REGIONE DEL VENETO

REGIONE DEL VENETO AZIENDA ZERO

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Agenzia Regionale per la Prevenzione e Protezione Ambientale del Veneto

IRSA CNR

UNIVERSITÀ DEGLI STUDI DI PADOVA

LIFE PHOENIX
FOR THE SCHOOL

TEACHING KIT

EXPERT INFORMATION FOR HIGH SCHOOLS

RAISING THE AWARENESS OF STUDENTS ON THE IMPORTANCE OF THE WATER, ON ITS CONSCIOUS USE AND ON THE ISSUES RELATED TO POLLUTION AND TO PFAS, IN PARTICULAR

Life Phoenix

Perfluorinated compounds
HOlistic ENvironmental
Interinstitutional eXperience

TEACHING KIT

FOR HIGH-SCHOOL TEACHERS AND STUDENTS

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1 THE LIFE PHOENIX PROJECT

The LIFE PHOENIX project aims at demonstrating how a new inter-institutional governance model, supported by innovative forecasting tools and targeted mitigation strategies, can manage the risks related to the water pollution caused by the emerging contaminants known as PMOC, in a more timely and effective way.

The LIFE PHOENIX model will be submitted in order to avoid, or at least to curb the public expenditure that is required to mend the damage caused by the emerging pollutants to the human health and the environment.

This project specifically focuses on a sub-class of the PMOC - the short-chain perfluorinated alkyl substances (PFAS) - and its presence in drinking and irrigation water.

A - The LIFE programme of the European Union

The LIFE programme is the financial tool of the European Union for the environment. The overall objective of LIFE is to contribute to the implementation, update and development of EU environmental policy and legislation by co-financing pilot or demonstration projects with added value at the European level.

The PHOENIX project is one of the many innovative projects in the environmental domain financed by the European LIFE programme. The total budget of the LIFE PHOENIX project amounts to over two million Euros, almost 60% of which is provided by the European Union.

B - Partners and duration of the project

The coordinating agency of the LIFE PHOENIX project is Regione del Veneto (Veneto Regional Government), with its Prevention, Food Safety, and Veterinary Science Department. The associate partners are Azienda Zero, ARPAV, IRSA-CNR and Università degli Studi di Padova. The project was started on September 1, 2017 and will come to an end on March 31, 2021.

C - Objectives of the LIFE PHOENIX project

The main objectives of the LIFE PHOENIX project are:

- Establish a stable system of inter-institutional governance of environmental pollution issues, based on a regional standing committee supported by a panel of experts.
- Develop guidelines for the prevention of the health and environmental risks caused by these contaminations, and provide operational instructions for immediate action in order to implement an effective work plan in case of emergency.

THE EXPERTS EXPLAIN

Which actions were implemented in similar instances of water pollution?

Previous cases of diffuse pollution of water intended for human consumption (for instance the atrazine case in the Lombardy region, Italy, in the 1980s or the more recent problem of natural arsenic in Central Italy) were addressed with administrative measures only, applying the derogation to the limit set by law, often delegating the responsibility for the actions to the various local parties (managers, mayors) who were not coordinated with each other, when not even opposed to each other.

The first added value of this model inspired by the Veneto Region and developed within LIFE will be the coordination and sharing of data and knowledge among all the parties involved; the second innovative aspect is that the coordinated management system will also study and implement all the prevention and mitigation measures that the scientific community provides

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With regard specifically to PFAS, since the early 2000s several studies in the United States have found the presence of PFOA, at ppb level, in the blood of more than 98% of the population. As a result of a class action lawsuit and an arrangement with DuPont (the largest producer of PFAS), three epidemiologists were commissioned to conduct studies on the population living near a chemical plant exposed to PFOA at higher levels than the general population. They found a correlation between high PFOA exposure and six health findings: renal carcinoma, testicular carcinoma, ulcerative colitis, thyroid disease, hypercholesterolemia (high cholesterol), and pregnancy-induced hypertension.

Following the problems that surfaced, the main PFOS producer - 3M (known as the Minnesota Mining and Manufacturing Company from 1902 to 2002) - began a phase-out of PFOS production since 2002 in response to concerns expressed by the EPA (United States Environmental Protection Agency). Since 2014 the EPA has also listed PFOA and PFOS (including their salts) among the emerging contaminants.

In the United States, a series of legal actions are still pending against PFAS manufacturers. Concern about these compounds has triggered the EPA's PFAS Action Plan since February 2019: this is a very substantial and articulated plan of studies and actions relating to PFAS, currently not expected to be closed.

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- Provide state-of-the-art forecasting tools to support risk analysis.

THE EXPERTS EXPLAIN

Which forecasting tools are available to us at present?

The forecasting tools used under the LIFE PHOENIX project are based on numerical modelling applied to groundwater and surface water. It consists in several software tools able to simulate all the chemical and physical processes related to the diffusion of pollution in water, and is therefore able to predict the evolution of the pollutant in space and time.

These capabilities allow these tools to provide answers to the many unknown factors of this issue (e.g. How many years will the pollution last? How much contaminant mass has been dispersed in the environment? etc.) and therefore to serve as an effective decision support tool capable of quantifying, interpreting, and predicting the spread of the contamination.

Numerical modelling has also been combined with a study on the toxicological effects of PFAS in living organisms, in order to identify those species that can provide a first "wake-up call" on their possible presence.

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- Propose mitigation strategies based on innovative technologies (for drinking water) and on natural solutions (for irrigation water).
- Develop a work method that can be replicated, so that the know-how and results of the project can be transferred to other Italian or European geographical contexts characterised by similar environmental contamination.
- Raise the awareness of the population and the stakeholders on the importance of an effective prevention and protection system for water as a resource.

D - Key actions of the project

- Creation of an information and statistical system that collects all the information – currently available in a fragmentary way in different institutions - on the structure and uses of the territory, on the sources of pressure, on the hydrographic network and irrigation districts, on the layout of water supply networks and on the results of environmental monitoring. The tool will enable the Institutions to monitor the situation immediately, comprehensively and in an integrated manner, thus making it easier to forecast and take strategic action.

THE EXPERTS EXPLAIN

The information system shall contain two different types of data:

- Data about land use: land use map (e.g. forests, agricultural areas, urban areas), hydrographic network, water catchment areas, irrigation districts associated with their irrigation sources, water supply networks with their sources of supply and users catchment area, sources of pressure (e.g. production plants differentiated by type, sewage treatment plants, incinerators, landfills), livestock farms, agricultural land, food production plants;

- Analytical data: results of the analyses carried out on different matrices (surface water, groundwater, drinking water before and after treatment, industrial wastewater, sludge, landfill leachate, soils, plant and animal species covered by the project).

Both the land use data and the sampling points of the various matrices analysed will be georeferenced on a map. All data will be updated periodically; regarding the analytical data, it will be possible to generate graphs that describe their trend over time.

The information system will therefore be able to create interconnections among the different data and will be easy to use by the experts of the institutions in order to promptly answer the most varied questions, some examples of which are given below:

- What are and where are located the sources of pressure that, depending on the type of substances or materials treated, could release certain pollutants into the environment? In which environmental medium could these pollutants be released (surface water, groundwater, soil)? Which matrices and points should be monitored to ensure that the environmental media at risk are not contaminated?
- Which production facilities are authorised to discharge wastewater into a specific watercourse? If so, where is the wastewater discharged and what are the results of ARPAV's analytical tests on wastewater to verify compliance with the discharge limits?
- In the case of landfills, what are the results of the analytical controls carried out by ARPAV on leachate? If these results show the presence of any pollutants, then has the underlying water table been contaminated?
- What are the concentrations of a given pollutant in a watercourse or water table (at the different sampling points) and how have they changed over time?
- What agricultural land is irrigated with water taken from a contaminated watercourse?
- Which water supply networks are supplied from contaminated water tables or watercourses? Have the purification treatments carried out been effective? How many people are living in the territory served by that specific water supply network, and could therefore be exposed to the pollutant?

Essentially, this information system will have a dual function:

- In the prevention and planning phase, it will allow to identify the sources of pressure, the environmental media that are potentially impacted and their geographical delimitation; to schedule the surveillance and analytical control activities required to identify and promptly remedy any critical issues.
- During the management of a pollution episode, it will enable to quickly trace back to the source of the pollution, to identify the contaminated environmental media and their extent, to understand whether the food and water supply chains may have been contaminated (in the latter case, quantifying the population exposed), to decide where the additional sampling points should be placed, to follow the evolution of the contamination over time by verifying the effectiveness of the control measures adopted.

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- Development of **hydrogeological forecasting systems** to analyse the evolution of pollution in space and time. These statistical models make it possible to simulate the spread of a pollutant through water, and to estimate where and how soon the pollutant will spread; these models can also be used to reconstruct the evolution of contamination in the past, using the current situation as a starting point.
- Development of **environmental "early warning" methods** based on bio-indicators, i.e. organisms or biological systems used to assess a (typically degenerative) change in the quality of the environment.
- Specifically, the selected **bioindicators** are earthworms, detritivore organisms considered to be a good soil quality indicator; it was also found that they are bioaccumulators of PFOS, PFOA and perfluorobutasulphonate (PFBS), a type of short-chain PFAS. Therefore, earthworm pools will be sampled from contaminated soils and tests will be carried out on them to detect the presence of **ecotoxicological biomarkers**, i.e. biochemical, cellular, physiological or behavioural changes due to the exposure and/or effect of one or more polluting compounds.

- In recent decades biomarkers have been developed as an innovative element in eco-toxicological investigations, since they provide quick and accurate answers to some basic questions: what effects do contaminants cause at the molecular, biochemical, cellular or tissue level on natural populations and/or communities? Can the correct assessment of these effects serve as an early signal of the stress caused by environmental contamination?
- The ultimate goal of the use of bioindicators and biomarkers is to estimate, predict and, consequently, take timely action to avoid ecologically unacceptable events.

  ▸ Development and application of **new technologies or methods that may mitigate the concentration of pollutants in the various matrices** (water, soil, plant and animal) present in the environment. More specifically, the project foresees:

  ▸ The construction of a pilot plant with **ion-exchange resins** to test the effectiveness of this technology compared to activated carbon filters, as a method to purify drinking water from PFAS. New generation ion-exchange resins that can be regenerated on site will be used, in order to cut the costs due to the disposal of activated carbon filters.

  ▸ The construction of a pilot plant to test the effectiveness of the common reed bed (Phragmites australis) as a method to absorb PFAS from irrigation water, and the subsequent upscale demonstration of the effectiveness of this **phytopurification** system for irrigation water in three wetlands in the Veneto region located in different places within the project area. The identified areas are the following: Monastero by Bevilacqua (Verona), inside the Red Area; Monselice (Padua), in the Yellow Area; Ca' di Mezzo at Codevigo (Padua), in the Green Area.

  ▸ Sampling of four matrices (water, soil, plants and animals) during the project running in order to assess how pollutants spread from one matrix to another. The chosen plant species are an epigeal vegetable (lettuce), a hypogeal vegetable (onion), an extensive cultivation (maize) and a wild plant (Phragmites australis). The animal species identified under the project is the earthworm.

THE EXPERTS EXPLAIN

How does the pilot plant work to absorb PFAS from irrigation water?

Phytopurification is a natural treatment technique that reproduces the natural purification processes in a controlled environment.

In the area around Lonigo, classified as high-pollution level, a pilot phytopurification plant has been installed to test the effectiveness of the common reed bed (Phragmites australis) as a method to absorb PFAS from water (see pictures on the next page).

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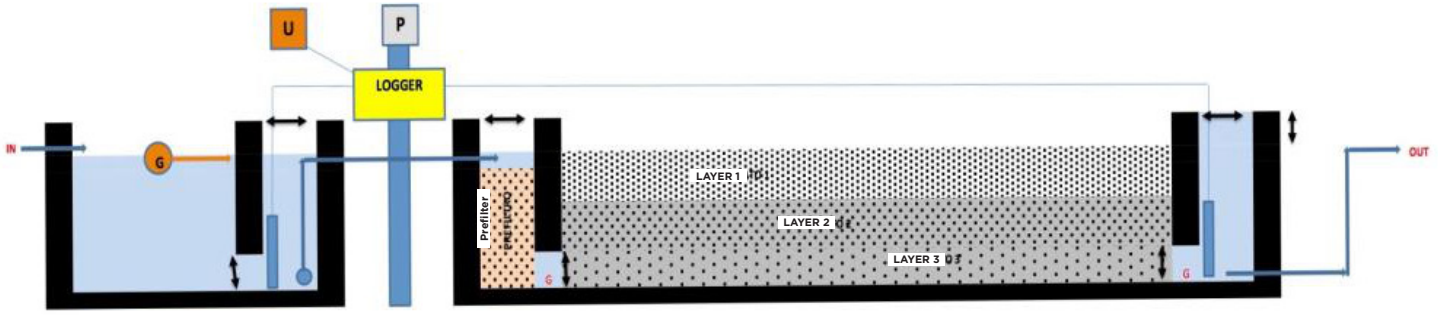
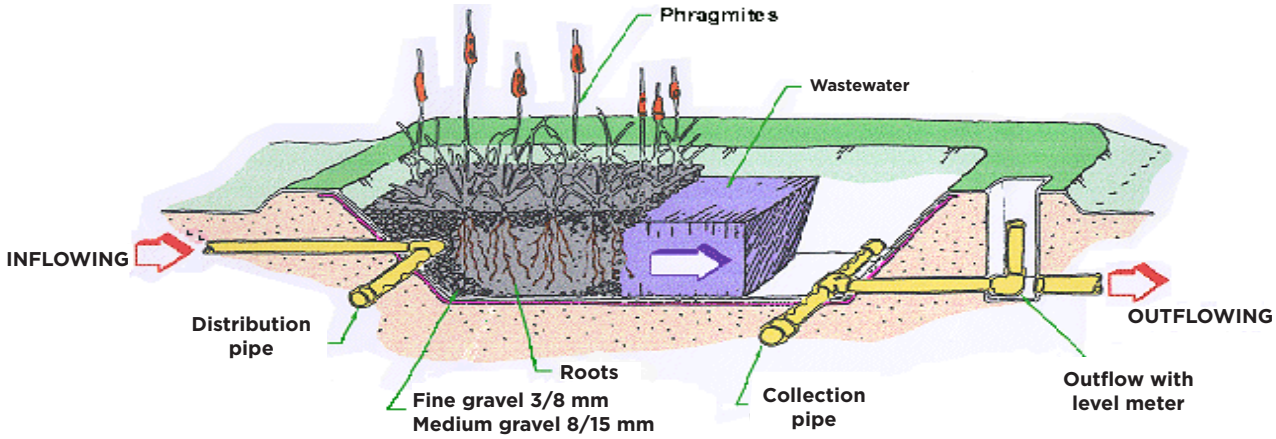
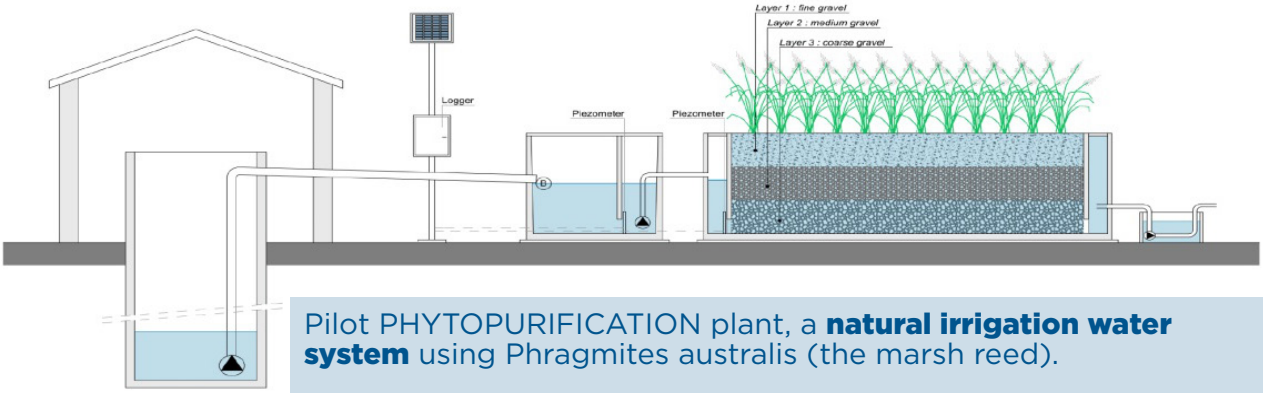


Design drawing of the phytopurification pilot plant



Pilot system for wetland with horizontal surface flow



Pilot PHYTOPURIFICATION plant, a **natural irrigation water system** using Phragmites australis (the marsh reed).

Pilot plant (3 m3) filled with contaminated water to evaluate the absorption capacity of the plants in removing PFAS.

Control unit for water supply pumps (a). The control unit is powered by solar energy (see panel, top left). Phragmites australis, Spring 2018: b) in April, c) in May.

2 WATER, A PRECIOUS RESOURCE

Water is an essential element to all living beings. The body of an adult person consists of about 50-60% in water and needs a minimum of 2 litres of water per day to compensate for fluid loss through sweating, breathing, urine and faeces.

Moreover, water is indispensable for personal hygiene, for washing and cooking food and, above all, for producing the food that forms the base of our diet: considerable quantities of water are needed to irrigate agricultural crops and even greater quantities are needed to raise livestock (both directly, to water animals, and indirectly, to produce the fodder used to feed them, to clean farms, etc.). The largest part of the processed food (bread, pasta, sauces, etc.) could not be produced without water either.

THE EXPERTS EXPLAIN

What is our daily consumption of water?

The daily volume of water that should be ingested by the human body, either in the form of water or through fruit and vegetables or food in general, is 2 litres.

Water consumption, i.e. the volume of water actually used per person per day and that is returned to the environment after undergoing qualitative degradation, is calculated at 241 litres/inhabitant in Italy. In Europe, average consumption stands at 180-190 liters

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In addition to these uses that directly affect the survival and health of the human being, water is indispensable to operate industrial plants and, particularly in Italy, as energy source as well: about 11% of all electricity produced nationwide comes from hydroelectric power plants.

THE EXPERTS EXPLAIN

Where does the remaining amount of energy we need come from? Does Italy purchase it from abroad, or are we self-sufficient?

The 2018 Electricity Balance Sheet (Statistical Department at Terna) shows that the 2018 electricity demand - equal to 321.4 TWh (plus 0.3% on 2017) - was met by domestic production in the amount of 86.3% (277.5 TWh: minus 1.9% on 2017) while the balance demand was met through net imports from abroad (43.9 TWh: plus 16.3% on 2017).

Gross domestic production, amounting to 289.7 TWh, consisted in thermoelectric production by 66.5% (192.7 TWh, or 8.0% less compared to 2017), hydroelectric production by 17.4% (50.5 TWh) with a significant double-digit increase (plus 32.8% compared to 2017) while the remaining 16.1% was covered by geothermal, wind and photovoltaic sources

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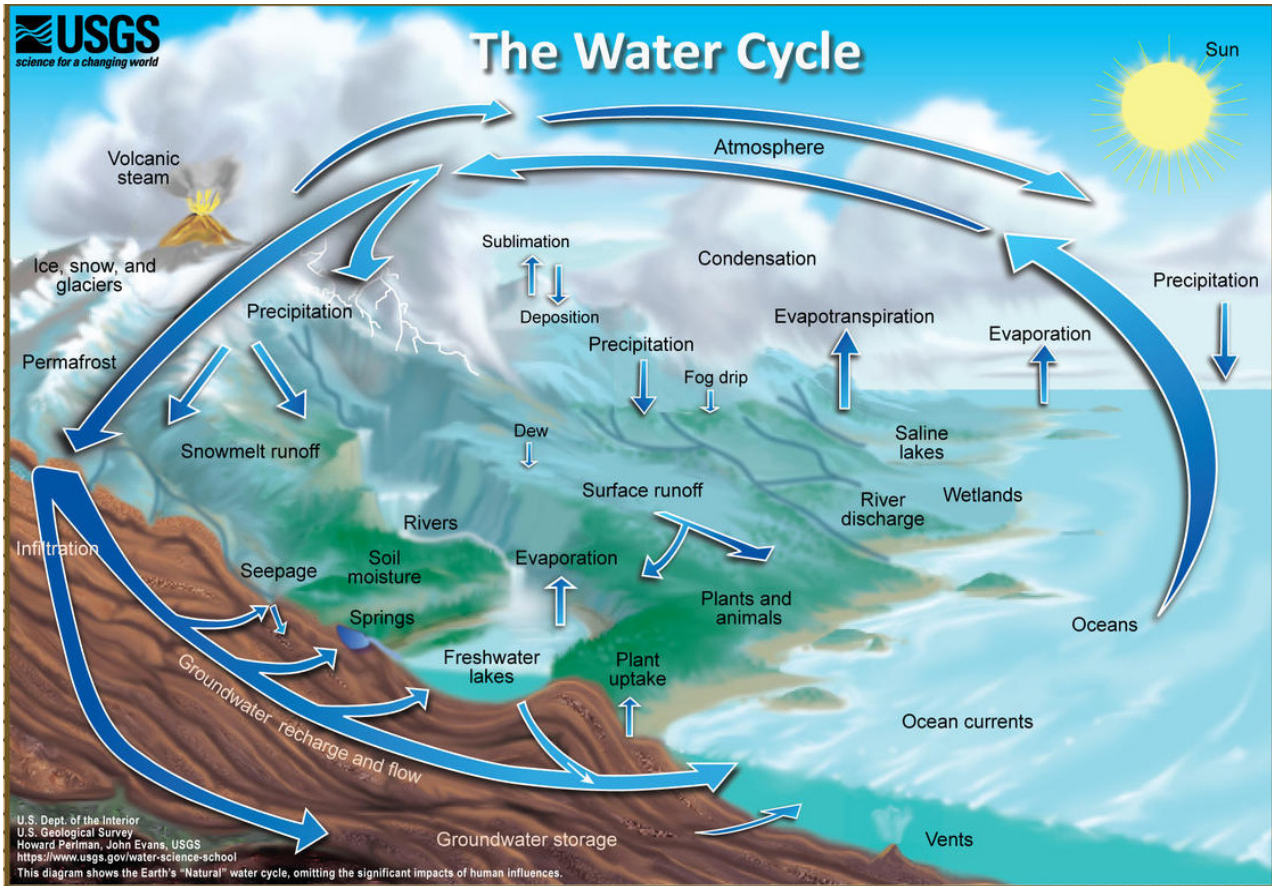
The water that humans need to drink, wash, cook and produce food must be of good quality, in addition to being available in sufficient quantities. Both lack of water and poor water quality can cause diseases. A typical example are gastroenteric diseases, which are frequent in many developing countries where water is often contaminated with bacteria and viruses, and water scarcity (of clean water in particular) prevents good hygiene.

Italy is naturally rich in water, especially in the North, but unfortunately here too the water resource is threatened in terms of both quantity and quality. Global warming is disrupting the availability of water in various ways: it is causing the melting of glaciers that have represented a very important water reserve for millennia; it is causing extreme weather events with alternating droughts and heavy rainfall, which violently hit the ground exceeding its absorption capacity and therefore, rather than feeding the groundwater, tend to runoff causing landslides and floods.

As for water quality, this resource is damaged by the continuous release of chemicals into the environment, many of which are not readily degraded and therefore pollute the water permanently.

3 THE WATER CYCLE

The water molecules on our planet are constantly moving within a hydrological cycle that interconnects the diverse solid bodies of water (glaciers, snowfields) and liquid reservoirs (water bodies) with the water that is found in the atmosphere in the form of vapour.



Water can be collected to form several types of **water bodies**:

- surface water bodies: lakes, rivers, streams, canals, lagoons, seas
- underground water bodies: water tables

A - River basins and hydrographic districts

From a hydrographical point of view, portions of land can be identified that constitute a unitary and interconnected system:

the river basin: this is the area of land on which all surface waters flow through a network of streams, rivers and, possibly, lakes into the sea at a single river mouth, in the form of estuary or delta;

the hydrographic district: this is an area - on land and at sea - made up of one or more neighbouring river basins together with their associated groundwaters and coastal waters; it forms the main administrative unit for the management of river basins.

Italy has seven Hydrographic Districts:

- *The District of the Po Valley - ITB*
- *The District of the Eastern Alps - ITA*
- *The District of Northern Apennines - ITC*
- *The District of Central Apennines - ITE*
- *The District of Southern Apennines - ITF*
- *The District of Sicily - ITH*
- *The District of Sardinia - ITG*

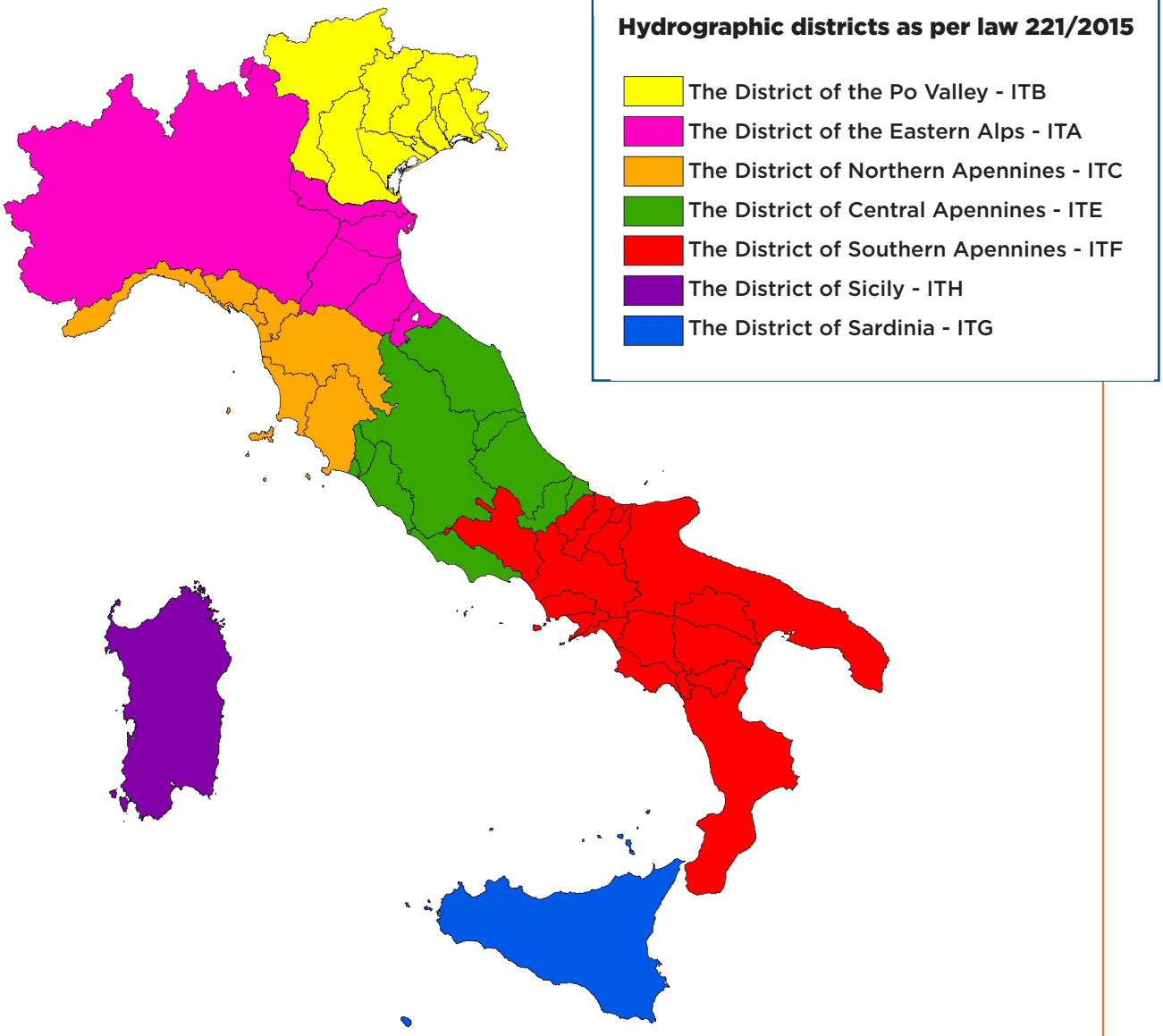
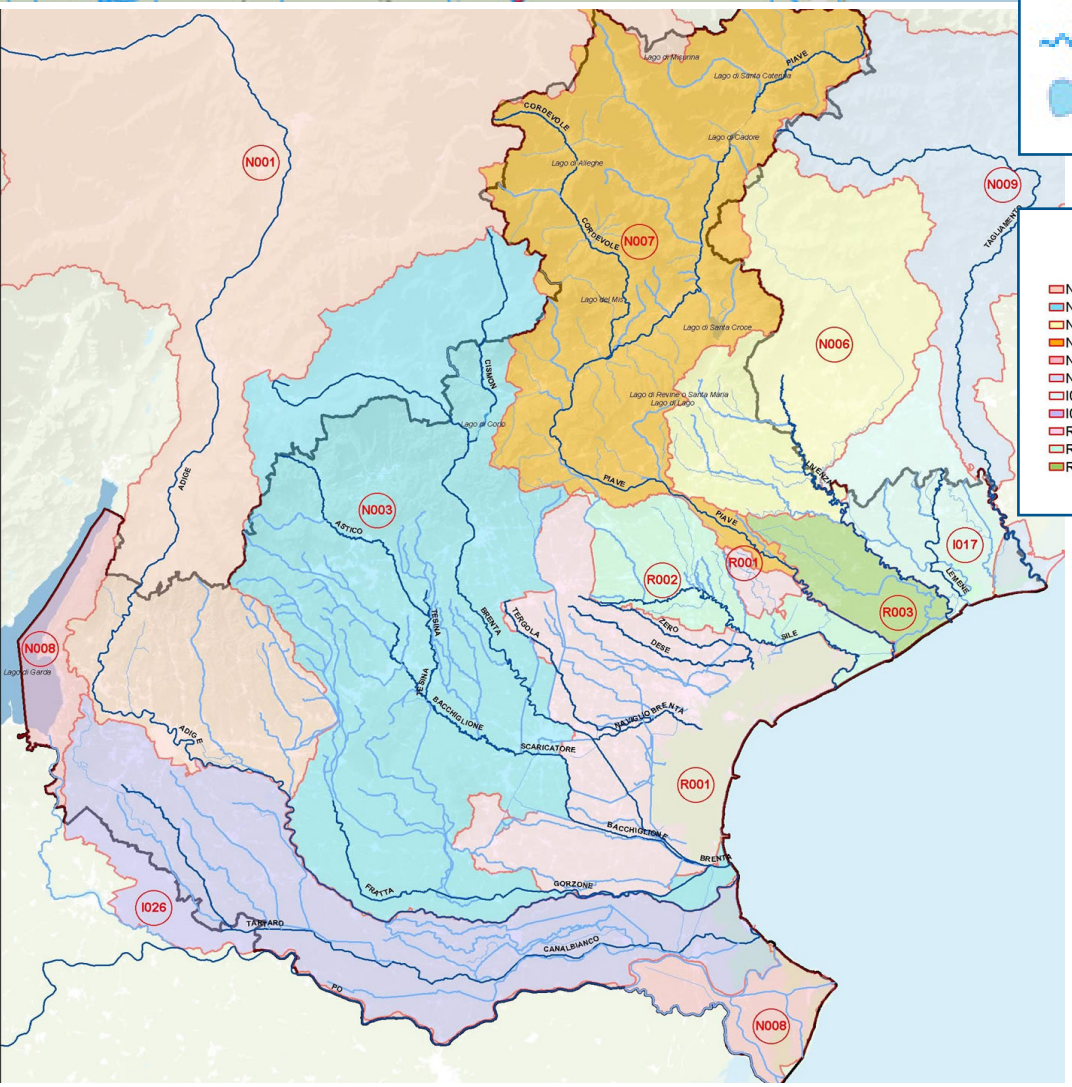


Figure 1: The Italian hydrographic districts with their relevant arrangement into river basins (Source: ISPRA - http://www.isprambiente.gov.it/pre_meteo/idro/UoM_CA.html)

Almost all the territory of the Veneto region falls within the Eastern Alps District, with the exception of a part of the Province of Rovigo lying along the Po Delta, and which is included in the Po Valley District.

The Eastern Alps district includes 13 river basins, 10 of which are located on the territory of the Veneto Region:

- *Adige*
- *Fissero-Tartaro-Canalbianco*
- *Brenta-Bacchiglione*
- *Piave*
- *Sile*
- *Livenza*
- *Drainage basin of the Venice Lagoon*
- *Livenza*
- *The plain between the Livenza and the Piave rivers*
- *Lemene*
- *Tagliamento*



RIVER BASINS

STATE BASINS
- N001 - Adige
- N003 - Brenta - Bacchiglione
- N006 - Livenza
- N007 - Piave
- N008 - Po
- N009 - Tagliamento

INTERREGIONAL
- I017 - Lemene
- I026 - Fissero - Tartaro - Canalbianco (F.T.C.)

REGIONAL
- R001 - Drainage basin of the Venice Lagoon
- R002 - Sile
- R003 - Plain between the Livenza and Piave rivers

Figure 2: Basins in the Hydrographic district of the Eastern Alps (Source: Autorità di bacino distrettuale Alpi orientali - http://www.alpiorientali.it/il-distretto/chi-siamo.html)

Figure 3: River basins in the Veneto Region (Source: ARPAV - http://www.arpa.veneto.it/temi-ambientali/acqua/acque-interne/acque-superficiali/bacini-e-sottobacini-idrografici)

B - The system of ground water tables

Groundwater is the drinking water resource most widely used by both water utility companies and individual citizens; unfortunately, it is not an inexhaustible resource but a "water stock" to be protected and safeguarded as a precious commodity.

When precipitations (rainfall, snow) reach the ground, the water never stops flowing. Part of it flows ("surface runoff") on the Earth surface until it flows into the hydrographic network (rivers, lakes); part is used by plants, part evaporates and returns to the atmosphere, and finally, some of it seeps underground.

The water that falls on the ground seeps underground only if the material that constitutes the soil has such properties as the ability to store water ("porosity") and to be penetrated by it ("permeability"). A portion of soil with pores communicating with each other, allowing water to pass through by gravity or pressure gradients, constitutes an aquifer. Aquifers are usually composed of gravel, sand, sandstone or fractured rocks. It is common to confuse the terms **aquifer** and groundwater; an easy way to distinguish them is to consider the aquifer as the container, and the groundwater as the water it contains.

Groundwater moves in aquifers at a slower rate than surface water, depending on the size of the cavities in the soil (or rocks) and on how interconnected these cavities are. The "engine" of groundwater is the hydraulic gradient, which represents the angle of the phreatic (or ground water) surface or the load loss produced by the energy losses that the water undergoes due to friction with the walls of the intergranular pores along its underground path.

Aquifers are classified as follows:

free reservoirs: they are limited only below by an impermeable layer and the **water sheet** contained in them, called **groundwater**, is free to oscillate in height depending on the water supply conditions.

confined aquifers under pressure: these are confined at the top and bottom by impermeable layers (e.g. clay) through which water does not pass; the **water sheets** contained in confined aquifers are called **artesian** (from the French region of Artois where this type of aquifer is located); when you drill a well into the ground and reach an artesian aquifer, pressurized water gushes out spontaneously without the need for pumps to extract it (**artesian well**).

The interactions between groundwater and surface water bodies such as rivers and lakes can be very complex, as they are strongly influenced by subsoil permeability and the seasonal changes in water levels (low and flood phases). In relation to the variability of these factors, under specific conditions the surface watercourses feed the groundwater, acting as a recharge factor, while in other conditions the surface watercourses drain the groundwater.

When groundwater encounters an obstacle that prevents its runoff (e.g. an impermeable layer of soil), it emerges from the Earth surface thus originating the springs, which are

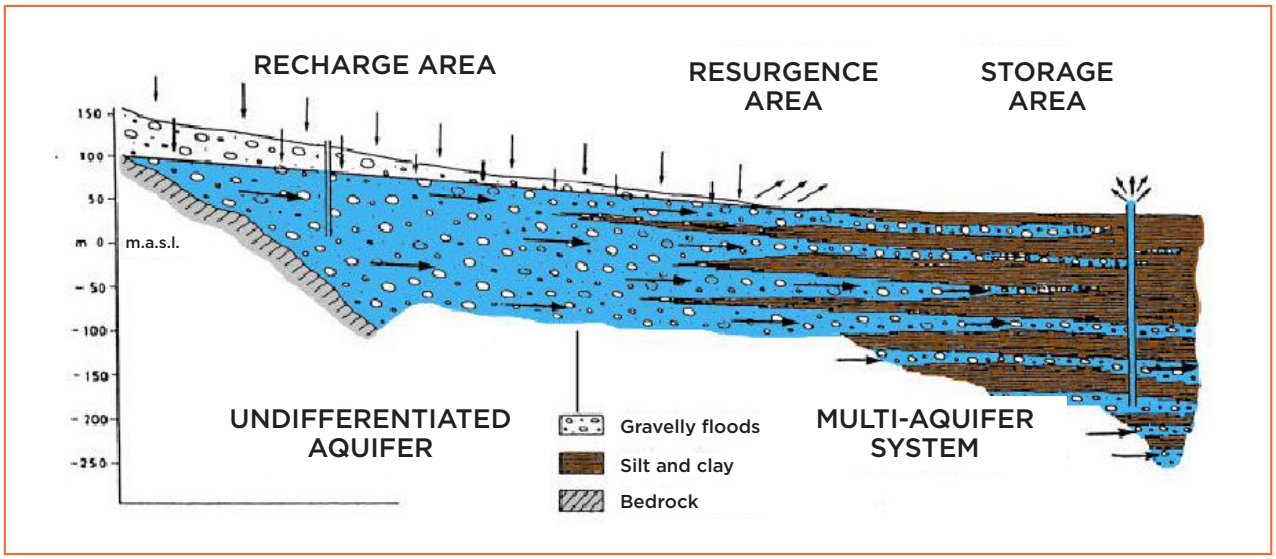


Figure 4: Passage from the undifferentiated aquifer to the multi-aquifer system

formed by the partial or total emersion of the water flowing underground. The underground runoff that feeds a spring can occur either inside the rock or in aquifers made of loose porous materials.

The hydro-geological system of the Veneto plain is divided into three sections: upper, middle, and lower plain.

The **upper plain** is composed of a layer of gravelly soil, deposited over the millennia by the water courses that flow from the mountains. This gravelly layer starts from the Pre-Alps and extends into the valley for about twenty kilometres, forming a single deposit that hosts a groundwater sheet that starts upstream, close to the reliefs. This is called the **undifferentiated aquifer of the upper plain**.

Much of the water contained in the large calcareous-dolomitic reservoirs of mountain areas is drained by the undifferentiated aquifer of the upper plain; moreover, thanks to the permeability of the gravelly soil above, the undifferentiated aquifer of the upper plain is also fed by precipitation, the dispersion of surface watercourses, and the infiltration of irrigation water.

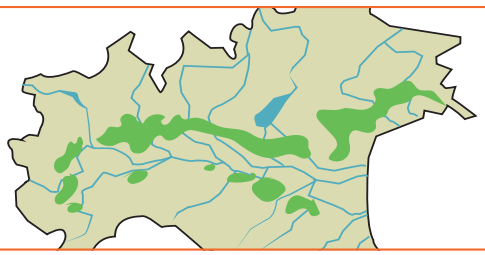
It is precisely because of the permeability of the soil, however, that the upper plain groundwater is extremely vulnerable to the infiltration of pollutants (e.g. pesticides, chemicals discharged into the soil or watercourses, air pollutants that are deposited on the ground). On the contrary, the undifferentiated upper plain aquifer should be preserved from any contamination, because it represents the **recharge area** of the entire aquifer system of the Veneto region, from which a large portion of the water intended for human consumption is taken. Indeed, 90% of the water distributed by the waterworks in our Region originates from wells and springs, while only 10% comes from surface water.

Going down from the upper plain area to the **middle plain** area, the soil composition changes and layers of clayey soil appear which progressively become more and more persistent.

A **multi-aquifer system (differentiated aquifer)** is thus formed, consisting of a shallow and very vulnerable surface aquifer, and a series of underlying water tables under pressure located in the permeable gravelly and/or sandy layers sandwiched between the clayey layers. Since the clayey layers have very low permeability, the deeper layers under pressure are much less vulnerable to the infiltration of pollutants than the surface groundwater. However, the system of aquifers under pressure is closely connected, upstream, to the only large undifferentiated groundwater table of the upper plain, which feeds it and conditions its basic quality.

THE SPRINGS AREA

Figure 5: The resurgence (or springs) belt in the Po Valley



The area that marks the transition from the undifferentiated aquifer to the multi-aquifer system is represented by a part of the territory developing east to west, a few kilometres wide, called the "**resurgence belt**".

A resurgence (or **spring**) is lowland spring generated by the surfacing of the undifferentiated groundwater at points where, as the water approaches the surface of the soil, it meets a clayey layer. The surfaced water forms water courses that are called resurgence rivers (e.g. Sile, Dese, Marzenego, Bacchiglione, Timonchio, Tartaro).

In the **lower plain** the deep gravel alluvial deposits are no longer present and the subsoil consists mainly of an alternation of silt, clay and sand. The artesian aquifers of the lower plain are therefore smaller in size and well protected by the clayey layers above.

Source: *"Le acque sotterranee della pianura veneta. I risultati del progetto SAMPAS" – ARPAV, 2008 http://www.arpa.veneto.it/temi-ambientali/acqua/acque-interne/acque-sotteranee*

4 THE PROTECTION OF THE WATER

As we have seen, water is a valuable asset and a fragile one as well, which needs to be preserved in terms of both quantity (avoiding waste) and quality.
Groundwater specifically, given its importance as a source of water for drinking and other uses (and for agricultural and livestock use in many areas of our Region), is a resource to be preserved with great care avoiding its over-exploitation and pollution. In fact, groundwater tables have a very slow flow so that once their quality has been compromised, it takes a very long time (several decades) to restore their initial state. Furthermore, groundwater remediation operations are extremely complex, time-consuming and expensive.
Every precaution must be adopted to prevent pollutants from reaching the groundwater, especially in the permeable gravel belt of the undifferentiated aquifer that is the most vulnerable zone, besides being the recharge area of the entire aquifer system.
Surface waters (lakes, rivers, the sea) must be protected against pollution as well, for various reasons:
they are interconnected with groundwater and they may contaminate it especially where the soil is permeable; they supply water for drinking and other uses to some areas of our Region; they are used for irrigation and may therefore contaminate the crops; their pollution damages the aquatic ecosystem, compromising the wealth and healthiness of fish products.
The European Union has adopted a complex regulatory system for the protection of water resources, the cornerstone of which is the so-called "Water Framework Directive" (Directive 2000/60/EC) implemented by Italy in the "Testo Unico in materia ambientale" (Legislative Decree 152/2006).
The Directive aims to facilitate sustainable water use, to prevent further deterioration of water quality, and to pursue the progressive abatement of pollution. To this end, it establishes the limit values of concentration of various types of chemical substances in surface and ground water; it publishes a regularly updated list of "priority" and "priority hazardous" chemical substances for which Member States must ensure the gradual elimination from wastewater, emissions, and leakages.
In order to ensure the achievement of the set objectives, Italy has set up a monitoring system for surface and groundwater quality based on regular sampling and analysis, which in the Veneto region is managed by the Regional Agency for Environmental Protection (ARPAV). The results of such monitoring contribute to updating knowledge on the contamination of water bodies and to adapting the Management Plans of the Hydrographic Districts accordingly.
Unfortunately despite the regulatory, control and management efforts, the challenge to ensure the quality of water as a resource is still open. A major issue to be tackled still is the continuous placing on the market (and consequently into the environment) of chemicals that are often but not necessarily newly released, and which properties are little known or for which no limits or regulatory requirements are available yet: these are the so-called "emerging contaminants".

5 THE EMERGING CONTAMINANTS

The term "emerging contaminants" refers to a heterogeneous group of substances that are not subject to regulations yet and have recently been identified as "causing concern".
These substances are often found in products used in large quantities in daily life, such as medicines, cosmetics, detergents, plasticizers and industrial additives.

Emerging contaminants are not necessarily new chemicals: in many cases these are substances that have been released into the environment for a long time, but the effects of which have not been fully understood yet. In addition, the methods to measure these substances in environmental matrices are often still under development, so that no standardised analytical methods exist at European level to allow comparability of data. One of the main sources of water pollution from emerging contaminants is urban wastewater treatment plants. As a matter of fact, the majority of these plants was not designed and equipped to treat wastewater from this type of pollutants, which are consequently released into water bodies.

A particularly alarming category of emerging contaminants is that of **Persistent Mobile Organic Compounds (PMOC)**: these are organic substances that show marked mobility within the water cycle, associated with considerable persistence. In other words, these substances spread very easily among the various water compartments (for example, they easily infiltrate through the earth reaching the aquifers and then spread through the groundwater flow) and also resist natural degradation processes, remaining unaltered for an extremely long time.
As a result, their continuous release results in their progressive build-up and spread in the environment, and possible long-term exposure of the population to PMOC through drinking water and food, with health effects that are largely unknown.

PMOCs include poly- and perfluoroalkyl substances (PFAS).
These are synthetic chemical compounds, not present in nature, consisting of a carbon chain of various lengths in which the carbon atoms are partially or completely fluorinated. These compounds have been developed by the chemical industry since the 1950s and are widely used for their heat-resistant, hydro- and oil-repellent and surfactant properties.

PFAS are found in many products of everyday use, such as household cleaning products, insecticides, paints and fire-fighting foams, and are also used in various industrial processes. They are also used for the waterproofing of clothing and footwear, for the production of non-stick pans and in the coating of food containers, such as fast-food or take-away pizza cartons.
PFAS are highly persistent and mobile in the environment; these properties, combined with their extensive use, have resulted in their spreading practically everywhere, to the extent that some of these substances are present in the blood of almost the entire population of various countries around the world and have even been detected in Arctic bears.

THE EXPERTS EXPLAIN

May we identify specific products or "classes of products" that contain PFAS?

- It is estimated that the PFAS currently under production correspond to around 5000 different chemical molecules, which find applications in virtually all products of daily and industrial use, from the coatings that make food paper grease-repellent, to surface treatments that make clothes and furniture water- and grease-repellent, to fire-fighting foams, water-repellent inks and paints for outdoor use and also in the boating industry, to surfactants and lubricants for special applications, for example in the aviation industry. They also have extensive application in the field of hospital medical devices.
- In short there are no specific products, but amongst the products that are widely used by everyone, definitely technical clothing and fast-food paper packaging make extensive use of PFAS-based coatings, which can be a source of pollution especially in landfills.
- PFAS-based products are also widely used in ski waxes.
- The major source of pollution is fire-fighting foams, but studies are underway to find equally effective substitutes in the extinguishing of large fuel fires (e.g. in airports, gas stations, ammunition powder magazines, fireworks warehouses).

Can we understand whether a product contains PFAS by reading its label?

- There is no evidence that PFAS are ever reported as a specific category on the label, as they can be included in the broader category of surfactants.
- PFAS are present in dental floss and cosmetic products such as eyeliner, face masks, etc., but they are not always mentioned on the label. It is nevertheless useful to learn how to read a label before purchasing a product.
- Some manufacturers of non-stick pans or technical clothing claim to be PFOA-free or PFAS-free following a specific Greenpeace campaign (of course you have to be careful, since PFOA-free generally means that there are other PFAS substitutes). Therefore let us all read the labels carefully, particularly those of technical clothing.

Could we list the items we had rather avoid?

- The basic concept is that materials based on per- or poly-fluorinated molecules have been and still are an invaluable support to our quality of life (in the healthcare field as well), but it is clear that in some applications these are tantamount to a "comfort" we could find some alternative solutions to, however less effective (e.g. for non-stick pans and the technical clothing used occasionally or in everyday life, but not under extreme conditions, we could resume the alternatives already in use decades ago, e.g. polished steel pans, waxed jackets, etc.).
- As for PFAS-based grease-repellent food packaging (indeed, any type of food packaging in general) we can also try to reduce its size, or choose those manufacturers who supply smaller-sized packaging. By way of example, just think of the giant hamburger boxes in fast-food restaurants that contain a tiny hamburger.
- We might therefore develop some alternatives for these products, non-stick pans, technical clothing, and food packaging made of treated paper-cardboard, baking paper, etc...
- However it is not easy (if impossible for us as technicians, imagine for the so-called "common person") to really know the materials these objects are made of.

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There are nearly 5000 different types of PFAS. The best known and studied are perfluorooctanoic acid (PFOA) and perfluorooctansulphonic acid (PFOS), which were used extensively until a few years ago.

However due to several alerts about the possible toxicity of these molecules, PFOS has been included in Annex B (restrictions on the use of some substances) of the Stockholm Convention since 2008 and, in 2019, PFOA and its salts have been included in Annex A as a substance to be removed.

In both cases the decision was taken after intense and complex discussions due to the use of these compounds and the difficulty or - in some cases, as with PFOS - the impossibility to replace them with different molecules having the same properties.
People are exposed to PFOA and PFOS mainly by ingestion, especially through food that can be contaminated during production (e.g. through soil, irrigation water, animals watering and livestock feed), but also afterwards when the food is cooked, heated and/or stored in certain types of non-stick or grease- and water-proof containers that may wear out over time.

ACRONYM	SUBSTANCE	n. CARBON	MW*	CAS NUMBER**
PFBA	Perfluoro-*n*-butanoic acid	4	214	375-22-4
PFPeBA	Perfluoro-*n*-pentanoic acid	5	264	2706-90-3
PFHxA	Perfluoro-*n*-hexanoic acid	6	314	307-34-4
PFHpA	Perfluoro-*n*-heptanoic acid	7	364	375-85-9
PFOA	Perfluoro-*n*-octanoic acid	8	414	335-67-1
PFNA	Perfluoro-*n*-nonanoic acid	9	464	375-91-1
PFDA	Perfluoro-*n*-decanoic acid	10	514	335-76-2
PFUnDA	Perfluoro-*n*-undecanoic acid	11	565	2058-94-8
PFDoDA	Perfluoro-*n*-dodecanoic acid	12	614	307-55-1
PFBS	Perfluoro-n-butane sulfonate	4	300	375-73-5
PFHxS	Perfluoro-n-hexane sulfonate	6	400	355-46-4
PFOS	Perfluoro-n-octane sulfonate	8	500	1763-23-1

9 perfluoro alkyl carboxylic acids

3 perfluoro alkyl sulphonic acids

* *MW: Molecular Weight;* ***CAS: Chemical Abstracts Service number*

Fig. 6: A table of the most widely used PFAS

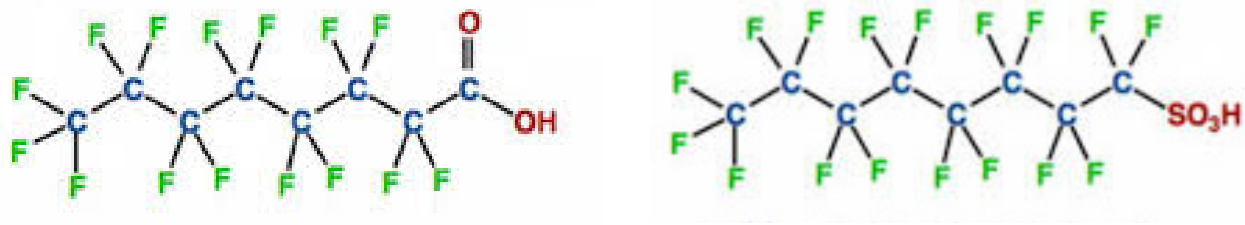

Fig. 7: The chemical structure of PFOA (perfluorooctanoic acid) and of PFOS (perfluorooctansulphonic acid).

Objects of daily use (e.g. stain- and water-proof fabrics, waterproof paper, cleaning products) might release PFAS during their use, hence could become a source of direct exposure through household dust.

Drinking water is a marginal source of exposure to most of the population, with the exception of a few localized cases of contamination as unfortunately happened in the Veneto.

There is no certainty yet as for the effects that PFOA and PFOS may have on human health, and several studies are under way to analyse this issue.

THE EXPERTS EXPLAIN

Is it dangerous to use non-stick pans?

- The coating of pans and pots may contain PTFE (polytetrafluoroethylene) that is known under several trade names - the most famous of which being Teflon. This coating has been applied for years on non-stick pans since it allows heating up or cooking food without any risk of seeing it char or stick to the pan bottom.
- PFOA is a surfactant used to produce PTFE, therefore it is dissolved in this polymer. It is released when heated up or when in touch with hot greases (frying operations typically). However studies show that after some cooking cycles the release of this substance stops. It is therefore advisable that when you buy a new pan, at its first use the oil is taken to the boiling temperature and then discarded, without using it to cook any food.
- PFOA has been banned from the production of PTFE, therefore there is no risk that it might be released from the pans manufactured after 2015. Of course PFOA has been replaced with other substances, the toxicity mechanisms of which are still little known. Nevertheless, the above advice remains applicable.
- US EPA advises not to exceed the temperature of 250°C and not to scratch the pans.
- If the PTFE coat is scratched this does not imply higher release risks, but increases the risk that plastic micro-fragments be released into the food. The issue of microplastic ingestion is under examination at present. As a precautionary measure, it is advisable not to use scratched pans and to replace them with polished stainless steel pans, or with Pyrex glass pots that have no coating of any kind. Most coatings are plastic-based and often contain PFAS (though being PFOA-free).

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The scientific community agrees on some hypotheses, i.e. that these compounds may increase cholesterol level in the blood and interfere with the immune response. Moreover high exposure to these compounds might favour the development of testicular and kidney cancer.

Despite uncertainties, and considering the highly problematic issues related to PFOA and PFOS (persistence, bioaccumulation, toxicity), the regulatory authorities of the European Union and other countries worldwide (including the USA) are progressively restricting the application fields of these two substances and regulating their concentration in the environmental matrices in an ever stricter manner. PFOA and PFOS are therefore doomed to progressively disappear from the manufacturing system, although it will take more time to see them disappear from the environment.

Unfortunately in these past few years the industry has replaced PFOA and PFOS with other kinds of PFAS, of a type that has a lower bioaccumulation potential but is equally persistent and mobile in the environment, and has practically unknown toxicological properties.

There is no regulatory limit imposed on most of these new PFAS. The never-ending story of the emerging pollutants continues!

6 THE "PFAS CASE" IN THE VENETO REGION

In Spring 2013, the Water Research Institute at the National Research Council (IRSA-CNR) published the results of a study commissioned by the Ministry of the Environment about the presence of PFAS in the main river basins in Italy. This study highlighted a remarkable contamination of the surface water bodies located in the provinces of Vicenza and Padua, as well as of the drinking water sampled in various Municipalities of that area.

The regional government of the Veneto was notified the issue in June 2013 and it immediately started an enquiry to safeguard the health of the population and the environment. One of the first, most urgent actions was to equip the purifying systems of the contaminated water supply networks with activated carbon filters, since these can absorb the PFAS. Within 3 months only, the PFAS concentration in the water supplied by the public network was drastically cut down.
At the same time environmental surveys were started to determine the extent of the contaminated area and identify the source of contamination. This was found in the chemical plant of the MITENI company in Trissino (Vicenza), in an area that extends above the undifferentiated aquifer of the upper plain.

The company has been active in the production of PFAS since the end of the Sixties and for decades it had discharged its wastewater - rich in polluting substances - into surface watercourses and underground after performing insufficient treatment; it had thus contaminated the rivers and the groundwater that supplies the water networks of the area.

By means of a complex environmental monitoring plan, the survey has mapped the extent of the contamination "plume" of the groundwater with growing precision, and it has identified the surface watercourses involved in this contamination.

In addition, the branching of the water supply network fed by contaminated sources was reconstructed to identify the municipalities or portions of municipalities where the population was exposed to PFAS through drinking water.
Overall, the portion of the regional territory involved in the environmental contamination extends over nearly 930 sq.km. and includes part of the Brenta-Bacchiglione river basin. More specifically, contamination was detected in the rivers Retrone, Bacchiglione, Togna, Fratta, Brendola, Guà, the Gorzone canal and the stream Poscola.

The contamination plume of the groundwater originated at Trissino and spread eastwards over the decades, reaching the borders of Vicenza, and southwards and southeast down to the municipalities of Montagnana, Pojana Maggiore and Noventa Vicentina, for a total extension of about 190 km. The contaminated water supply networks serve 30 municipalities in three different provinces (Vicenza, Verona and Padua) catering for an overall population of nearly 140,000 inhabitants.

Contamination management has been very complex since the beginning, not least because in 2013 PFAS were still unregulated substances, so there were no legal limits for concentrations in surface and groundwater, in soil, industrial wastewater and drinking water.
Since then much has been done in this respect: regarding the concentrations of some types of PFAS (including PFOA and PFOS) there are now legal limits for surface water and groundwater in force throughout Italy. A new European Directive is due soon, which will set some limits for drinking water as well.

THE EXPERTS EXPLAIN

Water control regulations and Water Safety Plans (Piani di Sicurezza dell'Acqua - PSA) as a means of protecting public health.

The Ministerial Decree of 14 June 2017 has integrated the legislation on the control of water intended for human consumption and has provided for the implementation of the Water Safety Plans in the national territory, which each integrated water service provider must prepare for approval by the Istituto Superiore di Sanità. These Water Safety Plans must be implemented by the year 2025.
The implementation of the Water Safety Plans (PSA) introduces the principle of risk assessment and risk management for the entire supply chain of drinking water intended for human consumption according to the WHO Water Safety Plan model, as reflected in the guidelines produced by the Istituto Superiore di Sanità (ISTISAN Report 14/21).

The rationale behind PSAs is to shift the focus from retrospective monitoring of the distributed water (as has been the case to date) to an assessment of the risks and dangers affecting the water supply chain, including the catchment areas of the water intended for such uses. This has led to a change in the function of the Authorities in charge of the monitoring of water intended for human consumption, such as the Local Health Authorities that, in addition to the traditional monitoring function, are required to act jointly with other Authorities in charge of environmental protection, including ARPAV, to provide specialized support for the correct preparation of the PSA, and provide all the necessary information to the Water Service Providers for them to identify the possible risks and dangers affecting that waterworks. The Water Service Provider will therefore be responsible for implementation of all the necessary actions to reduce that risk/hazard in a decisive and permanent way.

The PSAs provide for integration of the actions implemented by the authorities in charge of health protection and those in charge of environmental protection, at every governance level. Only in this way can the data from the environmental monitoring of the water matrix assist the impact assessment - including impact on human health - to safeguard the health of citizens and thus generate timely actions to reduce the risks for the population.

EDITED BY REGIONE DEL VENETO

Currently, thanks to the progressive upgrading of activated carbon filtering systems, the water supplied by the waterworks in the contaminated area has undetectable concentrations of PFAS and is therefore absolutely safe. However the activated carbon filters are extremely expensive and must be replaced frequently. For this reason, the Veneto Regional Government has resolved to start the construction of a new water supply network that will supply the 30 municipalities involved with uncontaminated water, solving the problem of water safety at its root.

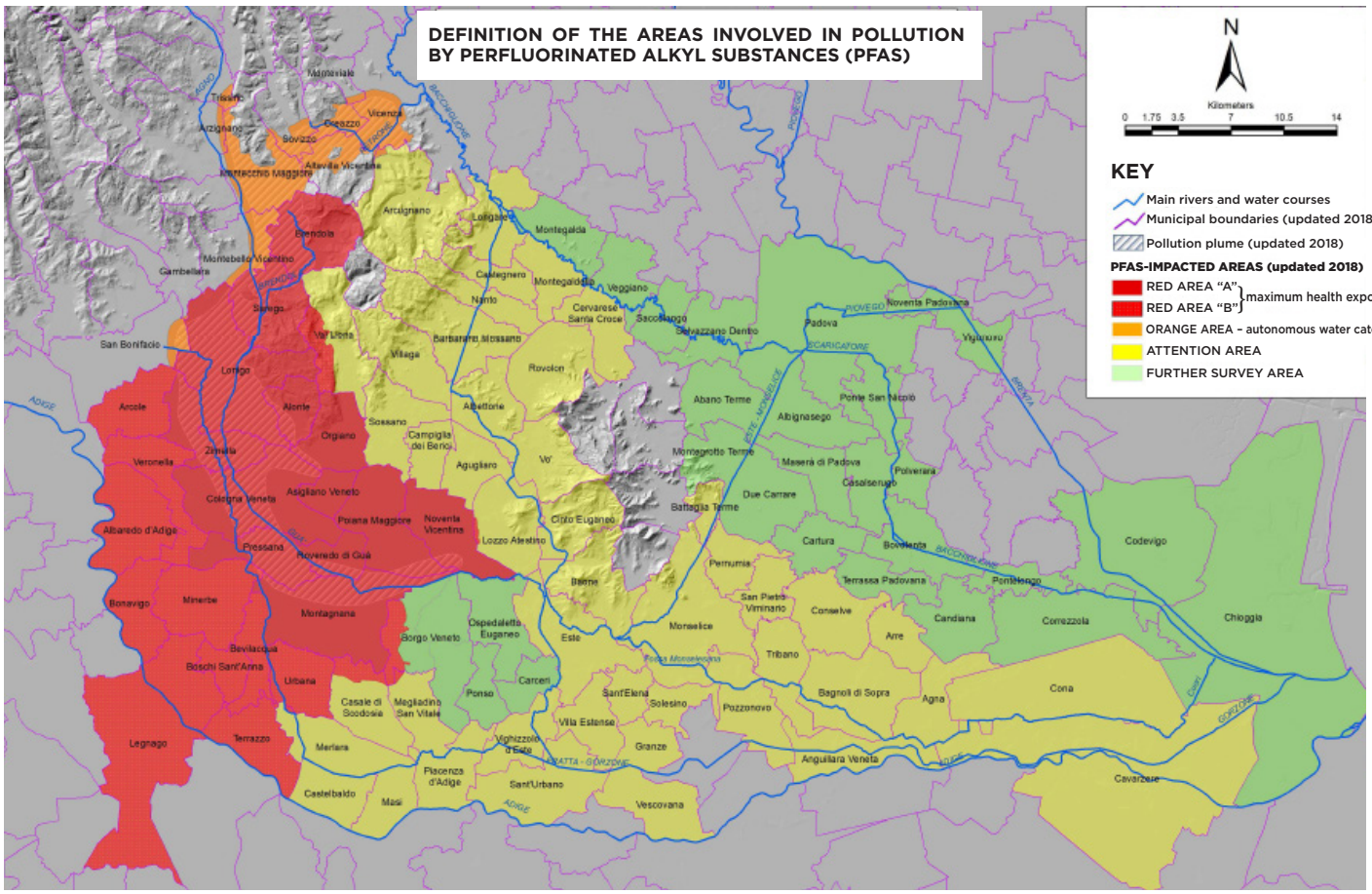

Figure 7: The PFAS-contaminated area in the Veneto

KEY:
Red Area: Municipalities supplied by the contaminated waterworks
Orange Area: Municipalities supplied by non contaminated waterworks, but which stand on the contaminated groundwater
Yellow Area: areas where surface waters have been contaminated
Green Area: areas requiring further analyses
Dotted Area: groundwater contamination plume

Although the emergency phase is now over, many issues remain unsolved. Despite the remediation work undertaken at the production site, the aquifer is still heavily contaminated and is likely to remain so for several years to come: a huge stock of water compromised in the long term and removed from safe use by the community. In addition, the contamination of surface water remains with all its negative effects on the aquatic ecosystem.

To make things worse in recent years the company MITENI, like the other PFAS producers in Western countries, has reacted to the increasingly stringent restrictions affecting PFOA and PFOS by replacing them with other types of PFAS, generally shorter carbon chain PFAS, which have a lower bioaccumulation potential but are just as persistent and mobile in the environment and, moreover, much more difficult to filter on activated carbon (due to the smaller size of the molecule).

THE EXPERTS EXPLAIN

Can you make a prediction of how long the contamination will persist?
PFOA and PFOS are extremely persistent in the environment and resistant to typical environmental degradation processes. The half-life of PFOA and PFOS in water is assessed at over 90 years for PFOA and over 41 years for PFOS, respectively, while it is of 114 and 90 days in the atmosphere (US EPA, 2014-2).

Early modeling results confirm that the contamination has occurred on a decades-long scale. Considering the characteristics of the aquifer, the extent of contamination and the persistence characteristics of the pollutants, it is estimated that considerable amounts of contamination will be present in groundwater over the next 50 years.

EDITED BY THE UNIVERSITY OF PADUA and ARPAV

A - What are the take-home messages of this story?

The PFAS case in the Veneto region has clearly shown that environmental and public health management based exclusively on existing knowledge and standards, and which neglects potential risks forecasting, runs the risk of acting when it is too late, leaving room to industrial practices that cause huge hard-to-remedy environmental damage.

A radical shift in perspective is therefore needed: we need to be able to predict in advance the pollution risks that threaten water and the environment in general, in order to implement all available preventive measures, combined with monitoring and control plans to detect if something goes wrong at an early stage.

To do all this, it is essential to gain an in-depth and systematic knowledge of the territory, of the possible sources of pollution that exist on it, of the water resources potentially threatened by those sources of pollution, of the areas where those water resources are used for drinking, irrigation or livestock farming purposes, and of the way a possible pollutant would spread in the environment. In addition, it is essential to seek new methods to remove pollutants from water, which are more effective and less expensive than those currently available.

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