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Radiostrontium levels in foodstuffs: 4-Years control activity by Italian reference centre, as a contribution to risk assessment

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ABSTRACT

^{90}Sr is considered an important contaminant relating to food supply chains. In this study, 176 liquid and 260 solid foods, were analysed in order to quantify ^{90}Sr.

Through ruggedness tests, the application field of radiochemical methods used was extended successfully to all most important types of foodstuffs.

Regarding liquid matrices, milk samples resulted the most important indicator about ^{90}Sr contamination, with mean ^{90}Sr activity concentration equal to 0.058 Bq L^{-1}. Among other liquid foods, wine/spirits and livestock watering resulted the most contaminated, with mean contamination levels equal to 0.022 and 0.035 Bq L^{-1}, respectively.

Concerning solid matrices, cheeses produced from sheep's milk and animal feeds resulted the most contaminated (mean levels: 1.237 and 1.557 Bq kg^{-1}, respectively). Meat products and seafood showed contamination levels not significant within this survey; while, among vegetables, cacao/chocolate and spices resulted in contamination levels comparable with those of cheese obtained from milk of cows origin.

1. Introduction

Strontium is an alkaline earth metal, which may be found in the environment as non-radioactive isotope (^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr) or as radioactive isotope (remaining 12 isotopes). Among radioactive isotopes, strontium-90 (^{90}Sr) is considered the most important, due to its large use in nuclear reactors, industry and medicine. Being a fission product of plutonium and uranium in nuclear reactors and weapons, ^{90}Sr may be present in the environment as a consequence of nuclear accidents, authorised or unauthorised releases from nuclear facilities and from atmospheric nuclear weapons testing (Vajda & Kim, 2010). The most important dispersions of ^{90}Sr in the environment occurred in the 1950 s and 1960 s in fallouts from atmospheric testing of nuclear weapons; moreover, after Chernobyl disaster of 1986, in Europe and Asia a large amount of this radionuclide was released in the atmosphere (Yablokov & Nesterenko, 2009).

^{90}Sr is considered a hazardous radionuclide because it is characterised by a long biological and physical half-life (28.6 years) (Wilken & Joshi, 1991). It decays, emitting high-energy beta particles (E_{max} = 546 keV), turning Yttrium-90 (^{90}Y) (Stamoulis, Ioannides, Karamanis, & Patiris, 2007). ^{90}Y is also a pure β-emitter (high energy beta particles, E_{max} = 2.27 MeV; half-life = 2.7 days) that decays, forming stable zirconium (United States Environmental Protection Agency, 2015).

If ^{90}Sr is present in the environment, it may be taken into animal and human body by eating food, drinking water, or breathing air. Belonging to second group of periodic table, this radionuclide is characterised by high chemical affinity with calcium (Torres, Garcìa, Llauradò, & Rauret, 1996); consequently, about 15% of what absorbed may be deposited in bone, by causing bone tumors and tumors of the blood-cell forming organs (Hodgson, Ham, Youngman, Etherington, & Stradling, 2004; United Nations Scientific Committee on the Effects of Atomic Radiation, 2000). The inhibition of calcification and consequent bone deformities in animals is another health concern related to ^{90}Sr absorption. In this regard, a maximum dose which may assure non-cancer effects in animals was established in 0.6 mg/kg b.w. per day (Peterson, MacDonell, Haroun, & Monette, 2007). It is important

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to remark that radiotoxicity is due to beta particles emitted by both ^{90}Sr and ^{90}Y.

Regarding food supply chains, ^{90}Sr is considered as one of the most important contaminants among radionuclides, together with cesium radioactive isotopes, ^{131}I and ^{40}K (Yamamoto et al., 2012). It may be accumulated in calcium-rich foodstuffs, such as milk, dairy products, vegetables and in animal feeds. Indeed, milk and dairy products are characterised by highest transferring coefficients from soil to foods (mean levels $\sim$ 0.28 Bq kg^{-1}), followed by wheat and meats (mean levels < 0.03 Bq kg^{-1}) (Annenkov & Averin, 2011). Although characterised by low accumulation capability, relating to ^{90}Sr, seafood is considered useful to investigate about sea pollution levels, as demonstrated by recent studies developed in Fukushima area, after recent accident (World Health Organization/Food & Agriculture Organization of the United Nations, 2011). ^{90}Sr significant contaminations in animal feeds were also underlined by different authors (Knizhnikov et al., 1991; Sapeika, 1974; Shandala, 1993).

In Council Regulation (Euratom) No 2218/89, the European Commission listed the maximum permitted levels of radioactive contamination of foodstuffs and of feedingstuffs, following a nuclear accident or any other case of radiological emergency (i.e. 75 Bq kg^{-1} for food for infants (4/6 months) and 125 Bq kg^{-1} or Bq L^{-1} for dairy products and liquid foods) (European Council, 1989). Consequently, reliable and accurate radioanalytical methods, together with significant risk assessment studies, should be available for Agencies in charge of food inspections. However, there is a substantial gap about this point. Indeed, some radioanalytical methods are available, but most of these are applicable only to milk or to environmental matrices (Brun, Kergadakllan, Boursier, Fremy, & Janin, 2003; Heilgeist, 2000; Kabai, Hornung, Savkin, Poppitz-Spuhler, & Hiersche, 2011; Kim, Al-Hamnwi, Törvènyi, Kis-Benedek, & Sansone, 2009; Linauskas & Leon, 1993; Maxwell & Culligan, 2009; Stamoulis et al., 2007; Vajda & Kim, 2010). Moreover, methods which employ spectrometric techniques may suffer to some extent from isobaric interference of ^{90}Sr, and abundance sensitivity (Maxwell & Culligan, 2009), while, regarding radiometric methods, the necessary validation procedures are lacking.

As it regards risk assessment studies, few data are available about ^{90}Sr accumulation in foodstuffs (Annenkov & Averin, 2011; Lopes, Madruga, Mourato, Abrantes, & Reis, 2010; Riond, 2004).

This study is collocated in this context. It may be considered a valid contribution to risk assessment about ^{90}Sr presence in the most important foodstuffs.

436 samples composed of different types of solid and liquid foodstuffs were analysed during official control activity at Italian National Reference Centre for the Detection of Radioactivity in Feed and Foodstuffs (Foggia, Italy) during the period 2012–2015. The radioanalytical determinations were carried out by validated and accredited methods by liquid scintillation counting (LSC), after achievement of ^{90}Sr / ^{90}Y secular equilibrium.

2. Materials and methods

2.1. Sampling

The samples were collected from 13 Italian regions and from Japan (Fukushima), during the period October 2011–October 2015. In Fig. 1 a description of sampling, subdivided by geographic regions, is shown. A total of 436 samples (176 liquid foods and 260 solid foods) were analysed.

Liquid matrices: 176 samples, composed of 61 Milk samples (47 cow and 14 ovicaprine), 12 alcoholic beverages (4 wines, 4 beers and 4 spirits), 12 non-alcoholic beverages (4 juices, 4 nerve stimulant beverages and 4 sugary drinks), 91 water (83 livestock watering, 4 mineral and 4 tap waters).

Solid matrices: 260 samples, composed of 64 cheese samples (24, 7 and 9 ripened samples obtained from cow, sheep and goat milk, respectively, and 24 soft cheeses (5 butter, 6 yogurt, 3 mascarpone, 3 Gorgonzola, 7 mozzarella)); 62 fresh meats (6 cow, 6 pork, 5 chicken, 11 boar, 2 deer, 16 sheep, 16 goat), 6 meat products (2 salami, 2 ham, 1 cotechino, 1 bologna), 14 teleosts (2 sea breams/sea basses, 2 tunas, 1 swordfish, 4 codfish, 5 other teleosts), 15 molluscs/crustaceans (2 bivalve shellfish, 8 squids, 3 shrimps, 2 cuttlefishes/octopuses), 3 eggs, 3 leafy vegetables (spinach and lettuce), 7 other vegetables (2 potatoes, 2 celery, 2 garlic and onion and 1 carrots) 5 honey, 4 spices, 4 tomatoes, 4 jam and toffees, 4 citrus, 3 wheat, 8 cacao and chocolate, 5 ice cream and 49 animal feeds (33 raw materials and 16 processed feeds).

The majority of samples (milk, livestock watering, cheeses, fresh meats, seafood and animal feeds) were collected during official surveillance activity, carried out at Italian National Reference Center for the Detection of Radioactivity in Feed and Foodstuff. These samples were representative of geographic area of sampling; i.e. cheese samples were processed in the milk region of origin, and fresh meats were obtained from animals grazed in the collecting region. The samplings were conducted by local veterinary services, directly from farms and producing factories. Remaining samples were collected during "Italian Total Diet Study 2012–2014", carried out by Italian Ministry of Health, under the supervision of the Istituto Superiore di Sanità (ISS), the Italian National Health Institute. These samples were commercial products, collected in 4 Italian regions: Apulia, Lombardy, Lazio and Emilia-Romagna.

Due to long radioanalytical procedure (total time required: three working days to add to fourteen days, necessary for achievement of ^{90}Sr/^{90}Y secular equilibrium), the determinations were carried out only once (no replicates).

2.2. Chemicals and working standard solutions

Oxalic acid dehydrate (100.6%), Sodium acetate (100%), Hydrochloric acid (37% w/v) and Toluene (99.8%) were purchased from VWR (Fontenay-sous-Bois, France); Ammonium hydroxide (30% w/v) and Hydrogen peroxide (33% w/v) were supplied by Panreac Quimica S.A.U. (Castellar del Vallès, Barcelona, Spain); Nitric acid ($\geqslant$65% w/v), Oxalic acid (99%) and Ethanol ($\sim$96%) were supplied by Sigma-Aldrich (Steinheim, Germany); Sodium hydroxide (50%, w/w) was supplied by J.T. Baker (Deventer, Netherlands); Hydrofluoric acid (48%) and Bis(2-ethylhexyl)phosphate (HDEHP, 97%) were purchased from Merck Schuchardt OHG (Hohenbrunn, Germany); Sodium sulphide nonahydrate (98%) was supplied by Carlo Erba Reagents (Rodano, Milan, Italy). Dowex cation exchange resin 50 WX-8 was supplied by Alfa Aesar (Karlsruhe, Germany). The scintillation cocktail, Ultima Gold AB, was purchased from Perkin-Elmer (Waltham, MA, USA). Strontium, Yttrium, Lead and Bismuth certified standard solutions (10000 mg L^{-1}) in 4% Nitric acid (HNO_3) were purchased from CPI International (Santa Rosa, CA, USA). The ^{90}Sr standardised solution at concentration of 7.441 kBq g^{-1} was obtained from Eckert&Ziegler Isotope Products (Valencia, California). All solutions were prepared with ultrapure water with a specific resistance of 18.2 MΩ-cm, supplied by Milli-Q RG unit from Millipore (Bedford, MA, USA).

2.3. Sample preparation

The most difficult analytical step which characterises this type of determination is the separation of ^{90}Sr from other alkaline earth elements, such as Ca and Ba. Once radiochemical separation of ^{90}Sr is achieved, the radionuclide reaches, after fourteen days, the ^{90}Sr/^{90}Y secular equilibrium, in which the activity concentrations