NORMAN – ICPDR cooperation during the JDS3

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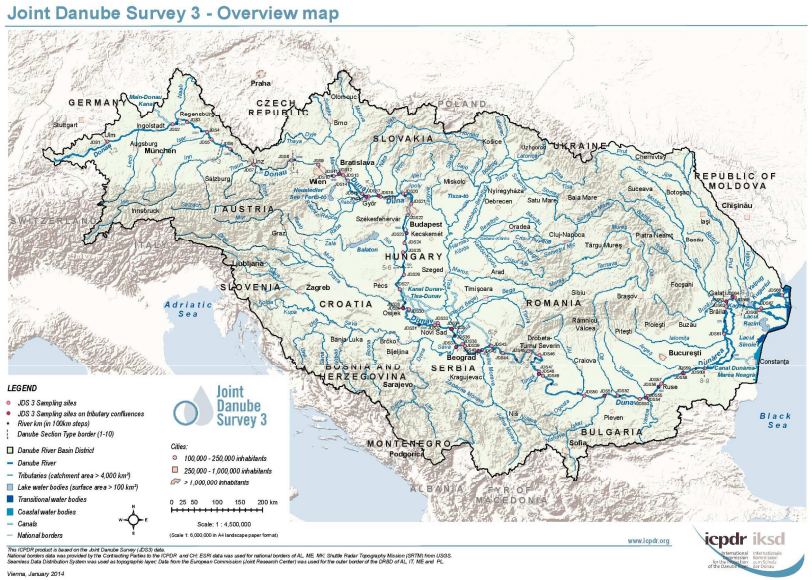
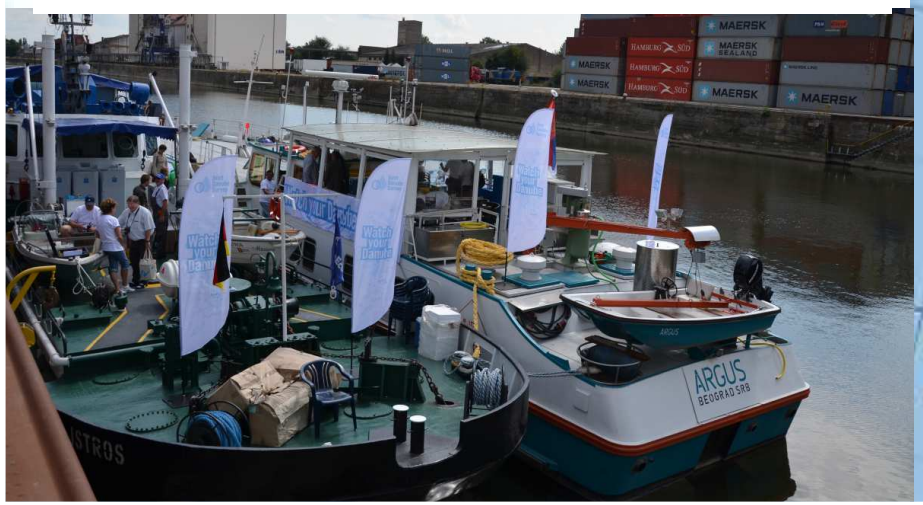
NORMAN – ICPDR Joint Danube Survey 4 (JDS4)
brainstorming workshop
Bratislava, 6 – 7 September 2018

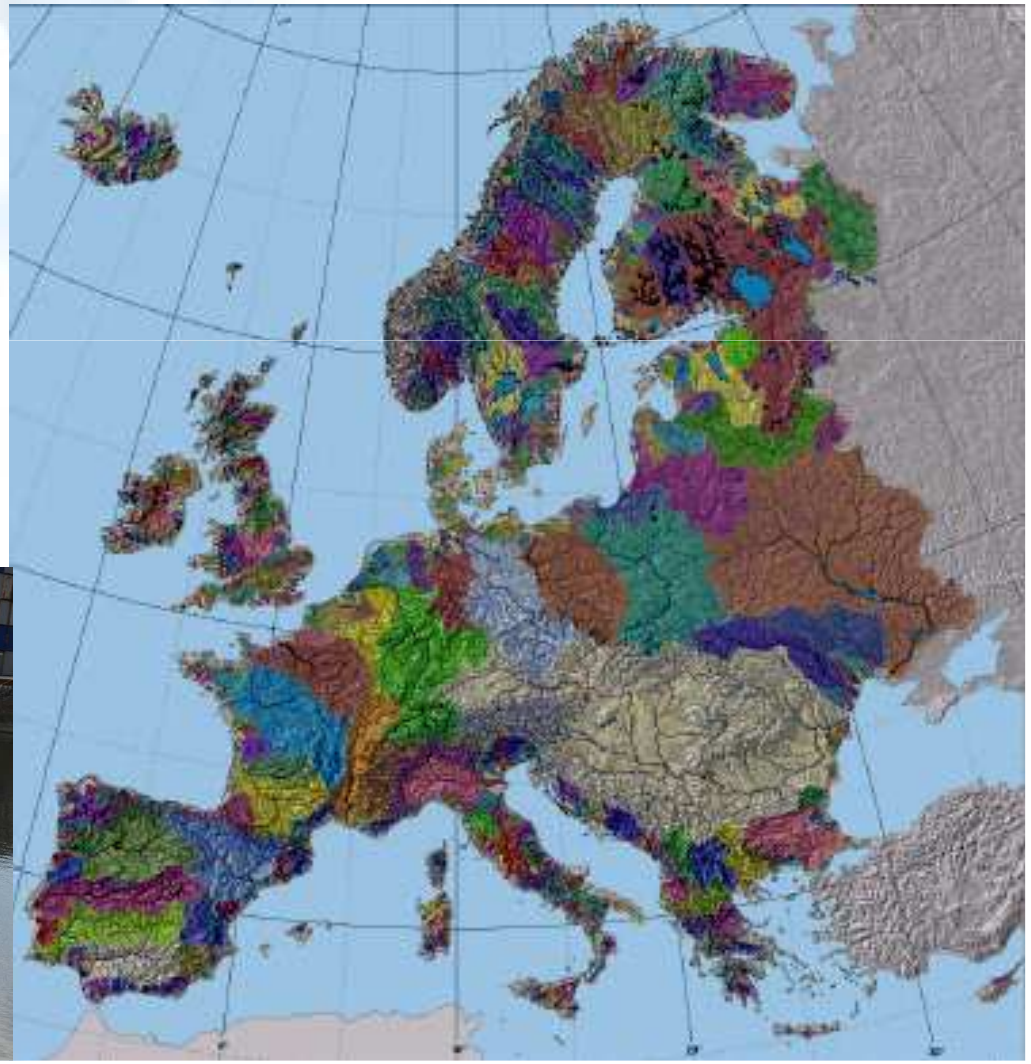
Joint Danube Survey 3

ICPDR, the biggest river expedition in the world

11 August – 26 September 2013



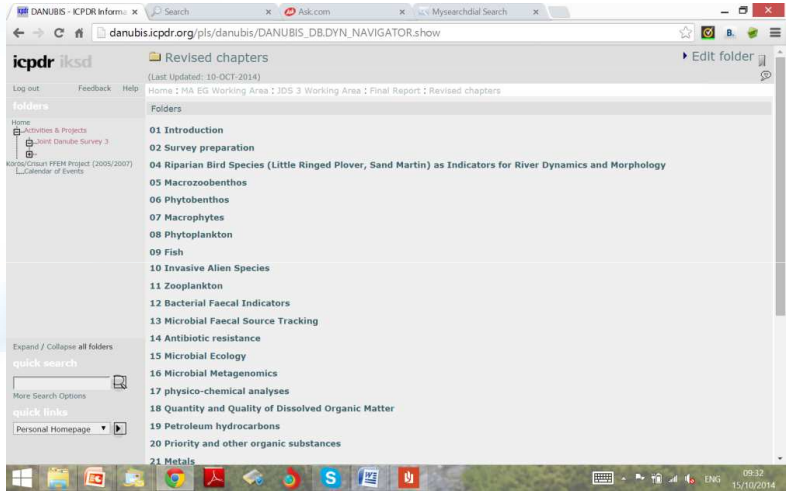




Overview – data collection

34 laboratories from 11 countries

- *Chemistry*
- *Biology*
- *Microbiology*
- *Exotoxicology*
- *Hydrobiology*
- *Hydromorpholgy*
- *Radiology*
- *Ornithology*



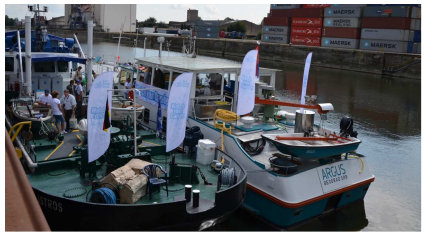
Chemistry - 618 substances

Water - river water, groundwater
Biota - fish muscle, fish liver, fish otolith, molluscs, leaves
Sediment
SPM
Soil

***JDS3 Final Report**, joint publications*

NORMAN Joint Programme of Activities 2013 - 2014

- **Joint Danube Survey 3**
- **NORMAN Collaborative Trial on non-target screening**
- **Prioritisation of non-target screening data**
- ChemProp
  - Automated collection of physico-chemical and ecotox properties of large number of emerging substances
- **Digital Sample Banking** – European archive for storage of raw MS chromatograms; **retrospective analysis**
  - Development of minimum requirements for storage of MS data in libraries
- **NORMAN MassBank**



Large Volume Sampling

NORMAN Collaborative Trial 2013 - 2014

Non-target screening of organic substances in river water samples

NORMAN CT – non target screening

Received datasets

	Name of organization / institute	Name of laboratory	Total DCTs	LC-MS	GC-MS
1	IAREN- Water Institute of the Northern Region	Laboratory of Chromatography			
2	NIVA	NIVA Oslo	1	1	
3	SUEZ Environment	CIRSEE	1	1	1
4	T. G. Masaryk Water Research Institue	Reference Laboratory for Environment Components and Waste			
5	University of Antwerp	Toxicological Centre	1	1	
6	Technische Universitaet Muenchen	Chair of Urban Systems Engineering	1	1	
7	University Jaume I (UJI)	Research Institute for Pesticides and Water	1		1
14	Ministry of the Environment of Canada	Laboratory Services Branch			
15	BRGM	Laboratory Division			
16	IRSTEA	LAMA	1	1	
17	Environmental Institute (EI), SK	Analytical Laboratory	1		1
18	Helmholtz-Centre for Environmental Research - UFZ	Effect-directed analysis	1	1	
19	University of Padua / Department of Chemistry	Group of Analytical Chemistry	1	1	
20	University of Bordeaux	team LPTC, laboratory EPOC (UMR 5805 CNRS)			
21	Masaryk University / Faculty of Science	RECETOX			
22	Bundesanstalt für Gewässerkunde	Gewässerchemie	1	1	
23	Zweckverband Landeswasserversorgung	Betriebs- und Forschungslaboratorium	1	1	
24	Croatian Waters	Central Water Management Laboratory	1	1	
25	University of Tuebingen	Environmental Chemistry	1	1	
26	University of Umea	Department of Chemistry	1		1
			18	**16**	**7**

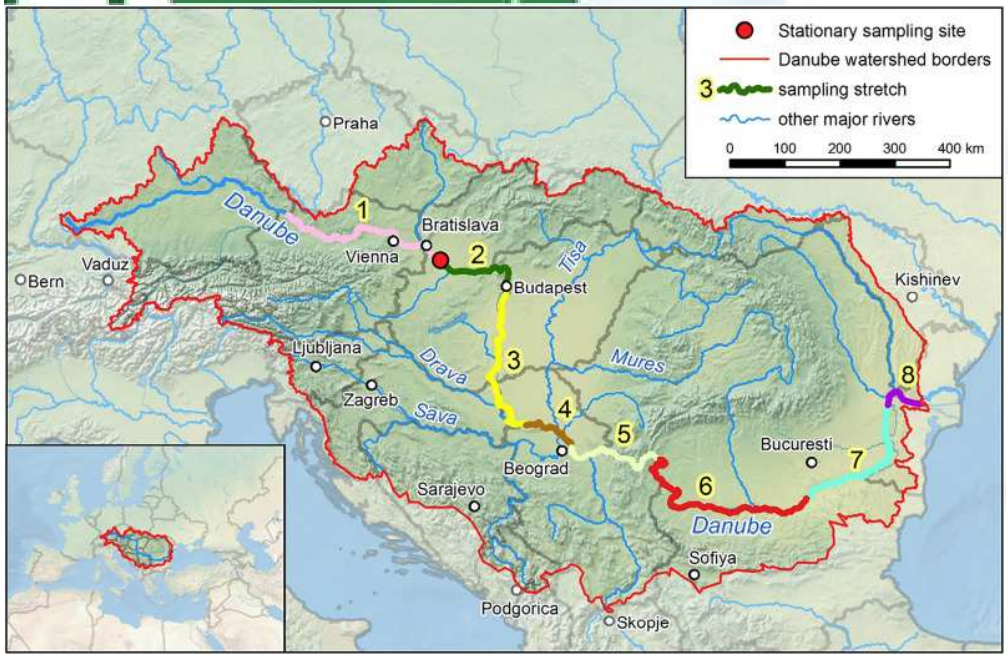
LC-HR-MS: T&S 1072; NT&Unknown 21380

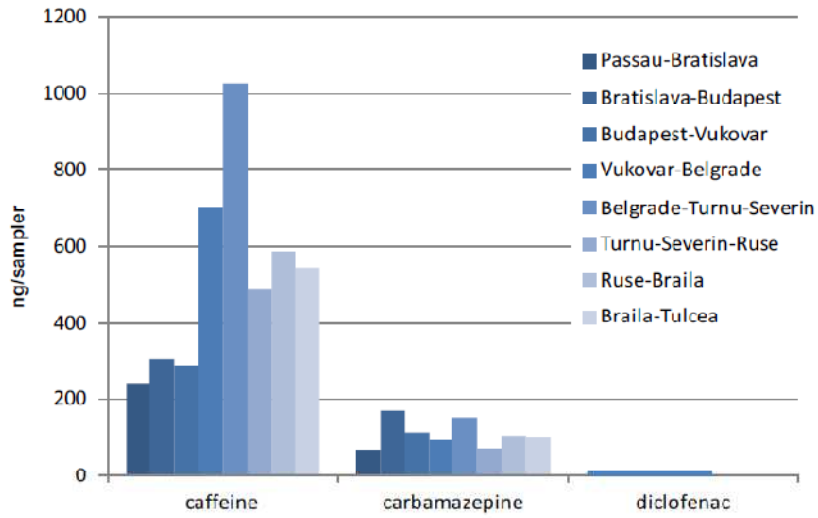
GC-MS: T&S 348; NT&Unknown 116

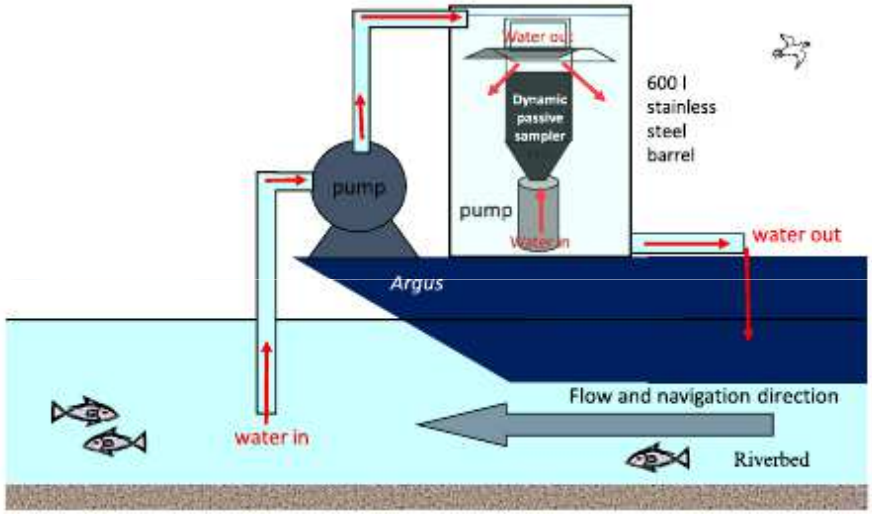
Less then 5% overlap

The “active” passive sampler

Spatial distribution of chemicals – Active passive sampling

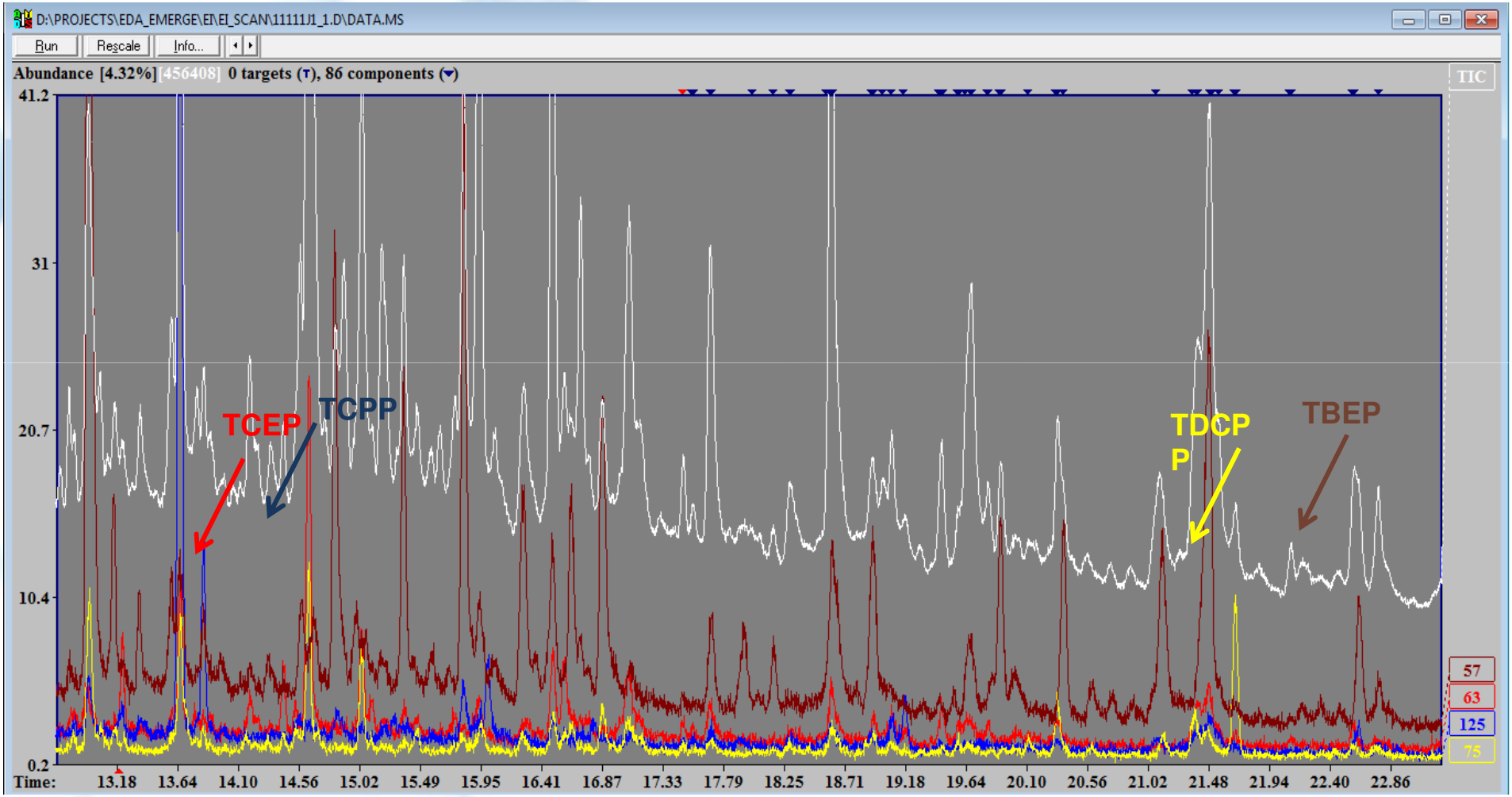






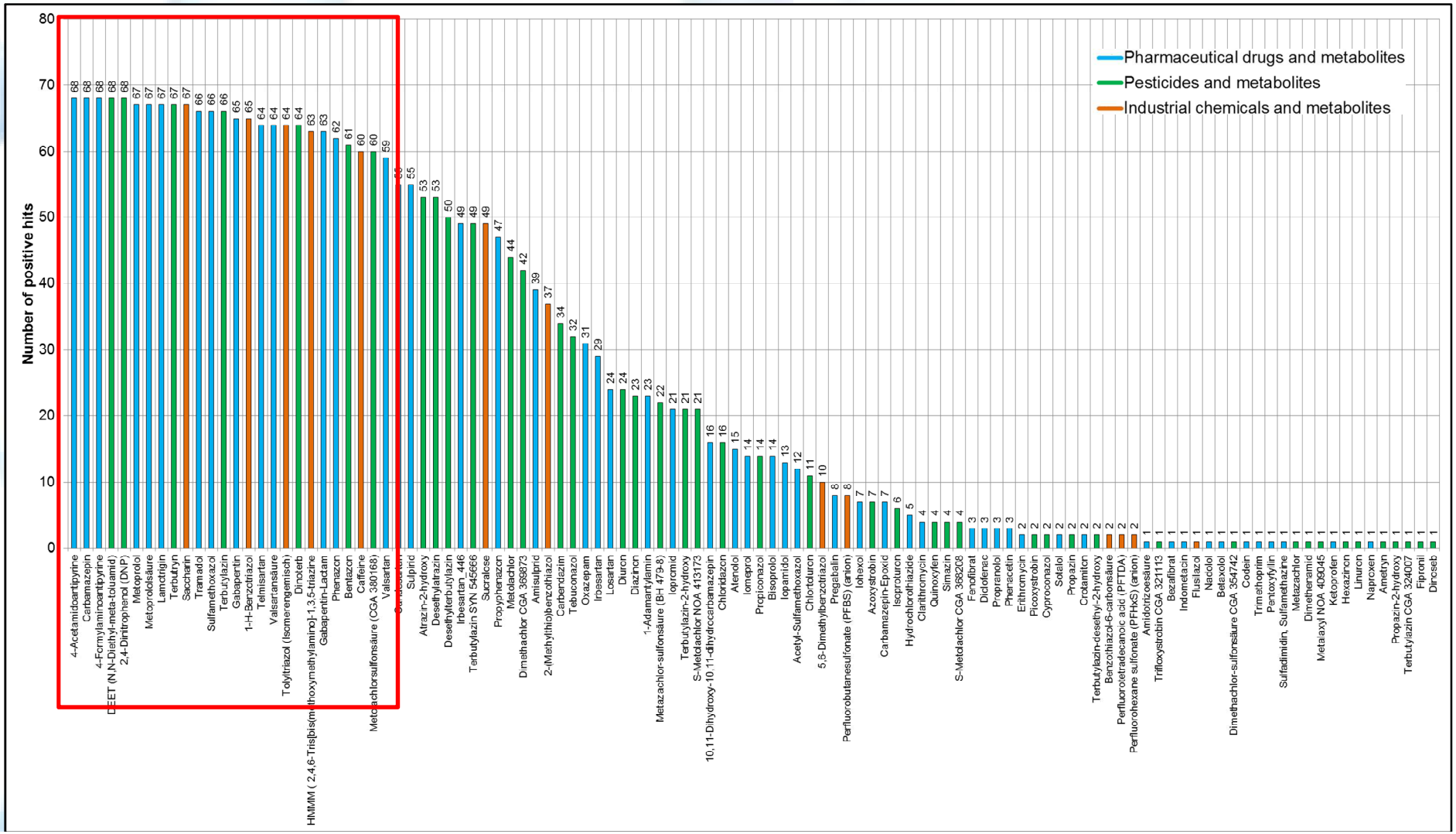
Vrana et al., Science of The Total Environment, 2018, https://doi.org/10.1016/j.scitotenv.2018.03.242

Retrospective analysis of full scan GC-MS chromatogram HR-X Organophosphorus flame retardants(TCEP – 50.8 ng/l, TCPP – 1081.8 ng/l, TDCPP – 120.2 ng/l, TBEP – 152.9 ng/l) found in sample 11111

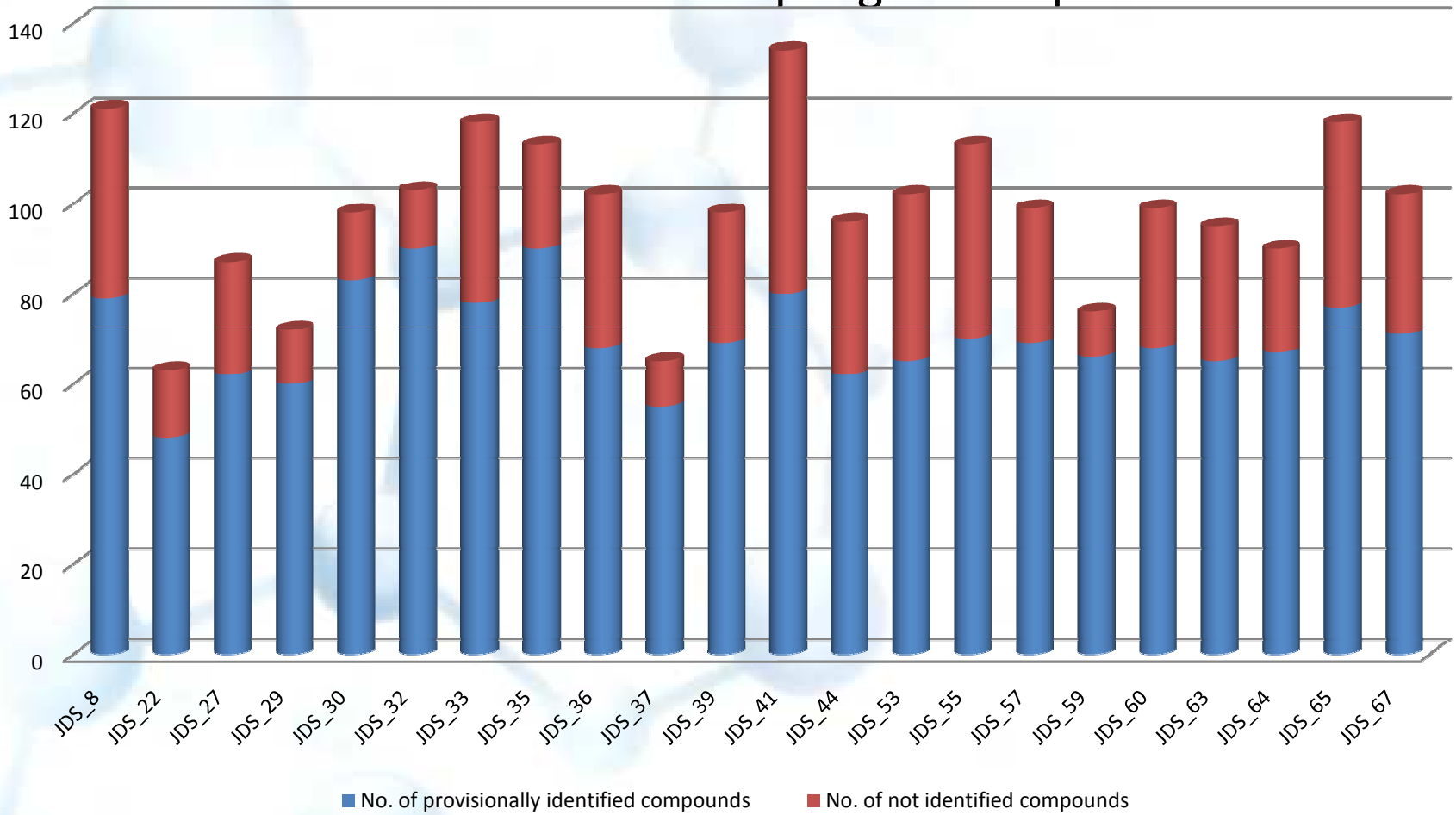


JDS3 - Frequency of appearance

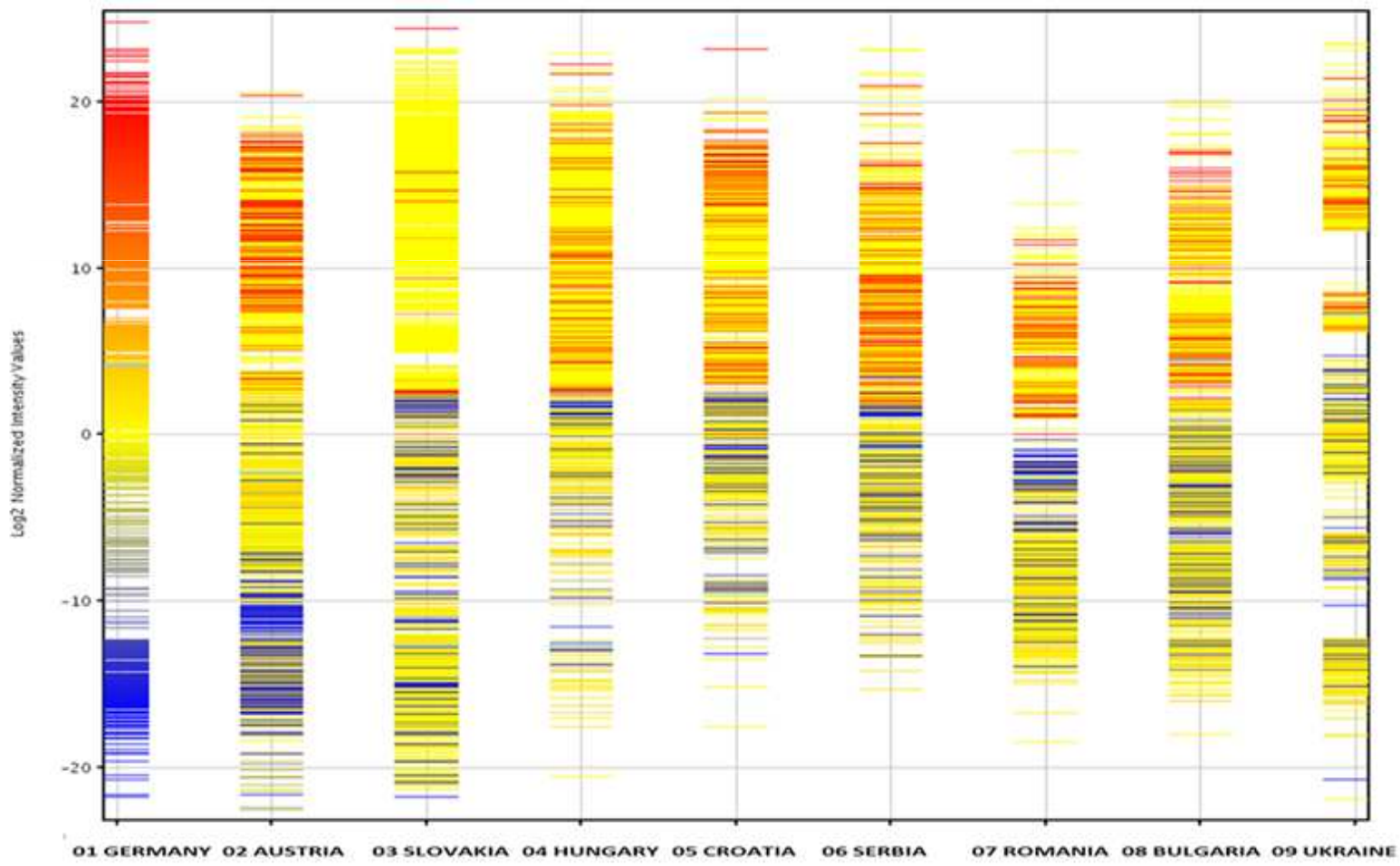
of 110 'identified' suspect pollutants (315 tested) in JDS3 surface water samples; results obtained from non-target screening workflow by HPLC-ESI-Q-TOF-MS operated in ESI⁺ and ESI⁻ modes



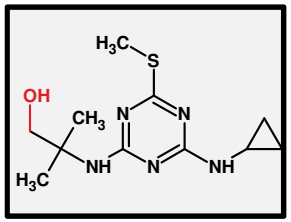
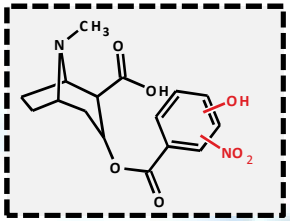
JDS3 - Number of compounds detected with LVI-GC-MS in the 22 JDS3 surface water samples obtained with the LVSPE sampling technique



Distribution of 7767 different mass spectral processed features through the Danube river and its tributaries; Danube countries are shown on x-axis and normalised signal intensity values are represented on y-axis; each single feature/compound is represented by a horizontal bar at a fixed position on the chart (position given by a unique combination of retention time, accurate mass spectrum, name, molecular formula, etc.) and the intensity of signal increase is indicated by blue (low) to red (high) colour



Non-target screening - prioritisation

Example	*Identification confidence*	*Minimum data requirements*
	***Level 1: Confirmed structure*** by reference standard	MS, MS^2, RT, Reference Std.
	Level 2: Probable structure a) by library spectrum match b) by diagnostic evidence	MS, MS^2, Library MS^2 MS, MS^2, Exp. data
	***Level 3: Tentative candidate(s)*** structure, substituent, class	MS, MS^2, Exp. data
$C_6H_5N_3O_4$	***Level 4: Unequivocal molecular formula***	MS isotope/adduct
192.0757	***Level 5: Exact mass*** of interest	MS

Schymanski, Jeon, Gulde, Fenner, Ruff, Singer & Hollender (2014) *ES&T*, DOI: 10.1021/es5002105

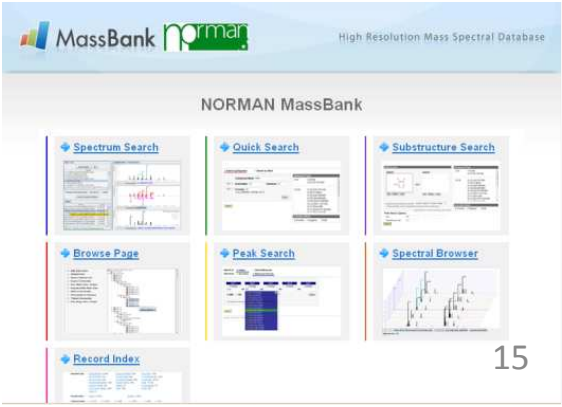
NORMAN MassBank – "let's share the knowns and focus on the unknowns"

- **VISION** =>> bringing together community of environmental chemists and set up of **a common and open access mass spectral database for identification purposes**

- Upgrade of the former NORMAN EMPOMASS database =>> hosted and maintained by UFZ, Leipzig
- NORMAN joined MassBank consortium (existing global platform *) in 2012
- Members of the NORMAN network committed to provide mass spectra to fill up the database

*MassBank Horai et al., 2010; www.massbank.jp

http://massbank.normandata.eu/MassBank/



Prioritisation – Danube TOP 20

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

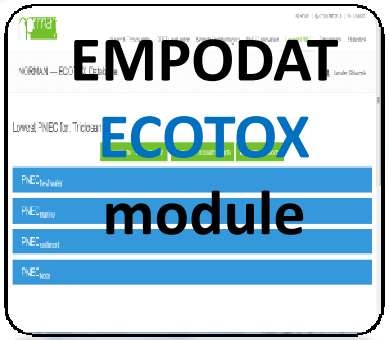
No.	Substance	CAS No.	No. of sites substance detected	C_{max}[1]	MEC_{95}[2]	Lowest PNEC/EQS	Key study	Type	EoE[3]	EoE score	FoE[4]	Final score
1	2,4-Dinitrophenol (DNP)	51-28-5	68	0.06	0.04	0.001	RIVM 2014	EQS chronic water[5]	40	0.2	1.00	1.20
2	PFOS (Perfluorooctansulfonate)	1763-23-1	63	0.026	0.02	0.00065	EU 2013	EQS chronic water[5]	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[5]	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[5]	10	0.1	0.76	0.86
6	Bromacil	314-40-9	31	0.19	0.14	0.01	INERIS 2013	EQS chronic water[5]	14	0.2	0.46	0.66
7	Dimefuron	34205-21-5	58	0.041	0.04	0.008	Oekotoxzentrum 2014	EQS chronic water[5]	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[5]	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[5]	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[5]			0.19	0.19
12	Linuron	330-55-2	32	1.42	1.12	0.26	Oekotoxzentrum 2014	EQS chronic water[5]	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[5]	1.1	0.1	0.03	0.13
15	17beta-estradiol	50-28-2	8	0.029		0.0004	CEC 2011	EQS chronic water[5]			0.12	0.12
16	Benzo(a)pyrene	50-32-8	3	0.002		0.00017	EU 2013	EQS chronic water[5]			0.04	0.04
17	Diclofenac	15307-79-6	51	0.318	0.036	0.05	Oekotoxzentrum 2014	EQS chronic water[5]			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[5]			0.01	0.01
20	Fluoranthene	206-44-0	58	0.02	0.006	0.0063	EU 2013	EQS chronic water[5]			0.01	0.01

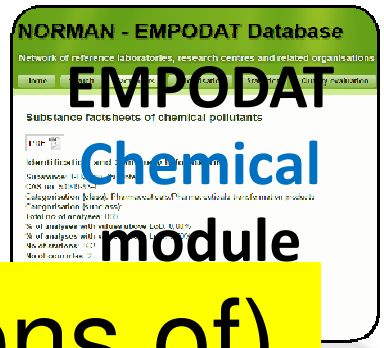
1 C_{max} – Maximum concentration in µg/L reported in case the substance has been measured by several JDS3 laboratories
2 MEC_{95} – 95th percentile of the Maximum Environmental Concentration in µg/L; calculated only if the substance has been found above LOQ at minimum 20 sites
3 EoE – Extent of Exceedance
4 FoE – Frequency of Exceedance
5 Equal to Annual Average EQS (AA-EQS)

The Danube River Basin District Management Plan, Update 2015

Feeding NORMAN Prioritisation system

MASTER TABLE

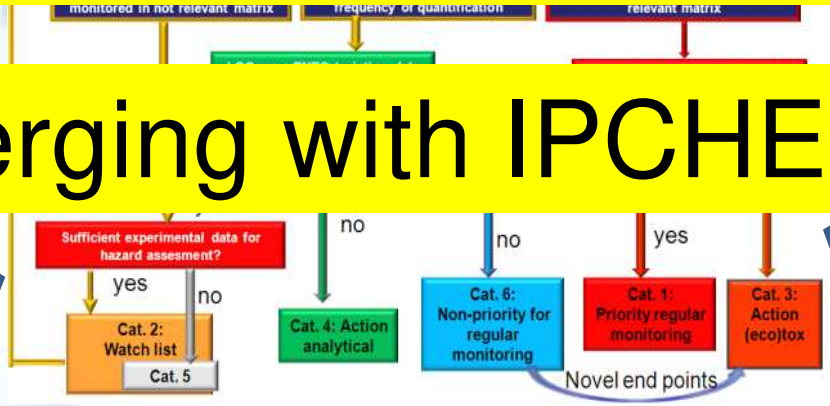




FACT

From HUNDREDS to (tens of) THOUSANDS substances

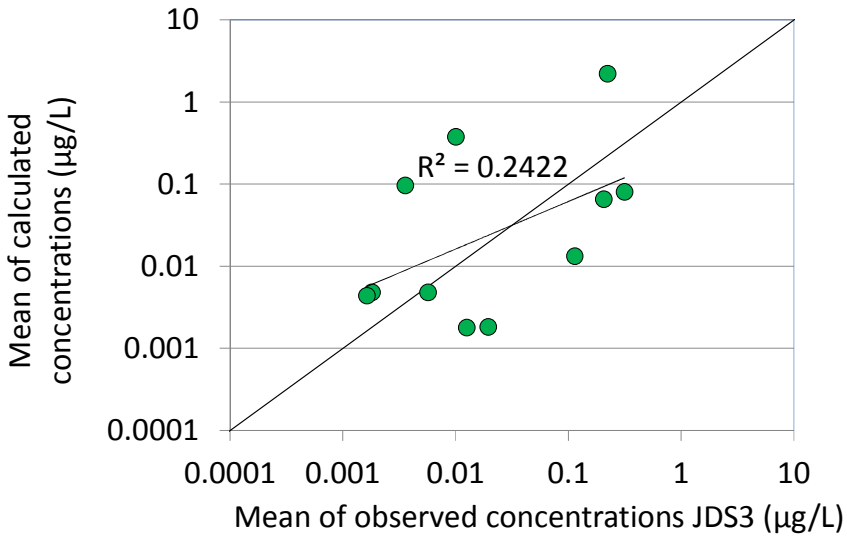
Merging with IPCHEM



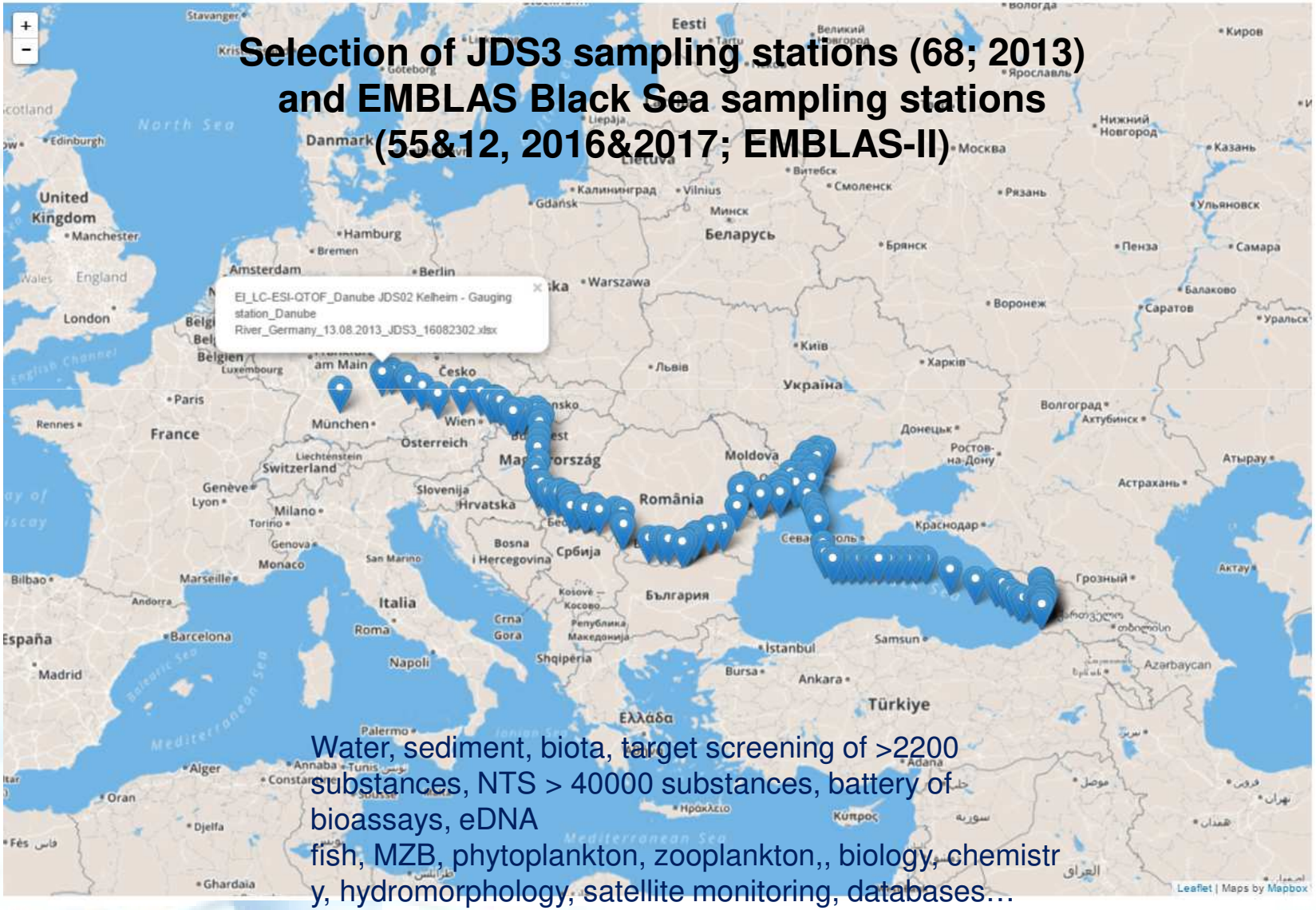
Modelling - First results for the Danube Basin

- Emission estimates and simulation of PFOS and PFOA
  Environmental Pollution 207 (2015) 97-106
  Chemosphere 144 (2016) 803-810

- 11 Industrial chemicals:
  - modelled emissions
  - modelled concentrations
- Comparison to measured concentrations at JDS3 stations:



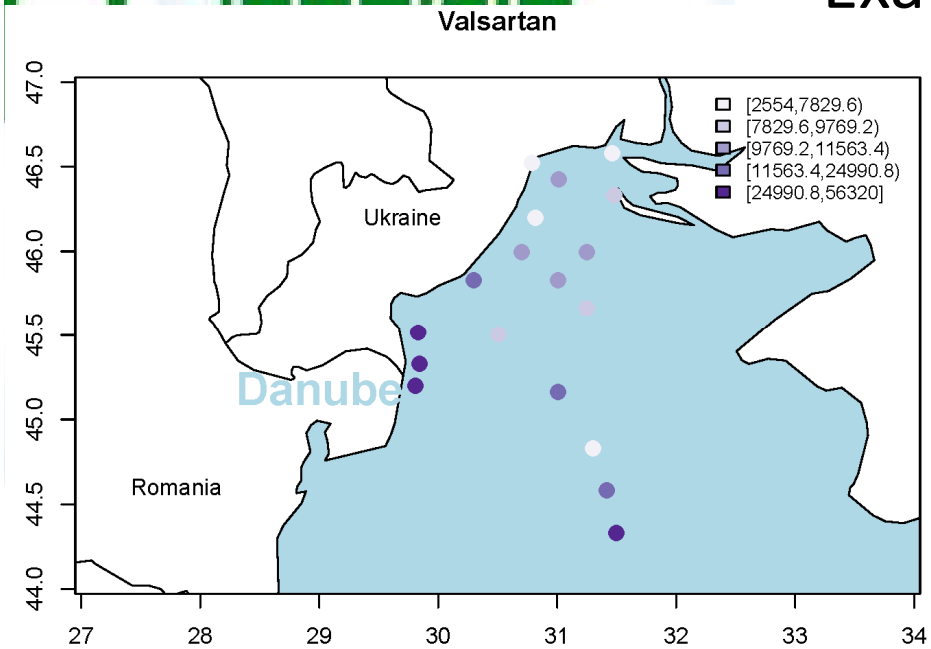
Test of the SOLUTIONS Tools/Methodologies in the Joint Danube Survey 4 (ICPDR) and Joint Black Sea Survey in June 2019
(EU/UNDP EMBLAS-Plus)

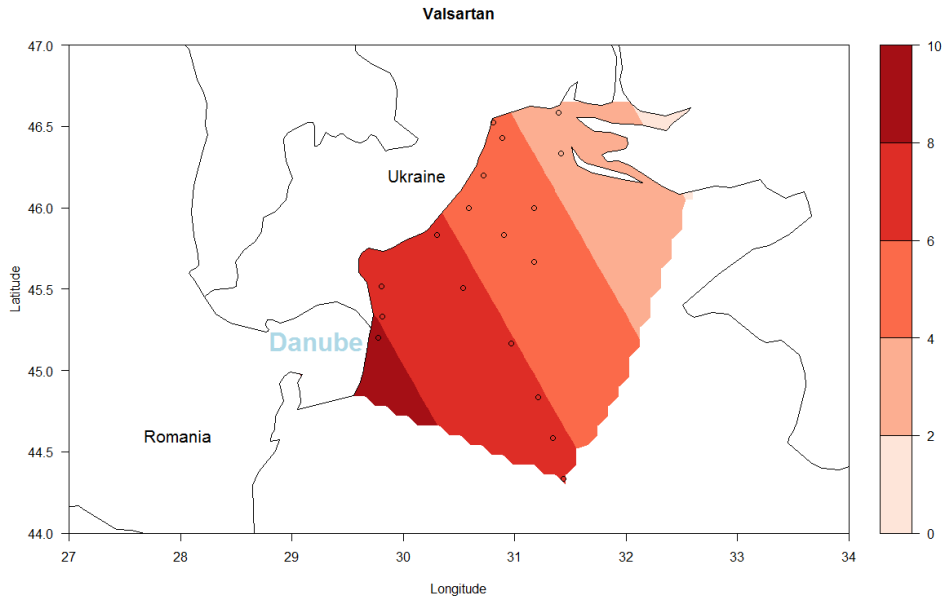


Selection of JDS3 sampling stations (68; 2013) and EMBLAS Black Sea sampling stations (55&12, 2016&2017; EMBLAS-II)

Water, sediment, biota, target screening of >2200 substances, NTS > 40000 substances, battery of bioassays, eDNA
fish, MZB, phytoplankton, zooplankton,, biology, chemistry, hydromorphology, satellite monitoring, databases…

Examples





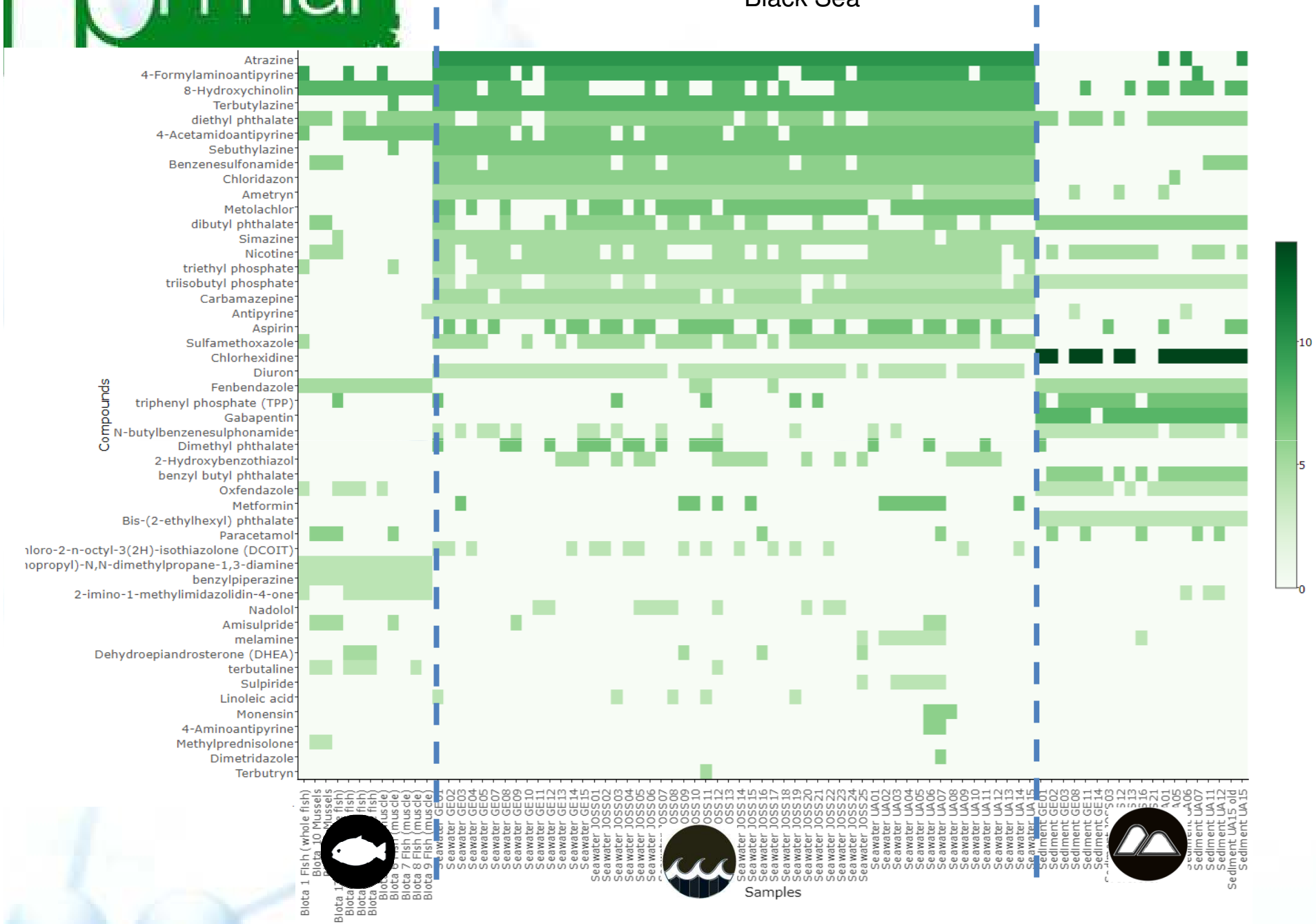
Name	[M+H]+	Molecular Formula	error [mDa]	error [ppm]	ΔRT	mSigma	Q1	Q2	Q3	Identification Level
Metolachlor	284.1412	C15H22ClNO2	-0.30	-1.06	0.17	25.4	252.1151	176.1427	212.0826	1
Metolachlor-ESA	330.137	C15H23N1O5S1	0.10	0.30	0.08	103*	298.1106	-	-	1
4-Acetamidoantipyrin	246.1237	C13H15N3O2	1.00	4.06	0.07	26.5	228.1127	204.1124	159.0905	1
4-Formylaminoantipyrine	232.1081	C12H13N3O2	0.50	2.15	0.06	17.2	214.0975	83.0604	187.0865	1
Benzotriazole (BTR)	120.0556	C6H5N3	-0.80	-6.66	0.01	35	92.0494	65.0384	-	1
Cotinine	177.1022	C10H12N2O1	-0.50	-2.82	0.13	38.5	80.0495	98.0600	70.06513	1
cotinine-Hydroxy	193.0972	C10H12N2O2	-0.40	-2.07	0.16	8.8	80.0495	134.0600	-	1
Metformin	130.1087	C4H11N5	-0.50	-3.84	0.13	6.1	71.0604	60.0556	85.0517	1
Carbamazepine	237.1022	C15H12N2O1	0.70	2.95	0.16	11.8	194.0964	192.0806	-	1
Dimethenamide	276.082	C12H18ClNO2S	0.00	0.00	0.13	19.3	244.0557	-	-	1
Atenolol acid (Metoprolol acid)	268.1543	C14H21N1O4	0.40	1.49	0.17	93.7*	191.0702	116.1070	-	1
Metoprolol	268.1907	C15H25N1O3	-2.40	-8.95	0.05	17.4	74.0607	116.1070	-	1

Poster:

"Exploring the extent of chemical pollution transfer from the Danube Rive to the Black Sea"

by Nikiforos Alygizakis et al.

DSFP - Screening of REACH compounds in samples from the Black Sea



Alex Vargin 2010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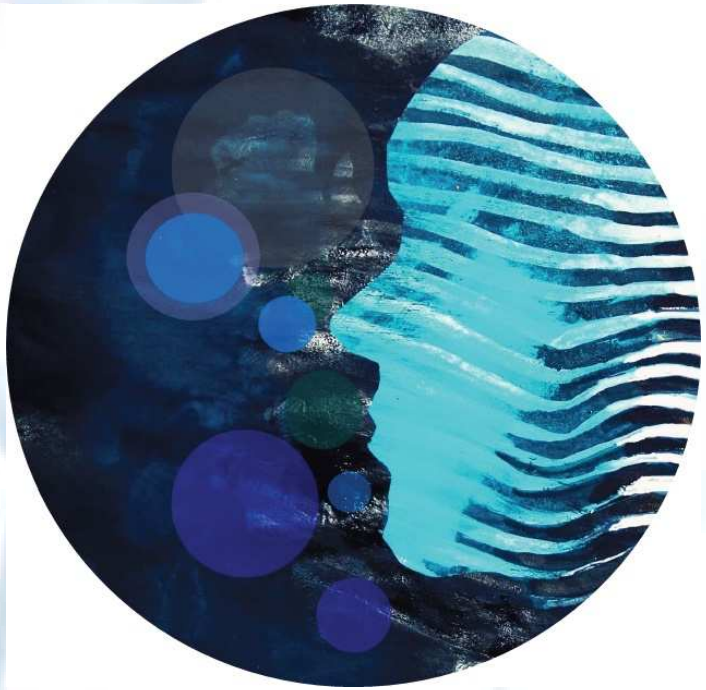

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