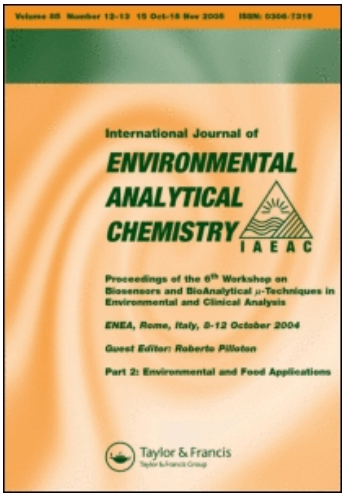

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Levels of radium in oily sludge

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Radium in oily sludge is unexplored, and this investigation could serve as a baseline study. We report elevated levels of ^{224}Ra and ^{226}Ra in 55 oily sludge samples that were collected from different sites and subjected to high-resolution gamma-ray measurement. The levels in our samples were more than five times higher than the estimated guidelines for soil and regular sludge. The period of investigation extended from January 2003 to January 2004. Both radium isotopes were identified by their characteristic gamma rays, whilst the short-lived one (^{224}Ra) was also identified by its half-life. Samples (1 kg dry weight) were counted for 12 hours, and activities between 150–1000 Bq/kg were recorded. The sludge is regarded as a useful building material and as an additive for soil enrichment, and remediation procedures are suggested to deplete the activity levels in the sludge prior to its use for these purposes.

Keywords: Radioactivity; ^{224}Ra; ^{226}Ra; Oily sludge; Gamma-ray spectroscopy

1. Introduction

The current method for the disposal of oily sludge is land farming [1]. The reuse of the sludge in asphalt paving mixtures was considered as an alternative [1]. The economic advantage of reusing the sludge as a substitute in asphalt is considerable. The component of the sludge in such mixtures could be as high as 50%, and the recycled product would be used to build roads, car parks, and shopping malls. The recycling of oily sludge, therefore, could result in immense savings in materials haulage and treatment costs and could help conserve natural resources. Radioactive contamination of the sludge would threaten the immediate biosphere, and from this perspective our study is significant [2–5].

Radium levels in soil and regular sludge can vary from location to location [6–8], but the average concentration is about 200 Bq/kg. A preliminary study showed that Ra levels in the oily sludge were relatively high, and our interest in this regard prompted the present study. ^{226}Ra and ^{224}Ra originate from the Uranium and Thorium series, respectively. Both are alpha- and gamma emitters, with respective half-lives of

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1600 years and 3.66 days. It is known [4–6, 9–15] that the accumulation of radium in the environment is a significant hazard. Exposure to elevated alpha- and gamma radiation creates serious biological problems [2–5], especially genetic damage, which usually arises from exposure to low doses over an extended period [4, 5]. Suitable protective measures should be put in place to shield the environment from such radiation [7, 13]. The thrust of our investigation, therefore, involved an assessment of the impact posed to our environment by the uses of oily sludge, and possible suggestions for remediation.

2. Experimental

2.1 *Sample collection and detection*

Fifty-five oily sludge samples were obtained from different sites in Oman. The collection period extended from Jan 2003 to Jan 2004. The samples were prepared for gamma-ray counting in standard Marinelli beakers. The detection system [16] consisted of a high-purity Ge detector (diameter: 59.0 mm, length: 74.2 mm) and standard electronics (EG & G Ortec, Oak Ridge, US). The detector resolution was 1.71 keV for the ^{60}Co 1.33 MeV gamma ray, and 0.807 keV for the ^{57}Co 122 keV line. The sample was shielded in a lead well to minimize the ambient background. Radioactive reference standards were used to calibrate the system and validate our methodology. In order to obtain statistically valid data the samples were counted overnight (12 h). The ambient background was monitored for an equivalent time. Prior to obtaining counts for each of the samples the system was checked for linearity. Specific procedures were used to identify ^{226}Ra and ^{224}Ra[16].

2.2 *Spectral analysis*

The recorded gamma-ray spectra were processed for radioisotope identification and specific activity. The software included a radionuclide directory, which was used to identify the detected radioisotopes [16]. Peaks in the spectra that were below the limit of detection (< 1 Bq/kg) were automatically omitted by the software. The most intense peaks were considered for computation of the total activities [17]. Some of the more prominent peaks are shown in figure 1, which represents a typical gamma ray spectrum.

3. Results and discussion

3.1 *Method validation*

The monitoring technique was validated in terms of repeatability and accuracy. A ^{60}Co reference standard and ^{208}Tl from a natural sample were counted six times, and these data, together with the means and relative standard deviations (RSD), appear in table 1. The RSDs were less than 2%, indicating that the reproducibility was acceptable. Apart from this, it was necessary to examine the accuracy to fully confirm the operational performance of the system. These measurements were obtained using standard reference sources (^{241}Am and ^{137}Cs), and their present activities were

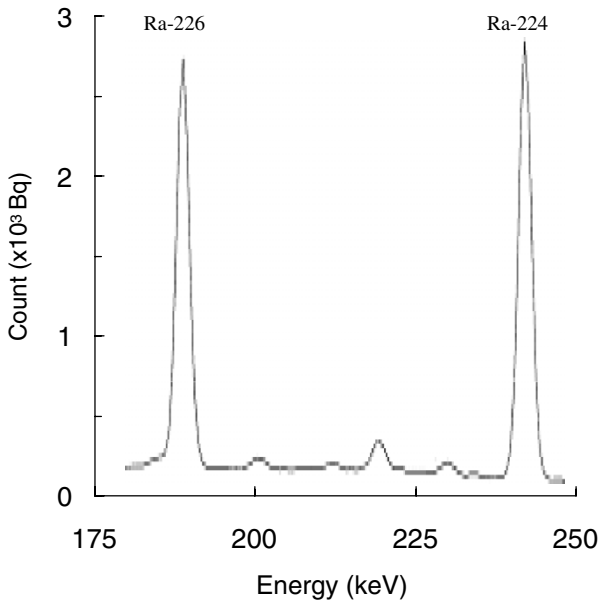

Figure 1. Gamma-spectrum of oily sludge showing typical assignments of ^{226}Ra and ^{2244}Ra. (Unassigned lines refer to other components of the general decay series).

Table 1. Repeatability measurements.

Measurement	Reference source	Natural source
	^{60}Co	^{208}Tl
1	1514	1167
2	1541	1153
3	1512	1187
4	1542	1151
5	1518	1158
6	1527	1120

Mean ± RSD: 1525 ± 0.85% 1156 ± 1.98%

measured against their corrected original certified activities [16]. In all cases the magnitude of the relative error did not exceed 2%, indicating that the accuracy attained was satisfactory.

3.2 *Presence of ^{226}Ra and ^{224}Ra*

^{226}Ra and ^{224}Ra originate naturally, but their intensities tend to increase with depth below the earth's surface [6]. Figure 2 represents the combined nuclear-energy level diagram of ^{224}Ra and ^{226}Ra and shows their appropriate decay by alpha emission to radon. Two methods [16] were used to establish the existence of ^{224}Ra. The first involved identification by detecting the energies of the characteristic gamma ray(s) [17] originating from its decay. This is evident from figure 1. The second method [18] was the 'half-life technique'. This is shown in figure 3, which is a plot of the natural logarithm of the activity against time. The slope yielded the appropriate decay

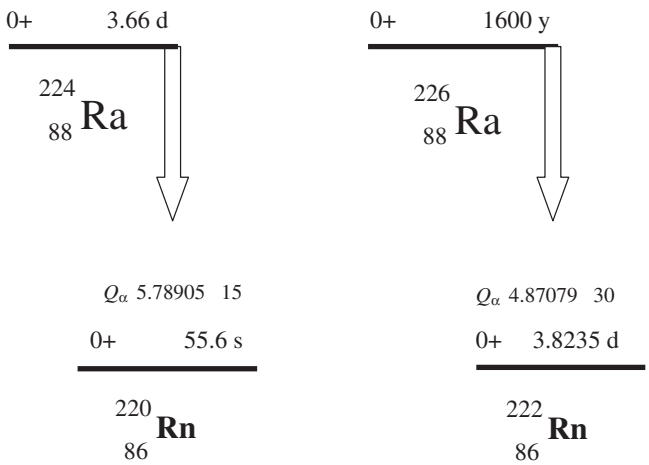

Figure 2. Nuclear-energy-level diagram showing decay schemes of ^{226}Ra and ^{224}Ra.

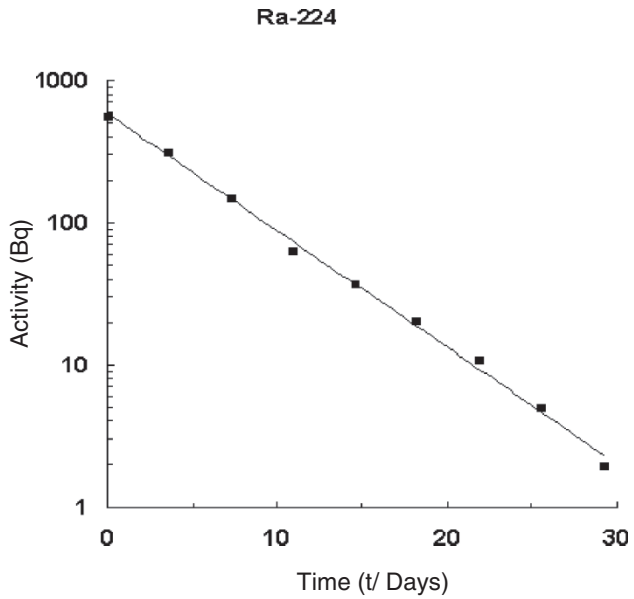

Figure 3. Activity *vs* time plot for computing the half-life of ^{224}Ra.

constant, thus confirming the presence of ^{224}Ra. In the case of ^{226}Ra it was not possible to establish its existence by the haf-life procedure, because of its long half-life of 1600 years. We therefore confirmed its existence only by its characteristic gamma rays [17] (figure 1). The 'room background count' showed minimal levels of these radionuclides.

3.3 *Elevated radioactivity*

The radionuclide of extreme significance in drinking water is radium [4], which is usually removed from water using the same chemical methods for calcium removal.

The maximum allowable contaminant level for radium in drinking water [4], as specified by the U.S. Environmental Protection Agency is, < 0.1 Bq/L. Therefore, elevated levels of radium activity in any medium should be noted with great concern, because such radioactivity could eventually contaminate water sources. The distribution of ^{226}Ra and ^{224}Ra from January 2003 to January 2004 appears in figures 4 and 5, respectively. The dispersion of the data in these figures was plotted in ascending order for convenience. Each data point represents the aggregrate of the relevant assignments associated with the most prominent gamma rays [17]. There is little information in the literature on the acceptable levels of ^{226}Ra and ^{224}Ra in oily sludge. However, the documented level [6] of such radioactivity in soil and regular sludge is around 200 Bq/kg. As can be seen from our results the levels in oily sludge were up to five times higher, and such activities could affect the environment when the sludge is used as a component in construction material or on sludge farms. We observe from figures 4 and 5 that over the one-year monitoring period the levels of radioactivity varied between 200–1000 Bq/kg (dry weight). This interval could be used as a possible guideline to other authors who wish to work in this area.

3.4 *Environmental impact and suggestions for remediation*

Use of radioactive sludge in our surroundings can be a cause for concern. First, there is the general contamination of the environment when the sludge is recycled in asphalt; and secondly, there is a possible contamination of water when the sludge is used on sludge farms. These points are considered in greater detail below.

(i) Some safety measures should be implemented to protect workers who handle and dispose of the sludge from exposure to the harmful alpha and gamma emissions. Even if the dose is low it is undesirable, and the sludge should be stored in

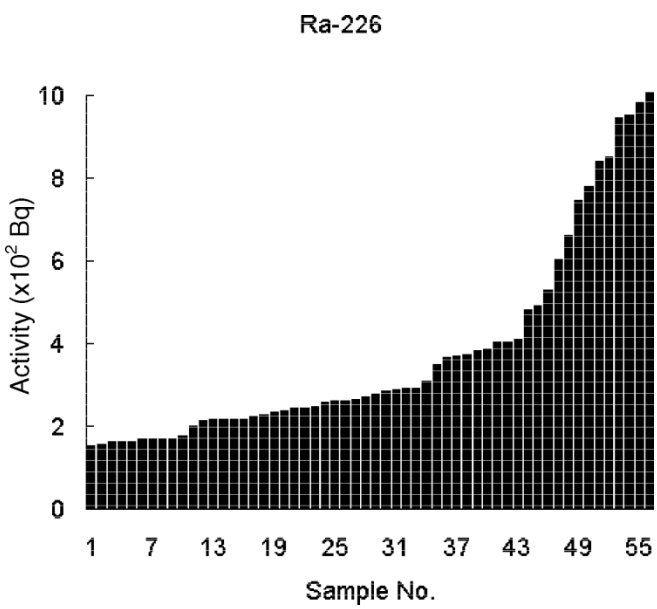

Figure 4. The distribution of ^{226}Ra over one year.

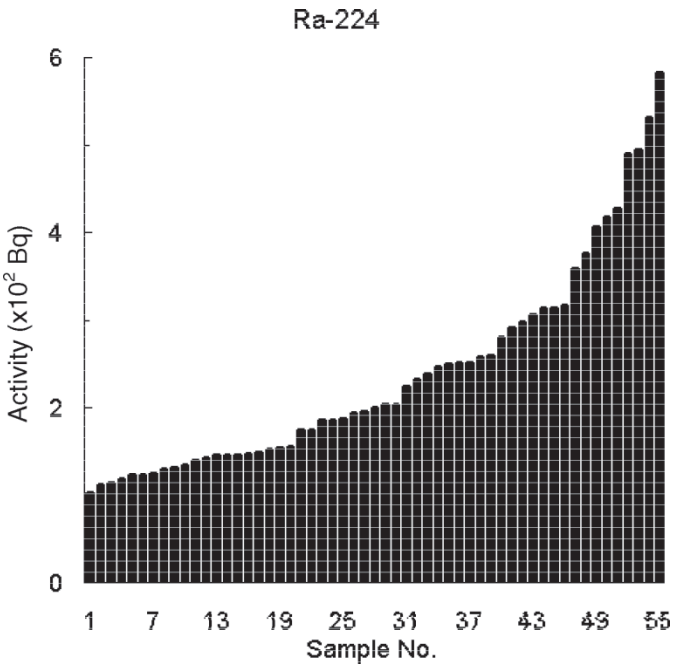

Figure 5. The distribution of ^{224}Ra over one year.

suitable lead-lined vessels that would adequately contain the radiation. On the other hand, these radionuclides could be leached from the sludge by rain water when the sludge is recycled in construction material. This can ultimately contaminate the general surroundings. One method of remediation would be to restrict levels of specific activity in the sludge during recycling. This can be done by dropping the proportion of sludge in asphalt to about 20%.

(ii) The effect of using radioactive sludge on farms needs to be considered in the light of possible contamination of plants and organisms found in these soils. This contamination can be spread by birds that feed on organisms found in the radioactive soil. The bioaccumulation of radioactivity in the food chain is, therefore, a potential hazard [19, 20] and merits further investigation. In addition, possible radioactive contamination of water supplies (such as streams and borehole sources) from agricultural run-off [19, 20] should be considered. The acceptable level of radium in potable water [4] is <0.1 Bq/L, so such contamination can pose a significant threat. Therefore, ceasing to use sludge on land farms can curb these particular problems.

4. Conclusions

The suggested remediation procedures could be implemented as a possible means to reduce the radioactivity in oily sludge to make it suitable for use as a construction material. For recycling of the oily sludge we propose a reduction in asphalt to 20%, but it would be in the interest of the environment to reduce this fraction even further. Possible contamination of the soil and water table would threaten the

immediate biosphere, and the only prevention to contamination is to stop using sludge on farms. A useful extension to this work would be a study of ^{223}Ra and ^{228}Ra.

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