Transactions of the Korean Nuclear Society Autumn Meeting
Yeosu, Korea, October 25-26, 2018

Marine Sample Analysis Using Statistical Methods: Distribution of Plutonium (Pu) Isotopes Using MC-ICP-MS (Multi-Collector Inductively Coupled Plasma Mass Spectrometry)

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1. Introduction

Environmental monitoring programs generate a large bulk of data, which can provide a great deal of information about pollution, trend, the effectiveness of policy, with suitable statistical analysis. However, to obtain meaningful statistical results, the data used for analysis must be accurate, reliable, and meet certain data quality objectives. So statistical analysis and quality assurance are two essential aspects of monitoring [1].

In modern days, plutonium isotopes has been released into the environment from atmospheric nuclear weapons testing, various accidents involving nuclear material and nuclear fuel reprocessing plants [2]. Plutonium (Pu) isotopes generally found in the environment are ^{238}Pu, ^{239}Pu, ^{240}Pu and ^{241}Pu, of which ^{239}Pu ($t_{1/2}$= 24100 year) and ^{240}Pu ($t_{1/2}$= 6571 year) are the two most important and abundant isotopes. From the viewpoint of toxicity and long half-life, many research programs has been carried out to study the distribution of Pu in environmental media so far [3-5].

This study concentrates on two common statistical methods and applied to distribute the Plutonium isotopes (concentration of $^{239}Pu+^{240}Pu$ and $^{240}Pu/^{239}Pu$ atom ratios) by using ICP-MS in sediment and seawater samples around the Nuclear Power Plant in South Korea. These are (1) confidence interval and (2) correlation coefficient. The confidence interval is the characteristics associated with data distribution whereas the correlation coefficient is a way to quantify the linear relationship between two random variables.

The statistical methods are using to discuss the various environmental problems [6-13]. For solving the environmental problems, it is usually concentrated on how common statistical methods can be used. Among them, few have focused on the inaccuracy of the statistical methods. This paper will discuss the two statistical methods as applied to collected marine sample analysis data.

2. Statistical method

2.1 Calculation of confidence interval

To evaluate environmental sample data relative to a singular value of a regulatory standard, a confidence interval for the sample mean is often calculated to compare with the standard [7]. Given data distribution mean and standard deviation of a normal distribution, the confidence interval is calculated as [14]:

$$X_{(1-\alpha)} = \overline{X} \pm Z{\alpha/_2} \times \frac{\sigma}{\sqrt{n}} \text{……….} (1)$$

Where $X_{(1-\alpha)}$ is the confidence interval for the mean of variable x at level of $1-\alpha$, $\overline{X}$ is the sample mean, $Z\alpha/_2$ is the confidence coefficient, σ is standard deviation and n is the sample size. Here, α is confidence interval of 95%. To find the value of $Z\alpha/_2$, convert the percentage to a decimal, 0.95, and divide it by 2 to get 0.475. Then, check out the z table to find the corresponding value that goes with .475 [15].

2.2 Correlation Coefficient

The correlation coefficient is a way to quantify the linear relationship between two random variables. The correlation coefficient is calculated as follows [8]:

$$\rho_{x_1,x_2} = \frac{1}{n}\sum_{i=1}^{n} \frac{(x_{1i}-\overline{X}_1)(x_{2i}-\overline{X}_2)}{(\sigma_{x_1}\times\sigma_{x_2})} \text{……….} (2)$$

Where ρ_{x_1,x_2} is the correlation coefficient between variables x_1 and x_2, $\overline{X}_1$ and $\overline{X}_2$ are the mean of x_1 and x_2, respectively, σ_{x_1} and σ_{x_2} are the standard deviation of x_1 and x_2, respectively, and n is the number of data points.

The correlation coefficient ranges from -1 to +1, which implies a negative and a positive correlation, respectively. In general, $\rho_{x_1,x_2} = 0$ means that there is no correlation at all, and increasing coefficient in absolute value means increasing degree of correlation. Equation (2) indicates that the correlation coefficient is actually an index of the sum of two respective comparisons between a variable with its mean [13].

3. Experimental

3.1 Study area and sampling

A total of 10 sediment and 10 seawater samples were analyzed. These samples were collected from the vicinity of the nuclear power plant during the year of 2017 for environmental monitoring [16].

3.2 Analytical procedure

For the purpose of environmental radiation monitoring, Pu is routinely analyzed in the sediment and seawater at the Korean Institute of Nuclear Safety (KINS), Daejeon, South Korea.

The collected sediment samples were ashed in the electric furnace at 500^0C for 8 hours to decompose organic matter. ^{242}Pu was spiked as a yield tracer and sample was leached with 8M nitric acid on a hot plate. After leaching, Pu was separated using extraction chromatography (TEVA·specTM resin). Plutonium isotopes (^{239}Pu, ^{240}Pu, and ^{242}Pu) and ^{238}U (as $^{238}U^1H^+$ monitor) were measured by MC-ICP-MS (Thermo Scientific. NEPTUNE, Germanly). The concentrations of ^{239}Pu and ^{240}Pu were calculated by the isotope dilution (ID) method, and then the ^{240}Pu/^{239}Pu atom ratio was calculated.

Since Pu isotopes concentration is very low, around a few femtograms (fg, 10-15g) per kg in the surface seawater, and U(uranium)/Pu ratio is quite high (> $1x10^6$), analysis of Pu in the environmental seawater sample demands highly sensitive instrument and an efficient U separation process. A MC-ICP-MS is an ideal instrument in the quantitative and qualitative analysis of Pu isotopes (^{239}Pu, ^{240}Pu, ^{241}Pu) in the seawater. However, measurement conditions and sample introduction system should be optimized so as to maintain low detection limit and good precision to guarantee reliable results even for low abundant Pu isotopes (^{240}Pu and ^{241}Pu) at below fg/ml level in the final measurement solution. A sequential rinsing system in the sample introduction system using weak hydrofluoric acid (HF) solution (0.5%) and HNO_3 (3%) helps Pu count rate return to its background level (a few cps) even after loading high level of Pu sample (> ~ ten thousand cps). Mixed HF (0.01M) and HCl (0.6M) as an eluent showed high recovery for Pu in the 1st and 2nd TEVA separation and also contributed high signal intensity by washing out effect in the sample inlet pathway before plasma.

Table I: Instruments and measurement conditions for high-resolution ICP-MS

RF power (kW)	1.2
Type of nebulizer	ARIDUS-II
Plasma gas flow (L/min.)	15
Auxiliary gas flow rate (L/min.)	1.0
Carrier gas flow rate (L/min.)	0.82
Dwell time (msec.)	1.029
Resolution	400
Cycle[1], Replicates	20,1

[1]Total measurement number (Cycle/Block x Block)

4. Results and discussions

This study reviewed two commonly used statistical methods for data analysis in marine samples. For estimation of confidence intervals, potential pitfalls include the automatic assumption of a normal distribution for environmental data. For correlation coefficients, the potential pitfall includes the use of a wide range of data in which the maximum data points may trivialize other smaller data points and consequently skew the correlation coefficient.

The confidence interval can be used to estimate pollutants concentration relative to a numerical standard, for example, a regulatory cleanup standard. To do so, we first need to know the data distribution, which will determine the confidence interval. Table II presents a set of sediment and seawater monitoring data for plutonium concentrations in the year 2017. We used the eq. (1) calculating the confidence interval.

For assessing the data quality of Pu contents in the sediment and the seawater determined in this study. By isotope dilution (ID) method and U separation process were used to analyze the sediment and seawater respectively. The Analyses were repeated 20 times. Analytical results are summarized in Table II, where average and uncertainty values for n (the number of analyses) =20 are also included [16]. Uncertainties are given as one standard deviations (1σ).

Table II: Table for confidence interval

Sampling spots	Sediment		Seawater	
	Concentration of ^{239}Pu +^{240}Pu (Bq/kg)	^{240}Pu/^{239}Pu	Concentration of ^{239}Pu +^{240}Pu (μBq/kg)	^{240}Pu/^{239}Pu
1	0.742±0.009	0.244±0.002	7.56±0.12	0.237±0.007
2	0.481±0.006	0.240±0.003	7.34±0.12	0.253±0.007
3	0.420±0.005	0.249±0.002	4.16±0.11	0.230±0.012
4	0.402±0.005	0.244±0.002	6.85±0.19	0.243±0.013
5	0.286±0.003	0.246±0.003	3.84±0.12	0.250±0.009
6	0.863±0.011	0.235±0.002	3.90±0.11	0.230±0.012
7	0.294±0.004	0.244±0.004	6.15±0.10	0.243±0.007
8	0.478±0.006	0.240±0.003	6.12±0.18	0.239±0.014
9	0.235±0.003	0.243±0.003	5.08±0.08	0.228±0.006

10	0.0556±0.0012	0.249±0.009	5.43±0.16	0.239±0.014
Sum	4.26	2.43	56.4	2.39
Mean	0.426	0.243	5.64	0.239
SD	0.225	0.004	1.32	0.008
Confidence interval[a]	0.426±0.068	0.243±0.001	5.64±0.40	0.239±0.002

[a]Error depends on 1σ

Correlation coefficients can be used to study relationships between sediment and seawater concentrations. For the analyzing data, the correlation coefficient is 0.106 which is very low. Therefore the sediment and seawater are independent of each other. This is because of the flowing of the seawater every time, whereas the sediment makes a layer, for this experiment, the sediment and seawater was collected during April and November respectively [16]. So due to the different sampling period there is lower correlation between them.

5. Conclusions

Environmental data management may cover a large range of evaluation objectives during the monitoring of the environment. At each stage, collecting relevant data to be able to draw the conclusions needed is quite a big challenge.

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