Marine Pollution Bulletin xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Baseline

Persistent organochlorine residues in fish and sediments collected from Eastern Aegean coast: Levels, occurrence and ecological risk

Shareef K.I. Muzyed[a], Filiz Kucuksezgin[a,*], Nalan Tuzmen[b]

[a] Dokuz Eylul University, Institute of Marine Sciences and Technology, Inciraltı, Izmir, Turkey
[b] Dokuz Eylul University, Faculty of Science, Chemistry Department, Tinaztepe Yerleskesi, Buca, Izmir, Turkey

ARTICLE INFO

Keywords:
Organochlorines
Fish
Sediment
Ecological risk
Risk assessment
Eastern Aegean

ABSTRACT

Organochlorines were determined in fish and sediment collected from Izmir and Çandarlı Bays. The results indicated that ΣCyclodiens were generally predominant contaminants. In all samples, *p,p′*-DDE was the predominant DDT congener. Aroclors were found in noticeably higher levels than OCPs in sediment and the highest levels of Aroclors, OCPs were found in Nemrut which can be attributed to industrial activities. According to Sediment Quality Guidelines, DDTs were lower than the values that may cause adverse biological risk in sediment samples. Aroclor 1254 in sediments only exceeded the TEL value at Nemrut site. The maximum values of ΣOCPs were found in fish collected from Gülbahçe, while Aroclors were measured in Aliaga. According to related indices, results indicate no recent influxes of DDT in the sampling areas. The estimated daily intake of DDTs, Aroclor1254 were below the acceptable daily intake level recommended by FAO/WHO.

Generally, organochlorines (OCs) are hydrophobic substances, with low water solubility, frequently at the μg or ng per liter level. These organic compounds are highly concentrated by living organisms and concentrations can biomagnify along the food chain. Also OCs are known for their environmental persistence and global concerns (Doong et al., 2002). Therefore, an investigation of the distribution of some OCs such as organochlorinated pesticides (OCPs) and polychlorinated biphenyls (PCBs) in fish and sediment samples can provide valuable data about contamination in a marine environment.

Among 24 chemicals targeted by the Stockholm Convention, listed in the annexes of the convention, there are 15 OCPs. Although their production, usage and disposal have been regulated or prohibited in most of the developed countries, OCPs are still used at present in many developing countries (Zhou et al., 2008). In many instances, derivates of DDT, including DDE, DDD have been detected in surface waters, in sediments and as suspended solids > 25 years after DDT was prohibited (Hung and Thiemann, 2002). The production and usage of many chlorinated compounds such as dieldrin, aldrin, endrin, chlordane, DDT, BHC, lindane and heptachlor were completely banned in Turkey in the 1990s. However total pesticide usage in Turkey in 1995 was 37,000 ton and this usage has shown a steady increase year by year (TCV, 1998).

PCBs are an industrial product; there are no known natural sources. Atmospheric depositions, runoff from the land, and food chain transport (Davis et al., 2007) have been regarded as the major sources of PCBs in aquatic environments. Although the use of PCBs was banned in Turkey in1995, the import of PCBs continued illegally until the 2000s.

A number of studies have been carried out on the concentrations of metals in sediments and biota (Kucuksezgin, 2011; Kucuksezgin et al., 2006; Kucuksezgin et al., 2011) in Izmir Bay, however few studies were performed on organochlorine levels in sediment (Pazi et al., 2011; Pazi et al., 2012; Kucuksezgin and Gonul, 2012) and no data are available from the published literatures on the organochlorine levels in fish from the sampling areas. The aims of this study were to evaluate the occurrence and distribution patterns of OCs in sediment and fish samples from Izmir and Çandarlı Bays, which gave the information about status of contamination, to assess the potential sources of DDTs using related indices, to provide possible sources as well as potential biological risk of DDTs, PCBs in the study areas.

Fish and sediment samples were collected from Izmir and Çandarlı Bays located in the Eastern Aegean coast (Fig. 1). Izmir Bay is one of the great natural bays of the Mediterranean. Izmir is an important industrial and commercial centre and cultural focal point. Pollution in the outer part of the bay is not significant according to the most pollution indicators. The Gediz River, which flows into the Outer Bay, is the second biggest river along the Eastern Aegean coast and densely populated and includes extensive agricultural lands and numerous industrial areas. The main sources of pollution are domestic and industrial effluents (Kucuksezgin, 2011).

Çandarlı Bay is a semi-enclosed bay in the Eastern Aegean. Great

* Corresponding author.
E-mail address: filiz.ksezgin@deu.edu.tr (F. Kucuksezgin).

http://dx.doi.org/10.1016/j.marpolbul.2017.04.040
Received 20 February 2017; Received in revised form 20 April 2017; Accepted 22 April 2017

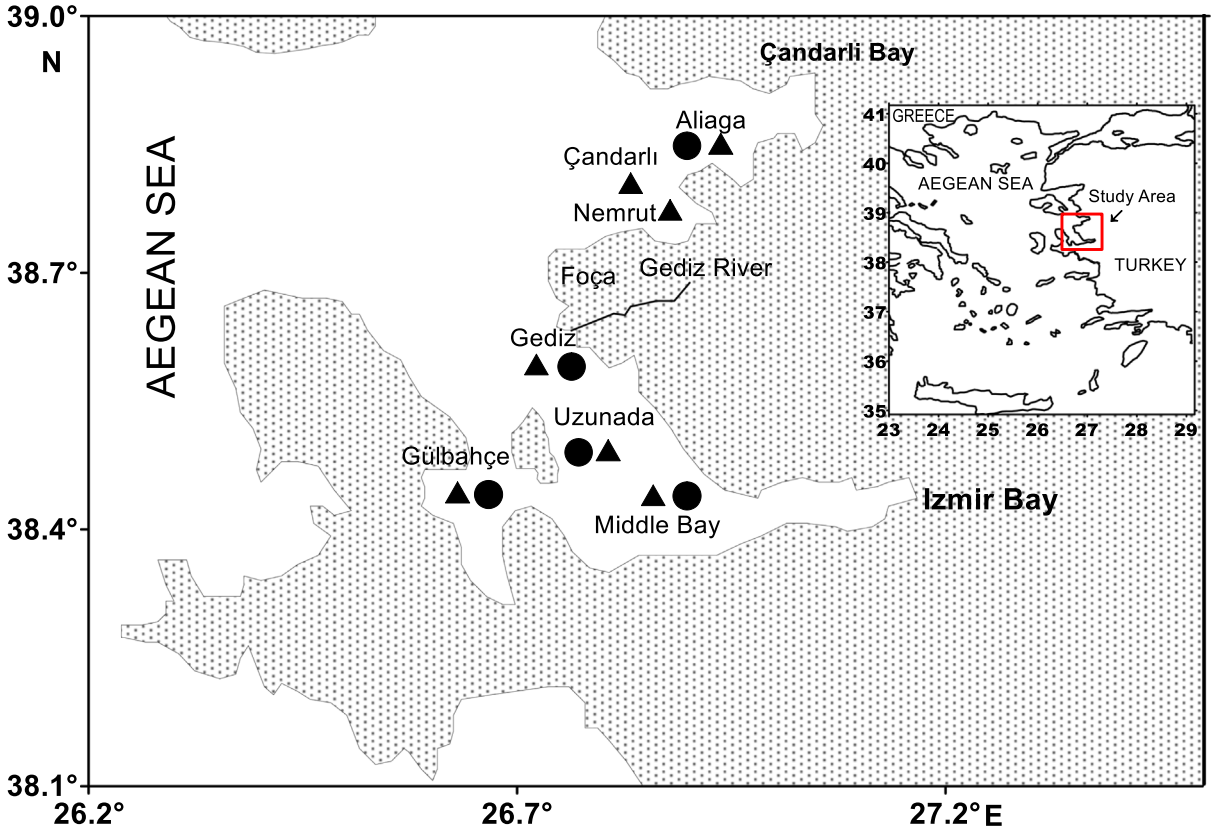

Fig. 1. Biota (●) and sediment (▲) sampling sites in Izmir and Çandarlı Bays.

industry settlements located in the coastal area of Çandarlı, have been discharging their wastes into Bakırçay River or Çandarlı Bay after limited treatment. Aliaga town located in the southern part of Çandarlı Bay, has been subjected to extensive industrial developments and is a ship dismantling area. There are iron and steel factories, coal storage yards, fuel storage yards, fertilizer factories, natural gas power plant, electrical substations, small industrial areas, and other medium and small establishments in the region (Pazi et al., 2012).

Fish (*Mullus barbatus*) were collected by trawling from five sites in Izmir (Gediz, Uzunada, Gulbahce, Middle Bay) and Çandarlı Bays during cruises of R.V. *K·Piri Reis* in 2014. Immediately, 25–30 organisms were dissected in the field from each sites and preserved at − 20° until transferring to labs. Muscle tissues were pooled and freeze-dried and then homogenized. Dry weight/wet weight was calculated as 0.28.

Surface sediments with three replicates were collected from the seven sampling sites (Gediz, Uzunada, Gülbahçe, Middle Bay, Çandarlı, Aliağa, Nemrut) using a box corer sampler, wrapped in aluminum foil and stored at − 20 °C for subsequent analysis in order to avoid degradation in 2014. The samples were freeze-dried, hand-sieved through 250 μm for grain size correction and homogenized, then kept until chemical analysis.

Three subsamples of each sample (approximately 5 g of dried fish sample) were extracted with a microwave digestion system using mixture of 30 ml hexane/acetone (90:10). For recovery of the method, internal standards (PCB29, PCB198, endosulfan Id4, ε-HCH) were added. The extract was then concentrated to about 10 ml and then the extract was dried with sodium sulfate and concentrated with nitrogen down to 1 ml. To avoid the lipid interfere during GC analysis sulfuric acid was used for saponification. Florisil column was used for fractionation of OCs for 3 groups using different solvents (UNEP/IOC/IAEA/FAO, 1990).

10 g of each sediment sample were extracted in microwave extraction system by adding 40 ml of a mixture of hexane/dichloromethane (1:1) and internal standards. After pre-concentration for the extracts sulfur was removed using activated elemental copper to avoid sulfur interferences during gas chromatography analysis. For fractionation, sediment samples were transferred into florosil column which was precleaned with dichloromethane and hexane and dried (UNEP/IOC/IAEA/FAO, 1990). Appropriate blank were analyzed. Quantitative analysis was performed with Agilent5975C 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.

All data were subject to strict quality assurance and control procedures. For each set of 10 samples, a procedural blank and a matrix sample spiked with standards were used to determine the accuracy. The recoveries for samples fell within a fairly narrow range, for internal standards between 70.0 and 96.1%. Also, the quality of the analytical data is assured using the reference materials of IAEA-451 and IAEA-417 for the biota and sediment samples (from IAEA, Monaco), respectively. The results for reference materials were given in Tables 2 and 4. The whole methodology was verified on these reference materials, obtaining results in good agreement with the certified values. The detection limits for OCPs were 0.10–0.57 pgg^{-1} and 2.4–4.5 pgg^{-1} for Aroclors.

The statistical analysis was done using the STATISTICA v.8.0 (STATSOFT) software package, and statistical significance was defined at the $p < 0.05$ level. Factor analysis, a multivariate analytical tool, was used to investigate the correlation of the determined parameters and facilitate the evaluation of pollution effects on the study area. This program based on Principal Component Analysis (PCA) as an extraction method and correlation matrix has been determined and Varimax Normalization rotation was performed.

The concentration of OCPs, cyclodienes, DDTs, Aroclors, EOM