Fate and behaviour of organic contaminants in the aquatic environment

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Summary

1. Contamination of water resources: causes and history

2. Organic contaminants: distinction between priority and emerging contaminants (including endocrine-disrupting compounds)

3. Factors affecting fate, transport and behaviour of environmental contaminants in the aquatic environment:
   Source
   Physical-chemical properties
   Environmental conditions
   Persistence/degradation
   Examples, case studies

4. Conclusions
Water

A scarce resource, indispensable for human life and for the sustainability of the environment.

**Reasons for its deterioration**

**Human and economic development**

(more than 60,000 chemical substances are routinely synthesised worldwide, and between 200 and 1000 new chemicals are added to this list each year)

**Use as elimination recipient** (man has released around 3 millions of synthetic chemical substances to the environment (UNEP, 2003))

**Contamination of water resources**

**Beginning of S. XIX: First signs.**

**1962. Scientific and social awareness and concern**

Publication of “Silent Spring” by Raquel Carson
(alterations in animal species ↔ DDT)

**Persistent organic pollutants (POPs)**

- Apolar
- Toxic
- Persistent
- Bioaccumulable

**Carcinogenic compounds**

- PAHS
- PCBs
- Pesticides
- Dioxines
- ...

**Priority contaminants**

List of priority substances
(2455/2001/EC)

| Anthracene | Brominated diphenylethers | Alachlor |
| Atrazine   | Cadmium and its compounds  | Benzene  |
| Chlorpirifos| C10-13-chloroalkanes       | Chlorfeninphos |
| Di(2-ethylhexyl)phthalate | Hexachlorobenzene | 1,2-dichloroethane |
| Diuron     | Hexachlorobutadiene        | Dichloromethane |
| Endosulfan | Hexachlorocyclohexane      | Fluoranthene |
| Isoproturon| Mercury and its compounds  | Nickel and its compounds |
| Lead and its compounds | Nonylphenol | Trichloromethane |
| Naphthalene| Pentachlorobenzene         |           |
| Octylphenol| Polycyclic aromatic hydrc. |          |
| Pentachlorophenol | Simazine |          |
| Simazine   | Tributyltin compounds      |          |
| Trichlorobenzenes | Trifuralin |          |
| Trifuralin |                        |          |

Subject to study for their identification as possible dangerous priority substances

Identified as dangerous priority substances

Persistent Organic Pollutants (POPs)

Common properties

- **Semivolatile** (Pv < 1000 Pa)
  - Long-range transport and distribution through the atmosphere and water bodies
- **Resistant to chemical, photolytic and biological degradation**
  - Persistent
- **High bioaccumulation and biomagnification potential**
  - They are found at higher concentrations at the higher levels of the food chains
- **Toxic to humans and wildlife**
  - Nervous system damage, endocrine disruption, diseases of the immune system, reproductive and developmental disorders, cancer,…
Emerging Contaminants

New and more sensitive analytical and biological methods

Def.: newly identified or previously unrecognized contaminants

Priority lines of research (WHO, EPA, UE)

Little or no investigated
Scarcity or lack of environmental data and analytical methods
Not regulated

Emerging contaminants

- Due to their physico-chemical properties (high water solubility and often poor degradability) they are able to penetrate through all natural filtration steps and man-made treatments
- Low elimination in WWTP
- Potential risk for drinking water supply
  - Large volume production/high fluxes in the environment (e.g. pharmaceuticals, surfactants, pesticides)
  - They do not need to be persistent in the environment to cause negative effects due to continuous introduction (pseudo-persistent contaminants)
  - Lack of data on their occurrence and behaviour
## Organic emerging contaminants

- Flame retardants (Brominated diphenylethers)
- Alkylphenol ethoxylate surfactants
- Chloroalkanes
- Phthalates
- Organotin compounds
- Drinking water disinfection by-products
- Pesticide transformation products
- Methyl tert-butyl ether and other gasoline additives
- Fluorinated surfactants (PFOA, PFOS)
- Pharmaceuticals
- Personal care products
- Algal toxins
- Bisphenol A

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## Endocrine Disrupting Chemicals (EDCs)

### Definition

“An exogenous substance that causes adverse health effects in an intact organism, or its progeny, consequent to changes in endocrine function”

(European Commission)

“An exogenous agent that interferes with the synthesis, secretion, transport, binding, action or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development and/or behaviour”

(EPA)
Categories of substances with reported endocrine-disrupting properties*

<table>
<thead>
<tr>
<th>SUBSTANCE</th>
<th>EXAMPLES</th>
<th>USES</th>
<th>MODES OF ACTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phytoestrogens</td>
<td>Isoflavones; lignans; coumestans</td>
<td>Present in plant material</td>
<td>Estrogenic and anti-estrogenic</td>
</tr>
<tr>
<td>Female sex hormones</td>
<td>17-β estradiol; estrone</td>
<td>Produced naturally in animals</td>
<td>Estrogenic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(including humans)</td>
<td></td>
</tr>
<tr>
<td>Synthetic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polychlorinated organic compounds</td>
<td>Dioxins</td>
<td>By-products from incineration</td>
<td>Anti-estrogenic</td>
</tr>
<tr>
<td></td>
<td>Polychlorinated biphenyls (PCBs)</td>
<td>and industrial chemical processes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Organochlorine pesticides</td>
<td>Insecticides</td>
<td>Estrogenic and anti-estrogenic</td>
</tr>
<tr>
<td></td>
<td>DDT; chlordane; lindane</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Organotins</td>
<td>Tributyltin</td>
<td>Anti-estrogenic</td>
</tr>
<tr>
<td></td>
<td>Tributyltin</td>
<td>Anti-fouling agent</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Alkylphenols</td>
<td>Nonylphenol</td>
<td>Estrogenic</td>
</tr>
<tr>
<td></td>
<td>Nonylphenol</td>
<td>Used in production of NPEOs and polymers, degradation product</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Alkylphenol ethoxylates</td>
<td>Dibutyl phthalate (DBP); butylbenzyl phthalate (BBP)</td>
<td>Estrogenic</td>
</tr>
<tr>
<td></td>
<td>Bisphenol-A</td>
<td>Component in polycarbonate plastics and epoxy resins</td>
<td>Estrogenic</td>
</tr>
</tbody>
</table>
|                                        | Synthetic steroids              | Ethinyl estradiol                         | Contraceptives         |}


How do the EDCs act?

Substances can interact with endocrine systems and cause a disruption to normal functions in several ways:

- They can act like a natural hormone and bind to a receptor. This causes a similar response by the cell, known as an agonist response.
- They can bind to a receptor and prevent a normal response, known as an antagonistic response.
- A substance can interfere with the way natural hormones and receptors are synthesized or controlled.

![Diagram of hormone receptor showing normal response, agonist response, and antagonist response.](image)
Well-documented effects of EDCs in wildlife

- Decreased fertility & growth
- Sex alteration
- Poor hatching/egg shell thinning
- Abnormal thyroid function

Some examples include:
- Reproductive effects in Baltic seals,
- Eggshell thinning in birds of prey,
- Decline in the alligator population in polluted lakes,
- General declines in frog populations,
- Effects on the reproduction and development of fish,
- Development of male sex organs in female marine organisms.

Aquatic animals, especially carnivores, are the most affected because they are at the top of the "food chain".

Suspected effects of EDCs in humans

- Malformations of newborns
- Undescended testicles
- Abnormal sperm
- Low sperm counts
- Abnormal thyroid function
- Possible breast, testicular, prostate cancer
- Other effects
Factors affecting distribution and fate of environmental contaminants in the aquatic environment

* Source

* Physical-chemical properties
  - Water solubility
  - Polarity (Kow)
  - Volatility (Henry’s constant, vapor pressure)
  - Acid-base properties
  - ...

* Environmental conditions
  - Temperature, Altitude, Latitude, Wind, Rainfall, pH, Organic matter, Flow rate...

* Persistence/degradation
  - Photo-, chemical-, and bio-degradation

Potential sources (↔ use)

Atmospheric Transport / Agricultural Runoff
  - Organochlorine Pesticides: DDT, Dieldrin, Lindane

Inceration, Landfill
  - Polychlorinated Compounds: Polychlorinated dioxins, Polychlorinated biphenyls

Industrial And Municipal Effluents
  - Alkylphenolics (Surfactants and Their Metabolites): Nonylphenol
  - Phthalates (Found In Plasticisers): Dibutyl Phthalate, Butylbenzyl Phthalate

Municipal Effluent And Agricultural Runoff
  - Natural Hormones, Synthetic Steroids: 17βEstradiol, Estrone, Ethynyl estradiol

Pulp Mill Effluents
  - Phytoestrogens: Isoflavones, Ligans, Coumestan

Agricultural Runoff
  - Pesticides Currently In Use - Atrazine, Trifluralin, Permethrin...

Harbors
  - Organotins: Tributyltin
**Physical-chemical properties**

**Solubility in water**

- **Def.**: maximum possible concentration of a chemical compound that can be dissolved in water at equilibrium.

- The higher the water solubility, the greater the tendency to remain dissolved.
- High water soluble substances are less likely to volatilize from water and likely to enter the aquatic environmental through run-off.
- Low water soluble substances volatilize more readily in water, tend to precipitate, to partition to soil, and to bioconcentrate in aquatic organisms.

- \(< 0.5 - 1 \text{ mg/L} = \text{very insoluble}\)
  - Most emerging contaminants are soluble in water
  - Most POPs have low water solubility

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**Physical-chemical properties**

**Polarity**

- **Octanol-water partition coefficient** (log $K_{ow}$) = the ratio of the concentration of a chemical in octanol and in water at equilibrium and at a specified temperature.

- It thus represents the tendency of a chemical to partition between an organic phase (e.g., fish, soil) and an aqueous phase.

  \[ \log P_{ow} \begin{cases} > 4.5 & \rightarrow \text{non polar comp.} \\ > 1.5 - 4 & \rightarrow \text{moderately polar comp.} \\ < 1.5 & \rightarrow \text{polar comp.} \end{cases} \]

- The higher the Log Kow the greater the tendency of a compound to absorb to solid phases and bioaccumulate in organisms.
### Physical-chemical properties

#### Volatility

**Def.** the property of changing readily from a solid or liquid to a vapor

**Vapor pressure**

Def.: pressure at which the gaseous phase of a substance coexists in equilibrium with its liquid or solid phase. 
It is characteristic for each substance and increases with T. 
Volatile substances have high vapor pressure values.

**Henry’s constant (H₀ Kᵢₐ)**

Def.: ratio between the concentration of a substance in air and its concentration in water in equilibrium. 
High values mean high volatilization 
< 9.9E-11 atm m³ mol⁻¹ → low volatile compounds

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### Physical-chemical properties

#### Acid-base ionization

Ionization capacity of a compound

Characteristic for each substance, increases with T

Ionization of a compound increases its solubility in water and decreases its lipophilicity.

In the water/soil media (pH 5-8)

* substances with pKa < 3-4: tend to move to the aquatic medium
  * substances with pKa > 10: tend to be retained in soil
Persistent Organic Pollutants (POPs)

Common properties

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  - Long-range transport and distribution through the atmosphere and water bodies
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- High bioaccumulation and biomagnification potential
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Atmospheric processes play a major role in their transport and fate
Polycyclic Aromatic Hydrocarbons in the NE subtropical Atlantic Atmosphere

Gas Phase

Aerosol Phase

Increased MW & Kow
Decreased volatility
Relative importance of air-water exchange processes for PAHs


Gobal distillation effect theory

(Fernández P, Grimalt, JO. Chimia 2003; 57: 514)
Seasonal effect of T

**Figure 3.** Illustration of the processes governing air–surface exchange of semi-volatile organic contaminants (SOCs) along a temperate mountain slope in different seasons. The balance of deposition (blue arrows) and resublimation (red arrows) will determine the change of SOC concentrations along an elevation gradient. SOCs of different volatility will differ in terms of their atmosphere–surface exchange.


Global distillation effect

<table>
<thead>
<tr>
<th>SOC</th>
<th>Py* (Pa, 25°C)</th>
<th>H* (Pa m²/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-HCH</td>
<td>3.0 × 10⁻³</td>
<td>1.1</td>
</tr>
<tr>
<td>HCB</td>
<td>2.4 × 10⁻³</td>
<td>139</td>
</tr>
<tr>
<td>PCB28</td>
<td>2.6 × 10⁻²</td>
<td>33</td>
</tr>
<tr>
<td>PCB180</td>
<td>8.1 × 10⁻⁵</td>
<td>102</td>
</tr>
<tr>
<td>DDT</td>
<td>3.8 × 10⁻⁵</td>
<td>6</td>
</tr>
<tr>
<td>DDE</td>
<td>8.6 × 10⁻⁴</td>
<td>34</td>
</tr>
</tbody>
</table>


**Uses of PCBs**


**Uses of PCB and latitudinal distribution in soils**
Global climate change

Increased T
↓
Iceberg & snow melting
↓
Release of contaminants

Bioaccumulation of POPs in Arctic Food Chain

Environmental conditions

Temperature

Wind Speed

- Henry’s constant
- Solubility
- Degradation rate
- etc.

- Atmospheric deposition
- Air-water exchange
- etc.

Influence of Sea Breeze on Air-Water Exchange

NW Mediterranean
Masnou harbor

(Pérez et al. ES&T 2003, 37, 3794-3802)
Influence of sea breeze on air-water exchange

PAH occurrence and Met data

(Pérez et al. ES&T 2003, 37, 3794-3802)
Emerging contaminants

- Due to their physico-chemical properties (high water solubility, low volatility, and often poor degradability) they are able to penetrate through all natural filtration steps and man-made treatments
- Low elimination in WWTP
- Potential risk for drinking water supply
  - Large volume production/high fluxes in the environment (e.g. pharmaceuticals, surfactants, pesticides)
  - They do not need to be persistent in the environment to cause negative effects due to continuous introduction
  - Lack of data on their occurrence and behaviour

Entering the water cycle

- Soil
  - Sewage sludge
  - Biota
- Ground water
  - Wastewater treatment plant
  - Run-off
  - Controlled/uncontrolled discharge
- Drinking water production
- Surface water
- Estuarine water
- Ocean water
- Sediment
- Biota
- Man
# Elimination in Sewage Treatment Plants (STP) (conventional activated sludge treatment)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbamezapine (anti-epileptic drug)</td>
<td>&lt; 10% (no removal)</td>
</tr>
<tr>
<td>Atenolol, Metoprolol (β-blockers)</td>
<td></td>
</tr>
<tr>
<td>Trimethoprim (antibiotic)</td>
<td></td>
</tr>
<tr>
<td>Diclofenac (anti-inflammatory)</td>
<td>10-39%</td>
</tr>
<tr>
<td>Methoxazole</td>
<td>50%</td>
</tr>
<tr>
<td>Gemfibrozil (lipid regulator)</td>
<td>43-71%</td>
</tr>
<tr>
<td>Naproxen (anti-inflammatory)</td>
<td>42-92%</td>
</tr>
<tr>
<td>Fluoroquinolones (antibiotics)</td>
<td>60%</td>
</tr>
<tr>
<td>Ibuprofen (anti-inflammatory)</td>
<td>&gt; 90%</td>
</tr>
<tr>
<td></td>
<td>Note: hydroxy and carboxy metabolites found in effluents)</td>
</tr>
</tbody>
</table>

*Removal efficiency is a function of the drug’s structure and treatment technology employed; the conjugates can be hydrolyzed back to the free parent drug.*

Source: REMPHARMAWATER final report

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# Deconjugation of glucuronide and sulfate metabolites of pharmaceuticals in sewers and STP

![Diagram of deconjugation](image)

- Estrone-sulfate (↓ activity)
- Estrone (↑ activity)
STP effluents: point-source contamination
Concentration of pharmaceuticals in treated sewage and surface water

Concentrations (ng/L) of the most ubiquitous anti-inflammatory, lipid regulators, psychiatric drugs and β-blockers detected in (A) wastewater effluent and (B) river water downstream the WWTP monitored.
Steroids in STP and receiving coastal waters in Catalonia

Study area

- WWTP Besós
- WWTP Depurbaix

⇒ Bi-monthly (Jun 02-Jun 03)

- B1: Mouth of Besós river
- B2: Emissary of WWTP Besós
- L1: Mouth of Llobregat river
- L2: Emissary WWTP Depurbaix (X1Y1)
- L3: Emissary WWTP Depurbaix (XmYm)
- L4: Emissary WWTP Depurbaix (X2Y2)

Average concentrations of estrone-3-sulfate and estrone in waste and coastal water

Concentrations in coastal water are approximately 100 times lower than in wastewater.
Breakdown during sewage treatment (AST): APEOs case.

(according Ahel, Wat. Res. 1995)

Ultimate biodegradation of NPEOs <40%

40-45% ends up in secondary effluent

20 % in sludge

### Breakdown pathway of NPEOs

- **Increasing polarity**
  - Possible contamination of groundwaters

- **Increasing toxicity**

- **Increasing persistence**

- **Increasing bioconcentration**

![Breakdown pathway of NPEOs](image-url)
Biosolids

~16000 municipal WWTP in USA → 12,5 billions dry lb/yr of biosolids

Estimated Mass and Use of Biosolids in US

- Land Application: 65%
- Incineration: 16%
- Landfills: 18%
- Other: 1%

Source: National Research Council of the National Academies

Human Medicine
- Excretion
- Sewage
- Treatment plant
- Sludge
- Surface waters
- Drinking water
- Overflow
- Leaks

Veterinary Medicine
- Excretion
- Manure
- Agricultural soils
- Ground waters
- Food chain
- Run-off
- Sea
- Drinking water

Aquaculture
- Excretion
- Manure

Domestic waste
- Excretion
- Disposal

Sewage
- Treatment plant
- Sludge

Agricultural soils
- Excretion
- Ground waters

Sea
- Run-off
- Drinking water
Manure

Soil Fertilization

- Lower cost of crop production
- Reduces soil erosion potential
- Improves soil/water infiltration

Concentration range of antibiotics in manure.

<table>
<thead>
<tr>
<th>Operation</th>
<th>Tetracyclines (µg/kg)</th>
<th>Sulfonamides (µg/kg)</th>
<th>Macrolides (µg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dairy</td>
<td>ND – 5130</td>
<td>ND – 46</td>
<td>ND – 5</td>
</tr>
<tr>
<td>Beef</td>
<td>ND – 585</td>
<td>ND – 258</td>
<td>ND – 846</td>
</tr>
<tr>
<td>Hog</td>
<td>ND – 23,140</td>
<td>ND – 38</td>
<td>ND – 6682</td>
</tr>
<tr>
<td>Sheep</td>
<td>ND – 10,900</td>
<td>ND – 419</td>
<td>ND – 31</td>
</tr>
<tr>
<td>Turkey</td>
<td>ND – 309</td>
<td>ND – 70</td>
<td>ND – 4</td>
</tr>
<tr>
<td>ND non-detectable</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: Ken Carlson, Antibiotics 2004 newsletter

Environmental Effects of Antibiotics

- Antibiotics are designed to affect microorganisms and bacteria found in humans and animals. This, therefore makes them potentially hazardous to other such organisms found in the environment.

- Excreted antibiotics (up to 90% of one dose in urine and 75% in feces) partially inhibit methogenesis in anaerobic waste-storage facilities, thus decreasing the rate at which bacteria metabolize animal waste products.

- The frequent use of antibiotics has promote the rise of populations of new strains of bacteria resistant to antibiotics. Some studies evidenced up to 70% increase in resistance to certain antibiotics when manure from a farm was applied to a garden soil.

- On release into the environment through manure/sludge application, antibiotics may end up on agricultural soils and can be taken up by plants, affecting the growth and development.

- In general, toxic levels of antibiotics for microorganisms, bacteria and micro-algae are 2-3 orders of magnitude below the toxic values for higher trophic levels.
**Entering the water cycle**

- Sewage sludge → Wastewater treatment plant → Surface water → Biota
- Rain → Controlled/uncontrolled discharge → Run-off
- Surface water → Estuarine water → Ocean water
- Surface water → Ground water
- Drinking water production
- Soil

**Sedimentation**

Favoured for:
- Non-ionic
- Low water solubility
- High Kow

**Concentrations of nonylphenolic compounds in river (Cardener) water and sediments**

Barcelona STP

- Water concentrations:
  - µg/L
  - µg/kg

- Sediment concentrations:
  - µg/kg

Cardener river

Llobregat river

C1

C2

C3

µg/L

µg/kg

µg/kg

µg/L
Inventory of PCB in the surface ocean and in soils

Entering the water cycle

Bioaccumulation
Favoured for lipophilic (high Kow)
Levels (ng/g) of hexabromocyclododecane (HBCD) in sediment and fish (*C. toxostoma*) - Cinca River (NE Spain)

Applications as flame retardant:
- Electronic circuitry
- Plastics
- Paper
- Wood
- Textiles
- Building materials

HBCD in fish from the Cinca River – Bioaccumulation

Fish length and weight are directly related to fish age

Length and Weight versus [HBCD]
Different profiles of HBCD isomers in sediment & fish

Questions?

Alpha is more bioavailable than gamma?
Or its bioaccumulation factor is greater?
Or does biotransformation from gamma to alpha occur?

Biomagnification in the food web

Polybrominated diphenyl ethers (PBDEs) in human milk

- Presence in:\n  - humans: milk, plasma, serum, fat tissue, fetus blood
  - animals: seafood, fish, birds, marine mammals
  - air, surface water, soils, sediments, sludge

- Possible effects:
  - neurotoxicity
  - endocrine disruption
  - cancer

PBDE # 47 & PBDE # 153 in human milk (Sweden)


Entering the water cycle

- Sewage sludge
- Wastewater treatment plant
- Surface water
- Estuarine water
- Ocean water
- Sediment
- Biota
- Soil
- Drinking water production
- Ground water
- Run-off
- Controlled/uncontrolled discharge
- Man

waterworks
Sant Joan Despí waterworks (Barcelona)

**PURIFICATION PROCESS**
- Prechlorination/predioxichlorination
- Sand filtration
- Ozonization
- Activated carbon
- Chlorination

**WATERWORKS OPERATION**
- SURFACE WATER
  - DAM
  - LLOBREGAT RIVER
  - TREATMENT PLANT
  - INDUCED SURFACE RECHARGING
  - AQUIFER
  - WELLS
  - GROUND WATER
  - NATURAL RECHARGING THROUGH THE RIVER’S BED

**Profile of total pesticide concentration throughout the water treatment process (SJD)**

- Cyanazine
- Simazine
- Tertbutylazine
- Desethylatrazine
- Atrazine
- Metolachlor
- Diuron
- Isoproturon
- Dimethoate
- Diazinon
- Molinate
- Propanil
- Mecoprop
- 2,4 D
- MCPA

Not detected: chlortoluron, linuron, alachlor and bentazone

Directive 75/440/EC: max. adm. conc. 5 ug/L for surface waters (intensive phys. & chem. treatment.)
Directive 98/83/EC: max. total pesticide conc. 500 ng/L water intended for human consumption
Directive 2006/118/EC: max. individual pesticide conc. 100 ng/L groundwater
Arraenas artificial recharge plant in Denmark

Levels (ng/L) of pesticides in DK samples (2004)

<table>
<thead>
<tr>
<th>Analyte/sample</th>
<th>Intake</th>
<th>SBW</th>
<th>SBE</th>
<th>IBW1</th>
<th>IBE2</th>
<th>I1</th>
<th>I3</th>
<th>M1</th>
<th>DGU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deisopropylatrazine</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>BAM</td>
<td>6.95</td>
<td>7.03</td>
<td>7.97</td>
<td>9.37</td>
<td>4.31</td>
<td>8.71</td>
<td>3.83</td>
<td>10.44</td>
<td>3.11</td>
</tr>
<tr>
<td>Desethylatrazine</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>0.31</td>
<td>0.34</td>
<td>0.87</td>
<td>0.25</td>
<td>nd</td>
</tr>
<tr>
<td>Dimethoate</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Simazine</td>
<td>11.57</td>
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</table>

2 sampling campaigns: Sept. 2003 / June 2004
17 target pesticides by on-line SPE(PLRP-s)-LC-ESI(PI)-MS/MS:
* 15 PI pesticides + propanil + BAM (2,6-dichlorobenzamide)
Cumulative levels of pesticides in water samples from DK

Formation of halogenated derivatives (SJD WW)

Average composition of nonylphenolic compounds after chlorination (calculated on a molar basis)

River water | Chlorinated river water | Flocculation sludge
--- | --- | ---
NPEC | NP | NPEO | halogenated derivatives

13% | 48%

After: Petrovic et al. ES&T, 2003

Formation of chlorinated derivatives of phenolic compounds

- Estrogens:
  Ethynyl estradiol + NaClO (5 min.) \( \rightarrow \) 4-CIEE + 2,4-diCIEE

- Phenol
- Bisphenol A
- ...

Chlorinated derivatives: $< \text{biodegradation}$ than parent comp. $> \text{estrogenicity}$
Water disinfection by-products (DBPs)

- Halogenated compounds are formed by reaction of disinfection agents with organic matter present in the source water.
- 1974: chloroform and other trihalomethanes, first identified DBPs.

**US EPA**


**Directive 98/83/EC**

(drinking water)

<table>
<thead>
<tr>
<th>Regulated Contaminants</th>
<th>MCL (mg/L)</th>
<th>MCL(C) (mg/L)</th>
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<tr>
<td>Total Trihalomethanes (THMs)</td>
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<tr>
<td>Chloroform</td>
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<td>Bromodichloromethane</td>
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<td>Bromoform</td>
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<td>For Haloacetic Acids (HAA5)</td>
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<td>Monochloroacetic acid</td>
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<td>Dichloroacetic acid</td>
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<td>Bromoacetic acid</td>
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<tr>
<td>Bromic acids (that use ozone)</td>
<td>0.010</td>
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<td>Chlorite (plants that use chlorine dioxide)</td>
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<td>0.6</td>
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</table>


More than 600 DBPs identified (< 50% total DBPs)

Very little information about the occurrence and toxicity of non-regulated DBPs

**Chemical analysis output for a typical environmental sample**

Adapted from:
C.G. Daughton
U.S. EPA July 2002

TIC – tentatively identified compounds
Conclusions

- Contaminants are widely distributed in the aquatic environment
- Sources, transport routes and final distribution in the various environmental compartments depend on the physical-chemical properties of the compounds and on environmental conditions
- Identified contaminants represent only a portion of those potentially present and their overall risk significance is largely ignored.
- Reduced emission and improved wastewater treatment to diminish occurrence, exposure and detrimental effects.

Acknowledgements

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