Evolution of Chemical Pollution in Catalan Coastal Sediments

Albert Palanques, Josep Caixach, Marc Belzunces, and Arantxa Bartolomé

Abstract In 2000 and from 2006 to 2011, a monitoring program was followed along the Catalan inner shelf, using homogeneous analytical methods and sampling strategies and focusing on the main sites of river sediment accumulation at present. Adjacent areas that are potentially vulnerable to pollution were also selected. Trace metals and organic pollutants were analyzed in surface sediment samples. Mean concentrations in each area show a distribution of organic and inorganic pollutants along the Catalan inner continental shelf. The highest concentrations are located on and around the coast of Barcelona city for most pollutants and locally on the coast of Tarragona city and the Ebre Delta for some of them. The concentrations tend to decrease gradually southward and sharply northward of Barcelona. The trace metal that shows the highest anomalies is Hg (max. enrichment factor, 34), whereas Cd, Zn, Cr, Pb, and Cu show more moderate anomalies. Sediment polycyclic aromatic hydrocarbons, 4-nonylphenols (metabolites of nonylphenol polyethoxylated, non-ionic surfactant), polybrominated diphenyl ethers, polychlorinated biphenyls, and dichlorodiphenyltrichloroethane are also significant. The time evolution of most trace metals shows a decreasing trend mainly between 2000 and 2006, whereas between 2006 and 2011 trends of trace metals and organic pollutants are not clear, as some of them increased and others decreased and many of them peaked in 2007 and 2009. The greatest decreases in trace metals were in the most polluted areas.

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Contents

Abbreviations

DDT	Dichlorodiphenyltrichloroethane (or dichlorodiphenyltrichloroethanes (DDTs) and metabolites DDE and DDD)
HCBz	Hexachlorobenzene
NPs	4-Nonylphenols (metabolites of nonylphenol polyethoxylated, nonionic surfactant)
PAHs	Polycyclic aromatic hydrocarbons
PBDEs	Polybrominated biphenyl ethers
PCBs	Polychlorinated biphenyls

1 Introduction

Contaminants discharged into rivers are transported downstream to the marine environment. However, they can also be trapped in dams or during periods of low water discharge, and they can be partially trapped on the inner side of meanders, in river banks, or in estuaries before reaching the sea. In the Mediterranean, the irregular regime of rivers and streams (most of them small) and the local nature of many discharges mean that pollutants reach the sea in sporadic pulses that are difficult to predict. Once discharged into the sea, pollutants are scavenged when flocculation occurs along the freshwater-saltwater interface [1], where they may also be affected by dilution, desorption, absorption, aggregation, and precipitation [2–5]. In addition, offshore dispersion of pollutants is controlled by dynamic marine processes (mainly currents and waves) that induce transport, accumulation, and/or resuspension of pollutants and determine their final fate [6–9]. In many zones of the oceans, energetic processes transport and dilute the marine pollution load in the transit to the deep sea. However, in the Mediterranean Sea, the transport capacity of the dynamic processes is lower than in large oceans, so a large part of the particulate pollutant load can quickly settle on the seabed near the coast, in some cases before being sufficiently diluted, thus generating persistent and anomalous concentrations in the bottom coastal sediments. Only extreme hydrodynamic events such as strong wave storms or strong wind-induced currents can resuspend coastal sediment and transport it again [10–13], and these events are not too frequent in the Mediterranean.

Trace metals are among the most common pollutants discharged into the marine environment and are indicators of domestic and industrial pollution. In most advanced countries of the European Community, the distribution of trace metals in the marine environment is being studied systematically and extensively in order to estimate the environmental impact and the economic and social effects of pollutants and to take preventive and corrective measures.

During the 1980s and 1990s, studies of trace metals in sediments of specific areas of the Catalan coast including Barcelona, the Llobregat River mouth, and the Ebre Delta coast [14–17] showed significant trace metal pollution at some sites. However, these studies were not continuous in time and did not always follow the same sampling strategies or methods of analysis. Organic pollutants were also studied on the Catalan coast, and it was found that the contamination of PCBs and PAHs was greater near the sites of urban and industrial impact [18, 19].

Because the Water Framework Directive (WFD, DIR 2000/60/EC) is not specific with respect to sediments, the monitoring of organic pollutants in them has been at the discretion of experts. In this context, to protect the environment, the Catalan Water Agency (ACA) has also been analyzing organic pollutants in different matrices. The WFD describes the monitoring of priority substances (PS) and other pollutants in fresh waters and coastal waters. The daughter directive 2008/105/EC defined environmental quality standards (EQS) for priority substances in water, with the aim of protecting the aquatic environment from their adverse effects. This directive includes 33 PS, mainly organic pollutants. In the recent revision of the list of PS (DIR 2013/39/EU), 12 new ones were added, the EQS of some existing PS was changed, and values for biota were introduced. Additionally, compliance monitoring for PS in the WFD requires the achievement of a limit of quantification (LOQ) equal to or below 30% of the relevant EQS. The formula for calculating the LOQ is therefore 0.3 × EQS. The WFD establishes the obligation to carry out programs to monitor and control the quality of water bodies and to establish management measures for them to achieve a good ecological and chemical status by 2015.

In 2000 the Marine Water Unit of the ACA started a surveillance program of heavy metal pollution in marine sediments of the Catalan inner shelf and established a monitoring network that prioritized the control of sediments in the vicinity of river mouths, where these elements tend to be more accumulated. This program provided homogeneity in the analytical methods and sampling strategies.

As a continuation of this work, the ACA started a second program to determine the levels of trace metals and organic pollutants in sediments of the Catalan coast in

2006, giving priority to the most affected areas of control according to the results of 2000 and also to water bodies that had not been evaluated at that time but were at risk of breaching the WFD [20]. Also, the monitoring of organic pollutants in sediment started at the discretion of experts. In the ACA program, which lasted until 2011, trace metals of some areas were analyzed annually, and organic pollutants were sampled at varying frequencies. In 2006, 2007, and 2009, all the sampling points of the monitoring network were analyzed, while in 2008 and 2010, only sampling points of the high-risk areas were analyzed.

1.1 Study Area

The fine sediment and pollutants that are present on the Catalan coast are mainly provided by the rivers, which develop mud belt prodeltas, particularly along the inner and mid-continental shelf [14, 15, 18, 21–24]. Outside these prodeltaic mud deposits, surface sediment can be relict from hundreds and thousands of years ago, when the sea level was lower than today [22, 25, 26]. Therefore, in this paper, we study the evolution of pollutants at selected sites of the present prodeltaic deposits of the rivers discharging on the Catalan coast (Fig. 1). The basic characteristics of the Catalan rivers are shown in Table 1. There are great differences between the Ebre River and the other eight rivers, which form the system known as the Inner Catalan River Basins. These eight rivers show a typical Mediterranean behavior, with short length, low discharges (extremely low in summer) and sporadic major floods typically in autumn and spring.

The system of the Inner Catalan River Basins occupies 16,600 km^2 (52% of the territory of Catalonia) and is densely populated, with about six million people accounting for 85% of the Catalan population. The most populated areas are the Barcelona Metropolitan Area and the Tarragona Bay. Heavily industrialized since the nineteenth century, the Barcelona Metropolitan Area is the sixth most populous urban area in the European Union (4.4 million inhabitants [2011]) and the second urban area on the Mediterranean Coast (Eurostat 2012). Tarragona Bay contains Tarragona city and one of the most important petrochemical clusters in the Mediterranean. The value of the production is equivalent to 0.75% of worldwide production, and the area produces 25% of the petrochemical products and 44% of the plastics for the Spanish market. Stockbreeding and agriculture are also important in the Inner Catalan River Basins. Stockbreeding is more important in the northern basins, while agriculture is more important in the southern ones. Finally, the Ebre River Basin occupies 85,362 km^2 in the north of the Iberian Peninsula, with a population of about three million people. The river flows through a major city, Zaragoza, but far away from the river mouth. In the lower Ebre River, although there is some local industrial activity, such as the Flix complex [27, 28], the main human activity is agriculture and stockbreeding.

2 Materials and Methods

2.1 *Sampling*

Surface sediment samples were taken from present-day prodelta deposits of the following rivers: Roses, Muga, Fluvià, Ter, Tordera, Besòs, Llobregat, Foix, Francolí, and Ebre. In addition, adjacent areas potentially vulnerable to pollution were also selected: Mataró, Masnou, Barceloneta, Castelldefels, La Falconera, Sitges, El Vendrell, Cambrils, Fangar Bay, and Alfacs Bay (Fig. 1).

In 2000, four transects of sampling stations were established in front of the mouth of each river perpendicular to the bathymetry. Considering that the main

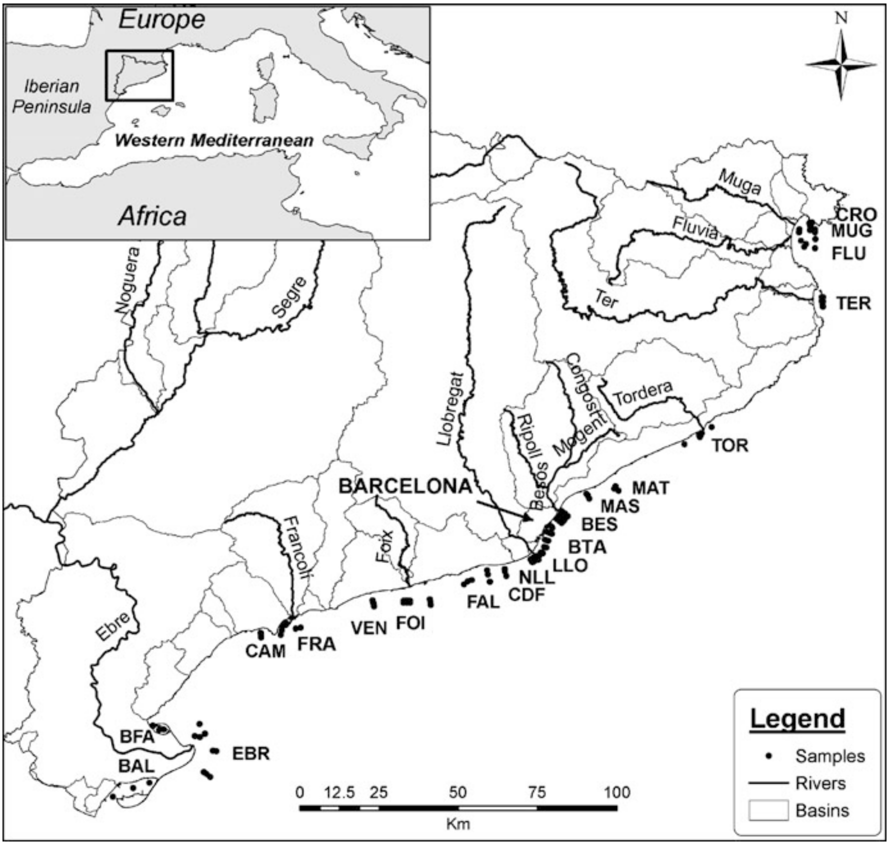


Fig. 1 Location of the study areas and samples in the context of the Catalan coast and the western Mediterranean (*CRO* Roses, *MUG* Muga prodelta, *FLU* Fluvià prodelta, *TER* Ter prodelta, *TOR* Tordera prodelta, *MAT* Mataró, *MAS* Masnou, *BTA* Barceloneta, *BCN* Barcelona city, *LLO* Llobregat prodelta, *NLL* new Llobregat, *CDF* Castelldefels, *FAL* La Falconera, *FOI* Foix prodelta, *VEN* El Vendrell, *FOI* Foix, *CAM* Cambrils, *EBR* Ebre prodelta, *BFA* Fangar Bay, *BAL* Alfacs Bay)

Table 1 Basic characteristics of the rivers flowing into the Catalan coast

River	Length (km)	Basin area (km^2)	Mean water discharge (m^3 s^{-1}, 2005–2011)
Muga	65	854	2.18
Fluvià	97	1,125	3.98
Ter	208	3,010	12.57
Tordera	54	894	0.39
Besòs	58	1,039	4.33
Llobregat	170	4,948	13.64
Foix	49	312	0.25
Francolí	85	838	0.83
Ebre	910	85,534	247.83

Data source: Statistical Institute of Catalonia (IDESCAT) and Ebre Hydrographic Confederation (CHE)

Table 2 Sampling areas and corresponding water bodies following IMPRESS 2005

Area	Water body
Roses (CRO)	C6
Muga prodelta (MUG)	C6, C7
Fluvià prodelta (FLU)	C7
Ter prodelta (TER)	C11, C12
Tordera prodelta (TOR)	C15
Mataró (MAT)	C17
Masnou (MAS)	C17
Besòs prodelta (BES)	C19, C20
Barceloneta (BTA)	C20
Llobregat prodelta (LLO)	C21
New Llobregat (NLL)	C21
Castelldefels (CDF)	C22
La Falconera (FAL)	C23
Foix prodelta (FOI)	C25
El Vendrell (VEN)	C25
Francolí prodelta (FRA)	C27
Cambrils (CAM)	C29
Fangar Bay (BFA)	T1
Ebre prodelta (EBR)	C33
Alfacs Bay (BAL)	T3

current of the Catalan coast has a dominant southwestward component [29], we established one transect north of the river mouth, one just in front of the mouth, and the other two south of the river mouth. In each transect, sediment samples were collected at 10, 20, 30, 40, and 50 m depth. In the following years, only the samples that showed significant pollution or were representative of an area were taken.

In this paper, we selected the stations in which sampling was carried out for 3 or more years. The correspondence between these areas and the coastal water bodies defined in [20] is presented in Table 2. Mean concentrations for all the samples from the same area were calculated for each sampling year and for the whole study period.

Sediment samples were taken with a grab collecting the first cm of surface sediment. Samples for metals were stored at 4°C and later lyophilized and ground. Samples for organics were air-dried and manually ground (2 mm) before extraction.

2.2 Analytical Procedures

2.2.1 Grain Size

The grain size analysis was performed using a SediGraph 5100 (<50 μm fraction) and a settling tube (>50 μm fraction). The results for both fractions were joined in order to obtain the total grain size distribution and the textural statistical parameters for each sample [30]

2.2.2 Trace Metal Analytical Procedures

A total digestion technique was carried out according to Querol et al. [31], using HNO_3, HF, and HCl suprapure acids. For every 18 samples, a blank, a PACS-2 reference material (National Research Council Canada), and a random-replicated sample were used for analytical quality control. Trace elements were analyzed (except Hg) by ICP-MS. Al was analyzed by ICP-AES. The overall analytical uncertainty was below 15% and typically between 5% and 10%.

For Hg analysis, a LECO AMA254 Mercury Analyzer complying with US EPA Method 7473 [32] was used. PACS-2 reference material from the National Research Council Canada, random-replicated for every ten samples and blank samples to avoid memory effects, was used for analytical quality control. The overall analytical uncertainty was below 2%.

Background trace metal levels of sediment samples from several areas were determined in previous studies [14, 16, 23]. Surface samples of the present study with these background trace metal levels were used to estimate the enrichment factor (EF). With these samples, aluminum-trace metal regression curves were established for every trace element in order to find the background levels in terms of aluminum content (Al normalization). The ratio between metal content and background level (Al normalized) for each sample was defined as the EF, which is a dimensionless value. To evaluate toxicity risk, we also used reference values following Long et al. [33], who defined two values for each trace metal, effect range low (ERL) and effect range median (ERM), which defined three ranges whose effects to the environment are predicted to be minimal (value $<$ ERL), occasional (ERL $<$ value $<$ ERM), and frequent (value $>$ ERM).

2.2.3 Organic Pollutants

About 5 g of dried samples were spiked with isotopic labeled standards. Five grams of copper powder was added to the sample to remove elemental sulfur. The extraction was carried out by sonication with hexane/dichloromethane (1:1, v/v). The extract was separated by centrifugation and the extraction process was repeated once again. The extracts were joined, and, after addition of isooctane, the whole extract was concentrated to a volume of 4 mL.

The extract was passed through a glass column containing 5 g of silica gel deactivated with 5% Milli-Q water, and the column was eluted with 100 mL of 95:5 hexane/dichloromethane at atmospheric pressure. The extract was concentrated to a volume of 500 μL and transferred to an amber glass vial. Finally, recovery standards were added. The extract volume was adjusted to 250 μL with gentle nitrogen flow.

The analyses of different families of organic compounds are based on the isotope dilution quantitation method and were performed by gas chromatography coupled to mass spectrometry of low and high resolution (HRGC-LRMS & HRGC-HRMS). These methods are based mainly on United States Environmental Protection Agency (USEPA) methods (e.g., 8270C, 1614, 1668) [19, 24, 34–36].

3 Results

3.1 Distribution of Pollutants

Distribution of mean trace metal concentrations (and EF) and mean organic pollutants in each sampling area during the whole monitoring period shows three main sectors of pollutant levels along the Catalan coast: the northern Catalan coast, where mean pollutant levels were mainly low or absent; the Barcelona city area, where mean pollutant levels were high; and the southern Catalan coast, where mean pollutant levels were mostly medium-high decreasing to low southward (Figs. 2, 3, and 4).

3.1.1 Northern Catalan Coast

The northern Catalan coast sector extends from the French border to Barcelona city area. This sector comprises the Roses, Muga, Fluvià, Ter, Tordera, Mataró, and Masnou areas, including the fluvial basins of the Muga, Fluvià, Ter, and Tordera Rivers (Fig. 1). The samples from the Roses, Muga, and Fluvià were mainly mud, with a fine fraction (silt plus clay) content higher than 60%, whereas the samples from the other areas were mainly muddy sand with a fine fraction of only 30%.

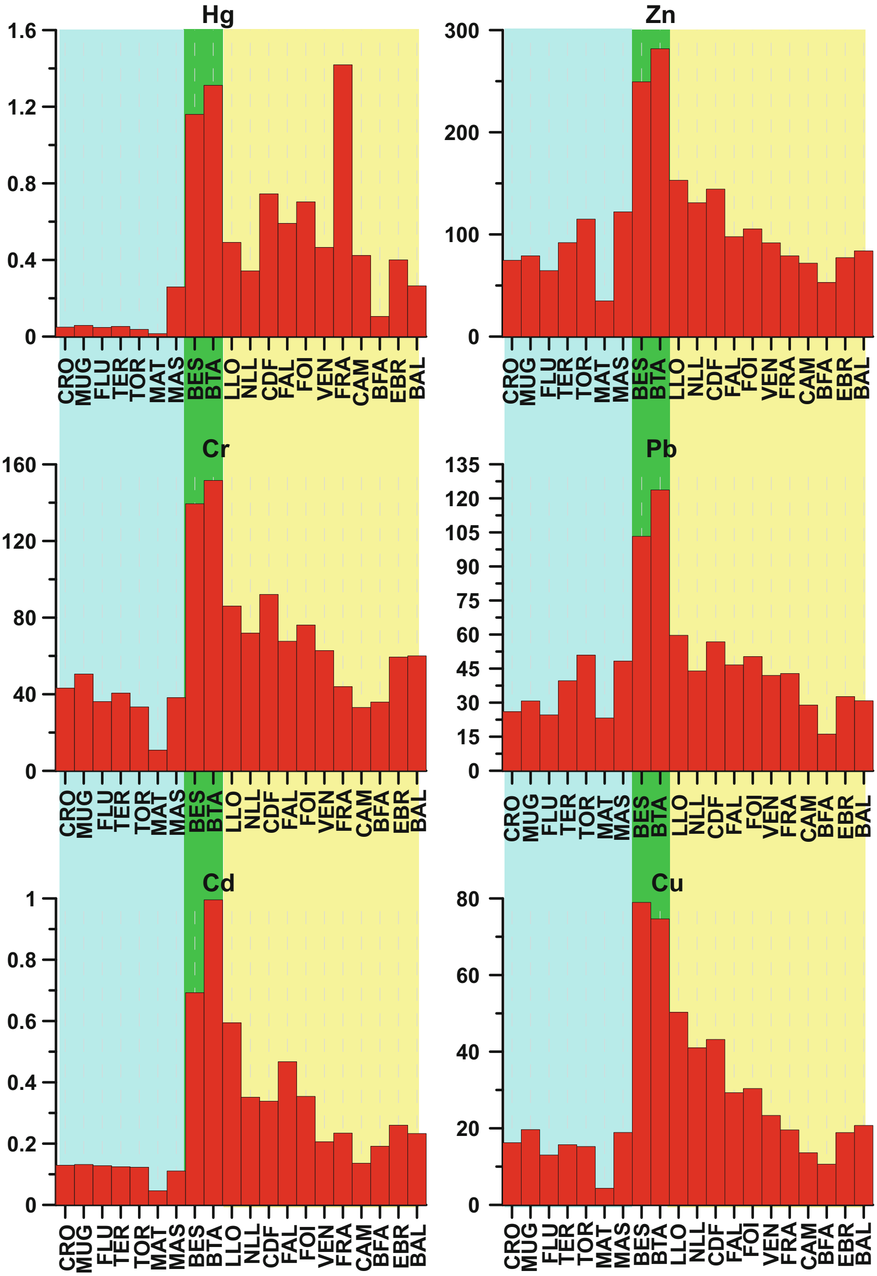


Fig. 2 Mean concentrations of trace metals (mg kg^{-1}) in the study areas during the whole monitoring period. Areas from the northern Catalan coast over *blue*. Areas from the Barcelona city coast over *green*. Areas from the Southern Catalan coast over *yellow*

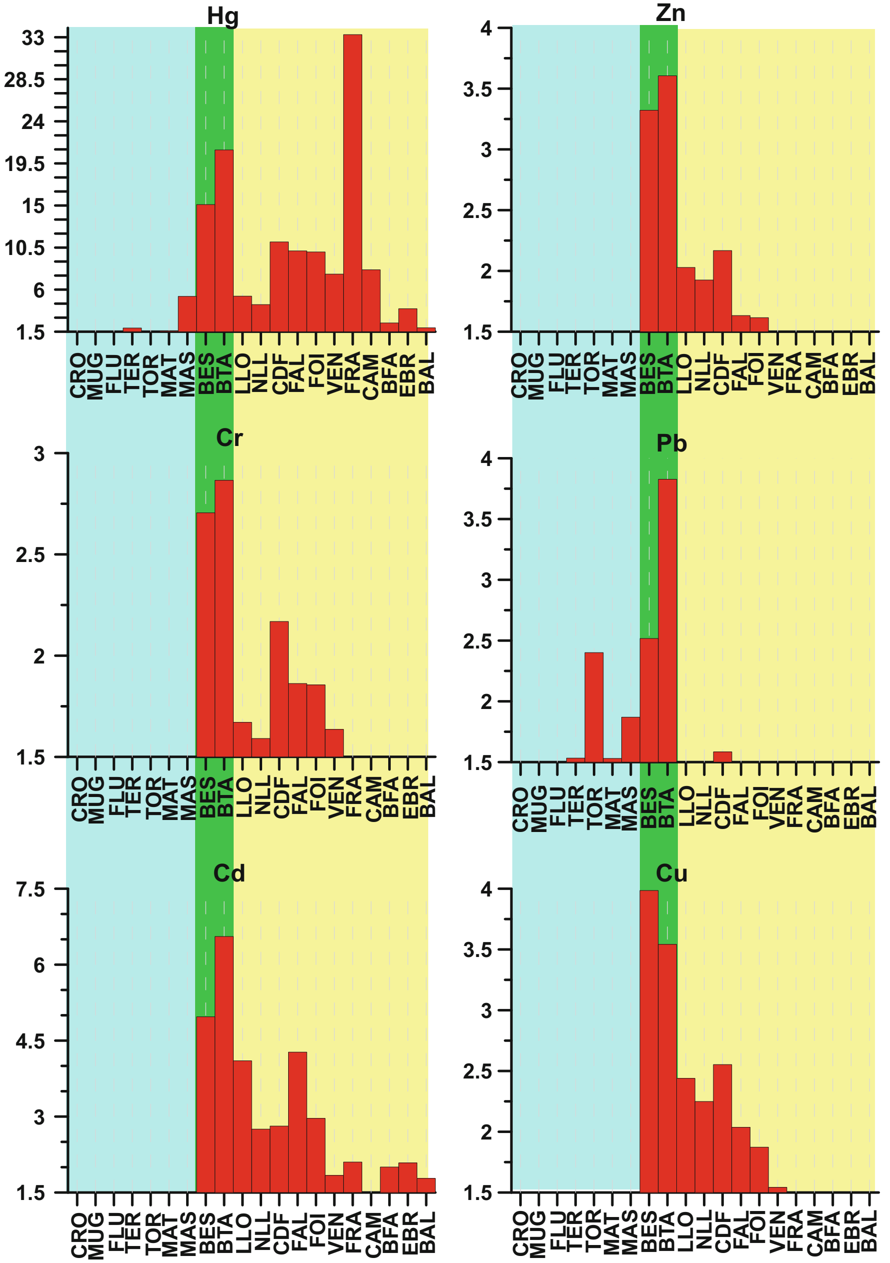


Fig. 3 Mean enrichment factors (EFs) of trace metals in the study areas during the whole monitoring period. Only EFs > 1.5 are considered significant and are represented. Areas from the northern Catalan coast over *blue*. Areas from the Barcelona city coast over *green*. Areas from the Southern Catalan coast over *yellow*

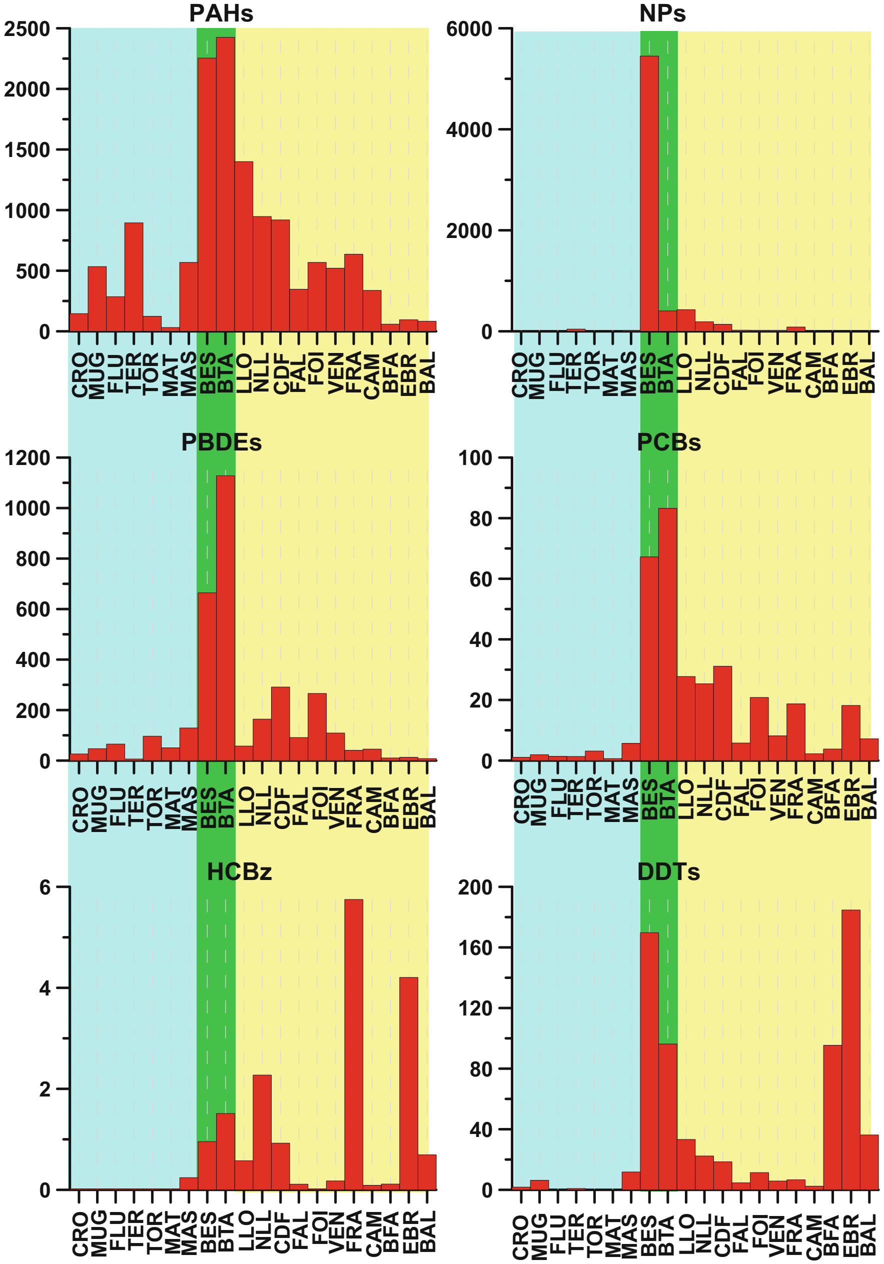


Fig. 4 Mean concentrations of organic pollutants (μg kg^{-1}) in the study areas during the whole monitoring period. Areas from the northern Catalan coast over *blue*. Areas from the Barcelona city coast over *green*. Areas from the Southern Catalan coast over *yellow*

Mean trace metal and organic pollutant concentrations in the areas of this sector during each monitored year are shown in Figs. 5 and 6.

In general, sediment samples taken in this sector showed natural or low levels of trace metal pollution, except in the case of Hg at Masnou where it showed a mean EF of 5.3 and concentrations between ERL and ERM values. Hg also reached a mean EF of 1.5 at Ter and Mataró (Fig. 3), where concentrations were below ERL values. Mean EFs for Pb of 2.4 were found at Tordera and of between 1.5 and 1.8 at Ter, Mataró, and Masnou, but only at Tordera did concentrations exceed ERL values without reaching ERM levels in 2000. Samples from all the other areas of this sector showed concentrations within the natural values below ERL for all the studied trace elements. Only Zn exceeded the ERL values slightly in 2009.

Regarding the organic pollutants, PAHs showed significant concentrations at Muga, Ter, and Masnou. PBDEs were identified at all the sites of this sector, increasing to the south, although significant values were only detected in 2007. The other families of organic compounds showed low concentrations, with only isolated increases in some areas (Figs. 4 and 6).

3.1.2 Barcelona City Coast

The coast of the Barcelona Metropolitan Area comprises the Besòs prodelta and Barceloneta and includes the fluvial basin of the Besòs River (Fig. 1). Most samples from this coast consisted of mud with more than 70% of fine fraction. This sector is where the Catalan coast showed the highest levels of most trace metals in sediments (Figs. 2 and 7). Hg is the element that showed the highest mean EFs (15 at Besòs and 21 at Barceloneta) in the area (Fig. 3). All the mean Hg concentrations on the Barcelona coast were above the ERM values during all the sampling years (Fig. 7). Anomalies of Cu, Zn, Cr, and Pb were lower (mean EF between 2.5 and 4) but relatively high for the marine environment, with concentrations between ERL and ERM values. Cd showed important anomalies in all the samples (mean EF 6.5) but only exceeded the ERL value in one sample (Fig. 7). In general, Besòs and Barceloneta showed the highest mean and absolute trace metal concentrations on the Catalan coast except for Hg, which was higher at Francolí (Fig. 2). However, these higher concentrations at Francolí were measured in only a few samples and mainly in 2000.

Mean organic pollutant levels were high in this sector, reaching maximum values for the PAH, NP, PBDE, and PCB families, which were significantly higher than those from other sectors. PAHs, PBDEs, and PCBs showed large increases in 2007. NPs increased strongly in 2009 at Besòs, which was the only area on the Catalan coast affected by high values of this family. DDT concentrations were also high in this sector, similar to those detected in the Ebre Delta area and increasing sharply in 2008 at Besòs. HCBz values were high but lower than the maximum values detected at Francolí and Ebre on the southern Catalan coast. A major increase in HCBz took place in 2010 at Barceloneta (Figs. 4 and 8).

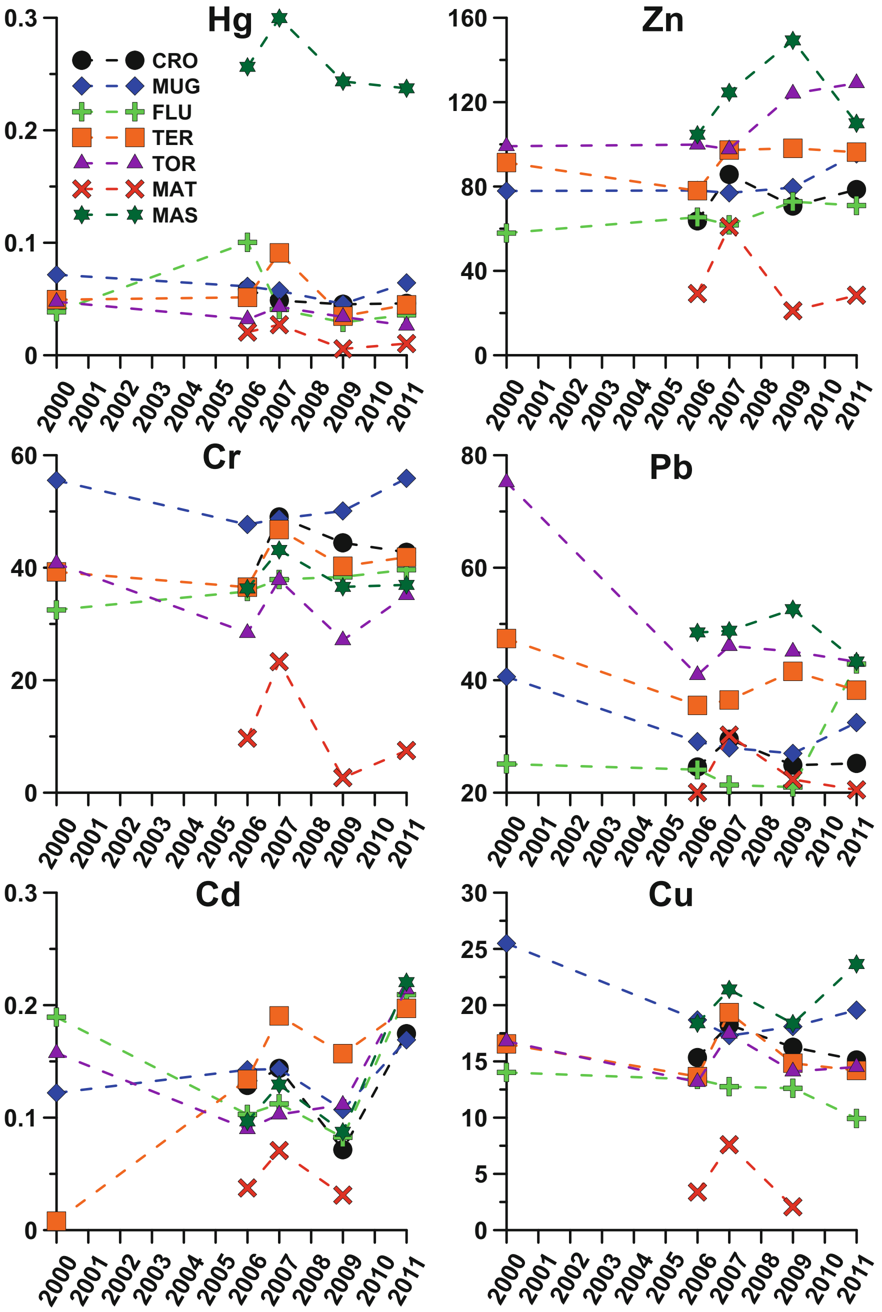


Fig. 5 Mean concentration of trace metals (mg kg^{-1}) in the study areas of the northern Catalan coast during each of the sampling years

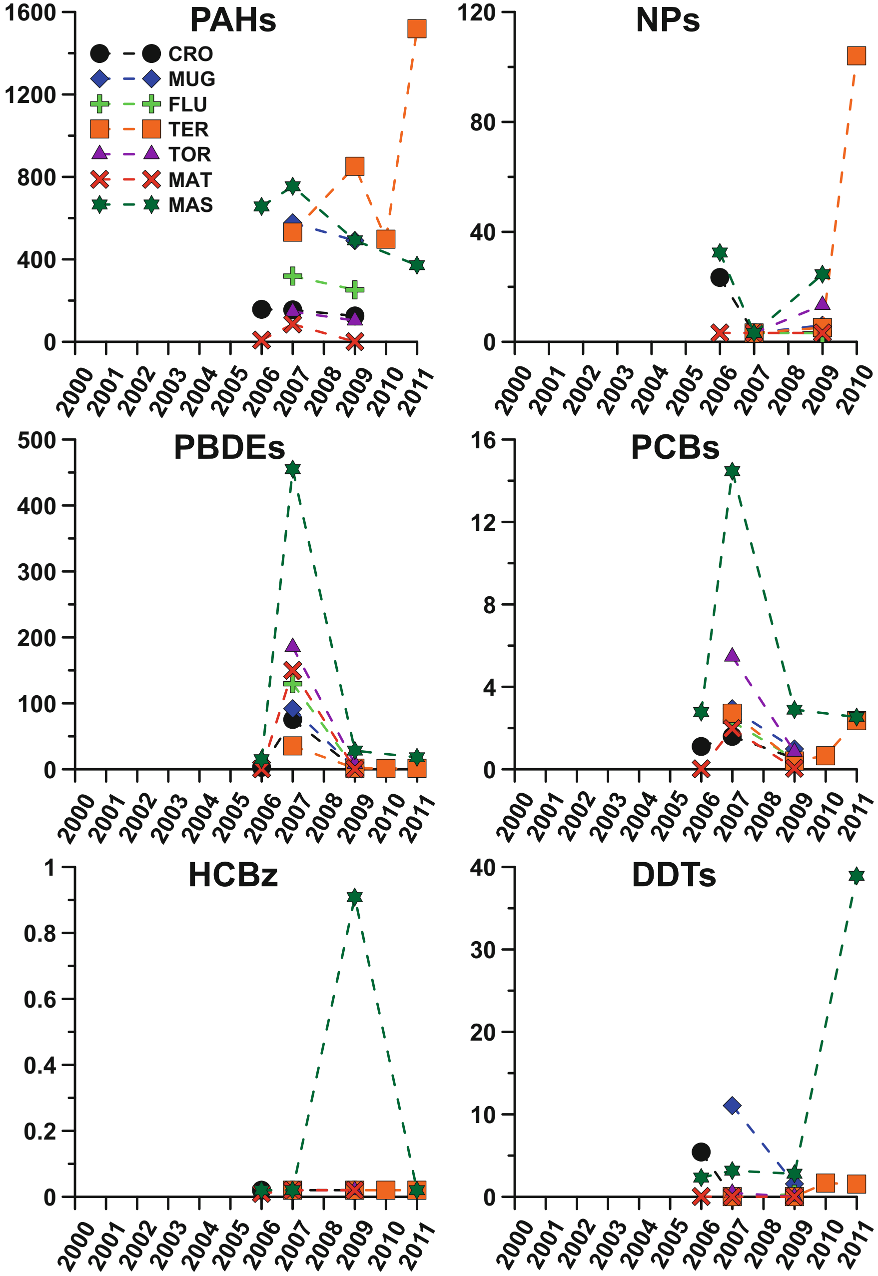


Fig. 6 Mean concentration of organic pollutants (μg kg^{-1}) in the study areas of the northern Catalan coast during each of the sampling years

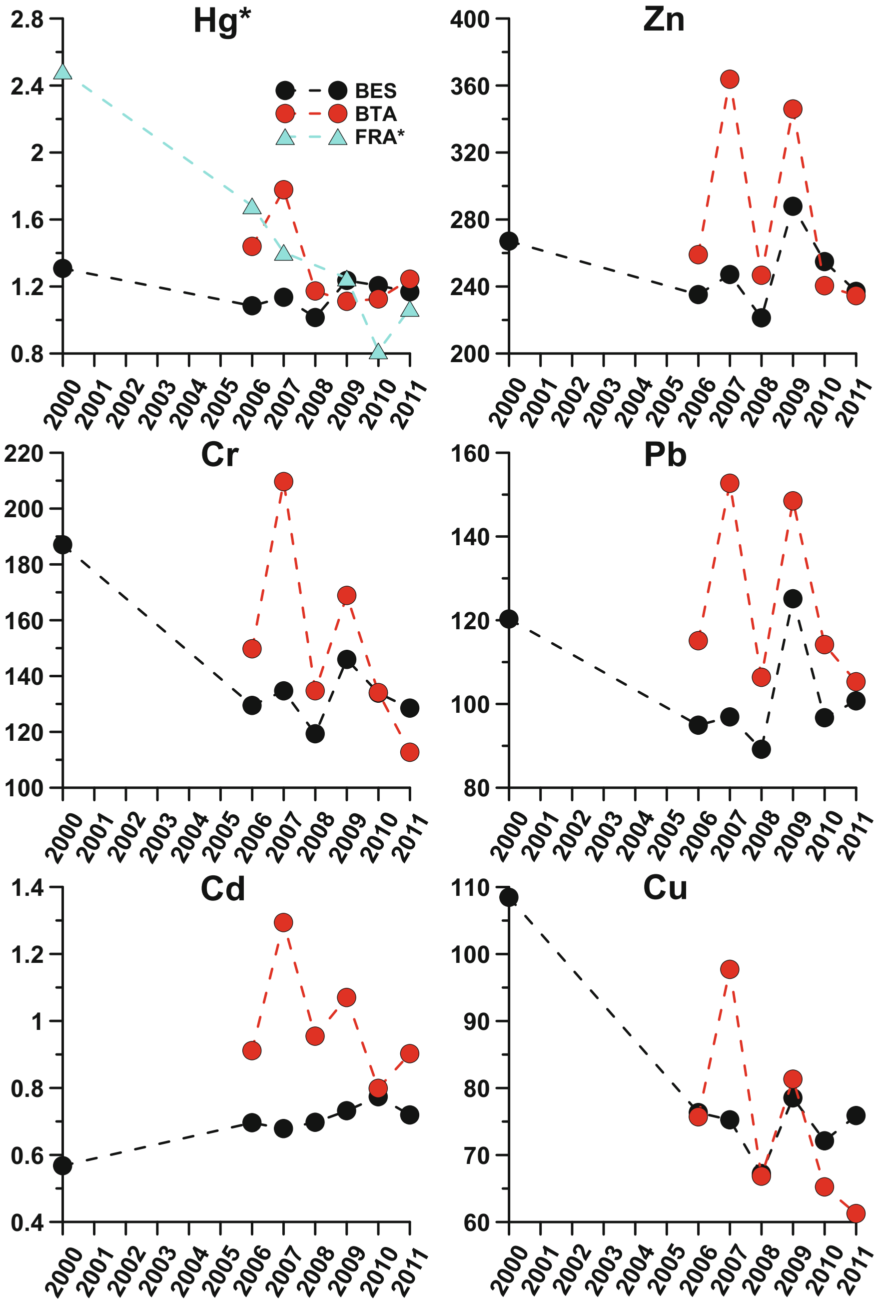


Fig. 7 Mean concentration of trace metals (mg kg^{-1}) in the study areas of the Barcelona city coast during each of the sampling years. *Hg of Francolí from the southern Catalan coast is represented in this figure because its concentration is of the same order of magnitude as those of the Barcelona city coast

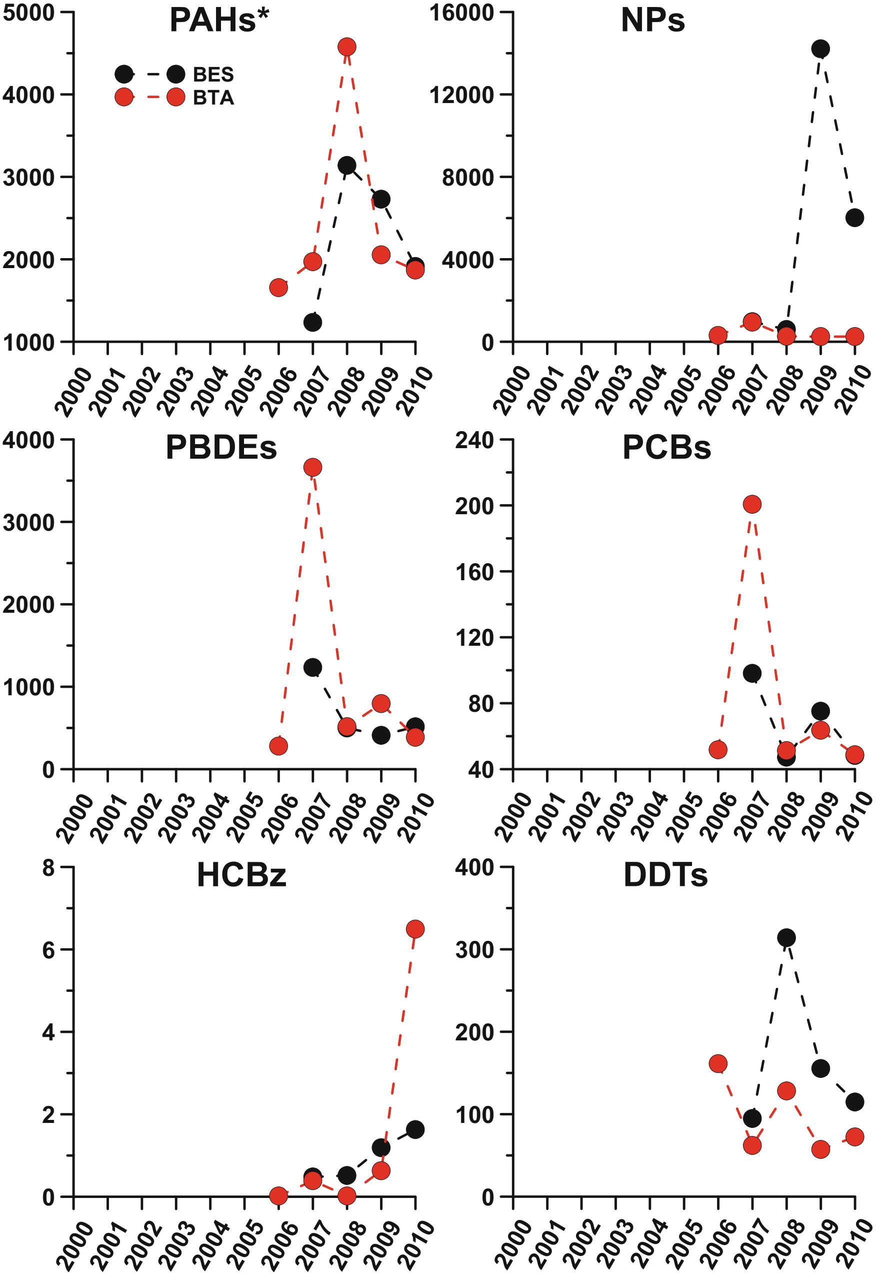


Fig. 8 Mean concentration of organic pollutants (μg kg^{-1}) in the study areas of the Barcelona city coast during each of the sampling years

3.1.3 Southern Catalan Coast

The areas of the southern Catalan coast are Llobregat, New Llobregat, Castelldefels, La Falconera, Foix, El Vendrell, Francolí, Cambrils, Fangar Bay, Ebre, and Alfacs Bay (Fig. 1). They include the basins of the Llobregat, Foix, Francoli, and Ebre Rivers. New Llobregat corresponds to the new Llobregat River mouth, which was moved 2 km southward artificially in 2004 to enlarge the Barcelona harbor. At La Falconera, there is a large dumpsite. The Francoli River mouth is in the harbor of the city of Tarragona. Most samples from this coast are mud with a fine fraction higher than 70%.

The southern Catalan coast was characterized by a gradual southward decrease of most trace metals, from significant pollution to near-natural levels and from general polluted areas to areas with only a few isolated points of pollution. The highest mean concentrations on the southern Catalan coast were at Llobregat and Castelldefels for Zn, Pb, and Cu; at Castelldefels for Cr; at Llobregat and La Falconera for Cd; and at Francolí for Hg. (Figs. 2 and 3). The highest mean Hg concentrations at Francolí were higher than those at Besòs and Barceloneta, with an EF of 34 and concentrations exceeding the ERM. However, the higher levels at Francolí only corresponded to a few samples with a maximum in those taken in 2000, whereas the high levels in the Barcelona city area (Besòs and Barceloneta) extended over a wider area than at Francolí. Hg concentrations of other samples at Francolí were similar to or lower than those at Besòs and Barceloneta. At Castelldefels the mean values and all the samples exceeded the ERM value for Hg (mean EF, 11), and at La Falconera and Foix, concentrations of Hg exceeded ERM values only in 2000. All the other samples from the southern Catalan coast exceeded the ERL value for Hg.

The mean and highest concentrations of Zn, Pb, Cr, and Cu only exceeded the ERL at Llobregat and Castelldefels, and Cd only exceeded the ERL at Llobregat and La Falconera in 2000 with an EF of 4. Toward the south of La Falconera, trace metal concentrations decreased to below the ERL. However, at Ebre trace metal concentrations increased slightly. Fangar Bay and Alfacs Bay are semi-enclosed bays that showed low pollution levels of Hg and Cd (EF around 2) and very low pollution levels of Zn and Cr (EF <1.4).

For the organic compounds, there was also a southward decreasing trend, except for HCBz and DDTs. HCBz showed maximum values at Francolí and Ebre, and DDTs concentrations also showed maximum values at Ebre. These two families of organic compounds are the only organic pollutants that reached the highest values on the southern Catalan coast in addition to the Barcelona city coast. PBDEs and PCBs showed great increases in all the areas of this sector in 2007. HCBz also showed high values at New Llobregat, Francolí, and Ebre in 2007 and at Ebre in 2011. DDTs increased at Ebre in 2007 and 2011 (Figs. 4 and 10). NPs values on the southern Catalan coast are low.

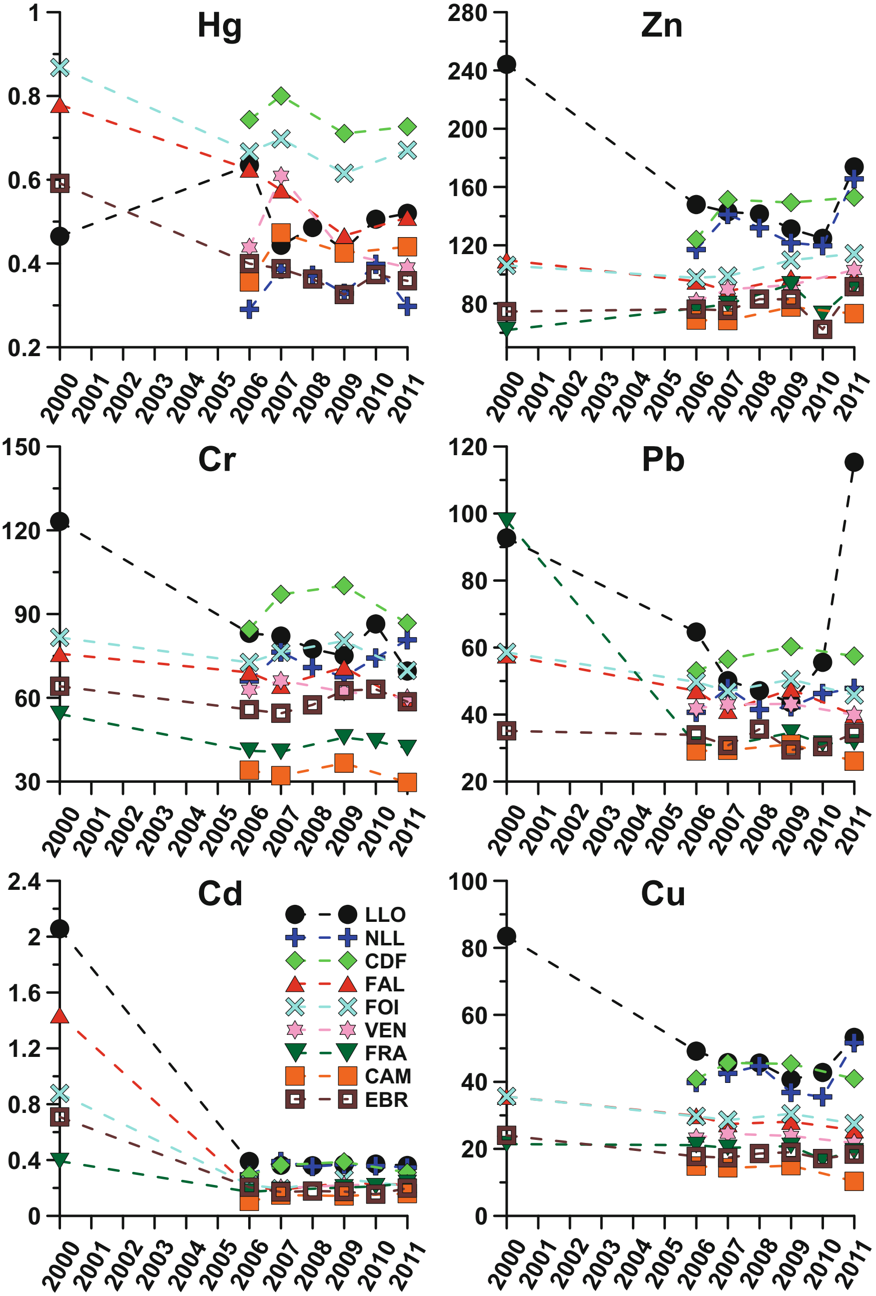


Fig. 9 Mean concentration of trace metals (mg kg^{-1}) in the study areas of the southern Catalan coast during each of the sampling years. Hg of Francolí is represented in Fig. 7 because its concentration is of the same order of magnitude as those of the Barcelona city coast

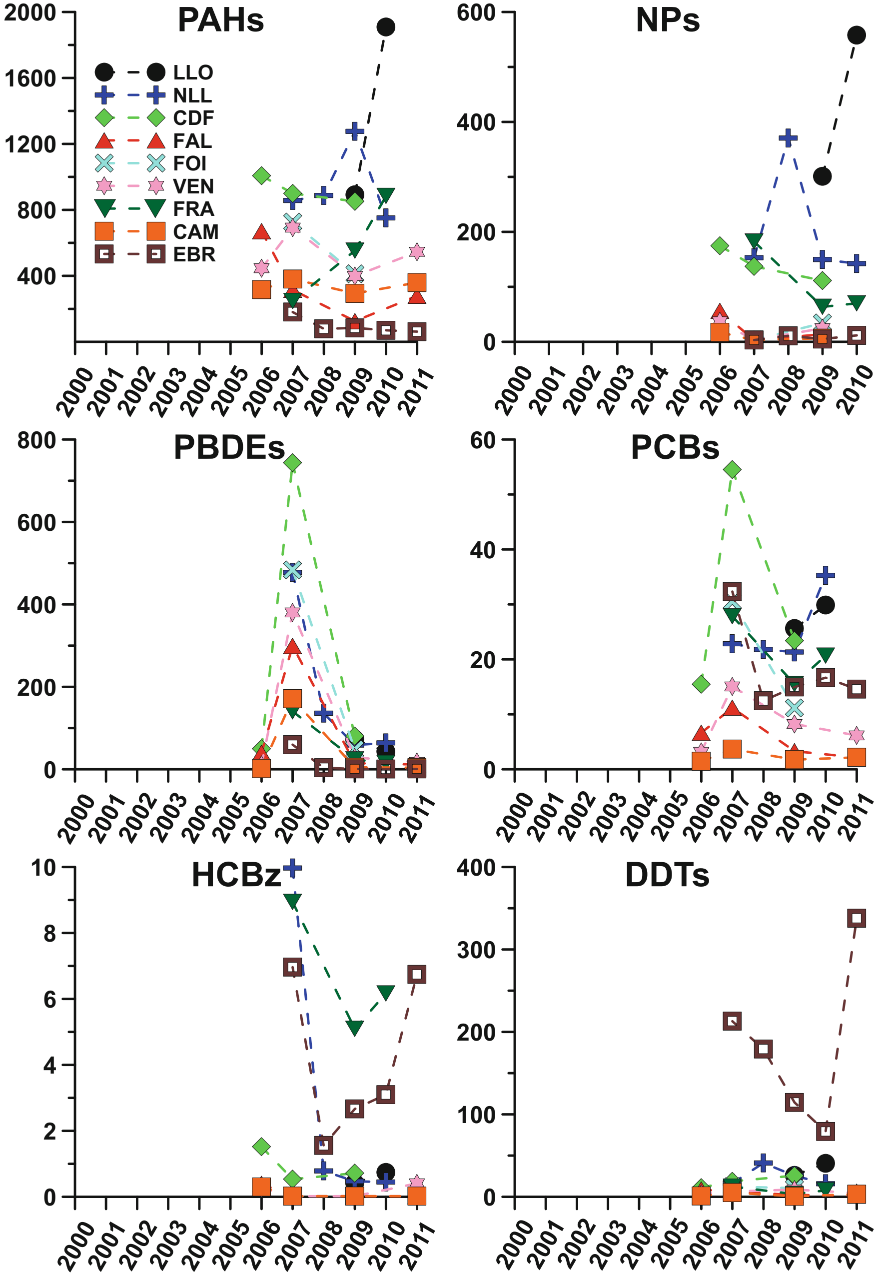


Fig. 10 Mean concentration of organic pollutants (μg kg^{-1}) in the study areas of the southern Catalan coast during each of the sampling years

3.2 Time Trends

Time trends of annual mean concentrations of trace metals in the monitored areas of the three sectors of the Catalan coast can be observed in Figs. 5, 7, and 9. On the northern Catalan coast, there are few clear trends because many samples have near-natural values of trace metals. Observing the difference between the samples taken in 2000 and those taken in 2006, Pb, Cr, and Cu decreased at Muga, Ter, and Tordera; Zn decreased at Ter; and Hg, Zn, and Cr increased slightly at Fluvià. However, comparing the samples taken in 2006 with those taken in 2011, Zn, Cr, Pb, and Cd increased in almost all the areas of this sector except Mataró. Other differences are small (Fig. 5). For organic compounds, there was no sampling in 2000 and in some years of the 2006–2011 period, so there are insufficient samples to define a trend in many areas. From the existing data, it seems that there was a major increase in PAHs and NPs at Ter and of DDTs at Masnou in 2011 and PAHs seem to have decreased at Masnou. Peaks of PBDEs and PCBs occurred in all the areas in 2007 (Fig. 6).

In the Barcelona city area, Hg, Zn, Cr, Pb, and Cu decreased at Besòs from 2000 to 2006 and only Cd increased in this period of time. However, considering only the annual mean concentrations from 2006 to 2011, these decreasing trends were not so clear (Fig. 7). At Barceloneta, there appears to be a decreasing trend for all the studied trace metals between 2006 and 2011, but there were peaks in 2007 and 2009. At Besòs, there were also peaks of some metals in 2009. For organic compounds, there were peaks of PBDEs and PCBs at Besòs and Barceloneta in 2007, of PAHs and DDTs at Besòs and Barceloneta in 2008, of NPs at Besòs in 2009, and of HCBz at BAR in 2011. HCBz seems to have shown an increasing trend at Besòs and Barceloneta, whereas PBDEs and PCBs decreased at Besòs and DDTs decreased at Barceloneta (Fig. 8)

On the southern Catalan coast, the trace metals decreased in all the areas between 2000 and 2006, with the exception of Hg at Llobregat and Zn at Francolí (Fig. 9). However, from 2006 to 2011, Zn increased in all the areas and Cd increased slightly. On the other hand, Hg, Cr, Pb, and Cu decreased slightly in most areas, and Cr, Pb, and Cu increased at New Llobregat and Castelldefels. For organic compounds, there were peaks of PBDEs and PCBs in all the areas in 2007. NPs and HCBz decreased at New Llobregat, Castelldefels, and Ebre (Fig. 10).

4 Discussion

Pollution on the Catalan coast is mainly associated with discharges from urban and industrial areas. The main urban area on the coast is Barcelona and its metropolitan area, and the second is Tarragona. Several small coastal cities and towns can also show local anomalies. The rivers transport trace metal and organic pollution from inland cities and industries. The main sources of industrial pollution in Catalonia

Table 3 Coastal cities with more than 20,000 inhabitants in the three sectors of the Catalan coast

Cities > 20 × 10^5 inh.	Population
Northern Catalan coast	
Lloret de Mar	40,282
Blanes	39,834
Premià de Mar	28,310
Pineda de Mar	26,040
Palafrugell	22,816
El Masnou	22,595
Mataró	123,868
Sant Feliu de Guíxols	21,814
Total	*325,559*
Barcelona city coast	
Barcelona	1,615,448
Hospitalet	256,065
Badalona	219,786
Santa Coloma de Gramenet	120,824
Sant Adrià de Besòs	341,57
Total	*2,246,280*
Southern Catalan coast	
Tarragona	134,085
Vilanova i la Geltrú	66,905
Viladecans	64,737
Prat de Llobregat	63,499
Castelldefels	63,139
Gavà	46,250
El Vendrell	36,454
Cambrils	33,008
Sitges	28,617
Salou	26,193
Calafell	24,984
Total	*587,871*

are located in the basins of the Besòs, Llobregat, Francolí, and Ebre Rivers [37]. In addition to rivers, other sources are wastewater plants, outfalls, storm sewers, and wind and rain events, which can also discharge significant amounts of pollutants.

On the northern Catalan coast, there are few populated coastal cities and few industrial areas. There are eight cities of more than 20,000 inhabitants which total about 325,000 inhabitants (Table 3). Landward, there are five cities with more than 20,000 inhabitants which total 226,000 inhabitants. Pollution load affecting this part of the coast is lower and is probably more diluted by the rivers discharging on it (the Muga, Fluvià, Ter, and Tordera) than is the case on the southern coast. The sediment discharged by rivers and accumulated on the northern coast often shows near-natural trace metal values and low organic pollution concentrations (Fig. 2). The Ter River has two large dams of 165 and 233 hm^3 along its course, whereas the

Muga River has a small one of 61 hm^3. Pollutants transported by these rivers are partially retained by these dams, but these rivers and the coastal towns produce some local anomalies at sea.

In contrast, in highly populated and industrialized areas, where the pollutant load affecting the rivers is higher, rivers are unable to dilute the concentration sufficiently to reach near-natural values. As a result, they are still discharging significant pollution into the sea and producing anomalies in the bottom sediments. This is the case of the Barcelona city coast, where more than two million inhabitants live in five cities (Table 3). In addition, more than 860,000 inhabitants live in 12 cities of more than 20,000 inhabitants located in the Besòs watershed. The Besòs River, the ancient Besòs wastewater treatment plant, and the sewers from Barceloneta have been generating high trace metal contents in the bottom sediment of the Besòs prodelta for decades [16, 38]. Also, most of the main representative families of organic pollutants are concentrated at Besòs and Barceloneta (Fig. 4). When the Besòs River discharge is low, most of it is treated in the Barcelona-Besòs wastewater treatment plant before being discharged into the sea, but when it is high, the plant is unable to process all of it and the rest goes directly into the sea.

DDT and its metabolites deserve particular consideration as their use was forbidden decades ago. There was an old industrial area of DDT affecting sensitive areas of the Besòs that was studied prior to the appearance of the WFD. However, our data indicate a recent contribution of DDT, apart from its known metabolites DDDs and DDEs.

In the case of NPs, although their use has declined significantly, probably due to their inclusion in the first list of priority pollutants [2455/2001/EC] and their values are low on most of the Catalan coast, a major isolated peak was still detected at Besòs, which should be noted as an exception to this decline.

On the southern Catalan coast, 11 coastal cities have a population of more than 20,000, totaling 580,000 people. A further 20 cities located inland in the watershed of the rivers discharging on this coast have a population of more than 20,000, bringing the grand total to one million people (Table 3). Some of the highest trace metal concentrations and organic pollutants are found around the Llobregat River mouth area, which receives the inputs from several populated cities and industries. The sediments from the Llobregat prodelta, although polluted, have lower trace metal contents than those of the Besòs prodelta. One of the reasons for this is that the Llobregat River has a mean water discharge three times higher than that of the Besòs River (Table 1 and Fig. 11). Therefore, the Llobregat has a higher dilution capacity, which probably helps to produce lower pollutant levels in the Llobregat prodelta sediments than in the Besòs prodelta sediments. The mouth of the Llobregat River was moved about 2 km southward in 2004 to enlarge the Barcelona harbor, and a wastewater treatment plant was built in 2006. However, our data show no clear effect of this move in the pollutants of the sediments of this area. Southward from the Llobregat River, there are eight coastal cities of more than 20,000 inhabitants between Castelldefels and Salou. The largest of these cities is Tarragona (133,000 inhabitants), where the Francolí River discharges into the harbor, causing major local anomalies of Hg and HCBz, as it is affected by the

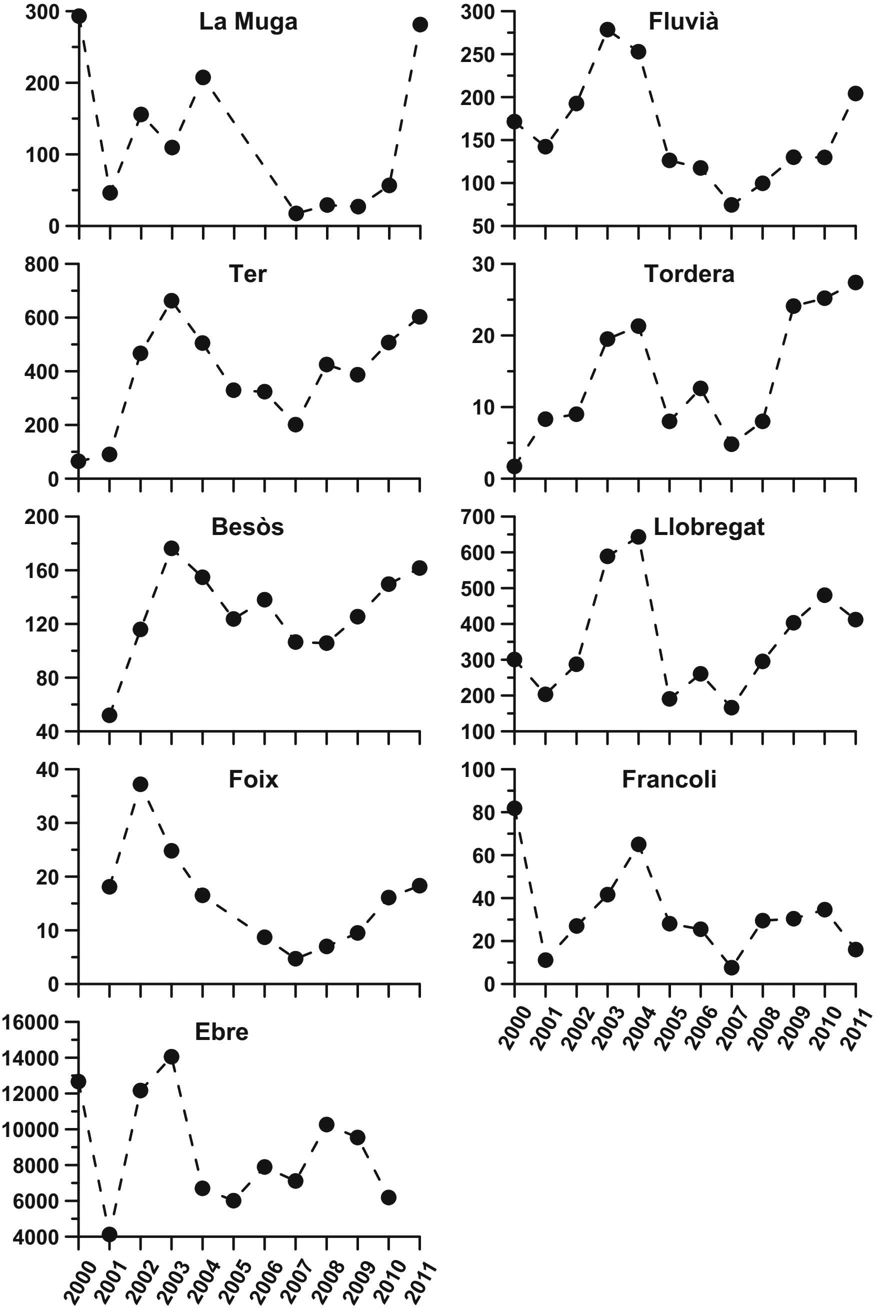


Fig. 11 Annual water discharge (hm^3) of the Catalan rivers from 2000 to 2011 (from idescat.cat)

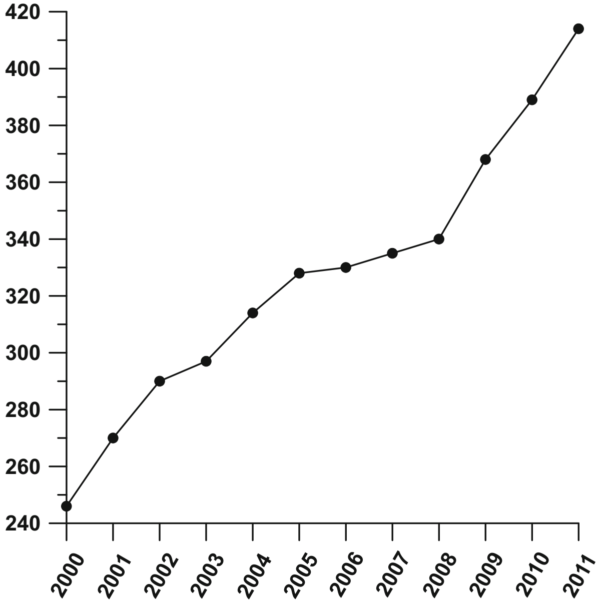


Fig. 12 Annual number of wastewater treatment plants working from 2000 to 2011 in Catalonia

activity of the city and the petrochemical industry. Southward from Salou, there are no populated cities and trace metals and organic pollutants decrease to low values. However, in the south, the Ebre River has a mean water discharge about two orders of magnitude higher than that of the other rivers (Table 1, Fig. 11). The lower part of this river is mainly affected by agriculture and some industry, such as the Flix Erkimia complex [28]. Upstream from the town of Flix, there are several dams along the Ebre River and its tributaries [39], which retain part of the pollutant load of this river [40]. Although this river has a much higher dilution capacity than the other Catalan rivers, there are Hg and Cd enrichments in the sediment accumulated around the Ebre Delta, as well as high values of HCBz and DDTs. As at Besòs, our data indicate a recent input of DDT. These pollutants break the southward decreasing trend. The explanation probably lies in the known contamination of the industrial chemical area of Flix (approx. 50 km from the river mouth), which is currently being treated.

Time trends in trace metals show a fairly general decreasing trend between 2000 and 2006. However, between 2006 and 2011, no clear trend is observed (Figs. 5, 7, and 9). Increasing trends are only observed for Cd at Ter and Besòs and for Zn at Tordera, Castelldefels, and Francolí. One of the reasons for the decreasing trend of trace metals between 2000 and 2006 is the continuous increase in the number of wastewater treatment plants in Catalonia (Fig. 12), including new plants on the Besòs and Llobregat Rivers. However, this increase does not explain why the trace metal levels remained similar from 2006 to 2011. The answer has more to do with the amount of water treated at these plants, which increased significantly from 2000 to 2003 and remained quite similar between 2006 and 2011 (Fig. 13).

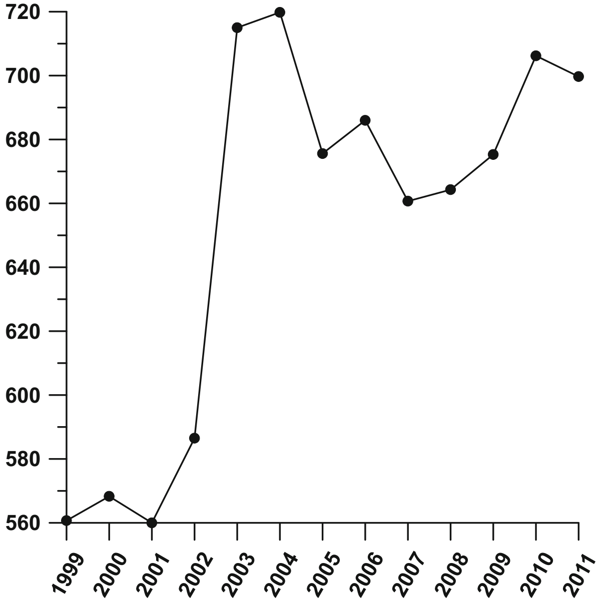


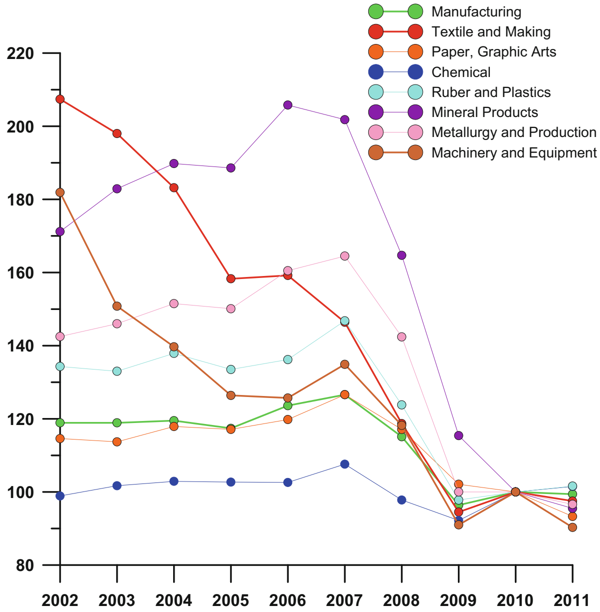
Fig. 13 Annual water outflow treated by wastewater treatment plants in Catalonia (hm^3)

Hydrodynamic processes must also be considered. From 2001 to 2006, 13 storm events with a significant deepwater wave height exceeding 3 m and a minimum duration of 70 h took place on the Barcelona city coast, whereas only six of these events occurred in the 2006–2011 period [41]. In addition, river water discharge also increased between 2002 and 2004 (Fig. 11). These storms and water discharge increases could have led to a decrease in trace metal levels of coastal sediments between 2000 and 2006 by resuspension and dilution.

Another cause of the trace metal decrease could be industrial production (Fig. 14). Textile and machinery and equipment production decreased sharply from 2000 to 2006 and continued to decrease until 2009. However, other industrial activities did not decrease until 2008. A strong decrease in all activities took place from 2008, but trace metal contents did not show this decrease in the monitoring carried out between 2008 and 2011.

In fact, some trace metals and organic pollutants increased in some areas in 2007, 2009, and 2011. These peaks of pollutants may have a variety of causes. The most general one could be the low water discharge of most rivers in 2007 (Fig. 11), which probably led to a lower pollutant dilution in most rivers and to peaks of several pollutants (PBDEs, PCBs, HCBz, Hg, Cr, Pb, Cd, and Cu) in 2007. In addition, the strongest storms of the 2006–2011 period occurred in 2008 and 2010 [41], with higher river discharge than in 2007 (Fig. 11), which could have reduced the levels of some pollutants on the Barcelona coast. The peaks in 2009 only occurred on the Barcelona city coast for NPs, Zn, Cr, Pb, Cd, and Cu and were related to an anomalous discharge of the Besòs wastewater treatment plant.

Fig. 14 Industrial Production Index (IPI). Annual means (Base 2010 = 100)



Finally, other causes could have contributed to these peaks. For example, (a) economic problems in management of wastewater treatment plants due to the crisis could have led to a lower reduction of the pollutant discharge, (b) industry could have invested less in environmental care, (c) the pollution generated during the pre-crisis times and retained in fluvial traps (meanders, small dams, etc.) could have been discharged in the following years, and (d) the pollution accumulated in coastal sediment could have been resuspended and redistributed on the coastal seabed.

If we compare the mean trace metal concentrations of the first and last year of monitoring in each zone, a dominant decreasing trend is observed on the Barcelona city coast and the southern Catalan coast (Figs. 7 and 9). In most cases, the most polluted zones (Besòs, Barceloneta, Llobregat, La Falconera, and Francolí) are the ones that show the highest decrease between the first and the last sampling year. The available data on organic pollutants show no dominant trend.

If we compare the data from this study with those from studies carried out in the 1980s and 1990s [14, 16, 17, 23, 42], in some areas, we observe that at Besòs maximum levels of Pb and Cd decreased by one order of magnitude, maximum levels of Cr and Cu decreased fourfold, and maximum levels of Hg decreased by half. At Llobregat, Cr, Pb, and Cu maximum concentrations decreased by a quarter. These comparisons must be taken with care, as methods and analytical equipment have changed, and the position of the compared samples is different. However, it is evident that this decrease is related to the installation of more efficient water treatment systems and the establishment of new environmental laws that have restricted the use of many pollutants over the last decades, as stated by Pinedo et al. [43], who monitored trace metals in shallow sediments (most of them taken between 6 and 12 m depth) along the Catalan coast in 2002, 2003, 2007, and 2010. Although most of these samples were sands with less than 10% of mud, these authors also detected maximum trace metal concentrations in Barcelona and Tarragona. However, most of the trace metal concentrations detected in this study were lower than those of our study, and pollution levels were not identified in several areas where we detected anthropogenic metal enrichments. Pinedo et al. [43] found increases between 2003 and 2007 and decreases in 2010.

5 Conclusions

This study allows the Catalan coast to be divided into three sectors in terms of trace metal pollution. The northern Catalan coast, from the French border to the town of Mataró, showed natural or near-natural levels, with isolated pollution at some points. The Barcelona city coast showed very high pollution for most of the studied pollutants, especially Hg, Cd, PAHs, PBDEs, and NPs. Finally, the southern Catalan coast showed significant pollution decreasing southward with isolated maximum values of Hg and HCBz at Francolí and maximum values of HCBz and DDTs at Ebre.

The Catalan coast showed considerable pollution of Hg along two-thirds of its length, between Mataró (Barcelona Metropolitan Area) and the Ebre Delta. The main Hg pollution is associated with areas of intense industrial and urban activities (Besòs, Barceloneta, Francolí). Mean Hg concentrations at Besòs, Barceloneta, and Francolí exceeded the ERM value in all years monitored, reaching a maximum mean EF of 33 at Francolí. Mean Hg concentration also exceeded the ERM value at La Falconera and Foix in 2000.

Cd exhibited a similar behavior to Hg but with lower anomalies, reaching maximum EF values of 6.5. It had maximum concentrations on the Barcelona city coast but not at Francolí. Although Cd concentrations were high, they rarely reached the ERL value. The sources were the same as those of Hg.

Cr, Pb, Cu, and Zn also showed levels indicative of pollution, but with a lower EF than Hg and Cd (EF: 3.5-4). They also showed higher values on the Barcelona city coast and decreasing values southward.

Similarly to trace metals, most of the main representative organic families are strongly concentrated on the Barcelona city coast, which receives the organic pollution of the industrial and urban conurbation of Barcelona. This includes the emerging pollution of the PBDEs family and exceptionally the NPs family at Besòs, although their use is declining. Maximum values of DDTs and HCBz at Ebre can be related to the Flix industrial complex and maximum HCBz at Francolí to the Francolí River inputs and the Tarragona harbor.

Rivers generate anomalies in coastal sediment depending on their pollutant load and their capacity to dilute it in their water discharge. In the case of the Besòs River, the pollutant load is too high to be sufficiently diluted by the river water and dispersed by coastal processes. Trace metals showed a dominant decreasing trend between 2000 and 2006 on the Barcelona city and southern Catalan coasts, the most polluted areas being the ones that show the sharpest decrease. This decrease can be due to an increase in the water treated in wastewater treatment plants and to natural causes (dilution by storms and water discharge). The pollutant peaks in 2007 can be associated with dryness and those in 2009 on the Barcelona coast can be associated with malfunctioning of wastewater treatment plants. Economic cuts reducing the observance of environmental policies and the redistribution of ancient pollutants could also have contributed to pollutant increases during some of the crisis years.

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