

Field Study on Heavy Metal Accumulation in a Natural Wetland Receiving Acid Mine Drainage

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The mechanism of surface water remediation in a natural wetland that is receiving heavy metal-rich acidic mine drainage was investigated. Selective sequential extraction was useful to derive the mechanisms of heavy metal removal in the wetland. In the upstream portion of the wetland, dissolved Fe was removed mainly as oxide-bounded mineral phases, such as hydroxides. These are important for the subsequent removal of other heavy metals. Other ion-exchangeable and carbonate-bounded heavy metals are also observed in the upstream, associated with Fe oxides. Organic matter and Fe–Mn oxides in the upstream remove Cu and Zn ions from the drainage, respectively. In the middle of portion of the wetland the removal of heavy metal ions in relatively low concentrations occurs by the emergent vegetation. Greater clay abundance and higher microbial activity of sulfate reducing bacteria in the downstream parts achieved low-level removal of metals. Multi-cell wetlands are recommended for the treatment of acidic metal bearing surface water drainage, if sufficient land area and expenses are available to construct.

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1. Introduction

Acid mine drainage (AMD) is a worldwide environmental problem. AMD arises when mining activities expose sulfide minerals in mine workings or in the form of tailings or rock dumps, to the near surface environment. In the presence of oxygen and water the sulfide minerals are oxidized, leading to the acidification and release of heavy metals and toxic elements, such as Ni, Co, Zn, and As, which are commonly associated with sulfide minerals.¹⁾

For several years, natural and constructed wetlands have been recognized as low-cost, low-maintenance systems that can lessen the impact of acidic metal rich drainage in areas downstream of mine sites.²⁾ Generally, the efficiency of a wetland for water remediation is based upon influent-effluent comparisons, where the ecosystem is treated as a 'black box'. This approach provides limited information about the geochemical processes occurring in the wetland. Accordingly, the information necessary to predict long-term efficiency and to improve planning and management in constructed wetlands is lacking.^{3,4)}

A natural wetland in southern part of Hokkaido, Japan, receives acidic heavy metal bearing water from the portal of abandoned mine workings. The drainage from the portal flows in two streams, one flowing through the wetland and one not (Fig. 1). Improved water quality was observed only in the wetland stream, therefore, the two streams make an excellent contrast. The aim of the present work is to understand the mechanism of heavy metal accumulation in a natural wetland receiving acid drainage and to extend the findings to the design of artificial wetlands. The knowledge may promote improved efficiency and effectiveness of artificial wetlands.

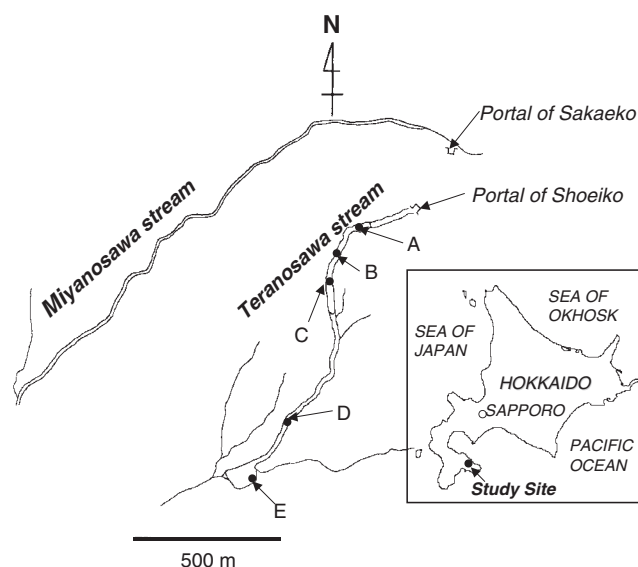


Fig. 1 Route map and sampling locations.

2. Experimental

2.1 Site location and sample collection

The wetland studied is 10–20 m wide and ~1000 m long with gentle slopes and is situated in the Teranosawa Marsh. The drainage basin of the Teranosawa Marsh includes discharge from sulfide mineral mine that closed 40 years ago. Sampling was done on 13th December, 1999. In winter, the water level in the marsh is low, and sides are exposed. In the spring, the snow melt raises the water table, and most areas are revert to traditional, wetland and aquatic zones 0.5–1.0 m in depth. Field sampling was done during the winter because access is difficult in other seasons. The two streams draining from the Sakaeko and Shoeiko mine portals (Fig. 1), have similar water composition when they discharge. The stream flowing from Shoeiko portal flows through a natural

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wetland in the Teranosawa marsh. The Miyanosawa mountain stream, which was from the Sakaeko portal, has no marsh.

The pH, oxidation-reduction potential (ORP), electroconductivity, and temperature are measured using by TOA HM-20P, RM-20P, and WM-22EP electrodes. The stream water concentrations of heavy metals, such as Fe, Mn, Cu, Pb, Zn, and Cd, were determined by atomic adsorption spectrometry (Hitachi Z-6000 AAS), the silicate concentrations by the molybdenum-yellow colorimetry, and major cations and anions by ionic chromatography (Yokogawa Analytical System IC 7000).

Sediment samples were also collected from the Teranosawa stream points A–E. These samples were packed in N₂-purged glass bottles and were stored cool. These samples would later be used for microbial activity-testing for sulfate-reducing bacteria (SRB) present by a Bio-checker Kit (Sanai Sekiyu Co. Ltd).⁵⁾

2.2 Sediment characterization

Prior to analysis the stream sediments were dried overnight at 50°C. Major elements in the sediments were analyzed using an energy-dispersive Horiba MESA-500 X-ray fluorescence spectrometer (XRF) under the following radiation conditions: Cu K α , 30 kV, 200 mA. In this method, elements with atomic numbers larger than Na can be determined, thus excluding compounds associated with organic substances. The mineral phases present in the stream sediments were determined by powder X-ray diffraction (XRD) using a JEOL JDX-3500 X-ray diffractometer with a monochromator under the following conditions: radiation, Cu K α , 30 kV, 200 mA; step scanning method; time constant, 0.5 second; angle range, 2.5–65 deg/2 θ . Minerals were identified based on the Joint Committee on Powder Diffraction Standards Data (JCPDS).

2.3 Sequential extraction

To identify the chemical forms of heavy metals in each sediment, acid sequential extraction was carried out in accordance with the modified Huerta-Diaz's method.⁶⁾ The samples are partitioned into three fractions by a three-step extraction using HCl, HF, and HNO₃ designed for mine tailings. Generally, HCl-soluble components belong to reactive group, HF-soluble components to silicate group minerals, and HNO₃-soluble components to sulfides and their related minerals, respectively. Detailed modifications of the procedure have been previously reported.⁵⁾

The HCl-soluble components include a wide range of chemical species in the sediments. To improve the definition of the reactive groups present, a selective sequential extraction method was also employed. This method was designed for river sediments, and identifies labile and weakly bound heavy metals.⁷⁾ One gram of dried sediment was subjected to 8 cm³ of 1 mol dm⁻³ MgCl₂ (pH 7.0) for 5 h at room temperature. In this step, exchangeable species are extracted. Second, the residue was extracted in 8 cm³ of 1 mol dm⁻³ NaOAc (pH 5.0) for 5 h at room temperature to release carbonate-bound species. Third, the residue was extracted in 20 cm³ of 0.04 mol dm⁻³ NH₂OH·HCl in 25%(v/v) HOAc for 6 h at 96°C to release the species bound to Fe–Mn oxides. Next, to release organic matter-bound

species the residue was extracted in 30 cm³ of 0.02 mol dm⁻³ HNO₃ and 5 cm³ of 30% H₂O₂ (pH 2.0 with HNO₃) for 2 h at 85°C, in 3 cm³ of 30% H₂O₂ for 3 h at 85°C, after cooling in 5 cm³ of 3.2 mol dm⁻³ NH₄OAc in 20%(v/v) HNO₃ for 30 min at room temperature.

The final residue was decomposed in a Mile Stone ETHOS PLUS microwave digester. 0.5 g of the residual sample was placed inside of a teflon vessel, with 7 cm³ of concentrated HNO₃, 2.5 cm³ of 49.5% HF, and 0.5 cm³ of 30% H₂O₂. After tightly capping the digestion vessel, the samples were decomposed by raising the temperature by 8°C/min and then heating continuously at 210°C for 20 min. The sample was completely decomposed by this procedure. The extracted liquid was diluted for the determination of heavy metals and the other elements by ICP-AES.

2.4 Vegetation analysis

The emergent vegetation was collected from several points in the wetland for analysis of heavy metals. The vegetation was washed with distilled water, dried at 85°C for 72 h, ground and then dried again at 85°C for 4 h, followed by decomposition in HF acid. Although other metals were analyzed, for this investigation only the Cu and Zn content of the plants is reported. The Cu and Zn contents were determined by AAS.

3. Results and Discussion

The pH, ORP, electroconductivity, temperature and water chemistry at several positions along the wetland stream are shown in Figs. 2–4. The pH was moderately acidic near the Sakaeko portal and does not change with the distance along the Miyanosawa stream, which is outside of the wetland. The pH of the Teranosawa stream discharge water was also moderately acidic near the vent, but gradually turns neutral as it flows through the wetland (Fig. 2). The improvement of water quality is not due to dilution by water from outside, because the phenomena are not observed in the Miyanosawa stream with the same water level. A thick growth of reed plants, such as *Phragmites australis*, thrives in the wetland through all seasons. With increasing distance from the vent, the ORP decreases. The flow rate of Teranosawa stream fluctuates between 100 and 600 dm³/min depending on the season and weather.

The Stiff diagrams of the water chemistry for sampling points A–E (Fig. 3) indicate that the total concentrations of major ions decrease dramatically from point A towards point D, and the decrease in sulfate ion concentrations is the most significant. The concentrations of heavy metals such as Fe, Mn, Cu and Zn, also decrease with increasing distance downstream from the portal (Fig. 4). The dissolved Fe was removed within a short distance (<300 m) from the vent. The other concentrations of heavy metals also decreased with distance, but did so more gradually. These results are in agreement with the decreasing electroconductivity trend along the stream, and clearly show that the stream water quality gradually improves toward the wetland. Further, these results suggest the possibility that the ecological system in the wetland is partly responsible for neutralization of the acidic drainage and removal of heavy metal ions and sulfate.

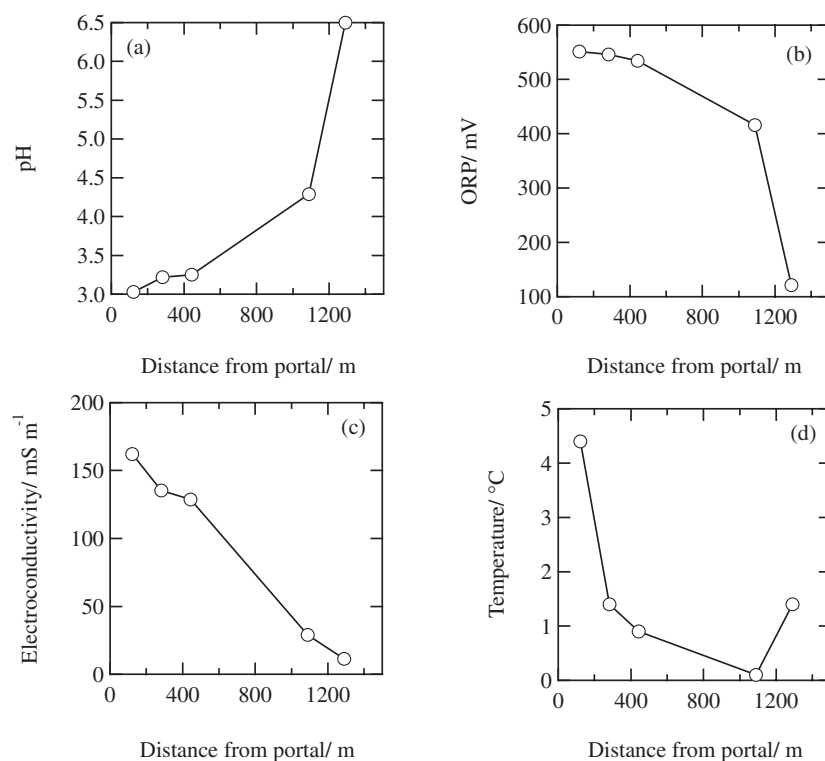


Fig. 2 Changes in pH, ORP, electroconductivity, and temperatures of water at points A-E in Teranosawa stream in the wetland.

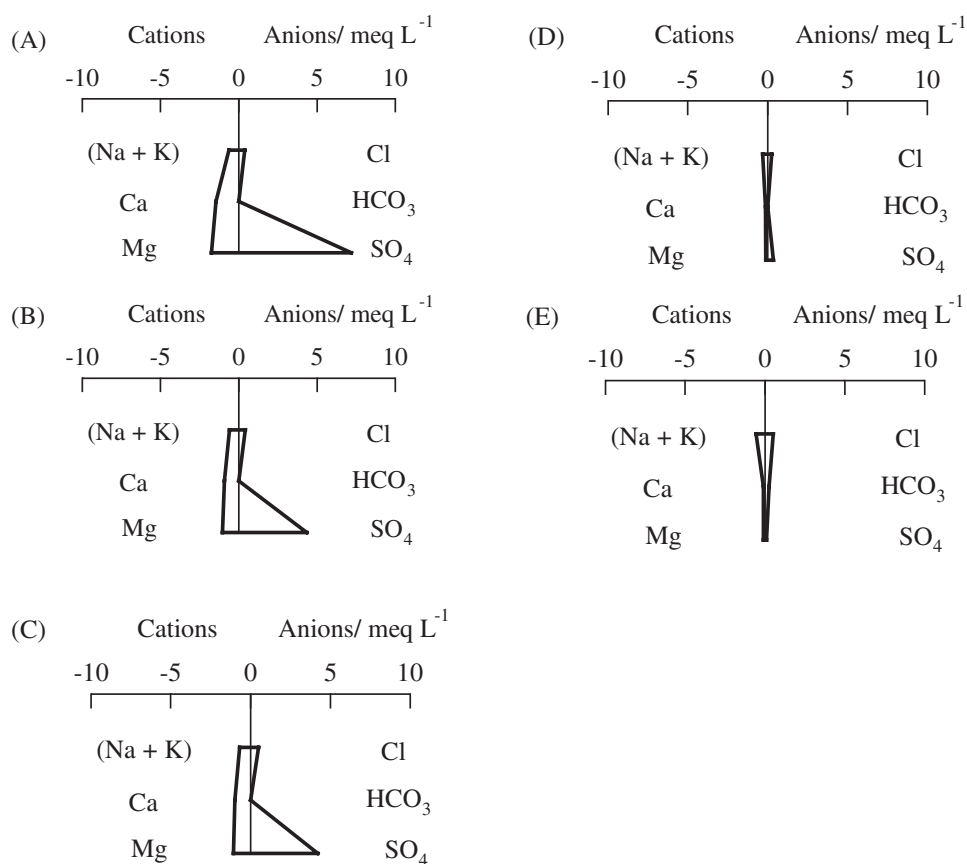


Fig. 3 Stiff diagrams of sampled waters at points A-E in Teranosawa stream.

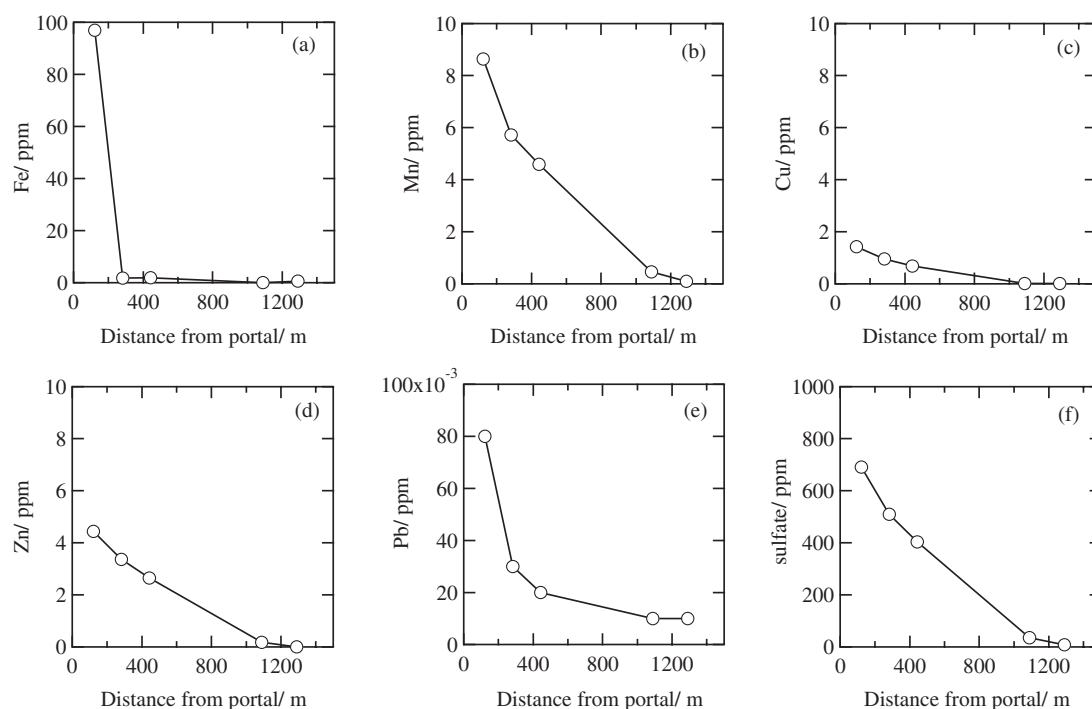


Fig. 4 Changes in dissolved Fe, Mn, Cu, Zn and sulfate concentrations along the Teranosawa stream.

The results of XRF analysis for the sediments (Table 1) indicate that Si, Fe, Al, Ca, and K are the major elements in all samples. Heavy metals, such as Cu, Zn, Pb, and Mn, are present in trace amounts. Any trend of decreasing heavy metal content of the sediments versus distance is not evident in this analysis.

The XRD patterns of the samples A–E (Fig. 5) show that the main crystalline component is α -quartz (JCPDS 5-0490). Likewise, small peaks assigned to andesine (0.62NaAlSi₃O₈, 0.38CaAl₂Si₂O₈) (JCPDS 10-359) are present. The relative intensity of andesine to α -quartz was larger in the downstream sediments than in the upstream. Heavy metal bearing minerals were not detectable by XRD in any minerals of the samples. Based on this evidence, it is reasonable to assume that the trace amounts of heavy metal ions are weakly bound

Table 1 Elemental compositions by XRF (mass%) for sediments collected at the points A–E shown in Fig. 1.

Element	A	B	C	D	E
Fe	14.9	31.1	24.6	22.4	20.6
Cu	2.77	0.388	0.0631	0.333	0.0288
Pb	n.d.	0.0882	n.d.	0.0785	n.d.
Zn	2.04	6.10	1.65	2.24	0.406
Mn	0.476	0.719	0.582	0.683	0.708
S	2.35	1.40	0.877	1.26	0.320
Na	0.0453	n.d.	0.0411	0.0409	0.0615
K	7.16	5.59	7.88	3.59	3.30
Mg	0.0595	0.0240	0.0586	0.111	0.0983
Ca	5.39	9.21	3.81	9.96	14.4
Al	8.07	4.65	9.87	10.0	8.45
Si	51.3	34.5	46.2	45.0	48.3
Others	5.44	6.23	4.37	4.30	3.33

n.d.: not detected.

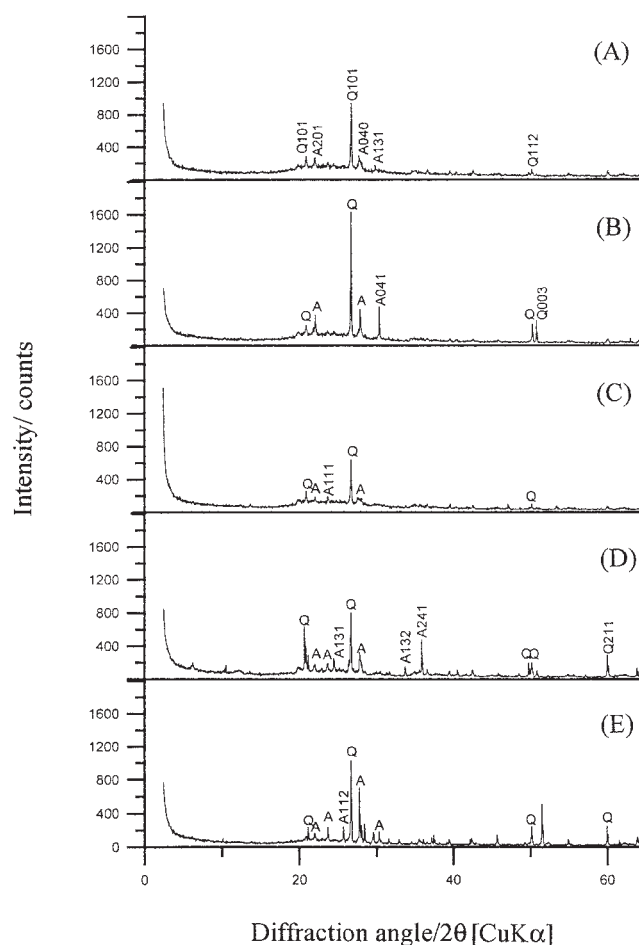


Fig. 5 XRD patterns for the sampled sediments. A: andesine (JCPDS 10-359), Q: α -quartz (JCPDS 5-0490).

to the sediment in non-crystalline phases or are not abundant enough to be detected by XRD.

For improved resolution about the presence of heavy metals in the sediments, chemical extractions were conducted. The results of the selective sequential extraction and acid

sequential extraction of heavy metals are shown in Figs. 6 and 7. These methods are related in that HCl-extractable species in the acid sequential extraction are partitioned into the 1st–4th fraction of the selective sequential extraction.⁸⁾ Iron in the sediments is primarily bound with HF-extractable

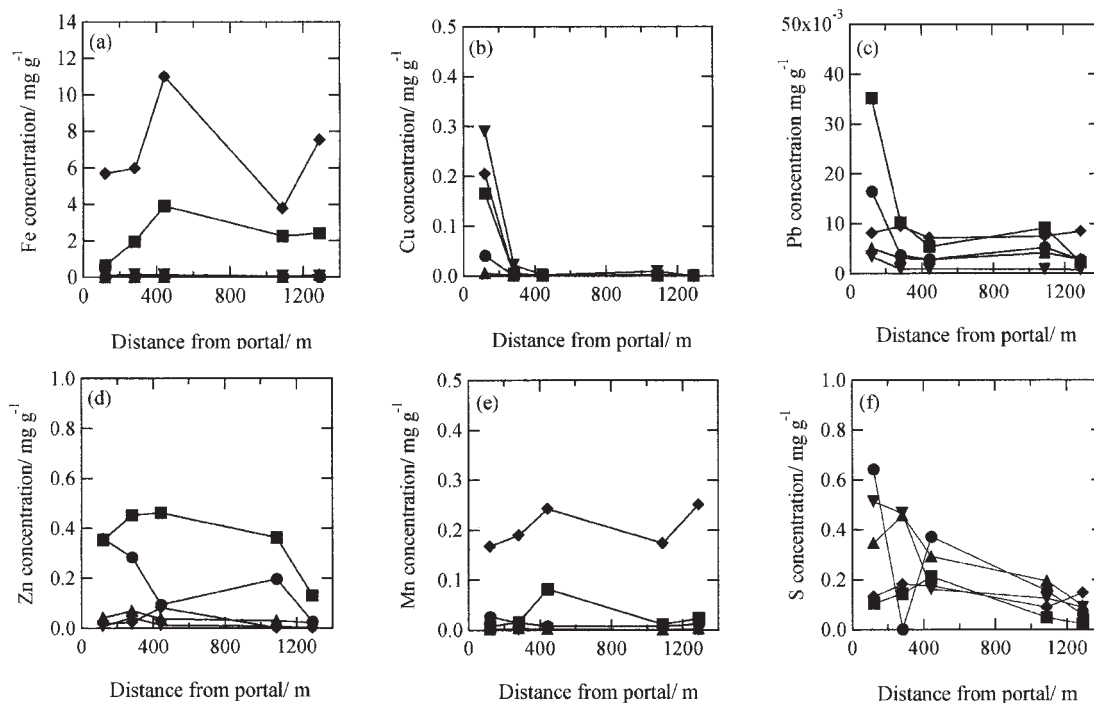


Fig. 6 Plots of Fe, Cu, Pb, Zn, Mn, and S contents in various fractions of the sediment as determined by selectively sequential extractions versus distance from the portal. The vertical axis expresses the amount of extracted elements in each step by mg/g-dry sediment. Symbols: ●, exchangeable; ▲, bound to carbonate; ■, bound to Fe-Mn oxides; ▼, bound to organic matter; ◆, residue.

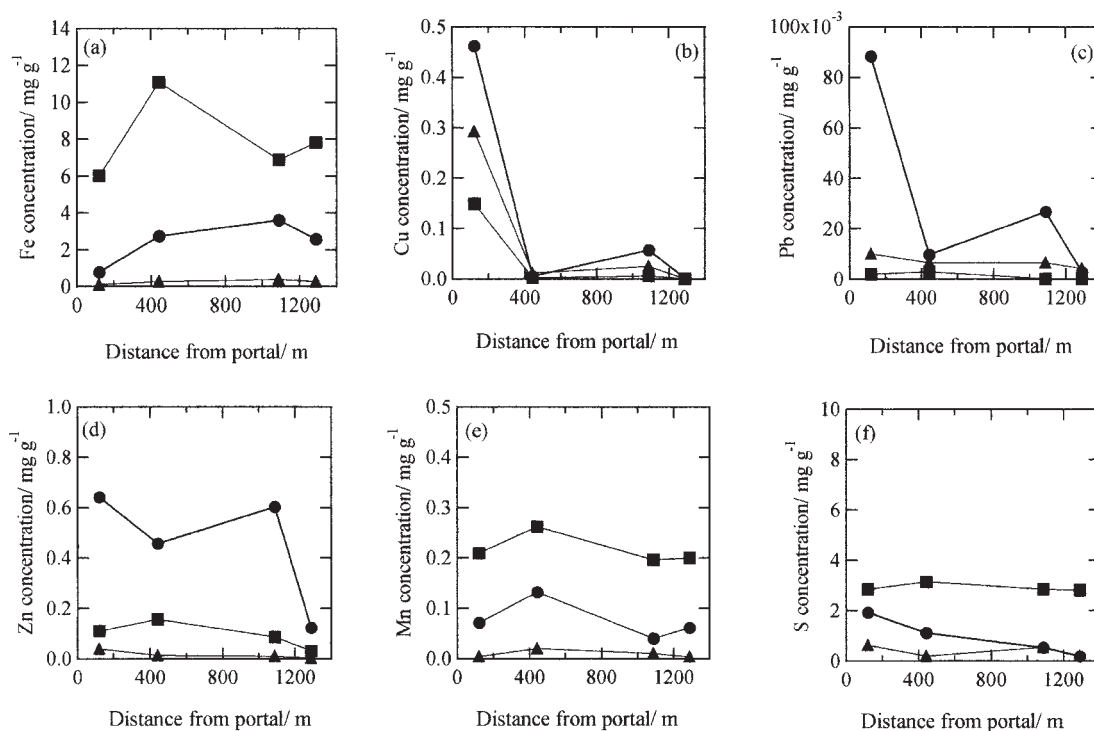


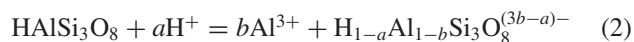
Fig. 7 Plots of Fe, Cu, Pb, Zn, Mn, and S contents in various fractions of the sediment as determined by acid sequential extractions versus distance from the portal. The vertical axis expresses the amount of extracted elements in each step by mg/g-dry sediment. Symbols: ●, HCl-extractable; ■, HF-extractable; ▲, HNO₃-extractable.

silicates (Fig. 7(a)). This fraction represents Fe present in the native sediments unaffected by drainage from the stream, but originally present. The Fe that is removed from solution is the most probable to change into the oxide-bounded types and be distributed all over the wetland (Fig. 6(a)). Mn is the most hardly removed and distributed in the sediment evenly in the wetland, bound to mainly oxides except for HF-extractable phase (Figs. 6 and 7(e)).

As shown in Figs. 7(b, c, d), the reactive phase (HCl-extractable phase) of Cu, Pb, and Zn shows a clear trend having higher contents in the upstream. Near the Shoeiko drainage vent, the Cu is primarily fixed in the organic matter (Fig. 6(b)). It is well known that Cu is easily complexed with carboxylic groups of humic substances, the representative organic compounds in the environments and probably is the case here. Although the dissolved Pb concentration in the stream was very low (Fig. 4(e)), oxides near the vent are enriched in Pb (Fig. 6(c)). Zn is distributed throughout the wetland, bound mainly to oxides and adsorbed predominantly near the portal (Fig. 6(d)). Sulfur contents represent to be mainly from sulfate in sediments. Reactive phases of sulfur are higher content in the upstream, other phases are constant independent of the distance from the vent (Figs. 6 and 7(f)).

The selective sequential and acid sequential extractions of major elements, Na, K, Mg, Ca, Al, and Si (Figs. 8 and 9) show that these elements are mostly extractable with HF and therefore are associated with silicates, and that Na and Mg are highly bounded to carbonate minerals in the upstream. It is reasonable to assume that the quartz and andesine detected by XRD (Fig. 5) are major components of HF-extractable

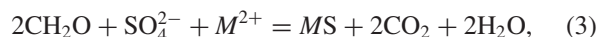
silicate phase. Andesine is an intermediate member of the plagioclase feldspar series with a composition range 70 to 50% albite, 30 to 50% anorthite. Under acidic conditions, feldspars are not stoichiometrically dissolved, but rapidly exchange the surface Na^+ , K^+ , and Ca^{2+} for H_3O^+ and release Al^{3+} to form activated complexes on the mineral surface as follows:⁹⁾



These activated complexes might remove heavy metals from solution by reactions such as cation-exchange, formation of complex, and adsorption.

Considering the molar ratio of Ca, Al, and Si in andesine, other aluminosilicates should be extracted in HF (Figs. 9(d), (e), (f)). The HF-extractable fraction of Mg, which is not a component of andesine, is more abundant in the downstream (Fig. 9(c)). The clay mineral components are more largely distributed in the downstream. It would be easier for suspended clay particles to settle out in the low velocity in distal part of the wetland. It is well known that clay minerals play an important part in ion-exchange, pH-buffering of soil water, and bridging for the formation of aggregated particles.

Sulfate-reducing bacterium (SRB) has been found to facilitate the precipitation of metals from solution in the anaerobic depths of wetlands and mine tailings,¹⁰⁾ as follows:



in which CH_2O and M^{2+} indicate a representative organic compound, and a divalent heavy metal, respectively. Sulfate

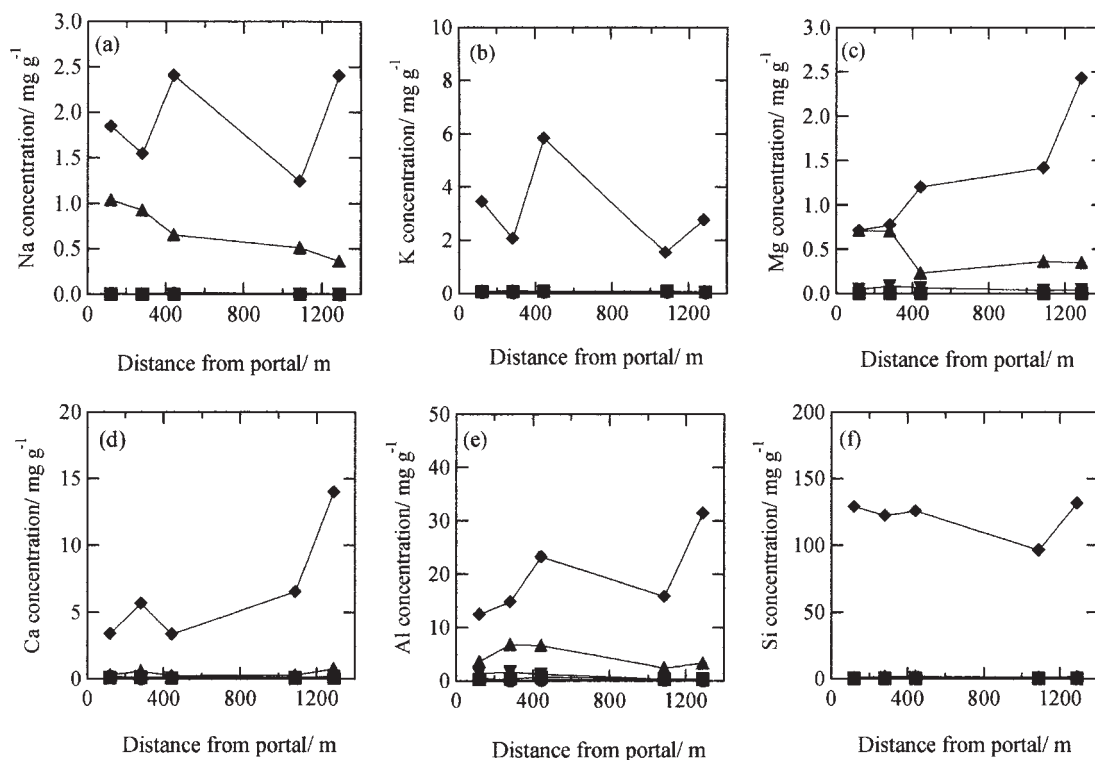


Fig. 8 Plots of Na, K, Mg, Ca, Al, and Si contents in various fractions of the sediment as determined by selectively sequential extractions versus distance from the portal. Symbols: ●, exchangeable; ▲, bound to carbonate; ■, bound to Fe-Mn oxides; ▼, bound to organic matter; ◆, residue.

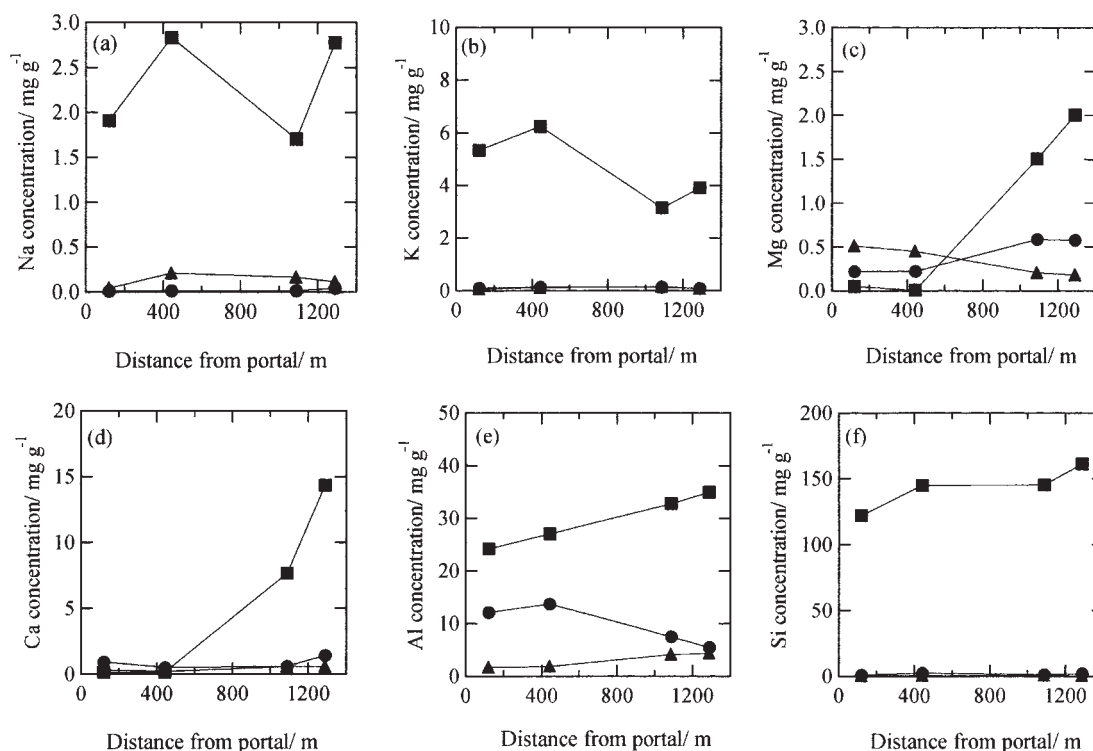


Fig. 9 Plots of Na, K, Mg, Ca, Al, and Si contents in various fractions of the sediment as determined by acid sequential extractions versus distance from the portal. Symbols: ●, HCl-extractable; ■, HF-extractable; ▲, HNO₃-extractable.

is reduced to sulfide through decomposition of organic compounds by the metabolic process of SRB.

This sulfate reduction and metal sulfide precipitation mechanism has been implemented for the treatment of mine drainage using permeable reactive barriers.¹¹⁾ Microbial tests for SRB proved positive only at location E. Where present in the wetland, these SRB might help in the remediation of natural or anthropogenic heavy metal-rich drainage.

Heavy metals, in addition to being accumulated in the mineral component of the stream, are also retained in the emergent vegetation. The Cu and Zn accumulated in the vegetation mostly around 600 m-downstream from the mine portal, at a level twice or three times greater than at other points along the stream (Fig. 10). The maximum Cu and Zn

contents in vegetation are not negligible, owing to being correspondent to much more amounts and around 25% in the sediment around 600-m downstream from the portal, respectively. These are caused by that heavy metals were absorbed from roots of emergent vegetations and accumulated in them. It has been reported that *Phragmites australis* is tolerant to widely acidic environments of pH 2–8. We observed an accumulation of 0.16 mg/g of Cu and 0.15 mg/g of Zn in the roots of *P. australis* through the investigation in a constructed wetland.¹²⁾ These values are close to the maximum Cu and Zn contents observed in the current investigation.

It follows from these results that the remediation of metal-rich acid drainage in this natural wetland involves sophisticated chemical and biological processes. Around the nearest the mine portal in the wetland, the removal of heavy metals is carried out primarily by soil function such as adsorption, and ion-exchange and formation of Fe–Mn oxides. Further down gradient, where the concentrations of dissolved metals are lower and pH is closed to neutral, metal removal is primarily through plant uptake. Plant growth and decay supplies further organic substances to the sediment. These organic substances facilitate the complexation of heavy metals and the growth of heterotrophic bacteria in the sediment. In the most distal part of the wetland, metal removal to low levels is accomplished by reactivity of clay minerals and microbial activity. The Mn removal mechanism was not clear from our investigation. In the pH ranges for the Teranosawa stream, it is unlikely that the dissolved Mn ions are oxidized chemically except for the contribution of Mn-oxidizing microorganisms.^{13,14)}

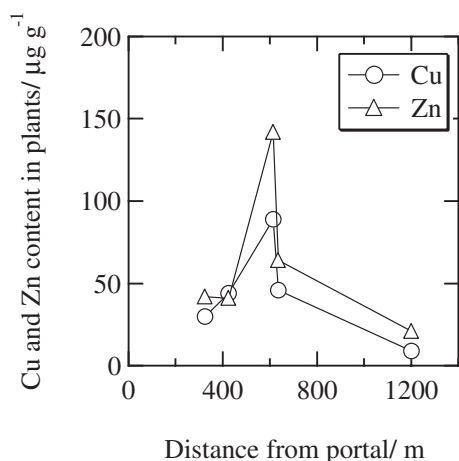


Fig. 10 Contents of Cu and Zn in plants (μg g⁻¹).

4. Conclusions

The mechanism of surface water remediation in a natural wetland that receives the heavy metal-rich acidic mine drainage was investigated through field research. The interpreted removal of heavy metals is as follows:

Soon after discharge from the vent, dissolved Fe oxidizes and precipitated near the vent mainly as hydroxides, which is important for the subsequent removal of other heavy metals in the wetland. In the upstream, other ion-exchangeable and carbonate-bounded types of heavy metals are also observed. Organic matter and Fe–Mn oxides are enriched in Cu and Zn, respectively. The Cu is bound to organic matter to form stable complexes and large molecule of polymer in the wetland soil.

Heavy metals are also absorbed by the roots of emergent vegetation. The growth of emergent vegetation, that has tolerance to heavy metals and weakly acidic waters, provides organic compounds to the sediments. These organic compounds support the microbial activity and the formation of complexes with heavy metals. In the most distant parts of the wetland, the low-level removal of metals is achieved by clay minerals and by microbial activity. Because of their ion-exchangeable capacity of the clay minerals have an affinity for divalent and trivalent metals. Sulfate-reducing bacteria remove heavy metals through reduction of sulfate and the precipitation of low solubility metal sulfides under conditions that are near neutral pH, anaerobic, and organic carbon-rich.

The design of a man-made wetland can be improved based on knowledge acquired from the above natural system. A multi-cell type of wetland with neutralizing reagent, vegetation, organic compost, and clay minerals could be constructed.

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