Marine Pollution Bulletin 109 (2016) 591–596

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Baseline

Organochlorine compounds in surface sediments from the northern coast of Cyprus, Eastern Mediterranean: Levels, possible sources and potential risk

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ARTICLE INFO

Article history:
Received 4 November 2015
Received in revised form 11 May 2016
Accepted 16 May 2016
Available online 24 May 2016

Keywords:
Organochlorines
DDTs
Sediment
Sediment quality
Northern Cyprus

ABSTRACT

Organochlorines (OCs) were determined in sediments collected from different regions of northern coast of Cyprus. The OCPs and Aroclors had a wide range from 2.78 to 306 and 15 to 325ng g^{-1}, respectively. The highest level was found at Yedi Dalga site. DDE was the most abundant compound. The ratios of metabolites to parent DDT showed that DDTs were derived mostly from the aged and weathered inputs. Comparing our results with the previous studies showed that POPs in sediments were found to be lower than those in samples for Mediterranean and Black Sea coasts. The SQG implied that, Aroclor1254 exceeded the TEL values, showing that adverse biological effects are expected occasionally at some of the sediment samples. DDTs were dominant and more ecotoxicological concern in the northern Cyprus. Altogether, it may be summarized that DDTs will impose ecologically hazardous impacts in the sedimentary environment at the present.

Organochlorine pesticides (OCPs), one of the persistent organic pollutants compounds, are ubiquitous in the environment. OCPs, such as DDTs, HCH and PCBs were produced and widely used for several purposes in the world since 1950s. Organochlorine pesticides have an extensive concern due to their environmental persistence (Zhang et al., 2007; Hu et al., 2009; Guan et al., 2009), high toxicity, trend in bioaccumulation (Yang et al., 2010), biomagnification (Wan et al., 2005) and health risks on humans and other animals (Jones and de Voogt, 1999).

The use of OCPs have been restricted in most of the developed countries in the world since 1970. The decreasing levels of OCPs were observed due to this restriction of organochlorines in monitoring programs. However, many developing countries are still using OCPs for agricultural purposes (Hong et al., 2003). They are still routinely measured in sediment, water, soil, air, and even foodstuff (Lee et al., 2001; Concha-Grana et al., 2006; Yang et al., 2010).

There are several sources that cause to the accumulation of organochlorines in the environment. These include domestic waste, industrial discharge, inputs from agricultural area, chemical spill and atmospheric fallout (Vallack et al., 1998; Zhou et al., 2001). This type of pollution is especially observed in the Mediterranean Sea because of its limited exchange with the open ocean (Basturk et al., 1980; Fowler and Elder, 1980; Stefanelli et al., 2004).

Some compounds have a strong tendency to bind to suspended particles; marine sediments have often been considered as the ultimate sink for nonpolar compounds (Salomons and Förstner, 1984). The relatively high lipophilic characteristic of OCs induces their accumulation in organisms and adsorption on suspended particles. Furthermore, resistance of OCs causes them to remain in the marine environment over long period and to be included in food chain (Borga et al., 2001).

The Mediterranean Sea is one of the semi-closed sea in the world, surrounded by intensively industrialized and densely populated areas, that shows a low capacity of exchange of waters with the Atlantic Ocean and other surrounding seas. The Mediterranean Sea has been extensively influenced from the land-based impacts. Mediterranean Sea has received considerable loads of anthropogenic organic/inorganic contaminants originated from human activities. Cilician Basin, located in the northeastern part of the Levantine Basin of the Eastern Mediterranean covers the area between Turkey and the Cyprus. Mersin and Iskenderun Bays locating next to wide continental shelves and Goksu, Seyhan, Tarsus and Ceyhan Rivers deltas are took place along the southern coast of Turkey that have been currently used for irrigation in this region. These rivers are reaching to the Cilician Basin of the NE Mediterranean. These sources supply a total fresh water flux of 870 m^3 s^{-1}, accounting for half the river discharge along the eastern Aegean and Mediterranean coasts (Ozsoy et al., 2008). This flux is much greater than the discharge of Nile in the eastern Mediterranean which is given to be 540 m^3 s^{-1}. A broad spectrum of pesticides was used for agricultural activities, especially cotton production is important in Adana. In Turkey, production and usage of aldrin, dieldrin, DDT, endrin, BHC, chlordane, heptachlor and lindane were completely officially banned in the 1990s.

Cyprus is the largest Mediterranean island after Sicily and Sardinia. Cyprus is situated in the extreme northeast corner of the Mediterranean; it is 71 km of Turkey and 105 km of Syria. Cyprus extends 227 km from Cape Andreas to Cape Drepanon and 97 km. The average

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http://dx.doi.org/10.1016/j.marpolbul.2016.05.034
0025-326X/

width is 56–72 km; the narrow peninsula known as the Karpas, which is nowhere 16 km wide, extends 74 km northeastward to Cape Andreas. Cyprus has a total coastline of 648 km. The southern part of Cilician Basin is threatened by industrial pollutants, pesticides used in agricultural areas, and the lack of adequate sewage treatment from the northern Cyprus.

The previous study about the potential ecological risk of PAHs in surface sediments in the present area has been reported by Kucuksezgin et al. (2013), however no information available from literatures to assess the organochlorinated contaminants in the Cilician Basin sediments. The purpose of this study was to determine organochlorinated contaminants in the sediments, to reveal the sources of POPs and to evaluate the ecological risk in the Cilician Basin.

17 surface sediment samples were collected using a Van Veen grab in 2011 from three regions in Cyprus coast of Cilician Basin (Northern Cyprus; Zeyko "Z" and Arpa Ambari "A", Western Cyprus; Yedidalga "Y") and samples were stored in a freezer until analysis (Fig. 1). Sediment samples were dried, homogenized and reduced fine powder. For grain size correction, the <250 μm fraction was chosen for analysis.

Extractions were performed by using microwave extraction system (CEM-MARS) with *n*-hexane and dichlorometane (1:1) mixture and internal organochlorine standards (PCB29, PCB198, α-endosulfan D_4, ε-HCH) followed by sulphur removal procedure using activated elemental copper. The sulphur-free extracts were cleaned up and fractioned, using 17 g of florosil (bottom), 1 g of anhydrous sodium sulphate (top) in a column with 70 ml hexane, 45 ml hexane–dichlorometane mixture and 70 ml dichlorometane. The florisil was precleaned with dicloromethane and hexane and dried in the beginning of analytical procedure. The eluates were collected and concentrated to 1 ml using nitrogen stream and injected to GC–MS. Same procedure was applied for both blanks and all samples.

Quantitative analysis was performed with Agilent 5975C GC–MS (DB-5MS column: 30 m × 0.25 mm × 0.25 μm). To analyze organochlorinated compounds, GC/MS was programmed initially 70 °C (2 min held), then increase to 150 °C with a velocity of 25 °C min^{-1} then increase to 200 °C with a velocity of 3 °C min^{-1} and up to 280 °C with a velocity of 8 °C min^{-1} held for 10 min. The nine OCPs (aldrin, dieldrin, endrin, *p*,*p*-DDT, *p*,*p*-DDE, *p*,*p*-DDD, HCB, heptachlor and lindane) and PCBs (commercial mixtures: Aroclor 1254 and 1260) were identified in Cilician Basin sediment samples.

The quality of the analytical data was assured using the reference material (sediment) of IAEA-417 the sediment sample from the International Laboratory of Marine Radioactivity, IAEA, Monaco. The whole methodology was verified on this reference material, obtaining results in good agreement with the certified values. Blanks were run periodically during the analysis. Blank values remained below detection limits (as 3:1 signal versus noise value). The method detection limits ranged from 0.10–0.57 pg g^{-1} for OCPs and 2.4–4.5 pg g^{-1} for Aroclors. And the recoveries for sediments ranged between 88% and 118%.

Sediments were analyzed for total organic carbon (TOC) content with the sulfochromic oxidation method by spectrophotometrically. The accuracy of this method is ±0.017% organic matter (Hach, 1988).

The sediment grain size analysis was performed using the procedure of Folk (1980) and sand, silt clay ratios were obtained. Hydrometer

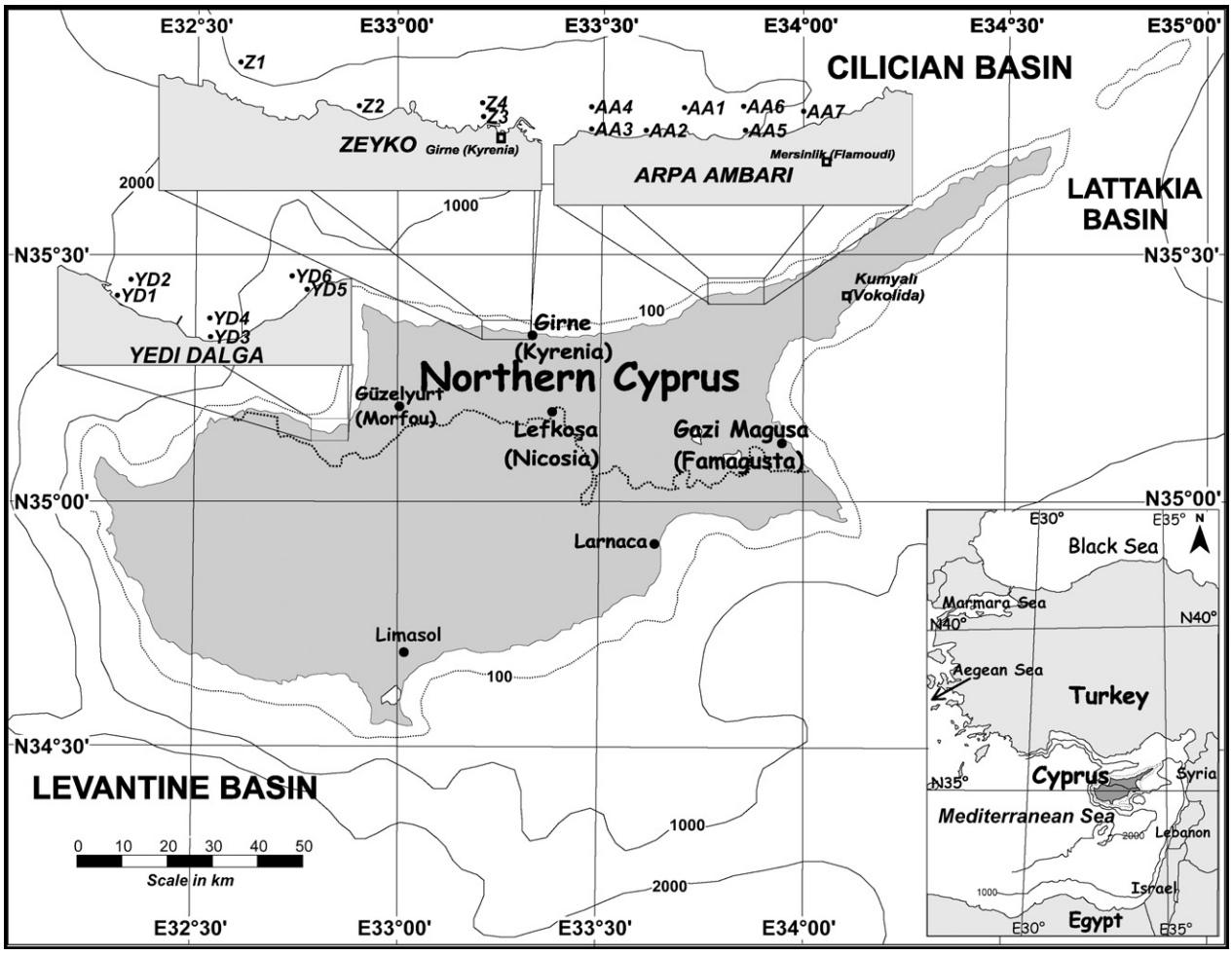

Fig. 1. Location of surface sediment sampling stations from Yedi Dalga, Zeyko and Arpa Ambarı regions. Sample locations (black dots) from each area and labelled water depths, while the map to the right corner show Cyprus and main basins in the eastern Mediterranean.