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AS, SR, ZN, FE, MN, PB AND CU CONCENTRATIONS OF SEAWEED AT THE KII PENINSULA, JAPAN

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ABSTRACT: Seaweed from locations ranging from Osaka Bay facing the metropolis to the southern top of the Kii Peninsula facing the Kuroshio Current at the Kii Peninsula were measured for concentrations of arsenic (As), strontium (Sr), zinc (Zn), iron (Fe), manganese (Mn), lead (Pb) and copper (Cu). Except for one location at Kanayama neighboring a closed Pb mine, metal concentrations in seaweed were variable but their average values agreed with the world data. Therefore the influence of the Kuroshio Current water and Osaka Bay water on metal concentration in seaweed was found to be small. As and Sr concentrations in brown seaweed were higher than those in red and green seaweed at the Kii peninsula except at Kanayama, Fe concentrations in green seaweed were higher than those in brown and red seaweed and Zn, Mn, Pb and Cu concentrations in brown, red and green seaweed were all the same. Total Fe, Zn, Mn, Pb and Cu loads of mine waste water from the closed mine into the Kanayama Bay were 4,000 to 6,000, 3,000 to 5,000, 180, 20 and several kg per year. Zn and Fe concentrations in seaweed at Kanayama were remarkably high being 10 to 100 times that of the world value. Mn and Pb concentrations in seaweed at Kanayama were 10 times higher than the world values. Cu concentrations of red and green seaweeds at Kanayama were little higher than the world values.

Keywords: Seaweed, heavy metal, mine waste, Kii Penisula, Kanayama Bay

1. INTRODUCTION

Many papers detailing metal concentrations in various kinds of seaweeds have been published [1]–[2]. The relationship between time or sea metal concentration and the bio-concentration factor was clarified. Metal concentrations in seaweed at heavily contaminated areas were published and metal concentrations in water and contaminated soil were also described [3]–[5]. The Kii Peninsula in central Japan, neighbors the metropolises of Osaka and Kobe at the north and contacts the Kuroshio Current in the south. Two different water resources, metropolitan sewage water and the Kuroshio Current, flow past the Kii Peninsula. Waste water from the now closed Pb Kanayama mine, located to the south, flows directly into Kanayama Bay [6]. Metal concentrations in seaweed were measured under several different sea conditions to clarify their relationship with that particular sea condition.

2. METHOD AND STDUY AREA

Fig.1 shows 15 sampling points, Ozaki, Misaki, Tomogasima Island north, Tomogasima Island west, Tomogasima Island south, Kada, Saikasaki, Tagui, Senjyo north, Senjyo, Kanayama, Hachijyuu, Susami, Tako and Kiitahara at the Kii Peninsula. All sampling points, except for Kanayama, were on the coast facing the outside sea.

Sampling dates were Ozaki March 2015, Misaki and Tomogasima January 2015, Kada March 2014,

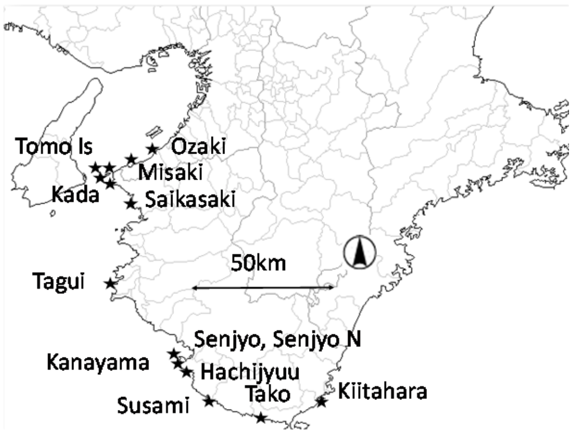


Fig. 1 Sampling points at the Kii Peninsula

Saikasaki May 2014, Tagui, February 2015, Senjyo and Senjyo N April 2013, Kanayama May 2013, Hachijyuu June 2014, and Susami, Tako and Kiitahara April 2015. Sampled seaweed was dried then dissolved with a concentrated nitric acid solution. Metal concentrations in the solution after filtration were analyzed by ICP-AS.

2.1 Kanayama Sampling Point

Kanayama sampling point was inside Kanayama Bay. Drainage water from two veins of Kanayama mine flows into Kanayama Bay. One drainage water pathway flows into the bay through the river.

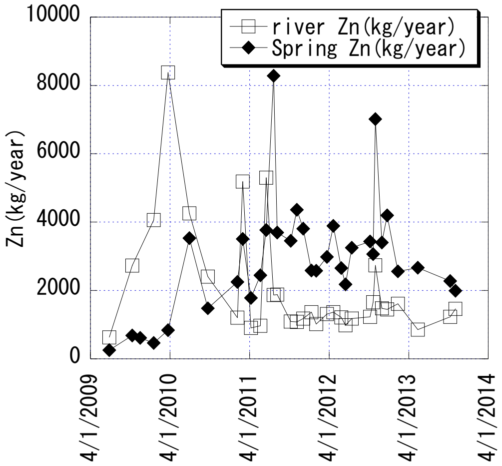


Fig. 2 Zn load of Kanayama mine.

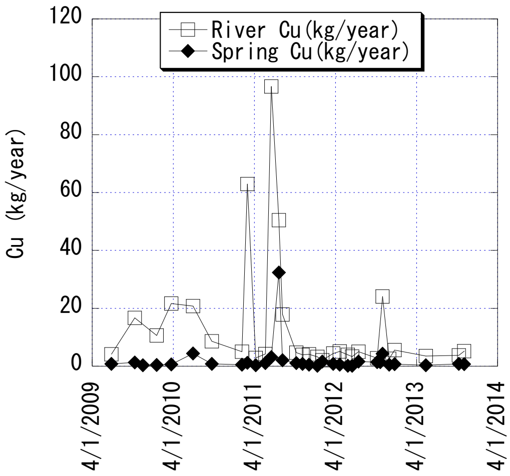


Fig. 3 Cu load of Kanayama mine.

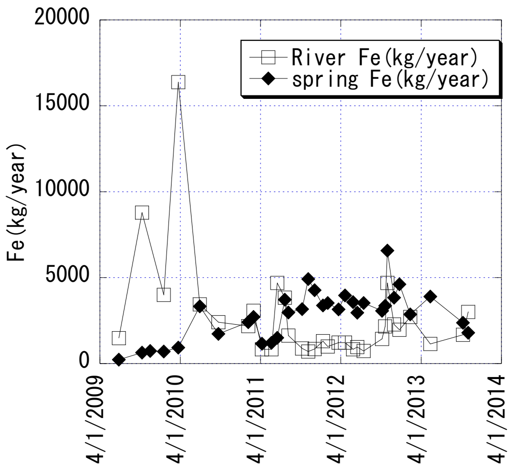


Fig. 4 Fe load of Kanayama mine.

The other drainage pathway is a spring on the coast facing the bay. Total Zn and Cu loads were 3,000 to 5,000 kg per year and several kg per year as shown in Fig. 2 and 3 [6]. Fig 4, 5 and 6 show the Fe, Pb and Mn loads of river and spring. Fe load from the

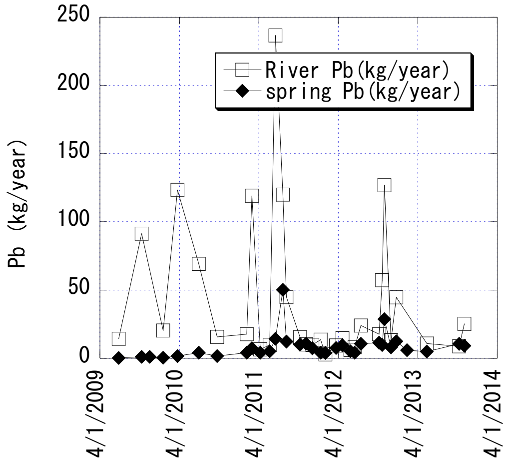


Fig. 5 Pb load of Kanayama mine.

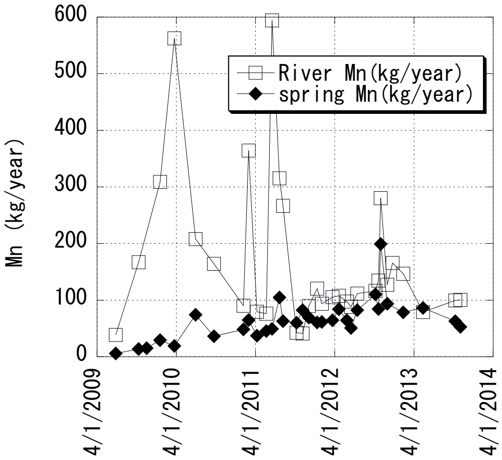


Fig. 6 Mn load of Kanayama mine.

spring varied from 2,000 to 4,000 kg per year and Fe load from the river was about 2,000 kg per year after 2011. Then total Fe load was about 4,000 to 6,000 kg per year. Pb load from the spring was stable, 10 kg per year and Pb load from the river varied around 10 kg per year. Then total Pb load was about 20 kg per year. Mn load from the spring was stable at 80 kg per year and Mn load from the river varied around 100 kg per year after 2011. Then total Mn load was about 180 kg per year.

2.2 Order and Species of Sampled Seaweed

Many kinds of seaweed were sampled and the order of representative seaweed was listed as shown in Fig, 7, 8, 9, 10, 11, 12 and 13. Order (species) of sampled brown seaweed were Laminariale 1 (Undaria pinnatifida), Laminariale 2 (Ecklonia cava, Undaria undarioides, Agarum clathratum), Fucales 1 (Sargassum muticum, Myagropsis myagroides, Sargassum ringgoldianum), Fucales 2 (Sargassum fusiforme), Fucales 3 (Sargassum thunbergii), Fucales 4 (Sargassum piluliferum), Dictyotales 1 (Dictyota dichotoma), Dictyotales 2 (Dictyopteris undulata, Dictyopteris prolifera), Ishigeales (Ishige foliracea, Ishige okamurae), Dictyotales 3 (Padina arborescens), Scytosiphonales 1 (Myelophycus simplex), Scytosiphonales 2 (Scytosiphon lomentaria), Scytosiphonales 3 (Colpomenia sinuosa, Colpomenia peregrine), and Scytosiphonales 4 (Petalonia binghamiae).

Order (species) of red seaweed was Gigartinales 1 (Chondracanthus tenellus, Chondracanthus intermedius), Gigartinales 2 (Grateloupia asiatica, grateloupia livida), Gigartinales 3 (Grateloupia lanceolata, Polyopes affinis, Polyopes prolifer, Polyopes lancifolius), Gigartinales 4 (Grateloupia elliptica, Chondrus ocellatus, Chondrus verrucosus), Gigartinales 5 (Gloiopeltis complanata), Gigartinales 6 (Ahnfeltiopsis flabelliformis), Gigartinales 7 (Gloiopeltis furcata), Gigartinales 8 (Caulacanthus ustulatus), Gigartinales 9 (Bonnemaisonia hamifera), Gelidiales (Gelidium crinale, Gelidium japonicum, Pterocladiella tenuis), and Bangiales (Pyropia yezoensis, Pyropia suborbiculata).

Order (species) of green seaweed were Cladophorales 1 (Cladophora wrightana), Cladophorales 2 (Chaetomorpha gracilis), Ulvales 1 (Ulva intestinalis, Ulva prolifera), and Ulvales 2 (Ulva pertusa, Monstroma nitidum).

3. RESULTS

3.1 As Concentration in Seaweed .

As concentrations in brown seaweed at the north and south Kii Peninsula were 10 to 300 ppm and 4 to 1,000 ppm as shown in Fig.7. As concentrations in red seaweed at the north and south Kii Peninsula were 0.3 to 40 ppm and 0.4 to 100 ppm. As concentrations in green seaweed at the north and south Kii Peninsula were 0.5 to 20 ppm and 1 to 100 ppm. As concentration in seaweed at the South Kii Peninsula was higher than that at the north of Kii Peninsula and As concentrations in brown seaweed was higher than those in green and red seaweed.

As concentration in brown seaweed, a kind of Fucales 1, Sargassum muticum, Myagropsis myagroides, and Sargassum ringgoldianum and a kind of Fucales 2, Sargassum fusiforme and a kind of Fucales 3, Sargassum thunbergii were much high, several 100 ppm. Sargassum fusiforme is a very popular brown seaweed food known as “Hijiki” in Japanese. Furthermore, As concentration in a kind of Laminariale 1, Undaria pinnatifida or “Wakame”, a very popular seaweed food, in Japanese was 10 to less than 100 ppm. As concentrations in another brown seaweed, Dictyotales, Ishigeales and Scytosiphonales were several to several 10s ppm and not very different from those of red and green seaweed.

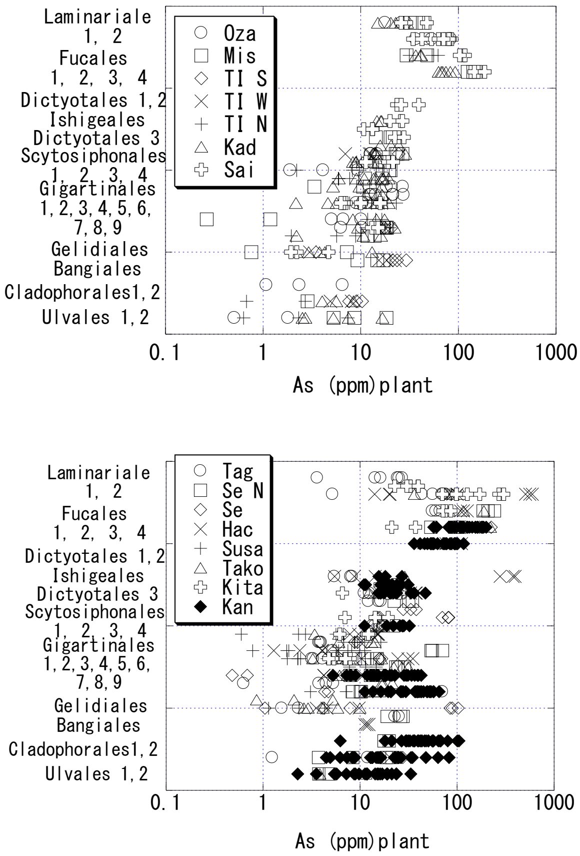


Fig.7 As concentrations in seaweed at north and south Kii Peninsula

As concentration in a very popular red seaweed food, a kind of Bangiales, Pyropia yezoensis, called “Nori” in Japanese were several 10s ppm. As concentration in the very popular green seaweed food, Ulvales 1, Ulva intestinalis, Ulva prolifera and Ulvales 2, Ulva pertusa, Monstroma nitidum, called “Aonori” in Japanese was 0.4 to 100 ppm. In particular, As concentrations in seaweed at Kanayama were not high compared to other areas.

3.2 Sr Concentration in Seaweed

Sr concentrations in brown seaweed at the north and south Kii Peninsula were 50 to 4,000 ppm and 70 to 4,000 ppm as shown in Fig.8. However, they were very high, 500 to 4,000 ppm and 400 to 4,000 ppm excluding Scytosiphonales 3 and Scytosiphonales 4. Sr concentrations in red seaweed at the north and south Kii Peninsula were 30 to 1,000 ppm and 30 to 1,000 ppm however most Sr concentrations in red seaweed were 30 to 200 ppm and 30 to 300 ppm. Sr concentrations in green seaweed at the north and south Kii Peninsula were 40 to 2,000 ppm and 70 to 400 ppm.

Sr concentration in brown seaweed was much high. Therefore, analysis of brown seaweed for concentrations of Sr was found to be an effective method of determining levels of radioactive Sr contamination in seawater surrounding atomic power stations.

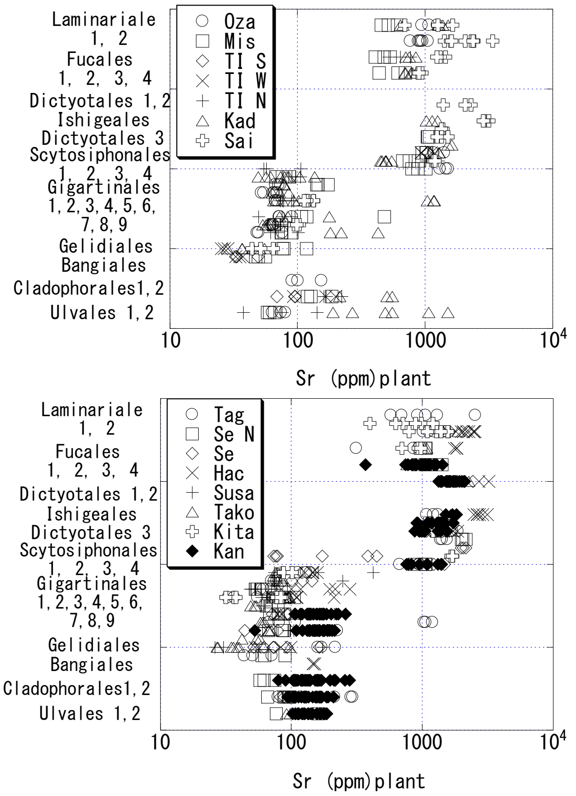


Fig.8 Sr concentrations in seaweed at north and south Kii Peninsula.

On the whole, Sr concentrations at the south Kii Peninsula were as the same as those at the north Kii Peninsula excluding Ulvales 1,2 at Kada. In particular, Sr concentration in seaweed at Kanayama was not high compared to other areas. Sr concentrations of green seaweed at Kada were moderate to high.

3.3 Zn Concentration in Seaweed

As shown in Fig.9, Zn concentrations in brown, red, and green seaweed at Kanayama were several 1,000s to 30,000, 2,000 to 30,000, and 500 to 30,000 ppm. These values were much higher than those at other areas. On the whole, Zn concentrations in seaweed at the Senjyo and Senjyo N were 10s to several 1,000s ppm and higher than those at the other area. The Senjyo and Senjyo N points were 1.2 km north of Kanayama sampling point and close to a large hot spring. The Hachijyu point was 1.6 km south of Kanayama sampling point. Zn concentration at Hachijyu was not as high compared to other areas.

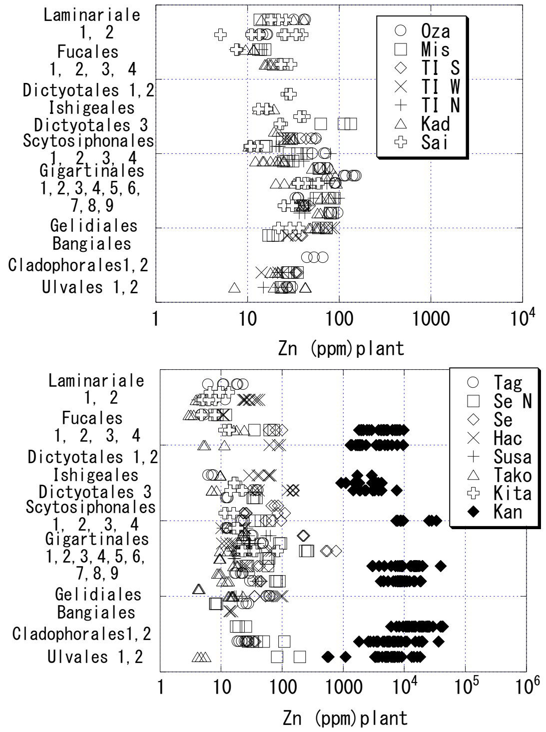


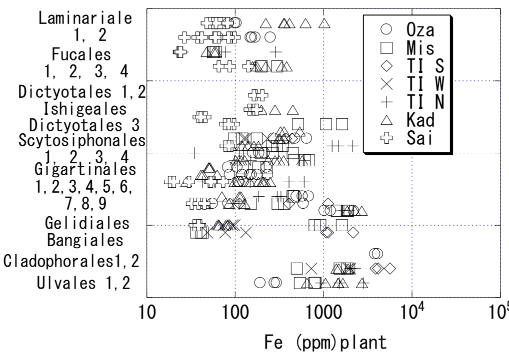
Fig. 9 Zn concentrations in seaweed at north and south Kii Peninsula.

Total Zn load into Kanayama Bay was 3,000 to 5,000 kg per year, influence of mine waste water on Zn concentration in seaweed in Kanayama Bay was found. Zn concentrations in seaweed at the Senjyo and Senjyo N were thought to be influenced by mine waste water or hot spring water. Zn concentrations in brown seaweed at the north and south Kii Peninsula were 5 to 200 ppm and 3 to 200 ppm excluding seaweed at Kanayama. Zn concentration in red seaweed at the north and south Kii Peninsula were 10 to 200 ppm and 4 to 1,000 ppm excluding seaweed at Kanayama. Zn concentration of green seaweed at the north and south Kii Peninsula were 7 to 70 ppm and 5 to 200 ppm excluding seaweed at Kanayama. Therefore Zn concentrations at the south Kii Peninsula were as the same as those at the north Kii Peninsula and the Zn concentration difference between brown, red and green seaweed were found to be small excluding seaweed at Kanayama..

3.4 Fe Concentration in Seaweed

Fe concentrations in brown, red, and green seaweed at Kanayama were 400 to 10,000, 2,000 to 50,000, and 1,000 to 200,000 ppm and much higher than those at other areas as shown in Fig.10. Total Fe load into Kanayama Bay was 4,000 to 6,000 kg per year and large as was the Zn load. However, Fe concentrations in seaweed at the Senjyo, Senjyo N and Hachijyu were not always high relative to other areas. Therefore, high Fe concentration in seaweed was found to be just at Kanayama Bay in spite of large amount of Fe load.

Fe concentrations in brown seaweed at the north and south Kii Peninsula were 30 to 3,000 ppm and 20 to 800 ppm excluding seaweed at Kanayama. Fe concentration in red seaweed at the north and south Kii Peninsula were 20 to 3,000 ppm and 10 to 3,000 ppm excluding seaweed at Kanayama. Fe concentration in green seaweed at the north and south Kii Peninsula were 200 to 7,000 ppm and 80 to 4,000 ppm excluding seaweed at Kanayama. Therefore, Fe concentrations at the south Kii Peninsula were the same as those at the north Kii Peninsula excluding seaweed at Kanayama and in general, Fe concentrations in green seaweed was higher than those in brown and red seaweed at the both Kanayama and other areas. “Aonori”, Ulvales 1, Ulva intestinalis, Ulva prolifera and Ulvales 2, Ulva pertusa, Monstroma nitidum, was relatively high, 100 to several 1,000s ppm.



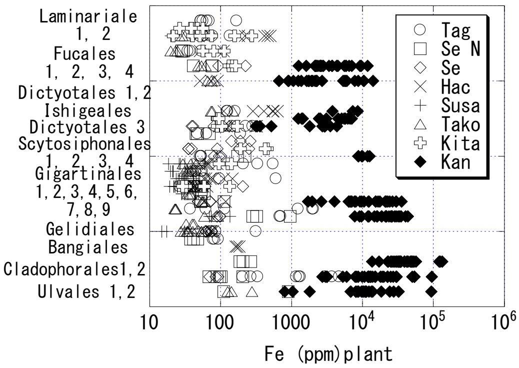
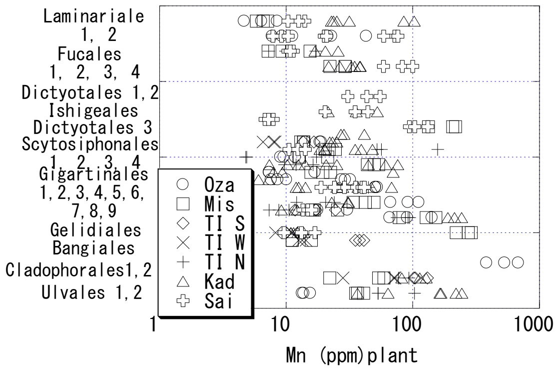


Fig. 10 Fe concentrations in seaweed at north and south Kii Peninsula

3.5 Mn Concentration in Seaweed

Total Mn load into Kanayama Bay was 180 kg per year. Mn concentrations in brown, red, and green seaweed at Kanayama were 7 to 500, 40 to 8,000, and 4 to 8,000 ppm and much higher than those at other areas as shown in Fig.11.

Mn concentrations in brown seaweed at the north and south Kii Peninsula were 4 to 300 ppm and 2 to 400 ppm excluding seaweed at Kanayama. Mn concentrations in red seaweed at the north and south Kii Peninsula were 5 to 400 ppm and 1 to 300 ppm excluding seaweed at Kanayama. Mn concentrations in green seaweed at the north and south Kii Peninsula were 20 to 700 ppm and 6 to 200 ppm excluding seaweed at Kanayama. Therefore, Mn concentrations at the south Kii Peninsula were the same as those at the north Kii Peninsula excluding seaweed at Kanayama and generally Mn concentrations in green, brown and red seaweed at the both Kanayama and other areas were the same.



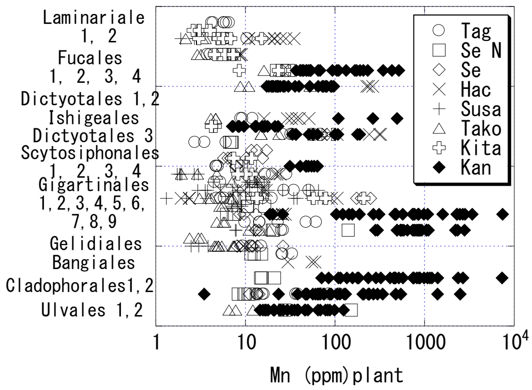


Fig. 11 Mn concentrations in seaweed at north and south Kii Peninsula.

3.6 Pb Concentration in Seaweed

Total Pb load into Kanayama Bay was 20 kg per year. Pb concentrations in brown, red, and green seaweed at Kanayama were 4 to 400, 30 to 1,000, and 4 to 1,000 ppm and much higher than those at other areas as shown in Fig.12. Pb concentrations in brown seaweed at the north and south Kii Peninsula were 0.2 to 20 ppm and 0.2 to 10 ppm excluding seaweed at the Kanayama. Pb concentration in red seaweed at the north and south Kii Peninsula were 0.3 to 40 ppm and 0.1 to 10 ppm excluding seaweed at Kanayama. Pb concentrations in green seaweed at the north and south Kii Peninsula were 2 to 40 ppm and 0.5 to 20 ppm excluding seaweed at Kanayama.

Therefore, Pb concentrations at the south Kii Peninsula were lower than those at the north Kii Peninsula excluding seaweed at Kanayama in spite of Pb load, 20kg at Kanayama, south Kii Peninsula and Pb load at Kanayama was found to be small at the Kii Peninsula. On the whole Pb concentrations in brown seaweed were lower those in green and red seaweed at Kanayama however no clear differences between brown, red and green seaweed were found in the other areas.

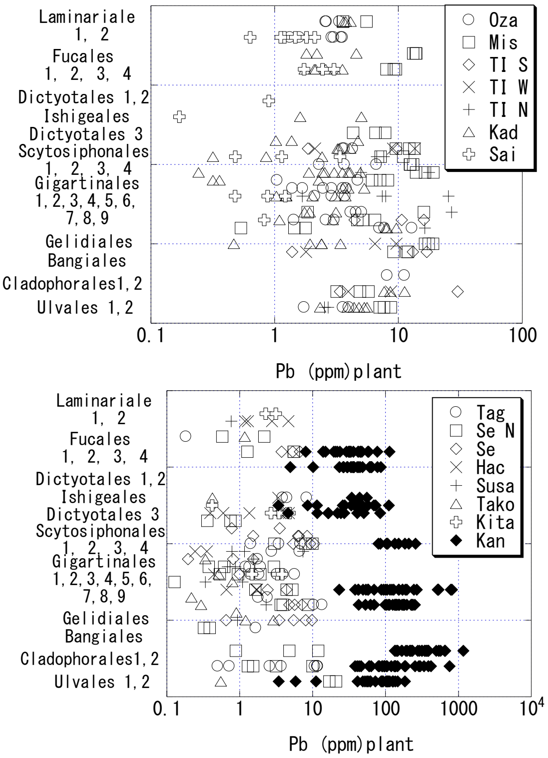


Fig.12 Pb concentrations in seaweed at north and south Kii Peninsula

3.7 Cu Concentration in Seaweed

Total Cu load into Kanayama Bay was several kg per year. Cu concentrations in brown, red, and green seaweed at Kanayama were 2 to 20, 2 to 100, and 2 to 300 ppm and little higher than those at other areas as shown in Fig.13.

Most of Cu concentrations in brown seaweed at the north and south Kii Peninsula were 1 to 20 ppm excluding some seaweed at the Senjyo North. Cu concentration in red seaweed at the north and south Kii Peninsula were 2 to 40 ppm and 0.8 to 40 ppm excluding seaweed at Kanayama and then most red seaweed concentrations at Kanayama were high, 20 to 100 ppm. Cu concentrations in green seaweed at the north and south Kii Peninsula were 3 to 20 ppm excluding seaweed at Kanayama which was little high, 2 to 80 ppm.

Therefore, Cu concentrations at the south and the north Kii Peninsula were almost the same values

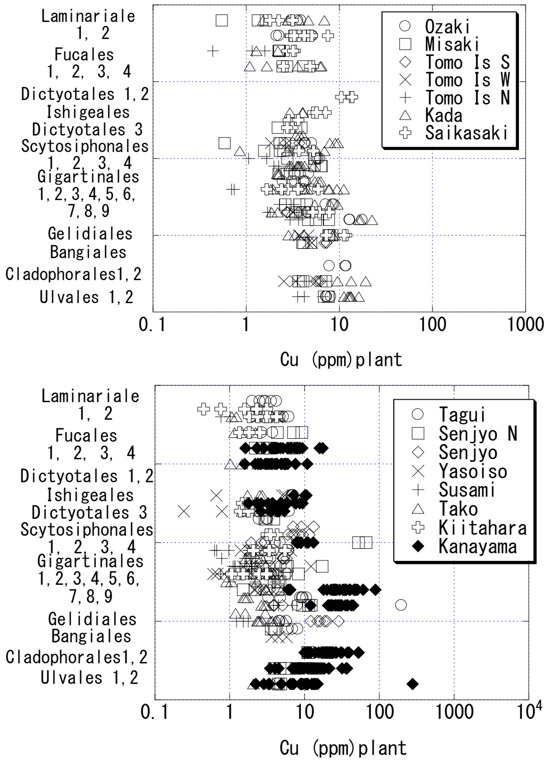


Fig.13 Cu concentrations in seaweed at north and south Kii Peninsula

excluding seaweed at Kanayama. On the whole Cu concentrations in brown seaweed were lower those in green and red seaweed at Kanayama however no clear differences between brown, red and green seaweed were found in the other areas.

4. DISCUSSION AND CONCLUSION

Table 1 shows As, Sr, Zn, Fe, Mn, Pb and Cu concentrations in brown, red and green seaweed between the north Kii Peninsula (north), the South Kii Peninsula (south) excluding Kanayama, Kanayama (Kan) and the world values (Ref) [7].

Metal concentrations in seaweed at Kanayama showed abnormally high values. The Kanayama sampling point was inside the bay and total Fe, Zn, Mn, Pb and Cu loads of mine waste water from the closed mine into the bay were 4,000 to 6,000, 3,000 to 5,000, 180, 20 and several kg per year. Zn and Fe concentrations in seaweed at Kanayama were 10 to 100 times relative to the world value. Mn and Pb concentrations in seaweed at Kanayama were 10 times higher than the world values. Cu concentrations of red and green seaweeds at Kanayama were higher than the world values.

Fe concentrations in brown seaweed and Sr concentrations in green seaweed at the north Kii Peninsula were higher than those at the south Kii

Peninsula and As concentrations in seaweed and Zn concentrations in red and green seaweed at the south Kii Peninsula were higher than at the north Kii Peninsula. Other seaweed metal concentrations at both the south and north Kii Peninsula had almost the same values.

Although As, Sr, Zn, Fe, Mn, Pb and Cu concentrations in seaweed from Osaka By to south top of the Kii Peninsula facing the Kuroshio Current at the Kii Peninsula were very variable, their average values were in good agreement with the world data except for Kanayama.

Therefore, As, Sr, Zn, Fe, Mn, Pb and Cu concentrations in seaweed at the Kii Peninsula except at Kanayama were normal values. In general, metal concentration distribution was uniform at the Kii Peninsula therefore the influence of the Kuroshio Current water and Osaka Bay water facing the metropolis on metal concentration in seaweed was found to be small. At the Kii peninsula except at Kanayama, As and Sr concentrations in brown seaweed were higher those in red and green seaweed, Fe concentrations in green seaweed were higher than those in brown and red seaweed and Zn, Mn, Pb and Cu concentrations in brown, red and green seaweed were all the same.

Table 1 Metal concentration (ppm) of seaweed at north and south Kii Peninsula

	site	brown	red	green
As	north	10~ 300	0.3~40	0.5~ 20
	south	4 ~ 1000	0.4 ~ 100	1 ~ 100
	Ref	62	6	1.2~6
Sr	north	50~4,000	30~1,000	40~2,000
	south	70~4,000	30~1,000	70~ 400
	Ref	800~ 1,600	95~450	60~220
Zn	north	5 ~ 200	10 ~ 200	7~ 70
	south	3 ~ 200	4 ~ 1,000	5 ~ 200
	Kan	1,000~ 30,000	2,000~ 30,000	500~ 30,000
	Ref	20~140	21~150	6~260
Fe	north	30~3,000	20~3,000	200~ 7,000
	south	20~800	10~3,000	80~ 4,000
	Kan	400~ 10,000	2,000~ 50,000	1,000 ~ 200,000
	Ref	13~1,900	200~ 1,800	160~750
Mn	north	4 ~ 300	5 ~ 400	20 ~ 700
	south	2 ~ 400	1 ~ 300	6 ~ 200
	Kan	7~500	40~8,000	4~ 8,000
	Ref	1~400	16~500	16~300
Pb	north	0.2 ~ 20	0.3 ~ 40	2 ~ 40
	south	0.2 ~ 10	0.1 ~ 10	0.5 ~ 20
	Kan	4 ~ 400,	30~1,000	4~ 1,000
	Ref	2~38	2.9	40
Cu	north	1~20	2~40	3~20
	south	0.2~90	0.8~40	3~20
	Kan	2~20	2~100	2~80
	Ref	2~68	3~24	4~58

5. REFERENCES

[1] Lunde G, "Analysis of trace elements in seaweed", J. of Sci. Fd. Argic., Vol. 21, Aug. 1970, pp. 416-418.

[2] Yamamoto T, and Ishibasi M, "The Content of Trace Elements in Seaweeds", in Proc. 7th Int. Seaweed Symposium, 1971, pp. 511-514

[3] Ghada F El-Said and Amany El-Sikaily, "Chemical composition of some seaweed from Mediterranean Sea coast, Egypt", Environmental Monitoring and assessment, July 2013, Vol. 185, Issue7, pp 6089-6099

[4] Alahverdi M and Savabieasfahani M, "Metal Pollution in Seaweed and related Sediment of the Persian Gulf, Iran", Bull Environ. Contam. Toxicol, Vol. 88, 2012, pp. 939-945.

[5] Griselda MRF, Evgueni S and Ignacio SR, "Heavy metal Pollution monitoring using the brown seaweed Padina durvillaei in the coastal zone of the Santa Rosalia mining region, Baja calfornia Peninsula, Mexico", J. Appl. Phycol., Vol. 21, 2009, pp. 19-26.

[6] Ii H, "Cu, Zn and As contamination of seaweed beside Shizuki and Kanayama metal mines in Japan", Int. J. of GEOMATE, Vol. 9, No.1, Sep. 2015, pp. 1411-1417.

[7] Asami T. and Chino M., "Elements in organism", Environmental Chemistry of the Elements, 1st ed. Hakuyusha, 1983, pp. 101–105. In Japanese.

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