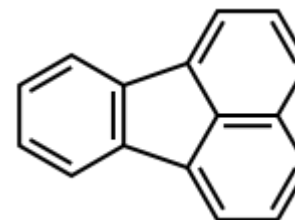
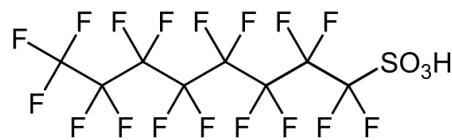
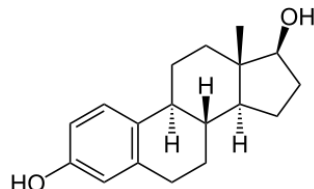
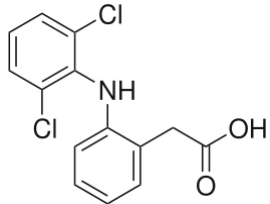
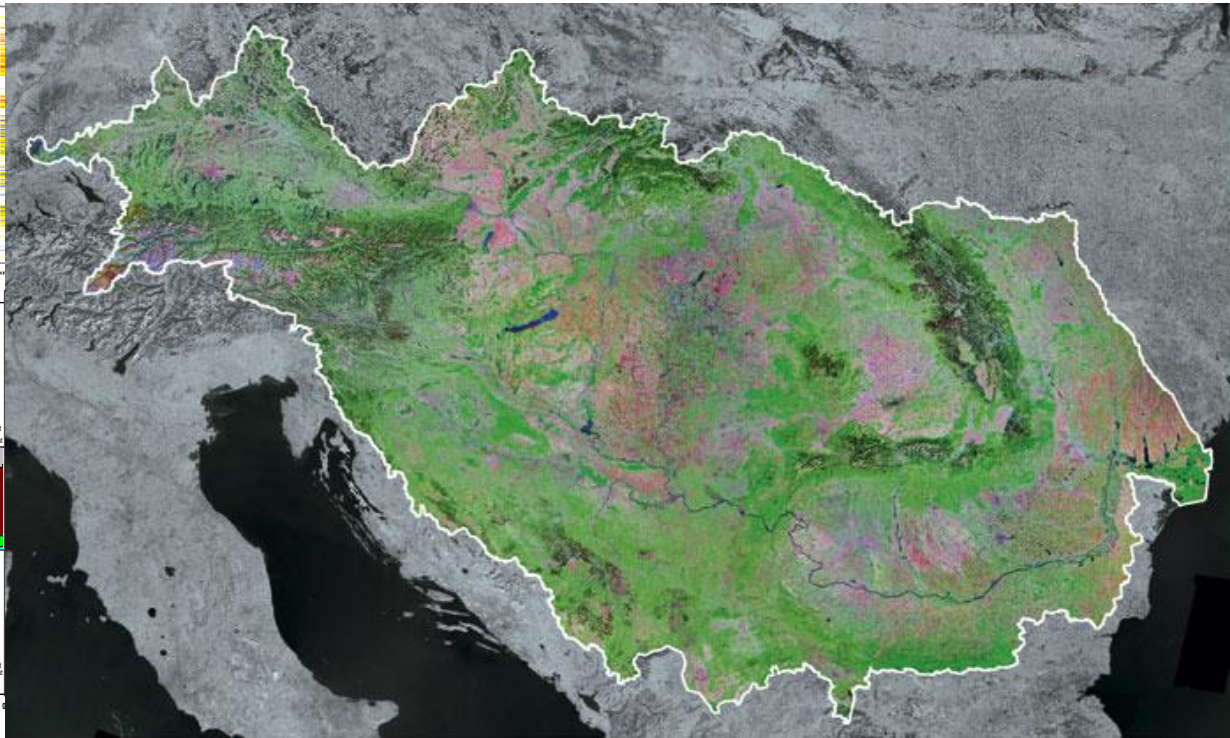
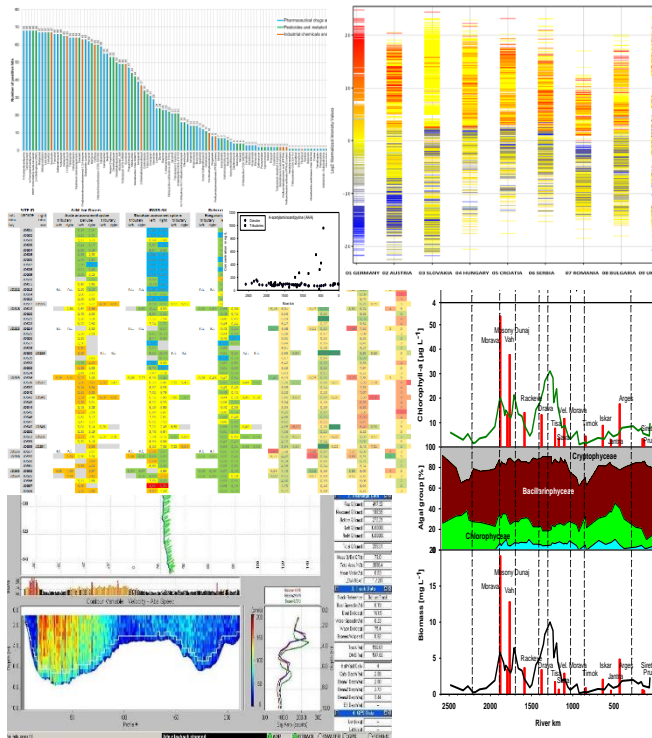


# Hazardous substances pollution in the Danube River Basin



Ivan Zavadsky

ICPDR



# Danube River Basin

International Commission  
for the Protection  
of the Danube River

Internationale Kommission  
zum Schutz der Donau



800 000 km<sup>2</sup>, 2900 km, 6500 m<sup>3</sup>/s, >85 M inhabitants, **19 countries**



# From Black Forest to Black Sea



**Large variety** of micro-climates, ecosystems, socio-economic status

# Human activities and their impact on the Danube

**ICPDR** IKSD

International Commission  
for the Protection  
of the Danube River

Internationale Kommission  
zum Schutz der Donau



Water **pollution**, **hydromorphological** alterations



# The DRPC as the legal mandate of the ICPDR

**ICPDR** IKSD

International Commission  
for the Protection  
of the Danube River

Internationale Kommission  
zum Schutz der Donau



Sustainable & equitable  
use of water



Protection of water &  
ecological resources



Reduce nutrients &  
hazardous substances



Manage floods  
& ice hazards

**ICPDR**: platform for **transboundary cooperation** on water management:

- Implementation of the **DRPC**(1998)
- Coordination of the implementation of EU **Water Framework** Directive (2000) & EU **Floods** Directive (2007)

# ICPDR

## Contracting Parties



**Germany**



**Austria**



**Czech Republic**



**Slovakia**



**Hungary**



**Slovenia**



**Croatia**



**Bosnia & Herzegovina**



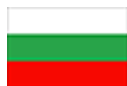
**Serbia**



**Montenegro**



**Romania**



**Bulgaria**



**Rep. of Moldova**



**Ukraine**



**European Union**

– EU Member States (9)

– Non-EU Member States (5)

---

# Managing hazardous substances

- ✓ The ICPDR's basin-wide vision for hazardous substances pollution is no risk or threat to human health and the aquatic ecosystem of the waters in the Danube River Basin District and Black Sea waters impacted by the Danube River discharge;
- ✓ Monitoring activities – TNMN (MA EG);
- ✓ Emission inventories / measures (PM EG).

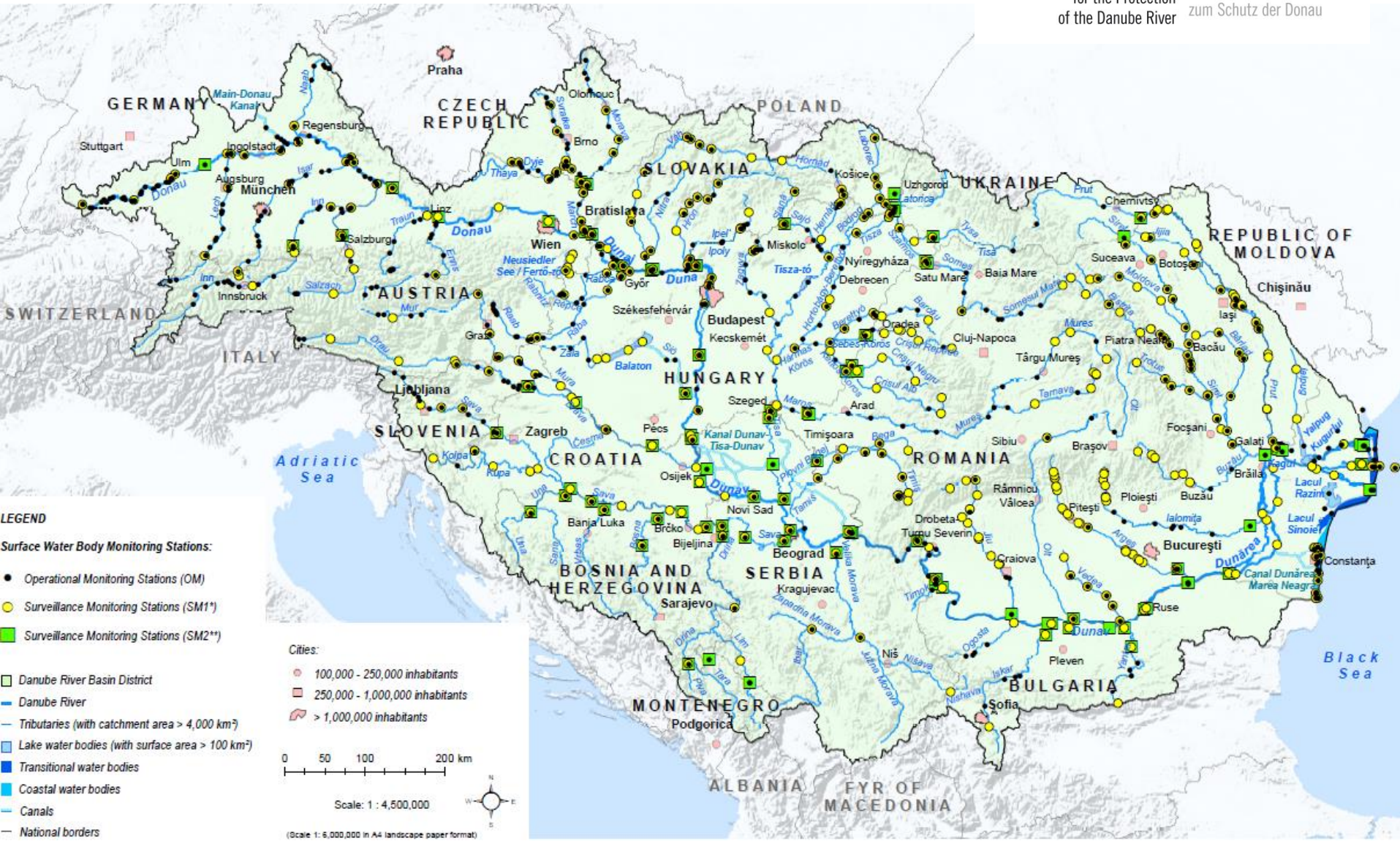


# Trans National Monitoring Network – TNMN

**ICPDR** IKSD

International Commission  
for the Protection  
of the Danube River

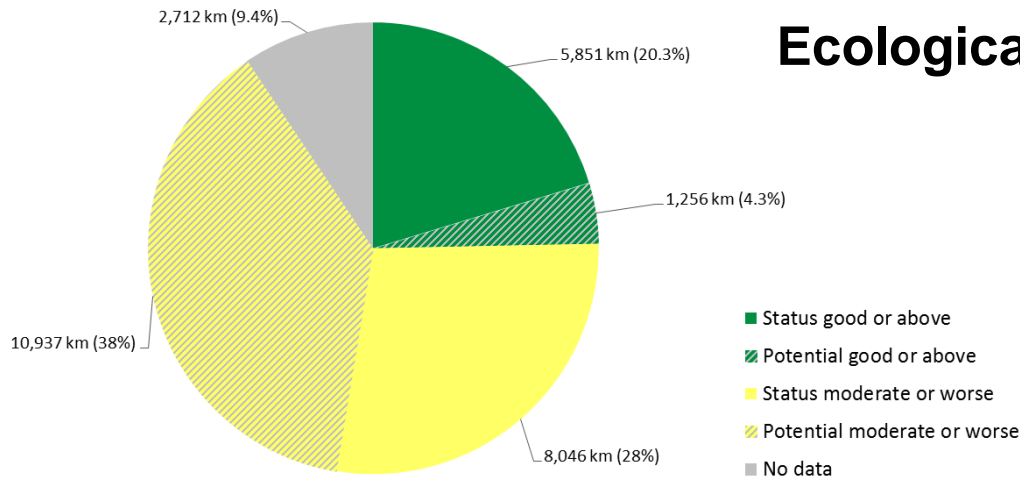
Internationale Kommission  
zum Schutz der Donau



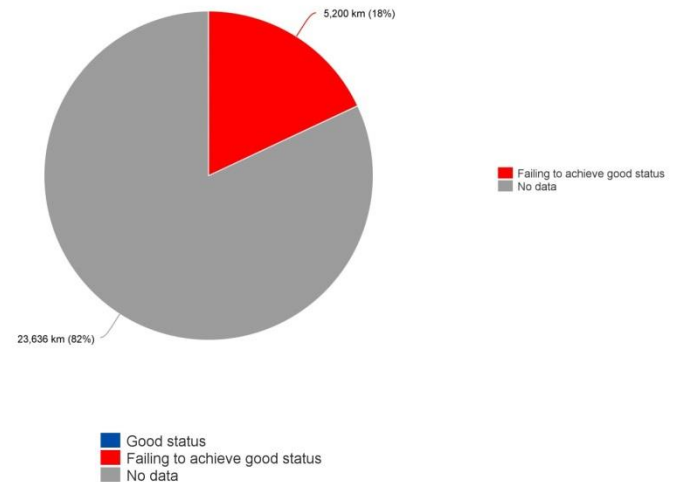


# Ecological & chemical status of surface waters (2015)

**Ecological status: ~ 25% good or above**



**Mercury in biota**



**Chemical status: ~ 70% good**  
\*excluding mercury in biota



In case of Czech Republic information on mercury in biota is also included in the chemical status presented on this map.

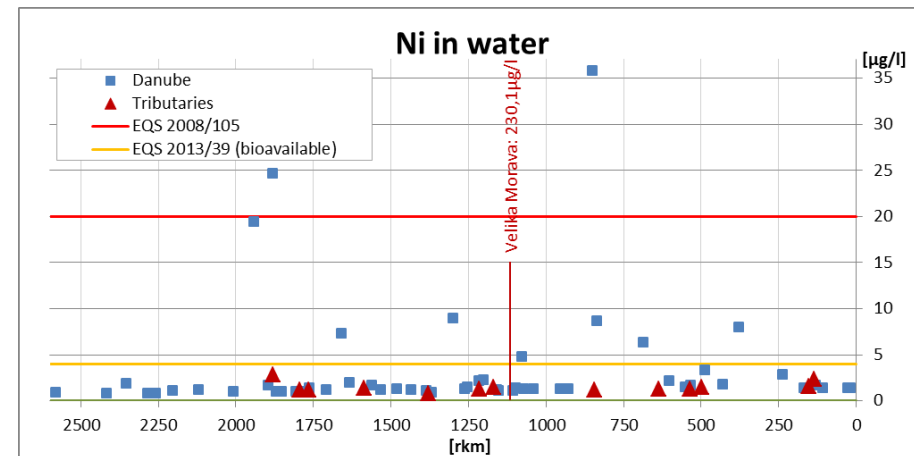
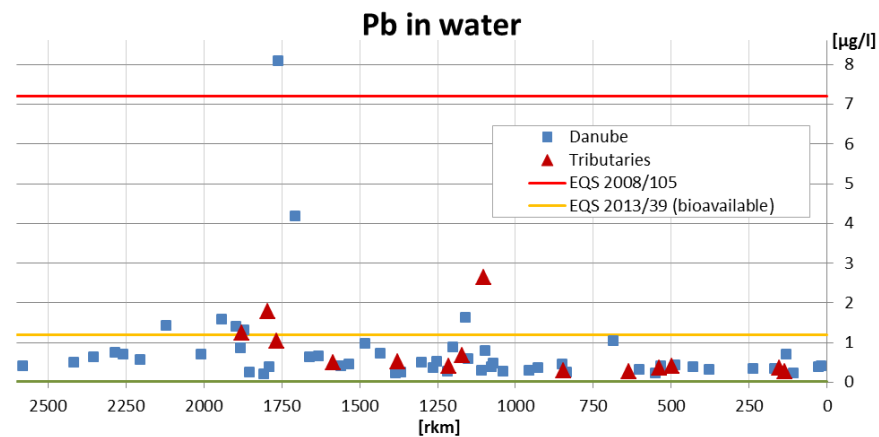
This ICOPDR product is based on national information provided by the Contracting Parties to the ICOPDR (AT, BA, BG, CZ, DE, HR, HU, ME, MD, RO, RS, SI, SK, UA) and CH. EuroGlobalMap data from EuroGeographics was used for all national borders except for AL, BA, ME where the data from the ESRI World Countries was used; Shuttle Radar Topography Mission (SRTM) from USGS Seamless Data Distribution System was used as elevation data layer; data from the European Commission (Joint Research Center) was used for the outer border of the DRBM of AL, IT, ME and PL.





# JDS3: Metals

- ⇒ Contents of metals in water, SPM and bottom sediments were similar to those observed during JDS1 and JDS2;
- ⇒ WFD EQS in water were exceeded occasionally for Ni & Pb;
- ⇒ In sediment the DE targets for metals were with one exception (Cu at JDS48) met at all sites for all elements;
- ⇒ Concentrations of Hg in all analysed fish samples exceeded the EQS significantly.





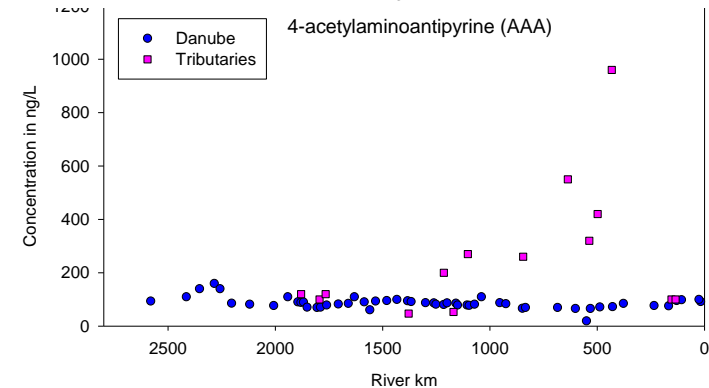
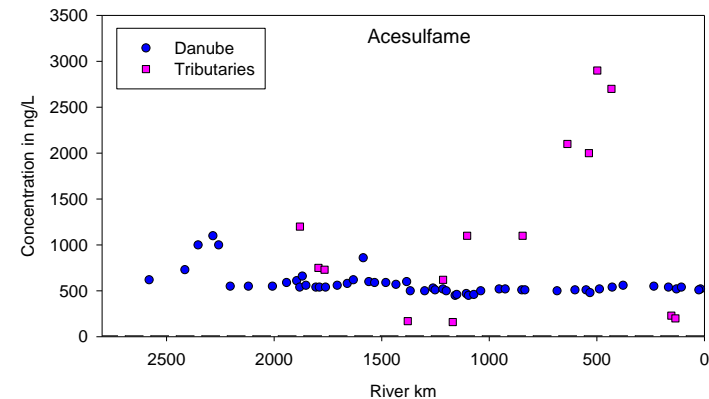
# JDS3: Organics – WFD PS

- ⇒ Most of the analysed WFD Priority Substances were found below the newly set EQS;
- ⇒ Concentrations of PFOS exceeded EQS at 94% of the sampling sites;
- ⇒ For PAH and tributyl-tin the AA-EQS for water was exceeded only at few sampling sites;
- ⇒ DEHP in water was present in all samples significantly below the AA-EQS;
- ⇒ For the first time C10-C13-chloroalkanes were analyzed, all concentrations in water were below the AA-EQS;



# JDS3: Emerging substances

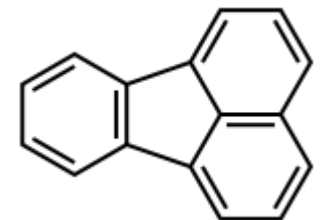
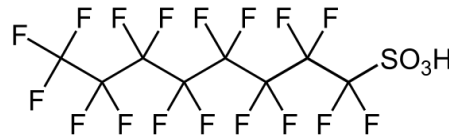
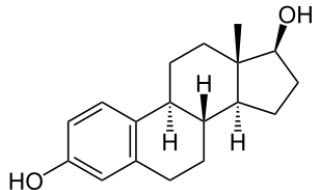
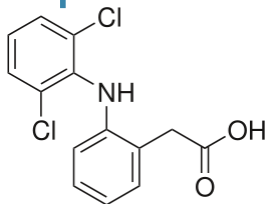
- ⇒ Large number of emerging polar organic substances was found but they were at very small concentrations;
- ⇒ Concentrations for most of the contaminants were lower in 2013 compared to JDS2 in 2007;
- ⇒ Pharmaceuticals mostly < 40 ng/l;
- ⇒ Elevated concentrations: metamizol metabolites FAA and AAA, artificial sweeteners acesulfame, cyclamate and sucralose, metformin, enalapril, triphenylphosphin oxide, iodinated X-ray contrast media, benzotriazoles, and the stimulant caffeine.





# RBSP prioritization

- ⇒ Prioritization methodology developed by NORMAN network produced a list of 22 substances suggested as relevant for the DRB based on the results of the JDS3 target screening of 654 substances in the Danube water samples by 13 laboratories;
- ⇒ PNEC values were available for 189 out of 277 JDS3 substances actually determined in the samples;
- ⇒ The list contains five WFD priority substances (three PAHs, fluoranthene and PFOS) and two EU Watch List candidate compounds (17beta-estradiol, diclofenac).



# RBSP prioritization 2015

**Table 96: Results of the prioritisation of pollutants determined in the JDS3 surface water samples**

No.	Substance	CAS No.	No. of sites substance detected	C <sub>max</sub> <sup>1</sup>	MEC <sub>95</sub> <sup>2</sup>	Lowest PNEC/EQS	Key study	Type	EoE <sup>3</sup>	EoE score	FoE <sup>4</sup>	Final score
1	2,4-Dinitrophenol (DNP)	51-28-5	68	0.06	0.04	0.001	RIVM 2014	EQS chronic water <sup>5</sup>	40	0.2	1.00	1.20
2	PFOS (Perfluorooctanesulfonate)	1763-23-1	63	0.026	0.02	0.00065	EU 2013	EQS chronic water <sup>5</sup>	31	0.2	0.93	1.13
3	Chloroxuron	1982-47-4	65	0.04	0.02	0.0024	James et al. 2009	PNEC acute	8.3	0.1	0.93	1.03
4	Desethylterbutylazine	30125-63-4	54	0.028	0.01	0.0024	RIVM 2014	EQS chronic water <sup>5</sup>	4.2	0.1	0.79	0.89
5	2-hydroxy atrazine	2163-68-0	53	0.06	0.02	0.002	EcoStat 2013	EQS chronic water <sup>5</sup>	10	0.1	0.76	0.86
6	Bromacil	314-40-9	31	0.19	0.14	0.01	INERIS 2013	EQS chronic water <sup>5</sup>	14	0.2	0.46	0.66
7	Dimefuron	34205-21-5	58	0.041	0.04	0.008	Oekotoxzentrum 2014	EQS chronic water <sup>5</sup>	5.0	0.1	0.56	0.66
8	Bisphenol A	80-05-7	30	1.94	1.03	0.1	Nendza 2003	EQS chronic water <sup>5</sup>	10	0.2	0.16	0.36
9	Benzo(g,h,i)perylene	191-24-2	65	0.029	0.003	0.002	CEC 2008	EQS chronic water <sup>5</sup>	1.5	0.1	0.26	0.36
10	Diazinon	333-41-5	21	0.009	0.01	0.001	Management Team PPDB 2009	PNEC acute	10	0.1	0.12	0.22
11	Indeno(1,2,3-c,d)pyrene	193-39-5	15	0.005		0.002	CEC 2008	EQS chronic water <sup>5</sup>			0.19	0.19
12	Linuron	330-55-2	32	1.42	1.12	0.26	Oekotoxzentrum 2014	EQS chronic water <sup>5</sup>	4.3	0.1	0.07	0.17
13	Amoxicillin	26787-78-0	33	0.28	0.08	0.078	van der Aa et al. 2011	PNEC chronic	1.0	0.1	0.03	0.13
14	Metazachlor	67129-08-2	30	0.03	0.02	0.019	INERIS 2014	EQS chronic water <sup>5</sup>	1.1	0.1	0.03	0.13
15	17beta-estradiol	50-28-2	8	0.029		0.0004	CEC 2011	EQS chronic water <sup>5</sup>			0.12	0.12
16	Benzo(a)pyrene	50-32-8	3	0.002		0.00017	EU 2013	EQS chronic water <sup>5</sup>			0.04	0.04
17	Diclofenac	15307-79-6	51	0.318	0.036	0.05	Oekotoxzentrum 2014	EQS chronic water <sup>5</sup>			0.04	0.04
18	Bentazon	25057-89-0	61	0.1	0.02	0.06	USEPA 2008	PNEC acute			0.01	0.01
19	Fipronil	120068-37-3	1	0.02		0.012	EU 2011	EQS chronic water <sup>5</sup>			0.01	0.01
20	Fluoranthene	206-44-0	58	0.02	0.006	0.0063	EU 2013	EQS chronic water <sup>5</sup>			0.01	0.01

<sup>1</sup> C<sub>max</sub> – Maximum concentration in µg/L reported in case the substance has been measured by several JDS3 laboratories

<sup>2</sup> MEC<sub>95</sub> – 95<sup>th</sup> percentile of the Maximum Environmental Concentration in µg/L; calculated only if the substance has been found above LOQ at minimum 20 sites

<sup>3</sup> EoE – Extent of Exceedance

<sup>4</sup> FoE – Frequency of Exceedance

<sup>5</sup> Equal to Annual Average EQS (AA-EQS)



# Sampling WWTP effluents for hazardous substances analyses

2017-2018



ICPDR  
UFZ Leipzig, Germany  
Environmental Institute,  
Koš, Slovakia  
Federal Environment  
Agency, Vienna, Austria

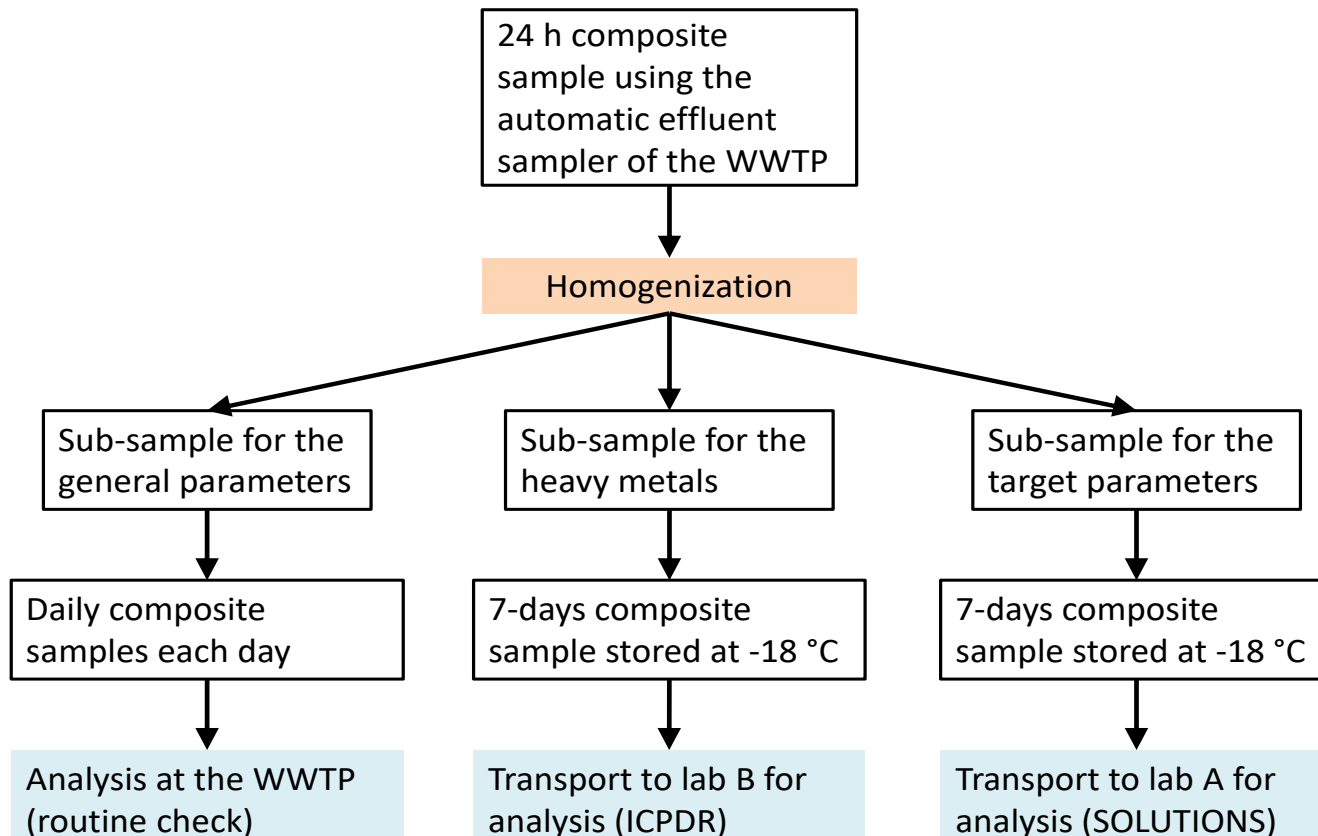


---

# Main goals

- ✓ Get representative chemical patterns from WWTP effluents with different treatment and from different Danube countries;
- ✓ Get representative effect-based patterns for the same WWTP effluents;
- ✓ Support RBSPs selection for the Danube basin;
- ✓ Provide the data to modelers for advanced exposure and risk modeling in the Danube river and comparison with JDS3 data;
- ✓ Starting point for the planning and implementation of JDS4;
- ✓ Support ICPDR and local stakeholders with valuable data for the Danube RBMP.

# Sampling scheme



General parameters (WWTP) – pH, conductivity, *COD and/or TOC, BOD<sub>5</sub>, NH<sub>4</sub>-N, NO<sub>3</sub>-N, TP, PO<sub>4</sub>*

Metals (UBA Vienna) – Cd, Cu, Cr, Pb, Ni, Hg, Zn, As

SOLUTIONS (UFZ, EI) – 7-days samples + LVSPE (20 l)



# WWTP samples – SOLUTIONS parameters

ICPDR IKSD

International Commission  
for the Protection  
of the Danube River

Internationale Kommission  
zum Schutz der Donau



## Chemical Analysis

Target screening of **2041 compounds**  
Highly sensitive determination of  
**antibiotics**  
**Suspect screening (>14,000  
substances)**  
**Non-target screening**



## Bioassays



## Genomics

Sequencing of  
whole DNA and  
determination  
of **ARGs**

# WWTPs in the Danube River Basin selected for effluent monitoring



International Commission  
for the Protection  
of the Danube River

Internationale Kommission  
zum Schutz der Donau

Country	Town	PE	Treatment type
<b>Romania</b>	Bucharest	1327995	tertiary
<b>Romania</b>	Cluj-Napoca	382031	tertiary
<b>Serbia</b>	Šabac	84000	tertiary
<b>Croatia</b>	Varaždin	97450	secondary
<b>Croatia</b>	Zagreb	842425	secondary
<b>Slovenia</b>	Ljubljana	462872	secondary
<b>Slovenia</b>	Vipap	152487	tertiary
<b>Hungary</b>	Budapest	1174643	tertiary
<b>Slovak Republic</b>	Žilina	139934	tertiary
<b>Czech Republic</b>	Brno-Modřice	397945	tertiary
<b>Austria</b>	Amstetten	150000	tertiary
<b>Germany</b>	Augsburg	659387	tertiary



---

# JDS4 Hazardous substances: Target analysis

- ✓ (New) priority substances from the Directive 2013/39/EU;
- ✓ Substances from the newly defined list of the Danube River Basin Specific Pollutants;
- ✓ Substances from the EU Watch List;
- ✓ Other emerging substances of concern in DRB;
- ✓ New techniques

---

# Hazardous substances: progress in measures

- ✓ Since 2006, 110 facilities have added specific technologies such as UV treatments and activated carbon filters to remove hazardous pollutants;
- ✓ A number of legislative measures have been put in place to stop the use of chemicals that cause water pollution, such as setting standard limits for priority substances like metals and pharmaceuticals;
- ✓ The release of agricultural chemicals is now minimized thanks to measures enforcing the use of less toxic substitutes, ensuring the safe application of biocides, and setting emission limits;
- ✓ In agriculture, the use of sewage sludge which could contain hazardous substances is now regulated to prevent harmful effects on soil, vegetation, animals, and people;
- ✓ Pollution from industrial accidents is also regulated and minimized through safety measures such as accident emergency plans and early warning monitoring systems.

Thank you for your attention!

[www.icpdr.org](http://www.icpdr.org)  
[secretariat@icpdr.org](mailto:secretariat@icpdr.org)