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Abstract

Plutonium isotopes, ^{239}Pu and ^{240}Pu were measured in liver samples from Surume squid using a sector-field high resolution ICP-MS after radiochemical purification. Surume squid samples were obtained from nine landing ports in Japanese inshore during fishery season from September to December 2002. Concentrations of ^{239}Pu and ^{240}Pu ranged from 1.5 to 28 and 1.1 to 24 mBq kg^{-1}, respectively. Plutonium ($^{239,240}Pu$) concentrations in liver were several thousand times higher than levels found in seawater. The concentration factor (*CF*) compared to seawater for $^{239,240}Pu$ and 13 other elements ranged from 10^0 to 10^7. The *CF* values for $^{239,240}Pu$, V and Th were 10^2-10^4. Pu had an intermediate *CF* between conservative and scavenged elements.

Atomic ratios $^{240}Pu/^{239}Pu$ in the squid liver ranged from 0.177 to 0.237 which were slightly higher than 0.178±0.014 for global fallout. The variations of $^{240}Pu/^{239}Pu$ atomic ratios in ocean currents with different source functions are important for interpreting high $^{240}Pu/^{239}Pu$

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atomic ratios in Surume squid liver. It seems likely that Pu with high $^{240}Pu/^{239}Pu$ atomic ratio is continuously transported through the solubilization and seawater transport from the North Equatorial Current to Kuroshio and its branch, the Tsushima Current. By assuming that Pu found in Surume squid liver is a mixture of global fallout Pu (0.178) and close-in fallout Pu with high $^{240}Pu/^{239}Pu$ atomic ratio (0.30-0.36) around Bikini Atoll, Pu contribution from Bikini close-in fallout Pu accounts for close to 35% of the whole plutonium in Surume squid liver. These results highlight that Surume squid is a useful organism for evaluating environmental Pu levels of larger sea area and facilitate the development of models to understand oceanic transport of close-in fallout Pu from Bikini Atoll.

Keywords : Plutonium, Trace elements, Squid liver, ICP-MS, Bio-indicator, Bikini

1. Introduction

Artificial radionuclides ^{110m}Ag and ^{60}Co appear in marine organisms as a result of metabolism during a growth processes (Folsom et al., 1965). This finding is useful for evaluating toxic metal elements and radionuclide pollution in marine environment (Folsom et al., 1970). Seawater is the most significant medium to migration processes in the marine environment. The man-made long-lived radionuclides, such as ^{90}Sr, ^{137}Cs and Pu isotopes, are distributed world wide as a result of global fallout from atmospheric nuclear weapons tests. Regarding Pu isotopes, it was estimated that, since 1945, about 11 PBq of $^{239,240}Pu$ has been deposited on the oceans as global fallout from 543 atmospheric nuclear weapons tests (UNSCEAR 2000).

The main island of Japan (Honshu) is surrounded by the Pacific Ocean and the Sea of Japan, which are different in their current and open/close areas. About 400 to 600 thousand

tons of squids were caught in each of the last five years, and the Surume squid (*Todarodes pacificus*) represents about half (or more) of the catch, and they are easily caught everywhere on the coast around Japan's islands (Living Information Center, 2003). Since their life span is only a year and trace elements are remarkably concentrated in their organs, levels of trace elements in seawater can be monitored by measuring these elements in their organs (Abe and Honma, 1997). In contrast to flat fish, seaweed and benthos which inhabit in quite small area, the squid moves long distance and pathways depending mainly on seawater temperature (Abe and Honma, 1997). Therefore, the squid may be useful for monitor of larger sea area. In our country, the Surume squid seems to be suitable for biological indicator for Pu in seawater, as shown from its habitats in Fig. 1. However, the habitable sea area is not uniform since Surume squid is migrant marine organism depending on sea temperature and ocean current.

We proposed that the Surume squid was a useful biological indicator for evaluating oceanic environments for pollution and radioactivity (Oikawa et al., 2003). Recently, Pu isotopes were measured in organs of squid collected over the last 20 years from the coast of Ishikawa, Japan sea side, and the coast of Chiba, Pacific Ocean side (Kishimoto et al., 2002). However, this investigation was carried out using squid samples cached in a broad sea area at the different time. Surume squid samples in nationwide landing at the same time are indispensable to get an expanded data concerning oceanic environments for pollution and radioactivity.

In this paper, a detailed work is reported on the radioanalytical and mass spectrometric analysis (by a sector-field high resolution ICP-MS) of Pu concentration in Surume squid liver collected from the coastal sea areas of Japan in 2002. Emphasis is put on the $^{240}Pu/^{239}Pu$ atomic ratio in Surume squid liver. In addition to Pu, levels of 13 elements (V, Mn, Fe, Co, Cu, Zn, Rb, Sr, Ag, Cd, Cs, Th and U) were measured for comparison. These data are discussed with emphasis on the potential use of Pu signatures in squid liver to trace the radioactive and

marine contamination of Pu.

2. Materials and methods

2.1. Sampling and pretreatment method

Surume squid samples were obtained from nine landing ports in Japanese inshore during fishery season from September to December 2002 as shown in Fig. 2, along with the location of nuclear power stations in/around our country. Surume squid that were born in winter season at East China Sea moves northward along the coast of the Japan islands in the Pacific Ocean and the Sea of Japan. Other groups born in summer or autumn around Japan islands also move northward in the Sea of Japan. An egg-laying area and season may be overlapped with each group. Thus, Surume squid samples landing during the autumn to winter season are ones which were born mainly at around East China Sea in winter season. Surume squid seems to be nocturnal habit marine organism and living at depth 100m-layer by day and raise to near surface by night. The habitat depth for landed Surume squid was estimated to be about 0-100m by the fishery practice of Japan. (Abe and Honma, 1997).

Refrigerated Surume squid samples were defrosted at room temperature and their livers were removed using polytetrafluoroethylene coating scissors and forceps. For plutonium analysis, raw livers were dried overnight at 105 °C and carefully ashed at 450 °C for 48 hours. Ashed samples were mixed well, sealed in polypropylene bags and stored in desiccators.

2.2. Measurements of Pu isotopes by sector field ICP-MS

Aliquots of 50 g ash were dissolved in 8M nitric acid with a few drops of hydrogen

peroxide, with the addition of known amounts of ^{242}Pu standard solution as a tracer (about 0.2 ng per sample). The ^{242}Pu standard solution was Standard Reference Material 4334G Plutonium-242 radioactivity standard, provided from National Institute of Standards and Technology. The sample solution was evaporated to dryness and dissolved in 8M nitric acid. Plutonium was separated by anion exchange resin column (Dowex 1-X8, 100-200 mesh, 5.5 ml volume). Plutonium adsorbed on the resin was successively washed by 8M nitric acid and 10M hydrochloric acid to remove interference elements such as Fe, Th and U. After washing, plutonium was eluted with 5% NH_4I-10M HCl solution. Finally, eluate was evaporated to dryness and then, to remove U completely, residue was dissolved in 4M acetic acid, and then passed through anion exchange resin column (Dowex 1-X8, 100-200 mesh, 2 ml volume). The eluate was evaporated to dryness and was dissolved into about 10 ml of 1M nitric acid (Kishimoto et al., 2002).

A sector field high resolution ICP-MS, Finnigan Element 2, Thermo Electron, Inc., Germany, working in the single collector, was used to measure Pu. The instrument was optimized for Pu measurement, also tuned for high sensitivity and low background.

Since a major problem in determining Pu isotopes by ICP-MS is the interference of $^{238}U^{1}H^{+}$ ion on ^{239}Pu peak area (Yamamoto et al., 2002), additional purification was performed using anion exchange resin from acetic acid solution before measuring ^{239}Pu and ^{240}Pu. Since resolution ($M/\Delta M$) more than 40,000 is required for accurate measurement, it is not possible to separate interference from ^{239}Pu peak at the resolution achievable with our instrument. Therefore, we assessed the influence of U on ^{239}Pu measurement. The increase in the *m*/*z* 239 mass peak was measured using a uranium standard solution. If the U content in the final solution was assumed to be 0.1 ng ml^{-1}, the expected influence was approximately 5 fg ml^{-1} for ^{239}Pu, which corresponds to the same order as the detection limit.

Through the measurements, the instrument was operated in the electric scanning (e-Scan)

mode by varying the accelerating voltage. Sample solution was introduced into the instrument at 0.3 ml min^{-1} using a pneumatic nebulizer. Measurements were carried out in the low resolution mode ($M/\Delta M = 300$).

For Pu isotopic measurements, ion signals were collected at *m*/*z* 239, 240 and 242 using fixed magnetic field. The magnetic field can be held constant very accurately by means of current control of the magnet, measurement of the peak-centered voltages provides a very accurate method for measuring differences in masses. Also, acceleration voltages can be scanned much faster than magnetic fields. The drawback to this method of operation is that a systematic error for the measurement of peak intensities is introduced because instrumental sensitivity also is a function of acceleration voltage (Montaser, 1998). Therefore, measuring parameters was configured to improve mainly statistical error, considering final sample volume. Total measurement time was about 20 minutes for each sample under following conditions; sample time of 0.1 s, 100 peaks per 10% mass window and 100 passes scans. The optimized operation conditions are summarized in Table 1.

Concentrations of ^{239}Pu and ^{240}Pu were calculated by isotope dilution method from the results of isotopic ratios relative to the ^{242}Pu spike. To check the accuracy of determination, certified reference material IAEA-135 (Irish Sea sediment) with a known $^{239,240}Pu$ concentration and $^{240}Pu/^{239}Pu$ atomic composition was used (Muramatsu et al., 1999 ; Miura et al., 2001). In case that any U is not contained in the sample, detection limit was about 1 fg ml^{-1} at final solution. Using a 50 g ash sample, detection limits as g-ash unit are achieved to be 0.5 μBq g^{-1} for ^{239}Pu and 2 μBq g^{-1} for ^{240}Pu.

2.3. Measurement of major metal elements

Aliquot of 5g raw liver sample was dissolved for measuring stable elements in

concentrated nitric acid with a few drops of hydrogen peroxide. The solution was evaporated to dryness and the residue was dissolved in 1 M ultra pure nitric acid. A quadrupole ICP-MS, Agilent 7500ce was used for 13 elements, except for Fe. An ICP-AES, Seiko SPS7800 was used for Fe measurement. An internal standard element was added to the sample solution to correct signal drift. Standard solution was XSTC-332 or XSTC-662 multi elements standard solution, and PL series single element standard solution provided from SPEX CertiPrep, Inc. The 13 elements were determined by interpolation method using a working curve with internal standard correction mode. For the purpose of internal standard correction, it was changed every target element as shown in Table 2. The internal standard correction techniques are one of the practicable and useful methods for the determination of trace elements by ICP instruments (Montaser, 1998).

3. Results and discussion

3.1. Concentrations of Pu isotopes and 13 elements in Surume squid liver

The liver of mature Surume squid is its largest internal organ and corresponds to about 10% of the squid's body weight. Plutonium isotopes were measured in liver samples, and the concentrations of the individual ^{239}Pu and ^{240}Pu isotopes and sum (^{239,240}Pu) of these isotopes were found in the range from 1.5 to 28, 1.1 to 24 and 2.5 to 53 mBq kg^{-1} raw liver (wet weight), respectively (Table 3). The concentrations of ^{239,240}Pu in the squid liver show a large variation. This seems due to the difference of the squid samples themselves rather than the difference of ^{239,240}Pu concentrations in seawater every landing port. The ^{239,240}Pu levels in liver at Pacific Ocean and Sea of Japan sides are about 10^3 times higher than typical levels

(^{239,240}Pu; about 15 mBq m^{-3}) for seawater found in about 200 m depth of the sea area (Yamada et al., 1996 ; Hirose et al., 1999 ; Livingston et al., 2001). While the mechanism is unknown, Surume squid concentrates Pu in their liver from seawater during growth. As a result, it is a useful organism for evaluating ^{239,240}Pu levels of larger sea area. Compared with the other marine products such as mussels, seaweeds and benthos, which habit in quite small coastal area, the Surume squid seems to surpass these marine products with regard to its relatively high concentration of ^{239,240}Pu within a year (Hirose and Haraguchi, 1990). In addition, in a brief life of a year Surume squid moves northward between nuclear power stations as shown in Fig. 2. Therefore, Surume squid is a useful for ^{239,240}Pu monitoring.

To know the relationship between Pu and trace elements, a comparison of trace elements found in squid liver and seawater is plotted as a logarithmic function together with the concentration factors (Fig. 3). The concentration factor (*CF*) in squid liver for each element compared to its mean seawater concentration was calculated as follows:

$$CF = \frac{C_{Liver}}{C_{SW}}$$

where C_{Liver} is elemental contents of the Surume squid liver (μmol kg^{-1}, raw liver, wet weight) and C_{SW} mean seawater concentrations of each element. The concentrations of trace elements in seawater vary with region, depth and other environmental factors. It is difficult to evaluate the C_{SW} mean seawater concentrations of each element every sampling area because data on these elements with depth profiles are not available. Therefore, the C_{SW} mean seawater concentrations of each element were represented for convenience by data from the Pacific Ocean (μmol kg^{-1}) estimated by Nozaki (1992).

The *CFs* found for Pu and the other 13 elements ranged from 10^0 to 10^7, although the content of each element varied within a factor of 1.2 to 2.4. Alkali metal and alkali earth metal elements, such as Rb, Sr and Cs, had *CFs* of 10^0 to 10^2 and were not generally concentrated in liver. Also U was barely concentrated in liver. On the other hand, transition metal elements,

Mn, Fe, Co, Cu, Zn, Ag and Cd had high *CF* values and were remarkably concentrated in liver. The *CF* for Pu, which are nearly same order as the *CFs* for V and Th, were found in the range from 10^2 to 10^4. Based on the chemical behavior of dissolved trace elements in seawater, the elements can be divided into three categories. These categories are (1) conservative elements (V, Rb, Sr, Cs and U), (2) nutrient elements (Fe, Cu and Zn) and (3) scavenged elements (Mn, Fe, Co, Cu, Ag, Cd and Th). The scavenged elements were selectively concentrated in Surume squid liver. Since Pu is well known to be particle reactive nuclides and is good tracer for the study of particle scavenging process, it was expected that Pu might be classified into scavenged element groups. However, as can be seen from the *CF* values for Pu, Pu had an intermediate *CFs* between conservative and scavenged elements. This difference can not be explained at present. One probable reason of this may be due to the following fact. Surume squid is an aggressive carnivorous species, and it feeds mainly on zooplankton species. The concentrations of major metals in zooplankton species are similar to those in squid liver. Therefore, most of metal elements concentrated in squid liver are derived from seawater via zooplankton species (Masuzawa et al., 1988) and fixed in liver tissue by proteins such as ferritin and metallothioneins (Durand et al., 1999, 2002). Probably, the same mechanism serves in case of Pu.

3.2. $^{240}Pu/^{239}Pu$ atomic ratio in Surume squid liver

As shown in Table 3, $^{240}Pu/^{239}Pu$ atomic ratios in squid liver ranged from 0.177 to 0.237, which are slightly higher than 0.178 ± 0.014 for global fallout (Krey et al., 1976), except for Wakayama. The $^{240}Pu/^{239}Pu$ ratio observed in Wakayama seems different from those observed in another 8 sampling ports. This may be due to the difference of egg-lying and born area between Surume squid landing in Wakayama and in another 8 landing ports. The $^{240}Pu/^{239}Pu$

ratios in liver from Surume squid collected from the Sea of Japan side appear to be a little higher than those from the Pacific Ocean side. Slightly higher $^{240}Pu/^{239}Pu$ values than in global fallout have been reported for sea sediments, seawater and marine products (Yamada et al., 1996 ; Buesseler, 1997 ; Kim et al., 2003 ; Kim et al., 2004 ; Zheng et al., 2004 ; Zheng et al., 2006).

The major origin of Pu isotopes in Surume squid liver is presumably due to global fallout from nuclear explosion tests. If Pu isotopes detected in their liver is only due to the global fallout, the $^{240}Pu/^{239}Pu$ atomic ratios are expected to have nearly the same values as those (0.178±0.014) observed in land. There are three large ocean currents flowing around Japan. These currents are the Kuroshio and Tsushima Currents that flow from the south and the Oyashio Current that flows from the north. The Kuroshio Current is a warm water current suitable for Surume squid. The principal axis of Kuroshio Current depends on seawater temperature in the depth from 100 to 200 m. The Kuroshio Current advances northward at 2-3 knot in east of Taiwan, East China Sea, the coastal sea area at Pacific Ocean side. The Tsushima Current advances northward at 0.5-1 knot along the coastal sea area in the Sea of Japan (Rika Nenpyo, 2006). Most of the Surume squids are born in East China Sea and move northward riding Kuroshio Current and/or Tsushima Current as they grow.

Along the path of the Kuroshio and Tsushima Currents, nuclear power stations and nuclear facilities are located in neighboring countries such as Taiwan, China and Korea. However, as far as we know, radionuclides, especially Pu, have not been released, based on environmental monitoring conducted in the countries. The Bikini Atoll is another potential source of Pu. The Kuroshio and Tsushima Currents are confluent current of the North Pacific Current passing through Bikini Atoll, which was contaminated by strategic explosion tests conducted in the 1950s. Annual discharge of Pu (as $^{239,240}Pu$) from Bikini Atoll (and Enewetak) is estimated to be approximately 0.2 TBq (Hamilton et al., 1996), and its $^{240}Pu/^{239}Pu$ atomic ratios are in the

range of 0.30-0.36 (Buesseler, 1997 ; Muramatsu et al., 2001). Contaminated particles with Pu isotopes deposited on lagoons, surrounding slopes and basin sediments have formed a reservoir and source for the marine environment after they are solubilized and transported in water. It seems likely that close-in fallout Pu with high $^{240}Pu/^{239}Pu$ atomic ratios are continuously transported through the solubilization and water transport from the North Equatorial Current to Kuroshio and its branch, the Tsushima Current (Kim et al., 2004; Zheng et al., 2006).

Therefore, it seems reasonable to assume that the Pu found in Surume squid liver is a mixture of global fallout Pu and close-in fallout Pu with high $^{240}Pu/^{239}Pu$ atomic ratio around Bikini Atoll (Muramatsu et al., 2001 ; Yamamoto et al., 2002). An attempt was made using simple two sources mixing model (Krey et. al., 1976) to resolve global fallout and Bikini close-in fallout Pu in Surume squid liver. Plutonium atomic ratio $^{240}Pu/^{239}Pu$ derived from global fallout was regarded as 0.178±0.014. For the Bikini close-in fallout $^{240}Pu/^{239}Pu$ atomic ratio, the values of 0.30 - 0.36, as mentioned above, were used for convenience. In case that global fallout $^{240}Pu/^{239}Pu$ atomic ratio was 0.178, except for Wakayama, the Bikini close-in fallout Pu accounts for ca. 35% (mean, ranges from 30-41%) of the whole plutonium in Surume squid liver using identification calculation method applied by Zheng and Yamada (2004). Identification of Bikini close-in fallout Pu in Surume squid liver will allow model calculations for better understanding oceanic transport of close-in fallout Pu from Bikini Atoll.

4. Conclusions

Plutonium isotopes and 13 stable elements (V, Mn, Fe, Co, Cu, Zn, Rb, Sr, Ag, Cd, Cs, Th and U) were measured in liver of Surume squid collected in the coastal sea areas of Japan

using ICP-MS/ICP-AES. Plutonium isotopes ^{239}Pu and ^{240}Pu were detected in liver samples. The concentrations of ^{239}Pu and ^{240}Pu and sum (^{239,240}Pu) ranged from 1.5 to 28, 1.1 to 24 and 2.5 to 53 mBq kg^{-1} raw liver, respectively. The Pu and the other 13 elements were concentrated with concentration factors (*CF*) ranging from 10^0 to 10^7. Alkali metal and alkali earth metal elements, such as Rb, Sr and Cs, were rarely concentrated with *CF* values of 10^0 to 10^2. Uranium was barely concentrated in liver. On the other hand, transition metal elements, Mn, Fe, Co, Cu, Zn, Ag and Cd were concentrated with high *CF* values. Plutonium, as well as V and Th, were concentrated in liver with *CFs* of 10^2 to 10^4. Scavenged elements (Mn, Fe, Co, Cu, Ag and Cd) were selectively concentrated in liver. Most metal elements concentrated in squid liver were probably derived from seawater via zooplankton species and fixed in tissues by proteins such as ferritin and metallothioneins. The same mechanism probably serves for Pu.

The ^{240}Pu/^{239}Pu atomic ratios 0.177 to 0.237 which were slightly higher than 0.178±0.014 for global fallout were found in squid liver. The ocean currents with their different source functions were an essential consideration in the interpretation of high ^{240}Pu/^{239}Pu atomic ratios. Three large ocean currents are flowing around Japan: Kuroshio and Tsushima Currents from south and Oyashio Current from north. Based on the habitat of the Surume squid, the Pu found in the liver is probably a mixture of global fallout Pu and close-in fallout Pu with high ^{240}Pu/^{239}Pu atomic ratio around Bikini Atoll. By assuming the two sources mixing model, Bikini close-in fallout Pu accounts for ca. 35% of the whole plutonium amounts. The results strongly indicate that the squid liver is very useful oceanic biological indicator for studying marine pollution of Pu and some other elements.

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References

Abe S. and Honma A., 1997. Modern Encyclopedia of Fish, 1st edition. NTS, Japan.

Buesseler K. O., 1997. The isotopic signature of fallout plutonium in the north pacific. Journal of Environmental Radioactivity, 36, 69-83.

Durand J. P. et al., 1999. ^{210}Po binding to metallothioneins and ferritin in the liver of teleost marine fish. Marine Ecology Progress Series, 177, 189-196.

Durand J. P. et al., 2002. Ferritin and hemocyanin: ^{210}Po molecular traps in marine fish, oyster and lobster. Marine Ecology Progress Series, 233, 199-205.

Folsom T. R. and Young D. R., 1965. Silver-110m and cobalt-60 in oceanic coastal organisms. Nature, 206, 803-806.

Folsom T. R. et al., 1970. Long-lived γ-ray emitting radionuclide silver-108m found in Pacific marine organisms and used for dating. Nature, 227, 941-943.

Hamilton T. F. et al., 1996. ^{137}Cs (^{90}Sr) and Pu isotopes in the Pacific Ocean: sources and trends. Radionuclides in the Oceans (RADOC 96-97) Inputs and Inventories, Gueguenia P., Germain P., Metivier H., Coodinators. Res Editions de Physique. Les Ulis, France, pp. 29-58.

Hirose A., and Haraguchi H., 1990. Bio-accumulation of trace elements in seawater. The Cell, 22, 8-12. (in Japanese)

Hirose K. et al., 1999. Anthropogenic radionuclides in seawater in the East Sea/Japan Sea: Results of the first-stage Japanese-Korean-Russian expedition. Journal of Environmental Radioactivity, 43, 1-13.

Kim C. K. et al., 2003. ^{240}Pu/^{239}Pu atom ratio in the bottom sediment of the NW Pacific

322 Ocean. Journal of Radioanalytical and Nuclear Chemistry, 258, 265-268.
323 Kim C. K. et al., 2004. Plutonium isotopes in seas around the Korean Peninsula. Science of
324 the Total Environment, 318, 197-209.
325 Kishimoto T. et al., 2002. Concentration of plutonium in squids collected from Japanese
326 inshore measured by HR-ICP-MS, 1981-2000. Journal of Radioanalytical and Nuclear
327 Chemistry, 252, 395-398.
328 Krey P. W. et al., 1976. Mass isotopic composition of global fall-out plutonium in soil.
329 Transuranium Nuclides in the Environment. IAEA-SM-199/39, IAEA, Vienna, pp
330 671-678.
331 Living Information Center, 2003. Statistical Databook on Fishes and Marine products 2003.
332 Living Information Center, Inc., Tokyo Japan.
333 Livingston H. D. et al., 2001. The behavior of plutonium in the Pacific Ocean. In A.
334 Kudo(Ed.), Plutonium in the Environment. Radioactivity in the Environment, Vol. 1, pp.
335 267-292. Amsterdam: Elsevier.
336 Masuzawa T. et al., 1988. A regularity in trace element contents of marine zooplankton
337 species. Marine Biology, 97, 587-591.
338 Miura T. et al., 2001. Rapid separation of plutonium in environmental samples using an anion
339 exchange resin disk. Journal of Radioanalytical and Nuclear Chemistry, 250, 449-452.
340 Montaser A., 1998. Inductively Coupled Plasma Mass Spectrometry. Wiley-VCH, Inc. USA.
341 Muramatsu Y. et al., 1999. Determination of plutonium concentration and its isotopic ratio in
342 environmental materials by ICP-MS after separation using and extraction
343 chromatography. Journal of Analytical Atomic Spectrometry, 14, 859-865.
344 Muramatsu Y. et al., 2001. Measurement of $^{240}Pu/^{239}Pu$ isotopic ratios in soils from the
345 Marshall Islands using ICP-MS. Science of The Total Environment, 278, 151-159.
346 Nozaki Y., 1992. Trace elements in sea water: Their mean concentrations and north Pacific

profiles. Chikyukagaku (Geochemistry), 26, 25-39. (in Japanese with English abstract)

Oikawa S. et al., 2003. Determination of trace elements in squid organs by inductively coupled plasma mass spectrometry and neutron activation analysis. Bunseki Kagaku, 52, 551-557. (in Japanese with English abstract)

Rika Nenpyo, 2006. Chronological Scientific Tables. National Astronomical Observatory (Edited). Maruzen Co. Ltd. Japan. (in Japanese)

UNSCEAR report, 2000. Sources and Effects of Ionizing Radiation; United Nations Scientific Committee on the Effects of Atomic Radiation Exposures to the Public from Man-made Sources of Radiation. United Nations, New York.

Yamada M., Aono T., Hirano S., 1996. ^{239,240}Pu and ^{137}Cs distributions in seawater from the Yamato basin and the Tsushima basin in the Japan Sea. Journal of Radioanalytical and Nuclear Chemistry, Articles, 210, 129-136.

Yamamoto M. et al., 2002. Some aspects of environmental radioactivity around the former Soviet Union`s Semipalatinsk nuclear test site: Local fallout Pu in Ust`-Kamenogorsk district. Journal of Radioanalytical and Nuclear Chemistry, 252, 373-394.

Zheng J. and Yamada M., 2004. Sediment core record of global fallout and Bikini close-in fallout Pu in Sagami Bay, Western Northwest Pacific Margin. Environmental Science & Technology, 38, 3498-3504.

Zheng J. and Yamada M., 2006. Determination of Pu isotopes in sediment cores in the Sea of Okhotsk and the NW Pacific by sector field ICP-MS. Journal of Radioanalytical and Nuclear Chemistry, 267, 73-83.

Figure captions

Fig. 1. Map of the location of born sea area of Surume squid with the schematic route to move northward.

Fig. 2. Map of the location of Surume squid landing port (sampling port) in Japan and surrounding sea, Sea of Japan, East China Sea, Sea of Okhotsk and Pacific Ocean with the schematic ocean current flowing patterns.

Fig. 3. Relationship between mean seawater concentration (C_{SW}) and elemental contents of the Surume squid liver (C_{Liver}) for plutonium and 13 elements in logarithmic scale.

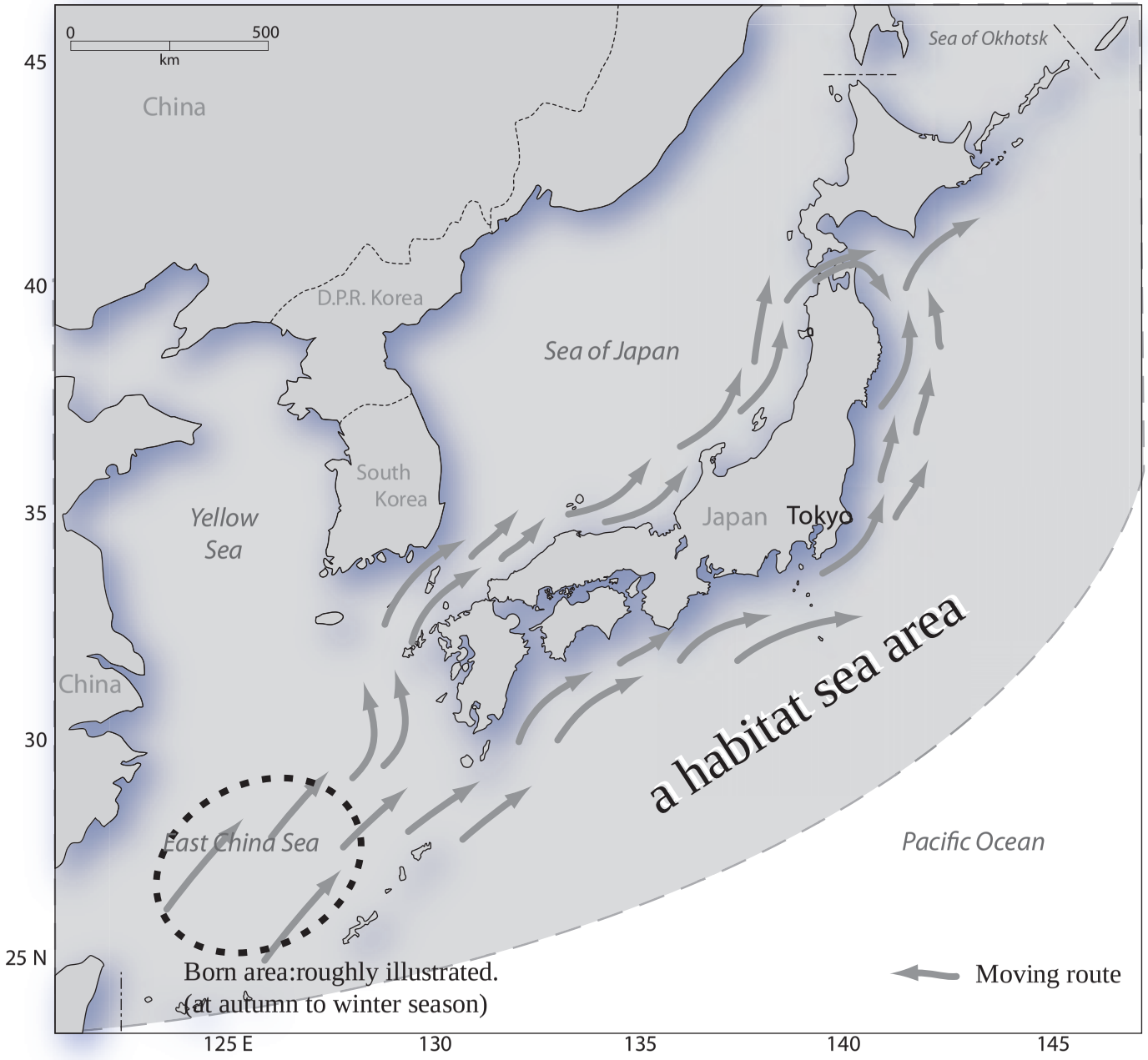

Fig. 1 Oikawa and Yamamoto

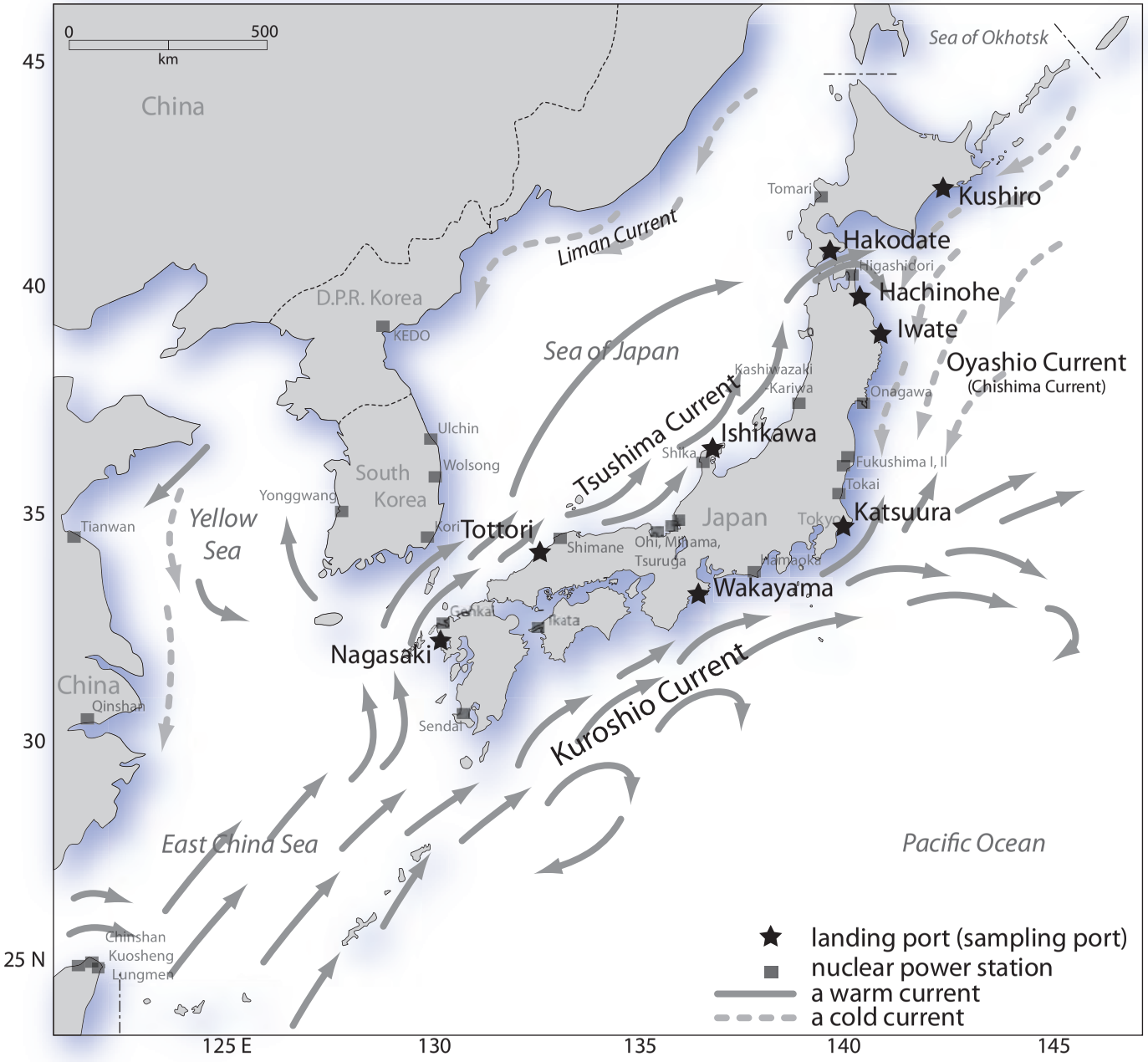

Fig. 2 Oikawa and Yamamoto

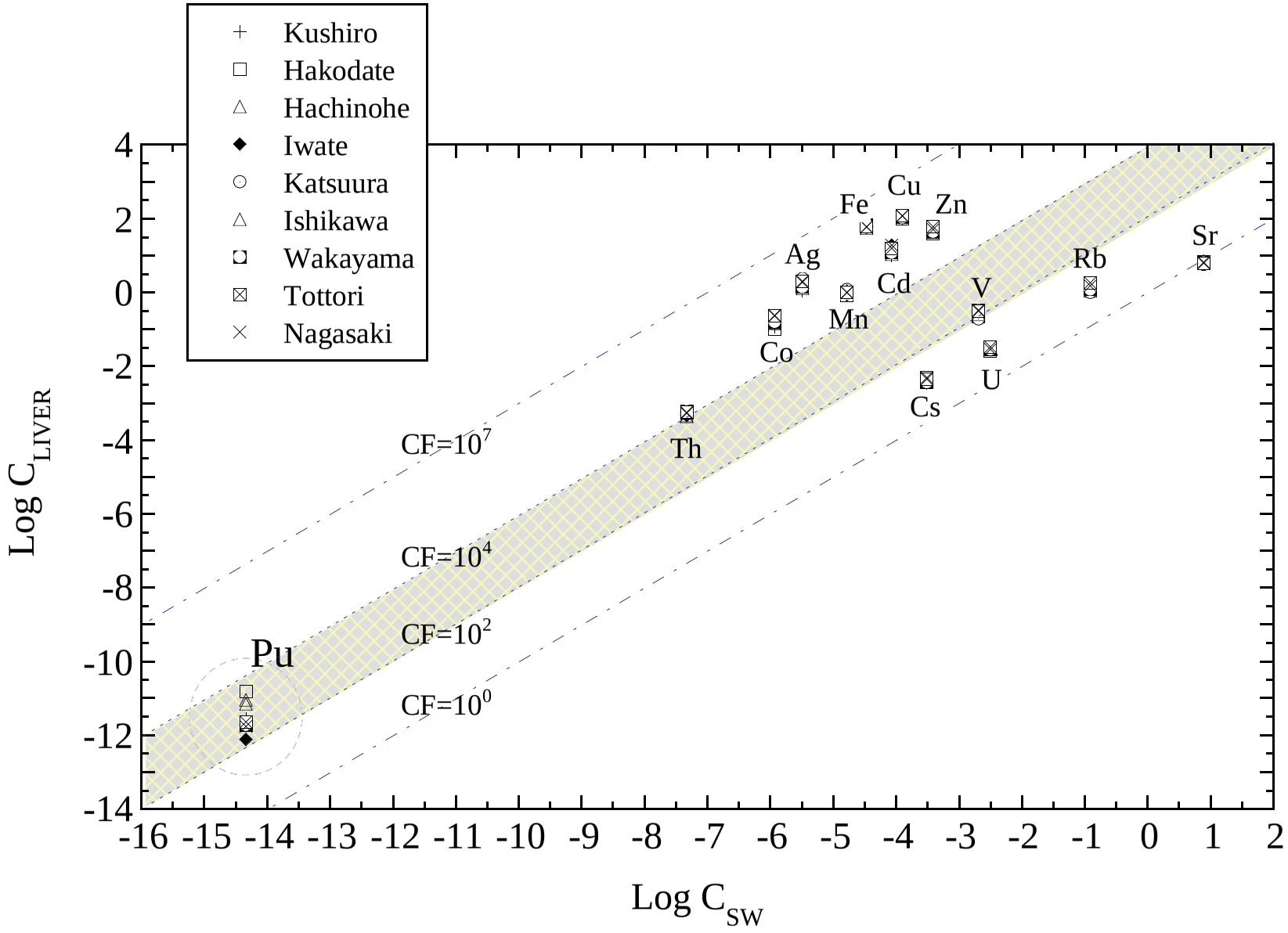

Fig. 3. Oikawa and Yamamoto

Table 1 : Operational conditions of ELEMENT 2 for Pu isotope measurements.

Plasma gas flow rate (L $min.^{-1}$)	16
Auxiliary gas flow rate (L $min.^{-1}$)	0.9
Plasma operation power (W)	1200
Peristaltic pump uptake rate (mL $min.^{-1}$)	0.3
Resolution	Low resolution mode ($M/\Delta M = 300$)
Scan mode	e-Scan
Accurate mass & range (a.m.u.)	^{238}U ; 238.0502 (238.011 - 238.090)
	^{239}Pu ; 239.0517 (239.012 - 239.092)
	^{240}Pu ; 240.0533 (240.013 - 240.093)
	^{242}Pu ; 242.0582 (242.018 - 242.099)
Magnet mass (a.m.u.)	238.050
Settling time per peak (s)	^{238}U ; 0.300
	^{239}Pu, ^{240}Pu, ^{242}Pu ; 0.001
Sample time per point (s)	^{238}U ; 0.0250
	^{239}Pu, ^{240}Pu, ^{242}Pu ; 0.100
Samples per peak	100
Mass window (%)	10
Segment duration (s)	^{238}U ; 0.250
	^{239}Pu, ^{240}Pu, ^{242}Pu ; 1.000
Detection mode	Counting, Analogue
Number of passes	100
Replicates	3

Table 2 : Internal standard element for ICP-MS/ICP-AES measurment.

Target element	*m* /*z*	Intrenal standard	*m* /*z*	Note
V	51	Sc	45	
Mn	55			
Fe	(238.204 nm)	Y	(371.030 nm)	by ICP-AES
Co	59			
Cu	62	Sc	45	
Zn	66			
Rb	85	Y	89	
Sr	88			
Ag	107	Rh	103	
Cd	111	In	115	
Cs	133			
Th	232	Bi	209	
U	238			

Table 3 : Concentration and atomic ratio of Pu isotopes in Surume squid liver collected from the coastal sea areas in Japan, 2002.

Landing port		Pu concentration（mBq/kg-raw）[*1]		$^{240}Pu/^{239}Pu$ atomic ratio[*2]	RSD (%)
		^{239}Pu	^{240}Pu		
Pacific Ocean side	Kushiro	5.23 ± 0.07	4.09 ± 0.25	0.213 ± 0.011	5.2
	Hachinohe	16.7 ± 0.16	14.1 ± 0.39	0.230 ± 0.005	2.1
	Iwate	1.45 ± 0.07	1.07 ± 0.03	0.196 ± 0.015	7.4
	Katsuura	3.46 ± 0.10	2.56 ± 0.09	0.202 ± 0.002	1.0
	Wakayama	3.69 ± 0.06	2.37 ± 0.07	0.177 ± 0.007	4.1
Sea of Japan side	Hakodate	28.2 ± 0.7	24.2 ± 0.9	0.234 ± 0.006	2.4
	Ishikawa	13.0 ± 0.2	11.4 ± 0.1	0.237 ± 0.002	0.63
	Tottori	4.24 ± 0.32	3.56 ± 0.32	0.230 ± 0.003	1.2
	Nagasaki	3.22 ± 0.02	2.67 ± 0.15	0.226 ± 0.012	5.4

[*1] Calcurate from isotope dilution method by using known amount of ^{242}Pu spike.

[*2] Standard deviation at three replicates acquisition (total 300 passes scans).