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ZN AND FE CONTAMINATION INDEX FOR RIVER USING RIVER INSECTS AND WATER PLANTS IN THE KINOKAWA RIVER CATCHMENT

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ABSTRACT: It has not been studied whether river insects and water plants are useful for an index of Zn and Fe contamination in the Kinokawa River catchment. Useful species as an index of Zn and Fe contamination needs a high concentration in a contaminated area, a low concentration in a non-contaminated area and a high and a wide range of their concentrations. Zn and Fe concentrations of crane fly larva around the closed Cu mine were high (88 to 420 and 1,300 to 9,300 mg/kg-dry for Zn and Fe). Zn and Fe concentrations of bryophyte around the closed Cu mine were high (34 to 8,900 and 110 to 58,000 mg/kg-dry for Zn and Fe). Crane fly larva (81 to 420 and 110 to 9,300 mg/kg-dry for Zn and Fe) in river insects and bryophyte (24 to 8,900 and 110 to 58,000 mg/kg-dry for Zn and Fe) in water plants had high and a wide range of Zn and Fe concentration. Therefore, it was thought that crane fly larva and bryophyte were useful species for an index of Zn and Fe contamination. Zn concentrations of Pottiaceae and Fe concentrations of Brachytheciaceae around the Cu mine area (75 to 8,900 for Pottiaceae and 940 to 58,000 mg/kg-dry for Brachytheciaceae) were high. Pottiaceae (75 to 8,900 mg/kg-dry for Zn) and Brachytheciaceae (220 to 58,000 mg/kg-dry for Fe) had high and a wide range of metal concentration. Therefore, Pottiaceae for Zn and Brachytheciaceae for Fe were useful species for an index of metal contamination.

Keywords: Zn, Fe, Pottiaceae, Brachytheciaceae, Crane fly larva

1. INTRODUCTION

Metal concentration of river water and river sediment (soil and mud) are measured in order to investigate the influence of heavy metals for aquatic life in river. However, metal concentration of river water is always very low and is changeable depending on the change of flow rate. Heavy metals of river sediment are soluble or insoluble. Many kinds of heavy metals of river sediment elute in river water. Then, total concentration of heavy metal of river sediment does not represent the heavy metal mass transferring in river. Therefore, the metal concentrations of river water and river sediment were not always useful for an index of the influence of heavy metals for aquatic life in river. On the other hand, it is thought that the metal concentrations of river insect and water plant to be useful for investigating the influence of heavy metals for aquatic life in river because river insect and water plant intake and accumulate heavy metal from river water and sediment in the long term.

At past, metal concentrations of caddice-worm [1,2], dobsonfly larva [3,4], stonefly larva [5], mayfly larva [5,6], reed [7,8], fern [9,10], bryophyte [11,12] have been studied. However, few reports were available on useful species as metal contamination index using river insects [13,14]. Then, we have studied Cu, Co and Ni concentrations of river insects and water plants in the Kinokawa River catchment and have determined useful species for an index of Cu, Co and Ni contamination for river [15]. However, it has not been studied whether river insects and water plants are useful for an index of other metal contamination, in particular Zn and Fe, in the Kinokawa River catchment. Therefore, Zn and Fe concentrations of river insects and water plants were measured in the Kinokawa River catchment and then the relation between Zn and Fe concentration of river insects and water plants and Zn and Fe contamination for river was analyzed. Useful species as an index of metal contamination needs a high metal concentration in a contaminated area and low metal concentration in a non-contaminated area. Moreover, it needs a high and a wide range of metal concentration and also very popular.

2. STUDY AREA

Figs.1 and 2 show location of study area and the Kinokawa River catchment. The Kinokawa River is located in the center of Kinki district and flows into the Kii Channel through the Kii plain. The Kinokawa River is classified into 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 [16]. The Sanbagawa Belt composed of metamorphic

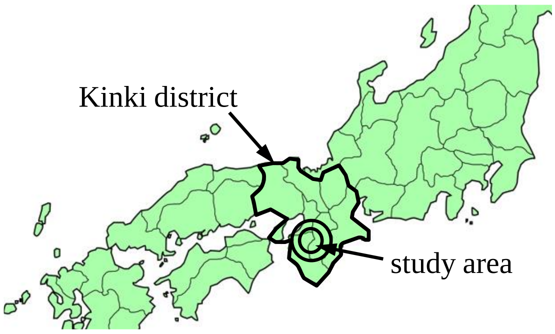

Fig.1 Location of study area.

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. The Izumi Group composed of sedimentary rocks, sandstone, mudstone and conglomerate is distributed in the northwest part of the catchment [17]. The Ryoke Complex composed of plutonic rocks, granite and gneiss is distributed in the northeast part of the catchment. In the Kinokawa River catchment, there are the closed Cu mines and serpentinite. The closed Cu mine produced a lot of Cu and Fe sulfide ore and the waste water was low pH and high concentration of sulfate with metal. The chemistry of serpentinite is quite different from the other rocks and in particular Mg and Ni concentrations of serpentinite are high.

3. STUDY METHOD

River insects and water plants in the river bed were sampled in the Kinokawa River catchment. Sampling points were shown in fig.2. Investigation period is July 2013 to April 2016. The number of sampling points was 109 points. Those sampling points were classified into three groups, the serpentinite area, the Cu mine area and the normal area. The kinds of sampled river insects were Japanese freshwater crab, caddice-worm, dobsonfly larva, dragonfly larva, stonefly larva, crane fly larva, mayfly larva and corixidae. However, crane fly larva was not sampled in the serpentinite area. The kinds of sampled water plants were reed, fern, bryophyte, Japanese knotweed and coix. However, reed was not sampled in the serpentinite area. Moreover, Japanese knotweed was not sampled in the normal area. The sampled bryophyte species were 12 species. Bryophyte species were determined by reference number 18 [18]. The kinds of sampled bryophyte were Pottiaceae, Brachytheciaceae, Marchantiaceae, Philonotis, Pelliaceae, Hedwigiaceae, Conocephalaceae, Bryaceae, Hypnaceae, Mniaceae, Thuidiaceae and Fissidentaceae. However, Marchantiaceae, Philonotis and Hedwigiaceae were not sampled in the serpentinite area. Moreover, Bryaceae and Hypnaceae were not sampled in the Cu mine area. And then, Mniaceae, Thuidiaceae and Fissidentaceae were not sampled in the serpentinite area and the Cu mine area. Zn and Fe concentrations of river insects and water plants were measured. The sampled river insects and water plants were desiccated by dryer at first. After drying, they were dissolved with concentrated nitric acid and it was

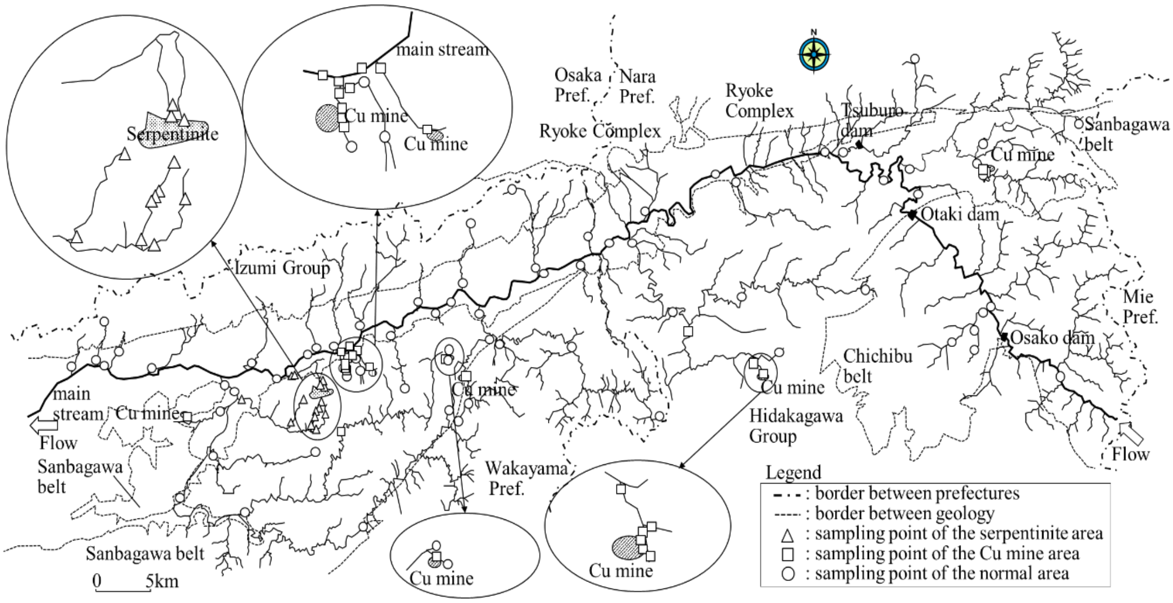

Fig.2 Study area.

filtered with the membrane filter with 0.45 micrometer of pore size before analysis. Zn and Fe concentrations of river insects and water plants were measured by ICP-AES (Seiko Instruments Inc., SPS1700HVR) in the laboratory of Wakayama University. The actual detection limit of ICP-AES is 0.01ppm for Zn and Fe. Water plants excluding bryophyte were divided into leaf, upper part stem, middle part stem, lower part stem and root and each part was separately analyzed.

4. RESULTS AND DISCUSSION

4.1 Zn Concentrations of River Insects and Water Plants

Fig.3 shows Zn concentrations of river insects and water plants. Solid mark indicates Zn concentration of water plant under the detection limit, 0.01 ppm of concentration for sample solution.

Zn concentrations of caddice-worm, dobsonfly larva, dragonfly larva, crane fly larva and corixidae in the Cu mine area were 76 to 250, 310, 88 to 260, 88 to 420 and 370 mg/kg-dry, respectively. Zn concentrations of caddice-worm, dobsonfly larva, dragonfly larva, crane fly larva and corixidae in the other areas were 79 to 180, 103 to 170, 70 to 173, 81 to 180 and 89 to 150 mg/kg-dry, respectively. Zn concentrations of reed, leaf and lower part stem and root of fern, bryophyte, stem and root of Japanese knotweed and upper and middle part stem and root of coix in the Cu mine area were 18 to 1,800, 20 to 2,200, 34 to 8,900, 24 to 220 and 23 to 940 mg/kg-dry, respectively. Zn concentrations of reed, leaf and lower part stem and root of fern, bryophyte, stem and root of Japanese knotweed and upper and middle part stem and root of coix in the other areas were 2 to 690, 8 to 130, 24 to 1,100, 7 to 40 and 2 to 130 mg/kg-dry, respectively. Therefore, their Zn concentrations in the Cu mine area were higher than those in the other areas. The closed Cu mine produced a lot of Cu and Fe sulfide ore and then the waste water was low pH and contained high concentration of sulfate with metal. It is reported that Zn concentrations of the cupriferous pyrite in the closed Cu mine in the Kinokawa River catchment were 100 to 25,000 ppm [19]. Therefore, it was thought that high Zn concentrations of caddice-worm, dobsonfly larva, dragonfly larva, crane fly larva, corixidae, reed, leaf and lower part stem and root of fern, bryophyte, stem and root of Japanese knotweed and upper and middle part stem and root of coix in the Cu mine area were caused by waste water and Cu and Fe sulfide ore from the closed Cu mines.

On the other hand, Zn concentrations of Japanese freshwater crab, stonefly larva, middle part stem of fern and Japanese knotweed leaf in the Cu mine area were 34 to 82, 137 to 440, 24 to 44

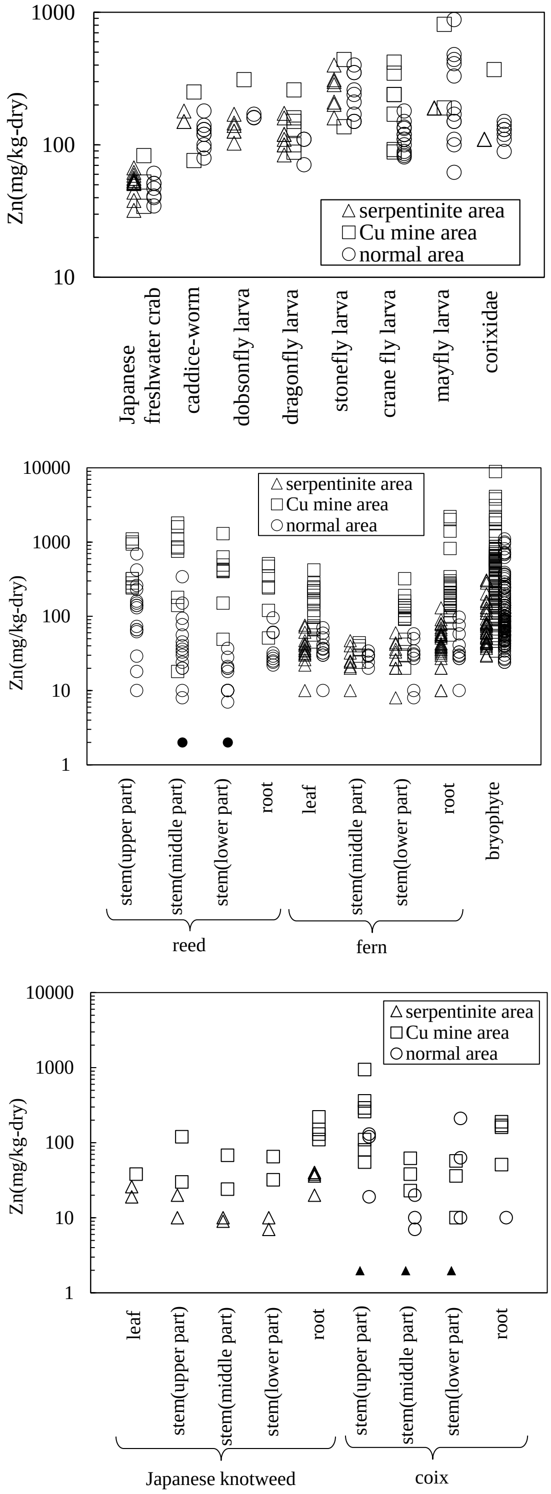

Fig.3 Zn concentrations of river insects and water plants.

and 38 mg/kg-dry, respectively. Zn concentrations of Japanese freshwater crab, stonefly larva, middle part stem of fern and Japanese knotweed leaf in the other areas were 32 to 67, 150 to 400, 10 to 47 and 19 to 26 mg/kg-dry, respectively. Therefore, their Zn concentrations in the Cu mine area were about the same as those in the other areas. Zn concentrations of mayfly larva and lower part stem of coix in the Cu mine area were 190 to 810 and 10 to 57 mg/kg-dry, respectively. Zn concentrations of mayfly larva and lower part stem of coix in the other areas were 62 to 880 and 2 to 210 mg/kg-dry, respectively. Therefore, their Zn concentrations in the Cu mine area were not higher than those in the other areas.

Zn concentrations of Japanese freshwater crab, caddice-worm, dobsonfly larva, dragonfly larva, stonefly larva, crane fly larva, mayfly larva and corixidae were 32 to 82, 76 to 250, 103 to 310, 70 to 260, 137 to 440, 81 to 420, 62 to 880 and 89 to 370 mg/kg-dry, respectively. Therefore, mayfly larva had the highest and a wide range of Zn concentration among river insects. Zn concentrations of reed, fern, bryophyte, Japanese knotweed and coix were 2 to 1,800, 8 to 2,200, 24 to 8,900, 7 to 220 and 2 to 940 mg/kg-dry, respectively. Therefore, bryophyte had the highest and a wide range of Zn concentration among water plants.

From the above results, mayfly larva had the highest and a wide range of Zn concentration among river insects. However, Zn concentrations of mayfly larva in the Cu mine area were not higher than those in the other areas. Useful species as an index of metal contamination needs a high metal concentration in a contaminated area and low metal concentration in a non-contaminated area. Therefore, mayfly larva was not useful species for an index of Zn contamination. On the other hand, crane fly larva also had high and a wide range of Zn concentration among river insects. Moreover, Zn concentrations of crane fly larva in the Cu mine area were higher than those in the other areas. Bryophyte had the highest and a wide range of Zn concentration among water plants. Moreover, Zn concentrations of bryophyte were high in the Cu mine area and were low in the other areas. Therefore, crane fly larva and bryophyte were useful species for an index of Zn contamination.

4.2 Fe Concentrations of River Insects and Water Plants

Fig.4 shows Fe concentrations of river insects and water plants. Solid mark indicates Fe concentration of water plant under the detection limit, 0.01 ppm of concentration for sample solution.

Fe concentrations of dobsonfly larva, dragonfly larva, crane fly larva and corixidae in the Cu mine area were 9,100, 280 to 9,100, 1,300 to 9,300 and 3,200 mg/kg-dry, respectively. Fe concentrations of dobsonfly larva, dragonfly larva, crane fly larva and corixidae in the other areas were 326 to 3,500, 250 to 2,500, 110 to 5,700 and 460 to 2,000 mg/kg-dry, respectively. Fe concentrations of middle and lower part stem and root of reed, leaf and root of fern, bryophyte, Japanese knotweed root and coix root in the Cu mine area were 10 to 13,000, 46 to 12,000, 110 to 58,000, 2,600 to 43,000 and 140 to 440 mg/kg-dry, respectively. Fe concentrations of middle and lower part stem and root of reed, leaf and root of fern, bryophyte, Japanese knotweed root and coix root in the other areas were 2 to 1,100, 79 to 3,500, 110 to 34,000, 1,600 to 6,000 and 130

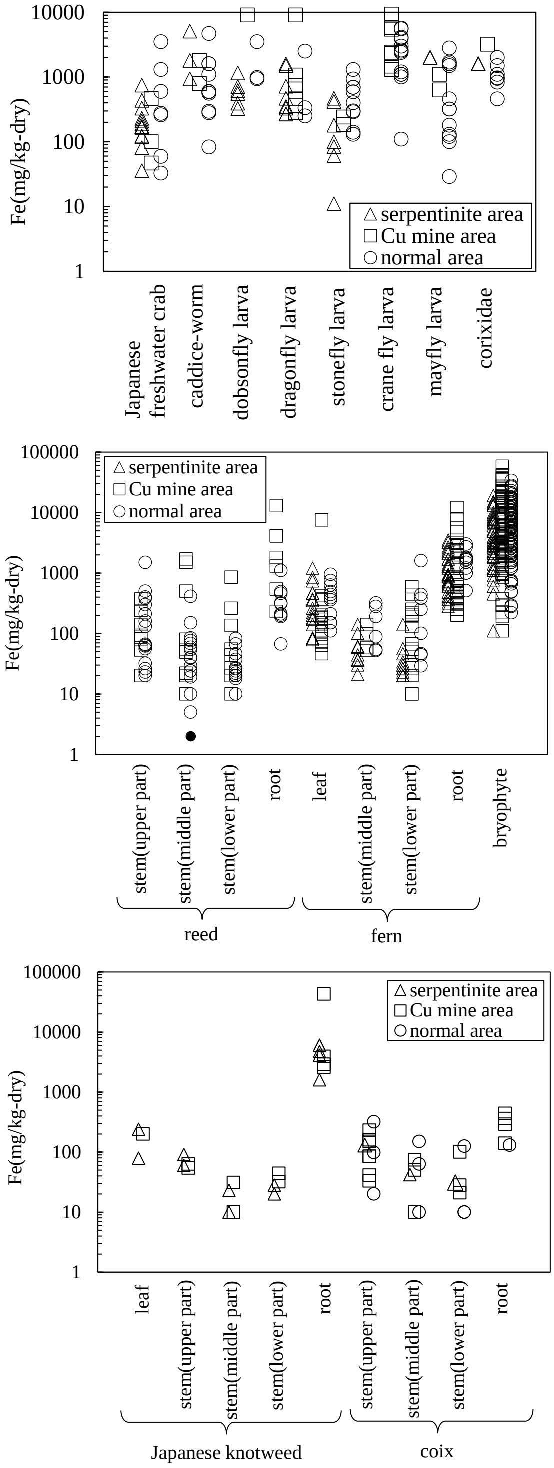

Fig.4 Fe concentrations of river insects and water plants.

mg/kg-dry, respectively. Therefore, their Fe concentrations in the Cu mine area were higher than those in the other areas. The closed Cu mine produced a lot of Cu and Fe sulfide ore and then the waste water was low pH and contained high concentration of sulfate with metal. It is reported that Fe concentration of the pyrite were 41.72% (417,200 mg/kg) [20]. Therefore, it was thought that high Fe concentrations of dobsonfly larva, dragonfly larva, crane fly larva, corixidae, middle and lower part stem and root of reed, leaf and root of fern, bryophyte, Japanese knotweed root and coix root in the Cu mine area were caused by waste water and Cu and Fe sulfide ore from the closed Cu mines. On the other hand, Fe concentrations of Japanese freshwater crab, caddice-worm, stonefly larva, mayfly larva, upper part stem of reed, fern stem and upper and middle part stem of coix in the Cu mine area were 46 to 465, 790 to 1,800, 183 to 240, 630 to 1,100, 20 to 370, 10 to 590 and 10 to 230 mg/kg-dry, respectively. Fe concentrations of Japanese freshwater crab, caddice-worm, stonefly larva, mayfly larva, upper part stem of reed, fern stem and upper and middle part stem of coix in the other areas were 32 to 3,500, 83 to 5,100, 11 to 1,300, 29 to 2,800, 20 to 1,500, 20 to 1,600 and 10 to 320 mg/kg-dry, respectively. Therefore, their Fe concentrations in the Cu mine area were not higher than those in the other areas. Fe concentrations of leaf and stem of Japanese knotweed and lower part stem of coix in the Cu mine area were 10 to 200 and 21 to 100 mg/kg-dry, respectively. Fe concentrations of leaf and stem of Japanese knotweed and lower part stem of coix in the other areas were 10 to 240 and 10 to 125 mg/kg-dry, respectively. Therefore, their Fe concentrations in the Cu mine area were about the same as those in the other areas.

Fe concentrations of Japanese freshwater crab, caddice-worm, dobsonfly larva, dragonfly larva, stonefly larva, crane fly larva, mayfly larva and corixidae were 32 to 3,500, 83 to 5,100, 326 to 9,100, 250 to 9,100, 11 to 1,300, 110 to 9,300, 29 to 2,800 and 460 to 3,200 mg/kg-dry, respectively. Therefore, crane fly larva had the highest and a wide range of Fe concentration among river insects. Fe concentrations of reed, fern, bryophyte, Japanese knotweed and coix were 2 to 13,000, 10 to 12,000, 110 to 58,000, 10 to 43,000 and 10 to 440 mg/kg-dry, respectively. Therefore, bryophyte had the highest and a wide range of Fe concentration among water plants.

From the above results, crane fly larva had the highest and a wide range of Fe concentration among river insects. Bryophyte had the highest and a wide range of Fe concentration among water plants. Moreover, Fe concentrations of crane fly larva and bryophyte were high in the Cu mine area and were low in the other areas. Therefore, crane fly larva and bryophyte were useful species for an index of Fe contamination.

4.3 Most Useful Species among River Insects and Water Plants

From figs.3 and 4, Zn concentrations of bryophyte and river insects and other water plants were 24 to 8,900 and 2 to 2,200 mg/kg-dry, respectively. Fe concentrations of bryophyte and river insects and other water plants were 110 to 58,000 and 2 to 43,000 mg/kg-dry, respectively. Therefore, bryophyte had the highest and a wide range of Zn and Fe concentrations among river insects and water plants. Moreover, Zn and Fe concentrations of bryophyte in the Cu mine area were higher than those in the other areas. River insects absorb heavy metals included in the water and food from the intestine. Reed, fern, Japanese knotweed and coix are vascular plant and absorb heavy metals included in the water and soil from the roots. Therefore, the absorption path of heavy metals of river insects and their plants are limited. However, bryophyte absorbs heavy metals from the whole surface of the body [21]. Therefore, bryophyte is easy to absorb heavy metals compared with river insects and vascular plants. Furthermore, bryophyte in the river bed absorbs heavy metals from not only river water but also high concentration of sulfate with metal from the closed Cu mines. It is thought that bryophyte is little metal consumption because growth rate of bryophyte is generally slow [22]. From the above reasons, it was thought that bryophyte had the highest and a wide range of Zn and Fe concentrations among river insects and water plants. Therefore, bryophyte was useful species for an index of Zn and Fe contamination among river insects and water plants.

4.4 Relationship between Bryophyte Species and Zn and Fe Concentrations of bryophyte

Figs.5 and 6 show Zn and Fe concentrations of bryophyte for each species. Zn concentrations of Pottiaceae and other species were 75 to 8,900 and 24 to 1,200 mg/kg-dry, respectively. Therefore, Pottiaceae had the highest and a wide range of Zn concentrations among bryophyte. Fe concentrations of Brachytheciaceae and other species were 220 to 58,000 and 110 to 37,000 mg/kg-dry, respectively. Therefore, Brachytheciaceae had the highest and a wide range of Fe concentrations among bryophyte. Zn concentrations of Pottiaceae in the Cu mine area and those in the other areas were 75 to 8,900 and 73 to 110 mg/kg-dry, respectively. Therefore, Zn concentrations of Pottiaceae in the Cu mine area were higher than those in the other areas. Fe concentrations of Brachytheciaceae in the Cu mine area and those in the other areas were 940 to 58,000 and 220 to 20,000 mg/kg-dry, respectively.

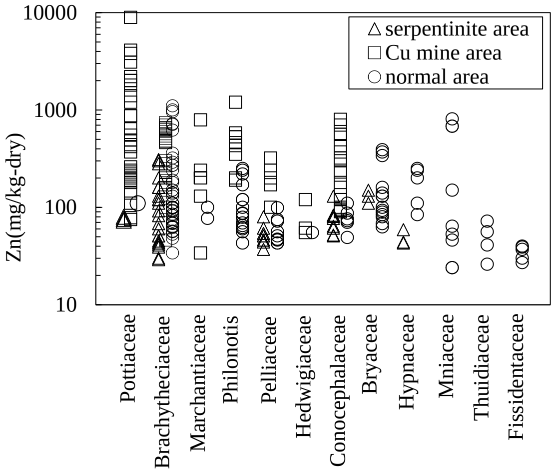

Fig.5 Zn concentrations of bryophyte for each species.

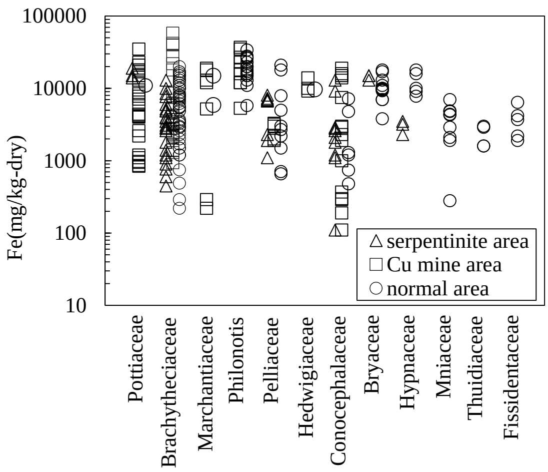

Fig.6 Fe concentrations of bryophyte for each species.

Therefore, Fe concentrations of Brachytheciaceae in the Cu mine area were higher than those in the other areas.

The closed Cu mine produced a lot of Cu and Fe sulfide ore and then the waste water was low pH and contained high concentration of sulfate with metal. It is reported that Zn concentrations of the cupriferous pyrite in the closed Cu mine in the Kinokawa River catchment were 100 to 25,000 ppm [19] and Fe concentration of the pyrite were 41.72% (417,200 mg/kg) [20]. Therefore, it was thought that high Zn concentrations of Pottiaceae and high Fe concentrations of Brachytheciaceae in the Cu mine area were caused by waste water and Cu and Fe sulfide ore from the closed Cu mines. It is reported that the tolerance ability of *Scopelophila cataractae*, a kind of Pottiaceae for Zn is high [23]. Moreover, it is known that *Scopelophila ligulata*, a kind of Pottiaceae accumulate Fe in the body [24]. Therefore, it is thought that Brachytheciaceae have the possibility of high Fe accumulation ability. And then, Pottiaceae and Brachytheciaceae can be sampled in all areas in the catchment.

From the above results, Pottiaceae was useful species for an index of Zn contamination among bryophyte. Moreover, Brachytheciaceae was useful species for an index of Fe contamination among bryophyte.

5. CONCLUSION

In this study, Zn and Fe concentration of river insects and water plants in the Kinokawa River catchment were investigated in order to find useful species for an index of Zn and Fe contamination for river. Useful species as an index of metal contamination needs a high metal concentration in a contaminated area and low metal concentration in a non-contaminated area. Moreover, it needs a high and a wide range of metal concentration and also very popular.

Zn concentrations of crane fly larva, mayfly larva and bryophyte in the Cu mine area were 88 to 420, 190 to 810 and 34 to 8,900, respectively. Zn concentrations of crane fly larva, mayfly larva and bryophyte in the other area were 81 to 180, 62 to 880 and 24 to 1,100, respectively. Zn concentrations of crane fly larva, mayfly larva and other river insects were 81 to 420, 62 to 880 and 32 to 440, respectively. Zn concentrations of bryophyte and other water plants were 24 to 8,900 and 2 to 2,200, respectively. Fe concentrations of crane fly larva and bryophyte in the Cu mine area were 1,300 to 9,300 and 110 to 58,000, respectively. Fe concentrations of crane fly larva and bryophyte in the other area were 110 to 5,700 and 110 to 34,000, respectively. Fe concentrations of crane fly larva and other river insects were 110 to 9,300 and 11 to 9,100, respectively. Fe concentrations of bryophyte and other water plants were 110 to 58,000 and 2 to 43,000, respectively.

Then, Zn and Fe concentrations of crane fly larva and bryophyte in the Cu mine area were higher than those in the other areas. Moreover, crane fly larva had the highest and a wide range of Fe concentration among river insects. Bryophyte had the highest and a wide range of Zn and Fe concentration among water plants. Mayfly larva had the highest and a wide range of Zn concentration among river insects. However, Zn concentrations of mayfly larva in the Cu mine area were not higher than those in the other areas. Useful species as an index of metal contamination needs a high metal concentration in a contaminated area and low metal concentration in a non-contaminated area. Therefore, mayfly larva was not useful species for an index of Zn contamination. On the other hand, crane fly larva also had high and a wide range of Zn concentration among river insects. Therefore, crane fly larva and bryophyte were useful species for an index of Zn and Fe contamination.

Bryophyte had the highest and a wide range of Zn and Fe concentrations among river insects and water plants. Therefore, bryophyte was useful species for an index of Zn and Fe contamination among river insects and water plants.

As a result of comparing Zn and Fe concentrations of bryophyte for each species, Zn concentrations of Pottiaceae (75 to 8,900 mg/kg-dry) and Fe concentrations of Brachytheciaceae (220 to 58,000 mg/kg-dry) were high. And then, Zn concentrations of Pottiaceae and Fe concentrations of Brachytheciaceae in the Cu mine area (75 to 8,900 for Pottiaceae and 940 to 58,000 mg/kg-dry for Brachytheciaceae) were higher than those in the other areas (73 to 110 for Pottiaceae and 220 to 20,000 mg/kg-dry for Brachytheciaceae). Moreover, Pottiaceae and Brachytheciaceae can be sampled in all areas in the catchment. Therefore, Pottiaceae was useful species for an index of Zn contamination and Brachytheciaceae was useful species for an index of Fe contamination among bryophyte.

6. REFERENCES

[1] Tochimoto H., Study of Aquatic Insect, Caddisfly, Stenopsyche marmorata as a Bio-monitor of Trace Element Contamination in Rivers and Streams: Cadmium and Copper, Journal of Japan Society on Water Environment, Vol. 17, No.11, 1994, pp.737-743.

[2] Aizawa S., Tsunoda A., Yasuda M., Tsunoda K., and Itabashi H., Concentrations of Heavy Metals in Caddisfly Larvae of the Tone River System and Their Seasonal Variations, BUNSEKI KAGAKU, Vol.58, No.4, 2009, pp.273-285.

[3] Tarras-Wahlberg N.H., Flachier A., Lane S. N. and Sangfors O., Environmental Impacts and Metal Exposure of Aquatic Ecosystems in Rivers Contaminated by Small Scale Gold Mining: The Puyango River Basin, Southern Ecuador, The Science of the Total Environment, vol.278, 2001, pp.239-261.

[4] Fujino A., and Ii H., Importance of Corydalidae as an Index of Metal Contamination of River, International Journal of Geomate, Vol.9, No.2, 2015, pp.1483-1490.

[5] Nehring R.B., Aquatic Insects as Biological Monitors of Heavy Metal Pollution, Bulletin of Environmental Contamination and Toxicology, Vol.15, Issue 2, 1976, pp.147-154.

[6] Ishizaki S., and Yamanouchi K., Benthic Communities and Heavy Metal Concentrations of Mayflies (*Baetis* spp. and *Epeorus latifolium*) in Sasu and Se Rivers, Annual Report of Nagasaki Prefectural Institute of Public Health and Environmental Sciences, Vol.30, 1987, pp.46-52.

[7] Ogino T., Endou Y., and Kurosawa K., Heavy Metal Concentration of Water, Soil and Plant in Wetland, Report of the Geological Survey of Hokkaido, Vol.72, 2001, pp.115-120.

[8] Sasaki S., Environmental Characteristics around River Area Based on Analysis of Chemical Contaminants in Reed, Soil Mechanics and Foundation Engineering, Vol.55, No.8, 2007, pp.28-30.

[9] Ogino T., and Endou Y., Basic data on the accumulation of metal component plant, Report of the Geological Survey of Hokkaido, Vol.80, 2009, pp.133-139.

[10] Okada H., Sakakibara M., Sueoka Y., and Sera K., Heavy Metals Accumulation of *Athirium yokoscense* in Polluted River Basin, Southeast Japan, NMCC Annual Report, Vol.22, 2015, pp.168-184.

[11] Aikawa Y., Nagano I., Sakamoto S., Nishiyama M., and Matsumoto S., Contents of Heavy Metal Elements in Copper Mosses: *Scopelophila ligulata*, *Scopelophila cataractae*, and *Mielichhoferia japonica* and Their Substrates, Soil Science and Plant Nutrition, Vol.45, Issue 4, 1999, pp.835-842.

[12] Laura R.E.B., Tanner B.H., and William B., Bryophytes of Adjacent Serpentine and Granite Outcrops on the Deer Isles, Maine, U.S.A., RHODORA, Vol.111, No.945, 2009, pp.1-20.

[13] Hatakeyama S., Satake K., and Fukushima S., Flora and Fauna in Heavy Metal Polluted Rivers I Density of *Epeorus latifolium* (Ephemeroptera) and Heavy Metal Concentrations of *Baetis* spp. (Ephemeroptera) Relating to Cd, Cu and Zn Concentrations, Research Report from the National Institute for Environmental Studies, No.99, 1986, pp.15-33.

[14] Ii H., and Nishida A., Effectiveness of Using River Insect Larvae as an Index of Cu, Zn and As Contaminations in Rivers, Japan, International Journal of Geomate, Vol.12, No.33, 2017, pp.153-159.

[15] Kubohara T., and Ii H., Cu Co and Ni Contamination Index for River Using River Insects and River Plants, International Journal of GEOMATE, Vol.11, Issue 26, 2016, pp.2651-2658.

[16] Ministry of Land, Infrastructure, Transport and Tourism Kinki Regional Development Bureau, http://www.kkr.mlit.go.jp/river/kasen/kinokawa.html

[17] Wakayama City Children’s Science Museum, Wakayama no Ishi, 2002, pp.7-10.

[18] The laboratory of Professor Kawakami in the Faculty of Education, Gifu Shotoku Gakuen University, http://www.ha.shotoku.ac.jp/~kawa/KYO/SEIBUTSU/syokubutsu/SogoZukan/koke/index.html

[19] Itoh S., Geochemical Study of Bedded Cupriferous Pyrite Deposits in Japan, Bulletin

of the Geological Survey of Japan, Vol.27, No.5, 1976, pp.245-377.
[20] Sakai N., Ishizaki C., Chida T., and Shimoiizaka J., A Kinetic Study of Pyrite Oxidation by Ferric Sulfate, Journal of the Mining and Metallurgical Institute of Japan, Vol.103, Issue 1192, 1987, pp.395-400.
[21] Yoshio H., Okayama University of Science, http://had0.big.ous.ac.jp/thema/moss/moss.htm
[22] Graduate School of Agricultural and Life Sciences, The University of Tokyo, https://www.a.u-tokyo.ac.jp/topics/2018/20180327-3.html
[23] Nomura T., Studies on Copper Tolerance and Cell Differentiation in *Scopelophila cataractae*, Abstract of doctoral thesis in the University of Tokyo, 2011, 4p.
[24] Nomura T., Itouga M., and Sakakibara H., Shokubutsu no Seibutsukinou wo Mochiita Kinzoku Kaisyu Gijyutsu, KAGAKU TO SEIBUTSU, Vol.52, Issue 2, 2014, pp.121-126.