12) μg g^{-1} Zn, a 92% recovery relative to the certified values (313.0 ± 8.0). The Al, Ca, Cu, Fe, K, Mg, Mn, P, Pb, S, and Zn contents of plant digests and water samples were then determined by ICP-OES (Optima 8300, Perkin Elmer, Waltham, MA, USA). The Zn, Cu, and Pb solid phases in the synthetic stormwater with and without ZnO-NP were modelled using the chemical equilibrium software Visual MINTEQ 3.1 (Gustafsson, 2020).

The translocation factor (TF) for each metal was calculated using eq. (1):

$$TF = \frac{[Metal]_{roots}}{[Metal]_{shoots}} \quad [1]$$

The bioconcentration factor (BCF) for each metal was calculated separately for roots and shoots, following eq. (2):

$$BCF_{plant} = \frac{[Metal]_{plant}}{[Metal]_{water}} \quad [2]$$

In this expression, $[Metal]_{water}$ refers to the metal concentration of the synthetic stormwater collected from the same box where plants were growing. A bioconcentration factor >1 is indicative of a species' phytoremediation potential.

2.3. Statistical analyses

The statistical analyses were conducted using R software version 3.4.0 for Windows (R Core Team, 2013) with the FSA package version 0.8.26[60]. Preliminary analyses of the data revealed that the conditions of equal variances and normal distribution were not met. Hence, the non-parametric Kruskal-Wallis (KW) ranks' test and Dunn's test with Benjamini-Hochberg adjustment (Dunn) were used instead of the standard analysis of variance (ANOVA) test. The scientific plotting package Veusz 1.23.2[61] was used to create graphs.

3. Results

3.1. Metal removal from the solution

The synthetic stormwater used in this study contained 411 ± 0.01 μg L^{-1} of Zn, 54.3 ± 0.67 μg L^{-1} of Cu, and 132.5 ± 1.4 μg L^{-1} of Pb (M ± SE). The solutions collected from the piezometers at the first sampling had much lower metal concentrations: 70–73% less Zn, 66% less Cu, and >99% less Pb. The Zn concentration of the solutions ($[Zn]_{sol}$) increased with each sampling ($P < 0.001$) (Fig. 1A).

However, $[Zn]_{sol}$ did not differ between controls and units treated with stormwater ($P = 0.9$) (Fig. 1B). It was only when the statistical test was applied separately to the results from sampling 3 (thus after the addition of ZnO nanoparticles) that we found significant differences in the $[Zn]_{sol}$. The treated units had $[Zn]_{sol}$ = 0.49 mg L^{-1} (0.46–0.58), which was significantly higher than the controls at 0.40 mg L^{-1} (0.40–0.40) ($P < 0.001$). Modelling with Visual MINTEQ predicted that Zn in synthetic stormwater would precipitate in the form of carbonates, which showed positive saturation indices (SI) (Table S3). When we added ZnO to the model as a finite solid, the SI for Zn carbonates

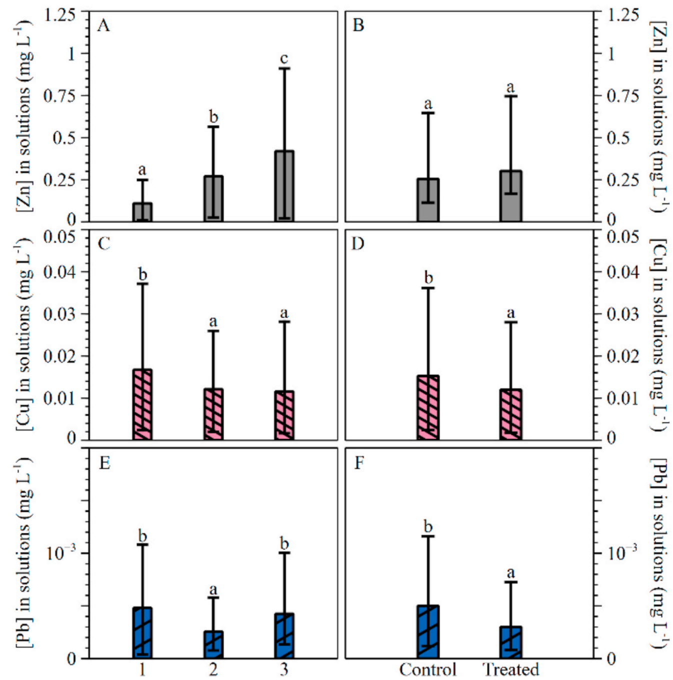

Fig. 1. Dissolved metal concentration in water samples collected from the bioretention system, per sampling (A, C, E) and per treatment (B, D, F). Samplings took place on 21/09/2017 (Sampling 1), 12/03/2018 (Sampling 2), and 25/06/2018 (Sampling 3). Control boxes contained tap water and treatment boxes contained stormwater. Each value is the median of either n = 24 samples (A) or n = 12 samples (B). Error bars correspond to interquartile ranges. Different letters indicate statistically significant differences between groups according to the Dunn's test with a Bonferroni correction.

increased and ZnO was predicted to remain mostly undissolved at equilibrium (97.9%). It must be noted here that Visual MINTEQ does not consider the effect of the nano-size when modelling dissolutions.

The Cu content of the solutions ($[Cu]_{sol}$) decreased up to the second sampling ($P = 0.004$) (Fig. 1A). The maximum Cu removal attained was 77% relative to the synthetic stormwater. Besides, $[Cu]_{sol}$ was lower in the treated units than in the controls ($P = 0.003$) (Fig. 1B). Modelling by Visual MINTEQ predicted that Cu in synthetic stormwater would precipitate in form of carbonates and hydroxides (Table S3), both before and after the addition of ZnO to the model as a finite solid.

The Pb content of the solutions ($[Pb]_{sol}$) varied between samplings ($P < 0.001$) and was higher at the first and third samplings than at the second sampling (Fig. 1A). Besides, the $[Pb]_{sol}$ was lower in the units containing stormwater than in the controls ($P < 0.001$) (Fig. 1B). Modelling by Visual MINTEQ predicted that Pb in synthetic stormwater would precipitate in form of carbonates, phosphates, and hydroxides (Table S3), both before and after the addition of ZnO to the model as a finite solid. For Zn, Cu, and Pb, the concentration in the solution was similar regardless of the plant species growing in each box, including those initially planted with *A. arenaria* (P = 0.3, 0.2, and 0.4, respectively).

3.2. Metal concentration in plant tissues

Zinc concentration ([Zn]) in plant tissues ranged approximately 100 to 8500 μg g^{-1} in roots and 60 to 3600 μg g^{-1} in shoots. The treatment with synthetic stormwater increased [Zn] 8x in the roots and 4x in the shoots, relative to controls ($P = 0.014$ and 0.006, respectively) (Fig. 2A). The species with highest [Zn] in both roots and shoots was *C. vulpina*, followed by *V. agnus-castus* and then *S. holoschoenus* ($P < 0.001$) (Fig. 2B). Further, the [Zn] of both roots and shoots was much higher in the third sampling compared to the first and second samplings, due to

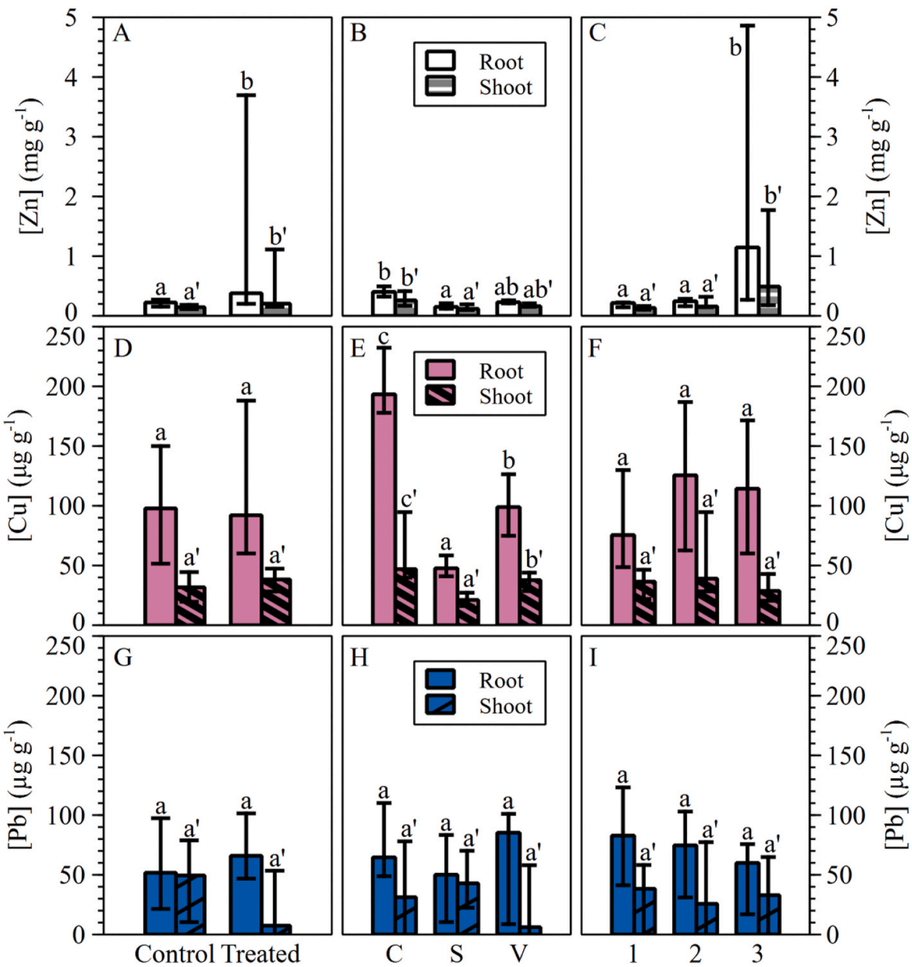

Fig. 2. Metal concentration in plants, per treatment (A, D, G), plant species (B, E, H), and sampling (C, F, I). Control plants were grown in tap water and treated plants in stormwater. Plant species were *Carex vulpina* (C), *Scirpoides holoschoenus* (S), and *Vitex agnus-castus* (V). Samplings took place on 21/09/2017 (Sampling 1), 12/03/2018 (Sampling 2), and 25/06/2018 (Sampling 3). Each value is the median of either n = 12 samples (A, D, G, and C, F, I), or n = 6 samples (B, E, H). Error bars correspond to interquartile ranges. Different letters indicate statistically significant differences between groups according to the Dunn's test with a Bonferroni correction, using "a, b, c …" for roots and "a', b', c' …" for shoots.

the addition of ZnO nanoparticles (Fig. 2C) ($P < 0.001$).

The [Cu] in plant tissues was much lower than the [Zn], ranging ~40–300 μg g^{-1} in roots and 10–140 μg g^{-1} in roots. The [Cu] in both roots and shoots was highest in *C. vulpina*, followed by *V. agnus-castus* and then *S. holoschoenus* ($P < 0.001$) (Fig. 2E). The [Cu] in roots and shoots did not respond to the treatment with stormwater and did not change between the samplings ($P > 0.1$) (Fig. 2D, F). However, when statistical analyses were performed on each species separately, some response to stormwater was noted. The [Cu] increased a 42% in *C. vulpina* roots ($P = 0.02$) and a 63% in *S. holoschoenus* shoots ($P = 0.004$), relative to controls. The Pb levels attained in plant samples were generally low compared to Zn and Cu and very similar between roots and shoots (approx. 0–200 μg g^{-1}). The [Pb] in roots was very similar in all the treatments ($P = 0.3$), species ($P = 0.4$), and samplings ($P = 0.3$) (Fig. 2G–I). The same trend was observed in the $[Pb]_{shoot}$ ($P = 0.4$, 0.052, and 0.98, respectively for species, treatment, and sampling).

3.3. Total metal extracted by plants

The total amount of each metal extracted by plants was calculated by multiplying the metal concentration attained in plant tissues by the dry weight of those same tissues. Each $Metal_{extr}$ value reported below corresponds to three plants collected in the same sampling and from the same box. The total amount of Zn extracted by plants (Zn_{extr}) ranged 1.9–443 mg. Of the three surviving species, *C. vulpina* reached the highest Zn_{extr} compared to *S. holoschoenus* and *V. agnus-castus* ($P < 0.001$) (Fig. 3B). Plants collected in the third sampling extracted 13x and 8x more Zn than those collected during the first and second samplings, respectively ($P < 0.001$) (Fig. 3C). The treatment with synthetic stormwater increased the median Zn_{extr} from 14 ± 3 mg in the controls to 86 ± 25 mg in the treated plants (Fig. 3A), but this effect was not significant ($P = 0.051$). For both Cu and Pb, the total amount extracted by plants (Cu_{extr} and Pb_{extr}, respectively) only showed clear differences between species (both $P < 0.001$) (Fig. 3D–I). In the case of Cu, *C. vulpina* extracted 7x more than *S. holoschoenus* and 9x more than *V. agnus-castus* (Fig. 3E). For Pb, *C. vulpina* extracted twice as much as *S. holoschoenus* and 7x more than *V. agnus-castus* (Fig. 3H). Plants extracted lower levels of these two metals compared to Zn, with Cu_{extr} ranging 0.6–25.5 mg, and Pb_{extr} 0–19.6 mg.

3.4. Bioconcentration factor

The bioconcentration factor for Zn (BCF_{Zn}) in plants were very high, ranging 313–21,155 in roots and 193–8977 in shoots. The BCF_{Zn} in roots relative to the solution was highest in *C. vulpina*, followed by *S. holoschoenus*, and finally *V. agnus-castus* (Fig. 4B) ($P = 0.03$).

The shoots followed the same trend ($P = 0.049$). Besides, the BCF_{Zn} of both roots and shoots was lowest at the second sampling during the cold season, compared to the first and third samplings ($P = 0.003$ and < 0.001, respectively) (Fig. 4C). However, neither the root BCF_{Zn} ($P = 0.9$) nor the shoot BCF_{Zn} ($P = 0.7$) responded to the treatment with stormwater (Fig. 4A). The bioconcentration factor of Cu (BCF_{Cu}) ranged 2.3–46 in roots and 0.8–7.9 in shoots, much lower than the BCF_{Zn}, and did not differ between treatments, samplings, or species (all $P > 0.1$) (Fig. 4D–F). The bioconcentration factor of Pb (BCF_{Pb}) in plants ranged 0–856 in roots and 0–524 in shoots, between those of Zn and Cu. The BCF_{Pb} was higher in roots collected during the second sampling compared to those collected during the first and third samplings ($P =$

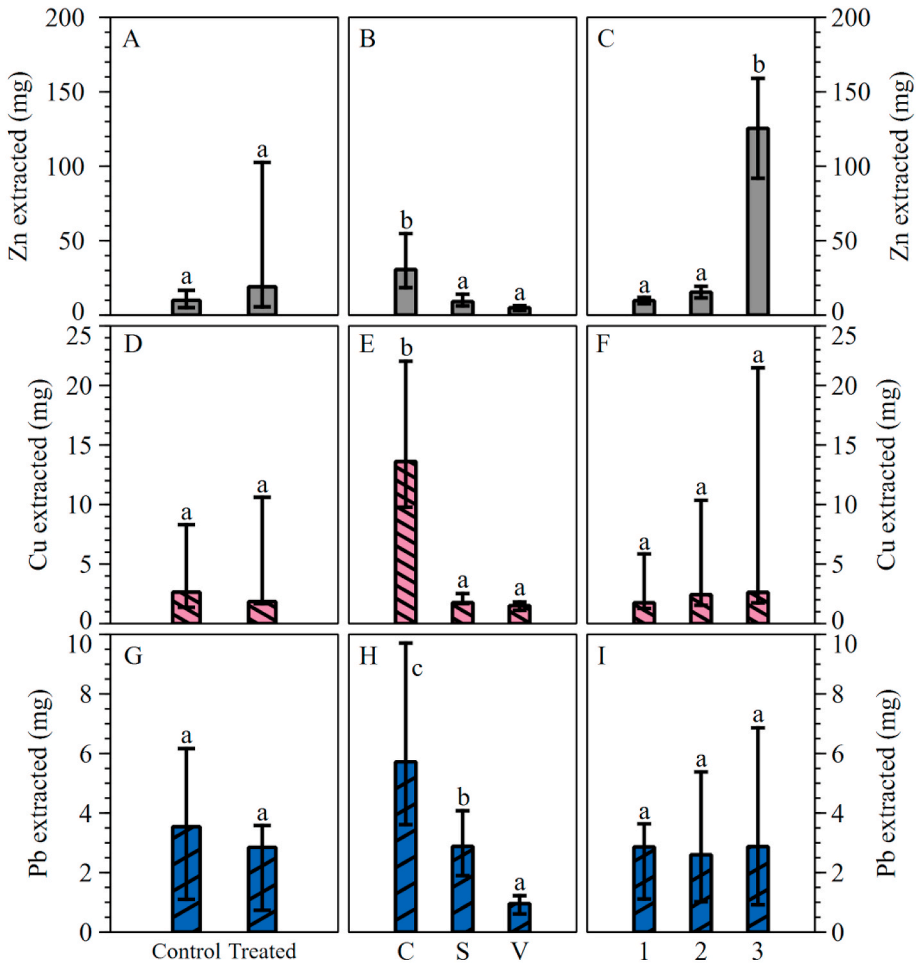

Fig. 3. Total metal extracted by plants, per treatment (A, D, G), plant species (B, E, H), and sampling (C, F, I). Control plants were grown in tap water and treated plants in stormwater. Plant species were *Carex vulpina* (C), *Scirpoides holoschoenus* (S), and *Vitex agnus-castus* (V). Samplings took place on 21/09/2017 (Sampling 1), 12/03/2018 (Sampling 2), and 25/06/2018 (Sampling 3). Each sample consisted of three plants collected during the same sampling and from the same box. Each value is the median of either n = 12 samples (A, D, G, and C, F, I), or n = 6 samples (B, E, H). Error bars correspond to interquartile ranges. Different letters indicate statistically significant differences between groups according to the Dunn's test with a Bonferroni correction.

0.008) (Fig. 4I). However, BCF_{Pb} in roots did not change between either species ($P = 0.6$) or treatments ($P = 0.8$) (Fig. 4G and H). In shoots, *V. agnus-castus* shoots showed the highest capacity to concentrate Pb, while *S. holoschoenus* and *C. vulpina* had lower BCF_{Pb} (Fig. 4H) ($P = 0.03$). By contrast, BCF_{Pb} in shoots did not vary between either treatments or samplings (both $P = 0.5$) (Fig. 4G and H).

3.5. Translocation factors

The translocation factors for Zn, Cu, and Pb (TF_{Zn}, TF_{Cu}, and TF_{Pb}, respectively) were generally >1, which indicates that metals were mostly retained in the roots (Fig. 5). The TF_{Cu} ranged 0.9–6.6 and was higher on average than TF_{Zn} (0.5–5.3) and TF_{Pb} (0–10.1). The TF_{Zn} was lowest in the plants collected during sampling 2, when the above ground tissues had died off, and highest in sampling 3, after the addition of ZnO-NPs ($P = 0.005$, Fig. 5C). The TF_{Zn} was similar across treatments and species (both $P = 0.15$, Fig. 5A and B). By contrast, the TF_{Cu} was highest in *C. vulpina*, followed by *V. agnus-castus* and then *S. holoschoenus* ($P = 0.04$, Fig. 5B). Plants collected during the third sampling had higher TF_{Cu} ($P = 0.04$, Fig. 5C), but there was not a significant difference between plants treated with stormwater and controls ($P = 0.16$, Fig. 5A). Finally, the TF_{Pb} did not differ between treatments, species, or samplings ($P > 0.1$, Fig. 5A–C).

3.6. Plant growth

The three species (*S. holoschoenus*, *C. vulpina,* and *V. agnus-castus*) which survived the adaptation period showed good tolerance to the treatment, since none of the biomass parameters studied differed significantly between controls and plants treated with synthetic stormwater ($P \geq 0.2$). However, plant growth differed between species and samplings. Shoots were shortest in plants collected during the second sampling and longest in the third ($P = 0.006$, Fig. 6A).

Most of the aerial biomass died off during the cold weather and grew back in spring (Fig. S3). The species with the longest shoots was *S. holoschoenus*, followed by *C. vulpina*, and finally *V. agnus-castus* ($P < 0.001$, Fig. 6B). However, *C. vulpina* shoot length increased 49.4% from the initial plant material to the end of the experiment. In comparison, *V. agnus-castus* shoot length increased only 10.5% and *S. holoschoenus* shoot length decreased 21.8%. Similarly, root length increased between the second and third samplings ($P = 0.005$, Fig. 6A). *Carex vulpina* had the longest roots followed by *V. agnus-castus* and *S. holoschoenus* ($P < 0.001$, Fig. 6B). Compared to the initial material, *C. vulpina* and *V. agnus-castus* greatly increased root length during the experiment (133% and 87% respectively), while *S. holoschoenus* did not (only 7%).

The dry weight of whole plants (DW_{plant}) and of the roots (DW_{root}) gradually increased during the experiment (both $P = 0.02$), while the dry weight of the shoots did not (DW_{shoot}) ($P = 0.06$) (Fig. 7A). Of the three surviving species, *C. vulpina* showed the highest DW_{plant} followed by *S. holoschoenus* and *V. agnus-castus* ($P < 0.001$) (Fig. 7B). Compared to the initial plant material, the DW_{plant} at the end of the experiment was ×12 higher for *C. vulpina*, ×8 for *S. holoschoenus*, and ×3 for *V. agnus-castus*. Most of the weight gain took place in the root. *Carex vulpina* had the heaviest roots followed by *S. holoschoenus* and *V. agnus-castus* (Fig. 7B) ($P < 0.001$). The DW_{shoot} was lower for *V. agnus-castus* than for the other two species ($P < 0.001$) (Fig. 7B). Since the shoots grew less than the roots, the distribution of plant biomass between roots and shoots (DW_{root}/DW_{shoot}) gradually increased during the experiment (*P*

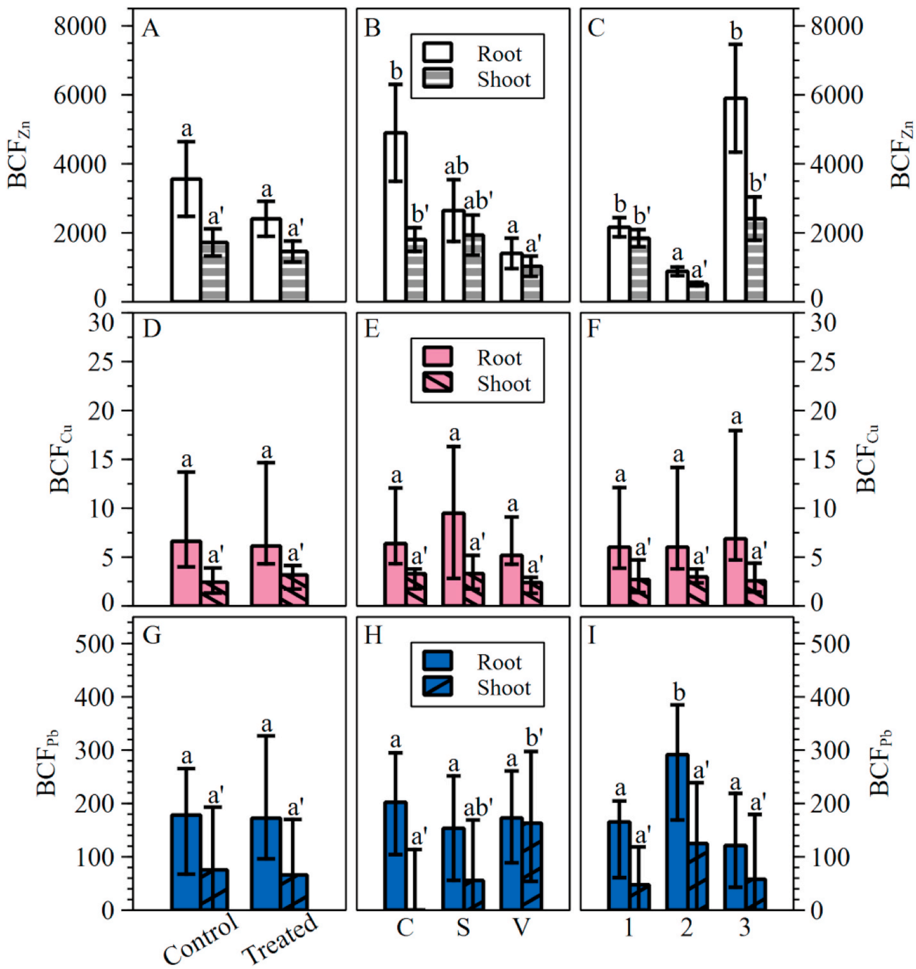

Fig. 4. Bioconcentration factor for Zn (A, B, C), Cu (D, E, F), and Pb (G, H, I) in plant tissues. Data are separated per treatment (A, D, G), plant species (B, E, H), and sampling (C, F, I). Control plants were grown in tap water and treated plants in stormwater. Plant species were *Carex vulpina* (C), *Scirpoides holoschoenus* (S), and *Vitex agnus-castus* (V). Samplings took place on 21/09/2017 (Sampling 1), 12/03/2018 (Sampling 2), and 25/06/2018 (Sampling 3). Each value is the median of either n = 12 samples (A, D, G, and C, F, I), or n = 6 samples (B, E, H). Error bars correspond to interquartile ranges. Different letters indicate statistically significant differences between groups according to the Dunn's test with a Bonferroni correction.

= 0.04) (Fig. 7A). *Carex vulpina* allocated more biomass to the roots followed by *S. holoschoenus* and *V. agnus-castus* (P < 0.001) (Fig. 7B).

3.7. Plants' nutritional status

The nutritional status of plants was not affected by the treatment with synthetic stormwater (P > 0.1, results not shown), again showing the good performance of the three surviving species in this experimental setting. However, the concentration of Al (present in the ZnO-NPs) and seven essential nutrients in plant tissues differed between the species studied (Table S4). In shoots, *C. vulpina* had the highest concentration of Al, Ca, Fe, K, Mg, Mn, P, and S ($P < 0.001$). In roots, both *C. vulpina* and *S. holoschoenus* had higher [Al], [Fe], and [Mn] than *V. agnus-castus* ($P < 0.001$). Besides, *C. vulpina* showed the highest [Mg] in roots of all three species ($P < 0.001$). By contrast, *V. agnus-castus* roots had higher [S] and [K] than *C. vulpina* and *S. holoschoenus* ($P < 0.001$). Three nutrients, Fe, Mn, and K changed their concentrations in plant tissues during the experiment (Table S5). Namely, [Fe] and [Mn] in roots were lowest at the third sampling relative to the first and second ($P = 0.048$ and 0.004, respectively), while [K] in shoots was highest at the third sampling ($P = 0.007$).

4. Discussion

4.1. Efficiency of the bioretention system for metal and nanoparticle removal

The present results demonstrate that a small-scale, low-cost treatment system based on wetland plants and coarse gravel is very effective in decreasing the metal load in stormwater and retaining ZnO-NPs. The metal concentration in the solution had greatly decreased for Zn, Cu, and Pb by the first sampling. The maximum removal rates recorded in our study were 99% for Pb, 73% for Zn, and 66% for Cu. In agreement, the removal efficiency of bioretention systems and constructed wetlands is generally around 70–100% for Pb, 60–100% for Zn, and 50–100% for Cu (Walaszek et al., 2018; Gill et al., 2017; Wang et al., 2017; Kadlec and Wallace, 2008; Walker and Hurl, 2002). Lead concentration in the initial synthetic stormwater was 133 $\mu g\ L^{-1}$, ~10x the maximum allowable [Pb] in surface waters in the EU (European Parliament and C, 2008) which is 14 $\mu g\ L^{-1}$. At the first sampling the $[Pb]_{sol}$ was only 0.54 $\mu g\ L^{-1}$, well below 1.3 $\mu g\ L^{-1}$ which is the environmental quality standard for Pb in the EU (European Parliament and C, 2008). Zinc and Cu are not yet considered priority pollutants and European environmental regulations do not specify safe concentration limits for them. However, we observed that the Zn concentration increased gradually from sampling 1 to sampling 3, even for controls. This points to external sources of Zn contributing to the metal load in our system. The most likely Zn source is atmospheric deposition from airborne pollution. As seen from Fig. 1, the experimental site is in an industrial area just ~200 m away from a heavily travelled highway. Zinc is a major pollutant associated to road traffic (Martín et al., 2018), coming mostly from tyre-wear particles, zinc-plated road furniture, and fuel burning (Świetlik et al., 2013; Councell et al., 2004; Hjortenkrans et al., 2007).

Concerning the behaviour of ZnO-NP, the Visual MINTEQ simulation indicated that only ~2% of ZnO would dissolve in the stormwater used in this study. Accordingly, our previous research (Caldelas et al., 2020) and other ZnO-NPs dissolution experiments (Reed et al., 2012) show that ZnO-NPs dissolve little in aqueous solutions. Instead, ZnO-NPs tend

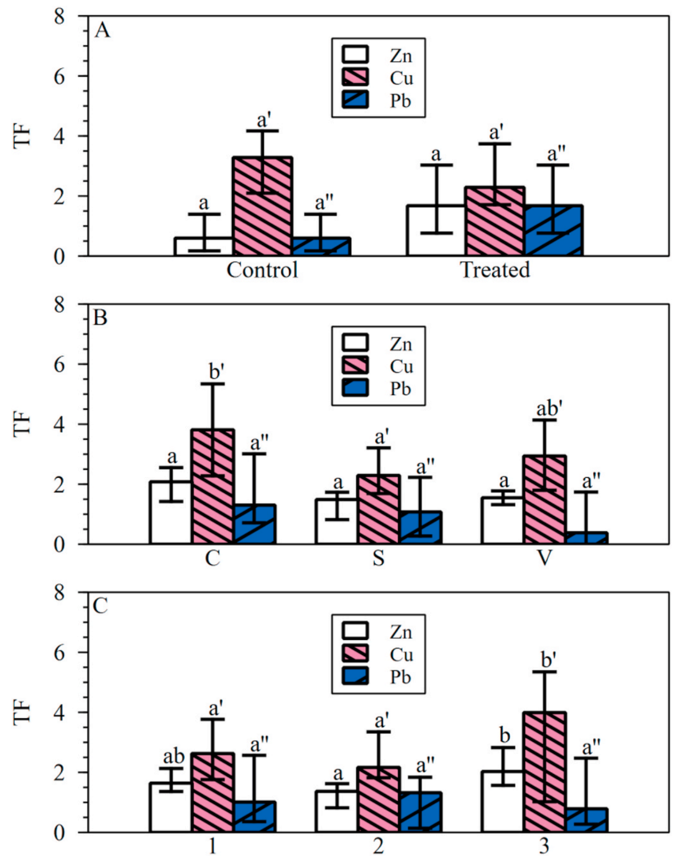

Fig. 5. Translocation factor for Zn, Cu, and Pb. Data are separated per treatment (A), plant species (B), and sampling (C). Control plants were grown in tap water and treated plants in stormwater. Plant species were *Carex vulpina* (C), *Scirpoides holoschoenus* (S), and *Vitex agnus-castus* (V). Samplings took place on 21/09/2017 (Sampling 1), 12/03/2018 (Sampling 2), and 25/06/2018 (Sampling 3). Each value is the median of either n = 12 samples (A and C), or n = 6 samples (B). Error bars correspond to interquartile ranges. Different letters indicate statistically significant differences between groups according to the Dunn's test with a Bonferroni correction.

to agglomerate and remain in the solid fraction. Reed and co-workers examined the dissolution of 100 mg L^{-1} ZnO-NPs in moderately hard water of similar pH and ionic strength to our stormwater and found that just 2 mg L^{-1} Zn dissolved (Reed et al., 2012). In our study, the $[Zn]_{sol}$ in the boxes treated with stormwater was different from controls by 0.11 mg L^{-1} in sampling 3, after the addition of ZnO-NPs. However, it is very improbable that the increased $[Zn]_{sol}$ originated from the total dissolution of all ZnO-NP, considering the results of the dissolution model and the literature. Most likely, the filters used to separate the ZnO-NPs suspended in stormwater did not completely remove all nanoparticles from the water samples analysed.

The processes involved in Pb, Zn, and Cu removal from stormwater in constructed wetlands include particulate settling, precipitation and co-precipitation, sorption (cation exchange) and plant uptake (Kadlec and Wallace, 2008). In our experimental setup, metal concentration in stormwater decreased to a similar extent in boxes with and without plants. Therefore, metal uptake by plants played only a small part in metal removal from the solution. In a long-term evaluation of metal removal from stormwater in constructed wetlands, most of metals were found in the sediments while plants took up a negligible amount (Gill et al., 2017). Similarly, particulate settling was not a relevant mechanism in our system because we used synthetic stormwater made from soluble salts and no particulate matter was added initially. The ZnO-NPs were incorporated to the system about six weeks before sampling 3, when most of the Zn, Cu, and Pb had already left the solution at the time of sampling 1. Simulation of the saturation indices in our stormwater indicated that several Zn, Cu, and Pb solids would precipitate, including carbonates, hydroxides, oxides, and phosphates. Besides, dissolved metals could have adsorbed onto the surfaces of the granitic gravel. Granite (biotite) thin sections can remove Cu and Pb from an aqueous solution through ion exchange with K and complexation (Farquhar et al., 1997). In summary, our results indicate that metal removal in this small-scale bioretention system was mostly controlled by precipitation and sorption onto the gravel.

We now discuss the possible interaction of ZnO-NPs with Pb. In our study, we observed that Pb levels doubled in sampling 3 after the addition of ZnO-NPs, as compared to sampling 1. The nanomaterial used contains only 2.7 μg g^{-1} Pb and 3.1 μg g^{-1} Cu (Caldelas et al., 2020). This amount is very small and could not explain the observed increase of [Pb] in the solution. Looking at the saturation indices in Table S3, we noted that plumbogummite decreased from 0.391 to −0.620 with the addition of ZnO as a solid phase. Hence, the presence of ZnO-NPs might increase the solubility of Pb phosphates, decreasing the efficiency of Pb removal and causing more Pb to reach aquatic ecosystems. This effect can be considered a synergistic interaction between Pb and ZnO-NPs as it would increase the bioavailability of Pb when ZnO-NPs are present in the stormwater chemical mixture. In wastewater treatment experiments, ZnO-NPs show good capacity to remove Pb through a combination of physical adsorption and photocatalytic reduction in the presence of UV radiation (Le et al., 2019). A similar mechanism could lead to Pb leaving the solid fraction and adsorbing onto ZnO-NPs, to be released back into solution once these dissolve. Even if the amount of Pb in solution is still low (0.51 μg L^{-1}) and well within legal limits, these results are concerning. Lead is universally recognised as a top priority water pollutant (European Parliament and C, 2008) due to the severe impact of Pb on human and environmental health. Releasing ZnO-NPs into the

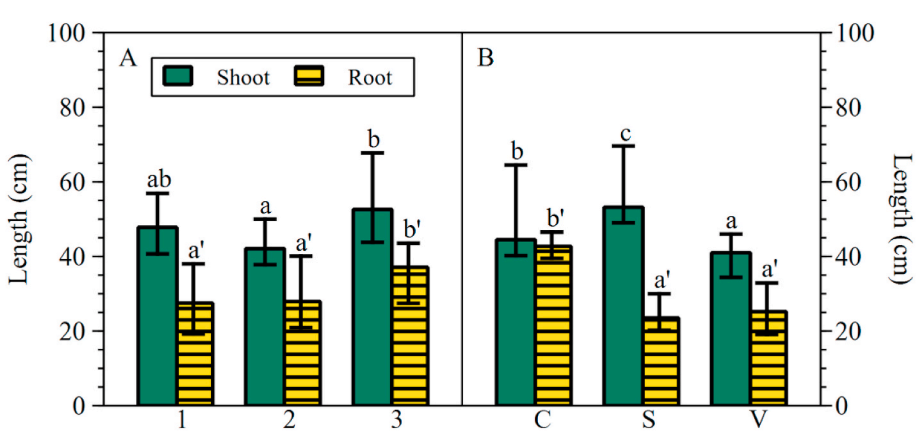

Fig. 6. Plant length per sampling (A) and per species (B). Samplings took place on 21/09/2017 (Sampling 1), 12/03/2018 (Sampling 2), and 25/06/2018 (Sampling 3). Plant species were *Carex vulpina* (C), *Scirpoides holoschoenus* (S), and *Vitex agnus-castus* (V). Each value is the median of either n = 12 samples (A), or n = 6 samples (B). Error bars correspond to interquartile ranges. Different letters indicate statistically significant differences between groups according to the Dunn's test with a Bonferroni correction.

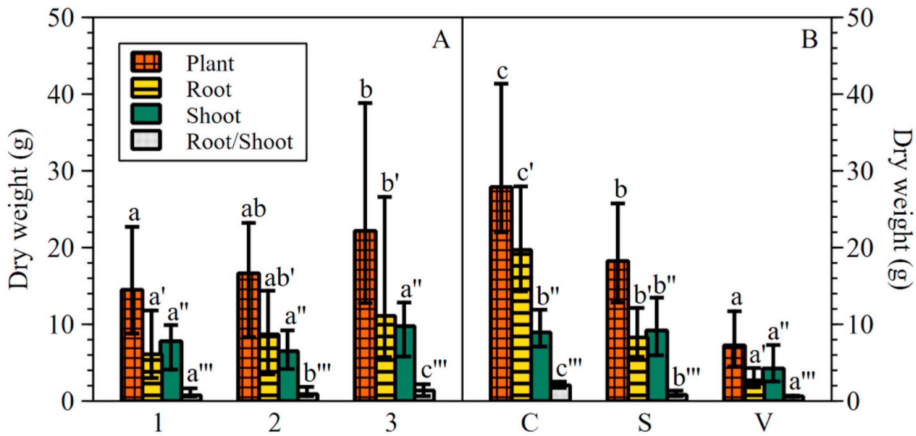

Fig. 7. Plant dry weight per sampling (A) and per species (B). Samplings took place on 21/09/2017 (Sampling 1), 12/03/2018 (Sampling 2), and 25/06/2018 (Sampling 3). Plant species were *Carex vulpina* (C), *Scirpoides holoschoenus* (S), and *Vitex agnus-castus* (V). Each value is the median of either n = 12 samples (A), or n = 6 samples (B). Error bars correspond to interquartile ranges. Different letters indicate statistically significant differences between groups according to the Dunn's test with a Bonferroni correction.

environment could potentially remobilise historic Pb deposits from sediments.

4.2. Metal removal by plants and implications for environmental health

The contribution of the chosen species to metal removal was relatively small in this experiment. This agrees with the literature, where plants have shown a limited capacity for extracting metals in bioretention systems (Dagenais et al., 2018). However, the high BCF attained clearly showed the potential of these species for metal phytoremediation, which has been widely reported for wetland plants (Caldelas and Weiss, 2017; Parzych et al., 2017; Rycewicz-Borecki et al., 2016). We explore the reasons for this discrepancy. Plants grown in high levels of metals or their nanoparticles exhibit toxicity symptoms like stunted growth and nutritional deficiencies, and accumulate excess metals preferentially in the roots where they can reach very high concentrations (Caldelas et al., 2009, 2011, 2012a, 2012b, 2020; Cyrusová et al., 2017; Freitas et al., 2004). By contrast, the synthetic stormwater in our study had much lower metal concentrations. Besides, most of the metals precipitated at an early stage, meaning that the metal concentrations in the solution collected from the piezometers was even lower and caused no impact on either the growth, the nutritional status, or the metal distribution within the plants. Hence, the metal levels present in solution in our bioretention system were not high enough to activate the plants' response to metal excess or to cause substantial bioaccumulation. Besides, the BCF and TF decreased during the winter pause, when most of the aerial part died. In this period there must have been little transpiration and consequently very little bulk flow, limiting metal uptake. This die-off of the aerial parts during the cold season could explain the limited contribution of wetland plants to metal extraction in stormwater treatment ponds. Nonetheless, plants maximize the benefits of bioretention systems by reducing the volume of stormwater through evaporation, increasing nutrient removal, promoting biodiversity, and providing aesthetic value (Dagenais et al., 2018), so it is still important to include them. Besides, root exudates can alter the surface activity of NPs, decreasing aggregation and promoting dissolution and uptake (Schück and Greger, 2020). This could contribute to the remediation of NPs in the biofilters, protecting aquatic ecosystems. Of the three species tested in our study, *C. vulpina* showed the best performance. It grew more than the other species, had better nutritional status, and extracted more metals while still producing flowers and seeds. In a review of 34 wetland plant species, Schük and Greger showed that the most important traits for efficient metal uptake are high total transpiration, high biomass production, and large numbers of fine roots and leaves, which are characteristics present in *C. vulpina* (Schück and Greger, 2020).

Author statements

Cristina Caldelas: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Supervision, Project administration, Funding acquisition; Rosa Gurí: Conceptualization, Methodology, Investigation, Resources, Writing – review & editing; Albert Sorolla: Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition; Jose Luis Araus: Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement NANOREM No 704957. We are thankful to Adriana Peña, Oriol García Antúnez, and Sebastián Angel Londoño for contributing to set up the experiment, maintain plants, and collect samples.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.131045.

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