



Conferenza d'Istituto 2019

21-22 maggio 2019



## Heavy metals and radionuclides mobility in food and environment: some recent research activities

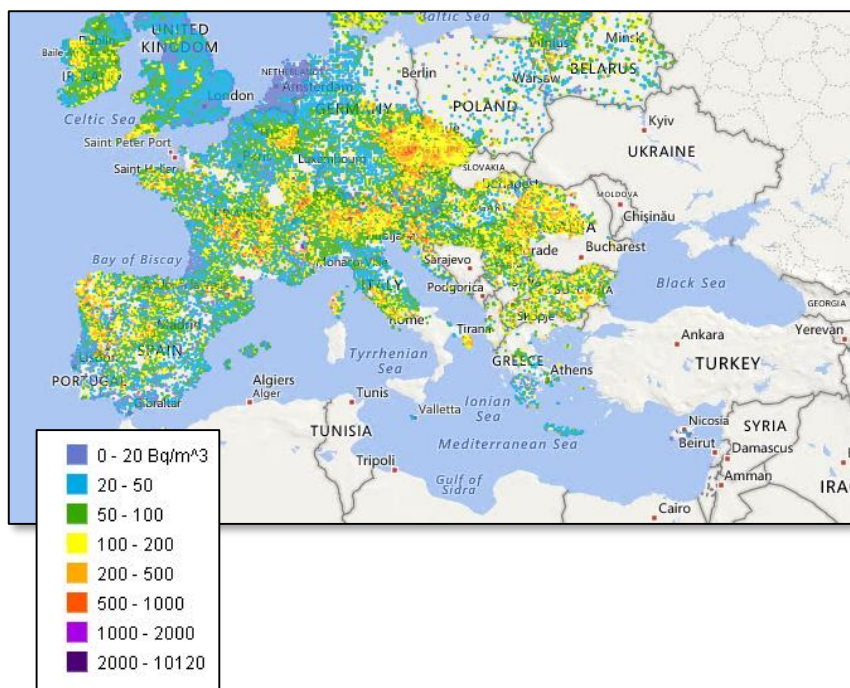
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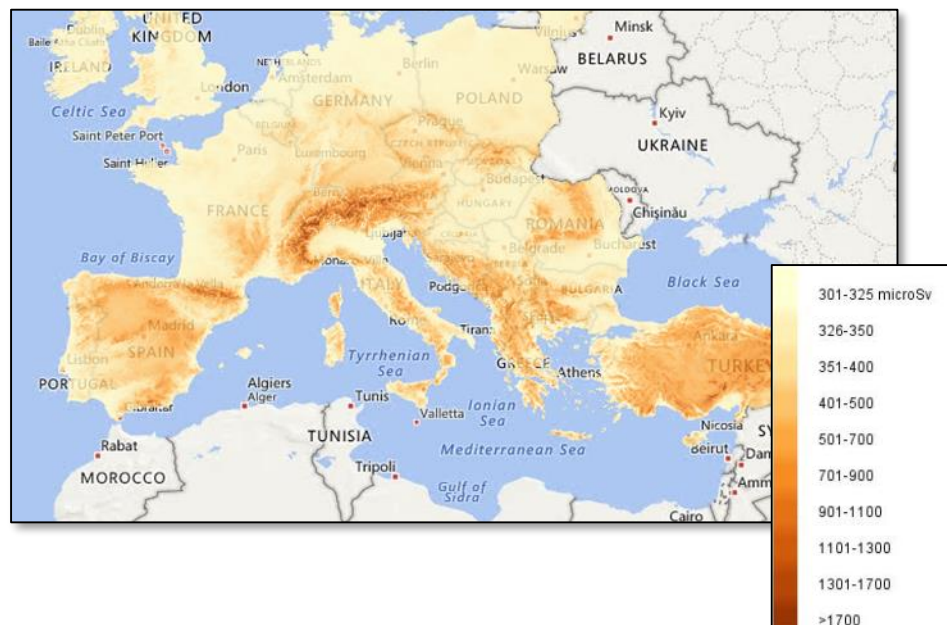
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We face natural radioactivity every day. Natural radiation sources are soil, bedrock and the sky. As living organisms in a naturally radioactive environment, evolution give us the right tools to cohabits with background radiation

## Indoor Radon Activity Concentration (Bq/m<sup>3</sup>)



## Annual Cosmic-Ray Dose (μSv/year)



Source: REMon (JRC, 2019)



## Natural and artificial radionuclides

The concentration of **naturally occurring** radioactive elements (e.g.  $^{40}\text{K}$ ,  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$ ,  $^{238}\text{U}$ ) is related to geological features (NORM). However, several technological treatments can enhance the activity concentration of such radionuclides (TENORM). TENORM sources are (EPA, 2019):

- **Energy**, e.g. coal combustion residuals, oil and gas production wastes
- **Industry**, e.g. mining wastes, fertilizers waste products, building materials
- **Water treatment**, e.g. sewage sludges

Many human activities are related to **artificial radioactive elements** (e.g.  $^{60}\text{Co}$ ,  $^{106}\text{Ru}$ ,  $^{131}\text{I}$ ,  $^{137}\text{Cs}$ ,  $^{192}\text{Ir}$ ,  $^{241}\text{Am}$ ):

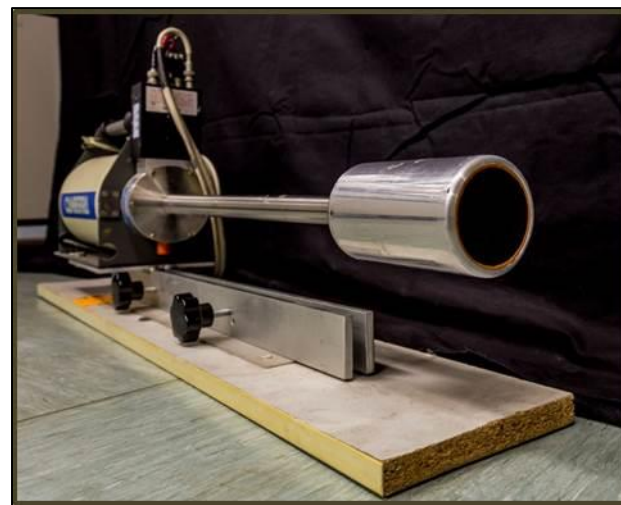
- **Energy**, short living fission products (not in Italy but the fallout of NPP accident is a global/regional issue)
- **Medicine**, e.g. external beam and internal radiotherapy, imaging
- **Industry**, e.g. thickness measurements, food sterilization
- **Research**, e.g. radioactive tracers/radiolabeling

The *Environmental Radiochemistry* group at CNR-ICMATE is specialized in radionuclide analysis and studies on radioactivity distribution among natural ecosystems, industrial settings, waste products and foods.

We are specialized in **low-level radioactivity** detection using alpha (2 Si(Li) detectors), beta (1 LSC) and gamma spectrometers (3 lead well + 1 portable HPGe detectors). The lab is also equipped with alpha counters and electret chambers for the determination of radon activity in the air.



For a complete survey of instrumental capability and methods, please take a look at **poster P29**



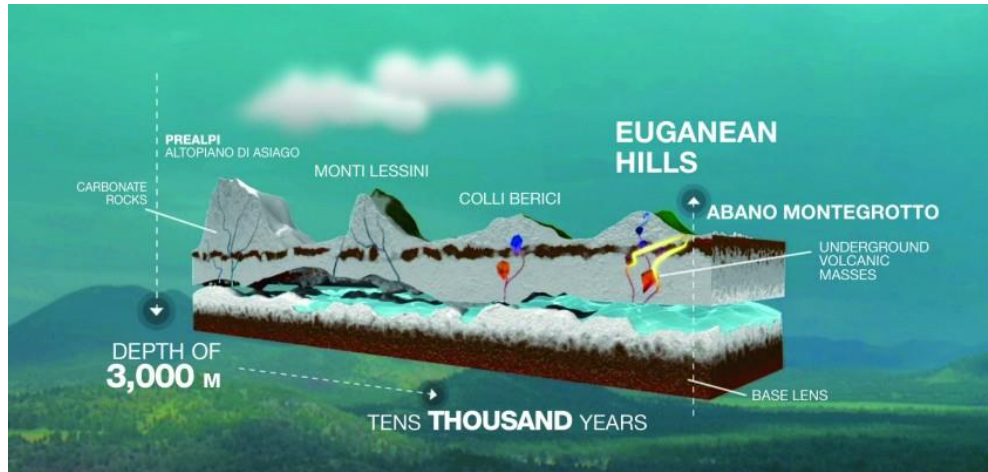


Recent research activities of the *Environmental Radiochemistry* group focused on the **distribution and mobility of radioactivity in the environment**

1. Radioactivity in thermal waters and mud
2. Radioactivity in drinking waters (focus on radon)
3. Radioactivity in food
  - ✓ Wild and bred animals
  - ✓ Food supplementations
  - ✓ Blueberries jams
4. Waste products
  - ✓ Phosphate fertilizer waste landfill
  - ✓ Urban wastewater treatment



Thermal waters are naturally radioactive with high variability on radionuclides concentration



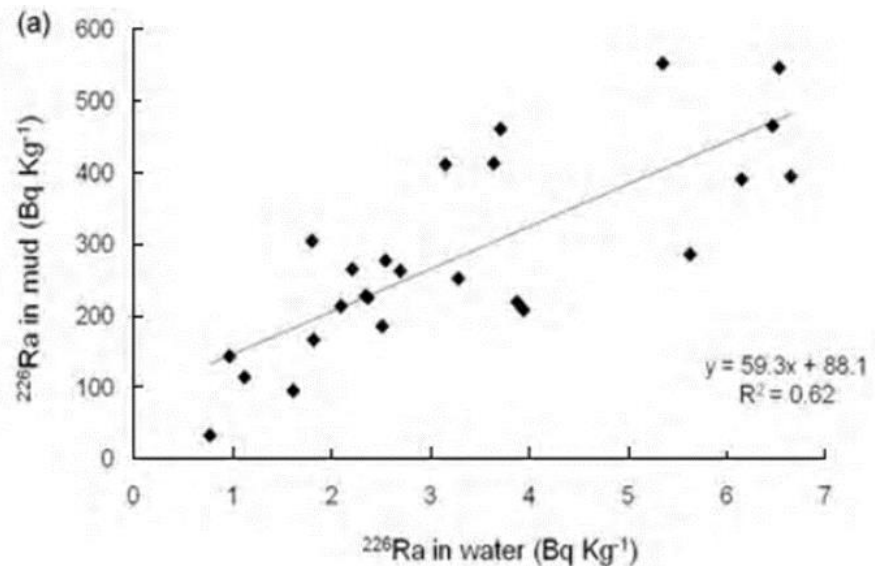
The Euganean Hills area is the largest thermal district in Europe.

**Deep groundwater leaches radionuclides from the hot and permeable deep rocks.**

Mud used for beauty and therapeutics treatments is originally non-radioactive lake sediment which had been in contact with radioactive thermal water. This “maturation” process turns the mud into a “radioactive mud”

**Biogeochemical transfer of  $^{226}\text{Ra}$  from water to the mud (enrichment).**

(Cantaluppi et al., 2014)

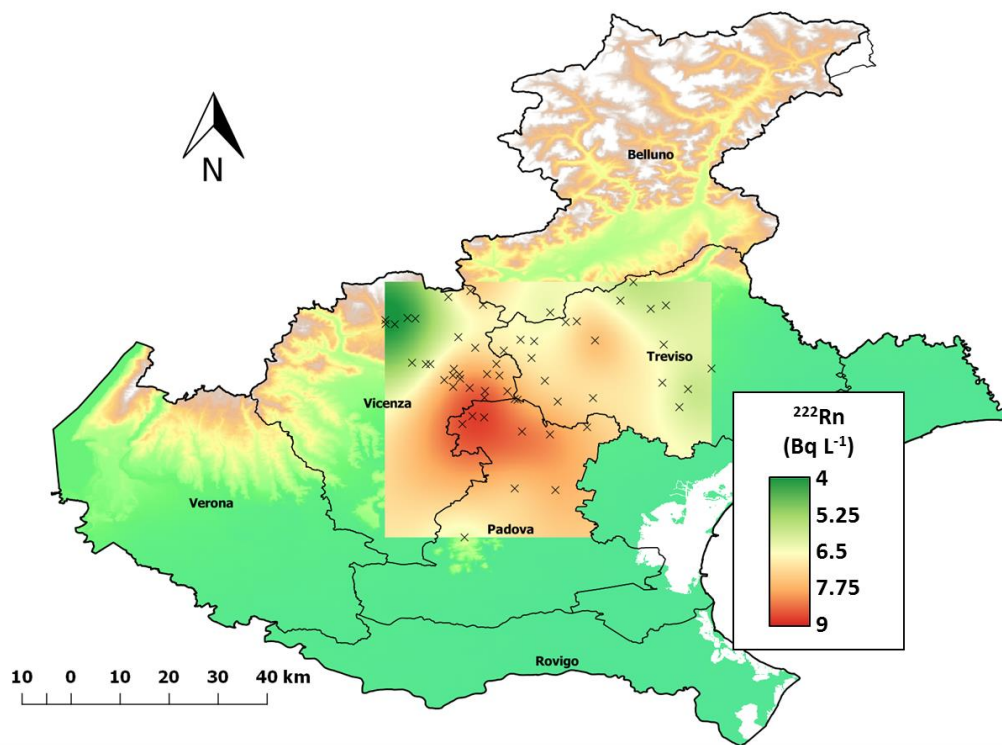


On the other hand, water used for human consumption (groundwater and surface water) is in general less radioactive than thermal water

Recent **European and national directives** require that government agencies and water supply companies perform seasonal campaigns for determining the radioactivity content of water

Radioactivity content in drinking water has **been poorly studied**, especially in the Veneto region

Mountain and plain area within the Veneto region display different concentration of  $^{222}\text{Rn}$  activity



(Cantaluppi et al., 2019 submitted)



Radioactivity in food is a matter of great concern. Real risk vs Perceived risk

Food industry represents 12% of the Italian GDP

**«Radioattività nella marmellata ai mirtilli», Tokyo blocca prodotti dall'Italia. L'azienda: tutta la frutta è garantita dalla nostra filiera**

Dal nostro corrispondente [Stefano Carrer](#) 25 ottobre 2013 Commenti (34)

TOKYO - Tutte le confezioni di marmellate ai mirtilli provenienti dall'Italia sono bloccate alle dogane giapponesi, dopo il ritiro dal commercio a Tokyo di oltre 5 mila barattoli di marmellata prodotta da una azienda veneta, in cui è stata riscontrata la presenza di radioattività superiore ai limiti di legge vigenti in Giappone.

Secondo un avviso del Comune di Tokyo, è stata rilevata presenza di Cesio 137 pari a 140 becquerel (Bq) al chilogrammo (contro il tetto massimo consentito in Giappone di 100) in confezioni di marmellata biologica "Fiordifrutta" ai mirtilli neri prodotte dalla Rigion di Asiago e importate dalla Mie Project. Secondo l'importatore, i mirtilli utilizzati proverrebbero dalla Bulgaria e l'elevata radioattività potrebbe risalire all'incidente.

**LA STAMPA** BIELLA

SEZIONI EDIZIONI

Con 330 mila presenze all'anno il Ricetto di Candelo simbolo del ... Insegue un'auto a Cossato per una mancata precedenza: fermato ... In 500 applaudono il segretario del Pd Nicola Zingales: «Vinci a ... Alpini, in mille da Biella sotto la Madonnina guidati dal decano Bisetti (100 ... "Nessuno credeva ai playoff, ma ora meritiamo di andare avanti!"

### Cesio nei funghi, sotto esame anche le castagne e i mirtilli

Legambiente: "Attenti agli alimenti in arrivo da zone contaminate"

**BIELLA**

A Cavaglià la fabbrica della plastica raddoppia: "I rifiuti diventano combustibile per i cementifici"

Gli oppositi si sfidano ai playoff: l'Edincol vuol frenare l'Orlandina-show

Bufere politica sul Reload festival. La Lega: "Una marchetta elettorale. Il sindaco: "Solo aria fritta"

L'Istituto Zooprofilattico Sperimentale ha scoperto cesio oltre la soglia di tolleranza in un fungo

### Allarme «cesio 137» nei cibi italiani

#### Catturati altri cinghiali radioattivi

*Dopo Vercelli animali contaminati anche in provincia di Verbania. Nel sangue la sostanza sprigionata da Chernobyl*



VERBANIA – Era un fenomeno privo di spiegazione certa; continua a esserlo ed è di dimensioni più estese del previsto. Esemplari di cinghiali «radioattivi», contaminati da tracce di cesio 137 (la stessa sostanza sprigionatasi in seguito all'esplosione di Chernobyl) sono stati individuati anche nella zona montana della provincia di Verbania, in particolare in valle Vigezzo.

COMMENTA  
Stampa  
Ascolta  
Email

NOTIZIE CORRELATE

- Chernobyl: linci, lupi e alci più numerosi di prima dell'incidente (06/10/2015)
- Marmellata Rigion bandita in

Sport Salute Tecno

Altri cinghiali radioattivi





Contents lists available at SciVerse ScienceDirect

## Food Control

journal homepage: [www.elsevier.com/locate/foodcont](http://www.elsevier.com/locate/foodcont)



### Radioactivity measurements and dosimetric evaluation in meat of wild and bred animals in central Italy

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#### ARTICLE INFO

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<sup>137</sup>Cs  
Meat  
Wild and farm animals

#### ABSTRACT

This research was dedicated to the study of the background activity concentration of natural radionuclides and <sup>137</sup>Cs in meat of wild and farm animals from central Italy. This meat is largely consumed by the local population and also exported to different countries. <sup>40</sup>K, <sup>210</sup>Pb, <sup>214</sup>Pb, <sup>214</sup>Bi and <sup>137</sup>Cs were determined by gamma spectrometry, <sup>210</sup>Po by alpha spectrometry. The mean <sup>40</sup>K activity concentration resulted 415 ± 56 Bq kg<sup>-1</sup> dw. In all samples, <sup>210</sup>Pb was below the detection limit (<18.9 Bq kg<sup>-1</sup> dw). The <sup>214</sup>Pb and <sup>214</sup>Bi activity concentration was detectable in only 33.1% of samples with a mean value of 3.5 ± 1.2 Bq kg<sup>-1</sup> dw. The <sup>210</sup>Po activity concentration ranged between 0.02 ± 0.002 Bq kg<sup>-1</sup> dw (pig) and 3.13 ± 0.31 Bq kg<sup>-1</sup> dw (deer) with a mean value of 0.48 ± 0.42 Bq kg<sup>-1</sup> dw. A significant difference can be noticed between the <sup>210</sup>Po concentration in the meat of wild specimens and the <sup>210</sup>Po concentration in those reared. Instead, no difference can be observed between male and female species and between adult and young species. The <sup>137</sup>Cs activity concentration resulted or not detectable or near to detection limit



- Dataset**
- Wild animals**
- 49 boars
- 29 deers
- Farm Animals**
- 52 cattles
- 18 pigs

**Table 2**  
<sup>210</sup>Po, <sup>214</sup>Pb – <sup>214</sup>Bi, <sup>40</sup>K and <sup>137</sup>Cs concentration (Bq kg<sup>-1</sup> dw) in deer's meat.

Sample number	<sup>210</sup> Po	<sup>214</sup> Pb – <sup>214</sup> Bi mean value <sup>a</sup>	<sup>40</sup> K	<sup>137</sup> Cs
<i>Roe deer</i>				
1	0.65	2.7 ± 0.5	387 ± 23.2	<2.0
2	0.53	<6.2	578 ± 34.7	<3.2
3	0.50	3.2 ± 0.6	401 ± 24.1	<2.5
4	0.60	<5.6	387 ± 23.2	1.8 ± 0.3
5	2.28	<6.4	448 ± 26.9	136 ± 5.6
6	0.51	<2.9	387 ± 23.2	<1.5
7	0.45	2.9 ± 0.6	380 ± 19.0	<1.7
8	0.22	–	–	–
9	3.13	4.3 ± 0.9	384 ± 23.0	54.9 ± 2.7
10	0.37	2.9 ± 0.6	386 ± 23.2	3.6 ± 0.2
11	0.77	<4.9	356 ± 21.4	<2.6
12	0.88	<4.1	404 ± 24.2	3.0 ± 0.2
13	0.30	<6.8	409 ± 24.6	<3.6
14	0.74	3.6 ± 0.7	377 ± 22.6	<1.8
15	0.62	<3.5	421 ± 21.1	<1.8
16	0.58	2.1 ± 0.4	478 ± 28.7	<1.7
17	0.22	<6.0	439 ± 26.3	<3.2
18	0.15	3.4 ± 0.7	422 ± 25.3	<1.9
19	0.31	<3.5	435 ± 26.1	<1.8
20	0.96	<4.5	430 ± 25.8	<2.3
21	0.83	<4.2	436 ± 26.2	1.3 ± 0.3
22	1.14	<5.9	456 ± 27.3	<3.2
23	0.97	4.4 ± 0.9	441 ± 26.3	<2.2
<i>Fallow deer</i>				
1	0.19	<5.8	396 ± 23.7	<3.1
2	1.18	4.0 ± 0.8	344 ± 20.6	<4.0
3	0.19	<9.9	425 ± 25.5	2.7 ± 0.6
4	0.37	<9.9	417 ± 25.0	3.8 ± 0.2
5	0.62	<4.4	459 ± 23.0	<2.3
<i>Deer</i>				
1	0.24	<5.4	431 ± 25.9	<2.8
Arithmetical mean <sub>dw</sub>	0.71	3.3	418	25.9
Standard deviation	0.63	0.8	44.6	48.1
Arithmetical mean <sub>fw</sub>	0.19	0.89	113	6.99
Geometrical mean <sub>dw</sub>	0.54	3.26	416	6.09
Geometrical mean <sub>fw</sub>	0.15	0.88	112	1.64

<sup>a</sup> Mean value of the activity concentration of the two radionuclides measured at 295.2 and 351.9 keV for <sup>214</sup>Pb and at 609.3 keV for <sup>214</sup>Bi.

<sup>137</sup>Cs detected in 14% of cases → the frequency of detection is higher for wild animals

<sup>210</sup>Po dose **0.03 - 0.11%** of the natural radiation exposure in Italy

(Meli et al., 2013)

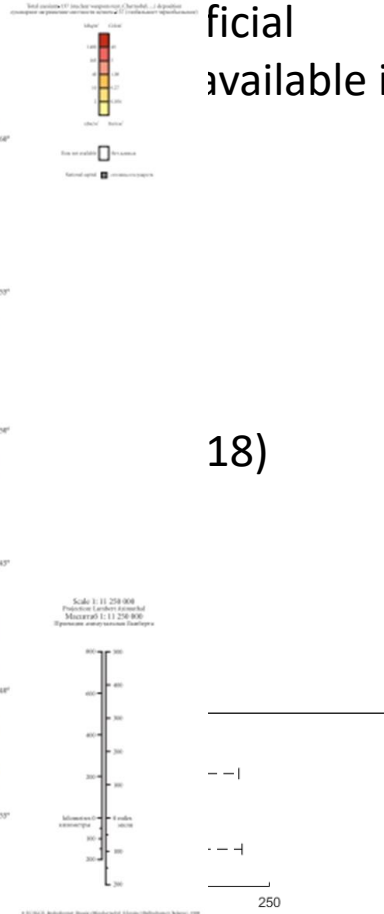
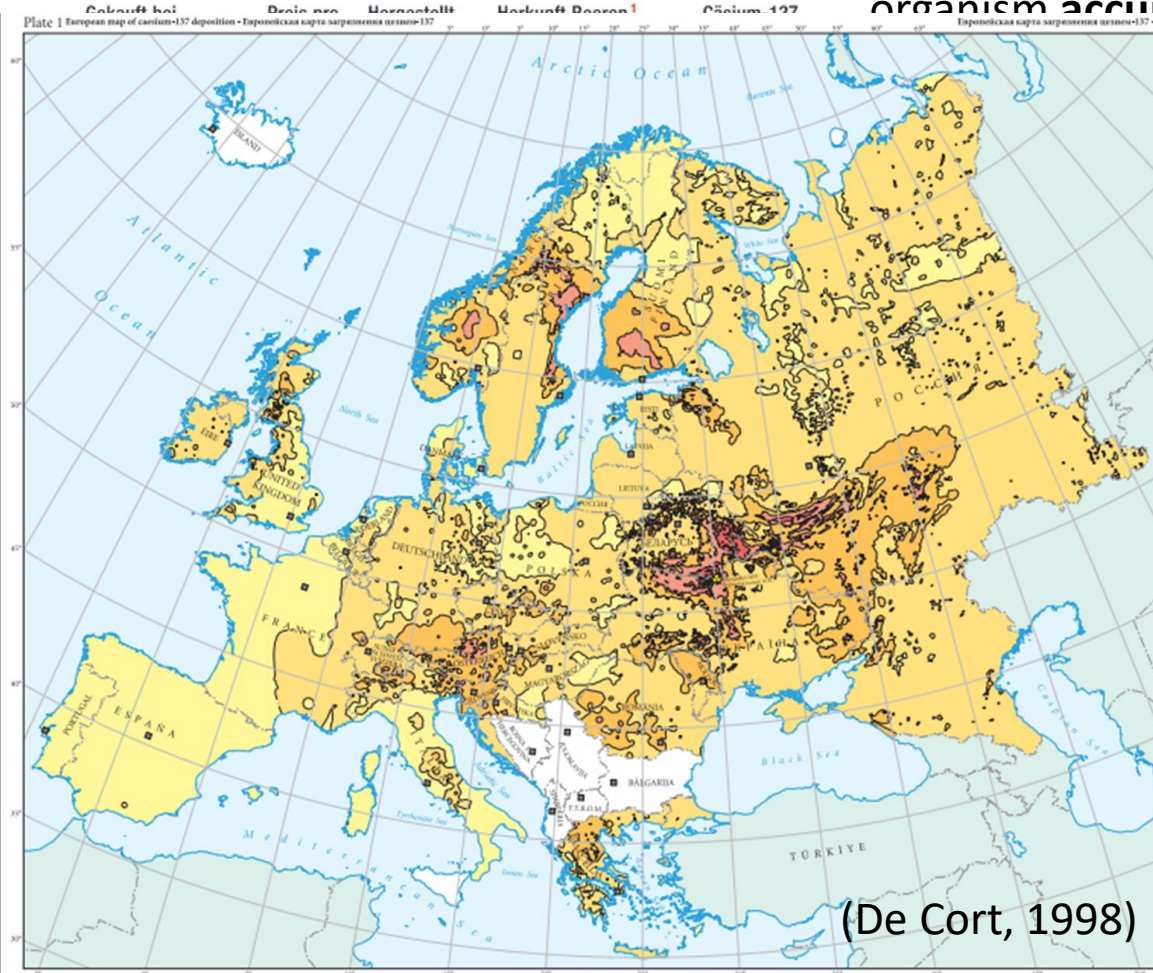
(<http://www.simplyinfo.org/?p=12058>)

Berries, mushrooms and other living organism accumulate natural (e.g. official available in

available in

18)

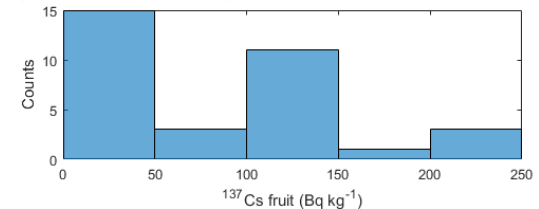
- Sorte
- Heidelbeer-Konfitüre
  - St. Dalfour Wilde Heidelbeere
  - Heidelbeeren Konfitüre (bio)
  - Naturgie Saveurs Attitudes Myrtille (b
  - Morga Heidelbeer Konfitüre extra
  - Staud's Wald-Heidelbeer Ost-Steierm
  - Maribel extra Heidelbeeren
  - Berg-Heidelbeer-Konfitüre
  - Sylt Blabär Wildheidelbeeren
  - Qualité & Prix Heidelbeeren Konfitüre
  - Hero Delicia Heidelbeere
  - Wilkin & Sons Ltd Wild Blueberry
  - Ottiger Heidelbeeren
  - Darbo naturrein Wildheidelbeere
  - Sonnentor, Die charmante Heidelbee
- Waldbeer-Konfitüre<sup>2</sup>
- Bonne Maman Waldfrüchte
  - Spar Konfitüre extra Waldbeeren
  - Maribel extra Mehrfrucht (Waldfrucht
  - Bonne Maman Erdbeeren u. Walderd
  - Favorit Waldbeeren Extra Konfitüre
  - Sonnentor, Die lustvolle Waldfrucht (
- <sup>1</sup> Angaben der Hersteller, muss auf Verp  
Heidelbeeren, beim Migros-Produkt Favor  
Bewertung: ■ = nicht nachweisbar ■



(De Cort, 1998)

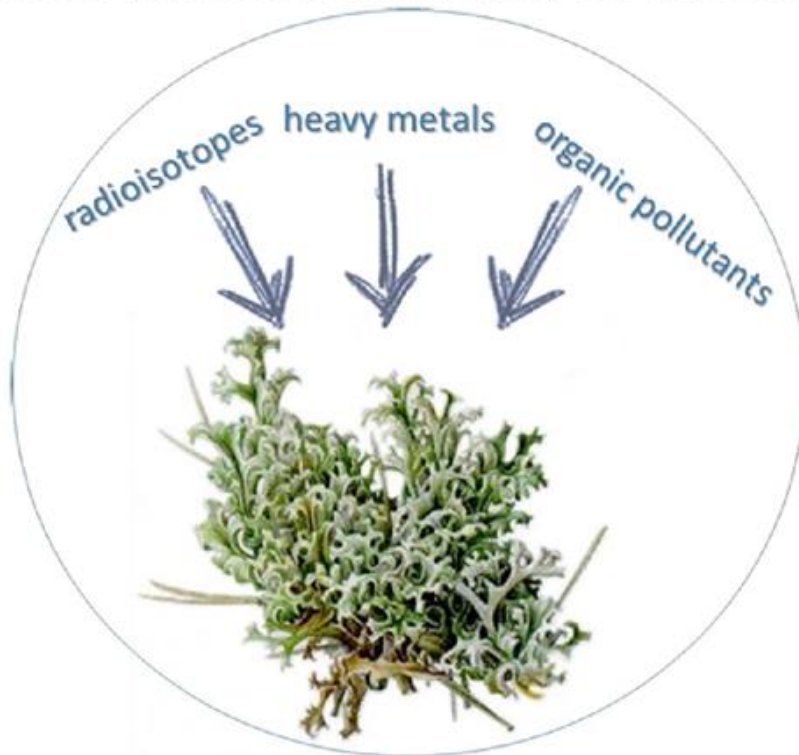
Determining the relationship between marmalade and blueberries from the radioactivity point of view?

(work in progress)



Other living organism accumulate pollutants (and radionuclides) from **airborne deposition**.  
*C. islandica*: the case of a lichen widely used in food supplementation and pharmaceutical products.

Airborne pollutants accumulation by *Cetraria islandica*



(Meli et al., 2018)

In addition to primordial radionuclides, the decay products  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  (father  $^{222}\text{Rn}$ ) return to Earth's surface via atmospheric deposition.

$^{210}\text{Po}$  sources include **natural** and **anthropogenic emissions** such as: coal-fired power stations, coal mining, metal smelting

$^{210}\text{Po}$  activity in *C. islandica* ranged [132 – 489] Bq kg<sup>-1</sup>dw

**Value higher than those reported by UNSCEAR for leafy vegetables** in the world [0.04–74] Bq kg<sup>-1</sup>dw.

The  $^{210}\text{Po}$  activity in *C. Islandica* accounts for **6% of annual intake from diet** (daily, liquid products), **~0.2% of natural radiation exposure** in Italy.



Phosphogypsum, a by-product of phosphate fertilizer production → acidic processing of phosphate rock with sulfuric acid → radionuclides partitioning into various phases

In the east sector of the Venetian Lagoon a large debris area (70000 m<sup>2</sup>) is characterized by the presence of **phosphogypsum wastes (400000 m<sup>3</sup>)** derived from fertilizer industries of Porto Marghera (1960-1980).

### No work of containment before 2000!

Main **radioecological and radiation protection problems** come up from

<sup>226</sup>Ra and daughters: <sup>222</sup>Rn, <sup>214</sup>Pb, <sup>214</sup>Bi, <sup>210</sup>Pb and <sup>210</sup>Po.

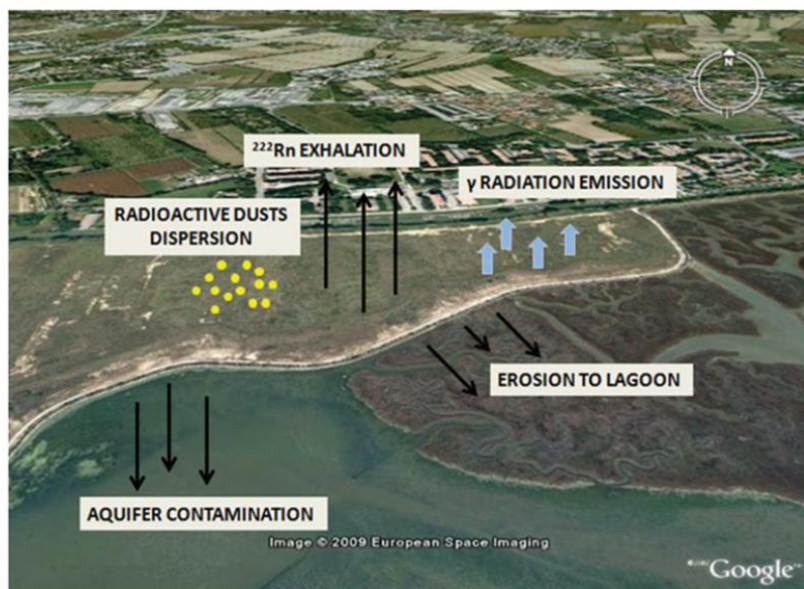


Fig. 1: Main environmental impacts of the phosphogypsum contaminated area (Passo a Campalto – Venice).

The main objective of the study was to determine how the implementation of a geochemical barrier **impacted on radon exhalation**

Research funded by *Magistrato alle Acque*

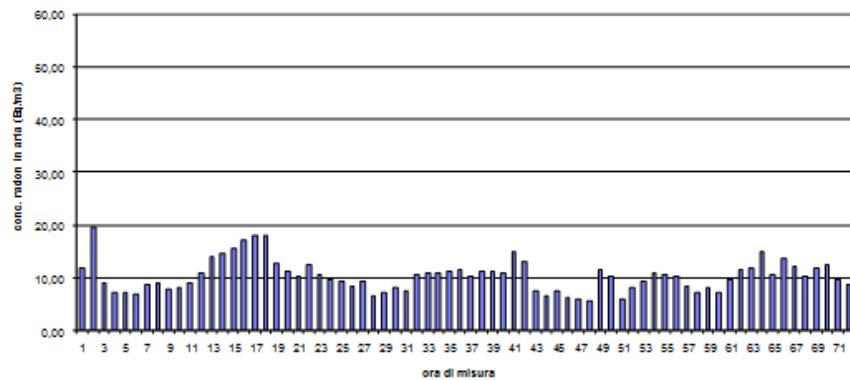
(Cantaluppi et al., 2012)

Table II: Comparison of averaged values of  $^{222}\text{Rn}$  flux in different cases.

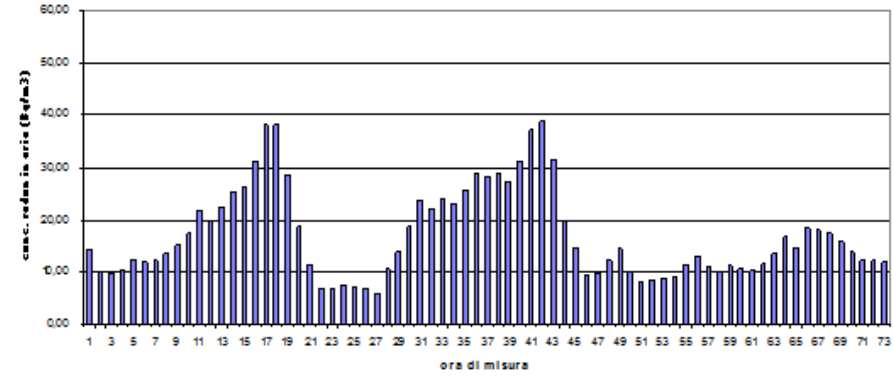
Average of $^{222}\text{Rn}$ exhalation rate <i>Anteoperam</i> ( $\text{Bq m}^{-2} \text{s}^{-1}$ )	Average of $^{222}\text{Rn}$ exhalation rate <i>Postoperam</i> ( $\text{Bq m}^{-2} \text{s}^{-1}$ )	Average of $^{222}\text{Rn}$ exhalation rate non-contaminated soil (CNR Research Area-Padua) ( $\text{Bq m}^{-2} \text{s}^{-1}$ )	Maximum permitted value of $^{222}\text{Rn}$ exhalation inside industrial areas (EPA 1998) ( $\text{Bq m}^{-2} \text{s}^{-1}$ )
0.72	0.020	0.060	0.74

(Cantaluppi et al., 2012)

Campalto (PG area)



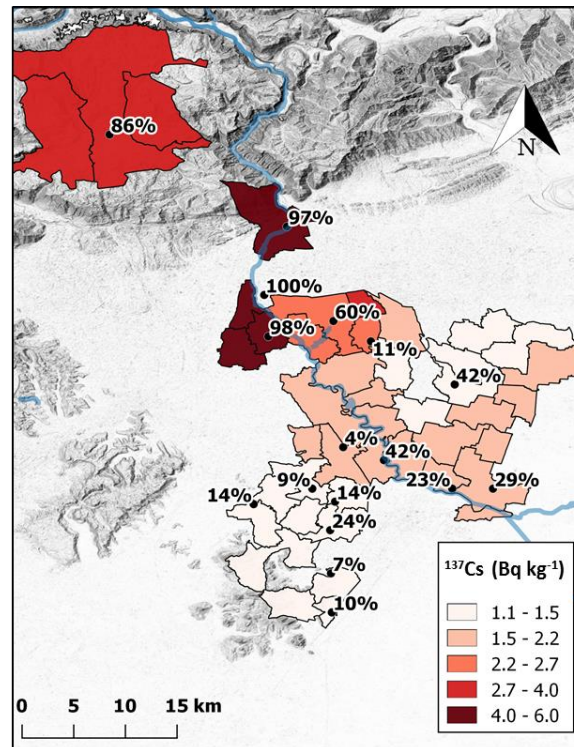
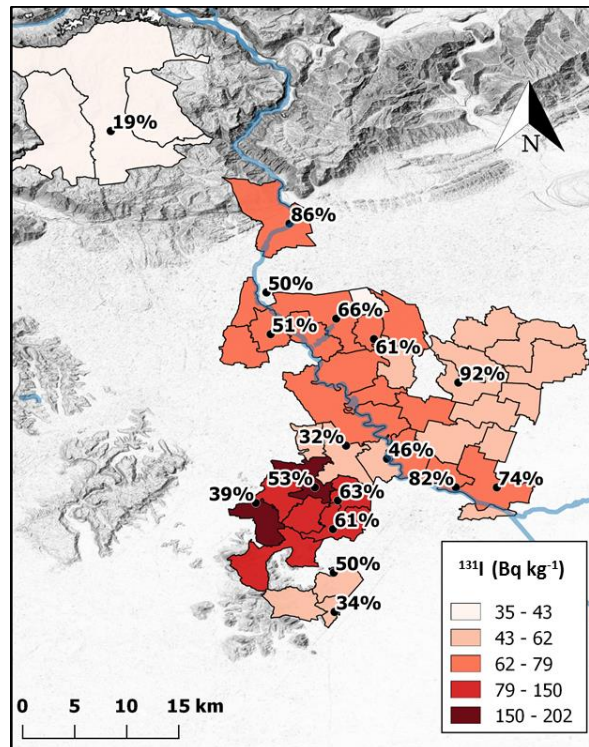
Padova (CNR)



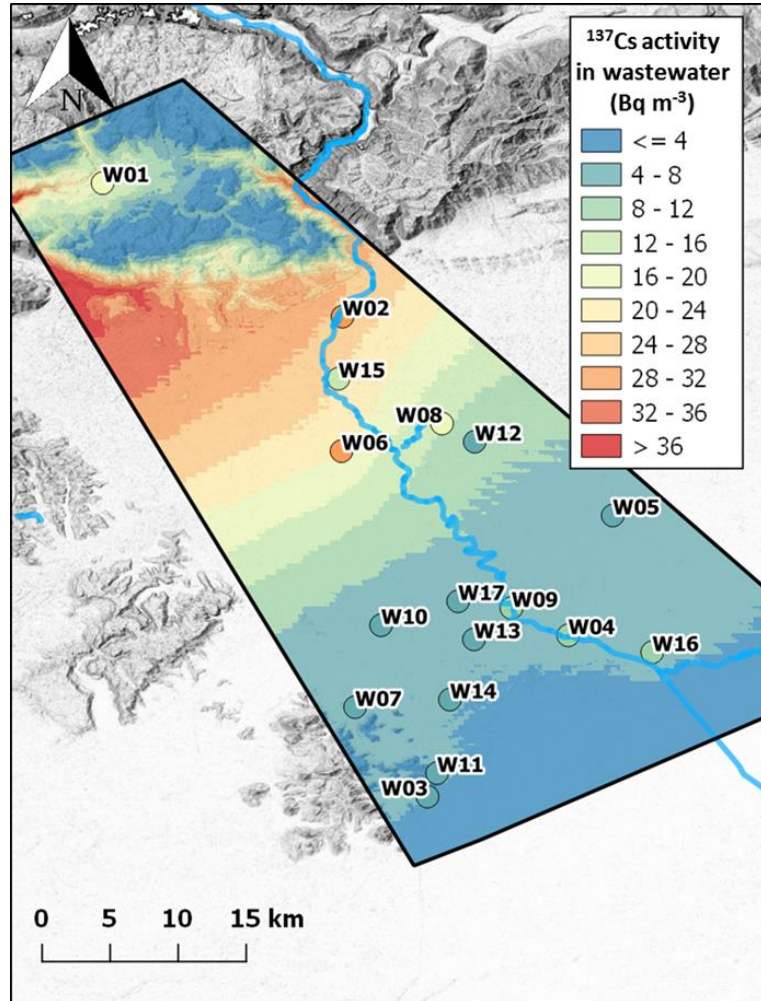


Wastewater treatment produces sludges that can be re-used in several application (e.g. agriculture, energy production).

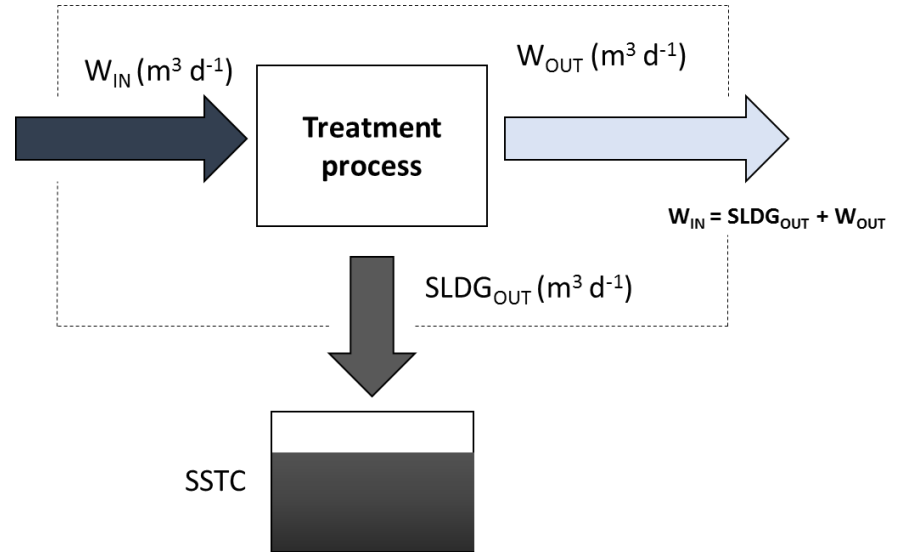
Sewage sludges **accumulate/concentrate** naturally occurring radioactive elements (TENORM) and man-made radionuclides.  $^{131}\text{I}$  and  $^{137}\text{Cs}$  in sewage sludges are two of the most occurring artificial radionuclides. Their activity is modulated by anthropogenic factors ( $^{131}\text{I}$ ) and by environmental factors ( $^{137}\text{Cs}$ )



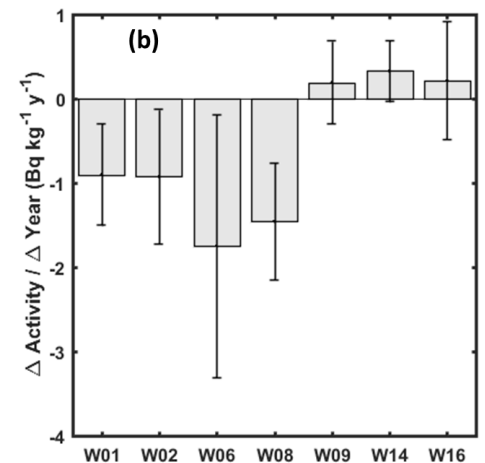
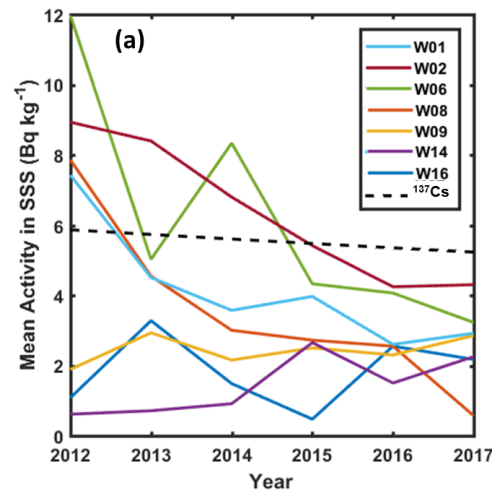




(Zannoni et al., 2019)



A five-years monitoring revealed the **displacement of  $^{137}\text{Cs}$**  from northern to southern areas





## Summary and Next Steps

Despite production of nuclear energy has been abolished in Italy in 1986, environmental radioactivity is still of great concern in our country.

Main issues are related to natural **radon activity in houses**, the **disposal of TENORM** and radioactivity content (artificial and natural) in **foodstuff**.

New European and national directives aim to set new limits and parameters for radioactivity in many matrixes (e.g. drinking water, building materials). This can be translated into a **new research effort**. For instance:

- the radionuclide content in foodstuff can be used in combination with other elements to **trace the origin of products**
- the radio-iodine analysis in wastewater treatment plant can be used **to improve engineering aspects of treatment plants** (iodine cycle and suppression → effect on aquatic environments)
- the radionuclides content in drinking water can be used with stable isotopes of water and trace elements to better understand the **dynamic of groundwaters** → better management of water resources. We are currently improving methods to detect extremely-low radioactivity levels in drinkable waters.

**Thank you**



## Reference list

- Calabrese, M., Calabretti, A., Chiara, C., Ceccotto, F., & Daniele, Z. (2018). Radiocesium Contamination in Samples of Blueberries Jams Collected in Stores of NE Italy (2013-2017).
- Cantaluppi, C., Ceccotto, F., Cianchi, A., Fasson, A., & Degetto, S. (2012). Radiological impact of phosphogypsum discharged into the Venice lagoon:  $^{222}\text{Rn}$ . In EPJ Web of Conferences (Vol. 24, p. 06001). EDP Sciences.
- Cantaluppi, C., Fasson, A., Ceccotto, F., Cianchi, A., & Degetto, S. (2014). Radionuclides concentration in water and mud of euganean thermal district. *International Journal of Environmental Research*, 8(1), 237-248.
- Cort, M. D. (1998). Atlas of caesium deposition on Europe after the Chernobyl accident.
- Meli, M. A., Cantaluppi, C., Desideri, D., Benedetti, C., Feduzi, L., Ceccotto, F., & Fasson, A. (2013). Radioactivity measurements and dosimetric evaluation in meat of wild and bred animals in central Italy. *Food Control*, 30(1), 272-279.
- Meli, M. A., Desideri, D., Cantaluppi, C., Ceccotto, F., Feduzi, L., & Roselli, C. (2018). Elemental and radiological characterization of commercial *Cetraria islandica* (L.) Acharius pharmaceutical and food supplementation products. *Science of the Total Environment*, 613, 1566-1572.
- Zannoni, D., Cantaluppi, C., Ceccotto, F., Giacetti, W., & Lovisetto, B. (2019). Human and environmental factors affecting the activity of  $^{131}\text{I}$  and  $^{137}\text{Cs}$  in urban wastewater: A case study. *Journal of environmental radioactivity*, 198, 135-146.