

Quantitative analysis using particle induced x-ray emission (PIXE)

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要約：浦の内湾の海底ヘドロと貝を粒子励起 X 線放射 (PIXE) 法によって定量的に分析した。この研究の目的は、ヘドロと貝類に対する重金属の影響をしらべることである。湾内の11ヶ所から採取されたヘドロを分析した結果、有害金属を含む17種の元素が検出された。また、湾の中心部が周辺部よりも汚染が進んでいる。貝の分析では、80ppm の銅、43ppm の亜鉛、9 ppm のストロンチウムが検出されるなど、スーパーで売られている商品よりも重金属濃度が高かった。

Abstract : We have done the quantitative analysis using Particle Induced X-ray Emission (PIXE). The seabed sludge and shellfish of Uranouchi bay were analyzed. The aim of this study is to find out the influence of heavy metals on the seabed sludge as well as shellfish. As a result of analyzing eleven sludge samples collected from different places in the bay, seventeen elements including some toxic were detected. The results suggest that the center region of the bay is seriously contaminated by heavy and toxic elements in comparison with the other areas in the bay. Our shellfish results indicate that they contain more heavy metals than that of Market shellfish such as Cu of 80 ppm, Zn of 43 ppm and Sr of 9 ppm etc.

1. Introduction

PIXE is an analytical technique which is highly sensitive and multi-elemental among others, already proved in all prospective areas such as thin films, water, air, archaeological and biological samples etc [1]. Though several analytical techniques have been used for elemental analysis, PIXE provides more accurate result. It has been widely used for analysis of environmental and biological samples in several decades [2-3]. In the present

study this technique is used to analyze the seabed sludge and shellfish to gather knowledge about the heavy elemental concentration in them. The samples were collected from different places of Uranouchi bay. Although Uranouchi bay in Kochi prefecture, Japan, is well-known for its natural landscape and fish culturing, sea water and the seabed of this bay are no longer clean now. It has been pointed out that increasing concentration of heavy elements is one of the causes of dirtiness of the bay.

It becomes now dirtier day by day which directly affect not only the sludge and shellfish but also the live bodies of this bay. This ecological environment of the bay has been changed due to several anthropogenic sources. Fishermen are growing fishes in this bay and put fish foods profoundly. The concentration of certain elements in fish foods is enriched. Although some portions of the food are taken by fishes, the rest of foods accumulate onto the seabed sludge. In addition, a large number of small boats sail inside the bay and their fuel is also the reason of creating the grimy sludge. Some household waste such as detergent and other natural waste fall onto this bay. The aim of the present study is to determine the influence of heavy metals on the seabed sludge and live bodies in the bay, shellfish has been chosen as the representative among the other live bodies.

2. Sampling

2.1: Seabed Sludge

The Uranouchi bay is about 12 km long and leads to the open Pacific Ocean through a shallow mouth (~100m wide). Samples were collected from eleven different places in this bay randomly; Ekman dredge sampler was used to collect the seabed sludge from the top of the bottom sediment. Then, samples were passed through a 2 mm metal sieve for removing stones, woods and algae type goods. After that, samples were preserved in a refrigerator in glass bottles with small amount of Ar gas. Fig.1 shows the sampling points in the Uranouchi bay.

2.2: Shellfish

Shellfish was collected from three different places of Uranouchi Bay. After washing with distilled water, they were preserved in a deep freeze. In Fig.1, No. from 12 to 14 is the sampling points of shellfish which indicates as zone1, zone2 and zone3,



Fig.1: Sampling points in Uranouchi Bay, No 1 to 11 is for seabed sludge and 12 to 14 for shellfish.

respectively in this paper.

3. Sample preparation:

3.1: Seabed Sludge

Wet sludge samples were dried at room temperature. For proper ingredient mixing of all elements, samples were made into powder form. Carefully weighed 10 mg dried sludge sample was mixed with 1 ml polyvinyl acetate (1000 ppm PVAc) and 0.5 ml Hiviswako (0.5%). After proper mixing, 15 μ l liquid sample was taken for analysis which contained 100 μ g sludge. A droplet of the acquired solution was then spotted onto a 4 μ m thick polypropylene film which was used as substrate for samples to form a circular target spot with a size of around 4 mm in diameter. At room temperature, samples were placed inside of desiccators until they were dried. The sample was then ready for PIXE measurement. From one sample solution, three targets were made and each target was measured separately.

3.2: Shellfish

The sample preparation procedure is shown in Fig.2. The shellfish was washed with distilled water after removing from the shell and waited sometime for removing water. Samples were dried by an oven for few minutes and then put onto the light (lamp) for

several hours to remove moisture from the samples. For proper ingredient mixing of all elements, samples were made into powder form using a small grinding hammer. A 10 mg powder sample was weighed carefully by electronic balance and was mixed with 1 ml polyvinyl acetate (1000 ppm PVAc). Carefully weighed 2 mg Mo was mixed in each sample as an internal standard. A 10 μ l re-

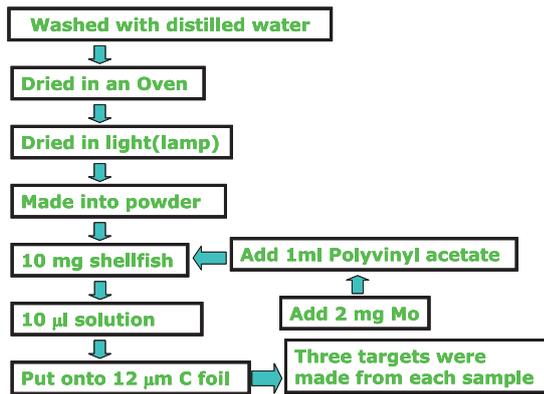


Fig.2: Flow chart of shellfish sample preparation technique.

sulting solution was taken by a micro pipette for analysis which contained 100 μ g of shellfish. The droplet of the obtained solution was then spotted onto a 12 μ m thick carbon foil which was used as substrate for samples to form a circular target spot with a size of around 2mm in diameter. All samples were placed inside of desiccators at room temperature until they were dried. The sample was then ready for PIXE measurements. From one sample solution, three targets were made and each target was measured separately.

4. Experimental

4.1: Seabed Sludge

The proton beam from the 2.5 MV Van de Graaff accelerator at Hiroshima University was used for this study. The samples were irradiated in a vacuum chamber with 6 mm in diameter ion beam which covered the entire area of target. Characteristic

x-rays from targets were measured with a Si(Li) SL80175 Canberra detector (25.4 μ m thick Be window). Detector was connected to a multi-channel analyzer for converting analog data to digital. Detector sensitivity area, resolution and Si thickness were 80 mm², 167 eV fwhm at 5.9 keV and 5 mm, respectively. Detector angle from the beam line was 150°. Two spectra were obtained for each target: the first one was for detection of $Z \geq 20$ elements with 2.5 MeV proton energy, 5 nA beam intensity and 2 μ C accumulated charge; the second one was for $Z < 20$ elements with 1.25 MeV proton energy, 1.5 nA beam intensity and 1 μ C accumulated charge. A 250 μ m thick mylar filter without any hole and a 2.4 mm hole (the so-called “funny” detector) were placed in front of detector for the first and the second case, respectively.

4.2: Shellfish

A 1.7 MeV tandem accelerator at Kochi University of Technology (KUT) Japan was used for the PIXE measurements. A He⁺⁺ beam of 4 MeV energy collimated to 1 mm diameter was used for irradiation of the samples which covered the quarter area of the samples. The shellfish samples were placed in a vacuum chamber straight to the beam line with a sample holder. Characteristic x-rays excited from targets were measured by an Si(Li) detector (8 μ m thick Beryllium with polymer coating window) positioned at 135° angle to the beam line for two-fold reduction in electron bremsstrahlung. Active area and Si thickness of detector were 10 mm² and 0.3 mm, respectively. A 125 μ m Mylar with an aluminum holder was used in front of detector which was acted as a filter to cut lower energy x-rays and reduce x-rays interference. The total distance from the target to Si(Li) detector was around 40 mm. The effective solid angle was 0.0063 sr. The collected charge was

measured by current integration from the sample holder which served as a Faraday cup. The charge around 30 μC was used for each sample irradiation. Detector was connected to a multi-channel analyzer via a preamplifier for converting analog data to digital.

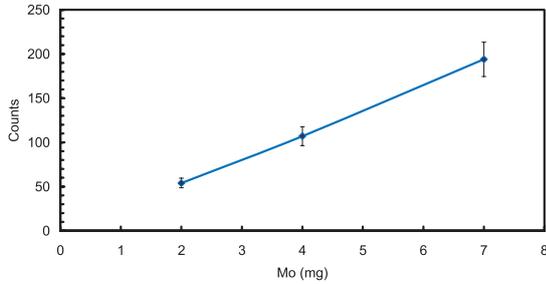


Fig.3: Count rate of Mo with respect to the concentration obtained with a 4 MeV He^{++} for 30 μC

Fig.3 shows the count rate vs internal standard (Mo) sample weight. The error bars shown are the experimental uncertainty at the approximately $\pm 10\%$ level. It is clearly seen from this figure that the count rate linearly increases with Mo concentration. Though, the homogeneity of the sample is difficult to maintain but in the present study it was carefully handled by proper mixing of sample during the time of making the powder form of the sample as well as before pipetting. The homogeneity of the sample has been checked at three different places each with one mm diameter which covered the three-fourth area of the sample. The collected fluorescence yields from different places of the sample are almost identical with an accuracy of around maximum $\pm 10\%$. This result indicates that the homogeneity within the sample is nearly uniform.

5. Results and Discussion

5.1: Seabed Sludge

Seventeen elements were detected in the analysis of the samples collected from eleven areas of Ura-

nouchi bay. Typical PIXE spectra of sample number Sam7 obtained with a 2.5 MeV proton beam is shown in Fig.4. Detected elements are designated in this figure. Though, Zr is detected in some samples in low amount, we do not consider Zr concentration in this paper. However, 4 extra peaks are clearly shown in Fig.4 as indicated by A, B, C and D at channel 504, 540, 640 and 672, respectively. Peak (A), (B), (C) and (D) are the sum peak of $\text{Ca}(\text{K}_\alpha) + \text{Fe}(\text{K}_\alpha)$, $\text{Ca}(\text{K}_\alpha) + \text{Fe}(\text{K}_\beta)$, $2 * \text{Fe}(\text{K}_\alpha)$ and $\text{Fe}(\text{K}_\alpha) + \text{Fe}(\text{K}_\beta)$, respectively. Experimental system has a function of pile-up rejection. Therefore, these peaks come when the system is unable to discriminate exactly simultaneous photons. Comparing Fig.4 (Sam7) with Fig.5 (Sam11), it is clear that the elemental concentration in Sam7 is much higher than that in Sam11.

Atomic Absorption Spectrometry (AAS) standard samples were used as calibration standards for the calculation of elemental concentration. The sensitivity of each element i is calculated using the following equation:

$$S_i = \frac{Y_i}{Q_i} \quad (5.1.1)$$

where S_i is the sensitivity for element i , Y_i is the peak height (counts per (μg)) for standard sample and Q_i is the value of charge (μC) accumulated during standard sample measurements. For calibration, the sensitivity versus atomic number curves are shown in Fig.6 (a) and Fig.6 (b).

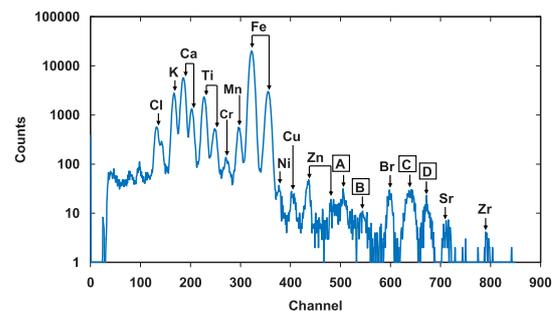


Fig.4: Typical PIXE spectrum of Sam7 obtained with a 2.5 MeV proton beam.

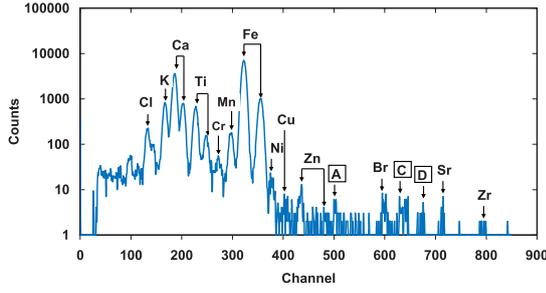


Fig.5: Typical PIXE spectrum of Sam11 obtained with a 2.5 MeV proton beam

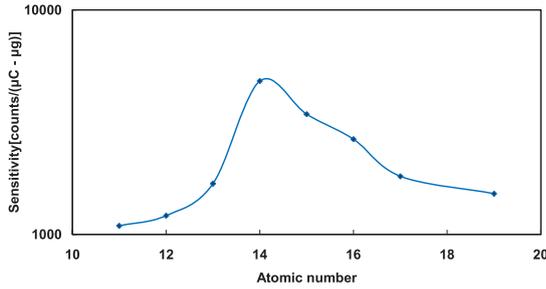


Fig.6(a): Sensitivity curve as a function of atomic number for the elements $Z < 20$.

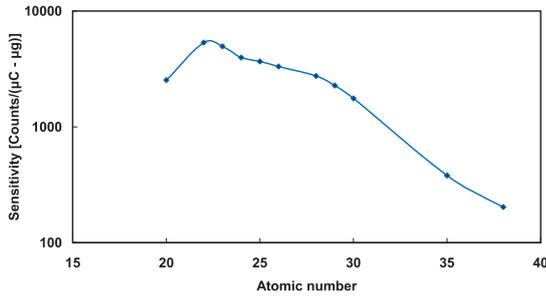


Fig.6(b): Sensitivity curve as a function of atomic number for the elements $Z \geq 20$.

The concentration of each element in the target t is calculated using the following equation:

$$C_{it} = \frac{Y_{it}/Q_{it}}{S_{it}} \quad (5.1.2)$$

where C_{it} and Y_{it} are the concentration and the average peak height of the element i in the target t , respectively. Q_{it} and S_{it} are the value of accumulated charge (μC) during the measurement of target and sensitivity factor for the element i , respectively.

Every sample was irradiated three times and then the

elemental concentration of one sample was calculated from the data after averaging peak height over measurements of three targets. It is noted that about 66 spectra from 11 samples are used for calculation. The elemental concentrations of the 17 elements are shown in Table 1. Na, Mg, Al, Si, S, Cl, K, Ca and Fe are detected as major elements whereas Ti, Cr, Mn, Ni, Cu, Zn, Br and Sr are detected as trace elements. Some toxic elements [4–6] such as Cr, Ni, Cu and Zn are significantly increased in some sampling area with respect to other areas.

Each sample shows characteristic features in the concentration of major elements depending on the collecting areas. Especially, Sam7 has a distinguished feature in comparison with Sam11. In Sam7 sulfur concentration is considerably higher by five times than that in Sam11. On the other hand, sulfur concentration is almost equal for the samples Sam2–5. Calcium concentration increases as the sampling points become inner from the inlet (Sam11) to the middle (Sam7) of the bay, and turns to decrease toward the inner side of the bay (Sam1–4), where its concentration shows similar values of around 45 ppm. Though the reason of decrease of calcium concentration is not clear, it can be said that such circumstance is not suited to fish culturing. With regard to the trace elements, chromium concentration is lower in Sam2 and Sam3 and is much higher in Sam7 in comparison with that in the other samples. Nickel concentration is higher in Sam9 and lower in Sam1 and Sam4. Iron, copper, zinc and strontium concentrations are much higher in Sam7 in contrast to that in Sam11.

The experimental errors were calculated in order to judge the significance of the differences in elemental concentration. The experimental errors mainly come from statistical errors of the x-ray peaks and partly from the value of x-ray transmis-

Table 1: Elemental concentration in the seabed sludge samples collected at 11 regions of Uranouchi bay. Results are shown in units of 100 $\mu\text{g/g}$.

Elements	Sam1	Sam 2	Sam 3	Sam 4	Sam 5	Sam 6	Sam 7	Sam 8	Sam 9	Sam 10	Sam11
Na	112.76	121.61	119.54	164.84	171.92	146.09	151.40	116.73	143.83	108.30	65.23
Mg	132.10	128.69	132.01	137.43	187.27	173.02	188.45	138.34	161.30	133.20	75.47
Al	421.83	385.77	455.21	352.59	456.06	309.68	569.06	339.96	409.90	332.92	179.00
Si	415.18	394.78	460.37	356.85	509.78	332.73	628.69	391.39	504.10	433.71	262.79
S	48.04	59.28	56.33	57.40	61.80	37.74	67.27	43.70	45.79	34.01	13.12
Cl	318.24	346.96	340.07	477.45	527.42	284.55	421.65	355.61	413.39	291.26	135.24
K	70.20	65.79	73.89	67.59	82.07	53.26	95.28	63.31	74.41	60.26	33.68
Ca	46.78	48.03	43.67	45.72	98.35	55.37	149.12	109.02	165.05	175.55	98.22
Ti	14.44	14.35	16.36	13.59	17.69	18.48	22.28	15.79	20.24	18.09	8.63
Cr	1.04	1.00	1.15	1.00	1.47	1.39	1.81	1.24	1.60	1.57	1.45
Mn	2.93	3.45	3.69	3.16	5.73	5.37	7.76	5.58	6.91	6.00	3.65
Fe	205.87	206.06	225.63	178.82	256.16	263.11	315.51	233.02	306.60	256.17	135.57
Ni	0.32	0.36	0.41	0.32	0.45	0.44	0.61	0.53	0.69	0.60	0.39
Cu	0.34	0.31	0.28	0.29	0.48	0.50	0.58	0.42	0.56	0.46	0.21
Zn	0.82	0.77	0.87	0.65	1.10	1.10	1.20	1.03	1.10	0.77	0.45
Br	2.85	2.46	3.20	3.86	3.90	3.64	3.68	3.51	3.64	2.11	0.96
Sr	1.48	1.48	0.90	0.99	1.23	1.40	2.05	1.15	1.89	2.05	0.90

sion and detection efficiencies. In this study, we only considered the statistical errors because the other errors were negligible with respect to the statistical errors. These errors were below 4 % for the elements $Z < 27$ except Cr whereas they become higher from around 15% to 50% for the heavy elements. For Cr the error was around 10 % because of less Cr count.

Fig.7 shows the ratios of concentrations of toxic elements, where all values are divided by the values for Sam11. It can be seen from the figure that the concentrations of Cr, Ni, Cu and Zn pronouncedly increase in Sam5-7 and Sam9 in comparison with those in the other samples. The concentrations of Cr, Zn and Cu in Sam7 are more than 2.48, 2.6 and 2.72 times higher, while that of Ni in Sam9 is 2.58 times higher in contrast to their lowest values. Although Zn and Cu are the essential trace elements for marine lives, they become toxic at higher concentrations[7]. In the present study, these elements show higher concentrations in the center region of the bay. Trace heavy metals as well as toxic elements have changed the

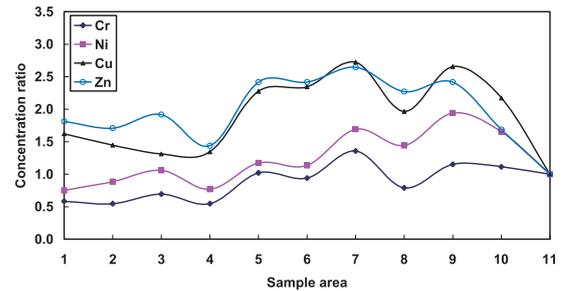


Fig.7: Concentration ratios of toxic elements at each sampling area with respect to the concentrations in Sam11.

ecological system of the bay and have caused deleterious effects on fishes and other aquatic organisms.

As there is no general agreement concerning the maximum acceptable limits of elemental concentration in seabed sludge, we discuss the concentration of various elements in reference to that for Sam11 collected at the inlet of the bay. As a result, it is found that all other samples collected in the inner regions in the bay are polluted. Among them, Sam7 collected in the center region in the bay is particularly contaminated.

5.2: Shellfish

The minimum detection of limit (MDL) defines the sensitivity of a measurement system. When the fluorescence spectrum is measured, the MDL is correlated with the signal peak and the background. Different methods have been reported for calculation of the minimum detection of limits in x-ray spectroscopy [8-10]. The detection limits are calculated in PIXE analysis by assuming that the minimum intensity of the peak is three times the square root of the background at full width half maximum intensity as indicated by equation,

$$MDL = \frac{3\sqrt{BG}}{S} * C \quad (5.2.1)$$

where, S and BG are the total number of counts in the peak and background areas, respectively. C is the known concentration of the standard element. Fig.8 shows that the minimum detection limits of our PIXE system which is calculated using equation 5.2.1.

If we use a single added internal standard into an unknown sample and for which the spectrum is collected in the same way as for the unknown sample then the concentration of each element for the unknown sample can be simply calculated by using the following equation [11],

$$C_U = \frac{Y_U}{Y_S} \times C_S \quad (5.2.2)$$

where C_U and C_S are the unknown and standard

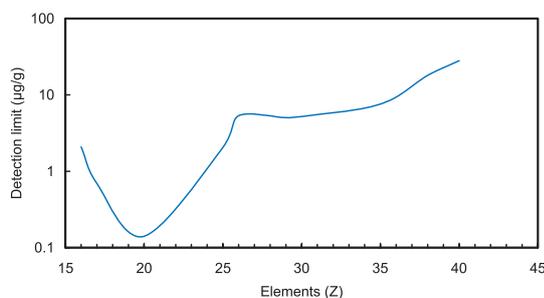


Fig.8: Limit of Detection obtained with a 30 µC of 4 MeV He⁺⁺ beam

samples concentration, respectively. Y_U and Y_S are the unknown and standard samples fluorescence yield, respectively.

Each sample was irradiated three times and then using a computer code the background was subtracted from each spectrum. The concentration of the element was calculated by using equation 5.2.2 from the data after averaging the peak areas from the three target spectrum at full width half maximum fluorescence yield. Three samples were analyzed for each zone i.e. total nine samples were analyzed. Average results are tabulated in table 2a. It is seen from this table that the S, Cl and Ca are detected as major elements whereas others are heavy elements. Due to high variation in the elemental concentrations, some elements show the higher standard deviation. Analyzing shellfish collected from different areas of Uranouchi bay, ten elements were detected. The concentration of major elements in all samples shows the characteristic features depending on the collecting areas. Especially, Ca shows the higher concentration among other major elements in all samples. It can be pointed out that the concentration of Ca is almost 17 and 8 times higher in zone 2 and zone 1, respectively in contrast of zone 1. Sulfur and chlorine show higher concentration in zone 3 and zone 1, respectively. However, sulfur decreases toward zone 2 and 1. On the other hand, Mn and Fe are shown as higher concentration in zone1 and zone 3, respectively.

The heavy element concentrations of Uranouchi shellfish was compared with Market shellfish as shown in table 2b. Three samples were analyzed which were collected from a supermarket and each sample was irradiated three times. The same procedure was applied for calculating the elemental concentration which followed in the Uranouchi cases. Fig.9 shows the comparison of elemental concentration on heavy elements between Uranou-

Table 2: The concentration of elements in shellfishes collected form Uranouchi bay and Market. Results are shown in units of 100 $\mu\text{g/g}$ (ppm).

Table 2a: For Uranouchi

Elements	Zone 1	Zone 2	Zone 3
S	23.19 (3.93)	32.53 (2.83)	46.48 (8.88)
Cl	53.97 (9.67)	21.59 (5.40)	26.33 (2.83)
Ca	622.05 (55.42)	1411.58 (253.27)	82.09 (6.99)
Mn	2.85 (0.50)	2.41 (0.13)	2.33 (0.13)
Fe	1.03 (0.17)	1.88 (0.54)	3.41 (0.51)
Cu	0.39 (0.08)	0.07 (0.01)	0.80 (0.15)
Zn	0.43 (0.06)	0.10 (0.05)	0.15 (0.04)
Br	0.23 (0.04)	0.23 (0.06)	0.04 (0.03)
Sr	0.05 (0.02)	0.09 (0.01)	0.04 (0.02)
Zr	0.04 (0.02)	0.02 (0.01)	0.01 (0.01)

Table 2b: For Market

Element	Market
S	41.18 (4.70)
Cl	151.30 (10.48)
K	66.74 (5.28)
Ca	18.46 (1.83)
Cr	0.31 (0.06)
Fe	1.51 (0.15)
Cu	0.16 (0.02)
Zn	0.14 (0.02)
Br	0.03 (0.02)
Sr	0.02 (0.01)
Zr	0.01 (0.01)

Numbers within parentheses refer to the standard deviation (\pm).

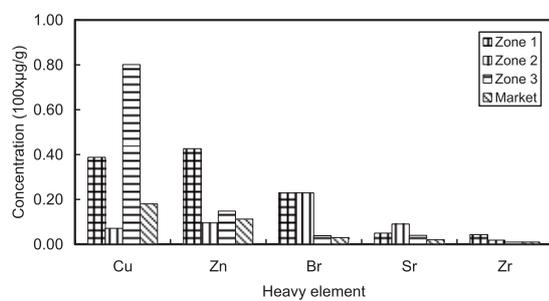


Fig.9: Comparison of heavy elements between Uranouchi and Market shellfishes

chi and Market shellfish. It is clearly seen from the figure that the all heavy elements of Uranouchi shellfish show much higher concentrations than Market shellfish except Cu. Cu has lower concentration in zone 2 in contrast of market but more than two and four times higher in zone 1 and zone 3, respectively. However Zn and Br are approximately four and eight times higher than market in zone 1, respectively. On the other hand, Sr is four time higher in zone 2.

Generally we consider that the market shellfish are cultivated in a good environment, put a balance food and strictly considered that they are not affected by other factors such as dirty water, chemicals, household and natural wastes etc. That's why in the present study we consider the market shellfish as a

reference. Results suggest that the different elements of Uranouchi bay shellfish have much higher concentration than Market shellfish. This is because this bay particularly the very sea shore where the samples were collected is polluted now. The reasons for the pollution of the bay can be classified as follows: 1) A large amount of fish is cultivated in this bay and fishermen have put a huge amount of foods, and they are partly taken by fishes but rest of them falls into the seabed [12]; 2) the household wastes including detergent and natural wastes come onto the bay; 3) leakage of fuel from sea boat and there might be some other causes which increase the elemental concentration of the heavy elements.

Conclusion:

Seventeen elements including toxic elements are detected from seabed sludge collected in Uranouchi bay. It is found that the center region of the bay is mostly polluted in contrast to the other regions. The highest values of copper and zinc concentration are found to be 2.72 and 2.6 times larger, respectively, in comparison with those for Sam11 collected from the inlet of the bay.

The heavy elements concentration were compared

between Uranouchi and market shellfish and found that almost all heavy elements in Uranouchi shellfish show higher concentration in contrast of market one except Cu in zone 2. The Zn concentration is four times higher than market shellfish. According to this result, live bodies of this bay are certainly affected by heavy metals in various ways.

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