Organic micropollutants in the framework of Water Directives

Dimitra Voutsa, Assistant Professor

Environmental Pollution Control Laboratory
Department of Chemistry
Aristotle University of Thessaloniki

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Organic chemicals in Europe

100,000 chemicals are registered in the European Inventory of Existing Commercial Substances before 1981
30,000 substances marketed in volumes above 1t/y
10,000 substances marketed in volumes above 10,000 t/y
3,800 new compounds came on the market since 1981

Organic micropollutants

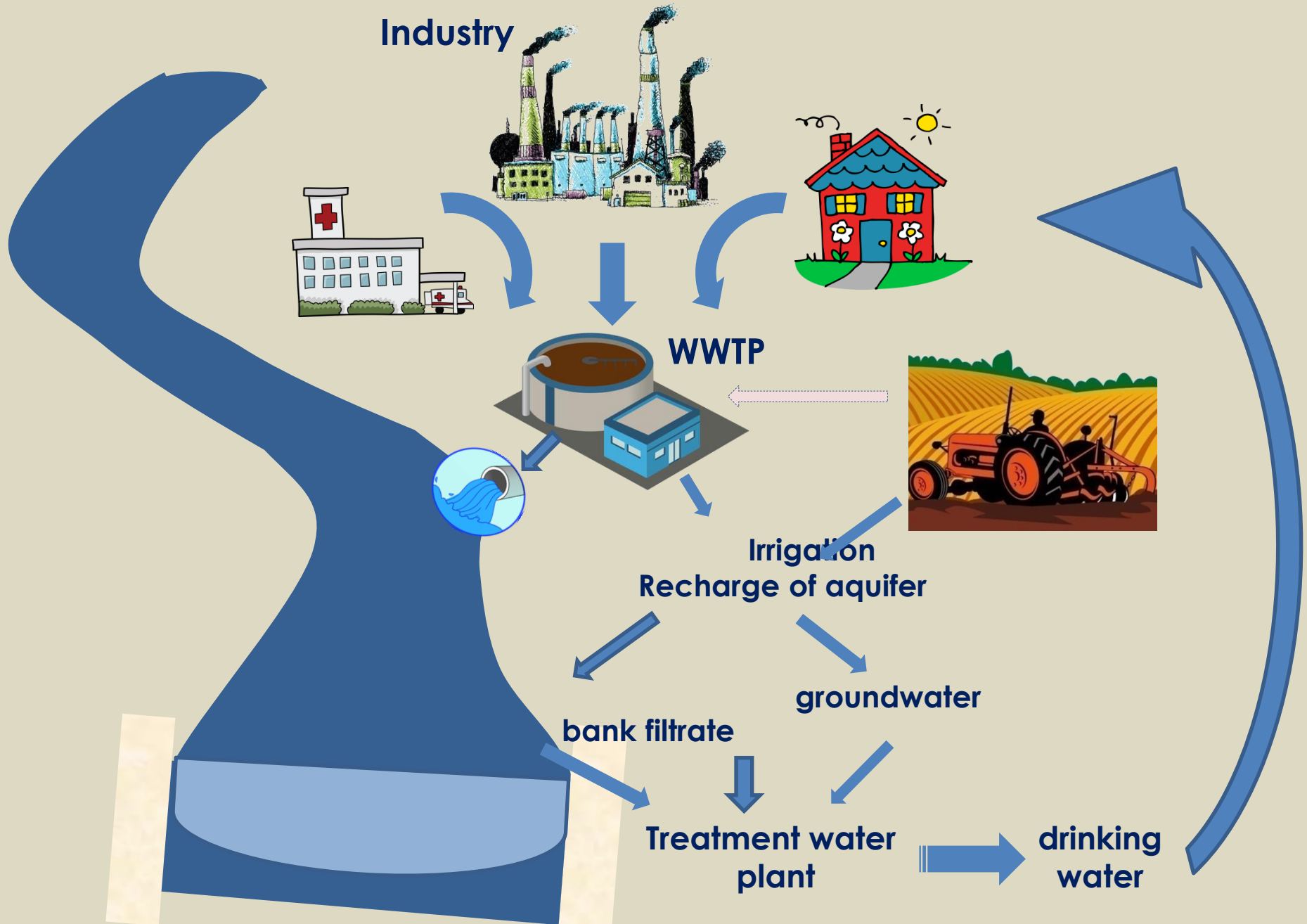
Compounds which are detected at the concentrations ≤ µg/L

Synthetic chemicals as well as natural substances

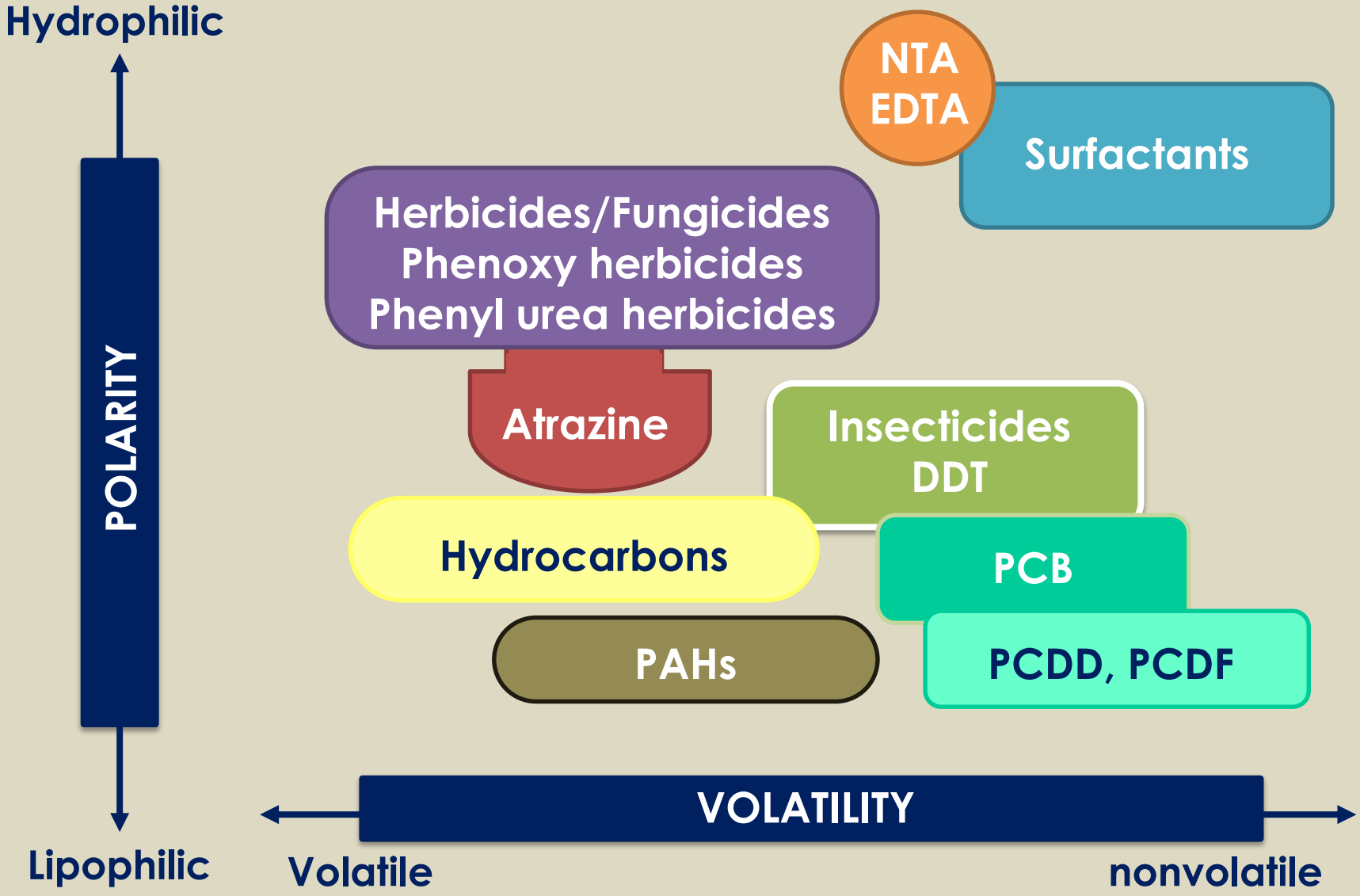
Sources of organic micropollutants

Source	Substance groups	Sources/Pathways
Urban activities	Personal Care products Pharmaceuticals Detergents, Biocides, Flame retardants Pesticides, Dyes	Wastewater Landfill sites
Agriculture	Pesticides (insecticides, herbicides, fungicides) Veterinary pharmaceuticals	Surface runoff Landfill sites
Industry	Industrial chemicals (polymers, dyes, varnishes, oxidants, reductants, detergents, biocides, corrosion inhibitors)	Wastewater Landfill sites
Traffic	Ingredients of motor oils, lubricants, combustion products	Surface runoff
Atmosphere	Combustion products, industrial chemicals	Wet and dry deposition

Organic micropollutants in water cycle

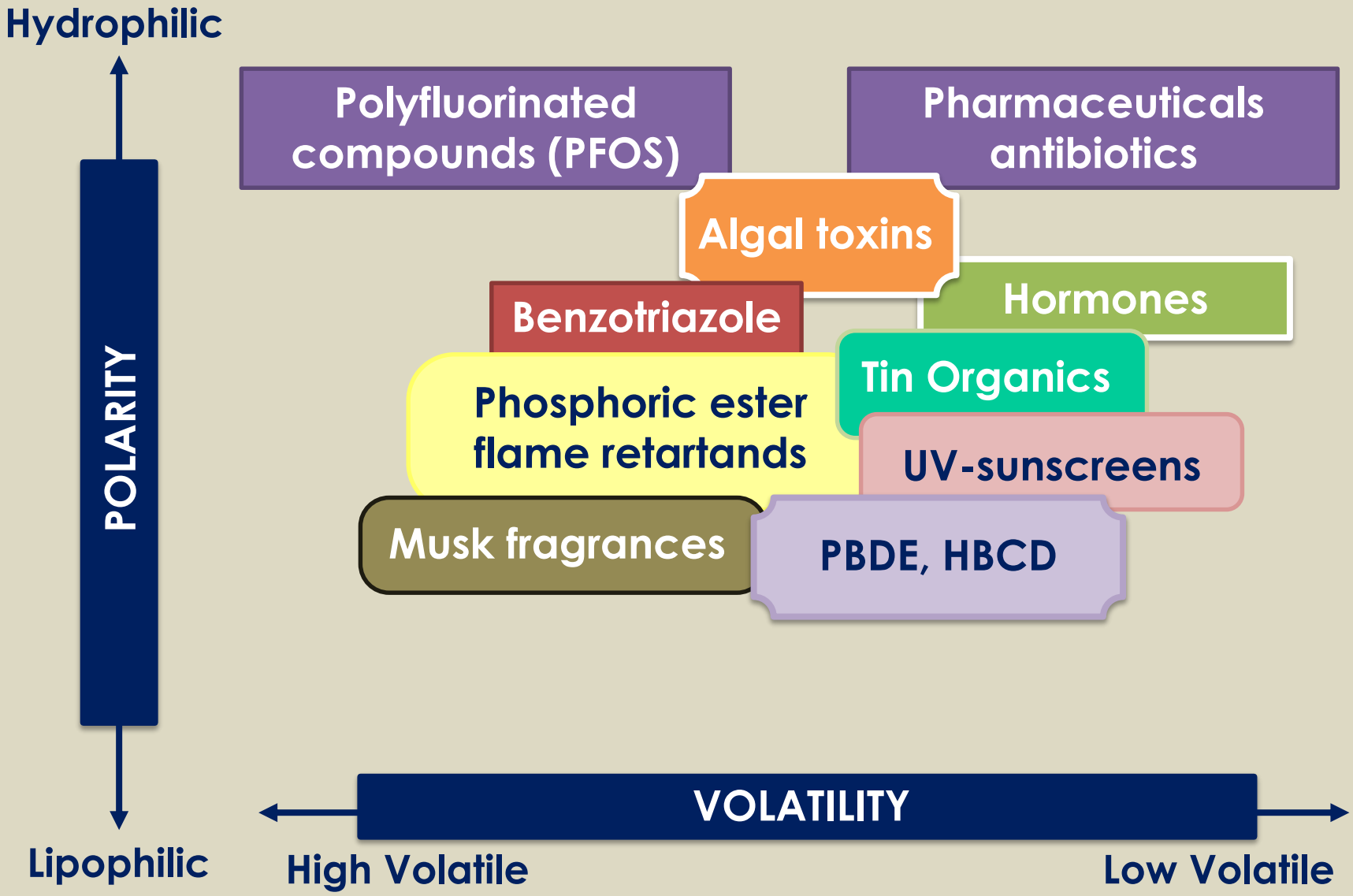


"Classic organic chemicals" detected in rivers



Giger, 2006

"Emerging" Contaminants in rivers

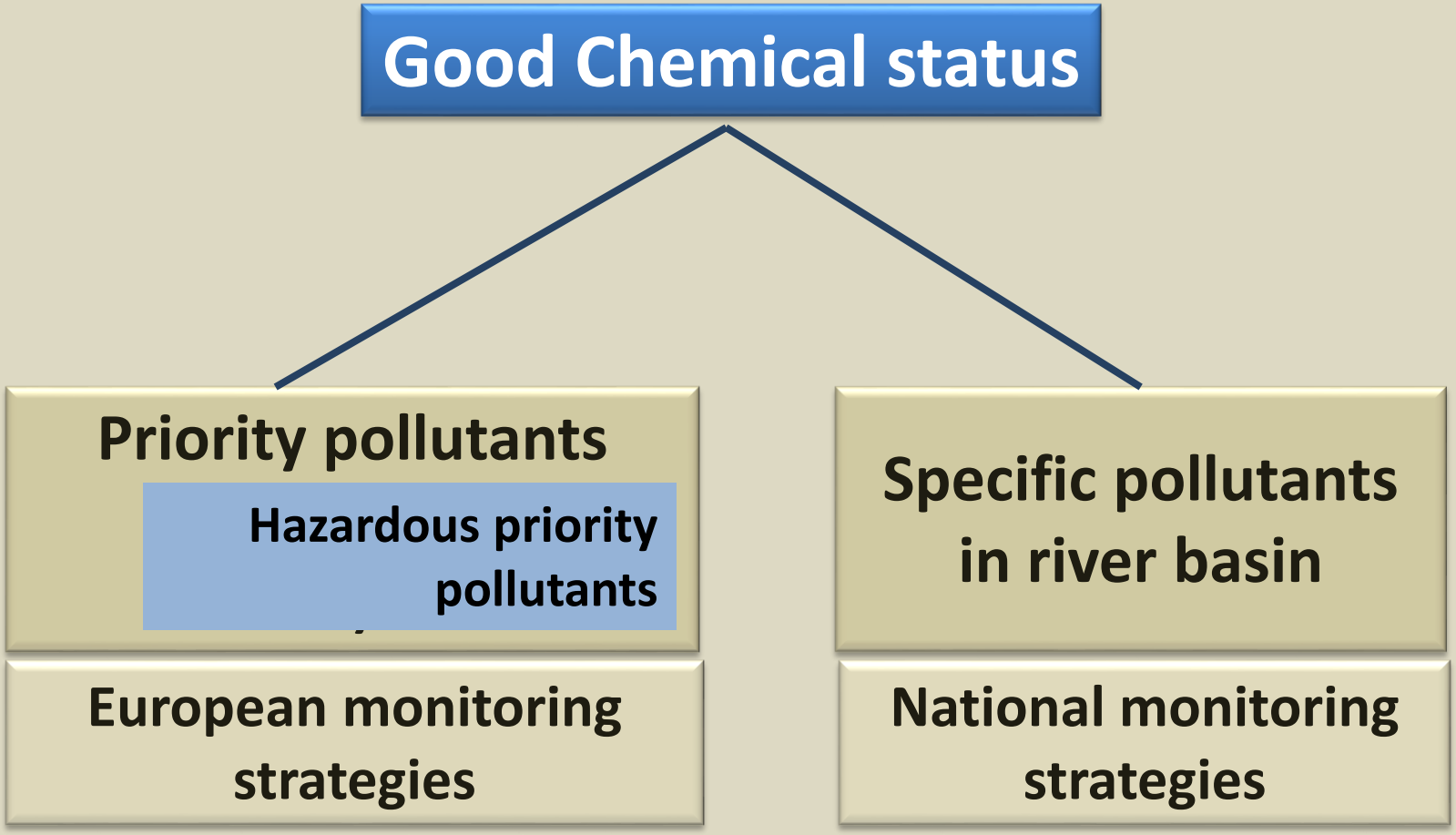


Ternes, 2006

Water Directives

Directive 2000/60/EC	**Water Framework Directive**
Decision No 455/2001/EC	**Establishing the list of priority substances**
Directive 2008/105/EC	**Environmental Quality Standards**
Directive 2009/90/EC	**Technical specifications for chemical analysis and monitoring of water status**
Directive 2013/39/EC	**Amending previous directives-priority substances**

Evaluation of chemical status



List of priority substances (2013/39/EC): 45 compounds

Priority Hazardous substances	Priority substances	Specific pollutants
Anthracene	Alachlor	DDT/p,p´-DDT
Brominated diphenylethers	Atrazine	Aldrin
Cadmium and its compounds	Benzene	Dieldrin
C10-C13-Chloroalkanes	Chlorfenvinphos	Endrin
Di(2-ethylhexyl)phthalate (DEHP)	Chlorpyrifos (ethyl)	Isodrin
Endosulfan	1,2-Dichloroethane	Carbon tetrachloride
Hexachlorobenzene (HCB)	Dichloromethane	Tetrachloroethylene
Hexachlorobutadiene (HCBD)	Diuron	Trichloroethylene
Hexachlorocyclohexane	Fluoranthene	
Mercury and its compounds	Isoproturon	
Nonylphenols	Lead and its compounds	
Pentachlorobenzene	Naphthalene	
Polyaromatic Hydrocarbons (PAHs)	Nickel and its compounds	
Tributyltin compounds	Octylphenols	
Trifluralin	Pentachlorophenol	
Dicofol	Simazine	
Perfluorooctane (PFOS)	Trichlorobenzenes	
Quinoxyfen	Tricholoromethane	
Dioxins-dioxin-like compounds	Aclonifen	
Haxabromocyclododecanes (HBDD)	Bifenox	
Heptachlor, heptachlor epoxide	Cypermethrin	
	Dichlorvos	

Environmental Quality Standards (2008/105/EC and 2013/39/EC)

Good chemical status

Priority substances– EQS

Annual average concentrations ≤ AA- EQS

Maximum allowable concentrations ≤ MAC-EQS

Specific river basin pollutants–national EQS

Performance criteria of analytical methods (2009/90/EC)

Limit of Quantification LOQ	≤	30% EQS
Uncertainty of measurement	≤	50%

Experience from the implementation of Directives

- **Many compounds have to be monitored-High cost**
- **Need for methods with very low quantification limits**

ie Heptachlor/epoxide EQS 0.2 pg/L (surface water) 10 fg/L (coastal waters)

- **Representative sampling design due to temporal variation of micropollutants**

Difficulties-problems in chemical characterization

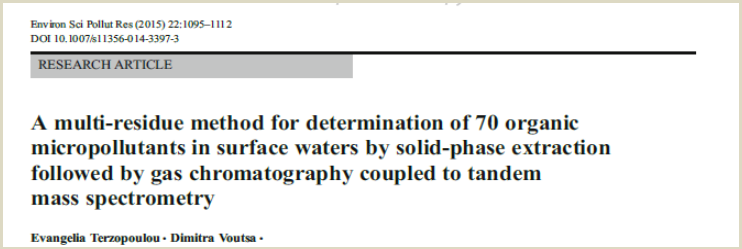
- Missing data for priority pollutants
- Method quality characteristics did not reported
- Method quality characteristics did not always fulfilled the proposed performance criteria
- Insufficient spatial or temporal coverage of measurements

Development of analytical method

- Multi-residue method based on gas chromatography-tandem mass spectrometry
- Determination of 70 organic micropollutants from various classes
- Validation according to the monitoring performance criteria -guidelines on quality assurance/quality control
- The method was applied in the basin of Strymonas River

PhD Thesis of E. Terzopoulou

Article, Terzopoulou et al., 2015


Environ Sci Pollut Res (2015) 22:1095–1112
DOI 10.1007/s11356-014-3397-3

RESEARCH ARTICLE

A multi-residue method for determination of 70 organic micropollutants in surface waters by solid-phase extraction followed by gas chromatography coupled to tandem mass spectrometry

Evangelia Terzopoulou · Dimitra Voutsa ·

70 organic micropollutants

Organochlorine compound- Chlorinated pesticides (a-HCH, b-HCH, lindane, d-HCH, heptachlor, heptachlor epoxide, endosulfan I, endosulfan II, endosulfan sulfate, aldrin, dieldrin, endrin, endrin aldeyde, p,p-DDE, p,p-DDD, p,p-DDT, methoxychlor, 4-chloro-o-tolyoxyacetic acid, mecoprop, dalapon, dichlorprop, dinoseb, dicamba, 2,4-D, silvex, alachlor, metolachlor)

Triazine pesticides (atraton, terbuthylazine, propazine, atrazine, simazine, prometryne, ametryne, simetryn, terbutryne)

Organophosphorus pesticides (fenthion, chlorfenviphos, chlorpyrifos)

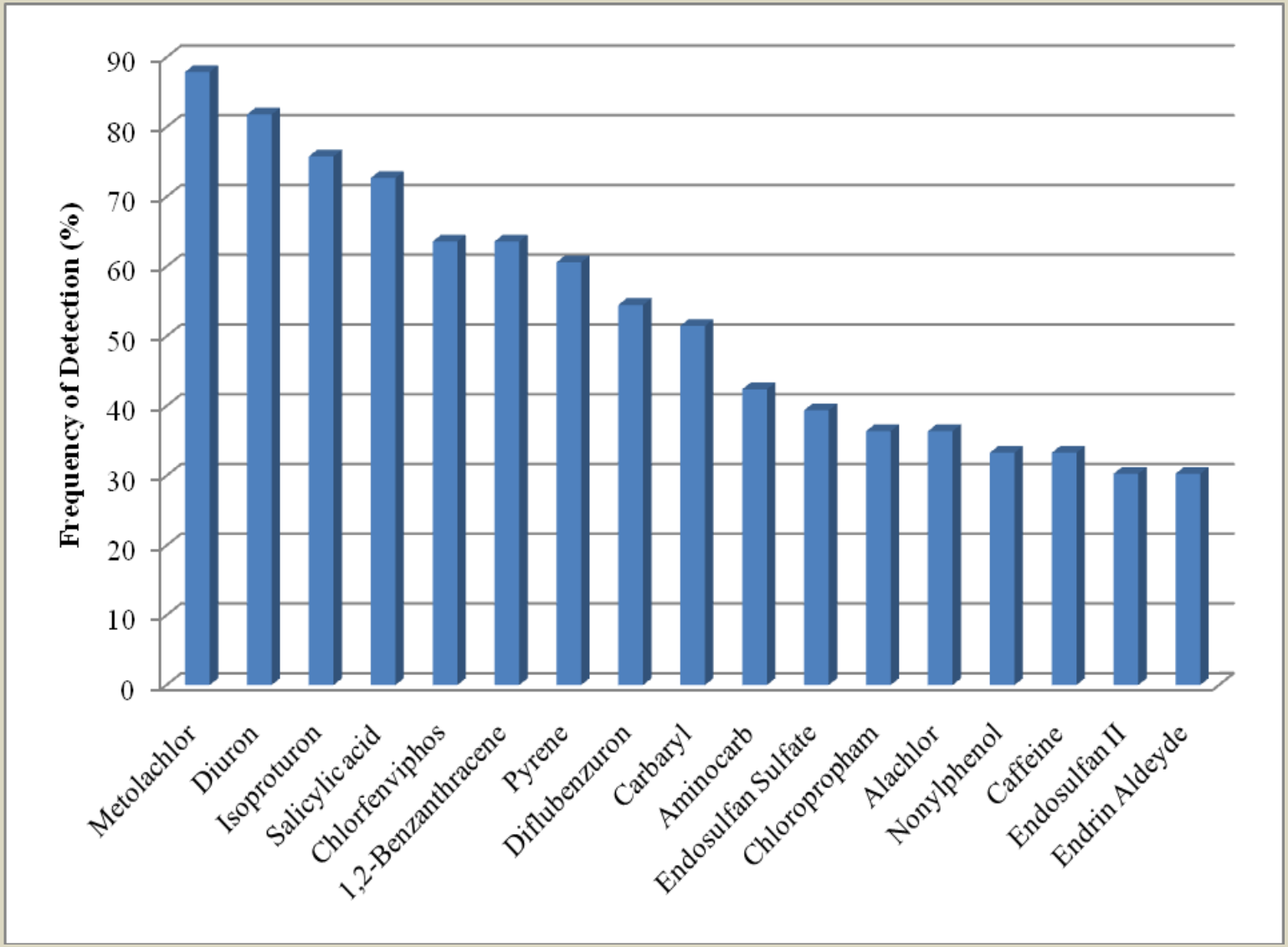
Carbamate & urea pesticides (swep, aminocarb, carbaryl, methiocarb, chloropropham, carbofuran, diuron, isoproturon, diflubenzuron)

PAHs (acenapthylene, fluorene, anthracene, phenanthrene, pyrene, 1-2,benzanthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene)

PCBs (PCB28, PCB52, PCB101, BPC138, PCB153, PCB180)

Other compounds: 1H-benzotriazole, salicylic acid, nitrophenol, 4-tert-octylphenol caffeine, nonylphenol, bishpenol A

Frequency of detection



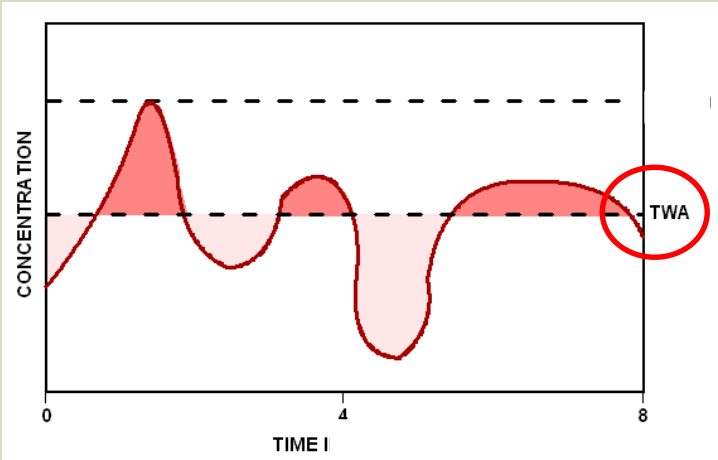
Passive sampling (an alternative tool)

- **Exposure of passive samplers devices over 2-4 weeks**
- **Accumulation and preconcentration of micropollutants**

This enables

- **improvement of limits of quantification (LOQ)**
- **integrate assessment of chemical status-**

time-weighted average concentrations (TWA)



Passive sampling

- **Recommended in the EC Guidance Document on surface water monitoring**

- **Recommended in Directive 2013/39/EC as complementary method to improve the level of confidence in water monitoring in comparison to spot sampling**

- **Could be used in conjunction with investigating monitoring as risk-based screening tool to**

a) evaluate the presence or absence of chemical compounds
b) identify pollution sources
c) estimate dissolved water concentrations
d) assess the exposure of biota to contaminants

Types of passive samplers

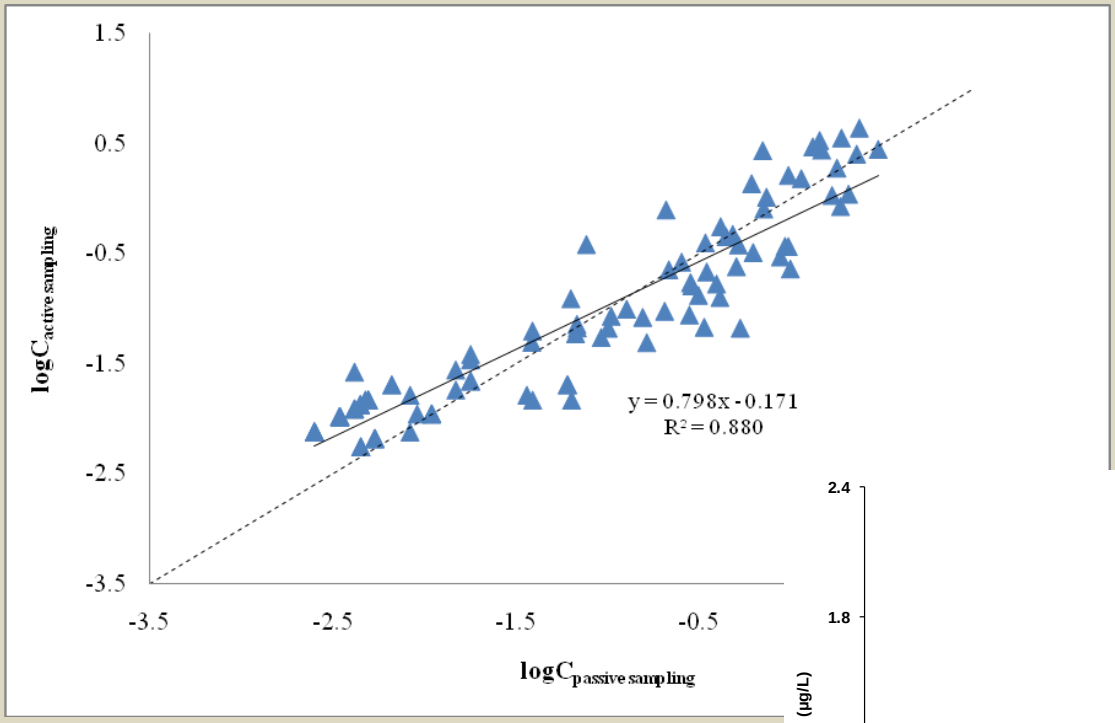
SPMDs: Hydrophobic compounds

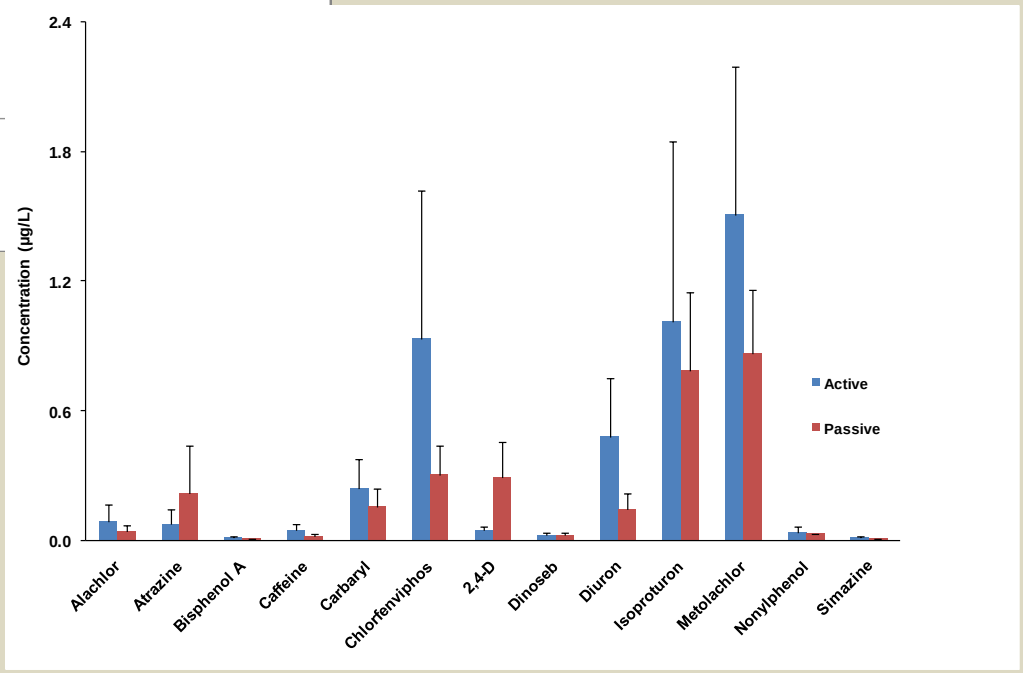
POCIS: Hydrophilic compounds

POCIs

Exposure for two weeks

Correlation between active & passive sampling





Passive sampling in Strymonas basin

- More compounds were detected by passive samplers
- Comparable data between active and passive sampling for polar compounds
- Describe satisfactory the exposure of organisms to hydrophobic compounds

- Passive sampling could be an additional tool for investigating monitoring and operational monitoring

- An extensive survey is needed to fully evaluate the efficiency of passive samplers under different conditions


Thank you