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Health and environmental impacts of a fertilizer plant – Part I: Assessment of radioactive pollution

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Abstract

The aim of the first part of this investigation is to assess the radioactive pollution caused by a production plant of complex fertilizers (that is to say containing nitrogen, phosphorus and, in some cases, potassium). Firstly, the authors determine the concentrations of natural radioactivity present in raw materials, end products and wastes of the industrial plant. Then, they carry out an assessment of radioactive releases into the atmosphere, hydrosphere and lithosphere as well as of their significance from the environmental point of view.

The second part of the investigation will be aimed at assessing the annual effective doses to plant workers and to members of the population surrounding the industrial site.

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Keywords: Natural radionuclides; Phosphate rocks; Fertilizers; Environmental radioactive pollution

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1. Introduction

Phosphate rocks together with potassium ores and nitrogenous compounds are the main raw materials used for fertilizers industrial production. As a matter of fact phosphorus, potassium and nitrogen are essential elements for plants growth. Phosphorus can be found in nature in a combined state in fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$, hydroxylapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ and chlorapatite $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ ores, the main constituents of phosphate rocks. Said rocks – which can be subdivided according to their origin into sedimentary, volcanic and biological – contain several trace elements, some of which have natural radioactive isotopes. In phosphate rocks, activity concentrations of uranium two isotopes (^{238}U and ^{235}U) and of their decay products are extremely variable and in some case quite high. For instance, deposits of volcanic phosphate rocks of Kola peninsula, Russia, show activity concentrations of ^{238}U equal to 40 Bq kg^{-1} (Guimond and Hardin, 1989), while phosphate deposits of Minjingu (Arusha – Tanzania) exceed 4000 Bq kg^{-1} (Makweba and Holm, 1993). As a rule, sedimentary phosphate rocks, or phosphorites, originated in a marine environment, are characterised by activity concentrations of uranium much higher than those of volcanic and biological rocks. The UNSCEAR (1988, 1993) indicates 1500 Bq kg^{-1} as the average concentration of ^{238}U in phosphate deposits of sedimentary origin.

The general goal of this investigation was to assess the environmental radioactive pollution and the radiological impacts caused by a large production plant of complex fertilizers (that is to say containing nitrogen, phosphorus and, in some cases, potassium). In particular the first part of the survey, aimed at analysing the environmental impact, starts by determining concentrations of natural radioactivity in raw materials, end products and wastes (solid wastes and wastewaters) of the plant. Afterwards, according to the process data and obtained results, the main dispersion routes of radionuclides in the environment have been identified. Finally, the quantity of natural radionuclides released into the different environmental compartments (water, air, soil) has been estimated and the significance, from an environmental point of view, of the different dispersion routes has been assessed.

In the second part of this investigation, the radiation exposure of workers and members of the population surrounding the industrial site has been determined.

2. Experimental work

2.1. Description of production process

The industrial complex involved in the survey is one of the main production plants of complex fertilizers in Italy. The plant is located in Ravenna, north-eastern Italy. It has been operating since the late fifties and afterwards the production process employed has been changed several times. The flowchart describing the production process is reported in Fig. 1. The phosphate ore is dissolved in HNO_3

with subsequent formation of $\text{Ca}(\text{NO}_3)_2$ and H_3PO_4 . The subsequent addition of $(\text{NH}_4)_2\text{SO}_4$ and ammonia leads to the formation of CaHPO_4 and NH_4NO_3 . The potassium, where required, is supplied by adding either KCl or K_2SO_4 . Finally, dolomite and limestone are added to the mixture. The achievement of desired concentrations of nitrogen and phosphorus is obtained through adequate dosages of NH_4NO_3 and of $\text{NH}_4\text{H}_2\text{PO}_4$ plus H_3PO_4 , respectively. The country of origin of raw materials employed in the production process is given in Table 1.

Fertilizers produced are called binary (containing N and P) and ternary (containing N, P and K); the company introduces to the Italian and foreign markets about 340 ktons of complex fertilizers per year (280 ktons of ternary fertilizers and 60 ktons of binary fertilizers).

2.2. Sampling and sample preparation

The investigation has been carried out during the years 2000–2003. In this way it has been possible to sample the whole range of fertilizers introduced to market by the company, some of which are produced quite rarely and in small amounts. The sampling related to measurements of activity concentrations has been carried out on the following materials:

- raw materials – samples of all raw materials which are involved in the production process in a significant way have been collected: phosphate ore, phosphoric acid, ammonium phosphate, ammonium sulphate, potassium sulphate, potassium chloride, ammonium nitrate, nitric acid, dolomite and limestone;
- intermediate products – on some products, especially those mostly commercialised by the company, measurements of activity concentrations have been performed also during the process;
- end products – all the fertilizers commercialised by the company have been analysed;

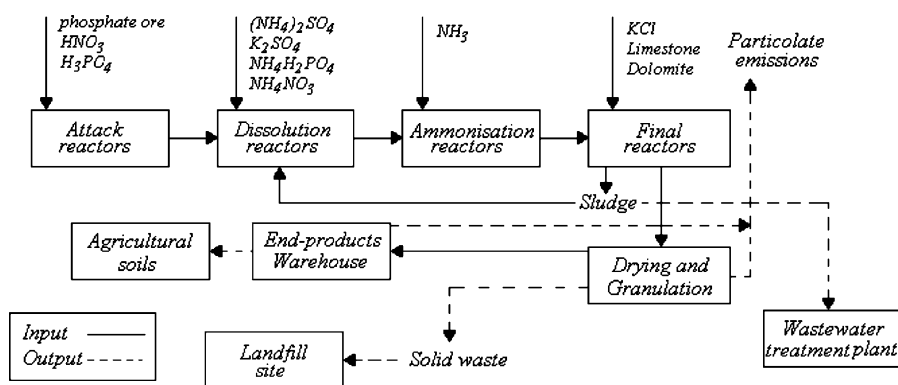


Fig. 1. Schematic illustration of the fertilizer production process.

Table 1
Country of origin of raw materials used in fertilizers production

| Material | Origin |
|--------------------|-------------------|
| Phosphate ore | Morocco |
| Phosphoric acid | Morocco |
| Ammonium phosphate | Morocco |
| Potassium chloride | Israel and Jordan |
| Potassium sulphate | Italy and Germany |
| Ammonium sulphate | Italy |
| Ammonium nitrate | Italy |
| Nitric acid | Italy |
| Dolomite | Italy |
| Limestone | Italy |

- process wastewaters – usually process wastewaters are completely reintroduced into reactors; only in the case of an emergency said waters may be piped into sewerage network and then conveyed to an industrial wastewater treatment plant. The first samples collected have shown negligible concentrations of radioactivity and therefore the sampling was stopped after few measurements;
- solid wastes – residues from the production process which may not be recycled are delivered to a special wastes landfill; their amount is very small (in terms of weight, just 0.14% of fertilizers). The sampling was performed before sending the waste to the facility for disposal;
- sediments – treated waters coming from the industrial wastewater treatment plant are conveyed to a nearby salt-marsh. Three samples of superficial sediments (5 cm high) were collected in this salt-marsh. Sample no. 1 was taken close to the inlet site of wastewater coming from the treatment plant, while samples no. 2 and no. 3 were collected, respectively, at 1000 and 3000 m downstream from the discharge point.

Solid samples have been dried for about 2 h at 105 °C and, if necessary, they have been crushed. Sediment samples have been sealed in 150 ml polyethylene containers while the other ones have been placed into 450 ml Marinelli beakers. All the samples have been sealed to avoid the release of radon gas. Measurements have been taken after an ageing period of about 30 days to allow the re-establishment of the conditions of secular equilibrium between ^{226}Ra and its short-lived decay products; as a matter of fact, said conditions might have been disturbed due to exhalation of ^{222}Rn during samples grinding.

2.3. Gamma-spectrometry

Activities concentrations have been determined by means of a multichannel analyser linked up to an n-type HPGe detector with 22.6% relative efficiency and FWHM of 1.9 keV and 1.33 MeV. The detector (diameter 54 mm, length 48.5 mm and volume 109 cm³) is placed in a well consisting of a layer 10-cm-thick of lead lined

with cadmium–copper coating at the inner side. Calibration has been carried out by using two sources, both supplied by the CEA (Commissariat à l’Energie Atomique – France). The first source was an aqueous solution containing ^{57}Co , ^{60}Co , ^{85}Sr , ^{88}Y , ^{109}Cd , ^{113}Sn , ^{139}Ce , ^{137}Cs , ^{241}Am . The second calibration source contained ^{125}I and was necessary to determine ^{210}Pb and ^{234}Th , both gamma-emitters with energies below 100 keV. The calibration curve thus obtained has made it possible to determine peaks included between 35.5 and 1836.1 keV. Two geometries of calibration have been used: the 450 ml Marinelli beaker and the 150 ml polyethylene container. Quality control of the calibration was performed by measuring natural matrix soil (IAEA-375) and sediment (IAEA-368) standards having radionuclide activity certified by the International Atomic Energy Agency.

Gamma-spectrometric measurements have made it possible to determine the activity concentration of the following radionuclides: ^{40}K , ^{238}U (via ^{234}Th), ^{226}Ra (via ^{214}Pb), ^{210}Pb , ^{228}Ra (via ^{228}Ac), ^{224}Ra (via ^{212}Pb) and ^{235}U . Peaks and relevant yields used for calculating concentrations are given elsewhere (Bruzzi et al., 2000; Righi et al., 2000). In the case of samples having an apparent density higher than 1.5 g cm^{-3} , self-absorption corrections were calculated using the coefficients suggested by Debertain and Ren (1989) for sands with apparent densities of 1.6 g cm^{-3} . The counting time was 4800 min for sediment samples and 60 000 s for the other samples; error confidence level is 95%.

2.4. Estimate of radioactivity released annually in the environment

The estimate of radioactivity released annually in the environment by the fertilizer plant has been carried out for those radionuclides that, according to gamma-spectrometric determinations, have resulted to be the most significant. The following formula has been adopted:

$$\overline{\text{AC}}_{ik} \times Q_k$$

where $\overline{\text{AC}}_{ik}$ is the average activity concentration of the i -th nuclide in the k -th material, expressed in Bq kg^{-1} and Q_k is the amount of k -th material released in the environment, expressed in kg per year.

Materials taken into account in the calculation are the following: fertilizers, process wastewaters, solid wastes, particulate matter emitted into the atmosphere by plant smokestacks. In the case of particulate matter emissions, in order to carry out the calculation, reference has been made to the average value of the activity concentrations measured in the fertilizer samples for the reason that most particulate matter emissions (>99%) come from the smokestacks of the fertilizer production department.

2.5. Analysis of dispersion of particulate matter emissions

The ground-level air concentration of the particulate matter emitted into the atmosphere by the plant has been estimated by using the ISCST3 simulation model.

The ISCST3 (Industrial Source Complex, Short Term, Version 3) is a steady-state Gaussian plume model developed by the U.S.EPA (1995).

Data input requirements for the model are sources, site and meteorological conditions characteristics. Parameters required to characterise the sources include stack height and diameter, and effluent temperature and velocity. The chemical–physical parameters of each emission have been drawn from the authorizations on emissions provided by the competent authority. Site parameters include the number and size of buildings adjacent to the plume, and the average ground surface roughness. The importance of site parameters has been shown in a previous study about this industrial plant (Righi et al., 2003). Hourly meteorological data over a whole year, for a total of 8760 records, have been used to carry out the simulations. The data specify: wind origin, wind speed, air temperature, stability class according to Pasquill Gifford, height of the mixing layer. The meteorological data were obtained from a meteorological station located only a few kilometres far from the investigated industrial plant.

3. Results and discussion

3.1. Natural radioactivity concentrations

Results of analysis carried out by gamma-spectrometry on raw materials, end products, intermediate products, solid wastes and sediments, as well as on wastewaters are indicated, respectively, in Tables 2, 3, 4 and 5. In all the samples analysed, activity concentrations of ^{235}U are in substantial accordance with uranium isotopic composition ($\cong 99.3\%$ of ^{238}U and $\cong 0.7\%$ of ^{235}U); those related to radionuclides belonging to the ^{232}Th chain turn out to be quite reduced (a few dozen Bq kg^{-1} at most) or even not detectable. For this reason the following discussion focuses on ^{40}K and members of ^{238}U decay chain only.

As it can be drawn from Table 2, ammonium sulphate and nitrate, nitric acid, dolomite and limestone show very low natural activity concentrations, in some cases lower than the instrument detection limits.

Potassium sulphate and chloride show high concentrations of ^{40}K (order of 10^4 Bq kg^{-1}) due to the natural abundance of this isotope in natural potassium ($\cong 93.26\%$ of ^{39}K , $\cong 6.73\%$ of ^{41}K and $\cong 0.0117\%$ of ^{40}K), while activity concentrations of radionuclides belonging to ^{238}U natural decay chain are always below detection limits. On the contrary, raw materials containing phosphorus show low activity concentrations of ^{40}K (equal to a few dozen Bq kg^{-1}) but significant activity concentrations of radionuclides belonging to ^{238}U chain. In phosphate ores, activity concentrations of ^{238}U , ^{226}Ra and ^{210}Pb are equal to about a thousand Bq kg^{-1} that is to say that they exceed the world average noticed in soils (UNSCEAR, 2000) and the natural background typical of the soils present in the study area (Sciocchetti et al., 1985) by two orders of magnitude. Uranium-238 activity concentrations noticed in phosphate ores taken into account in this survey (corresponding to about 100 ppm) fall within the range of values observed by several

Table 2
Activity concentrations in raw materials used in the production process (in Bq kg⁻¹)

| Sample | ⁴⁰ K | ²³⁸ U | ²²⁶ Ra | ²¹⁰ Pb | ²²⁸ Ra | ²²⁴ Ra | ²³⁵ U |
|--------------------|---------------------|---------------------|---------------------|---------------------|-------------------|-------------------|---------------------|
| Ammonium sulphate | (2.2 ± 0.3)E + 01 | <dl | <dl | <dl | <dl | <dl | <dl |
| Ammonium nitrate | (1.9 ± 0.2)E + 01 | <dl | (2.2 ± 0.3)E + 00 | <dl | <dl | (4.7 ± 1.3)E - 01 | <dl |
| Nitric acid | <dl | <dl | <dl | <dl | <dl | <dl | <dl |
| Dolomite | (5.1 ± 0.5)E + 01 | (9.5 ± 1.9)E + 00 | (8.5 ± 0.8)E + 00 | (1.30 ± 0.14)E + 01 | (3.0 ± 0.4)E + 00 | (2.9 ± 0.3)E + 00 | <dl |
| Limestone | (1.20 ± 0.11)E + 02 | (1.9 ± 0.4)E + 01 | (2.0 ± 0.2)E + 01 | (2.0 ± 0.2)E + 01 | (4.7 ± 0.5)E + 00 | (5.0 ± 0.5)E + 00 | <dl |
| Potassium sulphate | (1.30 ± 0.10)E + 04 | <dl | <dl | <dl | <dl | <dl | <dl |
| Potassium sulphate | (1.29 ± 0.11)E + 04 | <dl | <dl | <dl | <dl | <dl | <dl |
| Potassium chloride | (1.53 ± 0.11)E + 04 | <dl | <dl | <dl | <dl | <dl | <dl |
| Potassium chloride | (1.55 ± 0.13)E + 04 | <dl | <dl | <dl | <dl | <dl | <dl |
| Phosphate ore | (3.2 ± 0.4)E + 01 | (1.15 ± 0.18)E + 03 | (1.34 ± 0.10)E + 03 | (1.23 ± 0.10)E + 03 | (2.1 ± 0.2)E + 01 | (1.9 ± 0.2)E + 01 | (6.3 ± 0.7)E + 01 |
| Phosphate ore | (3.4 ± 0.4)E + 01 | (1.4 ± 0.2)E + 03 | (1.55 ± 0.15)E + 03 | (1.06 ± 0.09)E + 03 | (2.5 ± 0.2)E + 01 | (2.2 ± 0.2)E + 01 | (7.7 ± 0.8)E + 01 |
| Phosphate ore | (3.3 ± 0.4)E + 01 | (1.0 ± 0.2)E + 03 | (1.20 ± 0.10)E + 03 | (1.16 ± 0.10)E + 03 | (1.9 ± 0.2)E + 01 | (1.8 ± 0.2)E + 01 | (6.8 ± 0.7)E + 01 |
| Ammonium phosphate | (3.4 ± 0.4)E + 01 | (1.4 ± 0.2)E + 03 | (6.3 ± 0.6)E + 00 | (3.6 ± 0.4)E + 01 | <dl | (1.5 ± 0.2)E + 00 | (7.5 ± 0.7)E + 01 |
| Ammonium phosphate | (3.4 ± 0.3)E + 01 | (1.4 ± 0.2)E + 03 | (6.7 ± 0.6)E + 00 | (3.7 ± 0.4)E + 01 | (1.6 ± 0.2)E + 00 | (1.7 ± 0.2)E + 00 | (7.6 ± 0.7)E + 01 |
| Ammonium phosphate | (3.7 ± 0.3)E + 01 | (1.5 ± 0.2)E + 03 | (7.8 ± 0.7)E + 00 | (3.0 ± 0.3)E + 01 | (2.3 ± 0.3)E + 00 | (2.5 ± 0.2)E + 00 | (7.6 ± 0.8)E + 01 |
| Ammonium phosphate | (2.8 ± 0.4)E + 01 | (1.2 ± 0.2)E + 03 | (2.1 ± 0.2)E + 01 | (2.3 ± 0.2)E + 02 | (2.2 ± 0.3)E + 00 | (1.6 ± 0.2)E + 00 | (7.6 ± 0.7)E + 01 |
| Phosphoric acid | (1.5 ± 0.2)E + 01 | (1.7 ± 0.3)E + 03 | (5.5 ± 0.5)E + 00 | (1.01 ± 0.10)E + 01 | <dl | (4.5 ± 0.4)E + 00 | (9.5 ± 0.9)E + 01 |
| Phosphoric acid | (2.0 ± 0.3)E + 01 | (1.9 ± 0.3)E + 03 | (8.4 ± 0.8)E + 00 | (2.6 ± 0.3)E + 01 | <dl | (4.2 ± 0.4)E + 00 | (1.02 ± 0.10)E + 02 |
| Phosphoric acid | (2.9 ± 0.3)E + 01 | (1.6 ± 0.2)E + 03 | (2.4 ± 0.3)E + 00 | (6.8 ± 0.7)E + 00 | <dl | (4.4 ± 0.4)E + 00 | (1.02 ± 0.10)E + 02 |

Table 3
Activity concentrations in complex fertilizers (in Bq kg⁻¹)

| Sample | ⁴⁰ K | ²³⁸ U | ²²⁶ Ra | ²¹⁰ Pb | ²²⁸ Ra | ²²⁴ Ra | ²³⁵ U | |
|---------------------|-------------------|-------------------|---------------------|---------------------|-------------------|---------------------|-------------------|-----------|
| Fertilizer 01 (NPK) | (2.2 ± 0.2)E + 03 | (2.4 ± 0.4)E + 02 | (1.21 ± 0.10)E + 02 | (1.92 ± 0.17)E + 02 | (3.4 ± 0.9)E + 00 | (2.6 ± 0.3)E + 00 | (1.4 ± 0.2)E + 01 | |
| Fertilizer 02 (NPK) | (4.7 ± 0.4)E + 03 | (3.1 ± 0.5)E + 02 | (6.0 ± 0.5)E + 01 | (7.8 ± 0.7)E + 01 | (1.5 ± 0.5)E + 00 | (1.8 ± 0.2)E + 00 | (1.8 ± 0.2)E + 01 | |
| Fertilizer 03 (NPK) | (4.2 ± 0.4)E + 03 | (6.5 ± 1.1)E + 02 | (6.9 ± 0.6)E + 01 | (2.02 ± 0.18)E + 02 | (6.0 ± 1.1)E + 00 | (1.15 ± 0.11)E + 01 | (3.8 ± 0.4)E + 01 | |
| Fertilizer 04 (NPK) | (3.9 ± 0.3)E + 03 | (3.3 ± 0.5)E + 02 | (1.09 ± 0.10)E + 02 | (1.81 ± 0.16)E + 02 | (3.2 ± 1.0)E + 00 | (2.4 ± 0.3)E + 00 | (2.0 ± 0.3)E + 01 | |
| Fertilizer 05 (NPK) | (4.3 ± 0.4)E + 03 | (6.4 ± 1.1)E + 02 | (9.1 ± 0.8)E + 01 | (2.1 ± 0.2)E + 02 | <dl | (1.14 ± 0.13)E + 01 | (4.2 ± 0.4)E + 01 | |
| Fertilizer 06 (NPK) | (4.9 ± 0.4)E + 03 | (4.2 ± 0.8)E + 02 | (1.67 ± 0.14)E + 02 | (2.5 ± 0.2)E + 02 | (4.9 ± 1.2)E + 00 | (3.7 ± 0.4)E + 00 | (2.5 ± 0.3)E + 01 | |
| Fertilizer 07 (NP) | (3.0 ± 0.3)E + 01 | (2.3 ± 0.4)E + 02 | (1.24 ± 0.11)E + 02 | (2.00 ± 0.18)E + 02 | (2.9 ± 0.8)E + 00 | (1.9 ± 0.3)E + 00 | (1.3 ± 0.2)E + 01 | |
| Fertilizer 08 (NPK) | (5.2 ± 0.4)E + 03 | (4.7 ± 0.8)E + 02 | (1.48 ± 0.13)E + 02 | (1.92 ± 0.17)E + 02 | (4.7 ± 1.1)E + 00 | (3.3 ± 0.4)E + 00 | (2.8 ± 0.3)E + 01 | |
| Fertilizer 09 (NPK) | (4.3 ± 0.4)E + 03 | (3.4 ± 0.6)E + 02 | (1.31 ± 0.11)E + 02 | (1.81 ± 0.16)E + 02 | (4.4 ± 1.2)E + 00 | (2.8 ± 0.4)E + 00 | (2.3 ± 0.2)E + 01 | |
| Fertilizer 10 (NPK) | (2.9 ± 0.2)E + 03 | (2.6 ± 0.5)E + 02 | (1.44 ± 0.12)E + 02 | (2.23 ± 0.19)E + 02 | (2.8 ± 0.5)E + 00 | (2.3 ± 0.2)E + 00 | (1.8 ± 0.2)E + 01 | |
| Fertilizer 11 (NPK) | (2.8 ± 0.2)E + 03 | (3.5 ± 0.6)E + 02 | (2.3 ± 0.2)E + 02 | (3.5 ± 0.3)E + 02 | (8.0 ± 1.5)E + 00 | (4.3 ± 0.5)E + 00 | (2.2 ± 0.2)E + 01 | |
| Fertilizer 12 (NPK) | (4.5 ± 0.4)E + 03 | (3.1 ± 0.5)E + 02 | (6.2 ± 0.5)E + 01 | (9.8 ± 0.9)E + 01 | (1.9 ± 0.6)E + 00 | (2.2 ± 0.2)E + 00 | (1.9 ± 0.2)E + 01 | |
| Fertilizer 13 (NPK) | (4.0 ± 0.3)E + 03 | (2.0 ± 0.4)E + 02 | (1.26 ± 0.11)E + 02 | (1.56 ± 0.15)E + 02 | <dl | (2.5 ± 0.4)E + 00 | (1.5 ± 0.2)E + 01 | |
| Fertilizer 14 (NPK) | (2.4 ± 0.2)E + 03 | (2.2 ± 0.4)E + 02 | (1.15 ± 0.10)E + 02 | (2.1 ± 0.2)E + 02 | (4.0 ± 1.2)E + 00 | (2.0 ± 0.3)E + 00 | (1.4 ± 0.2)E + 01 | |
| Fertilizer 15 (NP) | (2.5 ± 0.3)E + 01 | (1.9 ± 0.3)E + 02 | (1.31 ± 0.11)E + 02 | (2.5 ± 0.2)E + 02 | (3.7 ± 1.1)E + 00 | (2.0 ± 0.3)E + 00 | (1.1 ± 0.2)E + 01 | |
| Fertilizer 16 (NPK) | (4.8 ± 0.4)E + 03 | (4.3 ± 0.8)E + 02 | (1.74 ± 0.15)E + 02 | (2.8 ± 0.3)E + 02 | (5.0 ± 1.5)E + 00 | (3.9 ± 0.5)E + 00 | (2.5 ± 0.3)E + 01 | |
| Fertilizer 17 (NPK) | (4.7 ± 0.4)E + 03 | (4.2 ± 0.7)E + 02 | (1.60 ± 0.13)E + 02 | (3.1 ± 0.3)E + 02 | (5.9 ± 1.5)E + 00 | (4.0 ± 0.5)E + 00 | (2.6 ± 0.3)E + 01 | |
| Fertilizer 18 (NPK) | (4.6 ± 0.4)E + 03 | (6.0 ± 1.0)E + 02 | (7.4 ± 0.6)E + 01 | (2.5 ± 0.2)E + 02 | <dl | (5.3 ± 0.6)E + 00 | (3.6 ± 0.4)E + 01 | |
| Mean | 4.0E + 03 | 2.8E + 01 | 3.7E + 02 | 1.2E + 02 | 2.1E + 02 | 3.5E + 00 | 3.9E + 00 | 2.3E + 01 |
| Min | 2.2E + 03 | 2.5E + 01 | 1.9E + 02 | 6.0E + 01 | 7.8E + 01 | <dl | 1.8E + 00 | 1.1E + 01 |
| Max | 5.2E + 03 | 3.0E + 01 | 6.5E + 02 | 2.3E + 02 | 3.5E + 02 | 8.0E + 00 | 1.2E + 01 | 4.2E + 01 |

Table 4
Activity concentrations in intermediate products, solid wastes and sediments (in Bq kg⁻¹)

| Sample | ⁴⁰ K | ²³⁸ U | ²²⁶ Ra | ²¹⁰ Pb | ²²⁸ Ra | ²²⁴ Ra | ²³⁵ U |
|----------------------|---------------------|-------------------|---------------------|---------------------|---------------------|-------------------|---------------------|
| Intermediate product | (3.4 ± 0.3)E + 03 | (4.9 ± 0.8)E + 02 | (1.28 ± 0.11)E + 02 | (1.70 ± 0.15)E + 02 | <dl | (3.3 ± 0.4)E + 00 | (1.13 ± 0.10)E + 01 |
| Intermediate product | (2.5 ± 0.2)E + 03 | (2.9 ± 0.5)E + 02 | (1.51 ± 0.13)E + 02 | (2.9 ± 0.3)E + 02 | <dl | (3.6 ± 0.4)E + 00 | (2.0 ± 0.2)E + 01 |
| Intermediate product | (3.8 ± 0.3)E + 03 | (2.8 ± 0.5)E + 02 | (6.7 ± 0.6)E + 01 | (1.10 ± 0.10)E + 01 | <dl | (2.1 ± 0.2)E + 00 | (1.04 ± 0.11)E + 01 |
| Mean | 3.2E + 03 | 3.5E + 02 | 1.2E + 02 | 1.9E + 02 | | 3.0E + 00 | 1.4E + 01 |
| Solid waste | (5.5 ± 0.5)E + 02 | (7.2 ± 1.2)E + 02 | (3.7 ± 0.3)E + 02 | (5.7 ± 0.5)E + 02 | (6.7 ± 0.8)E + 00 | (6.9 ± 0.7)E + 00 | (4.0 ± 0.4)E + 01 |
| Solid waste | (2.1 ± 0.2)E + 03 | (2.9 ± 0.5)E + 02 | (1.72 ± 0.14)E + 02 | (3.0 ± 0.3)E + 02 | (5.4 ± 0.6)E + 00 | (6.0 ± 0.6)E + 00 | (1.9 ± 0.2)E + 01 |
| Solid waste | (1.04 ± 0.10)E + 03 | (8.6 ± 1.3)E + 02 | (2.7 ± 0.2)E + 02 | (3.6 ± 0.3)E + 02 | (8.0 ± 0.9)E + 00 | (5.8 ± 0.5)E + 00 | (4.6 ± 0.5)E + 01 |
| Mean | 1.2E + 03 | 6.2E + 02 | 2.7E + 02 | 4.1E + 02 | 6.7E + 00 | 6.2E + 00 | 3.5E + 01 |
| Sediment no. 1 | (5.5 ± 0.5)E + 02 | (1.9 ± 0.2)E + 01 | (1.74 ± 0.16)E + 01 | (2.5 ± 0.3)E + 01 | (2.2 ± 0.2)E + 01 | (2.7 ± 0.3)E + 01 | <dl |
| Sediment no. 2 | (6.6 ± 0.6)E + 02 | (2.2 ± 0.2)E + 01 | (2.1 ± 0.2)E + 01 | (2.8 ± 0.3)E + 01 | (2.7 ± 0.3)E + 01 | (3.3 ± 0.3)E + 01 | <dl |
| Sediment no. 3 | (5.3 ± 0.5)E + 02 | (1.8 ± 0.2)E + 01 | (1.52 ± 0.14)E + 01 | (2.5 ± 0.3)E + 01 | (1.50 ± 0.14)E + 01 | (1.9 ± 0.2)E + 01 | <dl |
| Mean | 5.6E + 02 | 2.0E + 01 | 1.8E + 01 | 2.6E + 01 | 2.1E + 01 | 2.6E + 01 | |

Table 5
Activity concentrations in the wastewaters (in Bq l⁻¹)

| Sample | ⁴⁰ K | ²³⁸ U | ²²⁶ Ra | ²¹⁰ Pb | ²²⁸ Ra | ²²⁴ Ra | ²³⁵ U |
|-------------|-------------------------|-----------------------|-------------------------|-----------------------|-------------------|-------------------|------------------|
| Wastewaters | (2.7 ± 0.2) E + 02 | <dl | (1.7 ± 0.2) E + 00 | <dl | <dl | <dl | <dl |
| Wastewaters | (1.9 ± 0.2) E + 02 | (3.3 ± 0.7) E + 01 | (1.42 ± 0.10) E + 01 | (9.8 ± 1.1) E + 00 | <dl | <dl | <dl |
| Wastewaters | (1.58 ± 0.14) E + 02 | <dl | (2.0 ± 0.3) E + 00 | <dl | <dl | <dl | <dl |
| Mean | 2.1E + 02 | 1.1E + 01 | 6.0E + 00 | 3.3E + 00 | | | |

authors in phosphate ores of different origins (see [Khater et al., 2001](#)). As it can be observed from [Table 2](#), the conditions of secular equilibrium between ²³⁸U, ²²⁶Ra and ²¹⁰Pb differ depending on the type of phosphate raw material. The table highlights that phosphate ores show conditions of secular equilibrium in accordance with what indicated by other authors (e.g. [Boothe, 1977](#); [Guimond and Hardin, 1989](#); [Hussein, 1994](#); [Sam and Holm, 1995](#)). On the contrary, ammonium phosphate and phosphoric acid, show marked conditions of disequilibrium; as a matter of fact, while the activity concentration of ²³⁸U is around a few thousands Bq kg⁻¹, those of ²²⁶Ra and ²¹⁰Pb appear much lower (equal to a few hundreds Bq kg⁻¹ at most). The explanation of this is to be found in the phosphoric acid production process that disturbs the conditions of secular equilibrium existing in the source ore, remembering that the company imports the phosphoric acid and the ammonium phosphate used in the fertilizer production process. During the production of phosphoric acid, obtained from the reaction of the sulphuric acid with the phosphate ore, insoluble compounds of some radionuclides (in particular radium sulphate, an earthy alkaline element as calcium) coprecipitate together with calcium sulphate and concentrate in the waste product (phosphogypsum), while the most soluble ones remain in the phosphoric acid. [Poole et al. \(1995\)](#) highlighted, as to phosphoric acid, the following trend in activity concentrations: ²³⁸U = ²³⁴U > ²³⁰Th > ²¹⁰Pb = ²¹⁰Po > ²²⁶Ra and, obviously, an opposite trend in phosphogypsum. Said trend confirms the reason for ²³⁸U being detected in phosphoric acid samples in concentrations almost equal to the ore it is drawn from, while ²²⁶Ra and ²¹⁰Pb show activity concentrations which are much lower than those present in the phosphate ore. The different solubility, in phosphoric acid, of the compounds of some radionuclides also explains the disequilibrium present in ammonium phosphate samples, obtained by treating phosphoric acid with ammonia.

[Table 3](#) indicates the results of gamma-spectrometric measurements related to samples of end products. As it is possible to observe in [Table 3](#), ⁴⁰K activity concentrations in NPK and NP fertilizers are significantly different. Ternary fertilizers show higher concentrations of ⁴⁰K (average value 4000 Bq kg⁻¹) than binary fertilizers (average value 28 Bq kg⁻¹). This is due to the non-addition of potassium compounds – potassium sulphate and potassium chloride – to NP products. As to these fertilizers, ⁴⁰K derives from phosphate ores. All the fertilizers show concentrations of ²³⁸U equal to a few hundreds Bq kg⁻¹ (average value

370 Bq kg⁻¹, range 190–650 Bq kg⁻¹), while the values of ²²⁶Ra (average value 120 Bq kg⁻¹, range 60–230 Bq kg⁻¹) and ²¹⁰Pb (average value 210 Bq kg⁻¹, range 78–350 Bq kg⁻¹) result to be slightly lower. The disequilibrium between ²³⁸U, ²²⁶Ra and ²¹⁰Pb observed in fertilizers is to be attributed mainly to the different dosages of phosphorite, phosphoric acid and ammonium phosphate. In addition, as it can be seen from Fig. 2, a good linear correlation was observed between the fertilizer phosphorus content and the uranium concentration (²³⁸U and ²³⁵U), while no correlation was found between the fertilizer phosphorus content and the other determined radionuclides (the figure indicates ²²⁶Ra and ²¹⁰Pb).

The analysis of intermediate products has been carried out to better understand the distribution of radionuclides in the different matter flows of the production process. Unfortunately sampling of intermediate products is possible in a single spot of the chain of process phases; in said spot, samples analysed already show the same activity of end products (see Table 4); therefore it has not been deemed suitable to extend the survey to the remaining products. Waste products are generated during the production final phase only; as a matter of fact the production cycle does not provide for intermediate wastes such as the phosphogypsum which is generated by most of the plants during the production of superphosphate and triple superphosphate (e.g. Roessler et al., 1979; Makweba and Holm, 1993). In samples of solid wastes (see Table 4) radionuclides studied show average activity concentrations of the same order of magnitude of those of end products. This confirms that the production process does not provoke any partitioning of the ²³⁸U decay-series elements between the end product and waste product, as it was already assumable by observing the process scheme shown in Fig. 1. Sediment samples do not show

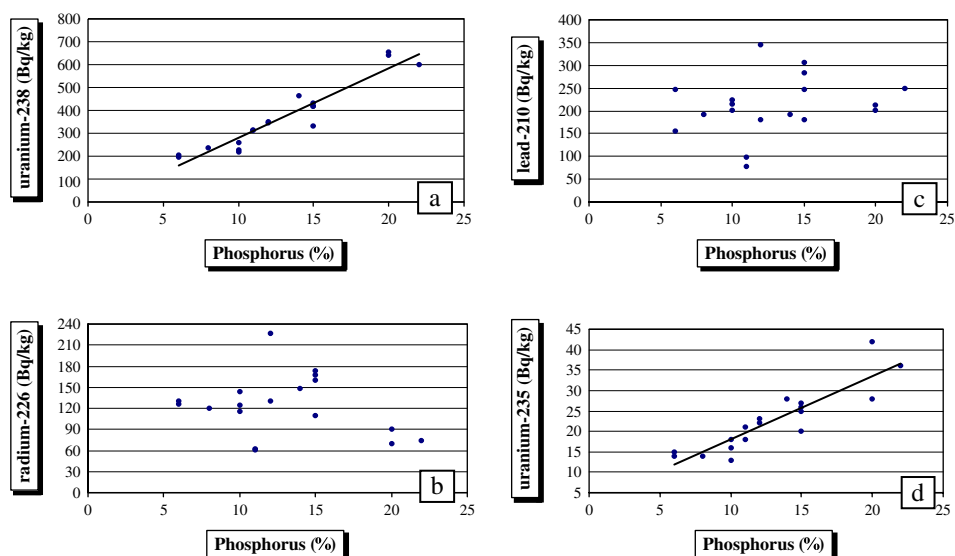


Fig. 2. Plot of activity concentration of ²³⁸U (a), ²²⁶Ra (b), ²¹⁰Pb (c) and ²³⁵U (d) (Bq kg⁻¹) vs fertilizer phosphorus content (%).

anomalous concentrations of natural radionuclides, having values within the range of 20–30 Bq kg⁻¹ for ²³⁸U and ²³²Th series and of 500–600 Bq kg⁻¹ for ⁴⁰K (see Table 4). Activity concentrations measured in these sediment samples are consistent with previous values found in the same area (Guerra et al., 2002). These figures show good agreement with the concentration values observed in lagoon and coastal sediments of North Adriatic Sea (Brondi et al., 1985; ARPA Emilia Romagna, 1998).

In wastewater samples (see Table 5) the activity concentrations of ⁴⁰K are a few hundreds Bq l⁻¹ and activity concentrations of ²²⁶Ra are up to a few dozen Bq l⁻¹. Considering that the concentrations of ⁴⁰K and ²²⁶Ra in fresh water are rather variable but almost always lower than 1 Bq l⁻¹ and that those of sea waters have, respectively, 11 Bq l⁻¹ and 1.1 mBq l⁻¹ as average values (Eisenbud and Gesell, 1997), it is possible to state that activity concentrations present in process wastewaters are remarkably higher than the natural condition.

3.2. Radionuclide releases into the environment

From the environmental point of view, it is interesting to note that the plant utilises a different process from the one normally used for the production of phosphate fertilizers. As described in Section 2.1, the phosphate ore acid attack does not occur with H₂SO₄ but with HNO₃, and reaction products – Ca(NO₃)₂ and H₃PO₄ – are both kept into the mixture. In this way it is possible to obtain a complex fertilizer – both nitrogenous and phosphatic – and to avoid the production of phosphogypsum, one of the main causes of radioactive pollution in the production of phosphate fertilizers (e.g. UNSCEAR, 1993; Bolivar et al., 1995; Haridasan et al., 2001).

Soil fertilizer, waste storage, release into the atmosphere of particulate matter from smokestacks and production of wastewaters result to be the main pathways of radionuclide release into the environment connected to the industrial production under examination. The estimate of the amount of radionuclides released into the environment by the plant is shown in Table 6. Calculations have been carried out as explained in Section 2.4. As it can be observed from the table, the majority of radionuclides are introduced into the environment through the use of fertilizers in agriculture. Only approximately 0.1% of radionuclides enter the external environment from storage of solid waste in landfills and only 0.04% results from the release

Table 6
Estimated releases of ⁴⁰K, ²³⁸U, ²²⁶Ra, ²¹⁰Pb and ²³⁵U from the complex fertilizer production plant at Ravenna

| Material | Annual production rate | Radionuclide (MBq y ⁻¹) | | | | |
|------------------------------|------------------------|-------------------------------------|------------------|-------------------|-------------------|------------------|
| | | ⁴⁰ K | ²³⁸ U | ²²⁶ Ra | ²¹⁰ Pb | ²³⁵ U |
| Fertilizers NPK | 280 000 (tons) | 1.1E + 06 | 1.1E + 05 | 3.5E + 04 | 5.9E + 04 | 6.7E + 03 |
| Fertilizers NP | 60 000 (tons) | 1.7E + 03 | 1.3E + 04 | 7.7E + 03 | 1.4E + 04 | 7.2E + 02 |
| Particulate matter emissions | 130 (tons) | 4.6E + 02 | 4.7E + 01 | 1.6E + 01 | 2.7E + 01 | 2.9E + 00 |
| Solid wastes | 480 (tons) | 5.7 + 02 | 3.0E + 02 | 1.3E + 02 | 2.0E + 02 | 1.7E + 01 |
| Wastewaters | 400 (m ³) | 8.4E + 01 | 4.4E + 00 | 2.4E + 00 | 1.3E + 00 | |

of particulate matter into the atmosphere. The contribution of wastewaters is even lower.

The impacts on the immediate area surrounding the fertilizer plant are essentially linked to the emission of particulate matter by smokestacks and release into the sewerage network of a small part of process waters. The amount of emitted particulate matter is about 130 ton y^{-1} . The results of the ISCST3 simulation model indicate that the maximum ground-level air concentration of particulate matter is $1.9 \mu\text{g m}^{-3}$ and occurs near the emission point, approximately 200 m ESE from the stacks. Downstream from this point, the particulate matter concentration decreases along with distance from the plant. Taking a dust loading of about $2 \mu\text{g m}^{-3}$ in ground-level air and assuming activity concentrations in airborne dust as those occurring averagely in end products, the activity concentrations in ground-level air are estimated to be about $0.7 \mu\text{Bq m}^{-3}$ of ^{238}U , $0.2 \mu\text{Bq m}^{-3}$ of ^{226}Ra , $0.4 \mu\text{Bq m}^{-3}$ of ^{210}Pb , $0.01 \mu\text{Bq m}^{-3}$ of ^{228}Ra , $0.01 \mu\text{Bq m}^{-3}$ of ^{224}Ra and $0.04 \mu\text{Bq m}^{-3}$ of ^{235}U . The predicted concentrations of ^{238}U -series radionuclides are about 2–4 times lower than the local ground-level air concentrations ($1.25 \mu\text{Bq m}^{-3}$ for ^{238}U -series radionuclides). Local background has been estimated in the manner suggested by UNSCEAR (1988, 1993, 2000) assuming a dust loading of about $50 \mu\text{g m}^{-3}$ and taking uranium-series radionuclide concentrations in local soil of 25 Bq kg^{-1} (Sciocchetti et al., 1985).

As anticipated in Section 2.1, when process waters may not be recycled inside reactors, they are piped to the nearby wastewater treatment plant, which also treats several other wastewaters coming from the industrial area. The fertilizer plant discharges about $400 \text{ m}^3 \text{ y}^{-1}$ of wastewaters, on average, to the sewerage network while the wastewater treatment plant treats about $800\text{--}900 \text{ m}^3 \text{ h}^{-1}$ of water. Therefore, it may be concluded that, thanks to both the purification treatment and the dilution effect with other waters, treated waters conveyed to a nearby salt-marsh do not result in a significant radioactive pollution of the environment. This conclusion is confirmed by the activity concentrations measured in sediment samples collected in the salt-marsh (see Section 3.1).

The introduction of natural radionuclides also occurs in areas far from the production zone through the utilisation of fertilizers for soil enrichment and the conveyance of solid wastes to landfills. The amount of radioactivity released into the environment, connected with the final placement of solid wastes seems to be not worrying from the point of view of environmental and human health protection, both due to the low activity concentrations and to disposal methods of said wastes, sent to controlled landfills equipped with the most modern technologies for environmental safeguard.

As highlighted above, about 99.9% of radionuclides yearly coming out from the production plant is transferred to the soil surface layer through fertilizing. Several studies on the subject indicate that the application of phosphate fertilizers to agricultural lands does not significantly affect the dose received from farmers and general population (e.g. Menzel, 1968; Ryan, 1981; Makweba and Holm, 1993; Santos et al., 1995; Sam et al., 1999). However, it is not yet known which long-term consequences might stem from the release of these small amounts of natural

radioactivity. Eisenbud and Gesell (1997) point out that continued application of phosphate fertilizers to soil over a period of many years could eventually increase the radium and uranium content of the soil, which would result in a corresponding increasing of the dose from this source. The prolonged use of phosphate fertilizers might also induce, in specific situations, a remarkable increase in natural radionuclides concentrations in surface and/or underground waters by migration of soluble compounds of uranium and its decay products, an event that has already occurred and has been widely documented (e.g. Spalding and Sackett, 1972; Zielinski et al., 1997). Therefore, it is not possible to exclude that, over the long period, a prolonged use of fertilizers containing natural radionuclides might induce significant radiological impacts on the environment (Eisenbud and Gesell, 1997; Ioannides et al., 1997; Sam et al., 1999). Impacts clearly depend upon conditions of fertilizer addition and whilst not impacting on radiological dose they may impact through exceeding of other regulatory drivers.

4. Conclusions

Radioactivity concentrations of fertilizers produced in this industrial plant are consistent with those reported in several other publications and with average values indicated in the UNSCEAR Report (1988).

From the environmental point of view, it is important to highlight that this plant utilises a process that avoids the production of phosphogypsum, one of the main causes of radioactive pollution due to production of phosphate fertilizers (UNSCEAR, 1993; Bolivar et al., 1995; Haridasan et al., 2001). This considerably simplifies solid and liquid wastes management. As a matter of fact, the survey shows that the radioactive pollution due to wastewaters and solid wastes is negligible. Particulate matter discharged into the atmosphere appears the most important additional release of natural radioactivity in the area surrounding the plant. Nevertheless, the predicted maximum ground-level air concentrations of ^{238}U -series radionuclides are about 2–4 times lower than the local background ($1.25 \mu\text{Bq m}^{-3}$).

However, even assuming that radioactive pollution from the production process might be negligible, it is underlined how chemical fertilizer application for long periods might induce an increase in natural radioactivity concentration in soils, thus entailing a possible dose increase to the population.

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