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CU, CO, CR AND NI OF RIVER WATER, RIVER INSECT AND WATER PLANT IN THE KINOKAWA RIVER CATCHMENT

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ABSTRACT: Metals concentration of insect and plant were useful for evaluating metal contamination and were proposed to be an effective index as metal contamination of river. Heavy metals of water, river insect and water plant were studied in order to clarify influence of geological condition on water, insect and plant metal contamination. Cu, Co, Cr and Ni concentrations of river water were lower than those of insect and plant. Cu and Co concentrations in river insect and water plant were affected by the Cu mines because their concentrations were high in the Cu mine area. Cr and Ni concentrations in river insect and water plant were affected by serpentinite because their concentrations were high in the serpentinite area. It was found that metals concentrations in moss and plant root were effective indicator for the influence of geological condition because Cu and Ni concentrations of plant root and Co and Cr concentrations of moss indicated highest concentration and wide range.

Keywords: Heavy Metals, Serpentinite, Cu Mines, Insects, Plants

1. INTRODUCTION

Generally, the environment of water area is mainly evaluated by water quality. Moreover, most of water quality standards are established in order to keep the human life safely. However, aquatic life is being taken seriously in recent years. Therefore, in Japan, the Environmental Quality Standards for water pollution and preservation of aquatic life were established in November 2003 [1]. And then, nonylphenol was added to the Environmental Quality Standards for water pollution and preservation of aquatic life in 2012 [2]. Moreover, linear alkylbenzene sulfonic acid and their salt was added to standards in 2013 [3]. However, under the Japanese Water Quality Standard values, heavy metal from natural source was thought to influence on river life. Natural metal resource in river depended on mainly geological setting. River insect and river plants were thought to be good indicators for heavy metal environment because insect and plant concentrations were higher than those of river water.

BOD value of the Kinokawa River was less than 2 mg/l [4] because of no big factory and low population density along the river. The river catchment has some copper mines and serpentinite with high Mg, Cr and Ni concentrations. No waste water with over the Japanese Environment Quality Standard flows into the Kinokawa River. Therefore, the purpose of this study is to clarify relation between heavy metal natural resource such as mines or rock type and concentrations of river water, river insect, and river plants.

2. STUDY AREA

Fig.1 shows the location of study area. The Kinokawa River is located in the center of Kinki district and flows to west along the median tectonic line from South Nara through Kii plain into the Kii Channel. The Kinokawa River is classified into A river based on the Ministry of Land, Infrastructure, Transport and Tourism of Japan and its length and total area are 136 km and 1,750 km^2 [5].

Izumi Group composed of sedimentary rocks as sandstone, mudstone, conglomerate and et al. is distributed in the northern part of the catchment. Sanbagawa belt composed of metamorphic rocks as serpentinite, crystalline schist and et al. is distributed in the southern part. Hidakagawa Group composed of sedimentary rocks as sandstone and shale is distributed in the southeast part [6].

The Kinokawa River catchment has serpentinite and the closed Cu mines. The chemistry of serpentinite is quite different from another rocks, in particular, serpentinite has high concentration of Mg, Cr and Ni. The closed Cu mine produced a lot of Cu and Fe sulfide ore and waste water was low pH and high concentration of sulfate with metal. Then, in this study, catchments were divided into three groups, serpentinite area, Cu mine area and normal area based on the geological aspect.

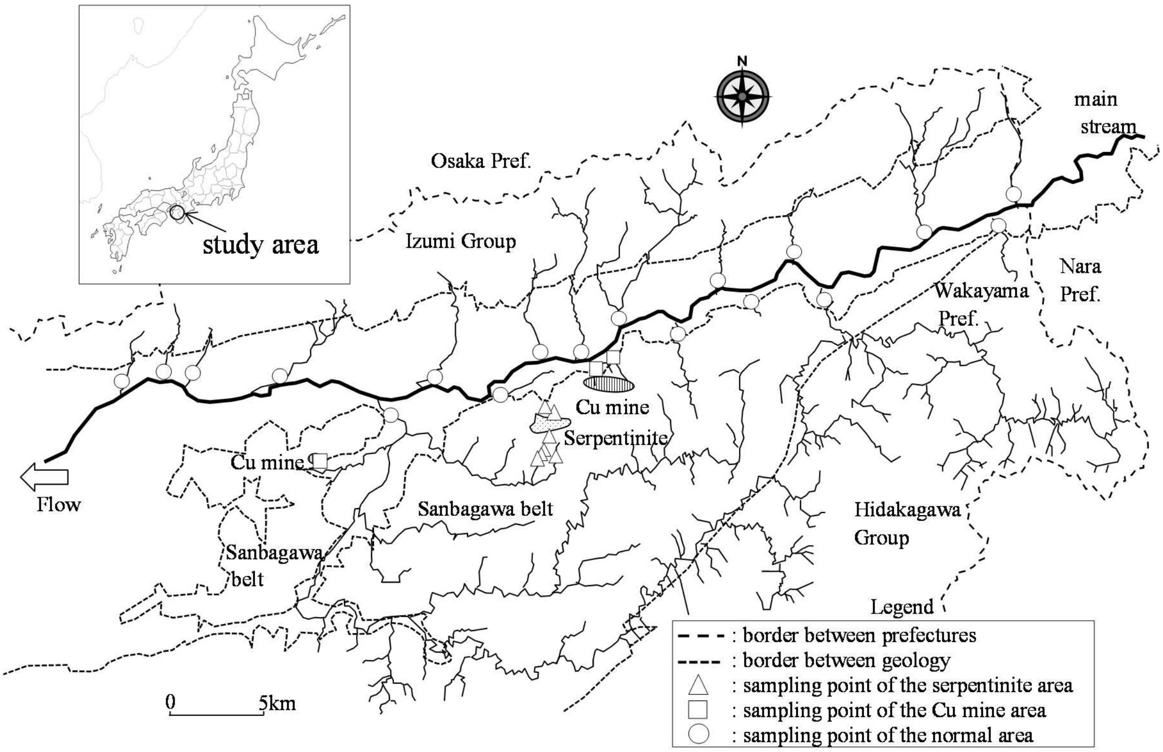

Fig.1 Study area.

3. STUDY METHOD

Chemistry of river water, river insect and water plant was studied. Mg^{2+}, Ca^{2+}, Cu, Co, Cr and Ni concentrations in river water and Cu, Co, Cr and Ni in river insect and water plant were measured.

River water samples were kept cool and it was filtered with the membrane filter with 0.45 micrometer of pore size before analysis in laboratory. 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 filtered with the membrane filter with 0.45 micrometer of pore size before analysis.

Mg^{2+} and Ca^{2+} were measured by ion exchange chromatography. Total Cu, Co, Cr and Ni were measured by ICP-AES. The actual detection limit of ICP-AES is 0.01ppm for Cu, Co, Cr and Ni.

Table.1 shows summary of field observation. The species of river insect were gammaridea, dobsonfly larva, caddice-worm, stonefly larva, dragonfly larva, crane fly larva, corixidae and rat tailed maggot. The species of water plant were fern, moss, coix, reed, Japanese silver grass, and paspalum. Water plant excluding moss was divided into upper part, middle part, lower part and root and each part is separately analyzed.

Table.1 Summery of field observation.

		the serpentinite area	the Cu mine area	the normal area	total
water	observation time	Sep.2013, Feb., Apr.2014	Dec.2013, Apr.2014	Dec.2013, Jan.2014	
	sampling points	7	3	18	28
	number of samples	14	4	18	36
river insect	observation time	July, Sep.2013, Feb., Apr.2014	Dec.2013, Apr.2014	Dec.2013, Jan.2014	
	sampling points	6	3	14	23
	number of samples	19	6	19	44
	species	gammaridea, dobsonfly larva, caddice-worm, stonefly larva, dragonfly larva	crane fly larva, dobsonfly larva, dragonfly larva, corixidae, rat-tailed maggot	crane fly larva, stonefly larva, dragonfly larva, corixidae	
water plant	observation time	Feb., Apr.2014	Dec.2013, Feb., Apr.2014	Dec.2013, Jan., Feb.2014	
	sampling points	7	3	18	28
	number of samples	33	27	73	133
	species	fern, moss	coix, reed, Japanese silver grass, fern, moss	coix, reed, paspalum	

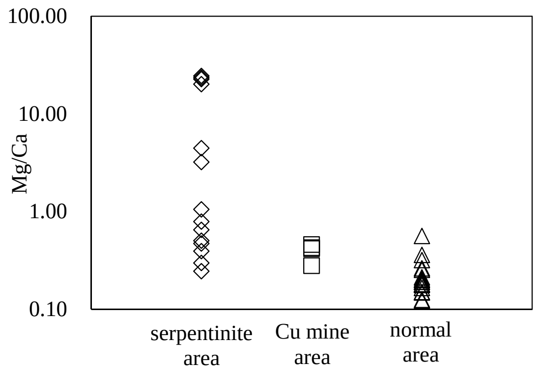

Fig.2 Mg/Ca equivalent ratios in river water.

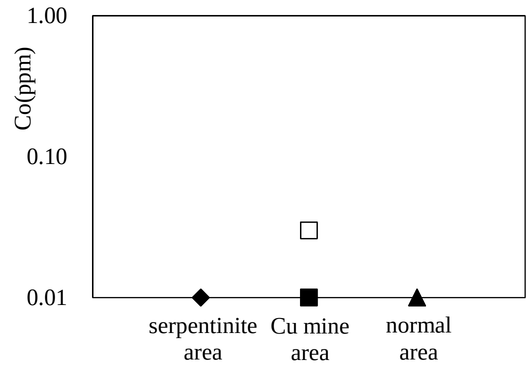

Fig.4 Co concentrations in river water.

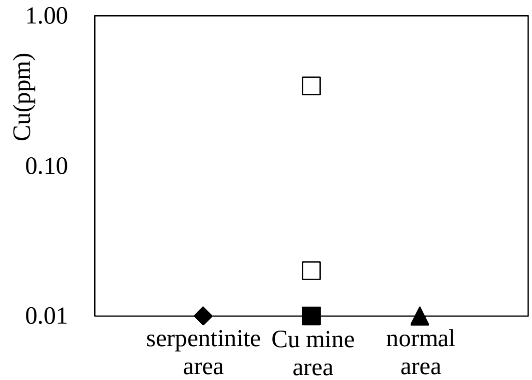

Fig.3 Cu concentrations in river water.

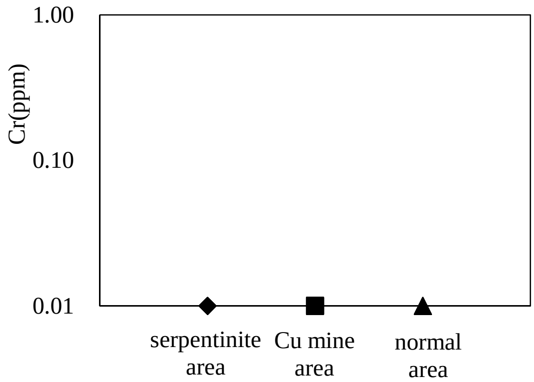

Fig.5 Cr concentrations in river water.

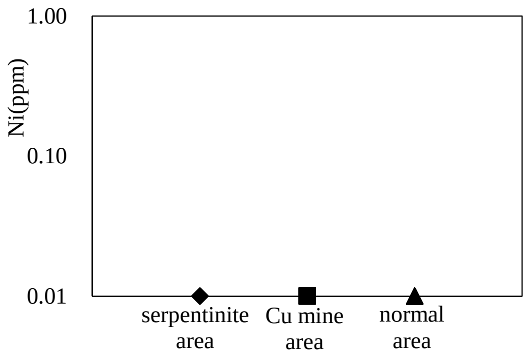

Fig.6 Ni concentrations in river water.

4. RESULTS AND DISCUSSION

4.1 Mg/Ca Equivalent Ratio in River Water

Fig.2 shows Mg/Ca equivalent ratios in river water.

Mg/Ca equivalent ratios in the serpentinite area were from 0.25 to 24, those in another two areas were from 0.12 to 0.56. Then, Mg/Ca equivalent ratios in the serpentinite area were higher than another two areas. Serpentinite contains a lot of Mg.

Therefore, river water in the serpentinite area was influenced by serpentinite.

4.2 Relationship between Heavy Metals in River Water, River Insect and Water Plant and Geological Condition

Figs.3, 4, 5 and 6 show Cu, Co, Cr and Ni concentrations in river water. Black solid markers indicate under detection limit.

Cu and Co concentrations in the Cu mine area were from under detection limit to 0.34ppm and from under detection limit to 0.03ppm, respectively. Their concentrations in another two areas were under detection limit. Then, Cu and Co concentrations in the Cu mine area were higher than another two areas. In particular, high Cu and Co concentrations were found at the mining sewage and the river water. Except high Cu and Co concentration data, Cu and Co concentrations were under detection limit in the area.

Cr and Ni concentrations were under detection limit in all areas.

Therefore, although there are Cu mines and serpentinite in the catchment, Cu, Co, Cr and Ni concentrations in river water were very low, under detection limit except some sewage and river from the Cu mine.

Figs., 7, 8, 9 and 10 show Cu, Co, Cr and Ni

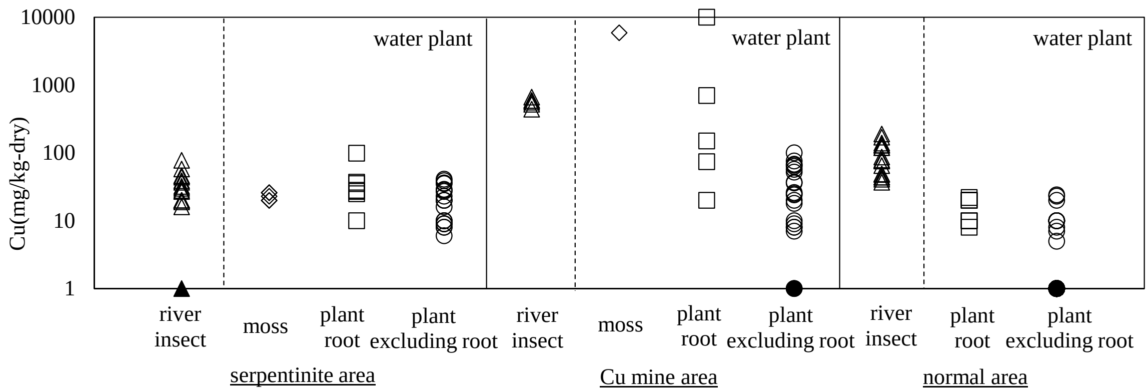

Fig.7 Cu concentrations in river insect and water plant.

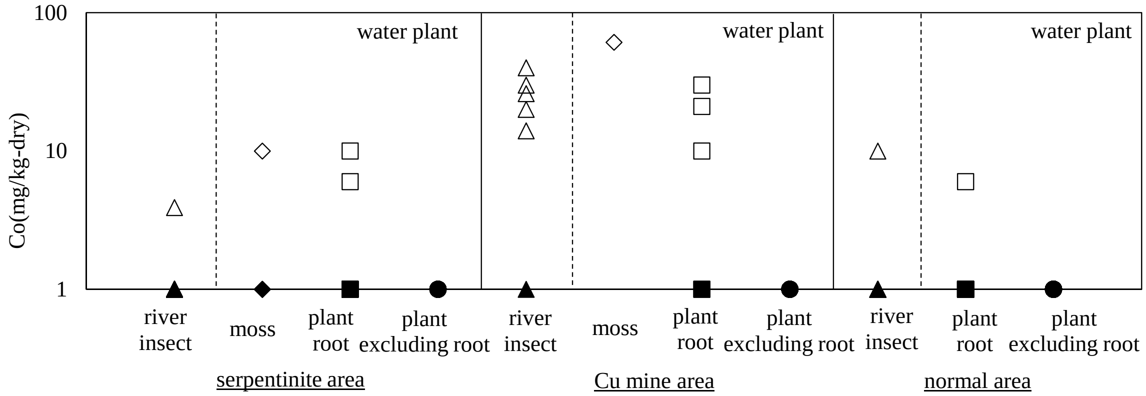

Fig.8 Co concentrations in river insect and water plant.

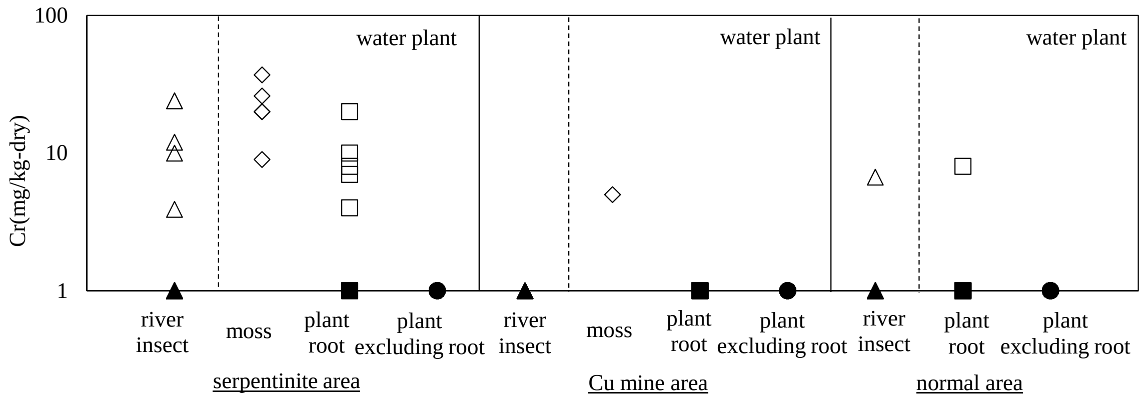

Fig.9 Cr concentrations in river insect and water plant.

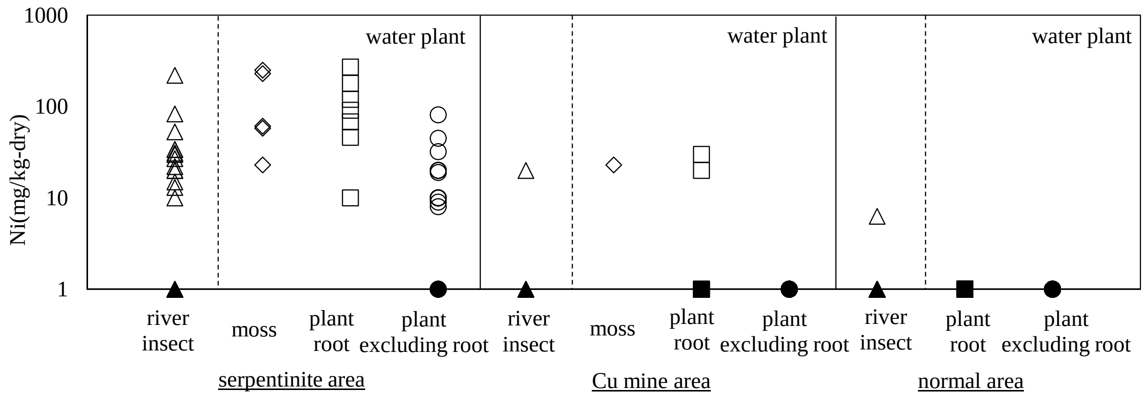

Fig.10 Ni concentrations in river insect and water plant.

concentrations in river insect and water plant. Black solid markers indicate under detection limit.

In the Cu mine area, metal concentrations of river insect were from 440 to 663 mg/kg-dry for Cu, from under detection limit to 40 mg/kg-dry for Co, respectively and metal concentrations of water plant were from under detection limit to 10,000 mg/kg-dry for Cu, from under detection limit to 61 mg/kg-dry for Co, respectively. In another two areas, metal concentrations of river insect were from under detection limit to 190 mg/kg-dry for Cu, from under detection limit to 10 mg/kg-dry for Co, respectively and metal concentrations of water plant were from under detection limit to 99 mg/kg-dry for Cu, from under detection limit to 10 mg/kg-dry for Co, respectively. Then, Cu and Co concentrations of river insect and water plant in the Cu mine area were higher than another two areas. The Cu mines in the Kinokawa River catchment have cupriferous pyrite [7]. It is known that the cupriferous pyrite contains Cu, Co, etc [8]. Therefore, Cu and Co of river insects and water plants in the Cu mine area were affected by Cu mines.

In the serpentinite area, metal concentrations of river insect were from under detection limit to 24 mg/kg-dry for Cr, from under detection limit to 220 mg/kg-dry for Ni, respectively and metal concentrations of water plant were from under detection limit to 37 mg/kg-dry for Cr, from under detection limit to 270 mg/kg-dry for Ni, respectively. In another two areas, metal concentrations of river insect were from under detection limit to 6.7 mg/kg-dry for Cr, from under detection limit to 20 mg/kg-dry for Ni, respectively and metal concentrations of water plant were from under detection limit to 8 mg/kg-dry for Cr, from under detection limit to 30 mg/kg-dry for Ni, respectively. Then, Cr and Ni concentrations in river insect and water plant in the serpentinite area were higher than another two areas. It is known that the serpentinite contains Cr [9] and Ni. Therefore, river insects and water plants in the serpentinite area were affected by the serpentinite.

Table.2 shows summary of the results. Heavy metals concentrations of insect and plant were higher than those of river water. Therefore, heavy metals in insect and plant were effective indicator for the influence of geological condition.

4.3 Compariosn of River Insect with Water Plant for Heavy Metals

Water plant were classified into moss (A), plant root (B) and plant stem and leaf (C). River insect was compared with them.

From Figs.7 and Table.2, Cu concentrations of river insect, moss, plant root and plant excluding root in all area were from under detection limit to 663 mg/kg-dry, from 20 mg/kg-dry to 5900 mg/kg-dry, from 8 mg/kg-dry to 10,000 mg/kg-dry and from under detection limit to 100 mg/kg-dry, respectively. From Figs.10 and Table.2, Ni concentrations of river insect, moss, plant root and plant excluding root in all area were from under detection limit to 220 mg/kg-dry, from 23 mg/kg-dry to 250 mg/kg-dry, from under detection limit to 270 mg/kg-dry and from under detection limit to 81 mg/kg-dry, respectively. Then, Cu and Ni concentrations of plant root indicated highest concentration and wide range. Moreover, highest metals concentrations of plant root were indicated in the Cu mine area for Cu and in the serpentinite area for Ni. Therefore, plant root was effective indicator of Cu and Ni for the influence of geological condition.

From Figs.8 and Table.2, Co concentrations of river insect, moss, plant root and plant excluding root in all area were from under detection limit to 40 mg/kg-dry, from under detection limit to 61 mg/kg-dry, from under detection limit to 30 mg/kg-dry and from under detection limit, respectively. From Figs.9 and Table.2, Cr concentrations of river insect, moss, plant root and plant excluding root in all area were from under detection limit to 24 mg/kg-dry, from 5 mg/kg-dry to 37 mg/kg-dry, from under detection limit to 20 mg/kg-dry and from under detection limit, respectively. Then, Co and Cr concentrations of moss indicated highest concentration and wide range. Moreover, highest metals concentrations of moss were indicated in the Cu mine area for Co and in the serpentinite area for Cr. Therefore, moss was effective indicator of Co and Cr for the influence of geological condition.

5. CONCLUSION

In this study, Cu, Co, Cr and Ni concentrations of water, river insect and water plant were studied in the serpentinite area, the Cu mine area and normal area of the Kinokawa River catchment in order to clarify influence of geological condition on water, insect and plant metal contamination.

It was thought that river water in the serpentinite area was affected by serpentinite because Mg/Ca equivalent ratios of river water in the serpentinite area were high.

Cu, Co, Cr and Ni concentrations of river water were lower than those of insect and plant. Cu and Co concentrations of river insect and water plant in the Cu mine area and Cr and Ni concentrations of them in the serpentinite area were high, although Cu, Co, Cr and Ni concentrations of river water in all area were under detection limit except some sewage and river from the Cu mine.

Table.2 The influence of geological condition for metals concentrations of river water, river insect and water plant.

			river water (concentration unit is ppm)	river insect	water plant		
					moss	plant root	plant excluding root
Cu	serpentinite area	concentrations (mg/kg-dry)	under detection limit	under detection limit to 78	20 to 26	10 to 99	6 to 41
		the influence of geological condition	small				
	Cu mine area	concentrations (mg/kg-dry)	under detection limit to 0.34	**440 to 663**	**5900**	**20 to 10,000**	**under detection limit to 100**
		the influence of geological condition	small	**large**			
	normal area	concentrations (mg/kg-dry)	under detection limit	37 to 190		8 to 22	under detection limit to 24
		the influence of geological condition	small			small	
Co	serpentinite area	concentrations (mg/kg-dry)	under detection limit	under detection limit to 3.9	under detection limit to 10	under detection limit to 10	under detection limit
		the influence of geological condition	small				
	Cu mine area	concentrations (mg/kg-dry)	under detection limit to 0.03	**under detection limit to 40**	**61**	**under detection limit to 30**	**under detection limit**
		the influence of geological condition	small	**large**			
	normal area	concentrations (mg/kg-dry)	under detection limit	under detection limit to 10		under detection limit to 6	under detection limit
		the influence of geological condition	small			small	
Cr	serpentinite area	concentrations (mg/kg-dry)	under detection limit	**under detection limit to 24**	**9 to 37**	**under detection limit to 20**	**under detection limit**
		the influence of geological condition	small	**large**			
	Cu mine area	concentrations (mg/kg-dry)	under detection limit	under detection limit	5	under detection limit	under detection limit
		the influence of geological condition	small				
	normal area	concentrations (mg/kg-dry)	under detection limit	under detection limit to 6.7		under detection limit to 8	under detection limit
		the influence of geological condition	small			small	
Ni	serpentinite area	concentrations (mg/kg-dry)	under detection limit	**under detection limit to 220**	**23 to 250**	**10 to 270**	**under detection limit to 81**
		the influence of geological condition	small	**large**			
	Cu mine area	concentrations (mg/kg-dry)	under detection limit	under detection limit to 20	23	under detection limit to 30	under detection limit
		the influence of geological condition	small				
	normal area	concentrations (mg/kg-dry)	under detection limit	under detection limit to 6.3		under detection limit	under detection limit
		the influence of geological condition	small			small	

Therefore, it was thought that Cu and Co of insects and plants in the Cu mine area were affected by Cu mines. Moreover, it was thought that Cr and Ni of insects and plants in the serpentinite area were affected by serpentinite.

It was thought that heavy metals in moss and plant root were effective indicator for the influence of geological condition because Cu and Ni concentrations of plant root and Co and Cr concentrations of moss indicated highest concentration and wide range.

Therefore, Cu and Ni concentrations of plant root and Co and Cr concentrations of moss were useful for determination of metal contamination and became an important index as contamination.

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