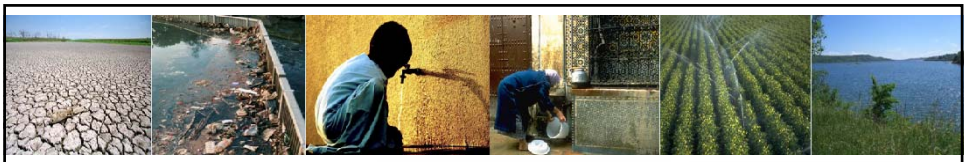


Parc Científic i Tecnològic Universitat de Girona

Universitat de Girona

Generalitat de Catalunya
Departament d'Innovació, Universitats i Empresa

Agència Catalana de l'Aigua

INNOVA-MED CONFERENCE

Innovative processes and practices for wastewater treatment and re-use in the Mediterranean region

8-9 October 2009, Girona, Spain

Evaluation of Ozone Waste Water Treatments and Studies Evaluating the Reuse of Treated Effluents

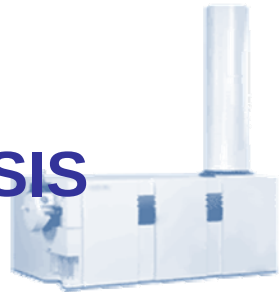
Amadeo R. Fernández-Alba
University of Almería, SPAIN

-Analysis of wastewater

-Advanced Oxidative Water Teatments (ozone and Ozone + H2O2)

-Life cicle assesment

ANALYSIS



GC-MS

LC-MS

ANALYSIS

Target compounds

Non target compounds

LC-QqQ-MS/MS and LC-LiT-MS/MS

LC-TOF-MS

GC-MS(MS)

MS/MS mode (Low mass acc.)

GC-Q-MS

Full scan mode (High mass acc.)

TARGET ANALYSIS

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Antibiotics
1. Metronidazole
2. Sulfamethoxazole
3. Trimethoprim
4. Ciprofloxacin
5. Cefotaxime
6. Ofloxacin
7. Erythromycin
8. Tetraciclyne
10.Norfloxacin
11.Clarithromycin
12.Lincomycin
13.Sulfamethazine
14.Sulfapyridine
15.Sulfadiazine
16.Sulfathiazole
17.Azithromycin
18.Mevastatin
19.Simvastatin

Analgesic/ Anti-Inflammatory
20. Acetaminophen
21. Indomethacine
22. Fenoprofen
23. Codeine
24. Mefenamic Ac.
25. Ibuprofen
26. Ketorolac
27. Naproxen
28. Diclofenac
29. Ketoprofen
30.Salicilic acid
31.Propyphenazone
32.Urbason

Contrast media
33. Iopromide
34. Iopamidol

Beta Blockers
35. Atenolol
36. Propranolol
37. Sotalol
38. Metoprolol
39. Nadolol

Antihistamines
40. Famotidine,
41. Lansoprazole
42. Ranitidine
43. Omeprazole
44. Loratadine

Diuretics
45. Furosemide
46. Hydrochlorothiazide

Antidepressants
47. Fluoxetine
48. Paroxetine
49. Venlafaxine
50. Citalopram
51. Amitriptyline
52. Clomipramine

Lipid regulators
53. Fenofibrate
54. Bezafibrate
55. Gemfibrozil
56. Pravastatin

Sympathomimetics
57. Salbutamol
58. Terbutaline

Antiepileptic Psychiatric drug
59. Carbamazepine
60. Diazepan
61. Primidone

Antineoplastics
62. Ifosfamide
63. Cyclophosphamide
64. Tamoxifen

Anesthetics
65. Mepivacaine

Corticosteroides
66. Methylprednisolone

Anti-Infective
67. Clotrimazole

Metabolites
68. 4-Acetoaminoantipyrine
69. 4-Formylaminoantipyrin
70. 4-Methylaminoantipyrine
71. 4-Dimethylaminoantipyrine
72. 4-Aminoantipyrine
73. Paraxanthine
74. Carbamaz.10,11-epoxide
75. Antipyrine
76. Fenofibric Acid
77. Clofibric acid
78. Cotinine

Pesticides
79. Atrazine
80. Clorpyriphos
81. Clorfenvinphos
82. Diuron
83. Isoproturon
84. Simazine
85. Permetrina

EDCs
86. Bisfenol-A

Disinfectants
87. Biphenylol
88. Chlorophene

Others
89. Nicotine
90. Caffeine

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Filtration
Filtros de fibra de vidrio
0.7 µm

OASIS HLB hydrophilic-lypophilic polymer

200 ml wastewater effluent, **pH 7-8**
400 ml river water, **pH 7-8**

Elution
4 + 4 ml MeOH

Drying
~ 5min N2

Wash
MIliQ water, pH = 7-8

Evaporation

SPE

Analysis
LC-ESI(+/-)MS
or GC-MS

Reconstitution:
- 1ml MeOH:H_2O, 10:90 (*v/v*)
- Filtro PTFE 0.45 µm

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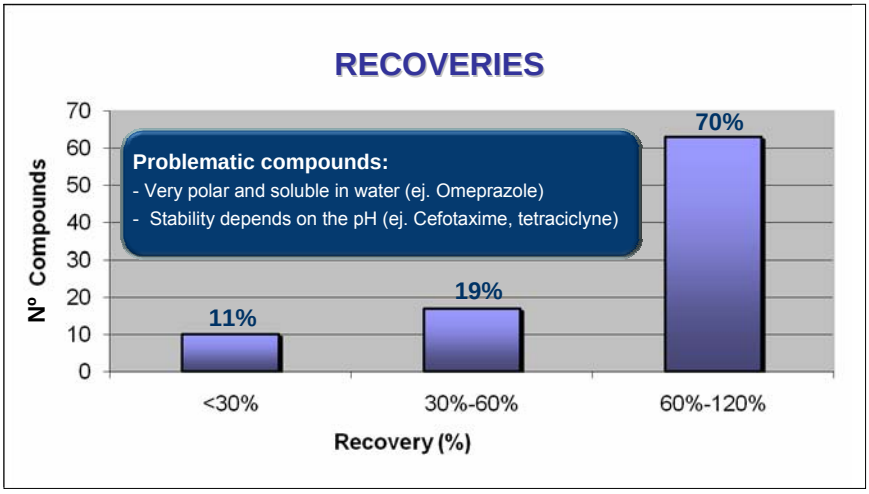
TARGET ANALYSIS
SAMPLE TREATMENT
INNOVA-MED CONF
6-9 October 2009, Gi



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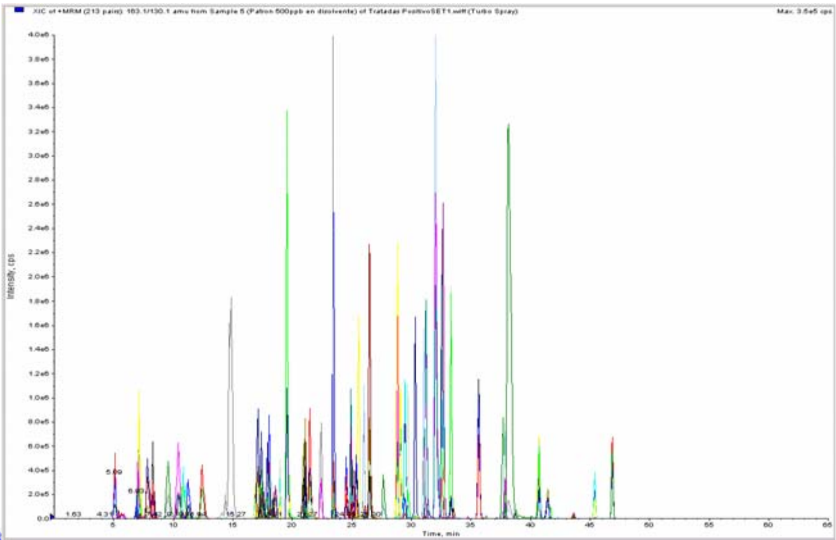
LC-QqQ-MS/MS

POLAR TARGET COMPOUNDS



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INNOVA-MED CONFERENCE
8-9 October 2009, Girona, SPAIN

POLAR TARGET COMPOUNDS

LC-QTRAP

Identification criteria

Compound	t_R (min) (%RSD)	Precursor Ion (m/z)	SRM 1*	SRM 2**	SRM 3**	[SRM2]/[SRM1] (%RSD)
Positive Ionization						
Nicotine	6.1 (5.6)	163.1	117.2	84.1	130.1	0.42 (14)
Salbutamol	7.1 (0.4)	240.3	148.2	166.2	222.2	0.28 (8)
Atenolol	7.2 (0.2)	267.3	145.2	190.2	116.1	0.72 (4)
Terbutaline	7.3 (0.1)	226.3	152.2	107.1	125.2	0.31 (2)
Ranitidine	7.9 (1.2)	315.3	176.2	130.1	224.2	0.66 (10)
Sotalol	[illegible]	[illegible]	[illegible]	213.2	255.2	0.73 (9)
4-MAA	[illegible]	[illegible]	[illegible]	97.2	159.2	0.38 (13)
4-DAA	[illegible]	[illegible]	[illegible]	[illegible]	111.2	0.31 (19)
4-AA	[illegible]	[illegible]	[illegible]	[illegible]	94.2	0.21 (11)
Parax[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.17 (12)
Ac[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.19 (16)
M[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.51 (11)
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.88 (7)
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.30 (8)
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.98 (6)
4[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.96 (7)
Tr[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0..85 (12)
Cefo[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.95 (4)
Ofloxaci[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	0.95 (5)
Ciprofloxacin	[illegible]	[illegible]	[illegible]	[illegible]	245.1	0.78 (16)
Mepivacaine	[illegible]	[illegible]	[illegible]	[illegible]	-	0.30 (9)
Metoprolol	[illegible]	[illegible]	[illegible]	133.2	159.2	0.64 (10)
Antipyrine	21.6 (0.3)	189.2	77.1	104.1	106.2	0.52 (7)
Omeprazole	22.3 (0.2)	346.3	198.2	136.2	151.2	0.60 (15)
Propanolol	24.9 (0.4)	260.0	116.2	183.2	155.2	0.71 (12)
Sulfamethoxazole	25.1 (0.4)	254.2	108.2	156.1	147.2	0.88 (6)
Carbam.10,11-epoxide	25.3 (0.2)	253.2	180.2	236.2	210.2	0.68 (11)
Erythromycin	25.5 (0.2)	734.6	158.3	576.5	316.1	0.24 (3)
Paroxetine	27.7 (0.1)	330.3	192.2	123.2	151.2	0.30 (14)

133 transitions
In the same time segment!!
In positive mode

Compound	t_R (min) (%RSD)	Precursor Ion (m/z)	SRM 1*	SRM 2**	SRM 3**	[SRM2]/[SRM1] (%RSD)
Positive Ionization						
Carbamazepine	28.9 (0.2)	237.2	194.3	192.1	-	0.34 (3)
Simazine	29.0 (0.1)	202.2	132.0	124.2	104.1	0.88 (7)
Fluoxetine	29.7 (0.2)	310.3	44.2	148.2	-	0.22 (20)
Ketorolac	30.4 (0.2)	256.2	105.1	178.1	-	0.01 (10)
Methylprednisolone	31.3 (0.2)	475.3	321.1	339.3	457.2	0.80 (11)
Isoproturon	32.4 (0.2)	207.3	72.1	165.1	134.2	0.20 (13)
Atrazine	32.6 (0.2)	216.1	174.1	104.1	132.1	0.41 (4)
Ketoprofen	33.3 (0.2)	255.2	209.2	105.1	177.2	0.78 (12)
Naproxen	33.6 (0.3)	231.2	185.3	170.1	-	0.36 (12)
Diazepan	35.6 (0.2)	285.2	193.2	154.2	222.3	0.98 (4)
Biphenylol	35.8 (0.3)	171.2	153.1	152.0	127.2	0.63 (5)
Indomethacine	37.7 (0.3)	358.2	139.1	174.3	-	0.10 (16)
Fenofibric Acid	37.9 (0.3)	319.1	233.1	139.1	121.0	0.33 (8)
Mefenamic Ac.	40.4 (0.3)	242.2	180.2	224.2	209.2	0.58 (12)
Chlorfenvinphos	40.7 (0.3)	359.1	155.2	127.1	205.1	0.96 (10)
Chlorpyriphos methyl	43.4 (0.3)	322.1	125.1	290.1	109.1	0.88 (13)
Fenofibrate	46.6 (0.2)	361.2	233.1	139.1	121.1	0.98 (6)
Negative Ionization						
Furosemide	5.0 (2.4)	329.1	205.1	285.1	126.2	0.86 (3)
Hydrochlorothiazide	5.7 (0.3)	296.0	269.1	205.0	126.0	0.97 (5)
Clofibric acid	5.9 (1.3)	213.0	127.1	85.0	-	0.25 (3)
Bezafibrate	7.9 (1.2)	360.1	274.2	154.1	85.0	0.62 (2)
Diclofenac	10.9 (0.7)	294.0	250.0	214.1	-	0.10 (6)
Diuron	11.6 (0.5)	231.1	186.1	149.8	122.1	0.24 (12)
Fenoprofen	11.8 (0.3)	241.1	197.1	93.1	-	0.67 (4)
Ibuprofen	12.5 (0.7)	205.1	161.2	-	-	-
Chlorophene	13.0 (0.3)	217.0	181.2	153.0	101.0	0.65 (10)
Gemfibrozil	13.4 (0.4)	249.2	121.0	127.1	-	0.10 (13)

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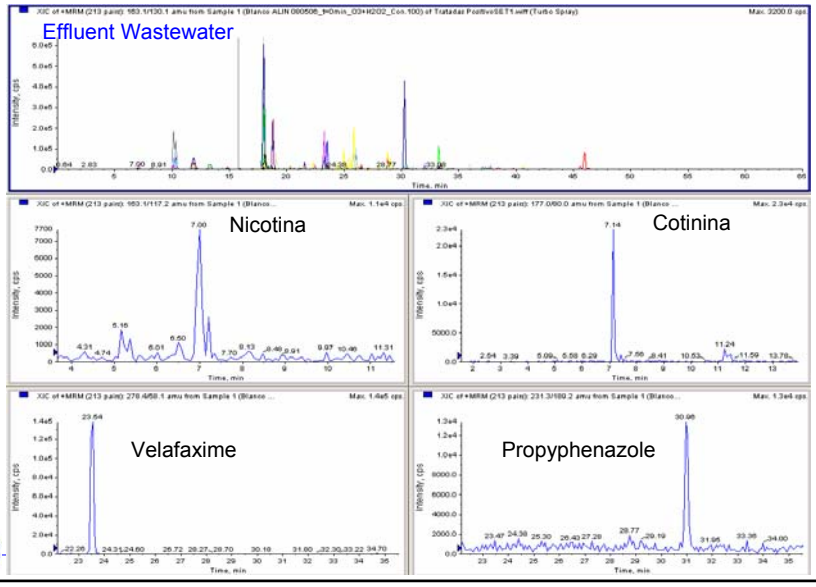
LC-QqQ-MS/MS

POLAR TARGET COMPOUNDS



Identification criteria for the SRM method by LC-QqQ-MS/MS

Compound	t_R (min) (%RSD)	Product Ion (m/z) SRM 1	Product Ion (m/z) SRM 2	[SRM2]/[SRM1] (%RSD)
Furosemide	3.7 (1.5)	205, $[M - H - CO_2SO_2NH_2]^-$	285, $[M - H - CO_2]^-$	0.9 (5)
Clofibric Acid	3.8 (0.7)	127, [M – H –	– H – $C_6H_4ClO]^-$	0.2 (8)
Bezafibrate	4			0.7 (3)
Hydroclhlorothiazi				0.9 (3)
Ketoprofen				
Naproxen				
Diclofen				
Fenopr				
Indometi				
Mefenamic				
Ibuprofen				
Diuron				0.2 (8)
Chlorophene	12.2 (0.2)			0.6 (11)
Gemfibrozil	12.3 (0.4)	121, $[M - H - CO_2C_6H_{12}]^-$	127, $[M - H - C_5H_9OH]^-$	**0.1 (8)**

SRM METHOD

IDENTIFICATION CRITERIA:

- ✓ t_R
- ✓ 2 SRM transitions per compound
- ✓ SRM2/SRM1 ratio

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LC-LiT-MS

QUALITATIVE ANALYSIS

QTrap instruments allows improving confirmatory information:

- Application of additional operation modes based on the use of the linear ion trap (LIT) mode.

Compounds for which the second transition:
- Not detected
- -Present at low intensity

Additional structural information is required for a suitable confirmation

Sequentially collect multiple SRM transitions and full scan MS/MS (Enhanced Product Ion, EPI mode) and/ or MS^3 spectra in one single run.

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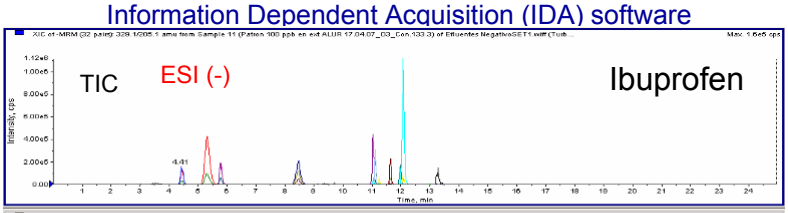
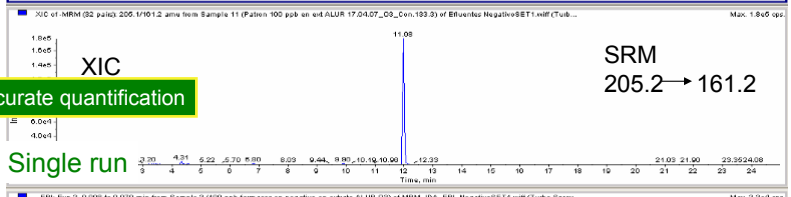
LC-QTRAP

QUALITATIVE ANALYSIS

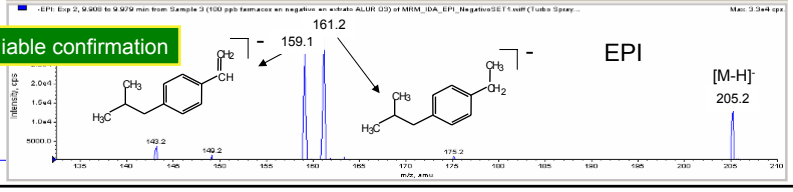
Information Dependent Acquisition (IDA) software





Accurate quantification

Single run

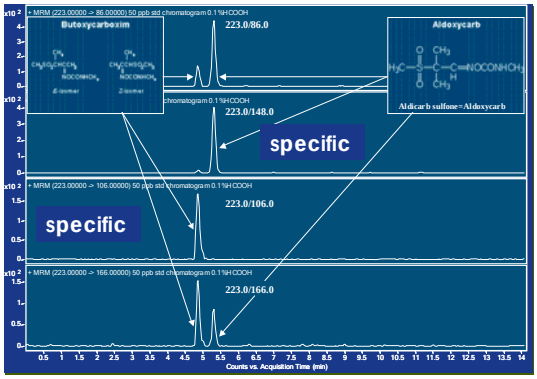


Reliable confirmation

Results

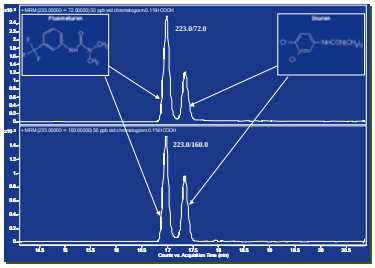
Examples for common transitions:

butoxycarboxin – aldicarb sulfone



scanned – unscanned transitions are common

fluometuron - diuron



both scanned transitions are common

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QUANTITATIVE ANALYSIS

LODs (ng/L)

	Compound	LC-QTRAP-MS/MS	LC-TOF-MS	LC-QTOF-MS
ESI (+)	Carbamazepine	0,4	5	0,7
	Mepivacaine	0,6	9	0,5
	Atenolol	2	10	0,2
	Ciprofloxacin	3	50	0,3
ESI (-)	Ibuprofene	1	100	2
	Diclofenac	0,4	8	2

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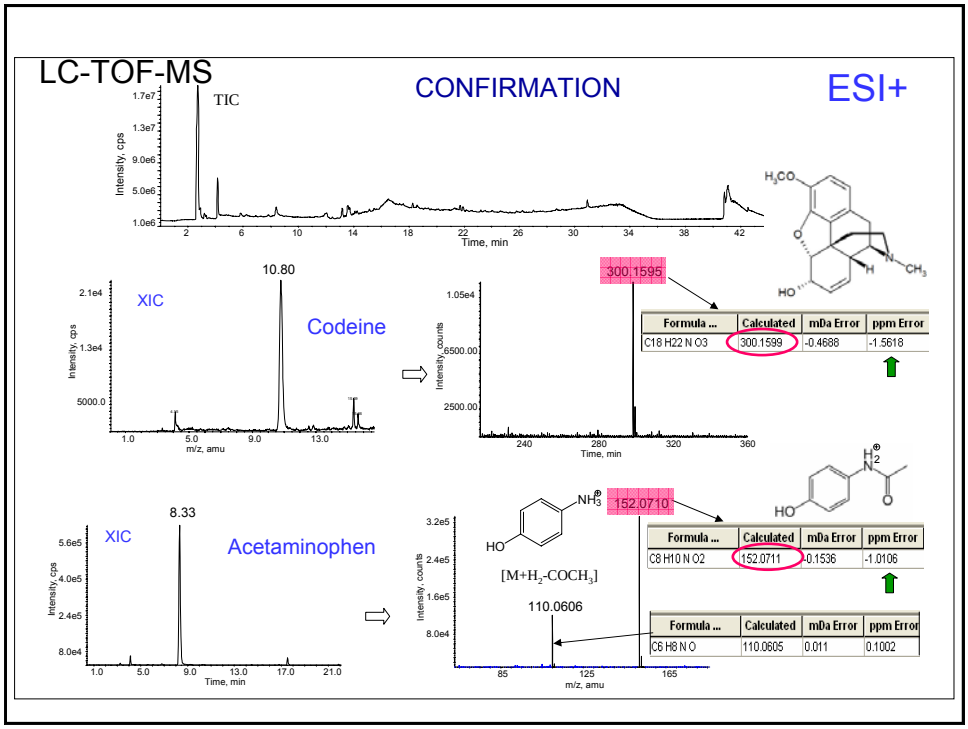
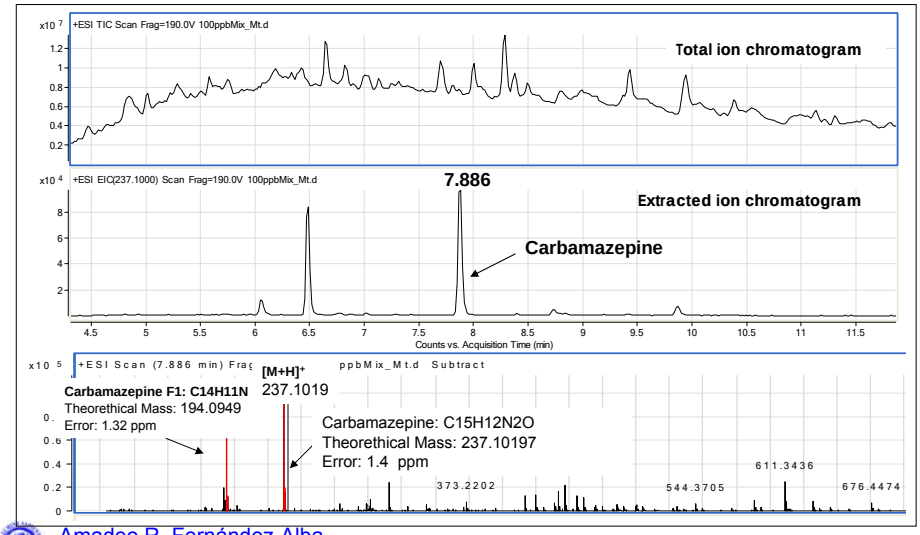
INNOVA-MED CONFERENCE
NON-TARGET ANALYSIS


LC-TOF-MS
CONFIRMATION
ESI+
TIC
Intensity, cps
Time, min
10.80
XIC
Codeine
Intensity, cps
m/z, amu
300.1595
Intensity, counts
Time, min
Formula ... | Calculated | mDa Error | ppm Error
C18 H22 N O3 | 300.1599 | -0.4688 | -1.5618
8.33
XIC
Acetaminophen
Intensity, cps
Time, min
152.0710
[M+H2-COCH3]
110.0606
Intensity, counts
m/z, amu
Formula ... | Calculated | mDa Error | ppm Error
C8 H10 N O2 | 152.0711 | -0.1536 | -1.0106
Formula ... | Calculated | mDa Error | ppm Error
C6 H8 N O | 110.0605 | 0.011 | 0.1002

LC-TOF-MS

Effluent wastewater



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LC-QTOF-MS
Accurate-Mass Database

Procedure:

- Preparación de Standards y Análisis
- Tabla de Datos Excel
- Creación de la Base de Datos
- Integración en el Software del equipo
- Screening Automático de Standards
- Screening Automático de Muestras Fortificadas
- Screening Automático de Muestras Reales

300 **pesticides** + in source fragments
93 **pharmaceuticals** + in source fragments

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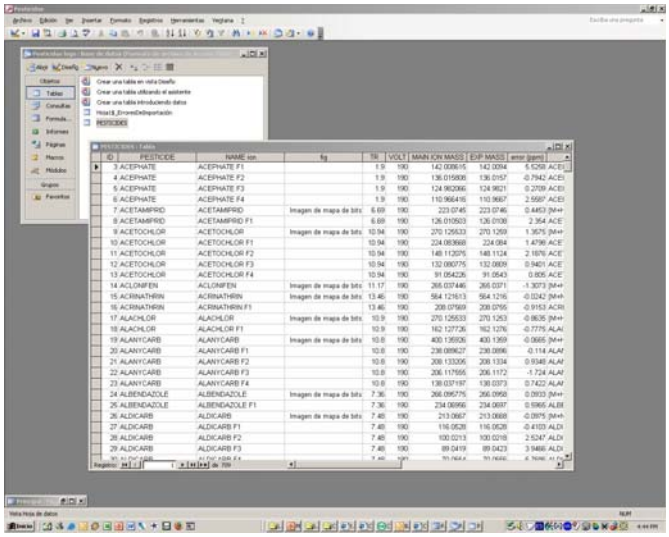
100 Pesticides + 618 Fragments= 918 entries in the database

Access

DATABASE



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LC-TOF-MS

COMPOUND	RT (min)	Theoretical Mass	Exp. Mass	Score	Error (ppm)	FORMULA [M+H$^+$]
…	…	…	…	…	…	…
AZOXYSTROBIN	10.15	403.1168	403.1168	95.56	0.01	C22H17N3O5
AZOXYSTROBIN F1	10.15	371.0901	371.0906	80.8	-1.47	C2H9NO2PS
…	…	…	…	…	…	…

Diazinón
DEET
Cyprodinil
Terbutryn
Diuron

Carbendazim
Clorfenvinfos
Azoxystrobin
Miclobutanil
Propiconazole

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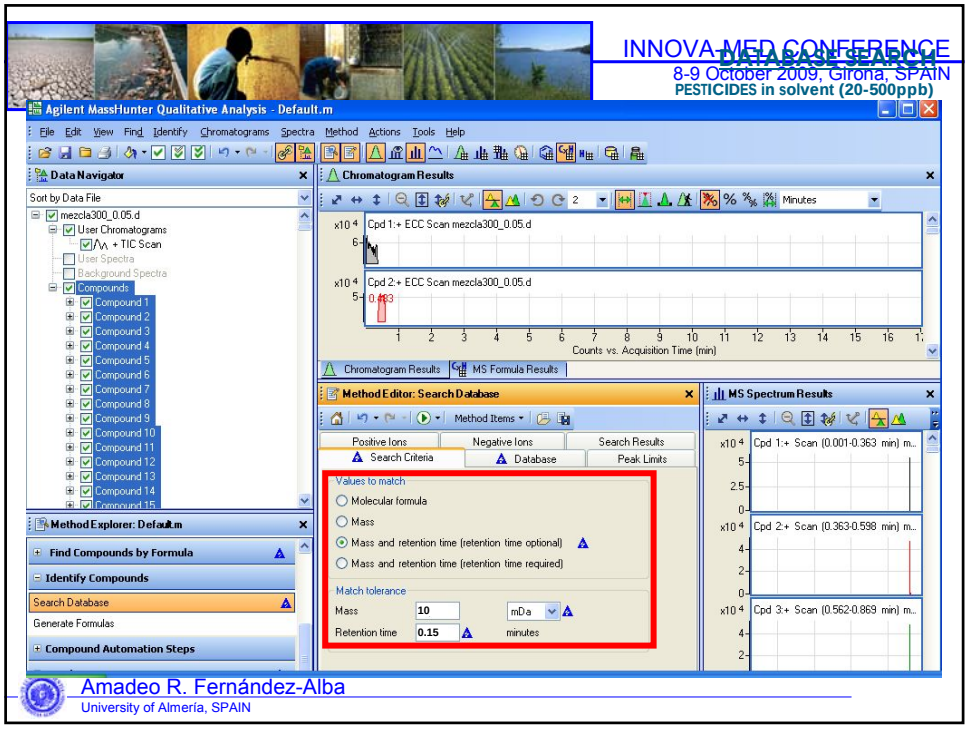
INNOVA MED CONFERENCE
DATABASE SEARCH
8-9 October 2009, Girona, SPAIN
PESTICIDES in solvent (20-500ppb)
Agilent MassHunter Qualitative Analysis - Default.m
Data Navigator
Chromatogram Results
Method Editor: Search Database
MS Spectrum Results
Method Explorer: Default.m
Find Compounds by Formula
Identify Compounds
Search Database
Generate Formulas
Compound Automation Steps
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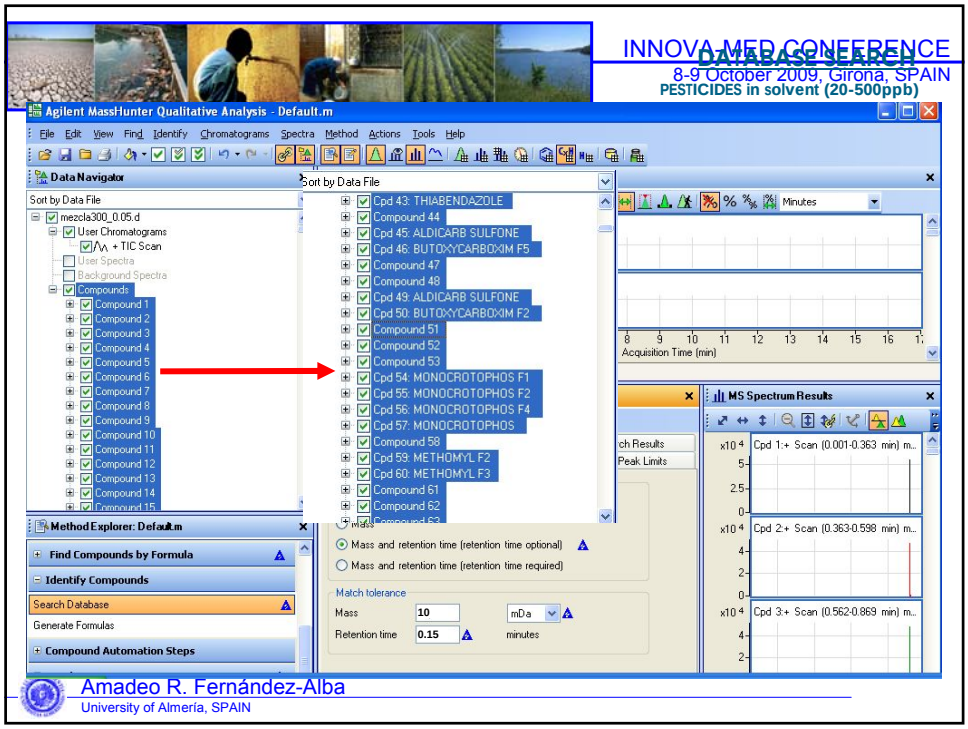
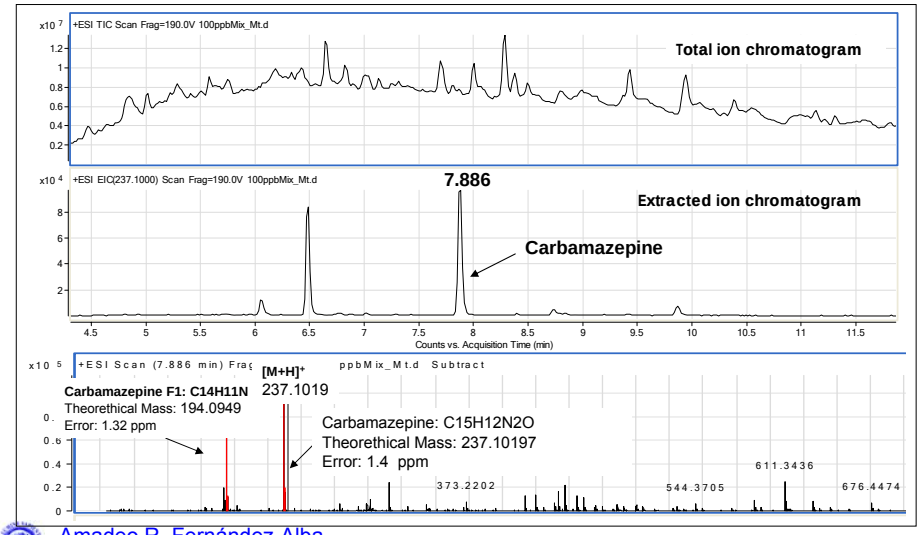

INNOVA MED CONFERENCE
DATABASE SEARCH
8-9 October 2009, Girona, SPAIN
PESTICIDES in solvent (20-500ppb)
Agilent MassHunter Qualitative Analysis - Default.m
Data Navigator
MS Spectrum Results
Method Explorer: Default.m
Find Compounds by Formula
Identify Compounds
Search Database
Generate Formulas
Compound Automation Steps
Amadeo R. Fernández-Alba
University of Almería, SPAIN

LC-TOF-MS

Effluent wastewater



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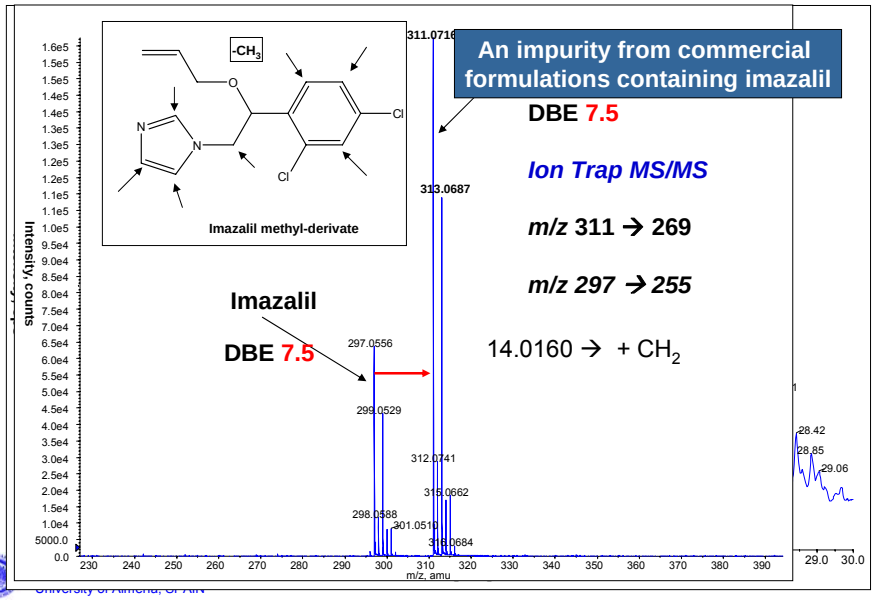
NON TARGET



TOF-MS REPORT

Effluent wastewater

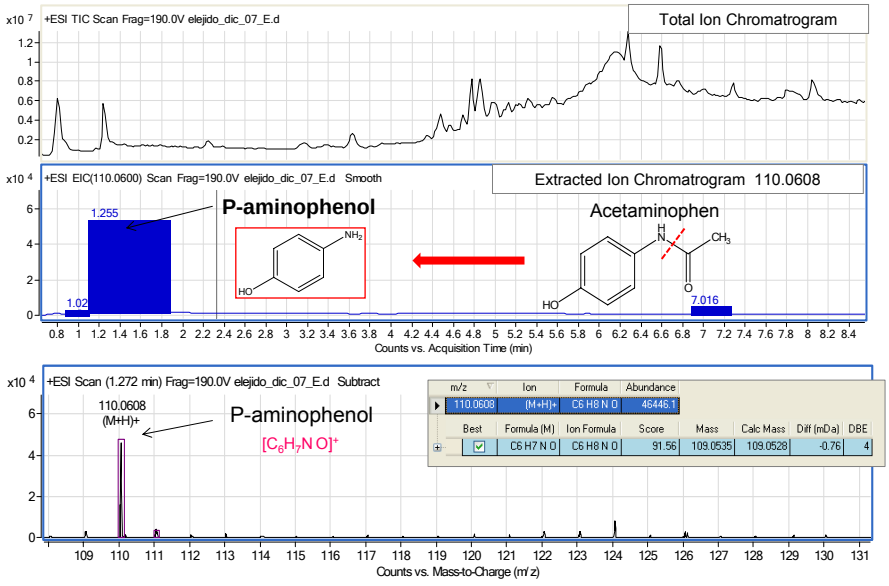
Name	RT	Mass	Mass (Tgt)	Diff (Tgt, ppm)	Formula (Tgt)	Score (Tgt)	Formula (DB)	Score (DB)
4AAA	4.85	245.1169	262.1192	-64864.74	C13 H16 N3 O3	95.82	C13 H16 N3 O3	92.93
4AAA	1.245	245.1166	262.1192	-64865.63	C13 H16 N3 O3	55.06		
4AAA	5.522	245.116	262.1192	-64867.91	C13 H16 N3 O3	75.66		
4FAA	4.864	231.1007	232.1086	-4342.33	C12 H14 N3 O2	80.13	C12 H14 N3 O2	94.89
4FAAF1	4.851	203.106	204.1137	-4936.73	C11 H14 N3 O	95.76	C11 H14 N3 O	97.99
4FAAF1	2.951	203.1058	204.1137	-4938.07	C11 H14 N3 O	85.47		
4MAA	2.76	217.1215	218.1293	-4620.35	C12 H16 N3 O	87.45		
AcetaminophenF1	1.241	109.053	110.0606	-9155.14	C6 H8 N O	80.51		
ACETOCHLOR F4	1.225	90.0462	91.0548	-11076.13	C7 H7	47.43		

			INFLUENT (ng/L)			EFFLUENT (ng/L)			
	pKa	Log kow	Max.	Min.	Average	Max.	Min.	Average	Removal Efficiency (%)
Acetaminophen	9.4	0.46	37458	1571	23202	< LOQ	< LOQ	< LOQ	100

Atenolol	11.492	266.1638	267.1709	-3769.3	C14 H23 N2 O3	77.79		
AZINPHOS-ETHYL F6	4.065	159.043	160.0511	-6298.71	C8 H6 N3 O	83.17	C8 H6 N3 O	73.79
AZINPHOS-ETHYL F7	9.908	152.0032	153.0123	-6594.68	C6 H5 N2 O S	68.29		
Azithromycin	14.368	748.5096	749.5164	-1343.22	C38 H73 N2 O12	63.62		
AZOXYSTROBIN	10.15	403.1159	404.1246	-2496.09	C22 H18 N3 O5	94.97	C22 H18 N3 O5	92.33
AZOXYSTROBIN F1	10.15	371.0901	372.0984	-2709.96	C21 H14 N3 O4	80.78	C21 H14 N3 O4	92.5
SULFURON-METHYL F1	10.55	148.0524	149.0603	-6761.34	C9 H9 O2	86.09		
Caffeine	4.779	194.0808	195.0882	-5164.06	C8 H11 N4 O2	97.32	C8 H11 N4 O2	88.56
CaffeineF1	4.78	137.0589	138.0667	-7299.41	C6 H8 N3 O	98.49	C6 H8 N3 O	88.96
Carbamaz1011epoxide	6.054	252.0898	253.0977	-3982.29	C15 H13 N2 O2	85.66		
Carbamazepine	7.853	236.0952	237.1028	-4249.49	C15 H13 N2 O	79.85	C15 H13 N2 O	96.23
Carbamazepine	6.456	236.095	237.1028	-4250.5	C15 H13 N2 O	85.28		
CARBOFURAN F1	7.634	164.0831	165.0916	-6108.56	C10 H13 O2	77.9		
FURAN-3-HYDROXY F1	7.283	162.0681	163.0759	-6179.69	C10 H11 O2	74.43		

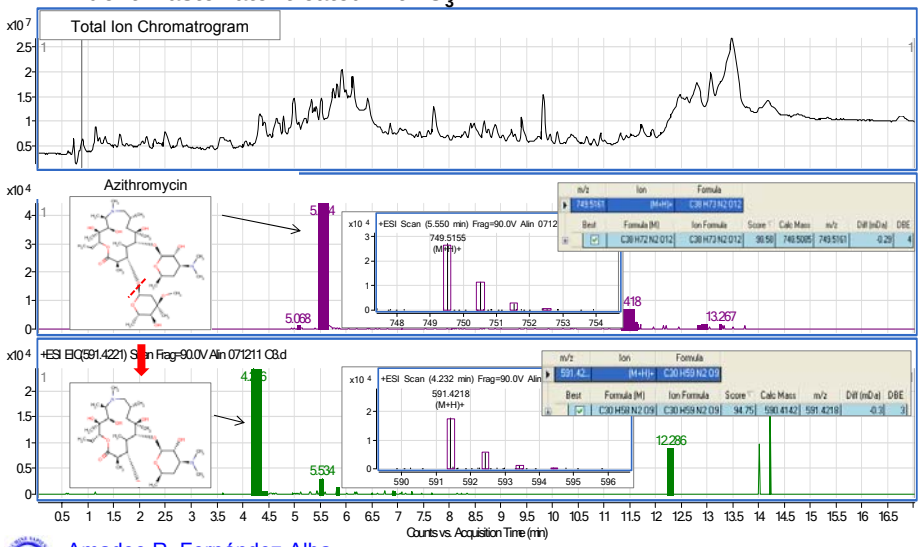
LC-TOF Chromatogram

Effluent Wastewater



LC-TOF Chromatogram

Effluent Wastewater treated with O_3



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QUANTITATIVE ANALYSIS

LODs (ng/L)

	Compound	LC-QTRAP-MS/MS	LC-TOF-MS	LC-QTOF-MS
ESI (+)	Carbamazepine	0,4	5	0,7
	Mepivacaine	0,6	9	0,5
	Atenolol	2	10	0,2
	Ciprofloxacin	3	50	0,3
ESI (-)	Ibuprofene	1	100	2
	Diclofenac	0,4	8	2

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CARACTERIZACIÓN

EDAR ALCALA OESTE (Aguas urbanas)

1989 (2002). 374.090 h.e. 3000 m^3h^{-1}
Sedimentación primaria. Fangos Activados con eliminación de nutrientes. Nitrificación/desnitrificación

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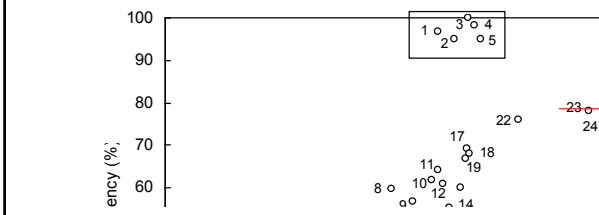
TABLE 1

Compound	pKa[1]	Log Kow[2]	Influent (ng/L) Maximum	Influent (ng/L) Minimum	Influent (ng/L) Average	Effluent (ng/L) Maximum	Effluent (ng/L) Minimum	Effluent (ng/L) Average	Removal Efficiency (%)
4-amino-antipyrine (4-AA)	4.3	0.07[3]	3325	262	1517	2253	127	676	55.4
4-methylaminoantipyrine (4-MAA)	4.3	0.39[3]	1894	314	880	1098	34	291	66.9
Acetaminophen	9.4	0.46	37458	1571	23202	< LOQ	< LOQ	< LOQ	100
Antipyrine	1.4	0.38	72	< LOQ	40	58	< LOQ	27	32.8
Atenolol	9.6	0.16	2432	660	1197	2438	517	1025	14.4
Bezafibrate	3.3	4.25	361	48	141	280	33	128	9.1
Benzophenone-3	7.6	3.82	904	< LOQ	393	121	< LOQ	86	78.2
Caffeine	10.4	0.07	65625	5010	22849	1589	< LOQ	1176	94.9
Carbamazepine	13.9	2.30	173	106	129	173	89	117	9.5
Ciprofloxacin	8.9	-1.08	13625	160	5524	5692	< LOQ	2378	57.0
Clofibric acid	3.2	2.57	127	< LOQ	26	91	< LOQ	12	54.2
Codeine	8.2	1.14	2087	150	521	319	< LOQ	160	69.3
Diclofenac	4.2	4.51[3]	561	< LOQ	232	431	6	220	5.0
Diuron	NA	2.78	196	30	109	81	2	42	61.5
Erythromycin	8.9	2.54	2310	< LOQ	346	760	< LOQ	331	4.3
Fenofibric acid	2.9	4.00[3]	117	< LOQ	79	129	< LOQ	78	1.3
Fluoxetine	10.1	1.95	1827	< LOQ	585	929	34	223	61.9

44 compuestos detectados al menos en 4 muestras del influente

Hydrochlorothiazide	7.9	-0.20	10018	617	2514	1702	679	1178	53.2
Ibuprofen	4.9	3.50	4113	< LOQ	2687	653	< LOQ	135	95.0
Indomethacine	4.5	4.27	113	< LOQ	42	59	20	37	11.1
Ketoprofen	4.5	3.12	801	< LOQ	441	539	277	392	11.2
Ketorolac	3.5	-0.27[3]	2793	< LOQ	407	607	< LOQ	228	43.9
Mefenamic Acid	4.2	5.12	220	101	141	163	87	138	1.8
Metoprolol	9.6	1.88	52	< LOQ	20	38	< LOQ	19	6.5
Metronidazole	2.4	-0.02	165	44	90	127	< LOQ	55	38.7
N-acetyl-4-amino-antipiryne (4-AAA)	4.6	-0.13[3]	22200	1760	8333	6745	< LOQ	4489	46.1
Naproxen	4.2	3.18	5228	1196	2363	2208	359	923	60.9
Metronidazole	2.4	-0.02	165	44	90	127	< LOQ	55	38.7
N-acetyl-4-amino-antipiryne (4-AAA)	4.6	-0.13[3]	22200	1760	8333	6745	< LOQ	4489	46.1
Naproxen	4.2	3.18	5228	1196	2363	2208	359	923	60.9
N-formyl-4-amino-antipiryne (4-FAA)	5.0	0.50[3]	71000	1005	17579	27444	< LOQ	5593	68.2
Nicotine	8.0	1.17	11671	< LOQ	4368	158	< LOQ	81	98.7
Ofloxacin	7.9	-0.39	5286	848	2275	1651	< LOQ	816	64.1
Omeprazole	7.1	2.23	2134	57	365	922	< LOQ	334	8.5
Paraxanthine	8.5	-0.39[3]	98500	4547	26722	1796	< LOQ	836	96.9
Propanolol	9.4	3.09	61	12	36	57	< LOQ	36	1.0
Ranitidine	1.9	0.27	1466	< LOQ	524	942	< LOQ	360	31.2
Sulfamethoxazole	5.7	0.89	530	162	279	370	104	231	17.3
Tonalide	-	5.70[3]	1932	< LOQ	952	315	< LOQ	146	84.7
Tridosan	7.8	4.53	2417	< LOQ	860	512	< LOQ	219	74.5
Trimethoprim	6.6	0.91	197	78	104	148	< LOQ	99	5.1



(27) atenolol, (36) propanolol, (30) metoprolol, (28) sulfamethoxazole, (40) erythromycin, (33) trimethoprim, (29) fenofibric acid, (31) bezafibrate, (32) ketoprofen, (34) Diclofenac, (35) indomethacine, (37) mefenamic acid, (38) omeprazole, (39) carbamazepine

$$D_{ow} = \frac{K_{ow}}{1 + 10^{pH - pK_a}}$$

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AOP

Procesos oxidativos donde se generan radicales hidroxilo en cantidad suficiente para influir en el tratamiento del agua

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \quad 70\,M^{-1}s^{-1}$$

$$O_3 + HO_2^- \rightarrow HO_2^\bullet + O_3^{\bullet -} \quad 2.2x10^6\,M^{-1}s^{-1}$$

$$HO_2^\bullet \underset{-k=5x10^{10}\ M^{-1}s^{-1}}{\overset{k=7.9x10^5\ s^{-1}}{\rightleftharpoons}} O_2^{\bullet -} + H^+ \quad pK=4.8 \qquad HO_3^\bullet \underset{-k=5.2x10^{10}\ M^{-1}s^{-1}}{\overset{k=3.3x10^2\ s^{-1}}{\rightleftharpoons}} O_3^{\bullet -} + H^+ \quad pK=8.2$$

$$O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2 \quad 1.6x10^6\,M^{-1}s^{-1}$$

$$HO_3^\bullet \rightarrow HO^\bullet + O_2 \quad 1.1x10^5\,M^{-1}s^{-1}$$

a pH 7 y valores de H_2O_2 10^{-5} – 10^{-3} M valores significativos de descomposición de ozono

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2.4 mgl^{-1} – 16.33 mgl^{-1}

TABLE 2

Ozonation time (min)	LOQ*	0	2	4	6	10	15	Ozone doses for remotion	k_R (M^{-1} s^{-1})
3-(4-methylbenzylidene) camphor	39	55	50	65	39	72	54	Not removed	
4-Aminoantipyrine	19	58	-	-	-	-	-	< 50 µM	
4-methylaminoantipyrine (4-MAA)	2	389	-	-	-	-	-	< 50 µM	
Antipyrine	8	30	16	-	-	-	-	< 90 µM	
Atenolol	3	911	655	265	24	-	-	< 220µM	

Grupo 27 - 40

Benzafibrato (4 ngl^{-1}) y ketoprofeno (3 ngl^{-1}) se detectan a dosis de ozono de 16 mgl^{-1}

No elimina

3-(4-methylbenzylidene) camphor 54 ngl^{-1}

Benzophenone-3 119 ngl^{-1}

Ethylkexyl methoxycinnamate 204 ngl^{-1}

Musk xylene 91 ngl^{-1}

Nicotine	4	81	12	10	13	10	14	Still detected at 340 µM
Norfloxacin	8	38	56	-	-	-	-	< 90 µM
Octocrylene	16	114	115	113	81	95	91	20% for 340 µM
Ofloxacin	3	3594	276	18	11	9	10	Still detected at 340 µM
Omeprazole	3	1015	231	7	-	-	-	< 130 µM
Primidone	5	80	86	65	40	-	-	< 220 µM
Propanolol	2	32	7	-	-	-	-	< 50 µM
Propyphenazone	2	23	-	-	-	-	-	< 90 µM
Ranitidine	2	111	3	-	-	-	-	< 90 µM
Sulfamethoxazole	8	95	39	19	15	-	-	< 220 µM
Sulfapyridine	12	60	-	-	-	-	-	< 50 µM
Tonalide	19	188	131	130	53	67	53	72% for 340 µM
Triclosan	52	246	55	72	79	70	53	Still detected at 340 µM
Trimethoprim	2	73	7	-	-	-	-	< 90 µM
Venlafaxine	8	179	127	21	-	-	-	< 130 µM

* LOQ calculated in ozonated samples. Cconcentration expressed as ng/L

3260 ± 780

680 ± 29

3890 ± 200

3040 ± 770

3100 ± 780

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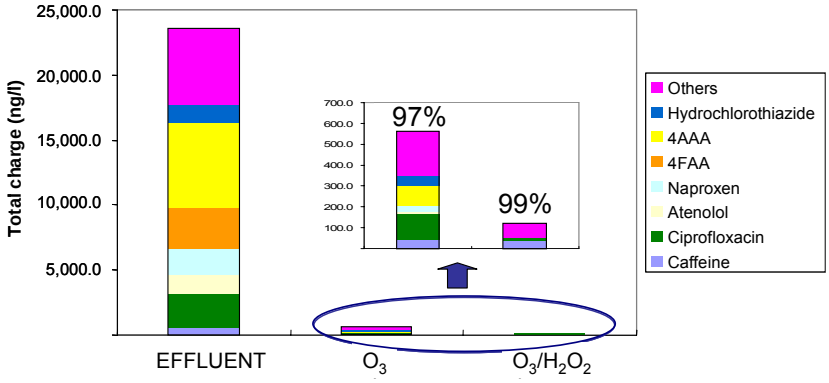
Tertiary Treatment



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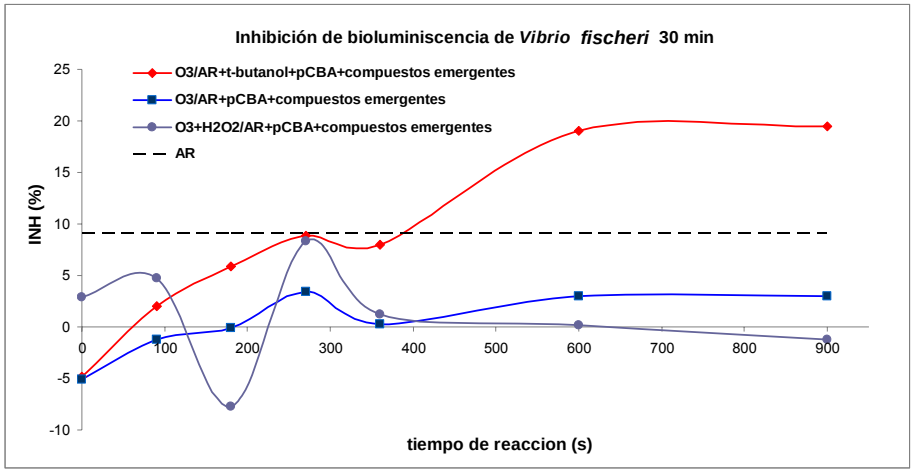
Norma ISO 11348-3



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PARAMETROS	Río Henares	U080311	U080506
SS (mgl^{-1})	1.85	3.95	6.35
ST (mgl^{-1})	410.00		
Turbidez (NTU)	2.35	4.93	6.30
Conduct. (μscm^{-1})	797	855	962
pH	7.83	7.08	7.31
DQO (mgO_2l^{-1})	26	61	58
$N\text{-}NO_3^-$ (mgl^{-1})	5.2	4.8	<0.5
$N\text{-}NH_4^+$ (mgl^{-1})	1.3	13.4	<16
$P\text{-}PO_4^{3-}$ (mgl^{-1})	0.5	0.38	0.54
DBO_5 (mgO_2l^{-1})	1.99	8.10	3.8
TOC (mgl^{-1})	4.36	5.09	5.84
IC (mgl^{-1})	43.04	59.10	62.75
Alcalinidad (mgl^{-1} $CaCO_3$)	230	200	270

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COMPUESTO	CONCENTRACIONES (ppb)
SULFAMETOXAZOL	2
ERITROMICINA	4
DICLOFENACO	10
IBUPROFENO	4
HIDROCLOROTIAZIDA	3
4-AAA	20
ATENOLOL	4
GEMFIBROZIL	1
CARBAMAZEPINA	2
TRICLOSAN	1
CAFEINA	2
DIURON	1
BEZAFIBRATO	1
PCBA	**1 ppm**
t-BUTANOL (sólo en muestras 22-05-09)	**10 mM**

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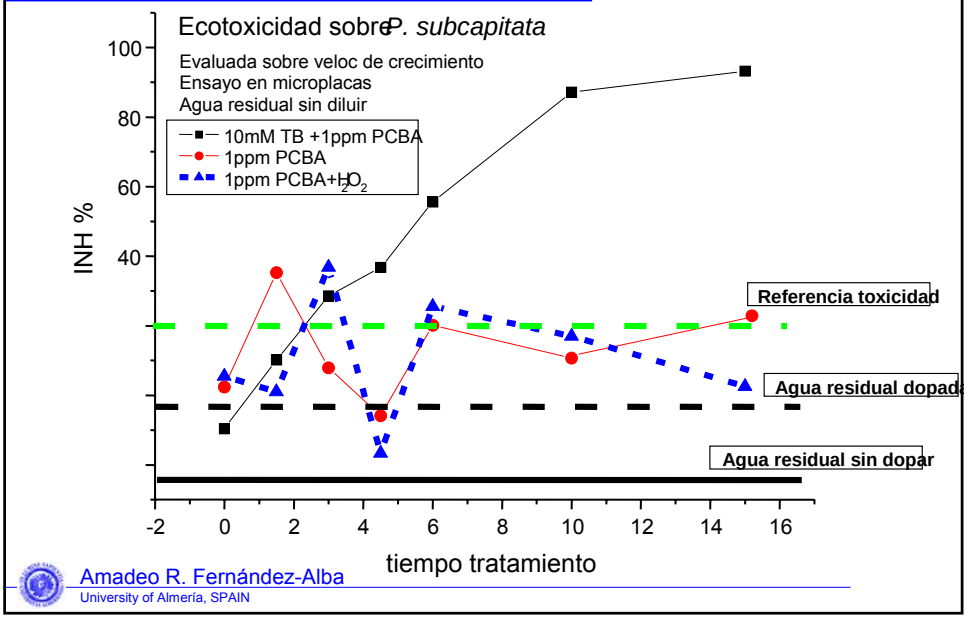

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Oxidation Technologies for Water and Wastewater Treatment, Berlin, april 2009
5th Specialist Conference/10th IOA-EA3 Berlin Conference

Water-reuse with ozone as an oxidant – a review about technical applications S. Shaefer, M. Sievers, A. Ried

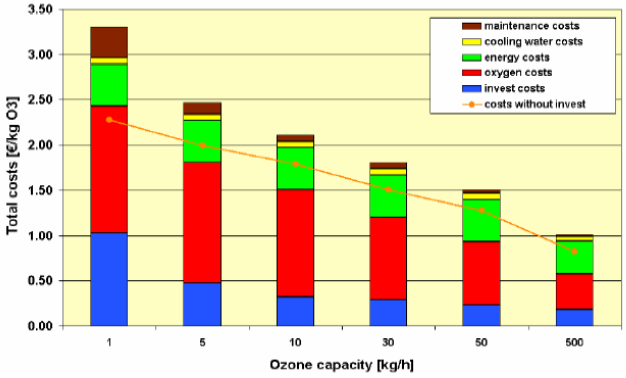

Figure 2. Specific costs of ozone-treatment

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7.5 kWhkg^{-1}O$_3$ - 12 – 15 kWhkg^{-1}O$_3$ (producción O3 + O2 + transporte O$_2$) //0.07 €kWh^{-1}

	Wastw	Obj.	Proc.	Flow (m^3/h)	Ozone (kgO$_3$/h)	Time (min)	Dos. (mg/l)	gen.O3 (€/m^3)	gen.O$_3$+O$_2$+ invest (€/m^3)
Tubli Tse Baharin 2002	sewag	Dis.	Bio-O3	8333	144	25	12	0.01	0.017
*WWTP Kalumburg (D) 2003	Ind. + sew	COD + dis.	Bio-O3-bio	1200	180	15	120/25	0.08	0.15
WWTP Ranica (I) 2006	sewag	COD + decolo.	Bio-O3	2000	56	10/30	10/20	0.02	0.042
Regensforf (S) 2007	sewag	EDC +Phar. +dis	Bio-O3-sandfil.	300	5	3/15		0.01	0.053
Ilkeston (UK) 2007	sewag	EDC	Bio-O3	42	0.8		3/15	0.01	0.06
Alcala	sewag	PPCP	Bio-O3	0.02	0.003	15	16	0.07	0.45
Alcala	sewag	TOC + PPCP	Bio-O$_3$/H$_2$O$_2$	0.06	0.016	5	29	0.14	0.88

* 20 % urbana, 80% industrial. Multinacional farmacéutica de fabricación de insulina

REUSE EVALUATION

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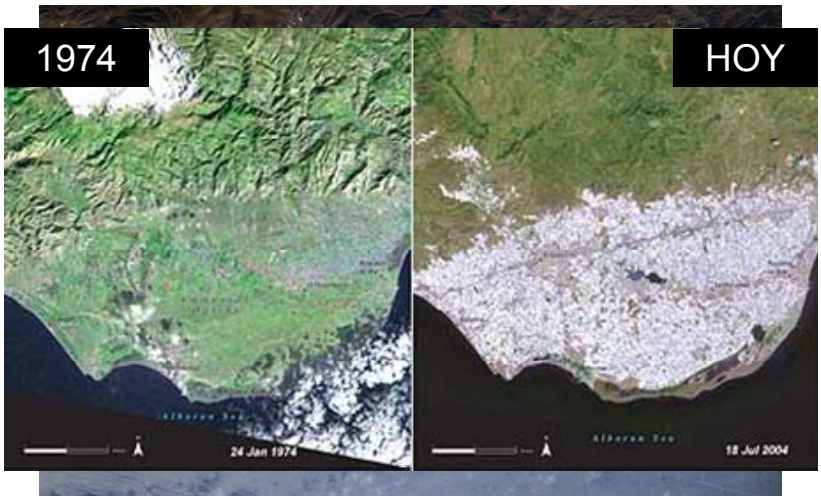

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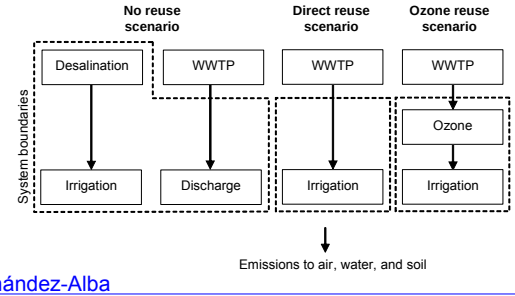
Life Cycle Assessment of ozonation and wastewater reuse

- Reusing wastewater in irrigation of agricultural land involves less environmental impact than obtaining water from other sources, taking into account a life cycle perspective?
- Reference technologies considered: ozonation and seawater desalination



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Life Cycle Assessment of ozonation and wastewater reuse

- We include the environmental impact of:
  - Oxygen production
  - Production of electricity for the ozonisator
  - Production of cooling water for the ozonisator
  - Transport of chemicals to the plant site (100 km)
  - Production of desalinated water from seawater
  - Pollutants in treated and untreated wastewater

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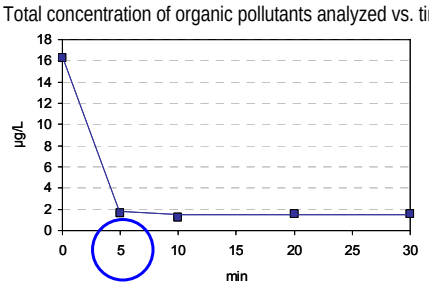
Life Cycle Assessment of ozonation and wastewater reuse

- Effect of ozone on the pollution load of a wastewater effluent from a urban WWTP



After 5 minutes there is little additional degradation

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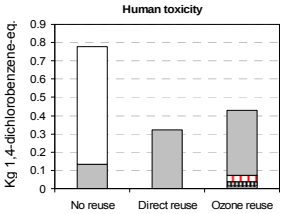
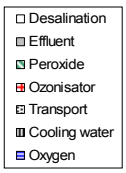
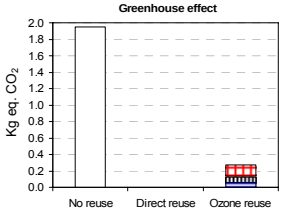
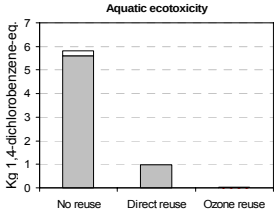
Life Cycle Assessment of ozonation and wastewater reuse

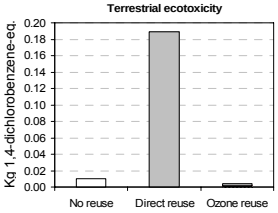
- RESULTS for environmental impacts assessed, per m^3 water
  - Aquatic ecotoxicity
  - Terrestrial ecotoxicity
  - Human toxicity
  - Greenhouse effect











TABACO

TOMATE


THANK YOU

GC-MS

Initial selected compounds

ANTIOXIDANT

Butylated hydroxytoluene- (BHT)

UV-FILTERS

Oxybenzone
2-Octyl-methoxycinnamate
4-methylbenzyledene camphor
ylene

SYNTHETIC FRAGANCES

Celestolide
Phantolide
Traseolide
Galaxolide
Musk xylene
Musk ketone
Tonalide.

ANTISEPTIC
Triclosan

DIOXIN

2,3,7,8-tetrachlolodibenzo-p-dioxin

INSECTICIDES

Endosulfan α
Endosulfan β
Endosulfan sulfate.

FIRE RETARDANT

TCPP oekanal.

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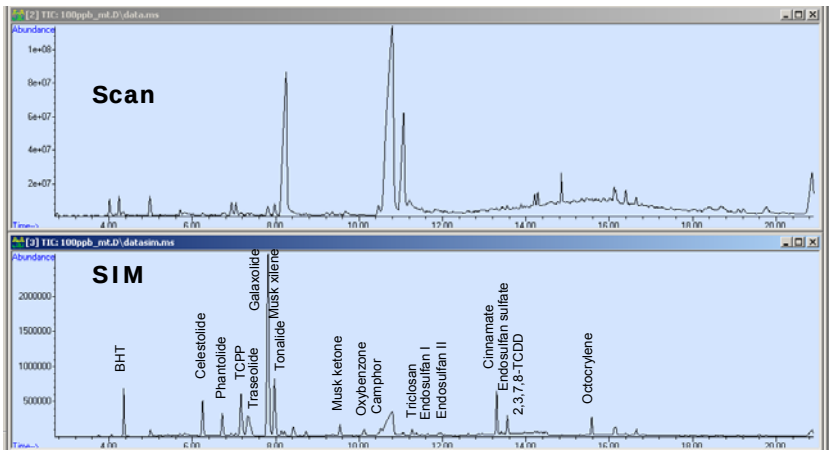
Screening and quantification of target compounds and "screening" of non-target compounds

10 ppb effluent wastewater matrix



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VALIDATION RESULTS OF THE ANALYTICAL METHOD

Compound	Linearity		MDL (ng/L)				Repeatability (RSD, %) n= 4
			Wastewater		River		
	Range (ng/L)	R^2	SIM	Scan	SIM	Scan	
BHT	25-1000	0,9999	16	16	6	6	6
Celestolide	10-1000	1,0000	7	7	3	3	6
Phantolide	25-1000	0,9996	7	7	3	3	4
TCPP Oekanal	50-1000	0,9976	36	66	14	27	7
Traseolide	25-1000	1,0000	18	22	7	9	7
Galaxolide	25-500	0,9932	17	20	7	8	7
Musk Xylene	10-1000	0,9999	1	4	0.4	2	6
Tonalide	25-1000	0,9998	16	22	6	9	8
Musk Ketone	25-1000	1,0000	21	21	11	11	4
EUSOLEX 6300	50-1000	0,9996	30	43	12	17	3
Oxybenzone	50-1000	0,9969	24	63	10	25	6
Triclosan	50-1000	0,9963	44	82	18	33	6
Endosulfan α	100-1000	0,9996	68	72	27	41	7
Endosulfan β	50-1000	0,9980	32	71	13	29	12
2-Octyl methoxycinnamate	25-1000	0,9976	10	17	4	7	5
Endosulfan Sulfate	50-1000	0,9993	35	35	14	14	6
2,3,7,8-TCDD	25-1000	1,0000	8	51	3	21	8
Octocrylene	25-1000	0,9977	11	47	5	19	2

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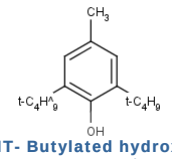
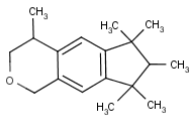
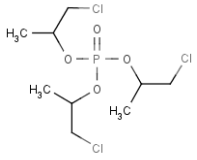
Introducción de compuestos en la base de datos AMDIS



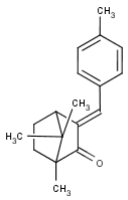
BHT- Butylated hydroxytoluene
Antioxidant



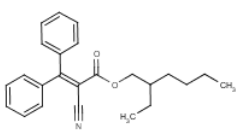
Galaxolide
Synthetic fragance



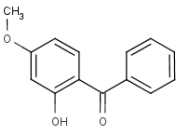
TCPP Oekanal
Fire retardant



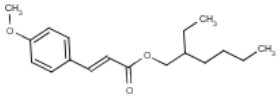
4- Methylbenzylidene camphor
UV-Filter



Octocrylene
UV-Filter



Oxybenzone
UV-Filter



2-Octyl methoxycinnamate
UV-Filter

934 compuestos

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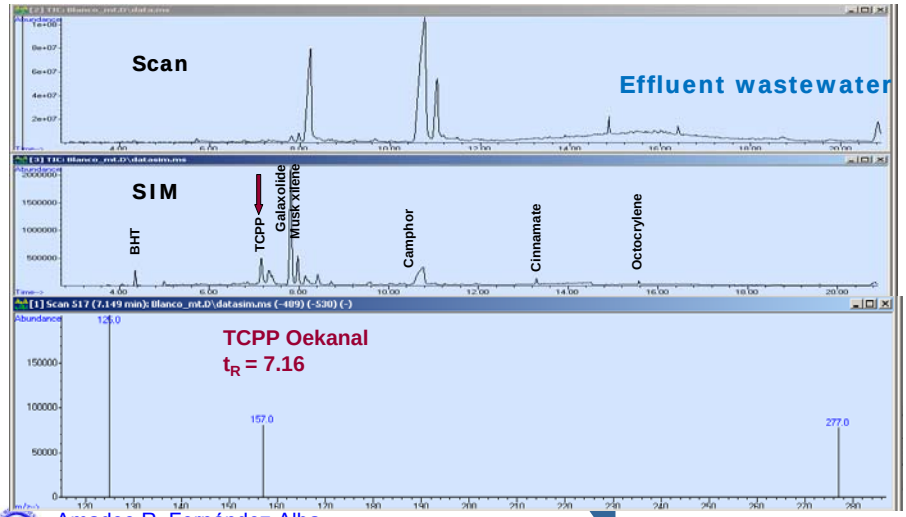
TARGET COMPOUNDS IDENTIFICATION AND CONFIRMATION



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			Amount (ug/L)	AMDIS		NIST	
R.T.	Cas #	Compound Name	Chem station Amount (ng/L)	Match	R.T. Diff sec.	Reverse Match	Hit Num.
2.9006	98533	Spiroxamine metabolite (4-tert-butylcyclohexanone)		77		69	6
3.1250	3228033	Promecarb artifact [5-isopropyl-3-methylphenol]		71	-4.7		
3.1250	3056642	4-tert-Butylphenyl acetate				76	1
3.1290	89838	Thymol		79	8.9	69	21
3.4469	88062	2,4,6-Trichlorophenol		48	6.2	59	60
4.1566	25013165	Butylated hydroxyanisole		85	5.1		
4.1566	121006	3-tert-Butyl-4-hydroxyanisole				80	1
4.3379	33704619	Cashmeran		77	4.0		
4.3379	64451769	2-(4-(But-2-yl)phenyl)propanoic acid				69	1
4.3558	**128370**	**BHT, Butylated hydroxytoluene**		**83**	**-0.7**	**81**	**1**
4.4208	90437	o-Phenylphenol		65	4.2	78	2
4.4891	90153	1-naphthalenol		55	21.1	74	32
4.8899	134623	N,N-Diethyl-m-toluamide		93	2.2	90	1
4.9780	84662	Diethyl phthalate		97	0.4	92	1
5.3543	119619	Benzophenone		94	3.0	90	1
5.4719	126738	Tributyl phosphate		75	2.0	74	1
6.0154	2631370	Promecarb		51	7.1		
6.0154	13743210	3-Buten-2-one, 3-methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-				71	1
6.6321	15323350	Phantolide		50	-9.8	60	15
7.0589	24691803	Fenfuram		49	-29.9		
7.0589	0000	Cis-8-thiabicyclo[4.3.0]nonane S,S-dioxide				71	1
7.0888	53112280	Pyrimethanil		71	3.2		
7.1674	**13674845**	**TCPP Oekanal**		**87**	**0.2**	**89**	**1**
7.3040	106025	Exaltolide [15-Pentadecanolide]		63	-30.0		
7.3040	629801	Hexadecanal				91	1
7.7754	**1506021**	**Tonalide**		**74**	**-24.2**	**84**	**4**
7.8110	**1222055**	**Galaxolide**		**87**	**-1.9**	**91**	**1**
7.9526	**81152**	**Musk xylene**		**68**	**-0.9**	**74**	**2**
7.9760	84695	Diisobutyl phthalate		75	3.4	89	9
8.2727	2164092	Chloranocryl		47	-11.5		
9.2224	84742	Di-n-butylphthalate		98	1.8	92	2
9.6223	2921882	Chlorpyrifos		49	0.7	36	27
10.5181	**38102644**	**EUSOLEX 6300, 4-methylbenzylidene camphor**		**63**	**1.6**		
10.5181	0000	1,7,7-Trimethyl-3-phenethylidenebicyclo[2.2.1]heptan-2-one				59	1
10.9303	470906	Chlorfenvinphos		86	18.4	71	1
10.9353	18708866	Chlorfenvinphos, trans-		84	18.0	74	1
13.2971	**5466773**	**Octinoxanate, 2-Ethylexyl methoxycinnamate**		**81**	**2.5**	**78**	**2**
13.5214	85687	Butyl benzyl phthalate		68	2.7	71	1
13.5249	84753	Di-n-hexyl phthalate		49	9.9	52	74
13.9729	51036	Piperonyl butoxide		69	3.3	84	2
14.0235	78513	Tris(2-butoxyethyl) phosphate		59	6.0	58	1
14.8555	117817	Bis(2-ethylhexyl)phthalate		96	4.4	90	3
15.5770	**6197304**	**Octocrylene**		**81**	**-0.1**		
15.5770	35871159	8-Phenylquinoline-6-carboxylic acid				63	1

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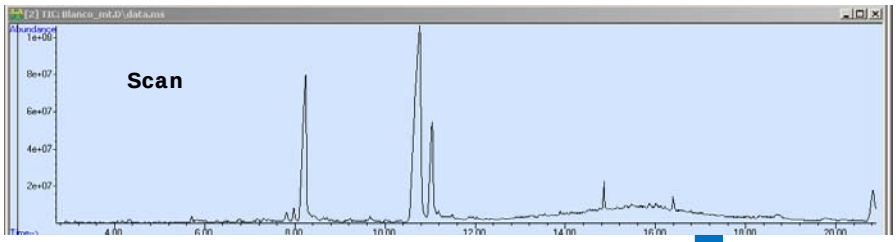
SCREENING
DRS NON TARGET COMPOUNDS

Effluent wastewater



DRS
Report in 90 seconds

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			Amount (ng/L)	AMDIS		NIST	
R.T.	Cas #	Compound Name	Chem station	Match	R.T. Diff sec.	Reverse Match	Hit Num.
3.1232	3228033	Promecarb artifact		72	-5.0		
3.1232	89838	Thymol		73	8.2		
3.1232	98544	Phenol, p-tert-butyl-				86	1
4.0483	**25013165**	**Butylated hydroxyanisole**		**68**	**-1.9**		
4.0483	0000	Undecane				72	1
4.3101	**33704619**	**Cashmeran**		**78**	**0.7**	**77**	**9**
4.3540	**128370**	**BHT, Butylated hydroxytoluene**	**205**	**54**	**-0.9**	**65**	**1**
4.8832	**134623**	**N,N-Diethyl-m-toluamide**		**78**	**1.4**	**79**	**2**
4.9778	84662	Diethyl phthalate		89	0.4	88	1
5.3506	**119619**	**Benzophenone**		**86**	**2.5**	**89**	**1**
5.4591	**126738**	**Tributyl phosphate**		**62**	**0.5**	**71**	**1**
6.0143	2631370	Promecarb		48	7.0		
6.0143	13743210	3-Buten-2-one				77	1
7.1447	**13674845**	**TCPP Oekanal**	**25**	**96**	**-2.6**	**90**	**1**
7.2180	**333415**	**Diazinon**		**69**	**-1.6**	**63**	**1**
7.8065	**1222055**	**Galaxolide**	**44**	**88**	**-2.5**	**92**	**1**
7.9687	84695	Diisobutyl phthalate		82	2.6	90	1
8.1999	**1506021**	**Tonalide**	**21**	**53**	**26.7**		
8.1999	52389158	Epistephamiersine				72	1
9.1963	84742	Di-n-butylphthalate		99	-1.3	94	1
9.5255	**81141**	**Musk Ketone**	**33**	**49**	**-1.6**	**84**	**9**
13.2728	**5466773**	**2-Ethylexyl methoxycinnamate**	**62**	**83**	**-0.4**	**83**	**1**
13.4991	85687	Butyl benzyl phthalate		72	-0.0	73	2
14.8361	117817	Bis(2-ethylhexyl)phthalate		96	2.1	88	3
15.5649	**6197304**	**Octocrylene**	**22**	**69**	**-1.6**		
15.5649	6132872	Benzocarbazole, 5,6-dihydro-3-methoxy-				57	1

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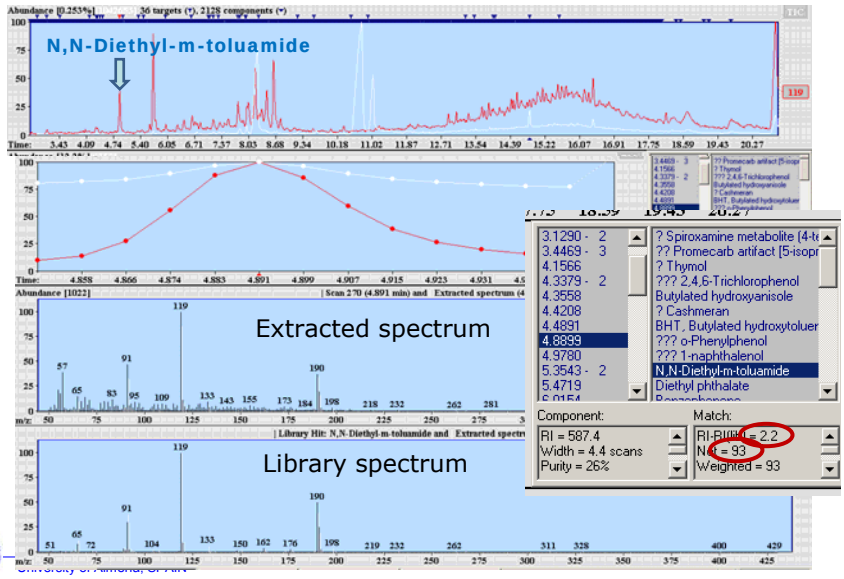
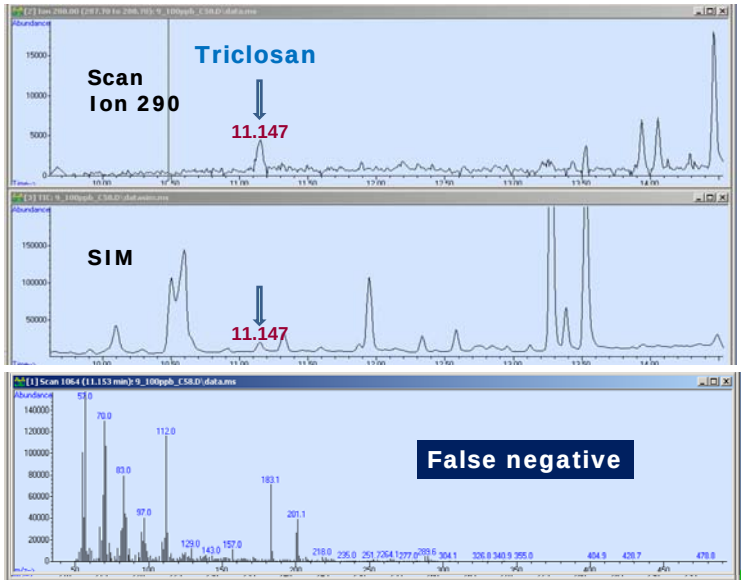
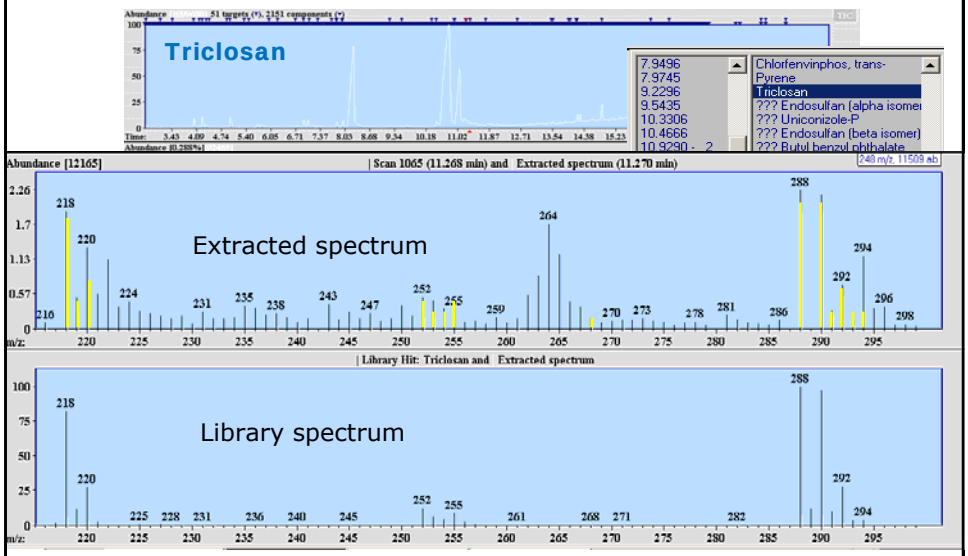
AMDIS Database



DECONVOLUTION



DECONVOLUTION



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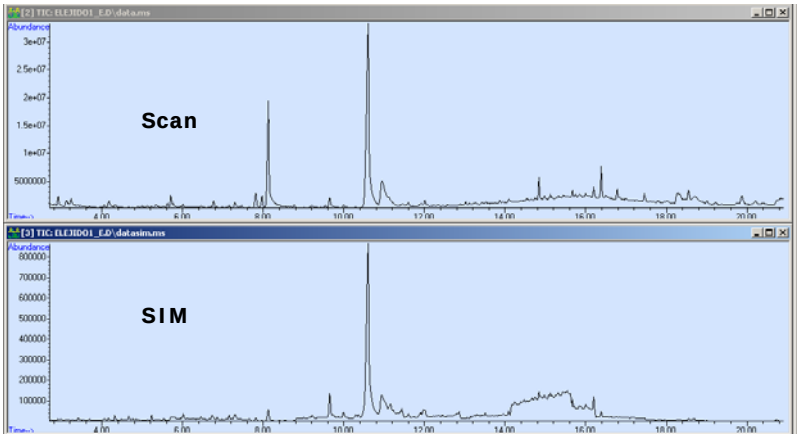
NON TARGET COMPOUNDS

Compounds not included in AMDIS or NIST databases

Retrospective analysis

Effluent wastewater



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NON TARGET COMPOUNDS

Compounds not included in AMDIS or NIST databases

Retrospective analysis