Cu, Zn and As pollution of river insect, plant and water along the metal mine tailing in Waidani area, Okayama prefecture, Japan

Hiroyuki Ii[1*], Shota Kumano[2], and Akio Nishida[3]

[1] *Faculty of Systems Engineering, Wakayama University, 640-8500, Wakayama, Japan*
[2] *Undergraduate School, Faculty of Systems Engineering, Wakayama University, 640-8500, Wakayama, Japan*
[3] *Graduate School, Faculty of Systems Engineering, Wakayama University, 640-8500, Wakayama, Japan*
**Corresponding author's e-mail: hiro@center.wakayama-u.ac.jp,*

Abstract

Comparing metal concentration and distribution for river insect larva in metal contaminated and not contaminated areas, dobsonfly was clarified to be an effective indicator for metal contamination. The Waidani area was selected as metal contaminated area. Although the maximum concentration of effluent for Cu, Zn and As was 0.18, 1.5 and 0.07 mg/l, under the Japanese Effluent Standard, the maximum metal load for Cu, Zn and As reached 35, 250 and 9 kg per year, abundant of Japanese diving beetles, were only found and then specialized condition was thought to be made by the effluent. Cu, Zn and As concentrations of dobsonfly and the other river insect larva were measured in the mine areas including the Waidani mine, limestone area and not contaminated area. Dobsonfly, just one specie, *Protohermes grandis,* was able to cover wide concentration range for Cu (several 10 to several 1000 ppm), Zn (several 100 to several 1000 ppm) and As (0.000 to 400 ppm) and had a wide distribution. Then, its concentration was depended on metal contamination. Although the other insects had wide concentration ranges and wide distributions as well as dobsonfly, they have many kinds of species. Therefore, their concentration did not depend on metal contamination but also species.

Keywords: Metal pollution, dobsonfly, mine, river insect larva

Introduction

Many papers about metal concentration of river insect larva were published and high concentration factor of heavy metal was found for many kinds of insects (Tochimoto H., *et .al* 1981; Hatakeyama S., *et al.* 1990; Hickey C.W. and Golding L.A. 2002). In particular, influence of metal from waste water or tailing on mines on river insects and relation between metal concentration for soil and water and metal concentration of insect were studied (Hatayama N. 2011; Iwasaki Y., *et al.* 2009; Leland H.V., *et al.* 1989). As a result, metal concentration of river insect larva was very high relative to no contaminated area and then, metal accumulation mechanism was studied using nitrogen and carbon stable isotope (Watanabe K., Yamamoto N., Kusano H. And Omura T. 2005).

Although a monitoring of water and soil is important for evaluating contamination, it spends long term sampling and large number of sampling for determining average value of metal concentration for water and soil because water and soil metal concentrations are variable with time and place. Metal concentration of river insect is higher than those of water or soil because of high bioconcentration factor for insects. River insect larva lives in a river for several years and its food from derived from upstream to the living point can cover wide metal information. Then, to measure metal concentration of insect larva is more effective to water and soil for time, area and concentration.

Dobsonfly is a common river insect larva in Japan as well as trichoptera. Dobsonfly is carnivorous with big jaws and lives in a river for 2 to 3 years and then its metal concentration is thought to depend on information for wide area and long term as well as trichoptera. In Japan, metal concentration for trichoptera was measured and its metal concentration was proposed for indicator organism for environmental pollution (Aizawa S., *et al*. 1994; Aizawa S., *et al*. 2009). However, trichoptera has many kinds of species and it is not easy to determine each species. Dobsonfly has just two main species, *Protohermes grandis* and *Parachauliodes continentalis* in Japan. Dobsonfly is thought to be more effective than trichoptera as for classification. Then the purpose of this study is to evaluate possibility of dobsonfly as indicator for metal environmental pollution.

High bioconcentration factor for metal, wide distribution and commonplaceness, and metal concentration of dobsonfly depending on metal concentration for soil and water are thought to be necessary for the evaluation of dobsonfly as indicator for metal contamination. Then, insect larva containing dobsonfly was sampled at both contaminated and no contaminated areas and their metal concentrations were measured. Comparing dobsonfly with the other insect, dobsonfly was evaluated to be indicator for metal contamination from their abundance and metal concentration range.

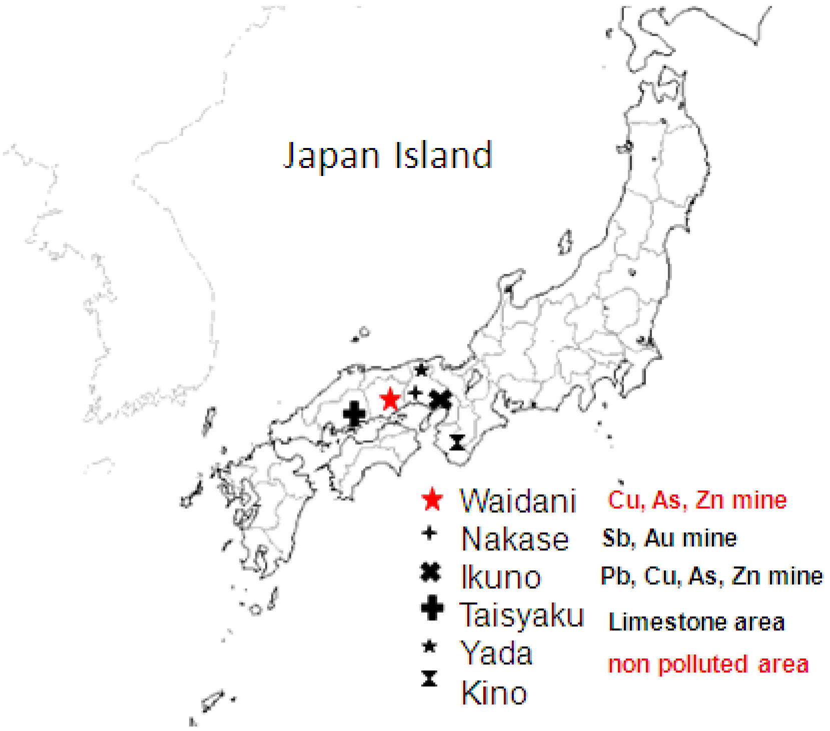

Figure 1 Study area. Mine: Waidani, Ikuno, and Nakase, Limestone:Taisyakukyo, No mine area: Yada, Kino.

Materials and methods

Figure 1 shows sampling sites. In this study, the closed mine area was selected to be metal contamination sites because drainage water and waste rocks from the mine contain metal higher than the other areas. Then, selected three metal mine areas were the Waidani area, Nakase and Ikuno mines.

In the Waidani area in Okayama prefecture, there were the closed some small copper mines operated till more than 70 years ago and waste rock containing ores and slag was disposed along the top of valley with no protection. Pyrite FeS_2, spharelite ZnS, chalcopyrite $CuFes_2$

and arsenopyrite FeAsS were found in the waste rocks. River insect larva was sampled along the downstream of the valley in May, June, November and December 2013. River water was sampled and flow rate was measured from December 2011 to March 2014.

The closed Nakase and Ikuno mines in Hyogo prefecture were at the east of the Waidani mine area. The Nakase mine produced Sb from stibnite Sb_2S_3 and Au from native gold and the Ikuno mine produced Au from native gold, Ag from Ag sulfide, Sn from Sn oxide and Sn sulfide, Cu from chalcopyrite, Pb from galena and Zn from spharelite. The other metal minerals were pyrite and arsenopyrite. River insect larva in the rivers around the mines was sampled in May 2013.

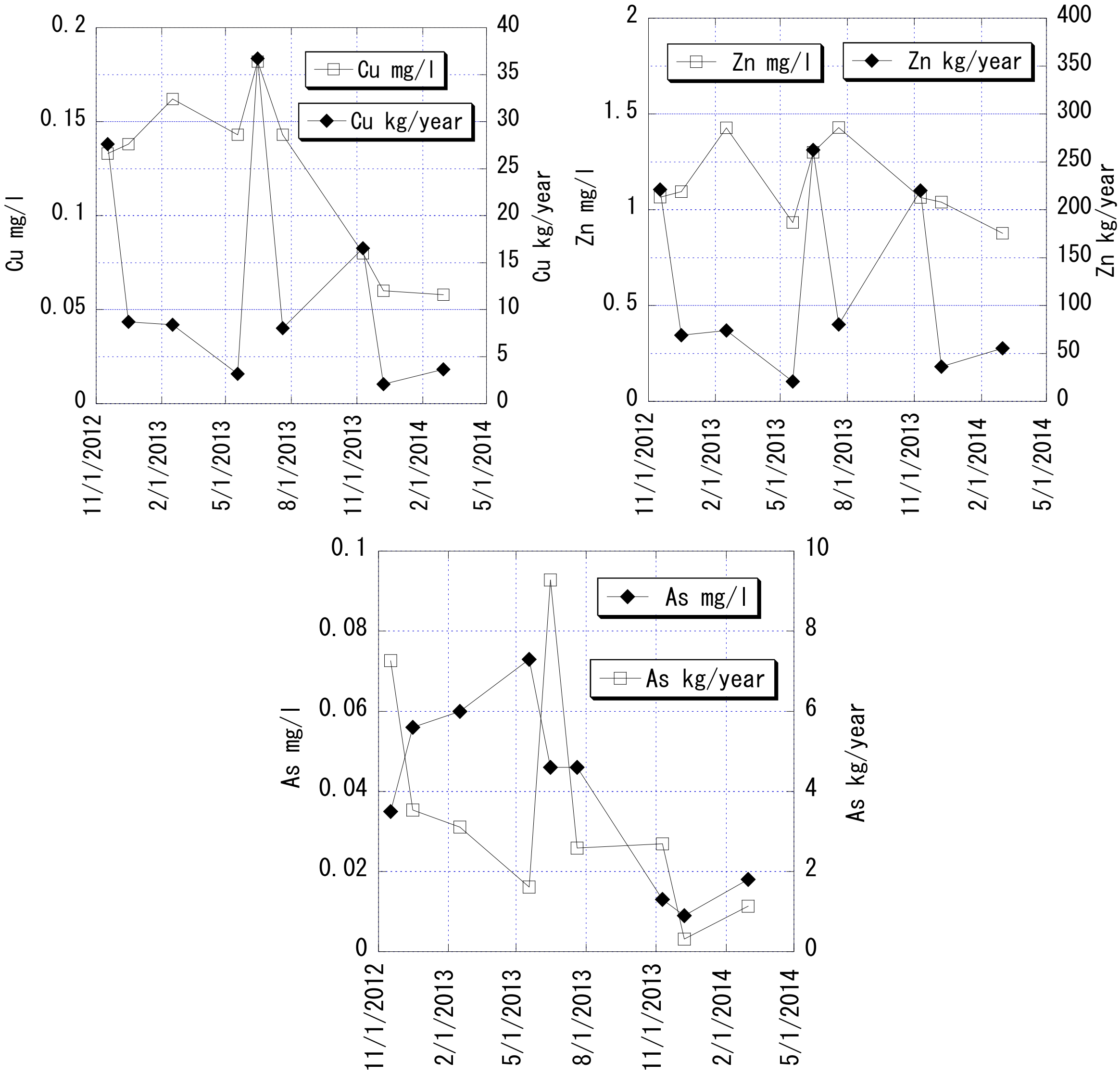

Figure 2, 3 and 4 Cu, Zn and As concentrations and their loads for waste water from the tailing in the head of the valley from November 2011 to March 2014In the Waidani mine area.

No metal contamination sampling was performed along the Taisyaku Valley (limestone valley) in Okayama prefecture, the Yada River in Hyogo prefecture and the upstream of the Kino River in Nara prefecture. River water and river insect larva were also sampled at the Taisyaku Valley in August 2013, the Yada River in July and December 2012 and the Kino River in December 2013.

Sampled insect larva was dried and then dissolved with concentrated nitric acid solution. The solution after filtration was analyzed to be metal concentration by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy). River water was also analyzed by ICP-AES.

Results and Discussion

Figure 2, 3 and 4 show Cu, Zn and As concentrations and their loads for waste water from the tailing in the head of the valley from November 2011 to March 2014 in the Waidani mine area. The maximum Cu, Zn and As concentrations were approximately 0.18, 1.5 and 0.07 mg/l and under the Japanese Effluent Standard (3 mg/l for Cu, 2 mg/l for Zn and 0.1 mg/l for As). The calculated maximum Cu, Zn and As loads reached approximately 35, 250 and 9 kg per year and metal load was not small for the small catchment with 3km length. At the several points down the stream of the valley, river insect larva was sampled to evaluate influence of river water metal on river larva insect. However, in the head of the valley, small number of Japanese diving beetle was only found with neither dobsonfly nor trichoptera. It was thought to indicate a very specialized environment although metal concentration of effluent was under the Japanese Effluent Standard.

Figure 5 show sampling points and sampled insects. "Wai S" is a south river from the waste rock place in the Waidani mine. "Up", "Me", and "Do" show upstream, medium stream and downstream of the river. "Do" was 3 km from the waste rock. "Wai N" is a nouth river from the waste rock place in the Waidani mine. "He" is the waste rock place at the head stream.

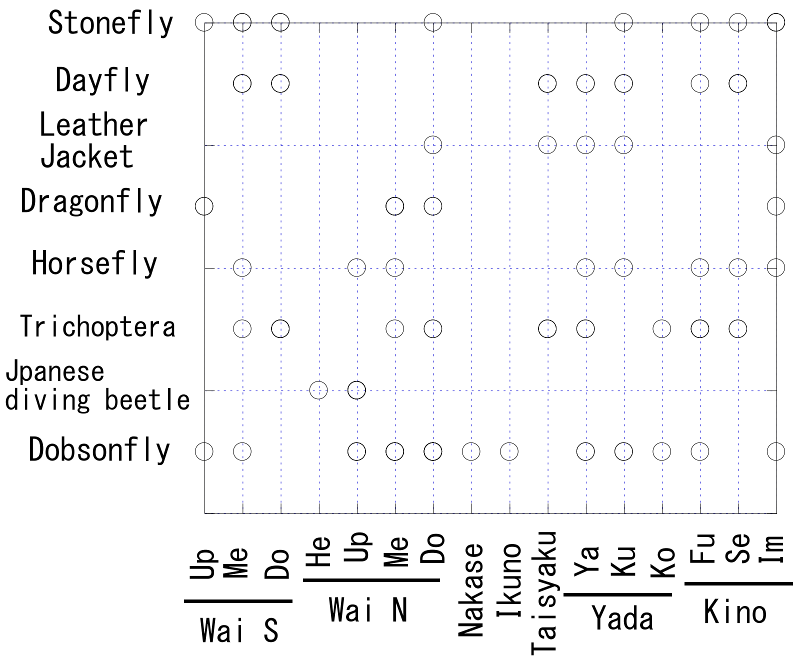

Figure 5 Sampling points and sampling sites.

"Ya", "Ku", and "Ko" in the Yada River are branch rivers, the Yamada River, Kumasaka River, and Konyo River. "Fu", "Se", and "Im" are along the Kino River. At the "He" site, dozens Japanese diving beetle were found with no other river insect larva. "Up" in the "Wai N" is close to "He", 20 m downstream. At the Up in the Waidani N there were dobsonfly and a lot of Japanese diving beetle and horsefly. From figure 5, dobsonfly is widely distributed excluding "He" and the Taisyakukyo. Taisyakukyo is limestone area. Dobsonfly is a just one species, *Protohermes grandis*. Trichoptera, stonefly and horsefly also were widely distributed. Leather jacket was not found in the mine areas. Then, dobsonfly can cover wide area including mine area excluding the Taisyakukyo, limestone area.

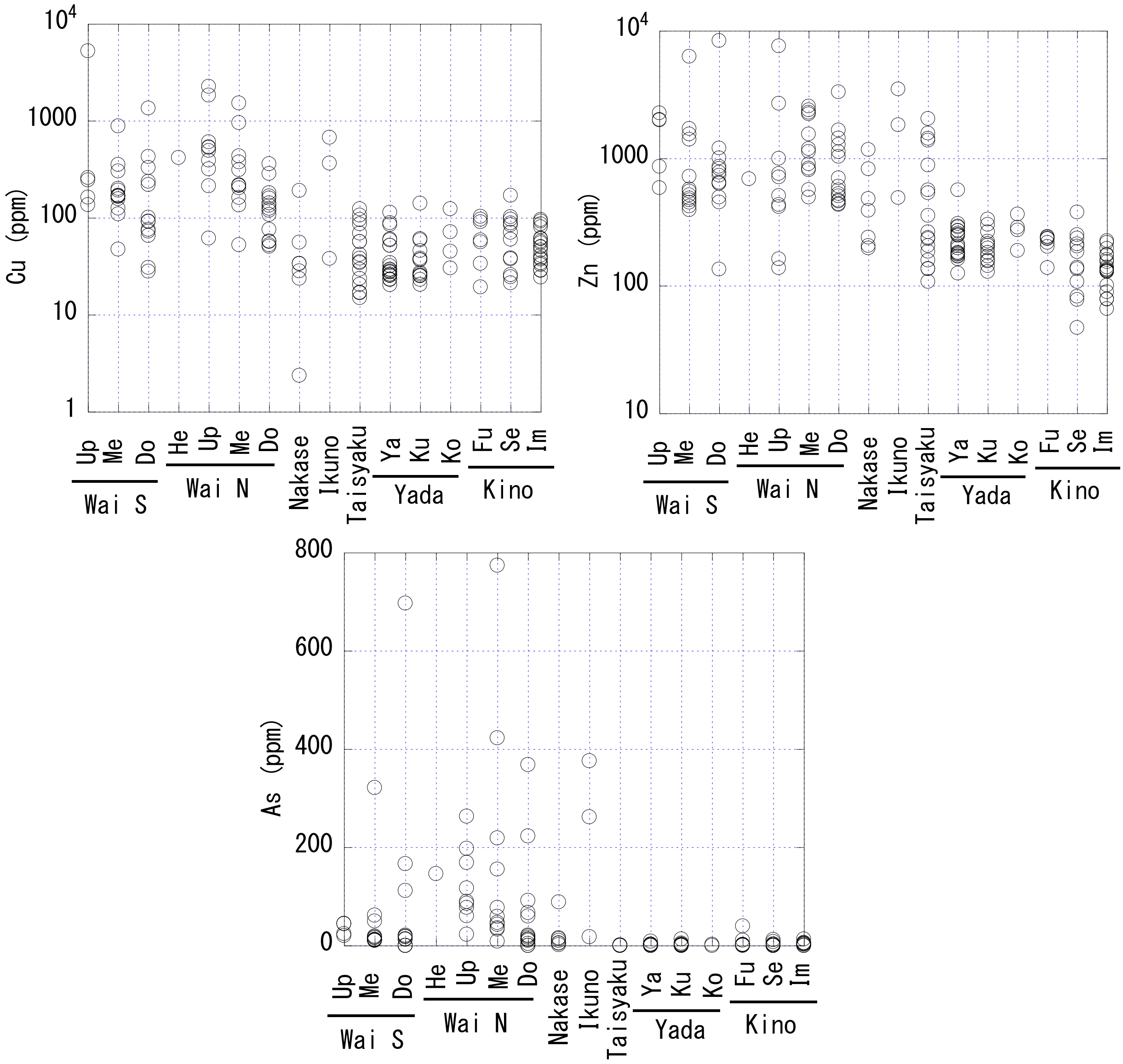

Figure 6, 7 and 8 Cu, Zn and As concentrations under dry weight samples.

Figure 6, 7 and 8 show Cu, Zn and As concentrations under dry weight samples for all sampled river insect. Cu concentrations of river insect larva in the Waidani north area were several 10 to several 1000 ppm and decreased from upstream to downstream. Cu concentrations in the Waidani south area also were several 10 to several 1000 ppm. Cu concentrations in the Ikuno mine area were several 10 to several 100 ppm. Cu concentration in the Taisyakukyo, Yada and Kino River, were uniform, 10 to 100 ppm and then Cu concentrations in mine area were higher than those in no mine area excluding the Nakase mine. The Nakase mine did not produce Cu although small amount of chalcopyrite is listed as a metal mineral. As a result, Cu concentration for river insect larva was thought to depend on the environment metal concentration. Although Cu concentration for river water in the head of the valley was under the Japanese Effluent Standard, Cu concentration for river insect larva even 3 km downstream were higher than those in no contamination area. Then, river insect is thought to be effective for indicator as Cu contamination indicator.

Zn concentrations of river insect larva in the Waidani south area were several 100 to several 1000 ppm and decreased from upstream to downstream. Zn concentrations in the Waidani north area also were several 100 to several 1000 ppm. Zn concentrations in the Waidani north area, the Ikuno mine area and the Nakase mine area were also several 100 to several 1000 ppm. Although Zn concentration in the Taisyakukyo is 100 to several 1000 pm as well as mine areas, Zn concentration in the Yada and Kino River were low, several 10 to several 100 ppm and then Zn concentrations in mine areas were higher than those in no mine area. As a result, Zn concentration for river insect larva was thought to depend on the environment Zn concentration. Then, river insect is thought to be effective for indicator as Zn contamination indicator.

As concentrations of river insect larva in the mine area, the Waidani, the Ikuno mine and the Nakase mine area were found to be over several 10 ppm, however As concentration in the Taisyakukyo, the Yada and Kino River were low, less than several 10 ppm. As a result, As concentration for river insect larva was thought to depend on the environment As concentration. Then, river insect is thought to be useful for indicator as As contamination indicator as well as Cu and Zn. Next, to find effective species for insect, the relation between metal concentration and insect species was studied.

Figure 9, 10 and 11 show the relation between Cu, Zn and As concentration and species for sampled insect and plant. Two plants, fern and mat rush were found at the waste rock area (“He”) in the Waidani mine. Cu concentrations in the fern and mat rush were low relative to those in the insect. Cu concentration in Dragonfly and stonefly were narrow range, several 10 to several 100 ppm. Cu concentration in trichoptera, horsefly, and dayfly were also wide range, several 10 to 1000 ppm. Japanese divining beetle was just only found at the waste rock place around the head stream in Waidani N. It is not common species and very abundant at the “He”. Its Cu concentration was very high, several 100 ppm. Wide concentration range and high concentration of insect is necessary for an indicator of metal contamination. Dobsonfly with wide range concentration, several to several 1000 ppm was thought to be very effective for Cu indicator as for wide range and high concentration.

Zn concentrations in the fern and mat rush were lower, 100 to 1000 ppm than those in the insects. Trichoptera is thought to be very effective for Zn indicator with wide range concentration, several 10 to 10000 ppm. Dobsonfly, dragonfly, horsefly, and dayfly also have a wide concentration range. Zn concentration for Japanese divining beetle was not very high relative to the other insects, several 100 ppm. As for Zn, Trichoptera is wider range than dobsonfly.

As concentrations in the fern and mat rush were low relative to those in dobsonfly, trichoptera, dragonfly. As concentrations in dobsonfly show wide range, 0 to 400 ppm. As concentration in trichoptera was 0 to 200 ppm. The other insects have narrow range concentration and most of samples were under the detection limit, 0.001 ppm. As concentration for Japanese divining beetle was high relative to other insect, 100 ppm depending on high As condition. Dobsonfly is thought to be very effective for As indicator as for wide range and high concentration.

As a result, effective metal contamination indicator for As is thought to be only dobsonfly because As concentration for the other insects were narrow range and very low. Dobsonfly is thought to be very effective for Cu and Zn indicator as well as trichoptera, other insect. Although main Dobsonfly, *Protohermes grandis* is found to be only one species in the sampled area, the other insects have many species. Next, each specie concentration range for Cu and Zn was studied for trichoptera, dragonfly, dayfly and stonefly with wide range.

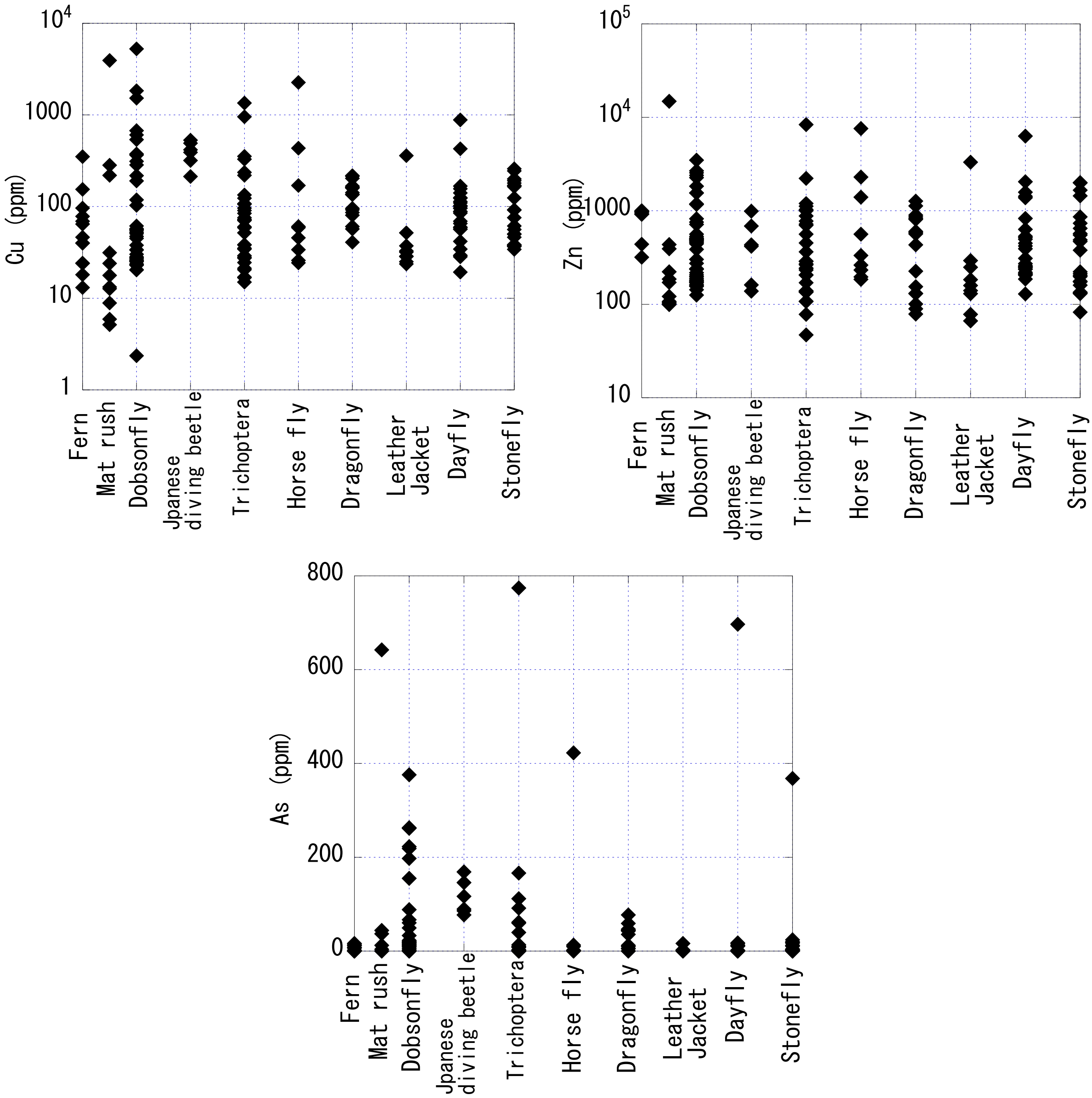

Figure 9, 10 and 11 Relation between Cu, Zn and As concentration and species for sampled insect and plant.

Figure 12 and 13 show the relation between Cu and Zn concentrations and in detail species in trichoptera, dragonfly, dayfly and stonefly. X axis is each detail species for trichoptera, dragonfly, dayfly and stonefly and they have approximately more than ten species in the sampled area.

Cu concentration in some species, *Stenopsyche marmorata*, of trichoptera ranged from 10 to 100 ppm. The other trichoptera species ranged from 100 to 1000 ppm. Two different ranges were found in trichoptera. *Stenopsyche marmorata* was a common trichoptera in the sampled area. Then, Cu concentration for trichoptera depended on detail species. For dragonfly, dayfly and stonefly, their Cu concentration changed with detail species and therefore one species was not able to cover wide rang. .

Zn concentration range in some species, *Stenopsyche marmorata*, of trichoptera also was concentrated to be several 10 to 1000 ppm as well as Cu. Other trichoptera species were concentrated to be 100 to 10000 ppm. There were two different ranges of Zn for trichoptera. Therefore, the concentration depended on detail specie of trichoptera. Although Zn concentration of *Kamimuria tibialis*, a kind of stonefly, had a wide range, several 10 to several 1000 ppm, the other stonefly species were concentrated to be several 100 ppm or 1000 ppm. Therefore, Zn concentration for stonefly also depended on detail specie. Zn concentration of dragonfly and dayfly were classified into two groups, several 100 and several 1000 ppm. Then, Zn concentration for trichoptera, dragonfly, dayfly and stonefly depended on detail species.

Finally, dobsonfly was thought to be a very effective indicator for evaluating water and soil contamination. Then, figure 14 shows picture of dobsonfly, *Protohermes grandis.* The scale is 1 cm length. It has big jaws. The larva is just before emergence.

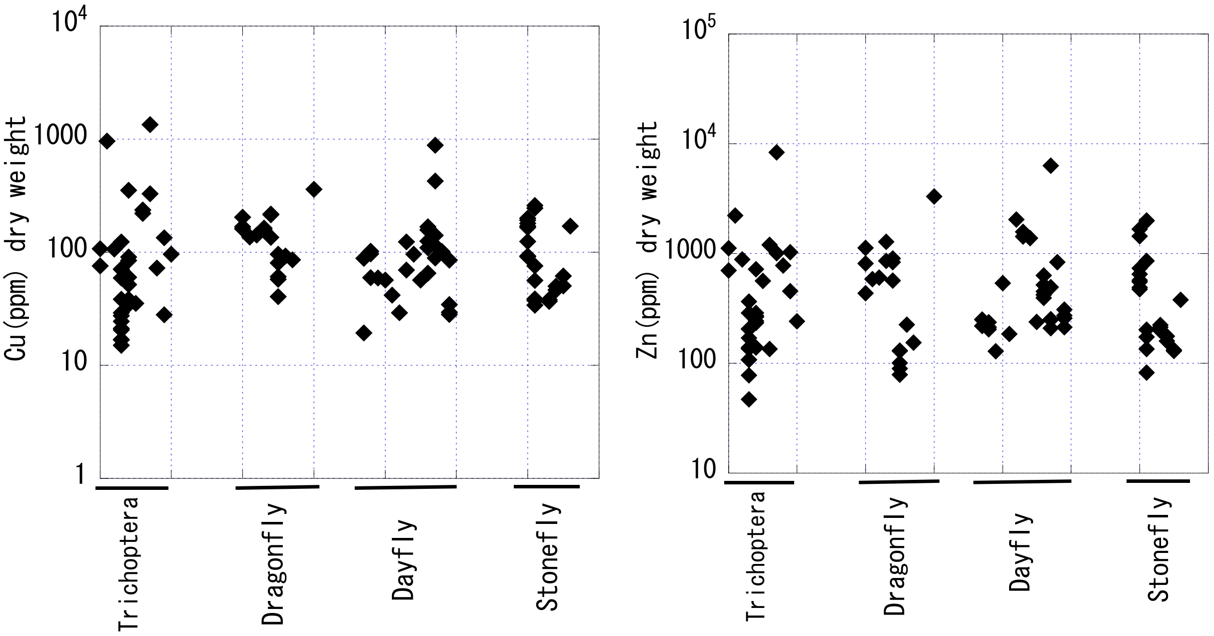

Figure 12 and 13 Relation between Cu and Zn concentrations and in detail species in trichoptera, dragonfly, dayfly and stonefly.

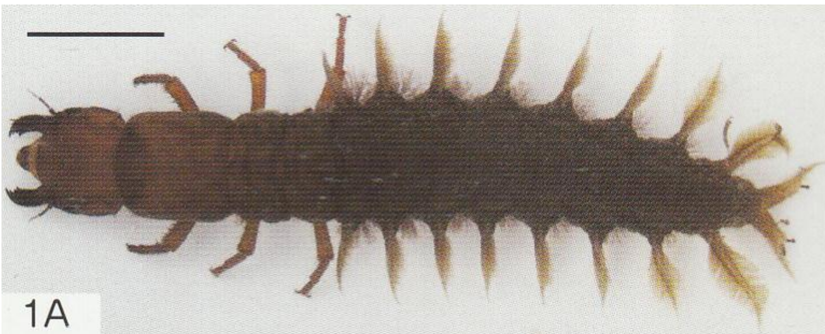

Figure14 Picture of dobsonfly, *Protohermes grandis*

Conclusion

Dobsonfly was widely distributed as well as trichoptera and the other river insects in metal contaminated area and not contaminated area excluding limestone area and just one specie, *Protohermes grandis*, was found as dobsonfly. *Protohermes grandis* was able to cover wide concentration range for Cu (several 10 to several 1000 ppm), Zn (several 100 to several 1000 ppm) and As (0.000 to 400 ppm) and its concentration was depended on metal contamination. Therefore, dobsonfly, *Protohermes grandis*, was an effective indicator for evaluating metal contamination. Comparing trichoptera and the other insects, they have also wide concentration range and wide distribution however, they have many species. Each species did not have wide range. Then, their concentration and distribution depended on species. Therefore, dobsonfly is thought to be the best indicator although dobsonfly was not distributed in a limestone area. It is necessary to confirm distribution of dobsonfly in limestone and clarify why dobsonfly is not abundant in limestone area

Although the Cu, Zn and As concentrations effluent at the top of the head of valley in the Waidani mine area were under the Japanese Effluent Standard, very limited insects, abundant of Japanese diving beetle, were only found and then specialized condition is made by the effluent.

References

Aizawa S., Kakuta K., Akatsuka M., Inoue S. and Akaiwa H. (1994). Evaluation of Trichoptera as an indicator organism for environmental pollution by heavy metals. *Japan Analyst*, 43(11), 865-871.

Aizawa S., Kakuta A., Yasuda S., Kakuta K. and Itabashi H. (2009). Concentrations of Heavy Metals in Caddisfly Larvae of the Tone River System and Their Seasonal Variations. *Japan Analyst*, 58(4), 273-285.

Hatakeyama S., Sugaya Y., Satake K., Miyashita M. And Fukushima S.. (1990). Macroinvertebrate communities in heavy metal-polluted rivers in the Shikoku district of Japan. *Verh. Internat. Verein. Limnol,* 24, 220-227.

Hatayama N. (2011). Determination of acceptable copper concentration for macroinvertebrate communities based on field investigations on metal-polluted rivers around abandoned mines in Japan. *Japan J. Environ. Toxicol..,* 14(1), 57-68.

Hickey C.W. and Golding L.A. (2002). Response of macroinvertebrates to copper and zinc in a stream mesocosm. *Environ. Toxicol. Chem.,* 21, 1854-1863.

Iwasaki Y., Kagata T., Miyamoto K. And Matsuda H. (2009). Changes in Riverine macroinvertebrate Assemblages after Discharge of Treated Mine Wastewater: A Class Study on Ikuno Silver mine. *Journal of Japan Society on Water Environment.*, 32(6), 325-329.

Leland H.V., Fend S.V., Dudley T.L. and Carter J.L. (1989).Effects of copper on species composition of benthic insects in a Sierra Nevada, California, stream. *Fresh-water. Biology.,* 21, 163-179.

Tochimoto H., Oshida Y., Kikuchi Y., Sasano H., Nakamura H. and Matsumoto M. (1981). Aquatic Insects in Streams as Biological Monitors of Heavy Metal Pollution. *Ann. Rep. Tokyo Metr. Res. Lab. P.H.,* 32(1), 296-303.

Watanabe K., Yamamoto N., Kusano H. And Omura T. (2005). Elucidation of Mechanisms of Heavy Metal Accumulation in Stream Aquatic Insects by Nitrogen and Carbon Stable isotope analysis. *Journal of Japan Society on Water Environment.,* 28(12), 737-744.