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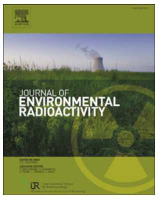

Gamma-spectrometric measurement of radioactivity in agricultural soils of the Lombardia region, northern Italy

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ABSTRACT

This work is part of a wider monitoring project of the agricultural soils in Lombardia, which aims to build a database of topsoil properties and the potentially toxic elements, organic pollutants and gamma emitting radionuclides that the topsoils contain. A total of 156 agricultural soils were sampled according to the LUCAS (Land Use/Cover Area frame statistical Survey) standard procedure. The aim was to provide a baseline to document the conditions present at the time of sampling. The results of the project concerning soil radioactivity are presented here. The aim was to assess the content of ^{238}U, ^{232}Th, ^{137}Cs and ^{40}K by measuring soil samples by gamma spectrometry.

^{238}U, ^{232}Th and ^{40}K activities range 24–231, 20–70, and 242–1434 Bq kg^{-1} respectively. The geographic distribution of ^{238}U reflects the geophysical framework of the Lombardia region: the soils with high content of uranium are distributed for the most part in the South Alpine belt, where the presence of magmatic rocks is widespread. These soils show an higher activity of ^{238}U than of ^{232}Th. The ^{238}U activities become lower than ^{232}Th when soils are located in the plain, originating from basic sedimentary rocks.

^{137}Cs activity ranges 0.4–86.8 kBq m^{-2}. The lowest activity of ^{137}Cs is in the plain, whereas the highest is in the North on soils kept as lawn or pasture. The ^{137}Cs activity of some samples suggests the presence of accumulation processes that lead to ^{137}Cs enriched soils.

This is the first survey of gamma emitting radionuclides in Lombardia that is based on the LUCAS standard sampling. The results from this monitoring campaign are important for the human radiation exposure and provide the zero point, which will be useful for assessing future effects due to external factors such as human activities.

1. Introduction

There is an increasing demand for soil data and information from policymakers to assess the state of soils at both the national and international levels. Agricultural soils are of special concern because they pose a direct threat to human and environmental health. To meet this demand, "Regione Lombardia" gave a mandate to the Università Cattolica del Sacro Cuore (UCSC) in Piacenza and to the Joint Research Centre – Institute for Environment and Sustainability (JRC-IES) in Ispra in 2011 to assess the quality of agricultural soils in the Lombardia region through a three-year environmental monitoring program: the "Soil Mapping" project.

Agricultural topsoils in Lombardia have been sampled and analysed to determine their main properties and for potential toxic elements, organic pollutants and gamma-emitting radionuclides. These analyses were complemented by biological analyses in the second phase of the project. The survey represents the first effort in Lombardia to build a database of topsoil properties based on standard sampling and analytical procedures (JRC, 2013).

This work presents the part of the project that concerns the radioactivity of the soils. The main aim of this survey was to assess

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the content of the natural and anthropogenic radionuclides ^{238}U, ^{232}Th, ^{40}K and ^{137}Cs by measuring soil samples by gamma spectrometry. Monitoring of radioactivity in the environment is important for human and environmental protection and provides a baseline of environmental radioactivity levels.

Various surveys of anthropogenic and natural radionuclides in the soils of Lombardia have been carried out for determining radon risk, due to soil emissions and to building materials and to check for compliance with European and Italian rules in the years since the Chernobyl accident in 1986 (ARPA Lombardia, 2003, 2006; Cardinale et al., 1972; Busuoli et al., 1984; Sciocchetti et al., 1984; Campos Venuti et al., 1988; Facchini et al., 1992; Bochicchio et al., 1999). However systematic data on natural and anthropogenic radioactivity of soils in Lombardia are scarce. Baseline radioelement data are increasingly being used in decision making processes relating to land use, the environment, agriculture and public health. They are essential for policy makers and regulatory agencies, for the human radiation exposure and the formulation of sound environmental policies. This is the first survey on gamma emitting radionuclides in Lombardia, which is based on LUCAS (Land Use/Cover Area frame statistical Survey) standard sampling (EUROSTAT, 2000). The aim is of contributing to, and establishing a baseline map to document the conditions present in 2011 and to scientifically assess future effects due to external factors such as human activities.

2. Materials and methods

2.1. The survey location and its geological context

Lombardia region covers an area of 23 834 km^2 in North Italy (Fig. 1). It borders with Swiss to the North and extends southwards to the Po river, is limited by Lake Maggiore and Ticino river to the west and by Lake Garda and Mincio river to the east. It is characterized by a succession of different geological and structural areas which are from North to South: Alps, Southern Alps, Po Plain and northern Apennines. 40.5% of the territory is mountainous, mainly located in the northern area, 12.4% is hilly and 47.1% is flat located in the south. A minor mountainous area lies south of the Po in the Apennines range. The region is characterized by the presence of lakes of glacial origin and is crossed by several water courses, among which the Po river, which gives its name to the Po Plain.

Geological maps show that, in the Alps belt, metamorphic basements display almost everywhere an Hercynian overprint and evidences of volcanic activity. Along the Periadriatic Lineament it is possible to recognize polyphase metamorphic complexes, widely intruded by plutonic bodies whose chemical composition shows a temporal progression from peraluminous to calcalkaline and finally high-K calc-alkaline character (APAT, 2004). Magmatic rocks, belonging to high-K calc-alkaline, to shoshonitic and ultrapotassic series present anomalous high values of U. The areas where these

Fig. 1. Geographical position of the Lombardia region in Europe.

rocks crop out are often characterized by high natural radiation background (Taylor and McLennan, 1995). Being uranium in soils due to the breakdown of rocks containing it, those soils derived by the weathering of uranium bearing rocks or minerals will present high values of uranium.

In the Lombardia region several uranium deposits contained in the tuffs of the series of Collio (Permo-Carboniferous) had been noted since the sixties in Alta Val Seriana. The areas more studied for economic purposes are located within the province of Sondrio (Val Vedello) and the province of Bergamo, on the south-western side of the Val Goglio (Novazza) (http://www.energiaminerals.com/italy/novazza-and-val-vedello-projects.html).

The Po Plain is characterized by quaternary deposits mainly made up of loose material with granulometry varying from gravel to sand and silt. According to Sesana et al. (2005) the following formations are present: (i) an older formation dating to the early Pleistocene, made up of the würmian fluvioglacial and fluvial formation, generally characterized by gravel and sand sediments; (ii) a more recent one, mainly lying along the present river courses, consisting of the fluvial deposits of the Holocene and which is mainly made up of gravel, sand, silt and clay (Sesana et al., 2005).

2.2. The survey design

The target population of this project was represented by the agricultural soils distributed over the whole area, including both croplands and grasslands. In the context of the LUCAS program croplands include: cereals, root crops, non-permanent industrial crops, dry pulses, vegetables and flowers, fodder crops, permanent crops, while grasslands include: pastures under sparse tree or shrub cover, grassland without tree/shrub cover, spontaneously re-vegetated surfaces. The soils to be examined were selected from the pre-existing network of LUCAS geo-referenced points (EUROSTAT, 2000) by the JRC-IES in the framework of a wider project which covered the whole Europe. A multi-stage stratified random sampling scheme based on land use and terrain information was adopted (McKenzie et al., 2008; cited by Carré et al., 2013). Details of the methodology for the selection of soil sampling sites are given in the JRC Technical Report (2013). This approach allowed the selection of sampling locations proportional to the agricultural land use, taking into account that LUCAS survey does not cover areas above 1000 m in elevation.

The sampling points resulting from the random selection were reduced to 156 by expert judgment, in a perspective of efficiency to optimize time and costs (ICRU, 2006). The final mean density of the sampling points was around one sample per 153 km^2.

2.3. The sampling points

The sampling team was provided with a triplet of points suitable for sampling, whose geodetic datum was the European Terrestrial Reference System 1989 (ETRS89) (Annoni et al., 2001, cited by EUROSTAT, 2005). In order to make either the tracking with common GPS devices and the exchange of information much easier, the sampling team decided to refer to the World Geodetic System Datum 1984 (WGS-84) by using the Transdat software (Killet Software Ing.-GbR).

A triplet is a group of three LUCAS points that have common properties such as slope, aspect and land cover. The triplet concept was established by LUCAS project to hold alternative locations for the surveyor to collect a soil sample should the initial point designated not be physically accessible (Carré et al., 2013). One of the three references chosen by the surveyors became the theoretical point of sampling. In the case of inability to sample at that predetermined location, the sampling team selected a nearby location, considering that the target soil had to be an agricultural land or a land interested by agricultural activity in the past, even in problematic areas as hills and mountains. The actual sampling point was tracked and reported, along with sampling details and a description of the area. The sampling campaign was carried out between September 2011 and half June 2012.

2.4. The sampling units

The sampling units were arbitrarily sized to have a mass to be easily processed and measured. Each sampling location was considered as being overlaid by a 20 × 20 m grid, subdivided in 25 cells of 4 × 4 m. An example of one of the possible randomizations is reported in Fig. 2.

Fifteen soil cores of 5.3 cm^2 × 30 cm were sampled in 15 cells selected by a random process. The 30 cm depth was chosen to cover the soil portion interested by the agricultural practices. The 15 cores were mixed and homogenized in field to meet a composite sample before analysis. Each sampling unit can be seen as cluster of fifteen points, corresponding to an actual area of 8.0×10^{-3} m^2 and a volume of 2.4×10^{-3} m^3. Stones, vegetation and other coarse material were removed in the field during the sampling procedures (Cenci, 2008).

Once in the laboratory the soils were oven dried at 40 °C until constant weight, disaggregated to pass through a 2 mm sieve, homogenized and then divided into two subsamples to be also sent to chemical analyses.

2.5. The analytical procedure

1.2 kg of the sieved soil was introduced in 1 L Marinelli beaker for analysis. ^{238}U and ^{232}Th (analyzed via their daughters), ^{137}Cs and ^{40}K were determined by direct gamma-spectrometry using a coaxial HPGe detector with relative efficiency (at 1.33 MeV of ^{60}Co) of 38% and a resolution (FWHM at 1.33 MeV of ^{60}Co) of 1.76 keV. The peak -to- Compton ratio calculated for the 1.33 MeV photopeak of ^{60}Co is 70.8. The software used by the spectrometry chain is the Genie 2000 of the Canberra Nuclear.

The efficiency calibration was experimentally determined for 1 L measuring geometry through certified source (density of 1.0 g cm^{-3}) containing gamma emitters of energy from 88 to 1836 keV. Each sample was measured for 60 000 s. The background was determined using both a Marinelli filled with 1 L of distilled

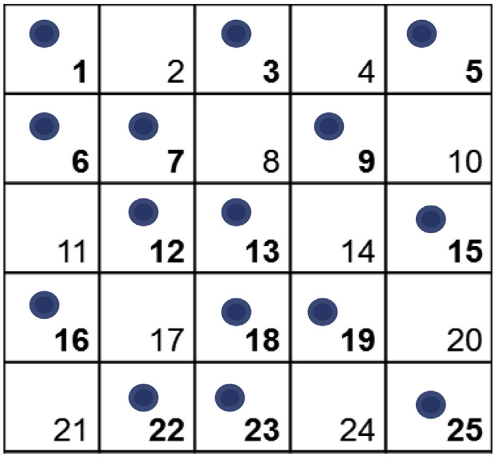

Fig. 2. Conceptual diagram of the 20 × 20 m grid subdivided in 25 cells, from which 15 (shown by spots) were selected randomly for sampling.

water and an empty one under identical measurement conditions. Intercomparisons for gamma-spectrometry were carried out with the Joint Research Centre (JRC) in Ispra.

The following radionuclides were measured:

2.5.1. ^{232}Th-series

The gamma emitting radionuclides ^{228}Ac (911.07 keV) and ^{212}Pb (238.63 keV) were used for analysis in soil samples. These radionuclides also gave information whether secular equilibrium was present, or not, within the decay chain for ^{228}Ra (^{228}Ac) and ^{228}Th (^{212}Pb). Within the uncertainty of the measurement, the radionuclides were found to be in equilibrium. Equilibrium of naturally occurring radioisotopes measured by gamma spectrometry is common in rocks older than 10^6 years, and the ^{232}Th series may be considered in equilibrium in most geological environments (Chiozzi et al., 2002). The average value for the activity ratio ^{228}Ra/^{228}Th was 1.06 ± 0.06. The activity concentrations of ^{228}Ra and ^{228}Th were therefore combined to give the ^{232}Th value.

2.5.2. ^{238}U-series

The analysis of ^{238}U by gamma spectrometry relies on the hypothesis of equilibrium conditions between parent nuclide ^{238}U and short-lived daughters ^{234}Th and ^{234m}Pa. The gamma-ray emitting radionuclides ^{234m}Pa (1000.9 keV), ^{214}Pb (295.2 keV) and ^{214}Bi (1764.5 keV) were used for analysis. The average value for the activity ratio ^{214}Bi/^{214}Pb was (0.96 ± 0.06). ^{226}Ra was therefore estimated combining the activity concentrations of ^{214}Pb and ^{214}Bi to give the ^{226}Ra value. However it was not possible to check if radionuclides are in secular equilibrium between the upper part of the decay chain given by ^{238}U (^{234m}Pa) and the bottom given by ^{226}Ra (^{214}Pb and ^{214}Bi), because samples in the Marinelli beaker were not hermetically sealed, to ensure the equilibrium between ^{226}Ra and ^{222}Rn and their decay products. The average value calculated for the activity ratio of ^{226}Ra/^{234m}Pa was 0.59 ± 0.23. Therefore only ^{234m}Pa data (1001.0 keV) were used further for representing the ^{238}U-series.

2.5.3. ^{235}U

The most predominant gamma transition 185.7 keV (57.2%) was used to measure the ^{235}U. Around ten percent of soil samples showed an activity concentration for ^{235}U lower than the minimum detectable activity: 0.14 Bq kg^{-1}. The average ratio of the ^{235}U to the ^{238}U activities is of 0.055.

2.5.4. ^{40}K

^{40}K was determined by measuring the gamma transition at 1460.8 keV.

2.5.5. ^{137}Cs

^{137}Cs was determined by measuring its gamma ray key line at 661.6 keV. The ^{137}Cs measured activities were decay corrected to the reference date 21st September 2011, the date of starting of gamma analyses.

The radionuclide concentration was expressed as Bq kg^{-1} dry soil. Only for ^{137}Cs, were data also expressed as Bq m^{-2} (Table 1). Bq kg^{-1} values were converted to Bq m^{-2} by the area and volume of the sampled unit and in the hypothesis that the average soil bulk density is $d = 1.2$ g cm^{-3}: Bq m^{-2} = Bq kg^{-1} × 360.0 kg m^{-2}.

The activity concentrations of ^{238}U, ^{232}Th and ^{40}K were then converted into concentrations of U, Th and K respectively (Table 2) according to the following relations (IAEA, 1989):

$$1\ \text{Bq}\ ^{238}\text{U kg}^{-1} = 81 \times 10^{-3}\ \text{mg U kg}^{-1}$$
$$1\ \text{Bq}\ ^{232}\text{Th kg}^{-1} = 246 \times 10^{-3}\ \text{mg Th kg}^{-1}$$
$$1\ \text{Bq}\ ^{40}\text{K kg}^{-1} = 3.2 \times 10^{-3}\ \%\ \text{K}$$

Table 1
Concentration of ^{235}U, ^{238}U, ^{232}Th and ^{40}K, expressed as Bq kg^{-1} dry soil, for 156 soils of Lombardia region. SD = standard deviation.

	^{235}U (Bq kg^{-1})	^{238}U (Bq kg^{-1})	^{232}Th (Bq kg^{-1})	^{40}K (Bq kg^{-1})
Arithmetic mean ± SD	4.8 ± 2.2	79 ± 31	48 ± 8.9	640 ± 150
Geometric mean	4.4	73	47	623
Geometric standard deviation	1.5	1.4	1.2	1.3
Median value	4.6	72	48	617
Range	1.2–20	24–231	20–70	242–1434
UNSCEAR (2000, Annex B)	–	35	30	400

These relationships are also valid for any daughter in the ^{238}U or ^{232}Th chain only if the chain is in equilibrium.

2.6. The correction factors

Despite the care taken in sample collection, some soil sample did not reach the volume of 1 L (mass of 1.2 kg) corresponding to the nominal height (h_0) of calibration. To adhere to the geometry of 1 L, correction factors (C_h) were empirically derived for the peaks at 661.7 keV of ^{137}Cs and 1460.8 keV of ^{40}K.

C_h is usually expressed as the ratio of spectrometer efficiency for the nominal sample height $\varepsilon\,(h_0)$ to the one obtained for the actual sample height $\varepsilon\,(h)$ (Jodłowski, 2007):

$$C_\text{h} = \varepsilon(h_0)/\varepsilon(h)$$

This works on the basis that this ratio is fairly constant above 400 keV (Debertin and Helmer, 1988). The efficiencies for the various sample heights $\varepsilon(h)$ were derived from the experimental efficiency calibration through a semi-empirical model as follows. In addition to the nominal sample, seven measurement geometries (h_i) were considered, where i corresponds to the soil mass of 0.50, 0.85, 0.90, 1.00, 1.05, 1.10, 1.15 kg. Gamma ray spectrometry measurements were performed for each of the geometries. Sample heights were the same as in spectrometry measurements.

Results were expressed as Bq kg^{-1} (h_0) for the nominal sample and Bq kg^{-1} (h_i) for the actual samples. Their values prove that the measured activity varies linearly with the sample height, in the range of mass and for the activity under study, showing a determination coefficient $r^2 = 0.994$.

Correction factors were then calculated as:

$$C_\text{h} = \text{Bq kg}^{-1}(h_0)\Big/\text{Bq kg}^{-1}(h_i)$$

where the sample material was less than 1.2 kg, to account for the difference in the height of the sample, the results from the gamma spectrometry were corrected as follows:

$$\text{Bq kg}^{-1}(h_0) = C_\text{h} \times \text{Bq kg}^{-1}(h_i)$$

3. Results and discussion

The object of this monitoring work was to ascertain the presence and the concentration of ^{238}U, ^{232}Th, ^{40}K and ^{137}Cs

Table 2
Concentrations of U, Th and K in 156 soils of Lombardia region.

U (mg kg^{-1})	Th (mg kg^{-1})	K (%)
6.4 ± 2.5	11.7 ± 2.2	2.07 ± 0.5

radionuclides in the agricultural soils of Lombardia, thereby providing baseline documentation of the conditions in 2011. The activity measured in soil samples expresses the average values of the radionuclides in the 0–30 cm layer, regardless of their distribution along the soil profile. All activity concentration values are associated with geographical points, each of which represents a 20 × 20 m^2 area.

3.1. ^{238}U, ^{232}Th, and ^{40}K spatial distribution

The activity concentrations of ^{235}U, ^{238}U, ^{232}Th and ^{40}K in soils, expressed as Bq kg^{-1} dry soil, are summarized in Table 1. The values of arithmetic and geometric mean, the median value and the range are reported.

The activity concentrations of ^{235}U will be omitted from here on, and ^{238}U activities will be used to illustrate results for uranium. The range of activities for ^{238}U varies of an order of magnitude, from 24 to a maximum of 231 Bq kg^{-1}. The frequency distribution of ^{238}U activities shows a lognormal trend with a tail shifted towards high values, where the median value of 72 Bq kg^{-1} for ^{238}U is closer to the geometric than to the arithmetic mean.

The ^{232}Th activities range from 20 to a maximum of 70 Bq kg^{-1} and show a normal frequency distribution. They are in general lower than ^{238}U activities, except for 13 samples, which are all located in the Po plain.

De Capitani and coworkers have measured natural radionuclides in the central sector of the southern alpine domain of Lombardia, not in the soils but in rock outcrops (De Capitani et al., 2007). They report values from 18 to 86 Bq kg^{-1} for ^{238}U and from 30 to 80 Bq kg^{-1} for ^{232}Th. Soil activities of our project agree with ^{232}Th values, but not with ^{238}U values. The Authors also comment on that intrusive acid rocks, such as granites, exhibit activities of ^{238}U only slightly higher than the ^{232}Th activity, while the opposite occurs in more basic rocks (De Capitani et al., 2007). This can explain the results from our work showing, as mentioned above, that for 13 soils located in the plain the ^{232}Th activity is higher than ^{238}U activity. One can assume that those soils in the plain originate from basic sedimentary rocks. Their pH ranges from 6.7 to 8.7, but no correlation is shown between ^{238}U content and soil pH.

The activity concentrations of ^{40}K are always higher than those of ^{238}U and ^{232}Th and range from 242 to 1434 Bq kg^{-1} (Table 1). The ^{40}K frequency distribution shows a short tail to the right. The Kolmogorov–Smirnov test demonstrates that the distribution does not deviate significantly from either a normal or a lognormal distribution, observation also made by other authors (Bunzl et al., 2000). Measures of ^{40}K activities in rock outcrops show values ranging from 431 to 1479 Bq kg^{-1}, higher than those found in our project (De Capitani et al., 2007).

The median values of ^{238}U and ^{232}Th series and of ^{40}K, 72, 48 and 617 Bq kg^{-1} respectively, are higher than the worldwide median values corresponding to 35, 30 and 400 Bq kg^{-1} respectively (UNSCEAR, 2000a,b) (Table 1).

A wide spatial dispersion of high and low activity for both ^{232}Th and ^{40}K can be observed both in the mountainous and plain regions. For ^{238}U instead, the areas at highest activity can be identified mostly in the North of the region, between the South Alpine belt and the plain. The range of variation of ^{238}U is higher than that of ^{232}Th and of ^{40}K and the frequency distribution shows a first mode around 55 Bq kg^{-1} and a second one around 105 Bq kg^{-1}. This variability indicates that the sampling areas are not situated on the same geological substrate, as predictable from the succession of mountain, hill and plain scenarios in Lombardia region. The most represented classes of ^{238}U are soils with activities lower than 100 Bq kg^{-1}, the 75th percentile, and the values of the highest frequency class range from 50 to 62 Bq kg^{-1}.

The 156 geo-referenced points, accompanied by the ^{238}U activity concentration in Bq kg^{-1}, are reported on a map of the Lombardia region (Fig. 3). The 95th percentile of the frequency distribution of ^{238}U identifies eight soils with the highest activity at 129–231 Bq kg^{-1}. The analysis of their geographic location shows that they are distributed for the most part in the South Alpine belt, with some few points in the plain.

The highest ^{238}U activity, 231 ± 44 Bq kg^{-1}, is from an area south of Lake Maggiore in Varese province. Geologic maps show a morein of the würmian period, with porphyritic formations, effusive magmatic rocks, typical of Varese area (Carta Geologica d'Italia, 2011). This sampling area is located approximately 10 km from Angera (Varese province), that is classified among the high radon areas in Italy (Facchini et al., 1992; Bonetti et al., 1992 cited by Sesana et al., 2005; Bochicchio et al., 1999).

The second highest sample for ^{238}U activity, 177 ± 52 Bq kg^{-1}, comes from Songavazzo in Bergamo province, at the foots of Alps Orobie. Geologic maps show a gravel fluvioglacial lithotype with marly limestones and bituminous shales. Only twenty kilometers farther, is located Novazza, one of those areas in Southern Alps investigated for the presence of uranium-rich ores in the seventies. Furthermore previous studies carried out by ARPA Lombardia reported an ^{238}U activity concentration of 160 ± 20 Bq kg^{-1} on the opposite side of the valley (Valtellina), at Chiesa Valmalenco; this value agrees with our results (Forte et al., 2001). Other measures on radon concentration in Valtellina also show quite high values in towns along the Insubrica fault (Facchini et al., 1992).

High activity concentrations of ^{238}U are also observed somewhere in the plain, in areas characterized by alluvial and Aeolian deposits and travertines from Pleistocene, locally up to Holocene. The east side of the Lombardia plain was previously investigated through indoor surveys, which indicated that the area to the North, towards the hills of Bergamo and Brescia, has higher radon concentrations than the area to the South (Sesana et al., 2005). However the areas identified in the present study are located in completely flat areas, such as the southern part of Mantova province. It is known that uranium is more soluble than thorium and can be leached from rocks and soils under certain weathering and ground conditions and deposited in sediments some distance away. High activities in the plain can be ascribed to the erosion and transport processes undergone by rich in uranium magmatic rocks and producing the sediments, sands and gravels that make the soils of the plain. Therefore it should not be unespected to find differences in radioelement concentrations between fresh bedrock, weathered regolith, and transported material (IAEA, 2010).

Other authors investigated natural radioactivity in Lomellina, a Southwestern region of the Lombardia. The soil, undisturbed for 30 years, shows an activity concentration of 48.0 ± 4.2 and 48.1 ± 5.5 Bq kg^{-1} for ^{238}U and ^{232}Th respectively. These values were determined by neutron activation analysis (Borroni et al., 1989). Our results from soil samples in the same area, south Pavia province, show higher agreement for ^{232}Th activity, 30–50 Bq kg^{-1}, than for ^{238}U activity, 50–80 Bq kg^{-1}.

Correlations among the measured radionuclides were investigated. No evidence of correlation between ^{238}U and ^{232}Th was found, nor between ^{238}U and ^{40}K. A weak correlation was instead evident between the activity concentrations of ^{238}U and ^{235}U, as expected, with a correlation coefficient $r^2 = 0.3$, and between ^{232}Th and ^{40}K, with $r^2 = 0.2$.

De Jong and coworkers refer to a correlation between the natural radionuclides and clay content of the parent material of Saskatchewan soils, in Canada (De Jong et al., 1994). The results of this project only confirm a positive correlation of ^{40}K with clay content

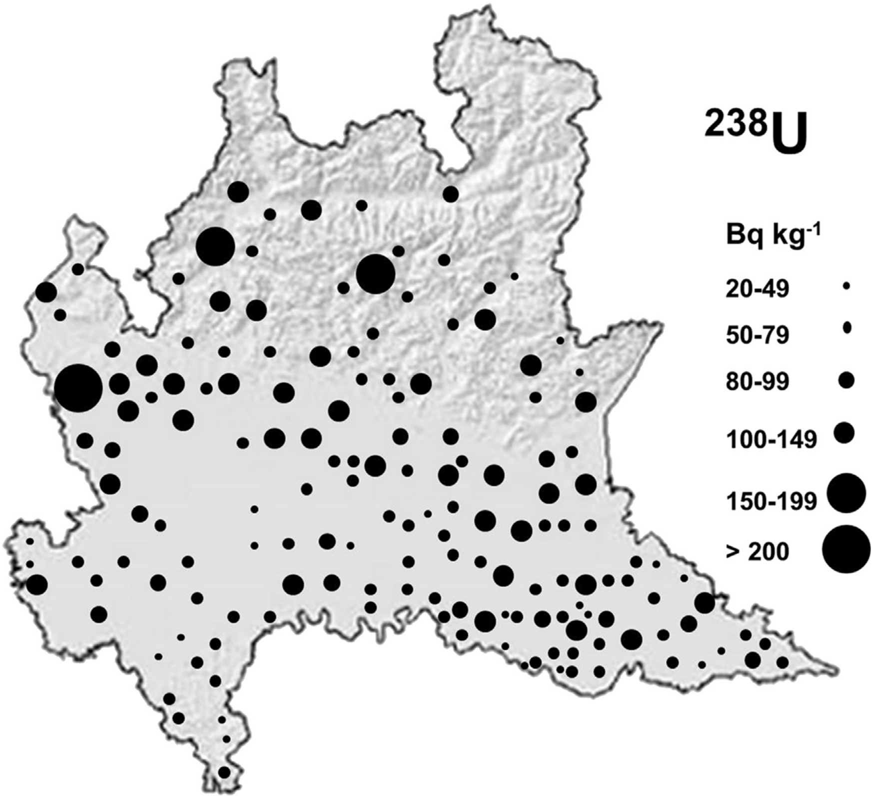

Fig. 3. Geographic distribution of ^{238}U in Lombardia region, expressed as Bq kg^{-1}.

and a negative correlation with sand content; however, neither is significant. Furthermore a positive weak correlation of ^{232}Th with silt is evident, with $r^2 = 0.2$. It has to be noticed that our results are on soils and, as commented on by de Jong and coworkers, the radioactivity of soils is largely affected not only by the mineral composition of the parent material, but also by the extent of weathering and leaching under different climatic conditions (Graham, 1964; Talibudeen, 1964; Osburn, 1965, cited by De Jong et al., 1994). It must also be remembered that this project deals with agricultural soils, that can be affected by farming practices such as the addition of potassium and phosphate fertilizers, that can bring traces of ^{40}K, ^{238}U and ^{232}Th to the soil.

Correlations were also investigated between the measured radionuclides and the trace elements content of soils. Various correlations were found between ^{232}Th and Ti, $r^2 = 0.55$, Al, $r^2 = 0.55$, Fe, $r^2 = 0.29$, Be, $r^2 = 0.23$ and Se, $r^2 = 0.30$. Negative correlations between ^{232}Th and Ca, $r^2 = 0.20$ and K, $r^2 = 0.11$. The ^{238}U activity concentration shows a weak correlation with Mo, $r^2 = 0.22$, with Pb, $r^2 = 0.11$ and with Tl, $r^2 = 0.10$. Other sources confirm that uranium in rocks is chemically associated with significant amounts of molybdenum (http://www.vivisulserio.it/content/view/120/65/).

The elemental contents of U, Th and K in these soils show that values are lower for U, 6.4 ± 2.5 mg kg^{-1}, than for Th, 11.7 ± 2.2 mg kg^{-1}. U and Th occur as trace elements in the rocks. Their crustal abundance or Clarke value corresponds to 2.30 (0.6–4.8 mg kg^{-1} for U) and 8.10 mg kg^{-1} (2.2–17 mg kg^{-1} for Th) respectively (Fortescue, 1992, cited by De Capitani et al., 2007). These values, in particular the U values, are lower than those calculated in this project. As before mentioned some magmatic rocks present high anomalous values, for example granitoids show a content of 4–5 mg kg^{-1} for U (Taylor and McLennan, 1995; APAT, 2004). And local concentrations of U can far exceed these values ranging up to 50 mg kg^{-1} disseminated in some granites, to much higher values in ore deposits.

The value of K average concentration in these soils is 2.07 ± 0.5%, value that agrees with the crustal abundance or Clarke value of 1.84% (Fortescue, 1992). Percentages of K ranging from 0.08 to 5.14% are reported in rocks in North Italy along the Alps–Apennines transition (Chiozzi et al., 2002). The percent K in the soils of this project, calculated by the 0.012% of ^{40}K in the earth's crust, corresponds to 0.163–4.51%, values that fall in the range measured by Chiozzi and co-workers (2002).

3.2. ^{137}Cs inventory

The concentration of ^{137}Cs in soils has been expressed as specific activity both in kBq m^{-2} and in Bq kg^{-1} dry soil. ^{137}Cs is detectable in all of the analysed samples. The values show a wide variability, ranging from a minimum of 0.4 to a maximum of 86.8 kBq m^{-2}. The position indexes for ^{137}Cs, expressed as kBq m^{-2} and Bq kg^{-1}, are reported in Table 3.

Table 3
Position indexes for ^{137}Cs activity, expressed both as kBq m^{-2} and as Bq kg^{-1} dry soil, for 156 soils in September 2011. SD = standard deviation.

Parameter	kBq m^{-2}	Bq kg^{-1}
Arithmetic mean ± SD	9.0 ± 10.4	25.0 ± 29.0
Geometric mean	5.8	16.2
Geometric standard deviation	2.5	2.5
Range	0.4–86.8	1.1–241.0
Mode	3.0	8.3
25th percentile	2.9	8.0
50th percentile/Median	5.1	14.3
75th percentile	11.9	33.0
95th percentile	27.7	77.0

The arithmetic mean (9.0 kBq m^{-2}) does not match the median (5.1 kBq m^{-2}) or the mode (3.0 kBq m^{-2}), indicating that this is a non-normal distribution. The curve must have a tail to the right because the median is lower than the mean. The analysis of the frequency distribution shows a lognormal trend, as expected when the value of the median (5.1 kBq m^{-2}) is closer to the geometric (5.8 kBq m^{-2}) than to the arithmetic mean (9.0 kBq m^{-2}), as commented on by other researchers (Blagoeva and Zikovsky, 1995).

This trend is confirmed by the Kolmogorov–Smirnov (K–S) test, which shows that the distribution significantly deviates from a normal one ($p < 0.05$). The same K–S test performed on the log-transformed data, log kBq m^{-2}, shows that the distribution does not significantly deviate from a normal distribution ($p > 0.05$).

The most represented classes of soils are those with values lower than 10 kBq m^{-2} (Fig. 4). This is confirmed by a 75th percentile value of 12 kBq m^{-2}. The values of the highest frequency class range from 2 to 4 kBq m^{-2}, as confirmed by a mode of 3 kBq m^{-2}. The median corresponds to 5 kBq m^{-2}. The 95th percentile value of 28 kBq m^{-2} identifies seven outliers, with the highest activity, at 30.8–86.8 kBq m^{-2}.

Historically ^{137}Cs in soils derives partly from the testing of nuclear weapons in the atmosphere from 1945 to 1980 and partly from the Chernobyl accident in 1986. The deposition density of ^{137}Cs from nuclear weapons was estimated to be approximately 5.2 kBq m^{-2} at 40°–50° North latitude at the end of the 1970s, which decay corrected to 2.5 kBq m^{-2} by September 2011 (UNSCEAR, 1982, 2000 Annex C). The mean ^{137}Cs deposition density over northern Italy from Chernobyl was estimated to be 10 kBq m^{-2} in 1986, which decay corrected to 5.6 kBq m^{-2} by September 2011. From the above findings, the average value for ^{137}Cs in soils of northern Italy can be mathematically estimated to be approximately 8 kBq m^{-2} at September 2011. The data on the averages obtained in this work are in good agreement with the historical data, showing an arithmetic mean of 9.0 ± 10.4 and a geometric mean of 5.8 kBq m^{-2} (Table 3).

The 156 geo-referenced points, accompanied by the ^{137}Cs activity density in kBq m^{-2}, are reported on a map of the Lombardia region (Fig. 4). The region shows the lowest concentrations of ^{137}Cs prevailing in the Po Plain in the South, lower than 7 kBq m^{-2}, and the highest concentrations in the Alps and Southern Alps in the North, at 22–87 kBq m^{-2}. It is known that ^{137}Cs from nuclear weapon tests was injected into the stratosphere and was deposited quite homogeneously with respect to latitude. In contrast, ^{137}Cs from Chernobyl was released into the troposphere, and its deposition exhibited very high spatial variability, concentrating in those geographical areas subject to abundant meteoric precipitations, particularly in the Alpine valleys (Bossew et al., 2001; Lettner et al., 2006).

The area in the North includes the seven soils with the highest ^{137}Cs activity: 30.8–86.8 kBq m^{-2}. They are located from the right side of Lake Maggiore to the western side of Lake Como in the province of Lecco at 200–600 m above sea level. These soils are kept as lawn or pasture and are classified as grasslands in the CORINE LANDCOVER 2000 dataset (APAT, 2005). Their activity reflects the measurements reported after the Chernobyl accident of 23–56 kBq m^{-2} in the area around Lecco and 11–23 kBq m^{-2} in the areas of Como, Lugano and Varese (De Cort et al., 1998; Forte et al., 2002; ARPA Lombardia, 2006).

However the activity in the literature does not explain the highest activity density of 86.8 kBq m^{-2}, which was measured in a sample in Como Province (Fig. 4). The information registered by the operator describes an organic, humid soil in a foothill area. The chemical analyses confirm the high content of organic matter: 17.7%. It is known from the literature that nutrient cycling and

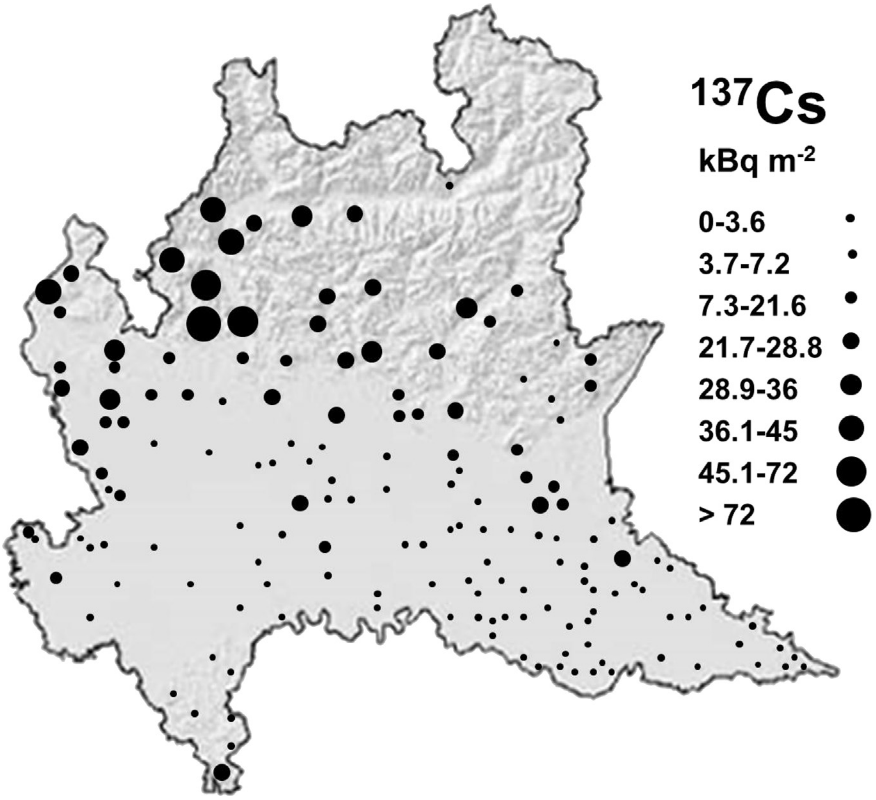

Fig. 4. Surface contamination of Lombardia territory by ^{137}Cs, expressed as kBq m^{-2}.

storage in organic soil horizons leads to a much longer persistence of radionuclides in semi-natural environments in comparison with cultivated agricultural land (Myttenaere et al., 1992, cited by Strebl and Tataruch, 2007). However, in this case, the activity was so high as to suggest soil affected by secondary transport processes, such as lateral migration, erosion and accumulation, which lead to a "^{137}Cs enriched soil". These processes have been described and studied by various authors, especially in the unprocessed mountainous soils (Pourcelot et al., 2003; IAEA, 2004; Agnesod et al., 2006; Schaub et al., 2010). This hypothesis needs to be confirmed by further sampling in the surrounding areas.

The activity of ^{137}Cs detected in the soils of the Lombardia region from 2011 to 2012 turns out to be a measure of the actual inventory, corresponding to the initial deposition minus the various ecological relocation processes that occurred between fallout and sampling, as commented on by Bossew and co-workers, who described contamination of Austrian soils with ^{137}Cs (2001). This confirms the importance of environmental monitoring that documents the current conditions of soils.

4. Conclusions

The increasing demand for agricultural soil data and information on a highly industrialized area, such as Lombardia, has been met through a project that monitors potentially toxic elements, organic pollutants and gamma-emitting radionuclides. The results on the monitoring of ^{238}U, ^{232}Th, ^{137}Cs and ^{40}K are discussed in this work. This is the first survey in Lombardia based on LUCAS standard sampling.

From the gamma analyses of 156 geo-referenced agricultural soils in Lombardia, we can conclude the following:

- The spatial distribution of the natural radionuclides: ^{238}U, ^{232}Th and ^{40}K is rather variable and affected by parent material characteristics, but also by weathering processes.
- The activities of the natural radionuclides determined in this project are generally higher than the worldwide median values; this point especially applies to ^{238}U.
- The geographic distribution of ^{238}U reflects the geophysical framework of the Lombardia region: the soils with the highest activity are distributed for the most part in the South Alpine belt, characterized by magmatic rocks with anomalous high content of uranium. These soils show an higher activity of ^{238}U than of ^{232}Th.
- A percentage of soils located in the plain shows higher activity of ^{232}Th than of ^{238}U. They are probably derived by sedimentary rocks, that present a lower content of uranium than igneous rocks.
- High ^{238}U activities are shown somewhere in soils of the plain. They can be ascribed both to the erosion and transport processes undergone by rich in uranium magmatic rocks, and to the higher solubility of uranium than thorium, that can therefore be deposited some distance away.
- The Lombardia is a region showing areas at quite high concentration of uranium. This agrees with the known mineral exploration in some areas North of the region, some decades ago, for the extraction of uranium.
- The ^{137}Cs is ubiquitous, but it shows highly variable levels of activity. The highest activity is in the mountains and the lowest on the plain.
- The ^{137}Cs activity of some samples suggests the presence of accumulation processes that lead to soils enriched with ^{137}Cs.
- While processed soils are generally subject to attenuation of pollutants, unprocessed semi-natural soils could undergo accumulation processes.
- Priorities for the future are to investigate those factors that can affect ^{238}U concentration in soil, such as the geological characteristics of the substrate, the climatic conditions and the anthropic intervention.
- The results from this project are important to assess the human radiation exposure and can provide a contribution to the study of the geological setting of the Lombardia region. They provide a baseline to document the conditions present in 2011 and will be useful when assessing future effects due to external factors.

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