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ASSESSING BENTHIC ANIMAL AND WATER PLANT USE IN ESTIMATING RIVER AL AND CR CONTAMINATION IN THE KINOKAWA RIVER CATCHMENT

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ABSTRACT: Benthic animals and water plants species useful for devising an index to indicate the extent of Al and Cr contamination in the Kinokawa River catchment area were studied. Studies revealed that the Al concentrations in crane fly larvae (260 to 5,260 mg/kg-dry) and bryophytes (640 to 20,000 mg/kg-dry) around a closed Cu mine were about 1.5 times higher than those around a non-mine area (530 to 3,100 for crane fly larvae and 220 to 13,000 mg/kg-dry for bryophytes). Cr concentrations in dragonfly larvae around the serpentinite (3 to 30 mg/kg-dry) were about 3 times higher than those around the non-serpentinite area (0.6 to 9 mg/kg-dry). Cr concentrations in bryophytes around the serpentinite (3 to 91 mg/kg-dry) were about 1.5 times higher than those around the non-serpentinite area (2 to 53 mg/kg-dry). Al concentrations in Pottiaceae, a kind of bryophyte found around a closed Cu mine (890 to 20,000 mg/kg-dry) were about 2.5 times higher than those around a non-mine area (6,300 to 8,000 mg/kg-dry). Cr concentrations in Pottiaceae found around the serpentinite area (91 mg/kg-dry) were about 3 times higher than those around the non-serpentinite area (3 to 29 mg/kg-dry). Additionally, crane fly larvae, dragonfly larvae, bryophytes, and Pottiaceae were widely distributed as they were sampled around both contaminated and non-contaminated areas. Therefore, it was concluded that useful species for devising an index to indicate contamination included the crane fly larvae for Al, dragonfly larvae for Cr, and the bryophytes, especially Pottiaceae for Al and Cr.

Keywords: Al, Cr, Pottiaceae, Cranefly larva, Dragonfly larva

1. INTRODUCTION

Metal concentrations in river water and river sediment were measured to investigate the influence of heavy metals on river aquatic life. Generally, metal concentrations in river water are very low. Moreover, they are changeable depending on the change of flow rate. Heavy metals in river sediment contain both soluble and insoluble metals, but river-dwelling aquatic life use only soluble metals. Therefore, not all heavy metals in river sediment are used for river aquatic life and the metal concentrations found in river water and river sediment were not always useful as an index of the influence of heavy metals on river aquatic life. Conversely, it is reported that the metal concentrations in benthic animals and water plants are indeed useful for investigating the influence of heavy metals on river aquatic life [1]-[6]. However, few studies have been done on whether benthic animals and water plants are useful as an index of river Al and Cr contamination. Therefore, Al and Cr concentrations in benthic animals and water plants in the Kinokawa River catchment were measured and species considered useful for an index of Al and Cr contamination for the river were determined. For a species to be considered “useful” as an index of Al and Cr contamination, it needs to possess a high concentration of Al and Cr in contaminated areas and a low concentration in non-contaminated areas. Additionally, the species needs to be common, widely dispersed, and possess a high and widely varying range of Al and Cr concentrations.

2. STUDY AREA

Figures 1 and 2 show the study area. The Kinokawa River is located in the center of the Kinki district and is classified as an “A” river based on the Ministry of Land, Infrastructure, Transport, and Tourism of Japan. The length and total area of the Kinokawa River are 136 km and 1,750 km^2 [7]. It flows into the Kii Channel through the Kii plain from South Nara. The Izumi Group, composed of sedimentary rocks, sandstone, mudstone, and conglomerate, is distributed in the northwest part of the catchment. The Sanbagawa Belt, composed of metamorphic rocks, serpentinite, and crystalline schist, is distributed in the southwest part and the northeast part of the catchment. The Hidakagawa Group, composed of sedimentary rocks, sandstone, and shale, is distributed from the southern part to the northeast part of the catchment. The Chichibu Belt, composed of sedimentary rocks, sandstone, mudstone, limestone, and chert, is distributed in the eastern part of the catchment [8]. The Ryoke Complex, composed of plutonic rocks, granite, and gneiss, is distributed in the northeast part of the

Fig.1 Location of study area.

catchment. In the Kinokawa River catchment, there is serpentinite and a closed Cu mine. The closed Cu mine produces large quantities of Cu and Fe sulfide ore. Wastewater from the closed Cu mine is low pH and has a high concentration of sulfate with metal. The chemistry in the serpentinite is quite different than that in other rocks with the Mg, Ni, and Cr concentrations in serpentinite being high.

3. STUDY METHOD

Riverbed benthic animals and water plants were sampled in the Kinokawa River catchment. Sampling points are shown in fig.2. A total of 73 sampling points were investigated between July 2013 and April 2016. Among sampled benthic animals were Japanese freshwater crabs, caddice-worms, dobsonfly larvae, dragonfly larvae, stonefly larvae, crane fly larvae, mayfly larvae, and Corixidae. Sampled water plants included reeds, ferns, bryophytes, Japanese knotweed, and coix. Sampling points were classified into three groups, the serpentinite area, the Cu mine area, and the normal area. The serpentine area comprised the sampling points around the serpentinite. The Cu mine area comprised sampling points around the Cu mine. The normal area was a sampling point excluding those areas. Crane-fly larvae and reed were not sampled in the serpentinite area. Moreover, Japanese knotweed was not sampled in the normal area.

In the laboratory, the sampled benthic animals and water plants were first rinsed with ultrapure water and then desiccated by a dryer. After drying, they were dissolved with concentrated nitric acid and filtered with a membrane filter in 0.45 micrometer of pore size. After filtering, the Al and Cr concentrations in benthic animals and water plants were measured by ICP-OES (AMETEK, Inc., SPECTRO ARCOS) in the laboratory at Wakayama University. The actual detection limit of ICP-OES is 0.01ppm for Al and Cr. Water plants, excluding bryophytes, were divided into leaf, upper part stems, middle part stems, lower part stems, and roots, and each part was separately analyzed.

4. RESULTS AND DISCUSSION

4.1 Al Concentrations in Benthic Animals and Water Plants

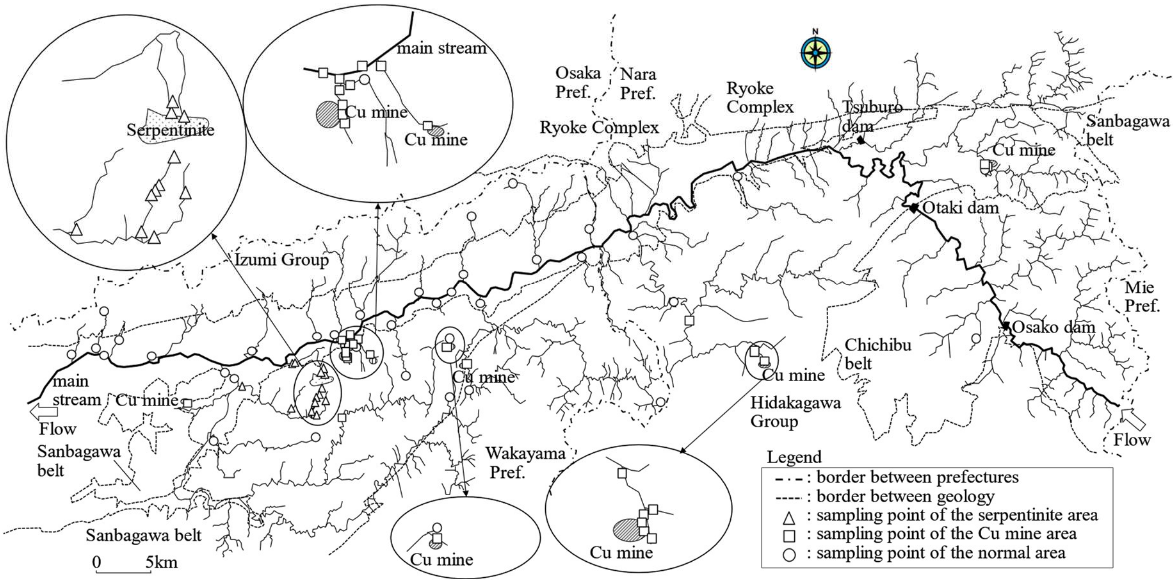


Fig.2 Kinokawa River catchment.

Figures 3 and 4 show Al concentrations in benthic animals and water plants. Al concentrations in dragonfly larvae and crane fly larvae in the Cu mine area were 151 to 3,100 and 260 to 5,260 mg/kg-dry, respectively. Al concentrations in dragonfly larvae and crane fly larvae in the other areas were 88 to 1,100 and 530 to 3,100 mg/kg-dry, respectively. Al concentrations in reed roots, leaves, and roots of ferns, bryophytes, upper- and middle-part stems, and roots of Japanese knotweed and coix roots in the Cu mine area were 610 to 1,600, 260 to 3,200, 640 to 20,000, 270 to 3,000 and 380 to 500 mg/kg-dry respectively. Al concentrations in reed roots, leaves, and roots of ferns, bryophytes, upper- and middle-part stems, and roots of Japanese knotweed and coix roots in the other areas were 440 to 590, 180 to 1,600, 220 to 13,000, 190 to 1,300, and 340 mg/kg-dry, respectively. Therefore, the Al concentrations in these species in the Cu mine area were higher than those in the other areas. Aluminum is widely distributed as feldspar and clay minerals in crustal rocks, where it is the third most abundant element following oxygen and silicon. The solubility of aluminum silicate and aluminum hydroxide in rocks is large under a low or high pH condition. The closed Cu mine produces low pH wastewater. Chemical equations of aluminum silicate and aluminum hydroxide with water in a low pH condition are shown below [9].

$$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2H_4SiO_4 + H_2O \quad (1)$$

$$Al(OH)_3 = Al^{3+} + 3OH^- \quad (2)$$

Therefore, it was thought that high Al concentrations in dragonfly larvae, crane fly larvae, reed roots, leaves and roots of ferns, bryophytes, upper- and middle-part stems and roots of Japanese knotweed and coix roots in the Cu mine area were caused by wastewater from the closed Cu mines.

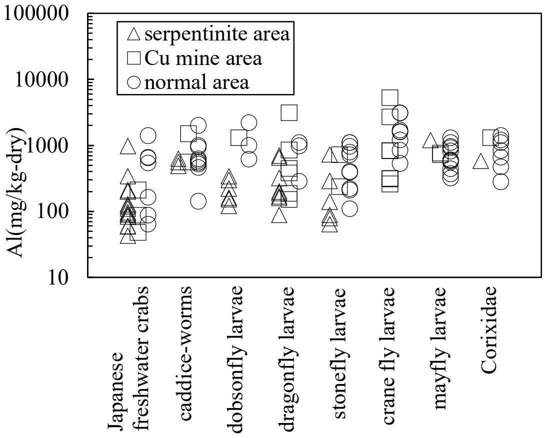
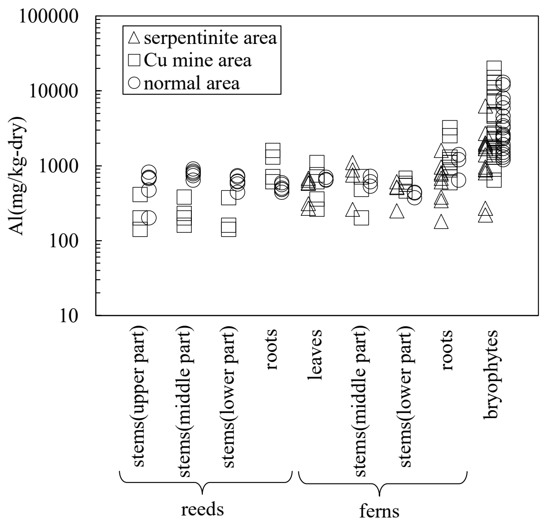


Fig.3 Al concentrations of benthic animals.



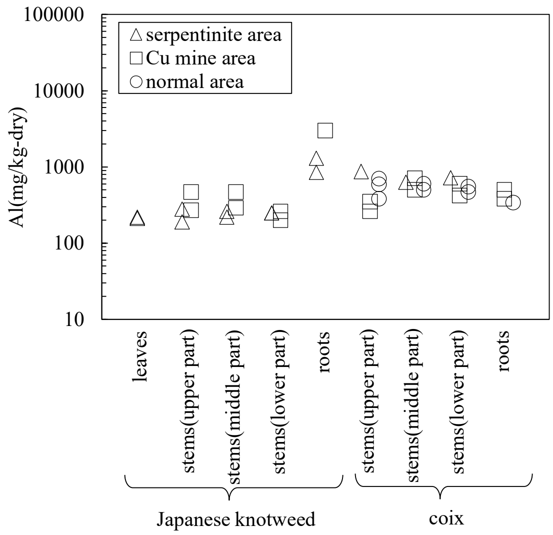


Fig.4 Al concentrations of water plants.

In contrast, Al concentrations in Corixidae, lower-part stems of ferns, lower-part stems of Japanese knotweed, and middle- and lower-part stems of coix in the Cu mine area were 1,300, 450 to 690, 200 to 260, and 420 to 710 mg/kg-dry, respectively. Al concentrations in Corixidae, lower-part stems of ferns, lower-part stems of Japanese knotweed, and middle- and lower-part stems of coix in the other areas were 280 to 1,400, 250 to 610, 250, and 470 to 720 mg/kg-dry, respectively. Therefore, their Al concentrations in the Cu mine area were almost the same as those in the other areas. Al concentrations in Japanese freshwater crabs, caddice-worms, dobsonfly larvae, stonefly larvae, mayfly larvae, reed stems, middle-part stems of ferns, and upper-part stems of coix in the Cu mine area were 48 to 210, 560 to 1,500, 1,300, 237 to 720, 720 to 760, 140 to 410, 200 to 710, and 260 to 350 mg/kg-dry respectively. Al concentrations in Japanese freshwater crabs, caddice-worms, dobsonfly larvae, stonefly larvae, mayfly larvae, reed stems, middle-part stems of ferns, and upper-part stems of coix in the other areas were 43 to 1,400, 142 to 2,000, 121 to 2,200, 64 to 1,100, 320 to 1,300, 200 to 900, 260 to 1,100, and 380 to 870 mg/kg-dry, respectively. Therefore, their Al concentrations in the Cu mine area were not higher than those in the other areas.

Al concentrations in Japanese freshwater crabs, caddice-worms, dobsonfly larvae, dragonfly larvae, stonefly larvae, crane fly larvae, mayfly larvae, and Corixidae were 43 to 1,300, 142 to 2,000, 121 to 2,200, 88 to 3,100, 64 to 1,100, 260 to 5,260, 320 to 1,300, and 280 to 1,400 mg/kg-dry, respectively. Therefore, among benthic animals, crane fly larvae had the highest Al concentrations, and these concentrations widely varied in range. Al concentrations in reeds, ferns, bryophytes, Japanese knotweed, and coix were 140 to 1,600, 180 to 3,200, 220 to 20,000, 190 to 3,000, and 260 to 870 mg/kg-dry respectively. Therefore, among water plants, bryophytes had the highest Al concentrations, and these concentrations widely varied in range.

Crane-fly larvae were sampled in the Cu mine area and the normal area. Bryophytes were sampled in the serpentinite area, the Cu mine area, and the normal area. Therefore, crane fly larvae and bryophytes were sampled in both contaminated and non-contaminated areas.

From the above results, among benthic animals, crane fly larvae had the highest Al concentrations, and these concentrations widely varied in range. While among water plants, bryophytes had the highest Al concentrations, and these concentrations widely varied in range. Moreover, Al concentrations in crane fly larvae and bryophytes were high in the Cu mine area and were low in the other areas. Crane-fly larvae and bryophytes could be sampled in both contaminated and non-contaminated areas. Therefore, crane fly larvae and bryophytes were deemed useful as species that could be used for an index of Al contamination.

4.2 Cr Concentrations in Benthic Animals and Water Plants

Figures 5 and 6 show Cr concentrations in benthic animals and water plants. Solid marks indicate Cr concentrations in benthic animals and water plants which were under the detection limit of 0.01 ppm in concentration per sample solution.

Cr concentrations in caddice-worms, dragonfly larvae, and mayfly larvae in the serpentinite area were 9 to 19, 3 to 30, and 20 mg/kg-dry respectively. Cr concentrations in caddice-worms, dragonfly larvae, and mayfly larvae in the other area were 0.3 to 10, 0.6 to 9, and 1 to 5 mg/kg-dry respectively. Cr concentrations in bryophytes and Japanese knotweed roots in the serpentinite area were 3 to 91 and 27 to 60 mg/kg-dry respectively. Cr concentrations in bryophytes and Japanese knotweed roots in the other area were 2 to 53 and 26 mg/kg-dry respectively. It is known that serpentinite contains a large amount of Cr. It is reported that Cr concentrations in the serpentinite were 400 to 31,300 ppm [10]-[11]. Therefore, it was thought that high Cr concentrations in caddice-worms, dragonfly larvae, mayfly larvae, bryophytes, and Japanese knotweed roots in the serpentinite area were caused by the serpentinite.

In contrast, Cr concentrations in Japanese freshwater crabs, dobsonfly larvae, stonefly larvae, Corixidae, ferns, Japanese knotweed stems, and coix in the serpentinite area were 0.2 to 8, 1 to 7, 0.7 to 4, 4, 2 to 10, 2, and 2 mg/kg-dry, respectively. Cr concentrations in Japanese freshwater crabs, dobsonfly larvae, stonefly larvae, Corixidae, ferns, Japanese knotweed stems, and coix in the other areas were 0.2 to 5, 2 to 7, 0.6 to 5, 0.8 to 5, 1 to 10, 2, and 2 to 3 mg/kg-dry respectively. Therefore, their Cr concentrations in the serpentinite area were virtually the same as those in the other areas.

Cr concentrations in Japanese freshwater crabs, caddice-worms, dobsonfly larvae, dragonfly larvae, stonefly larvae, mayfly larvae, and Corixidae were 0.2 to 8, 0.3 to 19, 1 to 7, 0.6 to 30, 0.6 to 5, 1 to 20, and 0.8 to 5 mg/kg-dry respectively. Therefore, among benthic animals, dragonfly larvae had the highest Cr concentrations, and these concentrations widely varied in range. Cr concentrations in ferns, bryophytes, Japanese knotweed, and coix were 1 to 10, 2 to 91, 2 to 60, and 2 to 3 mg/kg-dry respectively. Thus, among water plants, bryophytes had the highest Cr concentrations, and these concentrations widely varied in range.

Dragonfly larvae and bryophytes were sampled in the serpentinite area, the Cu mine area, and the normal area. Therefore, they were sampled in both contaminated and non-contaminated areas.

From the above results, therefore, among benthic animals, dragonfly larvae had the highest Cr

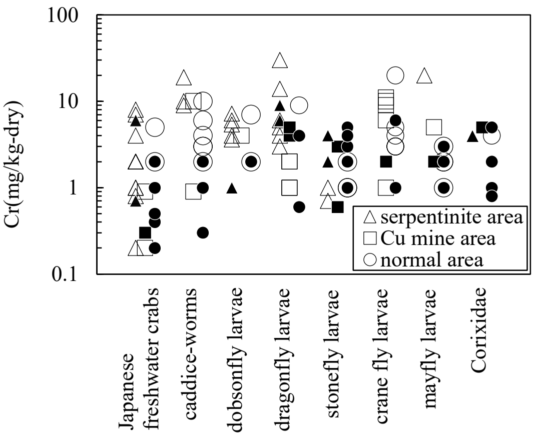


Fig.5 Cr concentrations of benthic animals.

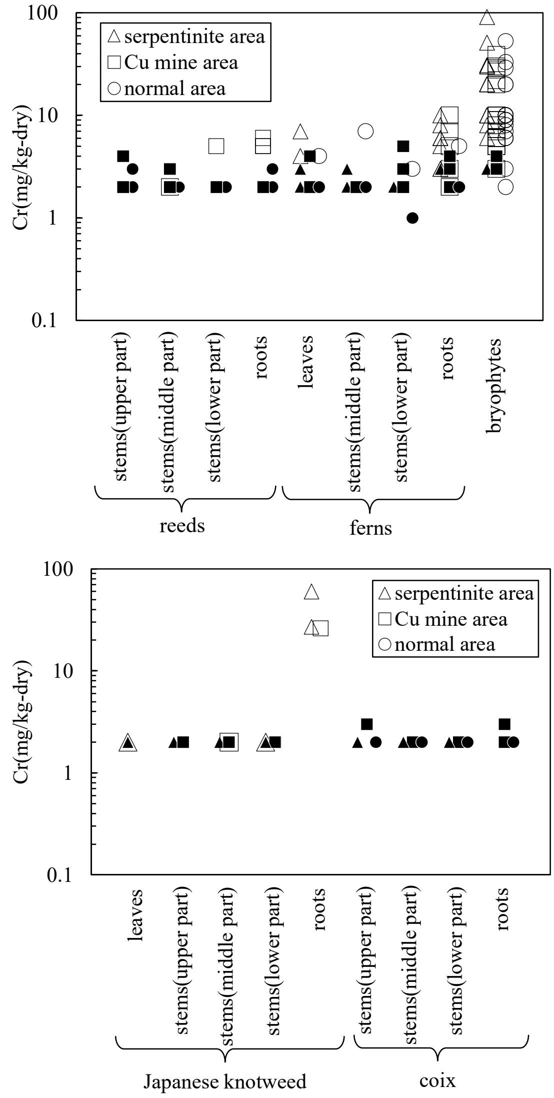


Fig.6 Cr concentrations of water plants.

concentrations, and these concentrations widely varied in range. Likewise, among water plants, bryophytes had the highest Cr concentrations, and these concentrations widely varied in range. Moreover, Cr concentrations in dragonfly larvae and bryophytes were high in the serpentinite area and were low in the other areas. Dragonfly larvae and bryophytes could be sampled in both contaminated and non-contaminated areas. Therefore, dragonfly larvae and bryophytes were deemed useful species for an index of Cr contamination.

4.3 Most Useful Species for determining River Al and Cr contamination

From figs.3 and 4, Al concentrations in benthic animals, bryophytes, and other water plants were 43 to 5,260, 220 to 20,000, and 140 to 3,200 mg/kg-dry respectively. From figs.5 and 6, Cr concentrations in benthic animals, bryophytes, and other water plants were 0.2 to 30, 2 to 91, and 1 to 60 mg/kg-dry respectively. Therefore, among benthic animals and water plants, bryophytes had the highest Al and Cr concentrations, and these concentrations widely varied in range. Moreover, Al concentrations in bryophytes in the Cu mine area were higher than those in the other areas. Furthermore, Cr concentrations in bryophytes in the serpentinite area were higher than those in the other areas. It is known that bryophytes absorb heavy metals from the entire surface of their structures [12]. Therefore, it is thought that bryophytes are better at absorbing heavy metals as compared with benthic animals and other water plants. Moreover, bryophytes consume little metal because the growth rate of bryophytes is generally slow [13]. For the above-stated reasons, it was deemed that among benthic animals and water plants, bryophytes had the highest Al and Cr concentrations and these concentrations widely varied in range therefore bryophytes were deemed useful as a species indexing Al and Cr contamination among benthic animals and water plants.

4.4 Relationship between Bryophyte Species and Al and Cr Concentrations in Bryophytes

Figs.7 and 8 show Al and Cr concentrations in bryophytes for each species. Solid marks indicate Cr concentrations in bryophytes under the detection limit, 0.01 ppm in concentration per sample solution.

Al concentrations in Pottiaceae and other species were 890 to 20,000 and 270 to 13,000 mg/kg-dry respectively. Therefore, among bryophytes, Pottiaceae had the highest Al concentrations, and these concentrations widely varied in range. Al concentrations in Pottiaceae in the Cu mine area and those in the other areas were 890 to 20,000 and 6,300 to 8,000 mg/kg-dry respectively. Therefore, Al concentrations in Pottiaceae in the Cu mine area were higher than those in the other areas. Aluminum is widely distributed as feldspar and clay minerals in rocks in the crust. The solubility of aluminum silicate and aluminum hydroxide in rocks is large under low or high pH conditions. The closed Cu mine produces low pH wastewater. Therefore, it was thought that high Al concentrations in Pottiaceae in the Cu mine area were caused by wastewater from the closed Cu mine. Cr concentrations in Pottiaceae and other species were 3 to 91 and 2 to 53 mg/kg-dry respectively. Therefore, among bryophytes, Pottiaceae had the highest Al concentrations, and these concentrations widely varied in range. Cr concentrations in Pottiaceae in the serpentinite area and those in the other areas were 91 and 3 to 29 mg/kg-dry respectively. Therefore, Cr

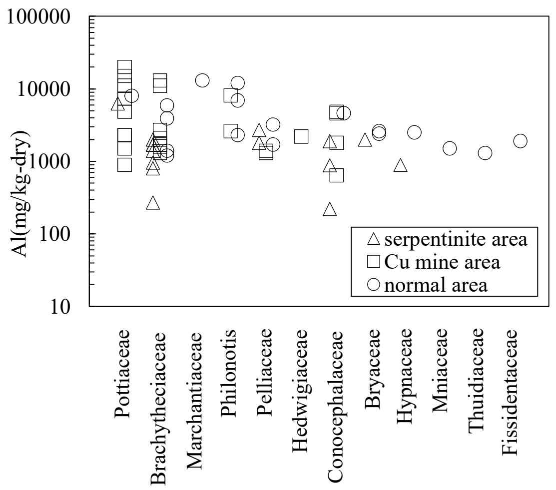


Fig.7 Al concentrations of bryophytes for each species.

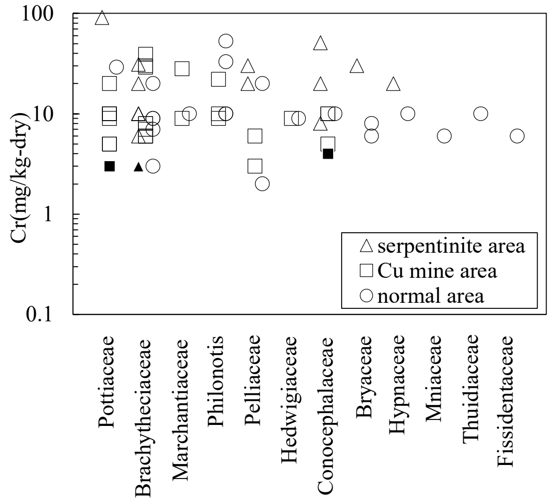


Fig.8 Cr concentrations of bryophytes for each species.

concentrations in Pottiaceae in the serpentinite area were higher than those in the other areas. It is known that the serpentinite contains a large amount of Cr. It is reported that Cr concentrations in the serpentinite were 400 to 31,300 ppm [10]-[11]. Therefore, it was thought that high Cr concentrations in Pottiaceae in the serpentinite area were caused by the serpentinite. It is known that *Scopelophila cataractae*, a kind of Pottiaceae, accumulates Cu, and *Scopelophila ligulata*, a kind of Pottiaceae, accumulates Fe in their structures [14]. Moreover, it is reported that Pottiaceae accumulates Co, Ni, and Zn in its structure [4]-[5]. Therefore, it is thought that Pottiaceae can accumulate high amounts of Al and Cr. Pottiaceae was sampled in the serpentinite area, the Cu mine area, and the normal area. Therefore, it could be sampled in both contaminated and non-contaminated areas.

From the above results, Pottiaceae was deemed a useful species for indexing Al and Cr contamination among bryophytes.

5. CONCLUSIONS

Al and Cr concentrations in benthic animals and water plants in the Kinokawa River catchment were investigated to estimate which species were useful for indexing Al and Cr contaminations in rivers. For a species to be considered useful in an index of Al and Cr contamination it needs a high concentration of Al and Cr in a contaminated area and a low concentration in a non-contaminated area. Moreover, it needs to be common and possess a high and widely varying range of Al and Cr concentrations.

Al concentrations in crane fly larvae and bryophytes in the Cu mine area were higher than those in the other areas. Cr concentrations in dragonfly larvae and bryophytes in the serpentinite area were higher than those in the other areas. Moreover, crane fly larvae for Al and dragonfly larvae for Cr possessed the highest and most widely varying range of concentrations among benthic animals. Bryophytes possessed the highest and most widely varying range of Al and Cr concentrations among water plants. Furthermore, crane fly larvae, dragonfly larvae, and bryophytes could be sampled in both contaminated and non-contaminated areas. Therefore, crane fly larvae for Al and dragonfly larvae for Cr were deemed to be useful species for an index measuring metal contamination among benthic animals. Bryophytes were found to be a useful species for an index of Al and Cr contamination among water plants. Bryophytes had the highest and most widely varying range of Al and Cr concentrations among benthic animals and water plants. Therefore, bryophytes were thought to be a useful species for an index of Al and Cr contamination among benthic animals and water plants.

As a result of comparing Al and Cr concentrations in bryophytes for each species, Pottiaceae possessed the highest and most widely varying range of Al and Cr concentrations. Moreover, Al concentrations in Pottiaceae in the Cu mine area and Cr concentrations in Pottiaceae in the serpentinite area were higher than those in the other areas. Furthermore, Pottiaceae could be sampled in both contaminated and non-contaminated areas.

Therefore, Pottiaceae was considered a useful species for an index measuring Al and Cr contamination among bryophytes.

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