Environ Monit Assess (2011) 176:385–401
DOI 10.1007/s10661-010-1591-4

Organochlorine pesticide residues in sediments from coastal environment of Cantabria (northern Spain) and evaluation of the Atlantic Ocean

Sonia Gómez · Daniel Gorri · Ángel Irabien

Received: 2 October 2009 / Accepted: 15 June 2010 / Published online: 10 July 2010

Abstract This paper documents levels of organochlorine pesticides (OCs) in coastal surface sediments from selected reference sites on the northern Atlantic Spanish coast. One hundred eight samples covering three estuaries in the Cantabrian Coast were sampled in 2006 and analyzed in the finer fraction (<63 μm) for 19 OCs by gas chromatography with electron capture detector after confirmation by mass spectrometry. Detected organochlorine pesticides were endosulfan α, endosulfan β, endosulfan sulfate, hexachlorobenzene (HCB), aldrin, dieldrin, methoxychlor, 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene (4,4′-DDE) and 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (4,4′-DDD). Total OCs concentrations ranged from 1.8 ng g^{-1} dry weight (dw) to 3.9 ng g^{-1} dw, showing a uniform distribution along the studied area, and being consistent with recorded levels in the literature for coastal sediments in other reference sites with low levels of pollution by OCs along the Atlantic Ocean. Endosulfan, 4,4′-DDD, HCB, aldrin, and dieldrin seemed to be ubiquitous as the legacy of past uses and deposition. OCs concentrations were significantly correlated to organic matter content and particle size distribution. No adverse biological effects derived from these pollutants are expected to take place as it can be concluded from the comparison with the existent marine sediment quality guidelines.

Keywords Organochlorine · Pesticides · Marine sediments · Cantabria · Ecotoxicological · SQGs

Introduction

Organochlorine pesticides (OCs) integrate the semi-volatile persistent organic pollutants (POPs) and as persistent, bioaccumulative, and toxic (PBT) substances present a risk to the environment because they have been associated to significant environmental impact in a wide range of species and at virtually all trophic levels (Lohmann et al. 2007; UNEP 1996). Due to their resistance to chemical, photochemical, and biological degradation they persist in various media to such extent that despite having been forbidden in most countries in 1970s they can be found in soils, sediments, biota, and even in human blood and tissues (Cerrillo et al. 2006; Lee et al. 2001; Fillmann et al. 2002; Hernández et al. 2002; Jan et al. 2009; Liu et al. 2003; Stern et al. 2005; Chang and Doong 2006; Fontcuberta et al. 2008; Gómez-Gutiérrez et al. 2007; Pikkarainen 2007; Hong et al. 2008; Porta

S. Gómez (✉) · D. Gorri · Á. Irabien
Departamento de Ingeniería Química y Química Inorgánica, ETSIIyT, Universidad de Cantabria, Avda. de los Castros s/n, 39005 Santander, Cantabria, Spain
e-mail: gomezs@gestion.unican.es

et al. 2008; Hu et al. 2009; Malik et al. 2009). Of major concern is the fact that POPs are even present in areas that can reasonably be considered not to have received many direct applications (Bard 1999; Macdonald et al. 2000). Values for coastal areas of Norway have been reported by Jiao et al. (2009), where total dichlorodiphenyltrichloroethanes (DDTs) can reach 0.28 ng g^{-1} dry weight (dw) or even 1.2 ng g^{-1} dw for hexachlorocyclohexanes (HCHs). They are distributed globally via atmospheric transport mechanisms (Wania and Mackay 1996) and a major fraction is known to be originated from some countries around the tropic and subtropic belts where some OCs (DDTs, HCHs, and endosulfan) are still used for agricultural and health purposes.

Another important property of organochlorines is lipophilicity and thus OCs are liable to bioaccumulate on fat tissues and may be biomagnified as they are transferred to higher trophic levels through the food web chain, mainly on aquatic environments (Lee et al. 2001). To reduce their potential to cause environmental and human harm, national and international controls on their production and use, such as the Stockholm Convention on Persistent Organic Pollutants (UNEP 2001) and Regulation 850/2004 (EC 2004) have been introduced. To develop an effective control mechanism, relevant research and more information on their sources, distribution, levels, and transport is needed. These instruments encourage European and signatory countries of the Stockholm Convention, among others, to assess regional contamination by OCs and POPs.

OCs have a great affinity for particulate matter so they can be deposited in the aquatic systems during sedimentation and can remain in sediments for very long due to their long half-life times. Important factors controlling sorption of OCs to sediments are mainly surface area and organic matter content, apart from other physico-chemical properties like pH, cation exchange capacity, or ionic strength (Karickhoff et al. 1979; Iwata et al. 1994; Delle Site 2001). OCs enter the marine environment from the agricultural cultivations, drainage, runoff, and atmospheric deposition (Odete and Vale 1999) so estuaries are one of the main reservoirs of pesticides and, in particular, sediments can act as long-term sinks for these anthropogenic contaminants or as a source from which residues can be released to the atmosphere, water, or living organisms (Kilemade et al. 2004). Sediments are one of the best media for monitoring of organic compounds as they provide a valuable record of contamination in aquatic environments (Chang and Doong 2006).

In Spain organic pollutants have been well documented in the Mediterranean Sea, based on the monitoring concentrations in sediments (Tolosa et al. 1995; UNEP 2002; Peris et al. 2005; Gómez-Gutiérrez et al. 2007) as well as the establishment of background concentrations in Mediterranean sediments (Gómez-Gutierrez et al. 2007). Nevertheless, the Cantabrian Coast, in northern Spain, shows only few available data for OCs in the Basque Country (Borja et al. 2005) and Galicia Coast (Observatorio Medioambiental de la Ría de Vigo 1996). Limited information is available regarding persistent organic substances in marine sediments from Cantabria, where only data of PAHs and PCBs are available (Viguri et al. 2002; González-Piñuela et al. 2006; Antizar-Ladislao 2009). There is not a comprehensive study of sediment pollution by organochlorine pesticides in the Cantabrian Coast, where important estuaries are subject to the discharge of rivers like Asón, Pas-Pisueña, and Nansa, with a total catchment area draining into the Sea that covers the major agricultural areas in the region.

Baseline and current concentration levels are needed in determining the effectiveness of present international and European controls. Therefore, the aim of this study is to provide information on the current status of organochlorine pesticides in the Cantabrian Coast in nature reserves and areas of low anthropogenic impact, and subsequently examines their possible sources and relationships with sediments characteristics. Furthermore, it compares the measured pollutants with those reported in the literature for other low contaminated areas in the world, emphasizing the Atlantic Ocean areas, and provides an ecotoxicological evaluation of the measured concentrations in the sediments. Bearing this in mind, this study provides, to our knowledge, the first published research about these contaminants in sediments from Cantabria and data gather very valuable baseline concentrations for the future evaluation.

Materials and methods

Studied area

Cantabria is located in the north of Spain and in its north face it is surrounded by the Cantabrian Sea, where many small rivers from the region flow into. Three sampling sites located in the estuaries of the main rivers (Fig. 1) were selected to accomplish the sampling: Santoña (ST), Mogro (MG), and Tina Menor (TM). Santoña site is located within the Santoña Marshes Nature Reserve, one of the most important ecosystems of the Spanish Cantabrian Coast, which receives water from the river Asón. It is affected by a nearby marina and fishing harbor, industrial effluents from foundry, and transformation of non-ferroalloys activities, from the extraction and manufacture of calcined and sinterized dolomite and effluents from municipal wastewater treatment plants. Mogro

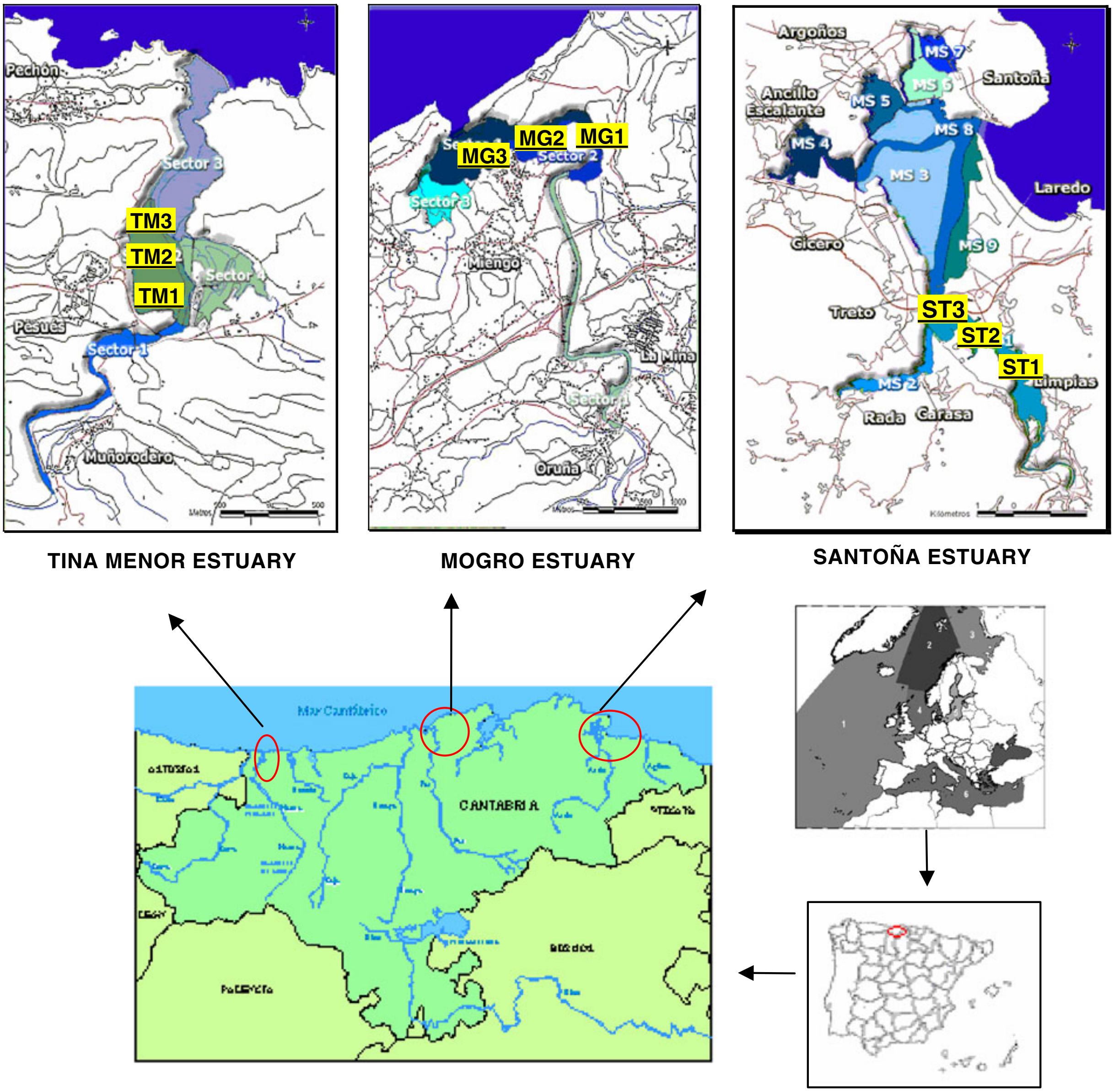

Fig. 1 Sediment sampling sites location in the region of Cantabria

estuary receives water from Pas-Pisueña rivers which are affected by effluents from municipal wastewater treatment plants and industrial effluents from dairy and other foodstuffs plants. Tina Menor estuary is affected by aquaculture activities and it receives water from the river Nansa, which is affected by effluents from small municipal wastewater treatment plants.

Samples

Inter-tidal surface sediments were sampled in triplicate at low tide from nine stations (Fig. 1) located in northern Spain according to standard protocols (UNE-EN ISO 5667-19 2004; US-EPA 2001). Squared patterns formed by cells of 1 m^2 were delimited prior to sample collection and the upper 10 cm of the surface sediments were sampled using a solvent-washed stainless steel spatula. Samples from each station were thoroughly mixed to ensure that the sediment collected was truly representative of each station. Sub-samples of the sediment were subsequently taken for analysis and stored in solvent-washed glass jars before transportation to the laboratory where they were air dried. Three surface sediment samples were collected during each season of the year 2006 per each one of the three stations in the estuary of Santoña (ST1, ST2, and ST3), Mogro (MG1, MG2, and MG3), and Tina Menor (TM1, TM2, and TM3), collecting a total of 36 samples per estuary during the four campaigns carried out in winter, spring, summer, and autumn. So a total of 108 sediment samples were collected for this survey.

Reagents and chemicals

Acetone, n-hexane, dichloromethane, and methanol Suprasolv® grade were provided by Merck (Darmstadt, Germany). Copper metal, nitric and hydrochloric acids for analysis were purchased from Panreac (Barcelona, Spain). Water was purified on a Milli-Q system from Millipore (Bedford, MA, USA).

Soil standard of hexachlorobenzene Pestanal® was supplied by Sigma-Aldrich (Steinheim, Germany). The standard of organochlorine pesticide mixture from Supelco consisted of a solution in n-hexane–toluene (1:1, *v*/*v*) at 2,000 μg mL^{-1} of α-hexachlorocyclohexane (α-HCH), β-hexachlorocyclohexane (β-HCH), γ-hexachlorocyclohexane (γ-HCH), δ-hexachlorocyclohexane (δ-HCH), endosulfan α, endosulfan β, endosulfan sulfate, aldrin, dieldrin, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (4,4′-DDT), 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (4,4′-DDD), 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene (4,4′-DDE), methoxychlor, and hexachlorobenzene (HCB).

A standard solution of 2,4,5,6-tetrachloro-*m*-xylene and dibutylchlorendate in n-hexane–toluene (1:1, *v*/*v*) at 2,000 mg mL^{-1} was purchased from Supelco to use as internal standard. A certified reference material 1944 was supplied by the US National Institute of Standards and Technology (Gaitherburg, ND, USA).

Physico-chemical characterization of the sediments

Physical characterization of the sediments included determination of loss on ignition (LOI), the total organic carbon fraction (TOC), the water content, and the <63 μm fraction as well as pH. Three replicates of all the physico-chemical properties were made. LOI was measured taking into account the standard procedure UNE-EN 12879 (2001) by means of a Hobersal Mod 12PR/300 furnace. Total organic carbon contents were determined by method UNE-EN 13137 (2002). Three grams of the dried sediment samples were acid-treated with 10% (*v*/*v*) hydrochloric acid for removal of inorganic carbon, mainly present as carbonate. After acid reaction is completed, samples were dried at 60°C. TOC was determined with an elemental analyzer (CHNS-O EA 1110 model from ThermoQuest- CE Instruments). The water content was determined by measuring the weight loss of a sediment subsample in an oven at 110°C until constant weight according to standard procedure UNE-EN 12880 (2001). Particle size distribution was performed by dry sieving according to method UNE-EN 77314 (2001). Sediments were divided into three fractions: silt and clay (<63 μm), sands (63 μm–2 mm), and gravel (>2 mm). Each fraction was weighed and expressed as percentage of the total weight. Standard procedure UNE-EN 77305 (1999) was followed to the pH determination.

Extraction and cleanup

EPA standard methods have been applied for the determination of OCs in sediments. The microwave-assisted extraction (MAE) of OCs in the sediments was performed according to the EPA 3546 standard method (US-EPA 1999). Aliquots (2 g) of air-dried and homogenized sediments (particle size <63 μm) were mixed with copper powder to remove elemental sulfur and prepared by treating the metal copper with diluted nitric acid and then rinsing it firstly with organic-free reagent water and secondly with methanol and dichlorometane. MAE was carried out in a CEM (Mathews, NC, USA) MARS 5X microwave accelerated reaction systems with 25 mL of n-hexane–acetone (1:1, *v*/*v*). The microwave extraction conditions were as follows: extraction temperature, 110°C; microwave oven power, 1,200 W (100%); and extraction time, 15 min. After cooling vessels at room temperature, the supernatants were filtered through 0.45 μm PTFE filters (Teknokroma, Barcelona, Spain). The volume of the extracts was reduced to 1 mL using a Zymark Turbo Vap LV evaporator (Hopkinton, MA, USA) provided with a nitrogen blowdown and a water bath at 45°C. The sample clean-up was performed by solid phase extraction (SPE), according to the EPA 3620B standard method (US-EPA 1996), in a SPE Vacuum Manifold (Waters, Barcelona, Spain). The SPE procedure was accomplished using Florisil® cartridges (6 cc, 1 g) from Waters, which were preconditioned with 4 mL of n-hexane. The sample volume was applied to the cartridge and finally, OCs were eluted with 9 mL of n-hexane–acetone (90:10, *v*/*v*). The solvent phase was concentrated gently under a nitrogen stream down to a volume of 0.5 mL for GC analysis.

Instrumental analysis

An aliquot of 2 μL of the final extract was injected into a gas chromatograph (Hewlett Packard HP 6890) equipped with a ^{63}Ni electron capture detector (ECD) and split/splitless injector. The column was a HP-5 capillary column (cross-linked 5% phenyl-methyl silicone, 30 m length, 0.25 mm i.d., and 0.25 μm film thickness). The oven temperature was programmed from an initial temperature of 110°C (1.5 min hold) to 150°C at a rate of 40°C/min, maintained at 150°C for 2 min, and then programmed to 275°C at 2.5°C/min, held for 2 min. Injector and detector temperatures were maintained at 230°C and 300°C, respectively. Helium was used as the carrier gas with a flow rate of 1.8 mL/min and nitrogen, as the make-up gas, was controlled at 60 mL/min. Quantification using the ECD was performed by reporting the measured integration areas in the calibration equation of the corresponding standards. The concentrations for each sample were calculated based on the peak area of the target analytes relative to the peak area of the internal standards 2,4,5,6-tetrachloro-*m*-xylene and dibutylchlorendate. For quantification of pesticides α-HCH, β-HCH, γ-HCH, δ-HCH, HCB, aldrin, heptachlor, and heptachlor epoxide, the standard 2,4,5,6-tetrachloro-*m*-xylene was employed and for the rest of the pesticides dibutylchlorendate was used. Calibration solutions for gas chromatographic analysis were prepared by the appropriate dilution of a standard solution containing the 19 pesticides. The concentration range of each pesticide was from 0.25 to 5 μg L^{-1} and the internal standards used in quantification at a concentration of 1 μg L^{-1}.

All of the sediment samples were triplicates and the relative standard deviation (RSD) for the method was determined. Confirmatory analysis was carried out by injecting an aliquot of 2 μL of the final extract in a 6890N gas chromatograph (Agilent Technologies, Barcelona, Spain) equipped with a 5975 inert mass spectrometer, also from Agilent Technologies. Injector temperature was 250°C, and the transfer line temperature was 280°C. MS detection was performed in single-ion monitoring mode after a solvent delay time of 3 min; the ion energy used for the electron impact was 70 eV. The selected mass/charge fragments (m/z) used for the identification are listed in Table 1. OCs identification was carried out by comparison of their retention times and mass spectra with those of the standards.

Table 1 Identification fragments of the OCs analyzed by GC/MS, limits of detection and quantitation, regression coefficients of the calibration curves for OCs in standard solutions, mean recoveries, and relative standard deviations (% RSD)

OCs	Identification fragments (*m*/*z*)	LOD (ng g^{-1}dw)	LOQ (ng g^{-1}dw)	Correlation coefficient	Mean recoveries (%)	RSD (%)
Hexachlorobenzene	284, 142, 249	0.11	0.31	0.9991	64	14
α-HCH	181, 219, 111	0.03	0.21	0.998	68	7
β-HCH	181, 219, 109	0.03	0.13	0.997	96	7
δ-HCH	181, 219, 109	0.04	0.20	0.994	80	11
γ-HCH	181, 219, 109	0.03	0.19	0.998	74	5
Endosulfan α	207, 195, 237, 170	0.06	0.21	0.9998	75	13
Endosulfan β	205, 195, 237, 159	0.06	0.21	0.998	95	5
Endosulfan sulfate	271, 229, 237	0.03	0.17	0.998	85	8
Aldrin	66, 263	0.09	0.20	0.996	69	22
Dieldrin	79, 262	0.10	0.29	0.998	79	8
Endrin	81, 262, 67	0.05	0.16	0.998	85	6
Endrin aldehyde	67, 250, 345	0.03	0.15	0.9993	64	3
Endrin ketone	67, 317	0.03	0.18	0.997	115	16
Heptachlor	100, 272, 65	0.21	0.38	0.9998	83	23
Heptachlor epoxide	81	0.05	0.21	0.997	67	8
Methoxychlor	227	0.06	0.18	0.998	99	4
4,4′-DDD	235, 237, 165	0.02	0.11	0.9991	84	10
4,4′-DDE	246, 248, 318	0.08	0.15	0.9995	84	5
4,4′-DDT	235, 237, 165	0.07	0.17	0.998	90	15

Statistical analysis

Bivariate correlations between OCs content and physico-chemical properties of coastal marine sediments were analyzed. All the statistical tests were conducted with SPSS Version 18.0. Statistical significance between paired values was considered for a confidence level greater or equal to 95%.

Results and discussion

Analytical performance

The quality assurance and quality control procedures included analyses of blanks, matrix spikes, triplicates, and certified reference material. A procedural blank was run in parallel with every batch of six samples using powder copper and then extracted in a manner identical to that of the samples. No OCs were found in blanks. The limit of detection (LOD) for each OC was estimated as three times the signal (peak height) of the background noise, and the limit of quantitation (LOQ), as ten times the signal (peak height) of the background noise or as the lower limit of the linear range of the calibration curve when this value was higher than the previous one. Table 1 shows LODs and LOQs for the 19 studied OCs as well as the regression coefficients of the calibration curves in standard solutions after GC-ECD analysis. It is shown that the LODs ranged from 0.02 ng g^{-1} dw for 4,4′-DDD to 0.21 ng g^{-1} dw for heptachlor and LOQs ranged from 0.11 ng g^{-1} dw for 4,4′-DDD to 0.31 ng g^{-1} dw for hexachlorobenzene. The correlation coefficients were in the range of 0.994–0.9998. Recoveries were determined by analyzing a separate set of matrix spikes, prepared by addition of 50 μL of a standard solution containing the 19 pesticides (10 μg L^{-1}) to sediment samples that do not contain the studied analytes and conducted through the entire analytical procedure in triplicates. Mean recoveries are shown in Table 1 and ranged from 64% for endrin aldehyde (RSD = 3%) and for HCB (RSD = 14%) to 115% for endrin ketone (RSD = 16%). Maximum RSD was found to be 23% for heptachlor, indicating that the analytical method in this study can accurately determine pesticides in sediment samples for most of the analytes studied. OCs measurements were corrected with recoveries. An appropriate standard reference material from the National Institute of Standards and Technology, NIST 1944, consisting of marine sediment containing five of the OCs studied (HCB, α-HCH, 4,4′-DDT, 4,4′-DDD, and 4,4′-DDE) was analyzed in triplicate to evaluate the method performance. Results are shown in Table 2.

Physico-chemical characteristics of sediment samples

The results of the physico-chemical properties of sediment samples from the three sampling sites in the Cantabrian Coast are shown in Table 3, expressed as the average value and their standard deviation for the analyses of the different sediments sampled at each one of the four seasons during 2006. These parameters included water content, TOC, LOI, silt–clay content, and pH. The water content ranged from 32% to 41%. The organic matter of sediment was in the range of 0.9% to 1.9%. LOI values ranged from 5.3% to 9.4%. The maximum values of organic matter were observed at Santoña Estuary. There were no significant differences in the <63 μm fraction, TOC, and pH among the three sites.

Levels of pesticide residues in sediments and comparison with previous reported concentrations

Table 3 shows the average concentrations of OCs in the seasonally analyzed surface sediment samples from the three estuaries in Cantabria, measured in the fraction of sediments <63 μm and expressed in terms of dry weight. The analyzed sediment samples show the presence of 4,4′-DDE, 4,4′-DDD, aldrin, dieldrin, endosulfan α, endosulfan β, endosulfan sulfate, methoxychlor, and hexachlorobenzene above the detection limits of the analytical method. Concentrations of OCs ranged from trace levels to 1 ng g^{-1} dw for hexachlorobenzene, trace levels to 0.3 ng g^{-1} dw for endosulfan β, n.d. to 0.6 ng g^{-1} dw for endosulfan α, 0.4 to 0.5 ng g^{-1} dw for aldrin, 0.4 to 0.7 ng g^{-1} dw for dieldrin, 0.3 to 0.4 ng g^{-1} dw for methoxychlor, 0.2 to 0.5 ng g^{-1} dw for 4,4′-DDD, and trace levels to 0.4 ng g^{-1} dw for 4,4′-DDE. For endosulfan sulfate, in all cases the concentrations were below the quantification limits. Throughout the studied area, it can be observed that the mean concentrations were 0.5–0.9 ng g^{-1} dw for total DDTs, 1.3–1.9 ng g^{-1} dw for cyclodiene pesticides (aldrin, dieldrin, endosulfan isomers, and endosulfan sulfate), and from trace levels to 1 ng g^{-1} dw for hexachlorobenzene. Aldrin, dieldrin, endosulfan isomers, endosulfan sulfate, and 4,4′-DDD were uniformly distributed among the studied sites as no significant differences were found for both the spatial distribution among the three estuaries and the temporal distribution along the whole year. The average ratio of total organochlorine pesticides for ST site was 1.8 ng g^{-1} dw, 3.7 ng g^{-1} dw for MG site, and 2.5 ng g^{-1} dw for TM site and for the whole study area, it can be deduced from the previous data that this amount is relatively constant at an average value of 2.6 ng total pesticides g^{-1} dw for surface marine sediments, which can be assigned to a relatively unpolluted site. Furthermore, it is noted that the detected total OCs concentrations in surface sediments from Cantabria is in the range of the Greenland sediments and other Arctic regions (<1–2 ng g^{-1} dw) (Cleeman et al. 2000). This suggests that the contamination levels of OCs found in the estuaries from Cantabria could be regarded as the baseline for OCs levels in the region.

Table 2 Certified concentrations (μg g^{-1} dw) for the five organochlorine pesticides in the standard reference sediment, NIST 1944, uncertainty for each one, measured values, and relative standard deviation

	Certified value	Uncertainty	Measured value	RSD (%) ($n = 3$)
α-HCH	2.0	0.3	1.3	10.1
4,4′-DDT	119	11	96	14.3
4,4′-DDD	108	16	85	12.7
4,4′-DDE	86	12	70	8.5
HCB	6.03	0.35	4.7	15.1

DDTs

It is well known that DDT isomer ratios act as useful indicators for understanding degradation

Table 3 Identification of the sampling sites, physicochemical properties, and detected concentrations of OCs (ng g^{-1} dw) in surface sediments from Cantabria (northern Spain) in 2006 in the fraction <63 μm

Sampling sites	ST1 ($n = 12$)	ST2 ($n = 12$)	ST3 ($n = 12$)	MG1 ($n = 12$)	MG2 ($n = 12$)	MG3 ($n = 12$)	TM1 ($n = 12$)	TM2 ($n = 12$)	TM3 ($n = 12$)
Geographic location	N 43°23′32″, W 3°27′29″	N 43°23′31″, W 3°27′28″	N 43°23′30″, W 3°27′27″	N 43°26′36″, W 3°57′34″	N 43°26′37″, W 3°57′33″	N 43°26′38″, W 3°57′32″	N 43°22′40″, W 4°28′42″	N 43°22′41″, W 4°28′41″	N 43°22′42″, W 4°28′40″
Physicochemical properties									
Water content (%)	41 ± 2[a]	39 ± 3	34 ± 6	33 ± 6	41 ± 7	40 ± 4	32 ± 2	35 ± 1	36 ± 4
TOC (%)	1.8 ± 0.1	1.8 ± 0.2	1.9 ± 0.2	1.2 ± 1.0	1.6 ± 0.5	1.4 ± 0.4	1.0 ± 0.2	0.9 ± 0.1	1.0 ± 0.1
LOI (%)	9.1 ± 1.9	8.9 ± 2.7	9.4 ± 2.2	6.1 ± 3.0	8.3 ± 2.2	7.4 ± 1.9	5.3 ± 1.7	5.4 ± 1.8	5.7 ± 1.6
Silt–clay content (%)	6.6 ± 6.1	5.5 ± 4.3	5.8 ± 4.3	3.9 ± 3.2	6.7 ± 2.3	4.3 ± 2.4	8.1 ± 6.0	8.4 ± 6.0	10.9 ± 6.8
pH	7.9	8.1	8.1	8.0	7.8	7.8	7.7	6.8	6.9
Temperature (°C)	20.8	20.3	20.2	20.6	20.5	20.4	20.7	20.7	20.6
Levels of OCs									
Hexachlorobenzene	t	t	t	1 ± 0.3	0.9 ± 0.3	1 ± 0.3	t	t	t
Endosulfan α	0.3 ± 0.1	0.3 ± 0.1	0.2 ± 0.1	0.5 ± 0.2	0.5 ± 0.1	0.6 ± 0.1	0.6 ± 0.2	0.5 ± 0.1	0.6 ± 0.2
Endosulfan β	t	t	t	0.4 ± 0.1	0.3 ± 0.1	0.3 ± 0.1	t	t	t
Endosulfan sulfate	t	t	t	t	t	t	t	t	t
Aldrin	0.4 ± 0.1	0.5 ± 0.1	0.5 ± 0.2	0.4 ± 0.1	0.4 ± 0.1	0.4 ± 0.1	0.5 ± 0.1	0.4 ± 0.1	0.5 ± 0.1
Dieldrin	0.7 ± 0.1	0.7 ± 0.2	0.6 ± 0.1	0.5 ± 0.1	0.4 ± 0.1	0.5 ± 0.2	0.7 ± 0.2	0.7 ± 0.1	0.7 ± 0.2
Methoxychlor	n.d.	n.d.	n.d.	0.4 ± 0.3	0.3 ± 0.2	0.3 ± 0.1	n.d.	n.d.	n.d.
4,4′-DDD	0.3 ± 0.2	0.2 ± 0.1	0.3 ± 0.1	0.5 ± 0.4	0.4 ± 0.3	0.5 ± 0.3	0.5 ± 0.3	0.5 ± 0.3	0.5 ± 0.2
4,4′-DDE	0.2 ± 0.1	0.3 ± 0.1	0.2 ± 0.1	0.4 ± 0.1	0.3 ± 0.2	0.3 ± 0.1	n.d.	n.d.	n.d.
Total DDTs	0.5	0.5	0.5	0.9	0.7	0.8	0.5	0.5	0.5
Σ OCs	1.8	1.9	1.7	3.9	3.5	3.9	2.5	2.4	2.6

ST Santoña Estuary (Asón River), *MG* Mogro Estuary (Pas-Pisueña River), *TM* Tina Menor Estuary (Nansa River), *n.d.* not detected (under the LOD), *t* trace levels (under the LOQ)

[a] Standard deviation

processes, sources, and transportation of these compounds, and what is more important, the observation of DDT is often taken as indicative of fresh DDT usage although not necessarily in the sampled region (Tavares et al. 1999). The pattern of DDT and its metabolites in all the sediment samples from Cantabria is that DDT metabolites account for 100% of total DDTs, indicating the absence of DDT and a total degradation of the parent compound. According to this, it can be denoted that there has been no recent input of technical DDT to the Coast of Cantabria. At TM site, DDD accounted for the total DDTs concentrations and at ST and MG sites it can be observed a dominance of DDDs over DDEs in the surface sediments, which can be indicative of a reductive dechlorination of DDT to DDDs under anaerobic conditions (Baxter 1990) as in general these estuaries are semi-closed areas with a restriction of water exchange with the open sea.

Sources of DDT in the Coast of Cantabria may be attributed to runoff from agricultural fields in the past, which finally enters rivers and streams, and from atmospheric deposition due to volatilization (Binelli and Provini 2003). Because of the low aqueous solubility of DDT, DDD, DDE (3, 40, and 160 μg L^{-1}, respectively) and high octanol–water partition coefficients (log $K_{\mathrm{ow}} = 6.36$, 5.69, and 6.02, respectively), they are strongly retained by soils and sediments, where they present a slow degradation process. In Table 4, the levels of organochlorine compounds in sediment samples recorded in this study are compared with those recorded for coastal sediments in other places, which do not take into account impacted areas. Total DDTs concentrations reported in the literature were in the range of <0.0018–31.92 ng g^{-1} dw as it can be observed in Table 4. The lowest values were found by De Mora et al. (2005) for sediments from Qatar, Bahrain, and Oman and in the North Sea (QSR 1993). Our results fit in the range reported by Gómez-Gutiérrez et al. (2007) as the background concentrations for sediments from the Mediterranean Sea, which ranges from 0.08 to 5 ng g^{-1} dw. The maximum concentration for total DDTs observed in this study is tenfold lower than the highest value for the background concentration range in the Mediterranean Sea. And our results show that DDT was present as metabolites DDD and DDE, indicating that inputs were not of recent origin, whereas Gómez-Gutiérrez et al. (2007) report the presence of parent compound DDT in the Mediterranean Sea, reaching a maximum value of 2.9 ng g^{-1} dw. Thompson et al. (1999) reported values of 1.06 ng g^{-1} dw for total DDTs concentrations in the Arcachon Bay and compared to the findings of Borja et al. (2005), the level of total DDTs found in this study is below these concentrations reported for the closest areas to the studied sites. Taking into account the levels reported in Table 4, it can be concluded that along the East Atlantic Ocean considering the areas bordering on Europe and Africa, the total DDT residue levels increase from north to south, being the minimum value 0.08 ng g^{-1} dw in the North Sea (Area I), while in Africa (Republic of Bénin; Area III) minimum values are around 2.96 ng g^{-1} dw, reaching a maximum at 31.92 ng g^{-1} dw in Ghana as it can be seen in Table 5. Furthermore, concentrations of DDT isomer is considerably higher in Africa, where values reach 5.52 ng g^{-1} dw. On the other hand, at northern latitudes the level of parent compound is in all cases less than 1 ng g^{-1} dw. Regarding the West Atlantic Ocean, total DDTs concentrations in the north (Area IV) are similar to those in the East Atlantic Ocean at higher latitudes (Area I and Area II) being higher at south latitudes (Area V).

HCB

Hexachlorobenzene is other OC present in all sediment samples analyzed in the Coast of Cantabria in 2006 below 1 ng g^{-1}. It is widely distributed in the environment and it is an ubiquitous environmental pollutant well known as an atmospherically transported pollutant (Strachan et al. 2001; Barber et al. 2005). It is likely to undergo global re-distribution in the environment and it is subject to cold condensation (Blais et al. 2003). The global distillation phenomena (Wania and Mackay 1996) and long-range transport have been given as a reason for the presence of HCB in polar regions (Meijer et al. 2003). Levels of HCB in remote areas away from sources are quite low, with values of <100 pg g^{-1} reported for the Persian Gulf region (De Mora et al. 2005) and <130 pg g^{-1} and <20 pg g^{-1} for Pacific islands of Vanuatu and

Table 4 Concentrations of organochlorine pesticides (ng g^{-1} dw) in marine sediments of different areas in the world

Site (country)	HCB	Endosulfan α	Endosulfan β	Aldrin	Dieldrin	4,4′-DDD	4,4′-DDE	4,4′-DDT	Total DDTs	Survey year	Reference
Cantabric Sea											
Cantabria	t–1	0.2–0.6	t–0.4	0.4–0.5	0.4–0.7	0.2–0.5	n.d.–0.4	–	0.5–0.9	2006	This study
Ría de Vigo, Galicia	0.1								2.0	1995	Observatorio Medioambiental (1996)
Basque Country				0.3–1.01	0.3–1.86				3	2004	Borja et al. (2005)
Atlantic Ocean											
Baltic Sea	0.0022–0.36					0.063–2.1	0.045–2.5	0.012–0.62	0.13–5.0	2001–2002	Pikkarainen (2007)
Bothnian Bay, Baltic Sea	0.84				0.39	0.34	0.48		1.9	1991	Strandberg et al. (2000)
Scotland, North Sea	0.03–0.07								0.08–0.14		QSR (1993)
Ballymacoda, Ireland	0.20	<0.10	<0.20	<0.09	0.40	<0.08	<0.09	<0.20	<0.37	2002	Kilemade et al. (2004)
Arcachon Bay, France						0.29	0.16	0.33	1.06	1997	Thompson et al. (1999)
Portugal		0.68–1.1		0.08–0.7	0.26–2.6	0.30–1.5	0.19–1.34	0.23–4.3	0.72–6.5	2007–2008	Carvalho et al. (2009a, b)
Merja Sidi Bourhaba, Morocco							10.11			–	Peters et al. (2001)
Lake Bosomtwi, Ghana		3.75–14.40		0.30–0.46	0.2–0.46		11.52–26.4	3.54–5.52	<15.06–31.92	2004–2006	Darko et al. (2008)
Houédo, Republic of Bénin		<0.014	<0.014	1.15[a]		1.55	0.95	0.15	2.96[b]	–	Pazou et al. (2006)
Savannah River Estuary, Georgia	1.5					0.42	0.37	0.45	2.05	1997	Loganathan et al. (2001)
Coast of Campeche, Mexico	0.001–0.0055	<0.00055	<0.00065–0.0072	<0.00042–0.0099	<0.00057–0.016	0.0024–0.190	0.0013–0.29	0.001–0.043	0.008–0.631	2000	Carvalho et al. (2009a, b)
Barahona, Dominican Republic	0.03			0.08	0.04	0.49	1.55	0.37	2.81[b]	1995	Sbriz et al. (1998)
Guanabara Bay, Brazil	0.60	0.68		0.47	0.28	1.72	0.66	0.28	10.61	2003–2004	Santos de Souza et al. (2008)
Mar Chiquita, Argentina		0.035–0.036	0.028–0.029		0.0052		0.45–0.74	0.42–0.51	0.63–1.05	2000	Menone et al. (2006)
Other areas											
Mediterranean Sea	0.04–0.8							0.02–2.9	0.08–5	1971–2005	Gómez-Gutiérrez et al. (2007)
Turkey, Black Sea	0.016–0.25			0.007–0.18	0.013–0.091	0.013–0.79	<0.008–0.03	<0.01–0.079		1993	Fillman et al. (2002)
Lan-Yang River, Taiwan		0.08–0.49	n.d.	0.04	n.d.	n.d.	0.17–0.26	0.45–0.74		2002	Chang Doong (2006)
Yangtze estuary, China		n.d.–1.23	n.d–0.16	0.1–1.76	n.d.–0.22	n.d.–0.34	n.d.–0.35	n.d.–0.21	n.d.–0.57	2001	Liu et al. (2003)
Persian Gulf	0.00056–0.027	<0.0002–0.016	<0.00095–0.029	<0.00025–0.019	<0.00035–0.15			<0.0018–0.097	<0.0018–0.43	2000	De Mora et al. (2005)

n.d. not detected (under the LOD), *t* trace levels (under the LOQ)

[a] Sum of aldrin, dieldrin, endrin, isodrin, and telodrin

[b] Sum of 4,4′-DDT, 2,4′-DDT, 4,4′-DDD, 2,4′-DDD, 4,4′-DDE, and 2,4′-DDE

Table 5 Concentration ranges of organochlorine pesticides (ng g^{-1} dw) in marine sediments along the Atlantic Ocean

Area	HCB	Endosulfan α	Endosulfan β	Aldrin	Dieldrin	4,4′-DDD	4,4′-DDE	4,4′-DDT	Σ DDTs
East Atlantic Ocean									
Area I	0.0022–0.84	<0.1	<0.2	<0.09	<0.39	0.063–0.34	0.045–2.5	0.012–0.62	0.08–5.0
Area II	0.1–0.98	0.1–1.1	0.06–0.25	0.22–1.01	0.3–1.86	0.07–0.55	0.07–0.32	0.07–0.33	0.16–3
Area III	–	0.014–14.4	<0.014	0.3–1.15	0.2–0.46	1.55	0.95–26.4	0.15–5.52	2.96–31.92
West Atlantic Ocean									
Area IV	0.001–1.5	<0.00055	<0.0072	<0.00042–0.08	0.00057–0.04	0.0024–0.49	0.0013–1.55	0.001–0.45	0.008–2.81
Area V	0.6	0.035–0.68	<0.03		0.0052–0.28	1.72	0.45–0.74	0.28–0.51	0.63–10.61

Data provided is from literature cited in Table 4

Area I latitudes <50° NE, *Area II* latitudes 35°–50° NE, *Area III* latitudes 0°–35° NE, *Area IV* latitudes 0°–50° NW, *Area V* latitudes 0°–50° SW

Tonga, respectively (Harrison et al. 1996). On the whole, HCB concentrations in source regions of the world average about 1 ng g^{-1} dw (Barber et al. 2005). In Table 4, HCB concentrations were found to be in the range of 0.00056–0.84 ng g^{-1} dw. At MG site at present study, concentrations reached 0.98 ng g^{-1} dw, which is comparable to the maximum value reported by Gómez-Gutiérrez et al. (2007) as background level for the Mediterranean Sea. These maximum values could be explained by the location of the sampling areas as they are influenced by river discharges and HCB had it most important use in agriculture in the past. Furthermore, waste treatment is also an important source as it can be deduced from the European Pollutant Release and Transfer Register (E-PRTR 2006) emission data for Cantabria in 2006 where emissions to air from a waste management activity are recorded to be 0.017 tonnes. Compared to the background or reference concentrations for HCB in surface sediments for application in the OSPAR areas southern Norway and Iceland Sea/Norwegian Sea, which are 0.07 and 0.04 ng g^{-1} dw, respectively, it can be observed that average value at the Coast of Cantabria is fivefold and eightfold, respectively, higher than these backgrounds. As conclusion it can be said that in the Northeast Atlantic Ocean (Area I and Area II) from the Baltic Sea to the Cantabrian Sea, HCB reaches similar maximum values about 1 ng g^{-1} dw as it is shown in Table 5. Reported values for this compound in Africa countries were not found. Regarding the West Atlantic Ocean bordering on America, values for HCB were quite low in both Area IV and Area V, reaching maximum values around 1 ng g^{-1} dw as it can be observed in Table 5 and being quite similar to values found in the east side.

Cyclodiene pesticides

Regarding cyclodienes aldrin and dieldrin, a uniform distribution along the three studied estuaries was observed. Average concentrations for aldrin were 0.4 ng g^{-1} dw and for dieldrin 0.6 ng g^{-1} dw (Table 3). Values for aldrin observed by Borja et al. (2005) for different estuaries in the Basque Country (Cantabrian Sea) were a bit higher as they reached values of 1.01 ng g^{-1} dw. The same happened to the levels found by these authors for dieldrin, but being below 2 ng g^{-1} dw in all cases (Table 4). Concentrations reported in the literature (Table 4) were in the range <0.00025–1.01 ng g^{-1} dw for aldrin. Values observed at present work are within this range. With respect to dieldrin, the concentration range was <0.00035–2.6 ng g^{-1} dw (Table 4). Residue levels detected in the Coast of Cantabria were comparable to values observed at the Bothnian Bay in the Baltic Sea and in Ballymacoda (Ireland), what Kilemade et al. (2004) established as a reference site. The uniform distribution of dieldrin throughout the studied region is in good agreement with its ubiquity and long-term existence as an environmental pollutant. Strachan et al. (2001) found a similar pattern in sediment samples collected in 1993, with an average concentration of 0.2 ng g^{-1} throughout the Bering-Chukchi Sea, an area which was not close to point sources.

In Table 5, and as conclusion it can be pointed out that in the Northeast Atlantic Ocean (Area I) aldrin is present at very low concentrations in the sediments being less than 0.09 ng g^{-1} dw, while concentrations for dieldrin are about 0.4 ng g^{-1} dw as this metabolite presents a slower degradation process in sediments. At lower latitudes near the studied area, in the areas bordering on Spain and France (Area II), minimum concentrations for aldrin and dieldrin are around 0.008 and 0.2 ng g^{-1} dw, respectively. Maximum detected concentrations for dieldrin (2.6 ng g^{-1} dw) are a bit higher than for aldrin (1.01 ng g^{-1} dw) while in areas bordering on the African continent (Area III) the residue levels of aldrin are higher than those of dieldrin, which indicates that in these countries there has been more recent inputs than at northern latitudes. In the West Atlantic Ocean maximum concentrations found for aldrin and dieldrin are 0.08 and 0.28 ng g^{-1} dw, respectively.

Endosulfan is a cyclodiene organochlorine widely used as an insecticide in agriculture. Nevertheless, plant protection products containing endosulfan cannot be applied any longer since 2006 as the European Decision EC/864/2005 established the withdrawal of the products containing endosulfan. Technical endosulfan contains two isomers, endosulfan α and endosulfan β, in approximately a 7:3 ratio along with impurities and degradation products (Rice et al. 1997). Concentrations of endosulfan α were higher than those of endosulfan β at the three studied sites. However, at ST and MG sites the concentration of isomer β was nearly negligible (trace levels). Stern et al. (2005) observed the presence of only endosulfan α in sediments from Lake DV09 in Canada as well as Hung et al. (2002) found in Arctic air. Furthermore, some studies have demonstrated that isomerization between the parent isomers can occur in aqueous systems, being the reaction favorable to the formation of the isomer α, which could explain the pattern at sites ST and TM. Endosulfan sulfate is the predominant residue of technical grade endosulfan, which finds its way into aerobic and anaerobic aquatic environments. It is less volatile than the parent compounds and more persistent than them. As the residue levels observed at this study were in all cases below quantitation limits, it can be deduced that an input of the parent compounds may have occurred relatively close to the sampling year in 2006.

Scarce data of endosulfan in sediments have been reported in the literature (Table 4), especially in the closest locations to the studied area. In the Coast of Cantabria the concentrations of endosulfan were comparable to the levels reported by Kilemade et al. (2004) in a reference site near Cork Harbor. Even though, much lower concentrations were reported by Menone et al. (2006) for Mar Chiquita (<0.04 ng g^{-1} dw), De Mora et al. (2005) for the Persian Gulf (<0.03 ng g^{-1} dw), and by Carvalho et al. (2009a, b) for the Coast of Campeche in Mexico (<0.008 ng g^{-1} dw). As conclusion it can be said that in the Northeast Atlantic Ocean (Area I) the residue levels of endosulfan are less than 0.2 ng g^{-1} dw (Table 5); being higher in the areas near France and Spain (Area II). However, at lower latitudes in the Atlantic Ocean (Area III), higher concentrations for endosulfan α have been reported in Ghana (14.4 ng g^{-1} dw) by Darko et al. (2008). In the West Atlantic Ocean concentrations of endosulfan α and endosulfan β in sediments can be found in the ranges 0.00055–0.68 ng g^{-1} dw and 0.00065–0.03 ng g^{-1} dw, respectively. The pattern is similar to the East Atlantic Ocean as residue levels are higher in the south than in the north.

Table 6 Correlation matrix of organochlorine pesticides, total organic carbon (TOC (%)), loss on ignition (LOI (%)), water content (WC (%)), and the percentage of the finer fraction of sediments (<63 μm (%)) in year 2006 for the 108 samples of the survey (two-tailed significant values)

	TOC (%)	LOI (%)	WC (%)	<63 μm (%)	∑OCs
TOC (%)	1				
LOI (%)	0.63**	1			
WC (%)	0.53**	0.23	1		
<63 μm (%)	0.04	0.34*	0.18	1	
∑OCs	0.05	0.35*	0.07	0.46**	1

$*p < 0.05$; $**p < 0.01$

Relationship between organochlorine pesticides and physico-chemical properties

Correlations between ∑OCs and physico-chemical properties were evaluated using the Spearman's rank correlation coefficient (ρ) for the total samples analyzed in the four campaigns carried out during 2006 (108 samples). The results are presented in Table 6. No significant relationship between ∑OCs and water content or total organic carbon was found. However, statistically significant correlations were found between OCs and both LOI ($p < 0.05$) and the finer fraction of the sediments ($p < 0.01$). These results suggest that higher concentrations of OCs in coastal marine sediments are influenced both by the amount of organic matter present and by adsorption to the silts and clays of the finer fraction due to the greater surface area of the smaller particles which provide a larger area. So the distribution of the contaminants is more related to these variables than to the proximity and importance of the sources. It is noticeable that sediments of the entire area of study present a very low TOC content, ranging from 1–2% and this can provide a possible explanation of the scarce relationship between TOC and ∑OCs.

Evaluation of ecotoxicological risk

Sediment chemistry data alone do not provide an adequate basis for evaluating the hazard posed by sediment-associated contaminants to aquatic organisms. Sediment quality guidelines (SQGs) represent a scientifically useful tool for the assessment of the potential effects of contaminants on aquatic organisms. Table 7 shows the comparison of the obtained data in this study for the residue of the OCs in the Coast of Cantabria with five international available guidelines from US-EPA, Florida, Canada, National Oceanographic and Atmospheric Administration (NOAA), and Wisconsin. It is important to point out there is not

Table 7 Sediment quality guidelines for OCs in marine sediments issued by different authorities and countries and comparison with the detected concentrations in the Cantabric Coast (northern Spain)

Pesticide	This work	US-EPA[a]	Florida[b]		Canada[c]		NOAA[d]		Wisconsin CBSQGs[e]	
		Screening Benchmark	TEL	PEL	ISQG	PEL	ERL	ERM	TEC	PEC
4,4′-DDD	0.2–0.5	2.07	1.22	7.81	1.22	7.81				
4,4′-DDE	n.d.–0.4		2.07	374	2.07	374	2.2	27	5.3	572
Total DDTs	0.4–0.9	3.89	3.89	51.7			1.58	46.1		
Aldrin	0.4–0.5								2	80
Dieldrin	0.4–0.7	0.72	0.71	4.30	0.71	4.30			1.9	62
Endosulfan sulfate	t	0.357								
Methoxychlor	n.d.–0.4	29.6								

Concentrations expressed as nanograms per gram dw

TEL threshold effects level, *PEL* probable effects level, *ISQG* Interim Sediment Quality Guidelines, *ERL* effects range—low, *ERM* effects range—medium, *TEC* threshold effects concentration, *PEC* probable effects concentration, *n.d.* not detected (under the LOD), *t* trace levels (under the LOQ)

[a] Marine Sediment Screening Benchmarks, Region III BTAG (2006)

[b] Florida Department of Environmental Protection (1994)

[c] CCME (2002)

[d] NOAA (1999)

[e] Wisconsin Department of Natural Resources, Consensus-Based Sediment Quality Guidelines (2003)

available sediment quality guidelines for all the pesticides detected. DDTs are the organochlorine pesticides for which guidelines are more extended. At their present levels, OCs in the studied area do not appear to pose a biological threat. Based on current sediment quality criteria for OCs for marine sediments, the concentrations of individual DDTs, aldrin, methoxychlor, and endosulfan sulfate show that they are not in excess of effects range—low or effects range—medium values, suggesting unlikely adverse biological effects. Only for dieldrin it was found in concentrations that were slightly above the threshold values established in Florida (threshold effects level), Canada (Interim Sediment Quality Guidelines), and by EPA (Benchmark screening) at three stations in Tina Menor site. However, all of the dieldrin residues are below the probable effect level, which denotes concentrations frequently associated with adverse effects.

Conclusions

This is, to our knowledge, the first survey reported for OCs in coastal marine sediments in Cantabria. Hexachlorobenzene, endosulfan, 4,4′-DDD, aldrin, and dieldrin were present in all samples of the nine monitored stations, showing their ubiquity in coastal marine sediments in Cantabria. Methoxychlor was only detected at Mogro estuary. Total OCs concentration ranged from 1.8 ng g^{-1} dw in station ST1 to 3.9 ng g^{-1} in station MG1. The higher concentration was found is samples from Mogro, which could be attributed to the higher industrial impact in the area as compared to Tina Menor. No significant differences were found among the concentrations measured at each one of the four seasons. It was shown that the organic matter content and the particle size distribution of particulates are the main parameters controlling the sorption of OCs onto studied sediments. Generally, the observed levels demonstrated a similar distribution along the studied areas and were comparable to that reported by different authors for areas catalogued to be low contaminated, reflecting both the legacy of historic usage of organochlorine pesticides and atmospheric deposition. From an evaluation of the concentrations found in the Atlantic Ocean, it can be pointed out that in general OCs residue levels observed at lower latitudes in the south areas are higher than in the north. Comparing the East and West Atlantic Ocean, concentrations are quite similar in the north while when comparing the residues found in the South Atlantic Ocean, concentrations are higher in the east areas. The comparison with the international SQGs for marine sediments shows no ecotoxicological risk for this area when considering these pollutants. However, to understand the organic pollutants accumulation patterns in the region, further work with more samples, including other matrices such as biota, and other POPs to be monitored, should be carried out.

Acknowledgements The Spanish Ministry of Education and Science (MEC) financially supported this research under National Project CTM2006-00317, and Sonia Gómez Lavín also thanks the MEC for the FPI fellowship BES-2005-9992.

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