Screening of emerging and priority contaminants in the Nalón, Arga and Besós rivers (Spain) by HPLC-DAD

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INTRODUCTION

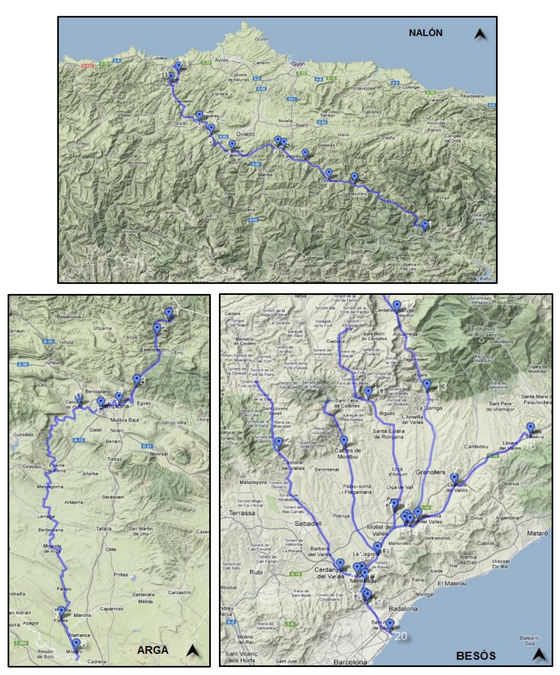
The monitoring of organic contaminants in water is important for legislative and environmental decision making purposes with the aim to improve the chemical quality of surface waters. During the last few years much effort has been made to establish and implement monitoring programs at river basins in order to measure and identify main contaminants, their transport and fate and the impact and risks they pose to the ecosystem. Because water monitoring programs have been or are being implemented across Europe, we have undertaken a technology transfer initiative where HPLC methods have been implemented in technical colleges and are part of the educative program. At this point, students gather knowledge on these methodologies that are of outmost importance for professional opportunities towards water agencies, analytical laboratories and research institutions. Therefore the aim of this study was to bring together teachers and students of technical colleges of environmental health and researchers from the Spanish Superior Council of Scientific Research (CSIC) in order to develop and validate an analytical methodology based on SPE and HPLC-DAD and to implement this know-how in three technical colleges in Spain. Following this, a monitoring program was carried out along Nalón, Arga and Besós rivers, from source to mouth in order to determine the presence of seven organic contaminants which are markers of industrial (nonylphenol, octylphenol and bisphenol A), urban (diclofenac, ibuprofen) and agricultural pollution (atrazine and terbutryn). The presence of these contaminants in the 3 river basins is discussed in terms of anthropogenic pressure, river flows and the different climatic conditions of each site.

STUDY AREA

ANALYTICAL METHODOLOGY

1. WATER SAMPLING

2. SAMPLES COLLECTED



3. PHYSICOCHEMICAL PROPERTIES

Target compounds	CAS nº	Formula	Molecular weight	Solubility g/100 mL	$t_{½}$ (h)	K_{ow}	pK
Atrazine	1912-24-9	$C_8H_{16}ClN_5$	217.69	0.007	50	2.61	1.7
Terbutryn	886-50-0	$C_{10}H_{19}N_5S$	241.36	0.0025	66	3.65	4.3
Diclofenac	15307-86-5	$C_{14}H_{11}NCl_2O_2$	296.15	0.00237	3.3	4.51	4.15
Ibuprofen	15687-27-1	$C_{13}H_{18}O_2$	206.29	Insoluble	4	3.14	5.2
Bisphenol A	80-05-7	$(CH_3)_2C(C_6H_4OH)_2$	228.28	0.12–0.30	1-150	3.32	9.73
Octyilfenol	67554-50-1	$C_{14}H_{22}O$	206.32	Insoluble	5	4.12	10.38
Nonylfenol	25154-52-3	$C_{15}H_{24}O$	220.35	0.006	8.2	4.5	10.7

4. EXTRACTION AND ANALYSIS

WATER
500 mL, unfiltered

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Oasis HLB (200 mg) SPE cartridges

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Conditioning with 6 ml methanol and 6 ml water

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Elution: 6 ml methanol

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N_2 evaporation to 0.5 ml

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Reconstitution: methanol

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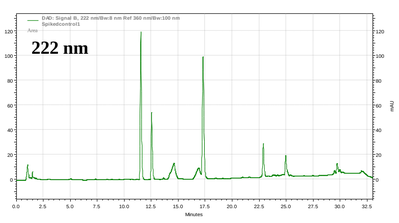
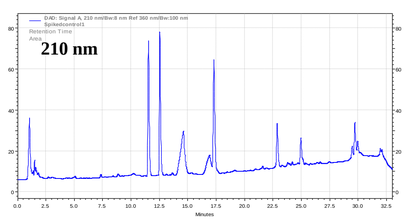
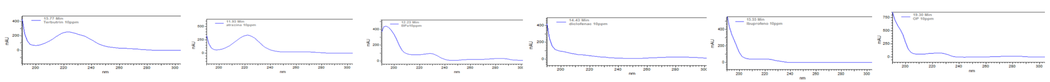
HPLC-DAD







Adsorption spectrum of target compounds

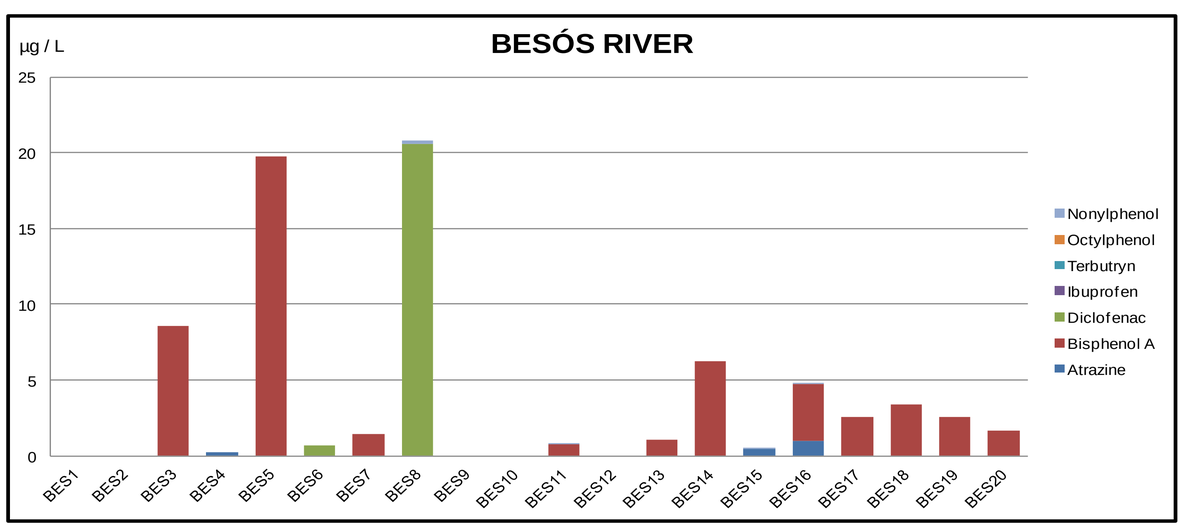
RESULTS

The three rivers originate from mountain areas with little or no anthropogenic impact but flow through very industrialized areas and gather effluents of large municipalities and agricultural run-off. The Arga flows into the Aragón, a tributary of the Ebro River, whereas the Nalón flows into the Cantabrian sea and the Besós into the Mediterranean sea, thus they have very different volume of flow, climatic conditions and impact. During the 1970s and 80, the Besós river became sadly famous for being the most polluted river in Europe.

None of the studied pollutants were found in the Nalón and Arga Rivers. It is assumed that both rivers have a high flow average; 56,40 m^3/s for Nalón River and 59,76 m^3/s for Arga River. In addition, the sampling was carried out in rainy season, reason by which we assume that the target contaminants were much diluted.

Besós River flows through an area densely industrialized and populated, and in addition has a flow of 4,33 m^3/s. Bisphenol A was the main compound detected at concentrations up to 19.8 µg/L, and was frequent in downstream waters close to the mouth. The maximum concentration of diclofenac was found in BES 8 (20.6 µg/L), a site where the Formula One and Grand Prix Motorcycle Racing Circuits of Montmeló is located. Atrazine was only detected in two sites, being the maximum concentration of 3.77 µg/L.

According to the Directive of the European Parliament and of the council, 2011/0429 (COD), as regards priority substances in the field of water policy, maximum limits were surpassed in some instances. For Bisphenol A, this Directive does not indicate the maximum admissible concentrations, but underlines that this substance has to be reviewed for possible identification as priority hazardous substance. Diclofenac is marked as "not applicable", since concentration values they are significantly lower than the acute toxicity threshold. For atrazine, the concentration exceeded the permitted maximum concentration of 2.0 µg/L.



In terms of method performance, the method optimized was validated in terms of recovery (% R), limits of detection (ng injected), repeatability (%), and linearity. Compounds were identified according to their elution time (Tr, minutes), maximum wavelength (λ max) and absorbance spectra. The system was linear over a concentration range of 0.05-10 µg/mL, except for diclofenac and ibuprofen. By performing a simple SPE procedure using methanol as eluting solvent, all compounds were recovered with very good efficiency. The method was implemented as laboratory practice subject in the 3 technical schools.

Target compounds	Rt (min)	λMax	Calibration curve	Linearity (µg/mL)	% R	Repetitivity	LOD (ng injected)
Atrazine	11.53±0.01	222	y=401123x+51143	0.05-10	64	7.1 %	0.23
Terbutryn	12.51±0.04	210	y=165784x+16574	0.05-10	85	8.5 %	0.17
Diclofenac	13.90±0.31	210	y=185029x–34665	1-10	81	18 %	0.62
Ibuprofen	16.42±0.23	210	y=75697x–35000	1-10	85	33 %	0.5
Bisphenol A	17.30±0.04	222	y=40791x+51361	0.05-10	66	7.7 %	0.6
Octylphenol	22.90±0.04	222	y=87789x+9715	0.1-10	68	9.0 %	0.33
Nonylphenol	25.02±0.05	222	y=81523x+44306	0.05-10	75	6.8 %	0.15

CONCLUSIONS

The main objective was that the procedures developed from sampling, extraction, analysis and quantification were transferred and implemented at technical colleges so that in future courses, water extraction and HPLC can be part of the formative program of the studies of environmental health. This study has been a first step to monitor systematically the quality of river waters using a relatively simple technique able to determine the presence of polar contaminants, in such a way that can be implemented for the long term screening of markers of environmental pollution.

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