# Legal issues pertaining waste water treatment and reuse

## - EU perspective -

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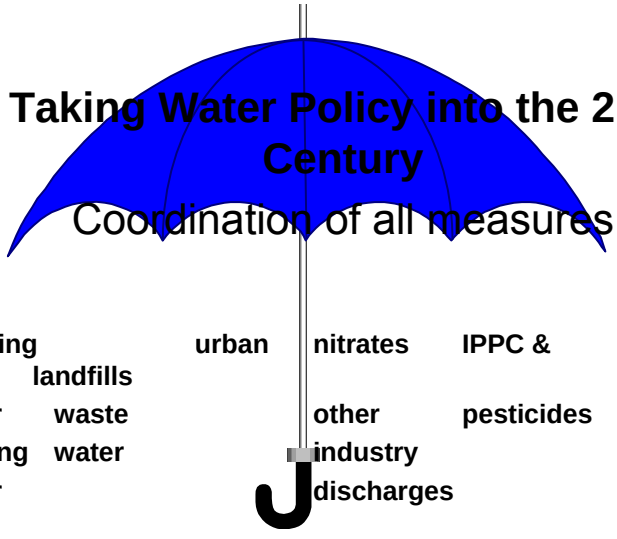
# Water Framework Directive

**Taking Water Policy into the 21st Century**

Coordination of all measures

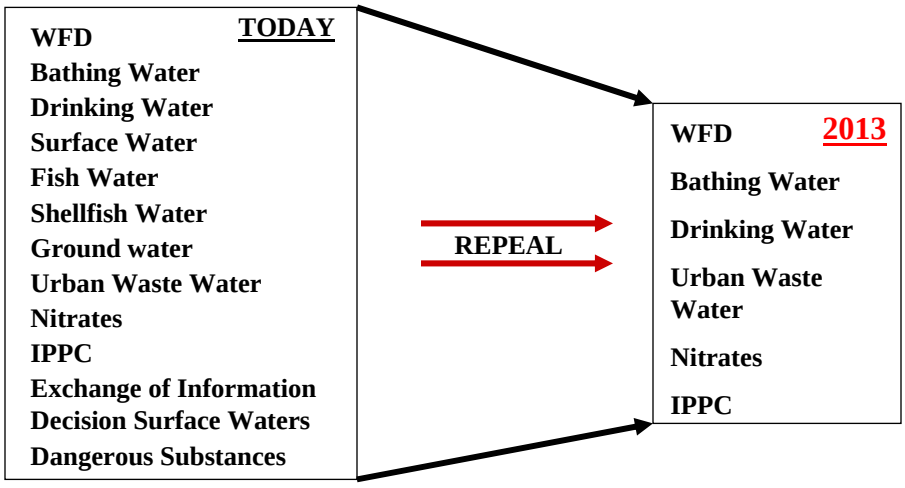


**drinking water**
**bathing water**
**landfills**
**waste water**
**urban**
**nitrates**
**other industry discharges**
**IPPC & pesticides**
**biocides**

# Water Framework Directive

- Sustainable water use into the 21st century
- Implement the polluter pays principle
- A coherent structure for water policy

# Evolvement of Water Legislation



## Research and Water
EU Water Framework Directive
GLOBAL VISIONS, LOCAL ACTIONS

- **Expands the scope of Water Protection to all waters, surface waters and groundwater - INTEGRATED APPROACHES**
- **Achieving good status for all waters by a set deadline**
- **Water management based on River basin**
- **"Combined approach of Emission limit" values and Quality standards, including common ecological objectives**
- **Monitoring and data collection**

# Common ecological objectives

Good status of all waters within 15 years

**Surface water**
- Chemical
- Ecological
- Phase out hazardous substances

**Groundwater**
- Chemical
- Quantitative
- Trend reversal

# What is Good Status?

## Surface water bodies

- Defined by poorer of chemical and ecological status.
- Ecological Status includes the elements of:
  - *morphology,*
  - *water quality,*
  - *biology,*
  - *hydrology.*
- Status is measured relative to undisturbed reference conditions.
  - *Defined by monitoring of pristine sites, modelling or expert judgement*

## *Groundwater*

- Objectives apply to "Groundwater Bodies" not groundwater per-se.
- Define by poorer of chemical & quantitative status but in essence:
  - *Abstraction must not exceed long term recharge.*
  - *No significant damage to terrestrial ecosystems (wetlands) from abstraction or pollution.*
  - *Associated surface waters do not deteriorate and achieve good status.*
  - *No saline intrusion*

# Delivering "Good Status"

## The Programme of Measures

- Split into compulsory *"Basic Measures"* and additional *"Further Measures"*.
- Basic Measures include:
  - **Implementation of existing European legislation.**
  - **Protection and improvement of water bodies used for drinking water.**
  - **Controls on abstraction & impoundment of surface and groundwaters.**
  - **Controls on point sources of pollution including prior authorisation.**
  - **Measures to prevent or control diffuse pollution.**
  - **Controls on aquifer recharge for geothermal, engineering or water resource purposes.**
  - **Measures to eliminate discharges of priority substances and progressively reduce other pollutants.**
  - **Measures to reduce accidental pollution.**

# Staged implementation schedule

## Obligations for Member States

| | |
|---|---|
| **Transposition into national legislation** | **Dec 2003** |
| **Analysis of impacts and pressures** | **Dec 2004** |
| **Economic analysis of water use** | **Dec 2004** |
| **Monitoring programmes operational** | **Dec 2006** |
| **Latest date for starting public participation** | **Dec 2006** |
| **River basin management plans** | **Dec 2009** |

## Obligations for the Commission

| | |
|---|---|
| **Daughter Directive Groundwater (Proposal)** | **Dec 2002** |
| **List of Priority Substances** | **✓ adopted** |
| **Daughter Directive emission controls - Proposal** | **Dec 2003** |
| **Daughter Directive quality standards - Proposal** | **Dec 2003** |
| **Inter-calibration of quality classification** | **Dec 2004** |

# Water Framework Directive

## List of priority substances in the field of water policy

| Priority hazardous substances | Priority hazardous substances under review | Priority substances not proposed as priority hazardous substances |
|---|---|---|
| **Brominated diphenyl ethers (penta)**<br>**Cadmium**<br>**Mercury**<br>**$C_{10}$-$C_{13}$ Chloroalkanes**<br>**Hexachlorobenzene**<br>**Hexachlorocyclohexane**<br>**Tributhyltin**<br>**Hexachlorobutadiene**<br>**Nonylphenols**<br>**PAH**<br>**Pentachlorobenzene** | **Anthracene**<br>**Atrazine**<br>**Chlorpyrifos**<br>**Di(2-ethtlhexyl)phthalate (DEHP)**<br>**Endosulfan**<br>**Lead**<br>**Naphthalene**<br>**Octylphenols**<br>**Pentachlorophenol**<br>**Trichlorobenzenes**<br>**Trifuralin** | **Alachlor**<br>**Benzene**<br>**Chlorfenvinphos**<br>**Dichloromethane**<br>**1,2-Dichloroethane**<br>**Diuron**<br>**Isoproturon**<br>**Nickel**<br>**Simazine**<br>**Trichloromethane** |
| Subject to phase-our or under consideration for phase-out (or severe restriction) on the international level | Shows properties similar to those identifed as "Priority Hazardous" (group 1)<br>Subject to a review for identification as possible priority hazardous substances by 31 December 2003. | Do not fulfil the criteria for being "toxic, persistent and liable to bio accumulate"<br>Classified as dangerous<br>Subject to emission controls and quality standards |

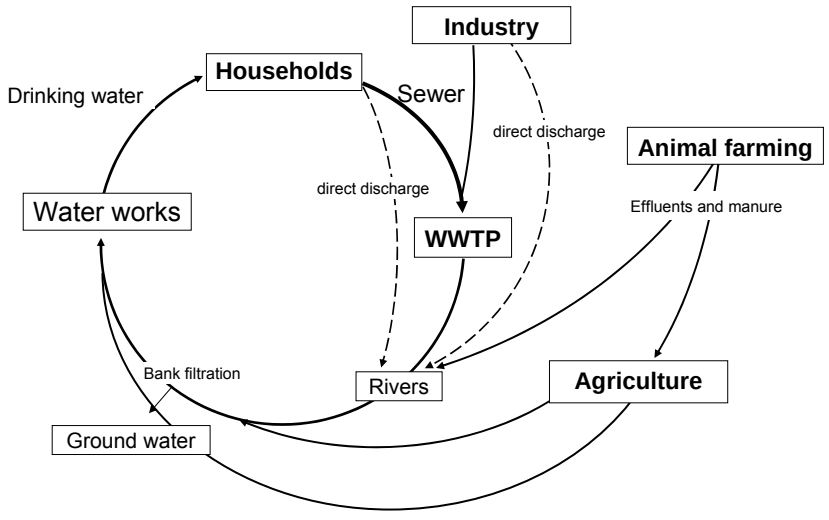
# Water Framework Directive
# Precautionary Principle

**Dynamic list – update every 4 years (2004)**

**Upcoming Priorities – Emerging Contaminants**
**(Future Candidates for Monitoring)**

- PPCPs (Pharmaceuticals and Personal Care Products)
  Diclofenac, Ibuprofen, Clofibric acid, Carbamezapim, Triclosan
- Veterinary pharmaceuticals for animal feeding (antibiotics)
- MTBE and related compounds
- Surfactants and their recalcitrant metabolites (LAS and SPC)
- Endocrine disrupting compounds (EDC)

# Important issue: Wastewater treatment and reuse



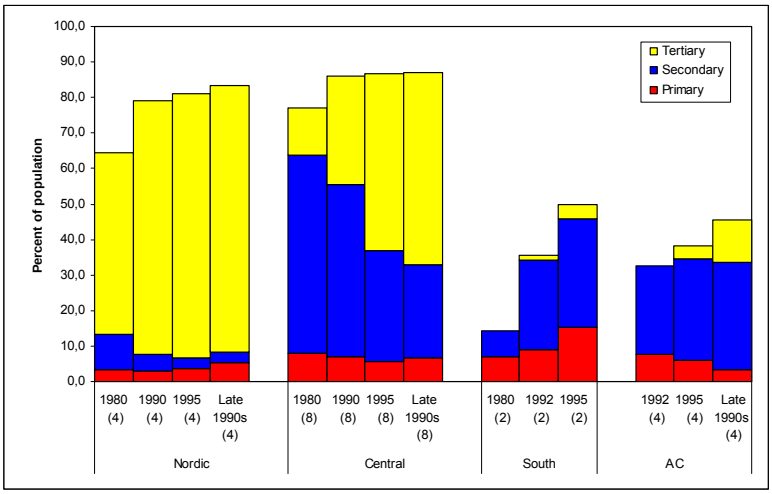
# EU Directives relevant to Waste Water

- **Directive on pollution caused by Dangerous Substances discharged into the aquatic environment (2006/11/CE )**
- **Directives daughters: 86/280/EEC, 88/347/EEC and 90/415/EEC**
  - **Quality objectives are fixed, sampling points, frequency**
  - **Emission limits and Quality Objectives for certain substances like HCB, Chloroform, carbon tetrachloride, dichloroethane, trichloroethylenes,**
  - **Emission at 1-2 ppm, chloroform and Quality objectives at 10 ppb**
  - **Spain, RD 995/2000 fixed 1 ppb for atrazine, metolachlor, simazine and terbuthylazine and 20-30 ppb for chlorobenzene, dichlorobenzene**
- **Directive on Urban Waste Water Treatment (91/271/EEC) to reduce pollution by municipal waste (relevant to endocrines)**

# Directive 91/271/EEC ( 98/15/EEC )
# Urban Waste Water Treatment

- **Till year 2000, urban centres >15.000 inhabitants and till year 2005 urban centres >2000 inhabitants should have treatment of wastewaters**
- **Construction of 40.000 treatment plants in EU (till year 2005)**
- **N & West Europe, 80-90 % of wastewater treated, S & East Europe, only 40-50 %**
- **More treatment plants ⇒ higher production of sludge (increase from 5.5 to 8.3 millions tons from1992 to 2005)**
- **It is necessary to increase the capacity of collection systems and treatment 22% and 69%, respectively (from 1992 to 2005)**
- **37 cities of more than 150.000 inhabitants do not have treatment of wastewaters (Brighton, Portsmouth, Brussels, Milan, Taranto, Coruña, Cadiz, Oporto, Costa Estoril)**

# Treatment of wastewaters in Europe

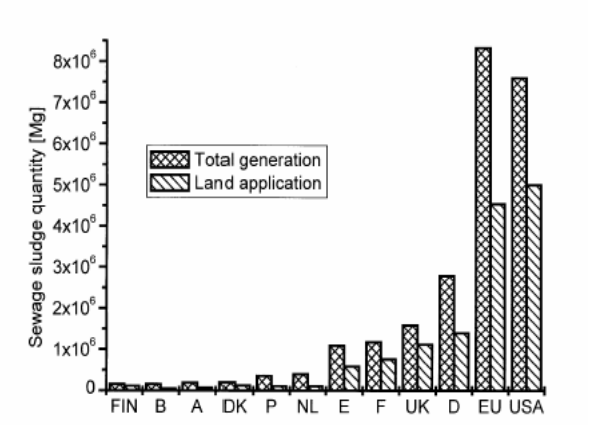


# The sludge problem
# Policy in the European Union: Fact and Figures

- Production of sewage sludge in European Union: 8 million tons/year
- **Increasing amounts** of sludge due to obligation to subject sewage to biological treatment prior to discharge (Directive 91/271/EEC)
- Aim to **enhance agricultural use** of sewage sludge (favorable properties as soil conditioner and fertilizer)
- **Agricultural application** regulated in terms of sludge quality, loading rate and crop type (Directive 86/278/EEC)
- Draft Directive (2000) setting **cut-off limits** for sludge contaminants: NP/NPEO, phthalates, PAH, PCB and PCDD/F

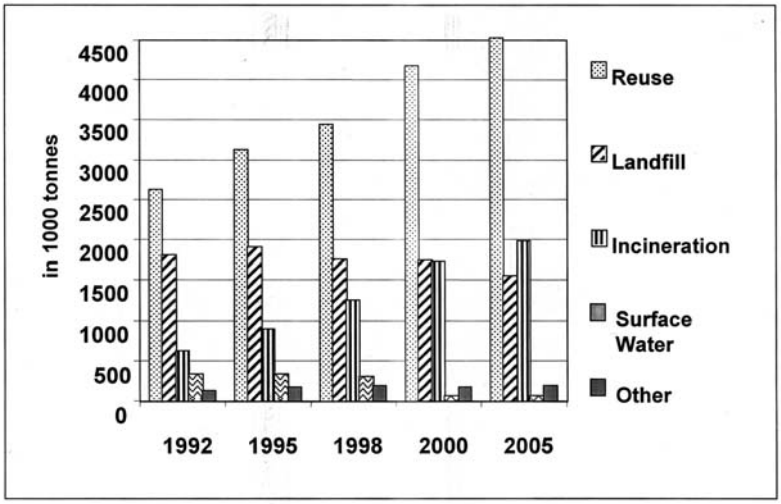
# Sludge production and utilization

**Expected sewage sludge production and utilization rates of EU member states compared to respective data of the USA in the year 2005**

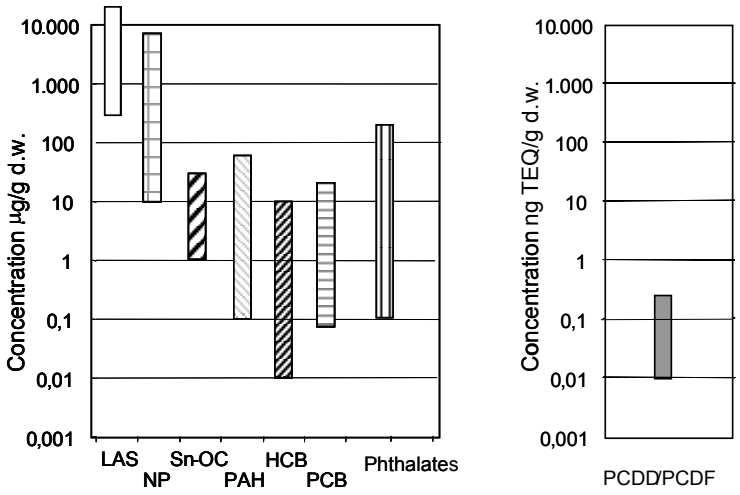



Source: Düring and Gäth, J. Plant Nutr. Soil. Sci (2002) 165, 544

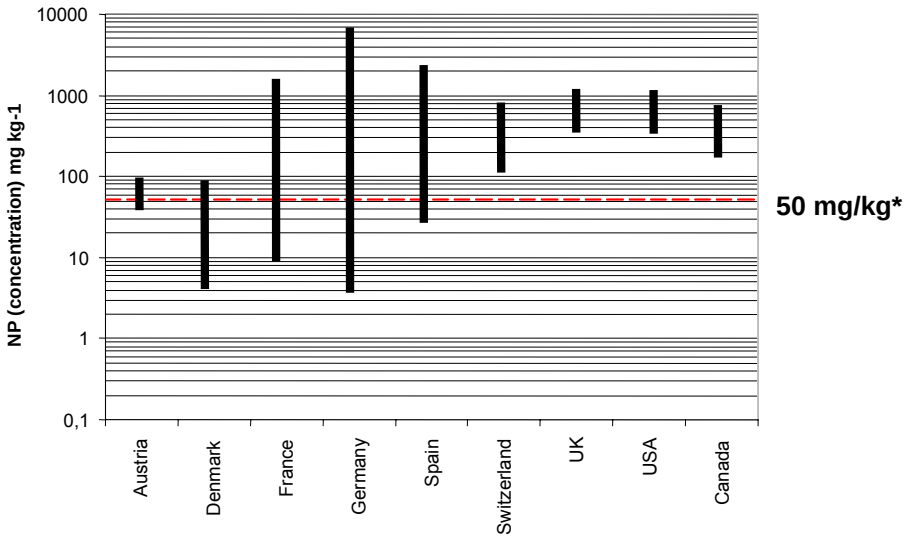
## Sludge destination
## (sea disposal prohibited in 1998)




## Levels of organic contaminants in sludge



# Concentrations of NP in sewage sludge

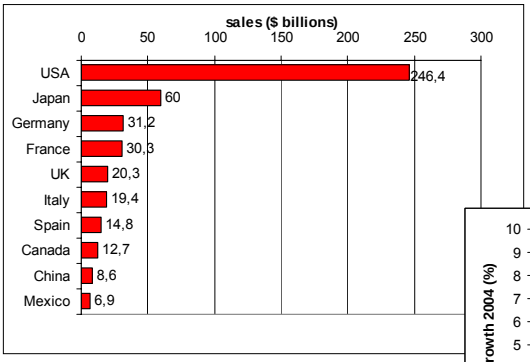



* Anex IV of the Working Document on Sludge, 3rd Draft, ENV E3/LM, 27 April 2000

# Case study

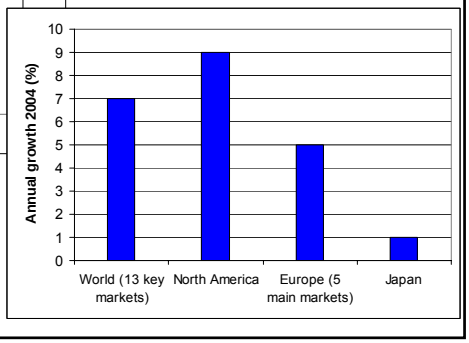
## Pharmaceuticals in wastewaters

# Usage/Consumption of pharmaceuticals




**Top ten markets (2005)**

**Annual growth (2004)**




Source: IMS Health

## Characteristics of Pharmaceuticals

- Pharmaceuticals are often large, complex, ionic and hydrophilic compounds; these properties influence their environmental fate.
- These characteristics are not typical of most non-pharmaceutical chemicals evaluated for environmental fate and effects.
- Most pharmaceuticals enter the environment daily through patient use.
- Sources are geographically diffuse and may be influenced by regional use patterns.
- Pharmaceuticals in the environment may be parent, metabolites or conjugates.
- Pharmaceuticals vary in their potency; in general, highly potent compounds will be used at lower volumes resulting in lower environmental concentrations.
- Some more potent compounds may be of environmental concern at lower concentrations.
- Designed to be biologically active

**Urinary excretion rates** of unchanged active ingredient for selected pharmaceuticals.

| Drug | Therapeutic class | Parent compound excreted (%) |
|---|---|---|
| Ibuprofen | Painkiller | 10 |
| Paracetamol | Painkiller | 4 |
| Amoxycillin | Antibacterial | 60 |
| Erythromycin | Antibacterial | 25 |
| Sulfamethoxazole | Antibacterial | 15 |
| Atenolol | β -Blocker | 90 |
| Metoprolol | β -Blocker | 10 |
| Carbamazepine | Antiepileptic | 3 |
| Felbamate | Antiepileptic | 40–50 |
| Cetirizine | Antihistamine | 50 |
| Bezafibrate | Lipid regulator | 50 |

- **Portions of most ingested drugs are excreted in varying unmetabolized amounts (and undissolved states, primarily because of protection by excipients) primarily via the urine and feces.**
- **Other portions sometimes yield metabolites that are still bioactive. Still other portions are excreted as conjugates.**

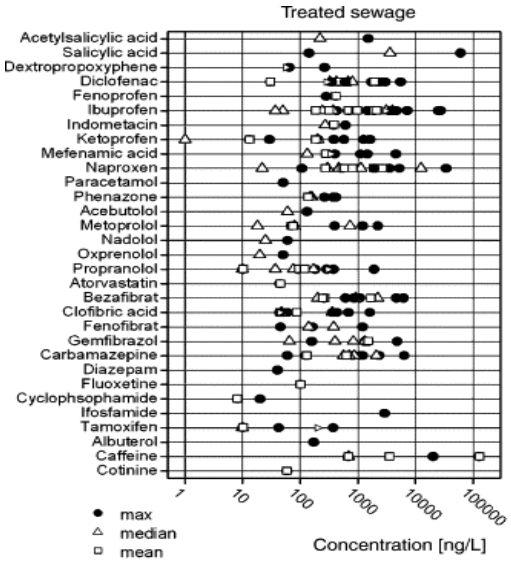
Jonathan P. Bound and Nikolaos Voulvoulis , Environ Health Perspect. 2005 December; 113(12): 1705–1711

# Removal in Sewage Treatment Plants (STP)

| Compound | Removal |
|---|---|
| Carbamezapine (anti-epileptic drug)<br>Atenolol, Metoprolol (β-blockers)<br>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%<br>Note: hydroxy and carboxy metabolites found in effluents) |

- In order to understand the process taking place in the WWTP and to increase the knowledge on biodegradation of contaminants in WWTP, **biodegradation studies of pharmaceuticals under laboratory controlled conditions** simulating WWTPs should be conducted.
- Free excreted drugs and derivatives can escape degradation in municipal sewage treatment facilities (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.**
- Implementation of an **improved technology** – MBR, AOP

## Concentrations of pharmaceutical residues in treated wastewater (secondary effluents)

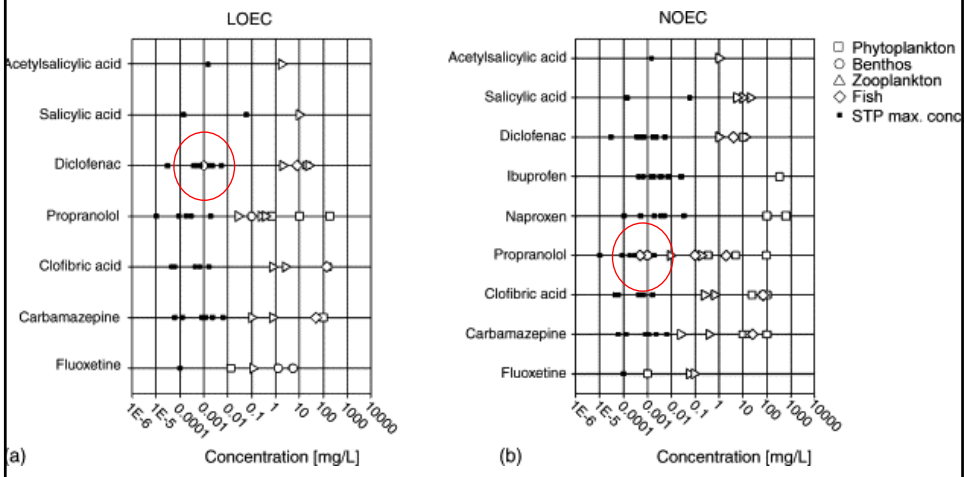



Fent et al. Aquatic Toxicology 76 (2006) 122.

## Selected pharmaceutical groups and their **environmental risk indicators**.

| Drug | Examples | Risk indicator |
|---|---|---|
| Painkillers | NSAIDS (e.g., ibuprofen), other analgesics (e.g., acetaminophen) | Very high prescription and OTC volumes; detected in the environment |
| Antibiotics | Penicillins, sulfamethoxazole | High volumes; detected in the environment; concerns over toxicity and antibacterial resistance |
| β -Blockers | Propranolol, metoprolol | High volumes; detected in the environment |
| Antiepileptics | Carbamazepine, phenobarbital | High volumes; long-term prescriptions; persistent |
| Lipid regulators | Statins (e.g., atorvastatin), clofibrate | Long-term prescriptions; commonly detected |
| Antidepressants | Fluoxetins, risperidone | Subject of toxicity testing |
| Hormone treatments | Contraceptive pills, 17α - ethinyl estradiol, hormone replacement | Most extensively studied toxicologic properties; widely detected |
| Antihistamines | Loratadine, cetirizine | Commonly held nonprescription medicine |

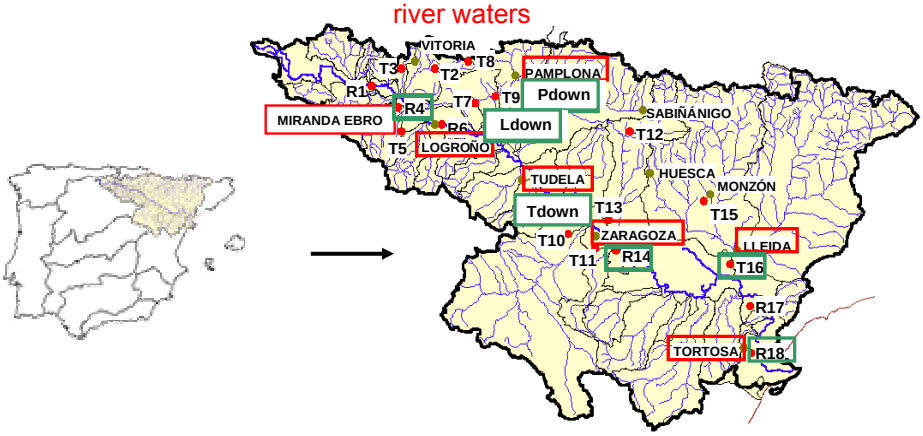
Jonathan P. Bound and Nikolaos Voulvoulis , Environ Health Perspect. 2005 December; 113(12): 1705–1711




Comparison between maximal concentrations of pharmaceuticals in treated wastewater and their chronic toxicity in aquatic organisms. (a) Lowest observed effect concentrations (LOEC); (b) no observed effect concentrations (NOEC) for different aquatic organism, different endpoints and exposure times.

# Example: pharmaceuticals in the Ebro river basin

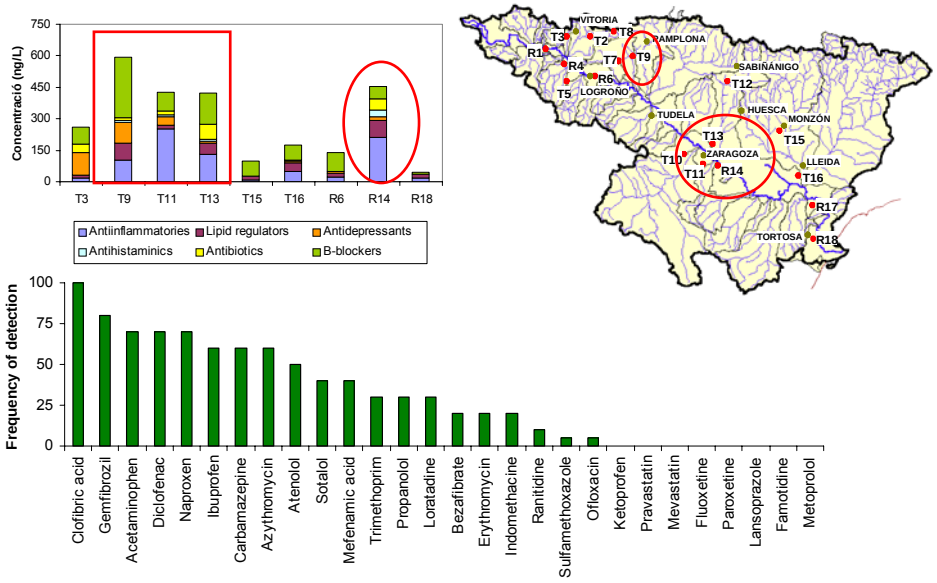
## Contribution of WWTP to the presence of pharmaceuticals in receiving river waters




**WWTP monitored: influent and effluent wastewaters**

**River water downstream the WWTP**

# River Ebro and its tributaries

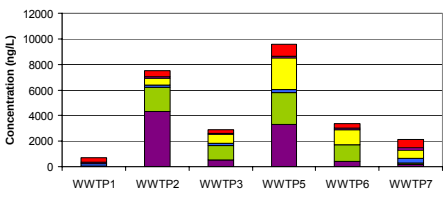


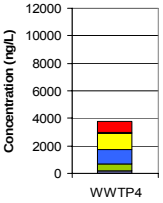




# Contribution of WWTP effluents

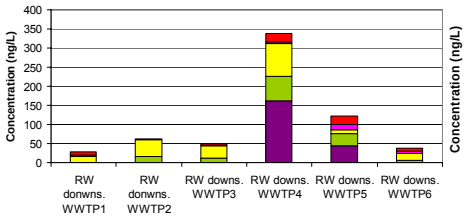
**WWTP effluent**

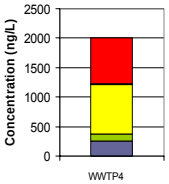



- There is an important **dilution factor**: Levels found in surface waters downstream WWTP are in the low ng/range, whereas in WWTP effluent concentrations of target compounds are between low µg/L-high ng/L range.

**River water downstream WWTP**



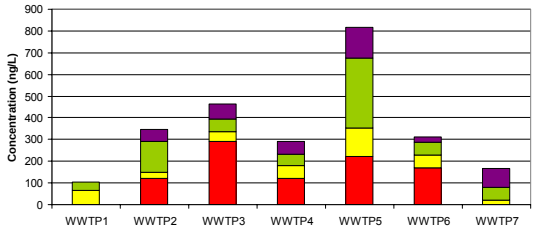




**Environmental risks are reduced in river water due to the important dilution**

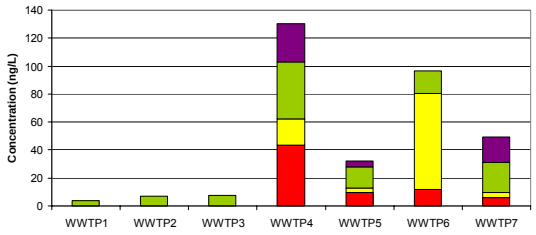
**Atenolol** **Gemfibrozil** **Diclofenac** **Naproxen** **Ibuprofen** **Carbamazepine**

# Contribution of WWTP effluents

**WWTP effluent**

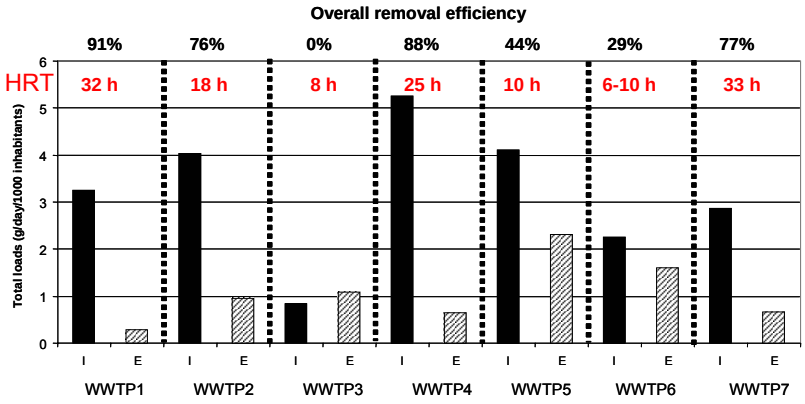



**River water downstream WWTP**





# Total load and removal efficiency




Loads expressed as g/day/1000 inhabitants

## Advanced treatment options

- **Membrane technology**
  Membrane bioreactors (MBR)
  nanofiltration/ultrafiltration
  reverse osmosis
- **Advanced oxidation** or reduction technologies (mainly catalytic or photocatalytic)
- Advanced bioactive technologies (aerobic or anaerobic)
- New solutions such as electrolysis/electro-dialysis, electromagnetic treatment, pulsed UV or arc discharge, ultra-sound, cold plasma, and new type of permeable reactive barriers.

## Why MBR?

Technical aspects

- (i) adsorption, improved physical sludge characteristics, with higher biomass concentration and more effective surface;
- ii) biodegradation, cultivation of metabolic speciation, with high sludge age, low mass organic load favouring biological synthesis of broader substrate spectrum
- iii) direct and complete separation through membrane with entire removal of all contaminants bound to colloids and particulate matter.

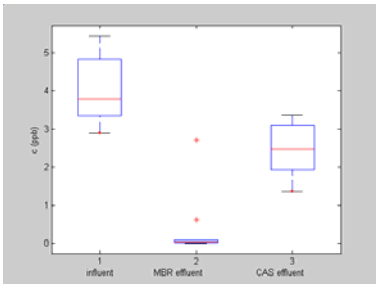
Financial aspect

- the cost of MBR drop from 2001 to 2004 and is estimated to be from 0.8 $ $m^{-3}$ to 0.5 $ $m^{-3}$

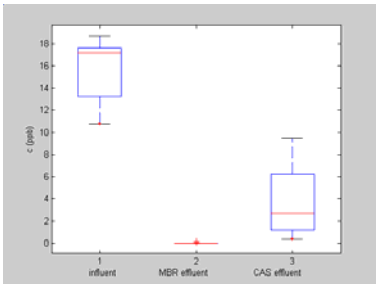
## MBR vs. CAS treatment

For most of the investigated compounds MBR treatment had better performance (removal rates>80%) and steadier effluent concentrations than the conventional system (e.g. diclofenac, ketoprofen, gemfibrozil, bezafibrate, ranitidine, pravastatin, ofloxacin).

**gemfibrozil**




**diclofenac**

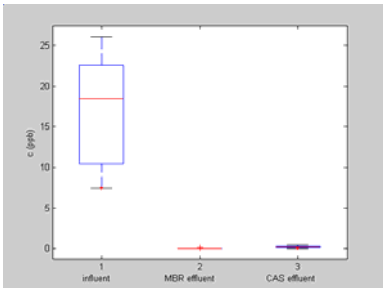



J. Radjenovic et al. Anal. Bioanal. Chem. 387 (4), pp 1365-1377

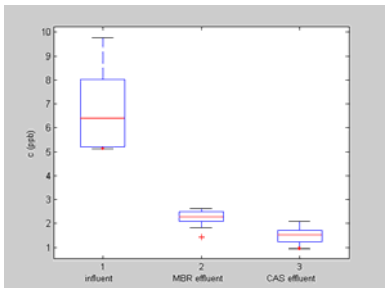
## MBR vs. CAS treatment

In some cases the removal efficiencies were very similar and high for bothtreatments (e.g. ibuprofen, naproxen, acetaminophen, hydrochlorothiazide, paroxetine).

**acetaminophen**




**hydrochlorothiazide**

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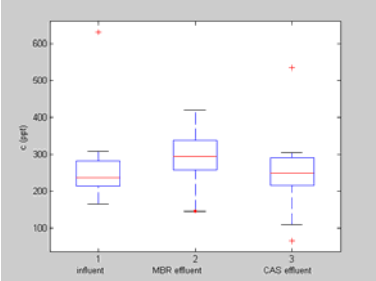
## MBR vs. CAS treatment

The antiepileptic drug carbamazepine turned out to be the most persistent pharmaceutical as it passed both through MBR and CAS system untransformed.

**carbamazepine**




J. Radjenovic et al. Anal. Bioanal. Chem. 387 (4), pp 1365-1377

## Research needs

### Occurance and behaviour

- There is a need to increase the knowledge about the fate of pharmaceuticals during sewage treatment for implementation of **better removal techniques**.
- Future work on WWTP **treatment optimization** will show to what extend pharmaceuticals can be removed from wastewater and to what extent the implementation of an improved technology is feasible, taking into account other macro- and micro-pollutants as well as the broad variety of complex wastewater matrices.
- Current monitoring programms focus on therapeutic form of the drug (What about **Conjugates**, Metabolites, Transformation products?
- Lack of studies concerning the formation of **transformation products** in the environment following natural degradation or water treatment.
- Biotic vs abiotic transformation?
- An important question that should be addressed is whether pharmaceutical residues are **bioavailable** and, if so, what the environmental impact will be.

## Research needs

### Effects/Chronic toxicity

- There is a general **lack of chronic toxicity data** on pharmaceuticals, in particular in fish.
- Need to find a **biomarker** for specific pharmaceutical classes (like vitelogenin for EDCs)
- Many pharmaceuticals need more investigation about potential long-term ecotoxicological effects, particularly with respect to potential disturbances in hormonal homeostasis (endocrine disruption), immunological status, or gene activation and silencing during long-term exposure.
- For better understanding of possible effects, a mechanism-based approach focused on target molecules, tissues and organs should yield more meaningful results and insights than traditional acute toxicity testing.
- Moreover, the potential of **combined effects** of pharmaceutical mixtures should be addressed. In the ecological context, subtle changes and disturbances may have negative consequences for the organism's fitness.

## Minimizing Pharmaceuticals' Environmental Disposition

***Drug Disposal/Recycling/Pollution Prevention***

- Responsible disposal and product stewardship – "smart disposal" USEPA, SIGRE (Spain)
- Source separation for domestic wastes. Advancement in, and implementation of, new technologies for dealing with waste at the source (e.g., urine separation)
- Sewage recycling. Upgrading sewage to potable water. By use of advanced water treatment technology such as reverse osmosis, nearly complete removal of all PPCPs can be achieved. However, all the solutes removed by reverse osmosis are concentrated in the rejected "brine"--a waste stream that must be disposed itself.
- Improvements to sewage infrastructure. Straight-piping of sewage to surface waters should continue to be identified and eliminated on an ongoing basis
- Recycling (reclamation). "Drug mining," such as hospital reclamation of highly toxic drugs from excreta and other wastes, could be pursued and expanded
- Responsible reuse, recycling, and donation.
- Public outreach/education--heightening public awareness.

# Reducing pharmaceutical loads to STPs

- Separate treatment of “hot spots”: hospital wastewaters (drugs)
- For drugs recommended actions are: Labelling (Sweden), urine separation, more environmental education (25-33% of drug disposal as household waste or directly to toilet) but still 1 dollar spent on drugs can save 6 dollars in hospital costs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