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Use of Fertilizers in Agriculture: Individual Effective Dose Estimate

Raffaella Ugolini *, Elena Caldognetto and Flavio Trotti

Servizio Osservatorio Agenti Fisici, ARPAV, Via Dominutti 8, 37135 Verona, Italy; elena.caldognetto@arpa.veneto.it (E.C.); flavio.trotti@arpa.veneto.it (F.T.)

* Correspondence: raffaella.ugolini@arpa.veneto.it; Tel.: +39-045-801-6811

Received: 18 November 2019; Accepted: 9 January 2020; Published: 14 January 2020

Abstract: Natural radioactivity might be present in fertilizers above ordinary levels, in particular for ^{40}K and for the radionuclides of the ^{238}U series. A modeling evaluation of the individual effective dose deriving from the use of fertilizers in agriculture is presented here. Dose assessment is useful in the transposition of Directive 2013/59/Euratom, which rules the individual exposure to commodities containing radionuclides of natural origin, such as fertilizers. The following input data have been considered for this study: the amount of fertilizers used in the region of Veneto and in Italy; the utilized agricultural area (to estimate the density of spread fertilizers); and, the average values of activity concentrations in fertilizers for ^{40}K and ^{238}U series radionuclides, derived from scientific literature. The individual effective dose was evaluated while using the Resrad calculation model, making assumptions on the characteristics of the interested soil. This study is focused on the region of Veneto, where the use of fertilizers is higher with respect to the rest of Italy, such providing a more conservative estimate of the individual effective dose to the population. The results show that the estimated individual effective dose values do not exceed few μSv per year. The category that most contributes to the dose is that of compound fertilizers and radon and ^{40}K are the most significant radionuclides.

Keywords: fertilizer; individual effective dose; natural radioactivity

1. Introduction

Naturally Occurring Radioactive Materials (NORM) consist of materials not usually considered radioactive, but containing natural radionuclides with activity concentrations higher than the average in Earth's crust. NORM can be raw materials, products, or wastes from several working activities, where the radiological risk is incidental and anyway lower than the chemical one. In Italy, the Legislative Decree 26 May 2000 n. 241 and related attachments regulate the management of these materials from the radiological point of view [1].

Fertilizers are included among NORM, because they can increase the exposure of the population to radioactivity.

Fertilizers are generally classified into 'straight' or 'complex/mixed', based on the presence of one or more primary plant nutrients (nitrogen, phosphorus, and potassium), respectively.

The natural radioactivity that is contained in fertilizers originates from the minerals used as raw material in their production. Significant levels of radioactivity can be contained in the phosphate and potassium fraction, while the nitrogen fraction is not radiologically significant.

Straight phosphate fertilizers are mainly derived from phosphorite, a mineral that is rich in calcium phosphate.

The treatment of phosphorite with sulfuric acid through the wet-process leads to the production of phosphoric acid and gypsum (phosphogypsum); in the balanced reaction of the phosphorite and sulphuric acid, the resulting product is the fertilizer known as superphosphate (SSP).

Triple superphosphate (TSP) with higher phosphorus content is obtained by chemical attack to phosphorite with phosphoric acid.

Straight potassium fertilizers are produced while using potassium salts taken from mineral deposits; the most widely used are potassium chloride and potassium sulphate.

Complex and mixed fertilizers are obtained as chemical combination of N, K, P, or by physical mixing of straight soil conditioners, respectively.

Monoammonium phosphates (also known as MAP) are widely used NP fertilizers that are obtained by adding a phosphoric acid solution to ammonia.

With regards to the presence of radionuclides in the different fertilizers, it is observed that:

- phosphorites are minerals that contain radionuclide of ^{238}U series in not negligible amounts; in the production of phosphoric acid through wet process, the radioactive equilibrium of phosphate rocks is disrupted during the chemical reaction, which leads to a redistribution of radionuclides. Previous studies have shown that radionuclides migrate according to their solubility in phosphoric acid or phosphogypsum. Accordingly, ^{226}Ra is incorporated in the phosphogypsum, as its chemical behaviour is similar to calcium, ^{210}Pb and ^{210}Po also concentrate into phosphogypsum. The behaviour of Thorium depends on the chemical reaction and it is distributed in the two reaction products. The isotopes of Uranium form highly soluble compounds that are predominantly incorporated in phosphoric acid [2–7];
- MAP fertilizers contain ^{238}U, but not ^{226}Ra, as they derive directly from phosphoric acid;
- in SSP and TSP [5] both ^{238}U and ^{226}Ra are present;
- high activity concentrations of ^{40}K are associated with the presence of potassium salts, with the ^{40}K isotope in a standard ratio with respect to stable potassium; ^{40}K makes up 0.012% of the total amount of potassium found in nature; and,
- in complex/mixed fertilizers the radionuclides content depends on the raw material used for phosphate and potassium components and on the production process.

With regard to production [8], Italy imports raw materials and intermediate products to manufacture different types of fertilizers. In the early 2000s, there were approximately 50 companies producing straight phosphate fertilizers, straight potassium fertilizers, and complex/mixed fertilizers, with 17 of them being main producers; among these, three companies produced superphosphate through balanced reactions between phosphorite and sulfuric acid. A subsequent 2013 census [9] that was conducted on companies authorized under the national law implementing Directive 2010/75/EU [10] registered 11 main fertilizer manufacturers.

In Italy, there are four areas where the radioactive waste from past processing (legacy sites) is deposited, which can represent a potential source of exposure for the population. These are the phosphogypsum storage areas of Venice-Marghera, Sicily-Gela, Sardinia-Porto Torres, and Calabria-Crotone. The impact due to the Marghera phosphogypsum disposal site was analysed for some time [11].

This article investigates the environmental impact that was generated in Italy by the use of fertilizers in agriculture in terms of individual effective dose to members of the public. It was considered to be appropriate to assess the resulting individual dose and the effect of accumulation due to the continuous spreading of the fertilizer over time. Dose estimates were carried out with recourse on Resrad calculation model [12]. Such evaluation is important in the view of the transposition of the Directive 2013/59/Euratom [13], where the phosphate and fertilizers industry is included in the list of NORM activities subject to regulation, while taking into account that the Directive itself provides that the population exposure to commodities containing natural radionuclides, such as fertilizers, should also be regulated.

2. Materials and Methods

2.1. Activity Concentration of Radionuclides in Italian Fertilizers

Radioactivity in Italian fertilizers was analysed on raw materials and final products in several investigations [8,14–16].

In the studies of Zampieri et al. [8] and Bruzzi et al. [15], the samples of phosphorite, phosphoric acid, phosphate fertilizers (SSP, TSP), potassium salts (KCl, K_2SO_4), and compound fertilizers (MAP and NPK products) were analysed by gamma-spectrometry with HPGe detector to quantify the activity concentration of ^{40}K and of radionuclides of ^{238}U series.

In Zampieri et al. [8], the detector was calibrated while using a certified multi-gamma solution with density 1 g/cm^3, ranging from 59 keV to 1836 keV. The samples were sealed in hermetic containers and then analyzed after thirty days, which is sufficient time to reach radioactive equilibrium between ^{226}Ra and its daughters ^{214}Pb and ^{214}Bi. The ^{226}Ra activities were determined by taking the mean of the photopeaks of its daughter nuclides: ^{214}Pb at 352 keV and ^{214}Bi at 609 and 1764 keV. The ^{238}U content of the samples was determined by measuring the intensity of 93 keV gamma-ray peak from ^{234}Th. The potassium content was determined from the 1460 keV gamma-ray peak of ^{40}K. Self-absorption correction was applied to take into account the variations of samples density and composition with respect to the reference standards.

Details regarding data and measurements techniques of survey carried out by Bruzzi et al. [15] are reported in the reference itself.

The average values for the activity concentration of radionuclides were derived by comparison of experimental data in Italian fertilizers that were obtained from those surveys [8,15]. Table 1 shows the average values of activity concentration for ^{238}U, ^{226}Ra, ^{210}Pb, and ^{40}K for the following groups of fertilizers: 'straight phosphate' (SSP, TSP), 'straight potassium' (KCl, K_2SO_4), and 'compound fertilizers' (MAP and NPK fertilizers). These data serve as reference levels to be used in the dose assessments by Resrad calculation model described later on.

Table 1. Average values of activity concentration (Bq/kg) of natural radionuclides in Italian straight and compound fertilizers samples [8,15]. The minimum and maximum values are shown in brackets.

Fertilizer	^{238}U	^{226}Ra	^{210}Pb	^{40}K
Straight Phosphate	670 (57–1500)	295 (34–500)	295 (34–500)	-
Straight Potassium	-	-	-	14,000 (13,000–15,000)
Compounds	262 (24–560)	107 (1–310)	157 (1–310)	3379 (0–9040)

2.2. Activity Concentration of Radionuclides in Agricultural Soil

The average values of activity concentration of the radionuclides in fertilizers of Table 1 were used to evaluate the radioactivity in the agricultural soil, together with literature data regarding the Utilized Agricultural Area (UAA) and amount of spread fertilizers.

The UAA is defined as "the total area taken up by arable land, permanent grassland, permanent crops and kitchen gardens used by the holding, regardless of the type of tenure or of whether it is used as a part of common land. It excludes mushrooms, unutilised agricultural land, woodland, other land occupied by buildings, farmyards, tracks, ponds, etc., utilised agricultural area which is a property of the owner but is leased or rented to someone else, common land which is not used" [17]. UAA is the only area where fertilizers are spread and this parameter must be taken into account to correctly evaluate the radionuclide density in the soil.

UAA is equal to 621,998 hectares for the region of Veneto and 8,808,140 hectares for all of Italy, according to the results of an elaboration [18] of the National Institute of Statistics (ISTAT) data on the area of herbaceous crops (cereals, industrial crops, vegetables, etc.), woody crops (fruit trees, etc.), and forage crops [19].

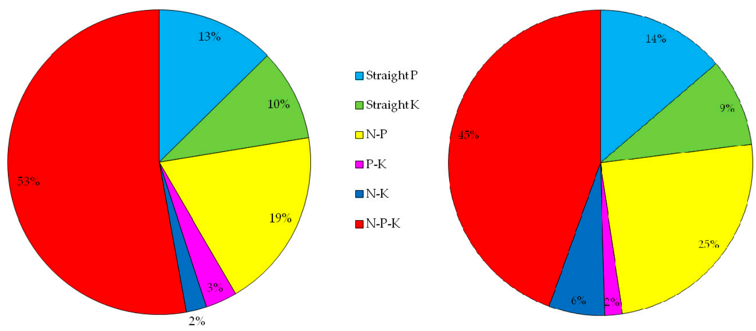
Table 2 shows the amounts and types of fertilizer used in Veneto and in Italy, based on the 2015 ISTAT census data [20].

Table 2. Fertilizers quantities spread in Veneto and in Italy in 2015 (10^3 kg/y) [20].

Area	Straight Phosphate	Straight Potassium	Compounds	Total
Veneto	15,700	12,100	96,200	124,000
Italia	113,700	77,000	636,400	827,100

The amounts that are reported in Table 2 can be considered to be representative also for more recent years, as the quantities of fertilizers of all types remained stable in the last years, whereas a sharp drop occurred from 2013 to 2015 [21].

Figure 1 shows the percentage distribution of straight and compound (disaggregated) fertilizers used in 2015, in Veneto (Figure 1a) and in Italy (Figure 1b) [20].



(**a**) (**b**)

Figure 1. Distribution of fertilizers used in 2015 by types [20]: (**a**) Veneto; (**b**) Italy.

Fertilizers density is obtained by dividing the total amounts of fertilizers spread of Table 2 by the UAA for Veneto and Italy (Table 3). In this assessment, a homogeneous distribution of all the fertilizers on the soil is assumed over the entire UAA.

Table 3. Fertilizer density on Utilized Agricultural Area (UAA) in Veneto and in Italy (kg/m^2) in 2015.

Area	Straight Phosphate	Straight Potassium	Compounds	Total
Veneto	0.0025	0.0019	0.0155	0.0199
Italia	0.001	0.0009	0.0072	0.0094

Assuming that the fertilizer is mixed with a layer of soil 0.5 m thick, the actual activity concentration of natural radionuclides from fertilizers in agricultural land can be calculated, as follows:

$$C_{act,i} = (C_i \cdot d)/(\rho \cdot s), \quad (1)$$

$C_{act,i}$ (Bq/kg) = Actual activity concentration of radionuclide i in the soil;
C_i (Bq/kg) = Activity concentration of radionuclide i in the fertilizer (Table 1);
d (kg/m^2) = Fertilizer density (Table 3);
ρ (kg/m^3) = Soil density (1300 kg/m^3); and,
s (m) = Soil mixing thickness (def. 0.5 m).

The values that were obtained from Equation (1) are shown in Table 4 and relate only to the region of Veneto. This represents a conservative condition for estimating the exposure to the overall Italian population, due to the higher density of fertilizer spreading (Table 3).

Table 4. Actual activity concentration of radionuclides in the soil in the region of Veneto (Bq/kg).

Fertilizer	^{238}U	^{226}Ra	^{210}Pb	^{40}K
Straight Phosphate	3×10^{-3}	1.36×10^{-3}	1.36×10^{-3}	
Straight Potassium				4.1×10^{-2}
Compounds	6.25×10^{-3}	2.55×10^{-3}	3.74×10^{-3}	8.06×10^{-2}

2.3. Calculating Model for Effective Individual Dose Evaluation for Use of Fertilizers in Agriculture

The data in Table 4 were used as input for the Resrad calculation model [12]. In model processing, more radionuclides of the ^{238}U series were taken into account with respect to those in Table 4: ^{234}U and ^{230}Th were included and assumed to be in equilibrium with ^{238}U, ^{210}Po was also included and assumed in equilibrium with ^{210}Pb; radon and its short lived progeny were considered in equilibrium with ^{226}Ra.

Resrad is a computer code for evaluating nine different exposure pathways for an individual living on top of radioactively contaminated soils. It requires specific input information regarding the characteristics of the contamination, properties of surface, sub-surface, and saturated soil strata, site-specific meteorological, hydraulic, and hydrogeological data, as well as exposure pattern of the receptor. Its typical application concerns materials that are confined to landfills. In the present study, the standard parameters of the program were maintained (with extension of the interested area equals to 10,000 m^2). For all radionuclides of compound and straight phosphate fertilizers the following pathways of exposure were considered: external irradiation due to a partial stay on the "contaminated" soil and indoors (house built on the same soil), inhalation of re-suspended particulate matter, ingestion of exclusively local water and food (fruits and vegetables, cereals, milk, meat; fish for 50% of local origin). Exposure due to the exhalation of radon gas from the ground has been also considered.

For straight potassium fertilizer, only the external irradiation due to ^{40}K was evaluated as an exposure pathway, because of the homeostatic behavior of this element within the human organism. For the same reason, the contribution to the effective dose deriving from the ^{40}K for compound and straight potassium fertilizers was separately evaluated, while only considering the external irradiation, and then added to the estimated effective dose for the other radionuclides.

3. Results

3.1. Occasional Spreading of Fertilizers

Table 5 shows the individual effective dose one year after performing the spreading, as estimated by the Resrad calculation model for the region of Veneto. In the conservative hypothesis where all types of fertilizers are distributed on the same agricultural area, the total dose can be calculated as the sum of the single contributions. This calculation shows that compound fertilizers give the greatest contribution to the individual effective dose.

Table 5. Annual individual effective dose (µSv/a) 1 year after the occasional spreading of fertilizers for the region of Veneto.

Fertilizer	Individual Effective Dose
Straight Phosphate	0.011
Straight Potassium	0.005
Compounds	0.032
Total	0.048

Figure 2 shows the trend of the effective dose of single radionuclides in the years following the spreading. The most significant radionuclide appears to be ^{226}Ra, with a not negligible contribution of ^{210}Pb and ^{40}K in the first 20 years.

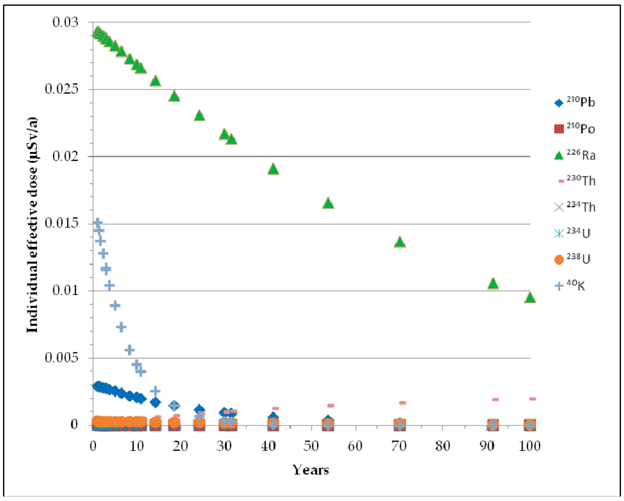


Figure 2. The trend of annual individual effective dose (µSv/a) for single radionuclides in the years following the occasional spreading of fertilizers.

The most significant pathway of exposure is the inhalation of radon (generated by ^{226}Ra in the soil), followed by external irradiation by ^{40}K.

3.2. Spreading of Fertilizers Over Time

It was assumed that the spreading of fertilizers on the agricultural area of Veneto had been carried out for 100 years with the same annual amounts being used in the previous scenario. The effective dose to an individual of the population was then estimated at the 100th year of treatment, therefore taking the accumulation of radionuclides occurred during that period into account. Table 6 shows the obtained values for each type of fertilizer and as a sum of all types. Again, these data indicate that compound fertilizers give the highest contribution to the dose.

Table 6. Annual individual effective dose (µSv/a) after one hundred years of fertilizer spreading on the same agriculture area in the region of Veneto.

Fertilizer	Individual Effective Dose
Straight Phosphate	0.71
Straight Potassium	0.04
Compounds	1.39
Total	2.14

Figure 3 shows the trend of the annual individual effective dose for each type of fertilizer due to the practice of spreading over time.

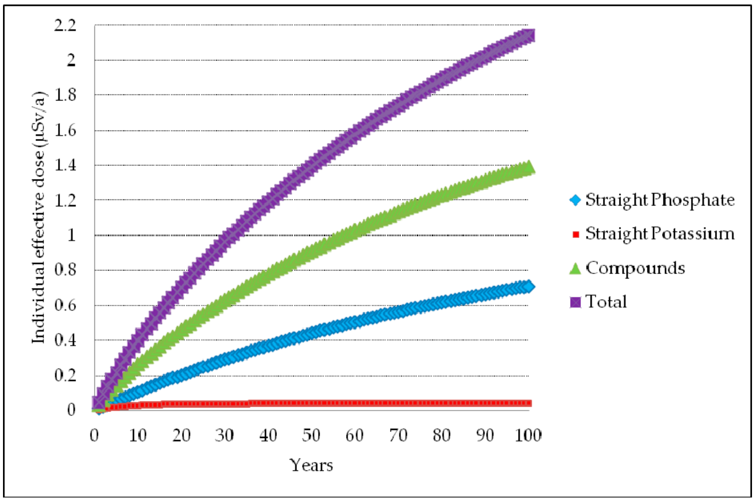


Figure 3. Trend of the annual individual effective dose (μSv/a) due to continuous spreading (100 years) on the same agricultural area, for single fertilizer.

4. Discussion

The individual effective dose for the population due to the use of Italian fertilizers in agriculture has been assessed through computer modeling, which is based on activity concentration values of natural radioactivity in fertilizers and on distribution data provided by ISTAT. The results show low values for both the occasional spreading over a year (maximum value of about 0.05 μSv/a) and for the continuous spreading over one hundred years (maximum value of about 2 μSv/a). These estimates are based on the density of fertilizer distribution documented by ISTAT for 2015 in the region of Veneto, but they can also be considered to be representative also at the national scale, as discussed before.

These are average estimates, being obtained by assuming that the single fertilizers are homogeneously spread over the entire available agricultural area. Further studies could be carried out while considering the specificity of the fertilizer with respect to the crop type and the subdivision of the UAA on the basis of the crop type (e.g., cereals, fruit trees, forage crops etc.).

These evaluations may be useful in view of the transposition into Italian law of Directive 2013/59/Euratom [13], which introduces radiation protection provisions for commodities containing radionuclides of natural origin, such as fertilizers. In particular, the Directive requires that the reference levels for the effective individual dose should be defined with regard to the exposure of the population to fertilizers. The estimates that were carried out in this study suggest that the radiological impact on the population deriving from the use of the investigated products is of negligible significance.

Author Contributions: Conceptualization, F.T.; methodology, F.T.; formal analysis, R.U.; investigation, R.U.; resources, E.C.; writing—original draft preparation, R.U.; writing—review and editing, F.T.; visualization, E.C.; supervision, F.T.; project administration, F.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The authors are grateful to Veneto Agricoltura for providing necessary data for this research. The authors would like to express sincere thanks to Giovanna Tedesco.

Conflicts of Interest: The authors declare no conflict of interest.

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