PhD DISSERTATION PROJECTS

Fluorinated organic pollutant assessment in agri-food-based matrices in different environmental scenarios

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Among the persistent organic pollutants are perfluoroalkyl substances, known as PFAS. The project aims to assess the content of targeted and non-targeted PFASs in agri-food products from areas of different anthropogenic impact, aimed at determining: current levels, sources of contamination, their trend over time, and possible correlation with other pollutants.

Valutazione degli inquinanti organici fluorurati in matrici agroalimentari in diversi scenari ambientali

Fra gli inquinanti organici persistenti vi sono le sostanze perfluoroalchiliche, note come PFAS. Il progetto ha come obiettivo la valutazione del contenuto di PFAS targeted e non-targeted in prodotti agroalimentari provenienti da zone a diverso impatto antropico, volto alla determinazione: degli attuali livelli, delle fonti di contaminazione, del loro andamento nel tempo e dell’eventuale correlazione con altri inquinanti.

# **1. State-of-the-Art**

The exponential industrial and scientific development of the last century has led to the production and use of many chemicals that have since been found to be harmful or potentially harmful to the environment and human health. Among the toxic substances classified as Persistent Organic Pollutants (POPs) are poly and perfluorinated compounds (PFAS), which are extremely important both from a toxicological and environmental aspect. These molecules are characterized by carbon chains containing fluorine atoms partially or completely replacing hydrogen atoms. They are found to be particularly recalcitrant and persistent in the environment because of the strong bond between carbon and fluorine, which gives them considerable chemical stability. Their use in many industrial fields is favored by the different chemical/physical characteristics given by the different substituents that can be linked to the alkyl chain. PFASs can be grouped into three macro-categories: i) perfluoroalkyl acid (PFAA) and its precursors, used for fire-fighting foams and to protect surfaces of textiles, clothing, leather, carpets and paper as well as for the production of fluorotelomers; ii) fluorotelomers, used for the production of plastics and rubbers and as water-repellent agents in paints; and iii) hydrofluorocarbons, used for the production of heat transfer fluids and detergents (Glüge *et al*., 2020). The scientific community's concern about such molecules is due to their identification as endocrine disruptors involving both female fertility problems-polycystic ovary syndrome and interference with normal mechanisms of pre- and postnatal development. Scientific studies have shown increased production of ROS and a possible association between their presence in the human body and cancers of the liver, testes, and pancreas. Some molecules including perfluorooctanoic acid (PFOA) have been shown to be harmful to the molecular structure of DNA by increasing the probability of genetic mutations (Bonato *et al*., 2020).

In Italy, major concern was raised by the analysis promoted in 2013 by the National Research Council (CNR) and the Ministry of the Environment and Protection of Land and Sea (MATTM) in the Veneto region, where large-scale PFAA contamination was revealed in drinking water (Bonato *et al*., 2020).

Furthermore, another substantial source of human intake of PFAS resides in food. The foods most susceptible to PFAS contamination are those of a protein nature, in fact in contrast to other POPs, PFAS preferentially accumulate in protein-rich (not lipid-rich) tissues with subsequent possible biomagnification. Thus fish products, wild game and edible animal offal represent one of the major sources of PFAS intake by humans, especially considering perfluorooctanesulfonic acid (PFOS) (Authority EFS, 2011).

The soil from which agri-food commodities are grown can be contaminated with PFASs either from irrigation water or from the use of sewage sludge used as a soil conditioner, which itself has contamination. It is the organic fraction of soil that promotes the accumulation of PFAS within the soil from which it subsequently migrates within plants. The breakdown within the plant is not homogeneous for all PFASs; the compounds that accumulate most in leaves and fruits are the short-chain C4-C6 compounds, compounds that nowadays are used to replace PFOA and PFOS. In contrast, the long-chain ones are more concentrated in roots (Ghisi *et al*., 2018).

Food packaging and cooking utensils can also be a source of PFASs in food given the use of these substances in lipophobic coatings and nonstick materials. Just as with other pollutants, there is a problem with PFASs migrating from the packaging or utensil to the food. The results of a recent study showed that it is the short-chain PFASs that are most affected by release into food. Migration is influenced by a number of factors such as: repeated reuse; exposure time; temperature; lipid, salt and pH content of the food (Ramírez Carnero *et al*., 2021).

For this reason, the European Food Safety Authority (EFSA) set a group safety threshold for PFAS in 2020 regarding the limit for tolerable weekly intake (TWI) of 4.4 ng kg-1 body weight (EFSA CONTAM Panel, 2020). Moreover, the EU has enacted Directive 2020/2184, concerning the quality of water intended for human consumption, setting limits for drinking water at 0.50 μg L-1 concerning the content of total PFAS, granting a transitional period until January 12, 2026, and Regulation 2022/2388 setting PFAS limits for certain foods. Nowadays, we speak of total PFASs because since 1940, many structural or isomeric variants of the original PFASs have been developed so the analysis of such molecules has shifted from a targeted to a non-targeted approach. The analysis of non-targeted molecules allows a comprehensive assessment of the content of PFASs that may be present in the analyzed matrix, and only in this way is it possible to make comprehensive estimates of the presence and abundance of these compounds in the environment-and thus in agri-food products and of their variation over time (Gonzalez de Vega *et al*., 2021). While food contamination for PFAS is often due to their use in other fields, foodstuffs are still affected by other chemical contaminants such as pesticides. These substances can be found in food as residues from treatments carried out on crops in order to increase production yield and meet food demand. They are a concern for human health because they can lead from simple headaches to more serious diseases such as cancer, as well as for the entire environmental ecosystem, and it is important to monitor their presence in foods to safeguard the health of consumers (de O. Gomes *et al*., 2020).

# **2. PhD Thesis Objectives and Milestones**

Within the overall objective mentioned above this PhD thesis project can be subdivided into the following activities according to the Gantt diagram given in Table 1:

A1) **Study of analytical method** starting with the choice of target molecules (A1.1) to develop an analytical method based on scientific knowledge and new analytical approaches (A1.2).

A2) **Sampling:** selection of sampling areas based on anthropogenic impact (A2.1) and sampling of agri-food products (A2.2).

A3) **Laboratory work** to analyze samples (A3.1) and check for chemical contaminants by data processing (A3.2).

A4) **Data analysis** to study sample clustering and correlations between molecules (A4.1) and to study sources of contamination (A4.2)**.**

A5) **Writing and Editing** of scientific reports and papers and the PhD thesis.

***Table 1***Gantt diagram for this PhD thesis project.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Activity Months | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** | **12** | **13** | **14** | **15** | **16** | **17** | **18** | **19** | **20** | **21** | **22** | **23** | **24** |
| A1) | ***Study of analytical method*** |   |   |   |  |  |  |  |   |   |  |  |  |  |   |  |  |  |  |   |   |  |  |  |  |
|  | 1) Choice of target molecules |   |  |   |  |  |  |  |   |   |  |  |  |  |   |  |  |  |  |   |   |  |  |  |  |
|  | 2) Development of an analytical method |   |  |   |  |  |  |  |   |   |  |  |  |  |   |  |  |  |  |   |   |  |  |  |  |
| A2) | ***Sampling*** |   |   |   |  |  |  |  |  |  |  |   |   |  |   |   |   |  |   |   |   |  |  |  |  |
|  | 1) Choice of sampling areas |   |   |   |  |  |  |  |  |  |  |   |   |  |   |   |  |  |  |   |   |  |  |  |  |
|  | 2) Sampling of agri-food products |   |  |   |  |  |  |  |  |  |  |   |   |  |   |  |   |  |   |   |   |  |  |  |  |
| A3) | ***Laboratory work*** |   |  |   |   |   |   |  |   |   |   |   |   |  |   |  |  |  |  |   |   |   |   |   |  |
|  | 1) Sample analysis |   |  |   |   |   |  |  |   |   |   |   |  |  |   |  |  |  |  |   |   |   |   |  |  |
|  | 2) Data processing |   |  |   |  |  |   |  |   |   |  |  |   |  |   |  |  |  |  |   |   |  |  |   |  |
| A4) | ***Data analysis*** |   |  |   |  |  |   |   |   |   |  |  |   |   |   |  |  |  |  |   |   |  |  |   |   |
|  | 1) Statistical analysis |   |  |   |  |  |   |   |   |   |  |  |   |   |   |  |  |  |  |   |   |  |  |   |   |
|  | 2) Study of sources of contamination |   |  |   |  |  |  |  |   |   |  |  |  |  |   |  |  |  |  |   |   |  |  |  |  |
| A5) | ***Thesis and Paper Preparation*** |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |  |   |   |   |   |   |   |   |

# **3. Selected References**

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