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APPLICATION OF SBSE-GCXGC-TOFMS FOR THE EFFICIENT EVALUATION OF ANTHROPOGENIC CONTAMINANTS IN WATERS

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entox

NATIONAL RESEARCH CENTRE FOR ENVIROMENTAL TOXICOLOGY

The University of Queensland (Australia)

Central role in the field of environmental toxicology and human health risk assessment.

The University of Queensland Australia

Queensland Government

national research centre for environmental toxicology

Entox is a joint venture between The University of Queensland and Queensland Health

University of Almeria

Pesticide Residue Research Group

Madrid institute for advanced studies, Spain

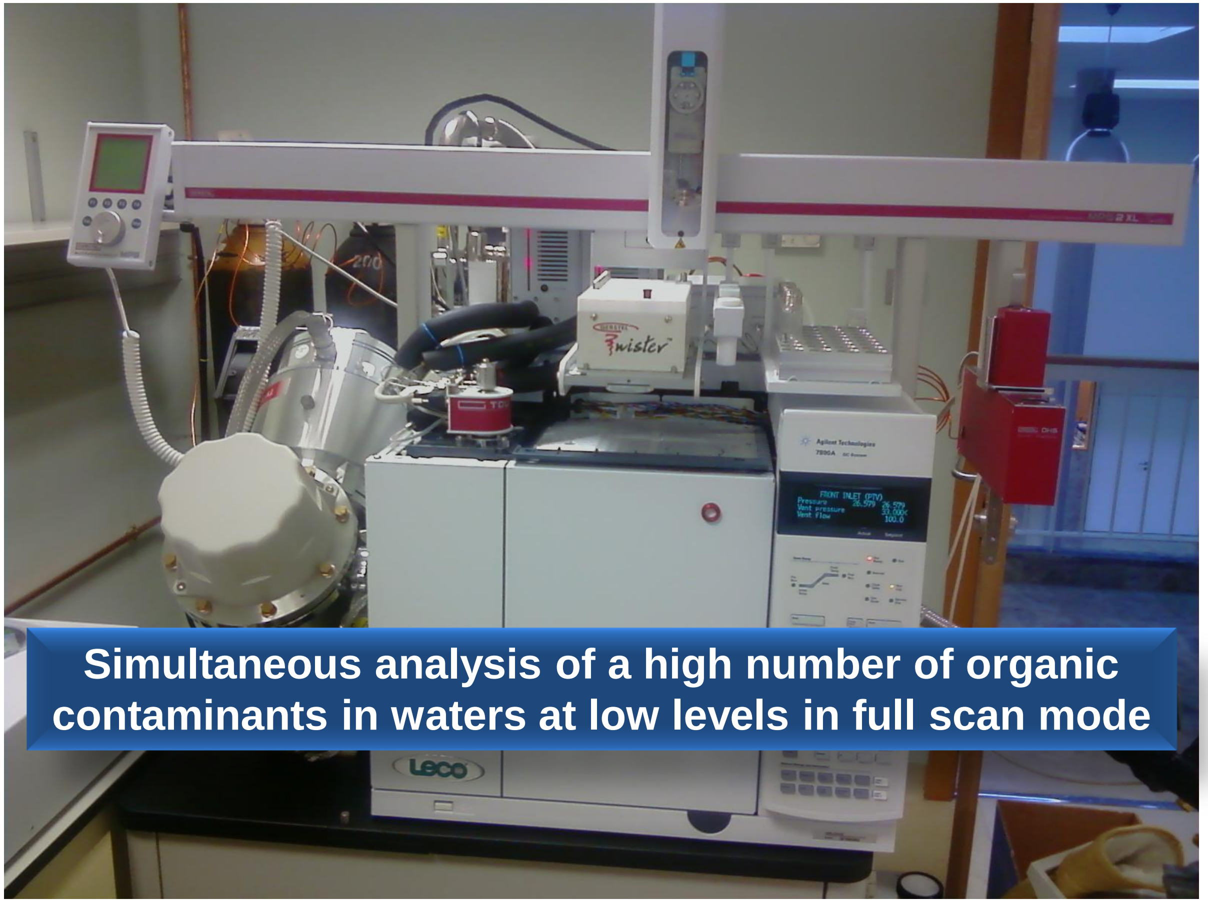
Water Quality Department

Analytical techniques
Sensitivity
More substances
target & non-target analysis

Pharmaceuticals, cosmetics, pesticides, surfactants, metabolites, transformation products...??

Ecological Risk? Fate? Behaviour?

SBSE-GCxGC-TOFMS



Simultaneous analysis of a high number of organic contaminants in waters at low levels in full scan mode

Analytes Selected

Non polar and semipolar organic contaminants

Log Kow: 2.61-6.93

Priority pollutants are marked in yellow

PESTICIDES	PESTICIDES	PAHs	PCPs
*Alachlor	*Methoxychlor	*Acenaphthene	*2-Ethylhexyl trans-4-methoxycinnamate
*Aldrin	*Metolachlor	*Acenaphthylene	*4-methylbenzyledene camphor (4-MBC)
*Atrazine	*Molinate	*Anthracene	*Biphenylol-2
*Chlorpyrifos-ethyl	*Procymidone	*Benzo[a]pyrene	*Bisphenol A
*Chlorpyrifos-methyl	*Simazine	*Benzo[ghi]perylene	*Butyl-hydroxy-toluen (BHT)
*Endrin	*Terbutryn	*Benzo[k]fluoranthene	*Celestolide
*DDT p,p'-	*Terbutylazine	*Chrysene	*Clorophene
*Diazinon	*Trifluralin	*Benz[a]anthracene	*Galaxolide
*Dieldrin	*Vinclozoline	*Fluoranthene	*Musk ketone
*Endosulfan I	*Chlorfenvinphos	*Fluorene	*Musk xylene
*Endosulfan II	*o,p'-DDE	*Indeno[1,2,3-cd]pyrene	*Oxybenzone
*Endosulfan sulfate		*Naphthalene	*Phantolide
* Hexachlorobenzene		*Phenanthrene	*Tonalid
*Iprodione		*Pyrene	*Traseolide
*Lindane			*Triclosan
*Methidathion			

Sample preparation

Because of the concentration of these contaminants in water is typically very low (ng/L or lower), it is necessary to incorporate a concentration step in the analytical procedure.

Extraction

The trend to simplify the analytical procedures have led to the development of new analytical approaches, that allow :

Determination of contaminants at trace level in complex matrix:

- Reduced clean-up and concentration steps
- Avoidance of toxic solvent
- Improved detection limits

SBSE

Filtration

SBSE optimization

Several parameters affect the SBSE procedure and have to be optimized:

100 ml river water sample
25 ml of WWE + 75ml MiliQ water

\+

Stir bar
20 mm x 0.5 mm
47 µL

\+

Sodium chloride (0, 10, **<u>20 g</u>**)
20 gr

\+

Methanol (5%, **<u>10%</u>**, 20%)
10%

Increased the recoveries of the most **hydrophobic compounds**, because reduce adsorption phenomena onto the glass walls and other surfaces.

TDU
Thermal Desorption Unit

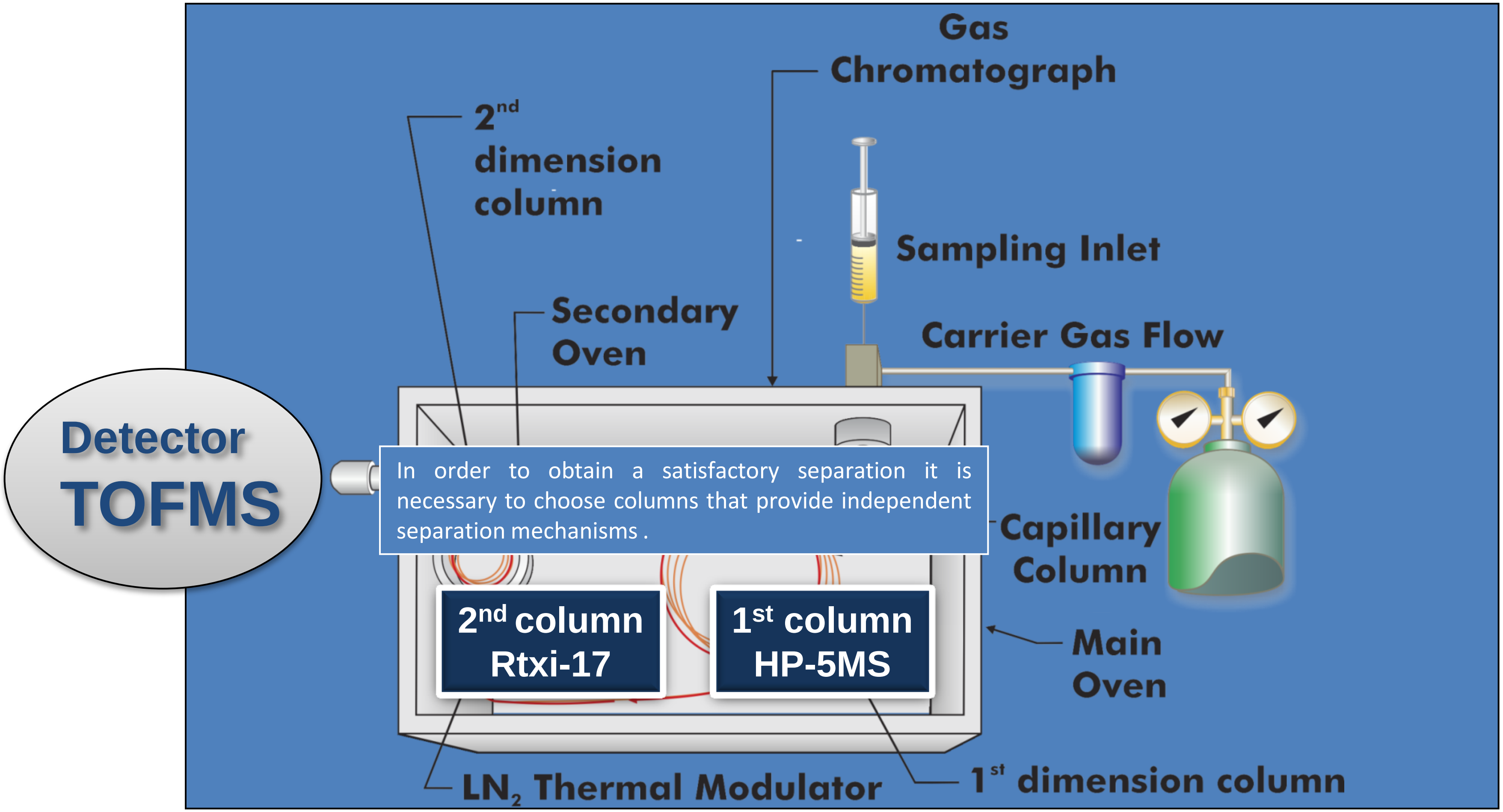
Rinse
Dry

2,4,8,**<u>14h</u>**
Overnight (~**14 h**)
Stirring at **900 rpm**

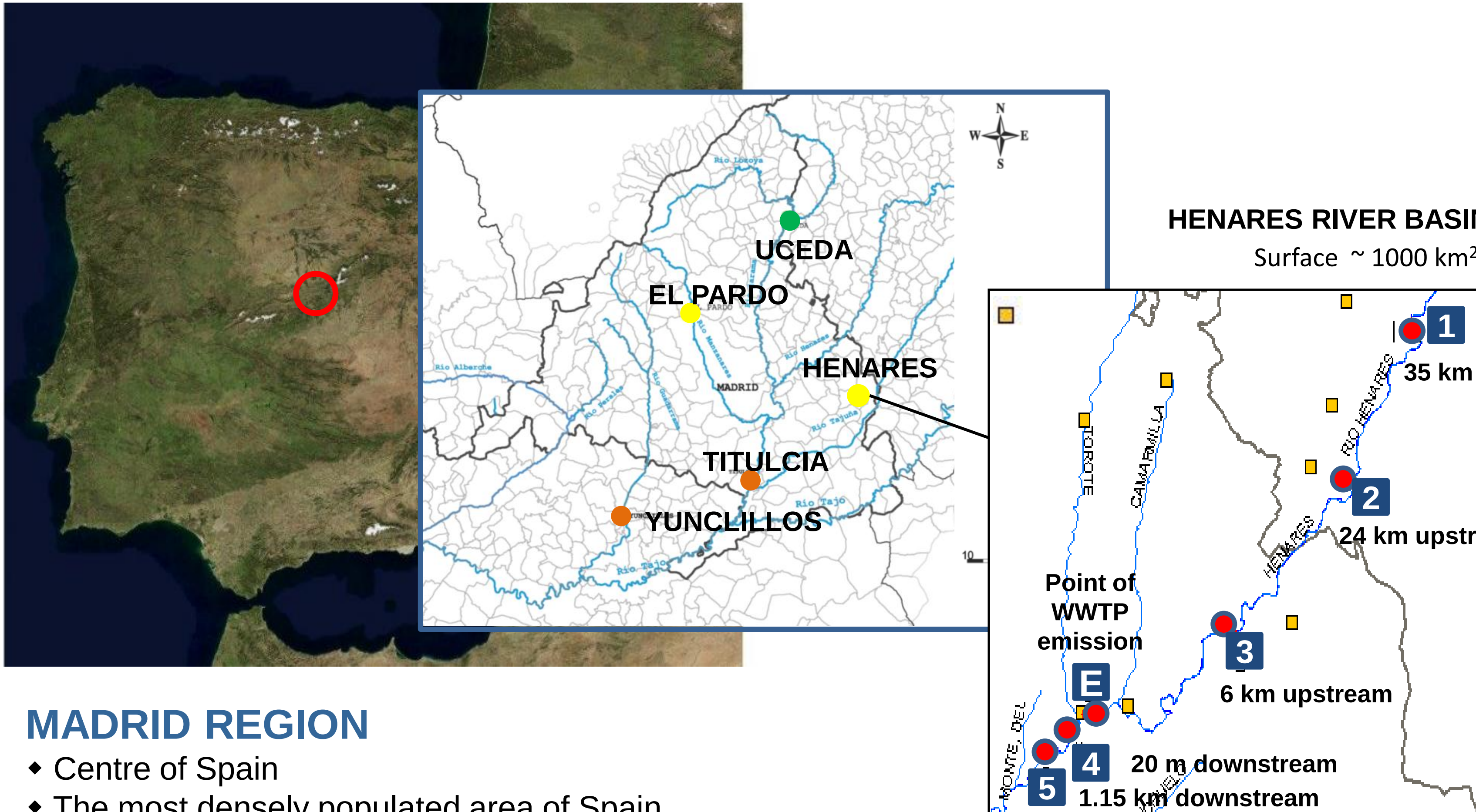
M.J. Gómez et al. ***Anal. Chem.*** *2011, 83,* 2638-2647

Instrumental analysis

GCXGC



Analysis of river waters by GCxGC-TOFMS



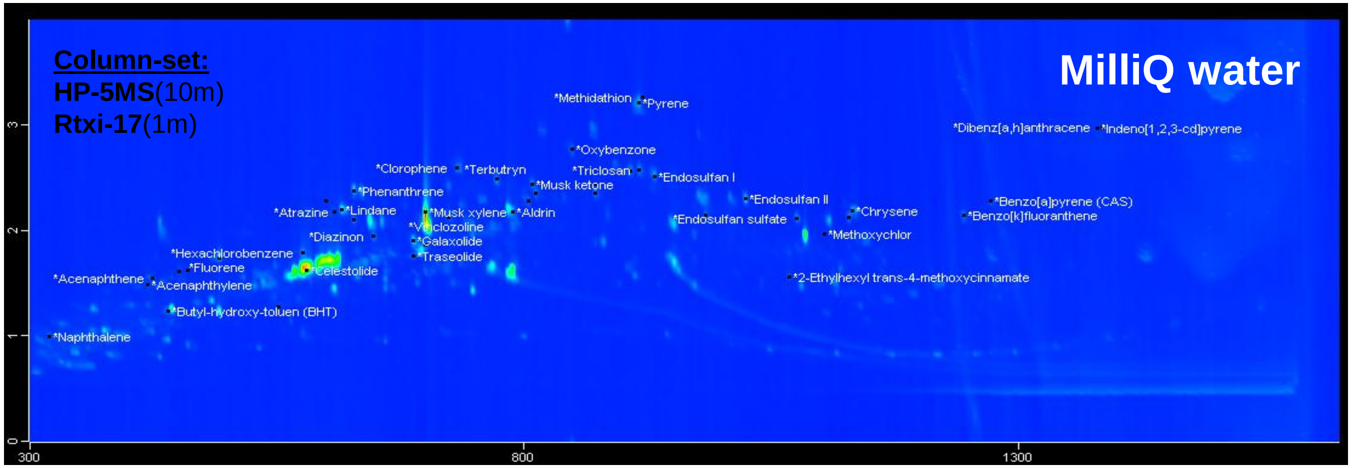
Henares river basin

MADRID REGION

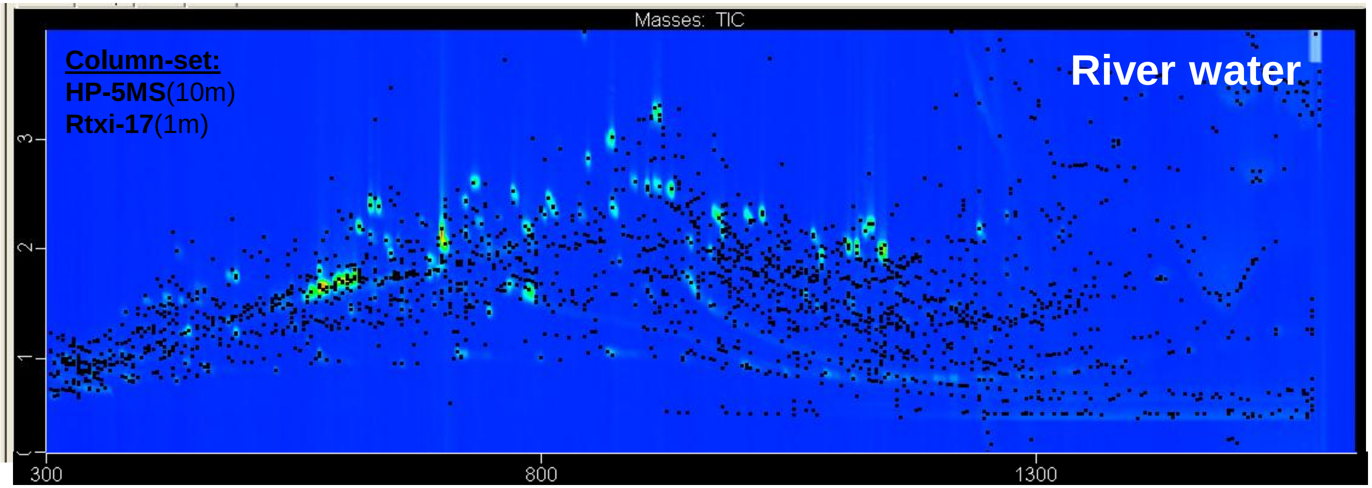
- Centre of Spain
- The most densely populated area of Spain
- Influence by a continental Mediterranean climate
- Rainfalls presentening substantial fluctuations along the different sasons

GCxGC separation

With the optimized conditions the analytes are all separed from one another:

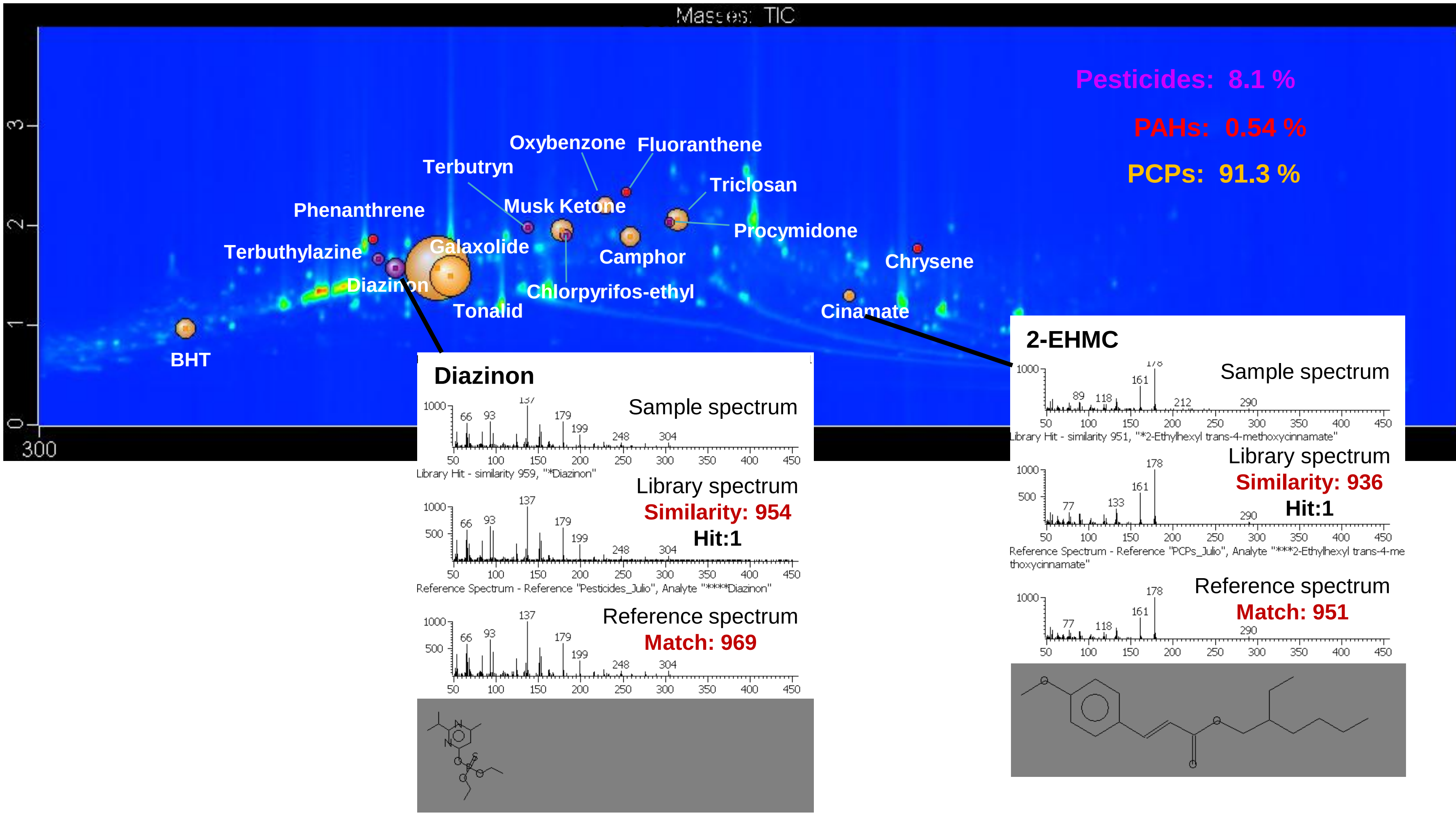


Also is achieve a good separation between target analytes and matrix constituents:



GCxGC-TOF-MS
Automatic analysis of target compounds

River water sample collected at 20 m downstream of the point of emission of a WWTP

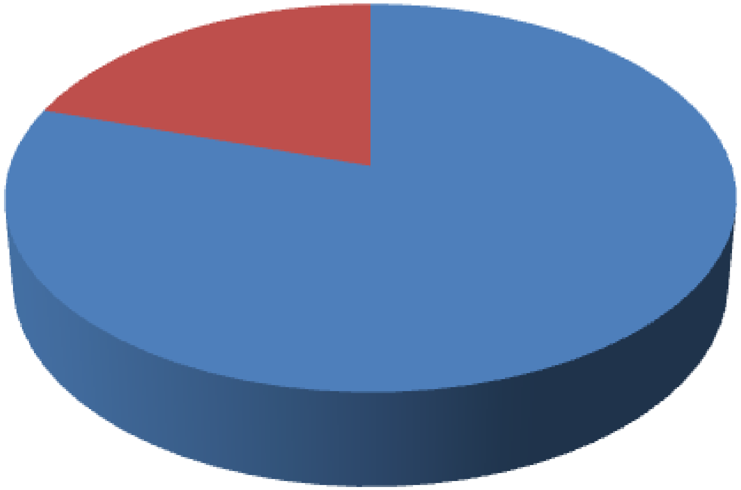


Method Performance

SBSE-GCxGC-TOFMS

Excellent results have been obtained in terms of separation efficiency and also in compound identification:

River water



MDLs

High factor of concentration

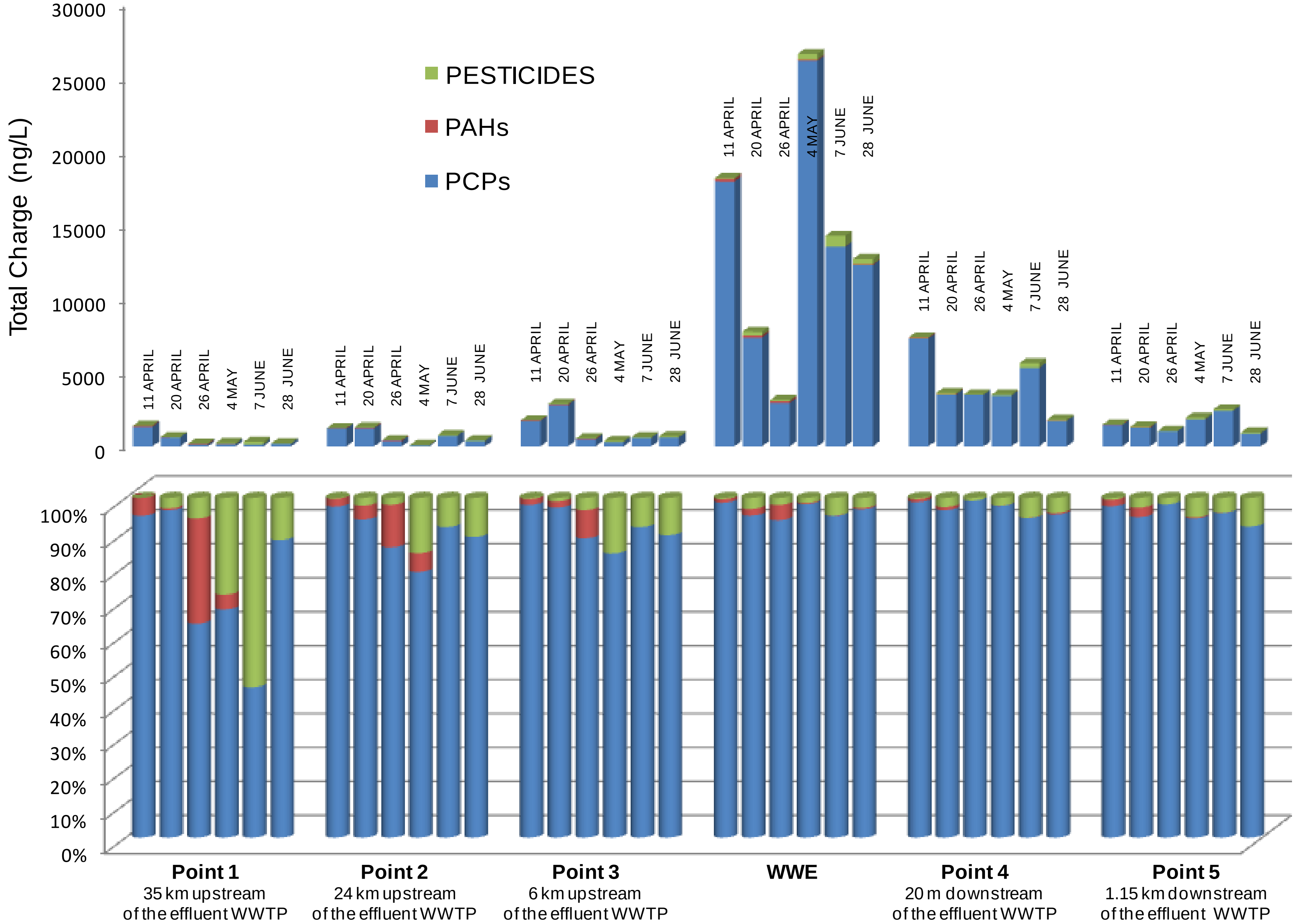
- **≤ 1 ng/L**
- **1-10 ng/L**

MQLs: 0.3-44 ng/L

Linearity: $r^2 \geq 0.98$

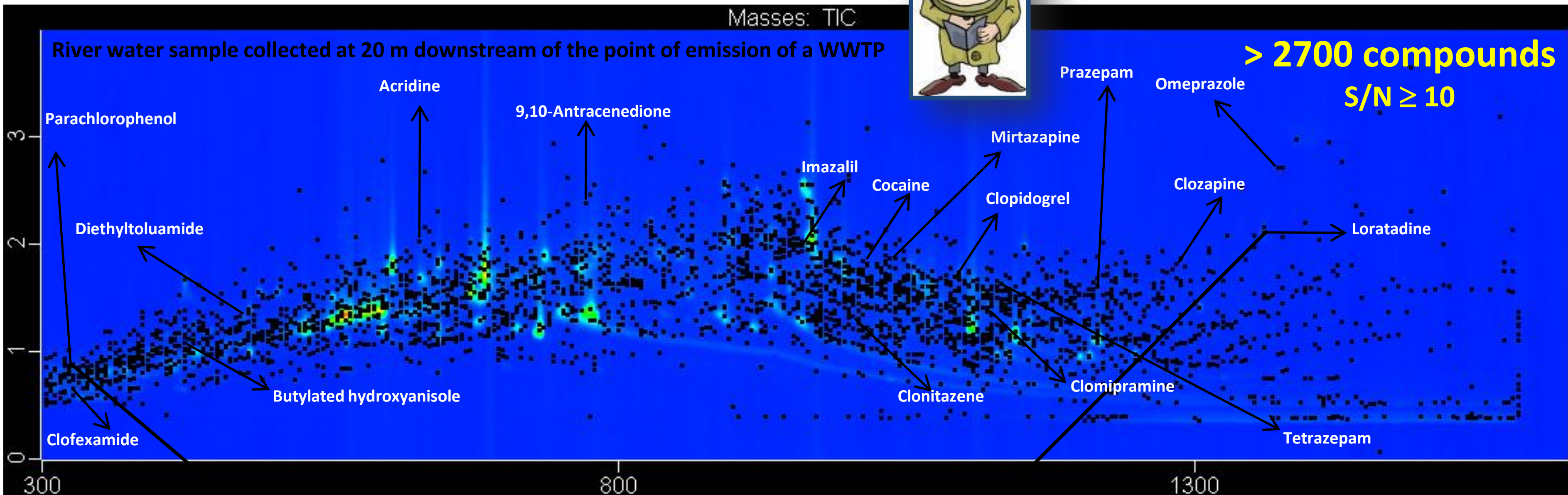
Precisions: RSD ≤ 28%

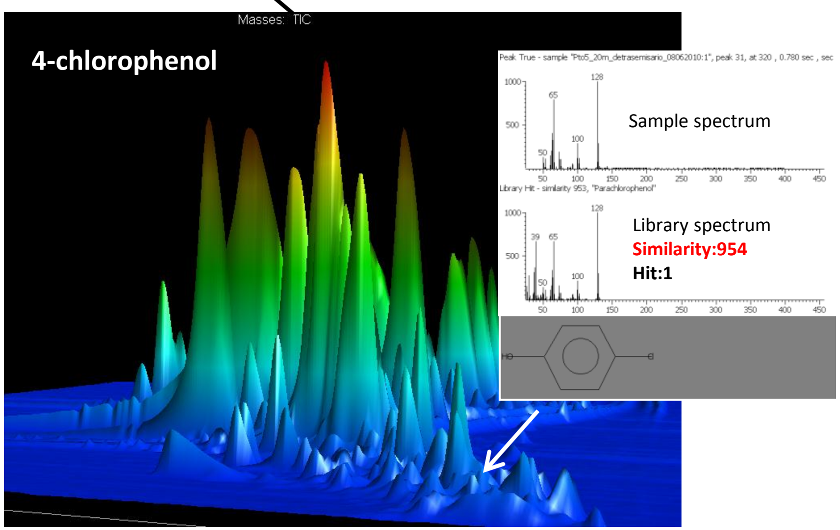
Recoveries: ≥ 83%

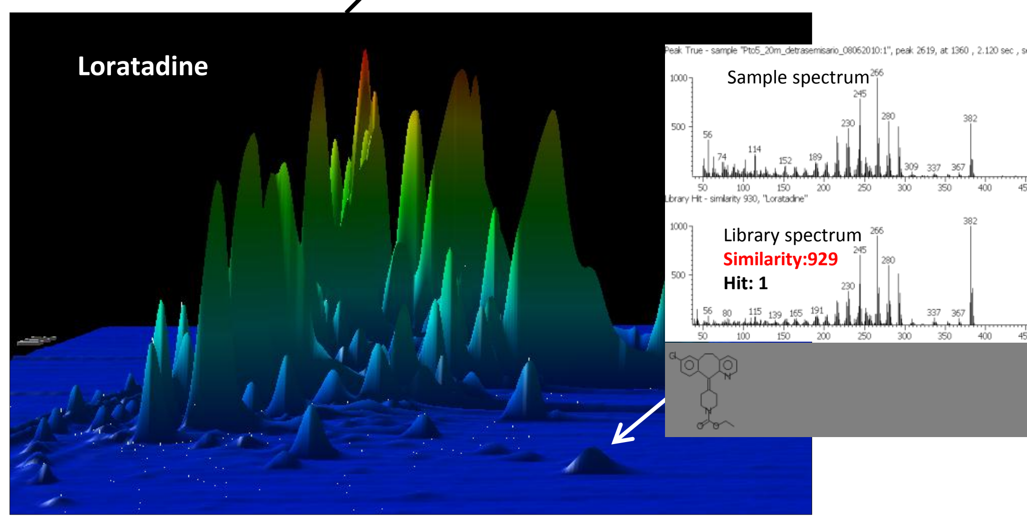


Total Charge (ng/L)
30000
25000
20000
15000
10000
5000
0
PESTICIDES
PAHs
PCPs
11 APRIL
20 APRIL
26 APRIL
4 MAY
7 JUNE
28 JUNE
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Point 1
35 km upstream of the effluent WWTP
Point 2
24 km upstream of the effluent WWTP
Point 3
6 km upstream of the effluent WWTP
WWE
Point 4
20 m downstream of the effluent WWTP
Point 5
1.15 km downstream of the effluent WWTP

Screening of nontarget compounds





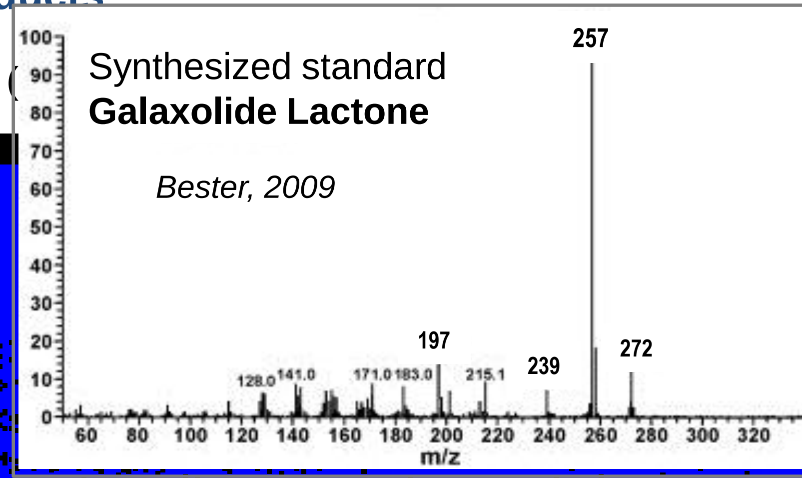


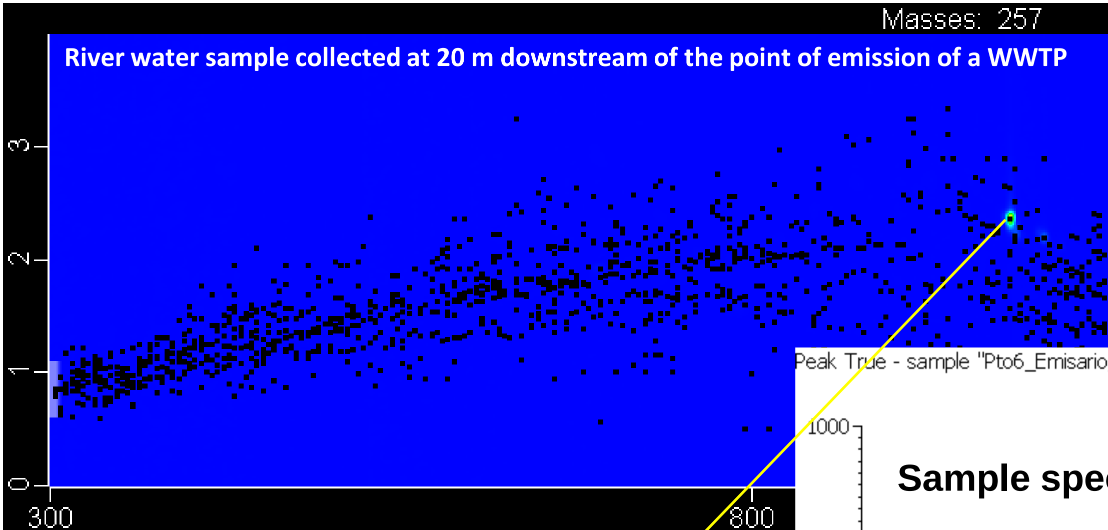
NON-TARGET COMPOUNDS

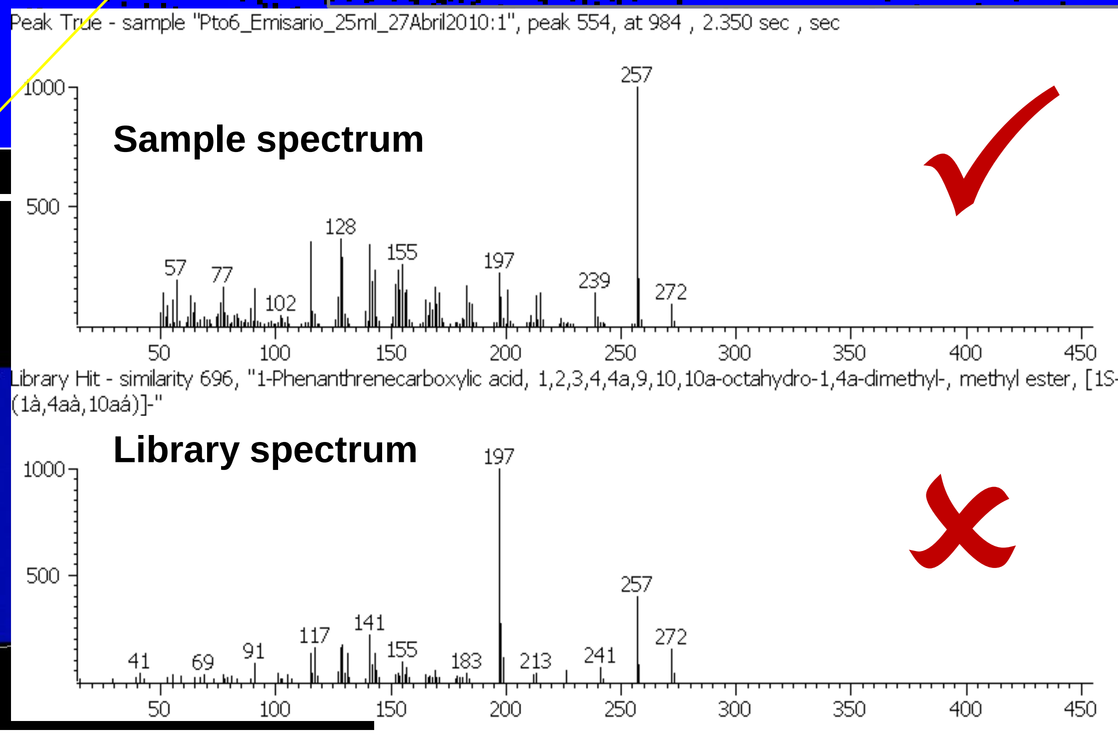
Chemical Class	Compound	Frequency of detection (%)	
		WWE (n=6)	RW (n=30)
Pharmaceuticals			
Antidepressant	Clomipramine	67	27
Antidepressant	Mirtazapine	100	50
Anxiolytic	Prazepam	67	23
Anxiolytic	Tetrazepam	50	43
Antipsychotic	Clozapine	17	7
Antihistamine	Loratadine	100	57
Antihistamine	Cloperastine	50	17
Cardiac drug	Clopidogrel	67	50
Local anesthetic	Lidocaine	17	7
Antiulcer agent	Omeprazole	83	17
Pesticides			
Herbicide	Oxadiazon	0	43
Herbicide	Chloropropham	17	7
Fungicide	Imazalil	17	3
Insect repellent	DEET	17	3
PCPs			
Antioxidant	BHA	100	13
UV-filter	Benzophenone	100	67
Fragrance	Patchouli alcohol	50	33
Steroids			
Sterol	Cholesterol	83	73
Faecal steroid	Chlolesta-4,6-dien-3-ol	67	50
Alkyl-PAHs			
Alkyl-phenanthrene	1-methyl-phenanthrene	17	20
Alkyl-phenanthrene	2-methyl-phenanthrene	33	7
Alkyl-phenanthrene	4-methyl-phenanthrene	17	17
Others			
Illicit drug	Cocaine	67	20
Illicit drug	Clonitazene	20	7
Flame retardant	TCPP	100	100
TPs			
Anthracene TP	9,10-anthracenodione	33	7
Musk xylene TP	4-amino musk xylene	100	77
Galaxolide TP	Galaxolide-lactone	100	100

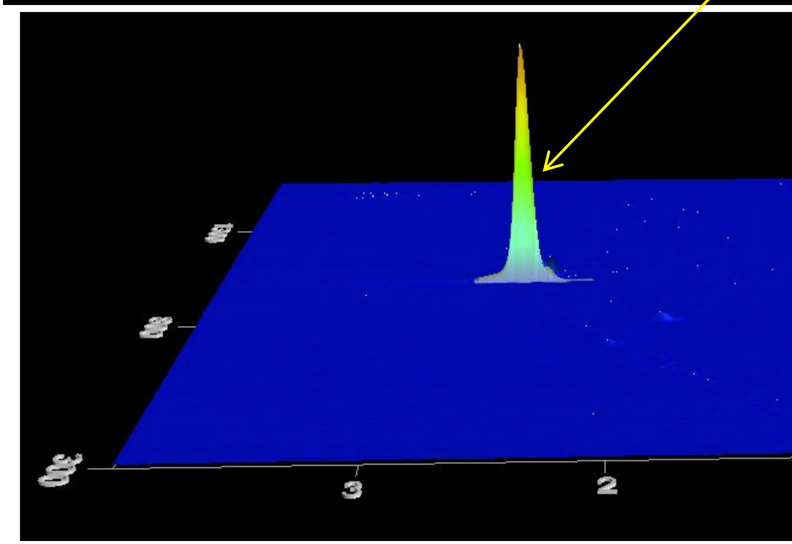
GCxGC-TOF-MS
Screening of nontarget compounds- degradation products

Galaxolide Lactone? M 272, **257 (100)**, 239 (21), 197 (





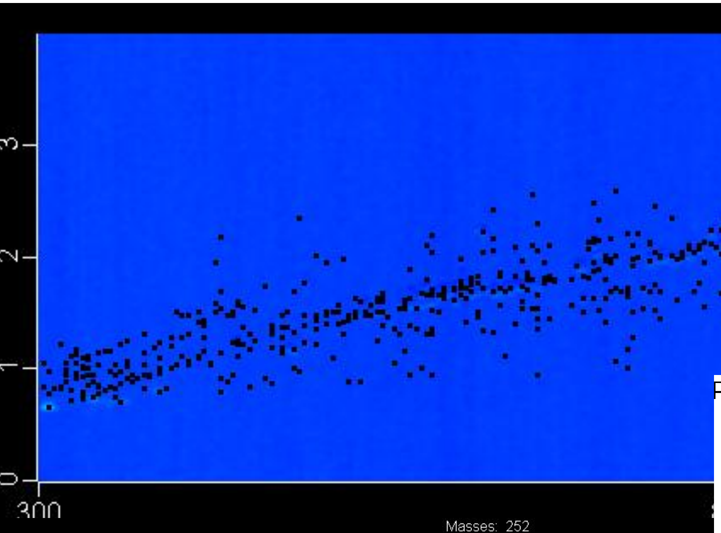


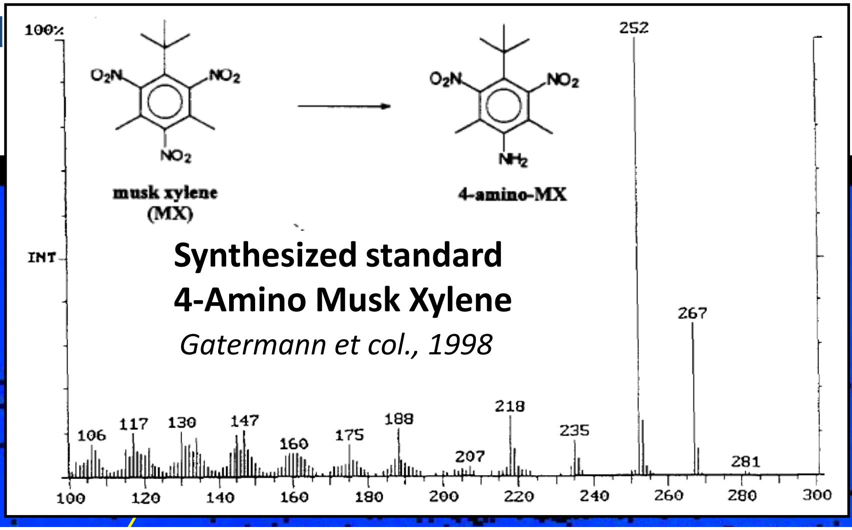


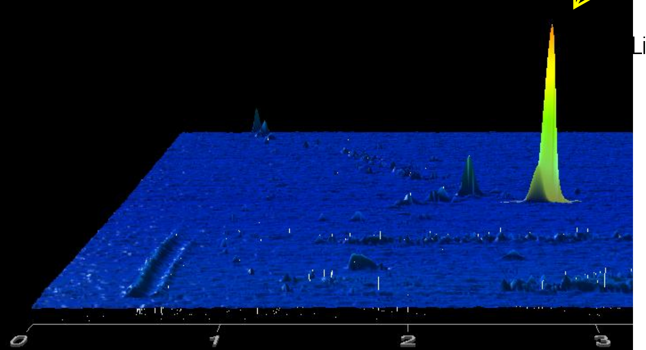
GCxGC-TOF-MS
Screening of nontarget compound

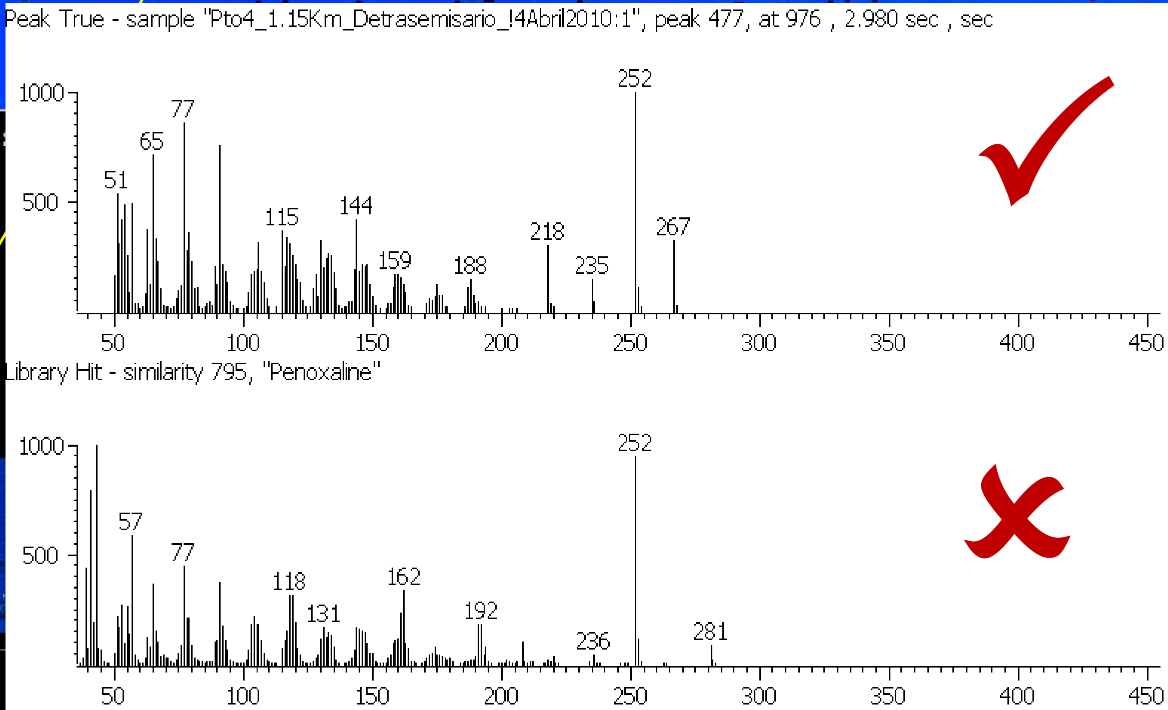
4-amino musk xylene?

Mass 252

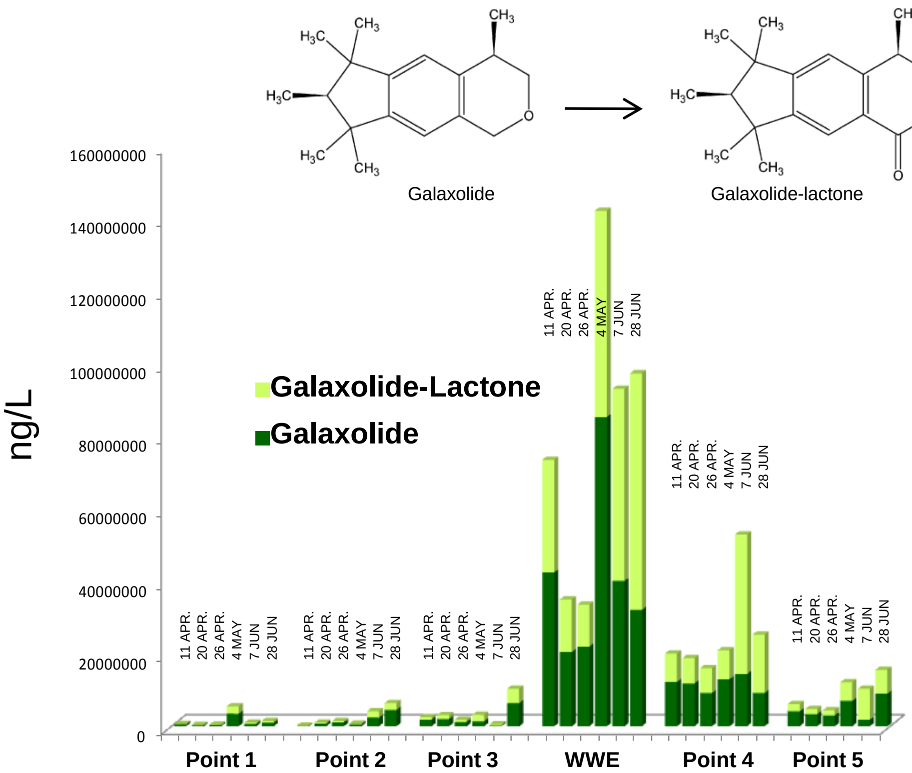


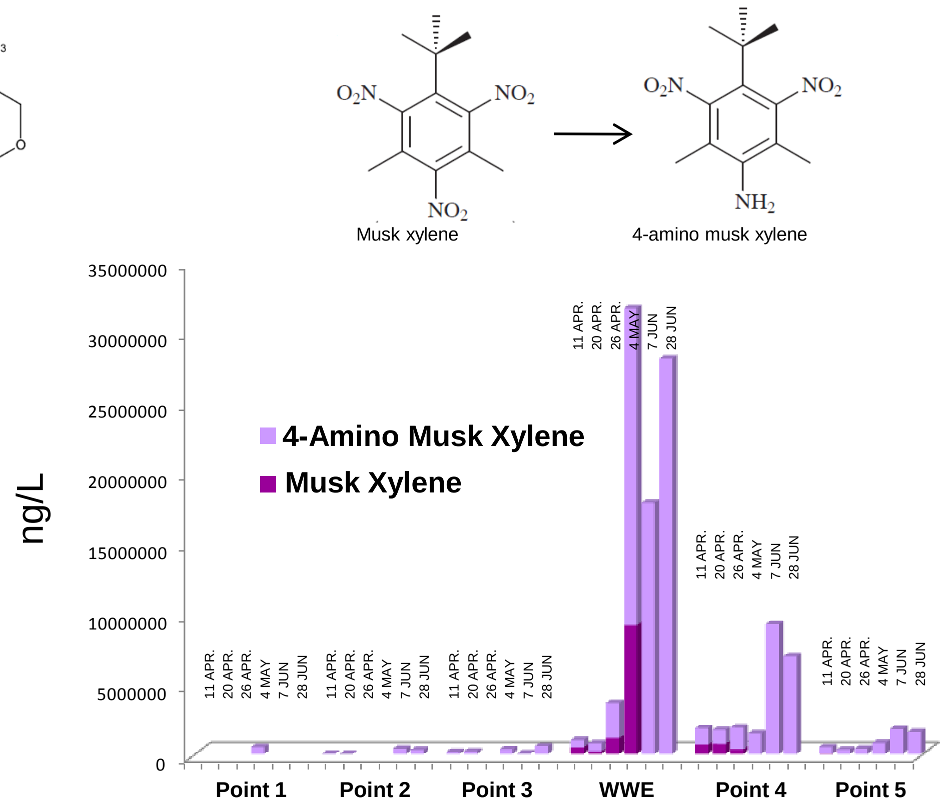






Temporal and spatial contamination variation of galaxolide-lactone, 4-amino musk xylene and their parents compounds along Henares River.





CONCLUSIONS

- In thsis study, SBSE-GCxGC-TOFMS has been demostrated as a powerful tool for the analysis of organic contaminants in waters.

With GCxGC has been achieved a considerable improved separation of analytes from each other and from matrix co-extract, compared with 1D-GC.

The method detection limits were very low (1-10 ng/L) and the reliable confirmation of analyte identity was possible at this low concentration levels.

The TOFMS data processing provide automatic peak findings using MS deconvolution and spectral searching versus different libraries.

In addition, with this technique it is possible to screening for non-target compounds

An approach has been described for examining and detect which of the contaminants present in the river samples could affect the macroinvertebrate community structure by using the developed screening method and statistical analysis. Have been identified contaminants that are unique to the bad and moderate ecological status.


Thank you for your attention!!

Validation data obtained with the SBSE-GCxGC-TOF-MS method for the analysis of target compounds in effluent wastewater and river water

COMPOUND	Log K_{ow}	Theoretical Recoveries (%)	Recoveries in Matrix (%)			MDLs (ng/L)		MQLs (ng/L)		Linearity (ng/L)				Precision RSD (%)	
										Range	R^2	Range	R^2	Rep.	Repr.
			WWE	WWE Diluted 1:4	River	WWE	River	WWE	River	WWE		River		WWE	WWE
2-EHMC	5,8	100	43	81	109	0.10	0.02	0,2	0,07	1-500	0,9917	1-500	0,9887	15	28
4-MBC	5,1	98	142	141	142	0.04	0.18	0,14	0,60	1-500	0,9950	1-500	0,9916	19	18
Acenaphthene	3,92	79	79	99	134	0.10	0.19	0,34	0,62	1-500	0,9908	1-500	0,9961	7	5
Acenaphthylene	4,07	84	17	67	136	0.16	0.24	0,52	0,81	1-500	0,9865	1-500	0,9996	4	5
Alachlor	3,52	60	157	124	134	1.74	0.75	5,82	2,51	5-500	0,9835	1-500	0,9856	21	13
Aldrin	6,5	100	15	30	123	0.89	0.46	2,96	1,53	1-500	0,9860	1-500	0,9911	18	17
Anthracene	4,45	93	121	110	139	0.02	0.04	0,06	0,14	1-500	0,9956	1-500	0,9830	17	16
Atrazine	2,61	16	149	148	115	3.07	0.98	10,23	3,28	5-500	0,9938	1-500	0,9880	15	9
Benzo [a] anthracene	5,79	100	81	97	98	0.30	0.10	1,01	0,32	1-500	0,9959	1-500	0,9900	27	15
Benzo [a] pyrene	5,97	100	21	57	67	0.18	0.27	0,61	0,89	1-500	0,9950	1-500	0,9921	17	17
Benzo [ghi] perylene	6,63	100	17	29	60	0.99	1.30	3,29	4,32	5-500	0,9980	5-500	0,9694	11	26
Benzo [k] fluoranthene	6,84	100	22	61	69	0.18	0.14	0,61	0,48	1-500	0,9988	1-500	0,9910	18	17
BHT	5,1	98	192	149	101	0.08	0.03	0,26	0,10	1-500	0,9838	1-500	0,9893	24	26
Biphenylol-2	3,09	36	130	116	131	1.77	1.08	5,9	3,61	5-500	0,9912	5-500	0,9856	9	21
Chlorfenvinphos (trans,cis)	3,81	75	124	125	121	0.52	0.09	1,75	0,3	1-500	0,9890	1-500	0,9890	18	12
Chlorpyrifos-ethyl	4,96	98	82	80	137	0.44	0.58	1,46	1,93	5-500	0,9927	5-500	0,9886	15	10
Chlorpyrifos-methyl	4,31	90	148	110	138	0.55	0.54	1,82	1,79	1-500	0,9918	10-500	0,9890	11	8
Chrysene	5,73	100	54	95	92	0.13	0.07	0,43	0,22	1-500	0,9854	1-500	0,9930	21	11
Clorophene	3,6	65	137	121	132	0.08	0.55	0,26	1,82	1-500	0,9914	1-500	0,9809	15	8
DDE (o, p)	6,51	100	171	138	114	0.76	0.60	2,55	2,00	1-500	0,9990	1-500	0,9957	18	28
DDT (p, p)	6,91	100	25	60	99	1.82	1.96	6,06	6,53	5-500	0,9954	5-500	0,9935	16	24
Diazinon	3,81	75	155	108	141	0.10	0.46	0,34	1,53	1-500	0,9879	1-500	0,9872	17	13
Dibenz [a,h] anthracene	6,5	100	18	34	59	1.16	0.75	3,86	2,52	5-500	0,9934	5-500	0,9886	17	19
Dieldrin	5,4	99	58	57	79	0.33	0.12	1,11	0,40	1-500	0,9890	1-500	0,9943	14	12
Endosulfan I	3,83	76	157	147	140	1.38	1.15	4,60	3,85	5-500	0,9907	5-500	0,9940	14	12
Endosulfan II	3,83	76	163	149	110	0.68	0.17	2,28	0,56	1-500	0,9897	1-500	0,9919	26	24
Endosulfan sulfate	3,66	68	139	121	129	1.79	1.60	5,96	5,32	5-500	0,9915	5-500	0,9910	17	13
Endrin	5,2	99	181	120	134	0.82	0.82	2,72	2,73	1-500	0,9997	1-500	0,9941	14	10
Fluoranthene	5,16	99	141	123	140	2.02	0.05	6.73	0,18	10-500	0,9962	1-500	0,9900	16	11
Fluorene	4,18	87	138	106	128	0.15	0.04	0,51	0,14	1-500	0,9959	1-500	0,9913	10	7