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-disruptng compounds)

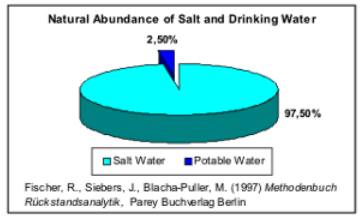
3. Factors affecting fate, transport and behaviour of environmental contaminants in the aquatic environment:
   - Source
   - Physical-chemical properties
   - Environmental conditions
   - Persistence/degradation

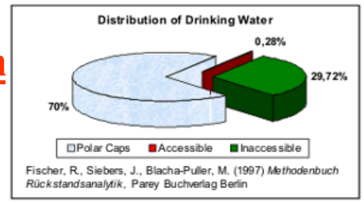
   } **Examples, case studies**

4. Conclusions

Water

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



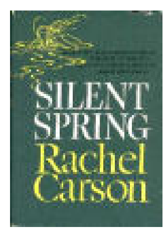


Reasons for its deterioration

human and economic development (more than 60.000 chemical substances are routinely synthetised worlwide, and beween 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

Water Framework Directive (2000/60/EC)

List of priority substances
(2455/2001/EC)

Anthracene
Atrazine
Chlorpirifos
Di(2-ethylhexyl)phthalate
Diuron
Endosulfan
Isoproturon
Lead and its compounds
Naphthalene
Octylphenol
Pentachlorophenol
Simazine
Trichlorobenzenes
Trifuralin

Subject to study for their identification as possible dangerous priority substances

Brominated diphenylethers
Cadmium and its compounds
C10-13-chloroalkanes
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclohexane
Mercury and its compounds
Nonylphenol
Pentachlorobenzene
Polycyclic aromatic hydroc.
Tributyltin compounds

Identified as dangerous priority substances

Alachlor
Benzene
Chlorfenvinphos
1,2-dichloroethane
Dichloromethane
Fluoranthene
Nickel and its compounds
Trichloromethane

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 bioacumulation 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

2455/2001/EC

- Organotin compounds
  Drinking water disinfection by-products
- Pesticide transformation products

Already regulated
New data

Methyl tert-butyl ether and other gasoline additives
Fluorinated surfactants (PFOA, PFOS)
- Pharmaceuticals
  Personal care products
  Algal toxins
- Bisphenol A
  . . . .

■ Endocrine disruptors

Not regulated
Insufficient data

*Susan D. Richardson (2004) Anal. Chem. 76, 3337-3364.

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*

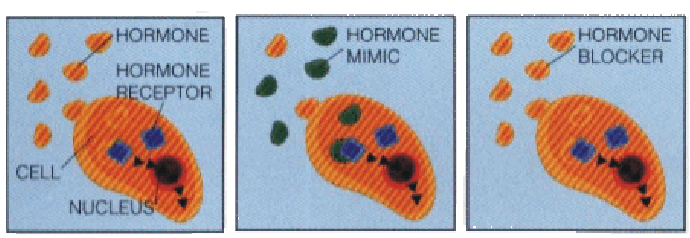
SUBSTANCE	EXAMPLES	USES	MODES OF ACTION
Natural			
Phytoestrogens	Isoflavones; lignans; coumestans	Present in plant material	Estrogenic and anti-estrogenic
Female sex hormones	17-β estradiol; estrone	Produced naturally in animals (including humans)	Estrogenic
Synthetic			
Polychlorinated organic compounds	Dioxins	By-products from incineration and industrial processes	Anti-estrogenic
	Polychlorinated biphenyls (PCBs)	Dielectric fluids	
Organochlorine pesticides	DDT; dieldrin; lindane	Insecticides	Estrogenic and anti-estrogenic
Organotins	Tributyltin	Anti-fouling agent	Anti-estrogenic
Alkylphenols	Nonylphenol	Used in production of NPEOs and polymers, degradation product	Estrogenic
Alkylphenol ethoxylates	Nonylphenol ethoxylate	Surfactants	Estrogenic
Phthalates	Dibutyl phthalate (DBP); butylbenzyl phthalate (BBP)	Plasticisers	Estrogenic
Bi-phenolic compounds	Bisphenol-A	Component in polycarbonate plastics and epoxy resins	Estrogenic
Synthetic steroids	Ethinyl estradiol	Contraceptives	Estrogenic

*Environment Agency, R&D Technical Summary P38, 1999.

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.



Normal response | Agonist response e.g. estogenic | Antagonist response normal response inhibited e.g. anti-estrogenic response

Well-documented effects of EDCs in wildlife

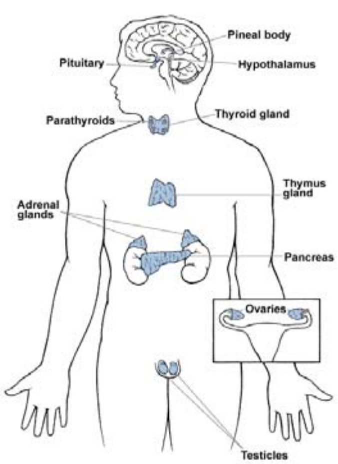
- Decreased fertility & growth
- Sex alteration
- Poor hatching/egg shell thinning
- Abnormal thyroid function

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

Incineration, Landfill

Polychlorinated Compounds: Polychlorinated dioxins, Polychlorinated biphenyls

Industrial And Municipal Effluents

Alkylphenolics (Surfactants and Their Metabolites): Nonylphenol

Phthalates (Found In Placticisers): Dibutyl Phthalate, Butylbenzyl Phthalate

Municipal Effluent And Agricultural Runoff

Natural Hormones, Synthetic Steroids: 17ßEstradiol, 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 mg/L = very insoluble**
- Most emerging contaminants are soluble in water
- Most POPs have low water solubility

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}
  - **> 4-5 → non polar comp.**
  - **> 1.5-4 → moderately polar comp.**
  - **< 1-1.5 → polar comp.**

- The higher the Log Kow the greater the tendency of a compound to absorb to solid phases and bioacumulate 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 gase 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 vapour pressure values.

Henry's constant (H o K_H)

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 m^3 mol^{-1} → low volatile compounds

Physical-chemical properties

Acid-base ionization

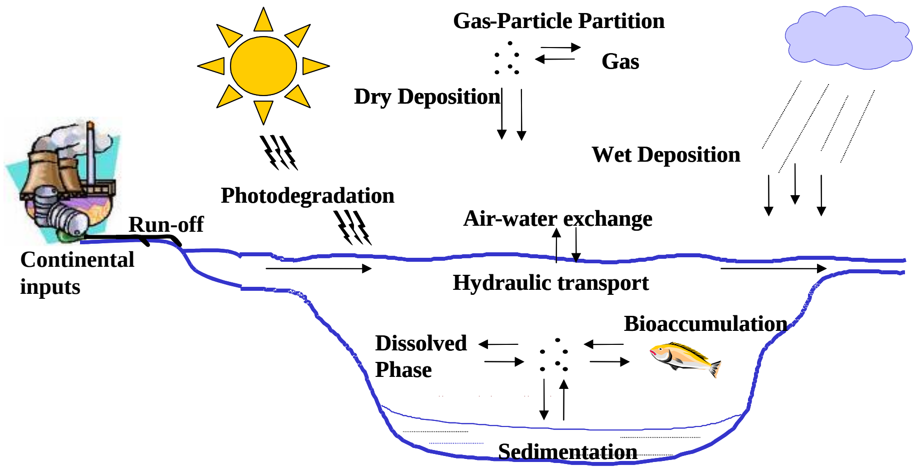
Ionization capacity of a compound

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

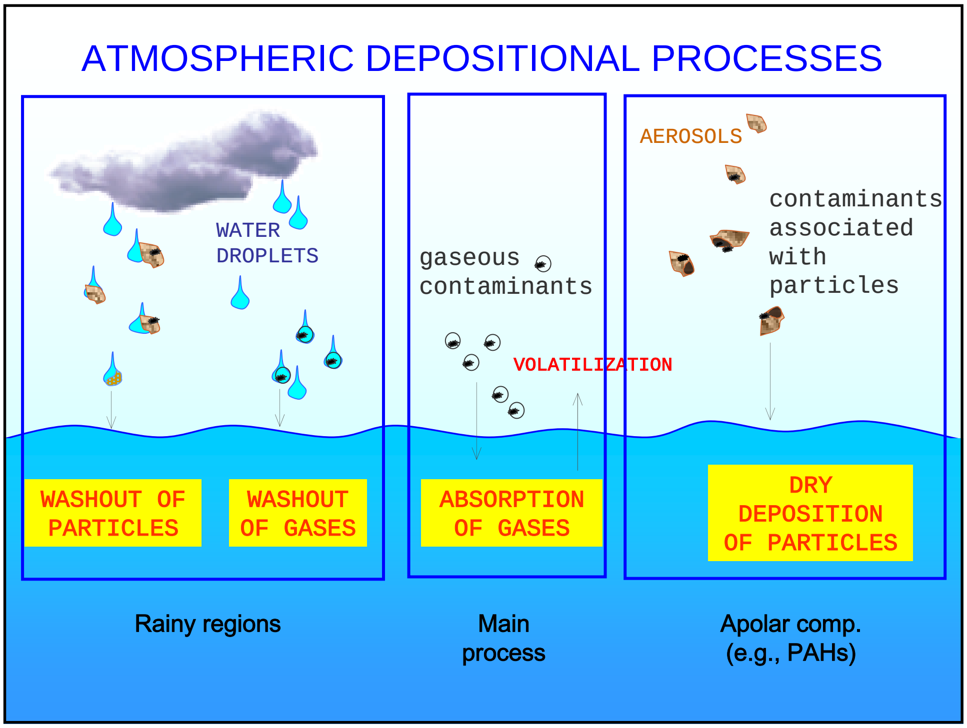
Global transport

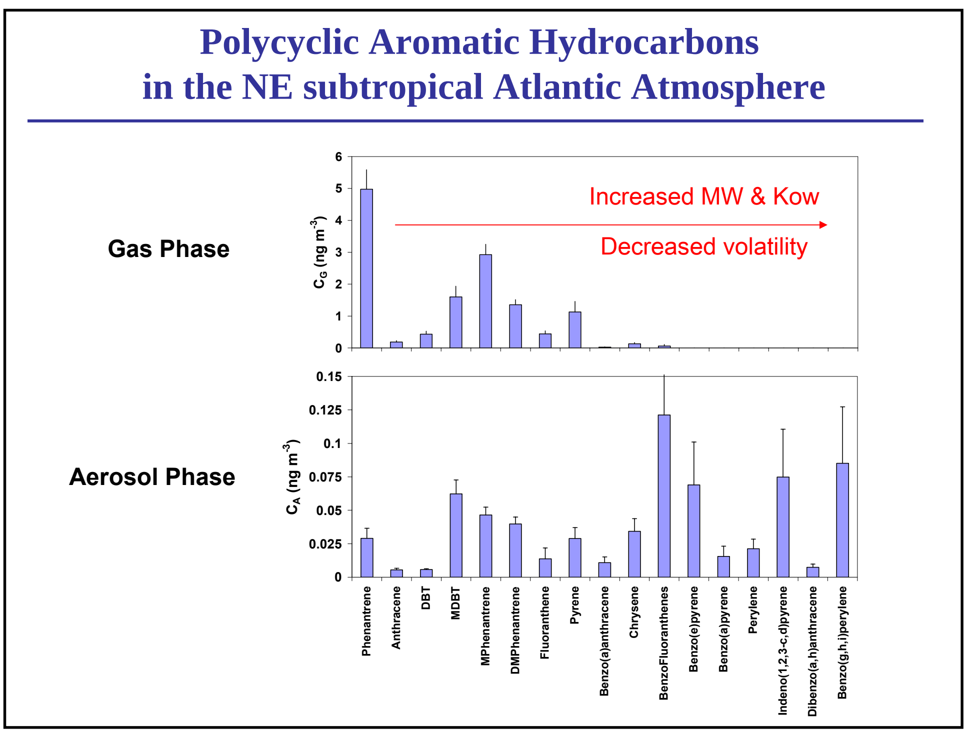


Persistent Organic Pollutants (POPs)
Common properties

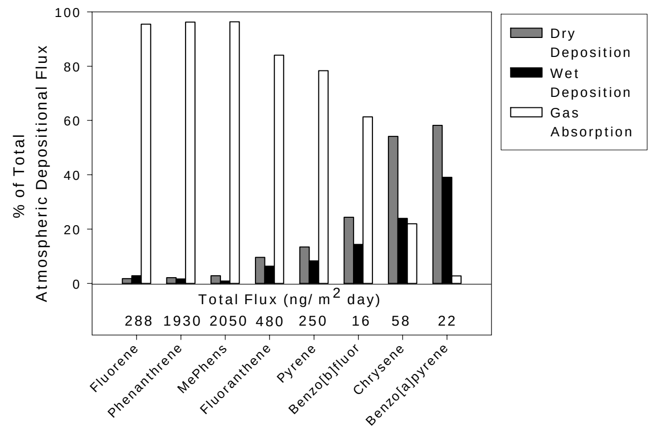
- **Semivolatile (Pv < 1000 Pa)**
  - Long-range transport and distribution through the atmosphere and water bodies
- Resistant to chemical ... biological degradation
  - Persistent
- High bioacumul... otential
  - They are foun... he higher levels of the fo...
- Toxic to humans a...
  - Nervous system dam... disruption, diseases of the immune system, reproductive and developmental disorders, cancer,…

Atmospheric processes play a major role in their transport and fate


ATMOSPHERIC DEPOSITIONAL PROCESSES
WATER DROPLETS
gaseous contaminants
VOLATILIZATION
AEROSOLS
contaminants associated with particles
WASHOUT OF PARTICLES
WASHOUT OF GASES
ABSORPTION OF GASES
DRY DEPOSITION OF PARTICLES
Rainy regions
Main process
Apolar comp. (e.g., PAHs)

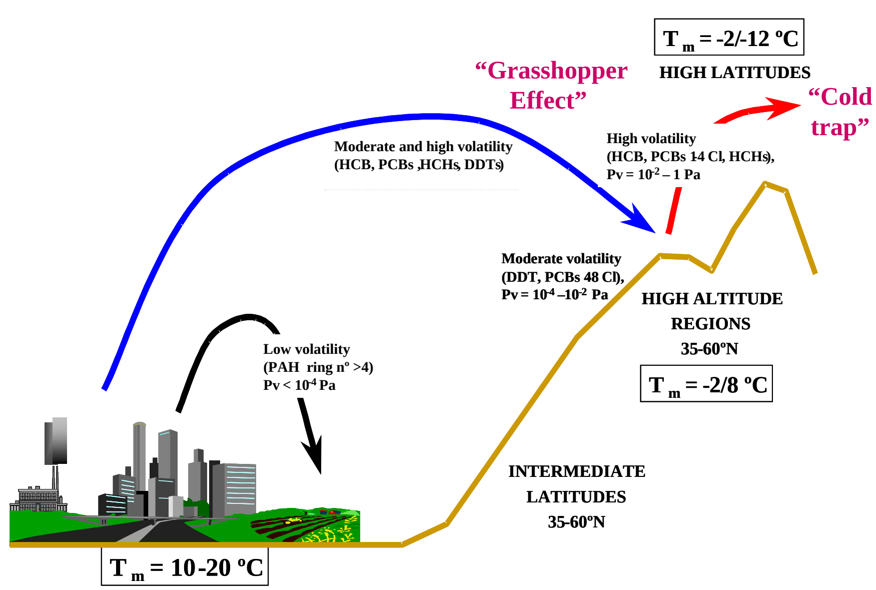

Polycyclic Aromatic Hydrocarbons
in the NE subtropical Atlantic Atmosphere
Gas Phase
Aerosol Phase
C_G (ng m^-3)
C_A (ng m^-3)
Increased MW & Kow
Decreased volatility
0
1
2
3
4
5
6
0.025
0.05
0.075
0.1
0.125
0.15
Phenantrene
Anthracene
DBT
MDBT
MPhenantrene
DMPhenantrene
Fluoranthene
Pyrene
Benzo(a)anthracene
Chrysene
BenzoFluoranthenes
Benzo(e)pyrene
Benzo(a)pyrene
Perylene
Indeno(1,2,3-c,d)pyrene
Dibenzo(a,h)anthracene
Benzo(g,h,i)perylene

Relative importance of air-water exchange processes for PAHs



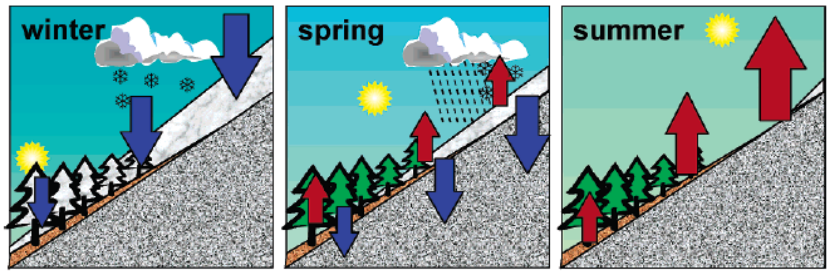
(Gigliotti et al. 2002, Environ. Toxicol. Chem 21: 235)

Goblal distillation effect theory



(Fernández P, Grimalt, JO. *Chimia* **2003**; 57: 514)

Seasonal effect of T



SOCs are deposited with falling snow and onto the snowpack, with higher rates of precipitation and higher SOC concentrations in the snow (colder!) at high elevation. Some volatile SOCs may evaporate from snow during initial metamorphosis (surface area loss)

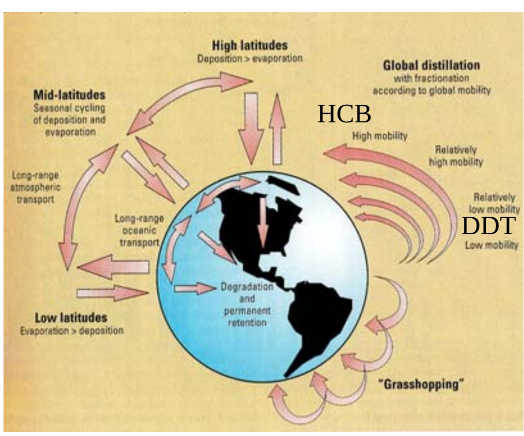
During snow melt, SOCs are released either back to atmosphere or to underlying surface (soils, lakes). Evaporative loss is largest for SOCs which are both relatively volatile and not very water soluble. Evaporative loss from melting snow may be reduced at higher elevations because of lower temperatures.

SOCs evaporate from or accumulate in surface compartments (soil, bedrock, foliage, glacier). Evaporative loss largest for volatile SOCs and for surfaces with low fugacity capacity (bedrock), smallest for less volatile SOCs and surfaces with high fugacity capacity (organic rich soils, forest canopy)

FIGURE 3. Illustration of the processes governing air−surface exchange of semivolatile organic contaminants (SOCs) along a temperate mountain slope in different seasons. The balance of deposition (blue arrows) and revolatilization (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.

Daly G, Wania F. *Environ. Sci. Technol*. **2005**; 39: 385.

Global distillation effect

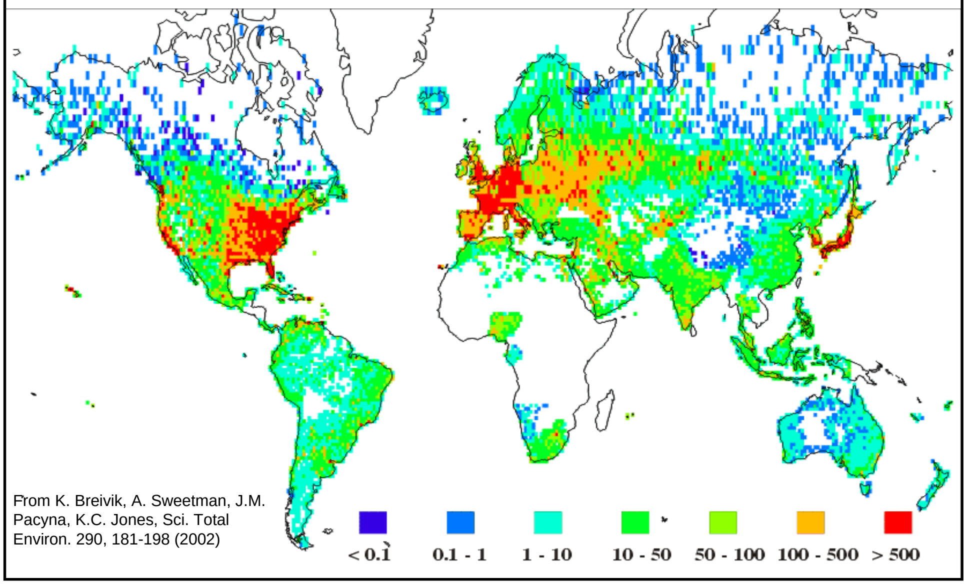


	Pv* (Pa, 25 °C)	**H*** (Pa m³/mol)
α-HCH	3,0 10^{-3}	1,1
HCB	2,4 10^{-3}	139
PCB28	2,6 10^{-2}	33
PCB180	8,1 10^{-5}	102
DDT	3,8 10^{-5}	6
DDE	8,6 10^{-4}	34

*Shiu y Mackay, *J. Phys.Chem.Ref. Data*, **15**, 911-929 (1986)

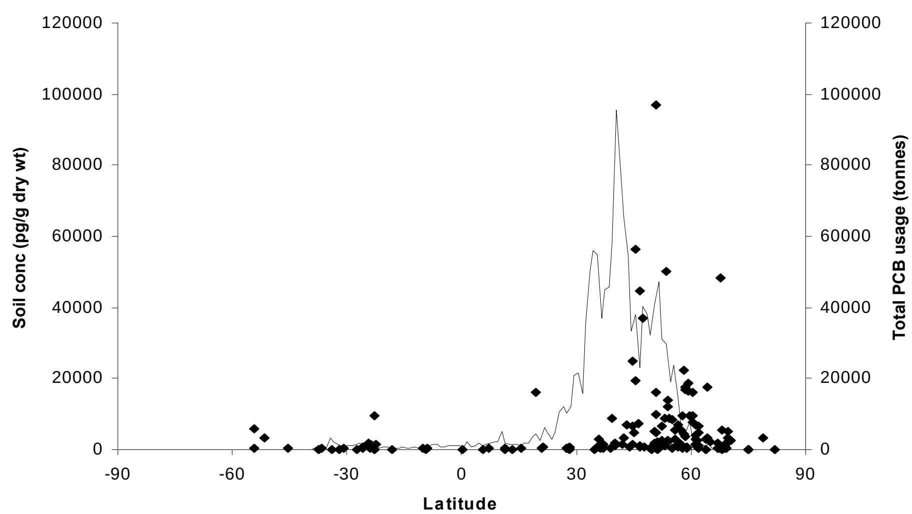
Adapted from Wania and Mackay, *Ambio*, **22**, 10-18 (1993) and *Environ. Sci. Technol.*, **30**, 390A-396A (1996)

Uses of PCBs



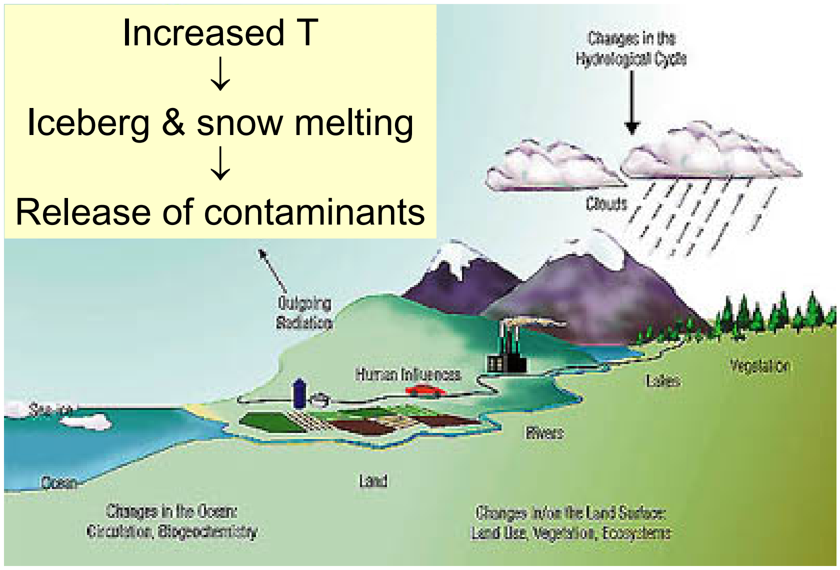
From K. Breivik, A. Sweetman, J.M. Pacyna, K.C. Jones, Sci. Total Environ. 290, 181-198 (2002)

Uses of PCB and latitudinal distribution in soils

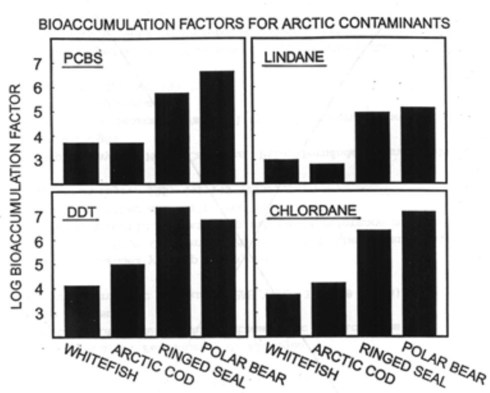


Global climate change

Increased T
↓
Iceberg & snow melting
↓
Release of contaminants



Bioaccumulation of POPs in Arctic Food Chain

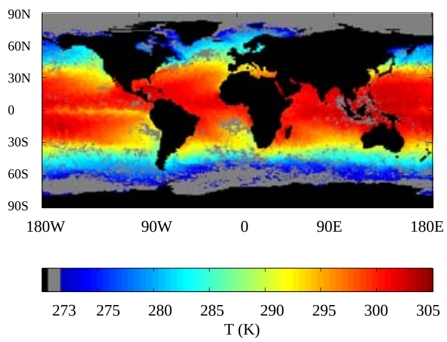


Food chain

Schindler *et al*., *Science of the Total Environment*, **160/161**, 1-17 (1995).

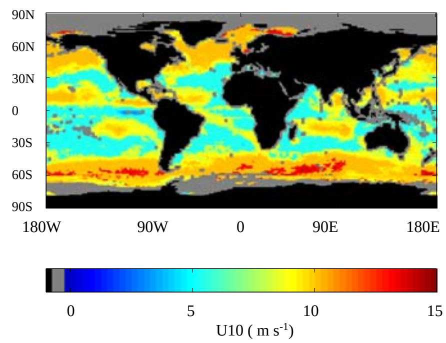
Environmental conditions

Temperature



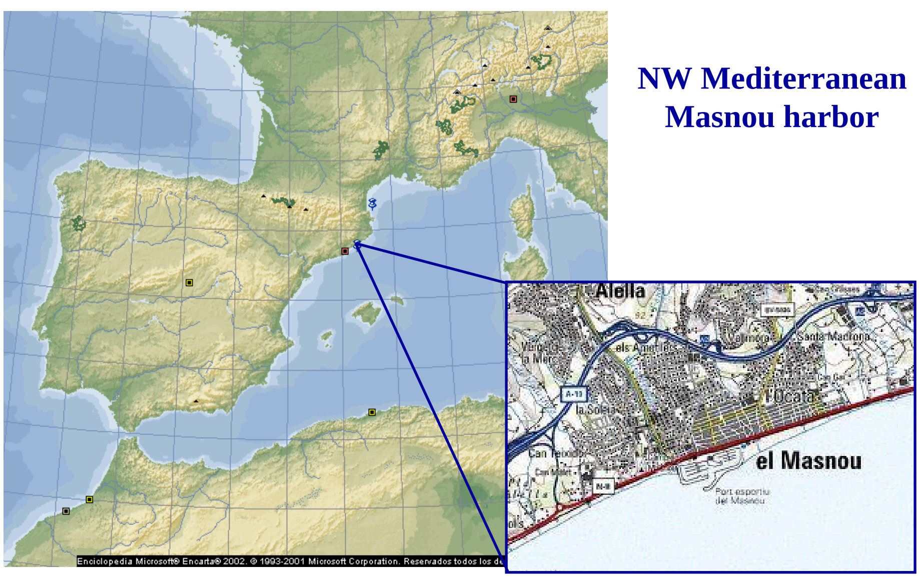
- Henry's constant
- Solubility
- Degradation rate
- etc.

Wind Speed



- Atmospheric deposition
- Air-water exchange
- etc.

Influence of Sea Breeze on Air-Water Exchange

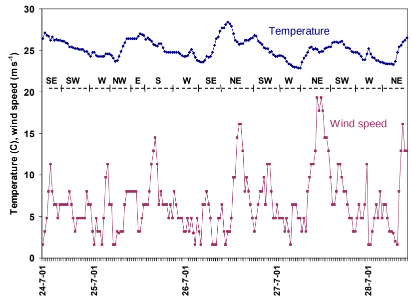


NW Mediterranean Masnou harbor

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

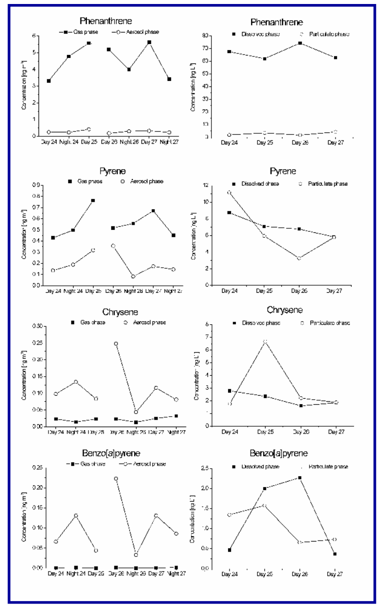
Influence of sea breeze on air-water exchange

PAH occurrence and Met data

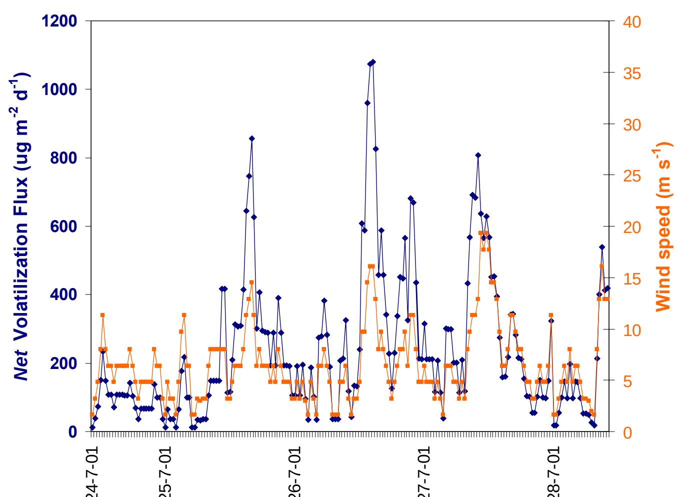


(Pérez et al. ES&T 2003, 37, 3794-3802)

Atmosphere **Water Column**



Influence of sea breeze on air-water exchange of PAHs



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)
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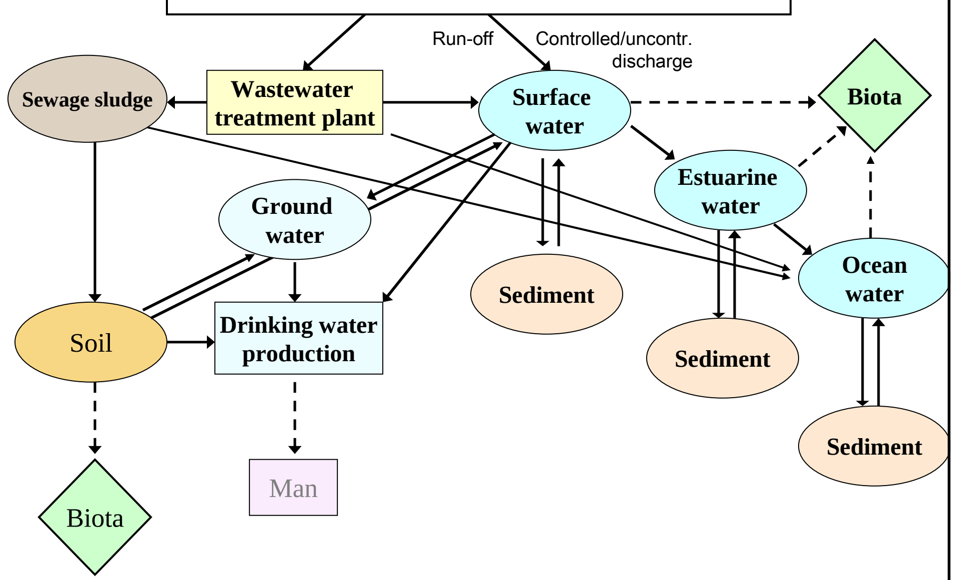
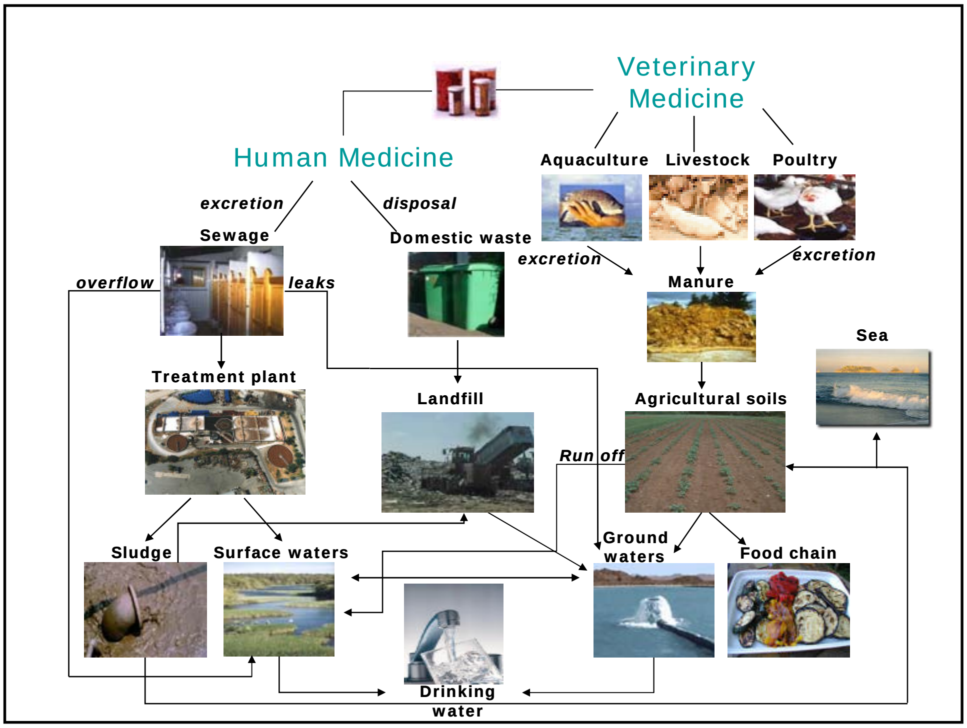
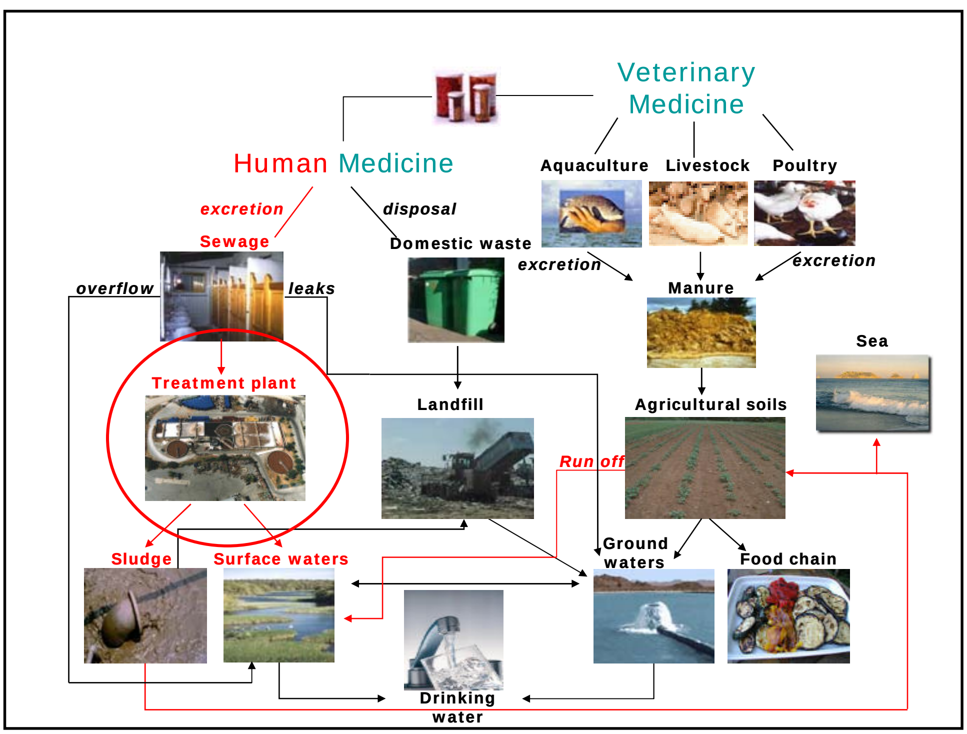
- Lack of data on their occurrence and behaviour

Entering the water cycle




Veterinary Medicine
Human Medicine
Aquaculture
Livestock
Poultry
excretion
disposal
Sewage
Domestic waste
excretion
excretion
overflow
leaks
Manure
Sea
Treatment plant
Landfill
Agricultural soils
Run off
Sludge
Surface waters
Ground waters
Food chain
Drinking water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Elimination in Sewage Treatment Plants (STP)

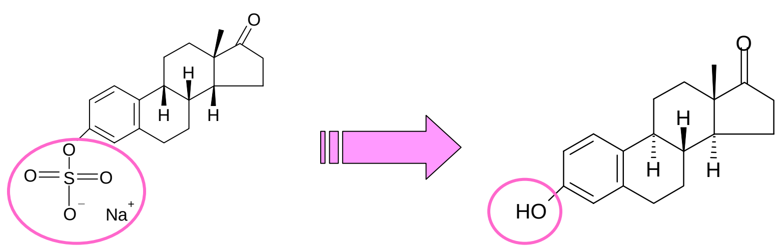
(conventional activated sludge treatment)

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

- **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

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

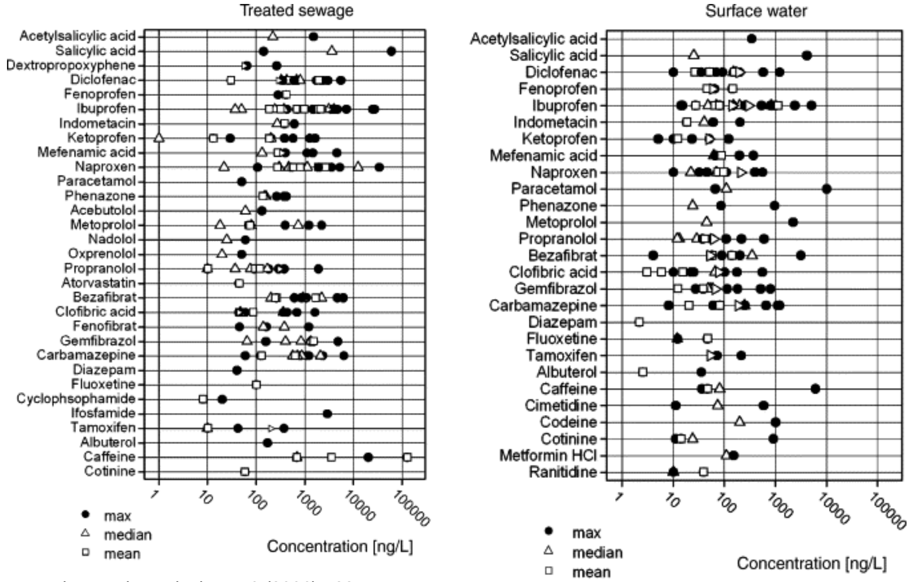


Estrone-sulfate
(↓ activity)

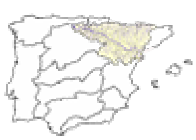
Estrone
(↑ activity)

STP effluents: point-source contamination

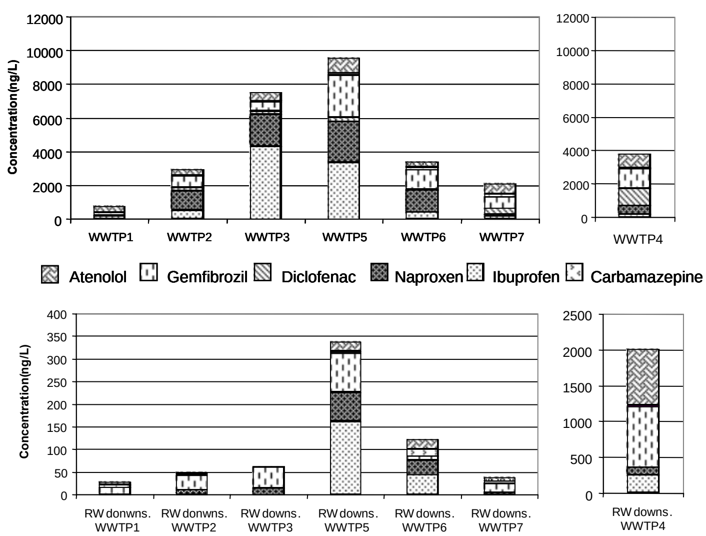
Concentration of pharmaceuticals in treated sewage and surface water



Fent et al. Aquatic Toxicology 76 (2006) 122.

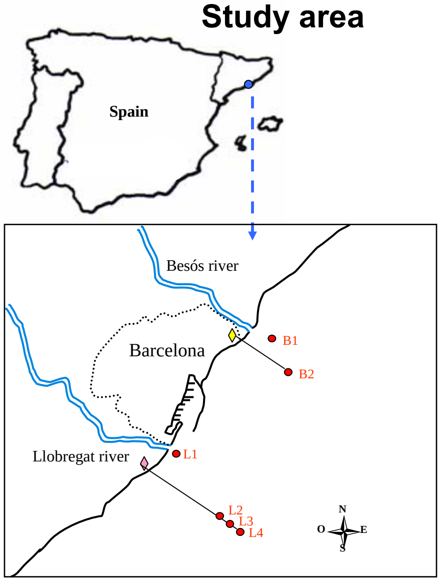


Concentrations (ng/L) of the most ubiquitous anti-inflammatories, lipid regulators, psychiatric drugs and ß-blockers detected in (A) wastewater effluent and (B) river water downstream the WWTP monitored



Steroids in STP and receiving coastal waters in Catalonia

Study area



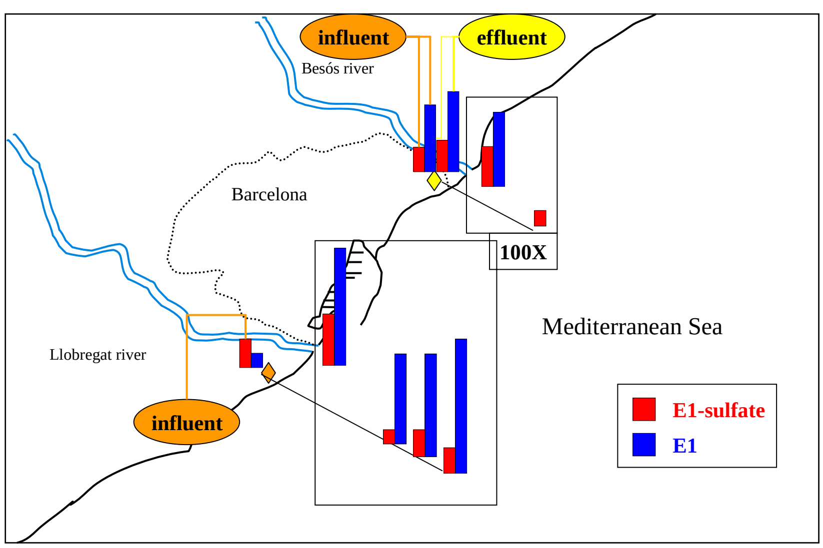
◊ WWTP Besós
◊ WWTP Depurbaix

⇒ 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

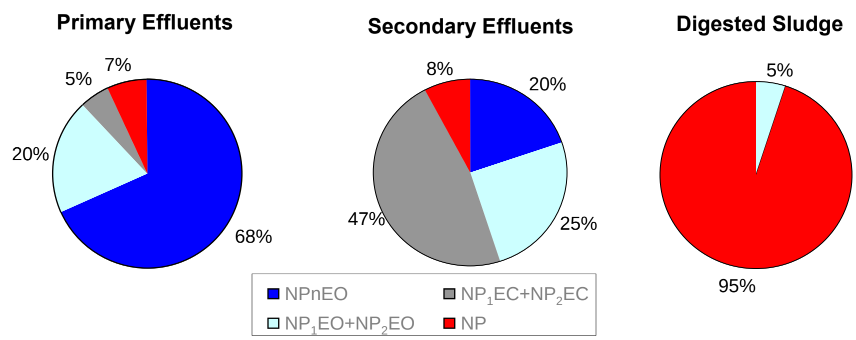
Breakdown during sewage treatment (AST): APEOs case.

(according Ahel, *Wat. Res. 1995*)

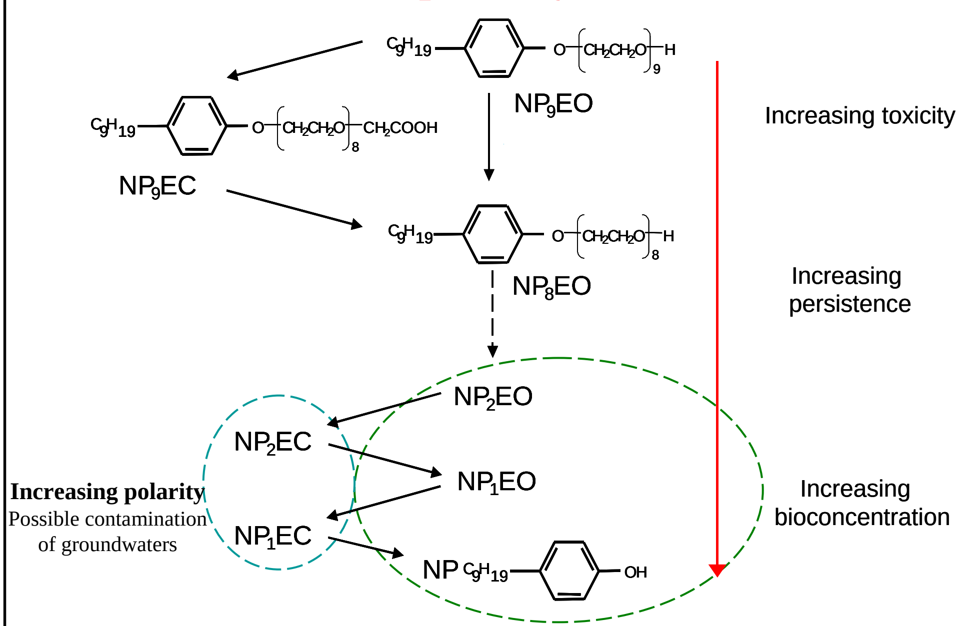
Ultimate biodegradation of NPEOs <40%

40-45% ends up in secondary effluent

20 % in sludge



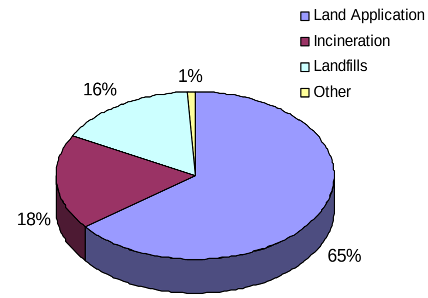
Breakdown pathway of NPEOs



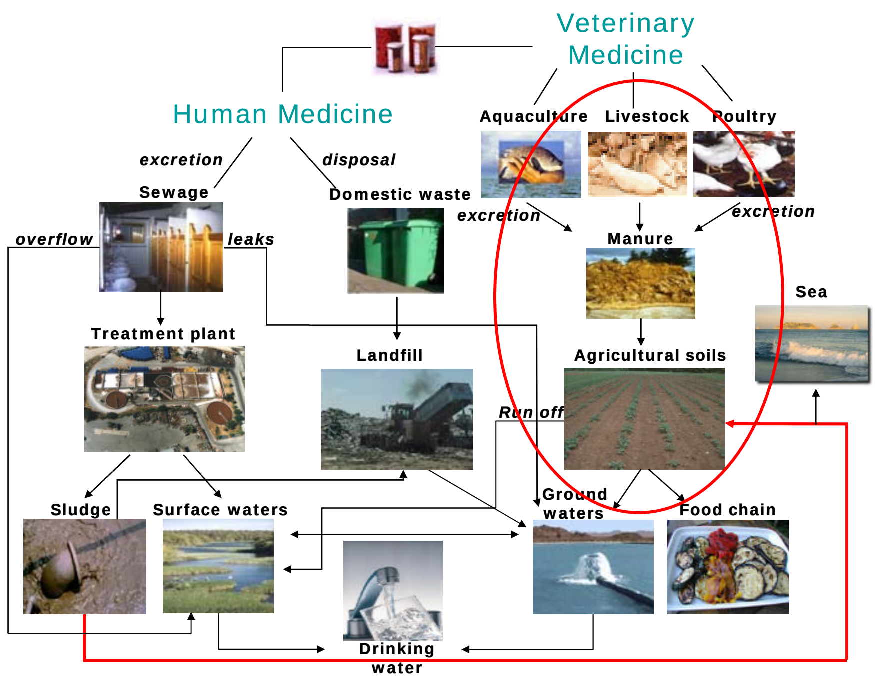
Biosolids

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

Estimated Mass and Use of Biosolids in US



Source: National Research Council of the National Academies



Manure

Soil Fertilization

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

Concentration range of antibiotics in manure.

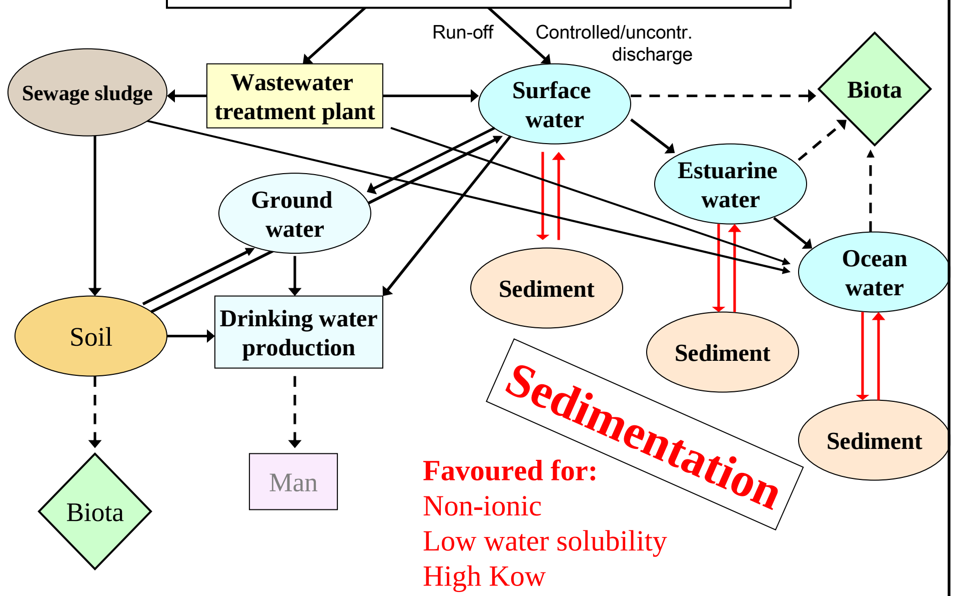
Operation	Tetracyclines (µg/kg)	Sulfonamides (µg/kg)	Macrolides (µg/kg)
Dairy	ND – 5130	ND – 46	ND – 5
Beef	ND – 585	ND – 258	ND – 846
Hog	ND – 23,140	ND – 38	ND – 6682
Sheep	ND – 10,900	ND – 419	ND – 31
Turkey	ND – 309	ND – 70	ND – 4
ND non-detectable			

Source: Ken Carlson, Antibiotics 2004 newsletter

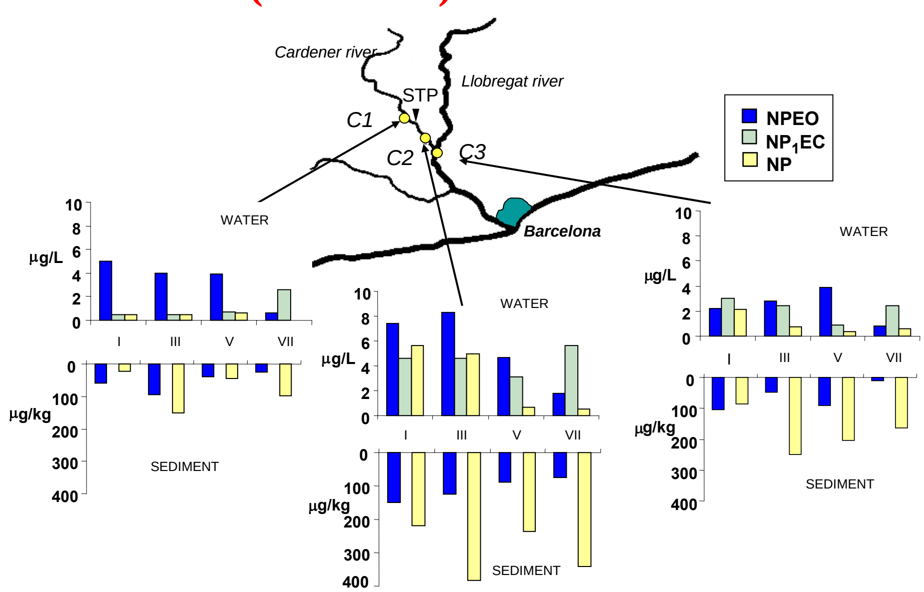
Environmental Effects of Antibiotics

- 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/sluge 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 magnitud below the toxic values for higher trophic levels.

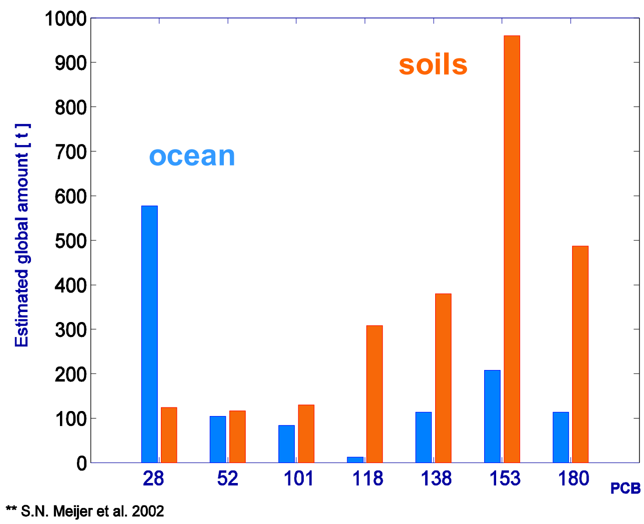
Entering the water cycle



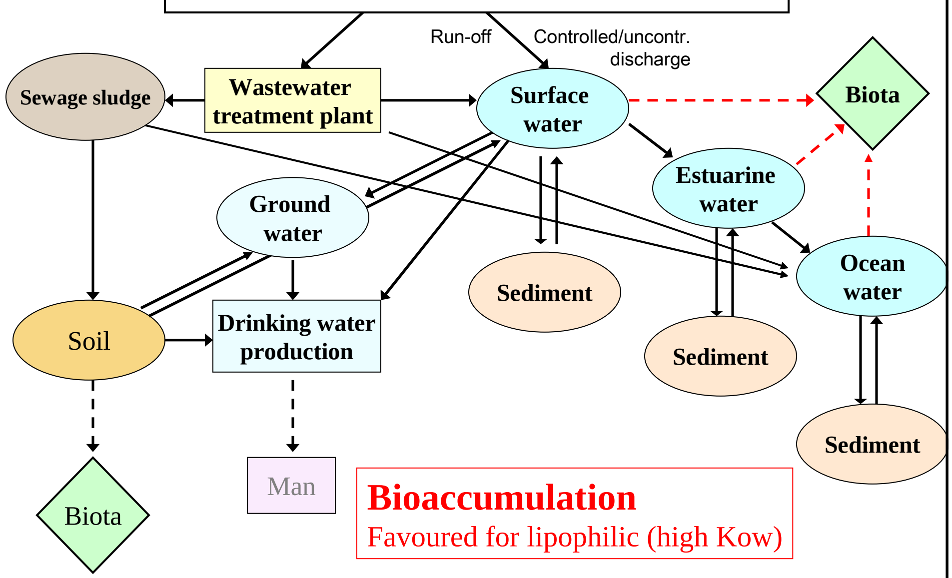
Concentrations of nonylphenolic compounds in river (Cardener) water and sediments



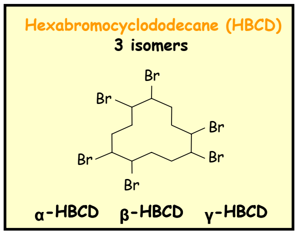
Inventory of PCB in the surface ocean and in soils



Entering the water cycle

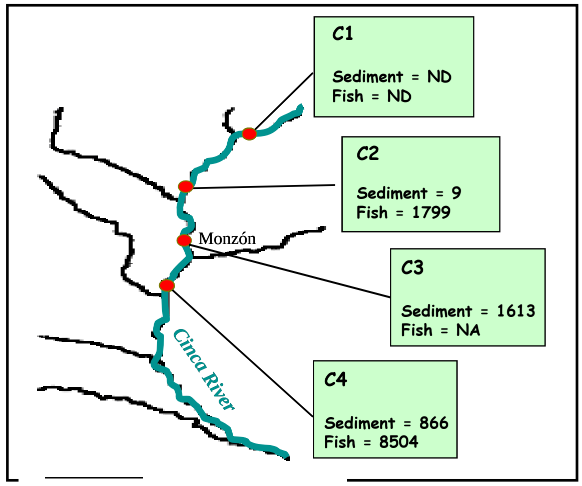


Levels (ng/g) of hexabromocyclododecane (HBCD) in sediment and fish (*C. toxostoma*) - Cinca River (NE Spain)



Applications as flame retardant:

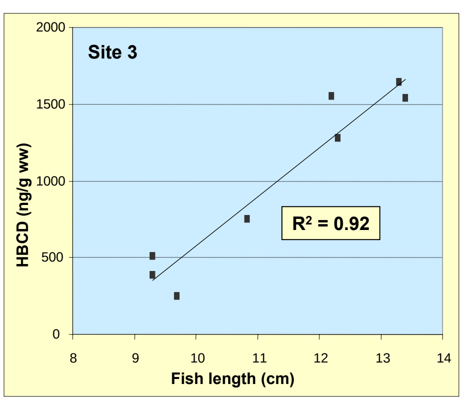
- Electronic circuitry
- Plastics
- Paper
- Wood
- Textiles
- Building materials

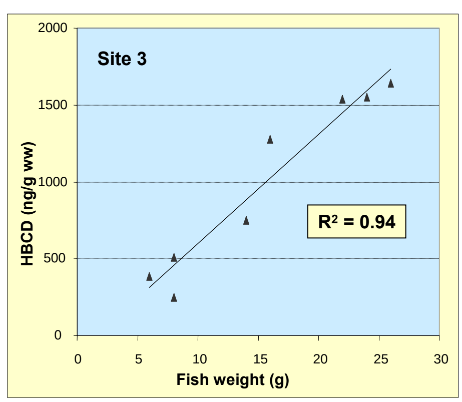


HBCD in fish from the Cinca River – Bioaccumulation

Fish length and weight are directly related to fish age

Length and Weight versus [HBCD]





Different profiles of HBCD isomers in sediment & fish

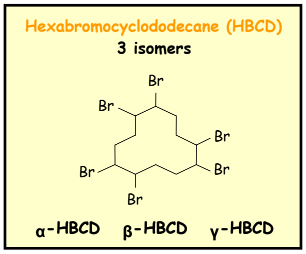
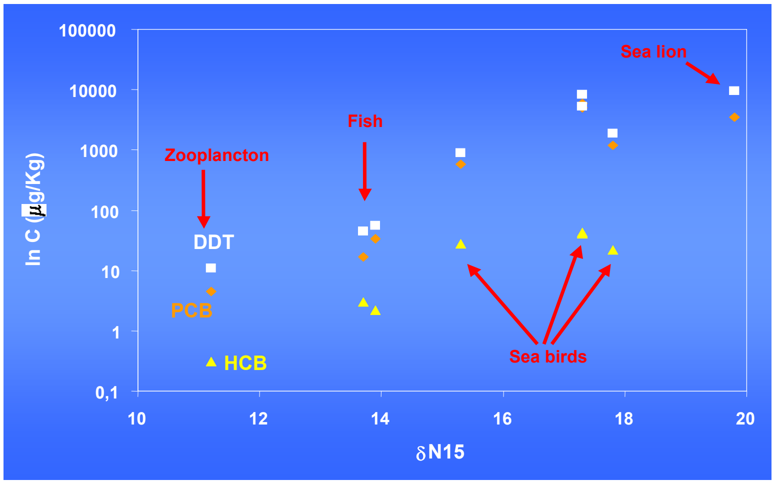


Fig. 2. HBCD diastereomeric distribution in an average technical HBCD mixture compared to different aquatic environmental compartments.

Questions?

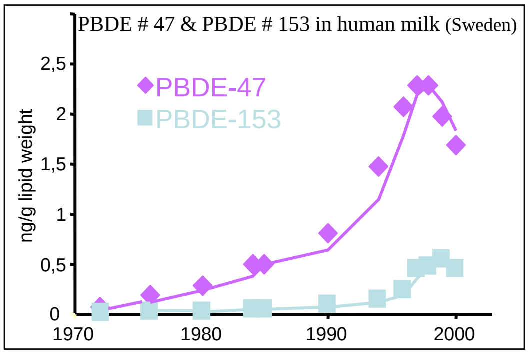
Alpha is more bioavailable than gamma?
Or its bioaccumulation factor is greater?
Or does biotransformation from gamma to alpha occur?

Biomagnification in the food web



(Jarman et al. *Environ. Sci. Technol.* 30, 654-660, 1996)

Polybrominated diphenyl ethers (PBDEs) in human milk



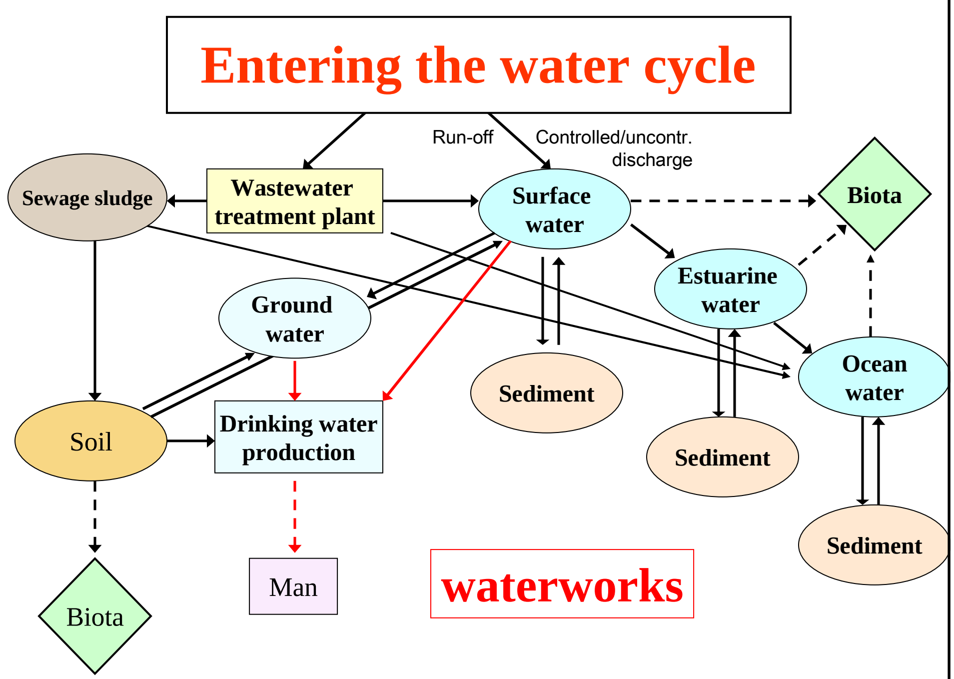
D.Meironyté y col., (1999)
J Toxicol Environ Health 58, 329.

K Noren ycol. (2000)
Chemosphere 40, 1111.

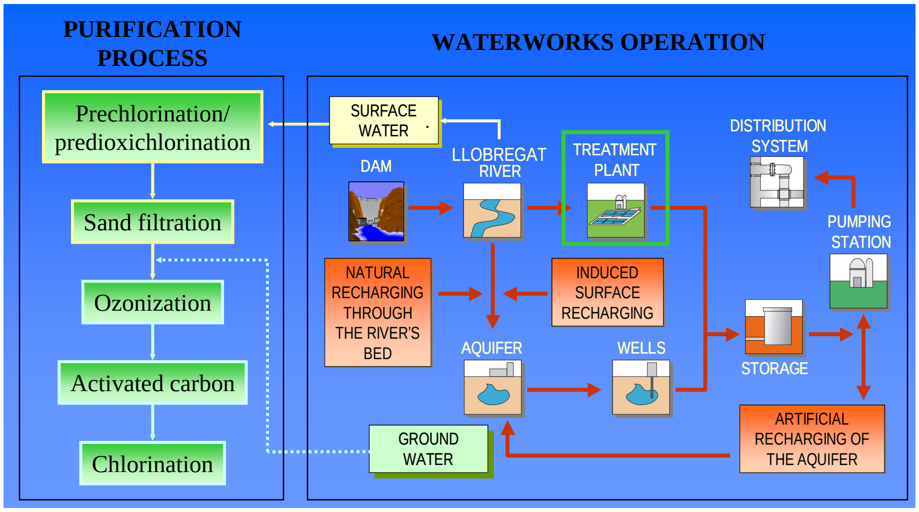
- **Presence in[1,2]:**
  - humans: milk, plasma, serum, fat tissue, fetus blood
  - animals: seafood, fish, birds, marine mammalians
  - air, surface water, soils, sediments, sludge

- **Posible effects:**
  - neurotoxicity
  - endocrine disruption
  - cancer

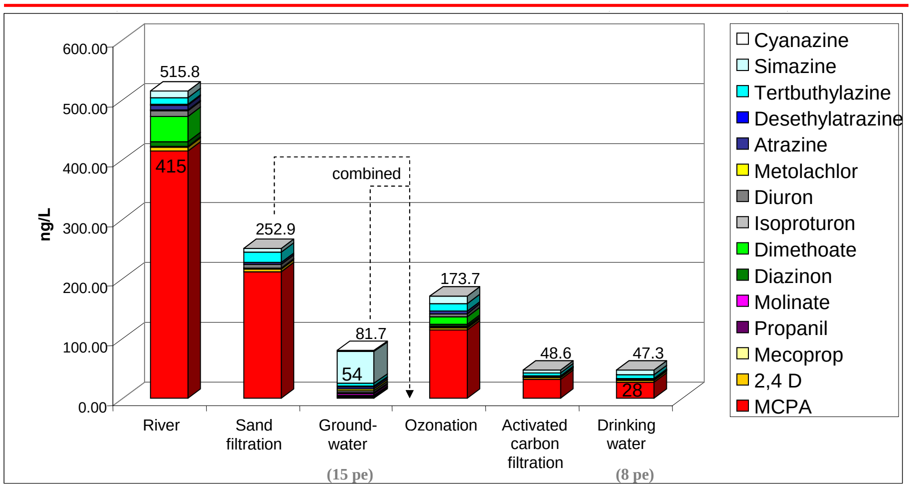
[1]Birnbaum LS, Staskal DF (2004) Environ. Health Perspect. 112, 9; [2]Alaee M (2003) Environ. Monit. Assess. 88, 327.



Sant Joan Despí waterworks (Barcelona)



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



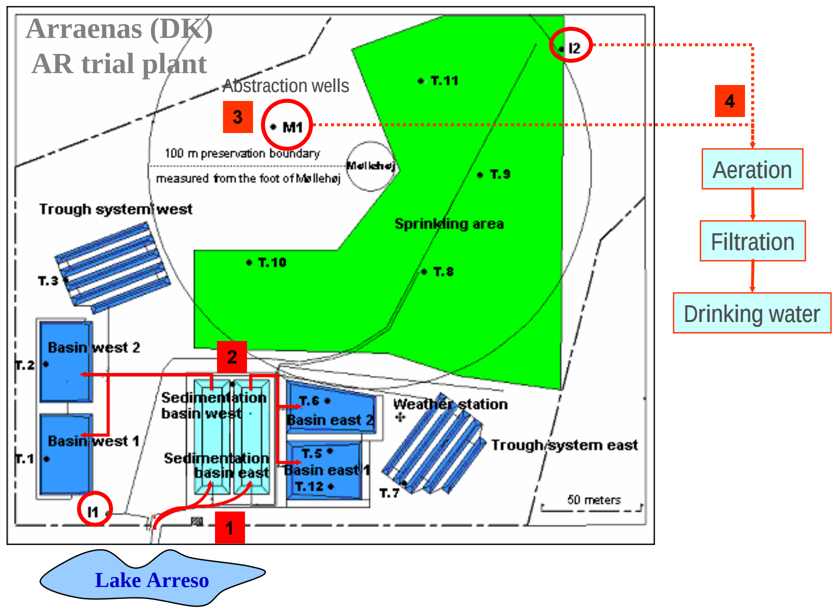
Not detected: chlortoluron, linuron, alachlor and bentazone

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

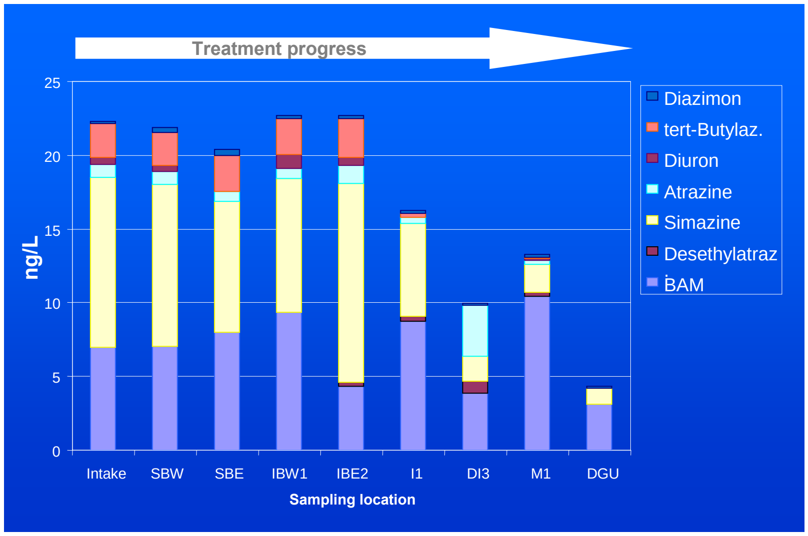


Levels (ng/L) of pesticides in DK samples (2004)

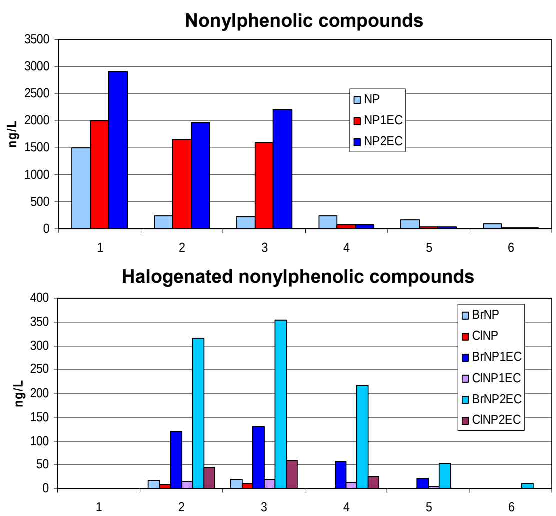
Analyte\Sample	Intake	SBW	SBE	IBW1	IBE2	I1	I3	M1	DGU
Deisopropylatrazine	nd	nd	nd	nd	nd	nd	nd	nd	nd
BAM	6.95	7.03	7.97	9.37	4.31	8.71	3.83	**10.44**	3.11
Desethylatrazine	nd	nd	nd	nd	0.31	0.34	**0.87**	0.25	nd
Dimethoate	nd	nd	nd	nd	nd	nd	nd	nd	nd
Simazine	11.57	11.02	8.93	9.09	**13.49**	6.33	1.68	1.93	1.09
Cyanazine	nd	nd	nd	nd	nd	nd	nd	nd	nd
Chlortoluron	nd	nd	nd	nd	nd	nd	nd	nd	nd
Isoprototuron	nd	nd	nd	nd	nd	nd	nd	nd	nd
Atrazine	0.87	0.82	0.62	0.65	**1.22**	0.41	3.43	0.22	nd
Diuron	0.46	0.45	nd	**0.97**	0.55	nd	nd	0.19	nd
Propanil	nd	nd	nd	nd	nd	nd	nd	nd	nd
tert-Butylazine	2.29	2.25	2.49	2.42	**2.61**	0.3	nd	0.07	nd
Linuron	nd	nd	nd	nd	nd	nd	nd	nd	nd
Molinate	nd	nd	nd	nd	nd	nd	nd	nd	nd
Metalachlor	nd	nd	nd	nd	nd	nd	nd	nd	nd
Alachlor	nd	nd	nd	nd	nd	nd	nd	nd	nd
Diazimon	0.18	0.31	**0.35**	0.23	0.2	0.19	0.15	0.16	0.16

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-dichlorbenzamide)**

Cumulative levels of pesticides in water samples from DK



Formation of halogenated derivatives (SJD WW)



1 – Influent (river water)
2 – Prechlorination
3 – Flocculation/Sand filter
4 – Ozonation
5 – GAC
6 – Chlorination

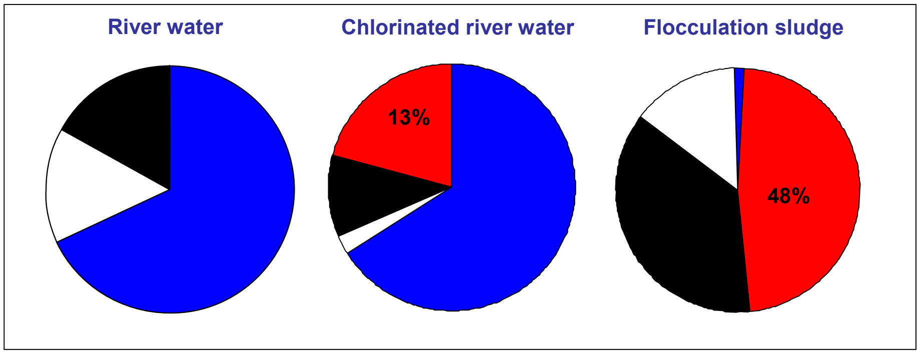
Elimination of total nonylphenolic compounds

Treatment step	Efficiency (%)
Prechlorination	20.4
Flocculation/sand filtration	7.3
Ozonation+ groundwater blending	86.3
GAC	72.7
Chlorination	42.8
TOTAL	97.9

Petrovic M y col. (2003) *Environ. Sci. Technol.* 37, 4442-4448

Average composition of nonylphenolic compounds after chlorination

(calculated on a molar basis)

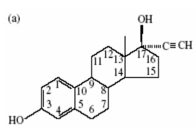


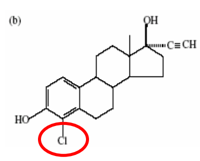
After: Petrovic et al. ES&T, 2003

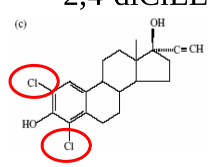
Formation of chlorinated derivatives of phenolic compounds

- Estrogens:

Ethynyl estradiol —(NaClO, 5 min.)→ 4-ClEE + 2,4-diClEE







estrogenic. ~ EE | estrogenic. 10^{-1}x EE

- Phenol

- Bisphenol A

- ...

Chlorinated derivatives: < biodegradation, > estrogenicity } than parent comp.

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

http://www.epa.gov/safewater/mdbp/qrg_st1.pdf

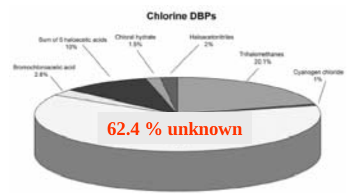
Regulated Contaminants	MCL (mg/L)	MCLG (mg/L)
Total Trihalomethanes (TTHM)	0.080	
Chloroform Bromodichloromethane Dibromochloromethane Bromoform		- zero 0.06 zero
Five Haloacetic Acids (HAA5)	0.060	
Monochloroacetic acid Dichloroacetic acid Trichloroacetic acid Bromoacetic acid Dibromoacetic acid		- zero 0.3 - -
Bromate (plants that use ozone)	0.010	zero
Chlorite (plants that use chlorine dioxide)	1.0	0.8

UE

Directive 98/83/EC (drinking water)

100 μg/L

10 μg/L

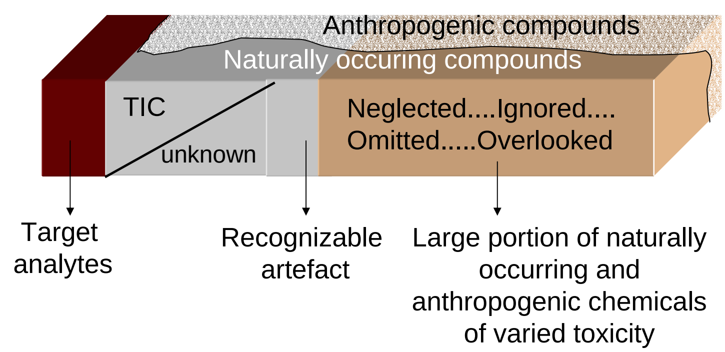


☝ More than 600 DBPs identified (< 50% total DBPs)

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

Richardson S, Simmons JE, Rice AG (2002) Environ. Sci. Technol. 36, 198A-205A.

Chemical analysis output for a typical environmental sample



TIC – tentatively identified compounds

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

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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- the EU (project INNOVA-MED [(INCO-2006-517728**])**

- the Spanish Ministry of Education and Science (project CEMAGUA [CGL2007-64551/HID])