2-2. Seasonal variations of chemical forms of heavy metals in the constructed wetland impacted by acid drainage

Seasonal variations of chemical forms of heavy metals in the constructed wetland impacted by acid drainage

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Abstract

Chemical transportation of heavy metals in the constructed wetland impacted by acid drainage was investigated seasonally using a combination of the monitoring water quality with the selective sequential extraction of the sediments in the wetland. It was found that the integration of the loading amounts at outlet was smaller than that at inlet, suggesting that there was the positive loading of heavy metals in the wetland. Based on the results of sequential extraction of the wetland sediments, Mn ions were dissolved from sediments at upstream area in the constructed wetland by the contact with acid drainage, and then precipitated again as ion-exchangeable forms in the sediments. However, it was estimated that total Mn contents in the sediments decreased with time. It was expected that a part of Mn bound to oxides were flown out of the wetland as suspended particulate matters. The similar trend was observed for transportations of Fe and Zn. On the contrary, the transportation of Cu clearly shows in a different behavior. The total Cu contents in the sediments were estimated to increase with time. It was considered that there was the decomposition of dissolved organic substances with high molecular weights by soil microorganisms in summer. The Cu ions were complexed with them,

and polymerized to precipitate as bound form with the organic matter in the sediments.

INTRODUCTION

The wetland is the integrated natural system consisting of underlying strata, hydric soils, detritus, water, and emergent vegetations. The standing water provides a habitat for aquatic organisms including fish, vertebrate animals, submerged- and floating-plant species, living algae and populations of microbes. The wastewater treatment is proceeded by remediation potential of each component and their interaction. Macrophytic plants provide much of the visible structure of wetland treatment system. There is no doubt that they are essential for the high levels of water quality improvement by means of evapotranspiration, transportation of oxygen to soils, providing a habitat for microbes in addition to the uptake, sorption of harmful substances, decomposition, and filtration. Wetland soils have a high trapping efficiency for a variety of chemical constituents, based on the abilities of cation-exchange, chelation of heavy metals, sorption and chemical decomposition of harmful substances. Soil microbial populations have significant influence on the chemistry of wetland. Important transformations of nitrogen, iron, sulfur, and carbon result from microbial processes. The microbial processes are typically affected by the concentrations of reactants as well as the redox potential and pH of the soils.

Constructed wetlands mimic the optimal treatment conditions found in natural wetlands but provide the flexibility of being constructable at almost any location and can be used for treatment of waste waters[1]. The use of constructed wetlands as biogeochemical systems for the treatment of acid mine drainage has developed rapidly over the last few decades in North America and Europe [2], [3], [4], [5], [6]. The wetland treatment has an advantage of low cost, low energy, and maintenance-free, as compared with chemical treatment by utilization of the ecological system. The treatment of various metal-mine drainage waters is a small but a growing application area for

constructed wetlands [7].

In the present work, we constructed the plant-sized wetland in the place where the acid Mn-rich drainage occurred under the construction of a dam, in order to investigate the water quality at outlet of the wetland, and the seasonal variations of the adsorption and accumulation of heavy metals to soil sediments. This is the first application of the constructed wetland to the treatment of acid drainage in Japan.

FIELD DESCRIPTION AND SAMPLES

Field description

Water chemistry of acid drainage occurred under the construction of a dam in the southern Hokkaido, Japan is as follows: Mn 121.05 mg/l, Fe 18.08 mg/l, Cu 6.77 mg/l, Zn 3.84 mg/l, Cd 0.066 mg/l, pH 3.17, as measured in May 2000. The high contents of Mn under low pH condition are characteristic of this water. The wetland was constructed in October 2000, which has 6 m in width, 16 m in length, and 1 m in average depth. An overview of the wetland is shown in Fig. 1. To prolong the residence time of drainage, several detours were installed in the wetland. The residence time was around one month. The flow rates of drainages were 0.04 l/min at inlet and 0.03 l/min at outlet on an average. The sand and lime stones were laid in the bottom and soil sediments were covered on them. *Phragmites australis,* which is representative to emergent vegetation, was implanted there. Acidic drainages have been introduced from 20th October 2000 to 31st August 2001, but temporarily stopped from the end of December 2000 to the beginning of April 2001, due to the frost damage in winter season.
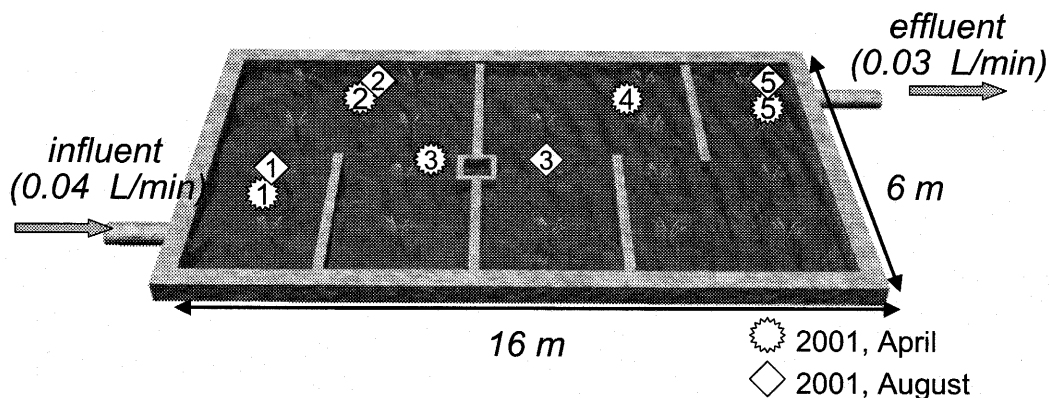

Fig. 1   Overview of the constructed wetland in the present work.

Samples

The flow rates, pH, temperature, electronconductivity of drainages water were automatically measured at inlet and outlet using a multi-water quality monitoring system U-22 (Horiba, Co. Ltd. Japan) at the field through the experimental term. Water samples were taken at inlet and outlet in the wetland every twice a week to analyze the concentrations of heavy metals and was carried to the laboratory with cooling. Sediment samples were taken from one site in the constructed wetland before the introduction of drainages, from 5 sites along the stream in April 2001 (before the 2nd introduction), from 4 sites in August 2001. Sampling sites were numbered from upstream to downstream as shown in Fig. 1.

ANALYTICAL METHODS

Water analysis

Water samples were acidified to pH 1 with HCl, and filtered to analyze dissolved Fe, Mn, Cu, Zn, and Cd concentrations by a Hitachi Z-6100 Atomic Adsorption Spectrometry.

Sequential extraction of sediments

Sediment samples were roughly de-hydrated at 40 ℃ for 72 h in a vacuum drier. The dried samples were ground to collect −100 mesh fractions by sieving and sent for XRF analysis and sequential extraction for heavy metals.

This method has been applied for river sediments in which labile and weakly bounded species of heavy metals are included[8]. One gram of dried sediment was extracted in 8 ml of 1 mol/l $MgCl_2$ (pH 7.0) for 5 h at room temperature. In this step, exchangeable species are extracted. Second, the residue was extracted in 8 ml of 1 mol/l $NaOCOCH_3$ (pH 5.0) for 5 h at room temperature to release the species bound to carbonate. Third, the residue was extracted in 20 ml of 0.04 mol/l $HONH_3Cl$ in 25 % (v/v) $HO COCH_3$ for 6 h at 96 ℃ to release the species bound to Fe-Mn oxides. Next, the residue, which was bound to organic matter, was extracted in 30 ml of 0.02 mol/l HNO_3 and 5 ml of 30 % H_2O_2 (pH 2.0 with HNO_3) for 2 h at 85 ℃, in 3 ml of in 30 % H_2O_2 for 3 h at 85 ℃, after cooling in 5 ml of 3.2 mol/l $NH_4O COCH_3$ in 20 % (v/v) HNO_3 for 30 min at room temperature.

The final residues were decomposed by a microwave decomposer Mile Stone ETHOS PLUS. The 0.5 g of residual sample was taken from the residue and thrown into a teflon vessel, where 7 ml of conc. HNO_3, 2.5 ml of 49.5 % HF, and 0.5 ml of 30 % H_2O_2 were added. The cap of teflon vessel was tightly set in a decomposer. Samples were decomposed by keeping at 210 ℃ for 20 min after heating with 8 ℃/min of the rising rate of temperature. The sample was completely decomposed by this procedure and diluted for ICP-AES analysis.

In the process of sequential extraction, the obtained leachate in each extraction was filtrated by membrane filter with 0.2 μm-pore size to determine Fe, Zn, Cu, and Mn concentrations by an ICP-AES SPS 7800 (SEIKO, Co. Ltd.).

RESULTS

Changes in water chemistry before and after wetland treatment

Figures 2 (a) ~ 2 (f) show the changes in dissolved Mn, Fe, Cu, Zn, and Cd concentrations at the inlet and outlet in the constructed wetland. There are blank periods from December 2000 to April 2001 due to water freezing in winter season. Except for Fe concentrations, it is difficult to recognize the pronounced difference at the inlet and outlet between in any metal ion concentration. Hence, these data were converted to transported amounts per day (gram/day) using flow rates, as shown in Fig. 3. Transported amounts per day (gram/day) are defined by the loading amounts multiplied the concentrations by flow rates per day. It was found that in any metal ion the transported amount was smaller at outlet than at inlet, suggesting that in particular these heavy metal ions seem to be accumulated in the wetland in early term from October to December 2000.

Seasonal variations in chemical forms of heavy metals fixed to sediments in the processes of wetland treatment

Selective extractions of three sediments were carried out, which were sampled in October 2000 (before the draining of acid water), April 2001 (at re-draining), and August 2001 (just before the stop draining), respectively. Figures 4 ~ 7 present the results of selective extraction for Mn, Fe, Cu, and Zn in sediments, in which the vertical

axis indicates the amount of each fraction expressed by mg/one kg-dry sediment, the horizontal axis is correspondent to the number of sampling site in Fig. 1, and the "initial" means the values in October 2000. There are five and four sampling sites in April 2001, and August 2001, respectively, which are numbered in order from upstream. It was assumed that the components of the sediment were uniform, independent of site in the wetland, during October 2000 before the draining of acid water.

Initially, Mn was mainly the oxide-bound type ('initial' in Fig. 4 (a)). In April 2001, they were partly dissolved by the impact of acid drainage in the sites 1 and 2 (upstream) and changed to ion-exchangeable type. In August, 2001, the replacement from oxide-bound type to ion-exchangeable type was enhanced all over the wetland, resulting in the content of ion-exchangeable type attained to be mostly equal to that of oxide-bound type (Fig. 4 (b)). Total content of Mn in sediment seems to have decreased from April to August 2001.

The Fe accounts the highest in heavy metal content in sediment (~23 g/kg). As shown in 'initial' of Fig. 5 (a), the fraction of 'residue' was the highest, followed by the fraction of oxide-bound. It indicates that the strongly bounded types are mainly for Fe. The compositional change of Fe in the sediment was not clearly observed even after leading acid water to the wetland (Figs. 5 (a), (b)). Total content of Fe in the sediment has decreased by 1 - 4 g/kg in August 2001.

There were not observable for Cu content in the initial sediment of the wetland ('initial' of Fig. 6 (a)). Even after 2 month-leading acid water, i.e., in April 2001, the trend was not changed (Fig. 6 (a)). However, a dramatic increase in Cu content was observed at the site 2 of Fig. 1 in August 2001 (Fig. 6 (b)). In particular, the content of the fraction bound to organic matters attained to 150 mg/kg of dry sediment.

The initial Zn content was determined to be 25 mg/kg of dry sediment mainly as the fraction bound to oxides, and few in the other fractions ('initial' of Fig. 7 (a)). In April 2001, the fraction 'the residue' has increased to reach equal or much more level to the fraction of oxide-bound type (Fig. 7 (a)). In August 2001, the fractions of weakly bound types of Zn were almost not observed, therefore, the re-dissolution of fixed Zn species was not expected. Total content of Zn in the sediment has decreased from April to August 2001.
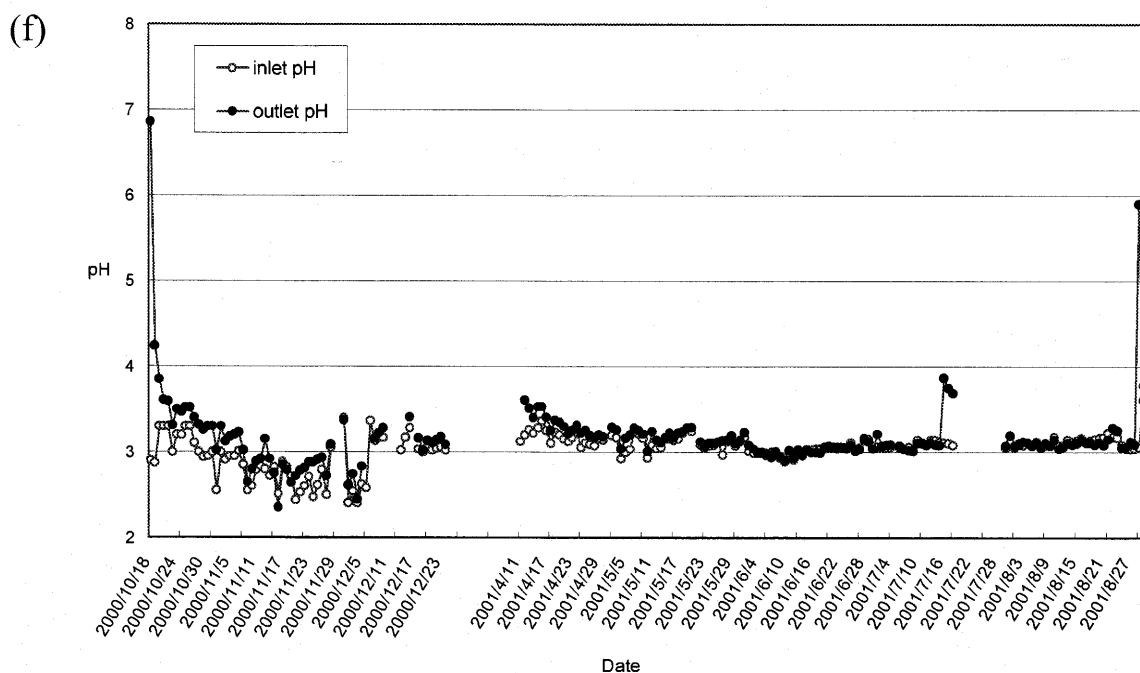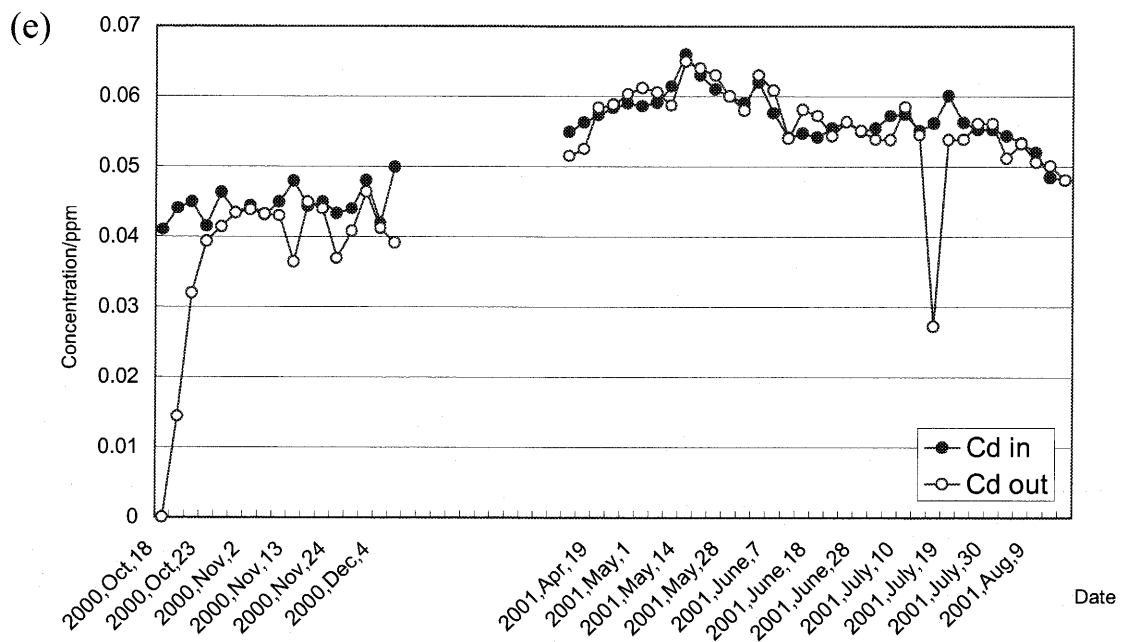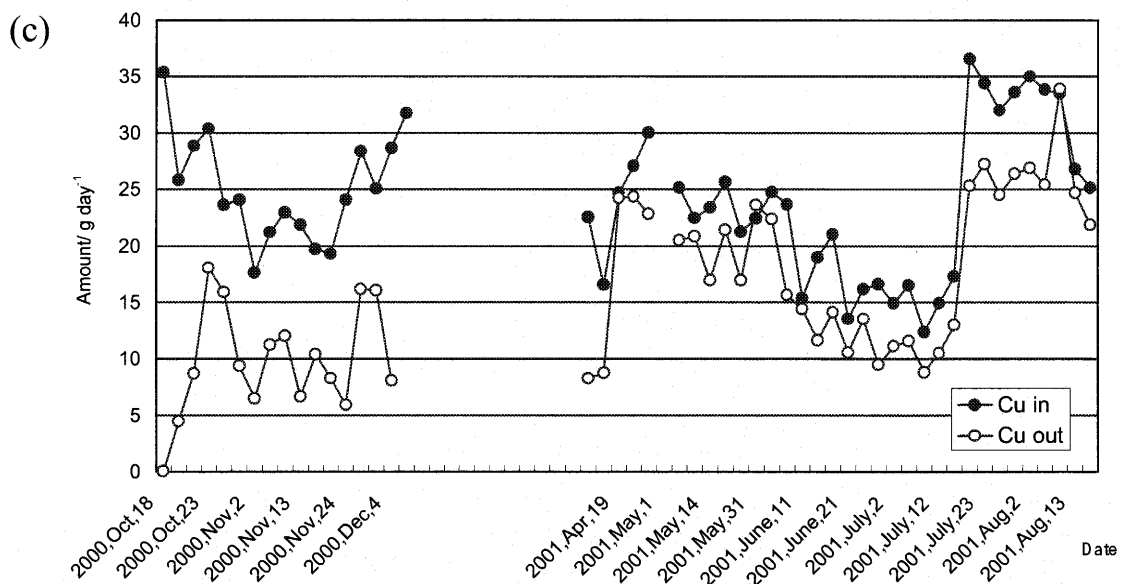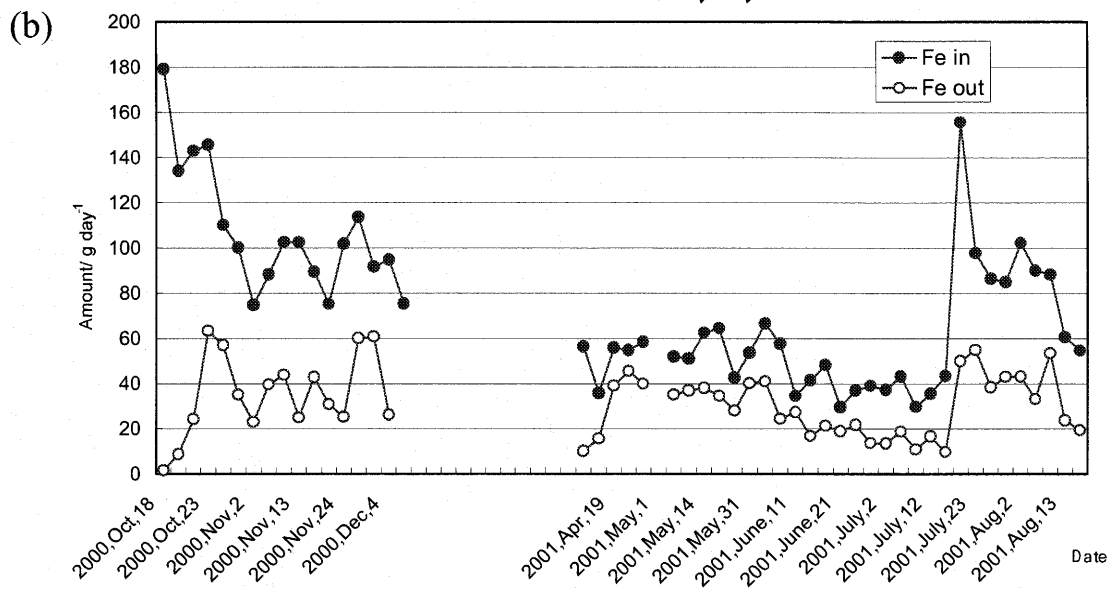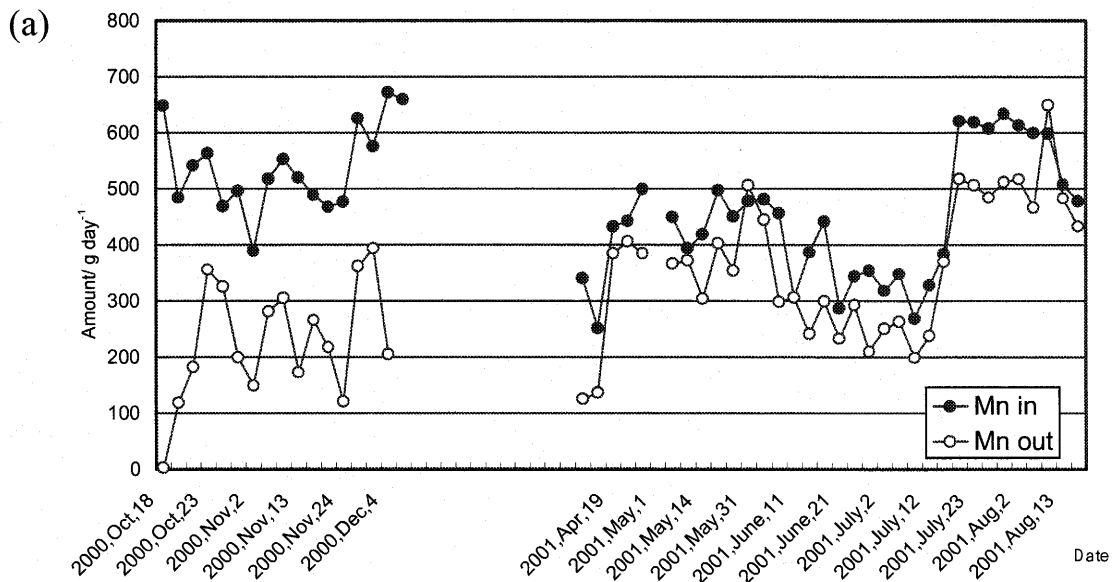
(a)

(b)

(c)

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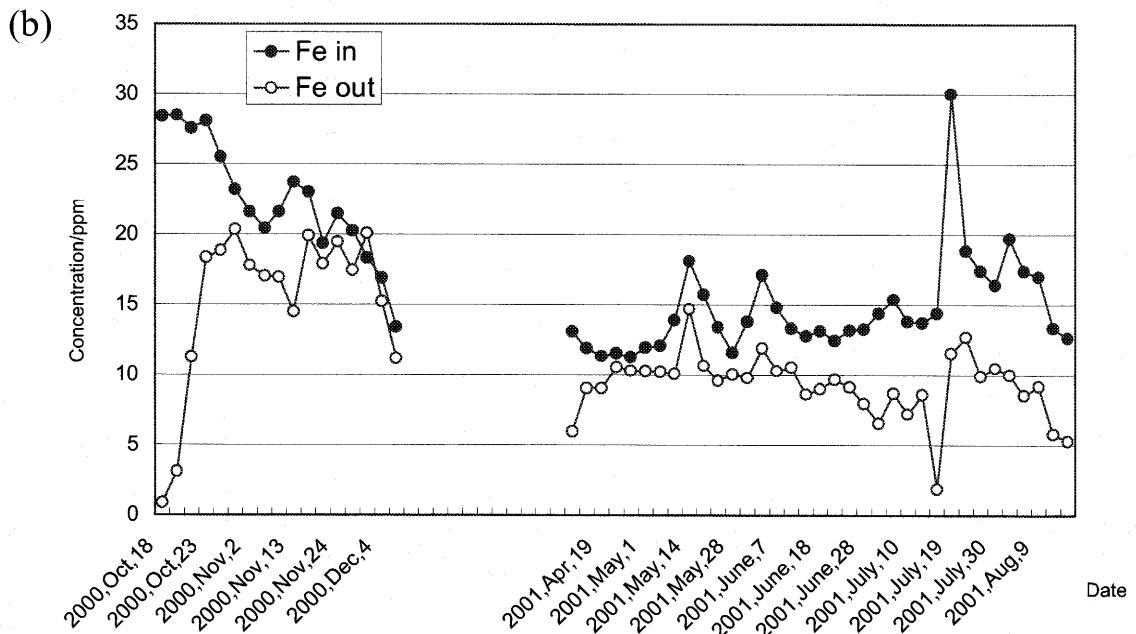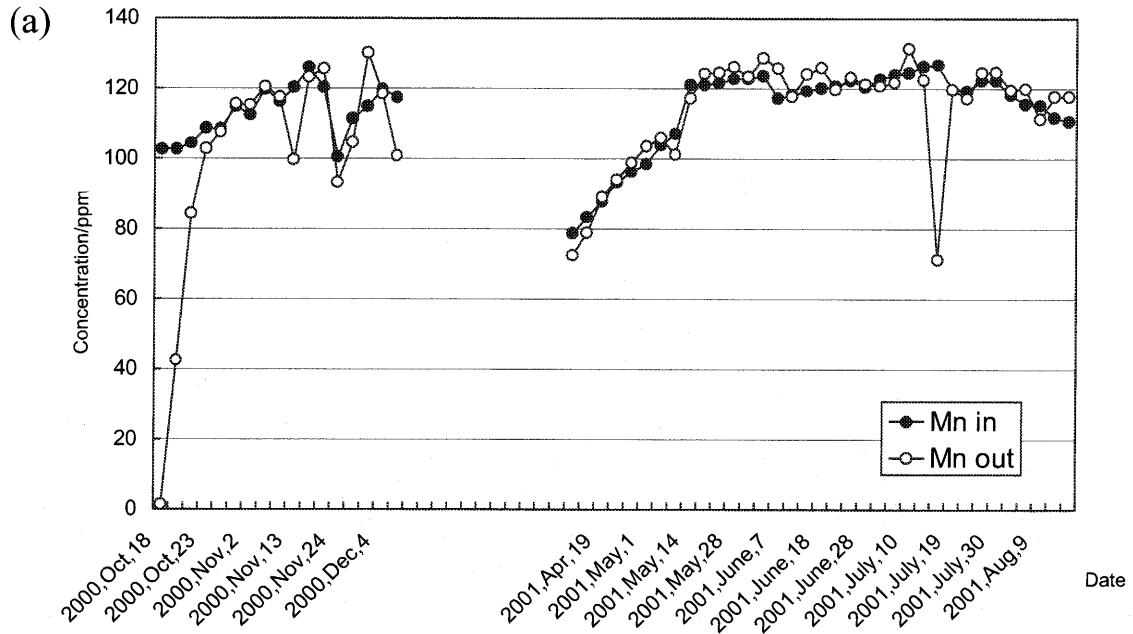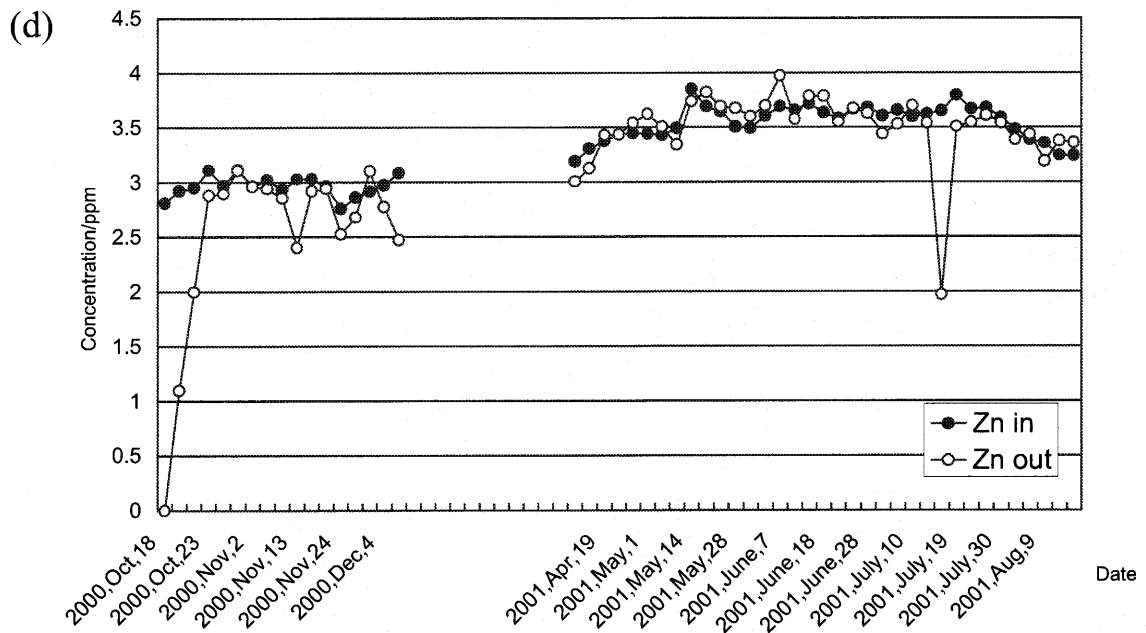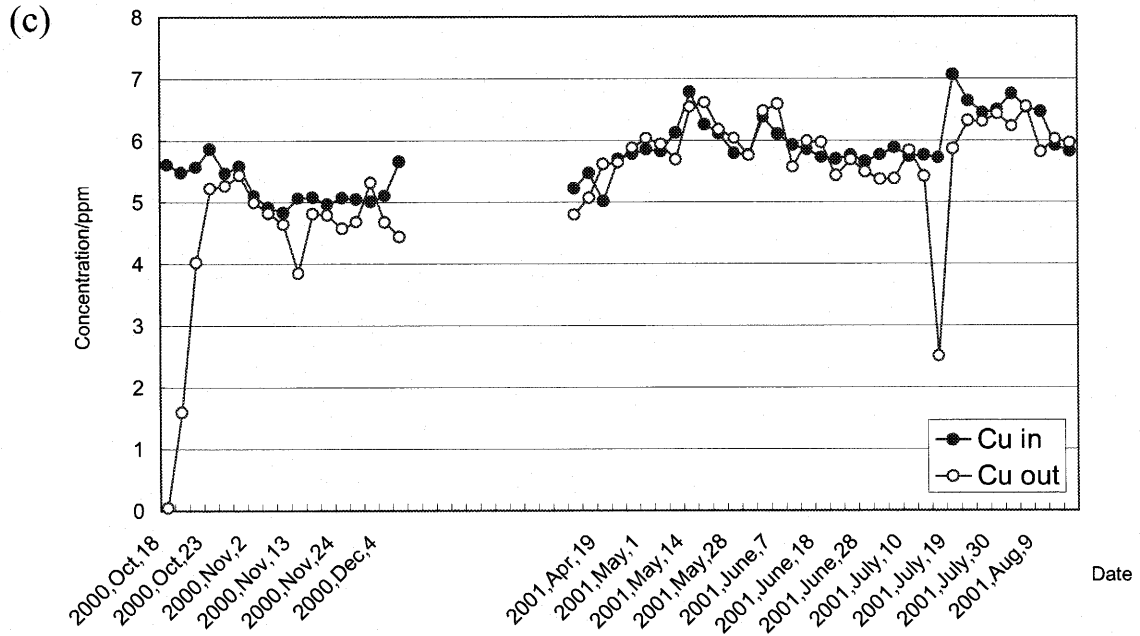
Fig. 2 Variation of the concentrations (mg/l) of (a) Mn, (b) Fe, (c) Cu, (d) Zn, (e) Cd and (f) pH at inlet and outlet of the wetland.
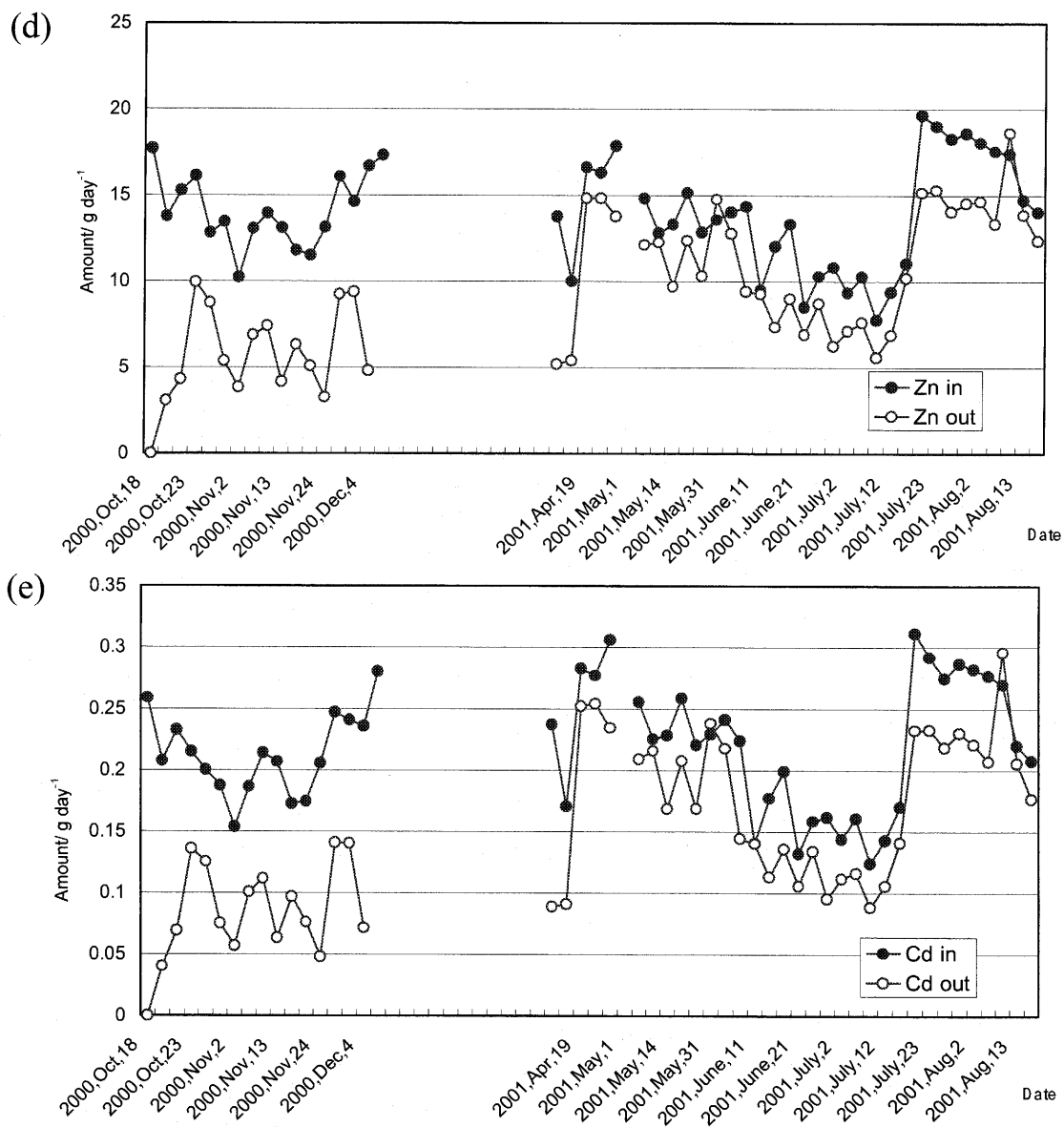
(a)

(b)

(c)

Fig. 3 Variation of the transported amounts (g/day) of (a) Mn, (b) Fe, (c) Cu, (d) Zn and (e) Cd at inlet and outlet.
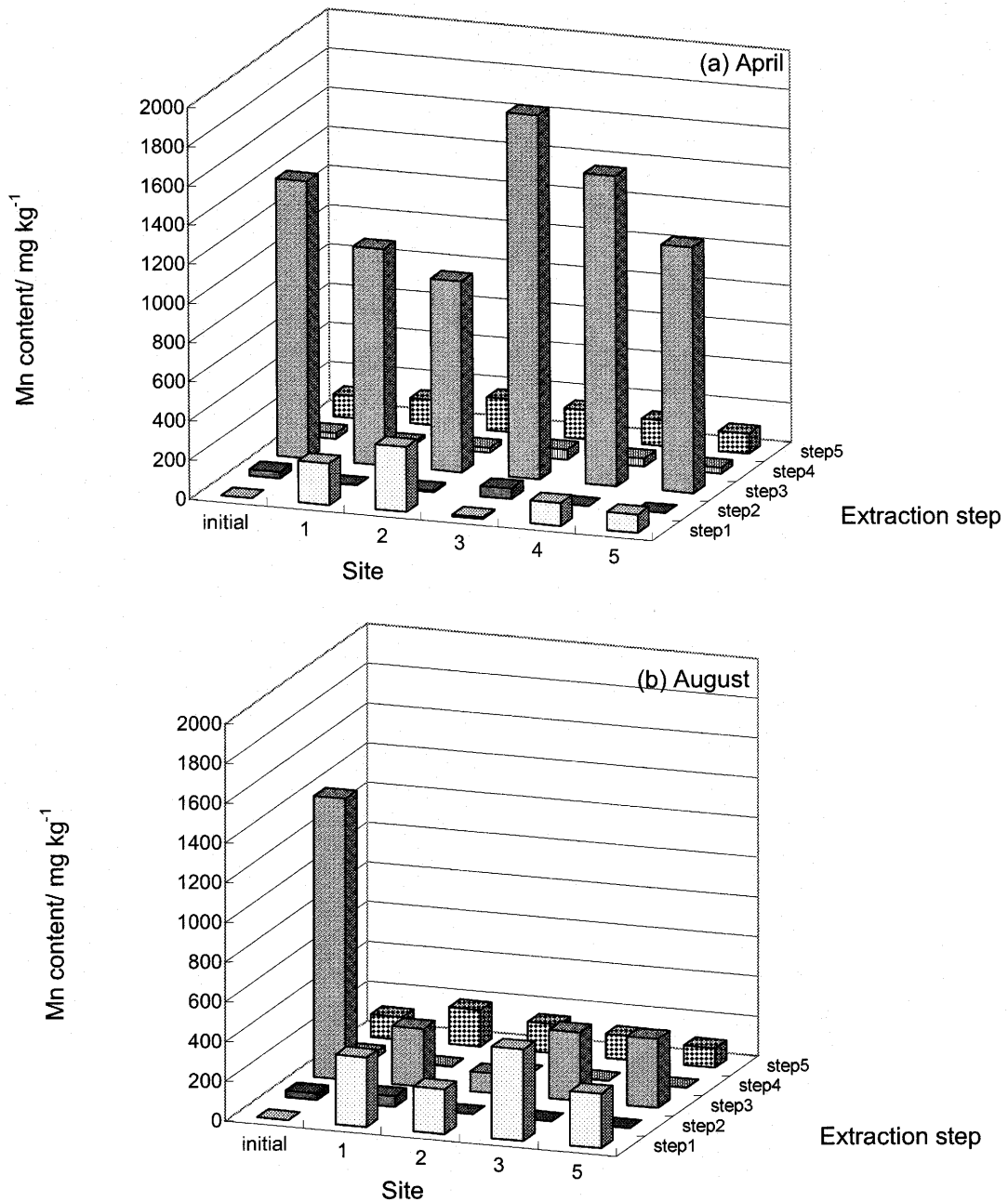
Fig. 4 Contents of sequentially extracted Mn from sediments taken from the constructed wetland in (a) April 2001, (b) August 2001. 'Initial' means October 2000. Step1, ion-exchangeable; step 2, carbonate-bound; step 3, oxide-bound; step 4, organic matter-bound; step 5, the residue.
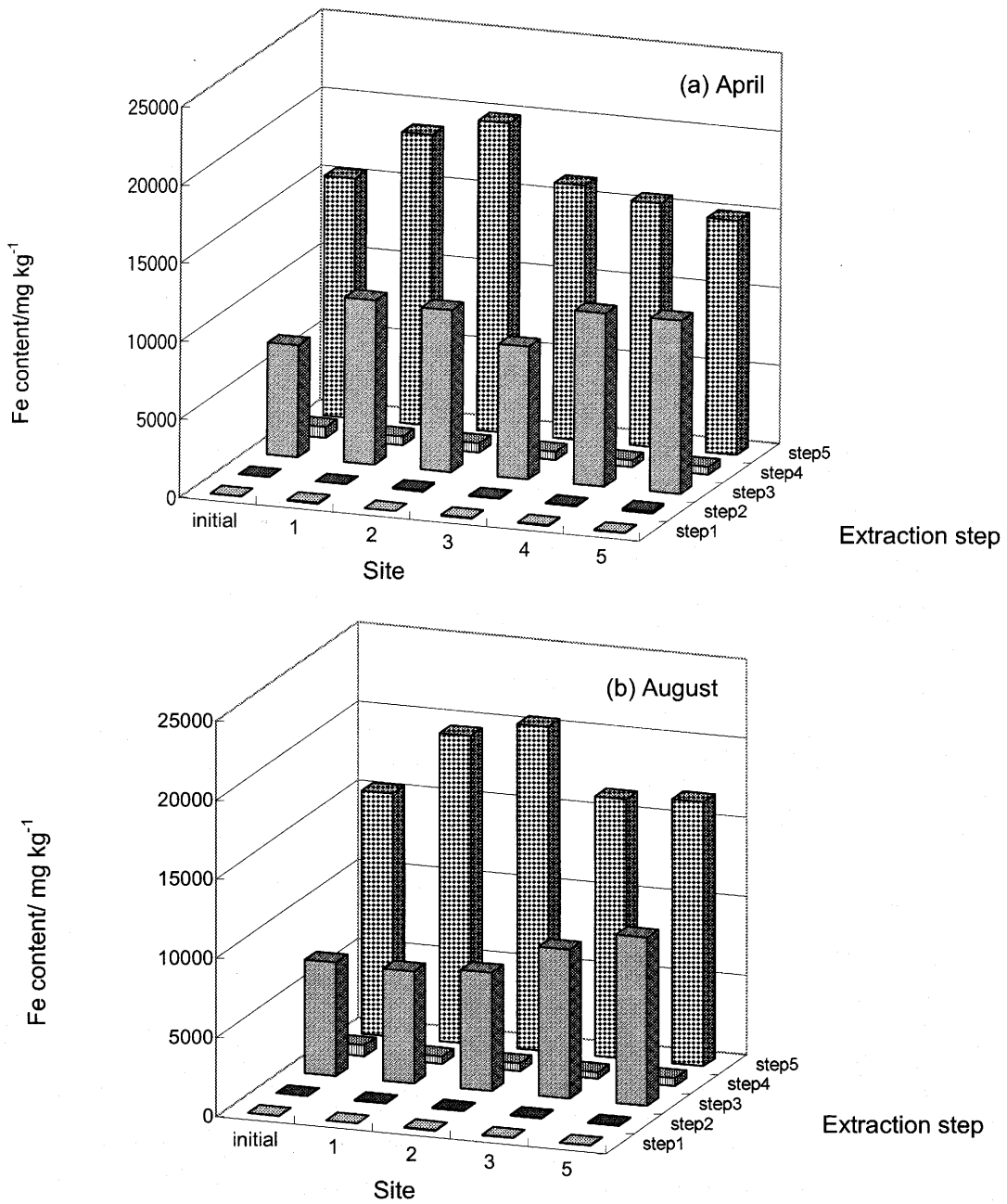
Fig. 5 Contents of sequentially extracted Fe from sediments taken from the constructed wetland in (a) April 2001, (b) August 2001. 'Initial' means October 2000. Symbols are the same as in Fig. 4.

Fig. 6 Contents of sequentially extracted Cu from sediments taken from the constructed wetland in (a) April 2001, (b) August 2001. 'Initial' means October 2000. Symbols are the same as in Fig. 4.

Fig. 7 Contents of sequentially extracted Zn from sediments taken from the constructed wetland in (a) April 2001, (b) August 2001. 'Initial' means October 2000. Symbols are the same as in Fig. 4.
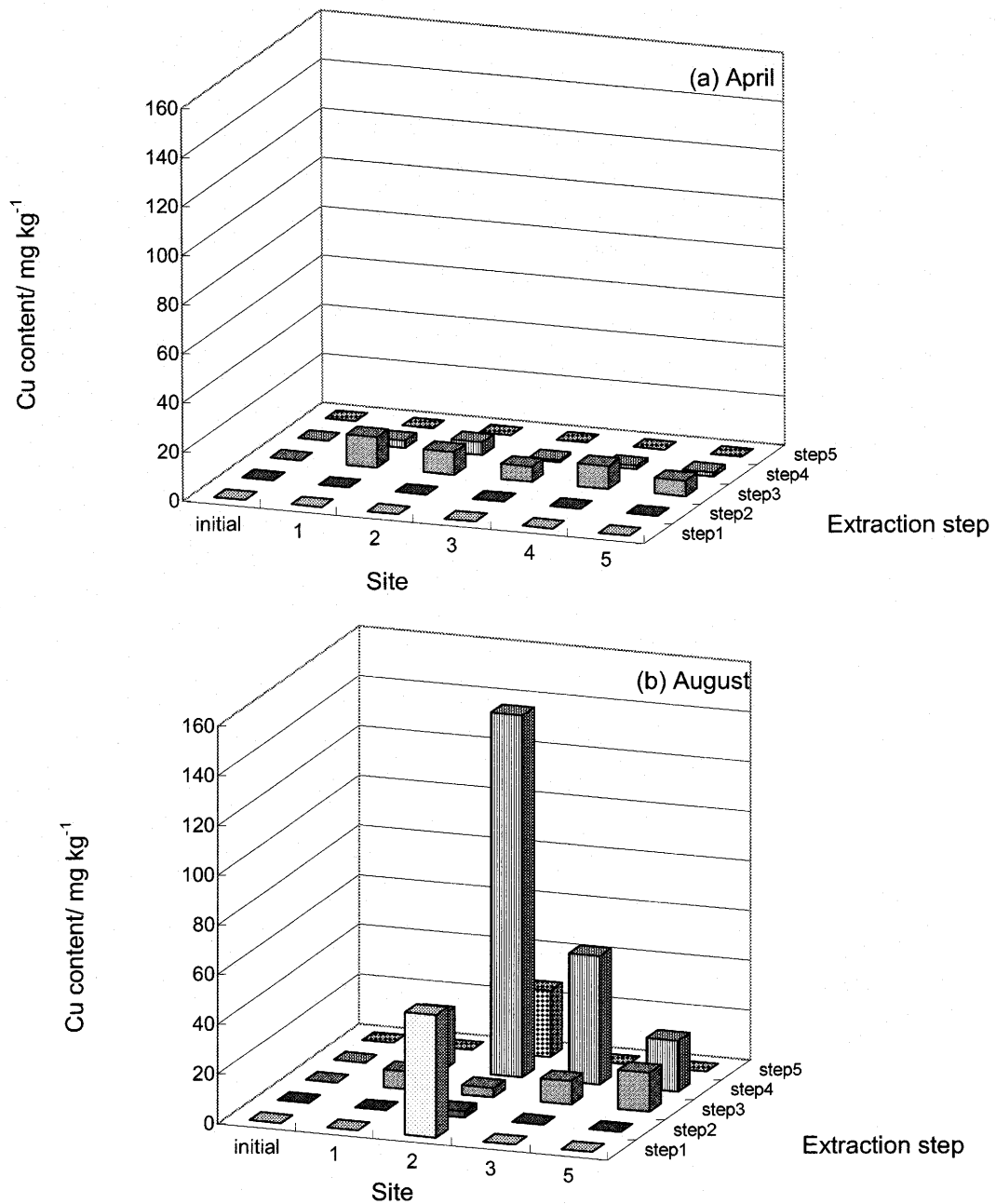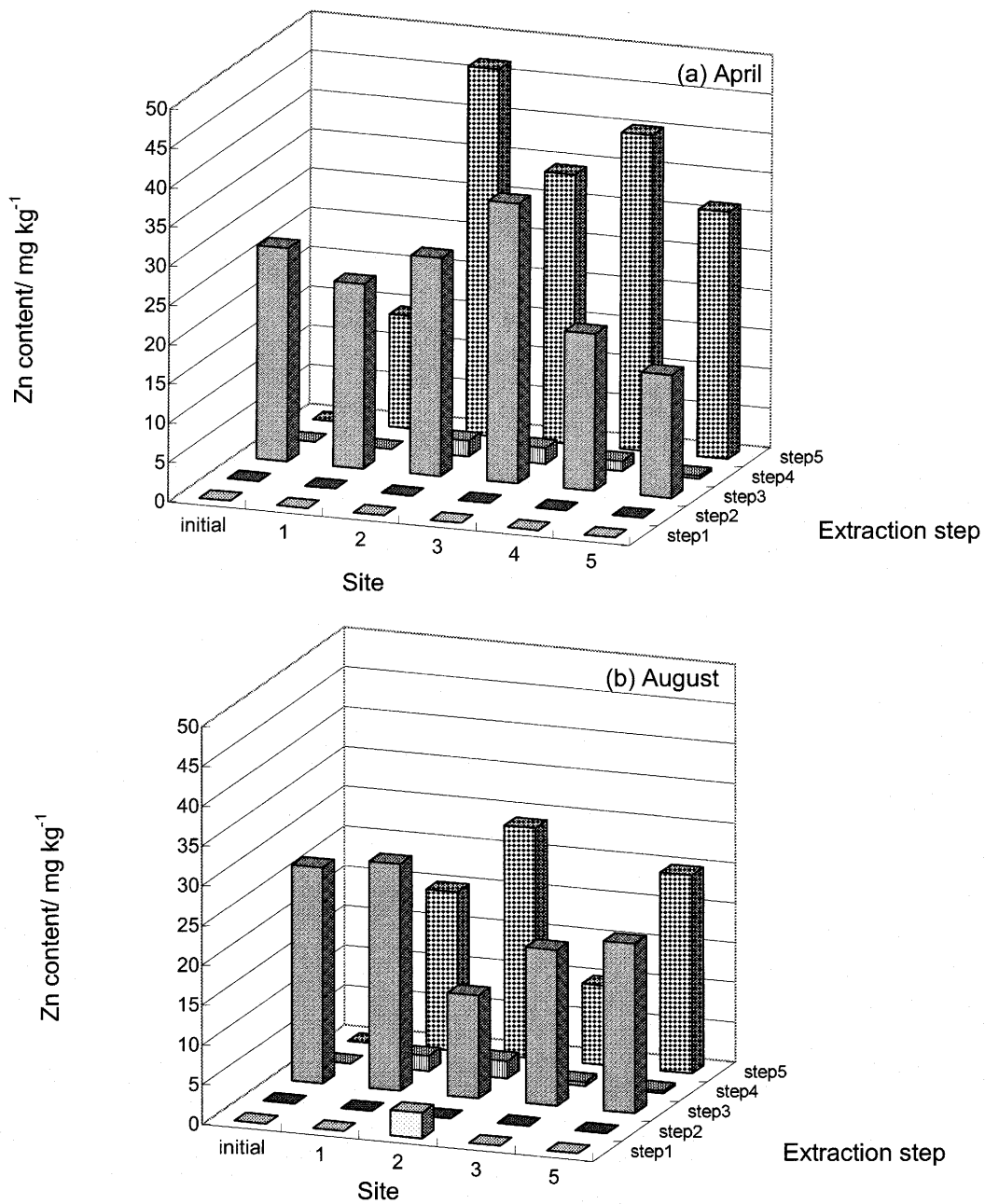
DISCUSSION

Neither increase in pH nor decrease in the dissolved Mn concentrations was observed during the period from October 2000 to August 2001, therefore, the preliminary purpose was not achieved. However, there are various changes in chemical transformations of sediments in the wetland. These are reflected to the biogeochemical changes of heavy metals related to seasonal variation of ecological system in the wetland.

Initially, the Mn content was about 1.4 g/kg-dry sediment which mainly consists of oxide-bound type. By contact with acid drainage, a part of sediment in upstream was dissolved and then bound to sedimentary particles as an ion-exchangeable type. The dissolved Mn concentrations did not dramatically change during the experimental period. Converting the concentration into the amounts of Mn by using the flow rate, it was found that there was the positive load in the wetland. In August 2001, the total Mn content was calculated to be 800 ~ 900 mg/kg-dry sediment. That is, 500 ~ 600 mg/kg of Mn was lost in the wetland from April to August 2001. However, the dissolved Mn concentrations did not increase, therefore, the re-dissolution of Mn is highly improbable.

The Fe also mainly occurs as stable forms in the sediment, as shown in Fig. 5. Around 1 ~ 4 g/kg-dry sediment of Fe was lost in the wetland from April to August 2001, though there were differences depending on the site of the wetland. It is considered that the oxide-bound Fe and Mn flowed out of the wetland as suspended particulate matters.

The behavior of Cu ion was quite different from those of Mn and Fe ions. The Cu content was scarcely observed in the initial sediment. In summer, heterotrophic microorganisms grow actively with increase in temperature and decompose the high molecular organic substances to low molecules such as humic substances, which easily form complexes with Cu (II) ions. It is considered that the complexes of Cu (II)-organic substances were polymerized to fix in the sediments. It is well known that the stability constant for the complex of Cu (II) ions and humic substances is large [9]. Because the element has already become the most stable in April 2001 (Fig. 7 (a)), it is assumed to be difficult for the plant to uptake.

CONCLUSIONS

In the experimental period, Mn ion was dissolved by contact of sediments with acid drainage, and fixed in the sediments as unstably bounded forms, that is, an ion-exchangeable type. The replacement occurred in order from the upstream of the wetland. Based on decrease in dissolved heavy metal ions and changes in total Mn and Fe-contents in the sediments, the eliminating route was estimated. The dissolved Mn and Fe ions get precipitated as the suspended particulate matters consisting of oxide-bounded Fe and Mn to remove away out of the wetland system by the flow of drainage.

ACKNOWLEDGMENTS

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