Introduction to Persistent organic pollutants: general environmental problems, regulations, toxic effects and environmental levels

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Throughout the twentieth century around 10 million chemical compounds were synthesized worldwide.

The global production is around 400.000.000 Tm/year

Among the different uses, the more important are:

• Industrial applications

• Pesticides

• Generated in as byproducts in combustion processes, production of chemicals and other industrial processes
Persistent organic pollutants

Persistent Organic Pollutants (POPs) are organic chemical substances, that possess a particular combination of physical and chemical properties that gives them four characteristics:

- **Toxicity**: they are toxic to both humans and wildlife in acute and chronic exposures
  - Chronic toxicity properties including: development, reproduction, carcinogenesis, immuno toxicity and neurological changes
  - Acute toxicity with continuous release/exposure

- **Persistence**: they are very stable and resistant to degradation processes and can remain intact in the environment for exceptionally long periods of time (many years)
  - Half-life in water > 2 months,
  - or half-life in soils > 6 months,
  - or half-life in sediments > 6 months
  - Alternatively, other chemicals even though degrading faster in the environment, are persistent due to continuous release
**Persistent organic pollutants**

**Persistent Organic Pollutants (POPs)** are organic chemical substances, that possess a particular combination of physical and chemical properties that gives them four characteristics:

- **Bioaccumulation**: these compounds are lipophilic and adsorb and concentrate in the fatty tissues of organisms, including humans. They are found at higher concentrations at higher levels in the food chain (biomagnification)
  - BCF > 5,000
  - or log Kow > 5
  - or if they show accumulation up in the food chain

- **Long distance transport**: they become widely distributed throughout the environment as a result of natural processes involving soil, water and, most notably, air. They are semivolatile compounds susceptible to atmospheric transport to remote areas where they have never been produced or used
  - vapour pressure > 1.000 Pa
  - atmospheric half-life > 2 days
  - alternatively, monitoring data showin that the substance can affect regions where use is non-existent
1962 Silent spring (Rachel Carson)
The most alarming of all man’s assaults upon the environment is the contamination of air, earth, rivers, and sea... This pollution is for the most part irrecoverable

1972 Dichlorodiphenylchloroethanes (DDTs) were banned by the EPA

1998 Rotterdam Convention
on international trade of certain hazardous chemicals

2001 Stockholm Convention
regulation of the popularly called “dirty dozen”

Legislation: directives

- Directive 76/464/EEC: established two lists of priority pollutants
- Directive 78/659/EEC: regulates the quality of freshwaters in order to support fish life
  - Decision 2001/2455/EC: approved a list of 33 priority pollutants
  - Directive 2008/105/EC: established the quality standards for the priority pollutants in water
- Other directives: 91/414/EEC for pesticides and other specific for one compound
- Conventions
  - Rotterdam Convention (1998): promotes shared responsibility in the international trade of chemical products
  - Stockholm Convention (2001): established the “dirty dozen”
**Legislation: conventions**

- Conventions
  - Rotterdam Convention (1998): promotes shared responsibility in the international trade of chemical products
  - Stockholm Convention (2001): initially established the “dirty dozen”
    - Initially 12 POPs: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, polychlorinated biphenyls (PCBs) polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF)
    - Extension to 3 annexes:
      - Annex A: Parties must take measures to **eliminate** the production and use of these chemicals (organochlorine pesticides, PBDEs)
      - Annex B: Parties must take measures to **restrict** the production and use of the chemicals listed (DDT)
      - Annex C: Parties must take measures to reduce the **unintentional releases** of these chemicals with the goal of continuing minimization and, where feasible, ultimate elimination (PCDD, PCDF, HCB, PCBs and Pentachlorobenzene)

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**Other POPs of interest**

- Other POPs of interest:
  - PAHs
  - Endosulfan
  - Hexabromocyclododecane
  - Short-chained chlorinated paraffins
  - Organo lead, mercury and tin compounds
**Effects**

- Specific effects of POPs can include:
  - Cancer, allergies and hypersensitivity
  - Damage to the central and peripheral nervous systems
  - Reproductive disorders, and disruption of the immune system PAHs
- Some POPs are also considered to be
  - Endocrine disrupters, which, by altering the hormonal system, can damage the reproductive and immune systems of exposed individuals as well as their offspring
  - They can also have developmental and carcinogenic effects

**Environmental distribution**

It reflects sources but also processes in between different environmental compartments
**PCB usage and soil data**

![Graph showing PCB usage and soil data](image)

- Normally the concentration decreases as we move away from the contamination source

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**Air-soil-water exchange processes: HCHs case**

![Diagram showing air-soil-water exchange processes](image)
Transport pathways of water soluble POPs

- These chemicals are so water soluble that they remain dissolved in the aqueous phase
- Efficient LRT in water requires high persistence in water
- Volatilisation is not required for long range transport (LRT) to occur

Examples: HCHs

Transport pathways of low volatile and low soluble POPs

- Efficient LRT is restricted to episodes favouring rapid horizontal air movement, limited vertical air movement and lack of precipitation
- Areas close to sources are affected more strongly than those further away
- Once deposited, contaminant will only move if the particles to which it sorbs are remobilised

Examples: heavy PCDDs/PCDFs, five ring PAHs (BaP), heavy PBDEs
Transport pathways of volatile POPs

- Persistent chemicals which change between the gaseous and condensed state within the environmentally temperature range
- Will hope more often and are most likely to travel far
- Less volatile POPs are being retained in soils, sediments and vegetation

- PCBs, light PCDDs/PCDFs, HCB, dieldrin

Global fractionation hypothesis
Groups of POPs: Polycyclic Aromatic Hydrocarbons

- **Sources**
  - Incomplete combustion of fossil fuels (transport, waste incinerators, industry, heating and at small scale, tobacco and barbecues)
  - Diagenetic processes of fossil fuel formation
  - In small quantities by natural processes (forest fires and microbiological synthesis)
  - Naphthalene has an application in the manufacture of pesticides, polymers, paints…

- **Characteristics**
  - Formed by aromatic rings
  - Low polarity
  - Carcinogenic and mutagenic properties increasing the number of rings
  - Hardly degradable, bioaccumulative
  - Incorporate in the organisms by ingestion, inhalation or dermal absorption
  - Accumulated in the soil organic matter, in plants and in certain organisms such as mussels (organisms that are an excellent bioindicator of pollution) while fish and mammals metabolize them
  - EPA recommends the control of 16 PAHs
Groups of POPs: Polycyclic Aromatic Hydrocarbons

<table>
<thead>
<tr>
<th>Naphthalene</th>
<th>Acenaphthene</th>
<th>Acenaphthylene</th>
<th>Fluorene</th>
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<table>
<thead>
<tr>
<th>Phenanthrene</th>
<th>Anthracene</th>
<th>Fluoranthene</th>
<th>Pyrene</th>
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<table>
<thead>
<tr>
<th>Benzo(a)anthracene</th>
<th>Chrysene</th>
<th>Benzo(b)fluoranthene</th>
<th>Benzo(k)fluoranthene</th>
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</table>

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<thead>
<tr>
<th>Benzo(a)pyrene</th>
<th>Dibenzo(a,h)anthracene</th>
<th>Indeno(1,2,3-cd)pyrene</th>
<th>Benzo(g,h,i)perylene</th>
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</thead>
</table>

The Netherlands | France | EE.UU. | Germany | Switzerland | Great Britain | Spain | Great Britain |

<table>
<thead>
<tr>
<th>Groups of POPs: Polycyclic Aromatic Hydrocarbons</th>
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<table>
<thead>
<tr>
<th>Matrix</th>
<th>Location</th>
<th>Level</th>
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</thead>
<tbody>
<tr>
<td>WATER</td>
<td></td>
<td></td>
</tr>
<tr>
<td>River water</td>
<td>Poland</td>
<td>ng L⁻¹</td>
</tr>
<tr>
<td>River water</td>
<td>Spain</td>
<td>76-312</td>
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<tr>
<td>Groundwater</td>
<td>EE.UU.</td>
<td>10-30</td>
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<tr>
<td>Sea water</td>
<td>Turkei</td>
<td>0.2-6.9</td>
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<tr>
<td>AIR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clean office</td>
<td>EE.UU.</td>
<td>ng m⁻³</td>
</tr>
<tr>
<td>Urban air</td>
<td>France</td>
<td>0.6-29</td>
</tr>
<tr>
<td>Elverum</td>
<td>Norwe</td>
<td>80</td>
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<tr>
<td>SEDIMENT/SOIL/SLUDGE</td>
<td></td>
<td></td>
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<tr>
<td>Freshwater sediment</td>
<td>The Netherlands</td>
<td>mg kg⁻¹</td>
</tr>
<tr>
<td>Freshwater sediment</td>
<td>France</td>
<td>7.5-8.5</td>
</tr>
<tr>
<td>Seawater sediment</td>
<td>EE.UU.</td>
<td>1.1-6.3</td>
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<tr>
<td>Urban soil</td>
<td>Germany</td>
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<td>Rural soil</td>
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<td>Urban sludge</td>
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<tr>
<td>Industrial sludge</td>
<td>Great Britain</td>
<td>1.1-5.5</td>
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</tbody>
</table>
Groups of POPs: organochlorine pesticides

- Designed to inhibit or destroy the proliferation of organisms
  - acute toxicity
  - endocrine disruption effects
  - carcinogenic activity
  - hepatic injury
- With one or more molecules of chlorine in its formulation
- Mainly all have insecticidal activity
- Abuse → contamination of soils → contamination of surface and groundwater

Groups of POPs: organochlorine pesticides

- Although the majority are banned, they can be found in the environment.
- They are adsorbed on the particulate matter and accumulated in sediments due to:
  - low solubility
  - hydrophobic nature
  - persistence to degradation
- Sediments are the final acceptors and their secondary contamination source
- When they degrade rapidly their degradation products can be both more persistent and toxic than their precursors
Groups of POPs: organochlorine compounds

Groups of POPs: organochlorine compounds

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<tbody>
<tr>
<td>WATER</td>
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<td></td>
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<tr>
<td>Rainwater</td>
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<tr>
<td>Ice</td>
<td>Artic</td>
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<td>BIOTA</td>
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<td></td>
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<td>Greece</td>
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<tr>
<td>Freshwater fish</td>
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<td>Crabs</td>
<td>Brasil</td>
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<tr>
<td>SEDIMENT/SOIL/SLUDGE</td>
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<td></td>
</tr>
<tr>
<td>Freshwater sediment</td>
<td>China</td>
<td>0.001-0.036</td>
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<tr>
<td>Freshwater sediment</td>
<td>Argentina</td>
<td>0.004-0.064</td>
</tr>
<tr>
<td>Freshwater sediment</td>
<td>Turkei</td>
<td>0.004-0.057</td>
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<tr>
<td>Seawater sediment</td>
<td>Brasil</td>
<td>0.028-0.217</td>
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<tr>
<td>Soil</td>
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<tr>
<td>Soil</td>
<td>Czech Republic</td>
<td>0.0001-0.0050</td>
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<td>Sludge</td>
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