Research article

Constructed wetlands for steel slag leachate management: Partitioning of arsenic, chromium, and vanadium in waters, sediments, and plants

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ABSTRACT

Constructed wetlands can treat highly alkaline leachate resulting from the weathering of steel slag before reuse (e.g. as aggregate) or during disposal in repositories and legacy sites. This study aimed to assess how metal(loid)s soluble at high pH, such as arsenic (As), chromium (Cr), and vanadium (V) are removed in constructed wetlands and how they accumulate in the sediments and the plants (*Phragmites australis,* common reed). The results show that reedbeds were very effective at removing calcium (98%), aluminium (81%), barium (98%), chromium (90%), gallium (80%), nickel (98%), and zinc (98%), and lowering pH and alkalinity. No statistical difference was found for As and V between leachate influent and wetland samples, showing that these metal(loid)s were not efficiently removed. As, Cr, and V were significantly higher in the reedbed sediments than in a reference site. However, sediment concentrations are not at levels that would pose a concern regarding reuse for agricultural purposes (average values of $39 \pm 26 \, \mathrm{mg \, kg^{-1}}$ for As, $108 \pm 15 \, \mathrm{mg \, kg^{-1}}$ for Cr, and $231 \pm 34 \, \mathrm{mg \, kg^{-1}}$ for V). Also, there is no significant uptake of metals by the aboveground portions of the reeds compared to reference conditions. Results show statistically significant enrichment in metal(loid)s in rhizomes and also a seasonal effect on the Cr concentrations. The data suggest minimal risk of oxyanion-forming element uptake and cycling in wetlands receiving alkaline steel slag.

1. Introduction

Highly alkaline leachates (pH > 12) can result from the current management practices of steel slag, a by-product of steel production, if water is allowed to contact and react with calcium oxide (CaO), calcium silicates and periclase (MgO) in the slag (Chaurand et al., 2007; Gomes et al., 2016b). Steel slags contain potentially toxic metal(loid)s (Chaurand et al., 2007) and oxyanions (e.g. As, Cr, Mo, Se, V) can be solubilised in the leachate (Cornelis et al., 2008; Fällman, 2000). Constructed wetlands have been increasingly used to treat highly alkaline leachates (Buckley et al., 2016; Higgins et al., 2015, 2017; Mayes et al., 2009b), and showed to be effective for improving water quality parameters (lowering pH, alkalinity, total dissolved solids and metal concentrations) (Banks et al., 2006; Buckley et al., 2016; Higgins et al., 2015; Mayes et al., 2009b; Valipour and Ahn, 2015). Given the multi-decadal timescales over which alkalinity generation can persist at legacy steel slag disposal sites (Riley and Mayes, 2015), constructed wetlands can offer an environmentally-sensitive and cost-effective alternative for leachate management (Gomes et al., 2018b).

Metal(loid)s can be efficiently removed in constructed wetlands, but there is the possiblity of making them readily-accessible to wildlife in wetland sediments or plant tissue (Mackintosh et al., 2016; PIRAMID Consortium, 2003). There is uncertainty and risks associated with the uptake of oxyanion-forming elements in wetlands, and a need to improve the understanding of the physical, chemical and biological processes, and how they affect metal(loid)s partitioning, especially at pH > 12. There is conflicting evidence about the accumulation of metals in macrophytes growing in highly alkaline waters (Chaurand et al., 2007). Different studies show As concentrations exceeding the phytotoxic level (Olszewska et al., 2016) and laboratory experiments show concentrations in plants below those levels (Buckley et al., 2016; Higgins et al., 2016). Recent field evidence has shown long-term cycling and uptake of As in macrophytes growing in waters subjected to historical release of bauxite processing residue (Olszewska et al., 2016). Arsenite has a similar geochemical behaviour to phosphate and that can be a potential pathway for biological uptake and subsequent cycling (Olszewska et al., 2016). Also, metal removal and bioavailability in wetlands are seasonal, with different removal processes (precipitation

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Table 1
Hydrochemical composition of the inflow and outflow waters (average values, standard deviation and number of samples) and maximal removal efficiency. Elements marked in bold are the focus of this study.

Determinand	Inflow	Reedbed 1	Reedbed 2	Efficiency (%)
pH	12.8 ± 0.3 (n = 40)	10.3 ± 0.8 (n = 139)	10.5 ± 1.4 (n = 16)	
Conductivity ($\mu S\ cm^{-1}$)	17,769 ± 6335 (n = 39)	7457 ± 2393 (n = 139)	4287 ± 2286 (n = 16)	
Na (mg L^{-1})	1713 ± 268 (n = 13)	987 ± 63 (n = 139)	924 ± 500 (n = 16)	46
K (mg L^{-1})	174 ± 9 (n = 19)	108 ± 12 (n = 139)	120 ± 45 (n = 16)	38
Ca (mg L^{-1})	138 ± 69 (n = 18)	2.5 ± 1.4 (n = 139)	2.4 ± 2.0 (n = 16)	98
Mg (mg L^{-1})	1.4 ± 1.5 (n = 16)	1.2 ± 1.1 (n = 139)	0.6 ± 0.6 (n = 16)	57
Al (mg L^{-1})	5.7 ± 6.8 (n = 3)	1.1 ± 0.6 (n = 139)	2.5 ± 1.7 (n = 16)	81
As (mg L^{-1})	**0.02 ± 0.01 (n = 6)**	**0.01 ± 0.02 (n = 139)**	**0.02 ± 0.06 (n = 16)**	**50**
Ba (mg L^{-1})	0.2 ± 0.2 (n = 5)	0.005 ± 0.002 (n = 139)	0.004 ± 0.002 (n = 16)	98
Cd (mg L^{-1})	0.002 ± 0.001 (n = 19)	< 0.001 (n = 139)	< 0.001 (n = 16)	50
Cr (mg L^{-1})	**0.01 ± 0.01 (n = 19)**	**< 0.001 (n = 139)**	**< 0.001 (n = 16)**	**90**
Cu (mg L^{-1})	0.04 ± 0.03 (n = 19)	0.01 ± 0.03 (n = 139)	0.01 ± 0.03 (n = 16)	75
Ga (mg L^{-1})	0.1 ± 0.1 (n = 5)	0.02 ± 0.02 (n = 139)	0.02 ± 0.1 (n = 16)	80
Li (mg L^{-1})	0.4 ± 0.04 (n = 5)	0.2 ± 0.02 (n = 139)	0.2 ± 0.1 (n+16)	50
Ni (mg L^{-1})	0.1 ± 0.2 (n+19)	< 0.002 (n = 139)	< 0.002 (n = 16)	98
Pb (mg L^{-1})	0.02 ± 0.01 (n = 19)	< 0.006 (n = 139)	< 0.006 (n = 16)	70
V (mg L^{-1})	**0.121 ± 0.1 (n = 12)**	**0.066 ± 0.03 (n = 139)**	**0.152 ± 0.1 (n = 16)**	**0**
Zn (mg L^{-1})	0.1 ± 0.1 (n = 19)	< 0.002 (n = 139)	< 0.002 (n = 16)	98

and adsorption) dominating in warm and cold seasons, respectively (Xu and Mills, 2018).

This study investigates, for the first time, the partitioning of As, Cr, and V in an alkaline steel slag leachate constructed wetland (pilot unit) installed at Scunthorpe, UK, as well as the accumulation of these elements in sediments and plants during two seasonal campaigns. The objectives were to understand the fate of those metal(loid)s in the wetland, providing field data to the accumulation of these elements, and to use the data produced to make recommendations for the effective design of passive treatments for industrial alkaline leachate treatment.

2. Materials and methods

2.1. Site characterisation

Two reedbeds (53°35′07.3″N 0°35′35.5″W, altitude 21 m) receiving alkaline steel slag leachate in Yarborough, Scunthorpe (UK) were studied. The reedbeds are separate treatments that were built on top of a clay-capped landfill cell that had been used for the disposal of steel slag processing residues in 2012, lined with > 1 m depth of local clay (Quaternary till of Devensian age) and planted with rhizome material of *Phragmites australis* (common reed) from an adjacent toe-drain already receiving highly alkaline (pH 12.4) leachate. The reedbeds receive groundwater that is pumped from a landfill containing steel slag and other inert process wastes. The pumping of groundwater is intermittent and triggered by high water tables in the landfill. There is a discharge overflow point from both the reedbed cells, but the majority of the water loss is via evaporative losses. Water depth in the reedbeds is variable and oscillates between 40 and 90 cm. Samples were also collected in a nearby reference site, which reflects an uncontaminated but otherwise similar lowland location – Oak Road Pond and Wetlands (Oak Road Park, Hull, 53°46′27.4″ N 0°20′40.8″W, altitude 2 m). This wetland was dug by the Environment Agency approximately 20 years ago to provide clay for reinforcing the River Hull flood banks. Half the area was allocated for angling, with the other half being designated for wildlife. The reference wetlands intercept shallow groundwaters in alluvial and tidal deposits of Quaternary age, which drain a predominantly urban catchment.

2.2. Water quality monitoring

Water quality in the reedbeds was continuously monitored, measuring pH, electrical conductivity (EC), temperature and total dissolved solids (TDS) using a Hanna Instruments HI-98195 Multiparameter Waterproof Meter, with parameters being logged every 15 min during the sampling campaigns. Auto sampling of water in reedbed 1 (South) was performed every 12 h using an ISCO 6712, besides weekly sampling of waters in both reedbeds. The autumn/winter campaign was from the 1st November to 26th December 2016, 11th – 27th January 2017. The spring/summer campaign was from the 4th May to the 02 June 2017, and it was discontinued because the reedbeds were not receiving leachate due to dry weather conditions. Water samples were collected from a sample station 5 m from where the pumped water discharged to the reedbed cells. Water samples were also collected at the reference site.

Total and carbonate alkalinity were measured in filtered (0.45 μm, MCE Membrane Millex HA) 50 mL samples using a Mettler Toledo T50 titrator. At the same time, 10 mL water samples were taken, filtered (0.45 μm, MCE Membrane Millex HA), and preserved with a few drops of HNO_3 (Romil SpATM Super Purity Acid). Trace metal analysis was done using a PerkinElmer Optima 5300 DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). A certified reference material (CRM-ES AT-1529, lot number 1319108) was used for quality control, and recoveries were 104 ± 78% for As, 85 ± 22% for Cr, and 95 ± 14% for V.

2.3. Metals in sediments and plants

A representative number of plants and sediment samples (respectively 20 and 25, in total) were collected in two seasonal campaigns – summer and autumn (June 2017 and November 2016, respectively) in the reedbed 1 and the reference site (Oak Road Park, Hull). After separating the aerial parts (leaves and shoot) from the rhizome, the samples were stored in polyethylene bags and taken to the laboratory. Samples were washed in running tap water and rinsed with deionised water to remove sediments attached. No visual signs of chlorosis and stress were observed in the plants. Lyophilisation (freeze-drying) was used to dehydrate the samples and to improve the determination of trace elements. Initially, the samples were frozen at −80 °C overnight, and then freeze-dried for 48 h. The drying was conducted at −40 °C under a vacuum of 0.8 mbar (Edward Modulyo freeze dryer).

A representative sample of the dried homogenised solid material (0.1000 g) was weighed into an Xpress microwave digestion vessel (CEM MARS microwave digestion system, CEM Corporation, Milton Keynes, UK) and 5 mL nitric acid (Romil SpA trace metal, Cambridge, UK) was added. After leaving to slowly digest at room temperature at least overnight with the vessel sealed, the gaseous products were vented
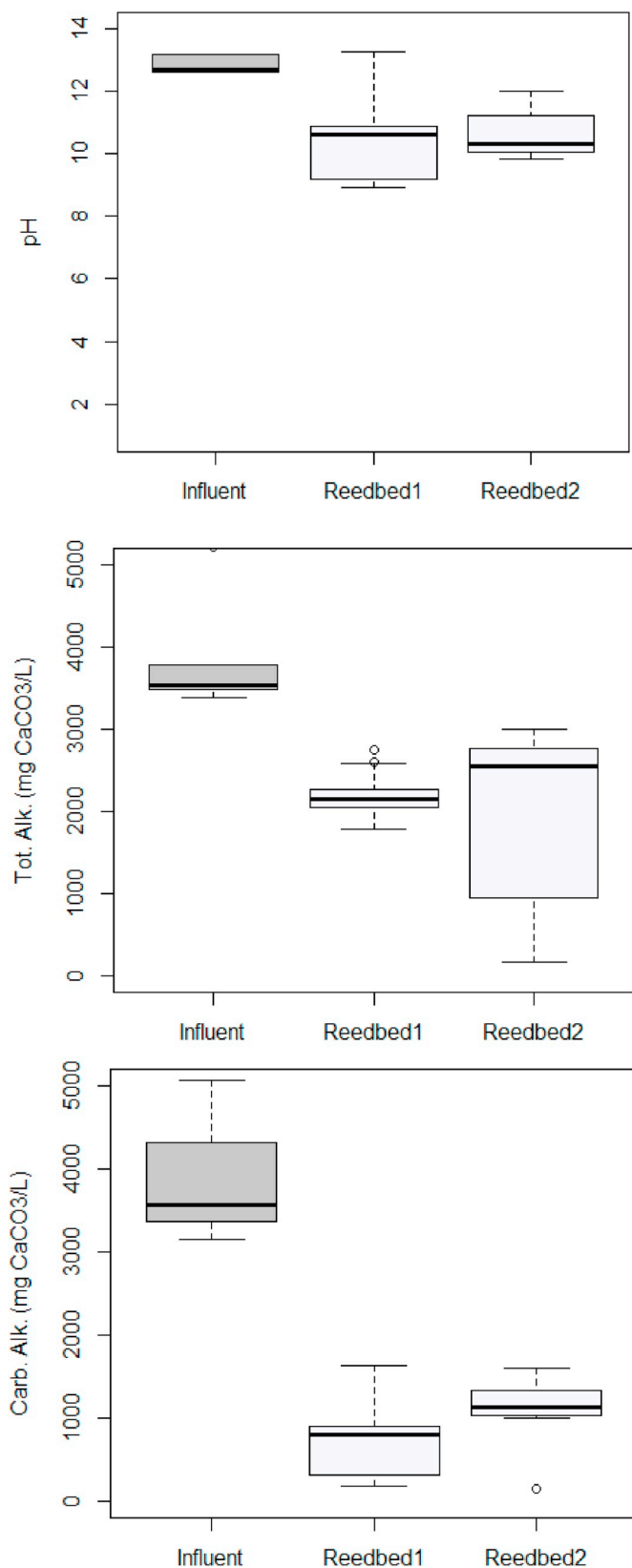
Fig. 1. Boxplots (data range, quartile range and median values) for pH, total alkalinity (mg CaCO$_3$ L^{-1}) and carbonate alkalinity (mg CaCO$_3$ L^{-1}) in the steel slag leachate (influent) and the reedbeds.

into a fume cupboard then resealed. A set of 40 vessels were prepared this way. The microwave heating was programmed to heat to 200 °C in 15 min, then held at that temperature for a further 15 min. When cooled to room temperature, the vessels were vented into a fume cupboard, and then the digests were diluted by weight with pure water (Elga Purelab, 18 Megohm conductivity) into tared 50 mL sample vials. Analysis was performed on PerkinElmer Optima 5300DV emission ICP instrument for 69 elements under high argon purge conditions. Comparison against certified reference materials (CRM-ES AT-1529, lot number 1319108) showed values within 96–106% for Cr, and V. Phosphorus was measured by ICP after acid digestion, and nitrogen analysis in plant samples by Kjeldahl digestion was performed by Beverley Analytical Laboratory.

Surface sediments (5 cm depth) were homogenised, air-dried, disaggregated with pestle and mortar, and sieved (2 mm aperture) before microwave-assisted total digestion (aqua regia and HF) following standard methods (USEPA, 1996). Three samples of secondary precipitates from the surface of emergent reeds were also collected to characterise the nature and composition of neo-formed minerals in the wetlands (Supplementary material). These were dried and analysed through total digestion and X-ray powder diffraction. This was performed on a PANAlytical Empyrean X-ray diffractometer (XRD) operating in Bragg-Brentano geometry using copper Kα1 radiation (λ = 1.540546 Å), and a PIXEL detector, in the range $3 \leq 2\theta/° \leq 70$ with a step size of 0.0393° and counting time 240 s per step.

2.4. Data analysis

Biological Concentration Factor (BCF) was calculated as metal concentration ratio of rhizomes to sediment, Translocation Factor (TF) was calculated as ratio of metals in leaves to that in rhizomes, while the Biological Accumulation Factor (BAF) was calculated as the ratio of metal in leaves to that in the sediment (Balabanova et al., 2015).

Statistical analysis was carried out in RStudio (R Development Core Team, 2017) using the "car" package (Fox and Weisberg, 2011). Since the Levene's test ($p < 0.05$) showed that the groups are not homogeneous, we used the non-parametric Mood's Median Test using the "RVAideMemoire" package (Hervé, 2017). A posthoc analysis was performed using the Pairwise Mood's Median Tests function and the Benjamini, Hochberg, and Yekutieli method with the "rcompanion" package (Mangiafico, 2017). When the concentrations were below the detection limit, we assumed that the value was half of the detection limit (Croghan and Egeghy, 2003).

The hydrochemical analysis was undertaken using PHREEQC Interactive 3.4.012927 (USGS) and the LLNL database to calculate saturation indices (SI) of relevant mineral phases using the values of the inflow leachate. SI was reported as an average of all the simulations.

3. Results and discussion

3.1. Hydrochemical composition

The reedbeds were very effective removing Ca (98%), Al (81%), Ba (98%), Cr (90%), Ga (80%), Ni (98%), and Zn (98%). There were marked decreases in various elemental concentrations between leachate and reedbed samples. Table 1 shows the difference in the hydrochemical composition between the steel slag leachate influent and the reedbeds. Pumping and sampling of the influent was intermittent according to the groundwater levels. Reedbed 1 was the most used and where the vegetation is more developed, so a higher number of samples was collected and analysed in the seasonal sampling campaigns.

The hydrochemical modelling with Phreeqc shows that calcium in the steel slag leachate is removed by precipitation as CaCO$_3$, with saturation indices (SI) for calcite and aragonite of 3.8 ± 0.1 and 3.7 ± 0.1, respectively. This contributes to the key buffering process operating in these systems (see Eq. (1)). The XRD results of the
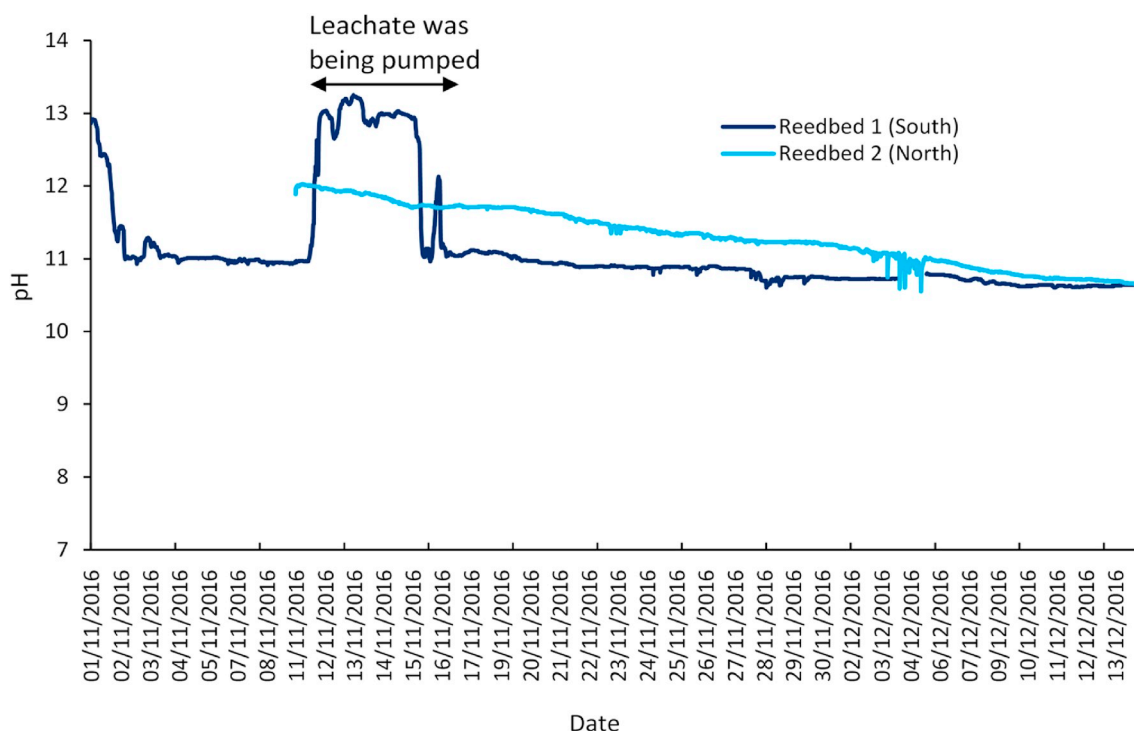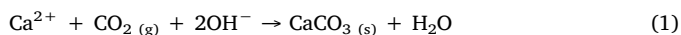
Fig. 2. pH variation (monitored every 15 min) in the reedbeds during the winter campaign.

secondary precipitates from plants (Supplementary material) confirm that calcite is the primary crystalline phase in the precipitate samples and acid digestion showed that Ca is the most abundant element (30 ± 2%) in the precipitates.

$$Ca^{2+} + CO_{2\,(g)} + 2OH^- \rightarrow CaCO_{3\,(s)} + H_2O \quad\quad (1)$$

These rapidly-forming secondary deposits are also likely to scavenge some of the dissolved metals of interest [e.g. Ni and Zn (Hobson et al., 2018; Zachara et al., 1991)] as has been documented at other steel slag disposal sites (Hobson et al., 2018). It is clear that dissolved Cr, Ni and Zn concentrations all rapidly fall to below detection limit concentrations in the reedbeds, which is very encouraging in showing that their environmental mobility is limited by the reedbeds.

The hydrochemistry shows that As is mostly present as $HAsO_3^{2-}$ at pH higher than 12, and as $H_2AsO_4^-$ and $HAsO_4^{2-}$ for pH between 2 and 11 (Panagiotaras et al., 2012). No statistical difference was found for As in the influent and both reedbeds, showing that this metalloid is not significantly removed in the constructed wetland.

Cr(VI) species dominates under high pH, forming the toxic, carcinogenic, and highly soluble oxyanions $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_4^{2-}$ (Watts et al., 2015). The Mood's median test for Cr showed that the concentrations were statistically different between the sites sampled (p < 0.01) and that Cr is effectively removed from solution in the reedbeds. The removal mechanism is likely to be dominated by sediment sorption, with Cr associating with the Fe–Mn oxide fraction (Hadad et al., 2018). The phytostabilization of this metal in the rhizomes and sediments also contributes for its removal (Mufarrege et al., 2018a, b).

Vanadium in alkaline leachate predominates as V(V), occurring as the vanadate oxyanion (e.g., $H_2VO_4^-$, HVO_4^{2-}), which exhibits a high mobility, but also strong affinity for hydrous metal oxide surfaces [e.g. Fe(III) oxides/oxyhydroxides], adsorbing via ligand exchange at neutral to low pH (Telfeyan et al., 2015). Vanadium is typically less well-removed from solution (Table 1) in the wetlands. No statistical difference was found for V in the influent and both reedbeds, showing that these metal(loid) are not removed in the constructed wetland. The vanadium removal is within the values reported in the literature (Kröpfelová

et al., 2009). This is consistent with the pH control on vanadate solubility in alkaline systems, where significant removal from solution typically occurs at pH < 10 (Burke et al., 2013). As V is a critical metal (EC, 2017) and simultaneously an emerging pollutant (Chen and Liu, 2017), it is important to implement measures that allow the removal and recovery of this metal from alkaline leachates (Gomes et al., 2016a, 2017), preferably before the constructed wetlands. Novel filter media can be used to remove V (Hua et al., 2018).

The reedbeds were also efficient in lowering pH and alkalinity (total and carbonate) (Figs. 1 and 2). However, the median pH value in the reedbeds is still higher than 9 [operational environmental quality standards (EQS)]. Fig. 2 shows clearly when fresh leachate is being pumped to the reedbed, and how the buffering from pH ∼ 13 to pH ∼ 11 is fast (takes approximately 8 h). Buffering to pH values lower than 11 takes longer, and it tends to stabilise above 10, given the Na enrichment of the leachate, when compared with the typical values measured in other steel slag leachates (Hull et al., 2014; Mayes et al., 2008). This is due to the presence of desulphurisation slags at this site, which provides a non-lime source of alkalinity. The steel plant has used Na_2CO_3 as the desulphurisation agent (current usage is minimal since magnesium is now used), which means that even after Ca equilibrates during $CaCO_3$ precipitation, there is still an excess of alkalinity in the system.

The statistical analysis (Mood's Median Test) showed that the median values of pH are significantly different between the influent and reedbed 1 (p = 0.04), the influent and reedbed 2 (p = 0.04), and between both reedbeds (p < 0.01). Reedbed 1 shows lower pH values that Reedbed 2 (Figs. 1 and 2), especially for the third quartile. One possible reason can be the higher biomass in reedbed 1 (visual observation) and subsequent biological activity present. Biological activity has been considered determinant in buffering alkaline waters through (1) microbial respiration increasing partial pressure of CO_2 in wetland substrates which aids buffering, and (2) the production of organic acids through decomposition and root exudates (Higgins et al., 2017; Mayes et al., 2009a). Reedbed 2 presents higher alkalinity values (Fig. 1) and a higher variation, which can be related with the sparse colonisation of this reedbed – the plants did not grow as much as in Reedbed 1 due to the water level variations in early years of operation
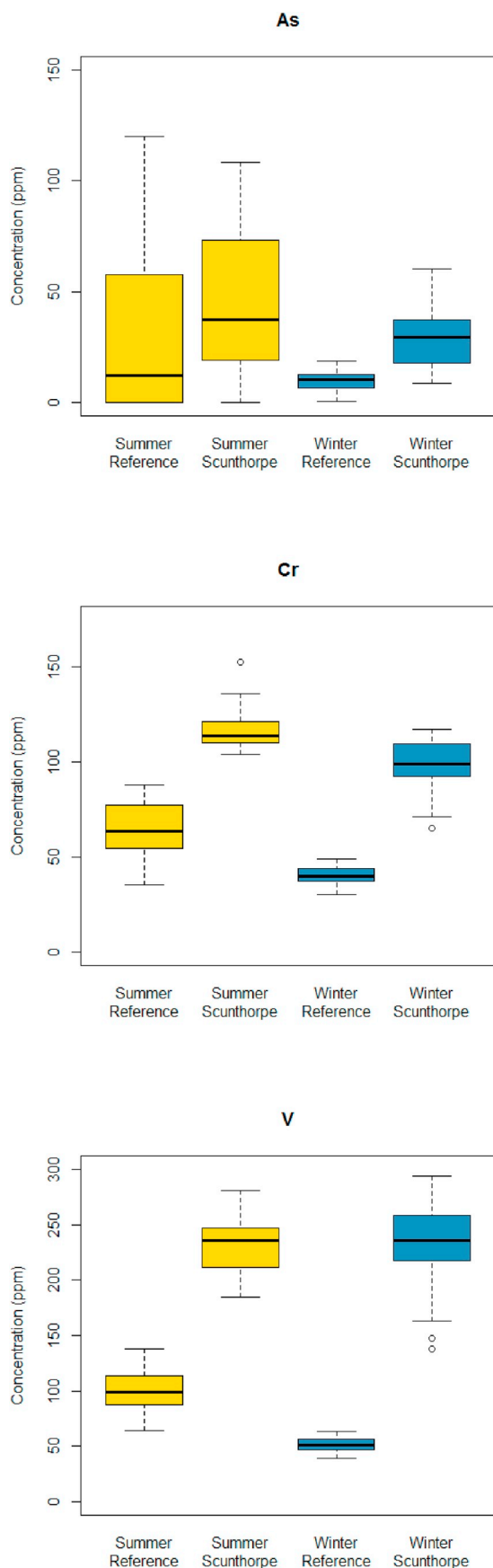
Fig. 3. Boxplots (data range, quartile range and median values) of the As, Cr and V concentrations in the sediments at the reference site and Scunthorpe during summer and winter.

Table 2
Average concentrations of metals in the sediments (mg kg^{-1}).

Site	Element		
	As	Cr	V
Scunthorpe (Spring)	50 ± 32	117 ± 11	232 ± 25
Scunthorpe (Winter)	30 ± 13	99 ± 14	230 ± 41
Reference (Spring)	45 ± 32	64 ± 15	100 ± 19
Reference (Winter)	10 ± 5	40 ± 5	51 ± 7

that were sub-optimal for reed growth.

3.2. Metal(loid)s concentrations in sediments

Sediment analyses (Fig. 3) show that As, Cr and V are significantly higher in the steelworks reedbed than in the reference site (Mood's median test, $p < 0.01$, $n = 25$). The average values measured in the sediments are presented in Table 2. The average values in the reference site are consistent with the average concentrations from the Geochemical Atlas of England and Wales (Rawlins et al., 2012). No statistical difference was found between the seasons where the sampling occurred ($p = 0.05$ for As, 0.23 for Cr and 1 for V, respectively).

Higher concentrations of the elements of interest at the reedbeds reflect either greater metal(loid) enrichment in the substrates used (unfortunately no samples before commissioning the site in 2012 were able to be collected) or accumulation of these from the water column. Except for V, there is clear evidence that the latter is apparent. Furthermore, isolated samples of secondary carbonate deposits taken from *Phragmites* stalks (Supplementary material) showed the average concentrations of 39 ± 7 µg g^{-1} of As, 4 ± 1 µg g^{-1} of Cr and 52 ± 2 µg g^{-1} of V.

The metal concentrations in the constructed wetland sediments are higher than those reported in constructed wetlands for municipal wastewater (Caicedo et al., 2015), but lower than the ones measured in wetlands treating mine water (Leung et al., 2017). Vanadium concentrations in both the reference site and the reedbed exceed the concentrations reported in the literature for a natural wetland (Hosseini Alhashemi et al., 2012), but this can be due to differences in the geological background. Vanadium enrichment in soils and superficial deposits overlying Jurassic Ironstones (as is the case at Scunthorpe) have been shown to exhibit relatively high V concentrations given the affinity for V with Fe-oxide-rich deposits (Hobson et al., 2018). It is informative to compare reported concentrations with statutory guidance to inform longer-term management options given routine de-sludging would be anticipated of full-scale wetlands treating alkaline steel slag leachate (PIRAMID Consortium, 2003). Considering the draft sediment quality criteria for England and Wales (Table 3), in both the constructed reedbed and the reference site the TEL (threshold effect level) is exceeded for As, Cd, Cr, Cu, Ni and Zn (Hudson-Edwards et al., 2008). The PEL (predicted effect level) is exceeded for As, Cr and Ni (Table 3). Comparing the measured concentrations in sediments with the trigger values (below these values phytotoxic or zootoxic effects are not expected) presented in Table 3, only 20% of the samples in the reedbed and 12% in the reference area exceed the threshold trigger concentration for As (50 mg kg^{-1}). When compared to the Dutch Soil Remediation Circular 2009 (MH, 2009) (Table 3), 12% and 2% of the samples exceed the soil intervention value for As, in the steelworks and the reference site, respectively. Assuming a conservative position and that all Cr is in its toxic form Cr (VI), 96% of the samples at the constructed reedbed exceed the intervention value when compared with 8% in the reference site. For vanadium, 20% of the samples in the constructed reedbed exceed the indicative Dutch level for serious contamination in soil. Considering the proposed values for metal concentrations in the European Commission Working Document on Sludge, 3rd Draft (EC, 2000), none of the samples exceeds the proposed values for metals and

Table 3
Percentage of samples that exceed quality criteria or regulatory levels (total number of samples for each site is 50). Values in square brackets refer to the reference site.

Element	England and Wales (Hudson-Edwards et al., 2008)					Netherlands (MH, 2009)
	Sediment		Soil (including overbank sediment)			Soil
	TEL	PEL	Threshold soils	Grazing livestock	Crop growth	Intervention value
As	**94 [70]**	**84 [22]**	**20 [12]**	0 [0]	0 [0]	**12 [2]**
Cd	2 [6]	0 [0]	0 [0]	0 [0]	0 [0]	0 [0]
Cr	**100 [88]**	**92 [0]**	*	*	*	**96[a] [8] [a]**
Cu	50 [40]	0 [0]	0 [0]	0 [0]	0 [0]	0 [0]
Pb	0 [24]	0 [0]	0 [0]	0 [0]	*	0 [0]
Ni	100 [44]	100 [2]	*	*	*	0 [0]
V	*	*	*	*	*	**20[b] [0]**
Zn	54 [22]	0 [0]	0 [0]	0 [0]	0 [0]	0 [0]

TEL – Threshold effect level (Hudson-Edwards et al., 2008), PEL – Predicted effect level (Hudson-Edwards et al., 2008).
* No value defined.
[a] Assuming all Cr as Cr(VI).
[b] The value for vanadium is 250 mg kg^{-1} (indicative level for serious contamination).

potentially the sludge could be applied in agricultural soils.

Resource recovery from sludge originated in metal-rich water treatment could still be considered a missed opportunity (Macías et al., 2017; Tyagi and Lo, 2013; Younger et al., 2002), as the high concentration and the possibility of leaching the metals make it an attractive alternative metal source with high economic potential (Gomes et al., 2018a). Another possibility is the metal recovery from the alkaline leachate before the passive treatment, using ion exchange resins (Gomes et al., 2016a, 2017), which could help offset long-term remedial costs in cases such as this.

3.3. Metal(loid)s concentrations in plants

As, Cr and V accumulate in the rhizomes of the plants (*Phragmites australis*) in the steel works reedbed and the reference site (Fig. 4), with the reference site showing the highest concentrations. Arsenic concentrations in the rhizomes and leaves from the reedbed 1 are consistent with the ones measured in other constructed wetlands (Caicedo et al., 2015). Cr concentrations measured in both leaves and rhizomes are within the ranges reported in the literature (Vymazal and Březinová, 2015), although Cr concentrations in the rhizomes at the reference site are higher than those reported for both natural and constructed wetlands. Vanadium concentrations in the rhizomes and the leaves are also consistent with the reported in the literature (Janadeleh et al., 2016). However, vanadium is typically a metal overlooked in constructed reedbeds, and more research is needed to better understand its behaviour and fate (Higgins et al., 2017; Kröpfelová et al., 2009).

Elemental concentrations in leaf material at both sites did not show any statistical variation between the reference site and the treatment reedbed during summer months (Pairwise Mood's Median Tests). In the winter campaign, As and V concentrations in the leaves from the reedbed were significantly higher than in the reference site ($p = 0.047$ for As and $p < 0.01$ for V). The rhizome concentrations were statistically different for As, Cr, and V between the reedbed and the reference site ($p < 0.01$), except V in the summer ($p = 0.113$). Altogether, the results show statistically significant enrichment in metal(loid)s in rhizomes (Table 4) and also a seasonal effect on the Cr concentrations (highest in both the reference site and the reedbeds in the winter campaign).

Comparing the rhizome/leaf ratio with the reference site, it is clear that macronutrients like P, K, S and Mg have lower rhizome/leaf ratios in the constructed reedbed (Table 5). Nutrient concentrations in the reedbeds receiving highly alkaline water are significantly lower than reference site data. This may in part be expected given the nutrient-poor source water (alkaline leachate which is generated from rainwater

ingress through an industrial by-product landfill: Table 1). Furthermore, nutrient deficiency has been highlighted as a constraint to plant growth on highly alkaline calcareous substrates due to the low organic matter content and strong P-binding with calcium minerals (Ash et al., 1994). Table 5 shows the comparison between the average concentration of macronutrients in rhizomes and leaves in the reedbeds studied and the reference site. It is clear that concentrations of N and P are lower in the alkaline leachate feed reedbeds. For the metal(loid)s of interest, in most cases, the concentrations are below the detection limit, but the rhizome/leaf ratio for Cr is low when compared with the average value (72.7) reported in the literature (Vymazal and Březinová, 2015). Regarding the translocation, bioaccumulation and bioconcentration factors in both sites, the reference site shows higher values for As (Table 6). The low values of BCF for Cr are similar to those reported for *E. crista-galli* in sediments contaminated with Cr and other metals (155 µg g^{-1}) (Basílico et al., 2018). For Cr and V, all factors have similar values in the summer campaign, but the translocation factor is higher in the reedbed in the winter campaign.

Metal(loid)s are successfully removed from solution in the wetlands (except V and As) and tend to accumulate in the wetland sediments, with modest concentrations apparent compared to reference site. However, none of the sediment concentrations is at levels that would pose a concern regarding reuse for agricultural purposes or soil amendment. Encouragingly, there is no significant uptake and translocation of metals to the aboveground portions of the reeds compared to reference conditions. Indeed, as mentioned before, it appears more likely that nutrient deficiency, rather than toxicity is likely to be a longer-term concern for managing wetlands treating highly alkaline leachate.

4. Conclusions

Constructed wetlands can be used to treat highly alkaline drainage (pH > 12). Reedbeds were effective at consuming the extreme alkalinity in the samples, typically lowering it by half in a relatively short residence time (< 24 h). Leachate pH buffering was also effective, showing initial rapid falls within < 10 h from pH 13-11. Removal percentages higher than 90% were obtained for calcium, chromium, nickel and zinc. However, arsenic and vanadium were not efficiently removed. There was accumulation of As, Cr and V in the reedbed sediments, but not at a level that raises concerns for the need to treat them as hazardous materials. Also, there is no significant uptake of metal(loid)s by aerial portions of the reeds, although there is accumulation in rhizomes. The data suggests minimal risk of As, Cr, and V uptake and cycling in wetlands receiving alkaline steel slag, but
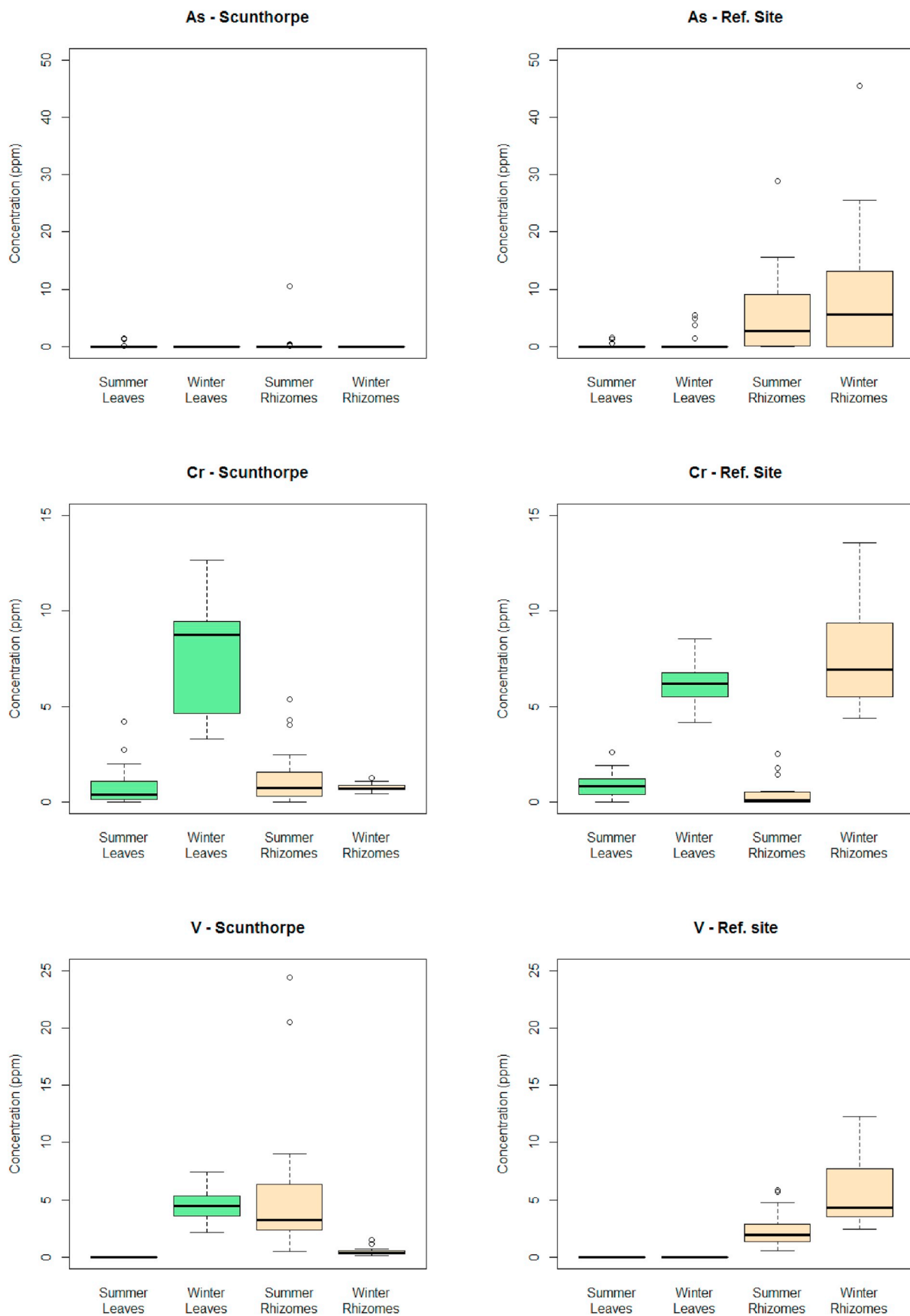
Fig. 4. Boxplots (data range, quartile range and median values) of the As, Cr and V concentrations in the plants (above and below ground) at the reference site and Scunthorpe during summer and winter. Common scales are used for each element for ease of comparison. Arsenic concentrations at Scunthorpe are below the detection limit (0.003 ppm).

Table 4
Value of p from the Pairwise Mood's Median Tests of the metal(loid)s levels in the plants. Values marked as bold are statistically significant.

Factor	Element		
	As	Cr	V
Site	0.103	0.212	0.09
Season	0.092	**< 0.01**	0.519
Part of the plant	**< 0.01**	**0.02**	**< 0.01**

Table 5
Average concentrations of macronutrients (g kg^{-1}) in rhizome and leaves in the study and reference site.

Element	N	P	K	Ca	S	Mg
Summer reedbed						
Rhizome	7.3 ± 9.5	0.5 ± 0.3	11.9 ± 4.3	7.9 ± 10.4	1.6 ± 0.5	0.6 ± 0.1
Leaf	26.3 ± 4.2	1.7 ± 0.3	22.4 ± 2.8	1.9 ± 0.7	3.8 ± 0.8	1.0 ± 0.32
Summer reference site						
Rhizome	11 ± 1.1	1.5 ± 0.2	18.6 ± 6.2	1.9 ± 1.0	2.0 ± 0.7	1.0 ± 0.3
Leaf	29.8 ± 5.4	2.0 ± 0.2	18.2 ± 2.1	3.5 ± 1.5	2.9 ± 0.7	1.2 ± 0.3
Winter reedbed						
Rhizome	6 ± 0.1	0.043 ± 0.02	1.0 ± 0.3	0.4 ± 0.2	0.2 ± 0.07	0.05 ± 0.02
Leaf	11.1 ± 0.3	0.4 ± 0.1	5.9 ± 1.7	11.9 ± 2.2	7.2 ± 1.3	0.8 ± 0.2
Winter reference site						
Rhizome	12.6 ± 0.5	1.9 ± 0.4	18.2 ± 4.5	1.9 ± 1.1	2.1 ± 0.5	1.0 ± 0.3
Leaf	19.6 ± 1.3	1.0 ± 0.1	7.2 ± 1.5	9.1 ± 1.2	5.7 ± 0.8	1.9 ± 0.3

Table 6
Average rhizome/leaf ratio, translocation, bioaccumulation and bioconcentration factors in the reedbed and the reference site during the summer and winter campaign for metal(loid)s and macronutrients.

Element	As	Cr	V	N	P	K	Ca	S	Mg
Summer reedbed									
Rhizome/Leaf ratio	< LOD	1.8 ± 0.5	< LOD	0.3 ± 0.02	0.3 ± 0.1	0.5 ± 0.1	3.3 ± 2.6	0.4 ± 0.04	0.6 ± 0.03
TF	< LOD	0.6 ± 0.2	< LOD	3.6 ± 0.3	4.1 ± 1.6	2.1 ± 0.6	0.4 ± 0.2	2.5 ± 0.2	1.8 ± 0.1
BAF	< LOD	0.01 ± 0.01	< LOD	na	3.3 ± 0.2	1.1 ± 0.1	0.05 ± 0.01	0.4 ± 0.05	0.1 ± 0.02
BCF	0.5 ± 1	0.01 ± 0.01	0.02 ± 0.02	na	0.9 ± 0.3	0.6 ± 0.2	0.2 ± 0.2	0.2 ± 0.03	0.1 ± 0.01
Summer reference site									
Rhizome/Leaf ratio	51 ± 78	1.1 ± 0.7	< LOD	0.4 ± 0.04	0.7 ± 0.005	1.0 ± 0.2	0.6 ± 0.03	0.7 ± 0.08	0.9 ± 0.1
TF	0.01 ± 0.03	13 ± 36	< LOD	2.7 ± 0.3	1.4 ± 0.1	1.0 ± 0.2	1.9 ± 0.3	1.5 ± 0.2	1.2 ± 0.1
BAF	0.1 ± 0.1	0.01 ± 0.01	< LOD	na	3.5 ± 0.2	1.3 ± 0.04	0.11 ± 0.03	2.1 ± 0.2	0.1 ± 0.02
BCF	5 ± 15	0.02 ± 0.02	0.02 ± 0.01	na	2.6 ± 0.1	1.3 ± 0.3	0.1 ± 0.02	1.4 ± 0.3	0.1 ± 0.02
Winter reedbed									
Rhizome/Leaf ratio	< LOD	0.1 ± 0.03	0.1 ± 0.03	0.3 ± 0.3	0.1 ± 0.02	0.2 ± 0.01	0.3 ± 0.01	0.03 ± 0.004	0.1 ± 0.01
TF	< LOD	10 ± 2	10 ± 2	1.9 ± 0.1	9.0 ± 1.3	5.9 ± 0.4	46 ± 25	38.3 ± 5.8	17.4 ± 2.3
BAF	< LOD	0.08 ± 0.02	0.02 ± 0.003	na	1.0 ± 0.2	0.3 ± 0.1	0.46 ± 0.03	1.1 ± 0.1	0.1 ± 0.02
BCF	5E-4 ± 2E-4	0.01 ± 0.001	0.002 ± 0.001	na	0.1 ± 0.02	0.1 ± 0.2	0.01 ± 0.01	0.03 ± 0.003	0.01 ± 0.002
Winter reference site									
Rhizome/Leaf ratio	< LOD	1.2 ± 0.2	< LOD	0.3 ± 0.4	1.9 ± 0.3	2.5 ± 0.2	0.2 ± 0.08	0.4 ± 0.04	0.5 ± 0.07
TF	< LOD	0.9 ± 0.1	< LOD	1.5 ± 0.02	0.6 ± 0.1	0.4 ± 0.03	6 ± 2	3 ± 0.3	2.0 ± 0.2
BAF	< LOD	0.2 ± 0.01	< LOD	na	3.1 ± 0.2	0.6 ± 0.1	0.42 ± 0.01	6.1 ± 0.3	0.3 ± 0.02
BCF	0.8 ± 0.9	0.2 ± 0.04	0.1 ± 0.05	na	5.8 ± 0.72	1.6 ± 0.2	0.08 ± 0.04	2.2 ± 0.3	0.1 ± 0.03

na – not available, < LOD – concentrations below the limit of detection of the analytical method Translocation Factor (TF) was calculated as ratio of metals in leaves to that in rhizomes, Biological Accumulation Factor (BAF) was calculated as the ratio of metal in leaves to that in the sediment, and the Biological Concentration Factor (BCF) was calculated as metal concentration ratio of rhizomes to sediment.

potential nutrient deficiency problems. Constructed wetlands can then be adopted as treatment for alkaline leachate. There is also potential to use sequenced reedbeds after chemical treatment, to minimise acid dosing and potentially offer a significant cost reduction.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2019.04.127.

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