Non-target screening of environmental pollutants in the context of risk assessment of European river basins: the NORMAN network perspective

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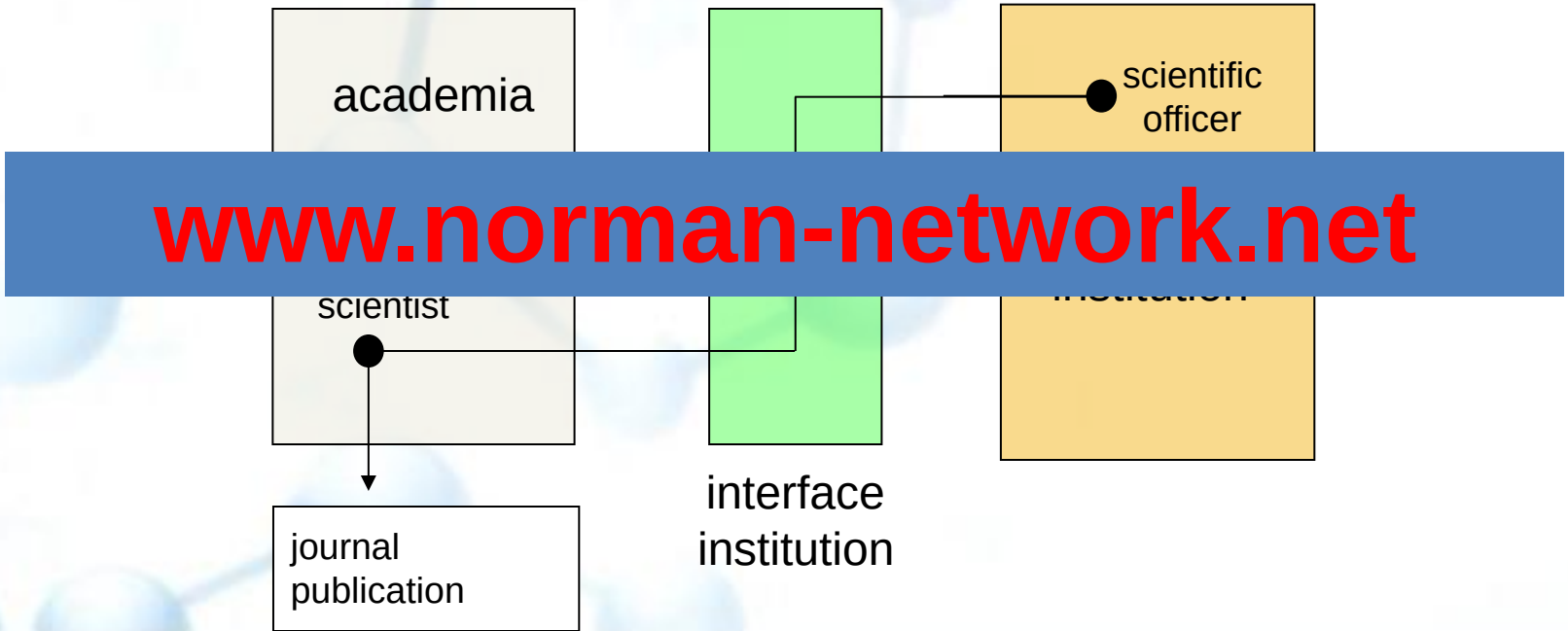
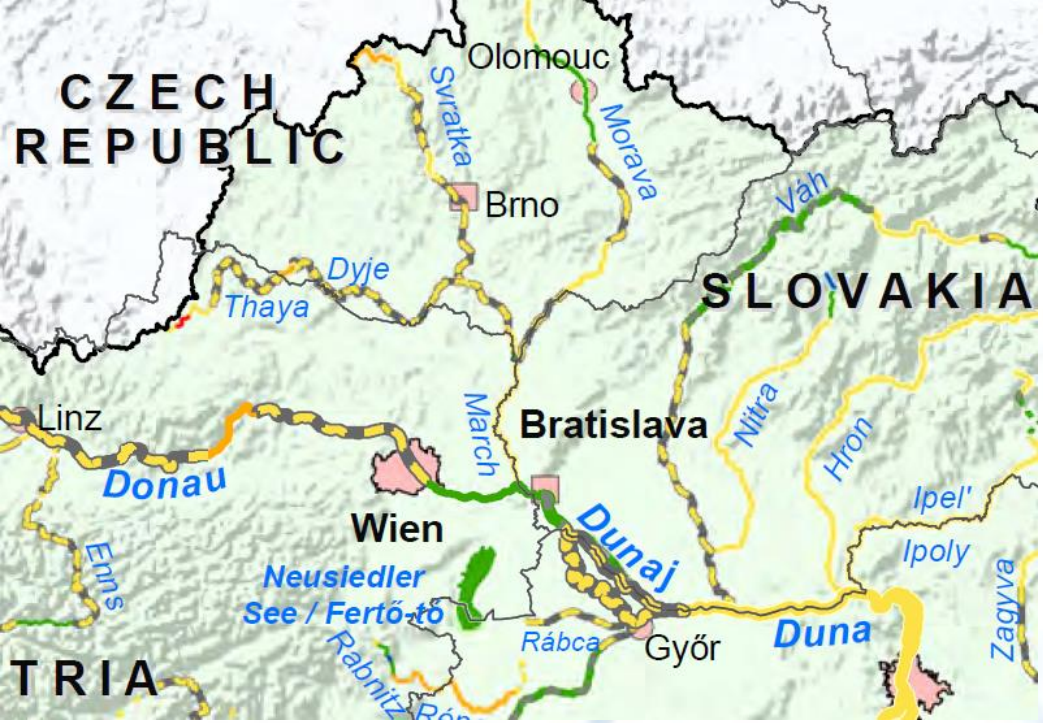
Science-to-policy interface

- Different inherent structure of academic science and political institutions
- **Possible solution:** institutional interface



www.norman-network.net

Danube River Basin District Management Plan 2009



Ecological status and ecological potential

Chemical status

NORMAN a s to identify the releva pollutants

Databases:
Monitoring
Toxicity
Properties dat

ge data/ Use
ndex

WFD 2000/60/EC – ecological status – River Basin Specific Pollutants

EQS Directive 2008/105/EC and 2013/39/EU – update of the WFD PS list and Watch List

Non-target screening

NORMAN Massbank – identification of unknowns

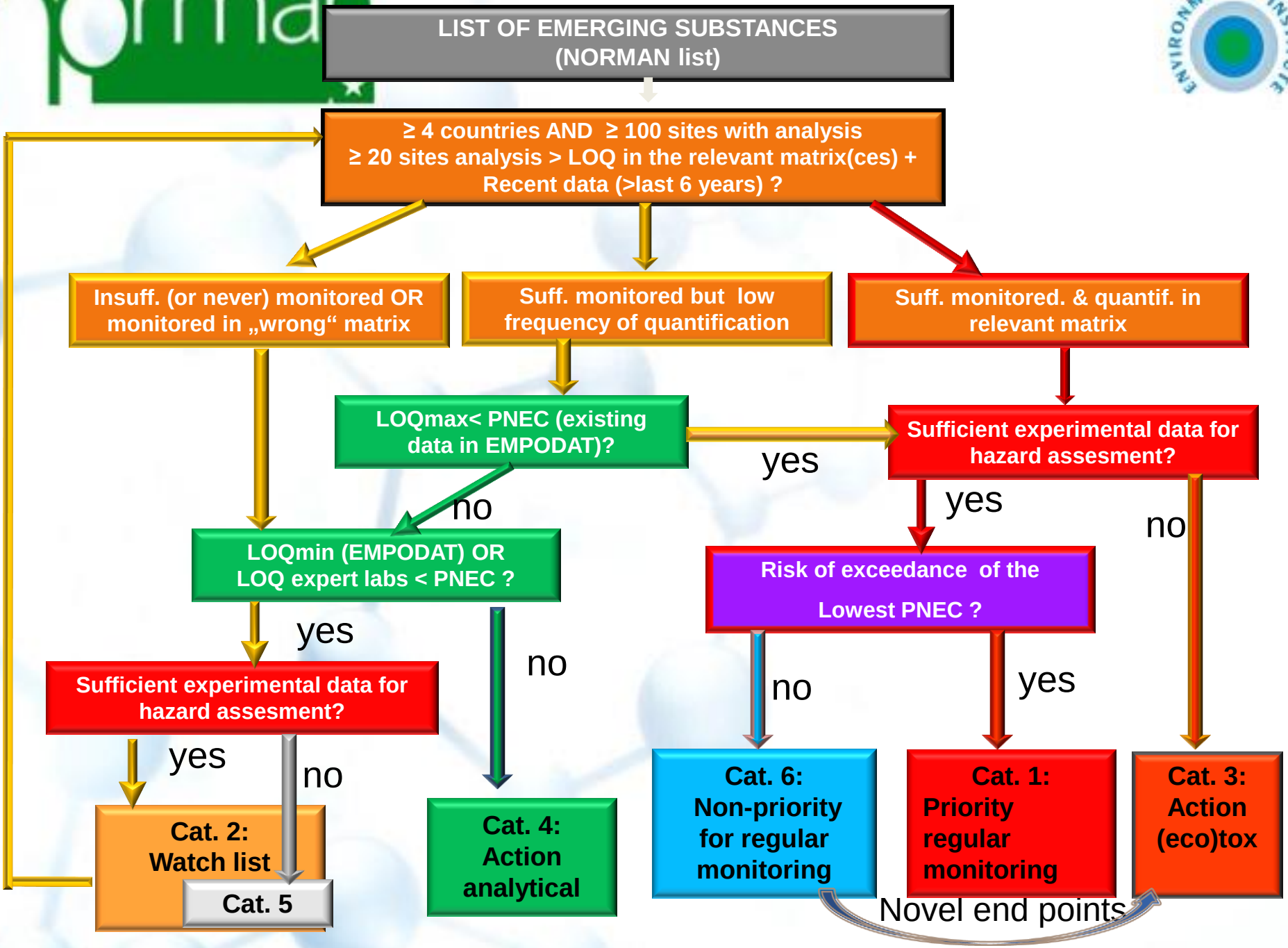
ect-Directed Analysis

NORM
pr
Measur
method

NORMAN scheme for Prioritisation of Emerging Substances

1. Categorisation – to allocate substances to **action categories**

2. Prioritisation – to define priorities within each action category


LIST OF EMERGING SUBSTANCES
(NORMAN list)
≥ 4 countries AND ≥ 100 sites with analysis
≥ 20 sites analysis > LOQ in the relevant matrix(ces) +
Recent data (>last 6 years) ?
Insuff. (or never) monitored OR monitored in „wrong“ matrix
Suff. monitored but low frequency of quantification
Suff. monitored. & quantif. in relevant matrix
LOQmax< PNEC (existing data in EMPODAT)?
yes
no
Sufficient experimental data for hazard assesment?
yes
no
LOQmin (EMPODAT) OR LOQ expert labs < PNEC ?
yes
no
Sufficient experimental data for hazard assesment?
yes
no
Risk of exceedance of the Lowest PNEC ?
no
yes
Cat. 2: Watch list
Cat. 5
Cat. 4: Action analytical
Cat. 6: Non-priority for regular monitoring
Cat. 1: Priority regular monitoring
Cat. 3: Action (eco)tox
Novel end points

NORMAN proposal for candidate substances for the 1st EU Watch List (Art 8 2013/39/EU)

Category 2 – WATCH LIST

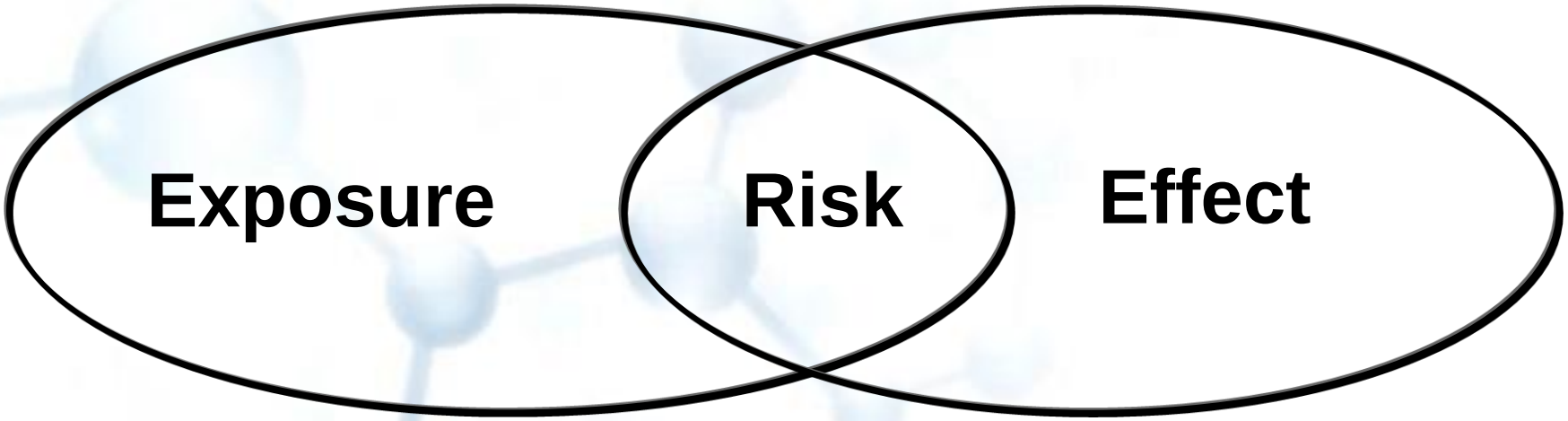
- Aminotriazole
- Azithromycin
- Ethylhexyl methoxycinnamate
- Diflufenican
- Ofloxacin
- Clarithromycin
- Erythromycin
- Triphenyl phosphate
- Ciprofloxacin
- Dimethenamid
- Methiocarb
- Oxadiazon

Category 1 - PS

- Bisphenol A
- Di-n-butylphthalate (DBP)
- Triclosan
- Diazinon
- Terbuthylazine
- Carbamazepine
- Estrone
- Diclofenac
- Ibuprofen
- Bentazone
- Metolachlor

http://www.norman-network.com/empodat/

Non-target screening – risk indicators



Tentatively identified

Predicted conc.

➔ MEC95

MEC95
P-PNEC

Predicted toxicity

AF of 1000

➔ P-PNEC

Non-target screening

Prioritisation based on GC-MS screening:

Table 7. Results of prioritisation based on the GC-MS screening data and (predicted) toxicity data

No.	CAS	Name	Max. conc.	MEC_{95}[a]	AA-EQS[b]	Source EQS	Lowest PNEC	Ref.[c]	TL[d]	Freq. PNEC[e]	Exceed. PNEC[f]	Priority[g]
1	629-62-9	Pentadecane	1.7	1.5			0.0015	B	A	0.20	1000	1.20
2	544-76-3	Hexadecane	3.6	2.4			0.0015	P	F	0.17	1600	1.17
3	95-16-9	Benzothiazole	30,958	4459	2	SK	2	E	D	0.12	2230	1.12
4	57-10-3	Hexadecanoic acid	15	3.7			0.021	B	F	0.53	176	1.03
5	629-50-5	Tridecane	8.0	4.3			0.023	B	F	0.50	187	1.00
17	92-52-4	Biphenyl		1.7	1	SK	0.36	E	D	0.22	5	0.32
18	2091-29-4	9-hexadecenoi		1.8			0.032	B	P	0.12	56	0.32
19	120-72-9	1H-indol	64	34			1	E	D	0.08	34	0.28
20	128-37-0	Me	10	2.6	1.4	SK	1.4	E	D	0.15	1.86	0.25
21	615-22-5		14.0	3.8			0.31	P	D	0.05	12	0.25
22	1620-98	-4-ethyl-	9.3	5.4			0.59	B	D	0.08	9	0.18
23	33		9.8	0.86			0.26	P	A	0.07	3	0.17
24			9.0	6.8			1.2	B	D	0.04	6	0.14
			208	8	10	SK	4.7	E	F	0.02	2	0.12
		ne	982	49	2.4	WFD	2.4	E	F	0.02	8	0.12
27		adecane	2.0				0.00024	P	F	0.11		0.11
28		Galaxolide	1.6				0.083	P	D	0.10		0.10
29		Cholesterol	4.1				0.0005	P	D	0.10		0.10
30	-21-4	Undecane	2.2				0.024	P	D	0.07		0.07

Name	MEC_{95}	Lowest PNEC	Freq. PNEC	Exceed. PNEC	Priority
Benzylbutylphthalate (BBP)	2.7	0.27	0.22	10	**0.42**

169 surface-water water samples!

Priority rank of the 11 polluters based on non-target analysis

SITE	CAS No.	Compound Name	Est. conc (ug/l)	Lowest PNEC (ug/l)	Exc.
I-3 Prevent Leather	59-48-3	2H-Indol-2-one, 1,3-dihydro-	50	0.50	100
I-3 Prevent Leather	620-92-8	Phenol, 4,4'-methylenebis-	33	1.69	20
I-3 Prevent Leather	106-44-5	p-Cresol	28	1.4	20
I-3 Prevent Leather	57-11-4	Octadecanoic acid	0.03	0.0013	20
I-3 Prevent Leather	141-02-6	2-Butenedioic acid (E)-, bis(2-ethylhexyl) ester	0.14	0.0094	14
I-3 Prevent Leather	3735-92-0	Carbamodithioic acid, dimethyl-, methyl ester	0.26	0.049	5
I-3 Prevent Leather	80-05-7	Bisphenol A	0.27	0.2	1
I-3 Prevent Leather	78-51-3	Tri(butoxyethyl)phosphate	8.9	6.8	1

Suspect screening – ONE JDS sample phase I -MS only

Data File	MS_JDS_58.d	**Sample Name**	MS_JDS_58
Sample Type	Sample	**Position**	P1-C4
Instrument Name	QTOF1	**User Name**	
Acq Method	MS_only_positive.m	**Acquired Time**	9/30/2013 7:43:37 PM
IRM Calibration Status	Success	**DA Method**	MS_POS.m
Comment			

Column4	Column3	Column4
Sample Group	**Info.**	
Funnel RF HP 150	**Funnel RF LP** 60	
Acquisition SW 6200 series TOF/6500		
Version series Q-TOF B.05.01 (B5125)		

Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)	MFG Formula	DB Formula	DB Diff (ppm)
Cpd 165: Fenchlorazole	1.065	372.87506	1016	Fenchlorazole	C10 H4 Cl5 N3 O2	372.87461	1.19	C10 H4 Cl5 N3 O2	1.45
Cpd 141: Fluorodifen	1.09	328.0309	1320	Fluorodifen	C13 H7 F3 N2 O5	328.03071	0.59	C13 H7 F3 N2 O5	2.44
Cpd 70: Cefazaflur	1.499	470.01153	3234	Cefazaflur	C13 H13 F3 N6 O4 S3	470.01125	0.59	C13 H13 F3 N6 O4 S3	-2.19
Cpd 95: 2,3-MDPEA / 2,3-Methylenedioxyphenethylamine	2.061	165.07883	3893	2,3-MDPEA / 2,3-Methylenedioxyphenethylamine	C9 H11 N O2	165.07898	-0.87	C9 H11 N O2	-0.21
Cpd 236: Merphos	2.078	298.10124	872	Merphos	C12 H27 P S3	298.10125	-0.04	C12 H27 P S3	1.89
Cpd 91: Vigabatrin	2.087	129.07889	7425	Vigabatrin	C6 H11 N O2	129.07898	-0.67	C6 H11 N O2	0.06
Cpd 78: o-Phenyleneurea (Benzimidazolone) (Droperidol-M)	3.381	134.048	8986	o-Phenyleneurea (Benzimidazolone) (Droperidol-M)	C7 H6 N2 O	134.04801	-0.07	C7 H6 N2 O	-0.02
Cpd 151: Anatoxin a	3.782	165.11506	1043	Anatoxin a	C10 H15 N O	165.11536	-1.87	C10 H15 N O	1.48
Cpd 255: (+)-cucurbic acid	3.799	212.14133	835	(+)-cucurbic acid	C12 H20 O3	212.14124	0.4	C12 H20 O3	-0.14
Cpd 212: L-Adrenaline	3.884	183.0896	1378	L-Adrenaline	C9 H13 N O3	183.08954	0.31	C9 H13 N O3	-0.55
Cpd 54: 6-Hydroxynicotine (S)	4.31	178.11061	9978	6-Hydroxynicotine (S)	C10 H14 N2 O	178.11061	-0.03	C10 H14 N2 O	-0.6
Cpd 51: Bufencarb	4.523	221.14166	15231	Bufencarb	C13 H19 N O2	221.14158	0.39	C13 H19 N O2	1.07
Cpd 265: Sotalol	4.676	272.11982	410	Sotalol	C12 H20 N2 O3 S	272.11946	1.33	C12 H20 N2 O3 S	-2.29
Cpd 129: Esculin (Polychrome)	4.702	340.07933	4476	Esculin (Polychrome)	C15 H16 O9	340.07943	-0.31	C15 H16 O9	0.8
Cpd 254: 4-[2-(Propylamino)ethyl]-1,3-dihydro-2H-indol-2-one	4.795	218.14194	691	4-[2-(Propylamino)ethyl]-1,3-dihydro-2H-indol-2-one	C13 H18 N2 O	218.14191	0.13	C13 H18 N2 O	-0.65
Cpd 1: Pramiracetam	4.864	269.21048	90695	Pramiracetam	C14 H27 N3 O2	269.21033	0.55	C14 H27 N3 O2	0.09
Cpd 248: Ciclacillin	4.957	341.14013	757	Ciclacillin	C15 H23 N3 O4 S	341.14093	-2.32	C15 H23 N3 O4 S	0.19
Cpd 121: Buformine	4.974	157.13254	3334	Buformine	C6 H15 N5	157.13275	-1.32	C6 H15 N5	-0.25
Cpd 79: N'-Hydroxymethylnorcotinine	4.983	192.08995	8963	N'-Hydroxymethylnorcotinine	C10 H12 N2 O2	192.08988	0.38	C10 H12 N2 O2	-0.26
Cpd 62: Pribecaine	5.059	277.16761	9104	Pribecaine	C16 H23 N O3	277.16779	-0.65	C16 H23 N O3	-0.05
Cpd 231: Tecomine	5.085	179.12958	674	Tecomine	C11 H17 N O	179.13101	-8	C11 H17 N O	6.81
Cpd 186: Diphacinone	5.179	340.11057	2460	Diphacinone	C23 H16 O3	340.10994	1.83	C23 H16 O3	0.09
Cpd 259: Aramite	5.196	334.10086	806	Aramite	C15 H23 Cl O4 S	334.10056	0.89	C15 H23 Cl O4 S	0.43
Cpd 193: Triazamate	5.204	314.14104	1211	Triazamate	C13 H22 N4 O3 S	314.14126	-0.71	C13 H22 N4 O3 S	-0.76
Cpd 170: 1-(3-Pyridinyl)-1,4-butanediol	5.264	167.09458	2380	1-(3-Pyridinyl)-1,4-butanediol	C9 H13 N O2	167.09463	-0.29	C9 H13 N O2	0.12
Cpd 125: Homatropine	5.383	275.15169	2890	Homatropine	C16 H21 N O3	275.15214	-1.63	C16 H21 N O3	0.75
Cpd 117: Gabapentin	5.4	171.12592	3718	Gabapentin	C9 H17 N O2	171.12593	-0.05	C9 H17 N O2	-0.71
Cpd 190: Arecoline	5.485	155.09469	665	Arecoline	C8 H13 N O2	155.09463	0.39	C8 H13 N O2	-1.22
Cpd 39: Ambenoxan	5.553	267.1468	30587	Ambenoxan	C14 H21 N O4	267.14706	-0.97	C14 H21 N O4	1.87
Cpd 63: Oxprenolol	5.57	265.16778	14740	Oxprenolol	C15 H23 N O3	265.16779	-0.06	C15 H23 N O3	0.46
Cpd 178: Gly Trp	5.681	261.11121	2204	Gly Trp	C13 H15 N3 O3	261.11134	-0.49	C13 H15 N3 O3	-0.05
Cpd 106: Theophylline	5.69	180.06446	4737	Theophylline	C7 H8 N4 O2	180.06473	-1.49	C7 H8 N4 O2	1.35
Cpd 86: Dacarbazine	5.724	182.09189	8310	Dacarbazine	C6 H10 N6 O	182.09161	1.56	C6 H10 N6 O	0.04
Cpd 42: Acetylhelenalin	5.826	304.13049	22757	Acetylhelenalin	C17 H20 O5	304.13107	-1.93	C17 H20 O5	0.37
Cpd 80: Ephedrine	5.869	165.11524	7912	Ephedrine	C10 H15 N O	165.11536	-0.76	C10 H15 N O	0.37
Cpd 75: O-Desmethyltramadol	5.979	249.17279	7869	O-Desmethyltramadol	C15 H23 N O2	249.17288	-0.34	C15 H23 N O2	0.42
Cpd 35: Arg Ser Ser	6.03	348.17585	37612	Arg Ser Ser	C12 H24 N6 O6	348.17573	0.33	C12 H24 N6 O6	-0.13
Cpd 163: 8-Hydroxychinolin (8-Hydroxyquinoline)	6.099	145.05283	2164	8-Hydroxychinolin (8-Hydroxyquinoline)	C9 H7 N O	145.05276	0.46	C9 H7 N O	-0.9
Cpd 243: Nifenazone	6.124	308.12719	537	Nifenazone	C17 H16 N4 O2	308.12733	-0.45	C17 H16 N4 O2	-0.93
Cpd 161: Acetylpheneturide	6.133	248.11601	2037	Acetylpheneturide	C13 H16 N2 O3	248.11609	-0.35	C13 H16 N2 O3	-0.83
Cpd 37: Cotinine	6.252	176.09515	33290	Cotinine	C10 H12 N2 O	176.09496	1.07	C10 H12 N2 O	-0.86
Cpd 245: Sudan 410	6.329	408.19579	789	Sudan 410	C26 H24 N4 O	408.19501	1.9	C26 H24 N4 O	1.5
Cpd 49: Thr Gln Gln	6.576	375.17526	24305	Thr Gln Gln	C14 H25 N5 O7	375.1754	-0.36	C14 H25 N5 O7	0.1
Cpd 131: Fencamine	6.601	384.22733	2617	Fencamine	C20 H28 N6 O2	384.22737	-0.13	C20 H28 N6 O2	0.19
Cpd 237: Propacetamol	6.644	264.14756	973	Propacetamol	C14 H20 N2 O3	264.14739	0.63	C14 H20 N2 O3	-0.98
Cpd 48: Etazolate	6.652	289.15384	22870	Etazolate	C14 H19 N5 O2	289.15387	-0.11	C14 H19 N5 O2	-0.14
Cpd 26: Octodrine	6.72	129.15172	21494	Octodrine	C8 H19 N	129.15175	-0.23	C8 H19 N	-0.15
Cpd 18: Thr Gln Asn	6.78	361.15968	50329	Thr Gln Asn	C13 H23 N5 O7	361.15975	-0.19	C13 H23 N5 O7	0.05
Cpd 195: Ampyrone	6.814	203.10596	12469	Ampyrone	C11 H13 N3 O	203.10586	0.47	C11 H13 N3 O	0.21
Cpd 73: Aminoantipyrine	6.814	203.10596	12469	Aminoantipyrine	C11 H13 N3 O	203.10586	0.47	C11 H13 N3 O	-0.28
Cpd 64: Dinaline	6.814	227.10595	13680	Dinaline	C13 H13 N3 O	227.10586	0.39	C13 H13 N3 O	-0.22
Cpd 33: Caffeine	6.916	194.08052	39014	Caffeine	C8 H10 N4 O2	194.08038	0.72	C8 H10 N4 O2	-0.08
Cpd 188: 8-Oxodeoxycoformycin	6.993	266.10146	3801	8-Oxodeoxycoformycin	C11 H14 N4 O4	266.1015	-0.19	C11 H14 N4 O4	0.17
Cpd 114: Sulfadimidine	7.061	278.08372	4822	Sulfadimidine	C12 H14 N4 O2 S	278.08375	-0.09	C12 H14 N4 O2 S	-0.44
Cpd 99: Isoproturon	7.197	206.14213	2214	Isoproturon	C12 H18 N2 O	206.14191	1.07	C12 H18 N2 O	-1.62
Cpd 46: Urapidil	7.248	387.22726	27154	Urapidil	C20 H29 N5 O3	387.22704	0.57	C20 H29 N5 O3	0.1
Cpd 269: Sulfamethoxazole	7.325	253.05192	632	Sulfamethoxazole	C10 H11 N3 O3 S	253.05211	-0.74	C10 H11 N3 O3 S	-0.89
Cpd 23: Clomiphene	7.359	405.18583	40060	Clomiphene	C26 H28 Cl N O	405.18594	-0.28	C26 H28 Cl N O	-0.31
Cpd 167: Arg Gln Arg	7.504	458.27174	2412	Arg Gln Arg	C17 H34 N10 O5	458.27136	0.82	C17 H34 N10 O5	0.35
Cpd 205: Aceclidine	7.657	169.11028	931	Aceclidine	C9 H15 N O2	169.11028	-0.01	C9 H15 N O2	0.13
Cpd 197: Gly Ser His	7.691	299.12272	984	Gly Ser His	C11 H17 N5 O5	299.12297	-0.83	C11 H17 N5 O5	-0.06
Cpd 105: Arg Gly Gly	7.87	288.15475	5239	Arg Gly Gly	C10 H20 N6 O4	288.1546	0.51	C10 H20 N6 O4	-0.18
Cpd 31: Vasicine	8.024	188.09511	43946	Vasicine	C11 H12 N2 O	188.09496	0.77	C11 H12 N2 O	-0.04
Cpd 230: Terbucarb	8.143	277.20392	1014	Terbucarb	C17 H27 N O2	277.20418	-0.94	C17 H27 N O2	0.65
Cpd 136: Homosalate	8.151	262.15673	2600	Homosalate	C16 H22 O3	262.15689	-0.61	C16 H22 O3	0.25
Cpd 68: N-Desmethylvenlafaxine	8.177	263.18848	10809	N-Desmethylvenlafaxine	C16 H25 N O2	263.18853	-0.19	C16 H25 N O2	0.08
Cpd 220: Congocidin (Netropsin)	8.296	430.2193	1313	Congocidin (Netropsin)	C18 H26 N10 O3	430.21893	0.86	C18 H26 N10 O3	-0.24
Cpd 41: 4-Nonynoic acid	8.509	154.09927	8665	4-Nonynoic acid	C9 H14 O2	154.09938	-0.73	C9 H14 O2	0.21
Cpd 16: Metoprolol	8.662	267.18347	1369	Metoprolol	C15 H25 N O3	267.18344	0.1	C15 H25 N O3	0.11
Cpd 43: Esaprazole	8.705	225.18421	15221	Esaprazole	C12 H23 N3 O	225.18411	0.44	C12 H23 N3 O	-0.05
Cpd 185: Anabaseine	8.773	160.10001	1443	Anabaseine	C10 H12 N2	160.10005	-0.24	C10 H12 N2	-0.68
Cpd 150: His Gly Thr	8.799	313.13853	3858	His Gly Thr	C12 H19 N5 O5	313.13862	-0.3	C12 H19 N5 O5	0.24
Cpd 101: Lamotrigine	8.85	255.0077	2929	Lamotrigine	C9 H7 Cl2 N5	255.00785	-0.6	C9 H7 Cl2 N5	0.4
Cpd 137: PYCC / 1-(Pyrrolidin-1-yl)cyclohexanecarbonitrile	8.867	178.147	1436	PYCC / 1-(Pyrrolidin-1-yl)cyclohexanecarbonitrile	C11 H18 N2	178.147	0.03	C11 H18 N2	-0.58
Cpd 210: Alprenolol	9.003	249.17255	1172	Alprenolol	C15 H23 N O2	249.17288	-1.33	C15 H23 N O2	1.01
Cpd 166: 2-Aminobenzimidazole	9.224	133.06415	3011	2-Aminobenzimidazole	C7 H7 N3	133.064	1.18	C7 H7 N3	-2.66
Cpd 158: Lomifylline	9.267	278.13863	2969	Lomifylline	C13 H18 N4 O3	278.13789	2.67	C13 H18 N4 O3	-1.56
Cpd 108: Leptacline	9.293	181.18291	3262	Leptacline	C12 H23 N	181.18305	-0.77	C12 H23 N	0.5
Cpd 249: Crenatine A	9.46	568.30585	1015	Crenatine A	C34 H40 N4 O4	568.30496	1.57	C34 H40 N4 O4	0.27
Cpd 57: Gly Ala Arg	9.531	302.17014	15617	Gly Ala Arg	C11 H22 N6 O4	302.17025	-0.37	C11 H22 N6 O4	-0.14
Cpd 160: Quinprenaline	9.625	246.13637	1504	Quinprenaline	C14 H18 N2 O2	246.13683	-1.84	C14 H18 N2 O2	1.73
Cpd 196: Arg Ser Ala	9.77	332.1804	1600	Arg Ser Ala	C12 H24 N6 O5	332.18082	-1.26	C12 H24 N6 O5	0.31
Cpd 222: Acetryptin	9.778	202.11051	1261	Acetryptin	C12 H14 N2 O	202.11061	-0.53	C12 H14 N2 O	-0.52
Cpd 184: Trepibutone	10.008	310.14128	1498	Trepibutone	C16 H22 O6	310.14164	-1.15	C16 H22 O6	2.64
Cpd 204: Dihydrocoumarin	10.255	148.05227	874	Dihydrocoumarin	C9 H8 O2	148.05243	-1.09	C9 H8 O2	0.21
Cpd 113: Ascaridole	10.315	168.11488	1730	Ascaridole	C10 H16 O2	168.11503	-0.86	C10 H16 O2	0.69
Cpd 25: 2-hydroxy-10-undecenoic acid	10.323	200.14137	21616	2-hydroxy-10-undecenoic acid	C11 H20 O3	200.14124	0.61	C11 H20 O3	0.17
Cpd 90: Cycluron	10.374	198.1732	3052	Cycluron	C11 H22 N2 O	198.17321	-0.05	C11 H22 N2 O	-0.02
Cpd 66: Methfuroxam	10.749	229.11018	11426	Methfuroxam	C14 H15 N O2	229.11028	-0.42	C14 H15 N O2	1.39
Cpd 93: Albuterol	10.826	239.15218	6144	Albuterol	C13 H21 N O3	239.15214	0.16	C13 H21 N O3	0.08
Cpd 14: 9-Riburonosyladenine	11.345	281.07622	58705	9-Riburonosyladenine	C10 H11 N5 O5	281.07602	0.72	C10 H11 N5 O5	-0.43
Cpd 98: 2-tert-Butyl-4-methoxyphenol	11.882	180.1148	4148	2-tert-Butyl-4-methoxyphenol	C11 H16 O2	180.11503	-1.26	C11 H16 O2	0.54
Cpd 110: Conhydrine	12.129	143.13091	4366	Conhydrine	C8 H17 N O	143.13101	-0.69	C8 H17 N O	-0.1
Cpd 45: 13,14-dihydro-16,16-difluoro Prostaglandin D2	12.367	390.22216	42117	13,14-dihydro-16,16-difluoro Prostaglandin D2	C20 H32 F2 O5	390.22178	0.97	C20 H32 F2 O5	0.11
Cpd 132: 2E,4E,6E-Nonatrienal	12.41	136.08868	1298	2E,4E,6E-Nonatrienal	C9 H12 O	136.08882	-0.97	C9 H12 O	-0.61
Cpd 97: Cyclobutoic acid	12.419	186.12577	4749	Cyclobutoic acid	C10 H18 O3	186.12559	0.93	C10 H18 O3	0.71
Cpd 118: 4-oxo-2E-Hexenal	12.47	112.05243	4669	4-oxo-2E-Hexenal	C6 H8 O2	112.05243	0.03	C6 H8 O2	-0.3
Cpd 198: p-Methoxycinnamaldehyde	12.58	162.06787	1321	p-Methoxycinnamaldehyde	C10 H10 O2	162.06808	-1.3	C10 H10 O2	-0.42
Cpd 252: Naphthalene	12.58	128.06252	1057	Naphthalene	C10 H8	128.0626	-0.63	C10 H8	-0.15
Cpd 47: DEET (Diethyltoluamide)	12.691	191.13106	27152	DEET (Diethyltoluamide)	C12 H17 N O	191.13101	0.25	C12 H17 N O	0.2
Cpd 52: Aspirin (Acetylsalicylic acid)	12.853	180.0423	19243	Aspirin (Acetylsalicylic acid)	C9 H8 O4	180.04226	0.22	C9 H8 O4	0.01
Cpd 20: Monoisobutyl phthalic acid	12.853	222.08938	20095	Monoisobutyl phthalic acid	C12 H14 O4	222.08921	0.79	C12 H14 O4	0.97
Cpd 138: Picaridin (Bayrepel)	13.228	229.16744	2962	Picaridin (Bayrepel)	C12 H23 N3 O3	229.16779	-1.55	C12 H23 N3 O3	1.58
Cpd 232: NECA / 5'-(N-Ethylcarboxamido)adenosine	13.415	308.12343	337	NECA / 5'-(N-Ethylcarboxamido)adenosine	C12 H16 N6 O4	308.1233	0.43	C12 H16 N6 O4	-2.06
Cpd 147: Triphenylphosphine oxide	13.466	278.08607	7248	Triphenylphosphine oxide	C18 H15 O P	278.08605	0.05	C18 H15 O P	-1.32
Cpd 214: Spectinomycin	13.594	332.15862	1023	Spectinomycin	C14 H24 N2 O7	332.15835	0.82	C14 H24 N2 O7	1.73
Cpd 175: Quercetin 3,3'-dimethyl ether 4'-(2-methylbutyrate)	13.671	414.13228	1348	Quercetin 3,3'-dimethyl ether 4'-(2-methylbutyrate)	C22 H22 O8	414.13147	1.95	C22 H22 O8	0.3
Cpd 85: Cyclandelate	13.679	276.17244	6069	Cyclandelate	C17 H24 O3	276.17254	-0.37	C17 H24 O3	-2.32
Cpd 262: Clebopride	13.688	373.15624	409	Clebopride	C20 H24 Cl N3 O2	373.1557	1.43	C20 H24 Cl N3 O2	-1.44
Cpd 38: Embelin	13.764	294.18254	9051	Embelin	C17 H26 O4	294.18311	-1.93	C17 H26 O4	0.54
Cpd 58: Torachrysone	13.798	246.08913	9027	Torachrysone	C14 H14 O4	246.08921	-0.31	C14 H14 O4	0.27
Cpd 267: Procinonide	13.977	508.22718	620	Procinonide	C27 H34 F2 O7	508.22726	-0.17	C27 H34 F2 O7	-0.34
Cpd 127: Precoxene II	14.667	220.11005	2686	Precoxene II	C13 H16 O3	220.10994	0.5	C13 H16 O3	-0.7
Cpd 28: His Lys Met	14.693	414.20389	19022	His Lys Met	C17 H30 N6 O4 S	414.20492	-2.5	C17 H30 N6 O4 S	0.03
Cpd 211: Benzylhydroxybenzoate	14.786	228.07865	1012	Benzylhydroxybenzoate	C14 H12 O3	228.07864	0.02	C14 H12 O3	0.22
Cpd 36: Xanthinol Nicotinate	14.795	434.19119	37453	Xanthinol Nicotinate	C19 H26 N6 O6	434.19138	-0.44	C19 H26 N6 O6	0.02
Cpd 227: Nifedipine	15.136	346.11705	1046	Nifedipine	C17 H18 N2 O6	346.11649	1.64	C17 H18 N2 O6	1.87
Cpd 111: Cyclandelate	15.221	276.1727	6588	Cyclandelate	C17 H24 O3	276.17254	0.56	C17 H24 O3	-2.53
Cpd 153: Triphenyl phosphate	15.408	326.07035	2806	Triphenyl phosphate	C18 H15 O4 P	326.0708	-1.36	C18 H15 O4 P	-0.47
Cpd 207: Dinocton	15.885	354.14327	1624	Dinocton	C16 H22 N2 O7	354.1427	1.61	C16 H22 N2 O7	-5
Cpd 77: Tributylphosphate	16.013	266.16479	43448	Tributylphosphate	C12 H27 O4 P	266.1647	0.37	C12 H27 O4 P	-0.36
Cpd 12: Caffeic acid	16.021	180.04231	56429	Caffeic acid	C9 H8 O4	180.04226	0.26	C9 H8 O4	-0.59
Cpd 72: Aspidodasycarpine	16.047	370.18858	11098	Aspidodasycarpine	C21 H26 N2 O4	370.18926	-1.84	C21 H26 N2 O4	0.33
Cpd 200: 6β-Hydroxyprednisolone	16.107	376.18804	1195	6β-Hydroxyprednisolone	C21 H28 O6	376.18859	-1.46	C21 H28 O6	1.49
Cpd 69: 3,5-Diprenyl-4-Hydroxyacetophenone	16.294	272.17721	7359	3,5-Diprenyl-4-Hydroxyacetophenone	C18 H24 O2	272.17763	-1.55	C18 H24 O2	0.34
Cpd 246: Simmondsin-2'-ferulate	16.328	551.19947	771	Simmondsin-2'-ferulate	C26 H33 N O12	551.20028	-1.47	C26 H33 N O12	0.24
Cpd 155: Butibufen	16.354	220.14626	16588	Butibufen	C14 H20 O2	220.14633	-0.33	C14 H20 O2	-0.26
Cpd 209: Met-Asn-OH	16.413	371.07672	1437	Met-Asn-OH	C14 H17 N3 O7 S	371.07872	-5.4	C14 H17 N3 O7 S	1.04
Cpd 171: Amicetin	16.524	618.30149	1473	Amicetin	C29 H42 N6 O9	618.30133	0.27	C29 H42 N6 O9	0.01
Cpd 174: Dipyridamole	17.342	504.31802	884	Dipyridamole	C24 H40 N8 O4	504.31725	1.53	C24 H40 N8 O4	2.73
Cpd 225: Milbemectin A3	17.35	528.30815	653	Milbemectin A3	C31 H44 O7	528.3087	-1.05	C31 H44 O7	-0.1
Cpd 208: Thr Trp Met	17.469	436.17847	989	Thr Trp Met	C20 H28 N4 O5 S	436.17804	0.98	C20 H28 N4 O5 S	-0.84
Cpd 164: Xibornol	17.529	258.19813	2462	Xibornol	C18 H26 O	258.19837	-0.89	C18 H26 O	0.25
Cpd 82: Palmitic amide	17.555	255.25634	8212	Palmitic amide	C16 H33 N O	255.25621	0.5	C16 H33 N O	-0.56
Cpd 270: 2-Formyl-1-indanone	17.589	160.05223	717	2-Formyl-1-indanone	C10 H8 O2	160.05243	-1.24	C10 H8 O2	-0.82
Cpd 256: Aspoxicillin	17.963	493.16354	772	Aspoxicillin	C21 H27 N5 O7 S	493.16312	0.85	C21 H27 N5 O7 S	2.56
Cpd 100: Gentamicin A	18.279	468.24328	4372	Gentamicin A	C18 H36 N4 O10	468.24314	0.3	C18 H36 N4 O10	0.25
Cpd 172: 3'-Deoxystreptomycin 6,3''-bis-phosphate	18.474	725.2024	1633	3'-Deoxystreptomycin 6,3''-bis-phosphate	C21 H41 N7 O17 P2	725.20342	-1.41	C21 H41 N7 O17 P2	3.04

Joint Programme of Activities 2013 - 2014

- **NORMAN MassBank**
- **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
- **Joint Danube Survey 3**
- **Digital Sample Banking** – European archive for storage of raw mass spectral data; **retrospective analysis**
- Development of minimal requirements for storage of MS data in libraries

- **SOLUTIONS - http://www.solutions-project.eu/**
  - FP7 project, 39 partners, 12 million EUR
  - 2013 - 2018

European Demonstration Programme

- Battery of 9 bioassays with 21 endpoints
- Extensive target analysis (N=140) + non-target screening

Top 10 target compouds:

Rank	*Frequency of occurrence (N=20+5 blanks)*
1	Benzotriazole (22)
2	Caffeine (22)
3	Perfluorooctanoic acid (PFOA) (22)
4	p-Toluenesulfonamide (22)
5	Bisphenol A (21)
6	5-Methyl-1H-benzotriazole (21)
7	Nonylphenol (NP) (20)
8	Carbamazepine (20)
9	Desethylatrazine (20)
10	Diclofenac (20) / Phenylbenzimidazole sulfonic acid (20)

Most frequent effects:

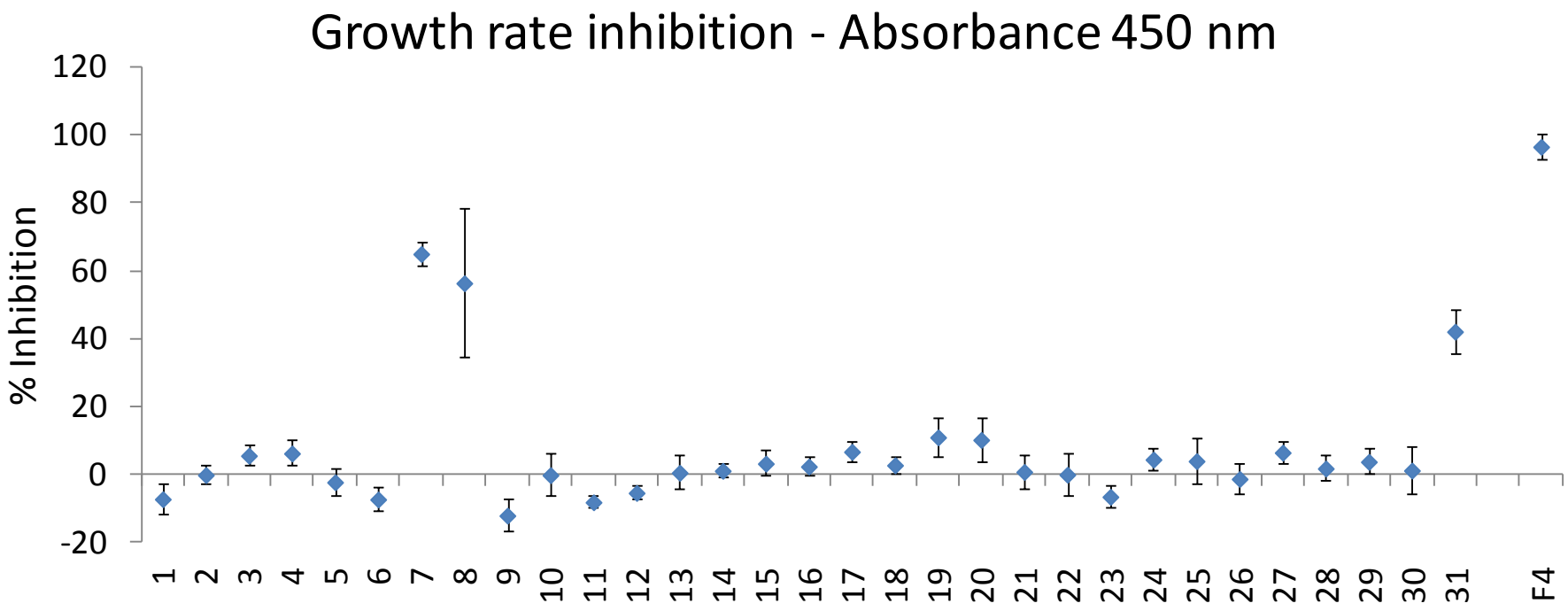
- Cytotoxicity
- Estrogenicity
- Algal growth inhibition
- AChE inhibition

HT EDA study – Morava RB

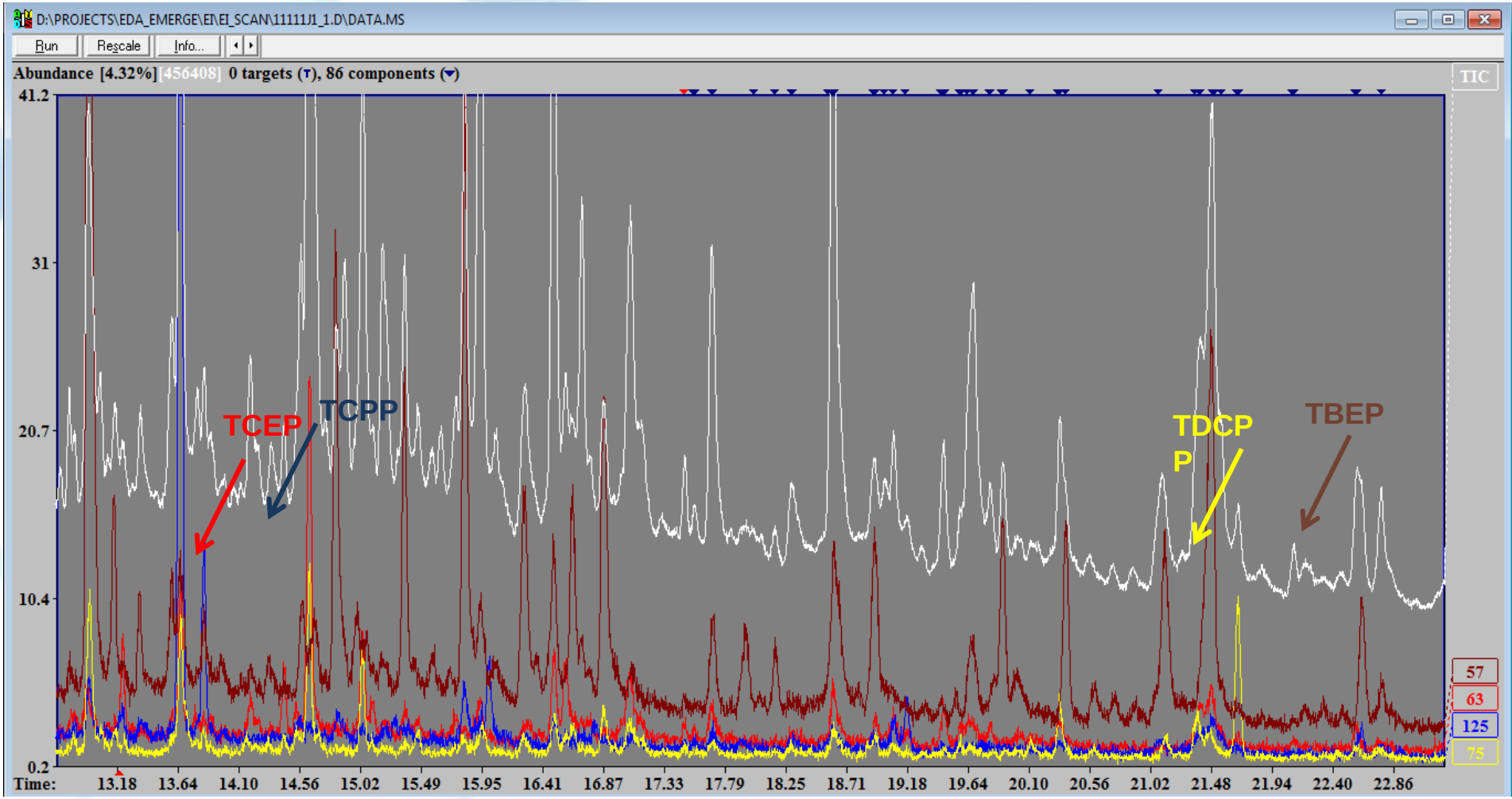
WWTP effl.

F7, F8, F31 – algal growth rate inhibition, photosystem II inhibition

F7, F8 – dioxin-like activity



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

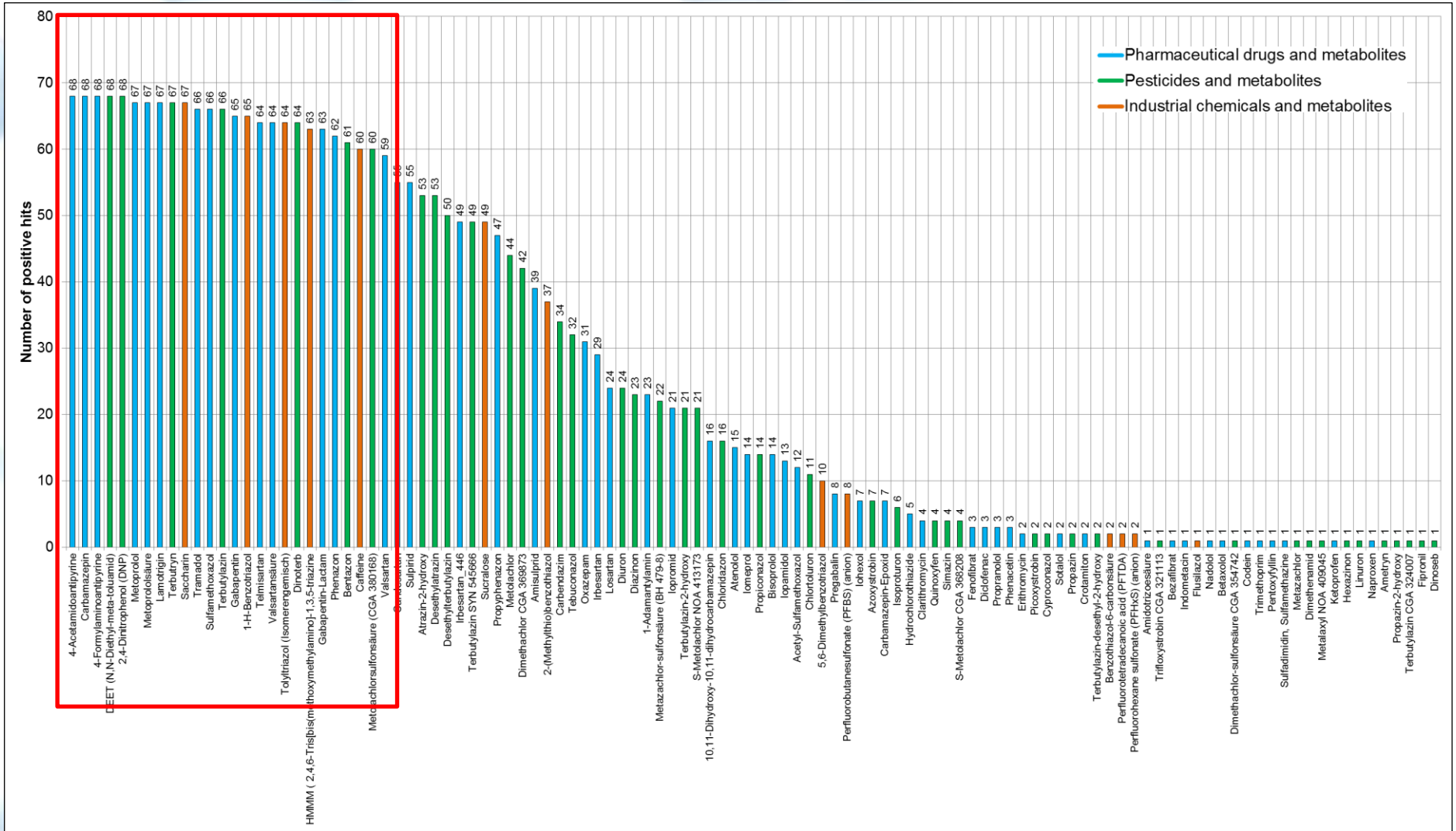


JDS3 – preliminary prioritisation

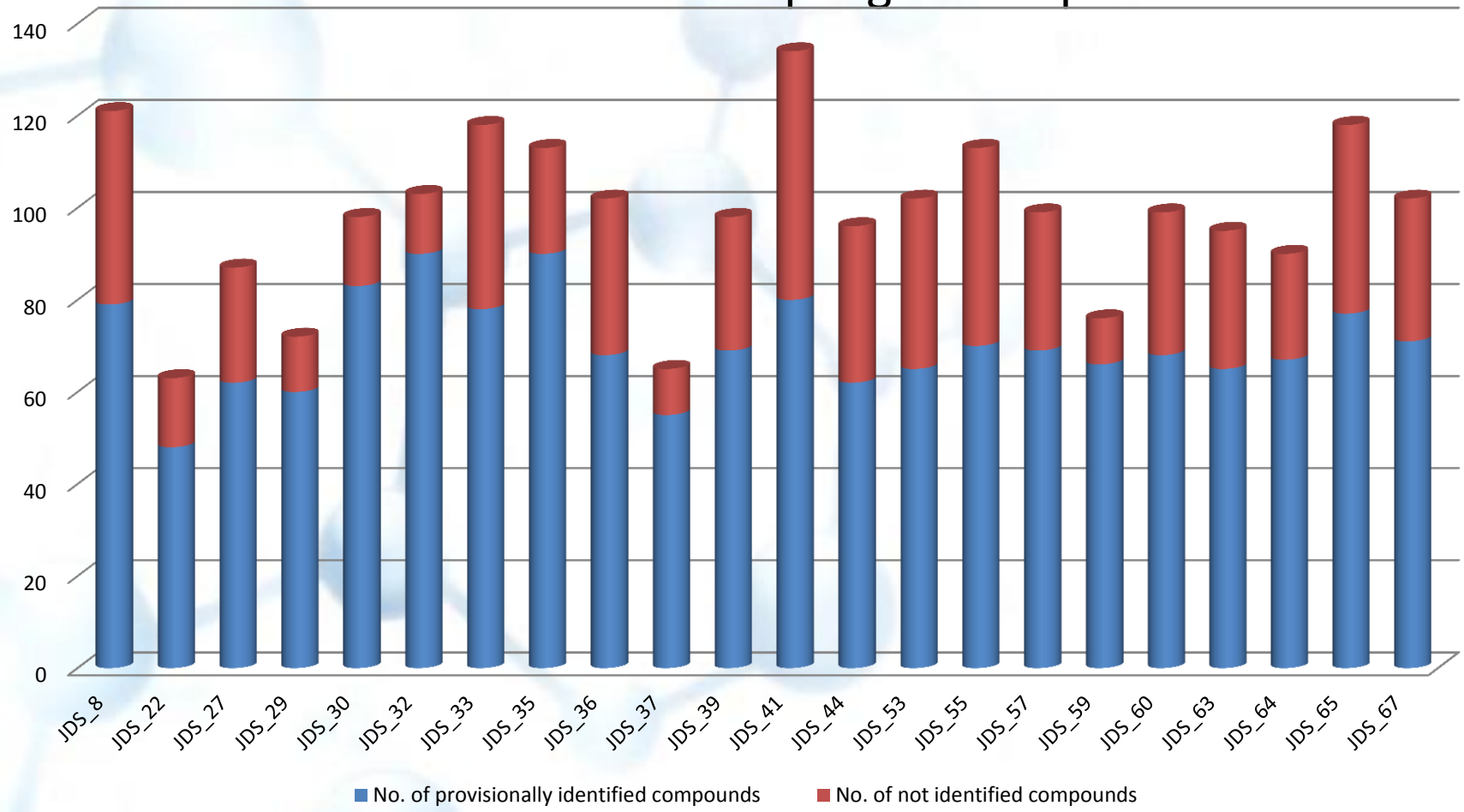
No.	Substance	No. of sites substance detected	C_{max}[1]	MEC_{95}[2]	Lowest PNEC/EQS	Type	EoE[3]	EoE score	FoE[4]	Final score
1	2,4-Dinitrophenol (DNP)	68	0.06	0.04	0.001	EQS chronic water[5]	40	0.2	1.00	1.20
2	PFOS (Perfluorooctansulfonate)	63	0.026	0.02	0.00065	EQS chronic water[5]	31	0.2	0.93	1.13
3	Chloroxuron	65	0.04	0.02	0.0024	PNEC acute	8.3	0.1	0.93	1.03
4	PFOA (Perfluorooctanoate)	66	0.036	0.02	0.0029	P-PNEC[6]	6.9	0.1	0.90	1.00
5	Desethylterbutylazine	54	0.028	0.01	0.0024	EQS chronic water[5]	4.2	0.1	0.79	0.89
6	2-hydroxy atrazine	53	0.06	0.02	0.002	EQS chronic water[5]	10	0.1	0.76	0.86
7	PFNA (Perfluorononanoate)	52	0.003	0.003	0.00039	P-PNEC[6]	7.7	0.1	0.76	0.86
8	Bromacil	31	0.19	0.14	0.01	EQS chronic water[5]	14	0.2	0.46	0.66
9	Dimefuron	58	0.041	0.04	0.008	EQS chronic water[5]	5.0	0.1	0.56	0.66
10	Bisphenol A	30	1.94	1.03	0.1	EQS chronic water[5]	10	0.2	0.16	0.36

JDS3 - Frequency of appearance

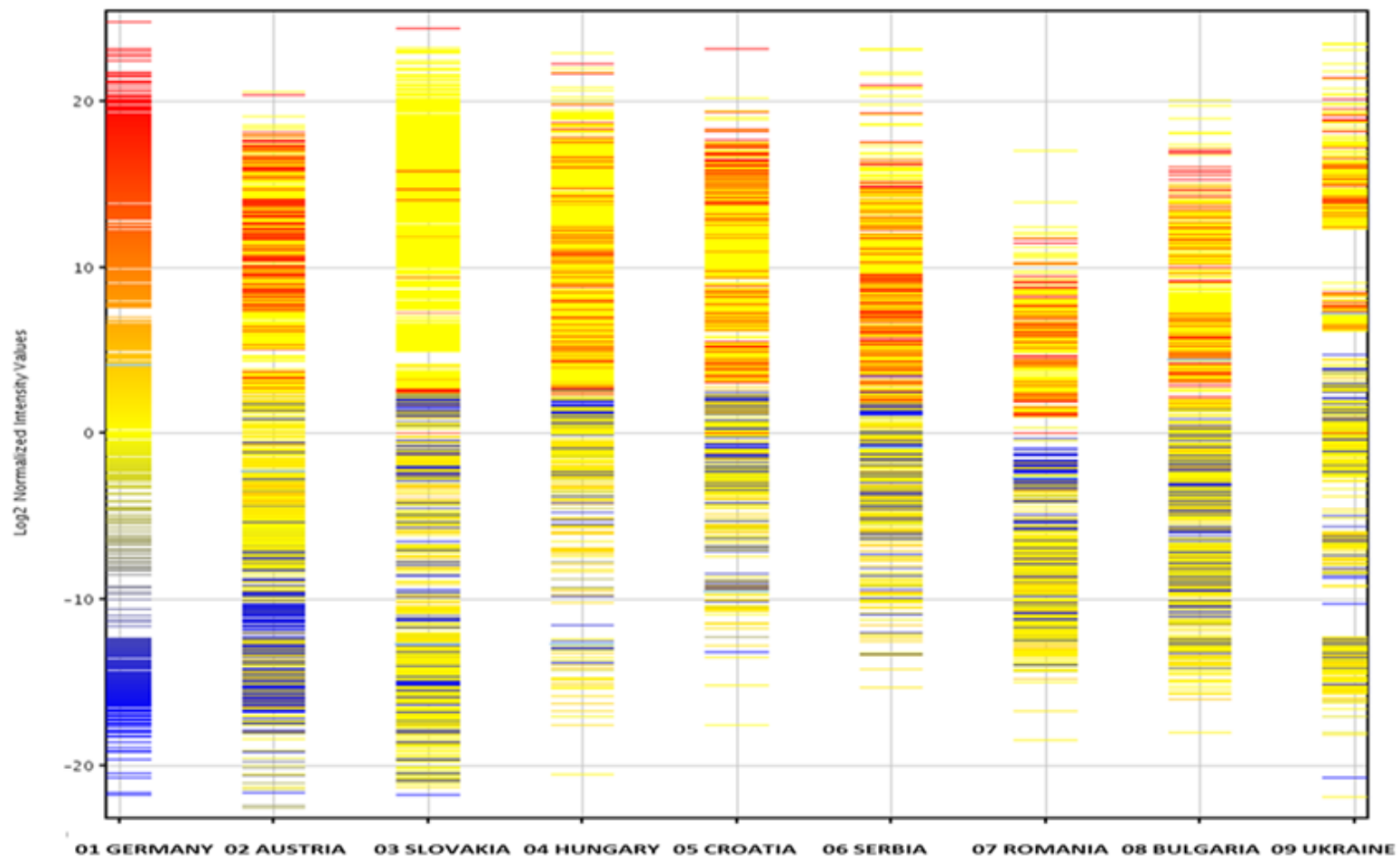
of 110 'identified' suspect pollutants (315 tested) in JDS3 surface water samples; results obtained from non-target screening workflow by HPLC-ESI-Q-TOF-MS operated in ESI⁺ and ESI⁻ modes



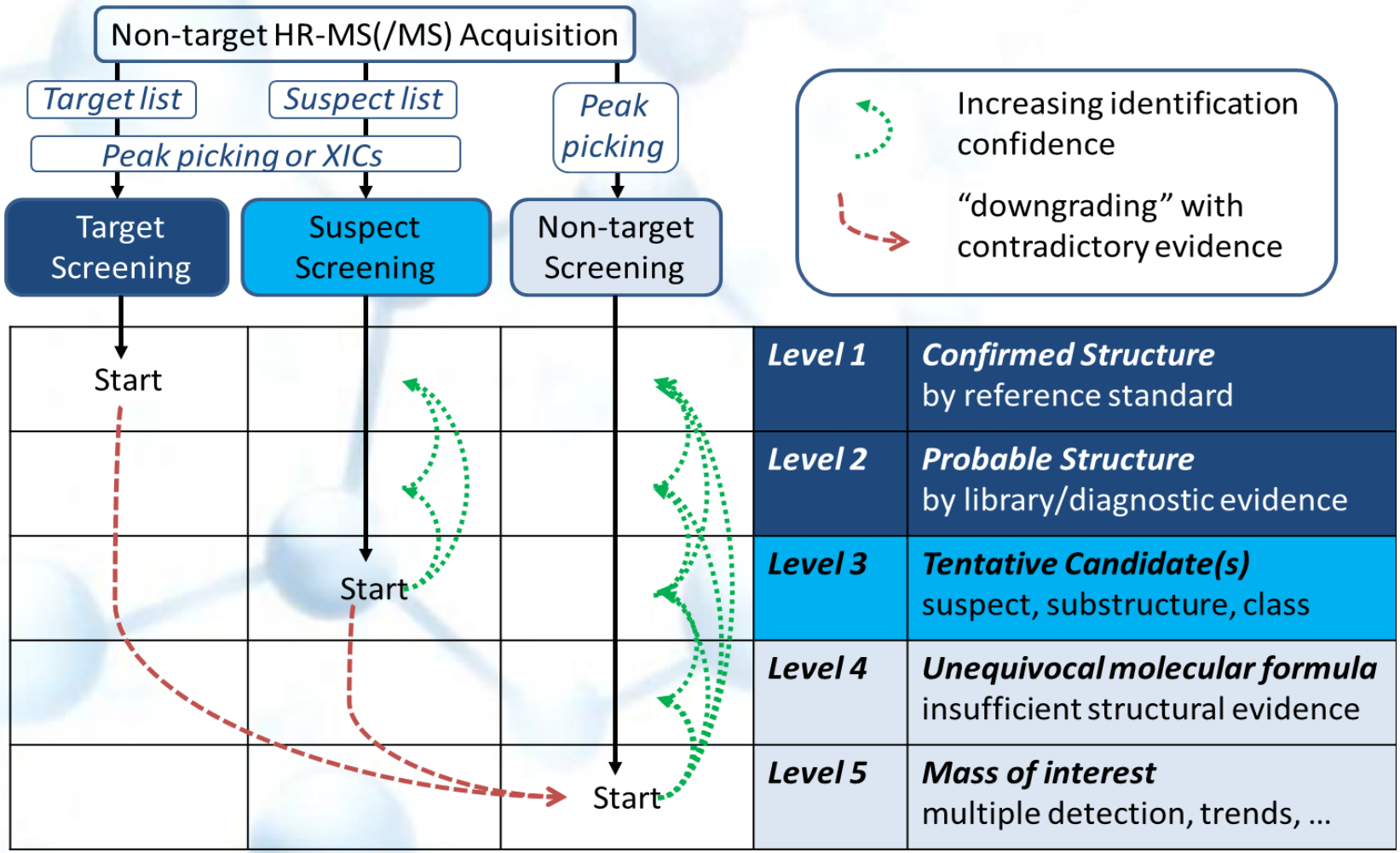
JDS3 - Number of compounds detected with LVI-GC-MS in the 22 JDS3 surface water samples obtained with the LVSPE sampling technique



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 – categorisation and prioritisation



Schymanski et al., 2015. Non-target screening with high resolution mass spectrometry: Critical review using a collaborative trail on water analysis. Analytical & Bioanalytical Chemistry, submitted.

JPA 2015

- **New Cross-Working Group Activity on Non-target screening**
  - Eawag, NIVA, EI, Umea University…

- **NORMAN network Early Warning System - NormaNEWS**
- **Exchange platform for targets, suspects and non-targets**
  - “screen smart” vs.“screen big”
- **EnviLights - Repository platform for raw chromatograms and sample associated metadata, data processing and profiling functions**
  - Support to prioritisation of compounds via non-target screening
  - MetaboLights platform
  - UFZ, UMEA, EAWAG, EI…
- **Collaborative Trial for non-target screening in dust from indoor environment**
  - NILU, EI…
- **Protocol for non-target screening in the Prioritisation methodology**
  - EI, INERIS…

Conclusions

- **It is not possible to develop the necessary knowledge and methodologies solely at the national scale**

  - **Usage data – exposure index**
  - Continuous **improvement of analytical expertise and data quality**
  - **European database** for storage of large dataset – raw full scan MS chromatograms for retrospective analysis
  - Common views of the scientific community on research needs and **priorities for future legislation**