Water Workshop 2023

Organic micropollutants and reuse of wastewater

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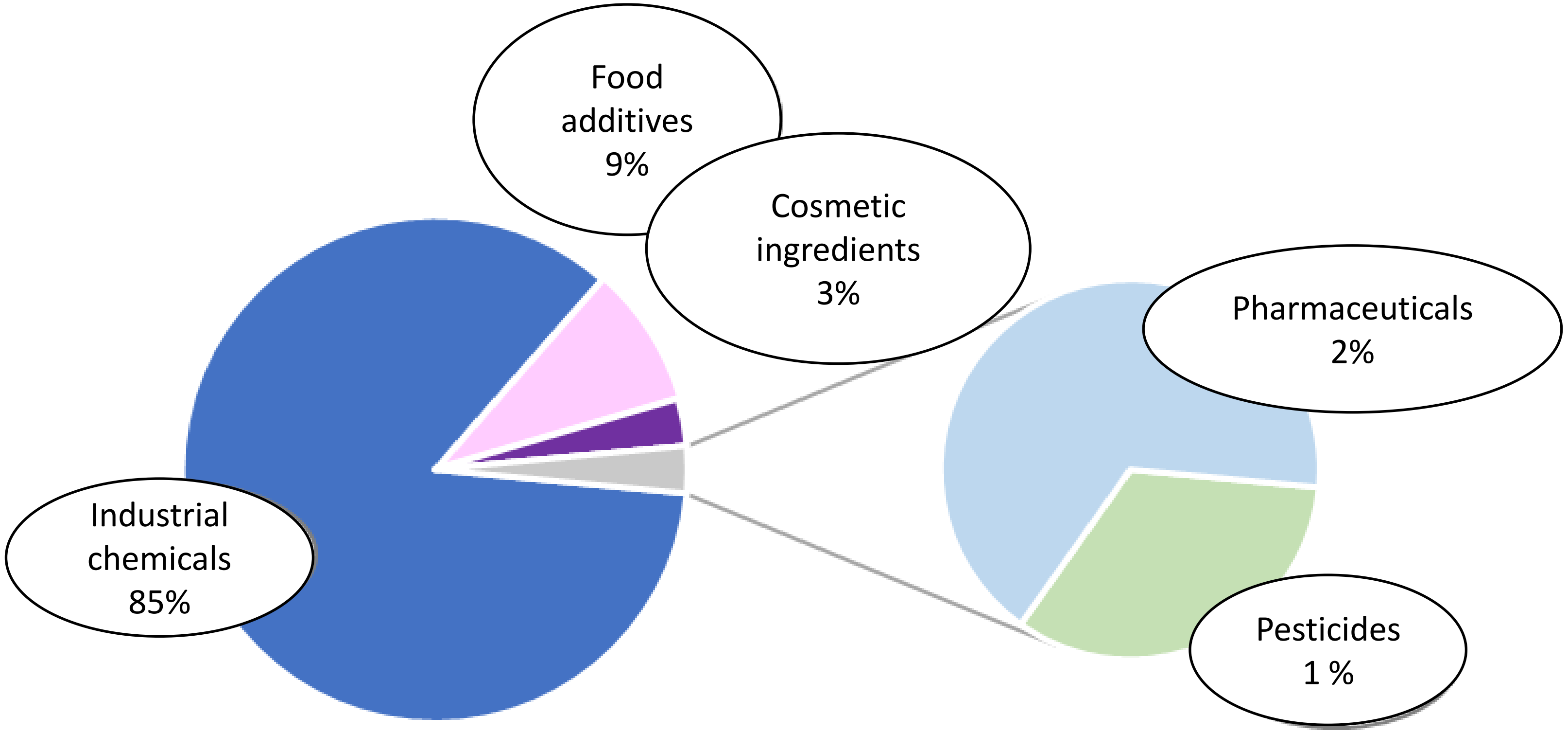
Growing use of chemicals by our technological society

CAS REGISTRYSM contains more than 106 million chemical substances, organic and inorganic

There are currently 350,000 chemicals and chemical mixtures registered for commercial production and use + over 2,000 new products are added each year

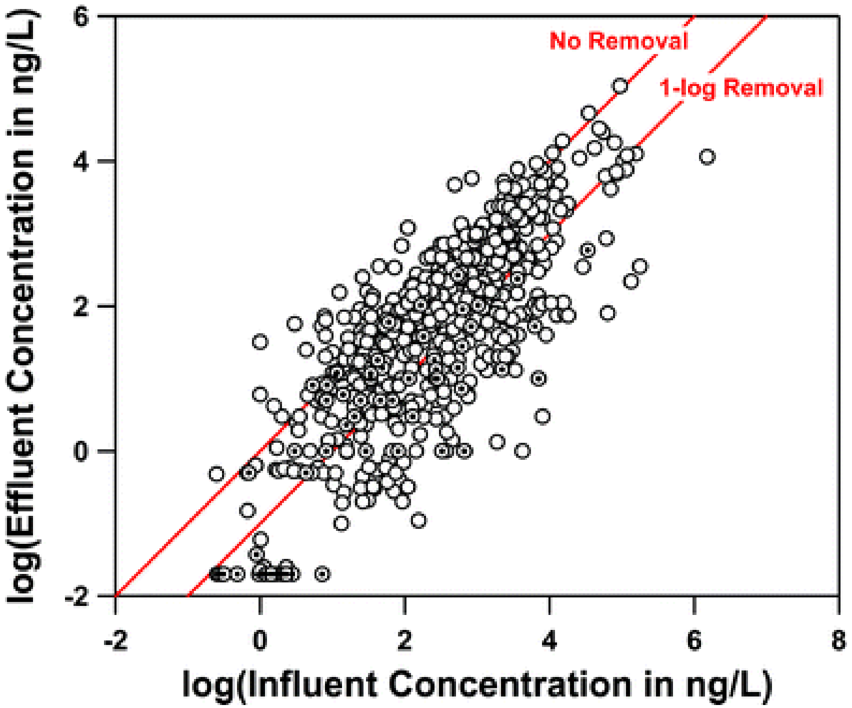
A total of 250 billion tons of chemicals are produced annually, representing a global market of $7.8 trillion.



Wastewater derived microcontaminants

Due to the fact that wastewater is generated by a variety of sources (bathing, cooking, manufacturing, cleaning, etc.), the contaminants found in wastewater are varied and numerous. They include, but are not limited to, nutrients, pathogens, metals, salt, ammonia, and a wide range of **organic compounds**.

At WWTP typically using secondary biological treatment (CAS – conventional activated sludge) not all organic contaminants are removed.



Comparison plot of pharmaceuticals and personal care products effluent concentration as a function of influent concentration for WWTPs utilizing traditional treatment operations (i.e., solids removal and CAS-conventional activated sludge)

Oulton et al. J. Environ. Monit., 2010, 12, 1956-1978

Wastewater Reuse Constraints

Reuse Category	Major Constraints
Irrigation	Surface or groundwater contamination
Landscape Irrigation	Public health concerns related to pathogens
Industrial Recycle & Reuse	Desires treated water quality
Groundwater Recharge	TDS, Nitrates & pathogens emerging contaminants
Non potable urban use (Toilet flushing, fire protection, AC)	Public health concerns related to pathogens desired treated water quality
Potable Reuse	Produced water quality trace organics

Priority (regulated) vs emerging (non regulated)

Regulated pollutants

Not regulated – emerging contaminants

Unknown toxicity

Priority (regulated) vs emerging (non regulated)

EU Water Framework (2000/60/EC)

1st List of Priority substances included compounds considered potentially toxic to human life, and for a number of years, a list of **33 compounds** was used as the basis for monitoring a range of pollutants in surface waters in order to determine the status of the water body.

List was revised in 2013 (Directiva 2013/39 / UE) including **12 new additions** to the Priority Hazardous and Priority Substances lists

This brings the total of **Priority Pollutants to 45**.

Watch list - A mechanism designed to allow targeted EU-wide monitoring of substances of possible concern to support the prioritization process in future reviews of the priority substances list.

4th Watch list (2022)

Name of substance/group of substances	Class
17-Alpha-ethinylestradiol (EE2)	Synthetic hormone
17-Beta-estradiol (E2), Estrone (E1)	Natural hormone
Erythromycin, Clarithromycin, Azithromycin, Clindamycin and Ofloxacin	Antibiotics
Metformin and its transformation product guanylurea	Pharmaceutical (diabetes)
Methiocarb	Pesticide
Neonicotinoids: Imidacloprid, Thiacloprid, Thiamethoxam, Clothianidin, Acetamiprid	Neuro-active insecticides
Azoxystrobin	Fungicide
Diflufenican	Herbicide
Fipronil	Insecticide
Avobenzone, octocrylene and oxybenzone	Sunscreen agents

Many classes of emerging contaminants are continually infused to the aquatic environment - essentially become “persistent” pollutants even if their half-lives are short — their supply is continually replenished.

These can be referred to as **pseudo- persistent chemicals**.

- Due to their physical-chemical properties (high water solubility and often poor degradability) they are able to penetrate through all natural filtration steps and man-made treatments
- Some with low elimination in conventional WWTP
- Potential risk for drinking water supply
- Large volume production/high fluxes in the environment

Old Pollutant – New Concern (not new pollutants but are newly identified in waters due to improved analytical techniques)

vs.

New Pollutant – Unknown Issues

Unregulated ≠ Little Risk

Annex XIII to the **REACH Regulation (Registration, Evaluation, Authorisation and restriction of CHemicals)** sets criteria for substances that are persistent, bioaccumulative and toxic (PBT) or very persistent and very bioaccumulative (vPvB).

Under REACH, a PBT/vPvB assessment is required for all substances for which a chemical safety assessment is carried out. A chemical safety assessment is required for substances manufactured or imported in amounts of 10 tonnes or more per year, unless exemptions apply. (All biocidal active substances have to undergo a formal PBT assessment).

PBT – persistent, bioaccumualtive and toxic
vPvB - very persistent, very bioacumulative

Example: anthracene, asbestos, cadmium and cadmium compounds chloroalkanes, C10-13 (short-chain chlorinated paraffins), p-Dichlorobenzene, hexabromobiphenyl, hexabromocyclododecane, hexachlorobutadiene, lead and lead compounds, mercury and mercury compounds, musk xylene, pentachlorobenzene

PMT – persistent, mobile and toxic
vPvM – very persistent, very mobile

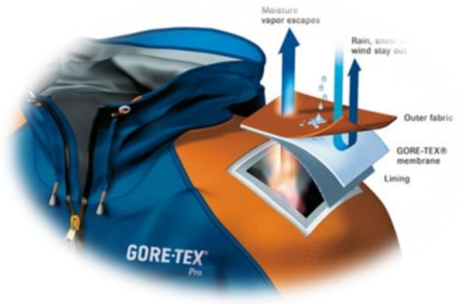
Example: perfluorobutane sulfonic acid (PFBS) and 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoic acid (HFPO-DA trade name GenX) were demonstrated to have an equivalent level of concern (ELoC) to PBT/vPvB substances owing to their PMT/vPvM properties.

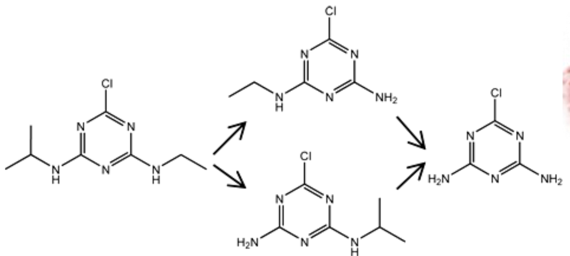
Special relevance for wastewater reuse

Emerging contaminants

- Global Organic Contaminants (flame retardants, perfluorinated compounds, siloxanes…etc.
- Pharmaceuticals
- Personal Care Products (preservatives, UV filters, biocides, insect repellents, fragrances, etc..)
- Nanoparticles
- Micro and nanoplastics
- Industrial Chemicals (new and recently recognized)
- Biological Metabolites and Toxins
- Transformation products

- ….
- ….
- ….





Pharmaceuticals and reuse of wastewater

- Global consumption 100,000 metric tons
- ≈ 15 g/person/year
- In industrialized countries - higher consumption (between 50 and 150 g / person / year)

- The consumption rates are expected to increase due to the increasing age of the population.

- They have benefits for human health. Medicine is essential to maintain and improve public health.
- They are not a single chemical substance; there are thousands!
- Human and veterinary medicines; Diagnostic Imaging Agents

- Generally, not regulated by existing environmental laws.

- Important properties:
  - Generally soluble in water; therefore, they move quickly in the environment
  - Made to be bioactive (concern for bioactivity in the environment)
  - Made to be stable in "patients"

- An environmental contribution is significant and unavoidable (excretion)

Pharmaceuticals and reuse of wastewater

Typical concentrations in raw wastewater - ng to hundreds of µg with very variable elimination during treatment

Effects on humans

Acute toxicity: Current evidence seems to indicate minimal risk

Chronic toxicity - Low dose long term exposure

- At the concentrations detected, too much intake is required to obtain a “therapeutic dose" of the drug. But we are not treating therapeutically through drinking water!
- Exposure to chemical cocktails
- Antibiotics → antibiotic resistence

Pharmaceuticals and reuse of wastewater

Irrigation and uptake by plants

Studies to date have provided clear evidence to suggest that PPCPs can transfer from soil to plants**-**when treated wastewater or biosolids are used in agriculture.

- Leafy greens (lettuce, spinach and cabbage) exhibited the largest number and the highest concentration of pharmaceuticals.
- Within the same crop, contamination levels varied due to wastewater source and quality of treatment, and soil characteristics.

The human health and ecological risks of plants contaminated with low levels of PPCPs are still unclear and more studies are needed

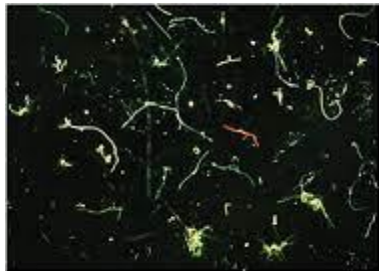
However, there is evidence on the adverse effects of PPCPs observed on non-target organisms such as aquatic organisms, leading to the conclusion that potential risks exist through dietary intake of PPCP-contaminated crops by human or animals.

Micro and nanoplastics

Classification

By size
Microplastics <5 mm
Nanoplastics < 1µm

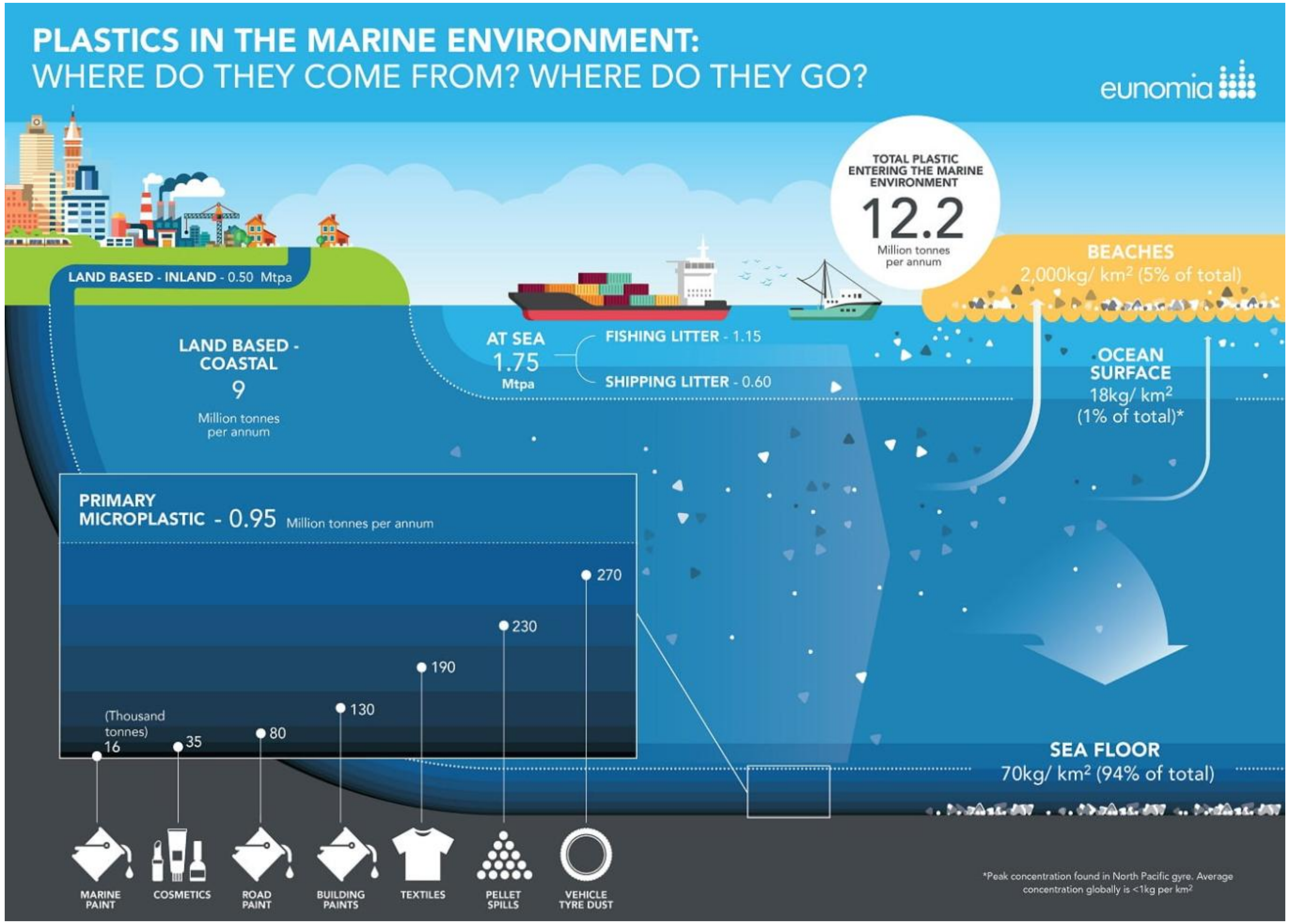
By origin
Primary – originally fabricated in that size
Secondary – formed by fragmentation of plastics of major size



By form
Synthetic fibers - Small strands or filaments produced artificially for the textile industry, to elaborate synthetic clothing (polyester, lycra, acrylic, etc.).
Microspheres - Plastic spheres that can be found in facial exfoliants, bath gels, toothpastes, and other cosmetics

By composition
Polyethylene (PE)• Polypropylene (PP)• Polyethylene terephthalate (PET)• Metacrylate polymethyl (PMMA)• Bisphenol A (BPA)• Nylon

Micro and nanoplastics in the environment



Source: *Plastics in the Marine Environment. EUNOMIA 2016*

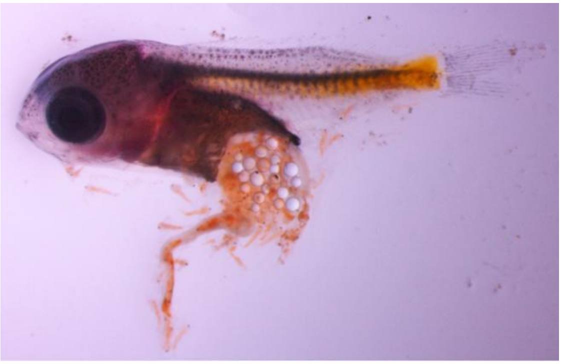
Micro and nanoplastics in the environment

Direct effect:
They can be ingested by smaller aquatic organisms obstructing their digestion and causing the death of these organisms.

In upper predators they would cause stomach problems, and additional stress by obstruction of their filtration/digestion system

Indirect effect:
Microplastics can adsorb disolved organic pollutants and facilitate their transport and affect bioavialability (so called Troyan horse effect).

They can also act as vectors for microorganisms.



It is important to consider that **the size of the microplastic matters**, and also that **different plastics** could have different dose/effect curves.

Micro and nanoplastics and water reuse

Water treatment generally does not specifically address the removal of microplastics (MPs).

Primary and secondary treatment processes **effectively remove MPs from wastewater** with removal efficiencies ranging from 75% to 90%. RE can be increased to >98% after tertiary treatment.

Although the removal efficiency of MPs in WWTP is relatively high, the quantity of these particles discharged into the environment is still very high, becoming one of the largest source of the introduction of MPs into the environment.

Most of the MPs eliminated from sewage **accumulate in the sewage sludge**. Incineration/thermal treatment of SS is the only effective way to destroy these plastic particles

Consesa and Ortuño, *Energies* **2022**, *15*(7), 2432; https://doi.org/10.3390/en15072432

Perfluorinated compounds

Forever chemicals

Per- and Polyfluoroalkyl Substances (PFAS) are a group of chemicals used to make fluoropolymer coatings and products that resist heat, oil, stains, grease, and water.

Used in products such as water-repellent clothing, furniture, adhesives, paint and varnish, food packaging, heat-resistant non-stick cooking surfaces and insulation of electrical wires.

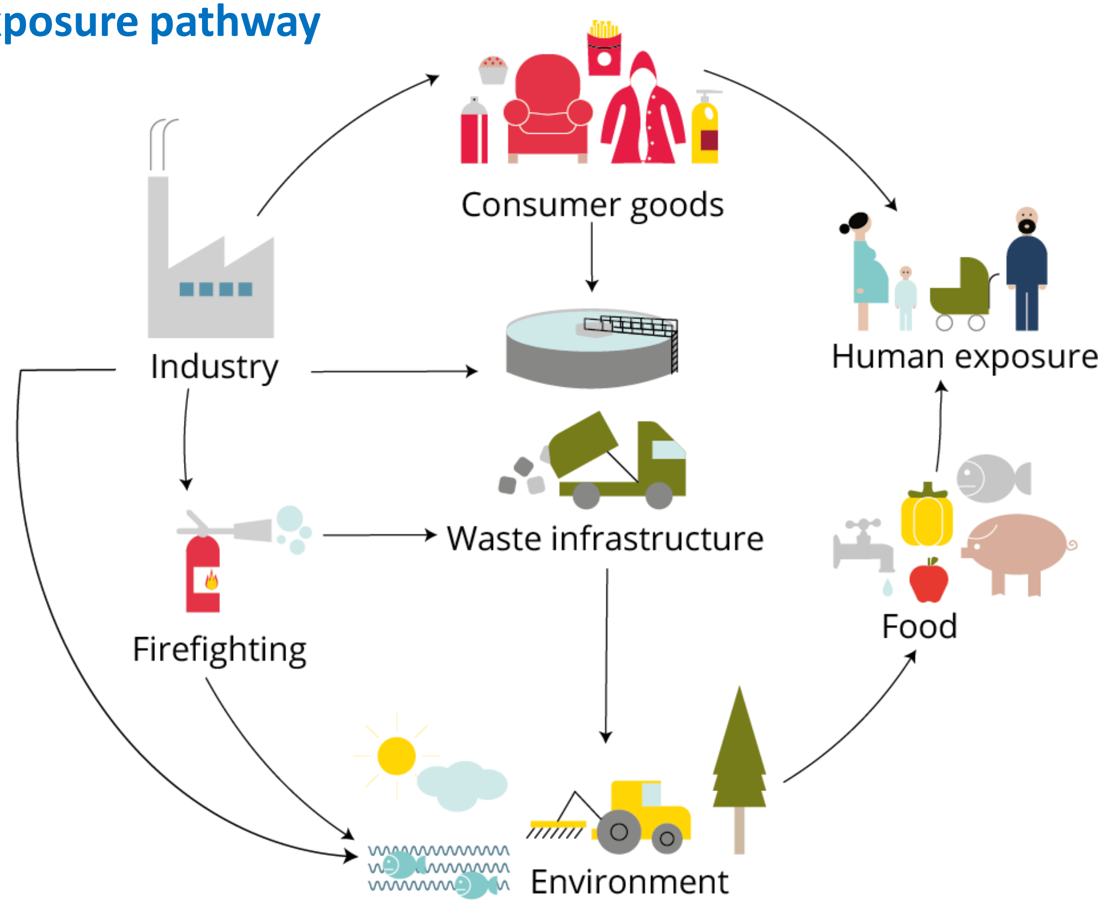
The majority of PFASs are persistent in the environment. **Some PFASs are known to persist in the environment longer than any other synthetic substance.** As a consequence of this persistence, as long as PFASs continue to be released to the environment, humans and other species will be exposed to ever greater concentrations. Even if all releases of PFASs would cease tomorrow, they would continue to be present in the environment, and humans, for generations to come.

Perfluorinated compounds

According to the OECD, at least **4,730 distinct PFASs** are known, which contain at least three perfluorinated carbon atoms.

The United States Environmental Protection Agency (EPA) toxicity database, DSSTox, lists **14,735 unique PFAS chemical compounds**.

Exposure pathway



PFAS and wastewater reuse

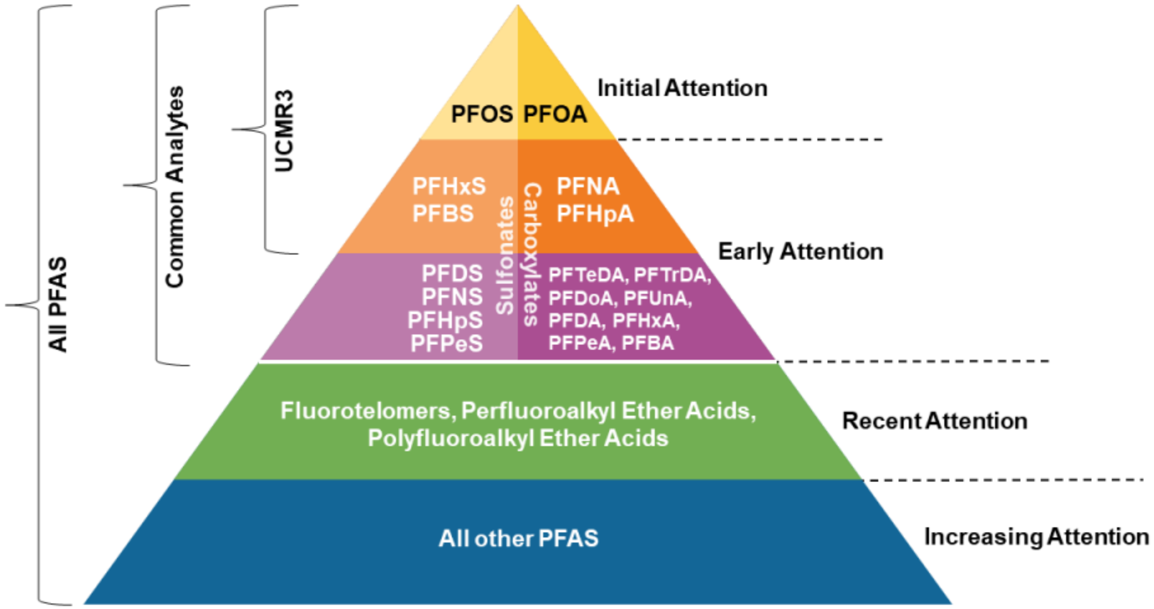
Per- and polyfluoroalkyl substances (PFAS) are commonly found in wastewater treatment plant (WWTP) effluents and therefore inadvertently introduced into the environment when treated wastewater is reused as an irrigation source or for recharge of aquifers

There is evidence on:
- uptake by plants
- entry to food chain (crops used by livestock)
- preferential for short chain PFAS

Perfluorinated compounds

Highly persistent in the environment
Global dissemination
Slightly water soluble
Low vapor pressure

Easily absorbed in humans
Elimination half-time in humans: several years
Pass the placental barrier
Lactational transfer results in peak exposures in infancy



Major adverse effects documented in laboratory animals and also reported in humans:

- Carcinogenicity
- Immunotoxicity
- Endocrine disruption, including delayed breast development
- Fetal toxicity and adverse pregnancy outcomes

Legislation at EU level

PFOS is restricted under the EU POPs Regulation (EU, 2019).

PFOA and its precursors are currently restricted under the REACH regulation (EU, 2006), including their presence in products made or imported into the EU.

PFOA and PFOS are priority hazardous substances under the Water Framework Directive (EC, 2017; EU, 2000).

Manufacturers have been developing replacement technologies, including reformulating longer-chain substances or substituting them with nonfluorinated chemicals, alternate technologies, or **shorter-chain perfluoroalkyl or polyfluorinated substances**. Some alternate PFAS include FTOH, PBSF-based derivatives, per- and polyfluoroalkylethers (for example, GenX chemicals and ADONA)

Due to the large number of PFAS chemicals, a substance-by-substance risk assessment and management approach is not adequate to efficiently prevent risk to the environment and human health from a single PFAS or mixtures of them.

As a result, complementary and precautionary approaches to managing PFAS are being explored.

Conclusions

The safety of water reuse has raised concern in recent years due to the presence of emerging contaminants..

In many countries, regulations or guidelines for water reuse mainly restrict conventional pollutants such as turbidity, COD, BOD, TSS, bacteria, residual chlorine, while emerging contaminants including microplastics are typically not included in the reuse standards

There is evidence that treated wastewater may be considered hazardous to human health when used for (*de facto*) potable reuse, or for irrigation of crops since some emerging contaminants may enter into the plants' roots, stems, leaves, and fruits.

The use of engineered pre-treatment or post-treatment methods needs to be based on a 'fit for purpose' principle and carefully integrated with the proposed water end use to ensure that human and environmental health risks are appropriately managed.

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Many thanks for your attention

SmartWaterTwin
Waste Water Management in Circular Economy Frame

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Unión Europea
Fondo Europeo
de Desarrollo Regional
"Una manera de hacer Europa"