Emerging chemical threats and radioactivity in drinking water resources

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Outline

- Introduction
- Examples for emerging chemical threats
  - Pharmaceutical residues
  - Endocrine disrupting compounds (EDC)
  - Nitrosamines
  - Perfluorinated compounds (PFC)
- Radioactivity in European source waters
- Conclusions

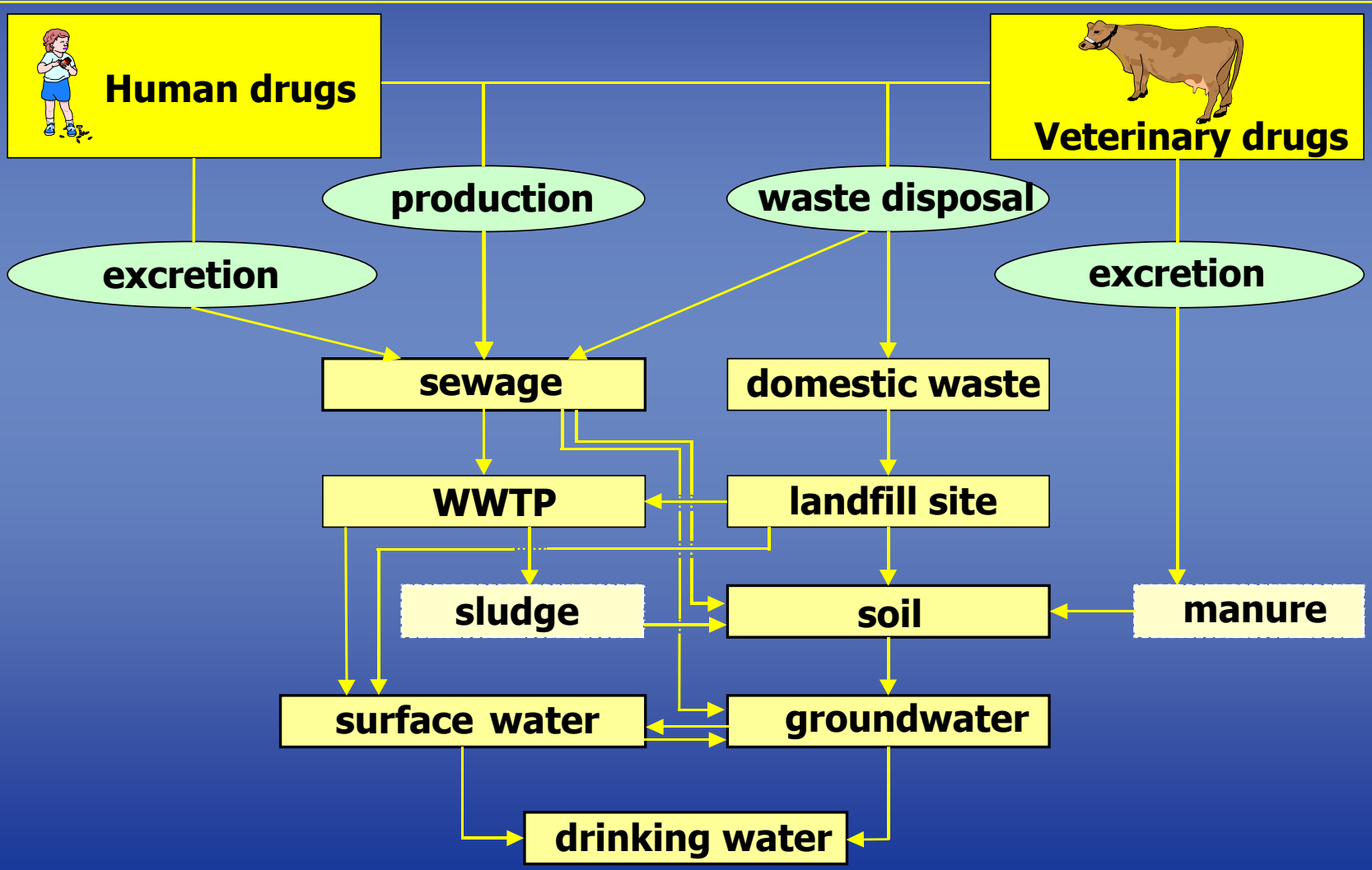
Relevance of emerging contaminants

no data on human and eco toxicology; no information on behavior during drinking water treatment

not included in official lists and monitoring programs; no regulatory values

?

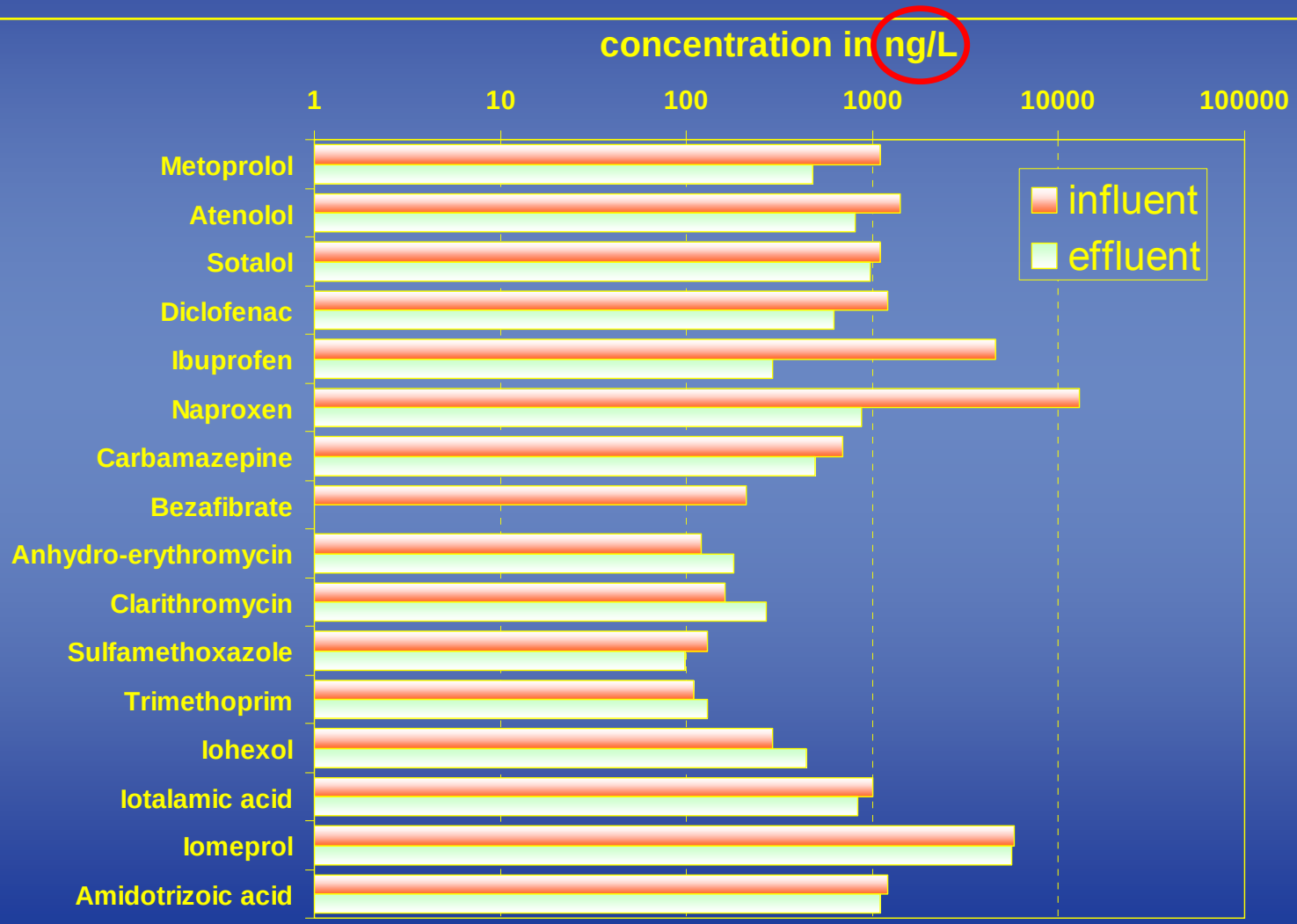
Pharmaceutical residues



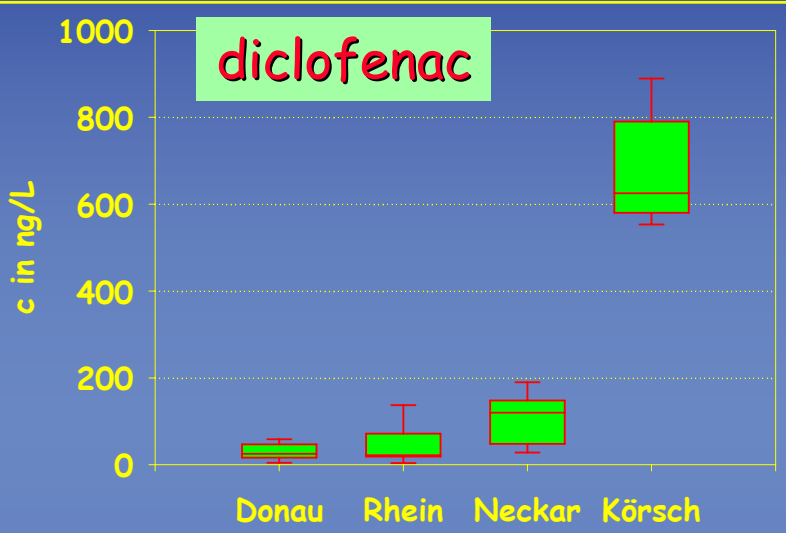
Classes of pharmaceutical residues

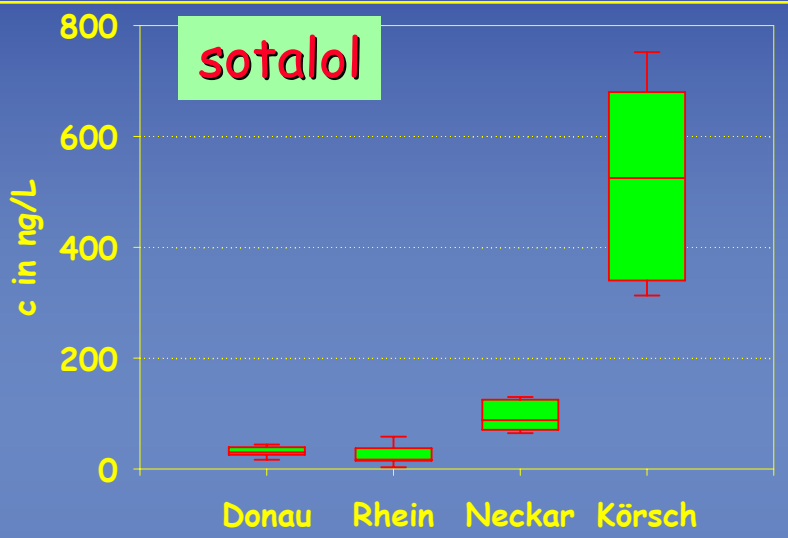
- analgesics
- anti-inflammatory drugs
- broncholytics, secretolytics
- lipid-lowering agents
- antiepileptic drugs
- antipyretics
- tranquillisers
- antibiotics (macrolides, sulfonamides, penicillins, tetracyclines, fluoroquinolones, cephalosporins,...)
- betablockers
- X-ray contrast agents
- antineoplastic drugs
- vasodilators

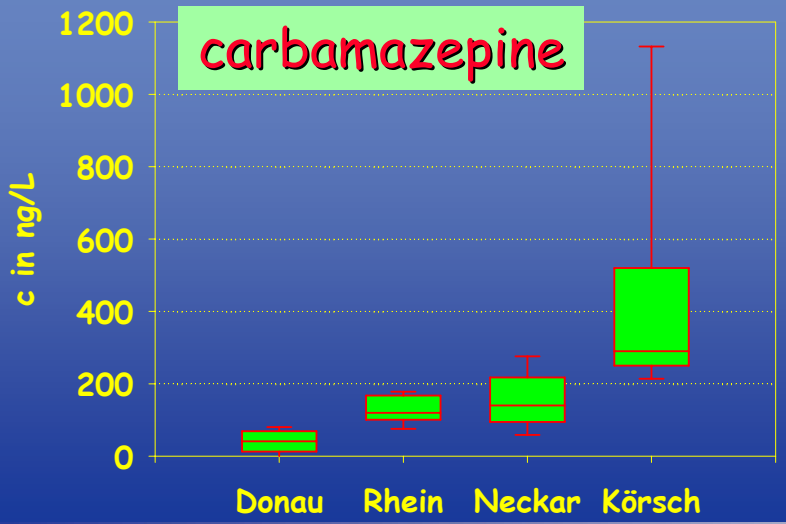
Pharmaceutical residues in WWTP

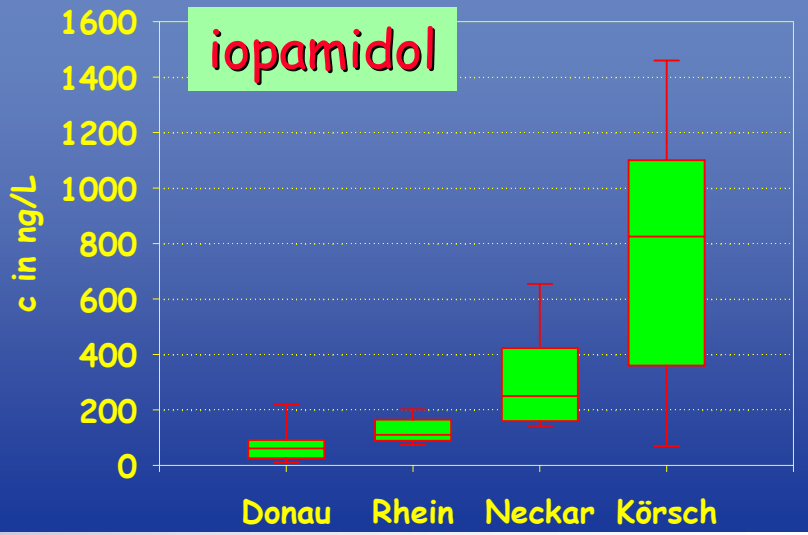


Pharmaceutical residues in surface waters

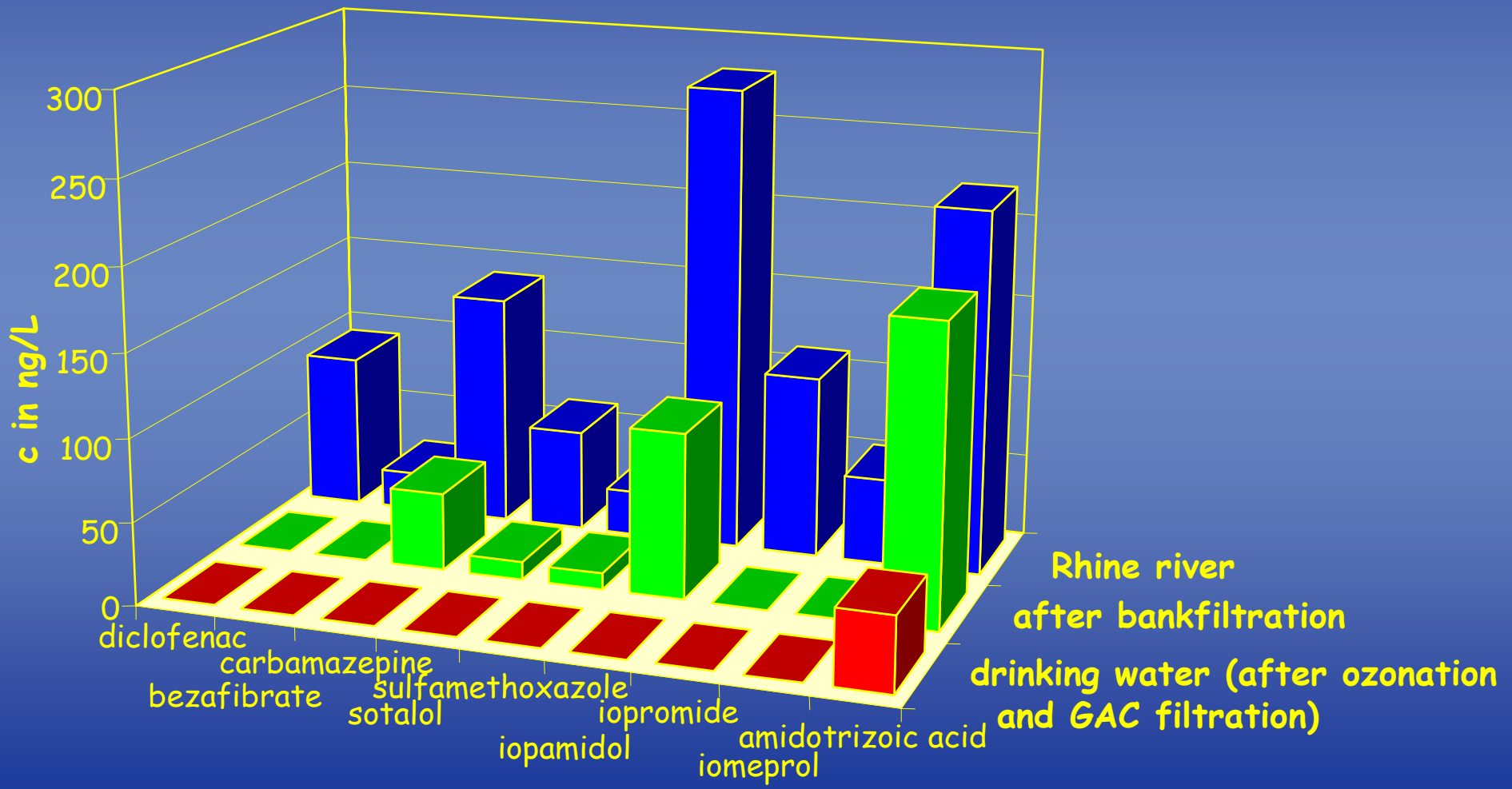








Pharmaceutical residues in drinking waters



Relevance of pharmaceuticals

- Concentration levels found in drinking waters are far below therapeutic doses
- At those concentrations, no adverse effects for humans are expected
- At the concentration levels found in the environment, no adverse effects for wild-life are expected
- **BUT:** Knowledge about long-term effects and effects of mixtures is scarce!!!

Endocrine disrupting chemicals (EDC)

- EU Weybridge definition: An EDC is „an exogenous substance that causes adverse health effects in an intact organism, or its progeny, consequent to changes in endocrine function“
- Possible effects of EDC: Reproductive disorders, inhibition of female characteristics, reduction of fertility,...

EDC

There are several hundreds of chemicals which are nowadays classified as EDC or potential EDC:

- natural hormones (estradiol, estrone)
- synthetic hormones (ethinylestradiol)
- phyto-hormones (ß-sitosterol)
- industrial chemicals (bisphenol A, nonylphenol, phthalates,...)
- pesticides (DDT, vinclozolin, linuron,...)
- metals (lead, cadmium, mercury)

Relative estrogenic potency

Compound	*relative potency*
17β-estradiol	1
17α-ethinylestradiol	0.9 – 1.2
estrone	0.09
estriol	0.08 – 0.8
diethylstilbestrol (DES)	0.7 – 1
p-nonylphenol	10^{-4} – 10^{-5}
tert-octylphenol	10^{-3} – 10^{-4}
bisphenol A	10^{-4} – 10^{-7}
dibutylphthalate	10^{-5} – 10^{-6}
diethylhexylphthalate	10^{-5}
DDT	10^{-7}
endosulphan	10^{-6}
4,4'-dihydroxybiphenyl	10^{-6}

Analysis of EDC

bio assays

- **in-vivo methods**
  vitelloginin test
- **in-vitro methods**
  E-screen assay
  YES assay
  ER CALUX assay

chemical analysis

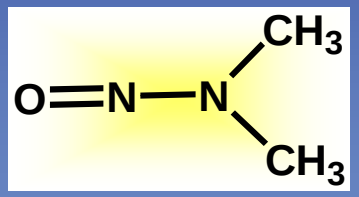
GC-MS(-MS)
HPLC-DAD
HPLC-MS(-MS)

effect-related analysis

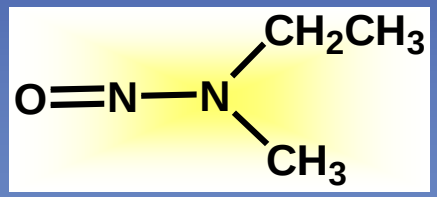
Relevance of EDC

- EDC are found in wastewaters, surface waters, and groundwaters
  - steroidal hormones
  - alkyl phenols (iso-nonylphenol, bisphenol A)
  - phthalates
- Steroidal hormones are found in low concentrations but also have very low no-effect levels (NOEL < 1 ng/L!!!)
- Endocrine disrupting effects due to anthropogenic chemicals have been found in the environment
- **But:** Most EDC are efficiently removed by conventional treatment technologies (ozonation, GAC filtration)
- **and:** There are a lot of other sources for EDC besides drinking water

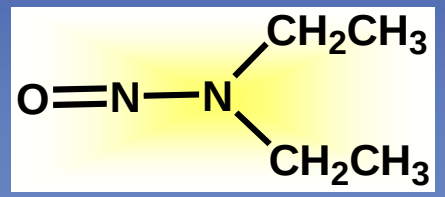
Nitrosamines



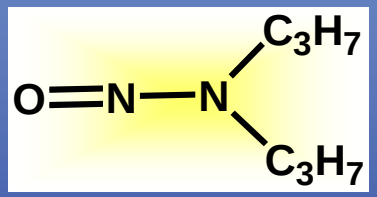
NDMA
(CAS 62-75-9)



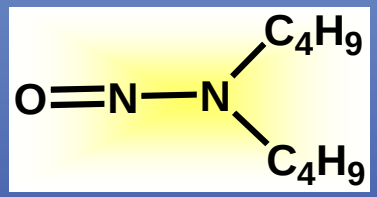
NEMA
(CAS 10595-95-6)



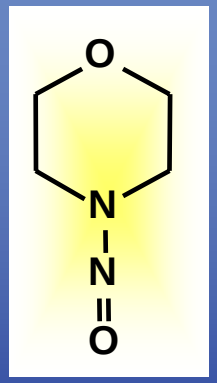
NDEA
(CAS 55-18-5)



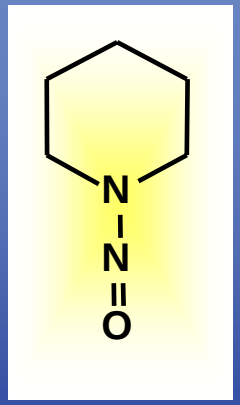
NDPA
(CAS 621-64-7)



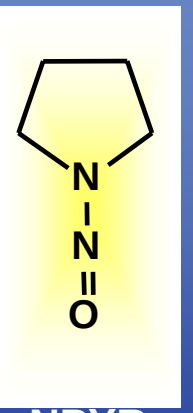
NDBA
(CAS 924-16-3)



NMOR
(CAS 59-89-2)



NPIP
(CAS 100-75-4)



NPYR
(CAS 930-55-2)

Toxicological relevance of nitrosamines

- Nitrosamines are genotoxic and mutagenic
- They are reasonably anticipated to be carcinogenic in humans
- German water pollution class: WGK 3 (very hazardous to water)
- Nitrosamines are toxic to aquatic organisms; they might cause harmful effects in surface waters for longer periods
- 10^{-6} cancer risk of nitrosamines in drinking water: **0.2 - 6 ng/L**
  (US EPA; related to 2 litres/day and exposure over 70 years)

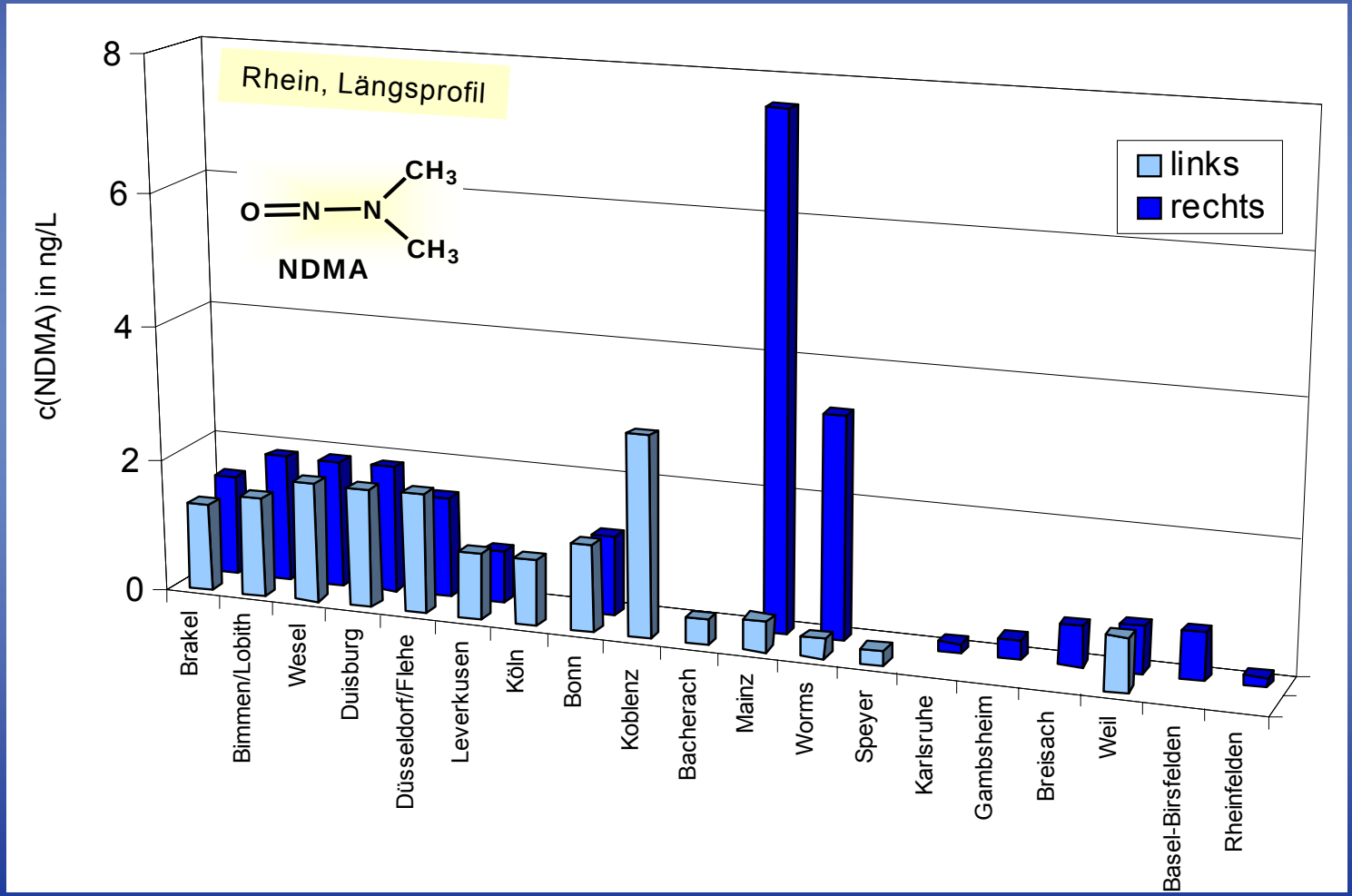
NDMA 0.7 ng/L (US EPA) 2.0 ng/L (OEHHA)
NMOR 0.8 ng/L (US EPA)

- „Preliminary action level“ for NDMA in drinking water: 10 ng/L
  (California Department of Health Services, DHS)

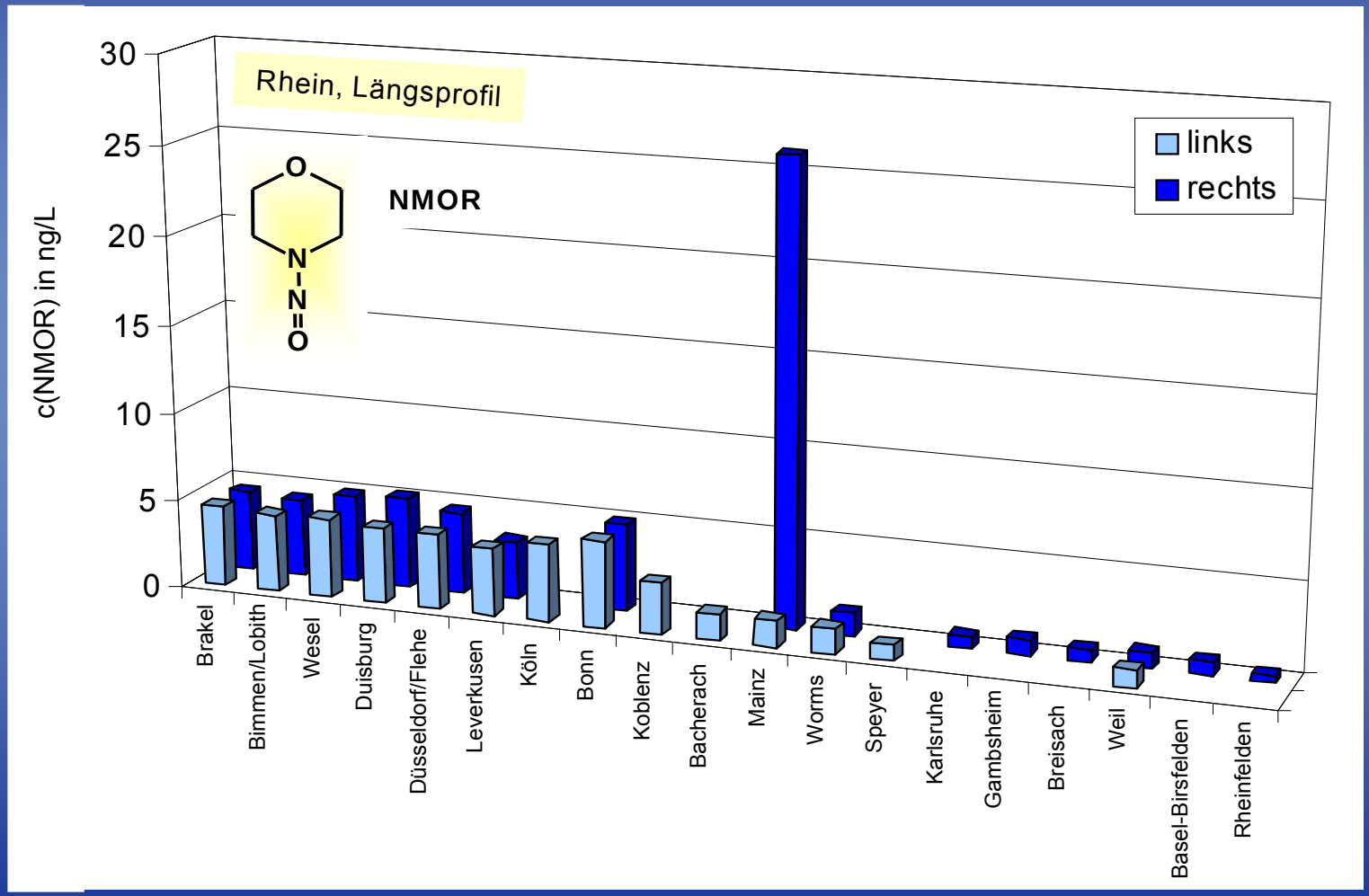
Sources of nitrosamines

- Industrial sector
  - chemical industry
  - metal-working industry
  - iron and steel industry
  - rubber and leather industry
- Consumer Products and Food
  - cosmetics and personal care products
  - products containing rubber
  - tobacco products
  - foods
- Natural Sources
  - natural amine precursors (fish, algae, urine, faeces) and nitrite

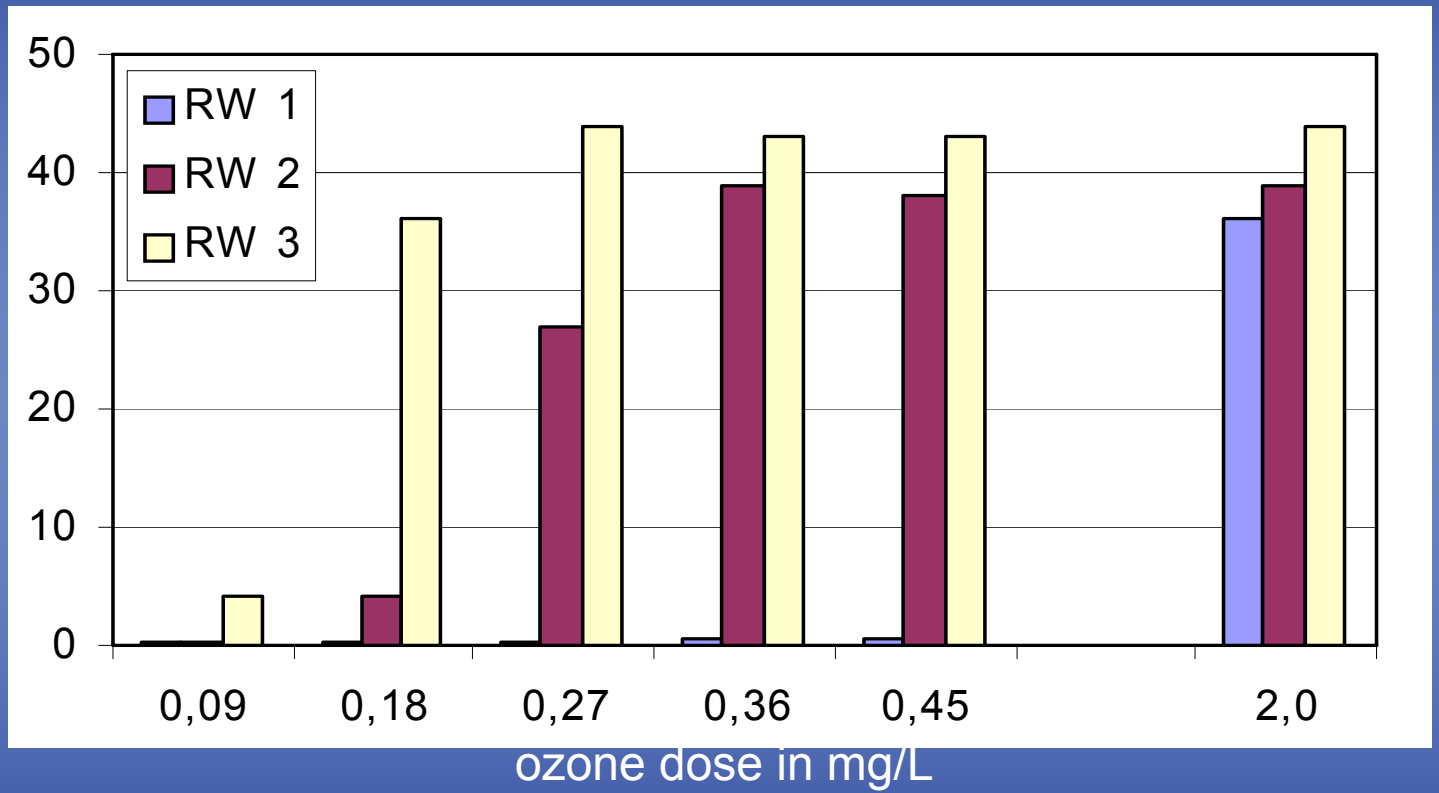
NDMA in the Rhine (spot samples)



NMOR in the Rhine (spot samples)

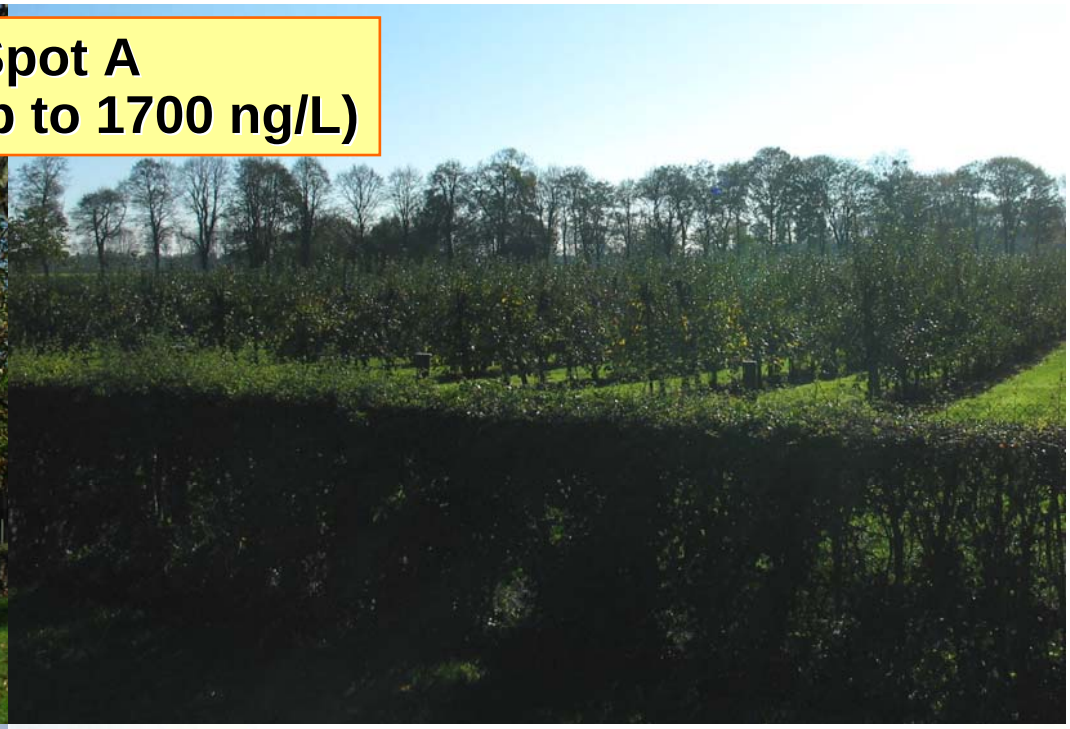


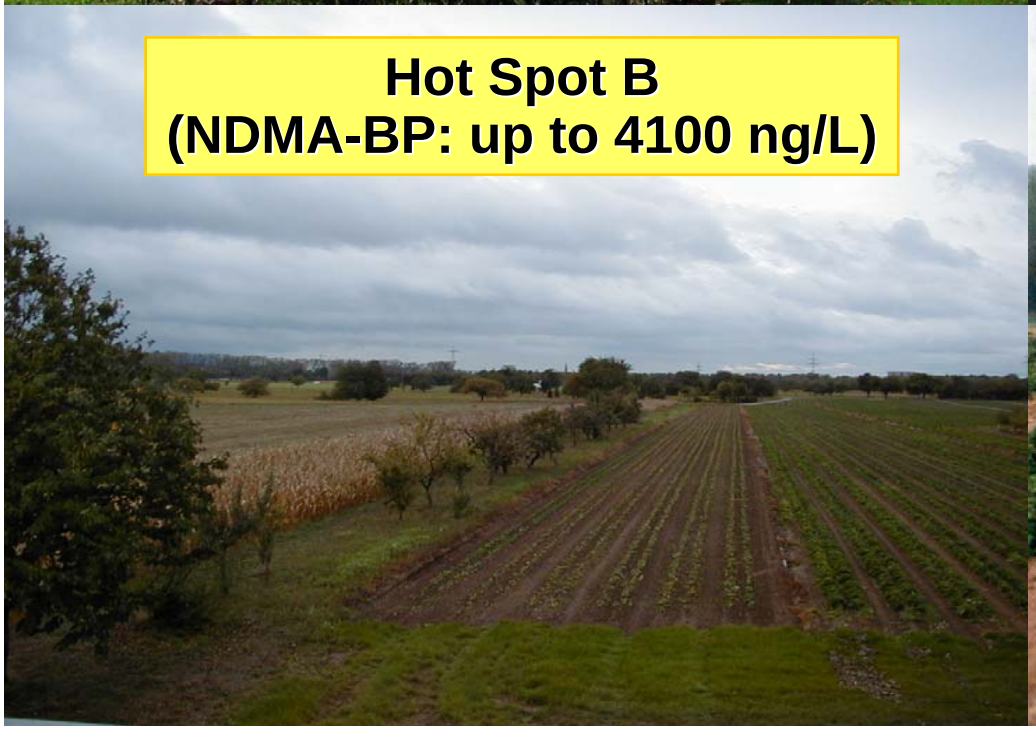
Another formation pathway discovered by TZW: NDMA formation during ozonation



- RW 1: 300 µg/L Mn, 16 µg/L Fe (strongly anoxic)
- RW 2: 3 µg/L Mn, 6 µg/L Fe (slightly anoxic)
- RW 3: aerob

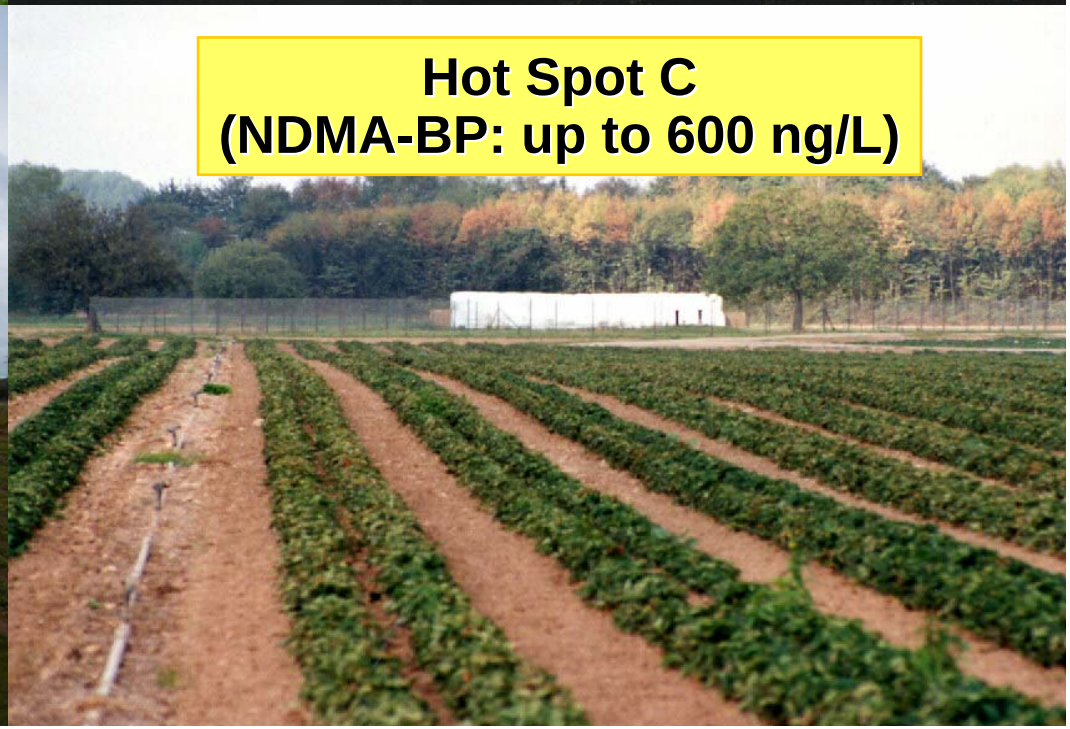
Hot Spot A
(NDMA-BP: up to 1700 ng/L)



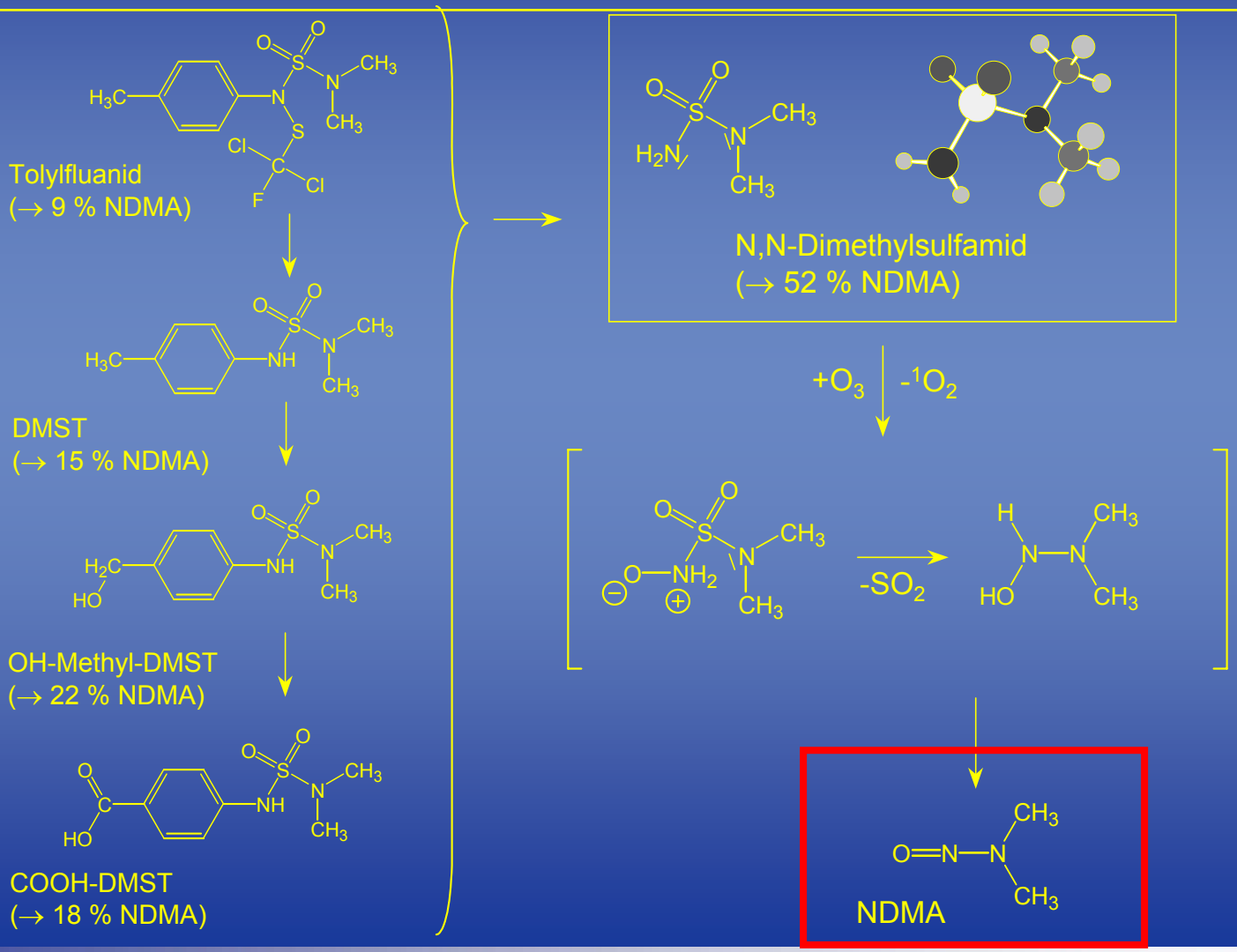


Hot Spot B
(NDMA-BP: up to 4100 ng/L)

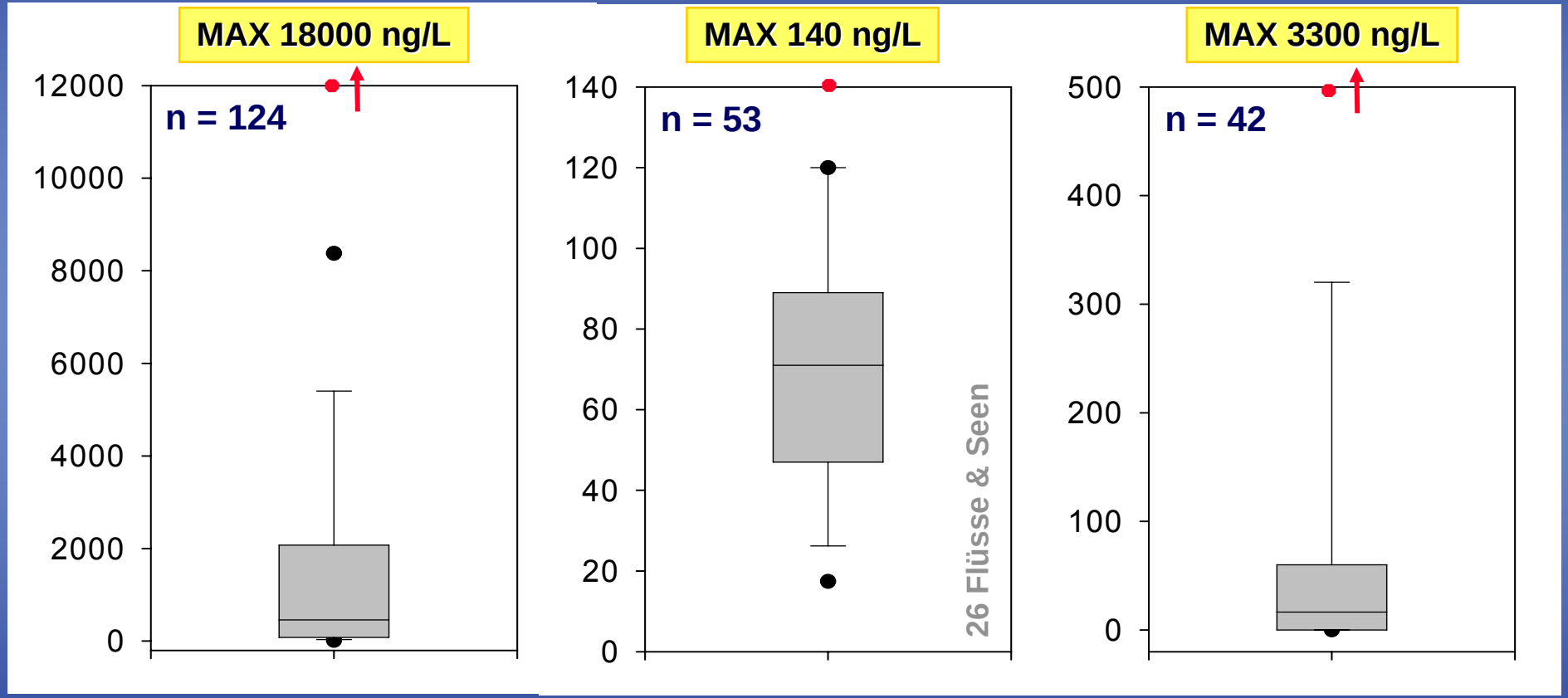
Hot Spot C
(NDMA-BP: up to 600 ng/L)



Formation of NDMA from dimethylsulfamide



Occurrence of Dimethylsulfamid (DMS) in the aquatic environment in Germany



Groundwater

median 460 ng/L

Rivers & Lakes

median 71 ng/L

Drinking Water

median 17 ng/L

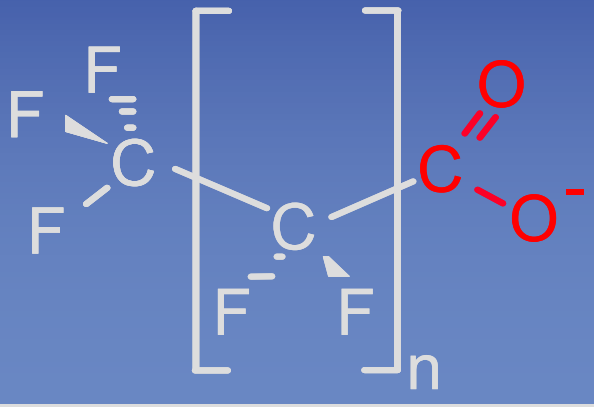
Relevance of nitrosamines

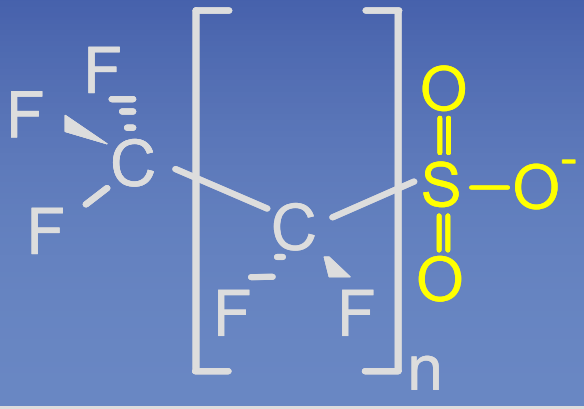
- Cancerogenic nitrosamines are by-products of chemical processes in industry and processing of food and consumer products
- Main nitrosamine pollutants in surface waters are NDMA and NMOR with typical concentrations in the low ng/L range
- At present, knowledge about occurrence of nitrosamines in European rivers and behaviour during drinking water treatment is scarce
- Due to their high toxicological relevance, nitrosamines should be regarded as priority pollutants


GUINNESS


SCOTCH
GARD

Structures of perfluorinated anionic surfactants





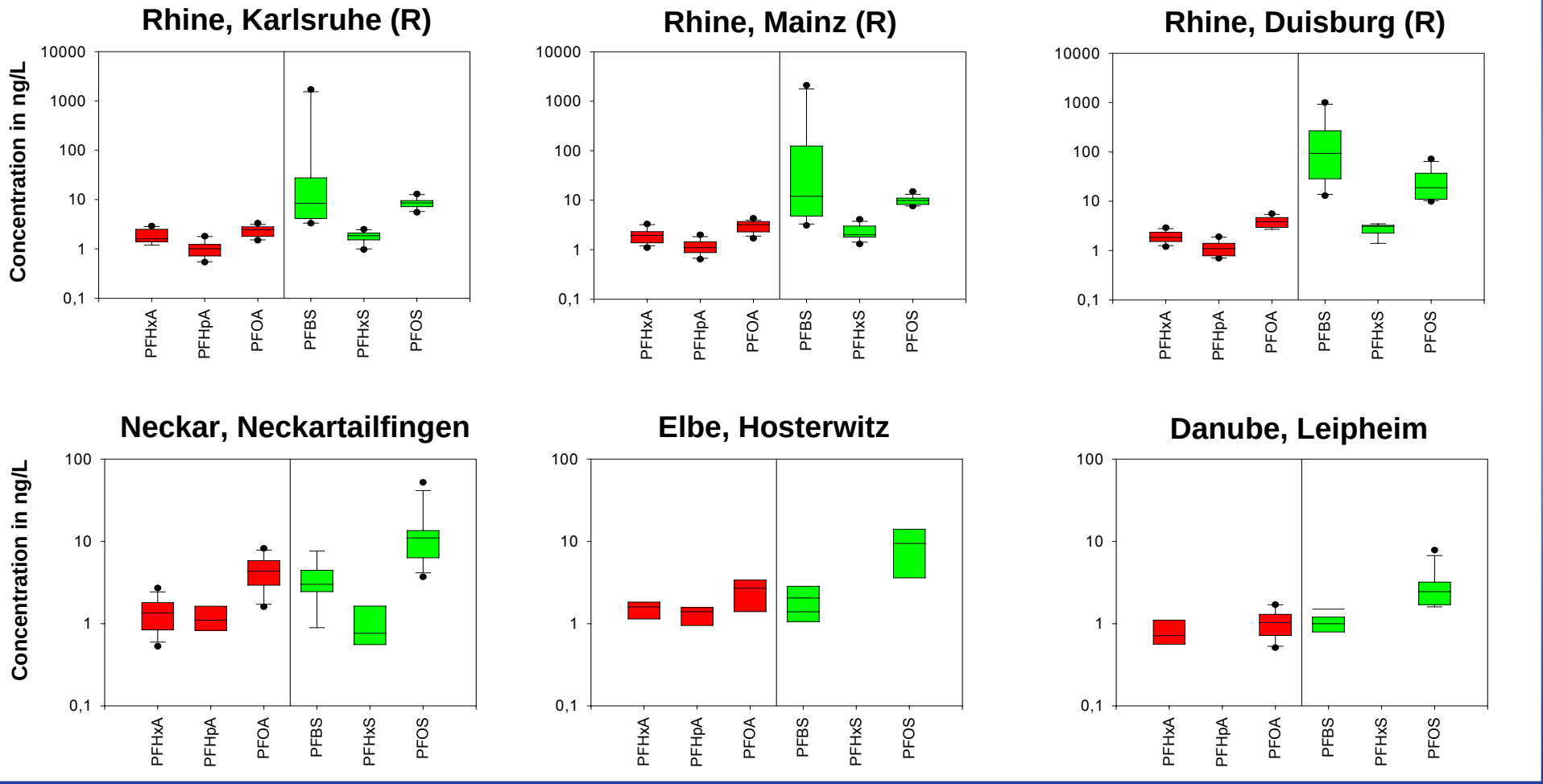
Perfluoroalkyl carboxylates

PFCA
C8 = PFOA
C4 = PFBA

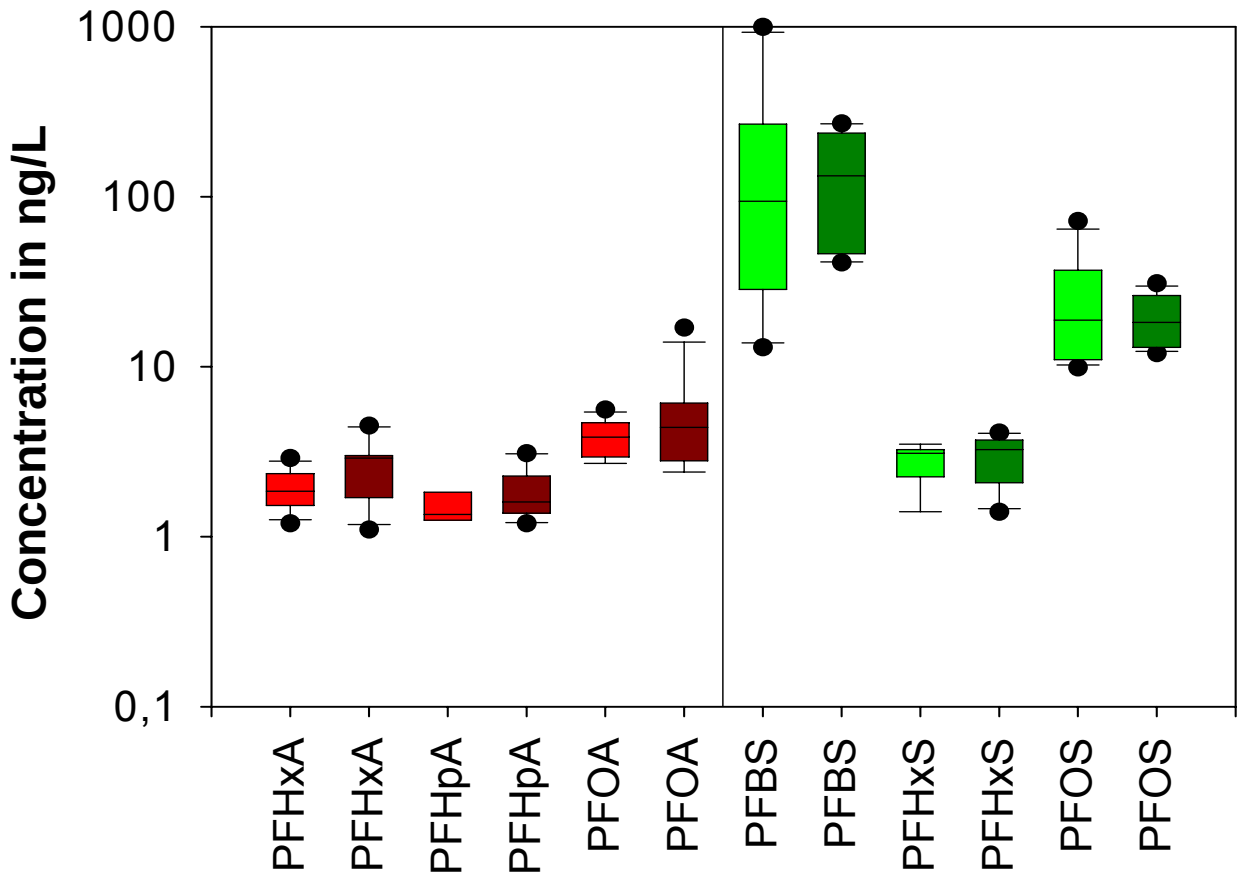
Perfluoroalkyl sulfonates

PFAS
C8 = PFOS
C4 = PFBS

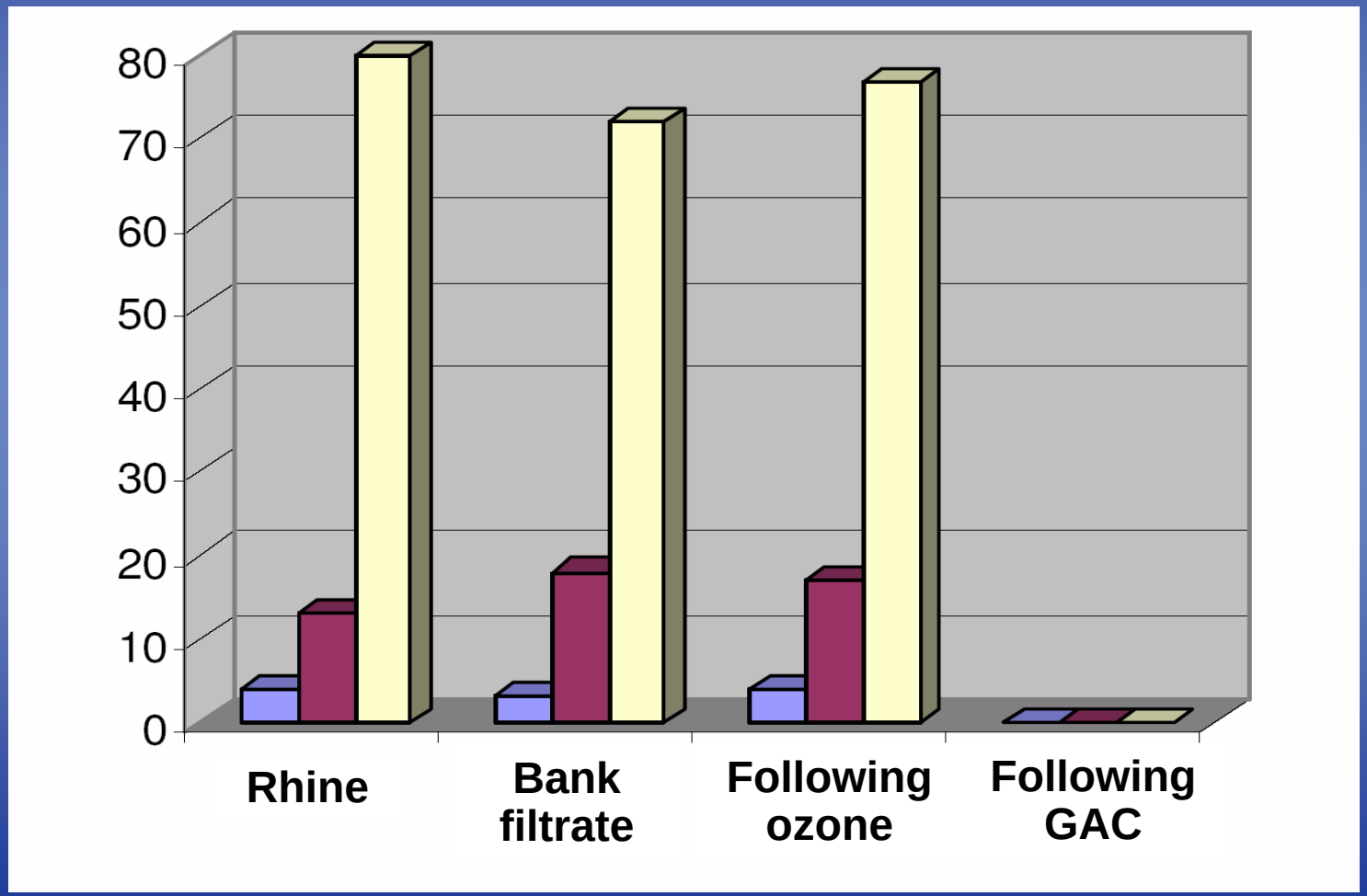
PFCA and PFAS in several German rivers in 2006



Behavior of PFCA und PFAS during bank filtration



Behavior of PFC in water treatment



Relevance of PFC

- **Due to persistency, bioaccumulation, toxicity and mobility: PFCA and PFAS are relevant to drinking water supplies**

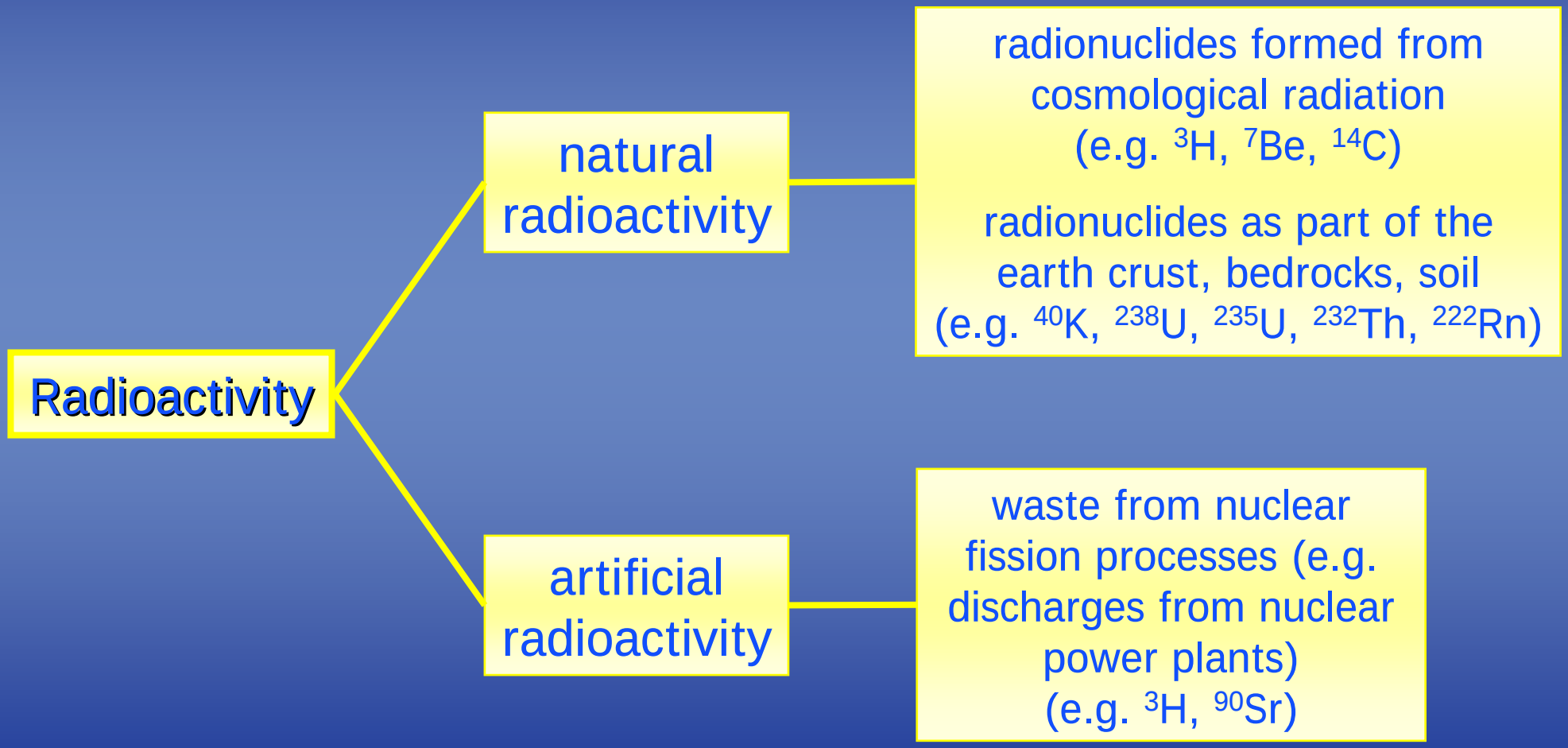
  The national situation is similar to global situation:

- **Diffuse background contaminations in surface waters typically lie in the single- to double-digit ng/L range for individual PFC.**
- **Spatial: „hot spots“ exist on a local/regional scale.**
- **Temporal: high short-term contaminations can occur.**
- **The concentrations found in hot spots or only sporadically are not representative for the general situation.**

Other emerging chemical threats

- pesticides (new pesticides, polar pesticides, metabolites)
- biocides
- algal toxins/cyanobacteria
- flame retardants
- complexing agents
- plasticizers/anti-oxidants
- fuel additives (MTBE/ETBE)
- fragrances
- ...

Radioactivity in European water resources



Radioactivity according to 98/83/EC

- Parametric values (Radioactivity is an indicator parameter):
  - Tritium (^{3}H): 100 Bq/L
  - Total indicative dose (excl. ^{3}H, ^{40}K, ^{234}Rn decay products): 0.1 mSv/year
- Monitoring:
  "A member state is not required to monitor drinking water for tritium or radioactivity to establish total indicative dose where it is satisfied that, on the basis of other monitoring carried out, the levels of tritium of the calculated total indicative dose are well below the parametric value..."
- Monitoring parameters:
  - gross alpha (total α activity)
  - gross beta (total β activity)
  - specific isotope monitoring if required

Survey in 22 European countries (by A. Hulsmann)

- Radioactivity occurs in some European waters
- Source waters are mainly affected by natural radioactivity
- Artificial radioactivity is of minor importance (few local exceptions)
- Exceedance of DWD level: mainly gross α followed by gross β
- Radioactivity can mainly be attributed to the occurrence of
  - Radon (^{234}Rn) and decay products
  - Radium (^{226}Ra, ^{224}Ra, ^{228}Ra)
  - Uranium (^{238}U, ^{234}U)
  - Lead (^{210}Pb)
- Most elements are only relevant on a regional scale (depending on the geological situation)

Conclusions

- An ever increasing number of chemicals is found in European water sources (mainly due to analytical improvements)
- Knowledge on effects and behaviour during drinking treatment of those compounds is limited
- In most cases, multi-barrier principle applied by water suppliers is able to cope with those chemical threats
- At the concentration levels found in drinking waters, no adverse health effects for humans are expected
- Problem for water suppliers: consumers‘ perception