NORM radionuclides in a soil profile from a former coal mine in southern Spain


NORM X, 9th-13th May 2022, Utrecht
Overview

1. Background
2. Main aim and working plan
3. Methodology
4. Results
5. Conclusions & Future works
1. Background

Villanueva del Río y Minas

Mining method: [Underground galleries, Opencast, Pit Lake]

NORM X, 9-13 May 2022, Utrecht
1. Background

Picture taken during the 80’s, before restoration

Picture taken in the second half of the 90’s, after environmental restoration.
1. Background

Environmental levels of NORM radionuclides were found in water, sediments and soil samples, except for soil 1A and 1B. At this spot…
1. Background

For n=33 spots, average 0.20 ± 0.10 μSv/h

232Th range: 1-7 Bq/kg
228Ra-228Th in secular equilibrium (range: 19-46 Bq/kg)
2. Main aim and working plan

Hypothesis: coal ash buried due to a small power plant to supply electricity.

To perform a deeper study at the “hot spot” on the restored area.

Working plan:
1\textsuperscript{st}. Measurement of a more detailed $H^*(10)$ around the spot
2\textsuperscript{nd}. Sampling of a soil profile
3\textsuperscript{rd}. Radiometrical Characterization
4\textsuperscript{th}. Element characterization
5\textsuperscript{th}. Mineralogical composition
3. Methodology

I). Ambient dose rate equivalent:

- Berthold, **UMo LB 123**
- Equipped with probe LB 1236-H10 (range 50 nSv/h-10 mSv/h)

II). Sampling of a soil profile

No information available about the amendment material used during the 80’s to cover the restored area.

Undisturbed soil? Or a “rocky” soil?
3. Methodology

II). Sampling of a soil profile

What we found was sandy soil, easy to excavate but highly inhomogeneous (mixed with debris: rocks, brick pieces, concrete blocks,…)

A 20x20x5 cm metal rack was hammered for soil sampling.

The profile reached 50 cm depth, split into 5cm layers.

Each layer (about 2kg wet weight) was cleaned of solid debris and homogenized:
- sieved to 2mm
- aliquots of about 300g were dried (80°C)
- One aliquot was ashed (organic matter content)
- One aliquot was sieved for grain size analysis
3. Methodology

III) Radiometrical techniques

γ-ray spectrometry

- XtRa Ge detector, 37% rel. eff.
- Ancient lead shielding
- N₂ evacuation system

Autoradiography:

Fujifilm BAS-TR 2040
3. Methodology

IV) Elementary characterization

X-ray Fluorescence

- **Majors**: WROXI PRO method (DL~ 0.05%)
- **Traces**: PRO-TRACE method (DL~ 1 ppm)

Scanning Electron Microscopy coupled to EDX detector (SEM-EDX)

- "Spot" mode
- "Mapping" mode

**ESEM: ZEISS EVO LS15**

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3. Methodology

V) Mineralogical characterization (X-ray Diffraction):

Quantitative analysis by the Rietveld method:

\[ \begin{align*}
\text{% of amorphous phase} & \quad \text{% of crystal phase} \\
\rightarrow \quad \text{Crystallographic structure}
\end{align*} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Code</th>
<th>PDF4</th>
<th>Formula</th>
<th>Conc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>00-066-0867</td>
<td></td>
<td>CaCO_3</td>
<td>53.1 ± 0.8</td>
</tr>
<tr>
<td>Quartz</td>
<td>00-046-1045</td>
<td></td>
<td>SiO_2</td>
<td>18.9 ± 0.4</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>00-058-2001</td>
<td></td>
<td>Al_2Si_2O_5(OH)_4</td>
<td>15.9 ± 0.7</td>
</tr>
<tr>
<td>Muscovite</td>
<td>00-058-2034</td>
<td></td>
<td>KAl_2(Si,Al)_4O_10(OH)_2</td>
<td>12.0 ± 1.0</td>
</tr>
</tbody>
</table>

Bruker D8 Advance A25(D8I-90)

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4. Results

Ambient dose rate equivalent $H^*(10)$

1st sampling screening (January 2019)

A higher resolution measurement revealed several inhomogeneities on a 30x30 m area

2nd sampling (December 2021)
4. Results

Humidity and organic matter profiles:

Sieve analysis (mesh 1000-25μm):

<table>
<thead>
<tr>
<th>Size (μm)</th>
<th>%</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000-80</td>
<td>78.1</td>
<td>Sand</td>
</tr>
<tr>
<td>80-25</td>
<td>13.9</td>
<td>Silt</td>
</tr>
<tr>
<td>25&lt;</td>
<td>8</td>
<td>Silt+Clay</td>
</tr>
</tbody>
</table>

Loamy sand

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4. Results

232Th series radionuclides

<table>
<thead>
<tr>
<th>Bq/kg</th>
<th>Range</th>
<th>Average±SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>232Th</td>
<td>14-31</td>
<td>20±5</td>
</tr>
<tr>
<td>228Ra</td>
<td>24-51</td>
<td>36±7</td>
</tr>
<tr>
<td>228Th</td>
<td>25-41</td>
<td>37±5</td>
</tr>
</tbody>
</table>

- Environmental levels were found
- 228Ra−228Th Secular Eq. found
- However a small disequilibrium of 228Ra/228Th with 232Th was found
4. Results

$^{238}$U series radionuclides

- Enhanced levels found
- Dosimetrical aproach needed
- Huge $^{226}$Ra-$^{238}$U disequilibrium.
- Identical behaviour (profile shape) with depth among $^{238}$U-$^{226}$Ra-$^{210}$Pb.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Range</th>
<th>Average±SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}$U</td>
<td>90-280</td>
<td>180±70</td>
</tr>
<tr>
<td>$^{226}$Ra</td>
<td>5.3-34.2</td>
<td>20±9</td>
</tr>
<tr>
<td>$^{210}$Pb</td>
<td>5.2-24.5</td>
<td>16.2±6.4</td>
</tr>
</tbody>
</table>
4. Results

238U series radionuclides

Neglecting “unsupported 210Pb” and 238U contribution to 226Ra, the imbalance can be used for dating the different layers:

Small disequilibrium 210Pb-226Ra found

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4. Results

Autoradiography

...or the “hunting” of hot particles.

A visual method to identify the distribution of beta/gamma emitters in any thin film after several days of being “irradiated” by the samples.

The different “grades of shade” inform us about the higher or lower level of activity in the sample and the presence of impurities from the radioactive perspective. Used to locate “hot particles” that will be measured later by SEM-EDX.
4. Results

Local (480x330 μm) element composition in **Mapping Mode**.

SEM-EDX of a “NORM aggregate”

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4. Results

SEM-EDX of a “NORM aggregate”

Spatial distribution of the different elements at a local scale:

Different location:
4. Results

Element characterization (major elements)

High content of organic matter ~ 38%

Low values of Si* (65%) and Na* (1.1%) but high levels of:

- Ca* (3-9%) ~ 20%
- Sr* (130-300 ppm) ~ 5000 ppm
- Ba* (80-400 ppm) ~ 15000 ppm
- Mn* (400-800 ppm) ~ 9000 ppm

Normal levels of: Al, Fe, K, Mg, Ti, P, S

* Geochemical atlas of Europe, 2006
4. Results

Element characterization (major elements)

Behaviour with depth:

Type I: maximum ~ 20 cm
Ca, Sr, Ba, S, Mn, Ti, Si

Type II: minimum ~ 20 cm
Al, Na, K, Zr

Type III
Fe, P, Cu, Mg
4. Results

Element characterization
(Trace elements)

Enhanced levels of:
- Pb* (10-50 ppm) ~ 170 ppm
- Cu* (15-30 ppm) ~ 100 ppm
- U* (2-5 ppm) ~ 17 ppm

Iodine:
- 5-200 ppm in recent sediments
- While igneous rocks averages 0.24 ppm

Normal levels*:
- REE: Ce, La, Y, Th
- Zn, Zr, V, Rb, Cr, As, Ni, Co

* Geochemical atlas of Europe, 2006
4. Results

Element characterization (Trace elements)

Behaviour with depth:

Type I
- Co, Cu, Ge, As, Ag, Bi, Cd, I
- Sb, Se, Sn, U, W, V, Zr

Type II
- Ce, Cs, La, Nb, Pb, Th, Y
- Ce, Cs

Type III: Cr, Ga, Br, Mo, Ni, Ta, Ti, Zn

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4. Results  

Mineralogical characterization

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Sample 5</th>
<th>Sample 20</th>
<th>Sample 50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite (CaCO₃)</td>
<td>14.8</td>
<td>46.3</td>
<td>38.2</td>
</tr>
<tr>
<td>Aragonite (CaCO₃)</td>
<td>6.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz (SiO₂)</td>
<td>19.1</td>
<td>7.96</td>
<td>13.6</td>
</tr>
<tr>
<td>Moganite (SiO₂)</td>
<td>5.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite (Al₂Si₂O₅(OH)₄)</td>
<td>7.50</td>
<td>3.59</td>
<td>11.5</td>
</tr>
<tr>
<td>Muscovite (KAl₂(Si,Al)₄O₁₀(OH)₂)</td>
<td>9.52</td>
<td>4.06</td>
<td>8.64</td>
</tr>
<tr>
<td>Calcium Aluminum Silicon (CaAlSi )</td>
<td>1.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bixbyite (Mn₂O₃)</td>
<td>1.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anatase (TiO₂)</td>
<td>1.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monohydrocalcite (CaCO₃·H₂O )</td>
<td></td>
<td></td>
<td>4.29</td>
</tr>
<tr>
<td>Barium Manganese Oxide (Ba₄Mn₃O₁₀)</td>
<td></td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>% amorphus</td>
<td>44.0</td>
<td>22.0</td>
<td>28.0</td>
</tr>
</tbody>
</table>

Elements as Sr or Fe were not found with crystallographic structures above the DL of this technique.
4. Conclusions & Future works

A hot spot was found in a restored area of a former coal mine with gamma external dose levels that drove us to sample a soil profile (0 – 50 cm).

The synergy among experimental techniques: radioactivity measurement, electronic microscopy, autoradiography and XR-Fluorescense revealed that:

• The highest activity concentration of natural radionuclides was due to $^{226}$Ra, reaching up to 35 Bq/g, having $^{40}$K or $^{232}$Th series radionuclides, environmental values.

• The origin of such high levels were found in the restored layer, not in deeper layers. So, where does the restoration material come from?
4. Conclusions & Future works

- Enhanced levels were found of Ca, Sr, Ba, Mn (as major elements) and of Pb, I, Cu and U (as traces).
- Radionuclides and stable elements presented three different behaviours depending upon the depth of the soil profile.
- The presence of “NORM aggregates” was also identified.
- An enhancement in **Barium manganese oxide** in the imported sand could be the origin of such a levels of natural radioactivity.

The experimental data will be used as the base for future dose assessments. Maybe, lixiviation experiments in the laboratory with the “NORM aggregates”?

The findings of this work are a clear example of the relevance and need of these type of studies associated to mining activities and restoration processes. This is especially relevant if there is human interaction in the restored area.
Thank you very much for your attention!

Picture taken in close contact with the topsoil