Title: Natural radioactivity content in groundwater of Mt. Etna's eastern flank and gamma background of surrounding rocks

Author: Beata Kozłowska, Agata Walencik-Łata, Giuseppina Imme, Roberto Catalano, Gabriella Mangano, Daniela Morelli i in.

Natural radioactivity content in groundwater of Mt. Etna’s eastern flank and gamma background of surrounding rocks

Beata Kozłowska¹*, Agata Walencik-Łata¹, Giuseppina Immè²,³, Roberto Catalano²,³, Gabriella Mangano², Daniela Morelli²,³, Salvatore Giammanco⁴

¹ University of Silesia, Institute of Physics, Department of Nuclear Physics and Its Applications, Katowice, Poland
² Università di Catania, Dipartimento di Fisica e Astronomia, Catania, Italy
³ Istituto Nazionale di Fisica Nucleare, Sezione di Catania, Catania, Italy
⁴ Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Etneo, Catania, Italy

ABSTRACT

Waters of Mt. Etna are the main source of drinking water for the local population and are also distributed in municipal supply systems to neighbouring areas. Radioactivity in underground waters and surrounding rocks from the eastern flank of Mt. Etna was investigated on the basis of 9 water and 8 rock samples from 12 localities altogether. Three samples were from water drainage galleries and six from water wells. All water intakes are used for consumption. Activity concentration of uranium isotopes ²³⁴,²³⁸U, radium isotopes ²²⁶,²²⁸Ra and radon ²²²Rn were determined with the use of different nuclear spectrometry techniques. The determination of uranium isotopes was carried out with the use of alpha spectrometry. The measurements of radium and radon activity concentration in water were performed with the use of a liquid scintillation technique. Additionally, rocks surrounding the intakes were examined with gamma spectrometry. All water samples showed uranium concentration above Minimum Detectable Activity (MDA), with the highest total uranium (²³⁴U + ²³⁸U) activity concentration equal to 149.2±6 mBq/L. Conversely, all samples showed radium isotopes activity concentrations below MDA. Radon activity concentration was within the range from 2.91±0.36 to 21.21±1.10 Bq/L, hence these waters can be classified as low-radon waters. Gamma natural background of the rocks surrounding the water sampling sites was found on the same levels as other volcanic rocks of Italy.

1. Introduction

There is a growing concern about the health effects produced by natural radioactivity in the environment. Natural radionuclides are present in water, air, soil, plants and animals and in consequence in the human diet. In groundwater, their presence is determined by their activity concentration in soil and bedrock. Groundwater reacts with the surrounding rocks and releases elements which can be dissolved in it. Long-lived isotopes of uranium, radium and potassium are mainly responsible for natural radioactivity content. The most extensively studied natural radionuclide in all types of natural environments is radon since this element was found to be directly or indirectly responsible of about 2% of all death from cancer in Europe [Darby et al. 2005]. In particular, indoor radon levels derived from groundwater use in the USA are thought to cause 1-7% of fatal lung cancers [Cothern et al. 1986].

Concerning an active volcanic environment such as Mt. Etna still few detailed studies exist on the levels of radionuclides other than radon in groundwater. Waters of Mt. Etna are the main source of drinking water for the local population and are also distributed in municipal supply systems to neighbouring areas. Moreover, they are used for both agricultural and industrial purposes.

A previous study on the determination of the activity concentration of ²³⁴,²³⁸U, ²²⁶,²²⁸Ra and ²²²Rn in Etna’s groundwater intakes was recently carried out [Kozłowska et al. 2009] showing values of uranium isotopes generally higher than the Minimum Detectable Activity (MDA), radium isotopes generally below MDA and low radon activity concentrations. The latter were in the same range as those found by D’Alessandro and Vita [2003], who performed an extensive survey in Mt. Etna’s groundwater for the specific determination of dissolved radon contents.

In this work we present geochemical data on the activity concentration of uranium isotopes ²³⁴,²³⁸U, radium isotopes ²²⁶,²²⁸Ra and ²²²Rn in collected un-
derground waters from the aquifers of the eastern flank of Mt. Etna volcano. This area was selected as a good case study because it is characterised by large volumes of groundwater, strong interaction between groundwater, volcanic rocks, volcanic gases and some hydrothermal fluids [Aiuppa et al. 2000, Brusca et al. 2001, Parello et al. 2001, Aiuppa et al. 2004]; it is also the area of Mt. Etna with the highest values of dissolved radon [D’Alessandro and Vita 2003] and the only area where radium isotopes were detected [Kozłowska et al. 2009]. All these facts stimulated the authors to perform detailed studies on natural radioactivity content in groundwater from this area. Moreover, gamma spectrometry measurements were performed on five samples from volcanic rocks surrounding water intakes and three samples from volcanic rocks taken close to summit craters, in order to investigate the natural background radioactivity of the area.

1.1. Sampling

Nine groundwater samples from aquifers of the eastern flank of Mt. Etna were collected for the purposes of this study. We chose sampling sites whose waters are continuously used for drinking purposes by the local population and whose sampling point was not too far from the water well/drainage gallery. There were other waters available for collection but they were either not used for drinking or their closest collection point was too far from the well/drainage gallery, so there was a high chance of losing radon by radioactive decay before collection.

Sampling was performed three times, in 2011, 2012 and 2013 year. Figure 1 presents the investigated area and the sampling sites. Three samples were taken from water drainage galleries and six from water wells. In the vicinity of five of these sites rocks samples were collected for the analysis of radioactive isotopes. Besides, three more rock samples were collected from the old-
est lavas outcropping in the uppermost slopes of the volcano, thus representing the rock types present in the recharge areas of the aquifers that contain the groundwater collected downslope. Table 1 presents a description of the intakes and the physical-chemical properties of the investigated waters, i.e. total dissolved solids (TDS), pH, electrical conductivity and temperature. The table also shows the values of partial pressure of dissolved radiactivity in waters and rocks of Mt. Etna.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Sample name</th>
<th>Sample description</th>
<th>Sample type</th>
<th>Rock surrounding water intake</th>
<th>pH</th>
<th>Depth [m]</th>
<th>T [°C]</th>
<th>Conductivity [mS/cm]</th>
<th>TDS [mg/L]</th>
<th>pCO2 [atm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_1</td>
<td>Fleri</td>
<td>water from drainage gallery, a village center, public water intake, drinking water</td>
<td>gallery</td>
<td>not taken</td>
<td>6.51</td>
<td>NA</td>
<td>17.5</td>
<td>0.75</td>
<td>360</td>
<td>0.124*</td>
</tr>
<tr>
<td>E_2</td>
<td>Valle San Giacomo</td>
<td>water from drainage gallery, drinking and irrigation water, local distribution</td>
<td>gallery</td>
<td>sample from the neighborhood</td>
<td>6.70</td>
<td>NA</td>
<td>18.85</td>
<td>1.37</td>
<td>668</td>
<td>0.026**</td>
</tr>
<tr>
<td>E_3</td>
<td>Milo</td>
<td>water from drainage gallery, local distribution, drinking water, public intake</td>
<td>gallery</td>
<td>not taken</td>
<td>7.54</td>
<td>NA</td>
<td>17.3</td>
<td>0.81</td>
<td>390</td>
<td>0.002*</td>
</tr>
<tr>
<td>E_4</td>
<td>Primoti</td>
<td>water from private well, irrigation water</td>
<td>well</td>
<td>lava and soil close to the well</td>
<td>6.67</td>
<td>150</td>
<td>18.5</td>
<td>4.52</td>
<td>2340</td>
<td>0.633§</td>
</tr>
<tr>
<td>E_5</td>
<td>Ilice</td>
<td>water - MPS, local distribution only, drinking water</td>
<td>well</td>
<td>sample from the neighborhood</td>
<td>6.55</td>
<td>120</td>
<td>18.4</td>
<td>0.74</td>
<td>357</td>
<td>0.124*</td>
</tr>
<tr>
<td>E_6</td>
<td>Macchia di Giarre</td>
<td>water from well San Paolo, drinking water, public intake</td>
<td>well</td>
<td>not taken</td>
<td>6.86</td>
<td>100</td>
<td>17.8</td>
<td>2.73</td>
<td>1360</td>
<td>0.022**</td>
</tr>
<tr>
<td>E_7</td>
<td>Fornazzo</td>
<td>water - MPS, drinking water, local distribution, private intake</td>
<td>well</td>
<td>sample from the neighborhood</td>
<td>7.61</td>
<td>&gt;100</td>
<td>17.4</td>
<td>0.81</td>
<td>391</td>
<td>0.010*</td>
</tr>
<tr>
<td>E_8</td>
<td>Linera</td>
<td>water used only for irrigation, private intake</td>
<td>well</td>
<td>not taken</td>
<td>6.39</td>
<td>&gt;100</td>
<td>17.2</td>
<td>2.01</td>
<td>987</td>
<td>0.120**</td>
</tr>
<tr>
<td>E_9</td>
<td>Guardia</td>
<td>water for drinking and irrigation, local distribution, public intake</td>
<td>well</td>
<td>sample from the neighborhood</td>
<td>6.40</td>
<td>&gt;100</td>
<td>19.0</td>
<td>1.54</td>
<td>756</td>
<td>0.156*</td>
</tr>
<tr>
<td>E_10</td>
<td>La Montagnola crater (1763)</td>
<td>-</td>
<td>rock sample</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E_11</td>
<td>Piano del Lago</td>
<td>-</td>
<td>rock sample</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E_12</td>
<td>1792 lava flow</td>
<td>-</td>
<td>rock sample</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Physical-chemical properties of investigated waters and samples description. NA = not available; MPS = municipal power supply; * pCO2 values from Parello et al. [2001]; ** pCO2 values from Giammanco et al. [1998]; § average pCO2 value for this site, from Giammanco et al. [2007a].
CO\(_2\) (pCO\(_2\)) measured in the corresponding sites during previous hydrogeochemical surveys [Giammanco et al. 1998, Parello et al. 2001, Giammanco et al. 2007a].

For radium and uranium determination the samples were collected in 2 and 0.5 volume polyethylene bottles, respectively. Samples were acidified to prevent the precipitation of iron as ferric hydroxide in the collecting containers. The initial chemical treatment for radium isotopes was performed at the Department of Physics and Astronomy of the University of Catania, Italy. Further treatment of the samples for radium and uranium determination was performed at the Department of Nuclear Physics and Its Applications, Institute of Physics, University of Silesia in Katowice, Poland.

For radon determination, samples of the volume of 10 ml were collected by disposable syringes directly at the intakes and immediately put into scintillation vials under 10 ml of scintillation cocktail [Suomela 1993a]. The measurements were performed at the Department of Physics and Astronomy of the University of Catania.

1.2. Hydrogeology and hydrochemistry of the area

The investigated area is the eastern flank of Mt. Etna volcano (Figure 1). The volcanic edifice of Mt. Etna has grown up during the last 500,000 years on the eastern coast of Sicily (southern Italy) with the alternate superimposition of lava flows and pyroclastic deposits [Romano 1982, Chester et al. 1985]. During the last 5000 years Etna has been almost continuously erupting and has emitted volcanic products essentially made of lavas, ranging in composition from alkali-basalt to hawaiite [Chester et al. 1985, Branca and Ferrara 2013]. The volcano built up its edifice over a sedimentary substratum with an estimated thickness common to many other basaltic volcanoes: fissure and highly permeable lava layers are interbedded with discontinuous layers of scarcely permeable pyroclastics. These volcanic products are superimposed on an impermeable sedimentary substratum, with a variable composition), pyroxene (~28%, having an average augitic composition), olivine (~3%) and oxides (~3%) such as magnetite and sometimes titanomagnetite and ilmenite. Other minerals present to a lesser extent are apatite, alkali feldspars and in some cases nepheline, leucite and biotite [Cristofolini and Romano 1982, Romano 1982, Chester et al. 1985].

According to the model first proposed by Anzà et al. [1989], Etna’s groundwaters are of meteoric origin, based on their Deuterium/Hydrogen and \(^{18}\)Oxygen/\(^{16}\)Oxygen isotopic ratios. When rain waters enter the aquifer, they become enriched in CO\(_2\) which, according to the \(^{8}\)C values already available in literature, is mostly of magmatic origin [Allard et al. 1997, Aiuppa et al. 2004]. This process is ubiquitous on Mt. Etna, although it is enhanced in the most fractured and seismically active zones of the volcano (i.e. the SW and E flanks) and it seems to mask any evolution of water chemistry from recharge to discharge areas [Aiuppa et al. 2004, and literature therein cited].

On the basis of structural, geological and geophysical data, three main hydrogeological basins were identified [Ogniben 1966, Ferrara 1990] (Figure 1). They roughly correspond to three sectors of the volcano: I) the eastern one, tributary of the Ionian Sea; II) the southwestern one, tributary of the Simeto River; III) the northern one, whose waters feed the Alcantara River.

The general chemical composition of Etna’s groundwater ranges from bicarbonate alkaline-earth to bicarbonate alkaline [Anzà et al. 1989, Dongarrà et al. 1993, Giammanco et al. 1996, Aiuppa et al. 2004]. As regards the major species in solution, the relative abundance is generally (Na\(^+\), Mg\(^{2+}\)) > Ca\(^{2+}\) > K\(^+\) among the cations, with magnesium prevailing on sodium in the waters with higher salinity, whereas among the anions bicarbonate (HCO\(_3\)\(^-\)) is always the prevailing dissolved species. Only very few samples show a chloride-sulphate alkaline-earth composition, normally due to the high concentrations of sulphate ions.

Values of Total Dissolved Solids (TDS) are normally well correlated with the corresponding values of calculated partial pressure of CO\(_2\) (pCO\(_2\)) in equilibrium with water. This indicates a strong chemical interaction among meteoric water, the host rocks, from

mano 1982, Chester et al. 1985, Branca and Ferrara 2013]. However, the concurrent presence of alkali olivine basalts ranging from “transitional” to sub-alkaline, belonging to the deepest basal lavas, is highly probable [Branca and Ferrara 2013].

Both of these magmatic series have a chemical composition ranging from basic to intermediate. The main mineralogical phases present in such products consist, in order of abundance, of plagioclase (~65%, with a variable composition), pyroxene (~28%, having an average augitic composition), olivine (~3%) and oxides (~3%) such as magnetite and sometimes titanomagnetite and ilmenite. Other minerals present to a lesser extent are apatite, alkali feldspars and in some cases nepheline, leucite and biotite [Cristofolini and Romano 1982, Romano 1982, Chester et al. 1985].

According to the model first proposed by Anzà et al. [1989], Etna’s groundwaters are of meteoric origin, based on their Deuterium/Hydrogen and \(^{18}\)Oxygen/\(^{16}\)Oxygen isotopic ratios. When rain waters enter the aquifer, they become enriched in CO\(_2\) which, according to the \(^{8}\)C values already available in literature, is mostly of magmatic origin [Allard et al. 1997, Aiuppa et al. 2004]. This process is ubiquitous on Mt. Etna, although it is enhanced in the most fractured and seismically active zones of the volcano (i.e. the SW and E flanks) and it seems to mask any evolution of water chemistry from recharge to discharge areas [Aiuppa et al. 2004, and literature therein cited].

On the basis of structural, geological and geophysical data, three main hydrogeological basins were identified [Ogniben 1966, Ferrara 1990] (Figure 1). They roughly correspond to three sectors of the volcano: I) the eastern one, tributary of the Ionian Sea; II) the southwestern one, tributary of the Simeto River; III) the northern one, whose waters feed the Alcantara River.

The general chemical composition of Etna’s groundwater ranges from bicarbonate alkaline-earth to bicarbonate alkaline [Anzà et al. 1989, Dongarrà et al. 1993, Giammanco et al. 1996, Aiuppa et al. 2004]. As regards the major species in solution, the relative abundance is generally (Na\(^+\), Mg\(^{2+}\)) > Ca\(^{2+}\) > K\(^+\) among the cations, with magnesium prevailing on sodium in the waters with higher salinity, whereas among the anions bicarbonate (HCO\(_3\)\(^-\)) is always the prevailing dissolved species. Only very few samples show a chloride-sulphate alkaline-earth composition, normally due to the high concentrations of sulphate ions.

Values of Total Dissolved Solids (TDS) are normally well correlated with the corresponding values of calculated partial pressure of CO\(_2\) (pCO\(_2\)) in equilibrium with water. This indicates a strong chemical interaction among meteoric water, the host rocks, from
which the ions in solution were extracted by leaching, and a gaseous phase mainly composed of CO₂. This gas is very abundant both in the ground waters and in the soils of Etna, besides its massive emission through the volcanic plume [Allard et al. 1991, Giammanco et al. 1995, D’Alessandro et al. 1997], and its origin is mostly magmatic [Anzà et al. 1989, Giammanco et al. 1995]. Dongarrà et al. [1993] also showed that the concentration of the major species in solution and particularly the calculated values of partial pressure of CO₂ with which waters equilibrated can be subject to marked variations in time. Such variations were found to be caused both by seasonal effects and, more significantly, by changes in the volcanic activity of Etna. Some minor chemical species are brought into water directly from the rocks or from the volcanic gases that carry them as volatile species. This is the case of radon, that is present both in the volcanic rocks of Mt. Etna and in the volcanic gases that leak through the flanks of the volcano along tectonic faults [e.g., Neri et al. 2011].

The surface of the area investigated by our sampling was about 120 km². The geological features of this area mainly consist of Etna’s volcanic products. The volcanic rocks that outcrop in the study area are essentially represented by lava flows belonging to the so-called Stratovolcano Supersynthem, whose activity started from 57 ka [Branca et al. 2011], although some minor outcrops belong to the Timpe Supersynthem, that started some 220 ka [Branca et al. 2011]. All of the samples of volcanic rocks collected belong to the former.

2. Measurement techniques

2.1. Water samples analysis

Since this project is a continuation of the research started in year 2009 the measurement techniques used for water samples studies were already described in the previous publication [Kozłowska et al. 2009]. There were two nuclear spectrometry techniques involved: liquid scintillation counting and alpha spectrometry. Determination of radon activity concentration was performed at the Department of Physics and Astronomy of University of Catania in Italy and in the Department of Nuclear Physics and Its Applications of the Institute of Physics at the University of Silesia in Poland. Apart from scientific purposes these studies served as inter-comparison measurement in the two laboratories. Collected samples were transferred to the laboratory in the Department of Physics and Astronomy of University of Catania where they were characterized, dried, crushed and ground to a fraction smaller than 0.2 mm for homogenization.

The measurements in both laboratories were carried out in Marinelli geometry, in 0.6 dm³ containers, where the rock samples were sealed for 30 days in order to allow secular equilibrium in the uranium and thorium series. The natural radioactivity of 226Ra, 228Ra(228Ac) and 40K in collected samples were determined using HPGe gamma spectrometers produced by ORTEC Company. The spectra were analyzed with the use of GENNIE gamma acquisition program and GANNAS spectra analysis program and MAESTRO-32 software. The energy calibration and the detector efficiency curves were obtained on the basis of standards prepared from certified materials from the International Atomic Energy Agency from Vienna, Austria and Central Laboratory for Radiological Protection from Warsaw, Poland.
<table>
<thead>
<tr>
<th>Sample code</th>
<th>$^{222}\text{Rn}$ [Bq/L] (from literature)</th>
<th>$^{222}\text{Rn}$ [Bq/L]</th>
<th>$^{226}\text{Ra}$ [mBq/L]</th>
<th>$^{228}\text{Ra}$ [mBq/L]</th>
<th>$^{234}\text{U}$ [mBq/L]</th>
<th>$^{238}\text{U}$ [mBq/L]</th>
<th>U [µg/L]</th>
<th>$^{234}\text{U}/^{238}\text{U}$</th>
<th>$^{222}\text{Rn}/^{238}\text{U}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_1</td>
<td>7.46±0.2 (2011 y)</td>
<td>-</td>
<td>&lt;40 (2011 y)</td>
<td>&lt;120 (2011 y)</td>
<td>4.8±1.3 (2011 y)</td>
<td>4.9±1.3 (2011 y)</td>
<td>0.4±0.1 (2011 y)</td>
<td>1.0±0.4 (2011 y)</td>
<td>1522±406 (2011 y)</td>
</tr>
<tr>
<td>E_2</td>
<td>2.91±0.36 (2011 y)</td>
<td>10.1 (2)</td>
<td>&lt;40 (2011 y)</td>
<td>&lt;120 (2011 y)</td>
<td>2.0±0.6 (2011 y)</td>
<td>1.5±0.5 (2011 y)</td>
<td>0.12±0.04 (2011 y)</td>
<td>1.4±0.7 (2011 y)</td>
<td>1940±690 (2011 y)</td>
</tr>
<tr>
<td>E_3</td>
<td>NA</td>
<td>4.8 (2)</td>
<td>&lt;40 (2011 y)</td>
<td>&lt;120 (2011 y)</td>
<td>12.5±1.8 (2011 y)</td>
<td>7.4±1.3 (2011 y)</td>
<td>0.6±0.1 (2011 y)</td>
<td>1.7±0.4 (2011 y)</td>
<td>-</td>
</tr>
<tr>
<td>E_4</td>
<td>12.52±1.38 (2011 y)</td>
<td>43 (2)</td>
<td>&lt;40 (2011 y)</td>
<td>&lt;120 (2011 y)</td>
<td>61.4±4.9 (2011 y)</td>
<td>64.5±5.1 (2011 y)</td>
<td>5.2±0.4 (2011 y)</td>
<td>1.0±0.1 (2011 y)</td>
<td>194±26 (2011 y)</td>
</tr>
<tr>
<td>E_5</td>
<td>15.79±0.65 (2011 y)</td>
<td>12.0±0.6;</td>
<td>&lt;40 (2011 y)</td>
<td>&lt;120 (2011 y)</td>
<td>4.1±0.8 (2011 y)</td>
<td>2.8±0.3 (2011 y)</td>
<td>0.23±0.05 (2011 y)</td>
<td>1.4±0.4 (2011 y)</td>
<td>5639±1231 (2011 y)</td>
</tr>
<tr>
<td></td>
<td>21.21±1.1 (2012 y)</td>
<td>28.1 (1.2)</td>
<td>&lt;40 (2013 y)</td>
<td>&lt;120 (2013 y)</td>
<td>4.0±0.7 (2012 y)</td>
<td>3.0±0.3 [1]</td>
<td>0.22±0.04 (2012 y)</td>
<td>1.5±0.4 (2012 y)</td>
<td>7856±1511 (2012)</td>
</tr>
<tr>
<td>E_6</td>
<td>3.49±0.76 (2011 y)</td>
<td>14.8 (2)</td>
<td>&lt;40 (2011 y)</td>
<td>&lt;120 (2011 y)</td>
<td>78.6±5.7 (2011 y)</td>
<td>70.1±5.1 (2011 y)</td>
<td>5.7±0.4 (2011 y)</td>
<td>1.1±0.1 (2011 y)</td>
<td>50±11 (2011 y)</td>
</tr>
<tr>
<td></td>
<td>8.03±0.6 (2012 y)</td>
<td></td>
<td>&lt;40 (2012 y)</td>
<td>&lt;120 (2012 y)</td>
<td>73.9±5.9 (2013 y)</td>
<td>71.0±5.7 (2013 y)</td>
<td>5.7±0.5 (2011 y)</td>
<td>1.0±0.1 (2012 y)</td>
<td>113±12 (2012 y)</td>
</tr>
<tr>
<td>E_7</td>
<td>&lt; 1.4 (2011 y)</td>
<td>1.6±0.5 (1)</td>
<td>&lt;40 (2011 y)</td>
<td>&lt;120 (2011 y)</td>
<td>8.0±1.5 (2011 y)</td>
<td>6.9±1.3 (2011 y)</td>
<td>0.6±0.1 (2011 y)</td>
<td>1.2±0.3 (2011 y)</td>
<td>417±79 (2012 y)</td>
</tr>
<tr>
<td></td>
<td>2.92±0.41 (2012 y)</td>
<td></td>
<td>&lt;40 (2012 y)</td>
<td>&lt;120 (2012 y)</td>
<td>8.3±1.0 (2012 y)</td>
<td>7.0±2.9 (2012 y)</td>
<td>0.57±0.07 (2012 y)</td>
<td>1.2±0.2 (2012 y)</td>
<td>1.4±0.1 [1]</td>
</tr>
<tr>
<td>E_8</td>
<td>NA</td>
<td>-</td>
<td>&lt;40 (2011 y)</td>
<td>&lt;120 (2011 y)</td>
<td>33.8±5.3 (2011 y)</td>
<td>36.8±5.6 (2011 y)</td>
<td>3.0±0.5 (2011 y)</td>
<td>0.9±0.2 [1]</td>
<td>-</td>
</tr>
<tr>
<td>E_9</td>
<td>17.95±1.35 (2012 y)</td>
<td>37.9 (2)</td>
<td>&lt;40 (2011 y)</td>
<td>&lt;120 (2012 y)</td>
<td>10.0±1.8 (2011 y)</td>
<td>9.8±0.8 (2011 y)</td>
<td>0.79±0.06 (2011 y)</td>
<td>1.0±0.1 (2011 y)</td>
<td>2040±318 (2012 y)</td>
</tr>
</tbody>
</table>

Table 2. Activity concentrations of $^{222}\text{Rn}$ [Bq/L] (both measured in this work and taken from literature for comparison), $^{226}\text{Ra}$ and $^{238,234}\text{U}$ [mBq/L] total uranium content [µg/L], $^{234}\text{U}/^{238}\text{U}$ and $^{222}\text{Rn}/^{238}\text{U}$ isotopic ratios in the investigated water samples from Mt. Etna.
The activity of $^{226}\text{Ra}$ was calculated as the weighted mean of the values obtained directly from the 186.2 keV line and the activities of $^{214}\text{Pb}$ (241.9, 295.2, 351.9 keV) and $^{214}\text{Bi}$ (609.3, 1120.3 keV) isotopes. The determination of the presence of $^{226}\text{Ra}$ and calculation of its activity was based on the following gamma-ray transitions: $^{212}\text{Pb}$ (238.6, 300.1 keV), $^{228}\text{Ac}$ (338.3, 911.1, 968.9 keV). $^{40}\text{K}$ was calculated from one 1460 keV line. The detection limit for radium measurements was 1 Bq/kg and 10 Bq/kg for potassium $^{40}\text{K}$.

3. Results and discussion

The results of the analyses of groundwater and volcanic rocks collected in the present survey for the detection of radionuclides are described in the following sections relatively to uranium isotopes, radium and radon and reported in Table 2 and corresponding figures.

3.1. Uranium

The activity concentrations for uranium isotopes varied from 1.5±0.5 mBq/L to 71.0±5.7 mBq/L for $^{238}\text{U}$ and from 2.0±0.6 to 78.6±5.7 mBq/L for $^{234}\text{U}$. A strong positive correlation (Pearson’s correlation coefficient $r=+0.99$) was observed between the concentration of $^{238}\text{U}$ and its daughter $^{234}\text{U}$. Moreover, a highly significant positive correlation ($r=+0.85$) between the total uranium content in water and TDS values was also noted. The highest total uranium ($^{234}\text{U}+^{238}\text{U}$) activity concentration was equal to 149.2±6 mBq/L, that is slightly higher than usual European values [Kozłowska et al. 2008, Walencik et al. 2012 and references herein]. Moreover, comparing the present results with uranium data published for 17 brands of drinking waters collected in the whole Italy one can state that they are comparable to the values obtained by Jia et al. [2009]. Our results confirm those of previous geochemical surveys of Mt. Etna groundwaters, underlining the important role both of uranium enrichment in water through rock leaching and of the redox state of the water in controlling the dissolution of uranium [Aiuppa et al. 2000]. This element is actually characterized by high mobility in the aqueous system under oxidized conditions, because it forms soluble o xo-hydroxocomplexes in its higher oxidation state (VI). Among the most common complexes in equilibrium with Mt. Etna waters are the uranyl-carbonates [Aiuppa et al. 2000]. This process would explain the highest uranium values found in this study. However, under more reduced conditions of waters, uranium can be scavenged by iron minerals and ferric oxyhydroxide, thus resulting to be depleted in those waters. This second process would explain the lowest uranium values found in our samples.

Interesting results were obtained for the $^{234}\text{U}/^{238}\text{U}$ activity ratios in the studied waters (Table 2, column 9), as they can be interpreted in terms of possible interference between groundwater and local precipitations (rain/melted snow) that easily percolate through highly permeable lava layers along major faults in the eastern flank of the volcano. The values varied in the range from 0.9±0.2 to 1.7±0.4, with values of arithmetic mean and median equal to 1.2 and 1.1, respectively. The results suggest achievement of secular equilibrium state for uranium isotopes (both arithmetic mean and median values are close to 1), rather than preferential leaching of $^{234}\text{U}$ (VI+) atoms from the mineral lattice of the host rocks, apparent for the disequilibrium state. Our results confirm a previous study performed for the Mt. Etna aquifers, where the highest value of $^{234}\text{U}/^{238}\text{U}$ was equal to 1.4±0.1 [Kozłowska et al. 2009]. As regards waters studied in the rest of Italy [Jia et al. 2009], the authors observed a slight disequilibrium between $^{234}\text{U}$ and $^{238}\text{U}$ activity concentration in most of the water samples, with mean isotopic activity ratios of 1.35±0.33. In the literature, groundwater flowing through rocks characterized by heterogeneous structure (e.g. presence of several deep faults and fractures) and where different weather conditions may also play a role, show $^{234}\text{U}/^{238}\text{U}$ values up to 30 [Osmond et al. 1983].

Plotting the $^{234}\text{U}/^{238}\text{U}$ ratio versus the inverse of total uranium content $1/\text{U}$ (expressed as l/µg) it is possible to infer processes that occur in waters in time. Groundwater characterized by constant $^{234}\text{U}/^{238}\text{U}$ values but variable contents of reversed uranium ($1/\text{U}$) in time is likely affected by mixing with other water devoid of uranium, such as, for example, fresh rainwater. Figure 2 presents the relation between $^{234}\text{U}/^{238}\text{U}$ and $1/\text{U}$ for some of our studied waters (i.e., those for which analyses were repeated twice or three times). The plot indicates only minor mixing between the selected groundwater samples and shallow infiltration waters, probably rainwater or surface runoff produced from melting of snow during early spring. Moreover, the variation of $1/\text{U}$ with time seems to be particularly evident only for the waters sampled at higher altitude (i.e., samples E_5 and E_7), thus confirming such hypothesis.

Besides activity concentrations, Table 2 presents also the results of uranium mass expressed in [µg/L], since the consumption limits are given in these units. In 2011, the World Health Organization (WHO) proposed a limit for $^{238}\text{U}$ in groundwater equal to 30 µg/L (0.19 Bq/L), based on the chemical toxicity of uranium as recommended by EPA [2000]. Our investigated waters are used for drinking purposes, so the calculation of the effective doses due to uranium absorption seems to be reasonable. Assuming a consumption of 2 L of water per day per person, based on the highest uranium activity con-
concentration measured in our samples one can calculate a yearly effective dose of 5.1 µSv, which is much below the proposed limit of 100 µSv/year [WHO 2011].

3.2. Radium and gamma background

All water samples analysed in this study showed activity concentrations of radium isotopes $^{226,228}$Ra below MDA. This is in apparent contrast with the general rule that high TDS values, such as those found in the investigated groundwater, correspond to high radium activity concentrations [Martín Sánchez et al. 1999, Dávila Rangel et al. 2002, Kralik et al. 2003, Godoy and Godoy 2006, Kozłowska et al. 2008]. On the other hand, activity concentrations of radium isotopes in other Italian waters [Jia et al. 2009] were also mostly below 10 mBq for both isotopes. Our previous hypothesis [Kozłowska et al. 2009] was that these results may point to a low radium content in the host rocks of Etna’s aquifers.

We performed gamma spectrometry measurements on rock samples collected in the vicinity of the water intakes sampled in this study. Activity concentrations of $^{226}$Ra varied from 45.5±2.2 Bq/kg to 85.2±4.4 Bq/kg, with average value of 61.8 Bq/kg. This value is almost identical to the median (61.4 Bq/kg), which confirms the normal distribution of the data. The activity concentration of $^{228}$Ra ($^{228}$Ac) varied from 28.8±0.9 Bq/kg to 67.7±2.6 Bq/kg, with average 53.3 Bq/kg and median 47.2 Bq/kg. The content of $^{40}$K in the studied samples varied from 331±15 Bq/kg to 725±35 Bq/kg. Our measured values, together with average values from other Italian magmatic rocks taken from literature for comparison, are presented in Figure 3.

Our study showed that the activity concentrations of $^{226}$Ra and $^{228}$Ra ($^{228}$Ac) found in the rocks of Mt. Etna are on the same levels as the average European values found in bedrock. IARC [1988] comprehensive studies concluded that $^{226}$Ra concentrations in soils span several orders of magnitude, but they are generally comprised between 10 and 50 Bq/kg, with an estimated average concentration of 25 Bq/kg. Similar values, from 10 to 100 Bq/kg, can be found in other publications [Cothren and Smith 1987, Nevissi and Bodansky 1987, Polanski 1988]. An average of 25.3 Bq/kg for $^{226}$Ra and of 24.4 Bq/kg for $^{228}$Ra can be found in soils of Poland [Radiological Atlas of Poland 2012]. By comparison, the Agency for Toxic Substances and Disease Registry reported on its web site concentrations of $^{226}$Ra in soils of northern Italy in the range 3-140 Bq/kg, excluding regions with extremely high levels of natural radioactivity.

Recently, Plant et al. [2003] stated that recent volcanic rocks such as those on Mt. Etna slopes, may be rich in uranium, which should result also in high radium contents. Chiozzi et al. [2001] published values of uranium levels in Lipari and Vulcano islands and Chiozzi et al. [2003] did the same for Stromboli, Salina, Filicudi and Panarea islands. These data were based on gamma spectrometric measurements of $^{214}$Bi line (1.76 MeV) or $^{208}$Tl line (2.62 MeV) so these results are representative of $^{226}$Ra or $^{228}$Ra radioactive decay, rather than that of uranium or thorium, for which radioactive equilibrium had to be assumed. Converting the results of Chiozzi et al. [2001, 2003] from ppm to Bq/kg, we obtain $^{226}$Ra values from 32 to 240 Bq/kg for Lipari and Vulcano and from 14 to 117 Bq/kg in the other volcanic islands of the Aeolian arc. Following the same procedure, we obtain $^{228}$Ra values in the range 37-268 Bq/kg.
for Lipari and Vulcano and 15-113 Bq/kg for the other Aeolian volcanoes.

Brai et al. [2002], using gamma spectrometry, investigated rock samples from Stromboli island obtaining similar results as those of Chiozzi et al. [2003] (226Ra values in the range 31-112 Bq/kg and 228Ra (from 228Ac line) values from 30 to 106 Bq/kg). It seems that the activity concentrations of 226,228Ra obtained for Mt. Etna rock samples in our study are very similar to the average results obtained for Stromboli, but slightly lower than those of Lipari and Vulcano. Volcanic products from the latter islands are richer in a wide variety of chemical elements, mostly silica, and hence they may be richer also in radioactive elements from the uranium chain, thus justifying the observed differences with Mt. Etna. This hypothesis is also supported by the results of D’Alessandro and Vita [2003], who found a significant positive correlation between median radon content in volcanic groundwater from several active volcanic areas of southern Italy (Mt. Etna, Vulcano, Pantelleria, Ischia) and the median total uranium content in the respective local reservoir rocks, with uranium being in turn more enriched in silica-rich volcanic rocks. As regards the apparent similarities between Mt. Etna and Stromboli, despite the two volcanoes are quite different in terms both of chemical composition of eruptive products and of styles of activity, these could be explained by a similar behaviour of Ra enrichment in the erupted fraction of the magmas from the two volcanoes by processes of magma formation, differentiation and eruption, as modelled by Capaldi et al. [1976], thus indicating similar pre-eruption histories for the magmas at both volcanoes.

In any case, the low radium activity in the groundwater of Mt. Etna would be explained mostly by the low affinity of this element for the aqueous environment, as radium tends instead to remain in the host rocks of the aquifers [Walencik et al. 2010]. Furthermore, as for uranium, the behaviour of radium in the aqueous environment is strongly controlled by redox conditions. Actually, under the typical Eh and pH conditions of groundwater of Mt. Etna, radium tends to form soluble Ra$^{2+}$ ions. However, in the presence of significant amounts of sulphate and/or carbonate ions in solution, insoluble complexes such as RaSO$_4$ or RaCO$_3$ are likely to form, thus removing radium from water. This process could be very efficient in the sampled waters, thus contributing to lower the contents of this element in solution.

3.3. Radon

The activity concentration of $^{222}$Rn varied from 2.91±0.36 Bq/L to 21.21±1.1 Bq/L. Obtained radon values are comparable to those of previous ground water surveys at Mt. Etna [D’Alessandro and Vita 2003, Kozłowska et al. 2009]. The variations in radon activity
observed within the presently analyzed waters cannot be simply explained by the different content of parent radionuclides in the Etna volcanic rocks, due to the rather homogeneous chemical composition of the latter, but rather they can be a result of different natural factors related to interaction between volcanic gases, water and volcanic rocks. The first is the enhanced water-rock interaction in the eastern flank of Etna that causes a strong release of major ions (described by TDS values) and hence of radon as a by-product of radium decay. This factor, however, seems to be effective only for some of the sampled waters. Figure 4 shows the correlation between values of dissolved radon and values of TDS in all of our samples. As evident from the plot, our samples show two distinct behaviors. In fact, samples E_1, E_5 and E_9 apparently show a much poorer correlation between radon activity in water and the corresponding TDS values than the rest of our samples. These three water samples come from the same aquifer, so the plot suggests an additional input of radon in the aquifer represented by these samples and therefore a radon source other than a simple dissolution of volcanic rocks. To study this, we plotted radon activity values versus the corresponding pCO₂ values in our water samples (Figure 5). Generally, the figure shows a correlation between the two parameters, indicating that radon activity in our sampled waters increases with increasing contents of dissolved CO₂. This evidence, therefore, supports the idea that radon is carried by magmatic CO₂ into the aquifers of the eastern flank of Etna, thus enriching water in both of these chemical species, and rules out the possibility of different radon/CO₂ ratios between the two group of samples highlighted in the plot of Figure 4. Therefore, a possible explanation for the higher-than-normal radon content in samples E_1, E_5 and E_9 is to assume that radon in these waters derives, if not solely at least in large part, from direct and strong input of magmatic gas in the aquifer in the proximity of these sampling sites. Actually, sites E_1 and E_5 are located very close to the Fiandaca Fracture Zone [Azzaro et al. 2012, De Guidi et al. 2012] and site E_9 is located very close to the Santa Venerina Fracture Zone [Azzaro et al. 2012, De Guidi et al. 2012], both being very active seismogenic faults. Therefore, it is reasonable to infer a large, CO₂-driven, radon release into local groundwater through active shallow rock fracturing along those major structural lines.

A specific discussion must also be made for site E_4, due to its peculiar characteristics. According to the above indications, the high amount of radon previously measured by other authors in the waters from this site (Rn = 43 Bq/L) [D’Alessandro and Vita 2003] would stem both from enhanced dissolution of volcanic rocks and from strong direct input of CO₂ gas into the aquifer, the latter testified by the very high pCO₂ values calculated for this water. However, it is worth noting from Figure 5 that at site E_4 the radon activity value that we measured is much lower than that expected according to the observed general correlation with pCO₂.
values. Actually, if we remove the point corresponding to this site, the general correlation is greatly improved ($r = +0.91$), thus suggesting some physical mechanism acting in the water from site E_4 that either leads to a removal of radon from solution or that hampers radon dissolution into the ground water at very high values of dissolved CO$_2$. The most reasonable explanation for this change in behavior is that the influx of the carrier gas (CO$_2$) in the ground water becomes so high that it overwhelms the shallow source of radon and thus dilutes it, so the gas entering the aquifer and dissolving into it has a much lower radon/CO$_2$ ratio. Actually, a similar process of radon dilution from high CO$_2$ flux was already observed by Giammanco et al. [2007b] in soil and fumarole gas emissions from Mt. Etna and by Bonfanti et al. [1995] in soil gas samples from South East Sicily. In our case, the “dilution” effect would start at values of pCO$_2$ higher than 0.2 atm (Figure 5).

Apart from the fact that the Mt. Etna waters can be treated as low radon activity waters, the values of the activity ratios $^{222}$Rn/$^{238}$U in waters (Table 2) varied in a wide range from 50±11 to 7856±1511. The obtained results indicated that $^{222}$Rn isotope was much better transported than $^{238}$U isotope.

4. Summary and conclusions

This paper presents the first full description of radionuclides ($^{234}$U, $^{238}$U, $^{226}$Ra, $^{228}$Ra, $^{222}$Rn) contents in groundwaters of the eastern flank of Mt. Etna volcano and of radioactivity background ($^{226}$Ra, $^{228}$Ra) in surrounding rocks. We studied nine groundwater samples from different local aquifers and eight rock samples from twelve localities altogether. Three groundwater samples were taken from water drainage galleries and six from water wells. All water intakes are used for drinkable purposes. Rock samples were assumed to represent the host rocks of local aquifers.

The present results confirmed those of a previous study performed on Mt. Etna [Kozłowska et al. 2009], taking into account a large number of aquifers, but with a much lower spatial density of sampling point in each aquifer. Activity concentrations of uranium isotopes $^{234,238}$U, radium isotopes $^{226,228}$Ra and radon $^{222}$Rn were determined with the use of different nuclear spectrometry techniques. Rocks surrounding the intakes were examined with gamma spectrometry.

Our new study showed that radionuclides levels in waters localized in the eastern flank of Mt. Etna are not different than the values obtained for the whole area of the volcano [Kozłowska et al. 2009]. Radionuclides are weakly leached by groundwater from the surrounding reservoir rocks, especially $^{226,228}$Ra that were at levels below MDA. The average $^{238}$U and $^{234}$U activity concentrations were 21.3 mBq/L and 22.7 mBq/L, respectively, whereas the average $^{234}$U/$^{238}$U activity ratio was equal to 1.2, thus proving achievement of secular equilibrium for uranium isotopes. Furthermore, all waters may be classified as low-radon waters, with maximum activity concentrations of 19.2 ± 0.8 Bq/L.

Gamma spectrometry studies of the rock samples...
collected in the vicinity of water intakes showed $^{226}$Ra and $^{228}$Ra mean values equal to 61.8 and 53.3 Bq/kg, respectively. These values are slightly lower than those of volcanic rocks from other active volcanoes in this geographic area.

References


EPA (2000). Environmental Protection Agency, National Primary Drinking Water Regulations; Radionuclides; Final Rule, Federal Register, 65 (236), December 7.


Jia, G., G. Torri and L. Magro (2009). Concentrations of $^{238}$U, $^{234}$U, $^{235}$U, $^{232}$Th, $^{230}$Th, $^{228}$Th, $^{226}$Ra, $^{228}$Ra, $^{224}$Ra, $^{210}$Po, $^{210}$Pb and $^{212}$Pb in drinking water in Italy: reconciling safety standards based on measurements of gross $\alpha$ and $\beta$, J. Environ. Radioact., 100, 941-949.


