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Türkiye'de, İzmit Körfezi'nde Yüzey Suyu ve Sedimentlerde Organik Klorlu Kirleticilerin Bölgesel ve Mevsimsel Dağılımı

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Özet: Türkiye'de İzmit Körfezi'nde yüzey suyu ve sedimentte, indikator poliklorlu bifeniller (PCB'ler) ile 1,1,1-trikloro-2,2-bis-klorofenil-etan (DDT) ve metabolitlerinin konsantrasyonları ve dağılımı tespit edilmiştir. Toplam PCB ve toplam DDT konsantrasyonları su örneklerinde sırasıyla <0.003 - 440 ng/L, ve <0.003 - 1255 ng/L olarak tespit edilirken, sediment örneklerinde <1 - 674 ng/g kuru ağırlık, ve <1 - 7286 ng/g kuru ağırlık olarak tespit edilmiştir. Sediment örneklerinde tespit edilen PCB ve DDT konsantrasyonları, bu hidrofobik maddelerin sediment fazına olan yüksek affinitelerine bağlı olarak, yüzey sularından çok daha yüksek bulunmuştur. 28, 52, 101 IUPAC No'lu PCB bileşenleri ve *p,p'*-DDT su ve sediment örneklerinde sıklıkla tespit edilmiştir.

Anahtar Kelimeler: PCB; DDT; Marmara Denizi; İzmit Körfezi

Spatial and Seasonal Distribution of Organochlorine Contaminants in Surface Water and Sediment from the İzmit Bay, Turkey

Abstract: The concentrations and distribution of indicator polychlorinated biphenyls (PCBs) and 1,1,1-trichloro-2,2-bis-chlorophenyl-ethane (DDT) and its metabolites were determined in surface water and sediments from the İzmit Bay, Turkey. The results showed that the levels of the total PCBs and total DDTs ranged from <0.003 to 440 ng/L, and <0.003 to 1255 ng/L in water, and from <1 to 674 ng/g dry weight, and <1 to 7286 ng/g dry weight in sediments respectively. Concentrations of PCBs and DDTs in sediment were significantly higher than those in surface water, due to the high affinity of these hydrophobic compounds for sediment phase. Congeners IUPAC Nos. 28, 52, 101 and *p,p'*-DDT were found frequently in water and sediment samples.

Keywords: PCB; DDT; Marmara Sea; İzmit Bay

• Doktora tezinden özetlenmiştir**.**

Introduction

Among a large number of man-made chemicals, organochlorines such as 1,1,1-trichloro-2,2-bis-chlorophenyl-ethane (DDT) and polychlorinated biphenyls (PCBs) are of great concern due to their highly persistent nature and global occurence (Glynn et al., 1995; Tkalin, 1996). These chemicals are bioaccumulative in nature, can biomagnify in the foodweb and induce various toxic effects in marine organisms (Fernandez et al., 1999; Maskaoui et al., 2005; Mora et al., 2005). Industries such as manufacture of adhesives, additives to hydraulic oil, capacitor and transformer fluids, paints, fire retardants, plastics, extenders in pesticide and carbonless copying paper have extensively used PCBs, because PCBs are extremely resistance to acid and base, heat stable and very inert (Alford-Stevens, 1986). The commercial production and usage of PCBs ceased in 1977, however illegal use and dumping of waste containing PCBs still pose serious environmental problems (Alford-Stevens, 1986; Connell et al., 1998). They have been reported to cause variety of effects including immunologic, teratogenic, carcinogenic, reproductive and neurological problems in organisms (Kodavanti et al., 1998).

Even after being banned, DDT is still being produced and used in many developing countries in agriculture to control pests effectively and in public health activities for the control of the diseases such as malaria and typhus (Pham et al., 1996; Tkalin, 1996; Wu et al., 1999; Nhan et al., 2001). Similar to PCBs, DDTs also cause endocrine disruption and are hazardous to human and/or environmental health (Babu-Rajendran et al., 2005). DDT and some of its metabolites are mutagenic, potentially carcinogenic, and are known to be environmental estrogens (Robinson et al., 1985). They are amongst the 12 Persistent Organic Pollutants (POPs) that are banned and included in the list of priority contaminants to be monitored regularly, and targeted for ultimate elimination under the international treaty (UNEP, 2001; Babu-Rajendran et al., 2005).

İzmit Bay, located south of İstanbul on the southeast of the Marmara Sea, is the most important semi-enclosed body of water on the sea of Marmara. Sea of Marmara is an inland basin located between the Black Sea and Aegean Sea, and has a two-layer stratification (Algan et al., 1999). İzmit Bay is one of the most polluted areas in Turkey. It is about 50 km in length, 2-10 km in width and has a surface area of 310 km^2 (Fig. 1). It consists of three district parts which behave semi-independently. The Eastern sector (inner part) is very shallow (30 m) and consists of the most polluted part of the Bay. While the industries of petroleum are based in the Central part, the entrance to the Marmara Sea through a wide and deep

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channel is located in the Western part (outer part) which is less polluted because of better water exchange (Okay et al., 2003). In addition, there are no industries with high polluting potential in Western part. The Central part is highly affected by the heavy industries discharging their wastewaters through Dil River into the Bay. The Eastern part is the most polluted, industrialized and the shallowest site of the Bay. One of the most-crowded cities of Turkey, İzmit, is situated on the coast of that part (Morkoç et al., 2007). There are more than 140 large industrial plants, such as petrochemical, pesticides and chlorine alkaline factories, scattered around the Bay and commissioning of these and, particularly, the consequent urbanisation of the coastal landscape have completely destroyed the İzmit Bay (Telli-Karakoç et al., 2002). The largest wastewater contribution comes to the Bay from İzmit city (Legovic et al., 1995).

On August 17, 1999, a powerful earthquake struck the Marmara region, and after the earthquake, most of the industrial treatment plants had been damaged and the refinery fire caused an increase in the levels of pollutant discharge through Petkim Channel (Okay et al., 2003; Morkoç et al., 2007).

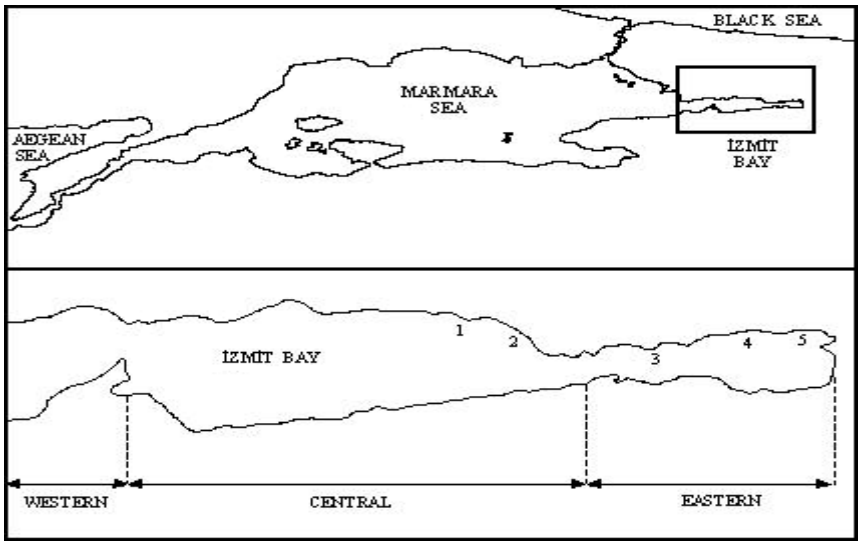

Figure 1. *Location of sampling stations (station 1: Kirazlıyalı; station 2: Petkim; station 3: Koruma Tarım; station 4: SEKA; station 5: Sarıdere) in the İzmit Bay in Turkey*

In this research, water and surface sediment samples collected from 5 different predetermined stations, (from west to east) Kirazlıyalı, Petkim, Koruma Tarım, SEKA and from the conjunction point of Sarıdere (the stream that İzaydaş, the waste incinerator plant, discharges the industrial and domestic wastes) and the Bay were analyzed monthly between December-2003 and November-2004 to measure the contamination level of indicator polychlorinated biphenyls and DDT compounds threatening environment and human health in İzmit Bay.

According to a study on the global distribution and budget of PCBs in surface soils, Turkey is in a global source region where 86% of the total global PCB usage occured (Meijer et al., 2003), and relatively higher emissions of PCBs would be expected on a global scale (Breivik et al., 2007). Nevertheless, very little is known on the PCB contamination and distribution in the environment and the biota of the İzmit Bay (Gedik and İmamoğlu, 2010, Gedik et al., 2010). Furthermore, in spite of the previous use of pesticides in İzmit city and other districts in Marmara Region, and Black Sea region, the DDT contamination in the Bay has never been measured in any previous studies. Also there is a contaminated site, an obsolete pesticide dump consisting of approximately 3000 tonnes of HCH and DDT. These chemicals are stored in improper conditions. The contaminated site is located in a heavily industrialized area and approximately 300 m to the shore. The nearest facilities are the oil distribution centers of the biggest oil companies. The facility, called Koruma Tarım, where the pesticides are produced is approximately 700 m from the site. No certain vegetation or animal life is documented in the area (Türkmen, 2005). Because of the reasons mentioned above, the primary purpose of this study is, therefore, to determine the levels and distribution of PCBs and DDTs comprehensively in the surficial water and sediments from the İzmit Bay. As PCB concentrations were determined in sea water of İzmit Bay before the quake (Telli-Karakoç et al., 2002), data in this study would provide valuable information on making comparisons and evaluating the effects of the Marmara earthquake of 1999 in İzmit, Turkey.

Materials and Methods

Sampling and sample treatment

Between 2003 (December)-2004 (November) subsurface (0.5 m) water and surface (0-10 cm) sediment samples were collected using the Ruttner and an Eckman-Grab respectively and placed in hexane-cleaned glass jars with foil cap liners at five locations. The stations in İzmit Bay were (from west to east) Kirazlıyalı (station 1 - station

close to industrial plants), Petkim (station 2 - petrochemical and chlorine substances factory), Koruma Tarım (station 3 - pesticide and chlorine alkaline chemicals factory), SEKA (station 4 - pulp and paper factory) and the conjunction point of Sarıdere (the stream that İzaydaş, the waste incinerator plant, discharges the industrial and domestic wastes) and the Bay (station 5). The sampling stations in İzmit Bay are shown in Figure 1. The water and sediment samples were stored at <4°C in dark until they were returned to the laboratory. The water samples were stored at <4°C in dark until analyzed and after discarding of excess liquid of the sediment samples, they were stored at <-10º C in dark until analyzed (USAEPA, 1999).

Standards

Reference PCBs (7 congeners and mix, each at 10 ng/µL) and DDTs (7 metabolites and mix, each at 10 ng/µL and mix, each at 100 ng/µL) were obtained from Dr. Ehrenstorfer. Working solutions were prepared by diluting the stock solutions with hexane to prepare solvent and matrix matched calibration solutions for GC analyses in the range of 3-500 ng/mL and also the single point calibration solutions for the values exceeding calibration solutions range.

Sample extraction

Sediment samples

Following open air drying for 2 days, sediment samples were sieved through a 1mm mesh and 5-10 g was oven-dried at 110ºC in order to determine the dry weight. All results for sediment samples were reported on a dry weight basis. Sediment samples (10 g) were mixed with anhydrous sodium sulphate and freshly prepared Cu granules, and then extracted in 300 mL mixture of aceton:hexane (1:1) for 16 hours. Following soxhelet extraction, the extracts were concentrated by rotary evaporator and purified by passing through Biobeads SX3 gel permeation chromatography system using ethyl acetate:cyclohexane mixture (1:1) as elution solvent with the flow rate of 1 mL/min. All the extracts were concentrated by rotary evaporator and gentle nitrogen blow, and then dissolved in 1 mL n-hexane (USAEPA, 1996; 1999).

Sea water samples

Sea water samples (1 L) were extracted with first 60 and then 20 mL portions of dichloromethane (3 times for each sample) and each portion was drained through the anhydrous sodium sulphate. Following separatory funnel extraction all the extracts were concentrated by rotary evaporator and gentle nitrogen blow, and then dissolved in 1 mL n-hexane (USAEPA, 1999).

Analyses

PCB and DDT determination was carried out on Hewlett Packard (HP) 6890 gas chromatoraph with a micro electron capture detector (µECD). An Agilent 19091S-433, HP-5MS, 30 m %5 phenyl-methylpolysiloxane capillary column, 0.25 mm i.d. and 0.25 µm film thickness was used with helium as the carrier gas at a pressure of about $1.5x10^5$ Pascal and nitrogen as the purge gas at a velocity of about 40 mL/min. Injection port was maintained at 250°C, and the sample was injected in splitless mode. Detector temperature was 350°C. Column temperature was held at 90°C for initial 4 min, and then programmed at 35°C/min to 160°C, held for 1 min, ramped at 3°C/min to 244°C and held for 10 min (CEN, 1996). The peaks were identified by matching the retention times of the peaks in the sample with those of authentic standards in the calibration solution. PCB/DDTs in samples were confirmed by GC/MS using primarily a HP 6890 gas chromatograph fitted with an HP 5973 quadropole mass spectrometer and a Agilent 19091S-433, HP-5MS, 30 m %5 phenyl-methylpolysiloxane capillary column, 0.25 mm i.d. and 0.25 µm film thickness was used with helium as the carrier gas at a flow rate of about 1.9 mL/min. Injection port was maintained at 250°C, and the sample was injected in splitless mode. Column temperature was held at 70°C for initial 2 min, and then programmed at 25°C/min to 150°C, held for 0 min, ramped at 3°C/min to 200°C and held for 0 min, ramped at 8°C/min to 280°C and held for 10 min (Meng and Szelewski, 2000). And secondly Varian CP3800 gas chromatograph with an electron capture detector was also used for confirmation.

Quality assurance

Before analysis, relevant standards were run to check column performance, peak area, height and resolution, and limits of detection (LoD). For each set of samples to be analysed, a field blank, a procedural blank and a standard mixture were run in sequence to check for contamination, peak identification and quantification.

Compounds were identified mainly by their retention times. To assure quality control, spiked samples were analysed for each set of samples. Recoveries of spiked water and sediment samples were 73%-108% and 72%-109% respectively. The detection limits for sea water and sediment samples were 0.003 ng/mL and 1 ng/g (dry weight) respectively for both PCB congeners and DDT metabolites. In addition, the errors involved in sampling were assessed by carrying out duplicate sampling of water and sediment from the same site and analyzing the samples.

Results and Discussion

PCB congeners

In water samples while the lowest total PCB concentration was determined as 0.003 ng/mL in January-2004 at station 4, the highest concentration was determined as 0.440 ng/mL in December-2003 at station 1. PCB concentrations of the water samples varied according to months and stations. Results are shown in Table 1. Generally highest concentrations were determined in the samples taken from Kirazlıyalı, SEKA and the conjuction point of Sarıdere and İzmit Bay. The water samples taken from İzmit Bay through the year were not so clear but especially the samples taken from these three stations indicated above were more turbid. Vuksanovic et al. (1996) also determined that PCB concentrations were higher in the zones that the turbidity was maximum.

Concentrations of PCBs in surface water depend on rain (WHO, 1993) and throughout the course of this study, a considerable amount of rainfall was experienced (Turkish State Meteorological Service, 2006). Konat and Kowalewska (2001) indicated that flood and too much rain affect the concentrations in water and carry the contaminated soils to water body. Furthermore, Robertson and Hansen (2001) determined that the solubility of PCBs in water may arise according to humic material or dissolved organic carbon content in water. In a related study it was found that the organic carbon content of the sediments taken from the Bay were extremely high (Tolun et al., 2001). The Bay's ecosystem is highly sensitive to increased concentration of organic matter. The most affected areas from industrialization; urbanization and fertilizer runoff from agricultural activities in the Bay ecosystem are located in the eastern part of the Bay (Morkoç et al., 2001). Organic matter accumulated on the sea bottom re-suspended by the extensive vibration due to the earthquake (Morkoç et al., 2007). Last but not least, in İzmit Bay -due to strong winds- anoxic bottom waters flow up and the suspansion of the contaminated sediment layer occurs, so adding these factors to the instability of the conditions of the sea water regarding the meteorologic changes, the bay is affected adversely and risk factors emerge (Okay et al., 2003).

Contamination levels in the sea water samples show values, in terms of PCB concentration, similar to those found in sea water samples by Telli-Karakoç et al. (2002), but in this study some of the concentrations were found to be higher. When the 17 August 1999 earthquake occurred, great loads of industrial wastes were released into the surface waters of the Bay and large quantity of particulate organic matter moved to the lower layer and eventually to the bottom (Morkoç et al., 2007). And also because of the earthquake, the PCB congeners deeper in sediment layers might have moved to upper layers and been released to the water column or tidal events might have carried the contaminated soils to the Bay waters.

It was also mentioned that factors like sediment composition, contamination level of the sediments with the PCB congeners and incubation temperature affect the levels of PCB concentration in water and the releasing ratio of these congeners from sediment to water (Sanders et al., 1997).

In this study, dominant congeners of the sea water samples were PCB 28, 52 and 101. Among the other congeners, higher concentrations of PCB 28 with the lowest chlorine substitution may be attributed to higher solubility of this congener in water comparison with the others. This finding is also in accordance with the Fu and Wu (2006) results. Robertson and Hansen (2001) mentioned that water solubility of PCB congeners decreases with the increasing number of the chlorine atoms of biphenyl ring. These results clearly point to the importance of atmospheric transport of CB28 in the İzmit Bay. Indeed this congener is recognised as having high mobility capacity (Shaw and Connely, 1984). Also Walker (2001) indicated that higher chlorinated PCB congeners degrade faster than the lower congeners in anaerobic sediments and if it is considered for anoxic waters then higher concentrations of lower chlorinated congeners in Bay's water can be explained.

PCB concentrations of sea water samples determined in this study were higher than those found in sea water samples by Lewis et al. (2001), Falandysz et al. (2002) and Nie et al. (2005). Limited ventilation and circulation of waters especially in the eastern part affect the PCB concentrations and higher concentrations found in this study may be attributed to this situation. On the other hand, PCB concentrations found in the sea water samples from İzmit Bay are actually lower than the results of some other studies (Kocan et al., 2001; EC. ELICC., 2004). Uptake by the phytoplankters appears to be the dominant mechanism of reducing the toxicity in the Bay. The second mechanism reducing the toxicity of the waste is dispersion by wind-induced current (Okay et al., 1996).

In water, PCBs are adsorbed on sediments and other organic matter; experimental and monitoring data have shown that PCB concentrations in sediment and suspended matter are higher than those associated water columns. Strong adsorption on sediment, especially in the case of the higher chlorinated PCBs, decreases the rate of volatilization. The substantial quantities of PCBs in aquatic sediments can therefore act as both an environmental sink and a reservoir of PCBs for organisms. Most of the environmental load of PCBs has been estimated to be in aquatic sediment (WHO, 1993). In this study the PCB concentrations were found to be higher in sediment samples either. In sediment samples while the lowest total PCB concentration was determined as 1.03 ng/g (dry weight) in January-2004 at station 4, the highest concentration was determined as 674 ng/g (dry weight) in January-2004 at station 3. Also the PCB concentrations of the sediment samples varied according to months and stations. Results are shown in Table 1. Generally highest concentrations were determined in the samples taken from Koruma Tarım, SEKA and Petkim stations. If the total PCB concentrations of January-2004 (674 ng/g dw), February-2004 (582 ng/g dw) and August-2004 (151 ng/g dw) in station 3 are not taken into account, no big difference was determined among the stations. In terms of individual congener distributions, in sediment samples, the congeners which made the largest individual contribution to total PCB concentrations were PCB 118, 138 and 153 at station 3.

It is hard to identify the source-occurence relationship because of the many discharge points surrounding the coastal line of the Bay. The tidal events cause sediment layer movements and sediment particules suspend in the water column thus chlorination increases depending on the movements from different sources (Tyler and Millward, 1996). The reason of established and high levels of moderate and higher chlorinated PCBs is low volatility, lipophilicity, tendency to adsorption on sediment surfaces and resistibility to microbial degradation (Shiu and Mackay, 1986; Tyler and Millward, 1996). Higher concentrations of moderate and higher chlorinated PCBs found in İzmit Bay support that finding. But generally, congeners found widespread in all

stations were the lower chlorinated congeners like PCB 28, 52 and 101. This finding is also in accordance with Wiegel and Wu (2000) since they indicated that in aquatic sediments, PCBs are reductively dechlorinated and degraded to lower chlorinated congeners due to microbial degradation in anaerobic conditions. Furthermore, the anoxicidity of the bottom layers of İzmit bay (Morkoç et al., 2007) supports Walker's (2001) findings that in anaerobic sediments higher chlorinated PCB congeners degrade faster than the lower ones.

During the last few decades, increased eutrophication appears to have affected the Bay's ecosystem negatively and become a serious problem (Morkoç et al., 2001; Okay et al., 2001). So, eutrophication could play a role in increasing the total PCB burden of the Bay.

The bottom sediments of the İzmit Bay consist of predominantly fine grained material with various proportions of silt and clay, however, sand–sized material contribute in varying degrees (Algan et al., 1999). Adsorption of contaminants on particules increases due to high organic matter burden and clayey type of sediment (Robinson et al. 1982a, b). Higher concentrations found in sediment samples can be attributed to high humic material content. It was mentioned that PCBs filter through sandy, silt and clayey sediments respectively in an increasingly harder fashion (WHO, 1993). But sediment samples collected from Kirazlıyalı were poorly sorted humic material and sand fraction was dominant. Moreover, high concentrations of PCBs in sea water samples in Kirazlıyalı can be attributed to this sandy structure and low adsorbance capacity of PCB congeners to sand particules.

The total PCBs concentration observed in the Bay in this study were comparable or occasionally higher than sediment PCB concentration determined in the study of Gedik et al. (2010). This finding indicates that the adverse effects of the earthquake is relatively reduced by the time. PCB concentrations of sediment samples were found higher than Fernandez et al. (1999), Kelderman et al. (2000), Miller et al. (2000), Fillmann et al. (2002), Nakata et al. (2005). The earthquake on 17 August 1999 have caused a vast deterioration of the sediment structure of the İzmit Bay and might have caused movement of contaminants to upper layers of sediment. But higher concentrations were also found in some studies (Metcalfe and Metcalfe, 1997; Chevreuil et al., 1998; Lewis et al., 2001; Fu and Wu, 2006).

Having found PCB 28, 52, 101 and 153 as dominant congeners and the other ones at high levels but not widespread is in accordance with Konat and Kowalewska (2001). The spatial distribution of PCBs in the Bay suggest that the sediments close to the former pulp and paper industry, chlorine alkaline industry and petroleum industry have relatively high PCB levels, indicating probable sources. This finding is also in accordance with Gedik et al. (2010).

DDT metabolites

In water samples while the lowest total DDT concentration was determined as 0.003 ng/mL in February-2004 at station 2, the highest concentration was determined as 3.180 ng/mL in January-2004 at station 5. DDT concentrations of the water samples varied depending on months and stations. Results are shown in Table 2. Generally highest concentrations were determined in the samples taken from the conjuction point of Sarıdere and İzmit Bay, Koruma Tarım and Petkim. Total DDT concentrations of water samples were found to be higher than the PCB concentrations. The levels of DDT and DDD in sea water samples in some of the sampling months were found to be above the limits mentioned in the Turkish National Aquaculture Regulation. It was mentioned that the maximum residue limits for DDT and DDD are 0.6 µg/L ve 3.0 µg/L respectively (Turkish National Aquaculture Regulation, 1995). *p,p'*-DDT concentrations were measured to be above the MRL in January-2004 except the 5th station and also *p,p'*-DDD concentrations of 5th station in January-2004 were found to be very close to MRL. Concentrations of DDT in surface water depend on the soil as well as on the rain. As it was indicated before, an excessive amount of rainfall was experienced throughout the study. DDT has a strong tendency to adsorb on surfaces. Most DDT that enters water is already firmly attached to soil particles, and remains attached. It was shown very early that, if DDT does find its way into clear water, it is gradually lost by adsorption on surfaces (WHO, 1979).

Concentrations of İzmit Bay were found to be lower than Ayas et al. (1997), Barlas (1999), Barlas (2002) but the order of the metabolites from higher to lower concentrations was the same as being DDD>DDT>DDE. This finding and also the concentrations were in accordance with Turgut (2003).

Dominant metabolites were determined as DDD and DDT in sea water samples in this study. In anoxic sediments DDD concentrations are higher than DDE concentrations and also DDT degrades to DDD and DDE in anaerobic and aerobic conditions respectively (Robinson et al., 1982a, b). DDD is a component of technical DDT and also DDD was sold as a pesticide called Rhothane and if it is considered that *p,p'*-DDT composing 70 % of technical DDT degrades to DDD then it is not a surprise to find DDD dominantly (Walker, 2001).

Tuncer et al. (1998), determined that 500 tonnes DDT discharge to Black Sea annually and proved illegal use of this chemical due to detection of DDT in all water bodies researched. In this study the DDE/DDT ratio was found to be less than 1, this finding also indicated new discharges to the Bay. To identify the real source of contamination is very difficult. The contaminations may have been sourced from Koruma Tarım (factory producing many chlorinated chemicals) or the abondoned depot near Koruma Tarım containing tonnes of DDT and the other organochlorine pesticides stored under improper conditions (Türkmen, 2005). There was considerably high amount of rain in December-2003, January-February-2004 but it was also

indicated that average rainfall in 2003 and 2004 years were higher than the overall average (Turkish State Meteorological Service, 2006). In these months finding of high concentrations of total DDT especially *p,p'*-DDT can be attributed to DDT metabolites leaking from contaminated area originating from pesticide dump by the rain. Concentrations of sea water samples of İzmit Bay were measured to be higher than Fernandez et al. (1999), Cataldo et al. (2001), Lewis et al. (2001). The differences can be attributed to the differences in geography, climate and industrial facilities.

In sediment samples while the lowest total DDT concentration was determined as 1.95 ng/g (dry weight) in October-2004 at station 1, the highest concentration was determined as 7286 ng/g (dry weight) in January-2004 at station 3. Also the DDT concentrations of the sediment samples varied depending on the time of the year and the stations. Generally highest concentrations were determined in the samples taken from Koruma Tarım, Sarıdere and SEKA. If the total DDT concentrations of December-2003 (610 ng/g dw), January-2004 (7286 ng/g dw) and February-2004 (4397 ng/g dw) in station 3 are not taken into account, no big differences were determined between the stations. In terms of individual metabolite distributions, in sediment samples, the metabolites which made the largest individual contribution to total DDT concentrations were *p,p'*-DDT, *o,p'*-DDT and *p,p'*-DDD in station 3. All results are shown in Table 2.

In practice, the most abundant and widespread residues of DDT found in the environment have been *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE (Walker, 2001). DDE metabolites were determined in almost all sediment samples in this study. However, high amounts of DDD and DDT metabolites were found at some point sources. These results highlight the known stability and persistence of DDE in the environment.

This study about contamination in sediment samples in İzmit Bay show values, in terms of DDT metabolites concentration, higher than those reported by Bakan and Ariman (2004), Nakata et al. (2005), Babu Rajendran et al. (2005), Thomas et al. (2005), Wurl and Obbard (2005). High concentrations of DDT metabolites at Koruma Tarım compared to the other stations in sediments collected in the rainy season are also likely to reflect the increased transportation of these contaminants from the depot containing chlorine pesticides near the Koruma Tarım by surface runoff.

Concentrations determined in this study were found to be lower than Barlas (1999) and also the congener pattern was different. This difference can be attributed to the depot near the third station since generally *p,p'*-DDE was dominant but high concentrations of DDD and DDT metabolites at third station could be sourced from new inputs of Koruma Tarım producing Dicofol containing interferences like *p,p'*-DDT, *p,p'*-DDD and *p,p'*-DDE. This finding is also in accordance with Fernandez et al. (1999). The concentrations found in this study are in accordance with Ayas et al. (1997), Barlas (2002), Fung et al. (2005) and except high concentrations found at Koruma Tarım also with Fillmann et al. (2002).

Sediments containing various inorganic compounds and organic compounds, biota, bacteria, dissolved cations and anions have a very complex structure and additionally the oxygen content of the sediments also make it hard to evaluate the results. It was mentioned before that in oxidative aerobic conditions DDT degrades to DDE and under reductive conditions DDD formation occurs (Robinson et al., 1982a, b). Higher concentrations found at Koruma Tarım in winter may have been caused by small earthquakes induced movements of contaminants to upper layers. Furthermore clayey and humic material rich sediment layer may have played a significant role since it was mentioned that it is harder for organic contaminants to move to the lower layers in the clayey sediment than in the sandy sediment (EC. ELICC., 2004), so little movements of sediment layer can cause contamination of the surface sediments.

Considering these observations, further investigations on the monitoring of PCB and DDT pollution are needed to assess the risks of wildlife and human health in İzmit Bay.

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References

Alford-Stevens, A.L. 1986. Analyzing PCBs: basic information about PCBs and how they are identified and measured. Environmental Science and Technology 20, 1194-1199.

Algan, O., Altıok, H., Yüce, H. 1999. Seasonal variation of suspended particulate matter in two-layered İzmit Bay, Turkey. Estuarine Coastal and Shelf Science, 49, 235-250.

Ayas, Z., Barlas (Emir), N., Kolankaya, D. 1997. Determination of organochlorine pesticide residues in various environments and organisms in Göksu Delta, Turkey. Aquatic Toxicology, 39, 171-181.

Babu Rajendran, R., Imagawa, T., Tao, H., Ramesh, R. 2005. Distribution of PCBs, HCHs and DDTs, and their ecotoxicological implications in Bay of Bengal, India. Environment International, 31, 503-512.

Bakan, G., Ariman, S. 2004. Persistent organochlorine residues in sediments along the coast of mid-Black Sea region of Turkey. Marine Pollution Bulletin, 48, 1031-1039.

Barlas, N.E. 1999. Determination of organochlorine pesticide residues in aquatic systems and organisms in upper Sakarya Basin, Turkey. Bulletin of Environmental Contamination and Toxicology, 62, 278-285.

Barlas, N.E. 2002. Determination of organochlorine pesticide residues in water and sediment samples in Inner Anatolia in Turkey. Bulletin of Environmental Contamination and Toxicology, 69, 236-242.

Breivik, K., Sweetman, A., Pacyna, J.M., Jones, K.C. 2007. Towards a global historical emission inventory for selected PCB congeners-a mass balance approach-3. An update. Science Total Environment, 377, 296-307.

Cataldo, D., Colombo, J.C., Boltovskoy, D., Bilos, C., Landoni, P. 2001. Environmental toxicity assessment in the Parana river delta (Argentina): simultaneous evaluation of selected pollutants and mortality rates of *Corbicula fluminea* (Bivalvia) early juveniles. Environmental Pollution, 112, 379-389.

CEN. 1996. European Standard. European Committee for Standardization. ICS 67.040. CEN 1528 (1-4). November 1996. Brussels.

Chevreuil, M., Blanchard, M., Teil, M.J., Chesterikoff, A. 1998. Polychlorobiphenyl behaviour in the water/sediment system of the Seine River, France. Water Research, 32 (4), 1204-1212.

Connell, D.W., Wu, R.S.S., Richardson, B.J., Leung, K., Lam, P.S.K., Connell, P.A. 1998. Occurence of persistent organic contaminants and related substances in Hong Kong marine areas: an overview. Marine Pollution Bulletin, 36, 376-384.

EC. ELICC. 2004. European Commission, Brussels. Dioxins and PCBs: Environmental levels and human exposure in candidate countries. Reference: ENV.C.2./SER/2002/0085. Final report. ELICC. Consortium:Environmental levels in candidate countries under supervision of Gunther Umlauf (JRC). BIPRO (Beratungsgesellschaft für integrierte problemlösungen). 333 pp.

Falandysz, J., Wyrzykowska, B., Puzyn, T., Strandberg, L., Rappe, C. 2002. Polychlorinated biphenyls (PCBs) and their congener specific accumulation in edible fish from the Gulf of Gdansk, Baltic Sea. Food Additives and Contaminants, 19 (8), 779-795.

Fernandez, M.A., Alonso, C. Gonzalez, M.J., Hernandez, L.M. 1999. Occurrence of organochlorine insecticides, PCBs and PCB congeners in waters and sediments of the Ebro River (Spain). Chemosphere, 38 (1), 33-43.

Fillmann, G., Readman, J.W., Tolosa, I., Bartocci, J., Villeneuve, J.P., Cattini, C., Mee, L.D. 2002. Persistent organochlorine residues in sediments from the Black Sea. Marine Pollution Bulletin, 44, 122-133.

Fu, C.T., Wu, S.C. 2006. Seasonal variation of the distribution of PCBs in sediments and biota in a PCB-contaminated estuary. Chemosphere, 62 (11), 1786-1794.

Fung, C.N., Zheng, G.J., Connell, D.W., Zhang, X., Wong, H.L., Giesy, J.P., Fang, Z., Lam, P.K.S. 2005. Risks posed by trace organic contaminants in coastal sediments in the Pearl River Delta, China. Marine Pollution Bulletin, 50 (10), 1036-1049.

Gedik, K., Demircioğlu, F., İmamoğlu, İ. 2010. Spatial Distribution and Source apportionment of PCBs in sediments around İzmit industrial complexes, Turkey. Chemosphere, 81, 992-999.

Gedik, K., İmamoğlu, İ. 2010. An assessment of the spatial distribution of polychlorinated biphenyl contamination in Turkey-Review. Clean-Soil, Air, Water, 38, 117-128.

Glynn, P.W., Rumbold, D.G., Snedaker, S.C. 1995. Organochlorine pesticide residues in marine sediment and biota from the Northern Florida Reef Tract. Marine Pollution Bulletin, 30, 397-402.

Kelderman, P., Drossaert, W.M.E., Min, Z., Galione, L.S., Okonkwo, L.C., Clarisse, I.A. 2000. Pollution assessment of the canal sediments in the city of Delft (The Netherlands). Water Research, 34 (3), 936-944.

Kocan, A., Petrik, J., Jursa, S., Chovancova, J., Drobna, B. 2001. Environmental contamination with polychlorinated biphenyls in the area of their former manufacture in Slovakia. Chemosphere, 43, 595-600.

Kodavanti, P.R.S., Ward, T.R., Derr-Yellin, E.C., Mundy, W.R., Casey, A.C., Bush, B., Tilson, H.A. 1998. Congener-specific distribution of PCBs in brain regions, blood, liver, and fate of adult rats following repeated exposure to Aroclor 1254. Toxicology and Applied Pharmacology, 153 (2), 199-210.

Konat, J., Kowalewska, G. 2001. Polychlorinated biphenyls (PCBs) in sediments of the southern Baltic Sea-trends and fate. Science of the Total Environment, 280 (1-3), 1-15.

Legovic, T., Morkoç, E., Okay, O.S., Egesel, L., Tüfekçi, V., Tüfekçi, H. 1995. Mass balance of total phosphorus in the İzmit Bay. Water Science and Technology, 32 (2), 193-198.

Lewis, M.A., Moore, J.C., Goodman, L.R., Patrick, J.M., Stanley, R.S., Roush, T.H., Quarles, R.L. 2001. The effects of urbanization on the chemical quality of three tidal bayous in the Gulf of Mexico. Water Air and Soil Pollution, 127, 65-91.

Maskaoui, K., Zhou, J.L., Zheng, T.L., Hong, H., Yu, Z. 2005. Organochlorine micropollutants in the Jiullong River Estuary and Western Xiamen Sea, China. Marine Pollution Bulletin, 51, 950-959.

Meijer, S.N., Ockenden, W.A., Sweetman, A., Breivik, K., Grimalt, J.O., Jones, K.C. 2003. Global distribution and budget of PCBs and HCB background surface soils: implications for sources and environmental processes. Environmental Science Technology, 37, 667-672.

Meng, K.C., Szelewski, M.J., 2000. Fast screening of PCB congeners using the Agilent 6890/5973N GC/MSD system. Agilent application note. Agilent Technologies, Inc. 2850 Centerville Road Wilmington, DE 19808-1610 USA, 4 pp.

Metcalfe, T.L., Metcalfe, C.D. 1997. The trophodynamics of PCBs, including mono- and non-*ortho* congeners, in the food web of North-Central Lake Ontario. Science of the Total Environment, 201, 245-272.

Miller, B.S., Pirie, D.J., Redshaw, C.J. 2000. An assessment of the contamination and toxicity of marine sediments in the Holy Loch, Scotland. Marine Pollution Bulletin, 40 (1), 22-35.

Mora, S., Fowler, S.W., Tolosa, I., Villeneuve, J.P., Cattini, C. 2005. Chlorinated hydrocarbons in marine biota and coastal sediments from the Gulf and Gulf of Oman. Marine Pollution Bulletin, 50, 835-849.

Morkoç, E., Okay, O.S., Tolun, L., Tüfekçi, V., Tüfekçi, H., Legovic, T. 2001. Towards a clean İzmit Bay. Environment International, 26, 157-161.

Morkoç, E., Legovic, T., Okay, O., Tüfekçi, H., Tüfekçi, V., Tolun, L., Karakoç, F. 2007. Changes of oceanographic characteristics and the state of pollution in the İzmit Bay following the earthquake of 1999. Environmental Geology, 53, 103-112.

Nakata, H., Hirakawa,Y., Kawazoe, M., Nakabo, T., Arizono, K., Abe, S.I., Kitano, T., Shimada, H., Watanabe, I., Li, W., Ding, X. 2005. Concentrations and compositions of organochlorine contaminants in sediments, soils, crustaceans, fishes and birds collected from Lake Tai, Hangzhou Bay and Shanghai city region, China. Environmental Pollution, 133, 415-429.

Nhan, D.D., Carvalho, F.P., Am, N.M., Tuan, N.Q., Yen, N.T.H., Villeneuve, J.P., Cattini, C. 2001. Chlorinated pesticides and PCBs in sediments and molluscs from freshwater canals in the Hanoi region. Environmental Pollution, 112, 311-320.

Nie, X., Lan, C., Wei, T., Yang, Y. 2005. Distribution of polychlorinated biphenyls in the water, sediment and fish from the Pearl River estuary, China. Marine Pollution Bulletin, 50 (5), 537-546.

Okay, O.S., Legovic, T., Tüfekçi, V., Egesel, L., Morkoç, E. 1996. Environmental impact of land based pollutants on İzmit Bay (Turkey): Short-term algal bioassays and simulation of toxicity distribution in the marine environment. Archives of Environmental Contamination and Toxicology, 31 (4), 459-465.

Okay, O.S., Tolun, L., Telli-Karakoç, F., Tüfekçi, V., Tüfekçi, H., Morkoç, E. 2001. İzmit Bay (Turkey) ecosystem after Marmara Earthquake and subsequent refinery fire: the long term data. Marine Pollution Bulletin, 42 (5), 361-369.

Okay, O.S., Tolun, L., Telli-Karakoç, F., Tüfekçi, V., Tüfekçi, H. Olgun, A., Morkoç, E. 2003. The changes of T-PAH levels and health status of mussels in İzmit bay (Turkey) after Marmara earthquake and subsequent refinery fire. Environment International, 28, 671-675.

Pham, T., Lum, K., Lemieux, C. 1996. Seasonal variation of DDT and its metabolites in the St. Lawrence River (Canada) and four of its tributaries. Science of the Total Environment, 179, 17-26.

Robertson, L.W., Hansen, L.G. 2001. PCBs Recent Advances in Environmental Toxicology and Health Effects. The University Press of Kentucky, 663 South Limestone Street, Lexington, Kentucky, USA, 449 pp.

Robinson, J.W., Chau, A.S.Y. and Afghan, B.K. 1982a. Analysis of pesticides in water. Volume I. Significance, Principles, Techniques and Chemistry of Pesticides. CRC Press, Inc. Boca Raton, Florida, United States.

Robinson, J.W., Chau, A.S.Y. and Afghan, B.K. 1982b. Analysis of pesticides in water. Volume II. CRC Press Inc., 2000 N. W. 24th Street, Boca Raton, Florida, United States.

Robinson, A.K., Schmidt, W.A., Stancel, G.M. 1985. Estrogenic activity of DDT: estrogen-receptor profiles and the responses of individual uterine types following *o,p'*-DDT administration. J. Toxicol. Environ. Health, 16, 493-508.

Sanders, G. Taylor-Hamilton, J., Jones, K.C. 1997. A microcosm experiment to assess the outgassing potential of PCBs from sediment-water systems. Chemosphere, 35 (4), 783-790.

Shaw, G.R., Connely, D.W. 1984. Physicochemical properties controlling polychlorinated biphenyl (PCB) concentrations in aquatic organisms. Environmental Science and Technology 18, 18-23.

Shiu, W.Y., Mackay, D. 1986. A critical review of aqueous solubilities, vapor pressures, Henry's Law constants, and octanol-water partition coefficients of the polychlorinated biphenyls. Journal of Physical and Chemical Reference Data, 15 (2), 911-929.

Telli-Karakoç, F., Tolun, L., Henkelmann, B., Klimm, C., Okay, O., Schramm, K.W. 2002. Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) distributions in the Bay of Marmara Sea: İzmit Bay. Environmental Pollution, 119, 383-397.

Thomas, R.L., Shaban, A., Khawlie, M., Kawass, I., Nsouli, B. 2005. Geochemistry of the sediments of the El-Kabir River and Akar watershed in Syria and Lebanon. Lakes and Reservoirs: Research and Management, 10, 127-134.

Tkalin, A.V. 1996. Chlorinated hydrocarbons in coastal bottom sediments of the Japan Sea. Environmental Pollution, 91, 183-185.

Tolun, L.G., Okay, O.S., Gaines, A.F., Tolay, M., Tüfekçi, H., Kıratlı, N. 2001. The pollution status and the toxicity of surface sediments in İzmit Bay (Marmara Sea), Turkey. Environment International, 26, 163-168.

Tuncer, G., Karakas, T., Balkas, T.I., Gökçay, C.F., Aygün, S., Yurteri, C., Tuncel, G. 1998. Land-based sources of pollution along the Black Sea Coast of Turkey: Concentrations and annual loads to the Black Sea. Marine Pollution Bulletin, 36 (6), 409-423.

Turgut, C. 2003. The contamination with organochlorine pesticides and heavy metals in surface water in Küçük Menderes River in Turkey, 2000-2002. Environment International, 29, 29-32.

Turkish National Aquaculture Regulation. 1995. Republic of Turkey Ministry of Agriculture and Rural Affairs National Aquaculture Regulation (22223), 29 pp.

Turkish State Meteorological Service. 2006. Republic of Turkey Ministry of Environment and Forestry Turkish State Meteorological Service. Official paper on meteorological observations 2006/B.18.1.DMİ.0.77.00.03/11834. Kocaeli Meteorology Station Meteorological Observations Records.

Türkmen, T. 2005. International POPs Elimination Project. Promotion of Active and Efficient Civil Society Participation in Preparation for Implementation of the Stockholm Convention. Derince Pesticides Depot, Kocaeli. 18 s., Türkiye. http://www.ipen.org.

Tyler, A.O., Millward, G.E. 1996. Distribution and partitioning of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polychlorinated biphenyls in the Humber estuary, U. K. Marine Pollution Bulletin, 32 (5), 397-403.

UNEP, 2001. The Stockholm Convention on Persistent Organic Pollutants, Geneva, Switzerland. United Nations Environmental Programme (UNEP) Chemicals (June, 2001).

USEPA. 1996. Method 3540C Soxhelet extraction. Revision 3. Environmental Protection Agency. December 1996. United States of America. 8 pp.

USEPA. 1999. Method 1668, Revision A: Chlorinated Biphenyl Congeners in water, soil, sediment and tissue by HRGC/HRMS. United States Environmental Protection Agency. Office of water (4303). EPA No. EPA-821-R-00-002, United States of America. 127 pp.

Vuksanovic, V., De Smedt, F., Van Meerbeeck, S. 1996. Transport of polychlorinated biphenyls (PCB) in the Scheldt Estuary simulated with the water quality model WASP. Journal of Hydrology, 174, 1-18.

Walker, C.H. 2001. Organic Pollutants. An Ecotoxicological Perspective. Taylor and Francis Inc., London, Great Britain, 282 pp.

WHO. 1979. DDT and its Derivatives. Environmental Health Criteria 9. 193 p. United Nations Environment Programme and The World Health Organization, GENEVA.

WHO. 1993. Polychlorinated Biphenyls and Terphenyls (Second Edition). Environmental Health Criteria 140. IPCS International Programme on Chemical Safety. 683 p. World Health Organization, GENEVA.

Wiegel, J., Wu, Q. 2000. Microbial reductive dehalogenation of polychlorinated biphenyls. FEMS Microbiology Ecology, 32, 1-15.

Wu, Y., Zhang, J., Zhou, Q. 1999. Persistent organochlorine residues in sediments from Chinese river/estuary systems. Environmental Pollution, 105, 143-150.

Wurl, O., Obbard, J.P. 2005. Organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in Singapore's coastal marine sediments. Chemosphere, 58, 925-933.

Table 1. *The concentrations of PCBs and DDTs in water (ng/ml) from İzmit Bay in Turkey (2003-2004)*

Compounds	Kirazlıyalı 1. station	Petkim 2. station	Koruma Tarım 3. station	SEKA 4. station	Sarıdere 5. station
PCB28	n.d.[a]-0.0165	n.d.-0.0115	n.d.-0.0190	n.d.-0.0245	n.d.-0.0120
PCB52	n.d.-0.1250	n.d.-0.1100	n.d.-0.0770	n.d.-0.1800	n.d.-0.1150
PCB101	n.d.-0.3150	n.d.-0.0250	n.d.-0.0170	n.d.-0.0230	n.d.-0.0550
PCB118	n.d.-0.0045	n.d.-0.0030	n.d.	n.d.-0.0120	n.d.-0.0100
PCB138	n.d.	n.d.	n.d.	n.d.	n.d.-0.0045
PCB153	n.d.-0.0075	n.d.-0.0045	n.d.-0.0035	n.d.-0.0035	n.d.-0.0045
PCB180	n.d.	n.d.	n.d.	n.d.	n.d.
o,o'-DDE	n.d.	n.d.	n.d.-0.0205	n.d.-0.0120	n.d.
o,p'-DDE	n.d.-0.0035	n.d.-0.0170	n.d.-0.0300	n.d.-0.0465	n.d.-0.0300
p,p'-DDE	n.d.-0.0045	n.d.	n.d.-0.0130	n.d.-0.0040	n.d.-0.0320
o,p'-DDD	n.d.	n.d.	n.d.-0.0085	n.d.	n.d.-0.0065
p,p'-DDD	n.d.	n.d.	n.d.-0.2045	n.d.-0.0030	n.d.-2.8750
o,p'-DDT	n.d.-0.0035	n.d.	n.d.-0.0355	n.d.	n.d.
p,p'-DDT	n.d.-0.7800	n.d.-0.7750	n.d.-1.2550	n.d.-0.7100	n.d.-0.3050
ΣPCBs	n.d.-0.440	n.d.-0.114	n.d.-0.094	n.d.-0.203	n.d.-0.170
ΣDDTs	n.d.-0.788	n.d.-0.775	n.d.-1.255	n.d.-0.710	n.d.-3.180

[a]not detected

Table 2. *The concentrations of PCBs and DDTs (ng/g dry weight) in sediments from İzmit Bay in Turkey (2003-2004)*

Compounds	Kirazlıyalı 1. station	Petkim 2. station	Koruma Tarım 3. station	SEKA 4. station	Sarıdere 5. station
PCB28	n.d.[a]-18.80	n.d.-4.86	n.d.-58.29	n.d.-2.66	n.d.-8.06
PCB52	n.d.-14.76	n.d.-28.10	n.d.-75.09	n.d.-48.43	n.d.-15.81
PCB101	n.d.-4.75	n.d.-3.05	n.d.-2.67	n.d.-12.10	n.d.-6.12
PCB118	n.d.-2.37	n.d.-2.84	n.d.-298.88	n.d.	n.d.-6.51
PCB138	n.d.	n.d.	n.d.-592.61	n.d.-1.81	n.d.
PCB153	n.d.-14.30	n.d.-25.43	n.d.-275.78	n.d.-18.80	n.d.-5.33
PCB180	n.d.	n.d.	n.d.	n.d.-3.34	n.d.-1.27
o,o'-DDE	n.d.-107.12	n.d.-9.74	n.d.-16.54	n.d.-58.77	n.d.-17.88
o,p'-DDE	n.d.-13.93	n.d.-1.69	n.d.-122.63	n.d.-13.23	n.d.-4.91
p,p'-DDE	n.d.-13.62	n.d.-63.33	n.d.-550.33	n.d.-42.65	n.d.-4.32
o,p'-DDD	n.d.-1.95	n.d.-6.43	n.d.-827.63	n.d.-35.62	n.d.-9.16
p,p'-DDD	n.d.-6.38	n.d.-7.52	n.d.-1702.49	n.d.-9.54	n.d.-391.74
o,p'-DDT	n.d.-5.05	n.d.-3.79	n.d.-2254.72	n.d.-7.28	n.d.-5.62
p,p'-DDT	n.d.-19.96	n.d.-16.00	n.d.-1819.27	n.d.-20.79	n.d.-21.28
ΣPCBs	n.d.-26.86	n.d.-46.48	n.d.-674.18	n.d.-61.91	n.d.-29.61
ΣDDTs	n.d.-107.12	n.d.-78.61	n.d.-7285.72	n.d.-138.82	n.d.-402.25

[a]not detected