



UNIVERSIDAD DE LAS PALMAS  
DE GRAN CANARIA



# NUEVAS TENDENCIAS EN CONTAMINACIÓN AMBIENTAL: CONTAMINANTES EMERGENTES

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Departamento de Química  
Universidad de Las Palmas de G.C.



UNIVERSIDAD DE LAS PALMAS  
DE GRAN CANARIA



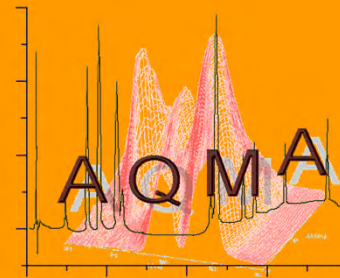
**GRUPO I+D**

**ANÁLISIS QUÍMICO**

**MEDIOAMBIENTAL (AQMA)**

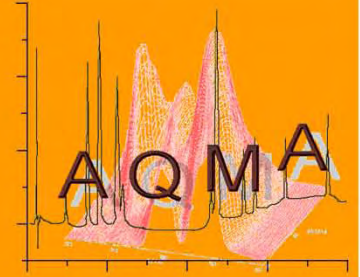


# ¿Dónde nos encontramos?



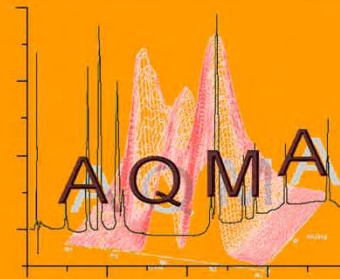
**Edificio de Ciencias Básicas. Departamento de Química.  
Universidad de Las Palmas de Gran Canaria.  
Teléfonos de contacto: 928 452915 / 928 454425  
Fax: 928 452922.**

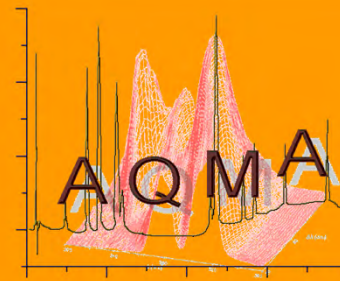
# Nuestro laboratorio



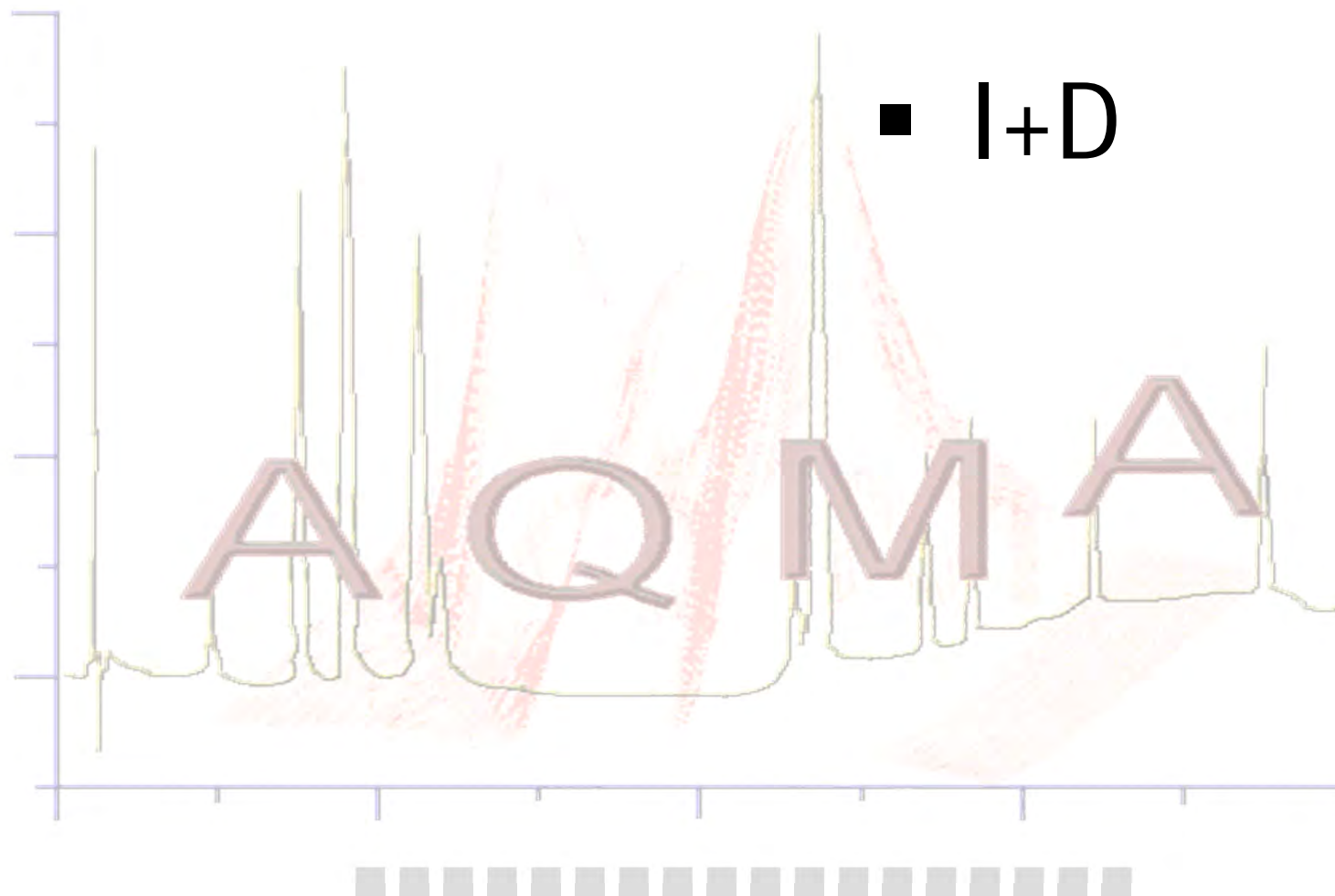


# Nuestros equipos





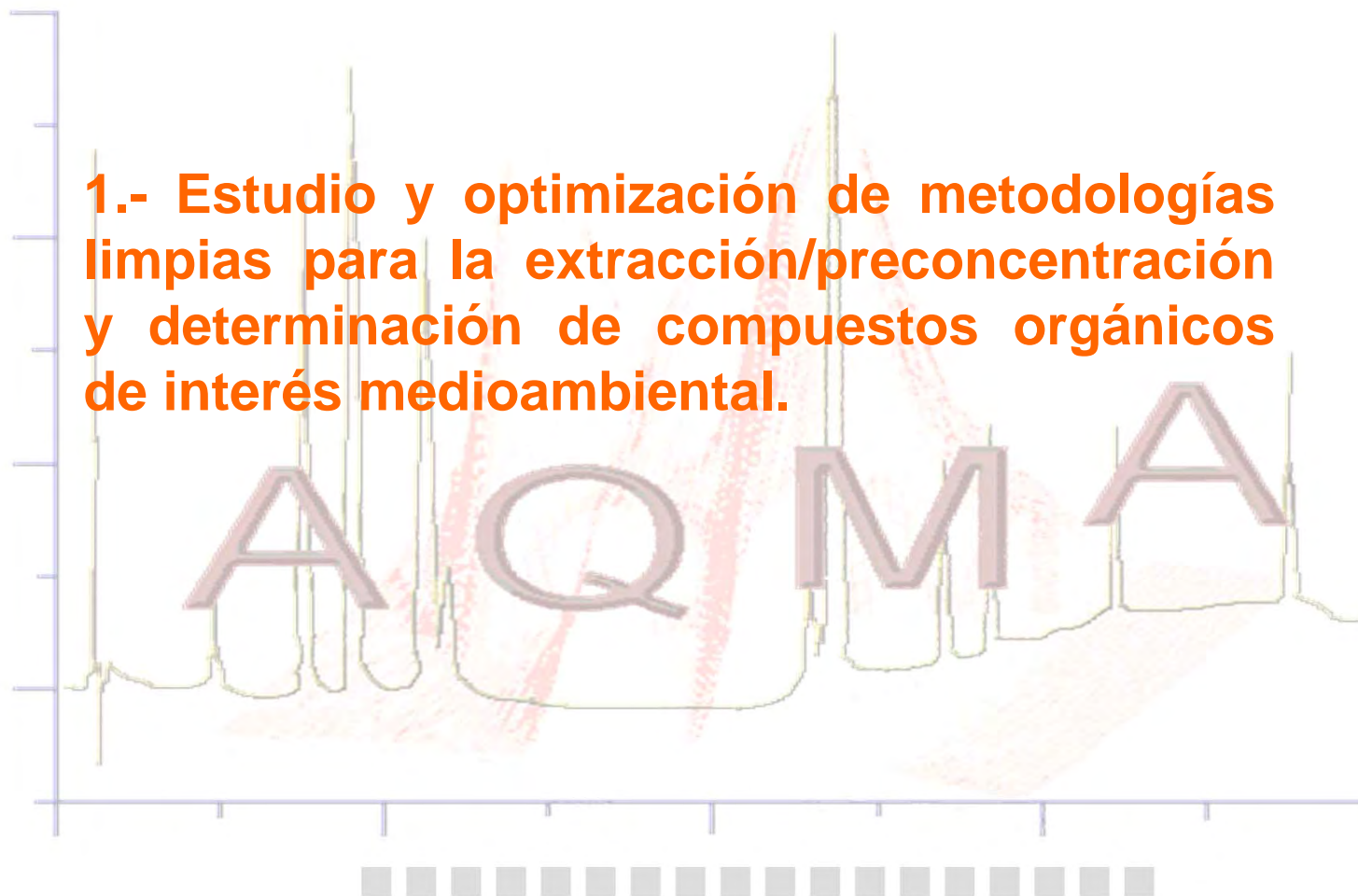
■ I+D



## Nuestras líneas de investigación

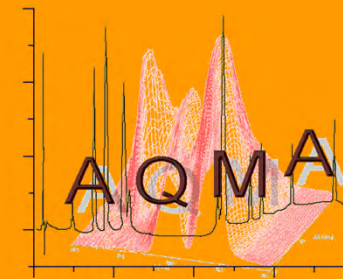


**1.- Estudio y optimización de metodologías limpias para la extracción/preconcentración y determinación de compuestos orgánicos de interés medioambiental.**





## Estudio y optimización de metodologías limpias para la extracción/preconcentración y determinación de compuestos orgánicos de interés medioambiental

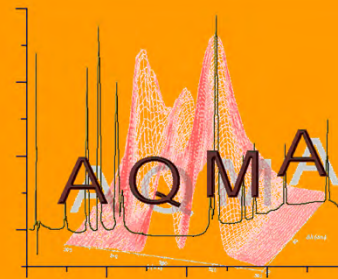


- Necesidad de determinar contaminantes en muestras medioambientales a concentraciones muy bajas (trazas y ultrazas)
- Métodos analíticos con alta sensibilidad y selectividad
- Aplicación a aguas, suelos, sedimentos y muestras biológicas





# Estudio y optimización de metodologías limpias para la extracción/preconcentración y determinación de compuestos orgánicos de interés medioambiental



~~DISOLVENTES ORGANICO~~

↓

SURFACTANTES

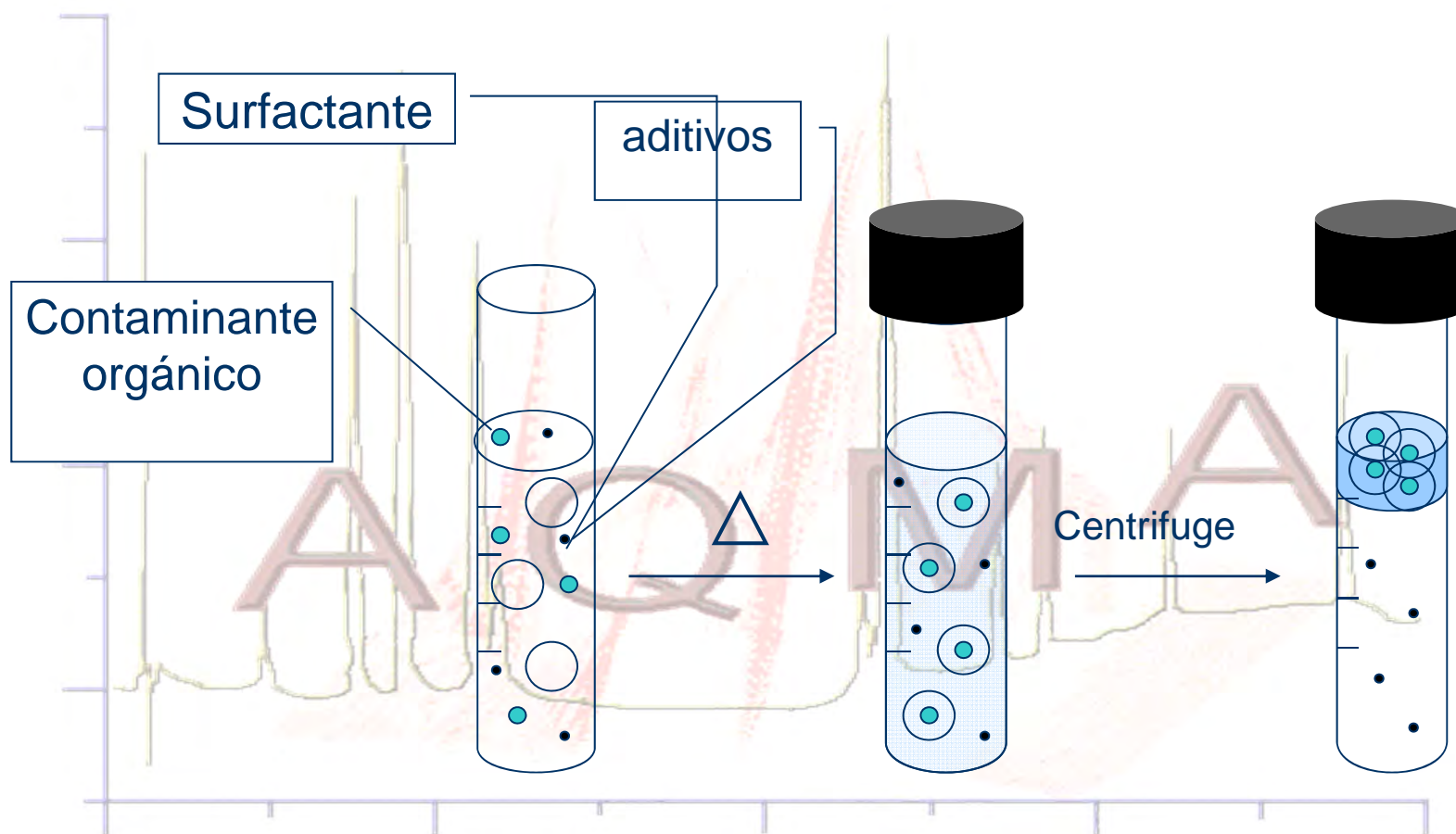
A Q M A

✓ Fácil de usar  
✓ No toxico  
✓ Barato  
✓ Biodegradable

The diagram shows three stages of micelle formation. On the left, surfactant molecules (represented by black wavy lines for non-polar groups and red circles for polar groups) are arranged in a bilayer. In the middle, a solute molecule (represented by a green hexagon) is being incorporated into the micelle. On the right, the solute is fully encapsulated within the micelle. A legend below the diagram identifies the wavy line as 'Micela' and the green hexagon as 'Soluto'.

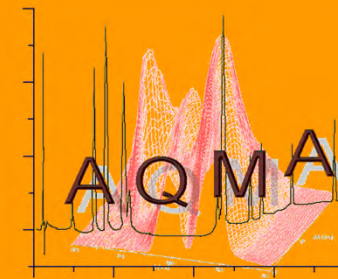
Anphipatic Structure:  
~ Non polar group  
● Polar group

# Estudio y optimización de metodologías limpias para la extracción/preconcentración y determinación de compuestos orgánicos de interés medioambiental

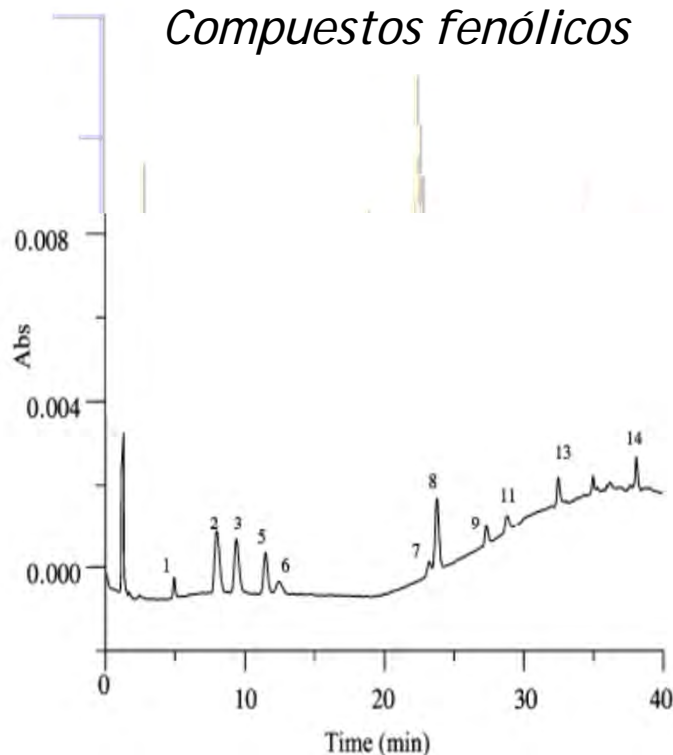


*Extracción en punto de nube (CPE, cloud point extraction)*

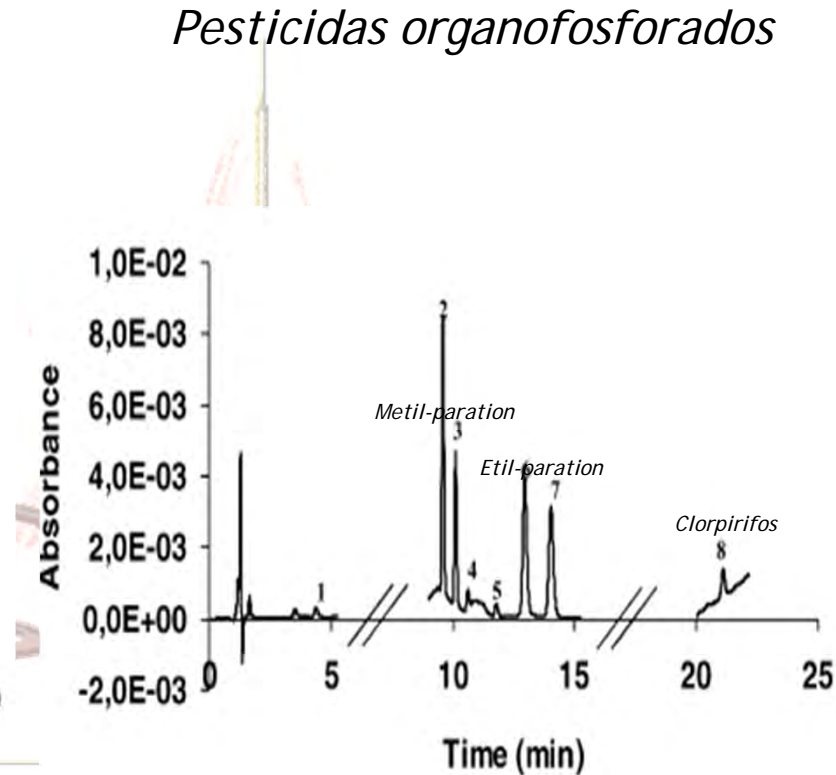
# Estudio y optimización de metodologías limpias para la extracción/preconcentración y determinación de compuestos orgánicos de interés medioambiental



*Compuestos fenólicos*



*Pesticidas organofosforados*

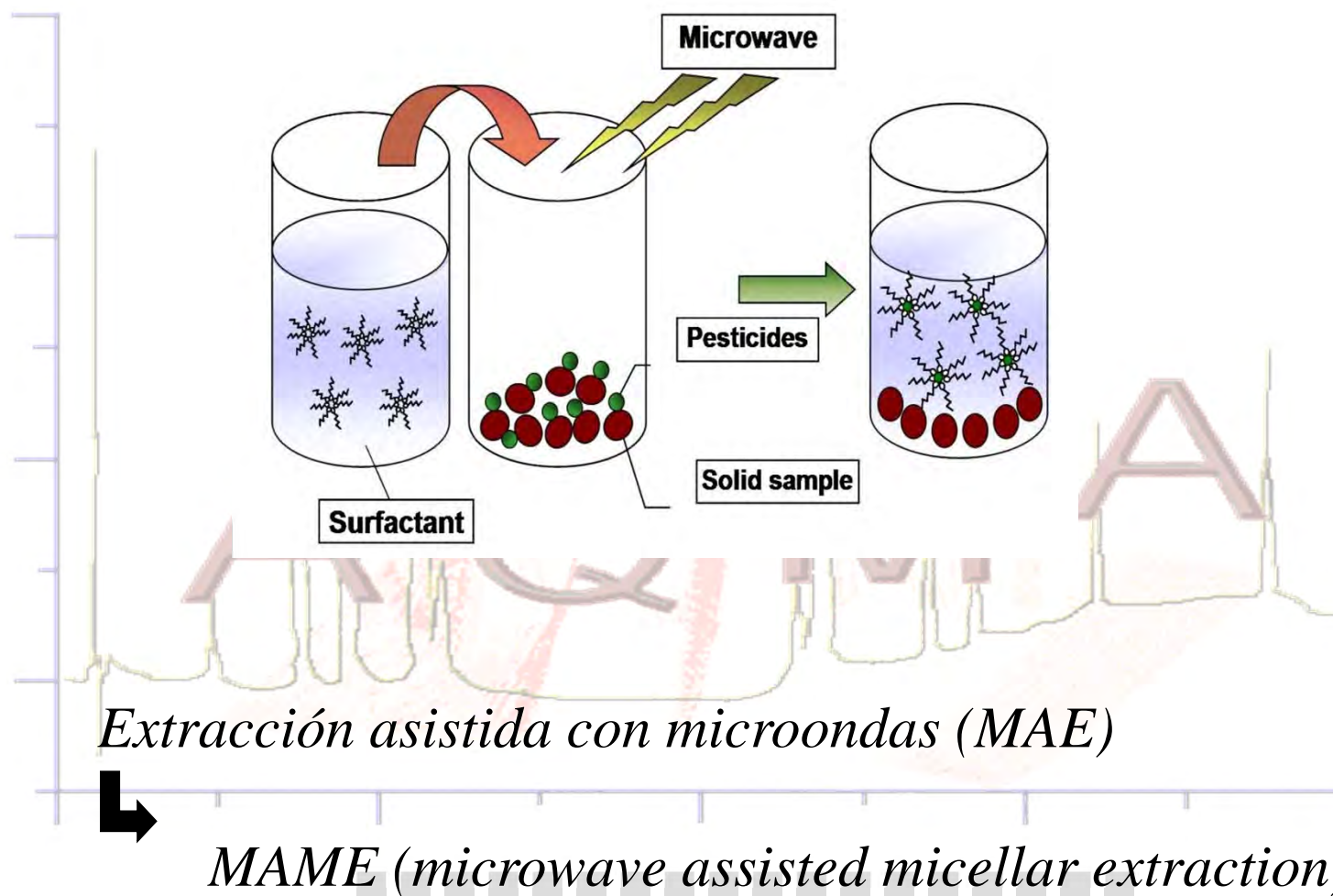
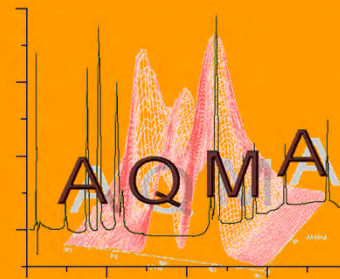


C. Mahugo Santana, Z. Sosa Ferrera, J.J. Santana Rodríguez, *Analyst* (2002), 127, 1031-1037

C. Padrón Sanz, R. Halko, Z. Sosa Ferrera, J.J. Santana Rodríguez, *Analytica Chimica Acta* (2004), 524, 265-270

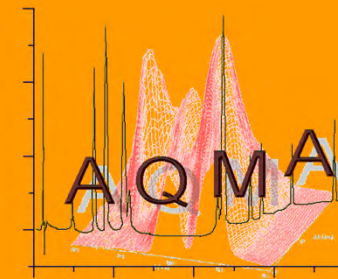


# Estudio y optimización de metodologías limpias para la extracción/preconcentración y determinación de compuestos orgánicos de interés medioambiental

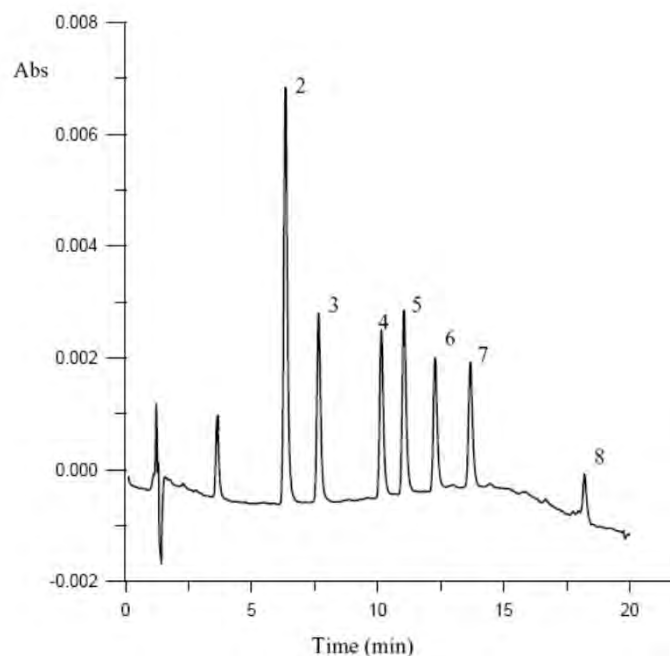




# Estudio y optimización de metodologías limpias para la extracción/preconcentración y determinación de compuestos orgánicos de interés medioambiental

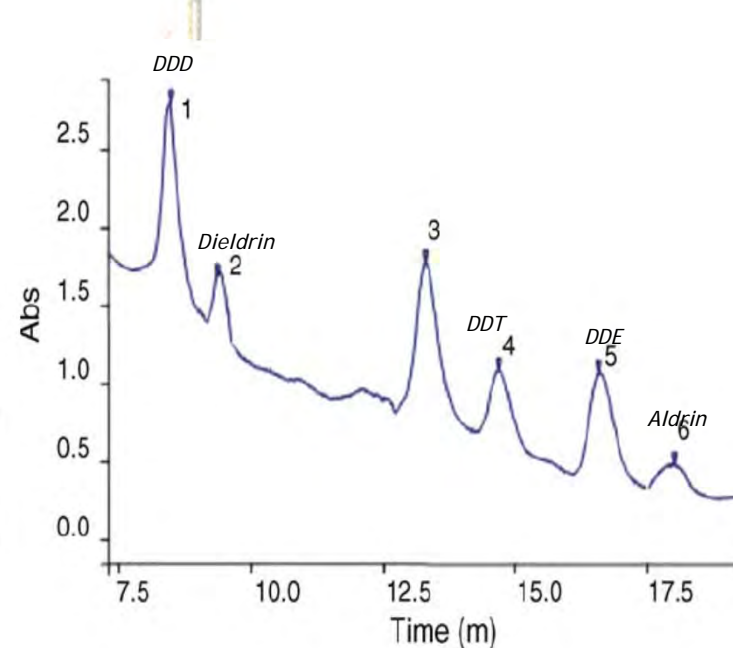


## Compuestos fenólicos



C. Mahugo Santana, Z. Sosa Ferrera, J.J. Santana Rodríguez, *Analytica Chimica Acta* (2004), 524, 133-139

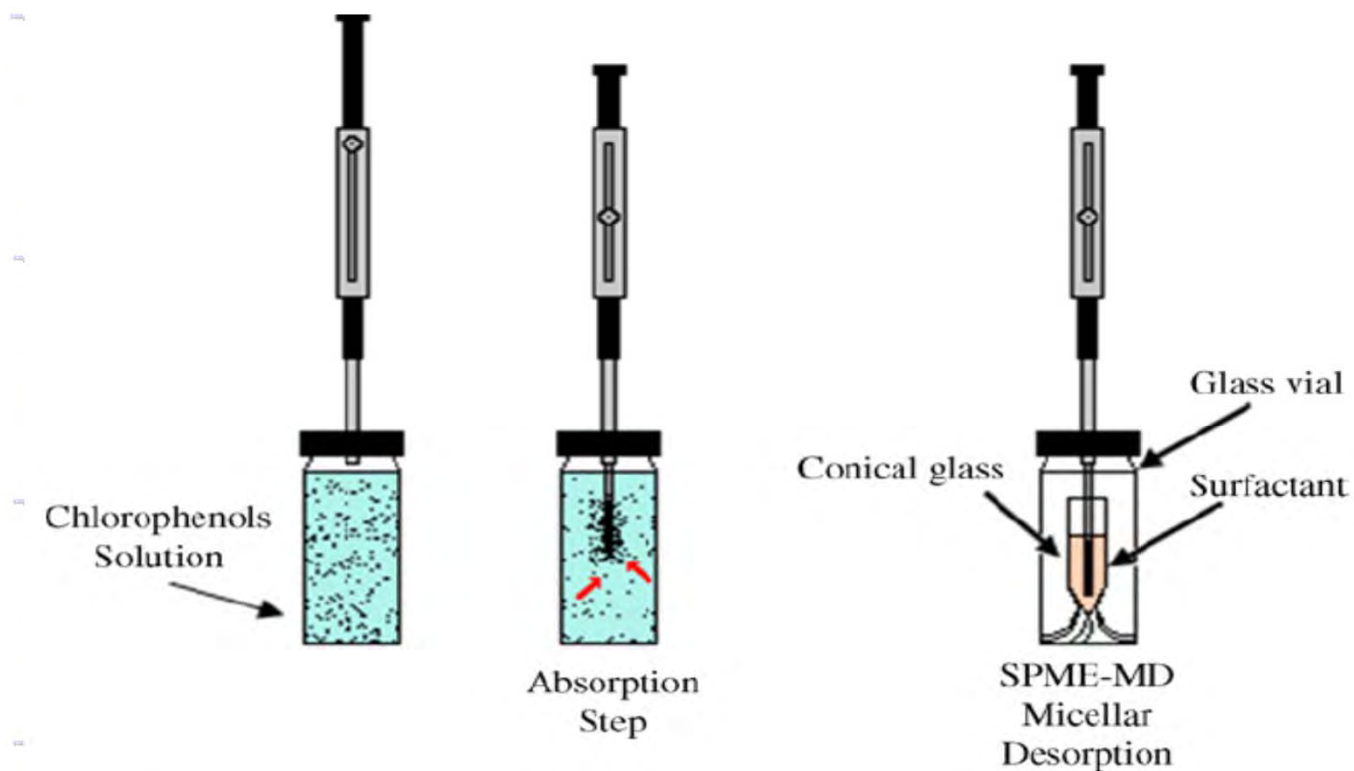
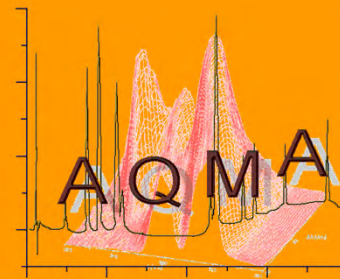
## Pesticidas organoclorados



D. Vega Moreno, Z. Sosa Ferrera, J.J. Santana Rodríguez, *J. Chromatogr. A* (2006), 1104, 11-17



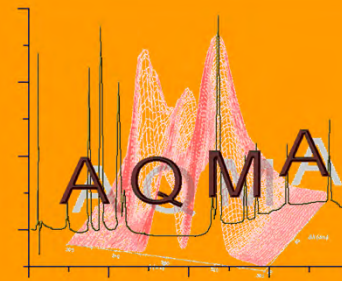
# Estudio y optimización de metodologías limpias para la extracción/preconcentración y determinación de compuestos orgánicos de interés medioambiental



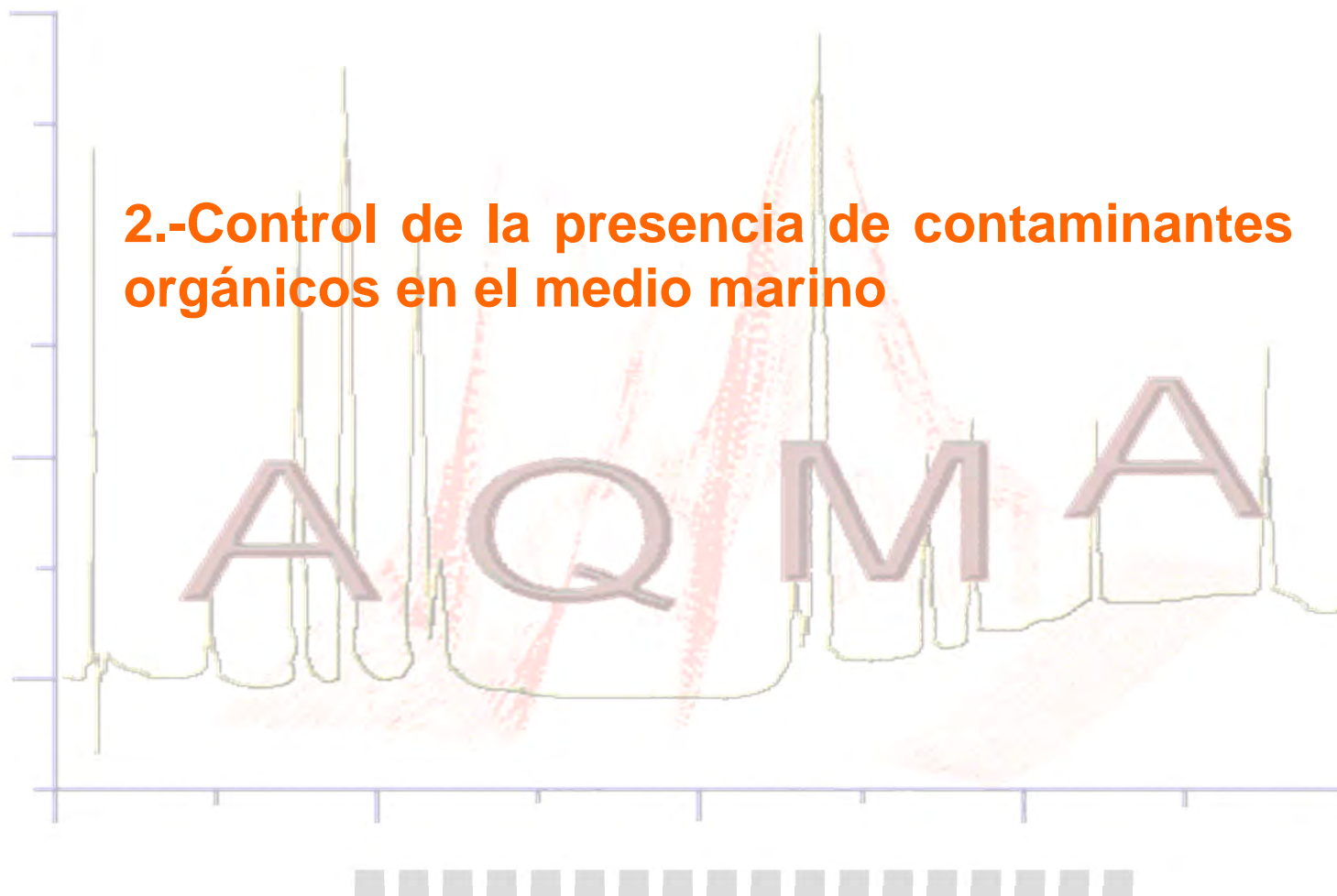
*Microextracción en fase sólida  
(SPME, Solid-phase microextraction)*



## Nuestras líneas de investigación y proyectos

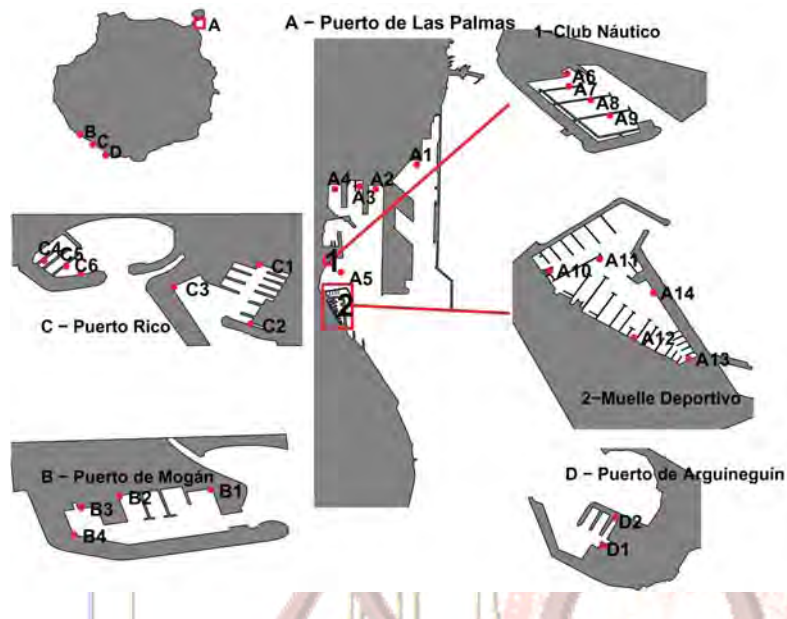
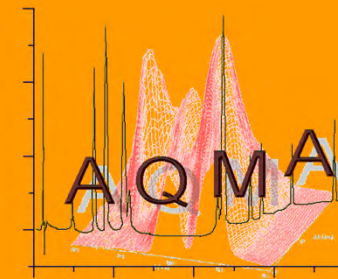


**2.-Control de la presencia de contaminantes orgánicos en el medio marino**

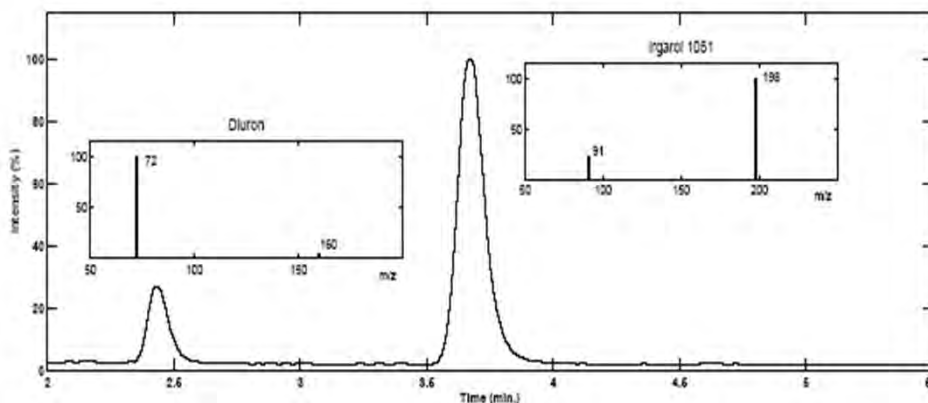




# Control de la presencia de contaminantes orgánicos en el medio marino

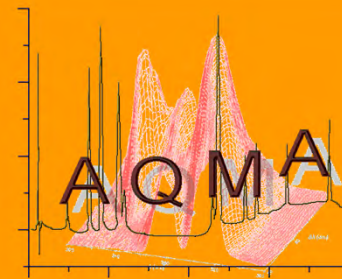


**PUNTOS DE  
MUESTREO EN  
DISTINTOS PUERTOS  
Y MARINAS DE GRAN  
CANARIA**

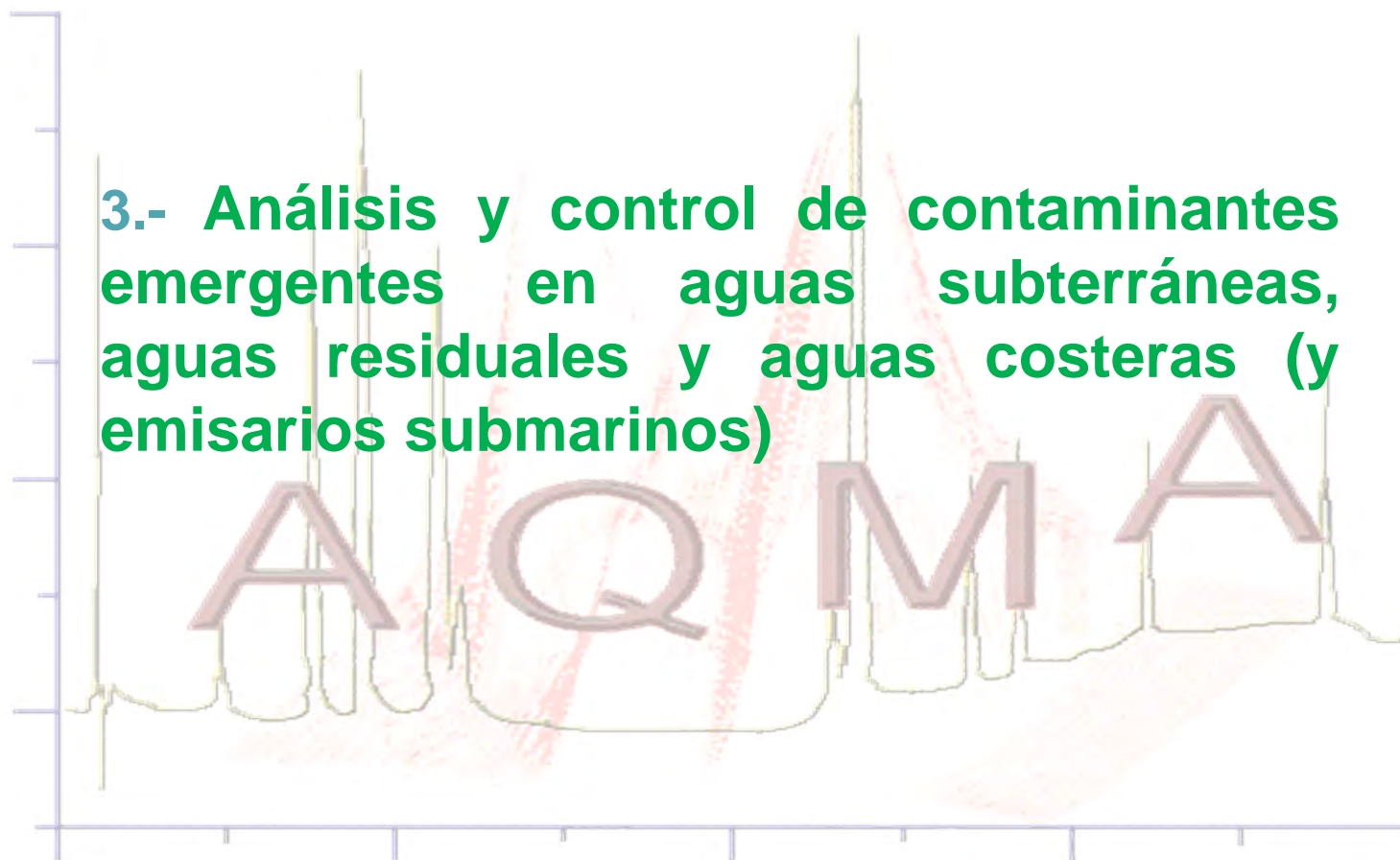


**COMPUESTOS  
ANTIFOULINGS  
ANALIZADOS POR  
TANDEM HPLC-  
ESPECTROMETRÍA DE  
MASAS**

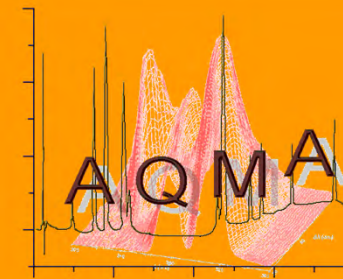
## Nuestras líneas de investigación



**3.- Análisis y control de contaminantes emergentes en aguas subterráneas, aguas residuales y aguas costeras (y emisarios submarinos)**



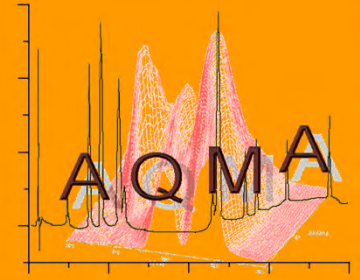
## Nuestras líneas de investigación



**4.-Desarrollo y aplicación de Nuevos Métodos Computacionales (Redes Neuronales Artificiales) en el tratamiento de datos en Análisis Medioambiental**



## Desarrollo y aplicación de Nuevos Métodos Computacionales (Redes Neuronales Artificiales) en el tratamiento de datos en Análisis Medioambiental



Detección y determinación de contaminantes  
(estructuras similares) en matrices complejas  
(medioambientales)



*(Colaboración con el Grupo COMCIENCIA  
de la ULPGC)*





# Análisis y control de contaminantes emergentes en aguas subterráneas, aguas residuales, aguas costeras y emisarios submarinos



Qué son los contaminantes emergentes?



## Análisis y control de contaminantes emergentes en aguas subterráneas, aguas residuales, aguas costeras y emisarios submarinos



Recently discovered

*Organic compounds degradation*

*Acumulation of contaminants in the natural medium*

- They are suspected of causing adverse effects in humans and wildlife
- In the past research priorities have focused on priority pollutants, such as POPs, pesticides, toxic metals, radionuclides
- Only recently, the attention of the scientific community has started to shift to emerging contaminants

# Análisis y control de contaminantes emergentes en aguas subterráneas, aguas residuales, aguas costeras y emisarios submarinos



## Sources



***Wastewaters treatment plants effluents (WWTPs)***

***Terrestrial run-offs and atmospherical deposition***

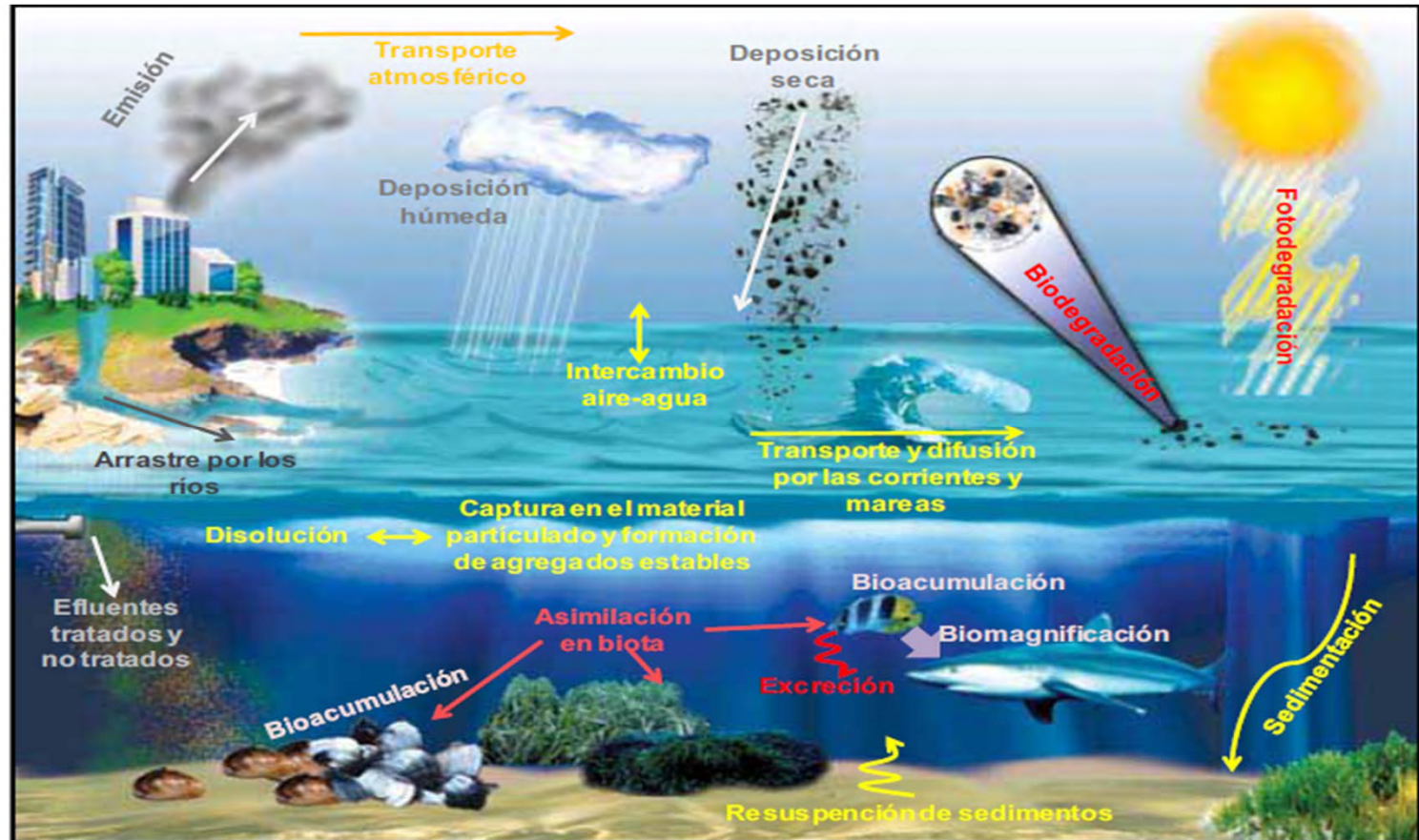
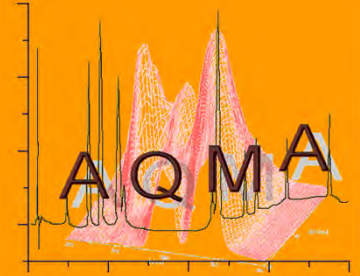
- Continuous introduction in the environment*
- Few studies about risk assessment and ecotoxicological effects*



difficult prediction of health effects on humans, terrestrial and aquatic organisms and ecosystems.

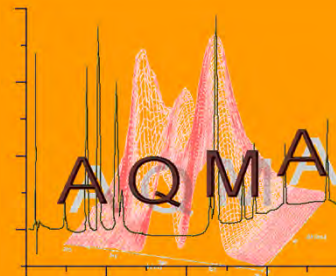


# Análisis y control de contaminantes emergentes en aguas subterráneas, aguas residuales, aguas costeras y emisarios submarinos





# Análisis y control de contaminantes emergentes en aguas subterráneas, aguas residuales, aguas costeras y emisarios submarinos



	Examples
<b>Pharmaceuticals</b>	
Veterinary and human antibiotics	Trimethoprim, erythromycine, lincomycin, sulfamethaxozole
Analgesics, anti-inflammatory drugs	Codein, ibuprofene, acetaminophen, acetylsalicylic acid, diclofenac, fenoprofen
Psychiatric drugs	Diazepam
Lipid regulators	Bezafibrate, clofibrac acid, fenofibrac acid
$\beta$ -blockers	Metoprolol, propranolol, timolol
X-ray contrasts	Iopromide, iopamidol, diatrizoate
<b><i>Steroids and hormones</i></b>	Estradiol, estrone, estriol, diethylstilbestrol
<b>Personal care products</b>	
Fragrances	Nitro, polycyclic and macrocyclic musks,
Sun-screen agents	Benzophenone, methylbenzylidene camphor
Insect repellents	N,N-diethyltoluamide
Antiseptics	Triclosan, Chlorophene
<b><i>Surfactants and surfactant metabolites</i></b>	Alkylphenol ethoxylates, 4-nonylphenol, 4-octylphenol, alkylphenol carboxylates
<b>Flame retardants</b>	Polybrominated diphenyl ethers (PBDEs), Tetrabromo bisphenol A, C <sub>10</sub> -C <sub>13</sub> chloroalkanes Tris (2-chloroethyl)phosphate
<b>Industrial additives and agents</b>	Chelating agents (EDTA), aromatic sulfonates,
<b>Gasoline additives</b>	Dialkyl ethers, Methyl- <i>t</i> -butyl ether (MTBE)

## Análisis y control de contaminantes emergentes en aguas subterráneas, aguas residuales, aguas costeras y emisarios submarinos



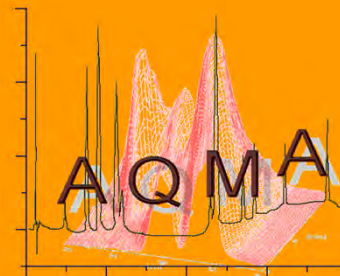
- *Legislated in 2455/2001/EC*
  - *Flame retardants*
  - *Ethoxylated alkylphenol surfactants*
  - *Chlorinated paraffins*
- *Not legislated.*
  - *Perfluorinated surfactants*
  - *Pharmaceutical compounds*
  - *Personal Care Products (PCPs)*
  - *Algal toxins*

# Análisis y control de contaminantes emergentes en aguas subterráneas, aguas residuales, aguas costeras y emisarios submarinos



Qué niveles de concentración?

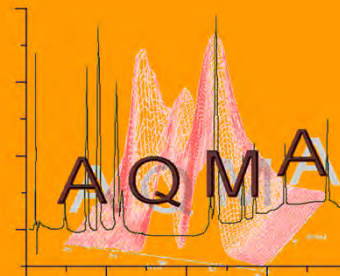




## - LC-MS/MS

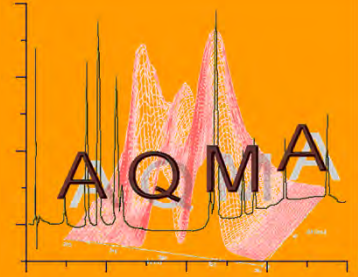






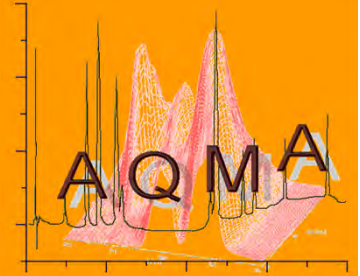
## - UHPLC-MS/MS





- **Objectives:**
  - *To develop a strong method to analyze different families of emerging pollutants, using LC – MS/MS and UPLC – MS/MS systems.*
  - *Monitoring of two Wastewater Treatment Plants in the Gran Canaria island which are based in different technologies.*

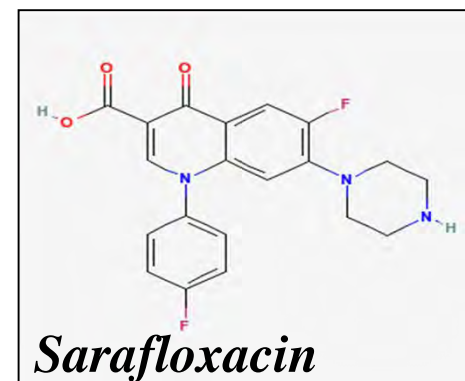
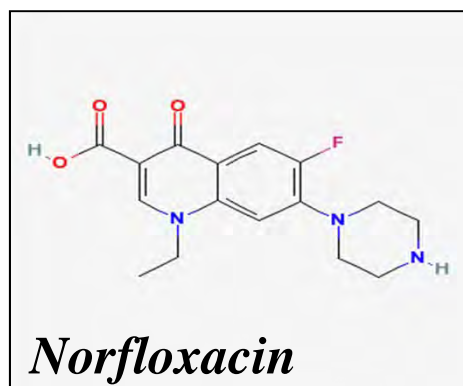
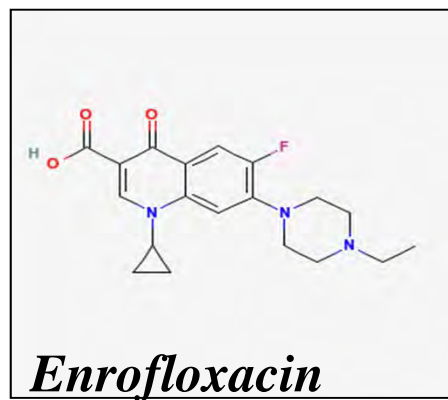
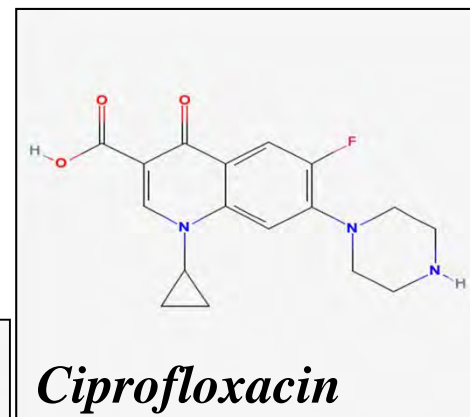
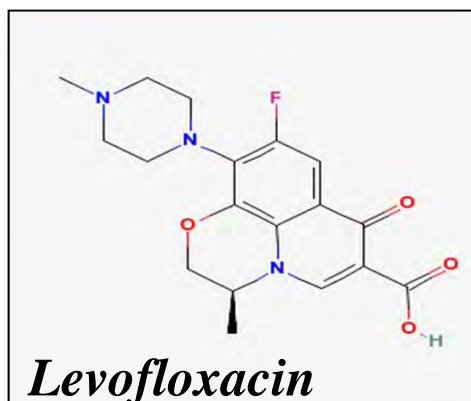




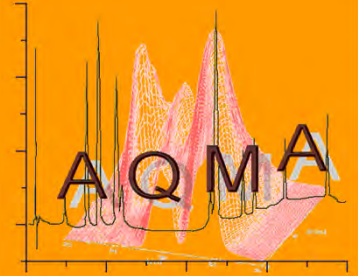
## ***Antibiotics: fluoroquinolones***

- *Synthetic generation of quinolone family with a fluoro group attached the central ring system, typically at the 6-position.*
- *Used in medicine and veterinary as antibiotics for treatment of many kind of infections:*
  - *Urinary tract*
  - *Respiratory*
  - *Typhoid fever*





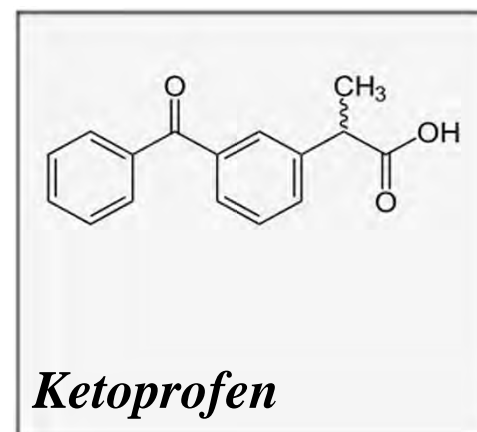
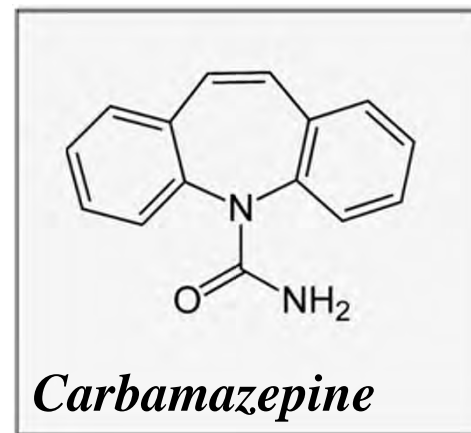
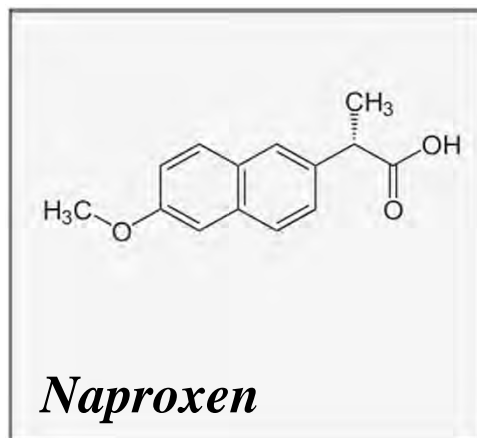
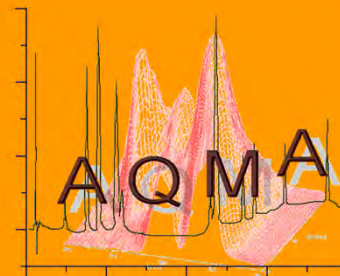


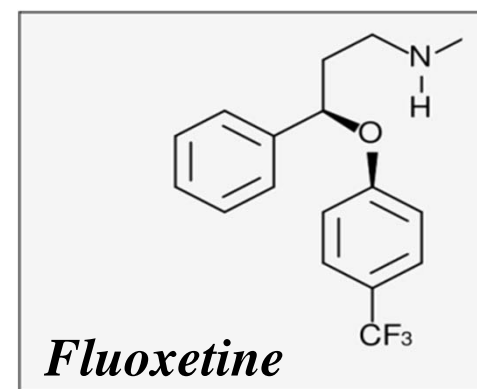
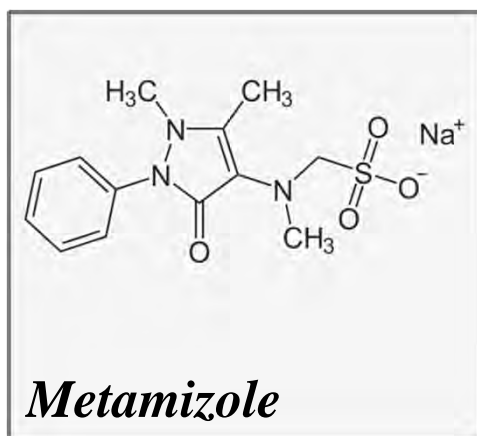
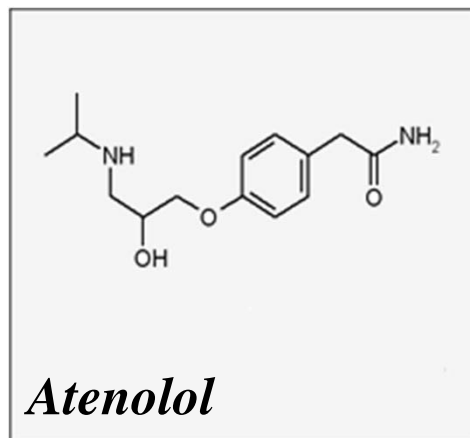
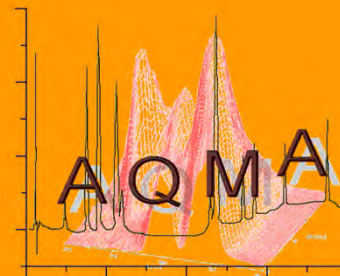


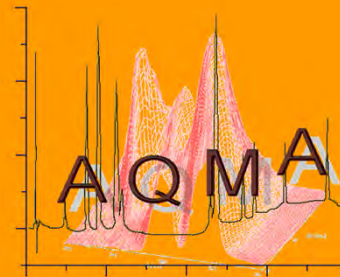
## ***Other pharmaceutical compounds.***

*Commonly used and belong to a wide range of treatments:*

- *Anti-inflammatory: **Ketoprofen, Naproxen.***
- *Analgesic: **Metamizole***
- *Regulators of cholesterol: **Bezafibrate***
- *$\beta_1$  receptor antagonist : **Atenolol***
- *Antidepressants: **Fluoxetine***
- *Stimulants: **Paraxanthine***
- *Anticonvulsant: **Carbamazepine***

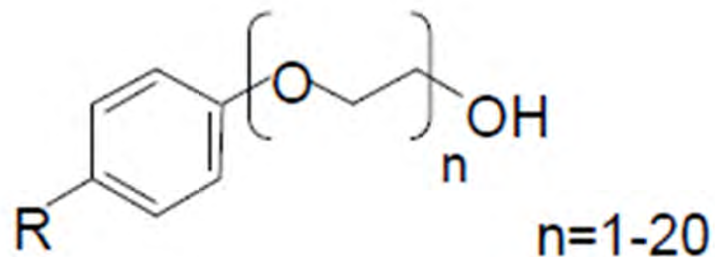






## ***Alkylphenols Ethoxylated***

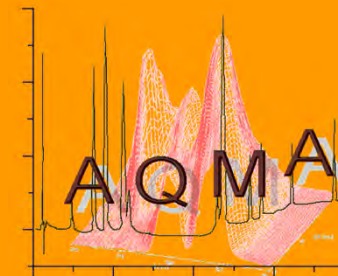
- *Octylphenol and Octylphenol poliethoxilated*
- *Nonylphenol and Nonylphenol poliethoxylated*



- *Used in **detergents**, as fuel additives, in lubricants, etc.*

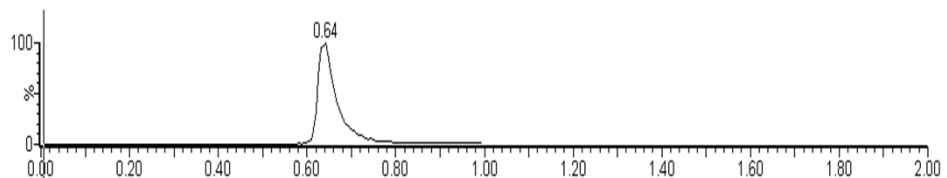
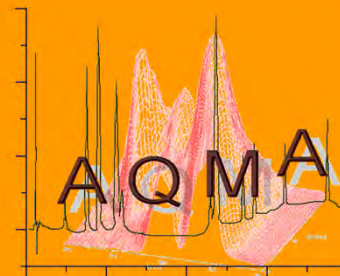




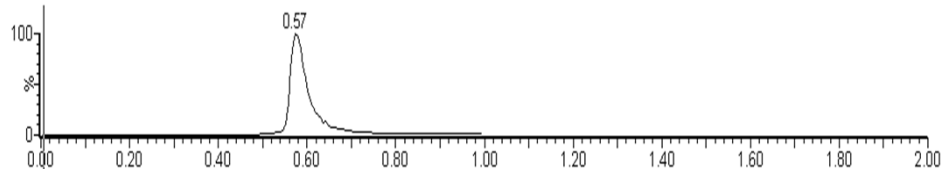


	WWTP 1	WWTP 2
Location	North of Gran Canaria	
Population	5,000	7,000
Inflow (m <sup>3</sup> /day)	500	700
Treatment process	Activated sludge	Membrane Bioreactor (MBR)
Sampling period	January, March, May and July of 2011	

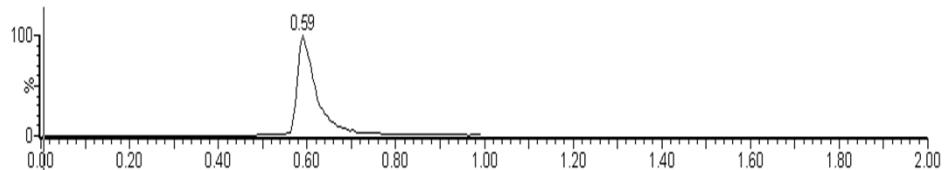




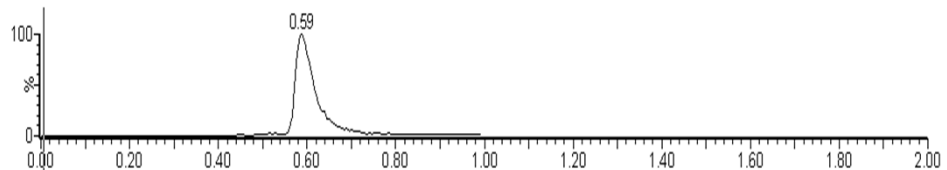
*Levofloxacin*



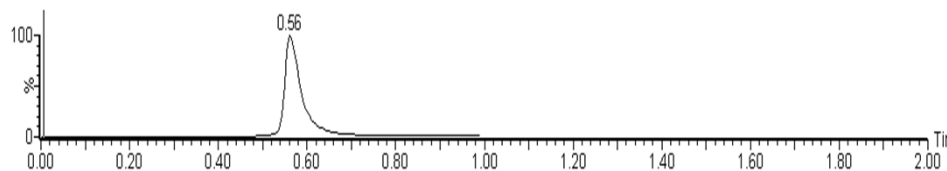
*Norfloxacin*



*Ciprofloxacin*



*Enrofloxacin*

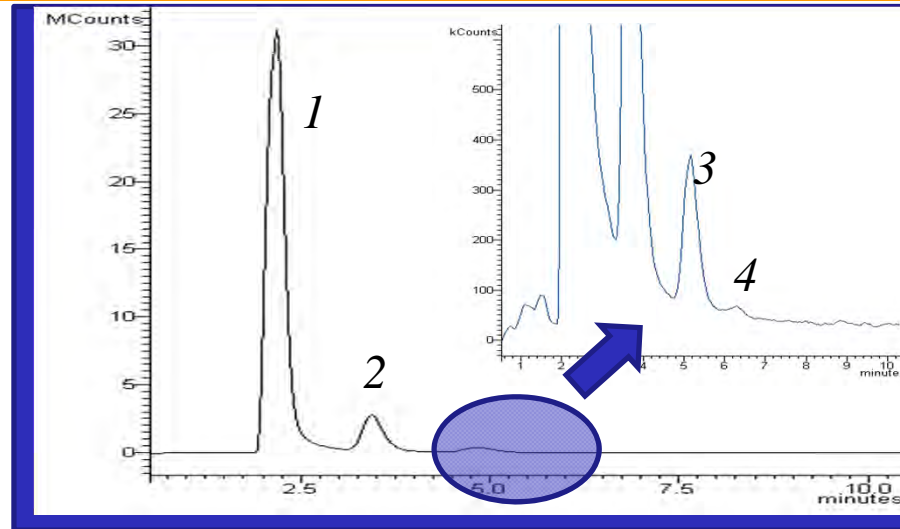
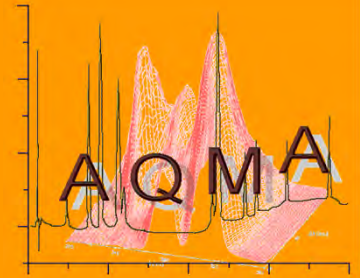


*Sarafloxacin*

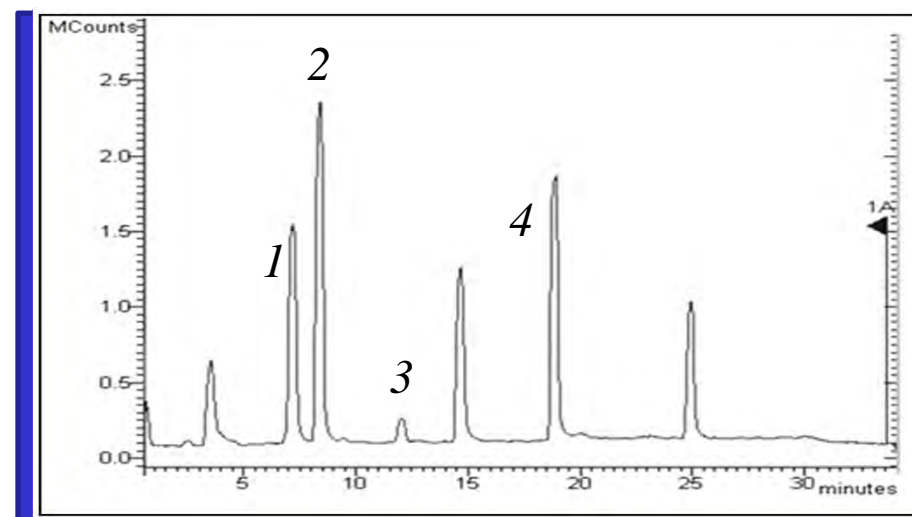




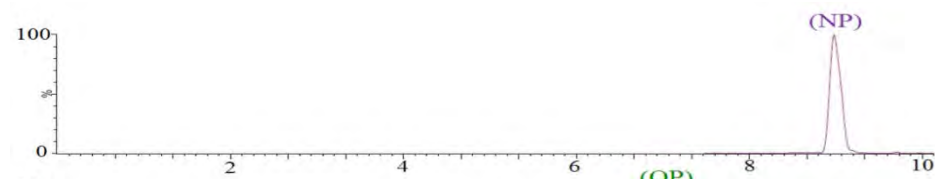
UNIVERSIDAD DE LAS PALMAS  
DE GRAN CANARIA



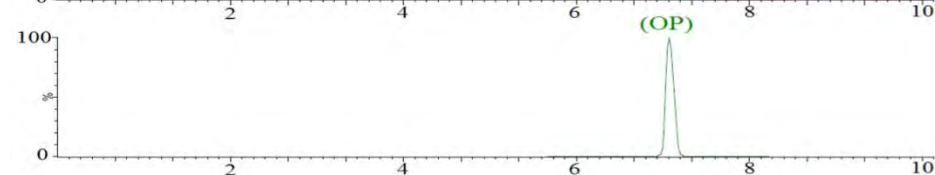
*1: carbamazepine  
2: ketoprofen  
3: naproxen  
4: bezafibrate*



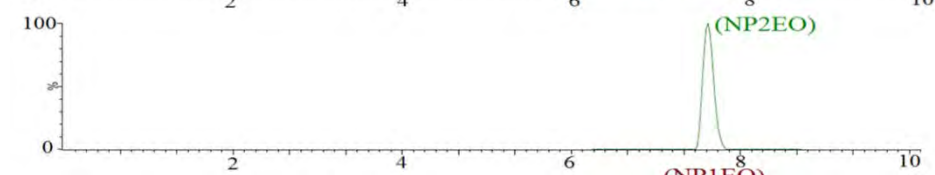
*1: atenolol  
2: metamizole  
3: paraxanthine  
4: fluoxetine*



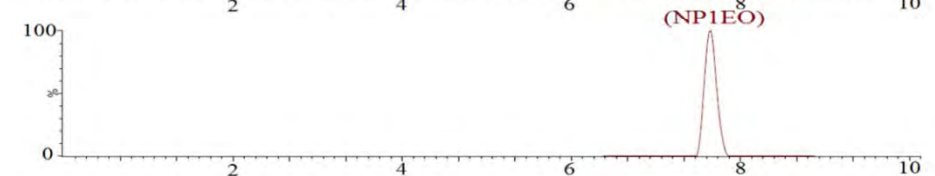
*NP*



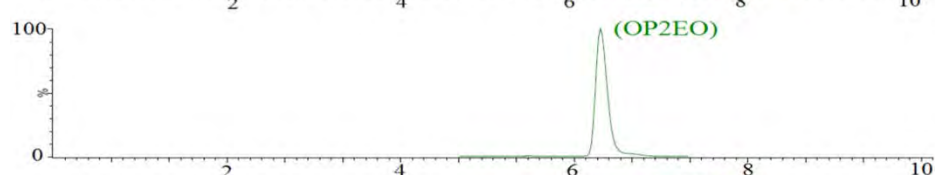
*OP*



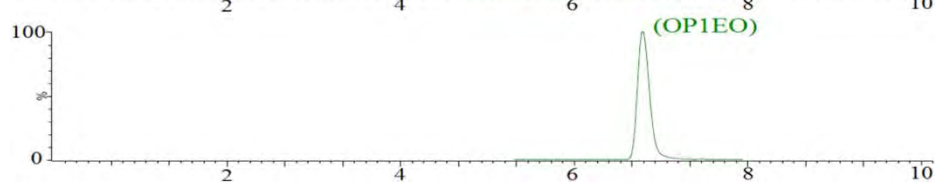
*NP2EO*



*NP1EO*

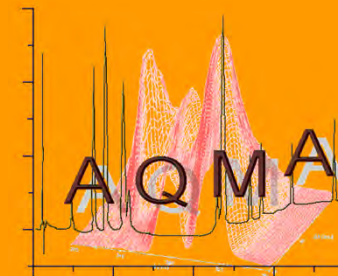


*OP2EO*



*OP1EO*

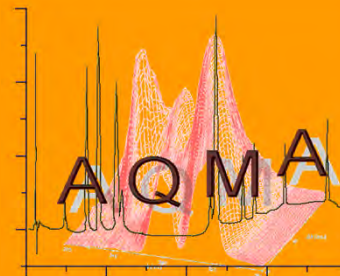




	Range of concentrations (ng/L) (Min – Max)	
	WWTP 1	WWTP 2
Levofloxacin	<b>(2,9 – 4,4)</b>	<b>(5,8 – 14,1)</b>
Norfloxacin	nd	nd
Ciprofloxacin	<b>(11,1 – 20,3)</b>	<b>(16,0)</b>
Enrofloxacin	nd	nd
Sarafloxacin	nd	Nd

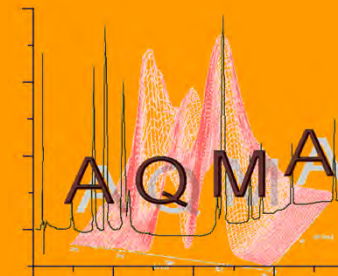


## Results: pharmaceuticals (A)



	Range of concentrations (ng/L) (Min – Max)	
	WWTP 1	WWTP 2
Naproxen	(62,1 – 252,4)	(52,9)
Carbamazepine	(20,9 – 505,0)	(77,5 – 974,5)
Ketoprofen	(218,5 – 1360,5)	(61,1 – 304,9)
Bezafibrate	<b>(9489,9 – 18850,7)</b>	<b>(18680,3)</b>

# Results: pharmaceuticals (B)



	Range of concentrations (ng/L) (Min – Max)	
	WWTP 1	WWTP 2
	Atenolol	(312,6 – 647,5)
Metamizole	<b>(414,7 – 3446,8)</b>	<b>(1189,3 – 8250,1)</b>
Paraxanthine	<b>(8362,0 – 12309,18)</b>	nd
Fluoxetine	nd	(23,67)

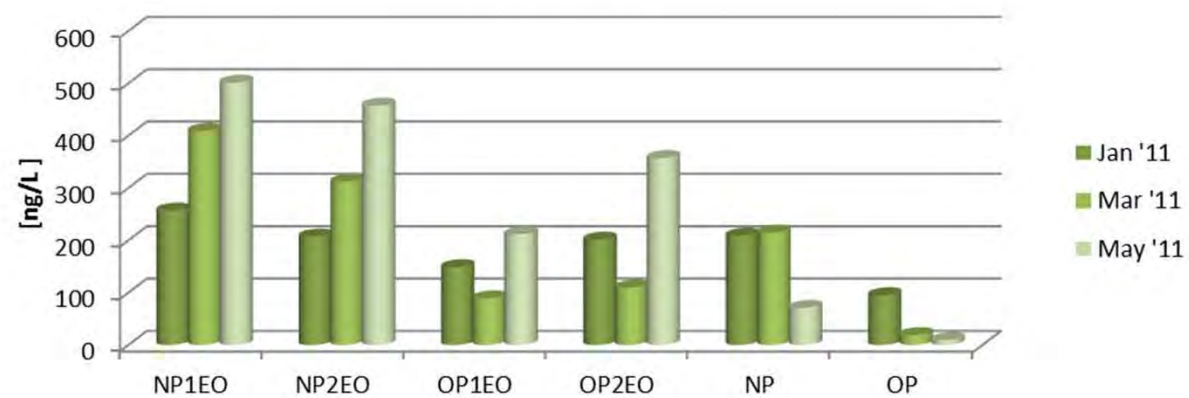
# Results: alkylphenols



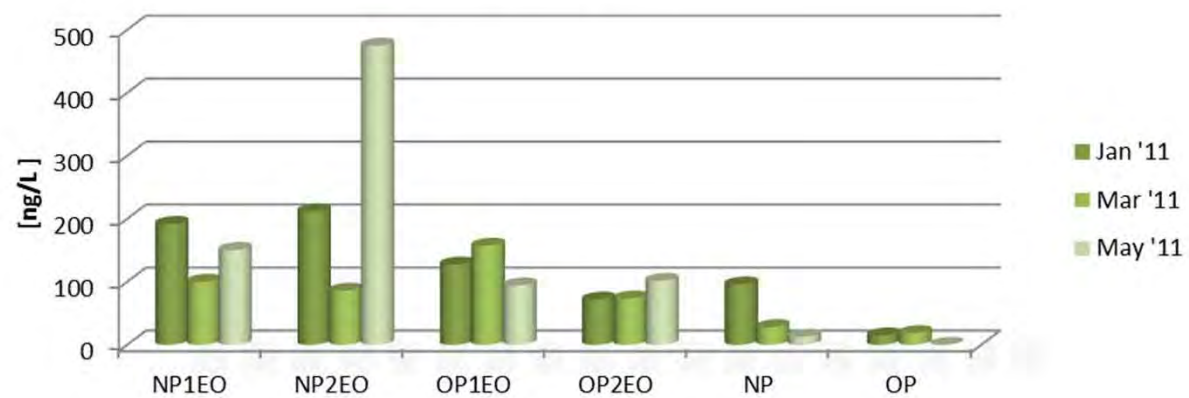
	Range of concentrations (ng/L) (Min – Max)	
	WWTP 1	WWTP 2
NP1EO	(257,0 – 501,4)	(100,1 – 191,9)
NP2EO	(207,3 – 457,5)	(85,9 – 474,8)
OP1EO	(89,3 – 211,7)	(94,2 – 157,3)
OP2EO	(109,9 – 357,3)	(71,8 – 101,6)
NP	(71,0 – 215,0)	(12,7 – 95,8)
OP	(9,7 – 95,2)	(14,9 – 18,5)



### WWTP 1



### WWTP 2

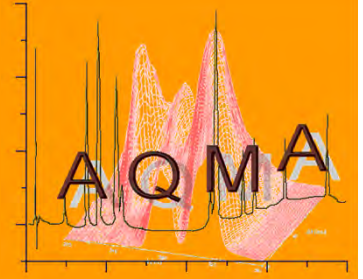


## Conclusions



- We identified and determined all the Pharmaceutical compounds and Alkylphenols studied, but only **two Fluoroquinolones** (Levofloxacin and Ciprofloxacin).
- Highest concentrations for **Bezafibrate** (19  $\mu\text{L}$ , regulator of cholesterol), **Metamizole** (analgesic) and **Parazanthine** (12  $\mu\text{L}$ ) (stimulant)
- **WWTP 2** (Membrane biorreactor) presents lower concentrations of the compounds detected (except Fluoroquinolones) than **WWTP 1** (Activated sludge)





Y en el medio marino ??



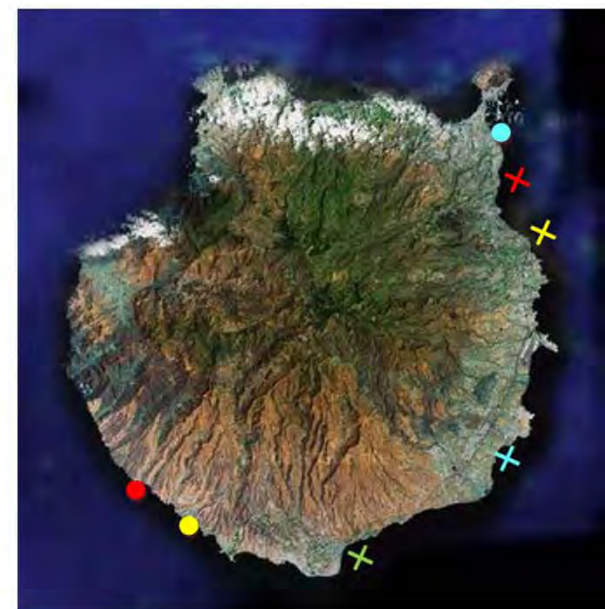
PROYECTO **CARMAC** (MEJORA DE LA CALIDAD DE LAS AGUAS RECREATIVAS Y COSTERAS DE LA MACARONESIA) (PCT-MAC)

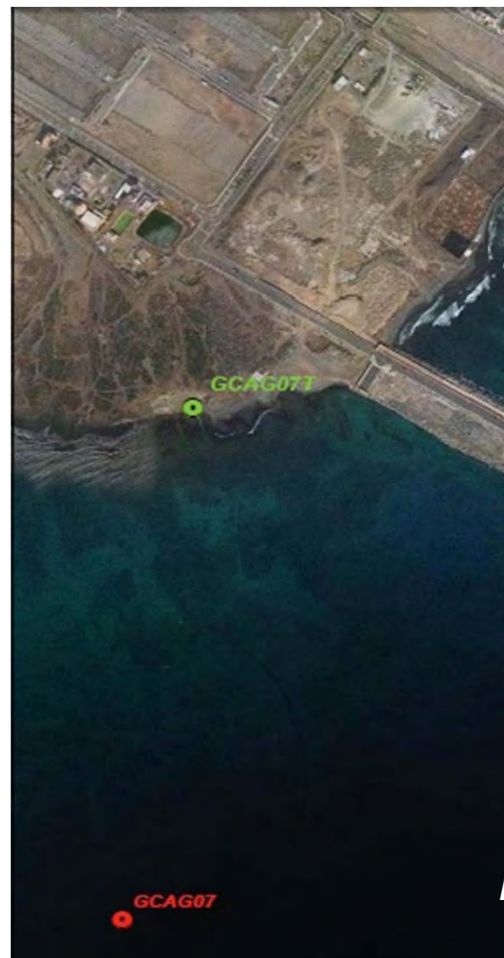


COMPOUNDS		
Antifoulings	Alquilfenoles	Fármacos
Diuron	Nonylphenol	Ketoprofen
Irgarol	Octylphenol	Acetaminofen
TBT	APEOs (1-12)	Diclofenac
		Carbamazepine
		Atenolol
		Norfloxacin
		Ciprofloxacin



ÁREA	MUNICIPIO	CODIGO
 Muelle Deportivo	Las Palmas de G.C.	MD00-11
 Puerto Escala Puerto Rico	Mogán	PR00-11
 Puerto deportivo de Mogán	Mogán	MG00-11
 EDAR Jinámar	Telde	JI00-11
 EDAR Sureste	Agüimes	AR00-11
 EDAR Las Burras	San Bartolomé de Tirajana	BU00-11
 EDAR Barranco Seco	Las Palmas de G.C.	BS00-11







*EDAR Jinámar*



*EDAR Las Burras*

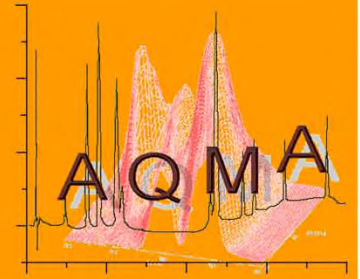


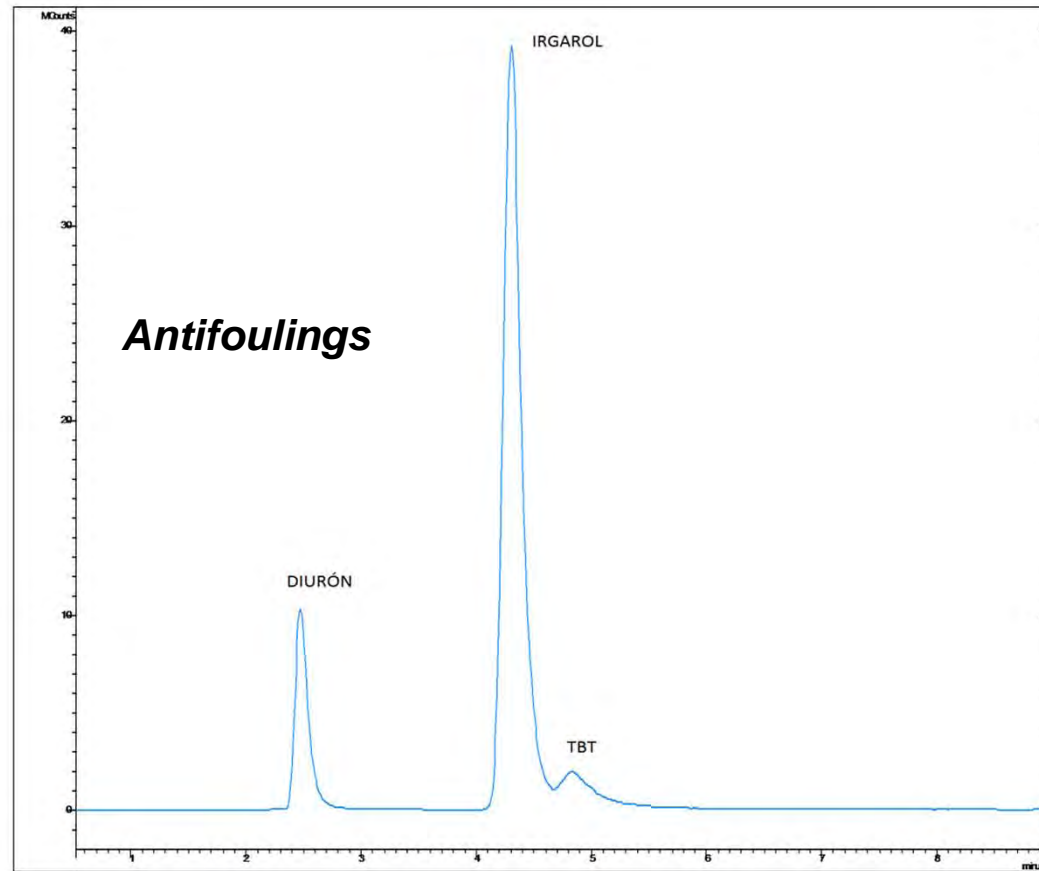
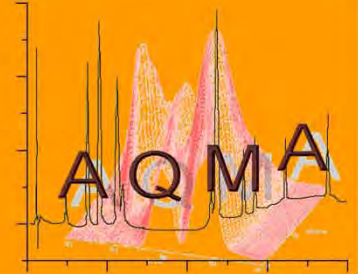




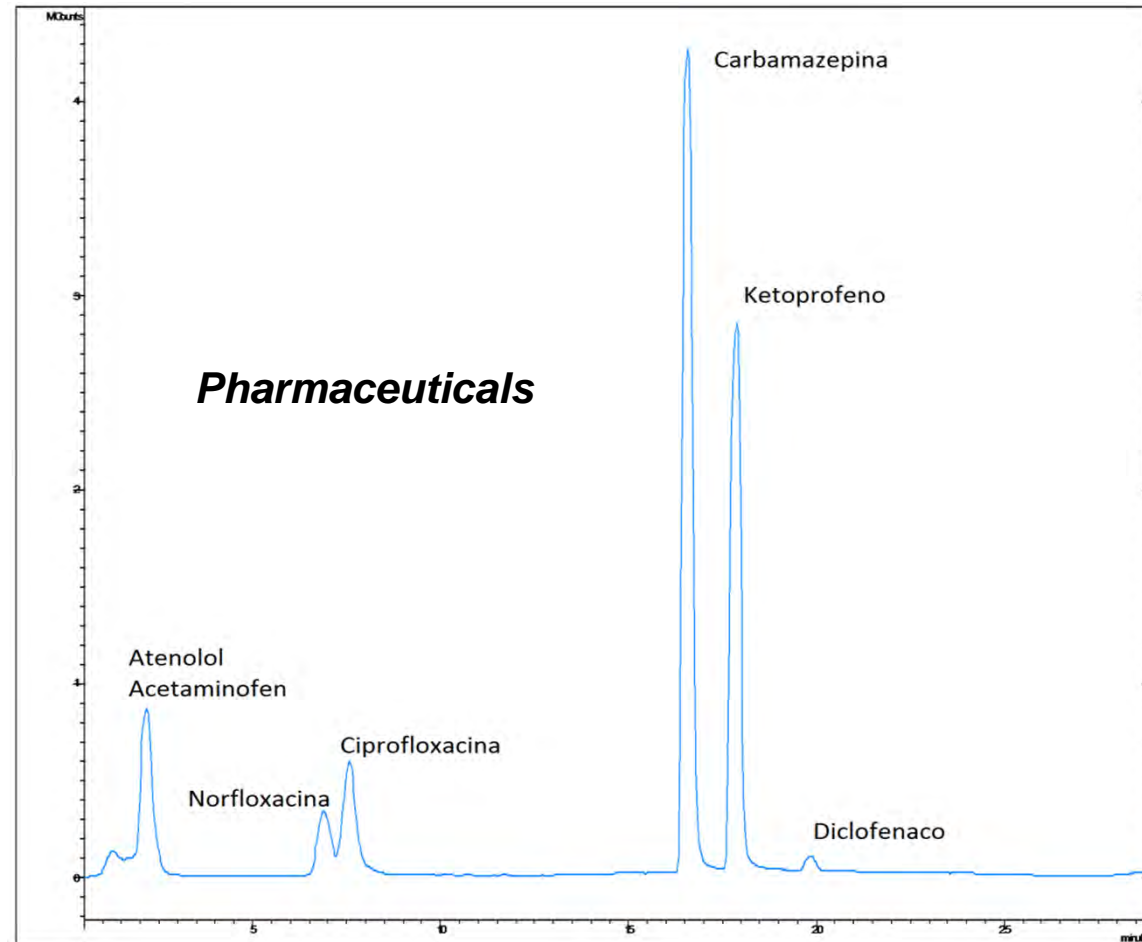
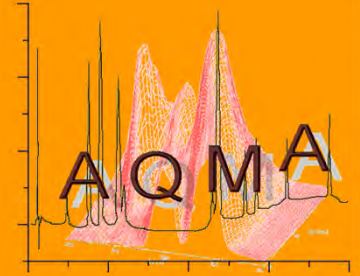








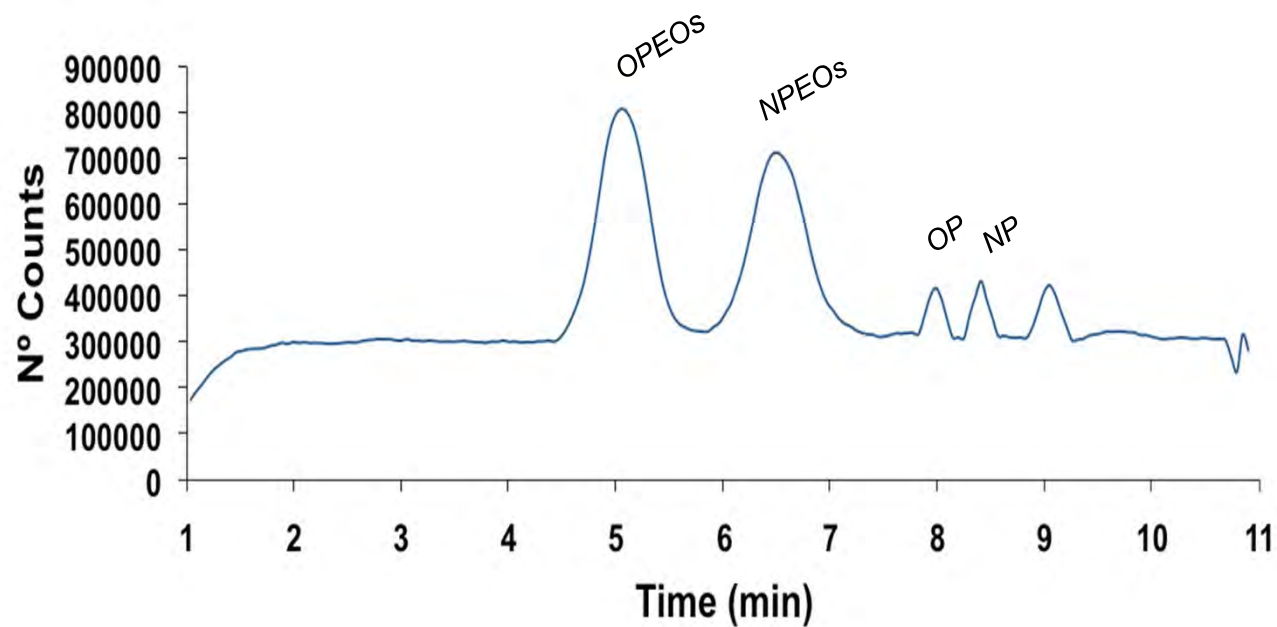
# Experimental







## Alkylphenols



# Results

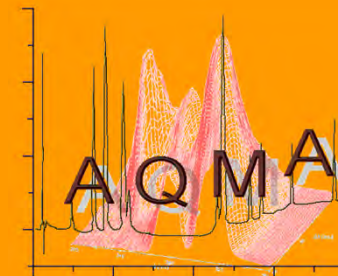


		MUELLE DEPORTIVO LPGC	PUERTO ESCALA PUERTO RICO	MUELLE DEPORTIVO DE MOGÁN
<b>DIURÓN</b>	Range	<b>25.5-119.0</b>	<b>25.0-99.0</b>	<b>24.5-138.2</b>
	Average	57.1	35.5	44.8
	Median	52.2	29.1	35.5
<b>IRGAROL</b>	Range	<b>42.1-92.1</b>	<b>40.6-72.3</b>	<b>40.3-108.9</b>
	Average	64.2	52.6	63.8
	Median	66.8	51.0	52.3

(\* ) concentration in  $ng.L^{-1}$



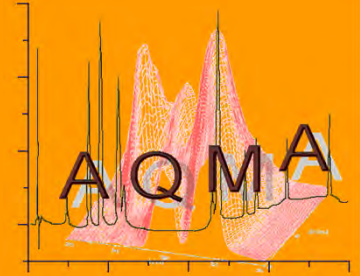
# Results



		EDAR BARRANCO SECO	EDAR JINAMAR	EDAR SURESTE	EDAR LAS BURRAS
<b>ACETAMINOFEN</b>	Range	21.5-297.0			
	Average	116.1			
	Median	29.7			
<b>NORFLOXACIN</b>	Range	11.3-3551.7	18.0-3179.1	22.9-1681.5	17.0-899.9
	Average	1039.8	1091.9	511.6	217.9
	Median	787.1	808.6	185.3	20.8
<b>CIPROFLOXACIN</b>	Range	18.9-303.6	9.0-303.4	18.8-101.0	4.4-80.1
	Average	92.1	91.9	48.4	33.1
	Median	63.1	68.4	30.8	14.7
<b>KETOPROFEN</b>	Range	41.6-67.8	106.3		
	Average	52.8	106.3		
	Median	49.0	106.3		
<b>DICLOFENAC</b>	Range	28.4-47.9	28.4	29.5-343.6	23.7-160.0
	Average	38.1	28.4	143.3	80.3
	Median	38.1	28.4	56.7	57.1

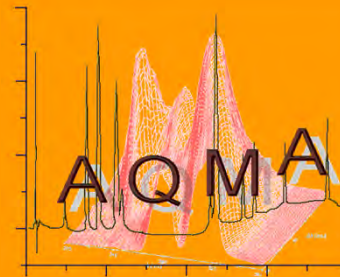


## Conclusions



- ❑ *Antifoulings*: presence of diuron and irgarol in all samples:  $46,4 \text{ ng}\cdot\text{L}^{-1}$  y  $60,2 \text{ ng}\cdot\text{L}^{-1}$  respectively.
- ❑ *Pharmaceuticals*:  $4.4\text{-}3551.7 \text{ ng}\cdot\text{L}^{-1}$
- ❑ *Alkylphenols*: *no presence*





## Benzotriazole UV Stabilizers (BUVs)

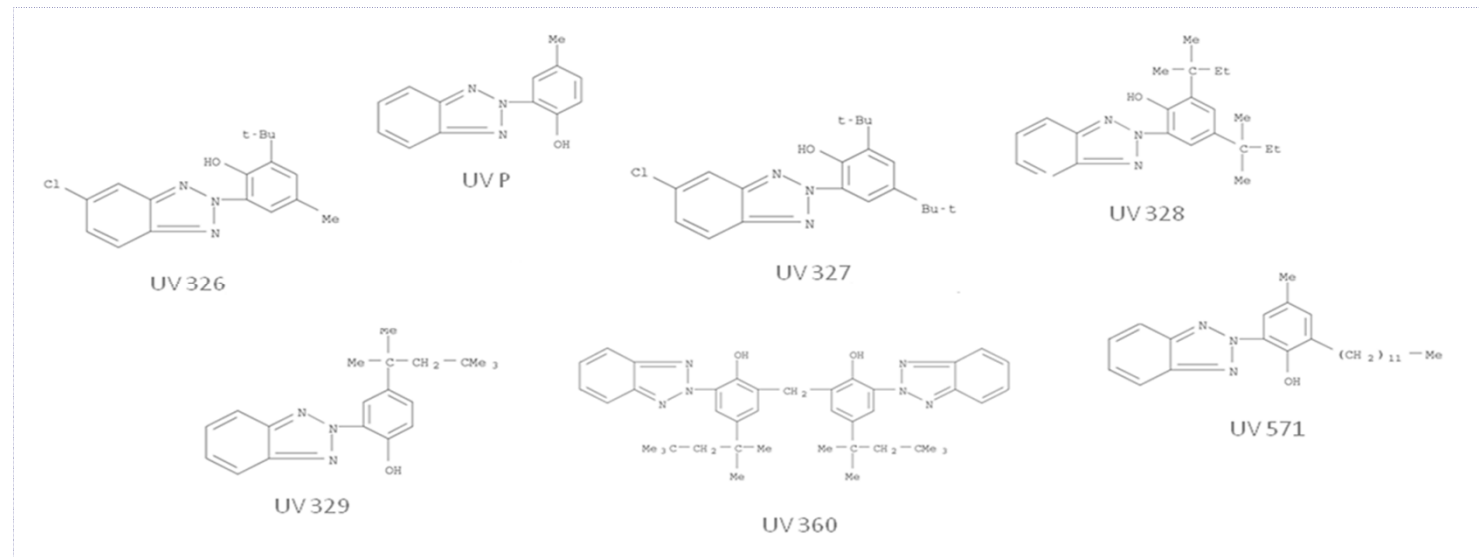
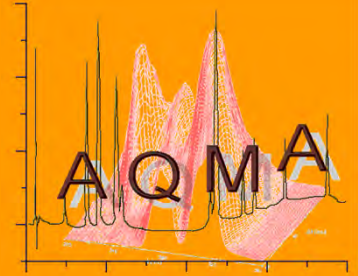
- Used in different **Personal Care Products** as reflecting and absorbing solar radiation: sunscreens, soaps, shampoos, lip gloss, hair dyes, etc.



May enter in the environment in **dissolved form**

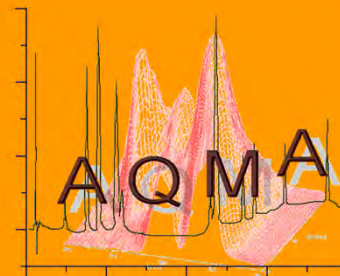
- Accumulation in sediments and bioaccumulation in organisms





- *Derivatives of BUVs :*

- \* *mutagenic in bacterial systems*
- \* *toxic in plants*
- \* *adverse effects on fecundity and reproduction of fish.*

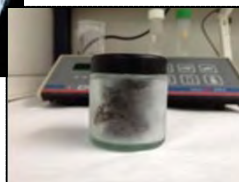


- ✓ **Optimization, development and application of a methodology for the determination of BUVSs in marine sediments and sewage sludges from WWTPs.**



## **MAE – On Line SPE-UHPLC-MS/MS**

*Extraction*



*Clean-up and  
preconcentration*



*Separation and  
determination*



# Experimental

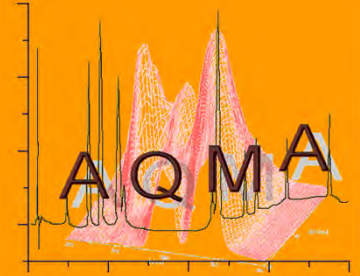


MAE	
EXTRACTANT	ACN
EXTRACTANT VOLUME	2 mL
EXTRACTION TIME	15 min.
POWER	300 W

ON-LINE SPE	
EXTRACTION COLUMN	Oasis HLB Direct Connect HP Column (2.1 x 30 mm, 20 $\mu$ m)
SAMPLE VOLUME	5 mL
pH	3
SAMPLE LOAD	Water 0.1 % formic acid (2mL/min)
WASH	Water:MeOH (70:30, v/v) (0.01 mL/min)
ELUTION	MeOH 0.1% acid 0.9 mL/min

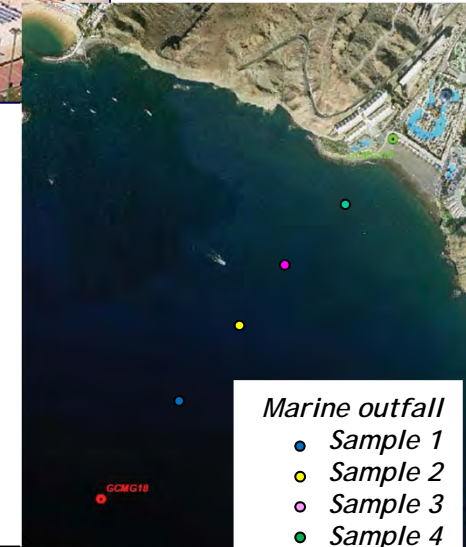
CHROMATOGRAPHIC CONDITIONS	
UHPLC COLUMN	ACQUITY UPLC BEH C18 1.7 $\mu$ m 2.1 x 50 mm
MOBILE PHASE	MeOH 0.1% formic acid
FLOW RATE	0.9 mL/min

# Results



## **Marine sediments**

- *Three samples from beaches sand*
- *Four samples close to a marine outfall from WWTP*

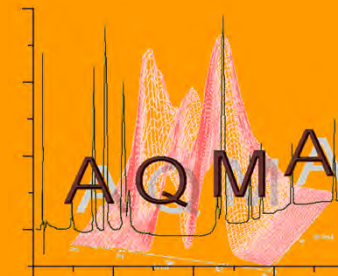


## **Sludges**

- *Three from WWTPs*



# Results



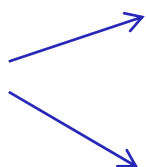
	UV P	UV 329	UV 326	UV 328	UV 327	UV 571	UV 360
Beach 1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Beach 2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Beach 3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Marine outfall 1	<LOQ	<LOQ	<LOD	24.0 ± 2.43	<LOD	<LOD	0.33 ± 0.04
Marine outfall 2	<LOQ	<LOQ	<LOD	22.0 ± 2.33	<LOD	<LOD	0.19 ± 0.02
Marine outfall 3	<LOD	<LOD	<LOD	20.7 ± 1.95	<LOD	<LOD	0.18 ± 0.02
Marine outfall 4	<LOD	<LOQ	<LOD	<LOQ	<LOD	<LOD	<LOQ
Sludge 1	<LOQ	<LOD	<LOD	12.2 ± 1.49	<LOD	<LOD	6.32 ± 0.92
Sludge 2	<LOQ	<LOQ	<LOD	<LOD	<LOD	<LOD	2.30 ± 0.31
Sludge 3	<LOD	<LOQ	<LOD	0.94 ± 0.11	<LOD	<LOD	<LOQ

(\* ) Concentrations in  $ng.g^{-1}$



## Conclusions



- Several BUVs were detected in **marine sediments** close to marine outfalls and **sludges** **but no** in beaches sand samples
- UV P and UV 329 were detected outfall **marine sediments and sludges** but were not quantified (< LOQs)
- UV 328 and UV 360 
  - marine sediments :**  
0.18 – 0.33 ng.g<sup>-1</sup>
  - sludges:**  
0.94 – 3.62 ng.g<sup>-1</sup>



## Remarks and trends



### Research and technology

- **Improvement of WWTPs treatments:**

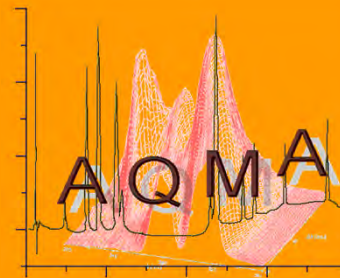


*New generation treatments*

*Ultrafiltration, Nanofiltration, Advanced Oxidation, Inverse Osmosis, etc.*

- **Metabolites identification:** more selective detectors Q-ToF, Orbit Trap, etc.





## Social

- *Consumption control of pharmaceuticals and drugs*
- *Collection control of pharmaceuticals in containers*
- *Use of biodegradable pharmaceuticals (Green Pharmacy)*

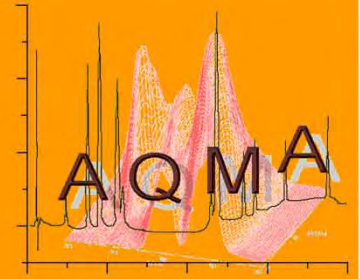


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Gracias por su atención

