SPECIFIC ACTIVITY IN SIZE-FRACTIONATED ALUM-SHALES. EFFECTS OF PARTICLE SIZE.

MASTER THESIS, 30 HP

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Abstract

The activity per unit mass of different radionuclides in size-fractionated samples has been shown to be strongly dependent on the size of the particles in the sample. Pulse height $\gamma$-ray spectrums from measurements of radionuclide content of $^{214}$Bi, $^{228}$Ac and $^{40}$K in samples of different particle size fractions prepared from Alum-shale rocks, collected at locations Andrarum and Billingen in Sweden, were reanalyzed and used as input data for a mathematical program, GraphPad Prism. The purpose with this study was to fit sample data to a theoretical equation of either type “$Y=P_1+P_2/X$” (two parameter adaptation) or “$Y=P_1+P_2/X+P_3/X^2$” (three parameter adaptation), in order to find the relation between $Y$, the sample activity concentration of a radionuclide and $X$, the particle size diameter by best fit values of the parameters $P_1$, $P_2$ and $P_3$. Results showed that data was insufficient in order to make a certain determination of these parameters, mainly due to the small amount of sample material in the finer particle size fractions and not enough number of particle size fractions.
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1 Introduction

Knowledge of the distribution of natural radionuclides in the environment plays an important role in geo-scientific research as well as in health physics. A lot of people are daily exposed to natural environmental radiation, for instance by working with the coal fuel cycle (mining, cleaning, transportation, combustion or conversion) or wastes from other fossil fuels (oil/peat) at power plants. The mining industry of rocks is also a source to increased human exposure of radioactivity. Determination of the amount of naturally occurring or fallout radionuclides in the ground is often based on measurements of either the activity per unit mass or the activity per unit area of the ground. These estimations may then be used for calculations of ambient dose rate by using dose constants given in the literature. The measurements are predominantly performed by calibrated field gamma spectroscopy \textit{(in situ)} measurements or by soil sampling and subsequent laboratory analysis with gamma-spectroscopy systems. Prior to the gamma-spectroscopic analysis the sample is often dried, homogenised and sieved through a 2 mm mesh. A subsample is then taken and placed in a small container for measurement with a high purity germanium (HPGe) detector. This subsample will then be composed of particles with a certain (mostly unknown) distribution in size, although sieving can be used to set an upper limit for the particle size.

The activity per unit mass of different radionuclides in size-fractionated samples has been shown to be strongly dependent on the size of the particles in the sample. Several measurements of gamma radiation from soil samples [1]; [2] and on fly-ashes in the µm-size region from coal-fired [3]; [4]; [5]; [6] as well as peat- and oil-fired [7] power plants have shown that the activity concentration of uranium- and thorium-series elements increases when the particle size decreases.

The above reported results thus suggest that certain elements are enriched on smaller particles in the samples and this enrichment seems to be independent of the origin of the sample. The aim of this study is to determine the activity concentration of naturally occurring radionuclides from the uranium and thorium series in alum-shales, which has a high abundance of U- and Th-series elements, and to find a simple model for the enrichment on the smaller-sized particles.
2 Theory

2.1 Naturally occurring radionuclides showing enrichment on smaller sized particles

The radionuclides investigated in this report was the concentrations of $^{214}\text{Bi}$ from the decay chain of $^{238}\text{U}$, $^{228}\text{Ac}$ from the decay chain of $^{232}\text{Th}$, and $^{40}\text{K}$ in the collected rock samples. The activity of $^{214}\text{Bi}$ was determined by using the measured pulse height analyzer photopeak from 609-keV $\gamma$-rays of $^{214}\text{Bi}$. $^{228}\text{Ac}$ content was given by the 911 keV and $^{40}\text{K}$ by the 1460 keV photopeak. All measurements were made prior to the present investigation (this work). The reasons for the choice of $^{214}\text{Bi}$ and $^{228}\text{Ac}$ were that both are located after Ra in the decay chains, but also due to their high $\gamma$-ray energies. This reduces the influences from self-attenuation in the samples (See 2.2.4). During the measurements each sample was placed in a 5 ml plastic container, which was sealed and left for at least two weeks to allow the U- and Th-series elements to reach equilibrium. $^{40}\text{K}$ was chosen due to its high $\gamma$-ray energy of 1460 keV and for comparison with earlier measurements done [1]; [8]; [9]. $^{40}\text{K}$ is also used as a normalisation nuclide when coal ashes are investigated, because its concentration remains more or less the same after combustion of the fuel. The enrichment factor ($EF$) is defined as the ratio of the concentration of a radionuclide ($X$) and $^{40}\text{K}$ in the sample divided by the corresponding ratio in the input coal.

$$EF = \frac{\frac{X_{\text{sample}}}{^{40}\text{K}_{\text{sample}}}}{\frac{X_{\text{coal}}}{^{40}\text{K}_{\text{coal}}}}$$

This effectively normalises the apparent enrichment of other nuclides resulting from loss of carbon during the combustion process [6].

2.2 Particle size dependent factors affecting the specific activity released from soil, rock or ash.

2.2.1 Emanation, recoil and diffusion

A lot of work has been spent in order to explain the reason why the activity concentration of uranium- and thorium-series elements increases when the particle size decreases. Most reports treats the behaviour of the $^{222}\text{Rn}$ released (emanation) from fly-ash particles, the waste product from fossil fuel power plants [7]; [6]; [5]; [3] and [4]. $^{226}\text{Ra}$ decays to $^{222}\text{Rn}$ which is a gas at
ambient temperatures. Once Rn has been formed, there is some probability it will diffuse out of or “emanate from” the material which contains the Ra parent. The fractional amount of Rn lost from the parent-containing material is called the emanation coefficient or emanating power [10], [11]. These reports all show that the emanation coefficient increases as the fly-ash particle size decreases. A couple of hypotheses are reported in order to explain this behaviour. One logical mechanism which would lead to enhanced emanation coefficients relates to the diffusion of $^{222}$Rn. Regardless of the location of the nucleus after it expends its kinetic energy, it must be able to diffuse into “sampleable” gas space before decay. The longer and/or more tortuous the diffusion course, the higher the probability of decay will be. Nuclei which decay before reaching this “sampleable” gas space cannot, in practical sense, be considered emanation. A qualitative explanation for the particle size effect is then based simply on the proportionality between particle size and length of diffusion course [4]. Other reports suggest a combination of recoil and diffusion. The proposed mechanism of $^{222}$Rn emanation is liberation with recoil from the individual grain in which $^{222}$Rn is formed. The $^{222}$Rn atoms generated within recoil range of the particle surface will be able to recoil directly outside the particle [3]. However, this effect can be achieved by a small fraction of $^{222}$Rn atoms since the recoil range is only about 0,04 µm in mineral grains [12]. The $^{222}$Rn atoms which recoil to positions within the mineral grains will diffuse by volume diffusion to the grain boundaries [3].

2.2.2 Surface adsorption

When particle size is comparatively large the amount of nuclide adsorbed on the surface will be very small compared with the nuclide originally contained in the soil because the surface area per unit mass of soil is comparatively small. For fine particles the surface area per unit mass is high. The amount of nuclide adsorbed on the surface is significant when compared to the amount originally contained in the soil. One report suggests 150 µm as a possible extreme point [1]. Some differences can be observed, depending on which type of samples that are investigated. When fly-ash samples are examined it can be shown that the concentration of U, Th and their radioactive decay products is much higher than in the source fuel (coal, peat, oil). This can be explained as a result from the combustion process. In combustion, both radioactive and stable elements and their oxides, which are volatile at furnace temperatures, are partly or completely evaporated from fly-ash particles. When the flue gases are cooled in the boiler, these elements condense on fly-ash particles. As a result, volatile elements are enriched on the particle surfaces [13]. Because of their high surface-to-mass-ratios, the
smallest or most irregular particles collect the highest concentrations of volatile elements [14]. The phenomenon has been explained in coal combustion [15], and verified in peat combustion [16]. Samples from different power plants show differences in the spectrum of adsorbed nuclides. One explanation is the differences in combustion temperatures between coal, peat and oil power plants. Nuclides are volatile at different temperatures, and as a result, will be enriched in different amounts on fly-ash particles when condensed as the gas stream cools.

When samples of soil originating from rock are examined other effects can be registered. Soil from rock is the result from long time weathering, and the concentration of nuclides in soil depends on many factors. Mineral composition is one of them, and lowest concentrations of $^{226}$Ra, $^{228}$Ra and $^{40}$K are found in soil samples composed mainly of amphibole, olivine and chlorite, the content in ultrabasic rocks. The highest values for these three nuclides are found in the soil samples composed mainly of microline, albite and biotite. This suggests that these soil samples may have originated mainly from the weathering of granite [9]. Samples can be measured with x-ray powder diffraction analysis in order to evaluate the mineral compositon. Another important factor is the environmental conditions. If the environmental is acid kaolin minerals can be formed by alteration of alkali feldspar and the K and Na ions released stabilize the silica in solution. The $^{40}$K concentrations from this type of soil therefore decrease as the particle size decreases. Montmorillonite, a solid type of rock, on the other hand seems to form most readily in a neutral or slightly alkaline environment and absorbs K ions selectively [17]. The $^{40}$K concentrations from those samples show no particle size dependence. The content of U and Th-series nuclides in all of the above mineral compositions shows an increment with surface area, but the ratio between different nuclides varies. An explanation for this is that during the weathering process some of the uranium and radium leaches as soluble ions or soluble complexes, while thorium and lead are less mobile [1].

The advantage of collecting rock samples and preparing different size fraction samples by crushing and sieving is that the elements are already in the matrix, and the weathering process has no influence on the result.
2.2.3 Water content

Measurement of radon and thoron (\(^{220}\text{Rn}\)) emanating coefficient as function of water contents in soil samples shows that the emanating coefficient is a little larger in slightly moist samples than in dry [18]; [19]. Wahl and Bonner (1958) indicate that the decreased emanation coefficient with dehydration is mainly a result of the increase in adsorption coefficient with dehydration. Test performed also shows that the thoron exhalation rate [Bq\(\text{cm}^{-2}\text{s}^{-1}\)] is greater when the soil is slightly moist than when it is completely dry. This result can be explained by the decrease in emanation coefficient of the sample for thoron, as earlier described. A possible explanation is that water that is not absorbed by particles will reduce the diffusion coefficient, and as a result, the exhalation rate. The capacity of water absorption decreases with increased particle size. As a result, the maximum exhalation rate occurs for less water content in smaller soil particles than in larger ones [18].

Tests performed on coal ash samples also shows that Rn emanation coefficient increases as a function of moisture content up to a point where it starts to decrease. This behaviour is more pronounced with smaller size particles, so it may represent the effect of an interaction between particle size and moisture on emanation [4]. This decrease could also be attributable to interstitial water and the lower diffusion coefficient of Rn in water than in air [11]. Thus it is very important that all samples in a test are all dehydrated in the same manner, and that the moisture content is documented.

2.2.4 Self-attenuation

Tests made with a set of different ore and soil sample matrices with the same densities and measurement geometry have shown that the \(\gamma\)-ray transmissions, \(I/I_0\), (where \(I\) denotes the intensity of photons with energy \(E\) after attenuation and \(I_0\) the intensity of photons of the same energy without attenuation) for nuclide energies between 661.6 and 1332.5 keV varies between 0.89-0.91. For energies around 100 keV the \(\gamma\)-ray transmission is about 0.75 [20]. Since all nuclide energies used in this report are above 600 keV no compensation for self-attenuation is made.
3 Material and methods

3.1 Material

3.1.1 Sample preparation
The Alum-shales in this work were sampled from two regions in Sweden: Andrarum and Billingen. These two regions are separated by at least 400 km and the shale formations are not interconnected. The samples from Andrarum was first measured at Lund, and a new preparation of this material was made some years later in Gothenburg.

The shale samples from Andrarum were crushed and sieved, separated into grain-size fractions of <63 µm, 63-125 µm, 125-250 µm and 250-500 µm. The distribution of particle size in each fraction is unknown and the particle sizes were therefore approximated with the midpoint of each interval: 94 µm, 187.5 µm and 375 µm. The fraction with particle sizes less than 63 µm was further fractionated by sedimentation in water. The settling times in the sedimentation process was chosen to give particles-sizes in the intervals <2 µm, 2-20 µm, 20-40 µm and 40-60 µm. The grain-size distribution in these fractions was measured and the particle size in the first three fractions was taken to be the median according to the grain-size analysis: 17 µm, 23 µm and 36 µm. For the first fraction the grain-size 2 µm was used.

X-ray analysis on the <2 µm fraction showed that the clay minerals were composed of quartz and Al-rich illite. These were the only well-crystallized phases found in this sample. A sample of the alum-shale from the fraction 20-40 µm was also oxidized with H₂O₂ before measurement to remove the organic material, leaving only the pure clay minerals. X-ray diffraction analysis on this sample suggested that the illite was not affected by the oxidation.

The sample from Billingen was crushed and sieved in fractions of <63 µm, 63-125 µm, 125-250 µm, 250-500 µm 500-1000 µm. As with the Andrarum sample the distribution of particle size in each fraction was approximated with the midpoint of each interval: 94 µm, 187,5 µm, 375 µm and 750 µm. The fraction with particle sizes less than 63 µm was again further fractionated by sedimentation in water to give particles-sizes in the intervals <2 µm, 2-6 µm, 6-20 µm and 20-60 µm. No measurements of the grain-size distribution were made on these.
samples and the distribution is again approximated by the midpoint of each interval: 4 µm, 13 µm and 40 µm. For the first fraction the grain-size 2 µm was used.

### 3.1.2 Radioactivity measurements

Each sample was placed in a 5 ml plastic container, which was sealed and left for at least two weeks to allow the U- and Th-series elements to reach equilibrium. The samples were then subjected to γ-ray spectrometry with a low-background Ge(Li)-detector connected to a 4096-channel pulse height analyzer. The detector was energy calibrated using standard reference sources and enclosed in a 10 cm thick lead shield. No efficiency calibration was made because the samples were only compared with each other in the analysis. In this work the above measured spectra were reanalyzed, and the $^{214}$Bi, $^{228}$Ac and $^{40}$K contents were determined from the areas of the photopeaks due to 609 keV γ-rays of $^{214}$Bi, 911 keV γ-rays of $^{228}$Ac and 1460 keV γ-rays of $^{40}$K respectively. To get the net counts in each photopeak from the corresponding channels in the pulse height analyzer the measured background spectrum was subtracted. The specific activity [cps/g] from each nuclide was calculated by dividing the net counts with the sample weight [g] and total measurement time [s]. The measurement error was calculated as plus minus one standard deviation (SD) of the mean.

### 3.2 Methods

#### 3.2.1 Mathematical models for the enrichment of radionuclides on smaller-sized particle

A simple model for the relation between the concentration of an element and particle size for fly ash was proposed by Davidson et al (1974) [21], where it is assumed that the element is uniformly distributed on the surface of the particle, as well as in the volume of the particle. The concentration $C_A$ may then be described by

$$C_A = C_V + \frac{C_S S}{\rho V}$$  \hspace{1cm} (1)

where

- $C_A$ = total activity concentration of the element (µg/g)
- $C_V$ = concentration of the element in the volume of the particle (µg/g)
- $C_S$ = surface concentration of the element (µg/cm²)
- $V$ = particle volume (cm³)
- $S$ = particle surface area (cm²)
ρ = particle density (g/cm³)

Assuming spherical particles with diameter $d$ and averaging over all particles in a sample, the above expression can be written

$$\bar{C}_s = \bar{C}_v + \frac{6\bar{C}_s}{\rho} \cdot \frac{1}{d}$$

(2)

It is seen that the concentration then follows a simple relation of the form

$$C_s = p + \frac{q}{d}$$

(3)

where $p$ and $q$ are parameters which may be determined by fitting the relation to experimental data. An expression of the same form is also proposed by Megumi and Mamuro (1974) [18] who measured the content of different radionuclides in soil samples.

The relation in equation (3) is also valid if small particles (e.g., clay mineral grains) together with some binding material cluster together to form larger particles. Under the assumption that the mineral grains have a surface as well as a volume distribution of an element (e.g., a radionuclide), the total activity, $A$, of the radionuclide in the larger particle is then proportional to the total grain area and total grain volume in the particle

$$A = k_1S_{grain} + k_2V_{grain}$$

(4)

where $k_1$ and $k_2$ are constants.

If the grains are of the same size the total grain area is proportional $d^2$ and equation (4) then becomes

$$A = k_3d^2 + k_2V_{grain}$$

(5)

where $k_3$ is a constant and $d$ is the particle diameter. The total grain volume is proportional to the particle volume, which yields

$$A = k_3d^2 + k_4d^3$$

(6)

where $k_4$ is a constant.

If some amount of the radionuclide is adsorbed on the surface of the particle from an outside source, an additional term describing this surface deposition and proportional to $d^2$ should be added to equation (6). The total activity can now be written

$$A = k_4d^3 + k_5d^2$$

(7)
The activity concentration, \( C_A \), is defined as the activity per mass unit and since the mass is directly proportional to the volume of the particle and hence to \( d^3 \), \( C_A \) is given by

\[
C_A = \alpha + \frac{\beta}{d}
\]  

(8)

an expression of the same general appearance as equation (3).

If we compare equation (3) and (8) and set \( p=\alpha=\alpha_1 \) and \( q=\beta=\beta_2 \) we get a general expression for a two parameter adaptation between element concentration and particle size:

\[
C_A = P_1 + \frac{P_2}{d}
\]  

(9)

Another hypothesis, more complicated to explain physically, is a three parameter adaptation. If starting with equation (1) a third term, \( C_d = \text{concentration gradient of the element (µg/cm)} \), can be added and we get:

\[
C_A = C_v + \frac{C_s \cdot S}{\rho V} + \frac{C_d \cdot d}{\rho V}
\]  

(10)

Again assuming spherical particles with diameter \( d \) and averaging over all particles in a sample, the above expression can be written:

\[
\bar{C}_A = \bar{C}_v + \frac{\bar{C}_s \cdot S}{\rho} \cdot \frac{1}{d} + \frac{6\bar{C}_d}{\pi \rho} \cdot \frac{1}{d^2}
\]  

(11)

and the concentration then follows the simple relation of the form

\[
C_A = p + \frac{q}{d} + \frac{s}{d^2}
\]  

(12)

Rewritten in the same form as equation (9) it gives:

\[
C_A = P_1 + \frac{P_2}{d} + \frac{P_3}{d^2}
\]  

(13)

One possible explanation for this third term can be related to the position of the particles relative to each other with varying particle size, which affects the sample packing and intermediate space, which in turn influence the diffusion and exhalation.

3.2.2 Calculation of parameters in mathematical models using nonlinear regression

In order to fit the parameters in equation (9) and (13) to a XY-graph by using the data from the measurements of the Alum-shales nonlinear regression (curve fit) was used. Nonlinear regression finds the values of those parameters that generate the curve that comes closest to the measured data. Those best-fit values of the parameters are the best possible estimates of
the values of those parameters. To perform this nonlinear regression a comprehensive and powerful program, GraphPad Prism (GraphPad Software, 2006) was used. By using an XY-graph all activity concentrations, \( C_t \text{ [cps/g]} = "Y" \) was computed as a function of particle size diameter, \( d \text{ [µm]} = "X" \). All Y values were normalised to the highest value of activity concentration for each nuclide energy measured, giving the limit of \( Y \leq 1 \). The error from each measurement was computed as plus minus one standard deviation (SD) of the number of counts, assuming Poisson statistics, also normalised to the highest value of the measured nuclide. An option, which was utilized in the program, made it possible to give each Y-value entered in the program a weight of \( 1/(SD)^2 \). Non-linear regression was performed on data from Andrarum and Billingen as well as on data collected from the literature.

4 Results

4.1 Measured activity concentrations in Alum-shales

Table 1, 2 and 3 shows the activity concentration versus sample fraction size prepared from the collected Alum-shales at Andrarum and Billingen. The measured activity concentrations from each nuclide are normalised to the highest value detected.

<table>
<thead>
<tr>
<th>Sample weight [g]</th>
<th>Fraction size (Ø) [µm]</th>
<th>214Bi (609 keV) Activity concentration [c/g·s] ( \times 10^{-3} )</th>
<th>Normalised Count rate</th>
<th>Activity concentration [c/g·s] ( \times 10^{-3} )</th>
<th>Normalised Count rate</th>
<th>Activity concentration [c/g·s] ( \times 10^{-3} )</th>
<th>Normalised Count rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.8</td>
<td>&lt;63</td>
<td>23.8±0.29</td>
<td>1±0.0122</td>
<td>0.673±0.091</td>
<td>1±0.1352</td>
<td>1.96±0.102</td>
<td>1±0.0520</td>
</tr>
<tr>
<td>5.1</td>
<td>63-125</td>
<td>14.2±0.19</td>
<td>0.597±0.0080</td>
<td>0.446±0.063</td>
<td>0.663±0.0936</td>
<td>1.64±0.078</td>
<td>0.837±0.0398</td>
</tr>
<tr>
<td>5.0</td>
<td>125-250</td>
<td>14.3±0.20</td>
<td>0.601±0.0084</td>
<td>0.624±0.065</td>
<td>0.927±0.0966</td>
<td>1.70±0.079</td>
<td>0.867±0.0403</td>
</tr>
<tr>
<td>5.3</td>
<td>250-500</td>
<td>13.0±0.18</td>
<td>0.546±0.0076</td>
<td>0.572±0.063</td>
<td>0.850±0.0936</td>
<td>1.63±0.076</td>
<td>0.832±0.0388</td>
</tr>
<tr>
<td>5.2</td>
<td>500-1000</td>
<td>14.3±0.19</td>
<td>0.601±0.0080</td>
<td>0.520±0.062</td>
<td>0.773±0.0921</td>
<td>1.80±0.079</td>
<td>0.918±0.0403</td>
</tr>
</tbody>
</table>
Table 2. Activity concentration versus sample fraction size from samples collected at Andrarum and measured in Gothenburg.

<table>
<thead>
<tr>
<th>Sample weight [g]</th>
<th>Fraction size (Ø) [µm]</th>
<th>Activity concentration [c/g·s]*10^3</th>
<th>Normalised Count rate</th>
<th>Activity concentration [c/g·s]*10^3</th>
<th>Normalised Count rate</th>
<th>Activity concentration [c/g·s]*10^3</th>
<th>Normalised Count rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.01</td>
<td>&lt;2</td>
<td>9.62±0.23</td>
<td>0.995±0.0238</td>
<td>0.285±0.069</td>
<td>0.869±0.2104</td>
<td>3.54±0.16</td>
<td>1±0.0452</td>
</tr>
<tr>
<td>3.44</td>
<td>2-20</td>
<td>9.67±0.12</td>
<td>1±0.0124</td>
<td>0.328±0.032</td>
<td>1±0.0976</td>
<td>2.52±0.07</td>
<td>0.712±0.0198</td>
</tr>
<tr>
<td>4.67</td>
<td>20-40</td>
<td>7.39±0.09</td>
<td>0.764±0.0093</td>
<td>0.271±0.026</td>
<td>0.826±0.0793</td>
<td>2.10±0.05</td>
<td>0.593±0.0141</td>
</tr>
<tr>
<td>4.76</td>
<td>40-63</td>
<td>6.76±0.09</td>
<td>0.699±0.0093</td>
<td>0.299±0.025</td>
<td>0.912±0.0762</td>
<td>2.26±0.05</td>
<td>0.638±0.0141</td>
</tr>
<tr>
<td>4.74</td>
<td>63-125</td>
<td>5.68±0.08</td>
<td>0.587±0.0083</td>
<td>0.250±0.023</td>
<td>0.762±0.0701</td>
<td>2.30±0.05</td>
<td>0.650±0.0141</td>
</tr>
<tr>
<td>5.25</td>
<td>125-250</td>
<td>5.72±0.06</td>
<td>0.592±0.0062</td>
<td>0.322±0.021</td>
<td>0.982±0.0640</td>
<td>2.25±0.04</td>
<td>0.636±0.0113</td>
</tr>
<tr>
<td>5.62</td>
<td>250-500</td>
<td>5.72±0.07</td>
<td>0.592±0.0072</td>
<td>0.277±0.021</td>
<td>0.845±0.0640</td>
<td>2.20±0.05</td>
<td>0.621±0.0141</td>
</tr>
</tbody>
</table>

*) Sample counts not significantly above background

Table 3. Activity concentration versus sample fraction size from samples collected at Billingen and measured in Gothenburg.

<table>
<thead>
<tr>
<th>Sample weight [g]</th>
<th>Fraction size (Ø) [µm]</th>
<th>Activity concentration [c/g·s]*10^3</th>
<th>Normalised Count rate</th>
<th>Activity concentration [c/g·s]*10^3</th>
<th>Normalised Count rate</th>
<th>Activity concentration [c/g·s]*10^3</th>
<th>Normalised Count rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0792</td>
<td>&lt;2</td>
<td>44.1±4.1</td>
<td>1±0.0930</td>
<td>*</td>
<td>*</td>
<td>3.07±2.75</td>
<td>1±0.8958</td>
</tr>
<tr>
<td>0.536</td>
<td>2-6</td>
<td>27.7±0.89</td>
<td>0.628±0.0202</td>
<td>*</td>
<td>*</td>
<td>2.18±0.43</td>
<td>0.710±0.1401</td>
</tr>
<tr>
<td>0.925</td>
<td>6-20</td>
<td>23.1±0.56</td>
<td>0.523±0.0127</td>
<td>*</td>
<td>*</td>
<td>2.12±0.28</td>
<td>0.691±0.0912</td>
</tr>
<tr>
<td>0.622</td>
<td>20-60</td>
<td>25.6±0.49</td>
<td>0.580±0.0111</td>
<td>0.22±0.16</td>
<td>1±0.7273</td>
<td>2.36±0.27</td>
<td>0.769±0.0879</td>
</tr>
<tr>
<td>5.045</td>
<td>63-125</td>
<td>21.5±0.24</td>
<td>0.487±0.0054</td>
<td>0.058±0.043</td>
<td>0.263±0.1954</td>
<td>1.69±0.08</td>
<td>0.550±0.0261</td>
</tr>
<tr>
<td>5.02</td>
<td>125-250</td>
<td>22.2±0.23</td>
<td>0.503±0.0052</td>
<td>0.046±0.041</td>
<td>0.209±0.1864</td>
<td>1.89±0.078</td>
<td>0.616±0.0254</td>
</tr>
<tr>
<td>5.224</td>
<td>250-500</td>
<td>22.1±0.18</td>
<td>0.501±0.0041</td>
<td>0.081±0.033</td>
<td>0.368±0.150</td>
<td>1.86±0.062</td>
<td>0.606±0.0202</td>
</tr>
<tr>
<td>5.08</td>
<td>500-1000</td>
<td>24.1±0.14</td>
<td>0.546±0.0032</td>
<td>0.12±0.025</td>
<td>0.545±0.1136</td>
<td>1.99±0.049</td>
<td>0.648±0.0160</td>
</tr>
</tbody>
</table>

*) Sample counts not significantly above background

4.2 Nonlinear regression (curve fitting) to measured Alum-shale data

4.2.1 Two parameter adaptation of 214Bi (609 keV)
The graphs in figure 3-5 show the result if GraphPad Prism fits the measured Alum-shale data of $^{214}\text{Bi}$ (609 keV) to the two parameter equation (9).

**Fig 3.** Best fit curve “Y=P1+P2/X” using nonlinear regression curve fit on Alum-shale samples collected at Andrarum and measured at Lund.

**Fig 4.** Best fit curve “Y=P1+P2/X” using nonlinear regression curve fit on Alum-shale samples collected at Andrarum and measured in Gothenburg.
Fig 5. Best fit curve “Y=P1+P2/X” using nonlinear regression curve fit on Alum-shale samples collected at Billingen and measured in Gothenburg

4.2.2 Two parameter adaptation of $^{214}\text{Bi}$ (609 keV), comparison with reference samples.

Table 4. Specification of nonlinear regression equation fit “Y=P1+P2/X” using GraphPad Prism on measured data from sample collected at Andrarum and Billingen and, as comparison, on data collected from other test reports worldwide

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sample type</th>
<th>Number of fractions</th>
<th>P1</th>
<th>Std. error</th>
<th>P2</th>
<th>Std. error</th>
<th>R² (un-weighted)</th>
<th>Weighted Sum of Squares (1/SD²)</th>
<th>Absolute Sum of Squares</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andrarum (Lund) Soil/Rock</td>
<td>5</td>
<td>0.52</td>
<td>0.036</td>
<td>13.60</td>
<td>3.219</td>
<td>0.9176</td>
<td>155.7</td>
<td>0.0115</td>
<td></td>
</tr>
<tr>
<td>Andrarum (Gbg) Soil/Rock</td>
<td>7</td>
<td>0.64</td>
<td>0.047</td>
<td>1.06</td>
<td>0.643</td>
<td>0.3237</td>
<td>893.1</td>
<td>0.1365</td>
<td></td>
</tr>
<tr>
<td>Billingen (Gbg) Soil/Rock</td>
<td>8</td>
<td>0.52</td>
<td>0.012</td>
<td>0.42</td>
<td>0.380</td>
<td>0.6053</td>
<td>182.0</td>
<td>0.0797</td>
<td></td>
</tr>
<tr>
<td>Fly-ash [4]</td>
<td>4</td>
<td>0.71</td>
<td>0.041</td>
<td>22.62</td>
<td>5.136</td>
<td>0.8597</td>
<td>6.276</td>
<td>0.0069</td>
<td></td>
</tr>
<tr>
<td>Fly-ash [6]</td>
<td>4</td>
<td>0.51</td>
<td>0.045</td>
<td>1.29</td>
<td>0.212</td>
<td>0.9326</td>
<td>1.044</td>
<td>0.0072</td>
<td></td>
</tr>
<tr>
<td>Fly-ash [5]</td>
<td>5</td>
<td>0.52</td>
<td>0.021</td>
<td>0.13</td>
<td>0.018</td>
<td>0.8926</td>
<td>7.810</td>
<td>0.0163</td>
<td></td>
</tr>
<tr>
<td>Fly-ash [5]</td>
<td>5</td>
<td>0.45</td>
<td>0.027</td>
<td>0.14</td>
<td>0.016</td>
<td>0.8147</td>
<td>17.09</td>
<td>0.0387</td>
<td></td>
</tr>
<tr>
<td>Fly-ash [5]</td>
<td>5</td>
<td>0.54</td>
<td>0.004</td>
<td>0.11</td>
<td>0.003</td>
<td>0.9989</td>
<td>0.7077</td>
<td>0.0002</td>
<td></td>
</tr>
</tbody>
</table>
4.2.3 Three parameter adaptation of $^{214}$Bi (609 keV)

The graphs in figure 6-8 show the result if GraphPad Prism fits the measured Alum-shale data of $^{214}$Bi (609 keV) to the three parameter equation (13).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>Std. Error</th>
<th>95% Confidence Intervals</th>
<th>Goodness of Fit</th>
<th>Degrees of Freedom</th>
<th>R² (unweighted)</th>
<th>Weighted Sum of Squares (1/SD²)</th>
<th>Absolute Sum of Squares</th>
<th>by.x</th>
<th>Number of points</th>
<th>Analyzed</th>
</tr>
</thead>
<tbody>
<tr>
<td>[3]</td>
<td>Fly-ash</td>
<td>0.40</td>
<td>0.049</td>
<td>2.68</td>
<td>0.474</td>
<td>0.9498</td>
<td>0.5532</td>
<td>0.0091</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[3]</td>
<td>Fly-ash</td>
<td>0.37</td>
<td>0.097</td>
<td>2.82</td>
<td>0.814</td>
<td>0.7857</td>
<td>1.185</td>
<td>0.0490</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[18]</td>
<td>Soil/Rock</td>
<td>0.18</td>
<td>0.038</td>
<td>21.96</td>
<td>5.562</td>
<td>0.6561</td>
<td>275.4</td>
<td>0.1847</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[18]</td>
<td>Soil/Rock</td>
<td>0.41</td>
<td>0.059</td>
<td>13.15</td>
<td>3.670</td>
<td>0.8071</td>
<td>63.16</td>
<td>0.0664</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[7]</td>
<td>Fly-ash</td>
<td>0.61</td>
<td>0.154</td>
<td>-0.26</td>
<td>0.282</td>
<td>0.0054</td>
<td>39.81</td>
<td>0.2523</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Fig 6.* Best fit curve “$Y=P1+P2/X+P3/X^2$” using nonlinear regression curve fit on Alum-shale samples collected at Andrarum and measured at Lund.
Fig 7. Best fit curve “Y=P1+P2/X+P3/X^2” using nonlinear regression curve fit on Alum-shale samples collected at Andrarum and measured in Gothenburg

Fig 8. Best fit curve “Y=P1+P2/X+P3/X^2” using nonlinear regression curve fit on Alum-shale samples collected at Billingen and measured in Gothenburg
4.2.4 Three parameter adaptation of $^{214}$Bi (609 keV), comparison with reference samples.

Table 5. Specification of nonlinear regression equation fit “$Y=P_1+P_2/X+P_3/X^2$” using GraphPad Prism on measured data from sample collected at Andrarum and Billingen and, as comparison, on data collected from other test reports worldwide

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sample type</th>
<th>Number of fractions</th>
<th>$P_1$</th>
<th>Std. error</th>
<th>$P_2$</th>
<th>Std. error</th>
<th>$P_3$</th>
<th>Std. error</th>
<th>$R^2$ (un-weighted)</th>
<th>Weighted Sum of Squares (1/SD²)</th>
<th>Absolute Sum of Squares</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anderstorp (Lund)</td>
<td>Soil/Rock</td>
<td>5</td>
<td>0.59</td>
<td>0.031</td>
<td>-4.84</td>
<td>6.845</td>
<td>-577.1</td>
<td>206.9</td>
<td>0.9858</td>
<td>31.83</td>
<td>0.0020</td>
</tr>
<tr>
<td>Anderstorp (Gbg)</td>
<td>Soil/Rock</td>
<td>7</td>
<td>0.55</td>
<td>0.027</td>
<td>6.64</td>
<td>1.196</td>
<td>11.48</td>
<td>2.396</td>
<td>0.9252</td>
<td>132.4</td>
<td>0.0151</td>
</tr>
<tr>
<td>Billingen (Gbg)</td>
<td>Soil/Rock</td>
<td>8</td>
<td>0.52</td>
<td>0.013</td>
<td>-0.22</td>
<td>0.924</td>
<td>-2.50</td>
<td>3.265</td>
<td>0.9621</td>
<td>162.9</td>
<td>0.0076</td>
</tr>
<tr>
<td>[4] Fly-ash</td>
<td>4</td>
<td>0.65</td>
<td>0.057</td>
<td>57.60</td>
<td>27.01</td>
<td>2372</td>
<td>1808</td>
<td>0.9456</td>
<td>2.305</td>
<td>0.0027</td>
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</tr>
<tr>
<td>[6] Fly-ash</td>
<td>4</td>
<td>0.43</td>
<td>0.012</td>
<td>2.49</td>
<td>0.150</td>
<td>2.73</td>
<td>0.333</td>
<td>0.9990</td>
<td>0.015</td>
<td>1.1e-4</td>
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</tr>
<tr>
<td>[5] Fly-ash</td>
<td>5</td>
<td>0.49</td>
<td>0.010</td>
<td>0.33</td>
<td>0.046</td>
<td>0.050</td>
<td>0.011</td>
<td>0.9920</td>
<td>0.711</td>
<td>0.0012</td>
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</tr>
<tr>
<td>[5] Fly-ash</td>
<td>5</td>
<td>0.41</td>
<td>0.015</td>
<td>0.45</td>
<td>0.077</td>
<td>0.076</td>
<td>0.019</td>
<td>0.9868</td>
<td>1.856</td>
<td>0.0028</td>
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<tr>
<td>[5] Fly-ash</td>
<td>5</td>
<td>0.54</td>
<td>0.003</td>
<td>0.096</td>
<td>0.006</td>
<td>-0.005</td>
<td>0.002</td>
<td>0.9998</td>
<td>0.133</td>
<td>2.24e-5</td>
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</tr>
<tr>
<td>[3] Fly-ash</td>
<td>4</td>
<td>0.24</td>
<td>0.025</td>
<td>6.71</td>
<td>0.608</td>
<td>14.88</td>
<td>2.213</td>
<td>0.9992</td>
<td>0.012</td>
<td>1.5e-4</td>
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</tr>
<tr>
<td>[3] Fly-ash</td>
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<td>0.059</td>
<td>0.054</td>
<td>11.42</td>
<td>1.359</td>
<td>31.53</td>
<td>4.940</td>
<td>0.9963</td>
<td>0.028</td>
<td>8.4e-4</td>
<td></td>
</tr>
<tr>
<td>[18] Soil/Rock</td>
<td>7</td>
<td>0.14</td>
<td>0.022</td>
<td>50.01</td>
<td>8.083</td>
<td>660.4</td>
<td>177.2</td>
<td>0.9632</td>
<td>61.59</td>
<td>0.0198</td>
<td></td>
</tr>
<tr>
<td>[18] Soil/Rock</td>
<td>6</td>
<td>0.36</td>
<td>0.072</td>
<td>27.21</td>
<td>12.04</td>
<td>290.0</td>
<td>237.8</td>
<td>0.8843</td>
<td>42.23</td>
<td>0.0398</td>
<td></td>
</tr>
<tr>
<td>[7] Fly-ash</td>
<td>4</td>
<td>0.54</td>
<td>0.390</td>
<td>0.14</td>
<td>2.225</td>
<td>0.43</td>
<td>2.359</td>
<td>-0.0394</td>
<td>39.16</td>
<td>0.2637</td>
<td></td>
</tr>
</tbody>
</table>

4.2.5 Two parameter adaptation of $^{228}$Ac (911 keV)

The graphs in figure 9-11 shows the result if GraphPad Prism fits the measured Alum-shale data of $^{228}$Ac (911 keV) to the two parameter equation (9).
Fig 9. Best fit curve “Y=P1+P2/X” using nonlinear regression curve fit on Alum-shale samples collected at Andrarum and measured at Lund.

Fig 10. Best fit curve “Y=P1+P2/X” using nonlinear regression curve fit on Alum-shale samples collected at Andrarum and measured in Gothenburg.
Fig 11. Best fit curve “Y=P1+P2/X” using nonlinear regression curve fit on Alum-shale samples collected at Billingen and measured in Gothenburg.

4.2.6 Three parameter adaptation of $^{228}$Ac (911 keV)

The graphs in figure 12-14 shows the result if GraphPad Prism fits the measured Alum-shale data of $^{228}$Ac (911 keV) to the three parameter equation (13).

Fig 12. Best fit curve “Y=P1+P2/X+P3/X^2” using nonlinear regression curve fit on Alum-shale samples collected at Andrarum and measured at Lund.
Fig 13. Best fit curve “Y=P1+P2/X+P3/X²” using nonlinear regression curve fit on Alum-shale samples collected at Andrarum and measured in Gothenburg

4.2.7 Two parameter adaptation of $^{40}$K (1460 keV)

The graphs in figure 15-17 shows the result if GraphPad Prism fits the measured Alum-shale data of $^{40}$K (1460 keV) to the two parameter equation (9).
Fig 15. Best fit curve “Y=P1+P2/X” using nonlinear regression curve fit on Alum-shale samples collected at Andrarum and measured at Lund.

Fig 16. Best fit curve “Y=P1+P2/X” using nonlinear regression curve fit on Alum-shale samples collected at Andrarum and measured in Gothenburg.
4.2.8 Three parameter adaptation of $^{40}$K (1460 keV)

The graphs in figure 18-20 shows the result if GraphPad Prism fits the measured Alum-shale data of $^{40}$K (1460 keV) to the three parameter equation (13).

**Fig 17.** Best fit curve “$Y=P_1+P_2/X$” using nonlinear regression curve fit on Alum-shale samples collected at Billingen and measured in Gothenburg

**Fig 18.** Best fit curve “$Y=P_1+P_2/X+P_3/X^2$” using nonlinear regression curve fit on Alum-shale samples collected at Andrarum and measured at Lund.
Fig 19. Best fit curve “Y=P1+P2/X+P3/X^2” using nonlinear regression curve fit on Alum-shale samples collected at Andrarum and measured in Gothenburg.

Fig 20. Best fit curve “Y=P1+P2/X+P3/X^2” using nonlinear regression curve fit on Alum-shale samples collected at Billingen and measured in Gothenburg.
5 Discussion

5.1 Results from $^{214}$Bi (609 keV)

If table 4 and 5 are compared it seems like the two parameter equation (9) overall is the best fit for $^{214}$Bi (609 keV). Some samples though fit better with the three parameter equation (13), but if the P1, P2 and P3 values received is used on other samples, it will not fit. In other words, equation (13) can not be used in general. The only trend that can be observed in table 4 is the value of the P1 parameter which can be estimated to approximately 0.50-0.52. This parameter however only tells the Y-level (activity concentration) of the curve when X (particle diameter) goes towards infinity. It has nothing to do with the slope of the curve at small particle sizes. As can be seen though, no matter of the geometric shape of larger particles, the maximum measured activity concentration will be about half of the measured value for the smallest particles.

5.2 Results from $^{228}$Ac (911 keV) and $^{40}$K (1460 keV)

For the $^{228}$Ac (911 keV) and $^{40}$K (1460 keV) measured from samples collected in Sweden no general solution could be fit either with two parameter equation (9) or the three parameter equation (13). Since the main goal with this work was to fit an equation to the Andrarum and Billingen samples, and to use other samples from test reports worldwide as a final confirmation of the equation calculated no comparison was made for these nuclids.

5.3 Sources to uncertainties and suggestions to improved sample preparation

Many suggestions can be made to the poor results received from the samples available, but some factors that in general improve the results can be mentioned.

Overall the sample weights are low compared to other test reports. The sieved samples had an average weight of approx. 5 g, while the wet-settled samples ranged between 0.08-1.0 g. This gives a weak signal especially from the interesting small particle size fractions. It is difficult to detect a clear energy peak in the multi-channel analyser spectrum, even if measurement time is up to 24 hours, which leads to an uncertain calculation of specific activity. The method
used to prepare these samples was by mechanical crushing, and for the smaller sizes, by grinding in a mortar. If new samples are to be made, some sort of electrical equipment should be used. A grinding machine with a diamond-grind-disc connected to a vacuum cleaner equipped with a special dust-filter would make the job.

Another problem is the number of fractions produced. In order to make a relevant curve fit more small size fractions with narrower size ranges need to be produced. Otherwise the parameter P2 (or P2 and P3) cannot be estimated. In order to reduce the measurement errors all fraction samples should be measured at least two times, preferably three or more. This will also reveal incorrect values received from troubling equipment. Since the samples used in this test are only measured one time each, it is hard to tell if a point in a graph is relevant and correct or not.

The wet sedimentation process is also a source of errors. The method used in this preparation was rather primitive, which leads to uncertainty if the sample content was representative for the fraction particle size recorded or not. Other more modern methods can be used today, both with water and air supplied equipment.
References


