Ecological risk assessment of plutonium in primary inlet of Indonesian through flow (ITF)

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Abstracts. The present study to understand the environmental radiological risk of plutonium to marine biotas in the primary inlet of Indonesia Through Flow (ITF), seawater, and sediment samples collected during the monitoring work 2018-2019. The activity concentration of $^{239/240}$Pu was measured both for them. The activity concentration of the $^{239/240}$Pu in seawater and sediment was low, where that low activity concentration of plutonium can use as an indicator of the release of plutonium in Indonesia or neighboring countries in the future. The environmental radiological risk of plutonium to marine biotas in this study uses the ERICA Tool, where the total dose rates to marine biotas and risk of resultant radiobiological impacts were assessed. As input data for the ERICA tools, activity concentrations of $^{239/240}$Pu in seawater and sediment, distribution coefficient (Kd), dose conversion coefficients, occupancy factors, uncertainty factor set as the default value in ERICA Tool. Results compared to background dose rates, also estimated by the ERICA Tools. The risk of radiobiological effects in marine biotas in the primary inlet of ITF can be considered negligible because the estimated total dose level is below the 10 μGy h$^{-1}$ screening dose. This study emphasizes that actual measurement data is needed in radiological risk assessment to reduce dependence on the ERICA Tool.

1. Introduction

Anthropogenic radionuclides in the Pacific Ocean, the Indonesian Ocean, and the Indian Ocean originate from the nuclear weapon test fallout conducted in the 1950s and 1960s. Local falls came from weapon tests conducted in the Marshall Islands, especially in the 1950s contributed significantly to anthropogenic radionuclides in the Pacific Ocean [1]. Based on the ASPAMARD database (Asia Pacific Marine Radioactivity Database), plutonium and cesium in marine sediments in the Pacific Ocean region are in the range of concentrations of 0.03 - 0.1 Bq/kg dry for $^{239/240}$Pu and 0.7 - 1.4 Bq/kg dry for $^{137}$Cs [2]. Because the ocean is a dynamic system, radionuclides that fall into surface water by wet and dry deposition do not stay constant, because of the currents and processes in the water column, they have been transported to various regions, as well as to bottom waters and sediments.

Movement of seawater from the Pacific Ocean to the Indian Ocean will enter Indonesian seawaters through the ITF - Indonesian Through Flow. The largest inflow from the Pacific Ocean will enter through the Makassar Strait (about 75%), the Lifamatola Canal, the Halmahera Sea Canal, and the Karimata Strait. The three main outflows through the Lombok Strait, Ombai Strait, and Timor Strait...
Thus, radionuclides from Pacific Ocean waters will enter Indonesian seawater through surface currents or deep currents. In several locations in Indonesia, plutonium databases are available in marine compartments from various regions in Indonesia, such as the coast of Bangka Island and the north coast of Java. The range of plutonium in the sediment is around $1.26 \times 10^{-2} - 5.17 \times 10^{-2}$ Bq/kg and in surface water from MDA to $1.03 \times 10^{-3}$ mBq/m$^3$ for seawater and 2.64 - 55.70 mBq/kg for sediment [4], 1.61x10$^{-3}$ Bq/kg in Jepara waters and the lowest activity is 1.38 x 10$^{-5}$ Bq/kg in Belitung waters.

In order to fulfill the lack of plutonium database in primary Indonesia through Flow (ITF), it is necessary to analyze plutonium in seawater and sediment samples from the Sulawesi Sea, Ambon Sea, and Sorong Sea. An ecological risk assessment must be done to determine the dose rate and risk quotient for specific biota.

2. Methodologies
2.1. Dissolution and preconcentration of sediment sample
Dry sediment samples weighed 20 grams. Put in a 250 mL beaker, then added concentrated HNO$_3$ and heated to dryness. Add concentrated HNO$_3$, concentrated HClO$_4$, and concentrated H$_2$O$_2$ then reheat until dryness. Add a mixture of 3M HNO$_3$-0.25 M Boric acid, 7M HNO$_3$, 2M Al(NO$_3$)$_3$, and 3M HNO$_3$, heat until the precipitate dissolves, then centrifuge. Add metal Fe and ascorbic acid, leave it for 3 minutes. Add 3.5 M NaNO$_2$ and 15.8M HNO$_3$. The sample is ready for the separation stage [6].

2.2. Pre concentration plutonium from big volume water
100 l of sea water used for the sample, add saturated KMnO$_4$ and stir for 5 minutes. Then MnSO$_4$ solution was added. Set the pH of the solution between 8 - 9 with the addition of NH$_4$OH and HCl until sludge formed. Sludge collected for the next step [6].

2.3. Separation of $^{239/240}$Pu from sediment sample using extraction chromatography of TRU resin
Soak the resin with H$_2$O for 1 hour. Add resin to the chromatography column in the amount of 2.5 cm height. Wash the column with H$_2$O, 2M HNO$_3$, and the mixture of 2M HNO$_3$ -0.01 M NaNO$_2$. Add the sample solution into the chromatography column, flow at a rate of 1mL/min. Rinse the beaker with a mixture of 2M HNO$_3$ -0.01 M NaNO$_2$. Rinse the column with a mixture of 2M HNO$_3$ -0.01 M NaNO$_2$. Rinse the column with 4M HCl and elute Pu from the column with a mixture of 4M HCl-0.01M TiCl$_3$ [7].

2.4. Electrodeposition
Pu elution heated to near dryness. Add 1 mL of concentrated HNO3 and five drops of concentrated HClO4, heat until dry. Add 10 mL 5% H2SO4, let stand until cool. Add thymol blue until it changes color (pink). Drop NH4OH 50% until it changes color (yellow). Drop 5% H2SO4 until it changes color (pink). Enter the solution into the electrodeposition device. Set the process at 1 A for 2 hours. Analysis with Alpha spectrometer [6].

2.5. Alpha spectrometer analysis
Plutonium in electrodeposition plates counted using an alpha spectrometer (Alpha analyst, Canberra) for 168 hours [8].

2.6. The ERICA Tools analysis
For risk assessment, we use The ERICA tool using Tier 2 with ten μGy.h-1 as a dose screening value. The ERICA Tool tier 2 used to calculate total doses and risk quotient by different biota. The ERICA Tool designed to model biota exposure of biota in aquatic ecosystems in the water column from both sediment and water. Concentration ratio (CR), dose conversion coefficients, uncertainty factor, and occupancy factors we use the default value in the ERICA tools data base [9], [10].
3. Result and discussion

3.1. Distribution of $^{239+240}$Pu activity in seawater

Seawater movement from the Pacific Ocean to the Indian Ocean will enter Indonesian Seawaters through the Indonesian Through Flow (ITF) with the largest inflow from the Pacific Ocean through the Makassar Strait (about 75%), Lifamatola Canal, Halmahera Sea Canal, and Karimata Strait, with three main outflows through Lombok Strait, Ombai Strait and Timor Strait [3]. Thus, radionuclides in Pacific Ocean waters will enter Indonesian Seawaters through surface currents or deep currents. Monitoring in the Sulawesi Sea, Ambon Sea, and Sorong Sea waters conducted in 2018 - 2019 to see the activity of radionuclide plutonium that entered Indonesian sea waters through eastern Indonesia.

Activity $^{239/240}$Pu was calculated from the spectrum of plutonium isotopes. The $^{239/240}$Pu peak isotope compared to the $^{242}$Pu tracer peak, which was measured together using alpha spectrometry. Because of alpha energies, $^{239}$Pu and $^{240}$Pu, are too close to be distinguished from each other, they are reported as a total of $^{239/240}$Pu. Activity data of $^{239/240}$Pu for the waters of the Sulawesi Sea, Ambon Sea, and Sorong Sea can be seen in Table 1.

Tabel 1. Activity of $^{239/240}$Pu in sea water from the Sulawesi Sea, Ambon Sea and Sorong Sea

| Sample Code | Coordinates          | Activity (Bq/m$^3$)      |
|-------------|----------------------|--------------------------|
| Wakatobi    | 123 35’ 51.3” E 005 23’ 22.5” N | 7.58 x 10$^{-4}$ ± 1.20 x 10$^{-4}$ |
| Mamuju     | 118 49’ 8.85” E 002 37’ 9.91” N | 9.23 x 10$^{-2}$ ± 5.10 x 10$^{-3}$ |
| Manado     | 124 50’ 20.4” E 001 30’ 3.6” N | 1.16 x 10$^{-4}$ ± 4.30 x 10$^{-5}$ |
| Tahuna     | 125 29’ 8.55” E 003 35’ 9.71” N | 1.49 x 10$^{-3}$ ± 4.81 x 10$^{-4}$ |
| Ambon      | 128 12’ 14.9” E 003 38’ 33.09” N | 2.89 x 10$^{-4}$ ± 1.08 x 10$^{-5}$ |
| Sorong     | 131 17’ 4.85” E 000 54’ 40.33” N | 2.43 x 10$^{-4}$ ± 5.32 x 10$^{-5}$ |

Figure 1. Latitudinal boxes in the Pacific and Indian Ocean [1]

The range of plutonium in the surface water in east Indonesia seawaters from 1.16 x 10$^{-4}$ in Manado to 9.23 x 10$^{-2}$ Bq/m$^3$ in Mamuju. This data indicates that the activity plutonium in East
Indonesia seawater comparable with other Indonesian seas. Plutonium in Jakarta bay range from MDA to 0.53 mBq/m³ [5], Bangka around 4.69 x 10^3 Bq/l [11], 3.01x 10^3 Bq/m³ [12].

Radionuclide distribution studies on surface seawater in the Pacific Ocean divided into 14 boxes divided according to current pattern systems, locations of nuclear weapons testing and uniformity of radionuclide distribution and data availability where 12 boxes in the Pacific Ocean and one box in the Pacific South and one box represent the Sea of Japan. The latitudinal boxes in the Pacific in Figure 2.

The picture above shows that the Indonesian sea included in Box 6, which is related to the Pacific Ocean. Compilation of research data conducted by Povinec [1] shown that the distribution of plutonium in surface seawater in Box 6, has an average activity of 239/240Pu was 3.6 µBq/L. Compared to data from this study, plutonium activity is still below the compilation data of the Pacific Ocean data.

3.2. Distribution of 239+240Pu activity in sediment

Based on the Asia Pacific Marine Radioactivity Database (ASPAMARD) data collection, the presence of plutonium and cesium in marine sediments in the Pacific Ocean region found a range of concentrations of 0.03 - 0.1 Bq/kg dry for 239/240Pu for coordinates 10° - 15° N which is the closest latitude with Indonesian waters. Plutonium in Jakarta bay sediment range prom 2.84-55.70 mBq/kg [5], Makassar Beach sediments found plutonium radioactivity of 0.008 - 0.43 Bq/kg, in the Muria Peninsula, ranging from MDA to 26.47 mBq/kg [13]. Activity 239/240Pu in sediments in the marine waters of Sulawesi and eastern Indonesia has an activity range of around 1.26 x 10^2 - 5.17 x 10^2 Bq/kg and comparable with other data. Data can be seen in Table 2.

| Sample Code | Coordinates                  | Activity (Bq/m³) |
|-------------|-----------------------------|-----------------|
| Kendari     | 122 36° 15.9” E 003 58’ 33” N | 1.52E-06 ± 2.53E-07 |
| Wakatobi    | 123 35° 51.3” E 005 23’ 22.5” N | 2.34E-03 ± 1.28E-03 |
| Makassar    | 119 24° 18.0” E 005 07’16.7” N | 2.49E-05 ± 3.22E-06 |
| Mamuju 1    | 118 49° 8.85” E 002 37’ 9.91” N | 5.26E-05 ± 8.55E-06 |
| Mamuju 2    | 119 05° 45.6” E 003 31’ 33.6” N | 3.17E-05 ± 4.95E-06 |
| Mamuju 3    | 119 25° 49.4” E 003 27’ 55.4” N | 1.42E-03 ± 7.27E-04 |
| Manado      | 124 50° 20.4” E 001 30’ 3.6” N | 1.51E-05 ± 2.47E-06 |
| Bitung      | 125 07° 4.27” E 001 25’ 1.99” N | 1.22E-05 ± 1.51E-06 |
| Tahuna 1    | 125 29° 8.55” E 003 35’ 9.71” N | 1.51E-05 ± 5.58E-06 |
| Tahuna 2    | 125 40° 1.20” E 003 23’ 9.6” N | 3.57E-05 ± 4.67E-06 |
| Ambon       | 128 12° 14.9” E 003 38’ 33.09” N | 2.89E-04 ± 1.08E-05 |
| Sorong      | 131 17° 4.85” E 000 54’ 40.33” N | 2.43E-04 ± 5.32E-06 |

3.3. Environmental Risk Assessment for 239/240Pu in marine biota

The ERICA tool used to assess the effects of post-accident radiation or normal conditions with radiation side effects, including pre-assessment of radiological study on Coastal ecosystems before the construction of nuclear installations. The ERICA Tool uses the bioaccumulation data obtained from laboratory experiments to understand the biota's dosimetric relationships of biota through various doses of received. This software also used to find the relationship between physicochemical kinetics and biological effects due to radiation in the environment [14]. The ERICA tool divided into three separate tiers, where Tiers 1 and 2 allow the user to release the assessment while the effects on biota are low, and Tier 3 is used to consider more complex situations. The differences of tiers, based on two calculations (1) estimation of the activity concentrations in biota and environmental media and (2) estimation of the dose rates to biota. Whereas Tiers 1 and 2, simply
recommend that no further testing be needed if the total dose obtained by the species is below the specified screening level. ERICA Tool uses the lowest dosage level (Tier 1 and 2) of 10 \( \mu \text{Gy/h} \) [10].

The ERICA Tool Tier 2 requires several constants, such as Concentration Ratio. The concentration ratio is the value of the ratio between radionuclide activity in specific biota divided by radionuclide activity in seawater. In this study, the default values for specific biota taken from the Erica tool database. Another value needed in the calculation is a Kd value, and the coefficient value of the sediment-water distribution is the ratio of radionuclide activity in the sediment to the activity in seawater. This value depends on environmental factors such as pH, temperature, and organic content, with values that can differ significantly, even in the same aquatic environment [15]. The Kd value can be seen in table 3.

**Tabel 3.** The sediment—water distribution constant of \(^{239/240}\text{Pu}\) in the Sulawesi Sea, Ambon Sea and Sorong Sea

| Sample Code | Coordinates          | Kd     |
|-------------|----------------------|--------|
| Wakatobi    | 123 35’ 51.3” E 005 23’ 22.5” N | 2.01E-01 |
| Mamuju     | 118 49’ 8.85” E 002 37’ 9.91” N | 5.70E-01 |
| Manado      | 124 50’ 20.4” E 001 30’ 3.6” N | 1.30E-01 |
| Tahuna      | 125 29’ 8.55” E 003 35’ 9.71” N | 1.01E-01 |
| Ambon       | 128 12’ 14.9” E 003 38’ 33.09” N | 3.67E-01 |
| Sorong      | 131 17’ 4.85” E 000 54’ 40.33” N | 8.31E-01 |

In this tier, the water-sediment distribution coefficient (Kd) of \(^{239/240}\text{Pu}\) choosing the highest value is 0.831 l/kg and suitable for Site-specific screening. The maximum activity of \(^{239/240}\text{Pu}\) used in this tier and all three kinds of biota (crustacean, mollusk, and pelagic fish) in the marine environment in the model [16] included in this process. The total Dose Rate and Risk Quotient, including the expected value (RQexp) and conservative value (RQcons), of reference organisms, are calculated and tabulated in Table 4.

**Table 4.** The total Dose Rate and Risk Quotient of reference biotas

| Biota        | Total dose rate (\(\mu\text{Gy/h}\)) | Screening Value (\(\mu\text{Gy/h}\)) | Risk Quotient (expected value (unit less)) | Risk Quotient (conservative value (unit less)) | ERICA Tool Notes | Notes                      |
|--------------|--------------------------------------|--------------------------------------|-------------------------------------------|---------------------------------------------|------------------|----------------------------|
| Crustacea    | 5.23E-6                              | 1.00E-1                              | 5.12E-7                                   | 1.54E-6                                     |                  | There was no statistically significant effect on DNA strand breakage |
| Bivalva      | 4.70E-5                              | 1.00E-1                              | 4.70E-6                                   | 1.41E-5                                     |                  | There was no statistically significant effect on the frequency of abnormal larvae regardless of the rearing temperature |
| Mollusk      | 7.15E-6                              | 1.00E-1                              | 7.15E-7                                   | 2.14E-6                                     |                  | There was no statistical effect on the phagocytic response of leucocytes to infection |
| Pelagic fish | 7.15E-6                              | 1.00E-1                              | 7.15E-7                                   | 2.14E-6                                     |                  |                           |
Risk analysis for the several biotas, like a mollusk, crustacean, and fish, indicated that all the total dose rates per that biota were lower than the screening rate (10 μGy/h). The results show no statistically significant effect on DNA strand breakage and no statistically significant effect on the frequency of abnormal larvae regardless of the rearing temperature for mussels from plutonium in sediment. For pelagic fish, plutonium from the water has no statistical effect on the phagocytic response of leucocytes to infection. Based on the ERICA approach, it can conclude that there is no statistical effect for marine biota because of the presence of plutonium in sediments and seawater from the Sulawesi Sea, Ambon Sea and Sorong Sea.

4. Conclusion
The range of plutonium in the surface water in Primary ITF (Sulawesi Sea, Ambon Sea, and Sorong Sea) from 1.16 x 10⁻⁴ to 9.23 x 10⁻⁵ Bq/m³ and for sediment is around 1.26 x 10⁻² - 5.17 x 10⁻² Bq/kg. These data were comparable with data from other Indonesia Sea and the Pacific Ocean. Risk analysis for the several biotas, like mollusk, crustacean, and fish, indicated that all the total dose rates per that biota were lower than the screening rate (10 μGy/h) and no statistical effect for marine biota.

References
[1] Povinec P P 2005 ⁹⁰Sr, ¹³⁷Cs and ²³⁹,²⁴⁰Pu concentration surface water time series in the Pacific and Indian Oceans - WOMARS results J. Environ. Radioact 81 no 1 pp. 63–87
[2] Hirose K, Aoyama M, Kim C S, Kim C K and Povinec P P 2006 Plutonium isotopes in seawater of the North Pacific: Effects of close-in fallout vol 8 (Elsevier Masson SAS)
[3] Metzger E J 2010 Simulated and observed circulation in the Indonesia Seas: 1/12 global HYCOM and the INSTANT observations Dyn. Atmos. Ocean vol 50 pp 275–300
[4] Makmur M 2013 Analisis plutonium di sedimen perairan Laut Bangka Prosiding Seminar Keselamatan Nuklir no 8 pp 32–37
[5] Suseno H, Budiawan, Muslim, Makmur M and Yahya M N Y 2017 Present status of marine radioecology in Jakarta Bay Atom Indonesia vol 44 no 2 pp 1–5
[6] Nakano M 2007 Manual of standard procedures for analysis of marine samples
[7] Levy I 2011 Marine anthropogenic radiotracers in the Southern Hemisphere: New sampling and analytical strategies Prog. Oceanogr. vol 89 no 1 – 4 pp 120 – 133
[8] Canberra 2016 Operation and calibration of the Canberra alpha analyst spectrometer
[9] Copplestone D Hingston J and Real A 2008 The development and purpose of the FREDERICA radiation effects database J. Environ. Radioact. vol 99 no 9 pp 1456–63
[10] Brown J E 2008 The ERICA Tool J. Environ. Radioact. vol 99 no 9 pp 1371–83
[11] Makmur M 2013 Penentuan nilai koefisien distribusi (Kd) ²³⁹,²⁴⁰Pu pada perairan laut Bangka Selatan J. Teknol. Pengelolaan Limbah vol 16 no 399 pp 23–30
[12] Makmur M Yahya M N Y and Putra D I P 2016 Concentration of selected radionuclides in sediment and surface seawater in Belitung Island, Indonesia 2nd Int. Conf. Sources, Eff. Risk Ioniz. Radiat. pp 29–34
[13] Nareh M and Warsona A 2000 Penentuan konsentrasi Cs-137 dan Pu-239/240 dalam sedimen di Semenanjung Muria dan daerah sekitarnya in Prosiding Presentasi Ilmiah Keselamatan Radiasi dan Lingkungan pp 23–24
[14] Vives i Battle J et al 2016 Inter-comparison of dynamic models for radionuclide transfer to marine biota in a Fukushima accident scenario J. Environmental Radioactivity vol 153 pp 31–50
[15] Patiris D L Tsabaris C Anagnostou C L Androulakaki E G Pappa F K Elefteriou G and Sgouros G 2016 Activity concentration and spatial distribution of radionuclides in marine sediments close to the estuary of Shatt al-Arab/Arvand Rud River, the Gulf J. Environmental Radioactivity vol 157 pp 1–15
[16] Ye S Zhang L and Feng H 2017 Marine ecological risk assessment methods for radiation accidents J. Environmental Radioactivity vol 180 pp 65–76
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