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Ecological modelling of a wetland for phytoremediating Cu, Zn and Mn in a gold–copper mine site using *Typha domingensis* (Poales: Typhaceae) near Orange, NSW, Australia

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ABSTRACT

Abstract: An artificial wetland was computationally modelled using STELLA®, a graphical programming tool for an Au–Cu mine site in Central-west NSW, the aim of which was to offer a predictive analysis of a proposed wetland for Cu, Zn and Mn removal using *Typha domingensis* as the agent. The model considers the important factors that impact phytoremediation of Cu, Zn and Mn. Simulations were performed to optimise the area of the wetland; concentration of Cu, Zn and Mn released from mine (AMD); and flow rates of water for maximum absorption of the metals. A scenario analysis indicates that at AMD = 0.75mg/L for Cu, Zn and Mn, 12.5, 8.6, and 357.9 kg of Cu, Zn and Mn, respectively, will be assimilated by the wetland in 35 years, which would be equivalent to 61 mg of Cu/kg, 70 mg of Zn/kg and 2,886 mg of Mn/kg of *T. domingensis*, respectively. However, should Cu, Zn and Mn in AMD increase to 3 mg/L, then 18.6 kg of Cu and 11.8 kg of Zn, respectively, will be assimilated in 35 years, whereas no substantial increase in absorption for Mn would occur. This indicates that 91 mg of Cu, 96 mg of Zn and 2917 mg of Mn will be assimilated for every kg of *T. domingensis* in the wetland. The best option for Cu storage would be to construct a wetland of 50,000 m^2 area (AMD = 0.367 mg/L of Cu), which would capture 14.1 kg of Cu in 43 years, eventually releasing only 3.9 kg of Cu downstream. Simulations performed for a WA of 30,000 m^2 indicate that for AMD = 0.367 mg/L of Zn, the wetland captures 6.2 kg, releasing only 3.5 kg downstream after 43 years; the concentration of Zn in the leachate would be 10.2 kg, making this the most efficient wetland amongst the options considered for phytoremediating Zn. This work will help mine managers and environmental researchers in developing an effective environmental management plan by focusing on phytoremediation, with a view at extracting Cu, Zn and Mn from the contaminated sites.

KEYWORDS

ecological modelling, heavy-metal removal, restoration ecology, phytoremediation, sustainable development, *Typha domingensis*

INTRODUCTION

Ground water pollution is a matter of grave concern because of severe ecological impact around the world (Gregory et al., 2013; Zheng & Liu, 2013). Heavy metals in water, when in excess, are a key risk to aquatic life, riparian vegetation and materials downstream (Gerald & Crawford, 1995; Gorelick & Zheng, 2015). Furthermore, heavy metals bioaccumulate through food chains causing irreversible negative impact for all life forms even at low levels in the environment (Pejman et al., 2015). Computational modelling tools have gained relevance in recent years with specific reference to ecological applications in agriculture (Altaweel & Watanabe, 2012), forestry (Bastos et al., 2012), fisheries (Johnson et al., 2013), meteorology (Krajewski et al., 2000) and hydrology (Michot et al., 2011), amongst several others (Svenning et al., 2011; Crookes et al., 2013; Gonzalez et al., 2013; Santos et al., 2013; Yue et al., 2013).

Using ecological modelling tools, attempts have been also made in extant mine sites to construct artificial wetlands to restore contaminated-land sites to near-total carrying capacity of pre-mining times (Jenkins et al., 2012). Specifically, useful efforts have been made in constructing artificial wetlands in the removal of heavy metals (Weis & Weis, 2004; Pimpan & Jindal, 2009; Naja & Volesky, 2011; He et al., 2013; Salem et al., 2014; Mander & Mitsch, 2017; Mohammed & Babatunde, 2017). Topical studies on the removal of Cu (Lim et al., 2001; Murray-Gulde et al., 2005; Galletti et al., 2010), Mn (Xu et al., 2009; Vymazal et al., 2013), Zn (Parviainen, 2014; Stein et al., 2007) and Hg (Chavan et al., 2007; Duong et al., 2011; Gomes et al., 2014; Windham-Myers, 2014) by free-water-surface (FWS) and subsurface-flow constructed wetlands (CWs) have resulted in considerable successes, demonstrating enhanced understanding of computational design of wetlands. From an environmental protection point of view, this means that future

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wetlands that are based on computer modelling could be designed to maximise the sequestration of heavy metals.

A computational model using STELLA® for Cd removal from the FWS of CWs in laboratory conditions is available (Pimpan & Jindal, 2009). STELLA® is the acronym for '**S**ystems Thinking, Experimental Learning Laboratory with Animation'. It is a visual programming language that enables researchers to execute models created as graphical representations of a system using fundamental building blocks. Using a similar computational tool, Water-Quality Analysis Simulation Program (WASP), a reasonably comprehensive model, the transport of Cu in a wetland that included *Nelumbo lutea* (Proteales: Nelumbonaceae) was computed. The program also computed total P in water column and dissolved Cu in sediments, further correlating both the simulated and experimental data (Lung & Light, 1996). Similarly, using a predictive-ecosystem simulation model, Mitsch and Wise (1998) designed a wetland that included *Typha latifolia* in which Fe contents dropped from 166 to 32 mg/L and that of Al dropped from 83 to 56 mg/L from the inflow to the outflow points. For further information on CWs that discuss computational analysis, specific metal removal, design and performance mechanisms, the readers are referred to the following research publications: Leguizamo et al. (2017), Syranidou (2017), Vymazal and Březinová (2016), Rezania et al. (2016), Cochard (2017), Nelson and Wolverton (2011), Sheoran and Sheoran (2006), Kumar and Zhao (2011), Golden et al. (2014), Türker et al. (2014), Philippe et al. (2014), Webb et al. (2012) and Vymazal (2013).

Whilst many modelling efforts validating existing wetlands exist along with information on the design, construction and functionality of artificial wetlands (Mitsch & Wise, 1998; Wood & Shelley, 1999; Villar et al., 2012; Nivala et al., 2013), little information is available on modelling unique heavy metals in a treatment wetland. This paper seeks to offer a predictive analysis of an ecological model of a proposed wetland at Cadia Valley Operations (CVO), an Au–Cu mine near Orange, NSW, Australia, for Cu, Zn and Mn removal using *Typha domingensis* as the agent.

Extensive volumes of soil and rock are excavated from the open-pit and underground mining activities at CVO for Au–Cu extraction. Low-grade ore and waste materials are stored in waste rock dumps. These waste rock dumps are the source of heavy metal leachate released via the oxidation of '$S–S_2$'-based minerals such as pyrite (FeS_2) (Salomons, 1995). Heavy metals in water, when in excess, are a key risk to aquatic life, riparian vegetation and materials downstream (Gerald & Crawford, 1995). Before mine closure, CVO proposes to construct a wetland planted with selected native wetland plants that can trap and store heavy metals from the leachate water that carries them. Presently, the leachate is stored in 'leachate ponds' and recycled for use in the ore extraction process; however, CVO is investigating the possibility of releasing the leachate into a CW that (pending water quality) would be eventually released into the Cadiangullong Creek (CAC), a tributary of the Belubula River at the time of mine closure in the next 20–30 years. Water from the Belubula River and CAC is used by downstream graziers and horticulturists.

T. domingensis was the plant of choice for wetland modelling in the present context, because the leachate ponds near the mining site were naturally colonised by extensive stands of this taxon (Adams et al., 2013). Pre-mining vegetation surveys have documented *T. domingensis* in waterways of mine locations (Bower & Medd, 1995). *T. domingensis* is an emergent perennial that naturally colonises and inhabits heavy-metal-contaminated waterways (Ye et al., 1998) and storage ponds at mine sites (Dunbabin & Bowmer, 1992). It can survive in aquatic environments contaminated by Cu, Mn and Cr (Boers & Zedler, 2008) and in those contaminated by P (Miao & DeBusk, 1999), Hg (Arfstrom et al., 2000) and SO_4 (Gilmour et al., 2007). It performs in such environments by creating an oxidised root zone that mobilises O_2 (Wang et al., 2008). It is preferentially used in CWs for decontaminating waterways (Dunbabin et al. 1988; Maine et al., 2009; Mufarrege et al., 2011; Vymazal, 2011; Eid et al., 2012; Bonanno, 2013; Gomes et al., 2014).

For the successful construction of a wetland, extensive analysis of important wetland characteristics and ecological factors that play key roles in trapping and storing heavy metals from the leachate are extremely vital. The objectives of this research work, therefore, were to (a) computationally design an artificial wetland using STELLA®, a graphical programming language; (b) study the influence of wetland area on metal absorption by *T. domingensis;* (c) analyse the influence of WA on Cu, Zn and Mn in the leachate, sediment and river downstream; (d) study the influence of AMD on metal adsorptions by *T. domingensis* in the CW; (e) explain the metal concentration downstream; and (f) further to calculate metal at the river fetch (mouth of the river that receives the metal).

1. MATERIALS AND METHODS

1.1. Study Site: Cadia Valley Operations

Newcrest Mining Ltd's CVO is situated 25 km south-west of Orange in the Central Tablelands of New South Wales (33°30′ E, 148°59′ N; 750 m asl). The mining lease area covers approximately 5,000 ha of the CAC Valley, which drains the southern portion of Mount Canobolas at 13 km north of mining area. Mining operations commenced in August 1998, following the finding of low-grade Au–Cu ore in 1992. Ore is extracted from the Cadia Hill open pit and the Ridgeway and Cadia East underground mines occurring within the current mining lease boundaries. The Au–Cu mineralisation is hosted by sheeted quartz veins and sheeted quartz S_2 veins that occur in Ordovician volcanics and sediments (MESH Environmental Inc. 2009). Waste rock is piled in the South Waste Rock Dump (SWRD), which occurs south of the open pit and spreads over 442 ha and includes approximately 430 MT of the excavated material, and the leachate draining from this waste rock dump is stored in the Northern Leachate Pond (NLP) and the Southern Leachate Pond (SLP) along the western side of SWRD (Fig. 1). The

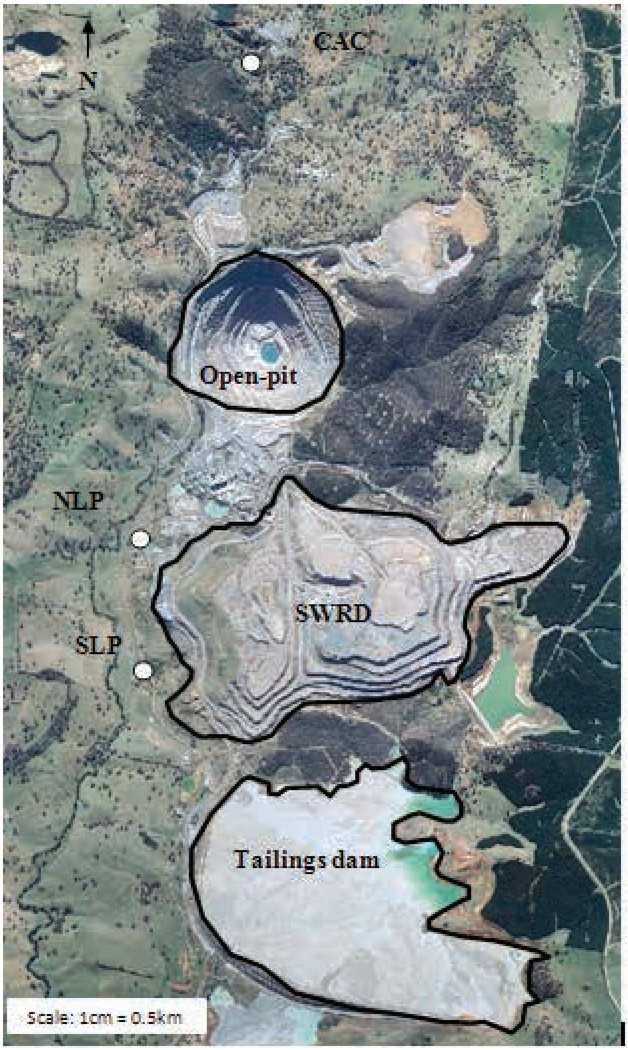

Figure 1. Aerial image of mine site showing the open pit, south waste rock dump and tailings dam. CAC, Cadiangullong Creek; NLP, Northern Leachate Pond; SLP, Southern Leachate Pond; SWRD, south waste-rock dump.

leachate flows from the toe of the waste rock dump along a natural drainage line to NLP and SLP. CAC is located less than 1 km away from the leachate ponds and is the first- and second-order upland stream that flows through the mining lease and drains into the Belubula River. CVO has constructed a dam on CAC upstream to ensure a water source for ore extraction purposes (King et al., 2003).

1.2. Experimental data for construction of the model

1.2.1 Sample Collection

This paper discusses the modelling of the wetland using experimental data ('f' multiplication factor [slope], 'mp' dry weight of the plant and 'c' constant [intercept] provided in Equation 6) obtained from NLP site previously published by our group (Adams et al., 2013). However, a brief description of experimental data collection, which was previously published (Adams et al., 2013), is described in the following text for clearer understanding as required by the reviewers.

T. domingensis covers approximately 0.17 ha at NLP and SLP. At the NLP, leachate passes through the *T. domingensis* stand before reaching the leachate pond, whereas at SLP, leachate resides at the toe of the dump where a large stand of *T. domingensis* occurs and exits at the southern end of the stand passing through several <5 m^2 patches of *T. domingensis*, before entering and settling in the leachate pond. At the CAC site, *T. domingensis* occurs scattered along the creek in stands occupying areas ranging from 1 to 5 m^2. At SLP, NLP and CAC, five sampling points at 10-m intervals were nominated along a 50-m transect, between the waste rock dump and leachate pond at NLP and SLP. At CAC, samples were also collected along a 50-m transect below the dam wall. Sampling was done to obtain data on the levels of Cu, Mn and Zn as the leachate travelled through naturally occurring populations of *T. domingensis* and away from the toe of the waste rock dump to the pond and at CAC to record natural concentrations in leachate, sediment and plant material. Leachate, sediment and root–shoot samples were collected along the transect at each site. Leachate was collected in 1-L polyethylene bottles. Sediment samples were collected at approximately 20-cm depth using an Undisturbed Wet Sampler (Model UWS35, Dormer Engineering Products, Murwillumbah, Australia), and the sample cores were collected at a depth of 15 cm in 4.4-cm wide removable plastic tubes. Sample material was collected over two seasons: Winter 2010 (11–14 July) and early Autumn 2011 (13–16 March). From each sampling point, one to three entire plants of *T. domingensis* were collected from a 2 × 2 m^2 plot, along with surrounding leachate and sediment. Taxonomic determination of *T. domingensis* was verified using Briggs and Johnson (1968).

1.2.2 Sample preparation and analysis

Leachate samples were sterilized through filtration at 0.45 µm with sterile-syringe driven filter units (Millex®—HP, Carrigtwohill Co, Cork, Ireland) before analysis. Each core sample of the sediment was divided into material from 0–5 cm and 5–15 cm depths, oven dried at 70°C for 48 h and pulverised in a hand-held mortar. The pulverised sediment was passed through a 500-µm sieve (Endecotts Ltd, Laboratory Test Sieve, London, ISO 3310-1:2000). For total metals, sediment subsamples (0.5 g) were digested with 10 mL of HNO_3 and 1 mL of HCl at 121°C until a colourless liquid was obtained. After cooling, the solution was adjusted to 50 mL with deionised water. For metals extractable in diethylene-triamine-pentaacetic acid (DTPA), 5.0 g of sediment was added to 12 mL of DTPA solution (0.005 M of DTPA, 0.01 M of $CaCl_2$, 0.10 M of triethanolamine [TEA], pH 7.3; Lindsay & Norvell, 1978).

Plant samples were separated into roots and shoots and oven dried at 70°C for 48 h. Dried plant samples were then pulverised in a plant grinder with a 0.5-mm mesh screen (J.P. van Gelder & Co. Pty Limited, Woy Woy, Australia). Subsamples (0.5 g) were digested with 10 mL of HNO_3 at 60°C for 18 h; after cooling, the suspension was adjusted to 50 mL with deionised water. Samples of leachate, sediment, plant roots and shoots were analysed for Cu, Mn and Zn using an ICP–OES (710 ES, Varian 710 ES, California, USA). Each sample was digested as three replicates (Adams et al., 2013). Accuracy and precision of the digestion procedure and analysis was verified with reference material CRM024-050 (Pasture grasses) and ASP 44-08 (Loamy sand). Plant root samples were also visually identified for the presence of any reddish brown coloured coatings, typical of Fe root plaques indicating the likely presence of Fe oxyhydroxides (Taylor et al., 1984).

1.2.3 Initial data analysis

Leachate sampling data collected in Winter 2010 and early Autumn 2011 were analysed using linear regression to determine the significance in the 'point–site' interaction (the specific site of interaction between the heavy metals and the strands of *T. domingensis*) for concentrations of Cu, Mn and Zn to evaluate any reduction in metal concentrations in the leachate as it passed through *T. domingensis* stands. Concentrations of Cu, Mn and Zn in sediment with DTPA extractable and the total acid digested were subjected to a one-way analysis of variance (ANOVA). All data were analysed using GenStat 14.2 (2011). Determination of metal translocation from roots to shoots was done with the translocation factor (TF) by expressing the ratio of $[\text{Metal}]_{\text{Shoot}}/[\text{Metal}]_{\text{Root}}$ (Stoltz & Greger 2002; Adams et al. 2013).

1.3. The Model

The computational model was developed using STELLA®, a graphical programming language (HPS Inc. 2001) useful in studying systems dynamics (HPS Inc. 2001). The developed model had three compartments referring to sites of metal accumulation in the wetland: (i) sediment, (ii) leachate and (iii) the plants (Fig. 2a–2d). The Freundlich Equation (FE) was applied to calculate metal concentrations as shown previously (Pimpal & Jindal 2009). Factors regulating Cu, Zn and Mn uptake by *T. domingensis* are presented in Section 2.3.1.3; the Cu, Zn and Mn discharged from the waste dump, entering the wetland, and their interaction with sediment are presented under Section 2.3.1.1, under 'Model Equations'. The discharged metal-including water entered the sediment and charged it until saturation. The preferential uptake of metals is by the sediments, because the sediments have outflow priority over the leachate, which is an artefact of the model. In reality, the plants would take up some of the metals simultaneously as the sediments are getting saturated. This does not, however, change the total metals taken up by the wetland in the end state. The remaining metal flowed into the river. There are two novel aspects of the developed model, in that the model (a) provides for downstream concentrations taking into account, water flow through waste ore pit/day (lit) and concentrations of metal released from the mine (see Table 2) and (b) calculates the total metal at the river fetch (mouth of the river that receives the metal).

1.3.1 Model Equations

1.3.1.1 Cu, Zn and Mn adsorption and removal in soil

FE enables estimating adsorption and removal of environmental contaminants including heavy metals in soil (Filella & Williams 2012). Adsorption and desorption computed in this paper are processes that are mutually exclusive, in that adsorption refers to physical binding in soils and desorption refers to the release of the metals from the soil (Wang et al., 2009). Equation (1) describes metal adsorption process in the soil.

$$Ms = K\ Mww + b \qquad (1)$$

where M is the metal, K is the adsorption coefficient (slope), and b is a constant (intercept). Using Equation (1), we regressed metal accumulation in soils (Ms) and its concentration in waste water (Mww) and obtained Equation (2).

$$Ms\ (mg/kg\ dw) = K\ (L/kg\ dw)\ X\ Mww\ (mg\backslash l) + b\ (mg/kg\ dw) \qquad (2)$$

Equation (2) was multiplied by the dry mass of soil, Ms (kg dw), (bulk density of soil, kgdw/m^3 ×soil volume, m^3), to obtain Equation (3).

$$Ms\ (mg) = \left[K\ (L/kg\ dw)\left(Mww(mg)\ /\ Vwater\ (L)\right)\right] + b\ (mg/kg\ dw)\ Ms(kg\ dw \qquad (3)$$

1.3.1.2 STELLA® Simulation of adsorption–desorption in the soil

The input variables applied in the present simulation are listed in Table 1**.** The input data were generated into basic equations by STELLA®. The basic model for metal accumulation in soil thus was transformed as shown in Equations (4) and (5):

$$Ms\ (t) = Ms\ (t\text{-}dt) + (adsorption - desorption)\ dt \qquad [4]$$

$$INIT\ Ms\ (mg) = Soil\ volume * initial\ Ms\ (mg/m3) \qquad [5]$$

where 't' is the current simulation time and 'dt' is the iteration time.

1.3.1.3 Cu, Zn and Mn uptake by T. domingensis

The biomass and mean growth rate of *T. domingensis* were experimentally determined, and the growth assumed to be linear with time. The rate of metal intake of plants is shown (mostly in their roots; however, for computational purposes, the uptake by the plants in their entirety has been computed) in Equation (6):

$$Mp = f * Mww * mp + c \qquad (6)$$

where f is the multiplication factor (slope), mp is the plant dry mass (kg dw) and c is a constant (the intercept). The relationship between rate of metal uptake by *T. domingensis* (Mp) and metal concentration in waste water (Mww) were obtained by

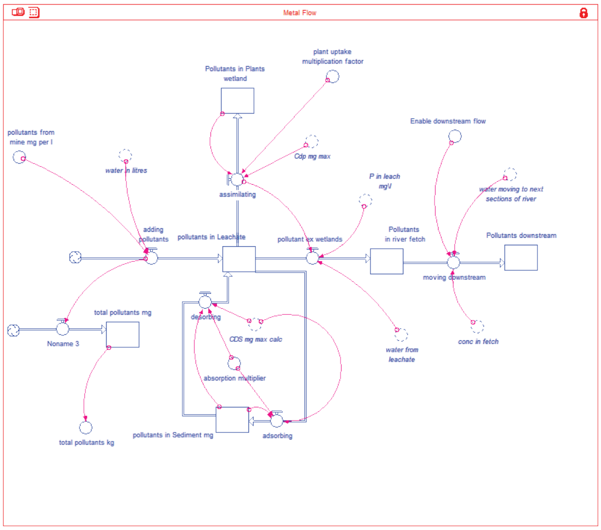

Figure 2a. Construction of the model – graphical representation of the metal flows.

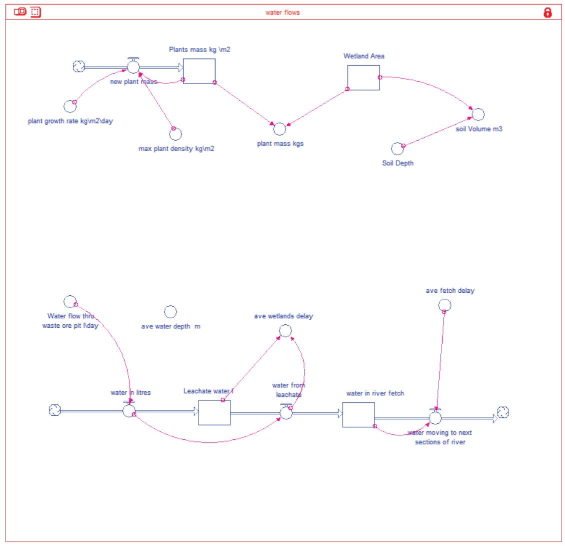

Figure 2b. Construction of the model – Graphical representation of the water flows.

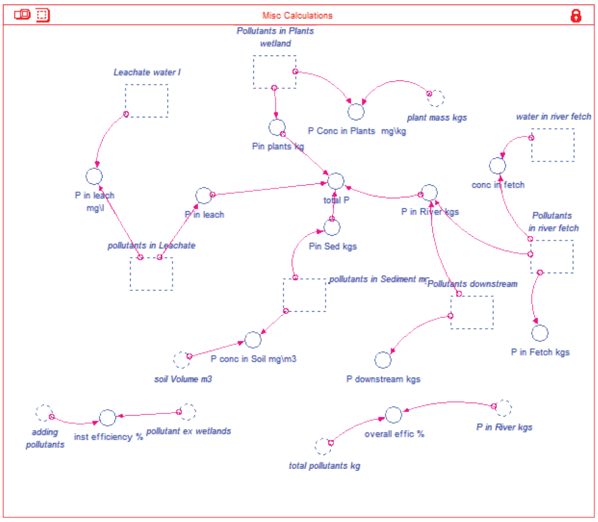

Figure 2c. Construction of the model – graphical representation of calculations for pollutants in leachate, sediment, wetland plants, river downstream and the river fetch.

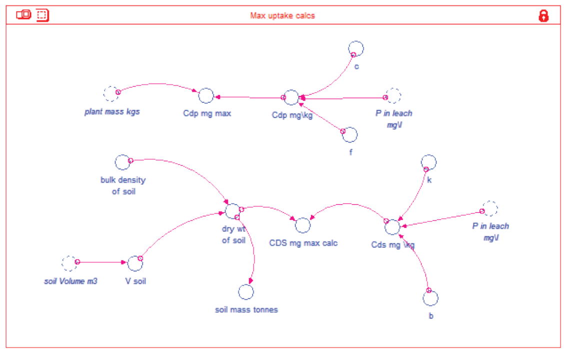

Figure 2d. Construction of the model – graphical representation of calculations for maximum metal uptake.

regression analysis (Equation 6) and the value of 'f' was determined applying Equation (7):

Mp (mg/kgdw) = f (L/kgdw2) Mww +c (mg/kgdw) (7)

1.3.1.4 STELLA Simulation for Cu, Zn and Mn uptake by T. domingensis

Metals in wetland are presented in Equation (8) and the inflow of metals is represented in Equation (9).

M in *Td*(t) = M in *T. domingensis* change as shown previously

(t–dt) + (assimilating) * dt INIT Metal in T. domingensis = 0 (8)

INFLOWS: assimilating = (Cup mg max – Cu in T. domingensis) * uptake multiplication factor (9)

1.3.1.5 STELLA Simulation for Cu, Zn and Mn concentrations in the leachate

Equations for STELLA simulation of Cu, Zn and Mn in leachate, inflow and outflows are provided in Equations (10), (11), and (12), respectively.

LEACHATE

M in Leachate(t) = M in Leachate(t – dt) + (M added + desorbing – assimilating – adsorbing – M exl wetlands)

* dt INIT M in Leachate = Leachate water in lit*initial M in water (mg\l) (10)

INFLOWS

M added = M from mine (mg\l) * water in litres

desorbing = (M in Sediment (mg CDS mg max calc) * absorption multiplier (11)

Table 1. Input data for the mode

Variable	Cu	Zn	Mn	Source
Bulk density of the soil (kg dw/m^3)		1210		Pimpan and Jindal, 2009
Initial concentration of heavy metal in soil (mg/m^3)		3		Experimentally determined
Depth of the soil (m)		0.8		Experimentally determined
Area of the wetland (WA) (m^2)		40,000		Estimated /designed based on the model
Average depth of water (m)		0.5		Experimentally determined
Initial concentration of heavy metal in water (mg/L)		0.001		Estimated
Plant growth rate (g^{-1} d^{-1})		0.4		Estimated based on field data
Maximum plant density (kg/m^2)		3.0		Estimated based on field data
Plant mass (kg/m^2)		0.3		Estimated based on field data
Water flow through waste ore pit/day (lit)		600,000		Experimentally determined
Concentration of metal released from mine (mg/L) AMD		0.367		Experimentally determined
c, (plant parameter) – constant (intercept)	51.50	61.10	2876	Calculated based on laboratory plant growth data
f, (plant parameter) – multiplication factor (slope)	881.94	764.55	902.88	Calculated based on laboratory plant growth data
b, (soil parameter) constant (intercept)	50	96.05	63.75	Calculated based on observed data from field experiments
k, (soil parameter) adsorption coefficient (slope)	1,861.11	1,484.54	1,644.55	Calculated based on observed data from field experiments

OUTFLOWS

assimilating = (Mp mg max–M in *T. domingensis*)*plant uptake multiplication factor

adsorbing = (Metal S mg max calc–M in Sediment mg)*absorption multiplier

M ex wetlands = M in leach (mg\l) * water from leachate + assimilating * 0 (12)

2. RESULTS

Sediment and plant analyses reported in Sections 3.1–3.3 were performed earlier by our research group reported elsewhere (Adams et al. 2013). None of the modelling-based data presented here was ever previously published.

2.1. Sediment analysis (DTPA extraction, 0–5 cm and 5–15 cm depths)

Mean concentrations of DTPA extractable Cu and Zn were the highest at 0–5 cm depth at the SLP, with 200 and 30 mg/kg, respectively, whereas the highest concentration of Mn at CAC was 384 mg/kg for the winter 2010. This trend also occurred in early autumn 2011 sampling at SLP, although the concentrations were lower with 103.2 mg/kg for Cu, 17.6 mg/kg for Zn and 131 mg/kg for Mn at CAC. Mn concentrations at 5–15 cm depths were the highest at CAC with 312 mg/kg in the winter 2010, whereas concentrations of Cu and Zn were the highest at NLP with 76 mg/kg and 11.4 mg/kg in winter 2010. For early autumn 2011, Cu concentrations were the highest at SLP with 61 mg/kg and Zn at CAC with 7 mg/kg, Mn concentration remained the highest at the CAC with 133 mg/kg.

2.2. Sediment analysis (total acid extraction, 0–5 cm and 5–15 cm depths)

Mean concentrations of total Cu and Zn in the 0–5 cm depth were the highest at the SLP with 2,042 and 480 mg/kg, respectively; Mn concentrations in the 0–5 cm depth were the highest with 5,529 mg/kg at CAC from winter 2010 sampling. For the early autumn sampling, Cu concentrations were the highest at NLP with 857 mg/kg, Mn was highest at SLP with 1297 mg/kg along with Zn with 142 mg/kg. Mean concentrations of total Cu and Zn at 5–15 cm depth were the highest in the NLP with 857 and 132 mg/kg, respectively, and the highest total mean concentration of Mn at the 5–15 cm depths at CAC was 1456 mg/

Table 2. Influence of WA on absorption of Cu, Zn, and Mn by T. domingensis *in the constructed wetland after 43 years*

WA, m	AMD, mg/L	Metal in leachate, kg			Metal in sediment, kg			Metal in wetland, kg			Metal downstream, kg		
		Cu	Zn	Mn	Cu	Zn	Mn	Cu	Zn	Mn	Cu	Zn	Mn
10,000	0.1	8.5	0	3.6	933	941.7	849.3	2.9	0	89.3	10.6	0	4.4
	0.367	63	53.72	58.1	3,329.3	3,333.6	3,311.2	3.6	2.4	89.8	77.8	66.3	72.6
	0.55	100.3	96.2	96.2	4,977.5	5,063.8	4,996.2	4.1	2.7	90.1	123.8	113.1	119.3
	0.775	144.5	144.5	142.2	7,150	7,123.8	7,067.9	4.7	3.0	90.5	180.5	171.1	176.8
	1.0	189.3	189.3	189.8	9,223.3	9,184.5	9,139.7	5.3	3.3	90.8	237.1	228.9	234.2
20,000	0.1	0	0	0	946.5	941.7	946.5	0	0	0	0	0	0
	0.367	51.1	31.6	42.1	3,435.8	3,401	3,269	6.2	4.3	178.9	31.6	19.2	25.7
	0.55	89.2	70.3	80.2	5,144.3	5,061.9	4,977.3	6.7	4.6	179.2	54.6	42.7	49
	0.775	134.5	117.8	127.2	7,244.9	7,104	7,077.8	7.3	4.9	179.6	82.9	71.6	77.8
	1.0	183	165.3	174.3	9,162.9	9,146.1	9,178.2	8	5.2	180	111.2	100.5	106.5
30,000	0.1	0	0	0	946.6	941.8	946.6	0	0	0	0	0	0
	0.367	40.2	10.2	24.9	3,408.5	3,446.4	3,195.5	8.9	6.2	268.1	16.2	3.5	10.1
	0.55	78.8	49.2	63.2	5,164.8	5,153.7	4,911.6	9.4	6.5	268.4	31.5	19.1	25.6
	0.775	124.7	95.3	110.2	7,274.8	7,157.8	7,021.7	10	6.8	268.8	50.4	38.4	44.8
	1.0	171.9	143.1	158.7	9,213.3	9,209.2	8,973.3	10.6	7.1	269.1	69.3	57.7	63.9
40,000	0.1	0	0	0	946.6	941.8	946.6	0	0	0	0	0	0
	0.367	28.2	0.1	7.6	3,425.5	3,456.1	4,832.2	11.5	0	357.2	8.5	0	2.2
	0.55	66.2	24.2	46.2	5,173.7	5,163.6	5,088.8	12	8.4	357.5	20	7.4	13.9
	0.775	113.2	72.5	94	7,288.5	7,195.4	6,855.3	12.6	8.7	357.9	34.2	21.8	28.3
	1.0	157.3	119.3	141.6	9,403.3	9,371.6	8,922.5	13.2	9	358.3	48.3	36.3	42.7
50,000	0.1	0	0	0	946.6	941.9	946.6	0	0	0	0	0	0
	0.367	16.2	0	0.1	3,439.6	3,456.1	3,436	14.1	0	37.6	3.9	0	0
	0.55	53.2	1.5	28.2	5,178	5,167.5	4,752.1	14.6	10.2	446.7	13.1	0.3	6.9
	0.775	100.2	49.4	76.6	7,295.7	7,226.5	6,793.5	15.2	10.6	447.1	24.4	11.9	18.4
	1.0	147.3	132.2	124.3	9,413.3	9,382.6	8,863.5	15.8	10.9	447.5	35.7	23.4	29.9

kg in winter 2010 sampling. For early autumn 2011 sampling, Cu and Zn concentrations were the highest at the NLP with 843 and 140 mg/kg, respectively. Mn concentrations were the highest at CAC with 944 mg/kg.

2.3. Plant analysis (Roots and shoots)

Mean root accumulation of Cu and Zn by *T. domingensis* was the highest at the SLP at 322 and 179 mg/kg, respectively; Mn accumulation was the highest at the CAC with 4276 mg/kg in winter 2010 sampling. Root accumulation of Cu and Zn in winter 2010 was the highest at the SLP with 225 and 101.6 mg/kg, respectively; accumulation of Mn was the highest at CAC with 1,932 mg/kg. Mean shoot accumulation of Cu by *T. domingensis* was the highest at the SLP with 83.2 mg/kg in winter 2010, whilst the highest accumulation of Mn and Zn was in early autumn 2011 sampling with 2324 mg/kg at CAC and 55.3 mg/kg at the SLP, respectively. Root samples of *T. domingensis* collected from CAC displayed a reddish brown colouring, whilst this colouring was not apparent on those collected from NLP (Adams et al., 2013).

2.4. Influence of wetland area on metal absorption by *T. domingensis*

The influence of WA on absorption of Cu, Zn and Mn by *T. domingensis* is presented in Table 2. The influence of WA on Cu absorption by *T. domingensis* and time (d) after which Cu becomes accessible to plants in the wetland are presented in Figure 3. When the model is simulated for a WA of 10,000 m^2, Cu becomes accessible to *T. domingensis* in 10.9 years; *vis-à-vis* in a projected area of 50,000 m^2, it would be 35 years. Similarly, for the simulation of Zn for a WA of 10,000 m^2, the time taken is 13.5 years; *vis-à-vis* in a projected WA of 50,000 m^2, the time would be 45 years. Simulation for Mn for a WA of 10,000 m^2 indicates that the time taken is only 10.5 years for plants to access the metal, whilst the time taken for the plants to access the metal would be 33.4 and 43 years for a WA of 40,000 m^2 and 50,000 m^2, respectively.

2.5. Influence of WA on Cu, Zn and Mn in the leachate, sediment and river downstream

Results of the influence of WA on metals in the leachate, sediment and downstream river are presented in Table 2. AMD represents concentration of Cu, Zn and Mn released from mine. Simulations indicate a general trend. The larger the WA, the greater is the holding capacity of metals in the sediment. In addition, if a WA of 10,000 m^2 was constructed, for AMD = 0.367 mg/L, 3,293.3 kg of Cu would be stored in sediments after 43 years, *vis-à-vis* in a projected WA of 50,000 m^2, it would be 3,439.6 kg of Cu. However, for Zn, if a WA of 10,000 m^2 is constructed, for the AMD = 0.367 mg/L, 3,333.6 kg of Zn would be stored in sediments after 43 years, *vis-à-vis* in a projected WA of 50,000 m^2, it would be 3,456.1 kg. For Mn, if a WA of 10,000 m^2 is constructed, for AMD = 0.367 mg/L, 3,311.2 kg of Zn would be stored in sediments after 43 years, *vis-à-vis* in a projected WA of 50,000 m^2, it would be 3,436 kg of Mn. The simulation further indicates that a WA as 10,000 m^2 would release 77.8 kg of Cu downstream, *vis-à-vis* 3.9 kg for a WA of 50,000 m^2. Simulations performed for Zn indicate that a WA of 10,000 m^2 would release 66.3 kg of Zn downstream (Mn = 72.6 kg), and if the WA is increased to 50,000 m^2, no amount of Zn or Mn would reach downstream the river. This is because, for AMD of 0.367 mg/L, there is enough sediment to capture all of Zn and Mn.

2.6. Influence of AMD on their absorptions by *T. domingensis* in the constructed wetland

Influence of AMD on metal absorption by *T. domingensis* is presented in Table 3. Five AMD data (0.1, 0.367, 0.55, 0.775 and 1 mg/L) were simulated. The current AMD release for Cu, Zn and Mn by CVO ranges between 0.3 and 0.45 mg/L. Therefore, it was important from the wetland point of view to simulate AMD that would reflect the current-release concentrations of Cu, Zn and Mn, as well as a greater or lesser AMD, that may prevail in future. The results of the simulation indicate a clear pattern: the greater the AMD, the shorter the time it takes for wetland plants to assimilate metals. For example, in a 10,000 m^2 WA, at AMD for Cu and Mn of 1 mg/L, *T. domingensis* starts assimilating in approximately 7 years; however, for the same WA, if AMD for Cu and Mn from the mine (0.1 mg/L) – a 10-fold reduction – the time taken would be 27.7 and 32.4 years, respectively, before the metals reach the wetland. Similarly, for a WA of 10, 000 m^2, at an initial AMD of 0.1 mg/L for Zn, even after 43 years, the metal does not reach the wetland. For Zn, if the AMD >0.7 mg/L, at a WA of 50,000 m^2, the time taken for the wetland plants to start assimilating the metal would be >68 years.

2.7. Influence of water flow rates on metal absorption in wetland, metals in leachate, and sediment

Currently, leachate flows from beneath the waste rock dump at a rate of 600,000 L/d. Therefore, investigating different flow rates and their effects on metal absorption in the wetland becomes essential. Either increasing or reducing the flow rate (between 400,000 and 800,000 L/d) do not change the quantity of Cu, Zn or Mn absorbed by *T. domingensis*, indicating that metal absorption by *T. domingensis* does not depend on water flow rate, whereas increasing water flow rate increases the Cu, Zn and Mn in leachate. This is because, as the water flow rate increases, it transports more metals with it. The increase in water flow rate results in greater volume of Cu, Zn and Mn in sediments.

2.8. Influence of AMD on final concentrations in leachate, sediment and river downstream

Scenario analyses for five dimensions of wetlands (10,000–50,000 m^2) and five AMD (0.1, 0.367, 0.55, 0.775 and 1mg/L) for Cu, Zn and Mn are presented in Table 2. A clear pattern emerged. Increase in AMD leads to increase in Cu, Zn and Mn concentrations in the leachate, sediment and the wetland. Furthermore, in almost all the scenarios, an AMD of 0.1 mg/L from the mine seems to be too low for the wetland to assimilate anything substantial before 43 years. It is also observed that an increase in AMD leads to increased load in the sediments. For instance, as shown in Table 2, WA of 40,000 m^2 would hold >3,500 kg of Cu at a current CVO AMD of 0.365 mg/L after 43 years. For a thorough analysis and establishments of patterns of wetland responses, we computed only one heavy metal in the influent water for each simulation. Therefore, more experimental data would be needed to computationally model competition of metals on adsorption sites. This would be an important study in future for sequestering specific heavy metals based on the AMD of each of the metals in the influent.

3. DISCUSSION

This study shows that WA is critical, because it determines total metal absorption and time at which metals become available for *T. domingensis*. However, with the increase in WA, a proportionate time delay in accessing metals occurs (Fig. 3). This is because in a larger WA, enough volume of sediment is available to retain metals for a longer period, resulting in reduced metal availability for plants. However, in the context of an exclusive wetland for Cu sequestration, for a WA of 40,000 m^2 (AMD = 0.367 mg/L), in totality approximately 12.5 kg of Cu would be assimilated in 29 years. For Zn, (AMD = 0.367 mg/L), the metal would not be available to the plants in the wetland

Table 3. Influence of AMD on Cu, Zn and Mn absorptions by T. domingensis *in the constructed wetland after 43 years*

WA, m^2	AMD, mg/L	Time (years) before start of absorption in the wetland		
		Cu	Zn	Mn
10,000	0.1	27.7	-	32.4
	0.367	11.7	17	12.9
	0.55	8.77	11.6	9.4
	0.775	7.8	9.3	7.8
	1.0	7.1	7.3	7
20,000	0.1	-	-	-
	0.367	18.4	30	21.6
	0.55	12.9	19.3	14.4
	0.775	10.6	14.6	11.5
	1.0	9.2	12.5	9.8
30,000	0.1	-	-	-
	0.367	25.2	-	30.2
	0.55	16.8	30	19.7
	0.775	13.5	31.2	15.1
	1.0	11.5	27.5	12.7
40,000	0.1	-	-	-
	0.367	32.1	-	38.9
	0.55	20.9	78.5	24.9
	0.775	16.2	69.6	18.8
	1.0	13.6	64.6	15.6
50,000	0.1	-	-	-
	0.367	38.7	-	-
	0.55	25	-	29.8
	0.775	19.1	75	22.5
	1.0	15.9	68.9	18.4

even after 35 years. However, for a greater AMD of 0.55 mg/L (WA = 40,000 m^2), 8.4 kg of Zn would be assimilated. For Mn sequestration, for larger WA, more metal sequestration occurs. This finding matches with the results of Li *et al*. (2003), who measured Ni using *Alysum corsicum* and sediment, and Chen *et al*. (2003), who measured Pb using *Raphanus sativus.* However, Manios et al. (2003), who researched on the removal of heavy metals (Cu, Ni and Zn) from a metalliferous water solution by *T. latifolia* and sewage sludge compost, confirm that the total amount of metals removed by the plants was considerably smaller than that of the substrate, due mainly to the small biomass development in the wetland. The concentration of metals in the roots and the leaves/stems was due to the use of metalliferous water solution and not from the metals pre-existing in the substrate (Manios et al., 2003), and the metal removing ability was less than 1% from within the wetland. However, our study also indicates smaller wetlands with Cu contamination and *T. domingensis* triggers a relatively early absorption. Whilst this is true for Zn and Mn absorption as well, inlet concentrations also play a major role on how early the plants in the wetland start absorbing the metals.

Apart from the role of *T. domingensis* in reducing overall metals downstream, sediment also plays a key role in storing the metals. This is true for almost all large wetlands. This is consistent with a study published by Mays and Edwards (2001) in which heavy metals Mn, Zn, Cu, Ni and Cr were re-

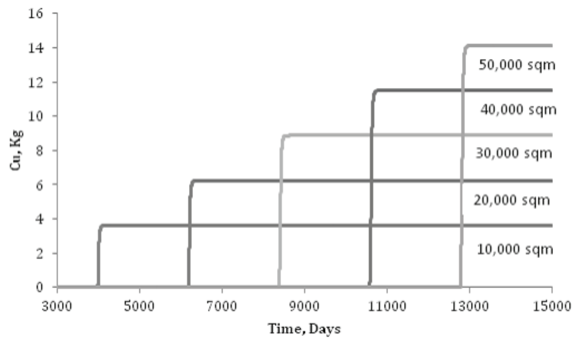

Figure 3. Influence of wetland area on Cu absorption by Typha domingensis.

ported to be accumulated in plants; however, the total plant accumulations were substantially less. Furthermore, Barley et al. (2005) report that Fe and As are preferentially taken up in plant roots more than the stems and that higher metal concentrations were recorded in sediments. As shown in Table 2, with higher metal retention in sediments in larger wetland, reduced quantities of Cu, Zn and Mn occur in the leachate, as WA increases. Our simulations reinforce that a WA of 10,000 m^2 (AMD = 0.367mg/L) would lead to 63 kg of Cu in leachate *vis-à-vis* 16.2 kg of Cu, for a WA of 50,000 m^2 in 43 years (Table 2). Under identical experimental conditions, simulations for Zn indicate that 53.7 kg in leachate for a WA of 10,000 m^2 and the absence of Zn in the leachate when the WA was increased to 50,000 m^2 in 43 years (Table 3). For a 10, 000m^2 WA at AMD = 0.1 mg/L, there will be no Mn in the leachate, because at lower AMD, the entire quantity of Mn would be adsorbed in the sediment. This is consistent with Hadad et al. (2006) who report substantially high accumulation of Fe, Cr, Ni and Zn in sediments in a wetland that treated industrial waste water.

Furthermore, simulations (Table 3) indicate that the greater the AMD, the shorter is the time for the wetland plants to assimilate metals, for (1) the capacity of the sediments to retain the metals at lower AMD is high, and (2) at lower AMD, it takes longer time for the metals to saturate sediments, before being available to plants in the wetland. A similar trend is evident for other WA (20,000–50,000 m^2).

Scenario analyses for five WA (10,000–50,000 m^2) and five AMDs (0.1, 0.367, 0.55, 0.775 and 1 mg/L) for Cu, Zn and Mn (Table 2) indicate that except in the 10,000 m^2 WA, if the Cu and Zn AMD ≤ 0.1 mg/L, even after 43 years, Cu and Zn will be retained in the sediment, indicating that constructing a wetland would be useless in such a scenario. Additionally, no Cu or Zn would occur in either the leachate or downstream. However, in a <10,000 m^2 WA (AMD = 0.1 mg/L) in 43 years, 2.9 kg of Cu will prevail in the wetland and 10.6 kg of Cu downstream. In similar experimental conditions, 2.4 kg of Zn would occur in the wetland, 66.3 kg of Zn downstream, the reason being non-availability of enough sediment to capture Cu and Zn because of a smaller WA. In the other scenarios, enlarging WA leads to greater capture of Cu. A greater efficiency occurs when WA is large, in that constructing a WA of 40,000 m^2 at the current AMD of 0.367 mg/L would lead to the capture of 11.5 kg of Cu after 43 years, eventually letting 8.5 kg of Cu downstream. Our computations indicate higher absorption capacity of Mn by *T. domingensis*. Earlier publications reinforce a similar outcome (e.g. Yun-Gu et al., 2006). Similar high removal rates of greater than 90.0% for Mn was observed by researchers studying distribution and removal efficiency of heavy metals in two CWs treating landfill leachate (Wojciechowska & Waara, 2011). WA, therefore, is not the limiting factor for Mn absorption at concentrations that are released by CVO; the greater the WA, lesser Mn would reach downstream.

Scenario analyses for two higher hypothetical AMDs for Cu, Zn and Mn (0.75 and 3mg/L) are presented in Table 4. At AMD = 0.75 mg/L, 12.5 kg of Cu is captured in the wetland in 35 years, *vis-à-vis* 8.6 kg for Zn and >350 kg of Mn. This consolidates to 0.21% of Cu, 0.14% of Zn and 5% of Mn that *T. domingensis* assimilates. Interestingly, an investigation on the efficiency of a continuous free surface flow wetland for the removal of heavy metals from industrial wastewater in Gadoon Amazai Industrial Estate Pakistan confirmed removal efficiency of 48.3% for Cu (Khan et al., 2009). Increasing AMD for Cu and Zn to 3.0 mg/L increases the total quantity of metals removed by *T. domingensis* to 18.6 and 11.8 kg, respectively, after 35 years; however, the removal rates for both these metals is higher, where for every kilogram of *T. domingensis*, 91 mg of Cu and 96 mg of Zn get removed. In the case of Mn, increasing the AMD released from mine from 0.75 to 3 mg/L does not substantially increase the absorption rate by *T. domingensis* in the wetland because a threshold is reached for Mn absorption at AMD = 0.75 mg/L. The trend, therefore, is higher the Cu and Zn AMD, higher is the ratio of removal by plant (till AMD of ~3 mg/L); however, for Mn, a threshold is already reached (AMD = 0.75 mg/L), where further absorption of Mn by *T. domingensis* is not possible. In contrast, the wetlands that use coke and gravel system treating wastewater containing Pb, at different hydraulic loadings, the inlet concentrations of 27.44 and 11.53 mg/L for coke system and inlet concentrations of 49.8 and 43.1mg/L all resulted in greater than 95.03% of removal efficiency (Chen et al., 2009). This confirms how wetlands that use plants have totally different dynamics of adsorption depending on a variety of factors, principal of them being the growth rate of plants and consequent rate of metal accumulation.

The Lim et al. study (2001) used *Typha angustifolia* and indicated <1% of Cu absorption in a scenario of reduced Cu concentrations. Similar absorption rates to those we obtained have been reported by Yeh et al. (2009) and Osaliya et al. (2011). Our study predicts that for every kg of *T. domingensis*, 61 mg of Cu and 70 mg of Zn get assimilated *vis-à-vis* 2,886 mg of Mn. Whilst higher absorption rates for Cu have been reported in other plants (Usmal et al., 2012, using *Iris ensata*, 263.8 mg/Kg of Cu and using *Typha orientalis,* 174 g/Kg of Cu), absorption capabilities comparable with our results were recorded for plants such as *Phragmites communis, Duchesnea chrysantha, Lactuca indica* and *Equisetum arvense* (Usman et al., 2012). Similarly, Sukumaran (2013) reported that after 15 days of treatment in a

Table 4. Scenario analysis for Cu, Zn and Mn absorption by T.domingensis*– Wetland (40000m2) vs No Wetland after 35 years*

	AMD, mg/L	Total metals, kg	Quantity In leachate, kg	In leachate, concentration reaching river, mg/L	In sediments, kg	Metals downstream, kg	Absorbed by wetland, kg after 35 years	Ratio of removal by plant weight, mg/kg	Notes
Cu	0.75	5,748.9	74.6	3.73	5,639.3	22.5	12.5	61	Wetland
	0.75	5,748.9	74.9	3.75	5,651.4	22.6	0	0	No wetland
	3.0	23,055.5	444.6	22.23	22,458.2	134.1	18.6	91	Wetland
	3.0	23,055.5	445.1	22.25	22,476.1	134.3	0	0	No wetland
Zn	0.75	5,784.9	34.2	0.011	5,729.7	10.3	8.6	70	Wetland
	0.75	5,784.9	34.5	0.012	5,739.9	10.4	0	0	No wetland
	3.0	23,409.5	414.9	0.45	22,857.1	125.3	11.8	96	Wetland
	3.0	22,995.2	415.3	0.46	22,868.1	125.7	0	0	No wetland
Mn	0.75	7,098.9	88.8	0.011	6,714.1	26.7	357.9	2,886	Wetland
	0.75	7,098.9	89	0.013	7,071.7	26.8	0	0	No wetland
	3.0	28,395.1	564.9	0.045	27,862.2	170.4	361.7	2,917	Wetland
	3.0	28,395.1	565.1	0.047	28,223.3	170.8	0	0	No wetland

CW, concentration of Cu in *T. latifolia* leaf increased from 0.005 to 0.086 mg/g with a bioconcentration factor of 895.83, and for *T. latifolia* root, the initial concentration was 0.031 mg/g, which then increased to 0.101 mg/g with a total bioconcentration factor of 1052.08. This is generally consistent with most studies that showcase high levels of metal uptake by *Typha* sp. than any other species for most effluents (Yang & Ye, 2009; Vymazal, 2010; Kumari & Tripathi, 2015; García et al., 2017). However, the rates of Cu and Zn absorptions are also dependant on the inlet concentrations. For example, Kanagy et al. (2008) showed that at very low inlet concentration of 0.89 mg/L, *Schoenoplectus californicus and T. latifolia could remove nearly 89% of Cu in a wetland. In general, T. domingensis has shown to tolerate* heavy metals and to maintain the contaminant removal efficiency of the CW, in that metal concentration (Cr, Ni and Zn) and total phosphorus have been reported to be significantly higher in tissues of plants growing at the inlet in comparison with those from the outlet and natural wetlands (Hadad et al., 2010). Furthermore, highest root and stele cross-sectional areas, number of vessels and biomass registered in inlet plants promoted the uptake, transport and accumulation of contaminants in tissues, confirming high adaptability to the conditions prevailing in the CW (Hadad et al., 2010).

4. CONCLUSION

This computational modelling effort has successfully designed artificial wetland with reference to its construction at CVO and critically evaluated its functionality. Simulations suggest that WA is a key factor that influences the quantity of Cu, Zn and Mn that would be assimilated in *T. domingensis*. The greater the WA, the greater is the plant biomass, and therefore, more metal absorption over time. Furthermore, plant parameters, such as growth rate and density, determine the quantity of metals that *T. domingensis* can store in the wetland. The best option for Cu storage would be to construct a wetland of 50,000 m^2 area (AMD = 0.367 mg/L of Cu), which would capture 14.1 kg of Cu in 43 years, eventually releasing only 3.9 kg of Cu downstream. When the Cu AMD is increased from 0.367 to 1 mg/L, it did not lead to proportional increase in Cu absorption by plants in the wetland. Similarly, for Zn, for a WA > 40,000 m^2, for an AMD of 0.367 mg/L, construction of wetland will serve no purpose. Simulations performed for a WA of 30,000 m^2 indicate that for AMD = 0.367mg/L of Zn, the wetland captures 6.2 kg releasing only 3.5 kg downstream after 43 years; the concentration of Zn in the leachate here would be 10.2 kg, making this the most efficient wetland amongst the options considered for phytoremediating Zn. However, for Mn, a wetland of 40,000 or 50,000m^2 can be constructed. The 40,000-m^2 WA would capture >350 kg of Mn discharging 2.2 kg downstream; the 50,000-m^2 WA will capture 37.6 kg in the wetland, letting no Mn downstream.

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