

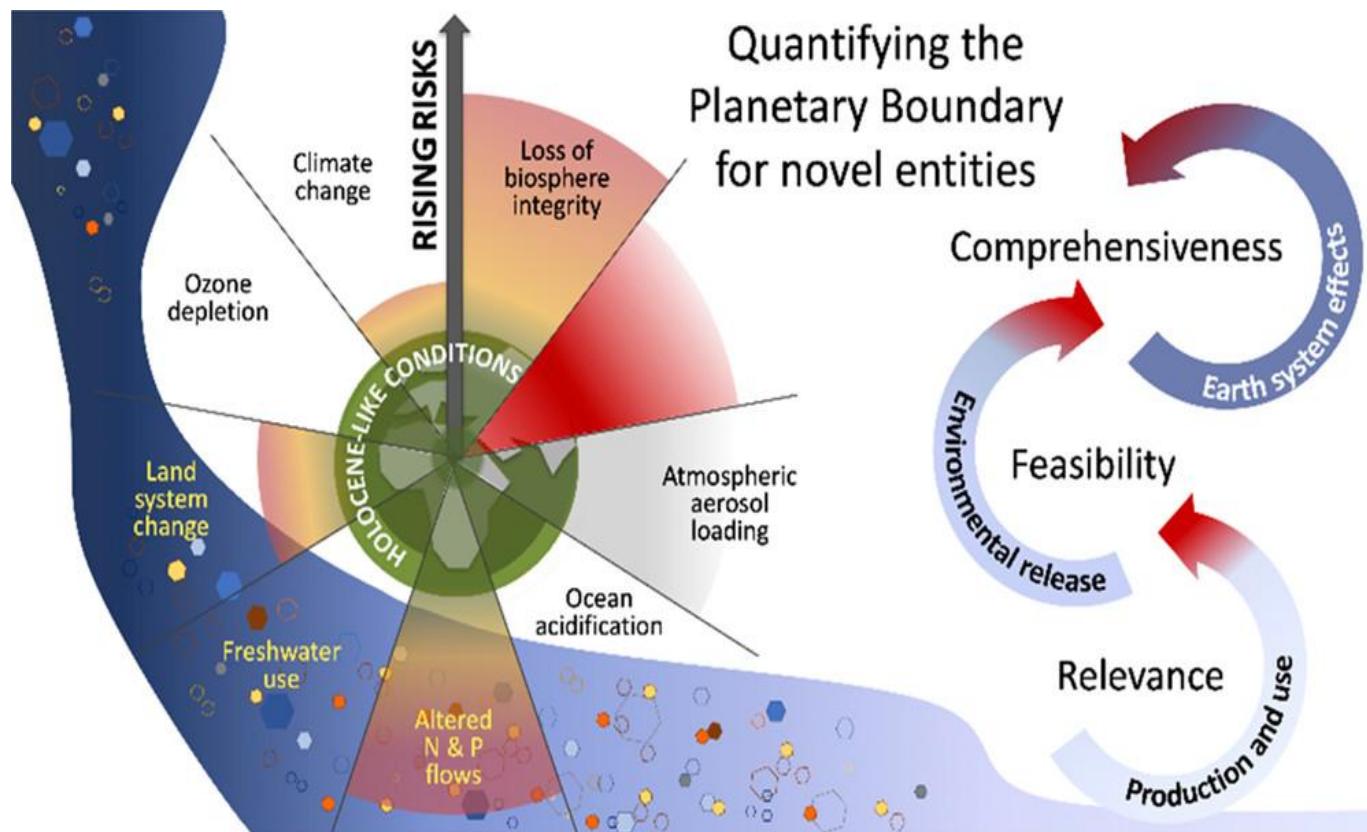
Comment la spectrométrie de masse permet-elle de caractériser l'empreinte de la pollution chimique des milieux aquatiques : enjeux, développements récents et limites

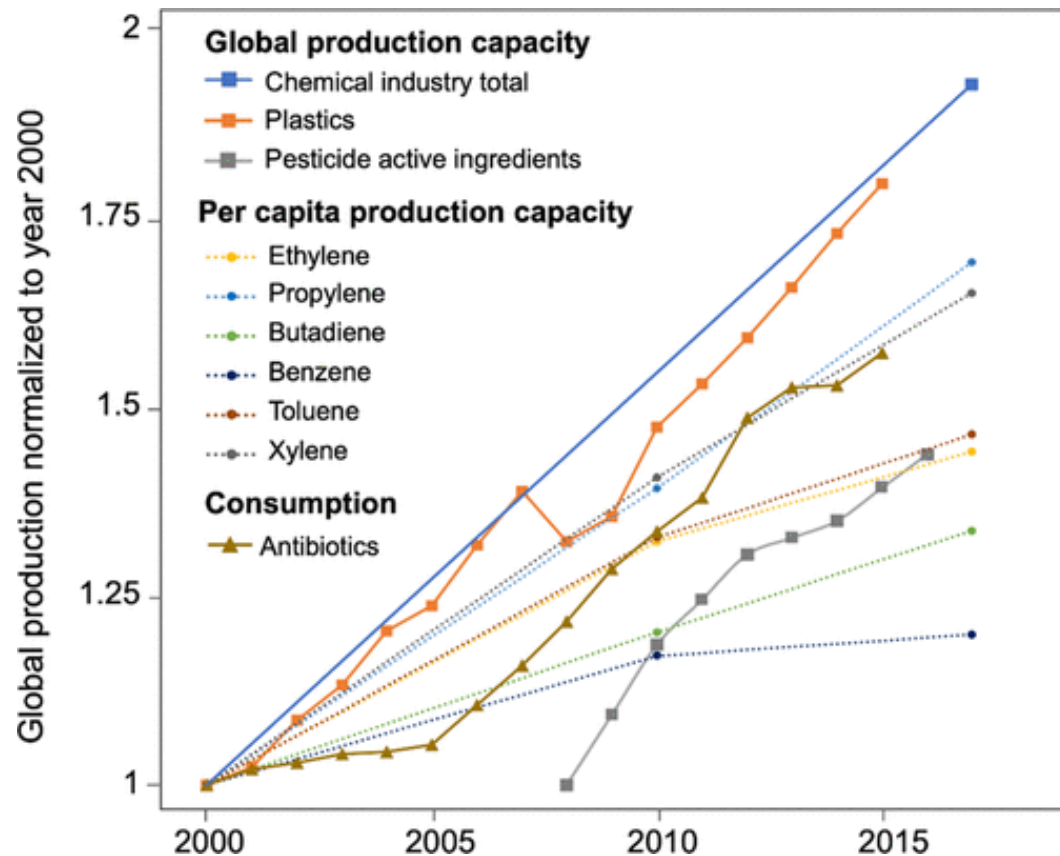
Hélène BUDZINSKI, Marie Hélène DEVIER

UMR 5805, EPOC, Université de Bordeaux/CNRS

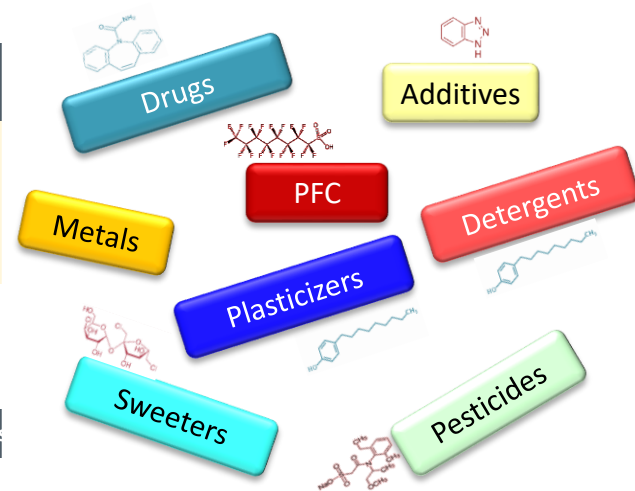
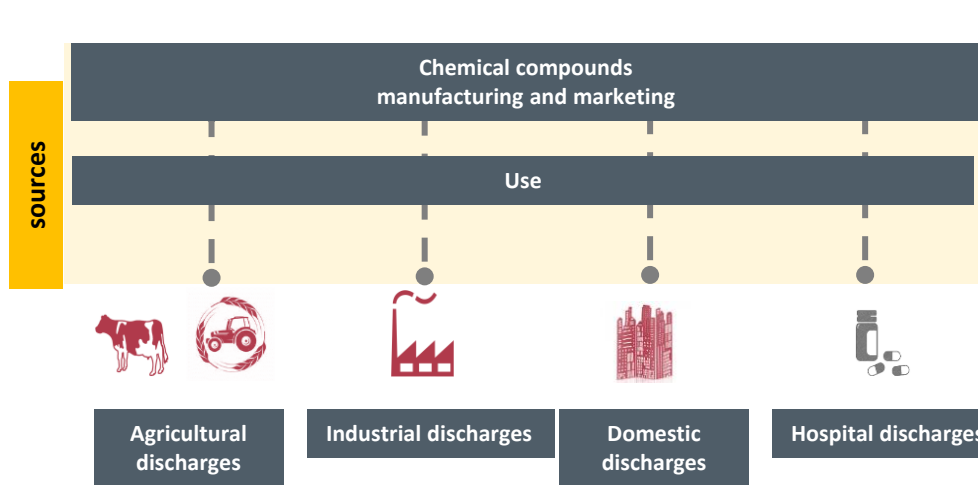


Chemical pollution: *Out of nine global limits on Earth, five have been exceeded (2022)*



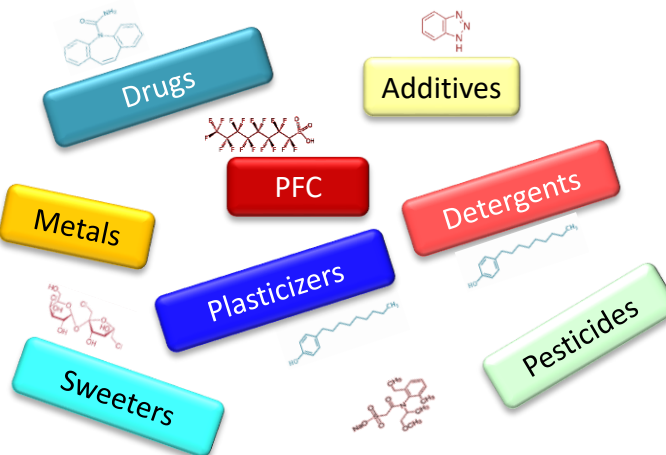
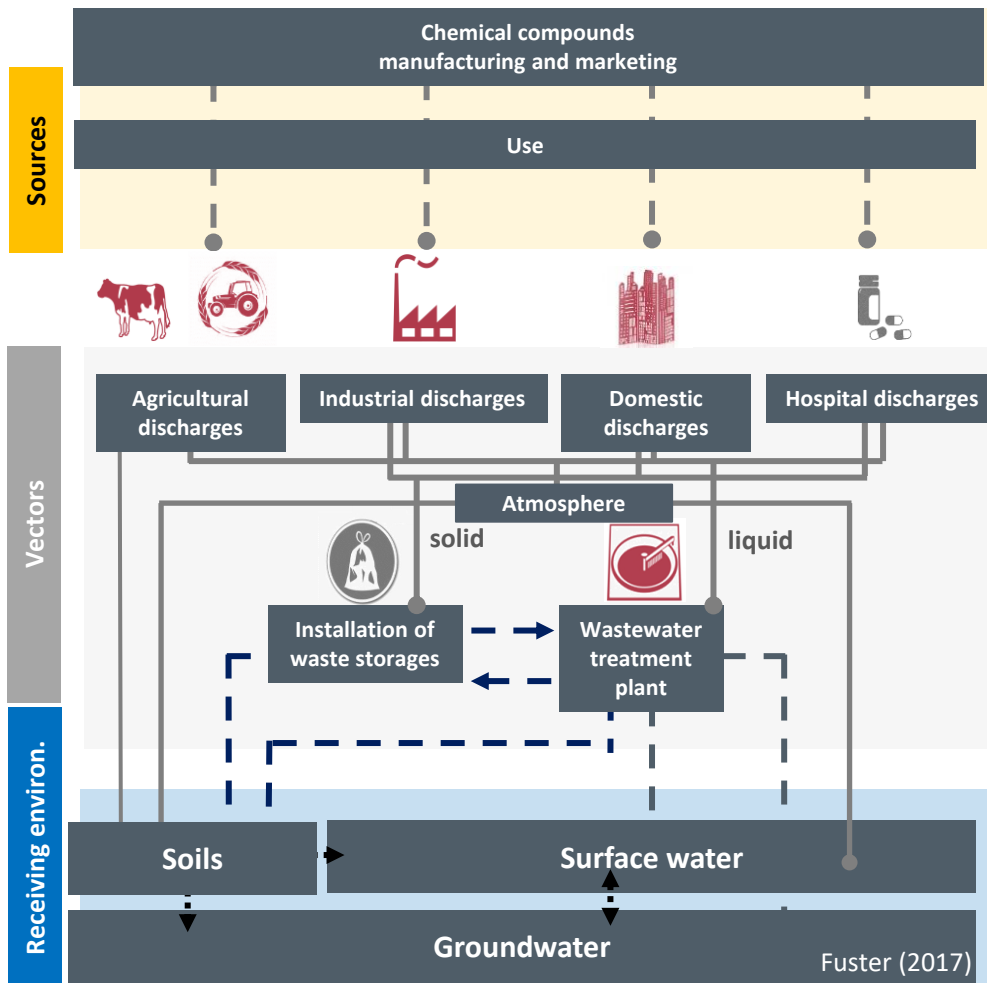


Chemical production has increased by a factor of 50 since 1950. And it is expected to triple again by 2050.
 Plastic production alone increased by 79% between 2000 and 2015



Fuster (2017)

Multi-use – Multi-sources – Multi-classes – Multi-compounds



Chemical compounds

Reg. 1907/2006/CE : **REACH**
 Reg. 1107/2009/UE : **Pesticides**
 Reg. 528/2012/UE : **Biocides**
 Dir. 2001/82-89/CE : **Drugs**

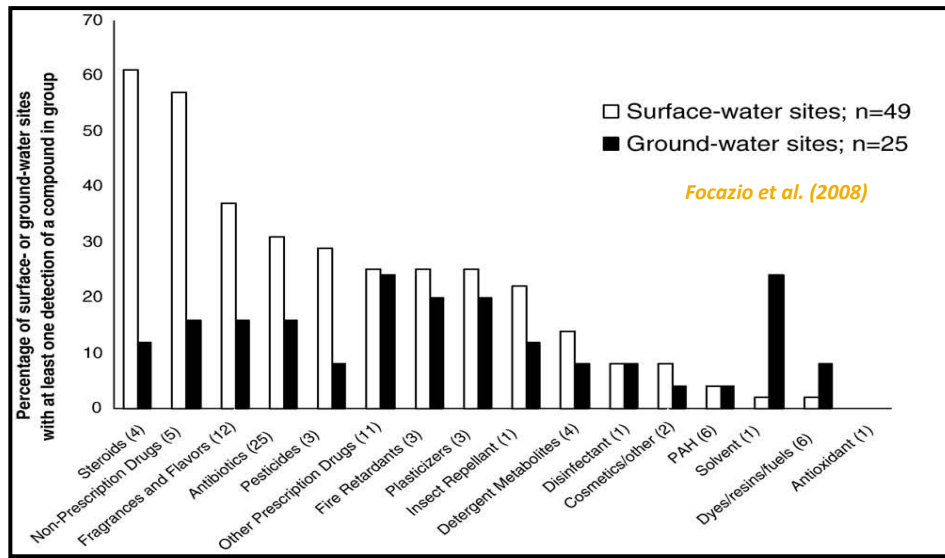
Emission and discharges

Dir. 2010/75/UE « **IED** » : industrial emissions
 Reg. 166/2006 « **E-PRTR** » : reporting of discharges : 91 comp.
 Dir. 91/271/CEE « **ERU** » : collection, transport and treatment of domestic wastewaters

Environment

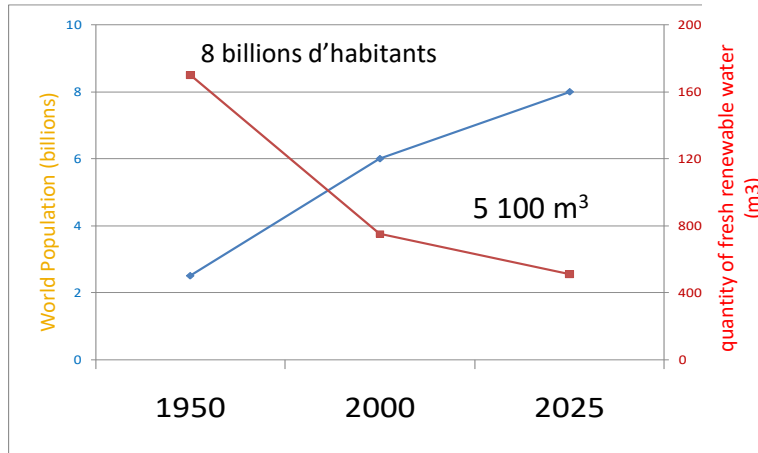
Dir. 2000/60/CE : **Water Framework Directive**
 Dir. 2006/118/CE : **Groundwater**
 Dir. 2008/56/EC : **Marine Strategy Framework Directive**
 ...

Fuster (2017)



IN THE CONTEXT OF :

- ➔ Generalization of water contamination
- ➔ Multi-class contamination
- ➔ Climatic and global changes

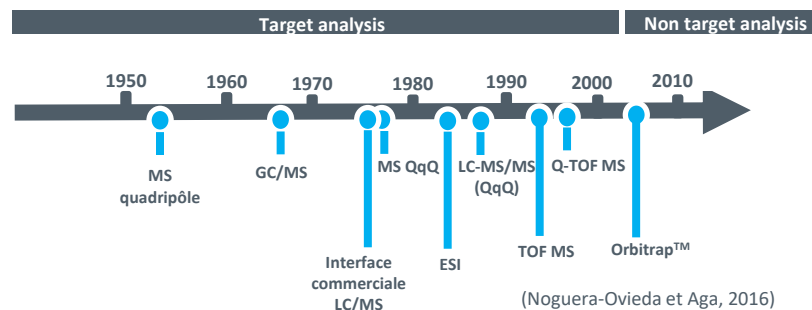
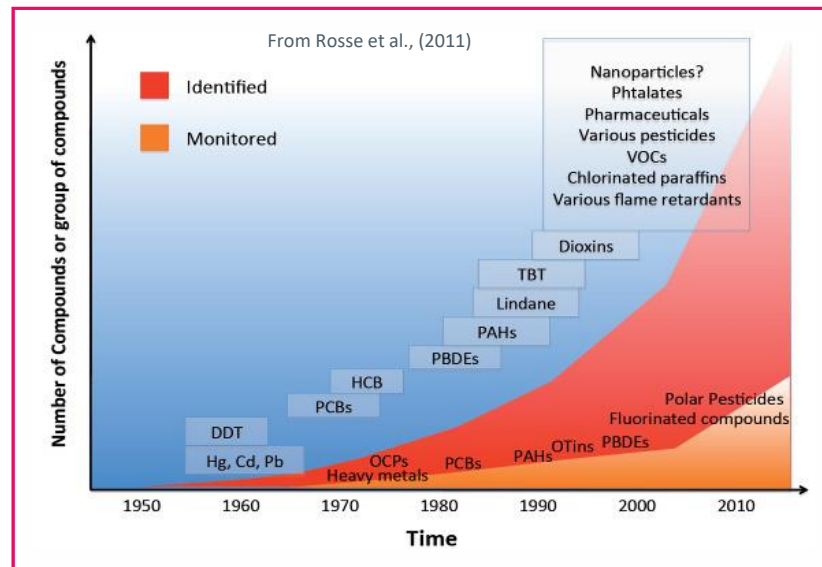


- ➔ Need to preserve the water resource (less than 1% of fresh water) from pollution
- ➔ Need to monitor water quality
- ➔ Need to identify sources - remediation - reduction at source

Regulated contaminants

Emergent contaminants of interest already identified

Unknown contaminants

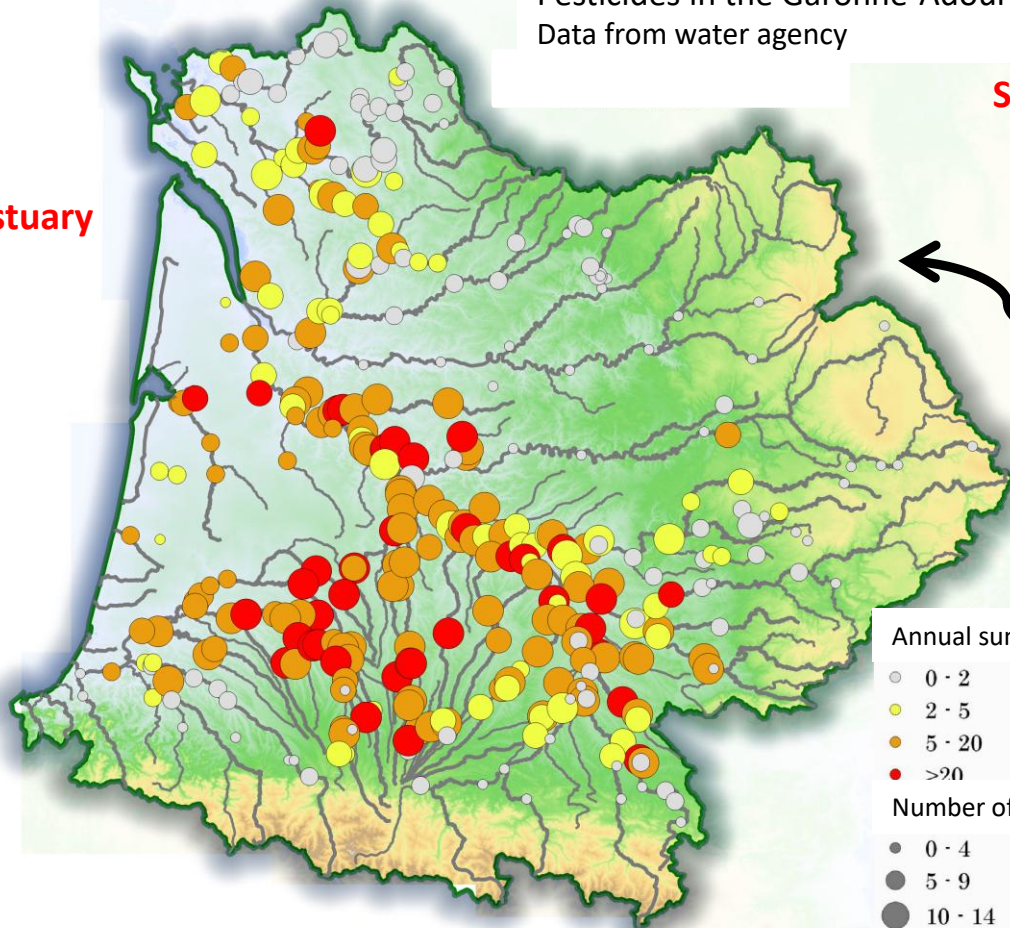


Screenings from Local, Regional scales to ...

Pesticides in the Garonne-Adour watershed (2021)
Data from water agency

Gironde estuary

South west coast
of France



Annual sum of concentrations ($\mu\text{g/L}$)

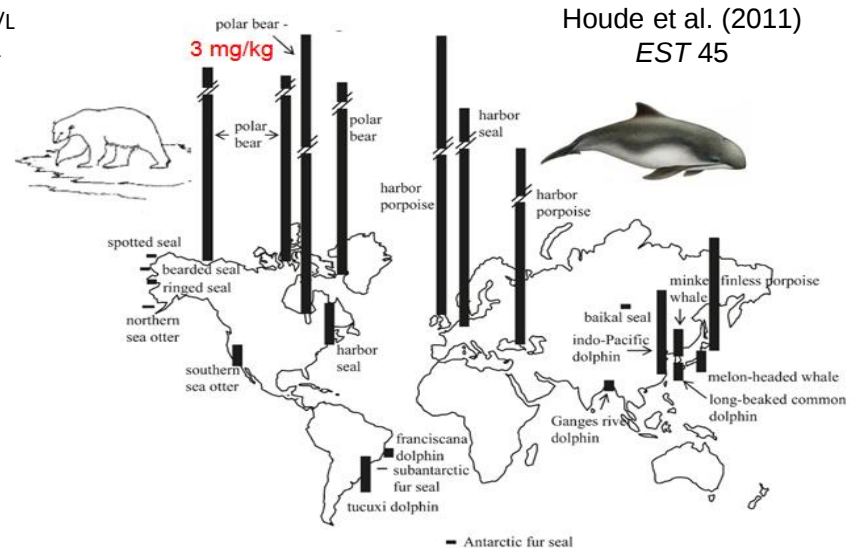
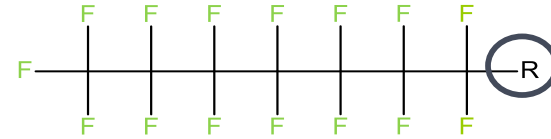
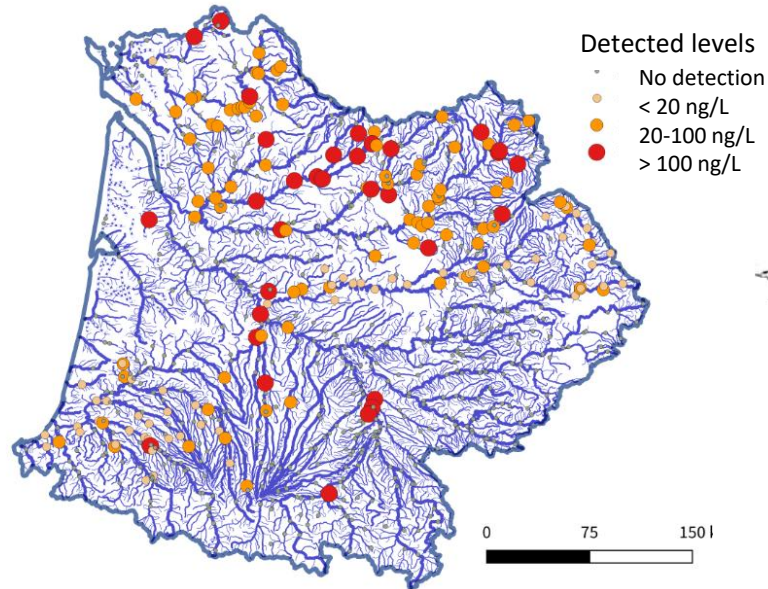
- 0 - 2
- 2 - 5
- 5 - 20
- >20

Number of detected molecules

- 0 - 4
- 5 - 9
- 10 - 14
- >15

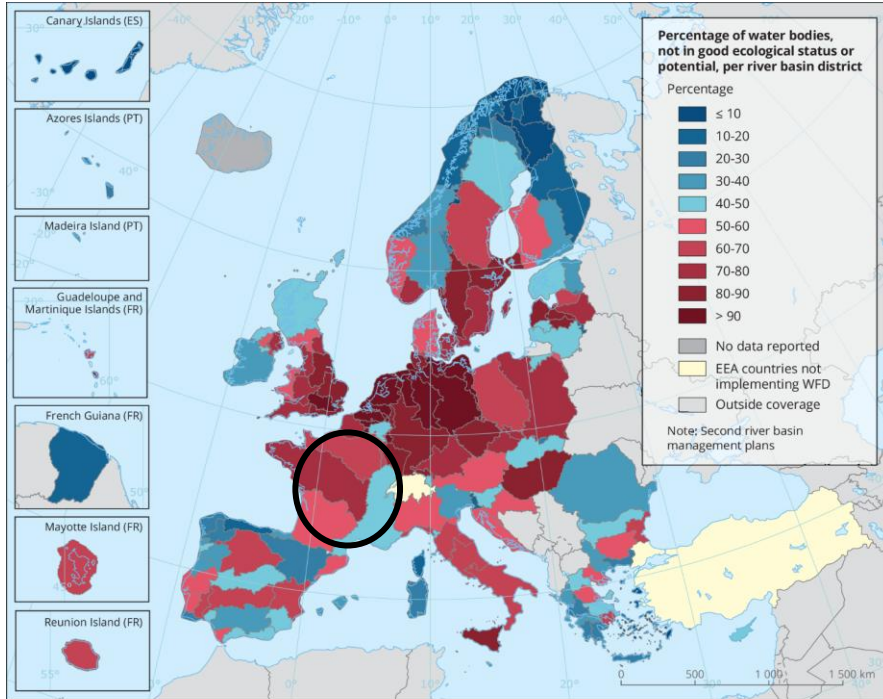
..... To Global scales

Contamination of rivers in the Garonne-Adour watershed – PFOS/PFAS(2021)
Data from water agency

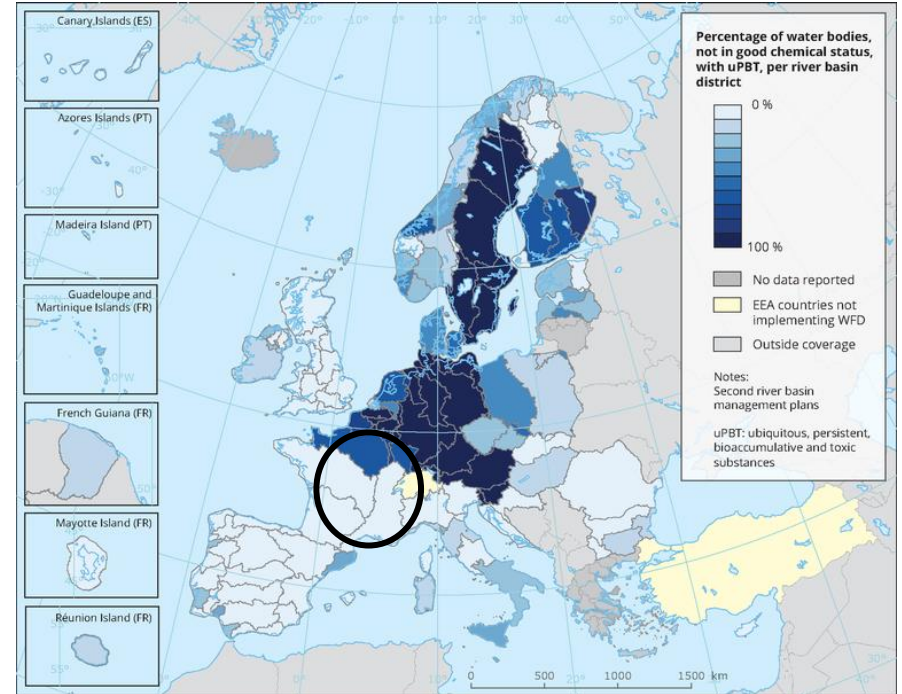


Levels of PFOS in marine mammals at large scale

- Linking chemical status to ecological status (2010-2015) not so easy nor trivial ?



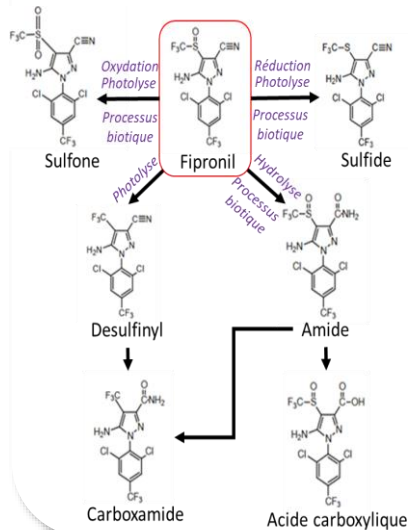
Reference data: ©ESRI | ©EuroGeographics



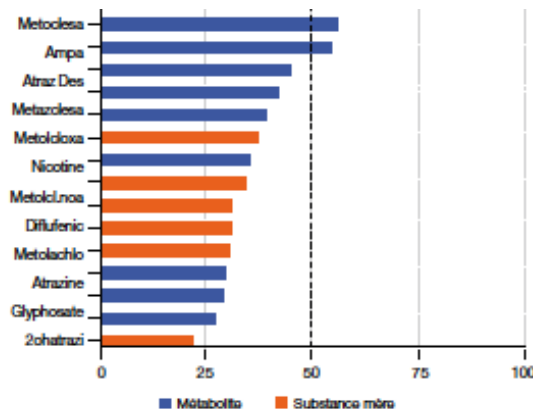
Stakes

- >130 millions of referenced organic and inorganic compounds (CAS registry)
- More than 110 000 chemical compounds present on the European market (with 30 000 to 70 000 daily used)
- In the environment, these figures are multiplied --> transformation products

One compound can lead to several products

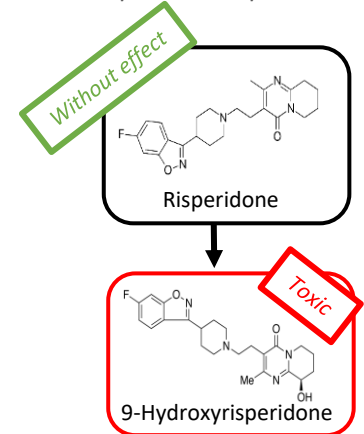


Top 15 of pesticides in french waterways (2018 to 2020) (%)

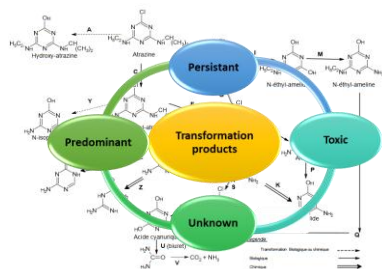


Chemical pollution in rivers and ponds in France from 2000 to 2020 (statistique publique juin 2023)

Transformation products can be more toxic (or stable) than parent compounds



OBJECTIVES

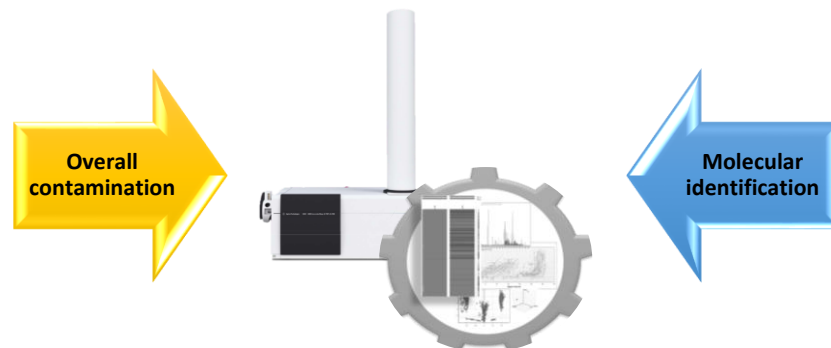


To date, main studies and assessments of chemical quality of aquatic environments are based on **target chemical analysis and pre-selected set of compounds**

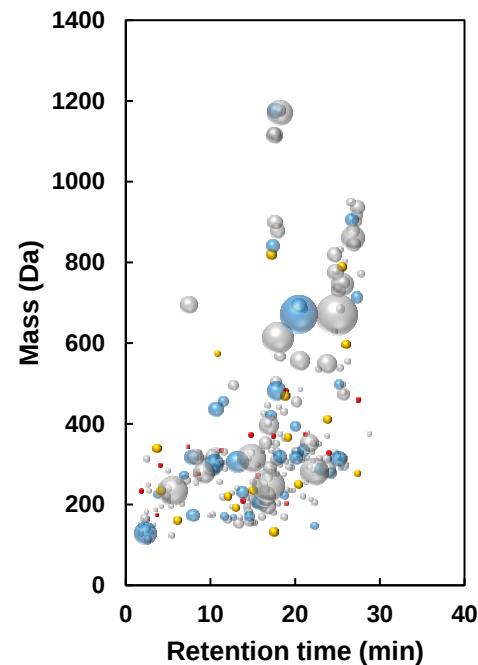
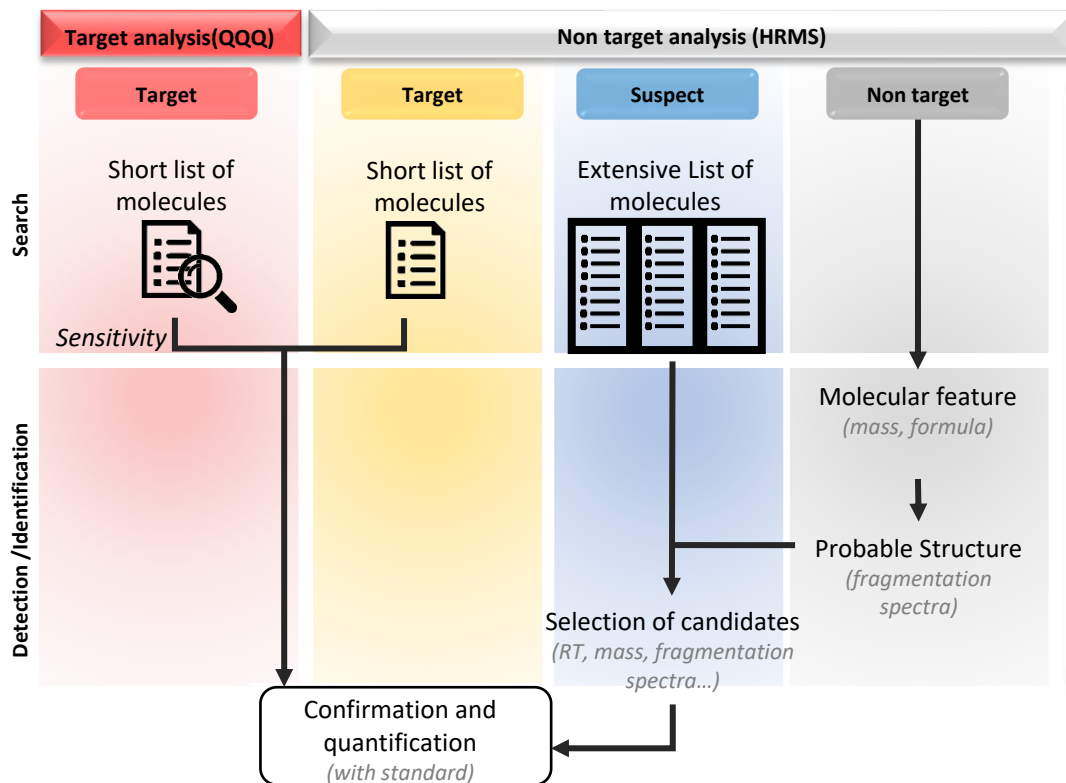


We are only looking for what we know

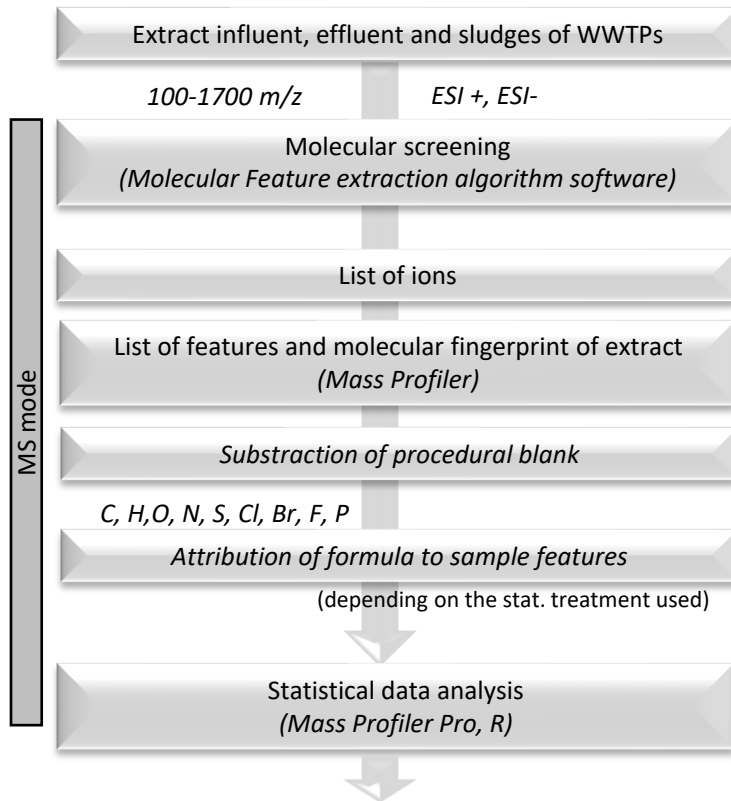
- Need to use new technologies and alternative approaches to characterise more deeply chemical contamination: Non target analysis by HRMS (High Resolution Mass Spectrometry)



Analytical strategies

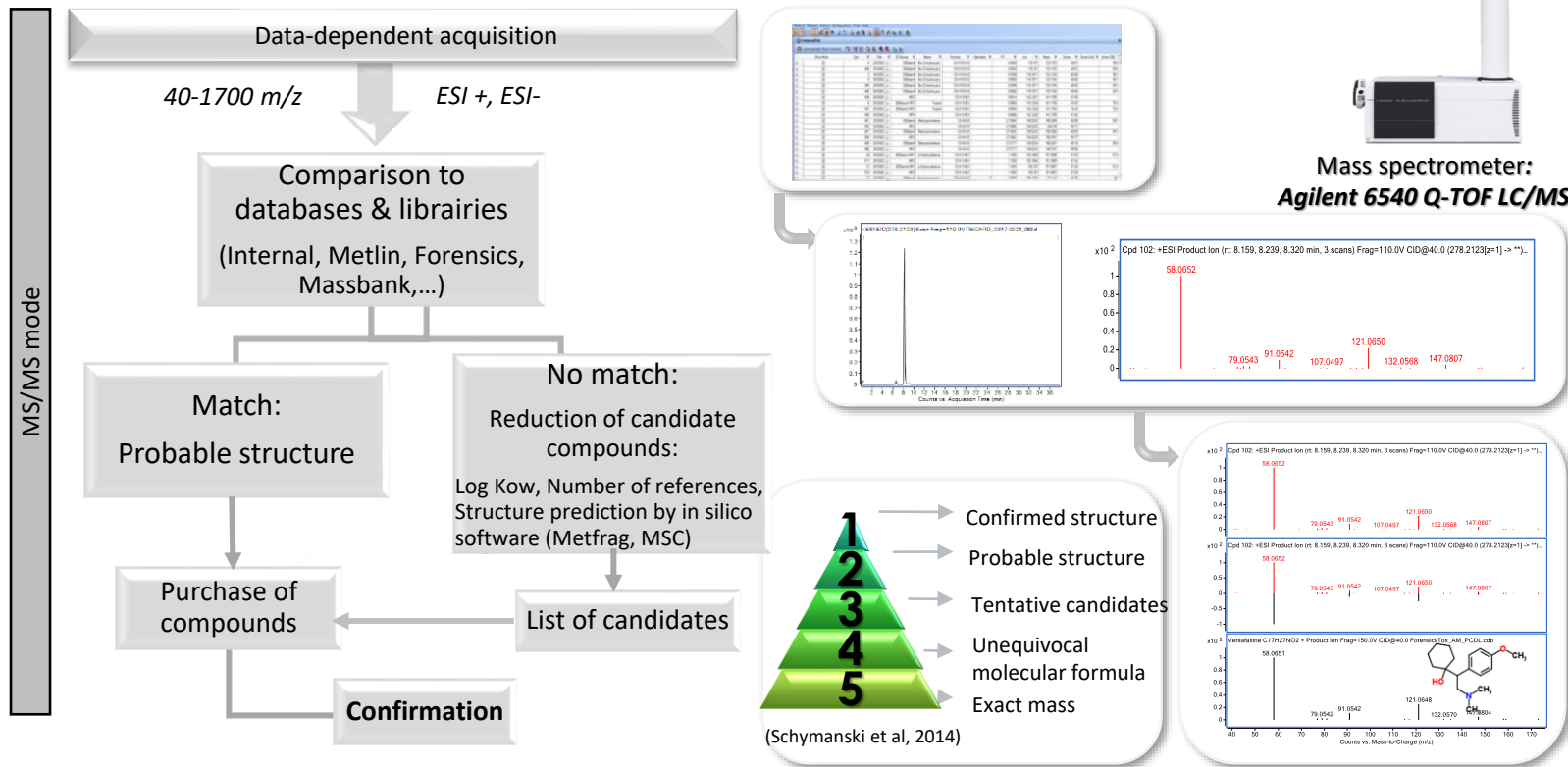


Non target analysis workflow

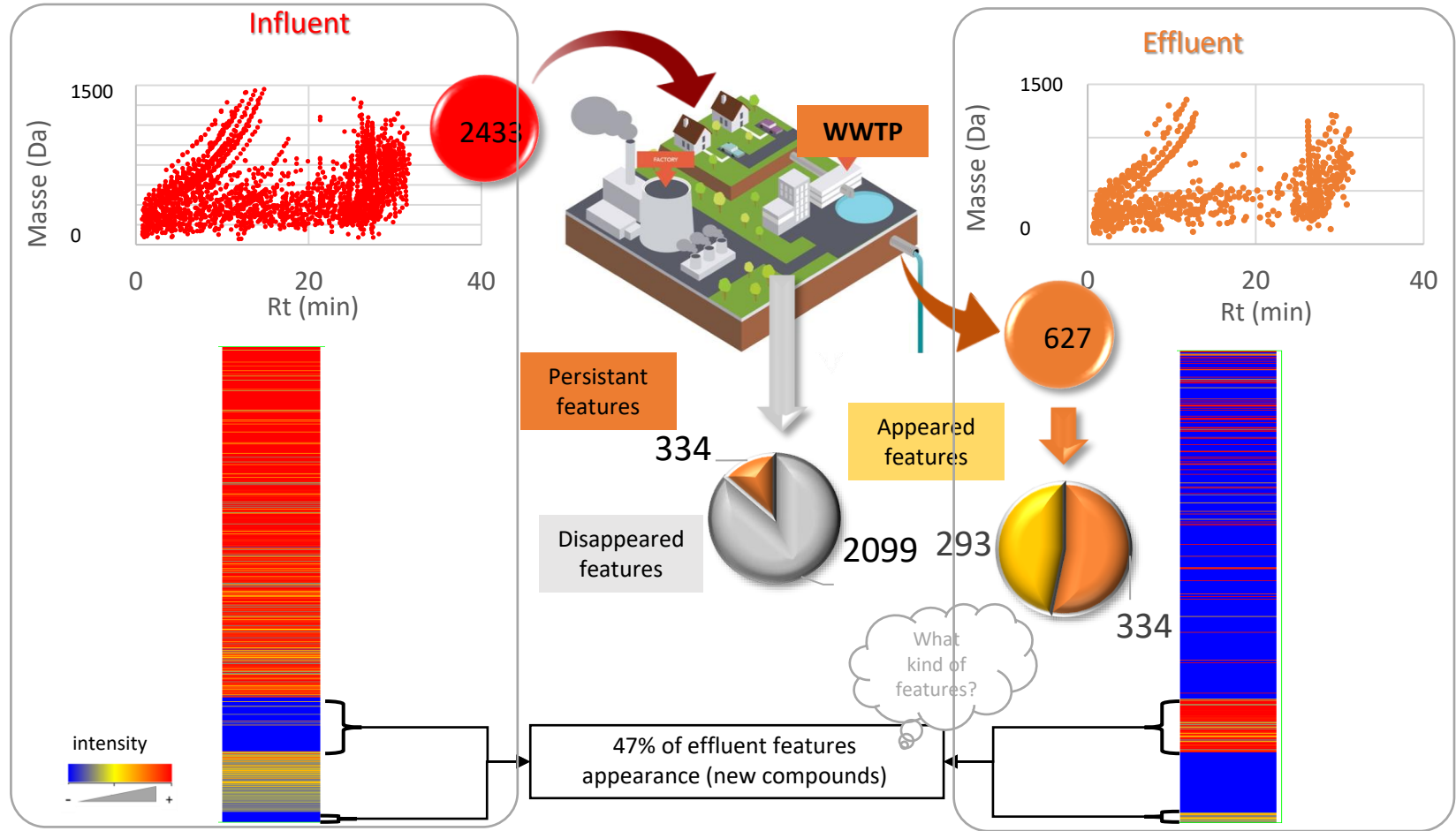


Retention Time (min)	Mass (Da)	Intensity
1.2	41	100
1.2	43	50
1.2	45	20
1.2	47	10
1.2	49	5
1.2	51	15
1.2	53	8
1.2	55	3
1.2	57	12
1.2	59	6
1.2	61	2
1.2	63	18
1.2	65	9
1.2	67	4
1.2	69	25
1.2	71	12
1.2	73	5
1.2	75	30
1.2	77	15
1.2	79	7
1.2	81	3
1.2	83	35
1.2	85	18
1.2	87	8
1.2	89	4
1.2	91	40
1.2	93	20
1.2	95	10
1.2	97	5
1.2	99	45
1.2	101	22
1.2	103	11
1.2	105	6
1.2	107	48
1.2	109	24
1.2	111	12
1.2	113	7
1.2	115	50
1.2	117	26
1.2	119	13
1.2	121	8
1.2	123	52
1.2	125	28
1.2	127	14
1.2	129	9
1.2	131	55
1.2	133	30
1.2	135	15
1.2	137	10
1.2	139	58
1.2	141	32
1.2	143	16
1.2	145	11
1.2	147	60
1.2	149	34
1.2	151	17
1.2	153	12
1.2	155	62
1.2	157	36
1.2	159	18
1.2	161	13
1.2	163	65
1.2	165	38
1.2	167	19
1.2	169	14
1.2	171	68
1.2	173	40
1.2	175	20
1.2	177	15
1.2	179	70
1.2	181	42
1.2	183	21
1.2	185	16
1.2	187	72
1.2	189	44
1.2	191	22
1.2	193	17
1.2	195	75
1.2	197	46
1.2	199	23
1.2	201	18
1.2	203	78
1.2	205	48
1.2	207	24
1.2	209	19
1.2	211	80
1.2	213	50
1.2	215	25
1.2	217	20
1.2	219	82
1.2	221	52
1.2	223	26
1.2	225	21
1.2	227	85
1.2	229	54
1.2	231	27
1.2	233	22
1.2	235	88
1.2	237	56
1.2	239	28
1.2	241	23
1.2	243	90
1.2	245	58
1.2	247	29
1.2	249	24
1.2	251	92
1.2	253	60
1.2	255	30
1.2	257	25
1.2	259	95
1.2	261	62
1.2	263	31
1.2	265	26
1.2	267	98
1.2	269	64
1.2	271	32
1.2	273	27
1.2	275	100
1.2	277	66
1.2	279	33
1.2	281	28
1.2	283	102
1.2	285	68
1.2	287	34
1.2	289	29
1.2	291	105
1.2	293	70
1.2	295	35
1.2	297	30
1.2	299	108
1.2	301	72
1.2	303	36
1.2	305	31
1.2	307	110
1.2	309	74
1.2	311	37
1.2	313	32
1.2	315	112
1.2	317	76
1.2	319	38
1.2	321	33
1.2	323	115
1.2	325	78
1.2	327	39
1.2	329	34
1.2	331	118
1.2	333	80
1.2	335	40
1.2	337	35
1.2	339	120
1.2	341	82
1.2	343	41
1.2	345	36
1.2	347	122
1.2	349	84
1.2	351	42
1.2	353	37
1.2	355	125
1.2	357	86
1.2	359	43
1.2	361	38
1.2	363	128
1.2	365	88
1.2	367	44
1.2	369	39
1.2	371	130
1.2	373	90
1.2	375	45
1.2	377	40
1.2	379	132
1.2	381	92
1.2	383	46
1.2	385	41
1.2	387	135
1.2	389	94
1.2	391	47
1.2	393	42
1.2	395	138
1.2	397	96
1.2	399	48
1.2	401	43
1.2	403	140
1.2	405	98
1.2	407	49
1.2	409	44
1.2	411	142
1.2	413	100
1.2	415	50
1.2	417	45
1.2	419	145
1.2	421	102
1.2	423	51
1.2	425	46
1.2	427	148
1.2	429	104
1.2	431	52
1.2	433	47
1.2	435	150
1.2	437	106
1.2	439	53
1.2	441	48
1.2	443	152
1.2	445	108
1.2	447	54
1.2	449	49
1.2	451	155
1.2	453	110
1.2	455	55
1.2	457	50
1.2	459	158
1.2	461	112
1.2	463	56
1.2	465	51
1.2	467	160
1.2	469	114
1.2	471	57
1.2	473	52
1.2	475	162
1.2	477	116
1.2	479	58
1.2	481	53
1.2	483	165
1.2	485	118
1.2	487	59
1.2	489	54
1.2	491	168
1.2	493	120
1.2	495	60
1.2	497	55
1.2	499	170
1.2	501	122
1.2	503	61
1.2	505	56
1.2	507	172
1.2	509	124
1.2	511	62
1.2	513	57
1.2	515	175
1.2	517	126
1.2	519	63
1.2	521	58
1.2	523	178
1.2	525	128
1.2	527	64
1.2	529	59
1.2	531	180
1.2	533	130
1.2	535	65
1.2	537	60
1.2	539	182
1.2	541	132
1.2	543	66
1.2	545	61
1.2	547	185
1.2	549	134
1.2	551	67
1.2	553	62
1.2	555	188
1.2	557	136
1.2	559	68
1.2	561	63
1.2	563	190
1.2	565	138
1.2	567	69
1.2	569	64
1.2	571	192
1.2	573	140
1.2	575	70
1.2	577	65
1.2	579	195
1.2	581	142
1.2	583	71
1.2	585	66
1.2	587	198
1.2	589	144
1.2	591	72
1.2	593	67
1.2	595	200
1.2	597	146
1.2	599	73
1.2	601	68
1.2	603	202
1.2	605	148
1.2	607	74
1.2	609	69
1.2	611	205
1.2	613	150
1.2	615	75
1.2	617	70
1.2	619	208
1.2	621	152
1.2	623	76
1.2	625	71
1.2	627	210
1.2	629	154
1.2	631	77
1.2	633	72
1.2	635	212
1.2	637	156
1.2	639	78
1.2	641	73
1.2	643	215
1.2	645	158
1.2	647	79
1.2	649	74
1.2	651	218
1.2	653	160
1.2	655	80
1.2	657	75
1.2	659	220
1.2	661	162
1.2	663	81
1.2	665	76
1.2	667	222
1.2	669	164
1.2	671	82
1.2	673	77
1.2	675	225
1.2	677	166
1.2	679	83
1.2	681	78
1.2	683	228
1.2	685	168
1.2	687	84
1.2	689	79
1.2	691	230
1.2	693	170
1.2	695	85
1.2	697	80
1.2	699	232
1.2	701	172
1.2	703	86
1.2	705	81
1.2	707	235
1.2	709	174
1.2	711	87
1.2	713	82
1.2	715	238
1.2	717	176
1.2	719	88
1.2	721	83
1.2	723	240
1.2	725	178
1.2	727	89
1.2	729	84
1.2	731	242
1.2	733	180
1.2	735	90
1.2	737	85
1.2	739	245
1.2	741	182
1.2	743	91
1.2	745	86
1.2	747	248
1.2	749	184
1.2	751	92
1.2	753	87
1.2	755	250
1.2	757	186
1.2	759	93
1.2	761	88
1.2	763	252
1.2	765	188
1.2	767	94
1.2	769	89
1.2	771	255
1.2	773	190
1.2	775	95
1.2	777	90
1.2	779	258
1.2	781	192
1.2	783	96
1.2	785	91
1.2	787	260
1.2	789	194
1.2	791	97
1.2	793	92
1.2	795	262
1.2	797	196
1.2	799	98
1.2	801	93
1.2	803	265
1.2	805	198
1.2	807	99
1.2	809	94
1.2	811	268
1.2	813	200
1.2	815	100
1.2	817	95
1.2	819	270
1.2	821	202
1.2	823	101
1.2	825	96
1.2	827	272
1.2	829	204
1.2	831	102
1.2	833	97
1.2	835	275
1.2	837	206
1.2	839	103
1.2	841	98
1.2	843	278
1.2	845	208
1.2	847	104
1.2	849	99
1.2	851	280
1.2	853	210
1.2	855	105
1.2	857	100
1.2	859	282
1.2	861	212
1.2	863	106
1.2	865	101
1.2	867	285
1.2	869	214
1.2	871	107
1.2	873	102
1.2	875	288
1.2	877	216

Identification workflow



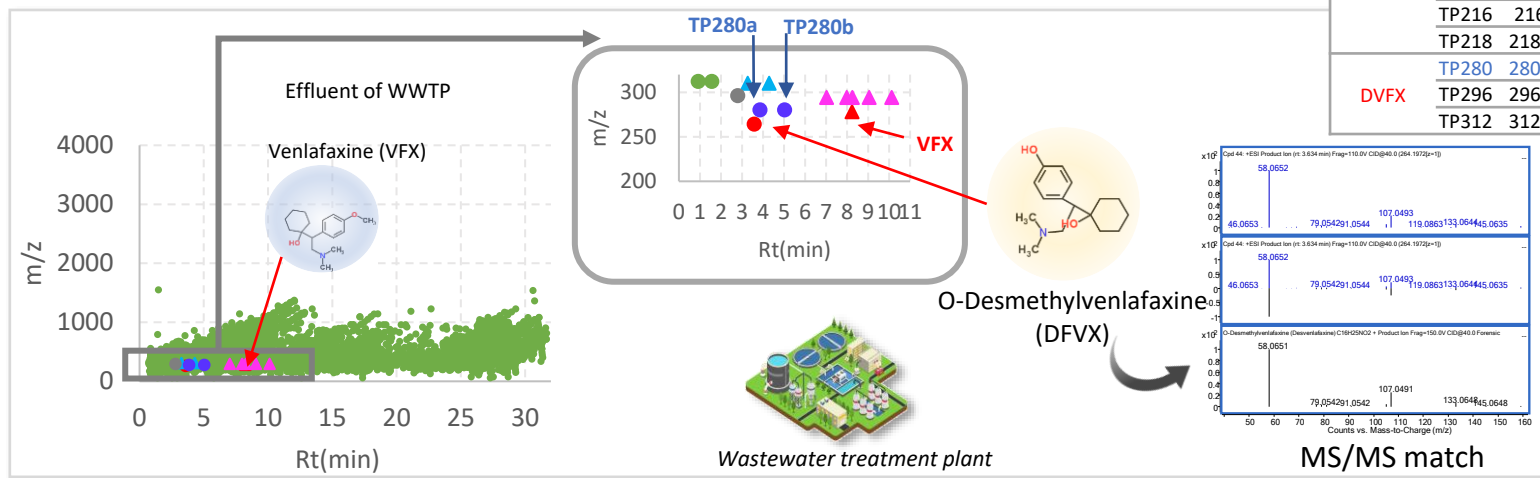
Overall analysis – Wastewater treatment plants (important source of MP in surface water)

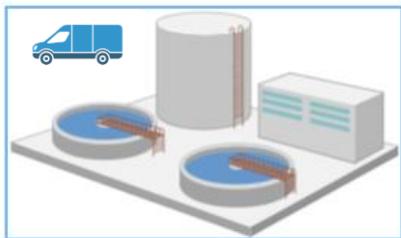


Transformation products in natural environment

List of suspected TPs

TPs	[M+H] ⁺
DVFX	264.1958
TP294	294.2053
Venlafaxine	TP310 310.2008
TP216	216.086
TP218	218.1012
TP280	280.1903
DVFX	TP296 296.1852
TP312	312.1799

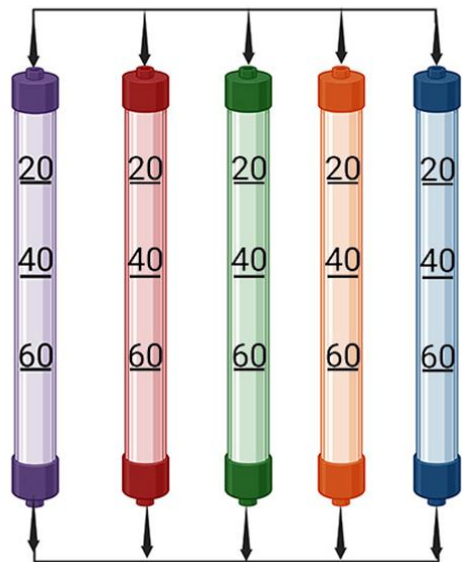




Treated urban wastewater (REUSE application)

Inlets filled with different types of treated waters

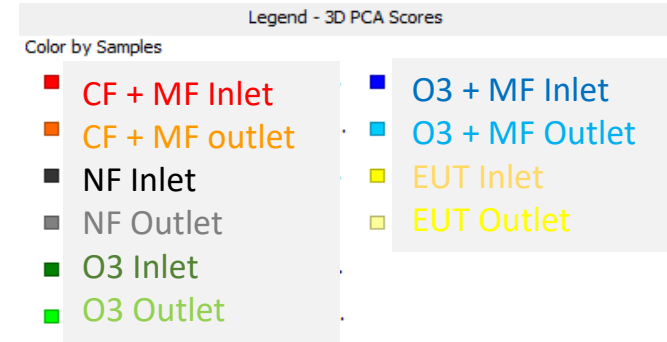
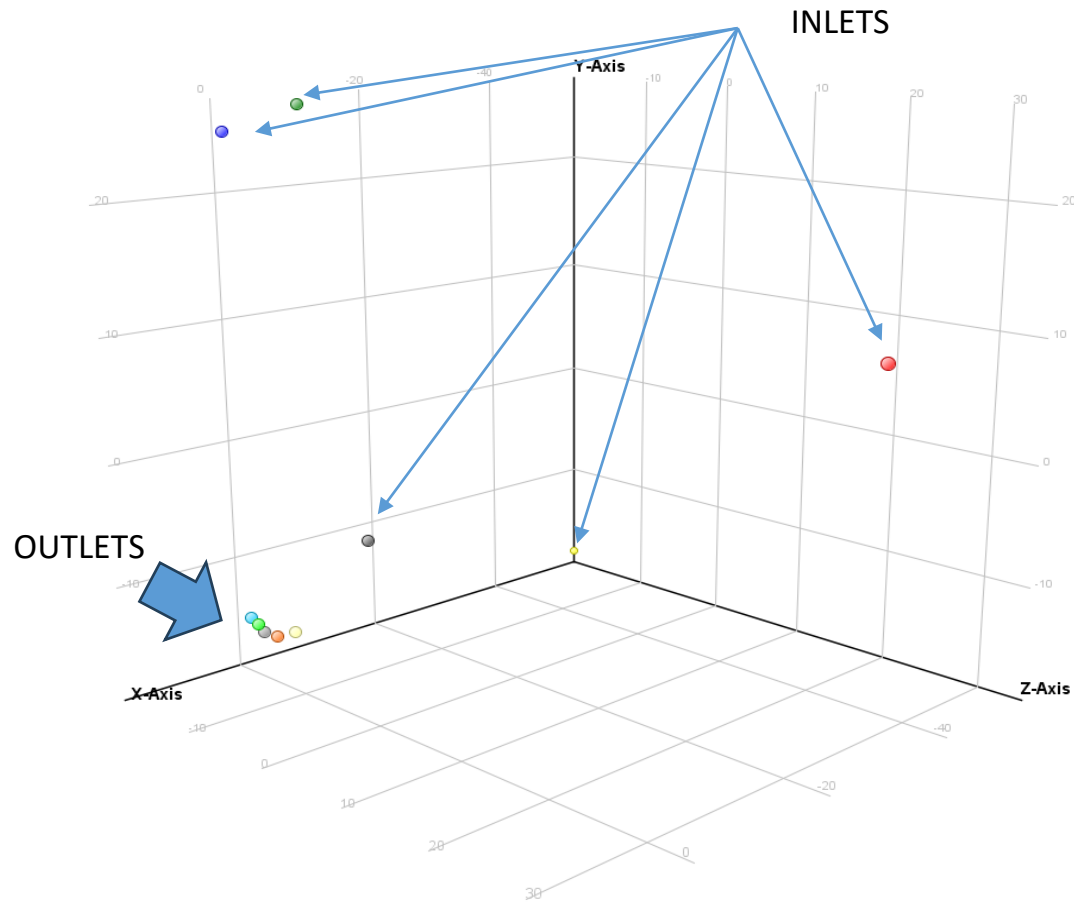
Five columns (1m) filled with sand and gravel to simulate the aquifer environment processes (soil/sand percolation)

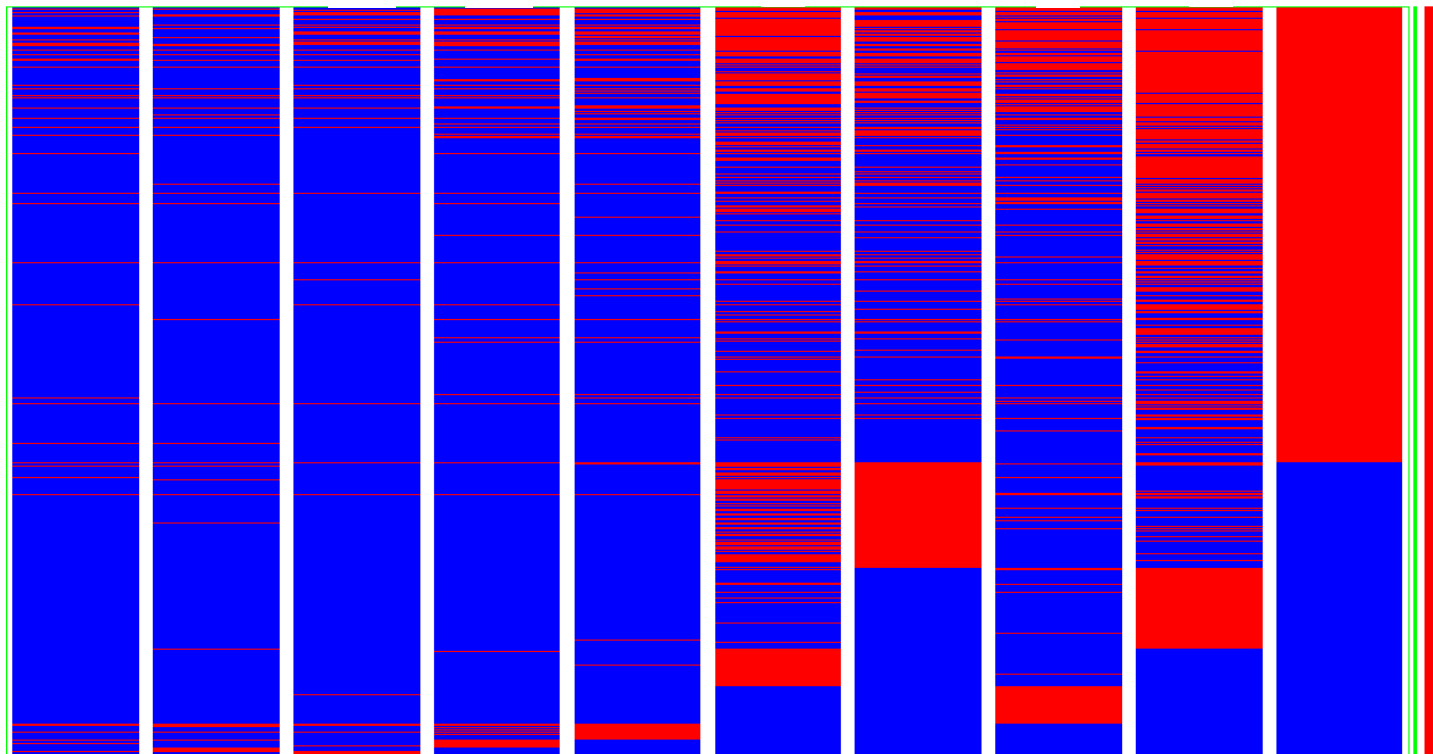
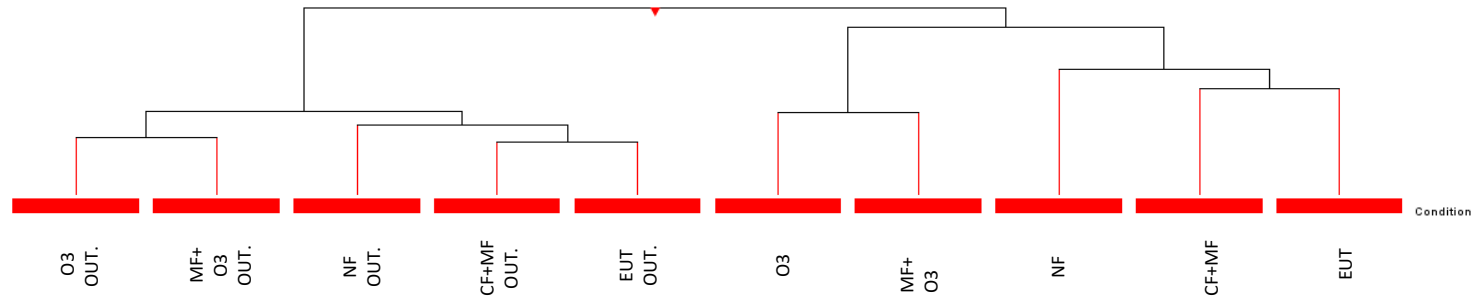


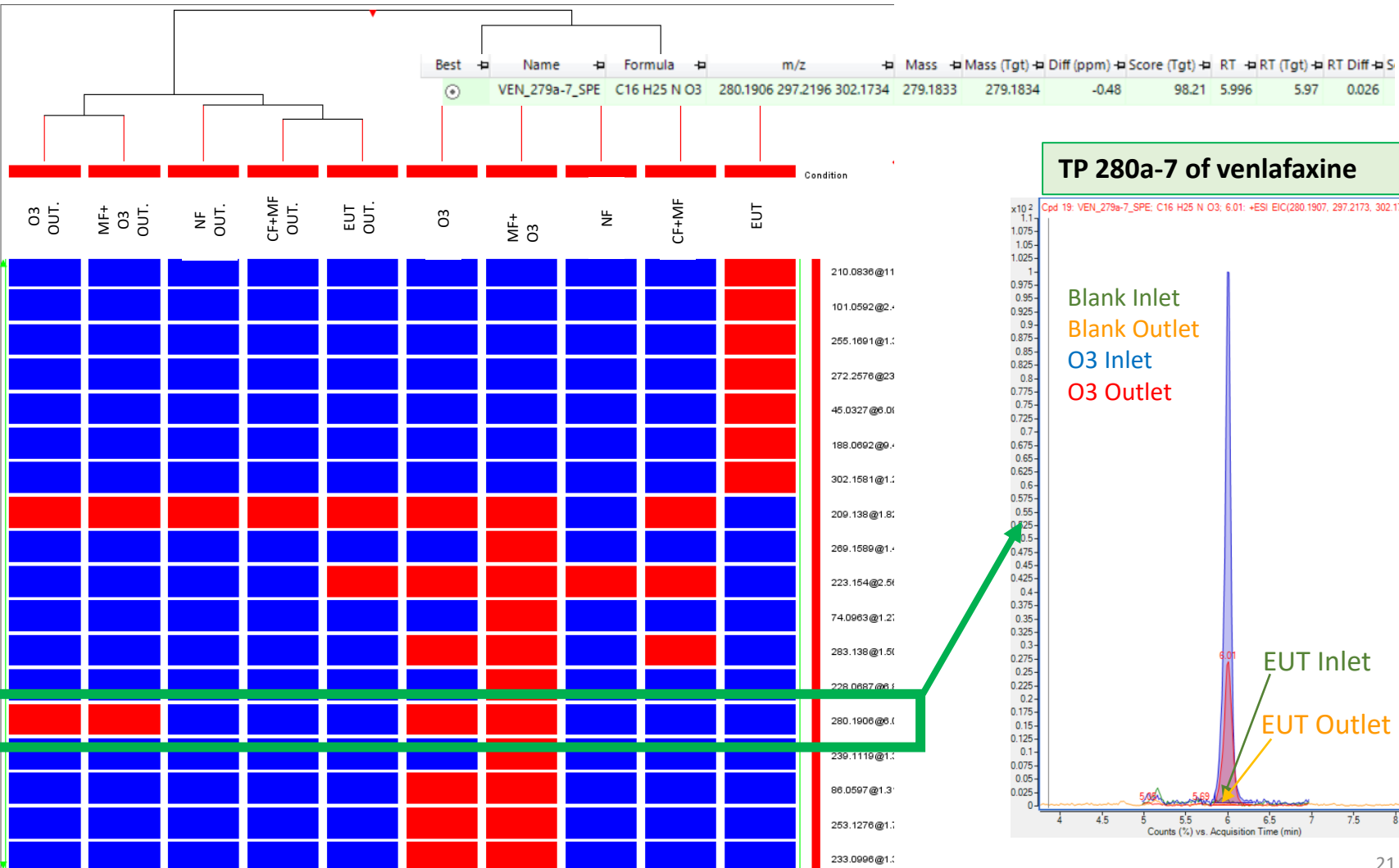
- **Column 1 (EUT):** Treated urban wastewater filtered at 10 μm .
- **Column 2 (CF+MF):** Coagulation-flocculation followed by ceramic filtration at 0.25 μm .
- **Column 3 (NF):** Nanofiltration with a molecular weight cutoff of 800 Da.
- **Column 4 (O3):** Ozonation (0.3–0.5 mg Ozone/mg DOC).
- **Column 5 (MF+O3):** Ceramic filtration at 0.25 μm followed by ozonation (0.3–0.5 mg Ozone/mg DOC).

Sample Information

Outlets for the different types of waters

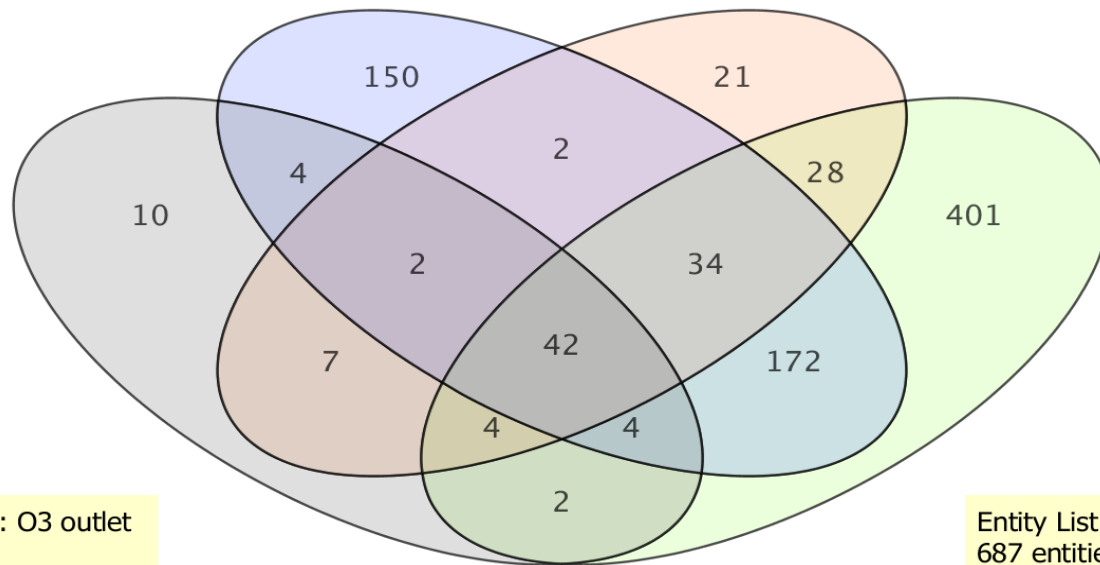






Entity List 1 : O3 inlet
410 entities

Entity List 4 : EUT Outlet
140 entities

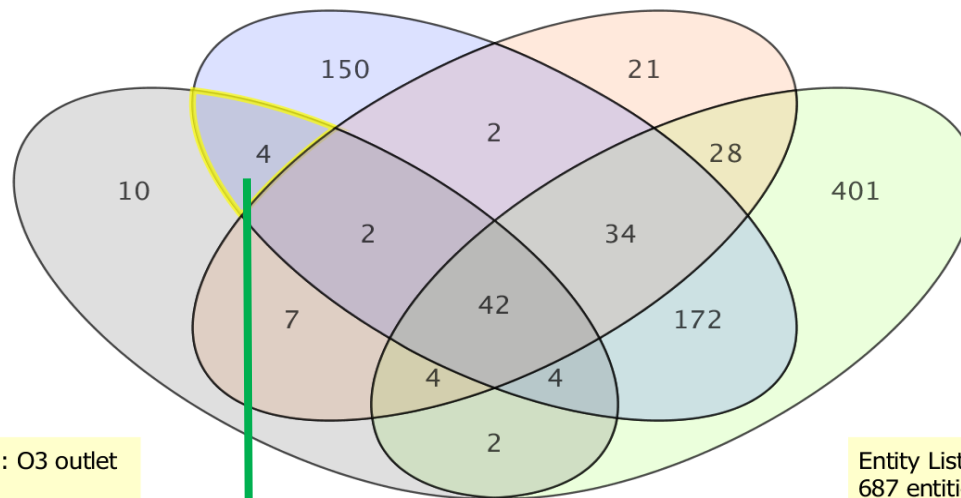


Entity List 2 : O3 outlet
75 entities

Entity List 3 : EUT Inlet
687 entities

Entity List 1 : O3 inlet
410 entities

Entity List 4 : EUT Outlet
140 entities



Entity List 2 : O3 outlet
75 entities

Entity List 3 : EUT Inlet
687 entities

	O3 Inlet			O3 Outlet		
Compound	Rt	Nb Ion	Abundance	Rt	Nb Ion	Abundance
280.1906@6.0008	6,001	3	1112274	6,002	2	300213
228.1955@18.951	18,948	3	301528	18,945	3	218877
386.1741@4.7342	4,736	2	359537	4,731	2	128748
333.3008@29.136	29,148	3	460684	29,135	2	87844

TP 280a-7 of venlafaxine

CONCLUSION AND NEEDS

- Demonstration of the presence of more and more compounds
- Characterization of more and more complex mixtures (Fingerprint/Footprint)
- Able to start to address TPs

But needs

- Lower LQ (HRMS towards LQ QQQ)
- To continue to characterize TPs (treatment of waste water - oxidation - « re-use »)
- **To improve treatment and storage of HRMS** data (databases, softwares, statistics, interoperability, ...) - Resolution
- Impossible to characterize all - Mixtures effects : strategies?
- Link presence/effects - Effect Directed Analysis

TEAM AND FUNDING

Special thanks Ye Geng (PhD)





Thank you for your attention 😊

