Chemosphere 94 (2014) 36–41

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in sediments from the Gulf of Batabanó, Cuba

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HIGHLIGHTS

- The first study on POPs in sediments from Gulf of Batabano (CUBA) was performed.
- Levels of DDTs, Lindane, HCB, Heptachlor, Aldrin, Mirex and PCBs were measured.
- The POPs concentrations indicated low contamination of the surface sediments.
- The Gulf of Batabano can be considered like a pristine environment.
- The levels of POPs found not have an adverse effect on sediment dwelling organisms.

ARTICLE INFO

Article history:
Received 17 April 2012
Received in revised form 18 August 2013
Accepted 2 September 2013
Available online 6 October 2013

Keywords:
Sediments
Organochlorinated compounds
DDT
PCBs
Gulf of Batabanó
Cuba

ABSTRACT

The spatial distribution of various organochlorinated compounds, e.g. PCBs, DDTs, HCB and HCHs, were investigated in sediments of the Gulf of Batabanó, Cuba. Among the target organochlorine compounds measured, ΣDDT isomers were the predominant contaminant with concentrations ranging from 0.019 to 1.27 ng g^{-1} dry wt. Lindane was present at very low concentrations in the range n.d. to 0.05 ng g^{-1}, while PCBs and other organochlorine pesticide residues, such as HCB, Heptaclor, Aldrin and Mirex were lower than detection limits (~0.010 ng g^{-1}). According to established sediment quality guidelines, the OCPs concentrations encountered in the surface sediments are probably not having an adverse effect on sediment dwelling organisms. Compared to concentrations reported in coastal environments from other parts of the world, PCBs and OCs concentrations in surface sediments of Batabanó Gulf were low and similar to the reported for remote and pristine environments. These results contribute to the sparse regional database for organochlorinated compounds in the Caribbean marine environment.

1. Introduction

Persistent organic pollutants (POPs) such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are ubiquitous contaminants in different compartments of the environments (Carvalho et al., 2002; Dietz et al., 2000; Leoni et al., 1995; Nhan et al., 1999; Sbriz et al., 1998; Villeneuve et al., 1999). In spite of numerous countries having withdrawn the registered usage of POPs for many years, these man-made chemicals still persist at considerable levels worldwide. These compounds are generally generated by anthropogenic processes and can be introduced into the environment through various routes. Due to their toxic, mutagenic, and carcinogenic characteristics, these persistent compounds are considered to be hazardous to the biota and environment (Gómez-Gutiérrez et al., 2007). Also, these compounds are strongly absorbed onto the surface of particles associated with the organic content of solid-phase matrix and can be deposited to the underlying sediments. Therefore, the investigation of POPs concentrations in aquatic environments is needed to provide important information on anthropogenic impact on the environment and serve as an indicator of contaminant loading (Hong et al., 2008; Zhao et al., 2010).

In Cuba, the use of pesticides has been reduced following the decline of farming activities over several decades. Since 1990, the use and importation of all pesticides included in the Stockholm Convention were prohibited. However, from the national inventory of polychlorinated biphenyls (PCBs) and chlorinated pesticides in disuse, there are in Cuba about 120 tons of dielectric fluid contaminated with PCBs and 9 tons of obsolete pesticides, principally: DDT, Heptachlor, and toxaphene (Abo-Balanza, 2005).

Nowadays, there is scarce information on the status of OCPs in many Caribbean coastal areas (Fernandez et al., 2007). For Cuba,

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0045-6535/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2013.09.007

some data is only available from the pesticide contamination in soils from the most agro-developed province of Cuba (Dierksmeier, 1996) and few data exist from the International Mussel Watch (Sericano et al., 1995). Recently, Tolosa et al. (2010) published the spatial distribution of various organochlorinated compounds in sediments from Cienfuegos bay. The concentrations reported appeared to be relatively low by global standards and only sediments receiving the impact from the residual waters of the city and thermo-electrical power approached the sediment quality guidelines for DDTs. Relatively higher ∑DDT concentrations and high DDT/(DDE + DDD) ratios in two sites near the outfalls of the city indicated a current DDT usage, probably linked to public health emergencies.

The Gulf of Batabanó is a large semi-enclosed water body in southern Cuba. Its approximate surface is 20850 km^2 with an average depth of 6 m. The coastal area is predominantly fringed by mangrove forests and the bottom is extensively covered by grass-beds with varying densities of *Thalassia testudinum*. Living coral reefs are found all along the shelf and generate many associated islets called 'cayos'. Biological studies have shown signs of environmental degradation in the Gulf, through loss of biodiversity, shift of benthic communities (Baisre et al., 2003; Cruz et al., 2001; Hernandez-Zanuy and Carballa, 2001) and reduction in size and capture levels of the spiny lobster *Panulirus argus* (Borrell et al., 2004; Puga et al., 1996). *Panulirus argus* is the most valuable species in the fishing industry in Cuba and accounts for approximately 15% of the total near-shore catches. The Gulf of Batabanó is one of the main four fishing areas in the island, providing 63% of the total lobster catches (Baisre et al., 2003).

In terms of inorganic pollution (heavy meals and radioactivity) the gulf environment is considered like a pristine area (Alonso-Hernandez et al., 2011). However, limited information is available on organic contamination produced by anthropogenic activities. In particular, little is known on pollution originated by the use of OCPs in the agricultural practices (rice and tobacco) present in the southern part of the La Havana and Pinar del Rio provinces.

In consideration of the above, the present study measures polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in sediments to ascertain the contamination status in the Gulf of Batabanó. In addition, a comparison of our results with those from other locations and sediment quality guidelines are included to evaluate the relative significance of the contamination.

2. Methods and materials

2.1. Sampling

Sixteen surface sediment samples were collected with a stainless steel grab in May 2005. Details of the samples sites are shown in Fig. 1 and Table 1. Approximately 2 cm of the top sediments were taken by a stainless steel spoon and stored in glass jar. Samples were cool transported to the laboratory where they were immediately stored in a freezer. Sediment were freeze-dried, hand-sieved (250 μm) and homogenized.

2.2. Chemical analysis

All analysis were carried out in the Marine Environmental Studies Laboratory at Environment Laboratory-IAEA, Monaco. The extraction and clean up of the OCPs and PCB were similar to those previously described by Tolosa et al. (2010).

Approximately 8 g portion of each sediment was spiked with internal standards (PCBs 29 and 198 for the first fraction and

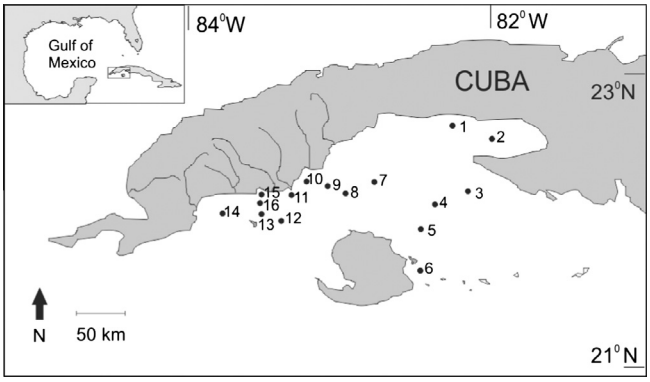

Fig. 1. Study area in the Gulf of Batabanó, Cuba. The inset shows the regional location of the study site. Sampling stations are indicated with black circles.

ε-HCH for the second fraction), and extracted with a hexane: methylene chloride mixture (50/50, v/v) in a microwave at 1200 W and 115 °C for 20 min. Sulfur was removed with activated copper and two fractions were obtained from silica/alumina columns, as described in Tolosa et al. (2010). PCBs, HCB, p,p′-DDE, Aldrin, Heptachlor and Mirex were eluted with 20 ml hexane followed by 20 ml hexane/methylene chloride (90:10). The p,p′-DDD, p,p′-DDT, and γ-HCH (Lindane) were eluted in a second fraction with 40 ml hexane/methylene chloride (80:20). The compounds were determined by HRGC with a ^{63}Ni electron capture detector (HRGC/ECD) on a Hewlett–Packard 6890HP equipped with a split/splitless injector, and an automatic liquid sampler (Hewlett–Packard, Palo Alto, USA). For all the analyses, a fused-silica capillary column HP-5 (30 m, 0.25 mm i.d. and film thickness 0.25 μm) was used. GC parameters were: injector temperature 250 °C; detector temperature 300 °C; helium at a flow rate of 1 ml min1 was used as carrier gas. The GC oven was temperature programmed from 70 °C (2 min isothermal) to 260 °C (at 3 °C min^{-1}) and held isothermally at 260 °C for 20 min.

The quantified analytes were: 25 polychlorinated biphenyl congeners (8, 18, 28, 44, 50, 52, 66, 87, 101, 104, 105, 118, 126, 128, 138, 153, 154, 170, 180, 187, 188, 194, 195, 201, 206), hexachlorobenzene (HCB); the DDT group (p,p′-DDT, p,p′-DDE, P,p′-DDT), γ-HCH, Aldrin, Heptachlor and mirex. The individual PCB congeners were determined by using individual standard congeners. The 25 selected congeners of PCBs are among the major 18 congeners of the NOAA NST list, which provides at least one representative congener from every homolog group. Total PCB estimates were derived from the sum of the 26 congeners analyzed, including the adjustment factor of 2 used by NOAA (Howell et al., 2008).

2.3. Quality control

All data were subject to strict quality assurance and control procedures. For each set of 7 samples, procedural blank and certified reference sediment (IAEA-408, International Atomic Energy Agency) were used to determine the accuracy. The concentration values of the target compounds always fell within the 95% confidence interval of the assigned reference value for concentrations of the analytes (Villeneuve et al., 2000).

The spiked recoveries for PCBs 29 and 198, in the surface sediments ranged from 56% to 80.9% and 61% to 83.9%, respectively.

The precision of the measurements obtained through replicates of the reference materials was better than 10% for all target compounds. The detection limit for each individual compound ranged between 10 and 30 pg g^{-1}.