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Risk management: Source control and emission reduction (waste water treatment, drinking water treatment)

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Content

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- Introduction: Problems and targets on different scales
- Risk assessment introduction
- Targets of different regulations
- Risk management methods
- Technical aspects
- Case studies

Problems on a global scale - hygiene

Water-related diseases in developing countries

- Half the people in the developing world are suffering from **one or more of the main diseases** : diarrhea, ascaris, dracunculiasis (guinea worm), hookworm, schistosomiasis (bilharzias, or snail fever) and trachoma.
- Approximately 4 billion cases of **diarrhea** each year cause 2.2 million deaths, mostly among children under five
- **Intestinal worms** infect about ten percent of the population of developing countries;
- Worldwide, over 2 billion people are infected with **schistosomiasis** and soil-transmitted helminthes, of whom 300 million suffer serious illness;
- **Arsenic** in drinking water is a major public health threat. In Asia, more than 50 million people per year drink arsenic-contaminated water.

Problems of the world (MDG)

Millennium Development Goals (MDG) issued in 2000, endorsed by 189 countries, was then translated into a roadmap setting out goals to be reached by 2015.

Keep the promise till 2015!!!!!

The Goals

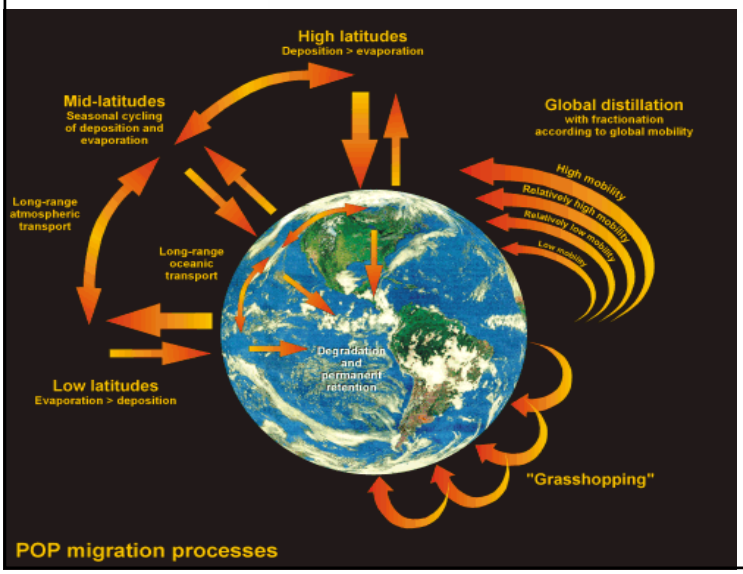
1. Eradicate extreme poverty and hunger
2. Achieve universal primary education
3. Promote gender equality and empower women
4. Reduce child mortality
5. Improve maternal health
6. Combat HIV/AIDS, malaria and other diseases
7. Ensure environmental sustainability
8. Develop a global partnership for development

Integrate the principles of sustainable development into country policies and programmes; reverse loss of environmental resources

Reduce by half the proportion of people without sustainable access to safe drinking water

Achieve significant improvement in lives of at least 100 million slum dwellers, by 2020

Problems on a global scale - POPs



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Many POPs (persistent organic pollutants), heavy metals and other contaminants from emissions further south are accumulated in Arctic food chains and ultimately in indigenous peoples.

Stockholm convention (UNEP)

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- Adopted in 2001 in response to urgent need for global action to protect human health and the environment from “POPs”
- Seeks the elimination or restriction of production and use of all intentionally produced POPS (i.e., industrial chemicals and pesticides) AND the continuing minimization and ultimate elimination of release of unintentionally produced POPs
- Entered into force - 5/17/04
- Provision for future additions of chemicals

Holistic approach (DPSIR – EEA)

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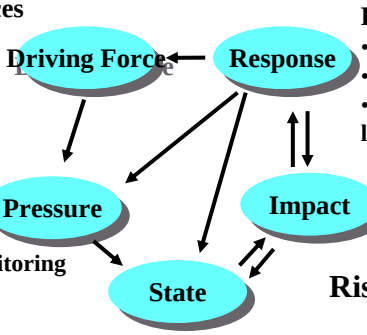
Contamination sources
natural, anthropogenic



Risk management
•prevention, ban
•technical measures
• national und international limit values and regulations

Emissions
•contamination monitoring and reduction
•technical measures

Effects on humans and the environment

Risk assessment

State of the water
•Surface water/groundwater
•drinking water
•bathing water
•irrigation water

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Risk assessment
(for humans and the environment)

Terminology: Hazard and Risk

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Hazard
The potential of a risk source to cause (an) adverse effect(s) /event(s).

Risk
The probability and severity of an adverse effect / event
occurring to man or the environment
following exposure, under defined conditions,
to a risk source(s) (EU_Risk).

Quantitative expression.
It characterizes the incidence of a defined adverse effect at given levels (doses).

Problem

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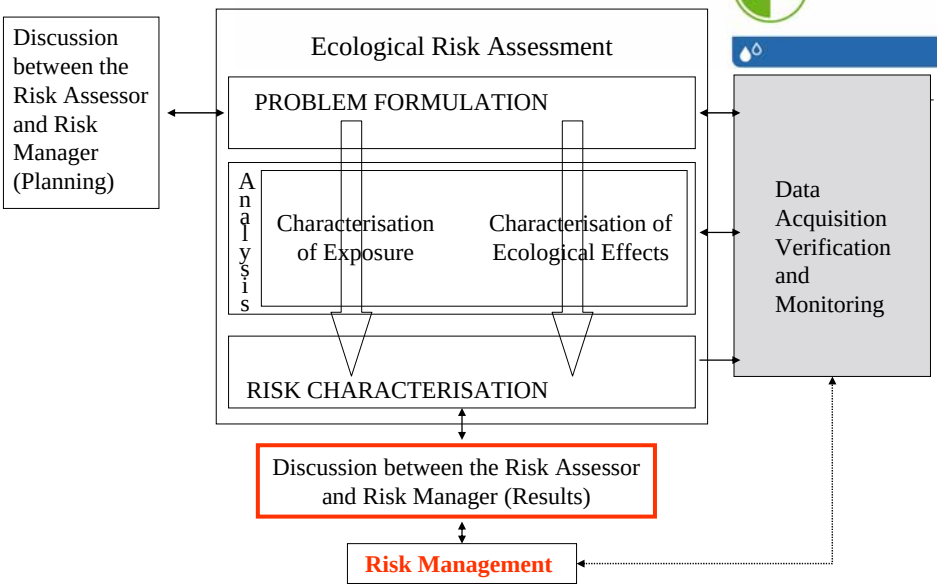
Before we can manage the risk, we have to know

- the problem and
- the magnitude and severity of the risk

Framework for ecological risk assessment



Criteria for the assessment of the fate in the environment

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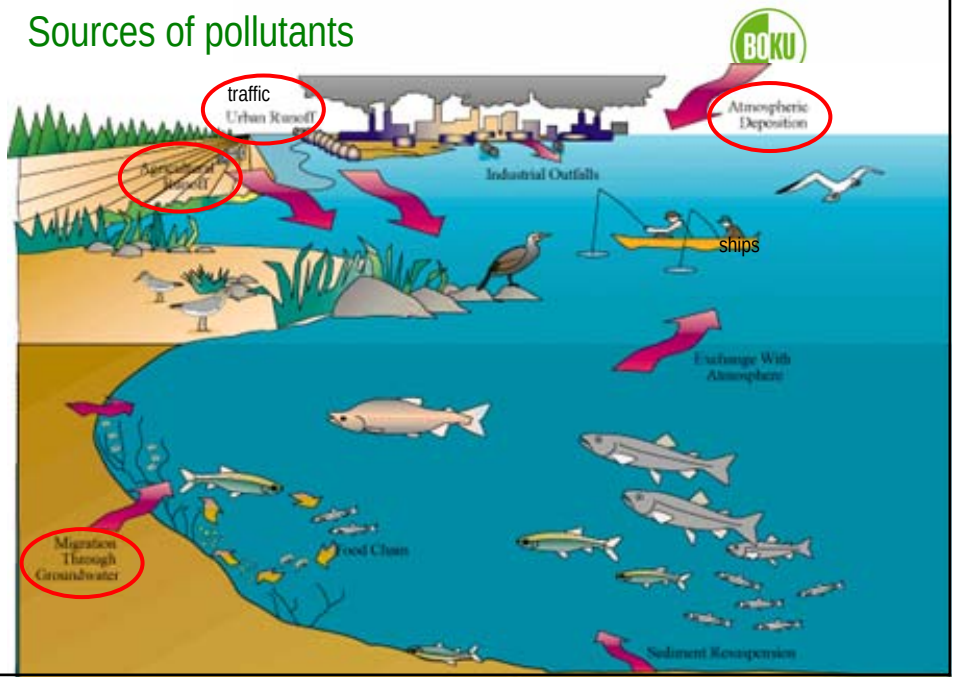
- Production volume
- Pattern of use
- Dispersion
- Persistance/accumulation
- Degradation

Sources of pollutants



Fate of Industrial Contaminants in the Environment

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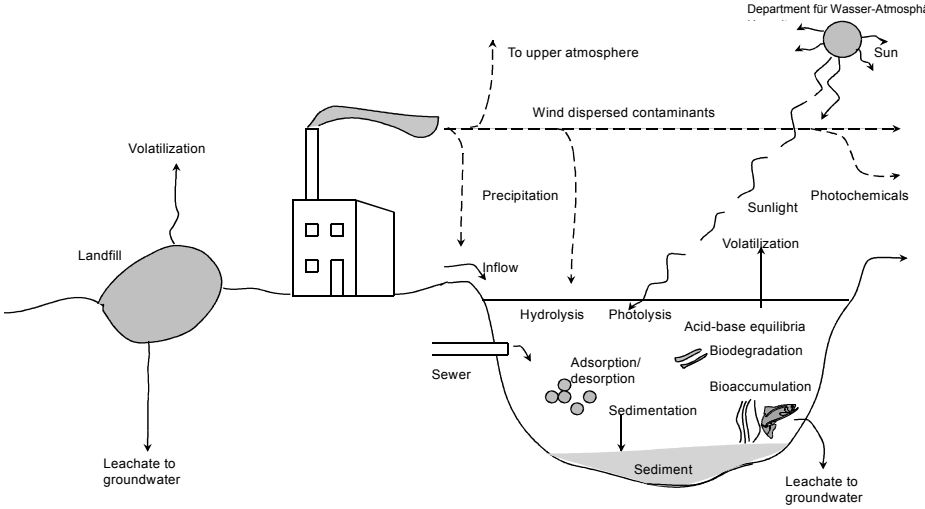

Effects: Dose - response evaluation

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Threshold - approach

Reference Dose (RfD), Reference Concentration (RfC),
Tolerably daily intake TDI (ADI) derived from NOEL, NOAEL, LOEL, LOAEL

The **TDI** is an estimate of the amount of a substance in food or drinking-water, expressed on a body weight basis (mg/kg or µg/kg of body weight), that can be ingested **over a lifetime** without appreciable health risk.

Nonthreshold - approach

Zero risk at zero concentration
(CMR..cancerogens, mutagens, toxics for reproduction)
model extrapolations from high ranges to low ranges

Substances with cancerogenic effects:

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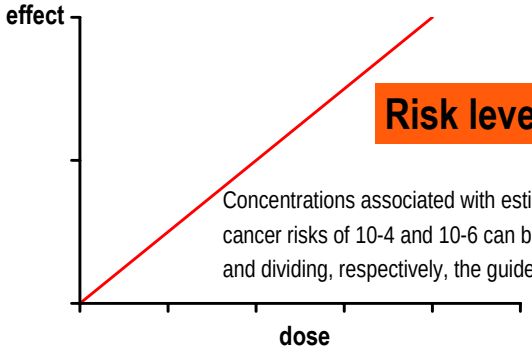
Dose-response relationship for substances with irreversible effects (e.g. teratogen and cancerogen) is linear



Risk level (10^{-4}) - 10^{-5}

Concentrations associated with estimated excess lifetime cancer risks of 10-4 and 10-6 can be calculated by multiplying and dividing, respectively, the guideline value by 10.

that means: effect "0" only at "0„ dose

TGD, 2003

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Technical Guidance Document on Risk Assessment (European Communities, 2003)

in support of

- Commission Directive 93/67/EEC on Risk Assessment for new notified substances
- Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances
- Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market

- This Technical Guidance Document (TGD) supports legislation on assessment of risks of chemical substances to human health and the environment.

OECD-Test systems

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- OECD 201 Alga, Growth Inhibition Test
- OECD 202 Daphnia spec., Acute Immobilisation Test
- OECD 203 Fish, Acute Toxicity Test
- OECD 204 Fish, Prolonged Toxicity Test: 14-Day Study
- OECD 210 Fish, Early-Life Stage Toxicity Test
- OECD 211 Daphnia magna Reproduction Test
- OECD 212 Fish, Short-term Toxicity Test on Embryo and Sac-Fry Stages
- OECD 215 Fish, Juvenile Growth Test

Calculation of the predicted no effect concentration (PNEC)

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concentration below which an unacceptable effect will most likely not occur

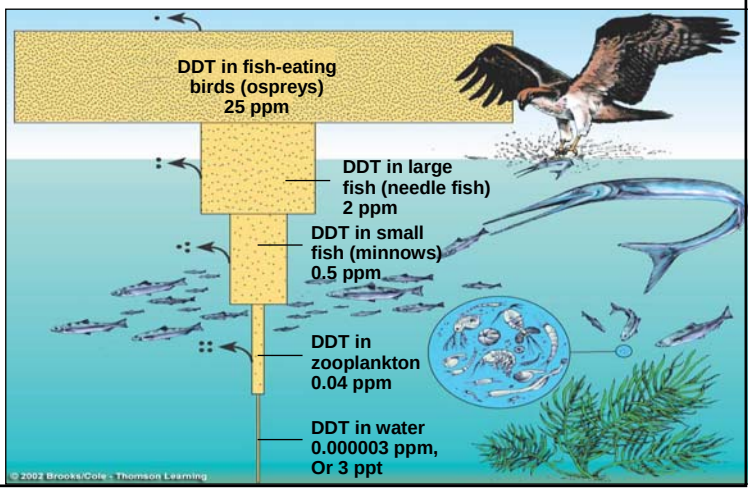
1. step: evaluation of data: non-standard organisms and/or non-standardised methods.

2. step: calculation of PNEC: lowest short-term L(E)C50 or long-term NOEC value divided by an appropriate assessment factor.

Secondary poisoning - bioaccumulation

Secondary poisoning: Lipophilic and persistence properties

Chemicals showing bioaccumulation and biomagnification may pose an additional threat due to exposure of organisms higher in the food chain, e.g. top predators.



Steps of the ecotoxicological risk assessment

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1. **Exposure assessment (humans and environment)**
   Predicted Environmental Concentration, PEC

2. **Effect assessment**
   Predicted-No-Effect-Concentration, PNEC

3. **Risk characterisation (Extrapolation of the resulting risk)**
   PEC/PNEC-Ratio

PEC/PNEC < 1: **no significant risk, no need for risk managment**

PEC/PNEC >1: **significant risk, need for risk managment measures**

Steps in toxicological risk assesment (TGD Part II)

Natural science

1. **Exposure assessment (humans and environment)**
   Predicted Environmental concentration, PEC
   Chemical analyses, bioindication, model calculation
2. **Effect assessment**
   Predicted-No-Effect-Concentration, PNEC
   - Identification of the adverse effects (qualitativ)
   - dose-response-relationship (strenght of the effect, threshold)
3. **Risk characterisation**
   Risk = The probability and severity of an adverse effect / event occurring to man or the environment following exposure, under defined conditions, to a risk source(s)

Politics, society

Risk-benefit-assessment
Risk management
Risk communication

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Legal requirements

Generell targets in the context of water

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Water management on a global and a local level needs to be done in a way to

- ensure sustainable use in terms of quality and quantity
- protect aquatic ecosystems and
- enable all different water uses e.g.
  - drinking water
  - irrigation water or
  - water for recreation purposes

Water related EU regulations

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Irrigation water requirements - microbiological and chemical parameters
Bathing Water Directive - microbiological parameters
Drinking Water Directive - microbiological and chemical parameters
WFD (surface and groundwater)– biological and chemical status

EU-Water quality standards

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Intergrated water quality management

⇧

EU – emission limits

UWWT (91/271/EEC)– eutrophication and oxygen depletion
IPPC (96/61/EEC)- chemical parameters
Nitrate Directive (91/676/EEC) – chemical parameters
Plant Protection Products (91/414/EEC)– chemical parameters

Basic approaches for standard setting

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Risk assessment

Environmental concentration (PEC)

Predicted no effect conc. (PNEC)

PEC/PNEC > 1

Take action

Precautionary principle

DW-values 0,1 µg/l — **for pesticides and metabolites (DWD, 1998)**

GW-values 0,01 µg/l — European Medicines Agency **EMEA, 2006 0,25*0,01 µg/l**; **LAWA, 2004 0,01 µg/l**

In case the knowledge for RA is not available at a proper time, no action is taken.
PP acts in advance // RA is lacking behind

Background of WFD (EEA)

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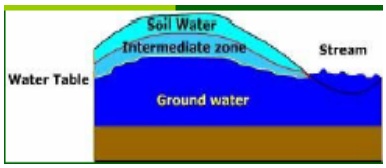
Today, the challenge lies in tackling the pollution and overexploitation of freshwater in agriculture, industry and other human activities.

According to Commission statistics:

- 20% of all surface water in the EU is **seriously threatened** with pollution;
- 60% of European cities **overexploit** their groundwater resources which supply around 65% of all drinking water in Europe;
- 50% of wetlands have **"endangered status"** due to groundwater over-exploitation, and;
- the area of **irrigated land** in Southern Europe has increased by 20% since 1985.
- An **opinion survey** showed that nearly half of Europeans (EU-25) are worried about water pollution (47%), with figures for individual countries going up as far as 71%.

Water Status Objectives

- Surface water status assessed using:
  - Ecological status e.g N&P
  - Chemical status: Priority substances (PS) and priority hazardous substances (PHS)
- Groundwater status assessed using:
  - Quantitative aspects
  - Chemical aspects: Nitrate, ..



• Objective is "good surface water / groundwater status"

Priority (PS) or priority hazardous (PHS)- The approach

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- PS and PHS in the WFD:
  PS: quality standards are defined (QS) ..
  minimization is required

- PHS must fulfill the P,T and B criteria or *„equivalent level of concern“*
  P...persistent, T... toxic, B... bioaccumulative
  PHS: phase out within 20 years !!!

Persistence-toxicity-bioaccumulation PTB Criteria

http://www.eurochlor.org/chlorine/publications/pops_pbts_ksis.pdf

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Criteria of the TGD – Guidelines (2003)

	Persistence	Bio-accumulation	Long-range transport potential	Toxicity [4]
EU PBT criteria	Half-life > 60 days in marine water **or** > 40 days in freshwater[1] **or** >180 days in marine sediment **or** > 120 days in freshwater sediment[1]	BCF > 2000	Not applicable	Chronic NOEC < 0.01 mg/l or CMR cat 1&2 or endocrine disrupting effects
EU vPvB criteria	Half-life > 60 days in marine or freshwater **or** >180 days in marine or freshwater sediment	BCF > 5000	Not applicable	Not applicable

(4) L(E) C50; NOEC - no observed effect concentration;
CMR - carcinogenic, mutagenic or toxic to reproduction.

Nr.	**E Q S for Priority Substances (WFD)** Name	PS/PHS	AA-EQS inland water µg/l	AA-EQS other SW µg/l	MAC-EQS Inland water µg/l	MAC-EQS other SW µg/l
1	Alachlor	PS (PHS)	0.3	0.3	0.7	0.7
2	Anthracene	PHS	0,1	0,1	0,4	0,4
3	Atrazine	PS (PHS)	0,6	0,6	2,0	2,0
4	Benzene	PS	10	8	50	50
5	Brominated Diphenylether	PHS	0,0005	0,0002	n.a.	n.a.
6	Cadmium and its compounds	PHS	≤ 0,08 (Class1)	0,2	≤0,45 (Class1)	
	(depending on water hardness classes[24])		0,08 (Class2)		0,45 (Class2)	
			0,09 (Class3)		0,6 (Class3)	
			0,15 (Class4)		0,9 (Class4)	
			0,25 (Class5)		1,5 (Class5)	
7	C_{10-13}-Chloralkanes	PHS	0,4	0,4	1,4	1,4
8	Chlorophenvinphos	PS	0,1	0,1	0,3	0,3
9	Chlorpyrifos	PS	0,03	0,03	0,1	0,1
10	1,2-Dichlorethane	PS	10	10	n.a.	n.a.
11	Dichlormethane	PS	20	20	n.a.	n.a.
12	Bis(2-ethylhexyl)phthalate (DEHP)	PS	1,3	1,3	n.a.	n.a.
13	Diuron	PS (PHS)	0,2	0,2	1,8	1,8
14	Endosulfan	PHS	0,005	0,0005	0,01	0,0004
15	Fluoranthene (Indikator of PAH)	PS	0,1	0,1	1	1
16	Hexachlorbenzene	PHS	0,01	0,01	0,05	0,05
	AA: annual average; MAC: maximum allowable conc.		n.a. = not applicable			

Nr.	**E Q S for Priority Substances (WFD)** Name	PS/PHS	AA-EQS inland water µg/l	AA-EQS other SW µg/l	MAC-EQS Inland water µg/l	MAC-EQS other SW µg/l
17	Hexachlorbutadiene	PHS	0,1	0,1	0,6	0,6
18	Hexachlorcyclohexane	PHS	0,02	0,002	0,04	0,02
19	Isaproturon	PS	0,3	0,3	1	1
20	Lead and its compounds	PS (PHS)	7,2	7,2	n.a.	n.a.
21	Mercury and its compounds	PHS	0,05	0,05	0,07	0,07
22	Naphthaline	PS (PHS)	2,4	1,2	n.a.	n.a.
23	Nickel and its compounds	PS	20	20	n.a.	n.a.
24	Nonylphenol	PHS	0,3	0,3	2,0	2,0
25	Octylphenol	PS (PHS)	0,1	0,01	n.a.	n.a.
26	Pentachlorbenzene	PHS	0,007	0,0007	n.a.	n.a.
27	Pentachlorphenol	PS (PHS)	0,4	0,4	1	1
28	PAH	PS	n.a.	n.a.	n.a.	n.a.
	Benzo(a)pyrene		0,05	0,05	0,1	0,1
	Benzo(b)fluouranthene		∑=0,03	∑=0,03	n.a.	n.a.
	Benzo(k)fluoranthene		∑=0,03	∑=0,03	n.a.	n.a.
	Benzo(g,h,i)perylene		∑=0,002	∑=0,002	n.a.	n.a.
	Indeno (1,2,3-cd)pyrene		∑=0,002	∑=0,002	n.a.	n.a.
29	Simazine	PS (PHS)	1	1	4	4
30	Tributyltin compounds	PHS	0,0002	0,0002	0,0015	0,0015
31	Trichlorbenzene	PS (PHS)	0,4	0,4	n.a.	n.a.
32	Trichlormethane	PS	2,5	2,5	n.a.	n.a.
33	Trifluralin	PS (PHS)		0,03	n.a.	n.a.
	AA: annual average; MAC: maximum allowable concentration	n.a.= not applicable				

Nr.	**E Q S for Priority Substances (WFD)** Name	PS/PHS	AA-EQS inland water µg/l	AA-EQS other surface waters µg/l	MAC-EQS inland water µg/l	MAC-EQS other surface waters µg/l
1	DDT total	(PHS)	0,025	0,025	n.a.	n.a.
	para-para-DDT	(PHS)	0,01	0,01	n.a.	n.a.
2	Aldrine	(PHS)	∑=0,010	∑=0,005	n.a.	n.a.
3	Dieldrine	(PHS)	∑=0,010	∑=0,005	n.a.	n.a.
4	Endrine	(PHS)	∑=0,010	∑=0,005	n.a.	n.a.
5	Isodrine	(PHS)	∑=0,010	∑=0,005	n.a.	n.a.
6	Carbontetrachloride	(PHS)	12	12	n.a.	n.a.
7	Tetrachloroethylene	(PHS)	10	10	n.a.	n.a.
8	Trichloroethylene	(PHS)	10	10	n.a.	n.a.
	AA: annual average; MAC: maximum allowable concentration	n.a.= not applicalbe				

Proposal for environmental quality standards (Directive 2000/60/EC) – Outcome of the European Parliament's first reading (Strasbourg, 21 to 24 May 2007)

(1)	Amidotrizoate	(19)	4-Methylbenzylidene camphor X
(2)	AMPA X	(20)	Musk ketone X
(3)	Bentazon X	(21)	Musk xylene X
(4)	Bisphenol A X	(22)	MTBE X
(5)	4 4'-Biphenol X	(23)	Naphthalene-1,5-disulfonate
(6)	Carbamazepine	(24)	Octyl-Methoxycinnamate X
(7)	Clotrimazole X	(25)	Perfluorinated Compounds (PFCs) X
(8)	dibutylphthalat (DBP) X		Perfluorooctane sulphonic acid (PFOS)
(9)	Diclofenac		Potassium salt
(10)	Dicofol X		Ammonium salt
(11)	DTPA X		Lithium salt
(12)	EDTA X		Diethanolamine (DEA) salt
(13)	ETBE X		Perfluorooctanoic acid (PFOA)
(14)	Free Cyanide		Ammonium perfluorooctanoate (APFO) X
(15)	Glyphosate X	(26)	Quinoxyfen (5,7-dichloro-4-(pfluorophenoxy)quinoline) X
(16)	HHCB X	(27)	Tetrabromobisphenol A (TBBP-A) X
(17)	Iopamidol	(28)	Tonalid (AHTN) X
(18)	Mecoprop (MCPP) X		

X This priority substance is subject to a review for identification as a possible "priority hazardous substance".

„Combined approach“ (article 10 of WFD)

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Biological quality components

hydromorphological and general chemical quality components (pH, T, conductivity) + specific pollutants

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good ecological status

Priority substances and „relevant“ substances

⇩

good chemical status

⇩

good status

Measures

EQS

BAT
BEP

→ EQS **(exceeded)**

BAT, BEP **measure**

→ EQS **(still exceeded)**

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More stringent measures

Environmental quality standards (EQS)

Point sources: best available techniques (BAT)

diffuse sources: best environmental practice (BEP)

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GOOD STATUS

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EQSs are exceeded!!

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Find the causes!!

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Risk management

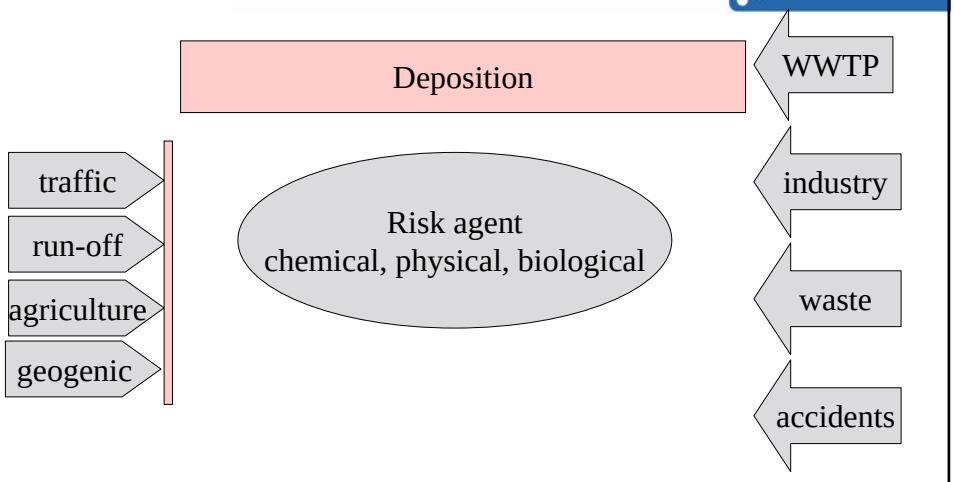
Evaluation, selection and implementation of **risk control actions**

- decisions are made in the risk analysis
- actions are part of the risk management

RM makes use of **tools** from

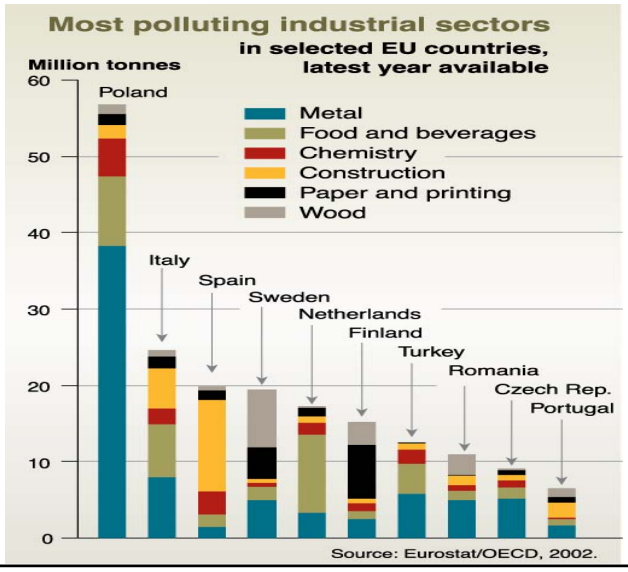
- economics, engineering, administration and the law to support efforts towards sound decisions and effective actions

Source and release assessment



Most polluting industrial sectors

Philippe Rekacewicz, UNEP/GRID-Arendal)
http://maps.grida.no/go/graphic/most_polluting_industrial_sectors



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The waste generated depends on the technology used, the nature of the raw material processed and how much of it is discarded at the end of the chain.
Very often manufacturing wastes end up in the hazardous category.

Measures to reduce pollution

Measures at regulatory level:
EU level: IPPC emission control
EU level: Substitution or outphasing
EU level: Limitations of use in certain applications

→ **Intern. Conventions**

Measures at production level:
Reduce discharges to water from point sources, either by **substitution, improved process control or modifications or effluent treatment or voluntary agreements**

→ **REACH**

Measures at use level :
consumers or in agriculture

Measures at community level:
Sewage treatment, waste disposal

→ **WWT**

Chemicals: testing and authorization

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REACH - Guideline EU

Registration,
Evaluation,
Authorisation of

Chemicals

REACH requires companies that produce and import chemicals to assess the risks arising from their use and to take the necessary measures to manage any risk they identify.

This would reverse the burden of proof from public authorities to industry for ensuring the safety of chemicals on the market.

Voluntary agreements

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Nonylphenol and NP-ethoxylates

- National voluntary agreements (e.g. in Denmark, Germany, Switzerland, Austria) with the trade association SPT (soap, perfume, technical chemical products) e.g. to phase-out their use of nonylphenolethoxylates in cleaning products/detergents

Mercury, lead and cadmium

WFD Measures

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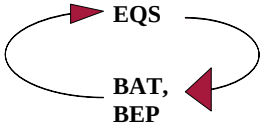
Point sources: best available techniques (BAT)

diffuse sources: best environmental practice (BEP)



EQS → BAT, BEP → EQS → More stringent measures

(exceeded) measure (still exceeded)

„combined approach“

(article 10 of WFD)

Selection for treatment processes for emerging contaminants (EC)

bio-degradable?

adsorbable?
K_D or K_{ow}
ionic substance?

oxidisable?

Biological WWTP MBR Soil passage biological active filter	Biomass Activated carbon Ion exchanger	Chlorination AOP Ozone/H_2O_2

Technical methods for drug removal

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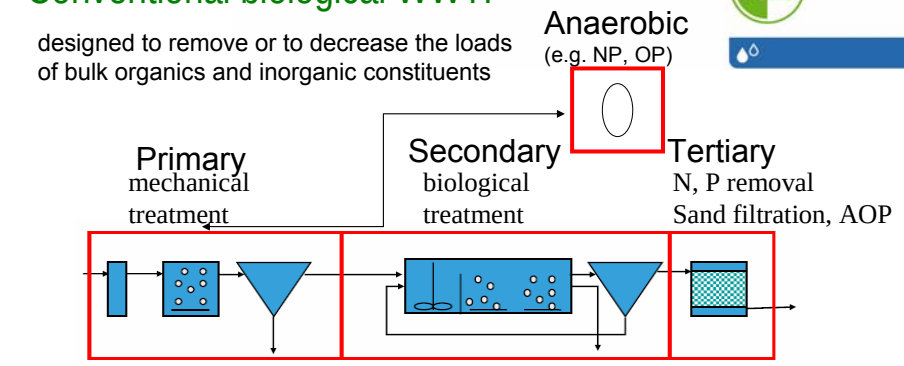
Activated carbon	**Diclofenac und Bezafibrate**	**< LOQ**
	Carbamacepine	**75 %**
	Clofibrinic acid	**20 %**
Ozone and AOP	**Carbamacepine und Diclofenac**	**fast**
	Bezafibrate, Diazepam,	**slow**
	Ibuprofen und Iopromid	**slow**
Membrane systems	**Depending on size and charge**	

Conventional biological WWTP

designed to remove or to decrease the loads of bulk organics and inorganic constituents



Pathogen reduction **0 - 1 log10 removal** **1 - 2 log10 for removal** **1 - 2 log10 for removal**

Removal of drug residues (mainly lipid regulators, antiphlogistics, betablockers , antiepileptic drugs) is often incomplete dependent on:

- the properties of the substances and
- the performance of the WWTPs (SRT>10 days at 10 ° C) incomplete removal of drug residues, more than 80% of the selected drugs

Membrane processes

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- pathogens reduction is very efficient
  - WHO (2006) considers membranes removing viruses and bacteria from 2.5 to >6 log10.
- removal of micro-pollutants:
  - Removal based on structure (MW, K_{ow}) and the membrane surface (pore size, charge, thickness)
  - efficient due to the low sludge load and long sludge retention time which gives bacteria time to adapt to these substances. MBR removes better substances attached to SS.
  - reverse osmosis (RO) and nanofiltration (NF) showed excellent removal (>95%) for all target analytes (esp. log Kow > 3)

Oxidation processes and disinfection

- Pathogen reduction (log unit reduction or inactivation) WHO (2006)
  - chlorination for viruses with 1 – 3 log10 and for bacteria with 2 – 6 log10;
  - for ozonation to be 3 - 6 log10 for viruses and 2 – 6 log10 for bacteria and
- removal of trace pollutants
  - Ozone (O3), O3/UV or H2O2/UV suitable for the reduction of pharmaceuticals in the municipal sewage plant effluents
  - But, objectionable daughter products may be formed

UV- Application and AOP

- Pathogen reduction (log unit reduction or inactivation) WHO (2006)
  - for UV radiation 1 - >3 log10 for viruses and 2 - >4 log10 for bacteria.
- removal of trace pollutants
  - Ineffective at disinfection dose
  - AOP: photochemical advanced oxidation processes include UV/H_2O_2, UV/O_3, UV/H_2O_2/O_3, UV/H_2O_2/Fe^{2+}(Fe^{3+}), and UV/TiO_2. The efficiency of the various AOPs depend both on the rate of generation of the free radicals and the extent of contact between the radicals and the organic compound – very suitable for removal

Acivated carbon

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- Removal of trace compounds
  - Efficient for ED and some pharmaceuticals
  - Compounds with < 50 % removal usually have Kow < 1
  - Showed good removal for ED
- Disadvantages
  - Must be regenerated
  - Efficiency reduced by natural organic matter (NOM)

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Risk management – drinking water

"Five F's" in water and sanitation

Fluid (drinking contaminated water and having too little water to wash)-waterborne fecal-oral diseases like cholera, typhoid, diarrhea, viral hepatitis A, dysentery and dracunculiasis (guinea worm disease).

Feces (the contamination of water, soil and food with human fecal matter)

Fingers (unwashed hands preparing food or going into the mouth)

Food (eating contaminated food)

Flies (spreading disease from feces to food and water or directly to people)

Water Safety Plan
(WHO GDWQ, 2003)

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Health based targets, esp. microbiological (public health and disease prevention)

Chatchment area – water treatment - disinfection

System assessment, including design criteria whole chain up to consumer

↓

Monitoring of control measures understanding and limits of the barriers

↓

Management plans documentation actions to be taken during operation and accidents

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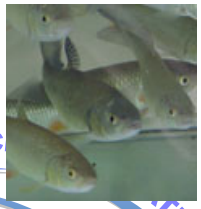
Case studies

Modul I
Monitoring
Scharf S.
Hohenblum P.,
Lorbeer G.,
Gands O.,
Moche W.
Schmid E.
Stanschitz B



Modul II
Bioindication
Grillitsch B.,
Gemeiner M., Gleiß A.,
Leitner M., Miller I., Möstl E.,
Schabuss M., Schmalwieser
Tschulenk W., Walter I.,
Jungbauer A. Beck, V.
Bursch W.

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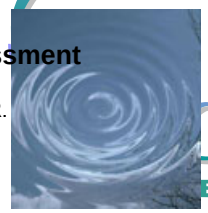
Modul III
Risk assessment
Bursch W.,
Sattelberger R.



Modul IV
Risk management
Kreuzinger, N.
Skutan S., Strenn B.,
Clara M., Fürhacker M.,
Lenz K., Staubmann K.,
Gaupp-Berghausen R.,
Vospernik P., Wegener S.

Modul V
Projektmanagement
Plankensteiner, B

Goals of ARCEM

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- **Material flow analysis**
  - Analysis of the most relevant material flows of endocrine disrupters in Austria as a basis to avoid an input into the waters
- **Monitoring:**
  - Study of concentrations of the most important endocrine disrupters in Austrian surface waters and groundwaters
- **Bioindication:**
  - Description of the pollution of selected running waters in Austria by endocrin disrupters using fish as indicator organisms
- **Risk Assessment:**
  - Assessment of the risk for the domestic fish fauna and for human health (consumption of fish, consumption of drinking water)
- **Risk Management:**
  - Study of the technical potential of various procedures to eliminate endocrine disrupters in the course of drinking water preparation and waste water treatment

Evaluated Substances

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Synthetic and natural estrogens:

- 17a-Ethinylestradiol (EE2)
- 17b-Estradiol (E2), 17a-Estradiol (E2a)
- Estrone (E1), Estriol (E3)

→ **used in lower quantities but strong hormonal activity**

Industrial chemicals:

- Nonylphenol (NP), NP1EO, NP2EO, NP1EC, NP2EC
- Octylphenol (OP), OP1EO, OP2EO
- Bisphenol A (BPA)

→ **used in higher quantities but lower hormonal activity**

Use of Bisphenol A

- used as raw material for synthetic materials (polymeres)
- use of Bisphenol A in Germany in 1995 (Leisewitz & Schwarz, 1997):

Polycarbonate
133 000 t

electrical engineering
data storage (CD,…)
lighting equipment
plates
vehicle construction

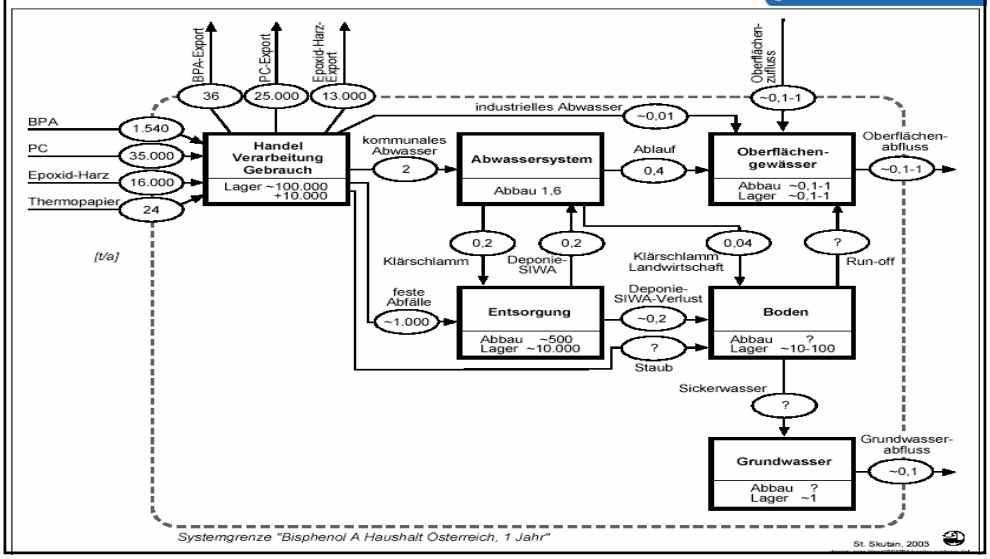
Total
190 000 t

others
700 t

Epoxy resins
56 000 t

electrical engineering
powder coating
coatings of cans/sheet
shipbuilding
vehicle construction

BPA material flow in A



Concentrations in groundwater in A (ng/L)

(ARCEM, 2003)

Risk assessment for fish and human health in case of fish consumption.
(LOD = limit of determination; - = no median or mean value calculated, more than 50 % <LOD
ng/l = nanogram per litre; n.d. = not detectable; PNEC = predicted-no-effect-concentration)

Substances	Number of samples (no. > LOD)	Measured in Austrian **groundwaters** (ng/l)			Risk for humans indicated when consuming ground-water?
		Median	Mean value	Min – Max	
17-α–ethinyl oestra-diol	112 (1)	-	-	n.d. – 0.94	no
17-β–oestradiol	112 (58)	0.07	0.13	n.d. – 0.79	
17-α–oestradiol	112 (4)	-	-	n.d. – 0.21	
Östron	109 (20)	-	-	n.d. – 1.6	
Östriol	112 (2)	-	-	n.d. – 0.16	
Nonylphenol (NP)	110 (77)	35	143	n.d. – 1,500	
NP1EO	112 (42)	-	-	n.d. – 150	
NP2EO	112 (47)	-	-	n.d. – 150	
NP1EC	112 (36)	-	-	n.d. – 260	
NP2EC	112 (14)	-	-	n.d. – 110	
Octylphenol (OP)	112 (5)	-	-	n.d. – 42	
OP1EO	112 (0)	-	-	n.d. – <10	
OP2EO	112 (0)	-	-	n.d. – <10	
Bisphenol A (BPA)	111 (65)	24	67	n.d. – 930	

Overview of measured concentrations of endocrine disruptors in surface waters in A

(ARCEM, 2003)

Risk assessment for fish and human health in case of fish consumption.
(LOD = limit of determination; - = no median or mean value calculated, more than 50 % <LOD
ng/l = nanogram per litre; n.d. = not detectable; PNEC = predicted-no-effect-concentration)

Substances	Number of samples (no. > LOD)	Measured in Austrian **surface waters** (ng/l)			PNEC (ng/l)	Risk for aquatic environment (in particular fish) indicated ?	Risk for humans indicated when consuming fish ?
		Median	Mean value	Min - Max			
17-α-ethinyl oestradiol	261 (4)	-	-	n.d. – 0.33	0.1	Fish: risk in all measured waters cannot be excluded	
17-β-oestradiol	250 (151)	0.13	0.19	n.d. – 1.2	1	no	
17-a-oestradiol	261 (17)	-	-	n.d. – 0.31	No effect		
Oestrone	243 (185)	0.35	0.58	n.d. – 4.6	3		
Oestriol	261 (20)	-	-	n.d. – 1.9	1		
Nonylphenol (NP)	261 (138)	11	31	n.d. – 890	330 ng/l: PNEC for generally toxic effects ----- 1.000 ng/l: threshold concentration for endocrine disruption	Risk for the aquatic environment cannot be excluded in Wulka, Leitha, Dombirner-Ach, Old Rhine, Vienna, Glan, Piesting, Schwechat, Danube, Traun, Ager, New Rhine rivers	no
NP1EO	261 (113)	-	-	n.d. – 170			
NP2EO	261 (97)	-	-	n.d. – 200			
NP1EC	261 (231)	54	158	n.d. – 2200			
NP2EC	261 (204)	29	82	n.d. – 1700			
Octylphenol (OP)	261 (1)	-	-	n.d. – 41	100	no	
OP1EO	261 (2)	-	-	n.d. – 20	100		
OP2EO	261 (1)	-	-	n.d. – 11	100		
Bisphenol A (BPA)	261 (58)	-	-	n.d. - 600	1600		

Bisphenol A in influent and effluents of 11 WWTPs

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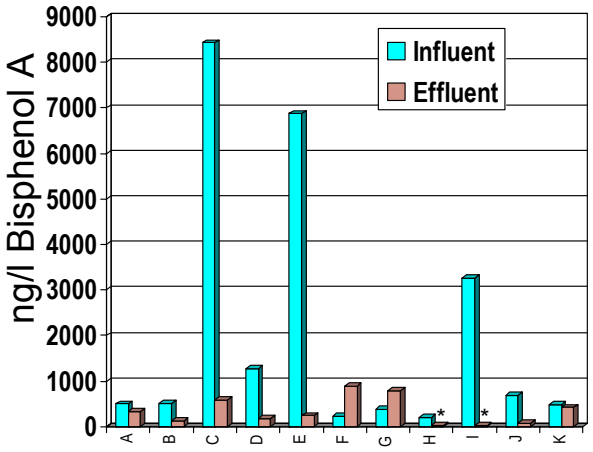

*….<LOD

Nonylphenol (Haskoning, 2002)

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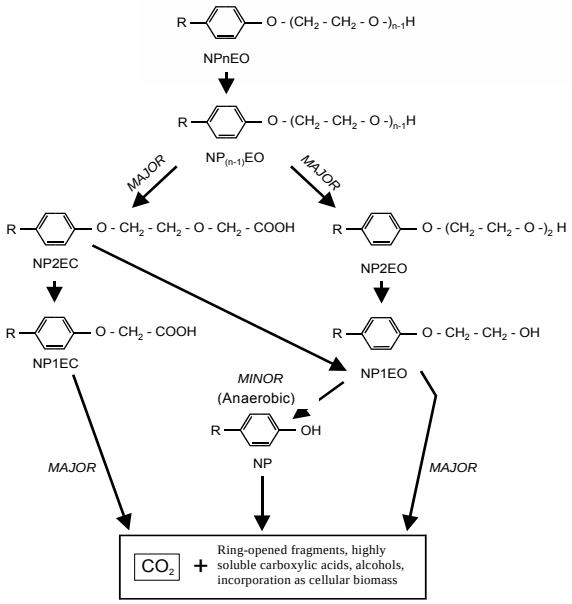
Nonylphenol is used in the production of:

- -Nonylphenol ethoxylates
- -Resins, plastics, stabilisers etc.
- -Phenolic oximes,
  used as a reagent for the extraction and purification of copper from ore *[EU RAR, 2001]*

AEROBIC BIODEGRADATION PATHWAYS OF NONYLPHENOL ETHOXYLATES



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Nonylphenol Ethoxylates

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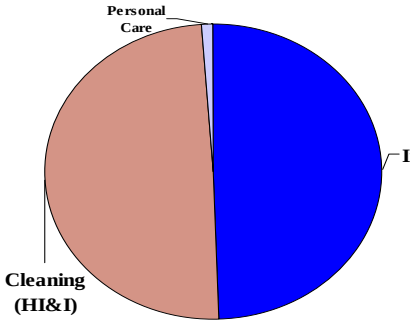

End use applications in the EU

- Household, Industrial, and Institutional Cleaners
- Industrial Processing
  - Emulsion Polymerization
  - Paints and Coatings
  - Textiles
  - Pulp and Paper
  - Agrochemicals

Elimination of 4-NP and NP(1,2)EO

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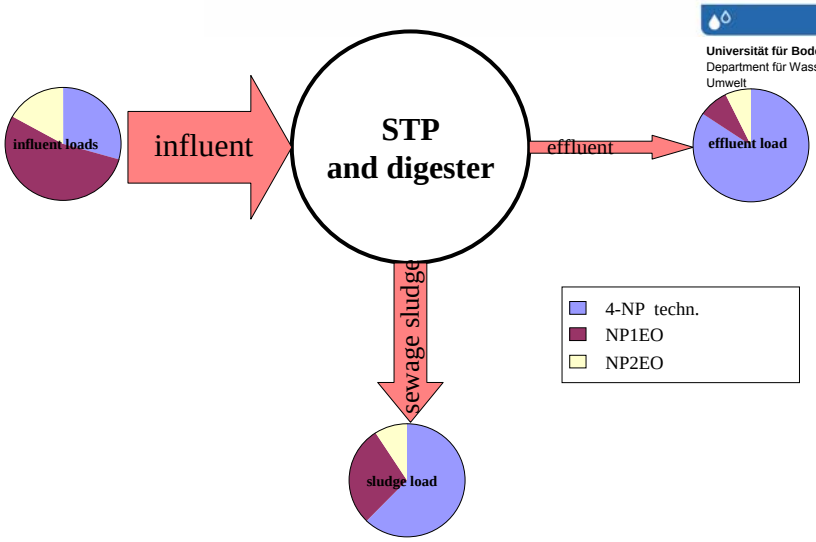

Results of ARCEM (RM - WW)

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- adsorption processes are of vital importance for the removal
- sludge retention time is important: denitrifying plants ensure a corresponding SRT
- anaerobic stage, accelerates the breakdown of nonylphenolethoxylates

- *The right SRT and a sequence of different oxygen conditions (aerobic, anoxic, anaerobic) are the most crucial factors in removing the substances.*

Results of ARCEM (Risk management – Drinking water)

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- **Chlorination with chlorine dioxide and ozone**:
  - reduce the endocrine disrupters to below the detection limit; with the exception of nonylphenolethoxylates
- **Sodium hypochlorite:**
  - reduction of more than 90% for bisphenol A, estrogens below DL (no increase in YES activity)
  - nonylphenolethoxylates no significant reduction
  - nonylphenol reduced (YES activity increased)
- **Activated carbon:**
  - estrogens good adsorption in high concentration ranges.
  - estrogens bad removal in low concentration ranges (e.g. Austria's groundwater level) Nonylphenol also adsorbs well to activated carbon only in high concentration ranges.
- **Precipitation** (Fe and Al): slight reduction in endocrine disrupters.

Study: Monitoring, removal and risk assessment of cytostatic drugs in hospital wastewater (Lenz et al., subm.. 2007)

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Katharina Lenz[1,2], Susanne Mahnik[2,3], Norbert Weissenbacher[2], Robert Mader[3], Petra Krenn[3], Stephan Hann[2], Gunda Koellensperger[2], Maria Uhl[1], Siegfried Knasmüller[3], Franziska Ferk[3], Wilfried Bursch[3] and Maria Fuerhacker[2]

[1]Umweltbundesamt Vienna

[2]University of Natural Resources and Applied Life Sciences, Vienna:
Institute of Sanitary Engineering and Water Pollution Control
Department of Chemistry - Division of Analytical Chemistry

[3]Medical University of Vienna, Department of Medicine I

Objective of the study (Lenz et al., subm.. 2007)

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- Calculation and chemical analysis of the selected substances in the wastewater of the oncologic in-patient treatment ward of a hospital in Vienna
- Treatment with a pilot membrane bioreactor system (MBR) in the hospital
- Adsorption to activated carbon and/ or UV-oxidation
- Biological effect monitoring (genotoxicity assay)

- Risk assessment for the selected substances

Selected substances (Lenz et al., subm.. 2007)

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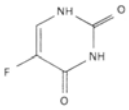
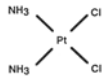
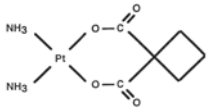


5-Fluorouracil

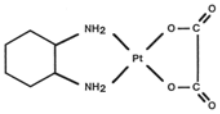
Cancerostatic platinum compounds (CPC)



Cisplatin

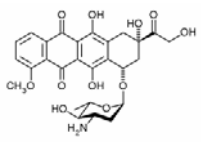


Carboplatin

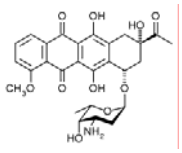


Oxaliplatin

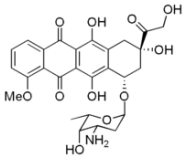
Antracyclines



Epirubicin



Daunorubicin



Doxorubicin

Treatment plant (Lenz et al., subm.. 2007)

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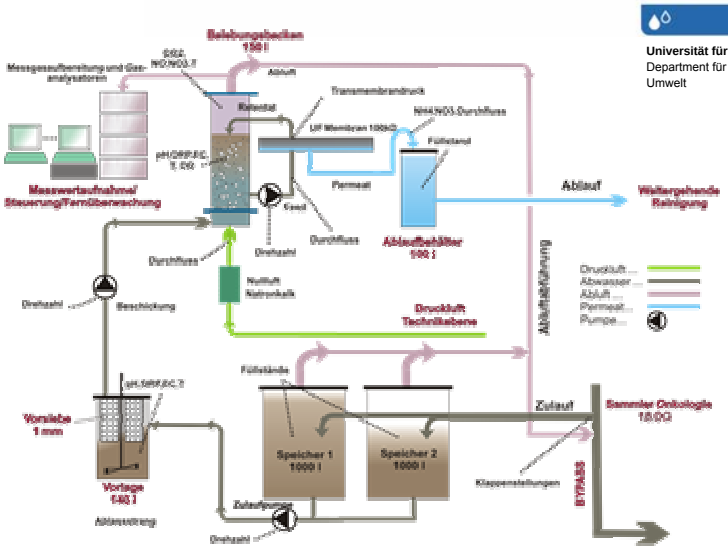

Treatment plant (Lenz et al., subm.. 2007)

- Ultra filtration membrane (cross-flow mode)
- Active area: 1 m²
- Nominal cut-off: 100kDa

Results (Lenz et al., subm.. 2007)

- Established model calculation suitable to estimate concentrations of selected cytostatic agents in hospital wastewater
- Significant amounts of the substances are emitted into municipial wastewater
- Wastewater treatment in an MBR removed chemical concentrations due to different mechanisms (adsorption to activated sludge, metablisation and biodegradation) as well as genotoxic effects
- Adsorption to activated carbon → further removal of CPC (17%)

Conclusions (Lenz et al., subm. 2007)

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According to „Guideline on the Environmental Risk Assessment of medical Products for Human Use“, data on ecotoxicity of the substances scarce → only preliminary risk assessment

➡ Risk from investigated cytostatic substances in hospital wastewater seems low

BUT: as classified as CMR they should be eliminated

Study: Quaternary ammonium compounds (QAC) (Kreuzinger et al., 2007)

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The aim of this study was:

- to form a broad and solid basis for environmental risk evaluation
- The study design involved
  - A) exposure characterization,
  - B) sources and the fate of QAC in waste water treatment plants (WWTP), and
  - C) ecotoxicological effect characterization.
- Selected compounds: Benzalkonium chlorides (BAC-C12 to C18) and dialkyldimethylammonium chlorides (DDAC-C10 to C18)

Flow scheme for the general approach chosen in the QAC Study (Kreuzinger et al., 2007)

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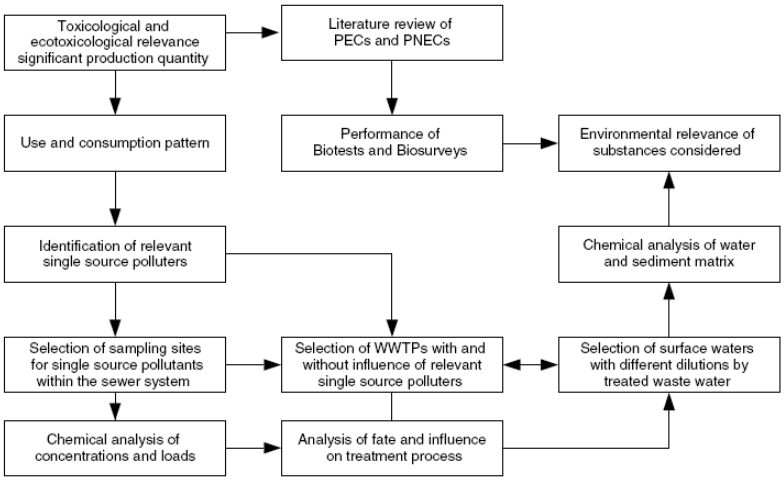
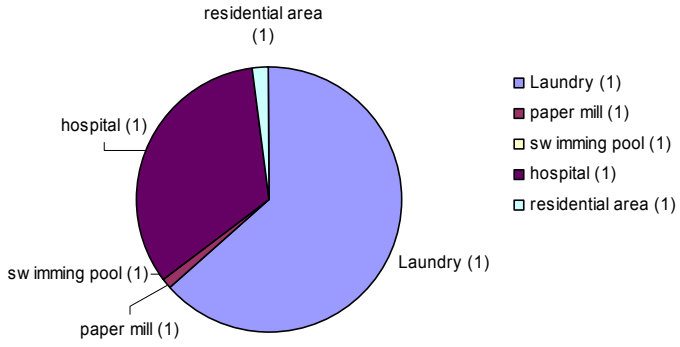


Distribution of molar BAC (C-12-C18) emissions (%) from single source waste water emission points based on total influent to the WWTP (Kreuzinger et al., 2007)



Comparison of PEC/PNEC for BAC-12 maximum and minimum concentration
(Grillitsch et al., 2007)

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Sampling sites Juni 2004 /September 2004	BAC-C12 ng/l		PEC/PNEC BAC-C12-	
Liesing oberhalb KA	1900	45	**47.5**	**1.13**
Liesing unterhalb KA	97	67	**2.43**	**1.68**
Ybbs Amstetten oberhalb KA	27	< BG	0.68	
Ybbs Gleis	25	25	0.63	0.63
Ybbs Neumarkt	15	< BG	0.38	
Schwechat Helenental	48	n.n.	**1.20**	
Schwechat Maria Lanzend.	290	26	**7.25**	0.65
Schwechat Albern	110	60	**2.75**	**1.50**
Donau- unter Kritzendorf	36	n.n.	0.90	
Donau- unter Albern Hafen	67	140	**1.68**	**3.50**
Donau-Haslau Fähre	52	45	**1.30**	**1.13**

Investigations of BAC and DDAC in the environment showed environmental concentrations (PEC) which are in some cases higher than the predicted no effect concentrations (PNEC).

Conclusions QAC-study

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- Database for environmental RA is still fragmentary – high assessment factors
- Influent concentrations were below effect concentration for micro-organisms in the WWTP
- The pollutant sources could be related to 2 single sources: hospital and laundries
- For surface water: the environmental risk could not be excluded

There is a need in treatment, but…..

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No treatment process will ever remove all organic compounds to below LOD of sensitive analytical instruments

- But, what %-removal is appropriate?
- Detection does not interfere toxicity
- We MUST understand the toxicological relevance at environmentally realistic concentrations!!!
- What is the cost benefit ratio?

Conclusions I

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- For the priorisation of risk management steps a risk assessment needs to be carried out.
- Substantial reductions (especially C and nutrients) in point source emissions to water was already achieved
- New forms of invisible, time-delayed and more systemic pollution and chemicals (e.g. emerging contaminants (persistent but polar) and CMR, endocrine disrupting or neuro-toxic effects) needs advanced forms of RA and RM

Conclusions II

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- For an effective risk management in terms of recreational, bathing water and drinking water use, the respective directives would need to be harmonized with the WFD, the UWWT and proposed BATs under consideration of pathogen and PS/PHS substance removal.
- Especially where water is scarce and reuse of wastewater is high, source control and treatment of ECs need sufficient attention.
- As drinking water contamination causes the most important loss of people the attention to the “5 Fs” and the implementation of a WSP is recommended - as there is way to go to reach the targets on the global level under the aspects of MDG.

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Thanks to
INNOVA-MED, especially to Prof. Ridvan Berber
to you for your attention

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