ASSESSING THE REMOVAL EFFICIENCY OF Zn, Cu, Fe AND Pb IN A TREATMENT WETLAND USING SELECTIVE SEQUENTIAL EXTRACTION: A CASE STUDY

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Abstract. The accumulation and speciation of Zn, Cu, Fe and Pb in the sediments of an artificial surface-flow wetland used to treat domestic wastewater near Christchurch, New Zealand, were examined. Water metal concentrations and total suspended solid (TSS) content were determined at the inflow and outflow both in winter and summer, and metal concentrations were analysed in shoots and roots of selected plants. Water and sediment data suggest that the wetland is acting as a sink for Zn, Cu and Pb, while Fe uptake is minimal and the wetland appears to be releasing Fe in the winter. Metal concentrations in the most mobile fractions (exchangeable and bound to carbonates) are negligible. Cu is mostly associated with the organic/sulphide phase, whereas Zn and Pb show a strong affinity for hydroxides and organics/sulphides. A large fraction of all metals is also present in the residual phase, and is therefore unlikely to be released into the overlying water. Metal concentrations are below the low trigger values of the ANZECC sediment quality guidelines, except for Pb near the inflow. However, results of sequential extraction suggest that a significant proportion of Pb occurs in the detrital phase and is therefore not bio-available. Metal concentrations were higher in the roots than in the shoots of both *Juncus* sp. and *Lythrum hyssopifolia.* This study shows that, although metal concentrations are low, TSS and metals, except Fe, are effectively removed by the wetland system. The low removal rate of Fe is possibly due to the young age of the wetland and low loading rates.

Keywords: copper, iron, lead, metal removal, plant uptake, speciation, wastewater treatment wetland, zinc

1. Introduction

Wetlands are increasingly being used for the treatment of wastewater, because of their ability to process waste material in a cost-effective way and to efficiently remove a range of contaminants, including BODs, nutrients, trace organics and metals (e.g. Kadlec and Knight, 1996). However, many studies assessing the efficiency of wetlands for the removal of metals usually only consider the total metal concentration at the input and output, and little is known about the fate and removal processes of metals in wetland sediments. The distribution of metals among various chemical phases determines their mobility, bio-availability and toxicity. Metals in wetland sediments may be loosely bound to exchangeable sites, associated with carbonates, bound to Fe- and Mn-hydroxides, fixed by organic matter and sulphides, adsorbed onto mineral phases or even form specific minerals (e.g. Gambrell, 1994). There

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are limitations associated with the chemical selective sequential extraction (SSE) procedure, due mainly to release and readsorption of metals into the residue after extraction and loss of material between extractions (e.g. Tack and Verloo, 1995). However, results of SSE provide an insight into the association and removal mechanisms for metals in the wetland, which cannot be obtained by determining the total metal concentration that only provides a measure of the level of contamination.

The purpose of this study was to determine the partitioning of Zn, Cu, Fe and Pb in the sediments of a constructed wetland used for municipal wastewater treatment, and to examine the variations in speciation with depth and between the inflow and outflow of the wetland. Metal analysis focussed on Cu, Zn and Pb not only because of their common occurrence in domestic wastewater, but also because of their potential toxicity (e.g. Rudd, 1987; ANZECC & ARMCANZ, 2000). Fe was also analysed, as Fe oxides are important adsorption sites for many metals and thus metal retention capacity of wetlands is largely controlled by the behaviour of Fe (e.g. precipitation on the surface of sediments or release) (e.g. Goulet and Pick, 2001). The total metal concentrations were also determined in sediments at both the inflow and outflow and in selected wetland plants. In addition, water samples were collected over a period of 8 h both in the winter and summer, and the metals and total suspended solids concentrations were compared between inflow and outflow. Discharge of treated effluent from the oxidation ponds into the wetland is fairly constant and influent quality does not vary significantly because of its source (domestic wastewater) showing little variation (R. Frizzell, pers. comm., 2002). However, temporal variations can be expected, thus the water dataset mainly provides a snapshot of the influent and effluent quality. Nevertheless, it is used in conjunction with the metal concentration in the sediment to give an indication of metal input and apparent reduction between inflow and outflow.

2. Study Site

The Kaiapoi sewage treatment plant is located 2 km east of the locality of Kaiapoi, north of Christchurch, South Island, New Zealand, and is used for the treatment of wastewater from Kaiapoi and Pines Beach/Kairaki, a nearby settlement 2 km to the northeast (average population 12,000). Sewage is first screened and treated by passage through an aeration lagoon and two oxidation ponds (average retention time of 30 days in the oxidation ponds), before being discharged into a 34 ha large constructed wetland (average retention time of 100 days, R. Frizzell, pers. comm., 2003). Further treatment occurs through a sand filter and UV sterilisation, before discharge into Jockey Baker Creek (Figure 1). The inflow and outflow of the treatment plant have been measured by the Waimakariri District Council since July 2001. Data from July 2001 to July 2002 (Figure 2) show that the inflow is fairly constant, with an average of 3421 ± 920 m^3/day, whereas the outflow has shown some significant variations, with an average of 1534 ± 1432 m^3/day, mostly due

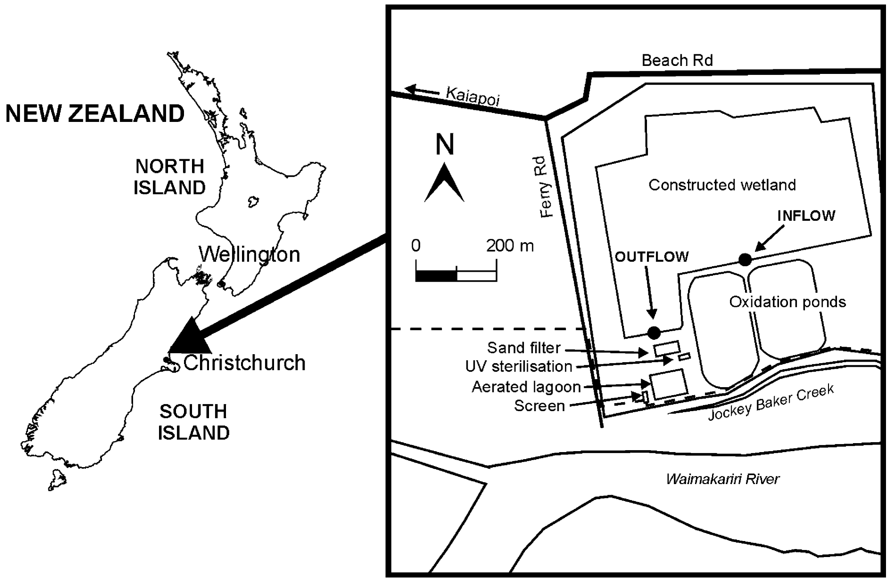

Figure 1. Location map of the Kaiapoi sewage treatment plant with sampling locations (inflow and outflow).

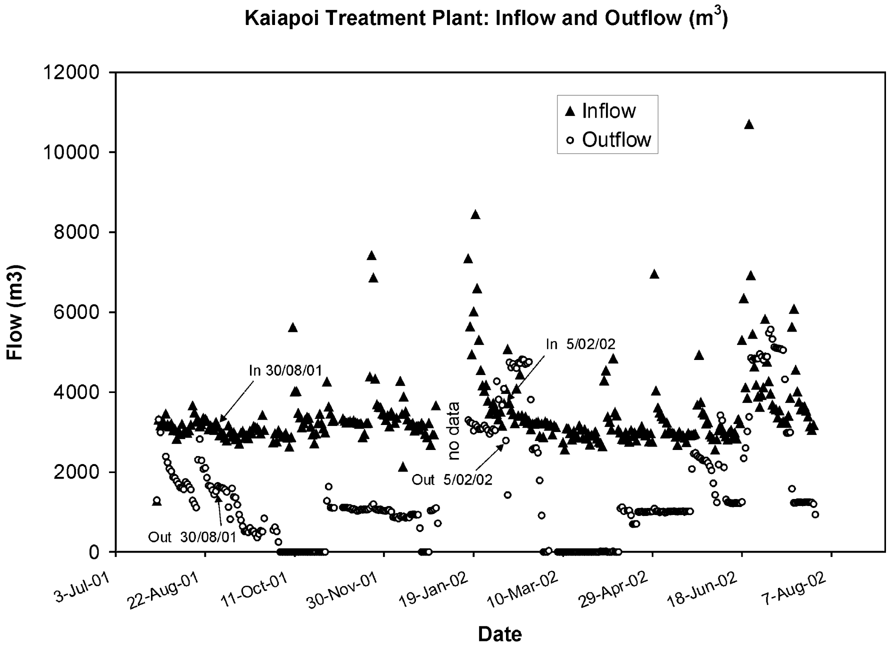

Figure 2. Total inflow and outflow from the Kaiapoi sewage treatment plant. Data from Waimakariri District Council. No data available from 29 December 2001 to 14 January 2002, because of malfunction in data transfer.

to variations in rainfall. In October 2001, as well as from 24 February to 9 April 2002, there was no discharge from the wetland, due to evapo-transpiration during a dry period without rain. Heavy rainfall at other times on the other hand is reflected in significantly higher inflow and outflow. The constructed wetland was commissioned in 1997 and has been planted with native plants, *Phormium tenax*, *Carex secta*, *Juncus pallidus*, *Schoenoplectus sp.*, *Bolboschenus sp.*, *Cortaderia richardii*, *Cordyline australis*, *Dacrydium dacrycarpus* and *Coprosma propinqua* (C. Glasson, pers. comm., 2001). The severe 1997 drought and the 1999 wet winter had an adverse effect on plant establishment, and continuous waterlogging has reduced the number of suitable species to *Carex, Phormium*, *Juncus*, *Schoenoplectus* and *Bolboschenus* (C. Glasson, pers. comm., 2001). With time, a number of *Juncus* species have become established in the wetland, including *Juncus effusus* and *Juncus gregiflorus*, while submerged exotic species (e.g. *Lythrum hyssopifolia*) are also abundant in the summer. Nevertheless, the vegetation cover is sparse (<20% of the total area) and the wetland is characterised by large areas of open water.

3. Methods

3.1. SAMPLING AND SAMPLE PREPARATION

Sampling of plants and sediments, as well as of a limited number of water samples, was carried out in May 2001. At the time of sampling, the wetland was waterlogged (c. 20 cm water depth near the inflow and c. 15 cm near the outflow), while only the eastern part of the wetland was inundated in April 2001, following a long period of drought in the Canterbury region. Redox conditions in the near surface sediments (10 cm depth) were measured at core sites before collection of cores. Platinum wire electrodes (Faulkner *et al.*, 1989) were pushed into the sediment, left for 3 h, and the redox potential measured against a silver/silver chloride electrode. 199 mV were then added to relate the readings to the standard hydrogen electrode. Three shallow sediment cores were collected from the wetland within 10 m of both the inflow and outflow, using PVC pipes lined with polyethylene tubing. Cores were stored at 4 °C pending analysis. Samples of the most common plant species found near the inflow, *Juncus sp.* and *Lythrum hyssopifolia*, were collected. In the laboratory, plant samples were washed with deionised water, roots and shoots were separated and dried overnight at 60 °C.

Water samples were collected in May 2001 (winter), and also over a period of 8 h both at the inflow and the outflow in the winter (August 2001) and in the summer (February 2002), in an attempt to assess the difference in removal efficiency between seasons. Temperature, conductivity, pH and redox were measured at the time of sampling. Acid-washed bottles were rinsed three times with sample water before sampling. Upon return to the laboratory, a representative sub-sample of each water sample was acidified with pure HNO_3, to be used for the analysis of total metals (dissolved and particulate). Another representative sub-sample was filtered through an acid-washed 0.45 μm filter and the filtrate acidified with pure HNO_3. This was used to determine the concentration of dissolved metals. Another sub-sample was subsequently filtered through a GF/C filter for total suspended solid (TSS) analysis.

3.2. ANALYTICAL METHODS

3.2.1. *Sediment*

Cores were sectioned at 1 cm intervals using a plastic cutter, and samples stored at 4 °C until analysed. One representative sub-sample of each interval was dried at 105 °C until constant weight was achieved and moisture determined. Weight loss on ignition (LOI) was determined by ashing at 500 °C overnight. Cores that appeared to provide the best stratigraphic record were chosen near the inflow (one core) and outflow (one core) for further analysis. Chemical analysis was carried out on each 1-cm interval of the organic-rich fine-grained top section of each core as well as selected samples from the lower, organic-poor, sandy section. One representative sub-sample (taken by mixing the sample and sub-sampling) was digested with a 3:1 mixture of hydrochloric acid and nitric acid (aqua regia). Sequential extraction of another representative sub-sample was carried out following modified procedures after Tessier *et al.* (1979). The equivalent of 4 g of dried sediment was used for the initial extraction, in order to obtain sufficient digest for analysis. However, the sediment used had not been dried, to avoid changes in chemical speciation, which might occur during the drying process. Acid-washed polyethylene centrifuge tubes (50 mL) were used for the extraction, to minimise sediment loss. The sequential extraction was divided into four steps, and separation between each extraction was achieved by centrifuging at 3500 rpm for 30 min. The supernatant was decanted into acid-washed polyethylene centrifuge tubes and kept at 4 °C until analysis. The residue was then rinsed with 32 mL of deionised water and centrifuged at 3500 rpm for 30 min. The supernatant was discarded and the residue extracted further. Step 1 – exchangeable fraction: extraction at room temperature with 32 mL of sodium acetate solution (1 M NaOAc, pH 8.2) with continuous agitation. Step 2 – bound to carbonates: extraction at room temperature and continuous agitation with 32 mL of sodium acetate adjusted at pH 5.0 with acetic acid. Step 3 – bound to Fe-Mn oxides: extraction with 40 mL of hydroxylammonium chloride (0.04 M $NH_2OH{\cdot}HCl$) in 25% (v/v) acetic acid. This extraction was carried out at 78 ± 3 °C (as the water bath could not achieve 96 °C) for 8 h with occasional agitation. The extraction time was increased to compensate for the lower temperature. Step 4 – bound to organic matter and sulphides: extraction with 6 mL of 0.02 M nitric acid and 10 mL of 30% hydrogen peroxide (adjusted to pH 2.0 with dilute HNO_3) at 78 ± 3 °C for 2 h with occasional agitation. After 2 h, 6 mL of 30% H_2O_2 (adjusted to pH 2.0 with HNO_3) were added and the extraction carried out for another 3 h at 78 ± 3 °C. After cooling, 10 mL of 3.2 M ammonium acetate in 20% (v/v) HNO_3 were added and the sample diluted to 40 mL. Ammonium acetate was added to prevent adsorption of extracted metals to the oxidised sediment (Tessier *et al.*, 1979).

The resulting solution from the total digestion by aqua regia and the extracts obtained from the sequential extraction procedure were analysed for Fe, Cu, Zn and Pb by atomic absorption spectrophotometry (AAS) using an air-acetylene flame. Calibration curves for each trace metal were prepared prior to every batch of sample determination. Blanks that had been digested by aqua regia and following the SSE procedure were also analysed, and their metal concentrations deducted from the results obtained for the sediment samples. The residual (detrital) fraction is calculated as the difference between the aqua-regia extractable metal content and the sum of the metals released by the sequential extraction. As aqua-regia is not a true total extraction, the residual fraction may have been slightly underestimated.

3.2.2. *Water*

The aliquot of the non-filtered water samples was digested with nitric acid following APHA method 3030E, and analysed for Fe, Cu, Zn and Pb by ICP-MS following APHA method 3125B. The filtered samples were analysed for Fe, Cu, Pb and Zn by AAS. However, only dissolved Fe concentrations are reported here, as dissolved Cu and Pb concentrations were below detection limit. Dissolved Zn concentrations were higher than the total concentrations, suggesting possible contamination, therefore data were not used.

3.2.3. *Plants*

Roots and shoots of the two types of plant specimens collected (*Juncus sp.* and *Lythrum hyssopifolia*) were digested with oxidising acids and analysed for Fe, Cu and Zn by ICP-AES and for Pb by ICP-MS.

4. Results and Discussion

4.1. SEDIMENT

Cores were shallow (maximum 20 cm thickness), consisting of a thin (5–8 cm) black muddy organic-rich layer overlying a dark brown-grey sandy layer. The thickness of the sandy layer varied between 8 and 12 cm, and represented the top part of the *c.* 2m thick sandy sequence forming the substrate of the wetland (R. Frizzell, pers. comm., 2003). The organic matter content and concentrations of total Zn, Cu, Fe and Pb at the inflow and outflow are shown in Figure 3.

Data show that, except for Fe, there is a significant decrease between the inflow and outflow. The highest measured *total* concentrations (reported on a dry weight basis) in the inflow cores are 13,000 mg/kg Fe, 72 mg/kg Zn, 19 mg/kg Cu and 75 mg/kg Pb, while the highest concentrations measured in the outflow core are 12,000 mg/kg Fe, 39 mg/kg Zn, 6 mg/kg Cu and 11 mg/kg Pb.

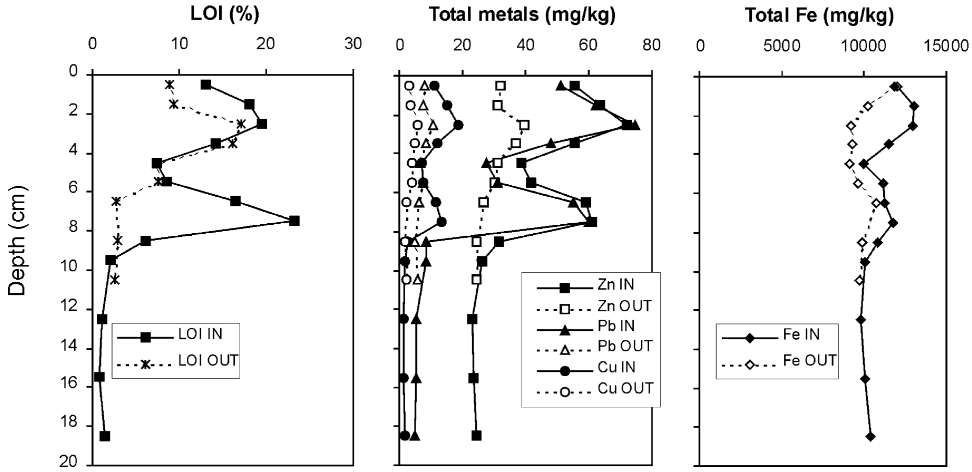

Figure 3. Total metal concentrations and organic matter content (weight loss on ignition: LOI) in two sediment cores taken near the inflow (IN) and outflow (OUT) in the Kaiapoi wetland.

As shown in Figure 3, Pb exhibits the most significant decrease in concentration between inflow and outflow. The vertical distribution of Zn, Cu and Pb also reflects the strong positive relationship between metals and organic matter content and grain size (Chagué-Goff, 2001), with higher metal concentrations in the organic-rich fine-grained upper part of the cores. However, Chagué-Goff (2001) also showed that lower metal contents occurred in wetland sediments near the outflow than near the inflow, despite a similar organic matter content (Figure 4), suggesting the uptake of metals in the wetland. Fe on the other hand exhibits only a weak positive relationship with organic matter. Furthermore, Fe data suggest that there is no significant decrease in Fe concentration between the inflow and outflow, and therefore there is possibly no Fe uptake in the wetland sediments (unless Fe from an unknown source is added to the system). There are no data available on the chemical composition of the sediments used to construct the wetland. However, the lower concentrations measured in the sandy sediments characterised by the lowest organic matter content are likely to represent background concentrations of the sediment substrate; *c.* 20–25 mg/kg Zn, *c.* 2 mg/kg Cu, *c.* 5–6 mg/kg Pb and *c.* 10,000 mg/kg (1%) Fe (see Figure 3). Furthermore, although there are no data on the rate of sediment accumulation since the construction of the wetland in 1997, four years prior to this study, the organic-rich top layer overlying the sandy substrate is likely to result from the decomposition of plants since 1997, as well as input from treated sewage.

As the sediment cores were taken near the inflow and the outflow, it is not known whether metal uptake is gradual and uniform throughout the wetland. Mungur *et al.* (1997) showed that metal uptake did increase as the influent moved away from the inlet, reaching a maximum near the middle of the laboratory scale wetland they studied. Nu Hoai *et al.* (1998) also found that Pb uptake by sediment was

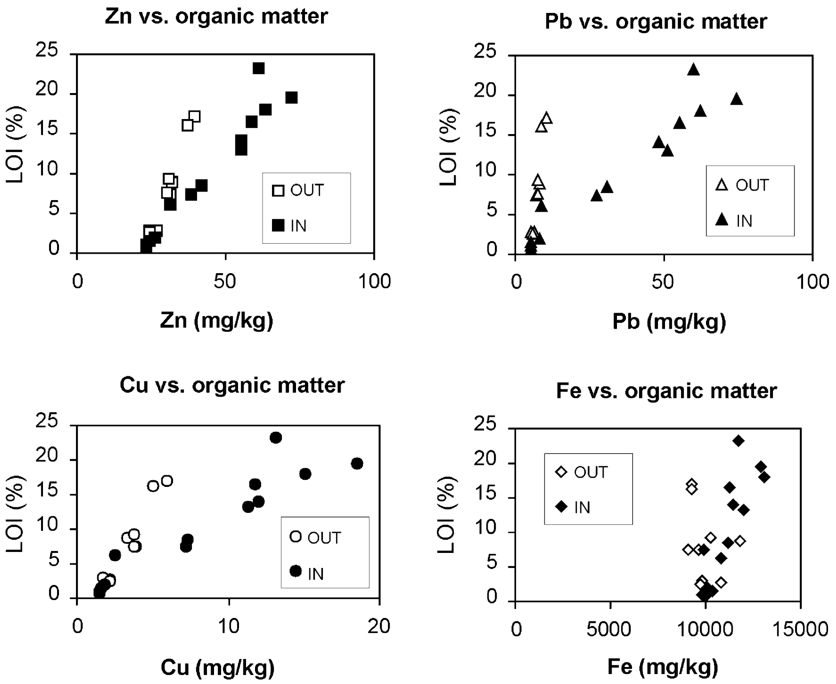

Figure 4. Metal concentrations in the Kaiapoi wetland sediments vs. organic matter content (LOI), suggesting strong affinity of Pb, Cu and Zn with the organic matter.

lowest near the inlet and the outlet. However, a number of other studies have reported a decrease in metal concentration with increasing distance from the inlet (e.g. Gillespie *et al.,* 2000; Chagué-Goff *et al.,* 1999; Chagué-Goff and Rosen, 2001). Walker and Hurl (2002) reported a similar trend and concluded that metal removal was mainly attributed to sedimentation, although biological assimilation and chemical transformation also contributed to metal retention. Further investigation would be required to assess whether metal uptake is gradual in the Kaiapoi wetland, but it was beyond the scope of this study.

Results of the sequential extraction procedure are shown in Figure 5 and are presented in percentage of the total concentration, which was determined by aqua regia digestion. The data suggest that the proportion of metals present in the exchangeable form (e.g. adsorbed and interstitial) and bound to carbonates is negligible. As seen in Figure 5, the residual fraction generally makes up a larger proportion of the total concentration in the lower part of both cores (sandy substrate) than in the top organic-rich section characterised by higher metal concentrations.

At the inflow, Zn occurs in association with organics/sulphides and oxides, as well as in the residual fraction, whereas at the outflow, more than 50% is present in the residual fraction, and the fraction bound to organics/sulphides is much smaller than at the inflow. Cu partitioning also differs at the inflow and the outflow. At the

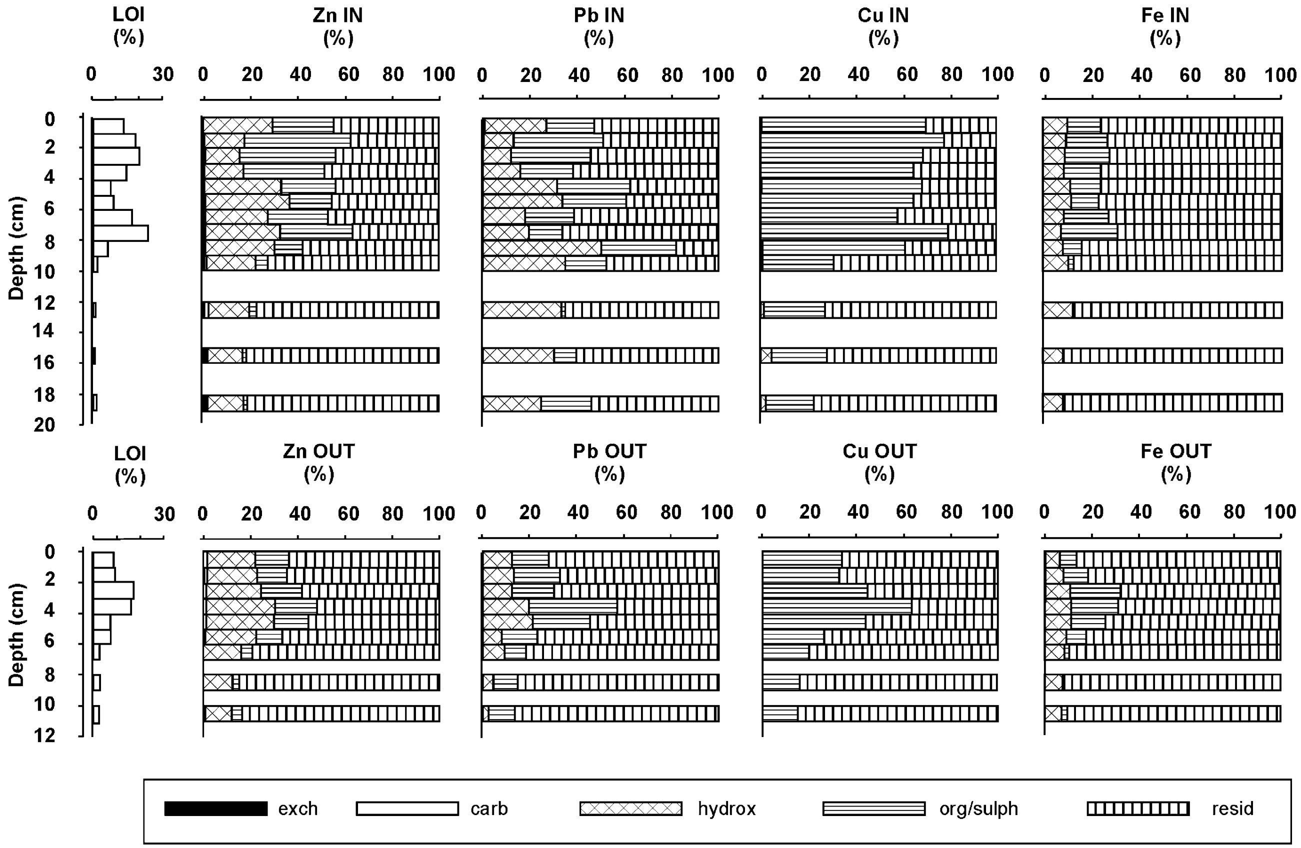

Figure 5. Metal speciation in the wetland sediments at the inflow (IN) and outflow (OUT) expressed as percentages of the total concentrations (exch = exchangeable, carb = bound to carbonates, hydrox = bound to Mn and Fe-hydroxides, org/sulph = bound to organics/sulphides, resid = bound to the residual/mineral fraction). The organic matter content (LOI) in each sample is also shown.

inflow, Cu is associated mainly with the organics/sulphides, with only a smaller proportion in the residual fraction, whereas the opposite is observed at the outflow. Almost none of the Cu is associated with hydroxides, except in the lower part of the core. Pb shows a strong association with the residual fraction (generally >40%), but also occurs with the organics/sulphides and hydroxides. The residual fraction is also larger near the outflow. Fe differs from the other metals analysed in that it is mainly associated with the residual fraction (>70%), with only a small part associated with organics/sulphides and hydroxides, and thus it is probably mostly present in mineral/detrital form.

Redox conditions in the sediments (*c.* 10 cm depth) are slightly reducing both at the inflow (126 ± 4 mV) and outflow (158 ± 5 mV). A lack of vertical variation in metal speciation also suggests that there was little change in redox conditions in the top part of the sediments at the time of sampling. In deeper wetland sediments overlaid by a thicker water column, changes in metal speciation have been reported, with the fraction associated with sulphides increasing with increasing depth and reducing conditions (Bostick *et al.*, 2001; Dollar *et al.*, 2001).

Bostick *et al.* (2001) also found that, under similar reducing conditions to those reported here and under similar water depth, sediments contained significant amounts of oxide-associated Zn and sulphide-associated Zn. In this study, Pb also exhibits a similar speciation. The oxide fraction represents metals scavenged by Fe and Mn oxides. The mobility of metals associated with this fraction is highly dependent on redox conditions, as oxides might be partially dissolved under the reducing conditions prevailing in the wetland, and the associated metals released into the overlying water. Under the reducing and anoxic conditions in wetlands, metal removal through precipitation with sulphides can represent a longer-term removal process, as this phase is most stable under reducing conditions. Microbial production of sulphide takes place in wetlands, as long as sulphate is present in the influent water and plants provide the organic substrate for growth of the sulphate-reducing bacteria. Metal ions can also be strongly bound as insoluble associations with organic matter, in particular with components of the humic fraction.

As shown by the results of sequential extraction in this study, Cu exhibits a high affinity for peat, humic substances and sulphides (e.g. Kadlec and Knight, 1996), which leads to high removal rates. The organics/sulphide fraction of Cu was also found to be the highest in other studies (e.g. Calmano *et al.*, 1993) in comparison to other metals. Pb is known for its relative insolubility when adsorbed and/or precipitated in sediments (Kabata-Pendias and Pendias, 1992). It has a strong affinity for organic ligands in sediments (Fergusson, 1990). However, under anoxic conditions, Pb is usually mostly bound to sulphides, if enough sulphate is available, and is therefore fairly immobile (Nriagu, 1978). Although Zn shows a strong association with organics and sulphides, a large proportion is also associated with hydroxides. Thus, Zn is more mobile (Kabata-Pendias and Pendias, 1992) and mobilisation and reprecipitation in wetland sediments between the inflow and the outflow is possible.

This study shows that at the inflow, metals are mostly associated with the organics/sulphides (except for Fe). This indicates that organics/sulphides represent the most important removal mechanism for Cu and Pb and to a lesser extent Zn, thus providing a long-term removal process, as long as anaerobic conditions are maintained. The relatively high percentage of metals present in the residual fraction, which are thus bound with minerals, in particular at the outflow, indicates that a large proportion of metals is unlikely to be released to the overlying water under natural conditions. The increase in percentage present in residual/mineral form at the outflow also reflects the diagenetic processes taking place in the wetland. As Fe is mostly associated with the residual fraction, this suggests that it should also be fairly well immobilised in the sediments of the Kaiapoi wetland.

Nevertheless, changes in redox conditions due to seasonal drying or flooding can result in metal mobilisation. Bostick *et al.* (2001) reported the conversion of oxides-associated Zn to sulphide-associated Zn with flooding in drier areas, whereas Calmano *et al.* (1993) observed a transformation towards more mobile fractions at the expense of the sulphidic fraction during oxidation-reduction cycles. During hot summers (e.g. summer 2001), the area around the outflow of the Kaiapoi wetland dries out, and therefore, the oxidation of sulphides might result in release of metals. At the time of sampling, the area was waterlogged. However, the proportion of Zn associated with sulphides shows a slight decrease relative to the proportion of Zn associated with the oxide fraction (Figure 5), possibly as a result of the seasonal drying of this area. This is thus likely to affect the efficiency of Zn removal in the wetland.

4.2. WATER

Only limited data are available and thus they only provide a snapshot of the water quality at the dates sampled (May 2001, August 2001 and February 2002). Nevertheless, used in combination with the sediment data, they can provide information about metal accumulation and apparent reduction rate.

Total suspended solids (TSS) were measured at the inflow and outflow of the wetland every 30 min for about 8 h both in the winter (August 2001) and summer (February 2002). The moderately high TSS at the outflow in summer are more likely to be attributed to windy conditions during sampling (strong southerly wind all day), which disturbed the sediment, while sampling in winter took place on a calm day. The wetland is shallow, with a water depth of 20–50 cm, and weather-dependent variations in TSS have previously been reported (C. Rowe, pers. comm., 2002; see also Table II). TSS concentrations at the inflow were lower in summer than winter (Table I; Figure 6), however measured concentrations are within the range of TSS measured over time by the Waimakariri District Council (see Table II). No removal rate can be calculated because of the limited dataset. Nevertheless, the data suggest that TSS removal is occurring in the constructed wetland.

There is little variation in pH between the inflow and outflow, with pH ranging between 7.3 and 8.4 (Table I). The increase in pH during the day on both sampling

TABLE I

Total suspended solids (TSS) concentrations, pH, water temperature, conductivity and redox potential in surface water at the inflow and outflow of Kaiapoi wetland in winter 2001 and summer 2002

	Winter 2001 (May)		Winter 2001 (August)		Summer 2002 (February)	
	Inflow ($n = 3$)	Outflow ($n = 3$)	Inflow ($n = 17$)	Outflow ($n = 17$)	Inflow ($n = 16$)	Outflow ($n = 16$)
TSS (mg/L)	96 ± 7	15 ± 3	66 ± 16	8 ± 2	47 ± 8	20 ± 3
pH	7.7	7.6	7.5–8.0	7.4–8.5	7.3–7.7	7.5–8.2
Temperature (°C)	9.6	6.5	11.1–12.6	10.2–14.4	18.4–19.5	16.8–18.2
Conductivity (μS/cm)	634	565	750–770	630–650	760 ± 20	671 ± 22
Redox (mV)	165	166	152–177	124–182	167–187	140–173

Note: Only four conductivity measurements available in August 2001.

TABLE II

Total suspended solids (TSS) data

	TSS (inflow) (mg/L)	TSS (outflow) (mg/L)	Comment
12/10/98		37	
07/98–09/99		<3–39	Below consent value of 50
11/06/99–29/10/99	29–87		Measured on a weekly basis
17/10/00		18	Heavy rain period
16/10/00		32	Heavy rain period
15/01/02	76		
12/06/03		24	
24/06/03		14	
25/06/03	62	14	

Source: Waimakariri District Council (R. Frizzell, pers. comm., 2003).

dates was also associated with a decrease in redox potential. Nevertheless, there was little difference in redox between the inflow and outflow, with slightly reducing conditions being measured at both sites (Eh ~ 120–180 mV). Electric conductivity on the other hand was higher at the inflow than at the outflow (Table I), and this decrease is likely to reflect the uptake of nutrients and metals in the wetland.

Results show that concentrations of Zn, Pb and Cu are lower at the outflow than inflow (Table III), both in winter and summer, suggesting uptake in the wetland. This is also inferred from the lower concentrations in sediments at the outflow than inflow (Figure 3). The level of removal in the summer might be underestimated, due to high TSS concentrations reported on the sampling day. Fe concentrations on the other hand were higher in the outflow than inflow in the winter and showed little variation in the summer (Figure 6). In May 2001, dissolved Fe was also higher at

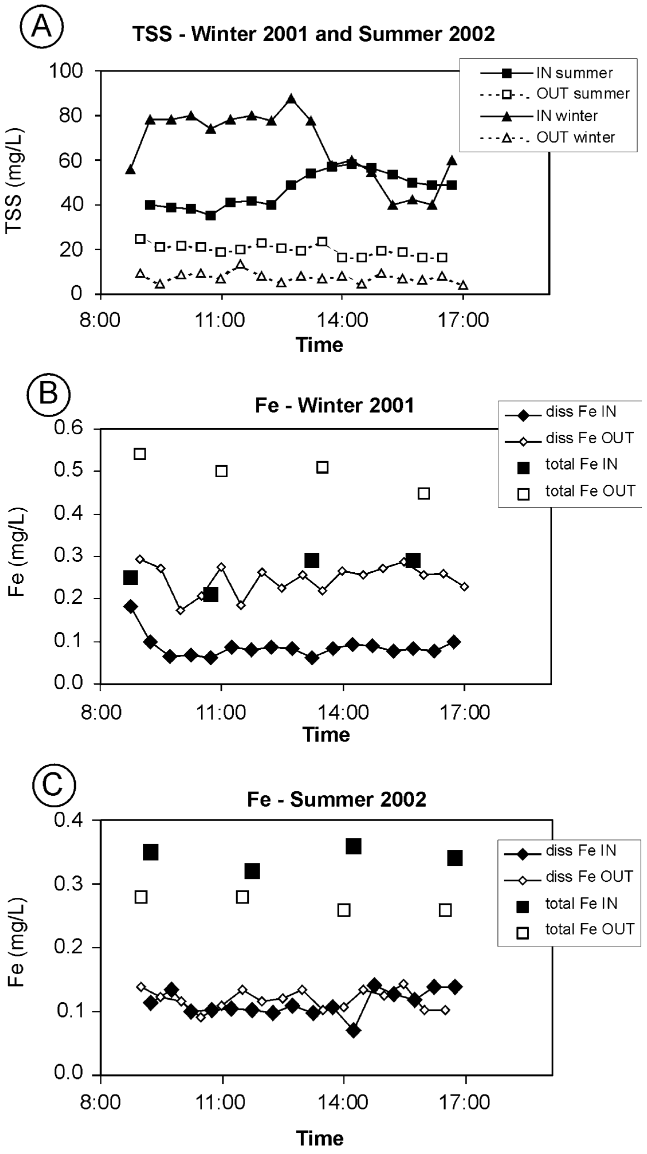

Figure 6. A: Total suspended solids (TSS) at the inflow (IN) and outflow (OUT) of Kaiapoi treatment wetland, in winter 2001 and summer 2002; B: Fe concentrations, total and dissolved (diss), at the inflow (IN) and outflow (OUT) in winter 2001. C: Fe concentrations, total and dissolved (diss), at the inflow (IN) and outflow (OUT) in summer 2002.

the outflow than inflow (inflow: 100 μl/L and outflow: 290 μl/L; no data available for total Fe, due to possible contamination). Although the dataset is limited, data appear to indicate that in winter (both in May and August) the wetland is a source of Fe, whereas in summer the wetland acts as a sink for Fe (although the removal

TABLE III

Metal concentrations at the inflow and outflow of Kaiapoi wetland in winter 2001 and summer 2002

	Inflow		Outflow	
	Total	Dissolved	Total	Dissolved
Winter 2001				
Fe (μg/L)	260 ± 40	90 ± 30	500 ± 40	250 ± 30
Cu (μg/L)	17 ± 12	<d.l.	3 ± 2	<d.l.
Pb (μg/L)	2.1 ± 0.1	<d.l.	1.9 ± 0.1	<d.l.
Zn (μg/L)	21 ± 4	n.a.	3.5 ± 1	n.a.
Summer 2002				
Fe (μg/L)	340 ± 20	110 ± 20	270 ± 10	120 ± 20
Cu (μg/L)	6 ± 0.7	<d.l.	1.3 ± 0.1	<d.l.
Pb (μg/L)	1.5 ± 0.2	<d.l.	1.1 ± 0.1	<d.l.
Zn (μg/L)	14.3 ± 3.3	n.a.	5.5 ± 4.4	n.a.

Note. Total metal concentrations were determined by ICP-MS ($n = 4$), whereas dissolved metal concentrations were determined by AAS ($n = 17$ in winter, and $n = 16$ in summer). <d.l. – below detection limit of the analytical technique, n.a. = not available due to possible contamination.

is negligible). Goulet and Pick (2001), who studied a young constructed wetland, reported that the wetland was a source of Fe in the winter. The results of their study suggested that anoxic conditions in the wetland promoted the release of Fe from the sediment, and thus the transformation of particulate to dissolved Fe. Fortin *et al.* (2000) found that it was related to low rates of photosynthesis and reduced Fe uptake by plants coupled with high microbial respiration. Fe retention was also attributed to the young age of the wetland and low inlet concentrations (average of 300 mg/L Fe), which are also features of the Kaiapoi treatment wetland. Similarly, Kadlec and Knight (1996) reported that wetland efficiency and removal rate for metals were correlated with inflow concentration and mass loading rate. Young wetlands are often dominated by phytoplankton (Mitsch *et al.*, 1998) and algal uptake has been suggested as a mechanism responsible for the release of particulate Fe (Goulet and Pick, 2001). As the wetland ages, emergent and submerged macrophytes take over by colonising the wetland surface area, and the processes of Fe removal change, as plants can provide a sink, directly or indirectly, for Fe (Goulet and Pick, 2001).

4.3. COMPARISON WITH ANZECC GUIDELINES

Near the outflow, Pb, Cu and Zn concentrations were all below the interim sediment quality guideline (ISQG) "low" values of 50 mg/kg, 65 mg/kg and 200 mg/kg, respectively (ANZECC & ARMCANZ, 2000). Near the inflow, Pb concentrations exceeded the ISQG "low" trigger value (however, remaining far below the ISQG "high" trigger value of 200 mg/kg). The ISQG trigger values represent a statistical probability of adverse effects (low: 10% and high: 50%) on biological species, and correspond to the effects range and guidelines developed by Long *et al.* (1995). The ANZECC guideline trigger values are based on total metal concentrations, and metal concentrations in this study were determined using aqua regia, and thus include fractions present in the detrital phase (as also shown by the results of SSE) that is not bioavailable. Thus, although some of the metal concentrations measured in this study are above the ISQG "low" trigger values, the bio-available fraction is most likely to be below the ISQG value. This therefore suggests that discharge of treated sewage in the Kaiapoi wetland is likely to have little adverse effect on the biota in the wetland, although further study would be required to assess Pb concentrations in other areas of the wetland. Metal concentrations in water measured in this study were not compared to the ANZECC water quality guidelines, as there were not enough data to allow for an assessment of the potential toxicity of metals released, both in the wetland and from the wetland into the receiving water. Water samples from the Kaiapoi wetland (inflow and outflow) have been analysed for metals at other times ($n = 3$), however concentrations were mostly below the detection limit of the analytical method used (R. Frizzell, pers. comm., 2003).

4.4. PLANTS

Metal concentrations in shoots and roots of two types of the most common plants occurring in the Kaiapoi wetland are shown in Table IV. Although the data are limited, they show that in both cases, metal concentrations are higher in the roots than the shoots. The roots of *Juncus* and *Lythrum* are fine roots that have a high surface area to volume ratio and this could explain the high metal concentrations. Higher metal concentrations in roots than in shoots has been reported elsewhere (e.g. Taylor and Crowder, 1983; Shutes *et al.*, 1993; Mays and Edwards, 2001) and often attributed to metals contained in root coatings. Iron plaques, which consist mainly of iron hydroxides, have been reported on roots of a number of aquatic

TABLE IV

Metal concentrations in shoots and root of *Juncus sp.* and *Lythrum hyssopifolia*

	Fe (μg/g)	Zn (μg/g)	Cu (μg/g)	Pb (μg/g)
Juncus sp. shoots	137 ± 5	14 ± 1	2.5 ± 0.5	<2
Juncus sp. roots	718 ± 100	23 ± 1	4	4.5 ± 0.5
Lythrum shoots	334	49	8	6
Lythrum roots	3985	86	10	15

plant species (e.g. Taylor *et al.*, 1984; Otte *et al.*, 1989; St.-Cyr and Crowder, 1990; Hansel *et al.*, 2001), and are likely to contribute to metal uptake on roots and possibly increase the metal tolerance of plants (Mungur *et al.*, 1997). Vesk *et al.* (1999) who investigated metal localisation in roots of water hyacinths, found that Fe levels were higher at the root surface and cell walls, whereas Cu, Zn and Pb concentrations were higher inside the cell walls.

The concentrations of all metals determined are also significantly higher in *Lythrum* than in *Juncus*. This finding is in agreement with previous studies that show that emergent species have lower metal concentrations than submerged or floating species (Sparling and Lowe, 1998; Mays and Edwards, 2001). *Lythrum* dies back in the winter and thus metals are likely to accumulate in the organic litter within the sediment.

The plant cover is sparse in the Kaiapoi wetland, due to a high die-back of plants attributed to a wet season following a drought shortly after the wetland was commissioned, which impeded the plant establishment, and thus no attempt was made to estimate the percentage of biomass nor the percentage of metal removal by plants. However, previous studies have reported that uptake by vegetation accounted for only a small percentage of metal removal (Mays and Edwards, 2001; Ye *et al.*, 2001).

5. Conclusions

Discharge of treated domestic sewage into the constructed wetland of the Kaiapoi sewage treatment plant has resulted in the accumulation of metals (Cu, Zn and Pb) in the top organic-rich layer of the sediments. Data show that, except for Fe, there is a marked decrease in metal concentrations between the inflow and outflow and metals are mainly associated with the organic/sulphide fraction. This is confirmed by the results of sequential extraction, which show that Pb and Cu, and Zn to a lesser extent, occur mainly in association with organics/sulphides, which represent a long-term removal process under anaerobic and reducing conditions in the wetland. A large proportion of these metals is also present in the residual/detrital fraction and is therefore unlikely to be released into the overlying water under natural conditions. The residual fraction makes up a larger proportion of the total metal content (usually >60%) near the outflow, probably as a result of diagenetic processes in the wetland. This suggests that less than 40–50% of the total metal concentration measured at the outflow might be remobilised if redox conditions (e.g. as a result of seasonal flooding/drying) change. The fraction of metals in the most mobile phases (exchangeable and carbonate-bound) is negligible, but a significant fraction is associated with the hydroxide phase, whose stability is strongly controlled by redox conditions. Zn speciation near the outflow suggests that Zn might be remobilised as a result of seasonal flooding and drying, as the proportion bound to organics/sulphides is reduced. Results of water and sediment analysis suggest that uptake is taking place in the wetland, and that the wetland acts as a sink for the anthropogenic metals studied (Pb, Cu and Zn), despite the low inflow concentrations. The wetland appears to act as a source of Fe in the winter, while minimal removal occurs in the summer. Minimal removal (summer) and release (winter) of Fe might also be attributed to the young age of the wetland and low loading rates. TSS removal appears to occur at all times. Metal uptake is higher in the roots than in the shoots of *Juncus* sp. and *Lythrum hyssopifolia*. *L. hyssopifolia*, a submerged floating species, is also characterised by higher metal concentrations than the emergent plants analysed. Based on sediment metal concentrations, this study suggests that the discharge of treated sewage into the wetland is unlikely to have any adverse effect, although Pb concentrations exceed the low trigger value sediment guidelines near the inflow. However, results of SSE analysis suggest that a significant fraction of Pb is bound to the mineral phase and is thus not bio-available. This study also shows that metal accumulation and speciation are strongly controlled by the amount of organic matter in the wetland, and that changes in redox conditions as a result of seasonal drying and flooding might affect the removal efficiency of the wetland for metals, particularly Zn.

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