Radiation Protection Dosimetry Advance Access published September 30, 2013

Radiation Protection Dosimetry (2013), pp. 1–6 doi:10.1093/rpd/nct237

NATURALLY OCCURRING RADIOACTIVE MATERIALS (NORM) IN ASHES FROM A FUEL-OIL POWER PLANT IN CIENFUEGOS, CUBA, AND THE ASSOCIATED RADIATION HAZARDS

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Received 21 June 2013; revised 3 September 2013; accepted 4 September 2013

The radioactivity of NORM was measured in ashes collected from a fuel-oil power plant in Cienfuegos, Cuba, using an HPGe gamma-ray spectrometer. The ^{226}Ra, ^{210}Pb, ^{40}K, ^{232}Th and ^{238}U activity concentrations reached 240, 77, 59, 70 and 15 Bq kg^{-1}, respectively. The potential radiological hazard of these residuals was assessed. The radium equivalent activities of the samples varied from 54 to 345 Bq kg^{-1}. The gamma index was calculated to be lower than that of the reference values, and the gamma absorbed dose rate was higher than the average reported for the earth's crust; however, the assessed annual effective dose was slightly lower than the annual effective dose limit for public, i.e. 1 mSv. Therefore, these bottom ashes were not dramatically enriched with radionuclides and may be used as an additive for building materials without restrictions from a radiological protection point of view.

INTRODUCTION

Naturally Occurring Radioactive Materials (NORM) are the radioactive residues from the extraction, treatment and purification of minerals, petroleum products or other substances obtained from parent materials that may contain concentrations of primordial radionuclides. Every year, hundreds of millions of metric tons (according to the International System of Units, one metric ton is equivalent to 1000 kg) of wastes containing NORM are generated from a wide variety of processes, ranging from uranium and phosphate mining to municipal drinking water treatment[1]. An example of NORM is the ashes produced from combustion of coal, gas and fuel oil in power plants[1]. If the radioactivity is much higher than the background level, handling NORM may cause problems in many industries. Eisenbud and Petro in 1964[2] noticed that in the use of fossil fuel for generating electricity, the concentration of radionuclides increased. Since then, several authors have reported radioactivity levels in coal- and lignite-fired power plants[3–10]. However, very few reports of NORM are available for fuel-oil power plants, even if the presence of naturally occurring radioactive material in the petroleum and gas extraction industry is a well-known fact[1]. In Cuba, there are no studies on the radioactivity levels in residual ashes from these industries.

Fuel oil is the main fossil fuel used to generate electricity in Cuba. Approximately 81 % of the electric demand in Cuba is generated by fuel-oil-fired power plants, and a total of 2.24 million tons of crude oil was consumed in 2011 to produce electricity in Cuba. In Cienfuegos province, a 370-MW fuel-oil power plant was established on the littoral zone of Cienfuegos' bay and it is operating since 1940. Several studies, carried out on sediments from Cienfuegos' bay, reflect that Cienfuegos' Power Plant (CPP) is one of the main sources of hydrocarbon and heavy metal pollution to the bay[11, 12]. High levels of heavy metals (V, Ni, Ti and Zn) were reported recently in bottom ashes from the fuel-oil power plant[13]. These ashes are considered as 'hazardous wastes' by the National Environmental Authority, through the resolution 136/2009[14]. From the radiological safety point of view, there are no special regulations for NORM in Cuba. However, studies carried out in Cuba demonstrated the existence of anomalous levels of the natural radioactivity in some environmental components[15–17]. High levels of ^{210}Po were reported in marine organisms of Cienfuegos Bay[18], which could be linked to the atmospheric emission or dumping of NORM radioactive wastes coming from CPP.

The aims of the present work are to investigate the activity concentrations of NORM in bottom ashes generated by the fuel-oil power plant in Cienfuegos, Cuba, and to assess the potential hazard of these residuals on man and its environment.

MATERIALS AND METHODS

Bottom ashes were collected from three disposal sites of waste materials from the thermal power plant 'Carlos Manuel de Céspedes', located near

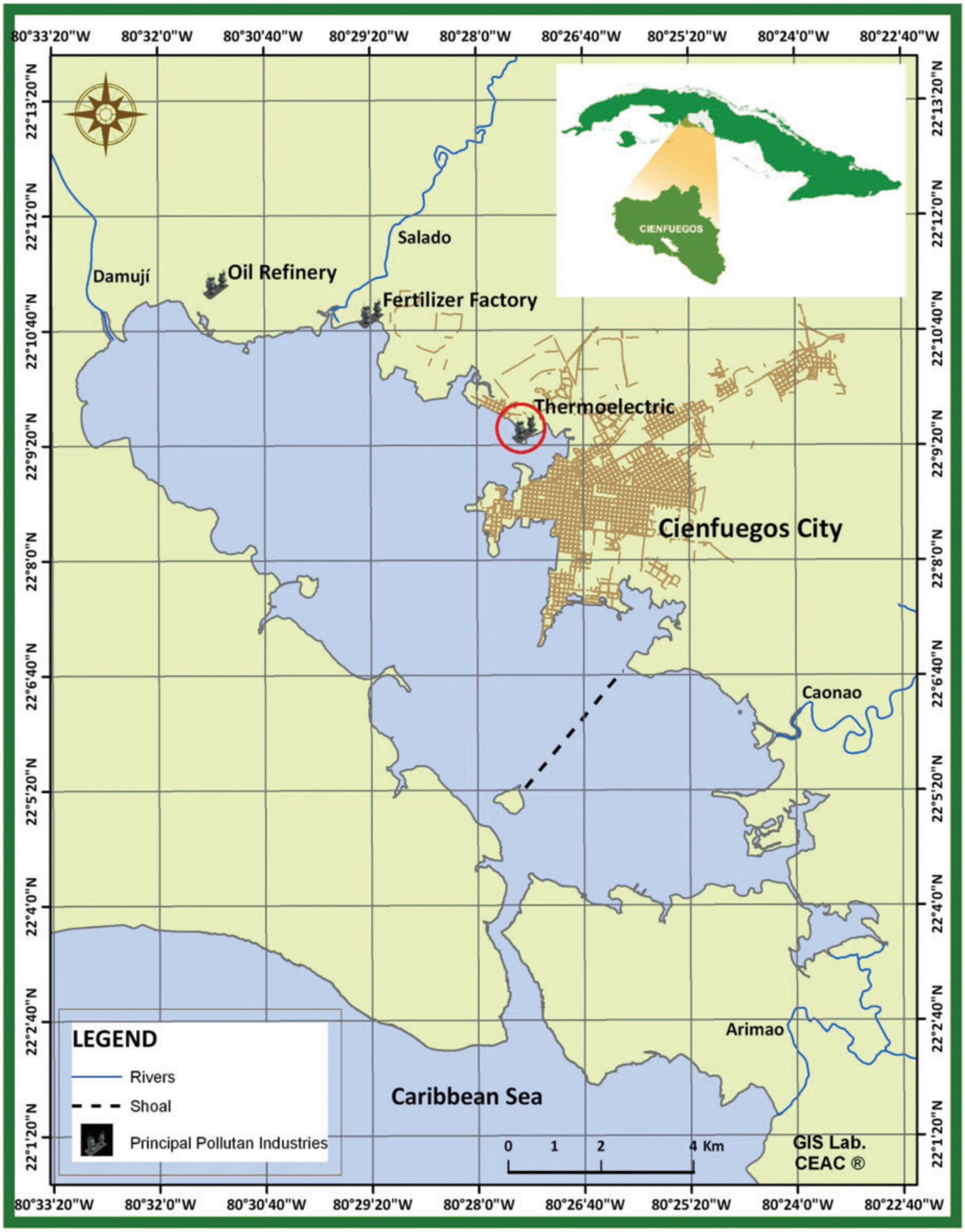

Figure 1. Location of Cienfuegos' Power Plant.

Cienfuegos bay (Figure 1). Ten random subsamples were taken for each sampling site to obtain a representative sample for each site. The ashes were dried at 110°C to reach a constant weight. All the samples were ground in a ball grinder, passed through a 0.5-mm-mesh-width sieve and homogenised. Aliquots of 86 g was inserted in PVC cylindrical containers (diameter=7.5 cm and height=2.5 cm) and immediately sealed to avoid ^{222}Rn and ^{220}Rn losses and to establish the secular equilibrium between ^{238}U and

^{232}Th with their short-lived decay products after four weeks. They were measured in a low-level gamma spectrometric system with an HPGe coaxial detector type NGC 3019 from Detector Systems GmbH, 30 % relative efficiency, 1.9 keV resolution at 1.33 MeV of ^{60}Co and an 8192-channel Multi-Channel Analyzer (MCA). An iron shield (30 cm thick) covered the active zone of the detector. The typical measurement time was 100 000 s. The gamma energies used for the analyses were 46.54 keV for ^{210}Pb, 63.28 keV from ^{234}Th for ^{238}U, 351.93 keV from ^{214}Pb for ^{226}Ra, 911.07 keV from ^{228}Ac for ^{232}Th and 1460.83 keV for ^{40}K. The activity concentration and its uncertainty were calculated using equations provided in the literature. The uncertainty was calculated as the result of the uncertainty propagation process using the net peak area, the detector efficiency and the mass uncertainties, and in all calculations, they were $<$10 %. This procedure was accredited by the National Office for Normalization for ISO-NC-17025, and it is recognised by the International Atomic Energy Agency through the ARCAL XXVI IAEA Regional Project since 2005. The Centro de Estudios Ambientales de Cienfuegos belongs to the IAEA-Network 'Analytical Laboratories for the Measurement of Environmental Radioactivity' and participates in proficiency tests organised by the IAEA.

RESULTS AND DISCUSSION

NORM activity concentrations in ashes

Results from the measurements of the NORM radionuclides in bottom ashes are shown in Table 1. ^{226}Ra was the main NORM radionuclide detected in ashes from the CPP. The ^{226}Ra activity concentrations reached 240 $\pm$ 8 Bq kg^{-1}. The detected radionuclides were distributed as follows: ^{226}Ra $>$ ^{210}Pb $>$ ^{40}K $>$ ^{232}Th $>$ ^{238}U (see Figure 2).

Results from this study were compared with the NORM ranges reported in the literature for fly and bottom ashes from other countries (Table 2). The values of ^{40}K and ^{238}U quantified in the bottom ashes from the CPP were lower than those reported in the literature for coal power plants, but the quantified values of ^{232}Th were similar to those reported. The ^{210}Pb activity concentrations were lower than those reported for Syria heavy fuel bottom ashes but were slightly higher than the values for bottom ashes from coal power plants. The ^{226}Ra activity concentrations were lower than the values for the coal bottom ashes from the Turkish Power Plant, but they were higher than the values for the rest of coal bottom ashes and slightly higher than the heavy fuel bottom ashes from the Syrian Power Plant.

Radium equivalent activity

A commonly used index, especially for radioactive raw materials and products, which is called radium equivalent activity, is the weighted summation of the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in studied materials[19]. The maximum value of 370 Bq kg^{-1} radium equivalent activity is regarded to be $<$1.5 mSv y^{-1} external dose that is considered to be safe for using NORM as an additive for building materials. The index was calculated from the following equation:

$$\mathrm{Ra_{eq}} = A_{\mathrm{Ra}} + 1.43 \times A_{\mathrm{Th}} + 0.076 \times A_{\mathrm{K}}$$

where A_{Ra}, A_{Th} and A_{K} are the mass activities of ^{226}Ra, ^{232}Th and ^{40}K, respectively. Radium equivalent activities of samples of bottom ashes from CPP had a mean value of 205 Bq kg^{-1} and ranged between 54 and 345 Bq kg^{-1}. As the maximum of this interval is still lower than the maximum reference radium equivalent activity, it is suggested that these ashes may be employed as an additive for building materials.

Activity concentration index (gamma index)

The activity concentration index or gamma index is used as a screening tool for identifying materials that might be of radiological concern[20]. The activity concentration index shall not exceed unity to assure the

Table 1. The activity concentrations of NORM radionuclides in the samples of bottom ashes.

Sample	Concentration, Bq kg^{-1} $\pm 2\sigma$				
	^{210}Pb	^{226}Ra	^{40}K	^{238}U	^{232}Th
I	61.8 $\pm$ 5.7	147.2 $\pm$ 6.1	58.6 $\pm$ 5.6	8.8 $\pm$ 3.7	69.3 $\pm$ 2.7
II	77.4 $\pm$ 6.1	240.2 $\pm$ 8.4	59.3 $\pm$ 7.1	$<$6.7	70.1 $\pm$ 3.1
III	62.6 $\pm$ 4.6	32.1 $\pm$ 1.1	55.9 $\pm$ 6.1	14.9 $\pm$ 3.6	13.6 $\pm$ 0.8
Mean	67.2	127.5	57.9	10.3	51.0
Min	61.8	32.1	34.1	$<$6.7	13.6
Max	77.4	240.2	59.3	14.9	70.1

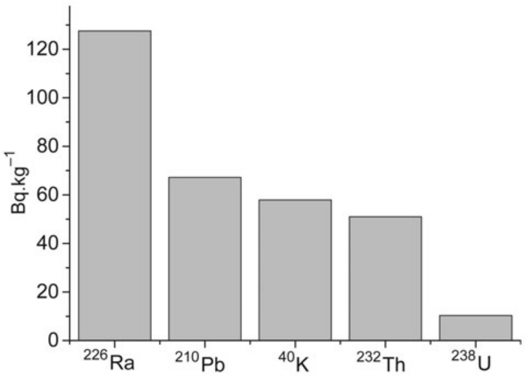

Figure 2. The activity concentrations of ^{226}Ra, ^{210}Pb, ^{40}K, ^{232}Th and ^{238}U in bottom ashes from fuel-oil Power Plant in Cienfuegos.

dose limit to general public (1 mSv). If the gamma index has a value of >6, then the material will have restricted use. In this study, the gamma index is calculated by the following formula recommended by the European Commission[20]:

$$I\gamma = 0.003 \times A_{\mathrm{Ra}} + 0.005 \times A_{\mathrm{Th}} + 0.0003 \times A_{\mathrm{K}}$$

where A_{Ra}, A_{Th} and A_{K} are the maxima of the mass activities (Bq kg^{-1}) determined for ^{226}Ra, ^{232}Th and ^{40}K, respectively. The gamma index of the samples from CPP calculated with this formula is $I\gamma$=1.1; this value is <6, so CPP bottom ashes have no restricted use from the radiological point of view.

Gamma absorbed dose rate and annual effective dose

The air-absorbed dose rate (nGy h^{-1}), at 1 m above the ground level, originated from ^{226}Ra, ^{232}Th and ^{40}K radionuclides in thermal power plant residues, is calculated with the following formula[21]:

$$D = 0.461 \times A_{\mathrm{Ra}} + 0.623 \times A_{\mathrm{Th}} + 0.0414 \times A_{\mathrm{K}}$$

where A_{Ra}, A_{Th} and A_{K} are the maxima of the mass activities (Bq kg^{-1}) determined for ^{226}Ra, ^{232}Th and ^{40}K, respectively.

The determined gamma absorbed dose rate from bottom ashes in CPP was D=157 nGy h^{-1}. According to the United Nations Scientific Committee on Effects of Atomic Radiation[22], the average air-absorbed dose rate, arising from the concerned radionuclides, at the earth's crust is 55 nGy h^{-1}, while for Cuba, a mean value of 34 nGy h^{-1} has been reported[19]. The value determined here is approximately three times higher than that of the earth's crust and five times higher than the mean dose rate for Cuba.

Table 2. The average concentrations of natural radionuclides in ashes from different coal- and heavy fuel-fired power plants.

Location/country	Power plant	Sample	Concentration, Bq kg^{-1}					Reference
			210Pb	226Ra	40K	238U	232Th	
Cienfuegos/Cuba	Heavy fuel	Bottom ash	67.2 (61.8–77.4)	127.5 (32.1–240.2)	57.9 (34.1–59.3)	10.3 (<6.7–14.9)	51.0 (13.6–70.1)	This work
India	Coal	Fly ash	—	77.7 (40.5–151.7)	373.8 (148–373.8	—	—	(6)
Langerlo/Belgium	Coal	Fly ash	—	450 (160–1100)	—	—	—	(5)
EC2 Lodz/Poland	Coal	Fly ash	112.4 (81–145.5)	85.6 (75–99.3)	608.4 (564.4–734.5)	116.4 (94.0–143.0)	66.4 (58.5–79.3)	(7)
		Bottom ash	26.1 (19.6–34.8)	55.7 (32.5–69.6)	432.2 (331.8–490.9)	58.0 (33.6–74.1)	46.3 (28.4–54.7)	(7)
EC3 Lodz/Poland	Coal	Fly ash	147.5 (43.5–264.3)	92.5 (54.2–117.2)	611.4 (448.5–727.4)	98 (169.9–130.5)	73.7 (47.5–91.5)	(7)
		Bottom ash	23.1 (11.1–39.6)	53.1 (36.1–70.9)	397.9 (307.1–518.1)	56.7 (37.6–72.7)	44.5 (32.5–54.9)	(7)
EC4 Lodz/Poland	Coal	Fly ash	182.9 (124–244.3)	104.2 (90.4–119.3)	720.8 (693.1–758)	155.8 (126.8–184.6)	84.0 (77.2–91.2)	(7)
		Bottom ash	59 (36–91.2)	77.8 (67.7–90.7)	570.8 (536–607.2)	82.8 (77.9–97.7)	66.9 (61.3–77.4)	(7)
Turkey	Coal	Fly ash	—	480–780	17–29	—	—	(8)
		Bottom ash	—	440–590	1–9	—	—	
Greece	Coal	Fly ash	275 (133–428)	366 (142–605)	297 (204–382)	—	—	(9)
Syria	Heavy Fuel	Fly ash	68–1083	<2.7–126		—	—	(24)
		Bottom ash	498–4023	77–135		—	—	

The annual effective dose (mSv) from bottom ashes is calculated by means of the following formula:

$$E = D \times 8766\,\mathrm{h} \times 0.7\,\mathrm{Sv\,Gy^{-1}}$$

where D is the air-absorbed dose rate (nGy h^{-1}).

According to the recommendations of the European Commission Report from 1999[20], the annual effective dose for adult people must be <1 mSv. The calculated annual effective dose from the samples of CPP bottom ashes was E=0.96 mSv; this value is slightly lower than the reference value 1 mSv and also lower than the value 2.5 mSv for residues of fired lignite reported from a thermal power plant in Turkey[23]. This result supports the possible use of the ashes from CPP as an additive for building materials without restrictions from the radiological protection point of view.

CONCLUSIONS

The activity concentrations of NORM radionuclides were measured in bottom ashes collected from a fuel-oil power plant in Cienfuegos, Cuba. Using the activity concentrations, the radium equivalent activity values, the gamma index, the air gamma absorbed dose rate and the annual effective dose from bottom ashes were calculated to allow comparisons with world average reference values and those given in the literature. The radium equivalent activities of the samples varied between 54 and 345 Bq kg^{-1}. The gamma index was lower than that of the reference value. The gamma absorbed dose rate was three times higher than that of the earth's crust average and five times higher than the mean dose rate for Cuba; however, the annual effective dose assessed was slightly lower than the annual effective dose limit for public, i.e. 1 mSv.

It is concluded that although some calculated parameters of CPP bottom ashes were found to be higher than some reference values, they are not dramatically enriched in comparison with other NORM given in the literature, and they may be used as an additive for building materials without restrictions from the radiological protection point of view. However, it would seem that a substantial amount of residues produced by the fuel-oil power plant could lead to a risk for workers of the related sector and members of public, who live near the waste or storage area, in the event that additional radiation doses were over the recommended limits. The radiation hazards can be reduced by the periodic control of the effective dose received by the occupationally exposed workers and by measures of the environmental radioactivity to check for the movements of probable radionuclides.

FUNDING

This research work was undertaken in the framework of the IAEA TC Project CUB/7/008 'Strengthening the National System for Analysis of the Risks and Vulnerability of Cuba's Coastal Zone through the Application of Nuclear and Isotopic Techniques'.

REFERENCES

1. International Atomic Energy Agency. *Extend of environmental contamination by naturally occurring radioactive materials (NORM) and technological options for mitigation*. Technical Report Series No. 419. IAEA (2003).
2. Eisenbud, M. and Petro, H. G. *Radioactivity in the atmospheric effluents of power plant that use fossil fuels.* Science **144**, 288–289 (1964).
3. Parami, V. K., Sahoo, S. K., Yonehara, H., Takeda, S. and Quirit, L. L. *Accurate determination of naturally occurring radionuclides in Philippine coal-fired thermal power plants using inductively coupled plasma mass spectrometry and spectroscopy.* Microchem. J. **95**(2), 181–185 (2010).
4. Papastefanou, C. *Escaping radioactivity from coal-fired power plants (CPPs) due to coal burning and the associated hazards: a review.* J. Environ. Radioact. **101**(3), 191–200 (2010).
5. Zeevaert, T., Sweeck, L. and Vanmarcke, H. *The radiological impact from airborne routine discharges of a modern coal-fired power plant*. J. Environ. Radioact. **85**(1), 1–22 (2006).
6. Mishra, U. C. *Environmental impact of coal industry and thermal power plants in India*. J. Environ. Radioact. **72**(1–2), 35–40 (2004).
7. Bem, H., Wieczorkowski, P. and Budzanowski, M. *Evaluation of technologically enhanced natural radiation near the coal-fired power plants in the Lodz region of Poland*. J. Environ. Radioact. **61**(2), 191–201 (2002).
8. Aycik, G. A. and Ercan, A. *Radioactivity measurements of coals and ashes from coalfired power plants in the southwestern part of Turkey.* J. Environ. Radioact. **35**(1), 23–35 (1997).
9. Papastefanou, C. *Radiological impact from atmospheric releases of ^{226}Ra from coal-fired power plants.* J. Environ. Radioact. **32**(1–2), 105–114 (1996).
10. Man-yin, T. and Leung, J. K. C. *Radiological impact of coal ash from the power plants in Hong Kong*. J. Environ. Radioact. **30**(1), 1–14 (1996).
11. Tolosa, I., Mesa-Albernas, M. and Alonso-Hernández, C. M. *Inputs and sources of hydrocarbons in sediments from Cienfuegos Bay, Cuba*. Mar. Pollut. Bull. **58**(11), 1624–1634 (2009).
12. Alonso-Hernández, C. M., Pérez-Santana, S., Muñoz-Caravaca, A., Díaz-Asencio, M., Gómez-Batista, M., Brunori, C., Morabito, R., Delfanti, R. and Papucci, C. *Historical trends in heavy metal pollution in the sediments of Cienfuegos Bay (Cuba), defined by ^{210}Pb and ^{137}Cs geochronology.* Nucleus **37**, 20–26 (2005).
13. Alonso-Hernández, C. M., Bernal-Castillo, J., Bolanos-Alvarez, Y., Gómez-Batista, M. and Diaz-Asencio, M. *Heavy metal content of bottom ashes from oil power plant and oil refinery in Cuba*. Fuel **90**, 2820–2823 (2011).
14. CITMA. Reglamento para el Manejo Integral de Desechos Peligrosos. 136. 2009.

15. Brigido-Flores, O., Barrera-Caballero, A., Montalvan-Estrada, C., Alonso-Hernández, C. M. and Tomas-Zerquera, J. *Exposición de la población cubana debido a la incorporación de Pb-210 y Po-210 a través de la dieta*. Nucleus **29**, 23 (2000).
16. Tomás Zerquera, J., Prendes Alonso, M. and Díaz Rizo, O. *Distribution of doses received by Cuban population due to environmental sources of radioactivity.* Radiat. Protect. Dosim. **123**(1), 118–123 (2007).
17. Tomás Zerquera, J., Prendes Alonso, M., Brigido-Flores, O. and Hernández Pérez, A. *Study on external exposure doses received by the Cuban population from environmental radiation sources.* Radiat. Protect. Dosim. **95**(1), 49–52 (2001).
18. Alonso-Hernández, C. M., Díaz-Asencio, M., Muñoz Caravaca, A., Suarez-Morell, E. and Ávila-Moreno, R. *^{137}Cs and ^{210}Po dose assessment from marine food in Cienfuegos Bay (Cuba)*. J. Environ. Radioact. **61**(2), 203–211 (2002).
19. Brígido Flores, O., Montalvan-Estrada, C., Rosa-Suárez, R., Tomás Zerquera, J. and Hernández Pérez, A. *Natural radionuclide content in building materials and gamma dose rate in dwellings in Cuba*. J. Environ. Radioact. **99**, 1834–1837 (2008).
20. EC. *Report on radiological protection principle concerning the natural radioactivity of building materials.* Radiation Protection 112 (Directorate-General Environment, Nuclear Safety and Civil Protection) Office of European Commission (1999).
21. UNSCEAR. *Sources and effects of ionizing radiation*. Annex A. Exposures from Natural Sources of Radiation. UNSCEAR (1993)
22. UNSCEAR. *Ionizing radiation: sources and biological effects.* UNSCEAR (2000).
23. Parmaksiz, A., Arikan, P., Vural, M., Yeltepe, E. and Tukenmez, I. *^{226}Ra, ^{232}Th and ^{40}K radionuclides enhancement rate and dose assessment for residues of lignite-fired thermal power plant in Turkey.* Radiat. Prot. Dosimet. **147**(4), 548–554 (2011).
24. Al Masri, M. S. and Haddad, K. *NORM emissions from heavy oil and natural gas fired power plants in Syria*. J. Environ. Radioact. **104**, 71–74 (2012).