

論文内容の要旨

Geochemical analysis of distribution and behavior of hazardous elements in

waters and sediments in a groundwater-recharged river, Santiago

(サンティアゴ市内の河川の水及び堆積物中の有害元素の分布と挙動の地球化学的分析)

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Water contamination has been paid much attention due to its impact on environments. The present study focuses on water contamination within the Lampa River in Santiago, Chile, which is recharged exclusively by groundwater. This study shows how the concentrations of both cations and anions are increased and diluted within the river by water and sediment analyses, emphasizing the behavior of hazardous elements (Cu, Zn, Ni, Co, Cd, Cr and Pb). Only a single area with high concentrations of cations and SO_4^{2-} was found at 0.8 km in length along the river out of 60 km examined. The phenomena observed in the high concentration area (HCA) were similar to those of acid mine drainage.

Samples were collected along the Lampa River during January-February 2006 and 2007: they were surface (runoff) waters, pore waters in saturated soil, groundwaters (well waters) and sediments from the riverbed. Measurements of pH, Eh, temperature and anion concentrations (SO_4^{2-} , HPO_4^- , Cl^- , NO_3^- , HCO_3^-) were done in the field mainly by colorimetry for the waters, and cation concentrations (Al, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si, Zn) were determined in the laboratory by inductively coupled plasma atomic emission spectrometry (ICP-AES). For the sediments, X-ray fluorescence spectrometry (XRF), X-ray diffraction analysis (XRD), ICP-AES and scanning electron microscopy equipped with energy dispersive X-ray spectrometer (SEM-EDS) were employed to measure the concentrations of major cations (XRF) and trace cations (ICP-AES), to identify minerals (XRD) and to observe textures (SEM-EDS). In addition, a sequential extraction technique

was used to examine how trace, hazardous elements were associated with sediment constituents. The geochemical calculations were done by Phreeqc and Geochemist Workbench software.

Analyses of pore and surface waters and sediments have revealed that the cation concentrations in the waters along the river in general are low and normal, and those in the sediments are constant except in the HCA. The HCA was characterized by sudden increase and subsequent decrease in cation concentrations (including those of the hazardous cations) and SO_4^{2-} in the waters, and by corresponding decrease and increase in pH. The cation and SO_4^{2-} concentration variations are well represented by a corresponding variation of ionic strength (Fig. 1), suggesting that ionic strength is a good indicator of contamination. On the other hand, the cation and anion concentrations in the groundwaters are generally low and normal everywhere along the river, which reflects those in the surface and pore waters in the other areas than the HCA due to the nature of the river system, groundwater recharging.

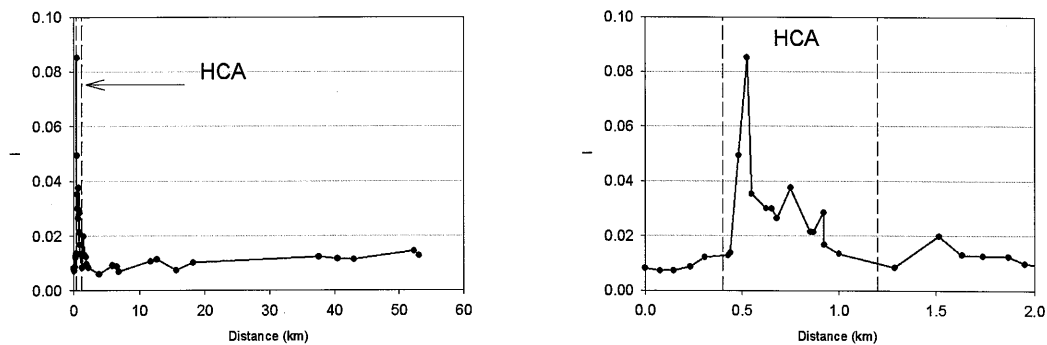


Figure 1 - Variations of ionic strength in waters along the Lampa River

The pH decreased to $\text{pH} \sim 3.1$ in the HCA from $\text{pH} \sim 7$ upstream (Fig. 2) resulting from dissolution of Cu/Fe sulfide (e.g., chalcopyrite). The presence of the sulfide and the dissolution texture were confirmed by SEM-EDS (labels A and B, respectively, in Fig. 3). The dissolution of Cu/Fe sulfide also caused the increase in Cu, Fe and SO_4^{2-} concentrations in waters in the HCA (Fig. 2), which consequently formed Fe and probably Cu sulfate minerals. The increase in concentrations of Mn, Zn, Ni, Co and Cd (Fig. 2) resulted probably from dissolution of sulfide minerals which further increased SO_4^{2-} concentration. The low pH induced by dissolution of sulfides, then, dissolved feldspars abundant in the Lampa River sediments, which increased the concentrations of Ca, Na, K and Al in the waters (Fig. 2).

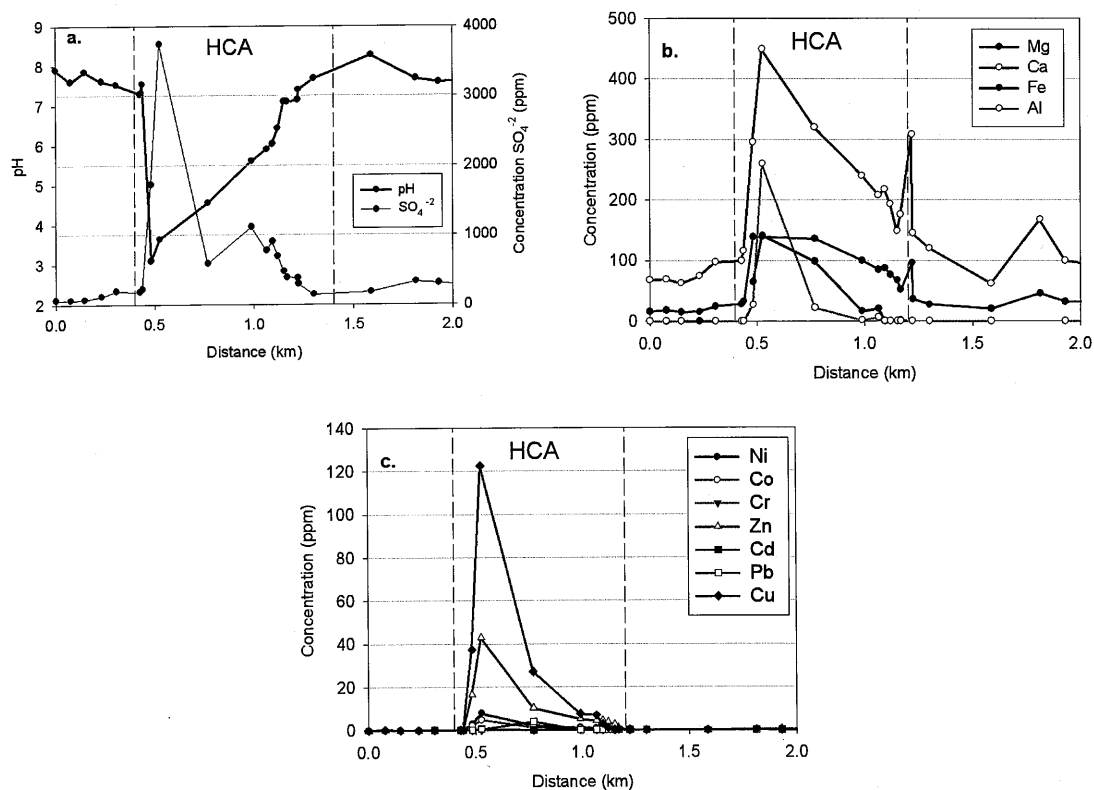


Figure 2 – Concentration variations of selected cations and SO_4^{-2} and variations of pH around the HCA for surface waters.

The decrease in SO_4^{-2} concentration in the HCA is concordant with the decrease in cation concentrations (Fig. 2). The decrease in SO_4^{-2} occurred by short-time consumption of SO_4^{-2} through precipitation of sulfate minerals such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$) and Al sulfate which were confirmed by XRD and SEM. Thermodynamic calculations suggested that Mg, Mn, Cu and Zn were all possible cations forming sulfate minerals. The decrease in concentrations of cations (excluding Cr and Pb) (Fig. 2) can be explained mainly by sulfate mineral formation. The slower decrease in Ca and SO_4^{-2} (Fig. 2) and the observation of gypsum even in water suspension indicated that gypsum formation is most effective to remove SO_4^{-2} , which has not been pointed out for acid mine drainage.

The increase and subsequent decrease in concentrations of Cu, Zn, Ni, Co, Cd, Cr and Pb occurred in the HCA for surface and pore waters. Similar increase and decrease were also observed for the hazardous elements in sediments only in the HCA but not in other areas along the river where their concentrations were generally quite low. Along with the concentrations variations (Fig. 2c), the sequential extraction (Fig. 4) revealed that Cu, Zn, Ni, Co and Cd behaved similarly in both waters and sediments. These hazardous elements are released by dissolution of sulfides, resulting in their high concentrations in water. The dissolved Cu, Zn, Ni, Co and Cd are then redistributed in sediments in a limited area and remain there but are not transported farther downstream. The sequential extraction results for Cr and Pb were different from those of the above hazardous elements in

addition to the difference in concentration variations between the two groups, which indicates that Cr and Pb concentrations in the waters are not affected significantly by dissolution of sulfides.

Dissolution of sulfides causes contamination but the contamination is present only in the HCA, at about 800 m in length along the river, and the river downstream returns to a normal one. No other contaminated sites were found along the river. However, if the contamination results from the characteristics of sediments in Santiago Valley, there remains the possibility that similar contamination occurs in other areas along the river.

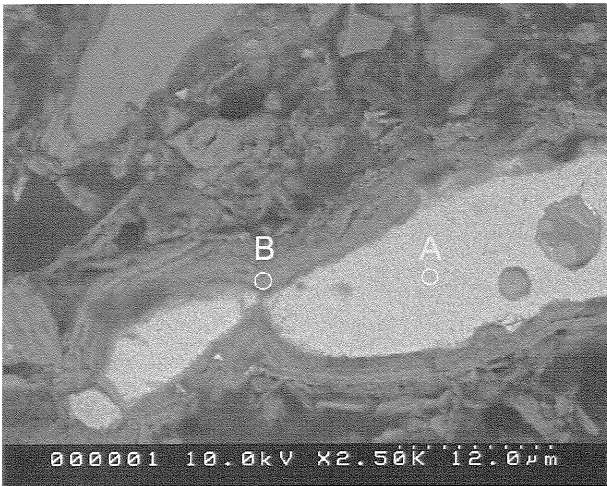


Figure 3 – Backscattered electron image of a sediment in the HCA

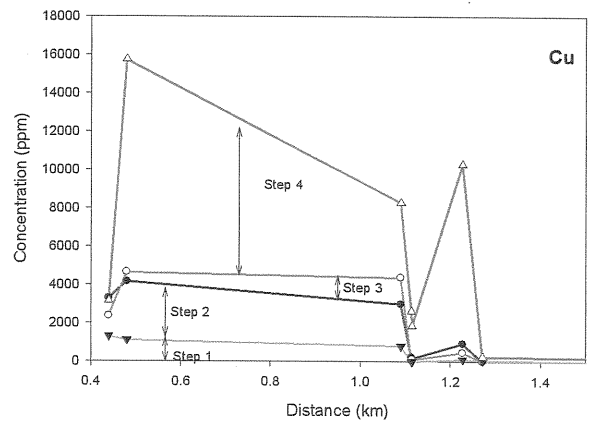


Figure 4 – Sequential extraction results for Cu in sediments expressed by concentration accumulation.