Journal of Hazardous Materials 480 (2024) 136494

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Assessment of natural radioactivity levels in polymetallic nodules and potential health risks from deep-sea mining

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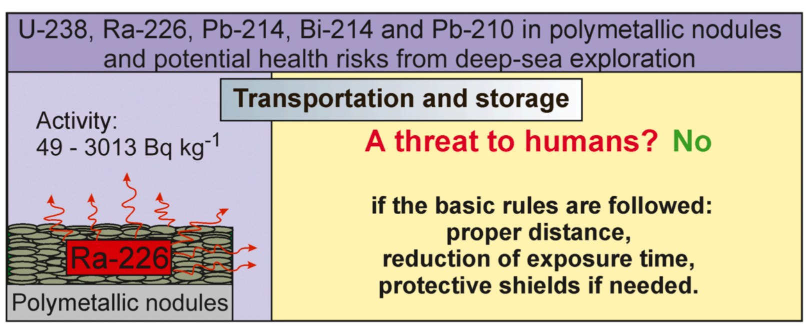
HIGHLIGHTS

- Polymetallic nodules contain radioactive elements of the U-Ra series.
- Radionuclide activity is arranged in the series U-238 <Ra-226 ≈Pb-214 ≈Bi-214 ≈Pb-210.
- Ra-226 belongs to the group of isotopes with the highest radiotoxicity.
- The tested nodule samples are characterized by large differences in Ra-226 activity.
- Observing the maximum exposure time effectively prevents exceeding the effective dose.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Polymetallic nodules
Clarion-Clipperton Zone
Pacific Ocean
Natural radioactivity
Radiological protection

ABSTRACT

The activity concentration of U-238, Ra-226, Pb-214, Bi-214, and Pb-210 was measured in samples of polymetallic nodules stored in the repository of the Interoceanmetal Joint Organization (IOM) based in Szczecin, Poland. The nodule samples were collected from the seabed of the Pacific Ocean, within the Clarion-Clipperton Zone, approximately 2000 kilometres west of Mexico. The activity concentration of U-238 in the studied samples ranged from 9 to 51 Bq/kg. The mean activity concentration of the other radionuclides, Ra-226, Pb-214, Bi-214, and Pb-210, was found to be at comparable levels at 350, 321, 323, and 287 Bq/kg, respectively. Also investigated was the potential radiological hazard to individuals involved in the storing and processing of the nodules, resulting from the radioactive decay of Ra-226 contained in the nodules. It was concluded that the effective dose limit (20 mSv) for individuals occupationally exposed to radioactive material can be exceeded in the case of prolonged and close contact with large quantities of nodules. Effective protective measures against the detected radiation include: observing the exposure time, ensuring safe distance from the source of radiation, and selecting suitable shielding where feasible within the operational constraints of the nodule transport or storage system.

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https://doi.org/10.1016/j.jhazmat.2024.136494
Received 25 September 2024; Received in revised form 6 November 2024; Accepted 11 November 2024
Available online 12 November 2024
0304-3894/

1. Introduction

In recent decades, interest in the extraction of nodules from the ocean floor, also known as polymetallic, ferromanganese, or manganese nodules, has gained global significance. This growing interest results from the relatively high content of economically valuable metals in their structure, including manganese, nickel, copper, cobalt, lithium, molybdenum, zirconium, and small quantities of rare earth elements [1]. Scientific research in the Area is governed by the legal framework established by the UN Convention on the Law of the Sea (UNCLOS). Part of this research focuses on developing extraction strategies for these ores and is conducted under contracts with the International Seabed Authority (ISA) – a UN body that has exclusive rights to grant exploration licences in the Area. Extensive research is being conducted, including studies on various technologies for nodule exploration [2] and extraction [3], as well as taxonomic and ecological research of species inhabiting the Area [4-7] and the impact of mining on deep-sea ecosystems (e.g. [8,9]). The impacts of deep-sea mining are being assessed through the implementation of numerous research projects, such as JPI Oceans Mining Impact (https://miningimpact.geomar.de/), Deep-Ocean Mining Environmental Studies and the joint US-Russian project called Benthic Impact Experiment [1]. Recently, a new topic has attracted a lot of attention, namely, serious concerns regarding potential threats to people working with nodules due to ionizing radiation resulting from the decay of radioactive isotopes accumulated in nodules [10].

Nodules were first extracted from the seafloor in 1873 during a scientific expedition on the British ship *Challenger* [11]. Twenty-five years later, in 1898, Maria Skłodowska-Curie and Piotr Curie announced the discovery of radioactive radium.

The radium isotope Ra-226 occupies the sixth position in the uranium-radium series initiated by uranium-238 (U-238 → Th-234 → Pa-234 → U-234 → Th-230 → Ra-226), with a half-life of 4.51×10^9 years (half-lives $T_{1/2}$ are based on [12]). The currently known radium isotopes, especially Ra-226 ($T_{1/2}$ =1600 years), together with their decay products are classified as some of the most dangerous Naturally Occurring Radioactive Materials (NORM) for the human body. Among the 30 known radium isotopes, only 4 (the most abundant being Ra-226) occur in nature [13]. The product of Ra-226 decay, which results in the release of alpha particles and gamma radiation, is the gaseous isotope radon-222 (Rn-222) with a half-life of 3.8 days. Subsequent decays of Rn-222 produce Po-218 ($T_{1/2}$ = 3.11 min), Pb-214 ($T_{1/2}$ = 26.9 min), Bi-214 ($T_{1/2}$ = 19.9 min), and Po-214 ($T_{1/2}$ =$1{,}64 \cdot 10^{-4}$ seconds), Tl-210 ($T_{1/2}$ = 1.32 min), Pb-210 ($T_{1/2}$ = 22.3 years), Bi-210 ($T_{1/2}$ = 5 days), Po-210 ($T_{1/2}$ = 138 days), and the stable Pb-206. Under adverse conditions, these isotopes can accumulate in the human body following Rn-222 inhalation, potentially leading to cancerous changes [14]. Depending on the matrix with which it is associated, the isotope Ra-226 can be absorbed into the body through the digestive tract, by inhalation, or through the skin. Under normal environmental conditions, the primary route of radon absorption into the body is via the digestive tract [15,16]. It is estimated that approximately 20 % of the ingested radon initially enters soft tissues [17], eventually becoming deposited in the skeletal system. Radon in the body chemically competes with calcium [18]. It is easily incorporated into mammalian bones owing to its chemical and biological similarity to other alkaline earth metals (Ca, Sr, and Ba). In bones, the cells most exposed to and sensitive to radiation from Ra-226 and its decay products are the marrow cells, osteoblasts, and the epithelial cells on the bone surface [18,19]. It has also been noted that in extreme situations, with continuous inhalation of Ra-226, a significant amount of this element may be deposited in the respiratory system, while its concentration in other organs remains relatively low [20].

As has already been mentioned, radon isotopes naturally occur in both soil and water, with Ra-226 being the predominant isotope in the oceans compared with other radon isotopes [21]. Several studies have focused on the baseline concentrations of natural radionuclides in coastal and marine sediments. Their results indicated that while natural radionuclide concentrations were present, they were within the global average limits. This study provides crucial baseline data for monitoring radionuclide levels in marine ecosystems [22]. In addition to studying radionuclides, Abbasi and Mirekhtiary [23] investigated the concentration of heavy metals and natural radioactivity in sediments from the Mediterranean Sea coast. The study found that although radionuclide levels were within safe limits, heavy metal contamination was a concern, suggesting anthropogenic pollution. This combined chemical and radiological risk requires integrated management strategies to safeguard marine environments. In a study, Zakaly et al. [24] evaluated naturally occurring radioactive materials (NORM) in aerosols dust. The findings highlighted the health risks associated with inhaling radioactive dust, particularly in areas with high NORM concentrations. This study is critical for regions where industrial activities or natural processes release significant amounts of radionuclides into the air.

In nodules collected from various locations on the ocean floor, more than 70 elements have been identified [1], including radioactive isotopes such as U-238, Th-230, Ra-226, Rn-222, Pa-231, Th-232 [10], Ra-226 and Pb-210 [25]. Therefore, it remains to be verified whether there are potential health risks associated with the handling of nodules due to ionising radiation caused by the presence of highly radiotoxic Ra-226. Along with its decay products, Ra-226 can significantly contribute to the effective dose from naturally occurring radioactive isotopes [26].

The goal of the present research was to assess the activity concentration of radioactive isotopes U-238, Ra-226, Pb-214, Bi-214, and Pb-210, which are present in the uranium-radium series and can be qualitatively and quantitatively detected in nodules using a gamma spectrometer. In this work, the material containing radioactive isotopes was treated as a volume/mass source (simplified as a point source) rather than as a source of NORM radiation concentrations in the surrounding environment, such as soil or sediments. Additionally, the study aimed to evaluate the potential radiological hazards associated with Ra-226 during technological processes, particularly those related to the transportation and storage of nodules, as indicated by the effective dose that a human might receive under specific conditions. Given the fact that nodule transportation and storage systems are still in the development phase, it was assumed that the technologies being developed effectively prevent dust generation, which is associated with additional human exposure. It was hypothesised that prolonged exposure to large quantities of polymetallic nodules during their transportation and storage poses a risk to human health.

2. Materials and methods

The research was conducted using polymetallic nodules stored in the IOM samples repository. The nodules were collected from the IOM exploration area located in the Clarion-Clipperton Fracture Zone (CCFZ) in the Eastern Pacific, approximately 2000 kilometers west of Mexico, where IOM has the exclusive rights for exploration licensed under the legal framework of the UNCLOS and administered by ISA.

Sixteen nodules with spherical or discoidal shapes and maximum diameters ranging from approximately 5 to 8 cm were examined. Polymetallic nodules from the CCFZ are composed of irregular layers of ore minerals (primarily Fe and Mn oxides and hydroxides) precipitated on nuclei formed from fragments of earlier-generation nodules, rock debris, or biogenic remnants (e.g. shark teeth). Metals of particular industrial value found in CCFZ nodules include Mn, Cu, Ni, Co, and Zn [27,28].

Nodules are heterogeneous in their structure. Particular laminae can form through direct precipitation either from seawater (hydrothermal type) or from pore waters following burial in sediments (diagenetic type) [29]. Hydrothermal laminae are characterised by high density, Mn/Fe ratio of less than 3, Cu+Ni content below 1.5 wt%, and Co content around 0.4 wt%. [30,31]. The significant porosity and active surface of hydrothermal laminae contribute to their enrichment with trace metals (e.g. Co) due to effective sorption processes (e.g. [32,33]).

Diagenetic laminae, composed of dendritic growth structures, are characterized by Mn/Fe ratio greater than 10, with Cu+Ni and Co content of approximately 3.9 wt% and 0.08 wt%, respectively [27]. Kozłowska and Mikulski (2019) differentiate between light and dark laminae in CCFZ nodules, which vary in metal content. Light laminae contain higher concentrations of Mn, Cu, and Ni oxides compared with dark laminae. According to Skowronek et al. [34], the internal structure of CCFZ polymetallic nodules includes not only metal-rich ore laminae (colloforms) but also areas of secondary infilling between them. These regions, known as intranoduliths, contain lithified and cemented trapped detrital material and have significantly lower metal concentrations [34].

2.1. Measurements of gamma activity concentration of radioactive isotopes in the uranium-radium series

The activity concentration of natural radioactive isotopes of the uranium-radium series, i.e. U-238, Ra-226, Pb-214, Bi-214, and Pb-210, was measured using a semiconductor gamma spectrometer manufactured by Canberra, equipped with a coaxial germanium detector of high resolution. The resolution (FWHM) for the 1.33 MeV line is 1.80 keV, and the relative efficiency is 40 % at 1.33 MeV. The spectrometer uses an HPGe detector containing germanium of very high purity. The detector was housed within a low-background lead shield to minimise gamma radiation background. The samples did not require chemical pretreatment prior to gamma spectrometric measurement, but they were stored in a measurement container for four weeks to achieve radioactive equilibrium. The standardised (homogenised, dried, etc.) samples were positioned in a specified geometric arrangement relative to the detector and analysed over a 72-hour regime.

Natural radioactivity was measured by using energy regions representing U-238, Ra-226, Pb-214, Bi-214 and Pb-210 at 92,60 keV, 186.21 keV, 351.9 keV, 609.3 keV and 46.56 keV, respectively.

Accuracy of the analytical method was evaluated by determining the Minimum Detection Activity (MDA), which represents the minimum radioactivity value of a radioactive isotope that can be detected by gamma spectroscopy. Many factors affect MDA for the nuclide of: detector efficiency, energy resolution (FWHM), peak background and measurement time. The Minimum Detectable Activity (MDA) for the radionuclides U-238, Ra-226, Pb-214, Bi-214, Pb-210 is 21.4 Bq/kg, 4.65 Bq/kg, 4.35 Bq/kg, 4.74 Bq/kg and 108 Bq/kg, respectively.

The accuracy of the analytical procedure was controlled by analysing the reference material IAEA 465 and IAEA 412 with certified values of natural radioactive isotope activity concentrations. The natural isotope activity concentration values obtained for both materials fall within one standard deviation of the certified limits.

Spectral analysis was conducted using Genie-2000 software (Gamma Analysis Option, model S501C). The results were expressed in becquerels calculated for a sample of 1 kg mass. The software also computed Type B measurement uncertainty.

The relative uncertainty was calculated as the square root of the sum of the independent relative variances of various components, including [35]:

- uncertainty in calculating the area under the signal peak recorded by the detector;
- uncertainty in determining the sample quantity;
- value of random uncertainty specified by the user;
- uncertainty of the effective efficiency of γ photon detection with a specified Energy;
- uncertainty related to the absorption of radiation by the material;
- uncertainty of the total correction factor, including: corrections related to, among others, measurement duration and time between taking the sample and starting the measurement.

The uncertainty value given in the table is expressed in Bq/kg and represents the expanded uncertainty (k = 2).

2.2. Estimation of maximum annual doses from Ra-226

The effective dose (E_{S1}) from the Ra-226 source was calculated using the following formula [36]:

$$E_{s1} = \frac{\Gamma_s \bullet A \bullet t}{k \bullet l^2} \tag{1}$$

where: E_{S1} – effective dose (mSv); Γs – constant characteristic of a given radioactive isotope, known as a unit power of the effective dose (mSv h^{-1} GBq^{-1} m^2); A – source activity (GBq); t – exposure time (h); k – attenuation factor; l – distance from the source (m).

The value of the unit power of the effective dose Γs for Ra-226 is 0.246 mSv h^{-1} GBq^{-1} m^2.

3. Results and discussion

Table 1 presents the results of measurements of the activity concentration of U-238, Ra-226, Pb-214, Bi-214 and Pb-210 in the studied polymetallic nodules. Also given is the measurement uncertainty (u) for each result.

The distribution of the results contained in Table 1 is presented in a graph form in Fig. 1.

Table 2 presents calculated mean and standard deviation (SD) values for the ratio of activity concentration of the measured radionuclides. Outlier measurement results were excluded from the calculations (sample nos.: 13, 14, 15).

The results presented in Fig. 1 and Table 2 indicate radioactive equilibrium between Ra-226, Pb-214, Bi-214, and Pb-210, as well as an increased activity concentration of these radionuclides relative to U-238.

Table 3 compares our research findings with those of other authors who investigated radionuclide activity concentration in polymetallic nodules collected from various locations on the Pacific seafloor. For example, the activity concentration of radionuclides measured by Moore [37] in particular layers of individual nodules revealed a non-homogeneous distribution of radionuclides within the nodule body. Table 3 presents the mean values for all the measurement results reported by various authors.

The results of our study, presented in Table 3, indicate significantly lower average activity concentration of Ra-226 in the samples compared to the average Ra-226 activity concentration reported by other authors. The considerable differences in average Ra-226 activity concentration may result from the location where the polymetallic nodule samples were collected. The data interpretation method might have an impact, as well. It is unclear whether the values reported by others (see Table 3) represent mean values calculated from multiple measurements within a nodule or are single point measurements. Therefore, the reported activity concentration measurements may not reflect accurately the actual Ra-226 activity concentration for whole nodules, as is the case in our study. No other articles have been found up to date that present Ra-226 activity concentration results for whole nodules.

Comparison of the results presented in Table 3 also reveals significant differences in the activity concentration of U-238 and Ra-226 in nodules collected from different locations on the Pacific seafloor. The U-238/Ra-226 ratios range from 0.05 to 0.60, compared with the U-238/Ra-226 activity concentration ratio close to or greater than one in coal and oil shale samples from various regions worldwide [42]. It can be inferred that in nodules, the radioactive decay equilibrium between U-238 and Ra-226 may be disturbed by multiple factors, one of them being the concurrent precipitation of U-238 and Ra-226 into the nodule from the surrounding water. It might therefore be that radon activity concentration is the sum of U-238 decay and the amount of precipitated

Table 1
Results of measurements of the activity concentration of the tested radionuclides in polymetallic nodules (Bq kg^{-1}).

Sample no.	U-238	*u*	Ra-226	*u*	Pb-214	*u*	Bi-214	*u*	Pb-210	*u*
1	51	18	241	169	231	19	217	13	252	154
2	9	11	412	26	369	16	393	16	269	133
3	40	13	314	20	310	24	289	13	258	128
4	20	13	394	20	375	28	368	12	315	126
5	21.2	9.5	48.5	4.3	47	5	42	5	80	80
6	36	14	371	24	347	27	324	15	399	158
7	23	14	367	24	330	27	322	16	327	156
8	19	12	329	17	288	22	308	10	219	83
9	38	13	385	20	346	26	361	13	193	127
10	42	16	658	34	607	45	617	20	497	198
11	18	11	337	17	294	23	317	11	312	22
12	34	12	313	20	284	24	296	12	383	132
13	202	64	2935	49	5053	75	2595	36	1884	50
14	165	51	3103	49	5298	74	2766	32	2015	202
15	37	13	1315	64	1216	80	1198	32	1235	393
16	17	12	375	19	349	26	350	12	222	111

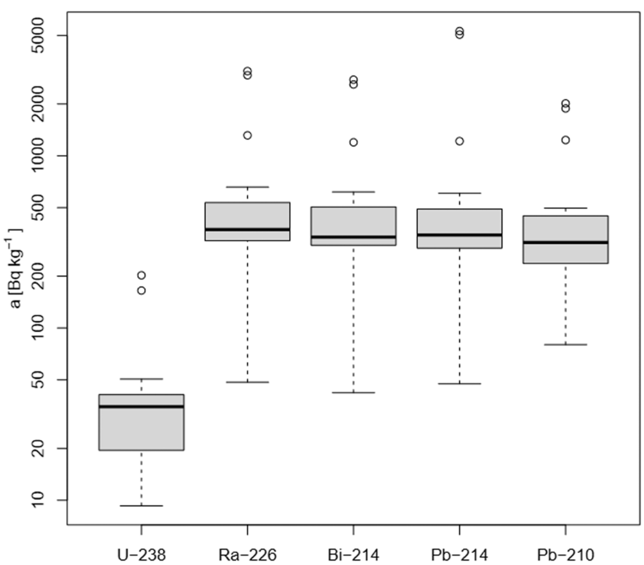

Fig. 1. Statistical distribution of activity concentration (*a*) of radioactive isotopes measured in polymetallic nodules.

Table 2
Mean and SD values for the ratio of radionuclide activity concentrations in the examined nodules, excluding outliers (samples nos.: 13, 14, 15).

Ratio	U-238/Ra-226	Ra-226/Pb-214	Pb-214/Bi-214	Bi-214/Pb-210
Mean	0.11	1.085	1.005	1.14
SD	0.11	0.042	0.062	0.37

Table 3
Comparison of mean activity concentration values for U-238, Ra-226, Pb-214, Bi-214 and Pb-210 in polymetallic nodules collected from various areas of the Pacific seabed (Bg kg^{-1}).

U-238	Ra-226	Pb-214	Bi-214	Pb-210	Data source
48	744	984	673	554	this research
-	4026	-	-	3367	[38]
786	1302	-	-	-	[39]
-	8933	-	-	-	[37]
73	3652	-	-	-	[40]
48	-	-	-	-	[41]
-	214	-	-	1074	[25]
196	3696	-	-	-	[10]

Ra-226. This is supported by a study of U-238 and Ra-226 activity concentration in different layers of nodules carried out by Moore et al. [39]. The study results show that in the outer layer up to a depth of 0.4 mm, the mean U-238/Ra-226 ratio is 0.33, whereas in the 2.2 to 4.0 mm layer, the mean ratio is 3.0. Considering the fact that both the formation of nodules and the half-life of U-238 last millions of years, whereas the half-life of Ra-226 is counted in thousands of years, it can be assumed that the activity concentration of these isotopes in the outer layers of nodules is relative to the concentrations of these isotopes in the surrounding waters, while equilibrium between these radionuclides is established in the deeper layers of nodules, which are isolated from sea water. Another factor influencing the U-238 and Ra-226 concentrations in water could be the varying solubility of the chemical compounds containing these radionuclides. Research by other authors indicates different ratios of these radionuclides depending on the type of water. For example, in thermal waters, U-238 activity concentration ranges from ≤ 0.5 to 8.95 mBq dm^{-3} , and Ra-226 activity concentration ranges from ≤ 5 to 29.2 mBq dm^{-3} [43]. In groundwater, U-238 activity concentration values range from $< 1.0 \times 10^{-4}$ to 8.0×10^{-2} mBq dm^{-3} , and Ra-226 activity concentration ranges from < 0.002 to 0.492 Bq dm^{-3} [44], whereas in uranium mine waters, the mean U-238/Ra-226 ratio is 0.29 [45]. For some types of water, inverse ratios of these radionuclides have been observed [46].

It is assumed that marine sediments are enriched in Ra-226 and U-238 with depth due to the decreasing quantities of carbonates containing Ra-226 and U-238, followed by the sorption of Ra-226 from sea water and the sedimentation of hydrolysed U-238 to the ocean floor [47]. The same enrichment mechanism may also take place in the case of nodules. In this case, the authors indicate two possible sorption mechanisms: chemical/ion exchange adsorption of Ra-226 and physical adsorption of U-238.

Among the isotopes of the uranium-radium series, Ra-226 is the most critical one from a radiological protection perspective, as it belongs to the group of radionuclides with the highest radiotoxicity (Recommendations, 2007). The results of the present study indicate that in the analysed samples, Ra-226 remains in radioactive equilibrium with Pb-214, Bi-214, and Pb-210 (Fig. 1, Table 2). Although U-238 is the parent isotope, its activity concentration is considerably lower compared with Ra-226 and its decay products. Therefore, when evaluating the effective dose, we focused on assessing the hazards posed by Ra-226.

4. Assessment of the effective dose from Ra-226

Council Directive, 2013 [48] lays down basic safety standards for protection against the dangers arising from exposure to ionising radiation, which establish the values of activity concentration and total activity concentration below which the handling of radioactive materials is exempt from notification or authorisation. For Ra-226, these values are set at 10 Bq g^{-1} and 1.0×10^4 Bq, respectively. In the case of the first value, all the examined samples are eligible for exemption (Table 1). Similarly, the mean Ra-226 activity concentration values measured by other authors do not exceed the 10 Bq g^{-1} exemption threshold (Table 3). The second value can be applied to the total quantity of nodules stored at a single location. In this case, the total activity concentration of as little as several tens of kilograms of nodules exceeds the exemption value. The Directive stipulates that if any of the two exemption values is not exceeded, no notification or authorisation is required for the handling of radioactive materials.

To assess the potential hazard to workers, effective dose values were determined for three parameters: the quantity of nodules, their radioactivity, and the distance between the worker and the source of radiation. Mean and maximum Ra-226 activity concentration values from our own research, as well as the highest values reported by other authors (Table 3) were used in the assessment. The annual effective dose E was calculated for 1, 2, 5 and 10 tonnes of nodules stored in a room, the distance from the radiation source being 0.5, 1, 5, 10 and 20 m for each the quantities. It was assumed that the annual working time of the person exposed to radiation was 2000 h (40 h per week in accordance with the provisions of the Polish Labour Law (Dziennik Ustaw [Journal of Laws] of 2023, item 1465, Chapter VI). The effective dose E calculated for the above assumptions is presented in Table 4.

The Council Directive 96/29/EURATOM of 13 May 1996 [49] laying down basic safety standards for the protection of the health of workers and the general public against the dangers arising from ionizing radiation [49] introduces two categories of exposed workers, A and B, based on the received annual effective dose. Category A includes workers who are liable to receive an effective dose greater than 6 mSv per year or an equivalent dose greater than 3/10 of the dose limits for the lens of the eye, skin and extremities laid down in Article 9 (2) of the Directive. Category B includes those exposed workers who are not classified as exposed category A workers. The annual effective dose limit is 20 mSv. Additionally, the Directive lays down that category A workers must be subject to systematic individual dose monitoring, while the exposure assessment for category B workers is based on measurements in the working environment.

The results presented in Table 4 indicate that the annual effective dose limit of 20 mSv for all worker categories is only exceeded when the distance from the source of radiation is ≤ 1 m (bold-typed values). In such cases, to protect exposed workers from exceeding the dose limit, simple preventive measures can be implemented: reducing the exposure time, ensuring that safe distance from the radiation source is maintained, wearing protective clothing, and installing protective shields and screens. Under extreme conditions assumed in this study, it is sufficient to ensure that workers maintain a minimum distance of at least 5 m from a 10-tonne mass of nodule.

Table 4
Annual effective dose E (mSv year^{-1}) from Ra-226 in polymetallic nodules.

Quantity (t)	Distance from the radiation source (m)				
	0.5	1	5	10	20
A_{Ra-226} = 744 Bq/kg					
1	2.9	0.37	0.015	0.004	$9.2 \cdot 10^{-4}$
2	5.9	0.73	0.029	0.007	$1.8 \cdot 10^{-3}$
5	**15**	1.8	0.073	0.018	$4.6 \cdot 10^{-3}$
10	**29**	3.7	0.146	0.037	$9.2 \cdot 10^{-3}$
A_{Ra-226} = 3103 Bq/kg					
1	**12**	1.5	0.061	0.015	$3.82 \cdot 10^{-3}$
2	**24**	3.1	0.12	0.031	$7.63 \cdot 10^{-3}$
5	**61**	**7.6**	0.31	0.076	$1.91 \cdot 10^{-2}$
10	**122**	**15**	0.61	0.153	$3.82 \cdot 10^{-2}$
A_{Ra-226} = 8933 Bq/kg[37]					
1	**18**	4.4	0.18	0.044	$1.10 \cdot 10^{-2}$
2	**35**	**8.8**	0.35	0.088	$2.20 \cdot 10^{-2}$
5	**88**	**22**	0.88	0.22	$5.49 \cdot 10^{-2}$
10	**176**	**44**	1.8	0.44	$1.10 \cdot 10^{-1}$

Another category of workers named is this research category C includes individuals not directly exposed to radiation from nodules. In this case, particular attention must be paid to the design of the work place (including, but not limited to, external walls and ceilings) so as to prevent the worker from receiving an annual effective dose of 0.3 mSv. The above guidelines, based on the recommendations of the International Commission on Radiological Protection (ICRP) [50], and the International Commission on Radiological Units and Measurements (ICRU), constitute a radiation protection system used in Europe and worldwide.

The results compiled in Table 4 indicate that the safe distance for each of the quantities of nodules is approximately 5 m. If the distance between the exposed worker and nodules is less than 5 m, proper shielding is required. The most cost-effective and efficient shield that can reduce the received dose is a layer of concrete with a density of 2.3 g cm^{-3} . For example, a 10 cm layer provides a twofold attenuation of radiation, while a 25 cm layer provides a tenfold attenuation [51]. Fig. 2 illustrates the effectiveness of concrete barriers in protecting category A, B and C workers. The graph was plotted using the highest Ra-226 activity concentration value from Table 3, which is 8933 Bq kg^{-1} , and the annual effective dose E calculated for 10 tonnes of nodules. The graph shows that a 10 cm concrete barrier reduces effectively the required safe distance for all categories of workers.

5. Conclusions and future research

Polymetallic nodules are increasingly recognised as a potential future source of critical metals for the global economy. Extensive research into the development of nodules extraction and processing technologies has been underway for decades. Concurrently, studies are being conducted on the environmental impacts and health risks associated with exploitation of nodules. As nodules contain radioactive isotopes from the uranium-radium series, including the highly radiotoxic Ra-226, it is feared that exposure to them during extraction and processing is potentially harmful to human health. Therefore, research on the radiological hazard posed by Ra-226 seems to be of great relevance to future exploitation projects.

The results of our study demonstrate that workers exposed to nodules are only liable to exceed the annual effective dose of 20 mSv in the case of prolonged and close contact with large quantities of nodules. However, the analysis of ionising radiation hazards based on Ra-226 activity concentration measurements shows that effective protection for workers in various exposure categories can be easily achieved through proper management of exposure time, maintaining safe distance from the radiation source, and using proper shielding.

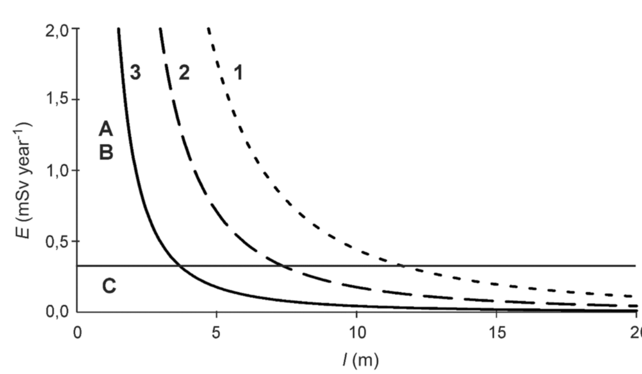

Fig. 2. Effectiveness of concrete walls in protecting category A, B and C workers from a radiation source (10 tonnes of polymetallic nodules having an activity concentration of 8933 Bq/ kg). E – annual effective dose; l – distance from the source of radiation; 1 – without shielding, 2 – 10 cm thick concrete barrier; 3 – 25 cm thick concrete barrier; A, B, C – categories of workers.

To ensure radiological safety of workers handling polymetallic nodules, our future research will include, among other topics, an assessment of the level of risk connected to high-energy alpha particle emitters. Alpha emitters are considered highly harmful, particularly when they enter the body, for example through inhalation. We consider this topic to be of high relevance to future exploitation projects, and therefore alpha emitters will be the focus of the follow-up to this study. At a later stage, we would like to broaden the scope of research by including actual technical designs of extraction, storage, transport and processing systems (i.e. case studies). If needed, a comprehensive approach to the handling of polymetallic nodules in exploitation projects will be developed and implemented, taking into account possible radiological hazards. Considering the type and level of radiation emitted from nodules, it can be expected that the costs of implementing such approach will not increase significantly the overall costs of nodules exploitation projects. Boundary technical conditions for exploitation technologies will depend on regulations regarding health risks arising from the radionuclides present in polymetallic nodules issued by ISA and other maritime regulators, e.g. classification societies.

Considering the growing significance of marine minerals mining and the planned pilot-scale nodules extraction projects, it is essential to intensify scientific research on technologies that would minimize the impact of exploitation on environment. It is also crucial to conduct in-depth studies assessing the associated risks, including radiological hazards, arising from the extraction and processing of these resources.

Environmental implication

Since nodules contain radioactive isotopes from the uranium-radium series, including the highly radiotoxic Ra-226, there are concerns that exposure during extraction and processing could be harmful to human health. Therefore, research on the radiological hazards posed by Ra-226 is highly relevant to future exploitation projects. Our study aimed to estimate the threat posed by the radioactivity of the nodules to human health and the environment surrounding processing facilities. Our data allow for the estimation of the radiation dose received by individuals working in nodule excavation, storage, and reprocessing plants.

CRediT authorship contribution statement

Agnieszka Strzelecka: Writing – review & editing, Supervision. **Kamila Mianowicz:** Writing – review & editing, Supervision. **Zbigniew Ziembik:** Writing – review & editing, Validation, Methodology, Formal analysis. **Artur Skowronek:** Writing – review & editing, Supervision. **Tomasz Abramowski:** Writing – review & editing, Supervision. **Agnieszka Dolhanczuk-Srodka:** Writing – review & editing, Writing – original draft, Visualization, Resources, Methodology, Investigation, Formal analysis, Conceptualization. **Andrzej Kłos:** Writing – review & editing, Writing – original draft, Supervision. **Daniel Janecki:** Writing – review & editing, Writing – original draft, Supervision, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The research was funded by the Interoceanmetal Joint Organization in relation with the research activities carried out in accordance with the contract for polymetallic nodules exploration with International Seabed Authority.

This work was carried out at MCBR UO (International Research and Development Center of the University of Opole), which was established as part of a project co-financed by the European Union under the European Regional Development Fund, RPO WO 2014–2020, Action 1.2 Infrastructure for R&D. Agreement No. RPOP.01.02.00–16-0001/17–00 dated January 31, 2018.

Data Availability

Data will be made available on request.

References

[1] Hein, J.R., Koschinsky, A., 2014. Deep-ocean ferromanganese crusts and nodules. In: Scott, Steven D. (Ed.), Treatise on Geochemistry, second ed., vol. 13. Elsevier, Amsterdam, pp. 273–291. https://doi.org/10.1016/B978–0-08–095975-7.01111–6 (Chapter 11).

[2] Guo, X., Xu, B., Yu, H., Burnett, W.C., Li, S., Lian, E., et al., 2022. Exploration of deep ocean ferromanganese nodule fields using radon as a tracer. e2022GL100726 Geophys Res Lett 49. https://doi.org/10.1029/2022GL100726.

[3] Kang, Y., Liu, S., 2021. The development history and latest progress of deep-sea polymetallic nodule mining technology. Minerals 11, 1132. https://doi.org/10.3390/min11101132.

[4] Błażewicz, M., Jóźwiak, P., Menot, L., Pabis, K., 2019. High species richness and unique composition of the tanaidacean communities associated with five areas in the Pacific polymetallic nodule fields. Prog Oceanogr 176, 102141. https://doi.org/10.1016/j.pocean.2019.102141.

[5] Drennan, R., Wiklund, H., Rabone, M., Georgieva, M.N., Dahlgren, T.G., Glover, A. G., 2021. Neanthes goodayi sp. nov. (Annelida, Nereididae), a remarkable new annelid species living inside deep-sea polymetallic nodules. Eur J Taxon 760, 160–185. https://doi.org/10.5852/ejt.2021.760.1447.

[6] Eichsteller, A., Martynov, A., O'Hara, T.D., Christodoulou, M., Korshunova, T., Bribiesca-Contreras, G., et al., 2023. Ophiotholia (Echinodermata: Ophiuroidea): a littleknown deep-sea genus present in polymetallic nodule fields with the description of a new species. Front Mar Sci 10, 1056282. https://doi.org/10.3389/fmars.2023.1056282.

[7] Neal, L., Wiklund, H., Rabone, M., Dahlgren, T.G., Glover, A.G., 2022. Abyssal fauna of polymetallic nodule exploration areas, eastern Clarion-Clipperton Zone, central Pacific Ocean: Annelida: spionidae and poecilochaetidae. Mar Biodivers 52, 51. https://doi.org/10.1007/s12526-022-01277-1.

[8] Gollner, S., Kaiser, S., Menzel, L., Jones, D.O.B., Brown, A., Mestre, N.C., et al., 2017. Resilience of benthic deep-sea fauna to mining activities. Mar Environ Res 129, 76–101. https://doi.org/10.1016/j.marenvres.2017.04.010.

[9] Jones, D.O.B., Ardron, J.A., Colaço, A., Durden, J.M., 2020. Environmental considerations for impact and preservation reference zones for deep-sea polymetallic nodule mining. Mar Policy 118, 103312. https://doi.org/10.1016/j.marpol.2018.10.025.

[10] Volz, J.B., Geibert, W., Köhler, D., Rutgers van der Loef, M.M., Kasten, S., 2023. Alpha radiation from polymetallic nodules and potential health risks from deep-sea mining. Sci Rep 13, 7985. https://doi.org/10.1038/s41598-023-33971-w.

[11] Belkin, I.M., Andersson, P.S., Langhof, J., 2021. On the discovery of ferromanganese nodules in the World Ocean. Deep Sea Res Part I: Oceanogr Res Pap 175, 103589. https://doi.org/10.1016/j.dsr.2021.103589.

[12] UNSCEAR 2000. Report to the General Assembly, with Scientific Annexes Vol I: Sources and effects of ionizing radiation, United Nations, New York, 2000.

[13] Molinari J., Snodgrass W.J.. The chemistry and radiochemistry of radium and the other elements of the uranium and thorium natural decay series. Technical Report Series No 310, The environmental behaviour of radium 1990; vol. 1, IAEA, Vienna, 11–56.

[14] Denton, G.N.W., Namazi, S., 2013. Indoor radon levels and lung cancer incidence on Guam., Procedia. Environ Sci 18, 157–166.

[15] Fisenne, I.M., Perry, P.M., Decker, K.M., Keller, H.W., 1987. The daily intake of 234,235,238U, 228,230,232Th and 226, 228Ra by New York City residents. Health Phys 1987 (53), 357–363.

[16] UNSCEAR 1993. Sources and Effects of Ionizing Radiation. Report to the General Assembly, with Scientific Annexes, United Nations, New York 1993.

[17] Stather, J.W., 1990. The behaviour and radiation dosimetry of radium in man. Technical Report Series No 310, The environmental behaviour of radium. I AEA, Vienna 2, 297–344.

[18] ICRP Publication 30, Part 1. Vol. 2, No. 3/4. Limits for Intakes of Radionuclides by Workers. Pergamon Press 1979.

[19] ICRP Publication 11. A review of the radiosensitivity of the tissues in bone. Pergamon Press 1967.

[20] Toxicological Profile for Radium. Tp-90–22, U.S. Department of Health & Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry 1990.

[21] Neff J.M., 2002, Chapter 11 - Radium Isotopes in the Ocean, Editor(s): Jerry M. Neff, Bioaccumulation in Marine Organisms, Elsevier, 2002, Pages 191–201, ISBN 9780080437163, https://doi.org/10.1016/B978–008043716-3/50012–9.

[22] Abbasi, A., Zakaly, H.M.H., Mirekhtiary, F., 2020. Baseline levels of natural radionuclides concentration in sediments east coastline of north cyprus. Mar Pollut Bull 161, 111793. https://doi.org/10.1016/j.marpolbul.2020.111793.

[23] Abbasi, A., Mirekhtiary, F., 2020. Heavy metals and natural radioactivity concentration in sediments of the Mediterranean sea coast. Mar Pollut Bull 154, 111041. https://doi.org/10.1016/j.marpolbul.2020.111041.

[24] Zakaly, H.M.H., Abbasi, A., Almousa, N., Savaşan, A., 2024. Naturally occurring radioactive materials (NORM) concentration and health risk assessment of aerosols dust in Nicosia, North Cyprus. J Radio Nucl Chem 333 (3), 1073–1082. https://doi.org/10.1007/s10967-023-09346-w.
[25] Lin, F., Lin, C., Yu, W., Sun, X., Lin, H., 2022. Radium and Lead Radioisotopes Composition of Sediment and Its Biogeochemical Implication in Polymetallic Nodule Area of Clario-Clipperton Zone. Molecules 27, 5061. https://doi.org/10.3390/molecules27165061.
[26] Nguyen, V.T., Huynh, N.P.T., Vu, N.B., Le, C.H., 2021. Long-term accumulation of ^{226}Ra in some agricultural soils based on model assessment. Agric Water Manag 243, 106453. https://doi.org/10.1016/j.agwat.2020.106453.
[27] Heller, C., Kuhn, T., Versteegh, G.J.M., Wegorzewski, A.V., Kasten, S., 2018. The geochemical behavior of metals during early diagenetic alteration of buried manganese nodules. Deep Sea Res Part I: Oceanogr Res Pap 142, 16–33. https://doi.org/10.1016/j.dsr.2018.09.008.
[28] Kotliński, R.A., 2011. Pole konkrecjonośne Clarion-Clipperton–źródło surowców w przyszłości. Górnictwo i Geoinżynieria 35 (4/1), 195–1214.
[29] Jung, H.-S., Lee, C.-B., 1999. Growth of diagenetic ferromanganese nodules in an oxic deep-sea sedimentary environment, northeast equatorial Pacific. Mar Geol 157, 127–144.
[30] Halbach, P., Friedrich, G., von Stackelberg, U., 1988. The Manganese Nodule Belt of the Pacific Ocean. Geological. Environment, nodule formation, and mining aspects. Ferdinand Enke Verlag,, Stuttgart.
[31] Wegorzewski, A.V., Kuhn, T., 2014. The influence of suboxic diagenesis on the formation of manganese nodules in the Clarion Clipperton nodule belt of the Pacific Ocean. Mar Geol 357, 123–138.
[32] Hein, J.R., Mizell, K., Koschinsky, A., Conrad, T.A., 2013. Deep-ocean mineral deposits as a source of critical metals for high- and green-technology applications: comparisons with land-based resources. Ore Geol Rev 51, 1–14.
[33] Koschinsky, A., Halbach, P., 1995. Sequential leaching of marine ferromanganese precipitates: genetic implications. Geochim Et Cosmochim Acta 59, 5113–5132.
[34] Skowronek, A., Maciąg, Ł., Zawadzki, D., Strzelecka, A., Baláž, P., Mianowicz, K., et al., 2021. Chemostratigraphic and textural indicators of nucleation and growth of polymetallic nodules from the clarion-clipperton fracture zone (IOM claim area. Minerals 11 (8), 868. https://doi.org/10.3390/min11080868.
[35] Canberra, Genie 2000. Customization Tools Manual. Meriden USA: Canberra, 2017.
[36] ICRP Publication 103, 2007.
[37] Moore, W.S., 1984. Torium and radium isotopic relationships in manganese nodules and sediments at MANOP Site S. Geochim Cosmochim Acta 48 (5), 987–992.
[38] Krishnaswami, S., Cochran, J.K., 1978. Uranium and thorium series nuclides in oriented ferromanganese nodules: growth rates, turnover times and nuclide behavior. Earth Planet Sci Lett 40 (1), 45–62.
[39] Moore, W.S., et al., 1981. Fluxes of metals to a manganese nodule radiochemical, chemical, structural, and mineralogical studies. Earth Planet Sci Lett 52 (1), 151–171.
[40] Huh, C.-A., Ku, T.-L., 1984. Radiochemical observations on manganese nodules from three sedimentary environments on the north Pacifc. Geochim Cosmochim Acta 48 (5), 951–963.
[41] Bollhöfer, A., Eisenhauer, A., Frank, N., Pech, D., Mangini, A., 1996. Thorium and uranium isotopes in a manganese nodule from the Peru basin determined by alpha spectrometry and thermal ionization mass spectrometry (TIMS): Are manganese supply and growth related to climate? Geol Rundsch 85, 577–585.
[42] Shpirt, M.Y., Punanova, S.A., 2014. Estimated radioactivity of solid fossil fuels. Solid Fuel Chem 48, 1–10. https://doi.org/10.3103/S0361521914010091.
[43] Van Duong, H., Nguyen, C.D., Nowak, J., et al., 2019. Uranium and radium isotopes in some selected thermal, surface and bottled waters in Vietnam. J Radio Nucl Chem 319, 1345–1349. https://doi.org/10.1007/s10967-018-6317-z.
[44] Almeida, R.M.R., Lauria, D.C., Ferreira, A.C., Sracek, O., 2004. Groundwater radon, radium and uranium concentrations in Região dos Lagos, Rio de Janeiro State, Brazil. J Environ Radioact 73 (3), 323–334. https://doi.org/10.1016/j.jenvrad.2003.10.006.
[45] Willett, I.R., Bond, W.J., 1998. Fate of manganese and radionuclides applied in uranium mine waste water to a highly weathered soil. Geoderma 84 (1–3), 195–211. https://doi.org/10.1016/S0016-7061(97)00129-8.
[46] Hakam, O.K., Choukri, A., Moutia, Z., Chouak, A., Cherkaoui, R., Reyss, J.-L., et al., 2001. Uranium and radium in groundwater and surface water samples in Morocco. Radiat Phys Chem 61, 653–654.
[47] Domanov, M.M., Gagarin, V.I., Bukhanov, M.V., 2022. Features of 226Ra, 232Th, 238U distribution in the surface layer of bottom sediments in the northern part of the Laptev Sea. Radiochemistry 64, 766–775. https://doi.org/10.1134/S1066362222060145.
[48] Council Directive 2013/59/Euratom of 5 December 2013 laying down basic safety standards for protection against the dangers arising from exposure to ionising radiation, and repealing Directives 89/618/Euratom, 90/641/Euratom, 96/29/Euratom, 97/43/Euratom and 2003/122/Euratom. Document 32013L0059.
[49] Council Directive 96/29/Euratom of 13 May 1996 laying down basic safety standards for the protection of the health of workers and the general public against the dangers arising from ionizing radiation. Document 31996L0029.
[50] ICRP, 2012. Compendium of Dose Coefficients based on ICRP Publication 60. ICRP Publication 119. Ann. ICRP 41(Suppl).
[51] Polish Standards, 1986. Protective materials and devices against X and gamma rays. Calculation of fixed screens, PN-86-J-800001.