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
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.