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IMPORTANCE OF CORYDALIDAE AS AN INDEX OF METAL CONTAMINATION OF RIVER

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ABSTRACT: Larva of Corydalidae, a kind of dobsonfly was useful for evaluating a metal contamination of catchment. Dobsonfly larva eats many kinds of aquatic insects as food. Then, metal derived from wide area of river soil and river water is concentrated in the dobsonfly larva for long term by food chain. The average Cu, Fe, Mn, Pb, Zn and As concentrations of dobsonfly larva under the polluted zone was high. Metal concentration of dobsonfly was clarified to be strongly influenced by river metal condition as well as mayfly and caddisfly. Cu, Fe, Mn, Pb, Zn and As concentration factors for dobsonfly were very variable depending on river metal concentration and totally the average factors for dobsonfly were almost similar values for mayfly and caddisfly. However, caddisfly and mayfly are clarified into many kinds of species and concentration factor depends on each specie. Dobsonfly is 2 or 3 species in Japan. Therefore, dobsonfly was thought to be useful for Cu, Fe, Mn, Pb, Zn and As contamination indicator.

Keywords: Metal contamination, aquatic insect, Corydalidae, larva, dobsonfly, concentration factor

1. INTRODUCTION

Metal concentration of river water is low and very changeable. There is a method to quantify a metal concentration of algae adhering to a stone of a river bottom or an aquatic life, etc. instead of analyzing water directly. It is expected that metal contamination degree of a river can be evaluated from metal concentration of an aquatic insect live. River contamination was caused by river sediments as well as river water. Then, to analyze river sediments is also necessary for determination of metal contamination. However, chemical analyzing for sediments is very difficult because of variability of concentration for each sediment grain. If an insect absorbed metal from water and river sediments is sampled and its metal concentration is analyzed, the concentration will become an index for metal contamination for river and sediments. The Baetidae, a kind of mayfly is reported to be useful as an environmental indicator for Cd and Zn and Stenopsyche marmorata, namely, a caddisfly for Cd, Zn, Al, Fe, Cu, Ni, Mn, and Co [1]. The Corydalidae, namely, dobsonfly eats many kinds of aquatic insects containing a mayfly and a caddisfly and then is thought to have a higher concentration factor. Comparing concentration factor of the dobsonfly with those for the caddisfly and the mayfly, effectiveness of the dobsonfly as a metal contamination index was studied.

The concentration factors of mayfly were 34,250 for Cu and 45,000 for Zn. The concentration factors of caddisfly were 51,900 for Fe, 6,410 for Mn, 25,490 for Zn and 18,700 for As [2]. A concentration factor of neither Cu of the caddisfly nor Pb was found.

The dobsonfly is distributed in Japan, the eastern part and southern part of Asia, South and North America, South Africa, Madagascar, Australia, and New Zealand [3]. Larva of the dobsonfly is living underwater for several years. Larva of the dobsonfly lives under a stone of a river bottom and catch the other insects [3]. The dobsonfly will be an imago in May and June [3]. Therefore, it can be expected that the metal concentration in the larva of the dobsonfly shows the pollution for river water and the river sediment around a sampling point.

2. INVESTIGATION AREA

The river sampling places for the dobsonfly were Waidani, Yoshinaga-cho, Bizen-shi, Okayama, Ota River in Yamaguchi, and the Kotako River and the Sugitani River in Nara, and the Kogawa of Kozagawa River branch in Kozagawa-cho, Higashi-Muro-gun, Wakayama.

The closed mine in the upstream of Waidani River produced gold, silver, copper, lead, zinc, and arsenic and mine waste water flowed into the river. Along the Waidani River, there were three sampling points of the lower reaches, the middle reaches and the upper reaches. Naganobori copper mine was along the upstream of Ota River in the center of Ymaguchi prefecture. The Naganobori copper mine was the historical Cu and Co mines and the Great Buddha of Nara was made of Cu produced from the Naganoboru mine.

The Kotako and the Sugitani River were the upper catchment of the Kino River. The limestone was along the fountainhead of the Kotako River. Hot spring water flowed into the Sugitani River and the sampling point was downstream of the mixing point. No mine and the Kumano acidic rocks were distributed along the Kogawa River [4]. The sampling points of the Kogawa River were in the upper reaches, the middle reaches, and the lower reaches. The Waidani and the Ota River were selected as contaminated area and the Kotako River, the Sugitani River and the Kogawa River were selected as non contaminated area.

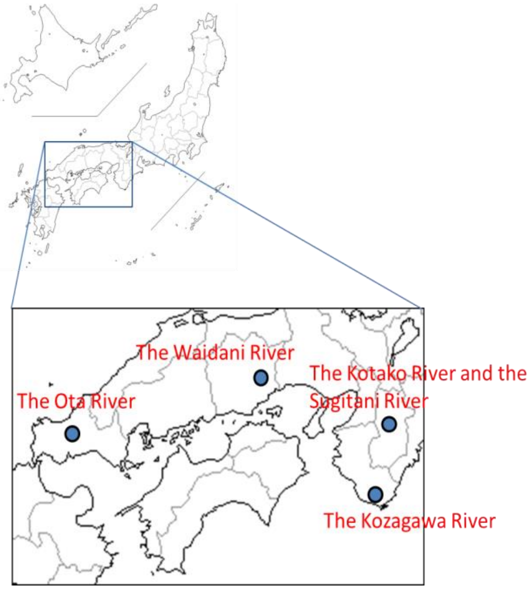

Fig. 1 Each investigation area in Honshu in Japan

3. RESEARCH METHOD

Table 1 is an investigation date. The sampling was performed in Waidani area 18th May 2013. As in this season, most of larva of dobsonfly becomes an imago, a big size larva just before imago was very rare. The last instar larva has been discovered in the Sugitani River and Kotako River 13th July 2013. It was performed in Kogawa River in 7th December 2013 and 22nd December, most dobsonfly larva was the last instar. It was performed in the Ota River 11th October 2014 and dobsonfly was also the last instar larva. Dobsonfly of the Ota River was sampled in fallen leaves accumulated in the river. At the other field, dobsnfly was found in both fallen leaves and river sediments.

Table 1 Investigation date

Month/day/year	Investigation area
May/18/2013	The Waidani River
July/13/2013	The Sugitani River and the Kotako River
December/7/2013	The Kogawa River
December/22/2013	The Kogawa River
October/11/2014	The Ota River

River water and dobsonfly were sampled and then the sampled dobsonfly was dried. Concentrated nitric acid was added to the sampled river water. The sampled dried dobsonfly was dissolved with concentrated nitric acid. After filtering the solution for river water with concentrated nitric acid and the dobsonfly solution of concentrated nitric acid, the solution was analyzed by ICP plasma-emission-spectrometry equipment.

Fig. 2 ICP plasma-emission-spectrometry equipment

An original metal concentration of the dobsonfly was calculated from weight of a dried sample and quantity of a used concentrated nitric acid using the equation (1). Concentration factor for the dobsonfly was calculated from metal concentration of the dobsonfly and metal concentration of river water using equation (2).

$$\text{The metal concentration of the dobsonfly} = \text{Analyzed result} \times \frac{\text{Quantity of concentrated nitric acid}}{\text{Weight of a sample}} \quad (1)$$

$$\text{concentration factor} = \frac{\text{Metal concentration of the dobsonfly}}{\text{Metal concentration of river water}} \quad (2)$$

4. RESULTS

Table 2 is the analyzed result of metal concentration of sampled river waters.

Cu concentrations of river water were 0.080 for the upper reaches of Waidani River, 0.021 for the middle of Waidani River, 0.006 for the lower reaches of Waidani River, N.D. for the Ota River, 0.001 for the Kotako River, 0.008 for the Sugitani River, 0.010 for the upper reaches of Kogawa River, 0.009 for the middle reaches of Kogawa River and 0.016 ppm for the lower reaches of Kogawa River.

Fe concentrations of river water were 0.067 for the upper reaches of Waidani River, 0.202 for the middle of Waidani River, 0.082 for the lower reaches of Waidani River, 0.007 for the Ota River, 0.008 for the Kotako River, 0.082 for the Sugitani River, 0.021 for the upper reaches of Kogawa River, 0.053 for the middle reaches of Kogawa River and 0.019 ppm for the lower reaches of Kogawa River.

Mn concentrations of river water were 0.007 for the upper reaches of Waidani River, 0.022 for the middle of Waidani River, N.D. for the lower reaches of Waidani River, N.D. for the Ota River, 0.001 for the Kotako River, 0.005 for the Sugitani River, 0.002 for the upper reaches of Kogawa River, 0.002 for the middle reaches of Kogawa River and 0.001 ppm for the lower reaches of Kogawa River.

Pb concentrations of river water were 0.027 for the upper reaches of Waidani River, 0.065 for the middle of Waidani River, 0.056 for the lower reaches of Waidani River, N.D. for the Ota River, N.D. for the Kotako River, 0.006 for the Sugitani River, 0.061 for the upper reaches of Kogawa River, 0.055 for the middle reaches of Kogawa River and 0.065 ppm for the lower reaches of Kogawa River.

Zn concentrations of river water were 0.700 for the upper reaches of Waidani River, 0.300 for the middle of Waidani River, 0.111 for the lower reaches of Waidani River, 0.001 for the Ota River, 0.001 for the Kotako River, 0.002 for the Sugitani River, 0.003 for the upper reaches of Kogawa River, 0.001 for the middle reaches of Kogawa River and 0.001 ppm for the lower reaches of Kogawa River.

As concentrations of river water were 0.013 for the upper reaches of Waidani River, 0.024 for the middle of Waidani River, 0.006 for the lower reaches of Waidani River, 0.008 for the Ota River, N.D. for the Kotako River, 0.028 ppm for the Sugitani River, N.D. for the upper reaches of Kogawa River, N.D. for the middle reaches of Kogawa River and N.D. for the lower reaches of Kogawa River.

Therefore, although the old closed copper mine was along the Ota River, metal concentrations of river water were not high relative to those for the non contaminated area. River metal concentrations of the Waidani area were totally higher than those of the non contaminated area. However, Fe concentration of the Sugitani River was high similar to the Waidani area

Table 2 Metal concentration of sampled river waters (ppm)

	Cu	Fe	Mn	Pb	Zn	As
The upper reaches of Waidani River	0.080	0.067	0.007	0.027	0.700	0.013
The middle reaches of Waidani River	0.021	0.202	0.022	0.065	0.300	0.024
The lower reaches of Waidani River	0.006	0.082	N.D	0.056	0.111	0.006
The Ota Riv	N.D	0.007	N.D	N.D	0.001	0.008
The Kotako Riv.	0.001	0.008	0.001	N.D	0.001	N.D
The Sugitani Riv.	0.008	0.082	0.005	0.006	0.002	0.028
The upper reaches of Kogawa River	0.010	0.021	0.002	0.061	0.003	N.D
The middle reaches of Kogawa River	0.009	0.053	0.002	0.055	0.001	N.D
The lower reaches of Kogawa River	0.016	0.019	0.001	0.065	0.001	N.D

Fig. 3 is Cu concentration of the dobsonfly larva in each investigation area. Cu concentration of the dobsonfly in the upper reaches of Waidani River was 600 ppm. Cu concentration of dobsonfly in the middle reaches of Waidani River was 300 ppm. Cu concentration of the dobsonfly in the lower reaches of Waidani River 400 ppm. It turns out that Cu concentration for the dobsonfly in the upper reaches of Waidani River was higher than those in the middle reaches and the lower reaches. Cu concentration of the dobsonfly in the Ota River was 10 ppm to 20 ppm. Cu concentration of the dobsonfly in the Kotako River and the Sugitani River was 50 ppm. Cu concentration of the dobsonfly in the upper reaches of Kogawa River was 22 ppm to 40 ppm. Cu concentration of the dobsonfly in the middle reaches of Kogawa River was 22 ppm to 35 ppm. Cu concentration of the dobsonfly in the lower reaches of Kogawa River was 15 ppm to 40 ppm.

The minimum, average and maximum of concentration factors of Cu for the dobsonfly were 76,00, 28,000, and 62,000 in the Waidani and 2,200, 6,700, and 13,000 in the Kogawa River, respectively. The concentration factor of Cu for the dobsonfly in the Ota River was not able to be calculated lack of river Cu concentration. The concentration factor of Cu for the dobsonfly in the Kotako River was 50,000. The concentration factor of Cu of the dobsonfly in the Sugitani River was 3,000.

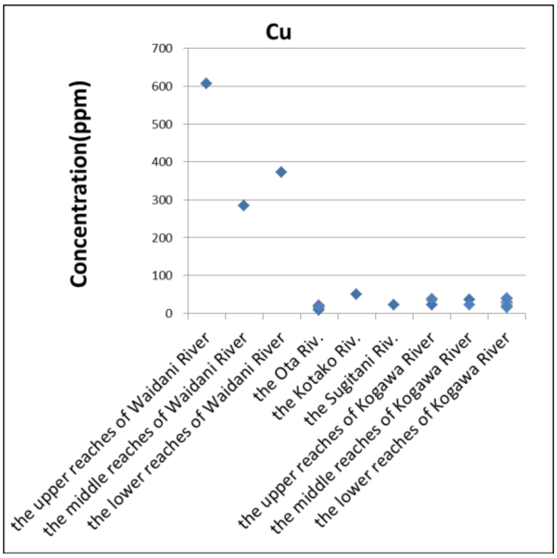

Fig. 3 Concentration of Cu for the dobsonfly larva in each investigation area (ppm)

Fig. 4 is Fe concentration of the dobsonfly larva in each investigation area. Fe concentration of the dobsonfly in the upper reaches of Waidani River and the middle reaches was 1,000 ppm. Fe concentration for the dobsonfly in the lower reaches of Waidani River was 4,000 ppm. Fe concentration of the dobsonfly in the Ota River was 20 ppm to 130 ppm. Fe concentration of the dobsonfly in the Kotako River was 1,000 ppm. Fe concentration of the dobsonfly in the Sugitani River was 3,500 ppm. Fe concentration of the dobsonfly in the upper reaches of the Kogawa was 300 ppm to 500 ppm. Fe concentration of the dobsonfly in the middle reaches of Kogawa River was 350 ppm to 500 ppm. Fe concentration of the dobsonfly in the lower reaches of Kogawa River was 300 ppm to 800 ppm.

The minimum, average and maximum of concentration factors of Fe for the dobsonfly were 4,500, 23,000, and 52,000 in the Waidani River and 3,000, 12,000, and 19,000 in the Ota River and 6,400, 34,000, and 73,000 in the Kogawa River, respectively. The concentration factor of Fe for the dobsonfly in the Kotako River was 78,000. The concentration factor of Fe for the dobsonfly in the Sugitani River was 43,000.

Fe concentration of the river water in the middle reaches was 0.053 ppm, and was higher than those in the upper reaches and the lower reaches. However, one of the Fe concentrations of the dobsonfly in the lower reaches was the highest concentration. Concentration of the dobsonfly did not relate with those in a river.

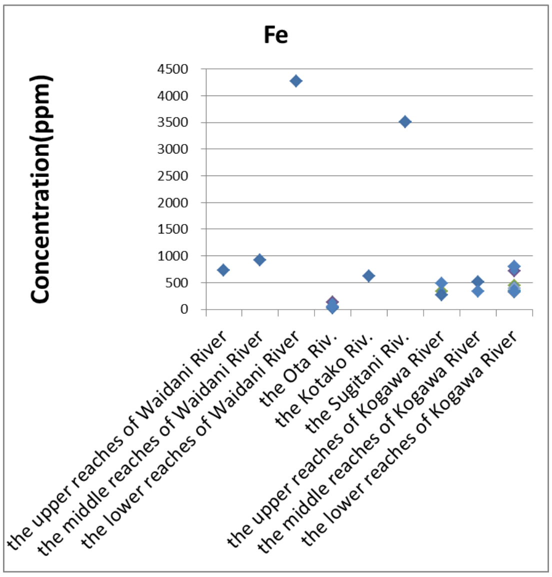

Fig. 4 Concentration of Fe for the dobsonfly larva in each investigation area (ppm)

Fig. 5 is Mn concentration of the dobsonfly larva in each investigation area. Mn concentration of the dobsonfly in the upper reaches of Waidani River and the middle reaches of the Waidani was 250 ppm. Mn concentration of the dobsonfly in the lower reaches of Waidani River was 2,000 ppm. Mn concentration of the dobsonfly in the Ota River was 5 ppm to 30 ppm. Mn concentration of the dobsonfly in the Kotako River and the Sugitani River was 250 ppm. Mn concentration of the dobsonfly in the upper reaches of Kogawa River was 50 ppm to 200 ppm. Mn concentration of the dobsonfly in the middle reaches of Kogawa River wast 50 ppm. Mn concentration of the dobsonfly in the lower reaches of Kogawa River was 25 ppm to 100 ppm.

The minimum, average and tmaximum of concentration factors of Mn for the dobsonfly were 9,800, 19,000, and 29,000 in the Waidani River and 20,000, 44,000, and 97,000 in the Kogawa River, respectively. The concentration factor of Mn for the dobsonfly in the Ota River was not able to be calculated lack of river Mn concentration. The concentration factor of Mn for the dobsonfly in the Kotako River was 140,000. The concentration factor of Mn for the dobsonfly in the Sugitani River was 29,000.

Most Mn concentration of the river water in the Kogawa River was not detected. However, Mn concentration for the dobsonfly in the Kogawa River was able to be detected to be 200 ppm and 100 ppm because of biological concentration.

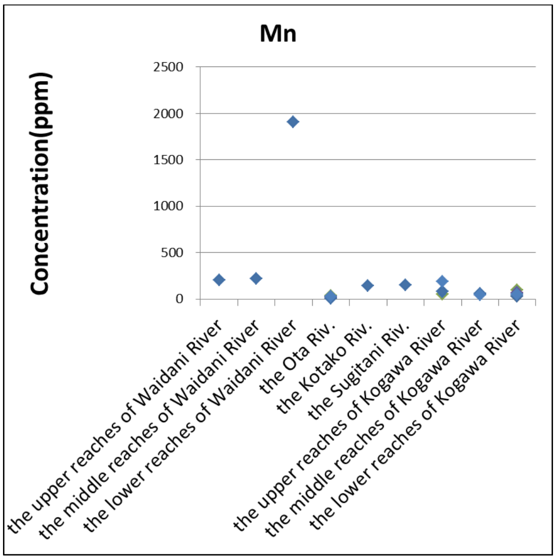

Fig. 5 Concentration of Mn for the dobsonfly larva in each investigation area (ppm)

Fig. 6 is Pb concentration of the dobsonfly larva in each investigation area. Pb concentration of the dobsonfly in the upper reaches of Waidani River was 90 ppm. Pb concentration of the dobsonfly in the middle reaches of Waidani River was 25 ppm. Pb concentration of the dobsonfly in the lower reaches of Waidani River was 10 ppm. Pb concentration of the dobsonfly in the Ota River was 1 ppm to 5 ppm. The Kotako River and the Sugitani River were also the almost same concentration. Pb concentration of the dobsonfly in the upper reaches of Kogawa River was 4 ppm. Pb concentration of the dobsonfly in the middle reaches of Kogawa River was 2 ppm to 4 ppm. Pb concentration of the dobsonfly in the lower reaches of Kogawa River was 1 ppm to 4 ppm.

The minimum, average and maximum of concentration factors of Pb for the dobsonfly were 100, 1,200, and 3,200 in the Waidani River and 20, 720, and 1,800 in the Kogawa River, respectively. The concentration factor of Pb for the dobsonfly in the Ota River, the Kotako River and the Sugitani River was not able to be calculated.

Pb concentration of the river water in the Kogawa River was 0.060 ppm. However, Pb concentration of the dobsonfly in the Kogawa River was 3 ppm, and was hardly condensed by biological concentration.

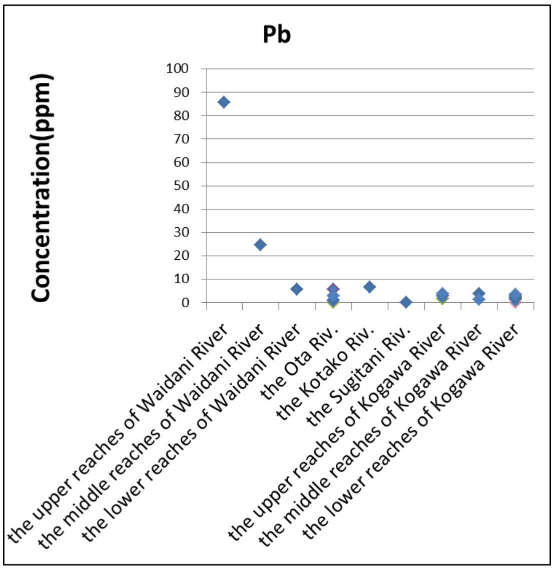

Fig. 6 Concentration of Pb for the dobsonfly larva in each investigation area (ppm)

Fig. 7 is Zn concentration of the dobsonfly larva in each investigation area. Zn concentration of the dobsonfly in the upper reaches of Waidani River was 700 ppm. Zn concentration of the dobsonfly in the middle reaches of Waidani River was 600 ppm. Zn concentration of the dobsonfly in the lower reaches of Waidani River was 1,200 ppm. Zn concentration of the dobsonfly in the Ota River was 25 ppm to 75 ppm. Zn concentration of the dobsonfly in the Kotako River and the Sugitani River was 100 ppm. Zn concentration of the dobsonfly in the upper reaches of Kogawa River was 140 ppm to 180 ppm. Zn concentration of the dobsonfly in the middle reaches of Kogawa River was 100 ppm to 160 ppm. Zn concentration of the dobsonfly in the lower reaches of Kogawa River was 70 ppm to 120 ppm.

The minimum, average and maximum of concentration factors of Zn for the dobsonfly were 1,000, 4,600, and 11,000 in the Waidani River and

25,000, 43,000, and 75,000 in the Ota River and 34,000, 62,000, and 150,000 in the Kogawa River, respectively. The concentration factor of Zn for the dobsonfly in the Kotako River was 120,000. The concentration factor of Zn for the dobsonfly in the Sugitani River was 57,000.

Most Zn concentration of the river water in the Kogawa River was not detected. However, Zn concentration of the dobsonfly in the Kogawa River was 140 ppm because of biological concentration as well as Mn.

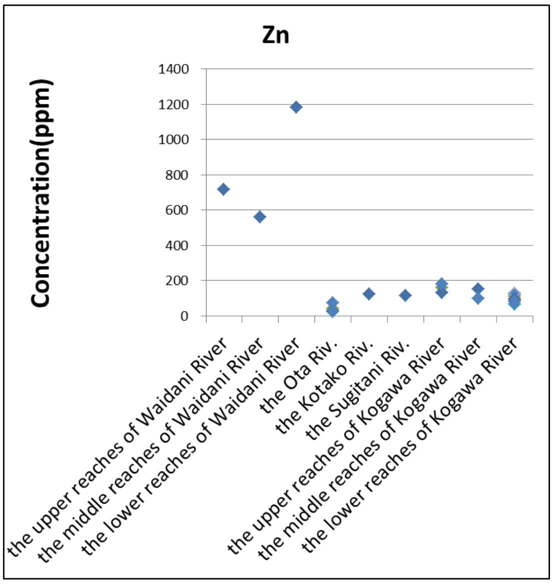

Fig. 7 Concentration of Zn for the dobsonfly larva in each investigation area (ppm)

Fig. 8 is As concentration of the dobsonfly larva in each investigation area. As concentration of the dobsonfly in the upper reaches of Waidani River was 250 ppm. As concentration of the dobsonfly in the middle reaches and the lower reaches of Waidani River was 220 ppm. As concentration of the dobsonfly in the Ota River was 1 ppm. As concentration of the dobsonfly in the Kotako River and the Sugitani River was 25 ppm. As concentration of the dobsonfly in the upper reaches of Kogawa River was 0.5 ppm to 2 ppm. Most As concentration of the dobsonfly in the middle reaches of Kogawa River was not detected. As concentration of the dobsonfly in the lower reaches of Kogawa River was 1 ppm to 5 ppm.

The minimum, average and maximum of concentration factors of As for the dobsonfly were 9,000, 22,000 and 36,000 in the Waidani River and 60, 80, and 100 in the Ota River and 300, 940, and 1800 in the Kogawa River, respectively. The concentration factor of As for the dobsonfly in the Kotako River was not able to be calculated lack of river As concentration. The concentration factor of As for the dobsonfly in the Sugitani River was 1000.

As concentration of the river water in the Kogawa River was not detected. However, As concentration of the dobsonfly in the Kogawa River was 3 ppm, and As can also be concentrated in the body because of a biological concentration as well as Mn or Zn.

Therefore, although the old closed copper mine was along the Ota River, metal concentrations of dobsonfly were not high relative to those for the non contaminated area. Dobsonfly metal concentrations of the Waidani area were totally higher than those of the non contaminated area. However, Fe concentration of dobsonfly in the Sugitani River was high similar to the Waidani area.

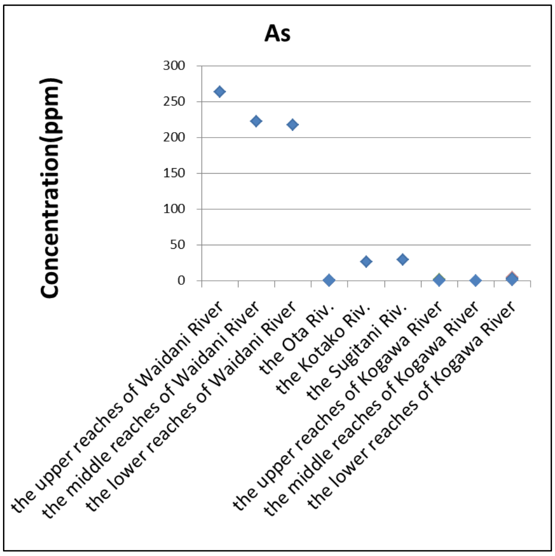

Fig. 8 Concentration of As for the dobsonfly larva in each investigation area (ppm)

Table 3 is the concentration factor of heavy metals for mayfly, caddisfly and dobsonfly. Concentration factor needs river and insect concentrations of metal. However, Cu, Mn, Pb and As concentrations for some river water were under the detection limit. Theefore, the maximum concentration factors of Cu, Mn, Pb and As can not be calculated. The maximum concentration factors of Fe and Zn for the dobsonfly were 78,000 and 150,000 which were higher than concentration factors of both mayfly and caddisfly.

The average concentration factors of Cu, Fe, Mn, Pb, Zn, and As for the dobsonfly were 12,000, 31,000, 46,000, 800, 53,000 and 5,200. The minimum concentration factors of Cu, Fe, Mn, Pb, Zn, and As for the dobsonfly were 2,200, 3,000, 9,800, 20, 1,000 and 60. Cu concentration factor for mayfly were over the average concentration facor for dobsonfly. Zn concentration factor for mayfly was similar value of the average value for dobsonfly. Fe and As concentration factors for caddisfly were over the average values for dobsonfly. Mn and Zn concentration factors for caddisfly were lower than the average values for dobsonfly. All metal concentration factors for mayfly and caddisfly were higher than the minmum concentration factors for dobsonfly. Therefore, metal concentration factors for donbsonfly were very variable depending on river metal concentration and totally the average factors for dobsonfly were almost similar values for mayfly and caddisfly.

Table 3 The concentration factor of heavy metals for caddisfly, dobsonfly and mayfly larva

Mayfly			
Cu	34,250		
Zn	45,000		
Caddisfly			
Fe	51,900		
Mn	6,410		
Zn	25,490		
As	18,700		
Dobsonfly			
	Minimum	Average	Maximum
Cu	2,200	12,000	—
Fe	3,000	31,000	78,000
Mn	9,800	46,000	—
Pb	20	800	—
Zn	1,000	53,000	150,000
As	60	5,200	—

5. DISCUSSION

The metal concentrations for river water and the dobsonfly in the polluted zone and the non-polluted zone were measured. It turns out that all metal concentrations for the dobsonfly and river waters in the Waidani area were higher than those in the non-polluted zone. In the waidani area, muck and mine dump were found at the upper reaches of Waidani River and muck and mine dump were thought to bring out river and insect metal contamination.

On the other hand, all metal concentrations for the dobsonfly and river waters in the the Ota River were low similar to the non contaminated area. Therefore, although there are along the closed old mine in the Ota River, the Ota River was not metal contaminated.

The Fe concentration of both dobsonfly and river water in Sugitani River were high similar to those of the Waidani area. Therefore, Fe contamination source was thought to be hot spring.

The average concentrations of Cu, Fe, Mn, Pb, Zn and As of the dobsonfly in the non-polluted zone were 28, 468, 60, 2, 117 and 2 ppm, respectively. The average concentrations of Cu, Fe, Mn, Pb, Zn and As of the dobsonfly in the Wanidani area were 421, 1970, 775, 38, 820 and 234 ppm, respectively. Metals, Cu, Fe, Mn, Pb, Zn and As were clarified to be concentrated in a body of the dobsonfly larva.

The average of the concentration factor of Cu for the dobsonfly was 12,000 and it was lower than 34,250 of the mayfly. The average of the concentration factor of Mn for the dobsonfly was 46,000 and it was higher than 6,410 of the caddisfly. The average of the concentration factor of Zn for the dobsonfly was 53,000 and it was higher than 25,490 of the caddisfly and the mayfly. The average of the concentration factor of Fe for the dobsonfly was 31,000 and it was lower than 51,900 of the caddisfly. The average of the concentration factor of As for the dobsonfly was 5,200 and it was lower than 18,700 of the caddisfly.

Cu, Fe, Mn, Pb, Zn and As concentration factors for donbsonfly were very variable depending on river metal concentration and totally the average factors for dobsonfly were almost similar values for mayfly and caddisfly. High concentration factor is useful for detecting metal contamination. Then, dobsonfly, mayfly, and caddisfly were candidate for indicator insect for metal contamination of river. Caddisfly and mayfly were clarified into many kinds of species and concentration factor depends on each specie [1],[2],[3]. Dobsonfly is 2 or 3 species, *Protohermes grandis*, *Parachauliodes japonicus*, and *Parachauliodes continentalis* in Japan. Terefore, dobsonfly was better than caddisfly and mayfly for indicator of Cu, Fe, Mn, Pb, Zn and As contamination sensor.

6. CONCLUSION

Larva of Corydalidae, a kind of dobsonfly was useful for evaluating a metal contamination of catchment. Metal concentration of river water was low and very changeable. River water contamination was caused by river sediments. However, chemical analyzing for sediments is very difficult to reach average values because of variability of sediment metal concentration.

However, as dobsonfly eats many another insects in river and lives in several years in river, metal derived from wide area of river sediment and from river water for long term is concentrated in dobsonfly body by food chain. It is easy to analyze metal concentration of dobsonfly because of high concentration factor. As a result, the average concentrations of Cu, Fe, Mn, Pb, Zn and As of the dobsonfly in the contaminated area were 421, 1970, 775, 38, 820 and 234 ppm, respectively. The average concentrations of Cu, Fe, Mn, Pb, Zn and As of the dobsonfly in the non-polluted zone were 28, 468, 60, 2, 117 and 2 ppm. Metals, Cu, Fe, Mn, Pb, Zn and As were clarified to be concentrated in a body of the dobsonfly larva. Metal concentration difference between polluted and the non-polluted areas was quite clear and then, dobsonfly was clarified to be very useful for index of metal contamination.

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