

The occurrence and environmental effect of persistent organic pollutants (POPs) in Taurus Mountains soils

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Abstract

Purpose Persistent organic pollutants (POPs) are of global concern due to their ubiquitous presence and toxicity. The occurrence of polychlorinated dibenzo-p-dioxins (PCDDs), -dibenzofurans (PCDFs), co-planar biphenyls (PCBs), hexachlorocyclohexanes (HCH), dichlorodiphenyltrichloroethanes (DDT), and organochlorine pesticides (OCPs) in forest soil collected from Taurus mountains may have adverse effects on the environment and health. The aim of the study was to investigate the outcome and distribution of POPs in the environment and the possible grasshopper

effect along an altitude transect from sea level up to nearly 2,000 m a.s.l at a spatial distance of about 60 km in the southeastern Turkish Mediterranean Sea.

Methods The samples were collected at a height of 121, 408, 981, 1,225, 1,373, 1,639, and 1,881 m above sea level from Taurus Mountains, Turkey. The results were confirmed using high-resolution gas chromatography–high-resolution mass spectrometry.

Results The levels of the PCDD in forest soil from Taurus Mountains varied from nearly 4 to 12 pg g⁻¹ dry weight (dw). PCDF concentrations ranged from 2 to 7 pg g⁻¹ dw. Considerably high DDT levels detected in five stations indicated (3,223–24,564 pg g⁻¹) its extensive local application or atmospheric transport. PCB levels were determined between 80 and 288 pg g⁻¹ dw. HCH concentrations ranged from 141 to 1,513 pg g⁻¹ dw. The other OCP was between 102 and 731 pg g⁻¹.

Conclusion Although the use of POPs has been banned, our results show that they could still be found in Turkey. Their presence may be attributed to the degradation of pesticides which are newly banned and, as well as to the atmospheric migration and deposition. The latitude of sampling sites, the chemical, and physical parameters of soil have observed no effect on the fate of POPs in the environment.

Keywords Persistence organic pollutants · Forest soil · Taurus Mountains · Turkey

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1 Introduction

Persistent organic pollutants (POPs) are a global concern. POPs released to the environment can travel through air and water to regions distant from their original source. They

travel on wind and water currents, especially through the process of evaporation and redeposition. For example, levels of lindane, used as a pesticide in China, recorded from the coast of China to the Beaufort Sea show a marked increase near the Arctic. Recent studies have shown that POPs are also present in the alpine regions (Belis et al. 2009; Iozza et al. 2009; Offenthaler et al. 2009; Voigt et al. 2010). The widespread migration of POPs have resulted in their detection in areas where they have never been used or produced (Nieuwoudt et al. 2009).

In May 1995, the United Nations Environmental Programme (UNEP) initiated work on the Stockholm Convention on POPs with the intention of reducing and ultimately eliminating these pollutants (Fenge 2000). Turkey signed and ratified the treaty on 4 September 2005 on POPs which into force for parties of the convention (Bouwman 2004). As a member of the convention, Turkey is legally obligated to abide by the objectives of the treaty and is encouraged to support research on POPs. Forests and their soils are important sinks for POPs in the environment. For example, the Taurus Mountains in Turkey are geographical and meteorological traps for atmospheric pollutants due to high precipitation and low ambient temperature. Organic forest soil is an important sink for pollutants deposited on needles and leaves during their life span and transferred to a litter, as well as for wet and dry deposition on the forest floor (Kukucka et al. 2009).

The UNEP has targeted Stockholm Convention to eliminate, reduce POPs in the environment because many POPs exists (Stockholm Convention 2001). Especially the initial list of 12 POPs, “the dirty dozen,” include: dichlorodiphenyltrichloroethanes (DDT), heptachlor, toxaphene, mirex, aldrin, endrin, dieldrin, chlordane, hexachlorobenzene, polychlorinated biphenyl (PCB), dioxins, and furans. Each of these compounds are subject to the final articles of elimination, reduction, and control mechanism.

Organochlorines were used extensively to control pests as a broad spectrum insecticide. Dioxins and furans were produced unintentionally as by-products of incomplete combustion as well as during the manufacture of pesticides and other chlorinated substances. They are emitted mostly in the burning of hospital, municipal, and hazardous wastes but also when burning peat, coal and wood, automobile emissions, and also improper fuels for heating (Tesar 2000).

Hexachlorobenzene (HCB) was used as a fungicide to kill fungi that affect food crops. It is also a by-product of the manufacture of certain industrial chemicals and exists as an impurity in several pesticide formulations, e.g., dicofol. HCB is also emitted during the thermal processes in substantial amounts worldwide due to its thermodynamic stability. PCBs were traditionally used in industry as heat exchange fluids in electric transformers and capacitors and as additives in paint, carbonless copy paper, and plastics (Tesar 2000).

The aim of this study was to investigate the occurrence of POPs residues in soils from Taurus Mountains, Turkey their spatial distribution and concentration in soils in order to evaluate the levels and possible sources of pollution, as well as the role of the long-range transport in contamination of mountain area with POPs.

2 Materials and methods

2.1 Sampling sites

Taurus Mountains soils were suggested for this study because of their potential to act as sink for organic pollutants, and it is expected that the atmospheric pollution is present in Turkey as well as in the neighboring countries, e.g., Arabia, Africa, and Russia. The Taurus Mountains are a mountain complex in southern Turkey, from which the Euphrates and Tigris descend into Iraq. It divides the Mediterranean coastal region of southern Turkey from the Central Anatolian Plateaus. Seven sampling sites were selected in Taurus Mountains (Fig. 1). The sampling sites were at 121, 408, 981, 1,225, 1,373, 1,639, and 1,881 m above sea level with the numbering in ascending order, respectively.

2.2 Sampling

The soil samples are often composited because of the high cost of extraction and analysis of POPs. Soil plots were divided in 10×10 m. Subplots and the humus layer were sampled separately with a steel cylinder of 30×30 cm diameter. The green and litter materials were excluded. The coordinates of the sample points were determined by GPS. The soil samples were taken at intervals of 2 m in one plot, and at least five samples were collected from one plot and mixed together in order to have one averaged sample. The soil samples were kept in labeled pre-rinsed glass jars in the dark until extraction and analysis.

2.3 Determination of physical and chemical parameters of forest soil

Soil texture was ascertained using a standard hydrometer method (Bouyoucos 1951). A standard micro-Kjeldahl method was used for the total nitrogen content. The pH was evaluated with a pH meter after the soil was exposed to 0.01 M CaCl₂ for 24 h. The percentage of the salt content was determined as described in the soil survey manual (Burt 2004). Exchangeable cations were determined using the method of Thomas (1982). After extraction, the Na and K content was assessed by spectrophotometer, whereas that of Ca and Mg was assessed by atomic adsorption. UV–visible spectrophotometer (Shimadzu UV-160A) was used

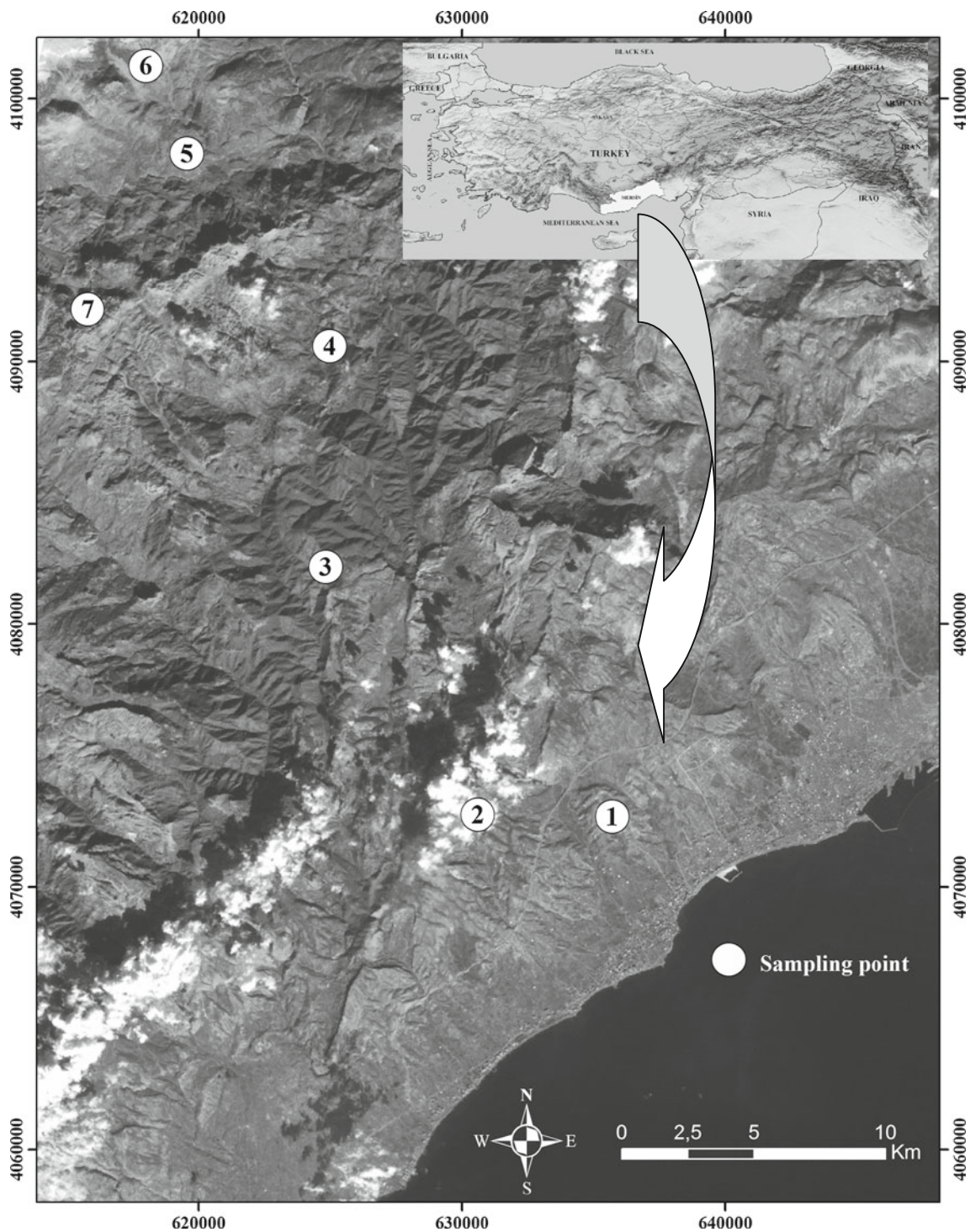


Fig. 1 The sampling point of Taurus Mountain

to determine the total organic matter and available phosphorous after extraction by the Walkey and Black (1934) and Olsen and Sommers (1982) methods. The Zn, Mn, Fe, and Cu contents were determined by the method of Lindsay and Norvell (1978). After digestion, the extract was analyzed using a Varian Atomic Adsorption Spectrophotometer (model AA 220/FS).

2.4 Extraction and cleanup of samples

Extraction of PCB and polychlorinated dibenzo-p-dioxin (PCDD)/F was carried out with 20 g of sample using an Accelerated Solvent Extractor (ASE 200) device (Dionex, Sunnyvale, CA, USA) according to Roots et al. (2004).

After spiking with the ^{13}C -labeled (^{13}C -organochlorine pesticides (OCPs) standards mixture, ^{13}C -labeled PCDD/F, and PCBs standard mixture) standard mixture (Cambridge Isotope Laboratories, Andover, MA, USA) for quantification, the extraction was performed using a mixture of n-hexane/acetone (75:25, v/v) at a temperature of 120 C and a pressure of 12 MPa. Two 10-min static cycles were applied for a complete extraction. To remove interferences, 60% of the concentrated crude extracts (ca. 1 ml) were cleaned up by several sequential liquid chromatography steps as follows: a multilayer chromatography column was filled with 5 g of anhydrous Na_2SO_4 , 2 g of activated silica gel, 4 g of silica gel treated with 10% AgNO_3 , 2 g of silica gel, 2 g of silica gel treated with 30% NaOH , 2 g of silica gel, 10 g of silica gel treated with 44% H_2SO_4 , 2 g of silica gel, and 5 g of anhydrous Na_2SO_4 (top) and washed with 50 ml of n-hexane.

A reversible carbon column (100 mg Carboxen 1016, Supelco) was rinsed with 25 ml of toluene and 25 ml of n-hexane, respectively and directly connected to the outlet of the multilayer column. The concentrated extract was added onto the top of the multilayer column and eluted with 200 ml of n-hexane. The PCDD/F and coplanar PCB were retained on the carbon column, whereas all other PCB congeners passed both columns. After disconnection, the carbon column is further eluted

with 30 ml of n-hexane/dichloromethane (9:1, v/v). Both eluates were combined, concentrated, and further cleaned on a C_{18} -modified silica column (1 g Isolute C_{18} , Biotage). The column was eluted with 4 ml of acetonitrile, and the eluate was reduced to a final volume of 20 μl for GC/MS analysis.

The PCDD/F and coplanar PCB were back-washed from the carbon column with 100 ml of toluene. This fraction was further cleaned on a chromatography column filled with 5 g of aluminum oxide (Alumina B, Super I, ICN) (Thielen and Olsen 1988). The first fraction with 35 ml of n-hexane/chloroform (88:12, v/v) was discarded; the second fraction with 50 ml of dichloromethane was reduced to a final volume of 10 μl and was analyzed by GC/MS.

Forty percent of the crude extract underwent cleanup using a mixed column (silica gel from Wesel Germany, grade 60; 3-cm diameter column containing, from the bottom upward, 10 g of silica, 5 g of alumina with 3% H_2O , 5 g of anhydrous sodium sulfate). The extracts were eluted with a 100-ml mixture of n-hexane and dichloromethane (1:1) and reduced to 1 ml. The residues were further purified through a C_{18} SPE cartridge for which acetonitrile was used as eluting solvent. After adding a recovery standard ($^{13}\text{C}_{12}$ -1,2,3,4-TCDD, Pentachlorotoluene, $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD, PCB111), the extracts

Table 1 GC/MS parameter for the isomer specific detection of PCDD/F, PCB, and organochlorine pesticides

	PCDD/F	PCB	Organochlorine pesticides
GC	Type: Agilent 6890 Column: Rtx-Dioxin2, 60 m, 0.25 mm ID, 0.25- μm film thickness (Restek) Temperature program: 130°C, 1.5 min, 45°C min^{-1} , 205°C, 5 min, 9°C min^{-1} , 305°C, 20°C min^{-1} , 310°C, 15 min Carrier gas: helium, constant flow: 1.5 ml/min Injector: cold injection system CIS 4 (Gerstel) Temperature program injector: 120°C, 12°C s^{-1} , 280°C, 5 min Temperature transferline: 300°C Autosampler: A200S (CTC) Injection volume: 1 μl pulsed splitless	Type: Agilent 5890 series II Column: Rtx-CLPesticides2, 30 m, 0.25 mm ID, 0.2- μm film thickness (Restek) Temperature program: 100°C, 1.5 min, 3°C min^{-1} , 270°C, 15°C min^{-1} , 300°C, 10 min Carrier gas: helium, head pressure: 16 psi Injector: cold injection system CIS 3 (Gerstel) Temperature program injector: 120°C, 12°C s^{-1} , 280°C, 5 min Temperature transferline: 300°C Autosampler: MPS2 (Gerstel) Injection volume: 0.5 μl splitless	Type: Agilent 6890 Column: Rtx-Dioxin2, 40 m, 0.18 mm ID, 0.18- μm film thickness (Restek) Temperature program: 60°C, 1.5 min, 25°C min^{-1} , 140°C, 8°C min^{-1} , 300°C, 20 min Carrier gas: helium, constant flow: 1.3 ml/min Injector: cold injection system CIS 4 (Gerstel) Temperature program injector: 120°C, 12°C s^{-1} , 280°C, 5 min Temperature transferline: 300°C Autosampler: A200S (CTC) Injection volume: 0.5 μl pulsed splitless
MS	Type: MAT 95S (Thermo) Ionization mode: EI, 50 eV, 260°C Resolution: >9,000 Detection: SIM mode	Type: MAT 95 (Thermo) Ionization mode: EI, 47 eV, 260°C Resolution: >8,000 Detection: SIM mode	Type: MAT 95S (Thermo) Ionization mode: EI, 50 eV, 260°C Resolution: >9,000 Detection: SIM mode

EI electron ionization

Table 2 Physical and chemical properties of soil samples

Station numbers	1 (121 m)	2 (408 m)	3 (981 m)	4 (1225 m)	5 (1373 m)	6 (1639 m)	7 (1881 m)
%Moisture	2.73	6.30	8.89	9.20	4.99	5.49	8.68
EC	318	381	457	306	307	344	424
%Salt	0.012	0.026	0.038	0.030	0.016	0.017	0.041
pH (1/2.5)	7.89	7.85	7.11	7.09	7.14	7.85	7.32
CaCO ₃ (%)	23.93	29.33	1.32	4.53	4.18	19.45	6.62
%Organic matter	7.34	19.50	22.57	24.27	11.78	10.62	25.77
%Sand	35.81	54.08	42.07	52.82	27.35	57.30	44.35
%Silt	32.87	28.40	33.45	27.00	32.25	15.53	37.73
%Clay	31.31	17.52	24.48	20.18	40.40	27.17	17.91

n.d. not detected

were concentrated with a gentle flow of nitrogen to 20 µl to be ready for analytical determination. Instrumental analysis of OCP was performed using a gas chromatograph coupled to a mass spectrometer (GC-MS). The GC-MS conditions are presented in Table 1.

2.5 Determination

PCDD/F and PCB analysis was performed by gas chromatography–high-resolution mass spectrometry; the instrumental parameters are listed in Table 1. The MS was

Table 3 Concentration of PCDD and WHO-TEQ_{PCDD} values in forest soil of Taurus Mountain (picograms per gram dw)

Station numbers	1 (121 m)	2 (408 m)	3 (981 m)	4 (1225 m)	5 (1373 m)	6 (1639 m)	7 (1881 m)
PCDD							
2.3.7.8-Tetrachlorodibenzo-p-dioxin	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
1.2.3.7.8-Pentachlorodibenzo-p-dioxin	0.17	0.16	0.12	0.08	0.21	<i>n.d.</i>	<i>n.d.</i>
1.2.3.4.7.8-Hexachlorodibenzo-p-dioxin	0.13	0.04	0.12	0.23	0.18	<i>n.d.</i>	0.09
1.2.3.6.7.8-Hexachlorodibenzo-p-dioxin	0.23	0.18	0.23	0.14	0.28	0.12	0.15
1.2.3.7.8.9-Hexachlorodibenzo-p-dioxin	0.13	0.11	0.11	0.15	0.15	0.10	0.10
1.2.3.4.6.7.8-Heptachlorodibenzo-p-dioxin	0.87	0.83	1.10	0.84	1.68	0.74	1.01
1.2.3.4.6.7.8.9-Octachlorodibenzo-p-dioxin	4.22	4.70	5.16	2.75	9.79	3.17	4.49
ΣPCDD	5.76	6.02	6.84	4.20	12.29	4.13	5.84
PCDD/OC	0.78	0.31	0.30	0.17	1.04	0.39	0.23
PCDF							
2.3.7.8-Tetrachlorodibenzofuran	0.30	0.20	0.33	0.26	0.51	0.16	0.15
1.2.3.7.8-Pentachlorodibenzofuran	0.35	0.26	0.40	0.28	0.59	0.23	0.32
2.3.4.7.8-Pentachlorodibenzofuran	0.41	0.41	0.56	0.17	0.71	0.13	0.33
1.2.3.4.7.8-Hexachlorodibenzofuran	0.63	0.49	0.83	0.20	1.01	0.22	0.46
1.2.3.6.7.8-Hexachlorodibenzofuran	0.49	0.49	0.64	0.23	0.89	0.17	0.45
1.2.3.7.8.9-Hexachlorodibenzofuran	0.14	0.14	0.25	0.08	0.21	0.06	0.09
2.3.4.6.7.8-Hexachlorodibenzofuran	0.42	0.48	0.55	0.20	0.91	0.19	0.42
1.2.3.4.6.7.8-Heptachlorodibenzofuran	1.75	1.28	1.98	0.50	2.63	0.62	1.53
1.2.3.4.7.8.9-Heptachlorodibenzofuran	0.16	0.13	0.26	0.12	0.25	0.06	0.15
1.2.3.4.6.7.8.9-Octachlorodibenzofuran	0.63	0.70	1.21	0.32	1.68	0.39	0.91
ΣPCDF	5.28	4.58	7.00	2.35	9.39	2.24	4.81
PCDF/OC	0.72	0.23	0.31	0.10	0.80	0.21	0.18
PCDD/F TEQ							
TEQ (NATO/CCMS)	0.60	0.53	0.70	0.30	0.96	0.20	0.41
TEQ (WHO 1998. Humans)	0.68	0.62	0.76	0.34	1.05	0.19	0.39

n.d. not detected

operated in SIM mode, and the two most intense ions of the molecular ion cluster were monitored for the unlabelled and labeled isomers (Henkelmann et al. 1996; Martens et al. 1998).

The quantification criteria included confirmation of retention times of the labeled standards and respective analytes. Routinely, the mass fragment of the highest intensity of the molecular ion was used for quantification. QC samples (laboratory blanks and solvent blanks) were included. The detection limit was defined as three times the average noise value measured on the individual mass traces used for quantification. Every signal below this limit was treated as not detectable. In the mean time, amounts smaller than the blanks by a factor of about 2 were not considered.

The recovery standards ($^{13}\text{C}_{12}$ -1,2,3,4-TCDD for PCB, PCT and $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD for OCP) were used for the calculation of the recoveries of ^{13}C -labeled internal standards. The recoveries of the internal standards were used to control the performance of the sample preparation step (extraction and cleanup). Low recoveries indicate an insufficient extraction and/or a failed fractionation on the

cleanup columns. The average recoveries of all ^{13}C -labeled and deuterated internal standards were between 40% and 100%.

3 Results and discussion

The chemical and physical soil-specific studies revealed merely minor standard deviation of pH, but moisture, EC, CaCO_3 , organic matter, clay, silt, sand contents showed larger standard deviation among the seven locations (Table 2). The mean values for forest soil from the results of individual investigations at the respective locations are listed. The content of organic matter (e.g., 7–25%) is important for the enrichment of POPs in soils (De Maagd et al. 1998). No significant differences were observed at the locations, and the pHs were found neutral (7.11–7.89). The moisture among stations varied from 2% to nearly 9% (Table 2). Different correlation methods were used to find any relation between chemical and physical parameters, but there was no correlation.

Table 4 Concentration of PCB and WHO-TEQ_{PCB} values in forest soil of the Taurus Mountain (picograms per gram dw)

Station numbers	1 (121 m)	2 (408 m)	3 (981 m)	4 (1225 m)	5 (1373 m)	6 (1639 m)	7 (1881 m)
2,4,4'/2,5,4'-Trichlorobiphenyl	6.68	9.07	10.76	5.29	6.95	7.94	8.10
2,2'.5,5'-Tetrachlorobiphenyl	7.30	8.64	9.99	4.63	7.79	7.62	9.31
2,2'.4,5,5'-Pentachlorobiphenyl	14.91	37.03	31.39	12.23	35.68	12.17	30.66
2,2'.3,4,4',5'-Hexachlorobiphenyl	23.03	47.28	52.90	13.77	58.21	14.07	40.08
2,2'.4,4',5,5'-Hexachlorobiphenyl	29.81	61.58	61.57	19.38	77.15	19.79	52.78
2,2'.3,4,4',5,5'-Heptachlorobiphenyl	16.86	31.27	30.07	7.27	42.52	9.21	26.17
∑Indicator PCB	98.59	194.88	196.69	62.56	228.30	70.78	167.11
Indicator PCB/OC	13.43	9.99	8.71	2.58	19.38	6.66	6.48
3,3'.4,4'-Tetrachlorobiphenyl	5.55	4.80	4.50	1.76	6.63	1.48	5.48
3,4,4',5-Tetrachlorobiphenyl	0.15	0.38	0.26	0.11	0.27	0.06	0.30
3,3'.4,4',5-Pentachlorobiphenyl	0.53	1.05	1.65	0.29	1.58	0.33	0.92
3,3'.4,4',5,5'-Hexachlorobiphenyl	0.38	0.34	0.54	0.33	0.54	0.44	0.25
∑Non-ortho PCB	6.62	6.57	6.95	2.49	9.02	2.32	6.94
Non-ortho PCB/OC	0.90	0.34	0.31	0.10	0.76	0.22	0.27
2,3,3'.4,4'-Pentachlorobiphenyl	5.86	13.87	13.94	4.08	14.95	4.23	10.73
2,3,4,4',5-Pentachlorobiphenyl	0.42	0.98	0.93	0.22	0.84	0.29	0.74
2,3'.4,4',5-Pentachlorobiphenyl	11.00	27.85	23.93	7.93	23.26	8.99	21.35
2'.3,4,4',5-Pentachlorobiphenyl	0.41	0.91	0.68	0.29	1.04	0.24	0.56
2,3,3'.4,4',5-Hexachlorobiphenyl	2.88	4.80	4.17	1.21	5.16	1.38	3.07
2,3,3'.4,4',5'-Hexachlorobiphenyl	0.77	1.28	1.21	0.26	1.68	0.37	1.03
2,3'.4,4',5,5'-Hexachlorobiphenyl	1.64	2.67	3.07	0.88	3.47	0.86	2.41
2,3,3'.4,4',5,5'-Heptachlorobiphenyl	0.69	0.99	1.02	0.30	1.16	0.22	0.65
∑Mono-ortho PCB	234.11	456.26	456.22	145.26	526.20	162.78	388.65
Mono-ortho PCB/OC	31.89	23.40	20.21	5.98	44.67	15.33	15.08
∑WHO-TEQ _{PCB} (WHO 1998, Humans)	0.06	0.12	0.18	0.03	0.18	0.04	0.10

Table 5 Concentration of HCH in forest soil of Taurus Mountains (picograms per gram dw)

Station numbers	1 (121 m)	2 (408 m)	3 (981 m)	4 (1225 m)	5 (1373 m)	6 (1639 m)	7 (1881 m)
α-HCH	10.80	57.52	70.57	74.34	79.99	47.19	69.32
β-HCH	55.41	141.94	76.28	201.55	165.25	61.58	152.22
γ-HCH	9.05	33.83	27.55	35.79	35.68	22.11	35.59
δ-HCH	4.11	4.27	7.13	55.40	7.05	4.44	6.79
ε-HCH	0.68	2.35	3.18	5.84	3.68	1.90	3.83
Pentachlorobenzene	13.67	56.03	65.09	40.53	48.31	90.46	33.51
Hexachlorobenzene	44.72	123.80	195.37	116.74	188.40	1,278.13	135.79
Pentachloroanisole	1.44	5.02	5.16	3.41	5.58	5.40	6.02
Octachlorostyrene	1.85	6.19	5.05	3.41	5.58	2.43	6.68
∑HCH	141.73	430.95	455.39	537.03	539.53	1,513.65	449.76
HCH/OC	19.31	22.10	20.18	22.13	45.80	142.53	17.45

Generally, sampling site 5 (at 1,373 m) showed higher levels of total PCDD and polychlorinated dibenzo-p-dibenzofuran (PCDF) compared to other the six sampling sites (Table 3). Similar studies have also reported detection of PCDF and PCDD residues in soil. In Turkey, Bakoglu et al. (2005) reported similar concentration ranges in soils from Kocaeli. Kukucka et al. (2009) documented levels of up to 104 pg g⁻¹ dry weight (dw) in forest soil in the Czech Republic. The results by Nieuwoudt et al. (2009) indicated that the findings of PCDDs in forest soil are similar to those in the present study. The levels of the toxicity equivalents (TEQ) of PCDD/F were calculated between 0.2 and 0.96 pg NATO TEQ per gram and 0.19 to 1.05 pg WHO-TEQ per gram (Table 3). This is in contrast to findings of Kukucka et al. (2009) which reported between 19 and 141 pg WHO-TEQ per gram in 2001 and in 2007 from Czech Republic between 19 and 79 pg WHO-TEQ per gram. In Turkey, Bakoglu et al. (2005) reported the level of TEQ as 0.40–4.26 ng I-TEQ per kilogram in deep soil from Kocaeli.

Indicator PCBs have higher levels than mono-ortho PCBs and non-ortho PCBs in all sampling sites. The total PCBs were detected at levels ranging from 62 to

228 pg g⁻¹ dw. The indicator PCBs were detected with levels of 76–79%, followed by mono-ortho PCBs with levels 18–21% and non-ortho PCBs with levels of 3–5% (Table 4). Similar studies have also reported residues of PCBs and metabolites in Turkey. Salihoglu and Tasdemir (2009) found a total concentration of PCBs between 161 and 251 pg g⁻¹ dw in Bursa and Meijer et al. (2003) reported the concentration of PCBs 344 pg g⁻¹ dw in Antalya, which is more comparable with present study because of the geographical similarity. In a study carried out in Turkish Electricity Distribution Corporation near Ankara, Turkey, Yeniova (1998) reported residues of PCBs as 464 μg g⁻¹ in the soil.

The results of the individual ∑HCH congeners in soil varies from 141 to 1,513 pg g⁻¹dw (Table 5). In terms of the present concentration levels, β-HCH is found to dominate in all sites except for station 6 which exhibited slightly higher α-HCH among HCH (Table 5). The HCH enrichment of HCH isomers was found at all stations for β-HCH, followed by α-HCH and γ-HCH. The main reason for this could be increased dechlorination reactions involving HCHs where γ-HCH isomer is most

Table 6 Concentration of DDT in forest soil of Taurus Mountains (picograms per gram dw)

Station numbers	1 (121 m)	2 (408 m)	3 (981 m)	4 (1225 m)	5 (1373 m)	6 (1639 m)	7 (1881 m)
4,4'-DDT	489.37	6,585.86	4,489.10	1,373.40	12,770.48	558.65	3,493.35
2,4'-DDT	231.32	1,498.39	680.50	364.55	1,633.54	142.84	1,088.52
4,4'-DDD	33.41	188.90	360.01	53.31	91.04	26.35	68.44
2,4'-DDD	20.05	84.52	83.96	27.53	47.05	9.21	45.23
4,4'-DDE	3,957.14	13,395.83	10,192.13	2,821.70	9,937.04	2,456.80	5,374.73
2,4'-DDE	156.27	73.00	94.94	89.43	85.36	29.52	42.71
∑DDT	4,887.57	21,826.50	15,900.64	4,729.92	24,564.53	3,223.36	10,112.98
DDT/OC	665.88	1,119.31	704.50	194.89	2,085.27	303.52	392.43

Table 7 Ratio of pesticides to detect recent inputs

	1	2	3	4	5	6	7
β -HCH/ γ -HCH	6.13	4.20	2.77	5.63	4.63	2.78	4.28
4,4'-DDE/4,4'-DDT	8.09	2.03	2.27	2.05	0.78	4.40	1.54
Endosulfan-I(α)/endosulfan-II (β)	0.27	0.4	0.17	0.22	0.21	0.31	0.17

already degradable by soil microorganisms. Isomerisation reactions in soil involving for example energetically more stable β -HCH have been described (Wu et al. 1997). The levels are comparable to those of typical forest soils from Germany, ranging from a hundred to 38,000 (Wenzel et al. 2002) HCH levels are similar to concentration of forest soil in Czech Republic (Kosubova et al. 2005). The relations of β/γ -isomers showed that β -HCH persists in forest soil, and its content is decreasing from the forest soil to needles. The more volatile γ -isomer shows an inverse tendency that refers to its more probable occurrence in the atmosphere, unlike β -HCH. The concentration of γ -HCH in the Alabama soils was 0.13 ng/g, but the soil concentrations varied spatially by up to two orders of magnitude and were largely dependent on the treatment history (Harner et al. 1999). The Czech forest soil concentrations of γ -isomers ranged from 0.19 to 1.69 ng g⁻¹ dw, which corresponds to the burden of the Czech background area.

Table 6 shows that total DDT residues were detected at levels ranging from 3,223 to 24,564 pg g⁻¹ dw. The DDT metabolite 4,4'-DDE was present in higher levels, except for station 5, than the associated 4,4'-DDT compound in all sampling sites. The high detection

frequencies and residue values of 4,4'-DDT compared to its metabolites suggest a recent input of technical DDT. A high DDE/DDT ratio indicates past input of DDT (Strandberg and Hites 2001). DDE/DDT ratios, especially when <1, indicate recent input. The low 4,4'-DDE/4,4'-DDT residue ratio of sampling station 5 suggests recent input of DDT in the forest (Table 7). DDTs and their residues are still detected in most environmental matrices in Turkey. The common concentrations of DDT up to 100 ng g⁻¹ in available soils. Our study shows the highest DDT levels in forest soils from the sampling sites 5 and 2. We suppose that the sampling sites were contaminated partially by long-range atmospheric transport, but also by extensive local application of DDT before the DDT was banned in 1987 in Turkey. We found no relation between organic carbon and concentration of POPs and high latitude of POPs. In station 5, it is expected that newly used DDT contaminated the soils, but this occasion is not possible because of the ban of DDT usage since 1985 in Turkey. We assume that this is caused by the long-range transport from neighboring countries. The dominant occurrence of DDT in relation to their metabolites is worth mentioning. Technical DDT includes 68–80% 4,4'-DDT, 15–20% 2,4'-DDT, and other minor components.

Table 8 Concentration of OTHER OCP in forest soil of Taurus Mountains (picograms per gram dw)

Station numbers	1 (121 m)	2 (408 m)	3 (981 m)	4 (1225 m)	5 (1373 m)	6 (1639 m)	7 (1881 m)
trans-Chlordane	7.92	27.11	17.89	7.82	22.63	2.75	14.13
cis-Chlordane	n.d.	24.23	30.40	13.00	31.79	5.93	23.11
oxy-Chlordane	n.d.	4.27	7.13	2.97	8.00	1.69	7.78
Heptachlor	n.d.	1.92	1.05	0.72	1.79	0.75	1.86
cis-Heptachloroepoxide	16.14	89.22	62.01	24.78	69.15	8.04	55.63
trans-Heptachloroepoxide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Aldrin	2.88	8.32	12.40	5.51	18.52	2.01	6.79
Dieldrin	32.80	144.08	187.69	143.18	232.61	26.45	150.03
Endrin	3.91	44.08	30.29	7.38	34.84	11.11	32.41
Endosulfan-I	24.47	79.08	38.53	18.61	53.36	9.52	37.34
Endosulfan-II	92.73	197.44	229.39	84.14	250.50	30.37	222.30
Methoxychlor	0.49	0.81	1.65	1.32	1.26	1.27	1.42
Mirex	2.47	3.95	5.71	1.98	7.26	2.86	4.93
Σ OCP	183.80	624.50	624.15	311.41	731.73	102.75	557.73
OCP/OC	25.04	32.02	27.65	12.83	62.11	9.67	21.64

n.d. not detected

The high DDT fractions found in the forest soils confirmed a very slow degradation of DDTs in the matrices rich in organic material, which is probably caused by their strong adsorption potential (Kosubova et al. 2005). In soil, DDTs are microbially transformed to their metabolites affected by moisture, organic carbon content, but this is not the case in our study.

The levels of chlordane in forest soils in Taurus Mountains were very low (Table 8). The mean value of chlordanes (trans-, cis-, oxy-) were in the range of ND-30 pg g⁻¹ dw. These levels are compatible to the concentrations measured in the Alabama arable soils (Harner et al. 1999). In all forest soils, chlordane was more abundant. Some constituents of the technical chlordane, as well as some of their metabolites (oxychlordane and heptachlor epoxide) are compounds that are very persistent in the environment.

The main constituents of technical chlordane are trans-, cis-, and oxy-, metabolites, and heptachlor. Heptachlor is one of the most active components of technical chlordane, and technical heptachlor was also used as pesticide (Moilanen et al. 1986). Heptachlor epoxide which is the degradation product of heptachlor adsorbs strongly to soil and is very resistant to biodegradation (Keith 1997). The levels found in the soils were below the detection limits at all sampling stations (Table 8). The chlordane and heptachlor were about ten to 100 times lower than in studies from the Czech Republic (Shegunova et al. 2007).

While aldrin was detected in lower concentrations, dieldrin was most abundant in forest soil since aldrin is quickly transformed in the environment into more toxic and persistent dieldrin (Falandysz et al. 1998). Thus, our results may also imply that aldrin used in Turkey in the past had already been degraded. Shegunova et al. (2007) detected dieldrin in all mountain soils sampled along the polish border in the concentration range of 0.58–2.78 ng g⁻¹. Endrin was detected in all the sampling stations with a maximum concentration of 44 pg g⁻¹ (Table 8).

Technical endosulfan consists of two isomers: alpha and beta endosulfan, which are mixed together in a ratio of approximately 7:3. The range of endosulfan I for all sampling sites was between 9 and 79 pg g⁻¹ dw in soil although the concentration of endosulfan II ranged from 30 to 250 pg g⁻¹ dw. The endosulfan I (α)/endosulfan II (β) ratios were observed below 1, which indicates recent inputs of endosulfan in the environment. However, endosulfan is widely used as insecticides and was banned in 2009.

4 Conclusions

Persistent organic pollutants (POPs) are stored mainly in the mountain soils over extended time periods as a result of long-range atmospheric transport, scavenging effect of

coniferous forests and high organic carbon content of forest soils. The physical and chemical properties of the soils demonstrated no effect of loading the pollution in the forest soil of Taurus. The sampling sites with higher altitude had no significant effect on chemical contamination in the soil. It can be concluded that soil is a good matrix for POP monitoring but in our case it was difficult to obtain any relationship between altitude and POPs contamination in the Taurus Mountains.

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