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CU, ZN AND AS CONTAMINATION OF SEAWEED BESIDE SHIZUKI AND KANAYAMA METAL MINES IN JAPAN

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ABSTRACT: Brown seaweed, Sargassum thunbergii is thought to be effective for As, Cu and Zn sensor. Green seaweed, Ulvales, red seaweed, Caulacanthus ustulatus and Ahnfeltiopsis flabelliformis are thought to be effective for just Cu sensor. High Zn concentration and large volume of Zn drainage water from the closed Kanayama mine flowed into sea and drainage water and groundwater containing Cu, Zn and As contacted with muck along the coast also flowed into sea in the closed Shizuki mine. Cu, Zn and As concentrations for many kinds of seaweed sampled at the two mines and no contamination places, the Kii and Izu Peninsula, were measured. Cu Zn and As concentrations for Sargassum thunbergii are 1000, several 100 and several 100 ppm at the Shizuki mine and 10, several 1000 and 100 ppm at the Kanayama mine, and 10, several 10 and 100 ppm at the no contamination places.

Keywords: Seaweed, Metal sensor, Metal mine, sea metal contamination

1. INTRODUCTION

Many papers about metal concentration of seaweed are published and high bioconcentration factor of heavy metal was found for many kind of seaweed [1]–[2]. The relation between time or sea metal concentration and bioconcentration factor was clarified [3]–[5]. Metal concentration of seaweed at heavy metal contamination area was published and metal concentration for water and contaminated soil were also described [6]–[8]. However a monitoring of water and soil is important for evaluating contamination, it spends long term sampling and large number of sampling for reaching average value of metal concentration for water and soil because water and soil metal concentrations are variable for time and place. To measure metal concentration of seaweed is easier than to measure those of water or soil because metal concentration of seaweed is higher than those of water or soil because of bioconcentration factor and seaweed has long term information. Then, the purpose of this study is to find effective seaweed as a metal sensor. There are many kinds of seaweeds and then each bioconcentration factor is variable. Therefore, effective seaweed as a metal sensor needs wide distribution and changeable concentration depending on metal concentration of water and soil. Then, comparing seaweed at contaminated area and non contaminated area, we select effective seaweed as a metal sensor. In this study, Cu, Zn and As were selected because Cu, Zn and As were popular heavy metals in Japanese metal mine contamination area..

2. METHOD

Fig.1 shows the study areas including 2 closed metal mines, Shizuki and Kanayama mines and 5 non contamination areas, North Senjyo, South Senjyo, Kada (Wakayama city), Saikasaki (Wakayama city) and Nawachi coasts. Both two small metal mines are facing sea. Drainage water and muck were accumulated on the coast. Seaweed was sampled along the coast. Sampling date for Kanayama is May 2013. Senjyo April 2013, Nawachi February 2014, Kada March 2014, Shizuki July and Aug 2013 and March 2014, and Saikasaki May 2014. Sampled seaweed was dried and then dissolved with concentrated nitric acid solution. Metal concentration for solution after filtration was analyzed by ICP-AS. Metal concentrations for spring water and river water including adit drainage were also analyzed by ICP-AS.

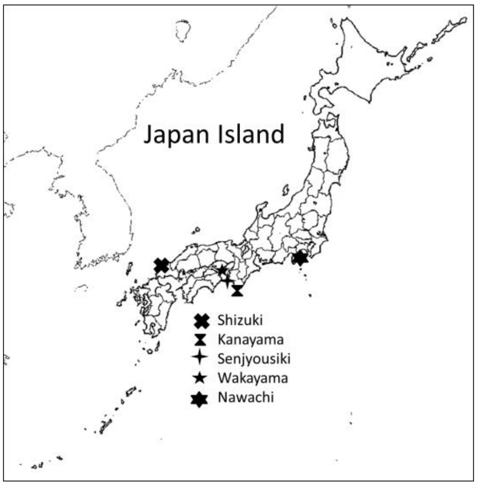


Fig. 1 Sampling points for seaweed

3. RESULTS

3.1 Condition for mine metal contamination area

Shizuki mine is copper mine at the Japan sea side and primary metal minerals are pyrite FeS_2, spharelite ZnS, chalcopyrite $CuFes_2$ and arsenopyrite FeAsS. In this mine, there is a lot of muck along the coast. As the secondary metal mineral, atacamite $Cu_2(OH)_3Cl$ was also found at the spring point and at the surface of muck stone along the coast, sea water was thought to react with spring water containing copper from mine. Table 1 shows flow rate and Cu, Zn and As concentrations for drainage and spring water. Cu concentration was high, a few mg/l and Cu load reached 5kg. Cu contamination was thought to bring out. Zn and As contamination was also thought to bring out because of drainage water and metal mineral including Zn and As.

Table 1 Flow rate and Cu, Zn and As concentrations for Shizuki mine

	spring at coast	drainage from adit	
date	2013/7/12	2013/7/12	2014/3/28
flow(l/min)	0	3	0.6
Cu(mg/l)	9.377	3.019	1.472
Cu(kg/year)		4.76	0.46
Zn(mg/l)	0.328	1.071	0.748
Zn(kg/year)		1.69	0.24
As(mg/l)	0.013	0.084	0.038
As(kg/year)		0.13	0.01

Kanayama mine is located at the Kanayama Bay in the Kii Peninsula facing the Pacific Ocean. Although main production was Pb (Galena PbS 5% of total metal mineral), main metal mineral is pyrite (50%) and spharelite (40%). Chalcopyrite (5%) was also found in the vein. Drainage water from two vein flows into the Kanayama Bay. One drainage water flows into the bay through the river. The other drainage is spring on the coast facing the bay.

Fig.2 and 3 show Zn concentration and Zn load for spring and river waters. Zn concentration of spring and river were less than 50 to 90 mg/l and 1 to 5 mg/l. Flow rate for spring increased since 2009 till 2011 and then Zn concentration decreased. However, Zn load increased with flow rate and since 2011 Zn load for spring was 2000 to 4000 kg per year. Zn load for river was 1000 kg per year since 2011. Then total Zn load for the Kanayama Bay 3000 to 5000 kg per year and it is quite large Zn load for the small bay with 100 m length and 50 m width. Total Zn concentrations for the sea water in the bay were 0.2 to 1.9 mg/l and soluble Zn concentration with 0.45 filtered sea water were also 0.2 to 1.6 mg/l. Most Zn was soluble style and sea water Zn concentration was also high.

Fig.4 and 5 show Cu concentration and Cu load for spring and river waters. Although Cu load reached several kg per year, Cu concentration was very low and 0.01 to 0.05 mg/l for spring and 0.005 to 0.01 mg/l for river since 2011. As concentrations for spring and river water were under detection limit 0.001 mg/l. Then, in the Kanayama mine area Zn contamination was quite large and Cu contamination was also thought to bring out. As contamination was not thought bring out or to be very small.

3.2 Condition for no contamination area

Senjyo coast is 3 km northwest from the Kanayama Bay. Wakayama coast, Kada and Saikasaki are 70 km northwest from the Kanayama Bay. Nawachi is located at the Izu peninsula in the center of Japan facing the Pacific Ocean. The all coast was located far from the big city and mine area and then heavy metal contamination was not thought to bring out. However the Senjyo coast is close to the Kanayama Bay and metal contamination may occur.

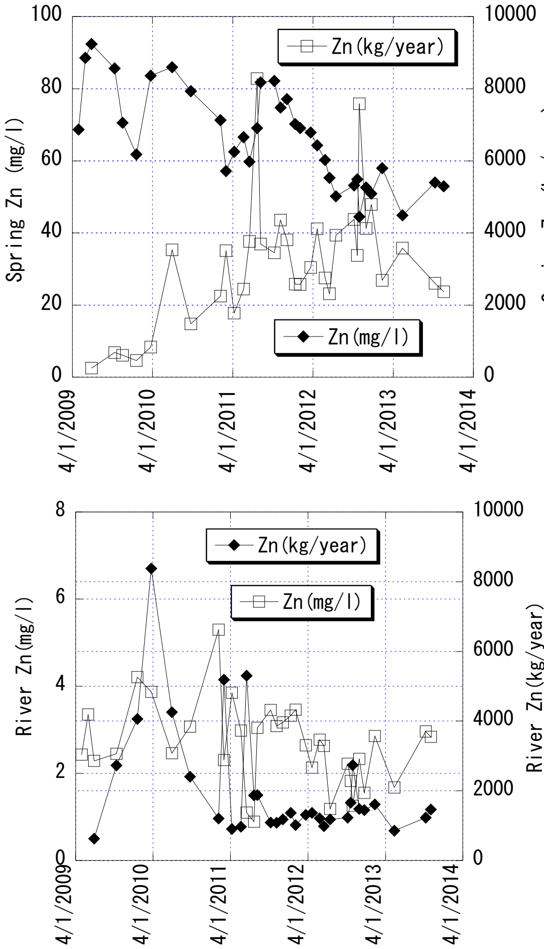
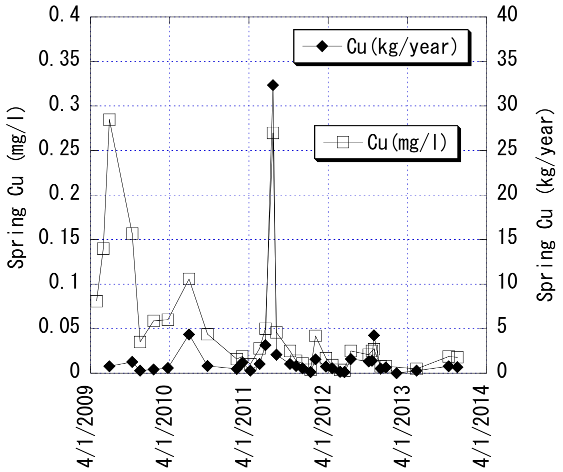


Fig.2 and 3 Zn concentration and Zn load from spring and river in the Kanayama mine

3.3 The relation between place and metal concentration of seaweed

Fig.6 shows Zn concentration of all sampled species of seaweed under the dry weight condition and place. In the Kanayama Bay, metal concentrations depend on distance from spring and the mouse of river and then sample points are described by distance from spring and river mouse. "UP" is close to spring or river mouse. Right direction from the "UP" shows far from spring. "O" is just located at the outside of the Kanayama Bay. "SS" and "SN" are south and north of Senjyo coast. "WS" and "WK" are Saikasaki and Kada coasts in the Wakayama city. "NW" is Nawachi coast. "SH" is Shizuki mine coast. Zn concentration in seaweed is extremely high in Kanayama Bay and reached several % down the spring. The maximum value is thought to be world record in natural. River stream area in the Kanayama Bay was also high. In the bay Zn minimum values for seaweed are 1000 ppm. Zn concentration just outside of the bay also keeps several 100 to several 1000 ppm. South of Senjyo coast is near the Kanayama Bay than North of Senjyo coast. Zn concentration at south of Senjyo coast is relatively high to north of Senjyo, Saikasaki, Kada, and Nawachi. Zn concentration in the Shizuki mine coast is wide variable and reached several100 ppm. Zn concentration at the



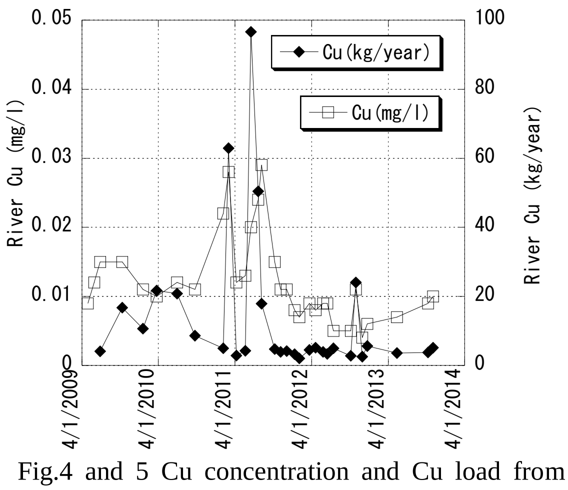


Fig.4 and 5 Cu concentration and Cu load from spring and river in the Kanayama mine

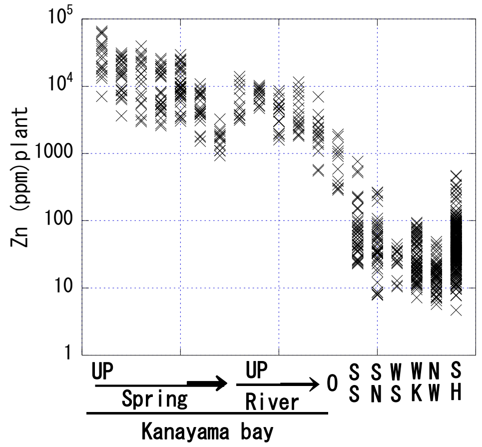


Fig.6 shows Zn concentration of all sampled species of seaweed and place.

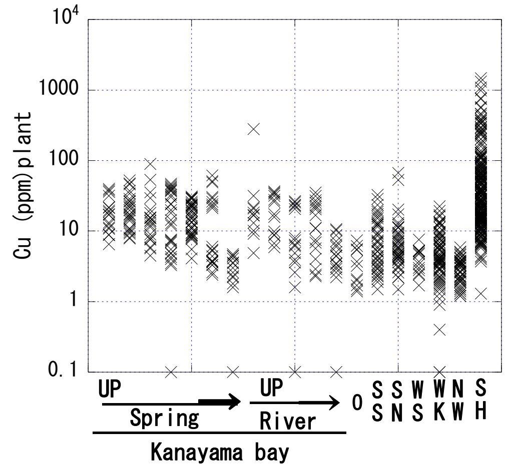


Fig.7 shows Cu concentration of all sampled species of seaweed and place

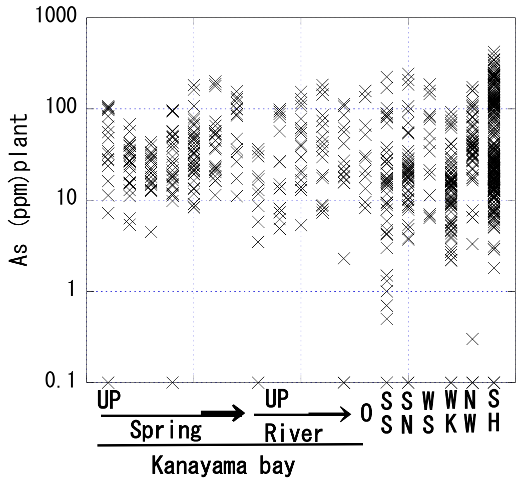


Fig.8 shows As concentrations of all sampled species of seaweed and place north of Senjyo is also high relative to no contamination coast and then Senjyo area is thought to be contaminated by Kanayama mine drainage. From the past study, Zn concentrations for green seaweed, brown seaweed and red seaweed were 20 to 140, 6 to 260 and 21 to 150 ppm [9] and Zn concentration of seaweed were 1.7 to 680 ppm [10]. Zn concentration of seaweed at the no contaminate areas were agreement with the past study results.

Fig.7 shows Cu concentration of all sampled species of seaweed under the dry weight condition and place. Cu concentration for seaweed at the Shizuki mine shows wide range and varied from several to 1000 ppm. Cu concentration of seaweed sampled at August and July 2013 in the Shizuki mine showed high values and it shows season changes. Cu contamination for seaweed was remarkable high for the Shizuki mine. Cu concentration of seaweed in the Kanayama Bay is several to several 10 ppm and the same value as Senjyo and Kada coasts. However, Cu concentration decreased with distance from spring or river mouse to outside the bay. Cu contamination was found from Cu concentration for seaweed in the Kanayama Bay. Cu concentration of seaweed at the Kada and Senjyo in the no contamination area were relative to high to those at the Nawachi and Saikasaki coasts. From the past study, Cu concentrations for green seaweed, brown seaweed and red seaweed were 4 to 58, 2 to 68 and 3 to 24 ppm [9] and Cu concentration of seaweed were 6.1 to 28 ppm [10]. Cu concentration of seaweed at the no contaminate areas were agreement with the past study results.

Fig.8 shows As concentration of all sampled species of seaweed under the dry weight condition and place. As concentration for seaweed in the Kanayama mine with no As mineral is not high relative to those sampled at another coast. As concentration for seaweed at the Shizuki coast shows wide range and varied from several to 100 ppm. As concentration of seaweed sampled at July and August 2013 in the Shizuki mine showed high values and it shows season changes for As as well as Cu. Muck from the Shizuki mine contains As mineral and drainage water contain 0.0n mg/l for As. Some samples shows high As values, however As concentration for seaweed was variable and some sample shows low values. Therefore, As concentration was thought to depend on species. From the past study, As concentrations for green seaweed, brown seaweed and red seaweed were 1.2 to 6, 62 and 6 ppm [9] and As concentration of seaweed were 1.2 to 130 ppm [10]. As concentration of seaweed at the no contaminate areas were agreement with the past study results. Then, next, relationship between species and metal concentration is shown.

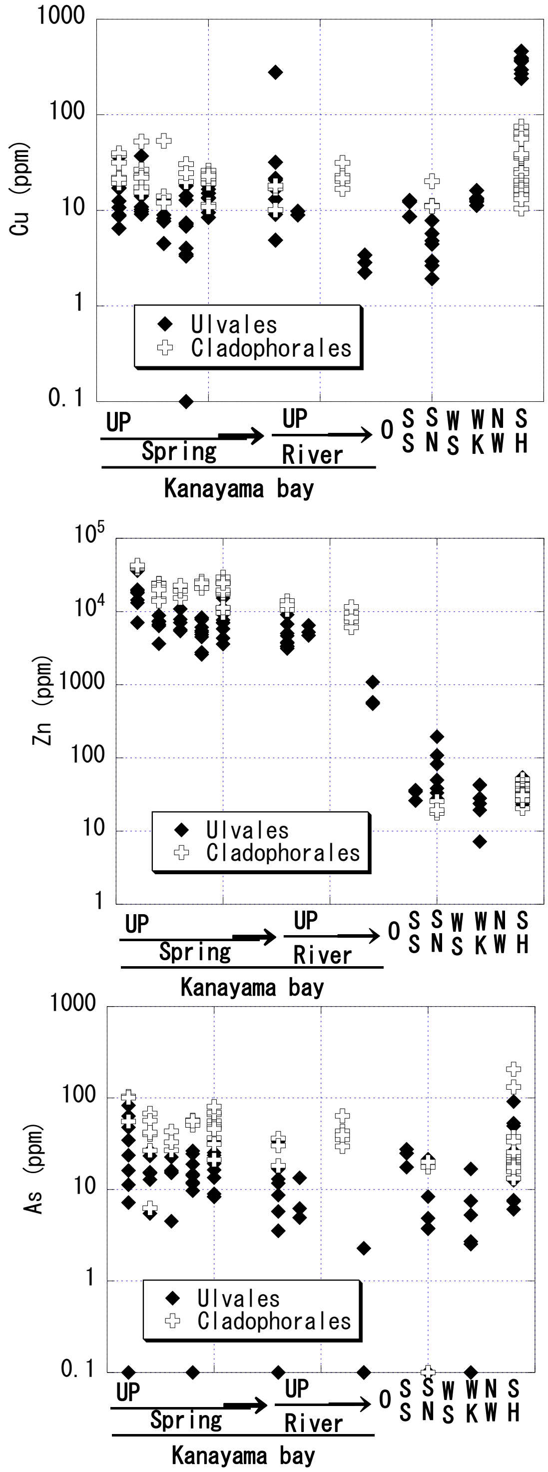


Fig.9 Cu, Zn and As concentrations for green seaweed (Ulvophyceae), Ulvales and Cladophorales

3.4 concentration of green, red and brown seaweed

Fig.9 shows Cu, Zn and As concentrations for green seaweed (Ulvophyceae), two order, Ulvales and Cladophorales. Ulvales and Cladophorales were popular green seaweeds at the sampling place and then effective candidates for a metal sensor covering a wide habitat. Cu concentrations of Cladophorales were uniform, 10 to 100 ppm under the different places. Cu concentrations of Ulvales were several 100 ppm at the Shizuku mine, several 10 ppm at the Kanayama mines and several ppm at the no contamination places. Ulvales is effective metal sensor for Cu because the concentration range was 100 times depending on the condition. Zn concentrations of Ulvales and Cladophorales were several 10000 ppm at the Kanayama mine and several 10 ppm at the no contamination places and the Shizuki mine. Both green seaweeds were not effective metal sensors for Zn because Shizuki mine was thought to bring out Zn contamination but Zn concentration of seaweeds at the Shizuki mine was low. As concentrations of Cladophorales were higher than those of Ulvales. As concentrations of Cladophorales were uniform, several 10 ppm to several 100 ppm and As concentration for Cladophorales of the Shizuki mine were not necessary high values. As concentrations of Ulvales were several 10 ppm at the downstream of spring in Kanayama mine and the Shizuki mine and several ppm at the no contamination places and at the downstream of the river in the Kanayama mine. Both Cladophorales and Ulvales were not effective metal sensor for As because of narrow range concentration.

Fig.10 shows Cu, Zn and As concentrations for brown seaweed (Phaeophyta), Pectalonia binghamiae and Sargassum thunbergii. They were popular brown seaweeds at the sampling place and then effective candidates for a metal sensor. Cu concentrations of Pectalonia binghamiae were uniform, several to several 10 ppm and not high at the Shizuki mine. Cu concentration of Sargassum thunbergii at the Shizuku mine were high relative to another area having wide concentration range from 10 ppm to several 1000 ppm. Cu concentrations of Sargassum thunbergii were 10 ppm at the the Kanayama mine and less than 10 ppm in the no contamination places. Therefore, Sargassum thunbergii was thought to be an effective metal sensor for Cu. Zn concentration of Pectalonia binghamiae were several 1000 ppm to several 10000 ppm at the Kanayama mine and several 10 ppm at the Shizuki mine and at the no contamination places. Zn concentration of Sargassum thunbergii were several 1000 ppm at the Kanayama mine, several 10 to several 100 ppm at the Shizuki mine and several 10 ppm at the no

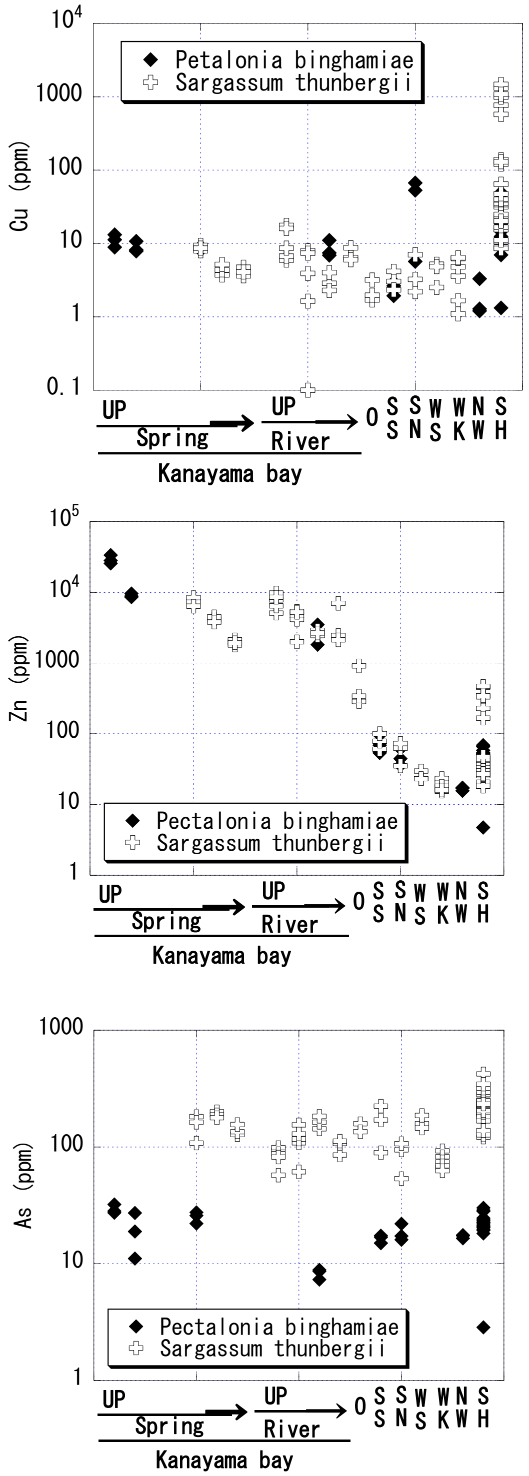


Fig.10 Cu, Zn and As concentration for brown seaweed (Phaeophyta), Pectalonia binghamiae and Sargassum thunbergii

contamination places. Then, both brown seaweeds were effective metal sensor for Zn. As concentration of Pectalonia binghamiae were uniform values, however As concentration of Sargassum thunbergii were over several 100 ppm at the Shizuki mine and several 10 to 100 ppm at the Kanayama mine and no contamination places. Sargassum thunbergii was thought to be effective metal sensor for As.

Fig.11 shows Cu, Zn and As concentratios for red seaweed (Rhodophyta), Caulacanthus ustulatus and Ahnfeltiopsis flabelliformis. They were popular red seaweeds at the sampling place and then effective candidates for a metal sensor. Unfortunately Ahnfeltiopsis flabelliformis cannot be found in the Shizuki mine however, another places, very common. Cu concentrations of both the red seaweeds were high at the Kanayama mine and low at the no contamination places. Cu concentrations of Caulacanthus ustulatus was high, several 100 ppm. Then, both the red seaweeds were thought to be an effective metal sensor for Cu. Zn concentrations of both red seaweeds were several 1000 ppm to several 10000 ppm at the Kanayama mine and several 10 ppm at the Shizuki mine and at the no contamination places. Then, both the red seaweeds were not effective metal sensor for Zn. As concentration of both the red seaweeds were uniform values, several ppm to several 10 ppm. Both the red seaweeds were not effective metal sensor for As. Totally Sargassum thunbergii is thought to be an effective seaweed for As, Cu and Zn sensor.

Although metal concentration of sea was measured by ICP-AS, metal concentration for most of water was under detection limit, 0.001 ppm. Zn concentration of sea for Kanayama Bay was over detection limit and then fig. 12 shows Zn concentrations of sea in the Kanayama Bay. Zn concentration of sea was extremely very high, 0.1 to several 10 ppm around the spring mouse because Zn concentration of spring reached 100 ppm. Similarly around river mouse, Zn concentration of sea reached several ppm. Zn concentrations for sea in the bay were several 0.01 to 1 ppm where spring and river water was mixed with sea water. Based on these values, concentration factor for each seaweed was measured.

Under extremely high Zn concentration for sea around the spring mouse, green seaweeds, Ulvales and Cladophorales, and brown seaweed, Pectalonia binghamiae were found and the concentration factor of Zn for Ulvales, Cladophorales, and Pectalonia binghamiae were 1,000 to 100,000. Around the river mouse, green seaweeds, Ulvales and Cladophorales were found and the concentration factor of Zn for Ulvales and Cladophorales were about 1,000 to 10,000. In the

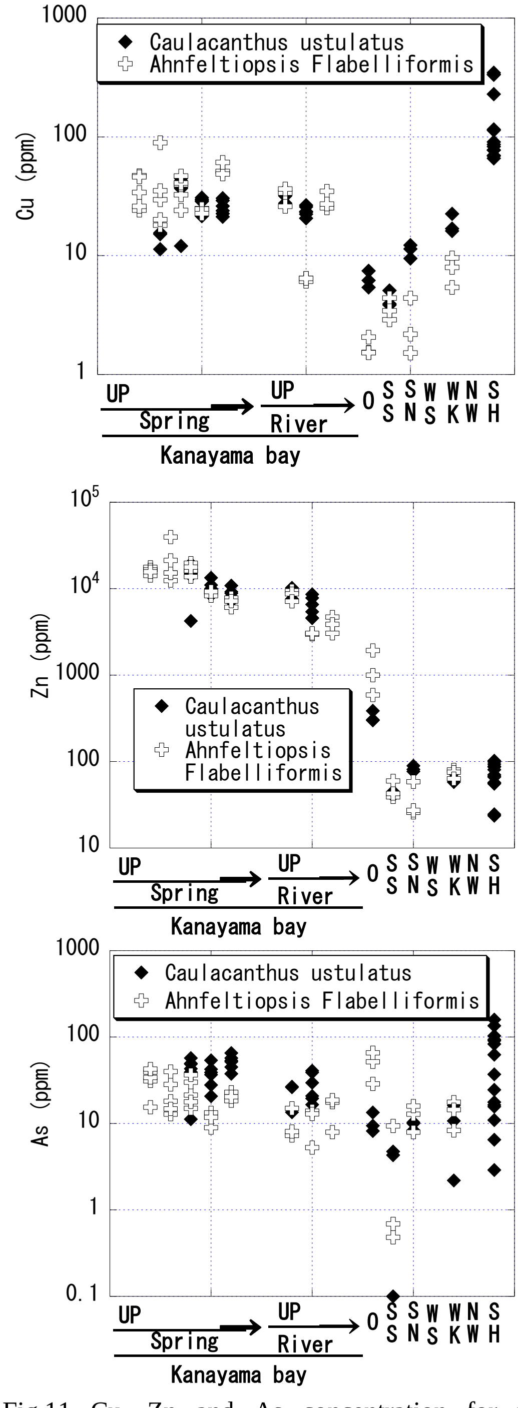


Fig.11 Cu, Zn and As concentration for red seaweed (Rhodophyta), Caulacanthus ustulatus and Ahnfeltiopsis flabelliformis

bay excluding spring and river mouse, green, brown and red seaweeds were found and the Zn concentration factors were about 10,000 and about 100,000 for Ulvales and Cladophorales, 1,000 to 100,000 for Pectalonia binghamiae, Sargassum thunbergii, Caulacanthus ustulatus and Ahnfeltiopsis flabelliformis. The concentration

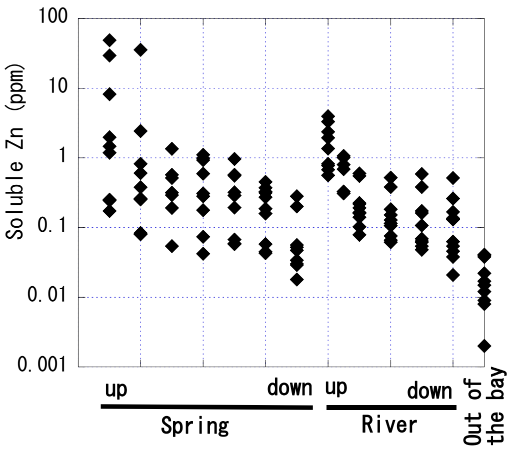


Fig.12 Zn concentrations of sea in the Kanayama Bay

factor was variable depending on Zn wide concentration for sea.

From the past study, Zn concentration for green seaweed, brown seaweed and red seaweed were 20 to 140, 6 to 260 and 21 to 150 ppm [9]. Zn concentration values for sea depended on depth [10] and Zn concentration of sea surface was quite low, 0.0003 ppm. Therefore, concentration factors of Zn for seaweed were 70,000 to 500,000 for green seaweed, 20,000 to 900,000 for brown seaweed and 70,000 to 500,000 for red seaweed. Zn concentration factor for seaweeds in Kanayama Bay were coincide with the Zn concentration factor for past study results and under the extremely high Zn condition, Zn concentration factor for seaweed was kept stable. Similarly, Zn concentration factor for seaweed sampled at Wakayama were 2,500 to 8,000 from the past study [3]. On the hand, Zn concentration factor for Ulva pertusa was low, 290 using Zn^{65} in laboratory test [4].

4. CONCLUSION

Under high metal concentration, the relation between metal concentration of seaweed and sea metal concentration was clarified. Kanayama mine was thought to be heavily Zn and medium Cu contamination place. Shizuki mine was thought to be heavy Cu and medium Zn and As contamination place. Comparing Cu, Zn and As concentrations for seaweed at the contamination and no contamination places, it was clarified whether metal concentration of the seaweed depended or did not on the contamination condition. As a result, brown seaweed, Sargassum thunbergii was thought to be effective for As, Cu and Zn sensor because the metal concentration for the seaweed changed with metal contamination. Ulvales, Caulacanthus ustulatus and Ahnfeltiopsis flabelliformis were thought to be effective for just Cu sensor. Zn concentration factor for seaweed was uniform even under high Zn concentration condition.

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