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Investigation of Soil Concentrations of Persistent Organic Pollutants, Trace Elements, and Anions Due to Iron–Steel Plant Emissions in an Industrial Region in Turkey

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Abstract The spatial distribution of several air pollutants emitted from iron–steel industries in Hatay-Iskenderun industrial region in Turkey was investigated by measuring their concentrations in soil. Collected soil samples (n=20) were analyzed for persistent organic pollutants (POPs; i.e., polycyclic aromatic hydrocarbons, polychlorinated biphenyls, polybrominated diphenyl ethers, and polychlorinated naphthalenes), anions, and trace elements. Generally, all measured POP concentrations and marker trace elements for iron–steel industry (Zn, Pb, and Cu) were high relative to those reported previously for rural and urban areas around the world, and they were comparable to those measured recently in a similar industrial region (Aliaga, Izmir, Turkey). For all investigated POPs, elements, and anions, the highest concentrations were measured at points located north of the iron–steel industries where their emissions are transported by the prevailing southerly winds. The spatial distribution and levels of POPs, elemental, and anionic concentrations indicated that the iron–steel plants in Hatay-Iskenderun region are important sources for these pollutants. Statistically significant relationships between several organic and inorganic pollutants further confirmed that they are emitted by common sources (iron–steel plants).

Keywords Iron–steel production · Electric arc furnaces · Trace elements · POPs · Soil pollution

1 Introduction

Previous studies have indicated that iron–steel plants are significant sources for air pollutants (IPPC 2001; Odabasi et al. 2009). Iron and steel could be produced either from iron ore at integrated steel plants or from ferrous scrap by electric arc furnaces (EAFs). Iron–steel production processes emit particle phase (zinc, chromium, nickel, lead, cadmium, and other metals/metal oxides) and gas phase inorganic pollutants (NO_x, SO_2, CO, HF, and HCl). Several organics (i.e., volatile organic compounds, chlorobenzenes, and polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs)) are also emitted (IPPC 2001). Other than these mostly regulated pollutants, persistent organic pollutants (POPs) like polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs),

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polychlorinated naphthalenes (PCNs), and polybrominated diphenyl ethers (PBDEs) are also emitted (IPPC 2001; Alcock et al. 2003; US EPA 2008). PAHs may be present in the scrap and are thermally desorbed during the production processes, or they may form as a result of incomplete combustion of scrap organic matter, fuels, and additives like coal. PCBs are also present in the scrap. They may also form by de novo synthesis during thermal processes, similar to PCDD/Fs (IPPC 2001). Ferrous scrap contains impurities like plastics and foam that could contain significant amounts of PBDEs (Alcock et al. 2003). PBDEs are emitted during the steel production process, during scrap charging (mostly in the particle phase), scrap preheating, and at the beginning of the melting cycle (mostly in the gas phase; Odabasi et al. 2009). PCNs may also be present in the scrap and are evaporated during production processes, or they may form by de novo synthesis in thermal processes (IPPC 2001). Some PCN congeners are combustion markers, and they could be used to assess their sources or formation mechanisms (IPPC 2001; Helm and Bidleman 2003). The major units of integrated steel plants (sinter plants, coke ovens, and blast furnaces) are also significant emitters of PAHs, PCBs, and PCNs. Significant amounts of PAHs are emitted by coke ovens (IPPC 2001). PBDEs are not formed during the steel production from iron ore. However, they could also be emitted from integrated steel plants since most of them use ferrous scrap in part during their production.

All these semivolatile POPs may be predominantly in the gas/particle phases or distributed between two phases, depending on their physicochemical properties and temperature. Transfer of POPs between air and natural surfaces (soil, water, vegetation) occurs especially through gas absorption/volatilization, dry particle, and wet deposition. Once deposited, POPs are persistent in soil for various periods of time where they are subject to various partitioning, degradation, and transport processes depending on their physical–chemical properties (Cetin and Odabasi 2007; Bozlaker et al. 2008a, b). Considering their large reservoir in soils, soil–air exchange by diffusion is an important process affecting the fate and transport of POPs between environmental compartments (Hippelein and McLachlan 1998; Backe et al. 2004).

Recent studies based on soil, ambient air, and stack-gas sampling have shown that the ferrous scrap processing steel plants with EAFs in Aliaga industrial region located in Izmir (the third biggest city in Turkey with several industrial activities) are important local sources of PAHs, PCBs, PBDEs, several other organic compounds (i.e., aromatic and aliphatic hydrocarbons, oxygen, sulfur, nitrogen, and chlorine-containing organic compounds), and trace elements (Cetin et al. 2007; Cetin and Odabasi 2007; Bozlaker et al. 2008a, b; Bayram et al. 2008; Odabasi et al. 2009). These previous studies have also indicated that soil is an important environmental medium reflecting the level and the spatial distribution of POPs emitted from stationary air pollutant sources (Cetin et al. 2007; Cetin and Odabasi 2007; Bozlaker et al. 2008a, b; Bayram et al. 2008; Odabasi et al. 2009). Using soil sampling to assess the level and spatial variation of air pollution is appealing when the technical, physical, and economical limitations of air sampling at several sites are considered. The Hatay-Iskenderun industrial region with several ferrous scrap processing steel plants, steel rolling mills, and an integrated steel plant is similar to the Aliaga industrial region that has been studied extensively (Cetin et al. 2007; Cetin and Odabasi 2007; Cetin and Odabasi 2008; Bozlaker et al. 2008a, b; Bayram et al. 2008; Odabasi et al. 2009). The plants in Aliaga and Hatay-Iskenderun regions have comparable production capacities, 7.99 and 8.10 million tyear^{-1}, respectively (Turkish Association of Iron-Steel Producers 2009). However, due to the locations of the plants and residential sites and prevailing wind directions, the population density that is exposed to iron–steel plant emissions may be significantly higher in Hatay-Iskenderun region compared to Aliaga region. The objective of this study was to confirm the results of previous studies indicating that steel plants are important local sources of PAHs, PCBs, PBDEs, and trace elements, polluting the air and soil. The effect of pollutants emitted from iron–steel industries on air and local soil was investigated by measuring their soil concentrations (that were shown to be good indicators for stationary source emissions) in Hatay-Iskenderun industrial region in Turkey.

2 Materials and Methods

2.1 Soil Sampling

The study area is located at north of Hatay and Iskenderun cities. The area contains several air pollutant sources including a large integrated steel plant (with a sintering plant, coke ovens, blast furnaces, a lime plant, and rolling mills), a cement plant, a fertilizer plant, and several scrap processing iron–steel plants with EAFs, scrap iron storage and classification sites, steel rolling mills, a very dense transportation activity of scrap iron trucks, heavy road and rail traffic, and busy ports. Payas county, Sincan village, and steel plant housings are the residential sites located in the region (Fig. 1).

Soil samples were collected at 20 different points in the study area on July 3, 2008. Sampling points were mostly in the industrial region (n=17). These consisted of sites in residential areas (4, 6, 7, 9, 10, 15, and 18), sites close to industrial activities (5, 8, 11, 12, 13, 14, 16, 17, 20), and a site in a rural area (19). All these sites had a potential to be affected by industrial emissions due to their locations and the prevailing wind directions, and therefore, they were classified as industrial sites. However, activities like scrap metal/raw material storage, and waste storage/dumping that are directly affecting the soil were not present at the sampling points. Samples from urban/suburban sites (Iskenderun, n=2, and from Mustafa Kemal University campus in Hatay, n=1), away from the industrial region were also collected (Fig. 1). Approximately 0.5–1 kg of sample was taken from the top 5 cm of the soil. After removal of the large stones and pieces of vegetation, samples were placed into airtight plastic bags and stored in a freezer.

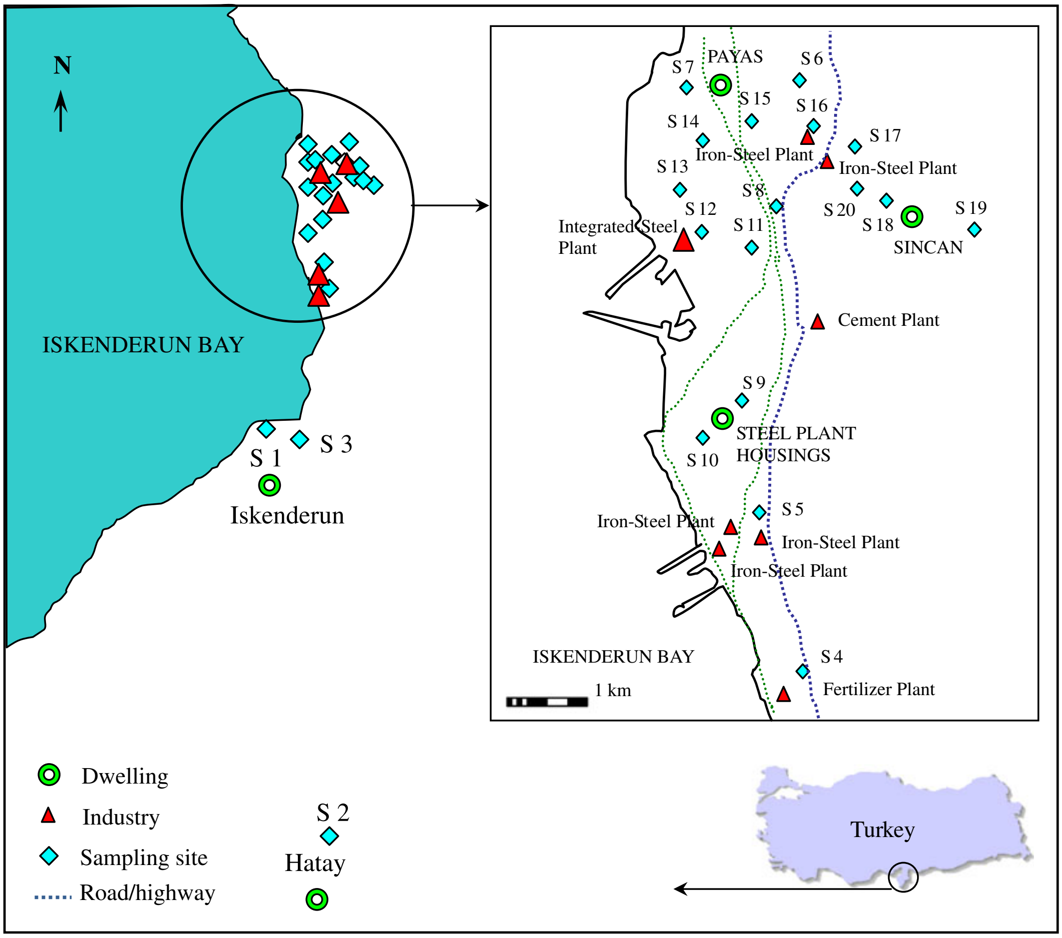

Fig. 1 Map of the study area showing the sampling sites, residential areas, iron–steel plants (ferrous scrap processing plants with electric arc furnaces), the integrated steel plant (iron ores and ferrous scrap processing plant), and other industries

2.2 Sample Preparation and Analysis

The soil samples were sieved through a 1.0-mm mesh sieve to remove large particles and organic debris. Soil moisture content was determined by weighing subsamples of soils before and after drying at 103°C in an oven for 24 h. The total organic carbon (TOC) content of the soil samples were analyzed using a Total Organic Carbon Analyzer (Shimadzu, TOC-V_{CPN}).

Prior to extraction, all samples ($n=20$) and blanks ($n=4$) were spiked with PCB, PAH, and PBDE surrogate standards to monitor the analytical recovery efficiencies. Five grams of soil samples were soaked in 40 ml of an acetone/hexane mixture (1:1) overnight. Then, they were ultrasonically extracted for 30 min. The extract volumes were reduced and were transferred into hexane using a rotary evaporator and a high purity N_2 stream. After concentrating to 2 mL, samples were cleaned up and fractionated on an alumina–silicic acid column containing 3 g silicic acid (deactivated with 4.5% deionized (DI) water) and 2 g alumina (deactivated with 6% DI water). The column was prewashed with 20 mL dichloromethane (DCM) followed by 20 mL petroleum ether (PE). Then, the sample in 2 mL hexane was added to the column, and PCBs, PBDEs, and PCNs were eluted with 35 mL PE (fraction 1) while PAHs and organochlorine pesticides (OCPs) were eluted with 25 mL DCM (fraction 2). The final extracts were solvent-exchanged into hexane by evaporating the extract to 5 mL under a stream of N_2, adding 15 mL hexane, evaporating to 5 mL, and adding 15 mL hexane. Then, they were concentrated to 1 mL under a stream of N_2.

For anion analysis, 1 g of sieved soil sample was ultrasonically extracted for 60 min at 60°C with 100 mL of 10 mM Na_2CO_3. Samples were filtered through 0.2-µm Teflon filters and stored in polypropylene vials prior to ion chromatographic analysis.

For elemental analysis, 0.5 g of sieved soil samples were extracted with 20 mL of concentrated acid (HNO_3/HCl, 1:3) in a microwave digester. Then, the samples were diluted to 100 mL with deionized water.

Samples were analyzed for POPs with an Agilent 6890N gas chromatograph equipped with a mass selective detector (Agilent 5973 inert MSD). Fractions 1 and 2 were combined and analyzed since significant amounts of lighter PAHs, heptachlor, aldrin, and *o,p′*-DDE are eluted with fraction 1. PAHs and PCBs were analyzed using electron impact ionization while negative chemical ionization (NCI) mode was used for PBDEs, PCNs, and OCPs. The capillary column used for PAHs, PCBs, PCNs, and OCPs was HP5-ms (30 m, 0.25 mm, 0.25 µm) while a DB5-ms column (15 m, 0.25 mm, 0.1 µm) was used for PBDEs. Helium was the carrier gas, and high purity methane was the reagent gas for NCI. All POPs were analyzed in selected ion monitoring mode (SIM). Compounds were identified based on their retention times, target and qualifier ions, and were quantified using the internal standard calibration procedure.

Anions (F^-, Cl^-, NO_3^-, and SO_4^{2-}) were analyzed using an ion chromatograph (Dionex DC-3000) equipped with a guard column (AG9-HC), analytical column (AS9-HC), a suppressor (AMMS-II), and a conductivity detector. Na_2CO_3 (10 mM) was used as the eluent.

Elements in soil samples (Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Sb, Sn, Sr, V, Zn) were analyzed with inductively coupled plasma optical emission spectrometer (ICP-OES; Perkin Elmer DV-2100).

Further details of sample preparation and instrumental analysis could be found elsewhere (Cetin et al. 2007; Cetin and Odabasi 2007; Bozlaker et al. 2008a, b; Odabasi et al. 2009).

Average recoveries for the surrogate standards were 60±11% (acenaphthene-d_{10}), 62±10% (phenanthrene-d_{10}), 65±12% (chrysene-d_{12}), 65±10% (perylene-d_{12}), 91±15% (PCB-14), 80±11% (PCB-65), 74±10% (PCB-166), and 81±16% (PBDE-77). Instrumental detection limits were determined from linear extrapolation, based on the lowest standard in calibration curve and using the area of a peak having a signal/noise ratio of 3. For 1-µl injection, the quantifiable amounts were 0.15, 0.10, 0.05–0.35, 0.01–37 pg for PAHs, PCBs, PBDEs, and PCNs, respectively. Blanks were also analyzed. The limit of detection of the method (LOD, nanogram) was defined as the mean blank mass plus three standard deviations (LOD=mean blank value + 3SD). Instrumental detection limit was used for the compounds that were not detected in blanks. Average analyte amounts in blanks were generally <14%, <7%, and <10% of the amounts found in samples for POPs, anions, and trace elements, respectively. Sample quantities exceeding the LOD were quantified and blank-corrected by subtracting the mean blank amount from the sample amount.

3 Results and Discussion

3.1 Soil Concentrations

Persistent organic pollutants PCB, PBDE, PCN, and PAH concentrations measured in soil samples are presented in Table 1. $\sum_{16}$PAHs in soil were dominated by medium to high molecular weight compounds (fluoranthene, chrysene, pyrene, benzo[*b*]fluoranthene, and benzo[*k*]fluoranthene). Although there are no dominating compounds for PCBs, medium to high molecular weight congeners (4, 5, 6, and 7-Cl) had relatively higher concentrations. These observed soil PAH and PCB profiles were similar to those recently measured in Aliaga, Turkey (Bozlaker et al. 2008a, b). PBDE-209 was the most abundant compound in $\sum_7$PBDE concentrations, and it was followed by PBDE-99 and 47. A similar profile for soil concentrations was recently reported by a recent study conducted in Izmir, Turkey (Cetin and Odabasi 2007). The abundance of PBDE-209 could be due to the fact that it is the most widely used commercial PBDE, and use of penta and octa-BDEs have been banned within the European Union since August 2004 (Leung et al. 2007). PCN-59 (5-Cl), PCN-46, 38+40, 35 (4-Cl), and PCN-62 (5-Cl) were the congeners with highest concentrations while PCN-36+45, 38+40 (4-Cl), PCN-66+67, 64+68 (6-Cl) were the most frequently detected ones in soil (n=17). POP concentrations were also measured in urban and suburban sites (sites 1, 2, and 3; Table S2 in the Electronic Supplementary Material). Generally, POP concentrations at these sites were lower (two-tailed t test, p<0.01) than those measured in the industrial region (3.9, 3.9, 3.8, and 1.7 times for $\sum_{41}$PCBs, $\sum_{16}$PAHs, $\sum_7$PBDEs, and $\sum_{32}$PCNs, respectively). Concentrations at sites 1 and 3 (urban) were generally higher (2.9, 9.7, 15.2, and 3.1 times for $\sum_{41}$PCBs, $\sum_{16}$PAHs, $\sum_7$PBDEs, and $\sum_{32}$PCNs, respectively) than those measured at site 2 (suburban, university campus).

Soil POP concentrations measured in the present study were compared to those reported for several rural/background/agricultural, urban/suburban, and industrial sites reported recently in the literature (Table 2). Concentrations reported in the previous studies have a large variation within a site category. However, in general, soil POP concentrations show the following trend: rural/background/agricultural sites < urban/suburban sites < industrial sites. Soil POP concentrations measured in the present study were higher than those measured in rural/background sites, and they were within the ranges reported for urban, especially for industrial sites (Table 2).

Several studies measuring soil POP concentrations have been conducted in the Izmir region (Cetin and Odabasi 2007; Bozlaker et al. 2008a, b; Odabasi 2009). Those studies covered urban, suburban, and several industrial sites in Aliaga region that is similar to the area covered in the present study. Soil concentrations at points close to the iron–steel industries were comparably higher than those measured at urban, suburban, and rural sites in Aliaga (Cetin and Odabasi 2007; Bozlaker et al. 2008a, b; Odabasi 2009). Soil POP concentrations measured in the present study were also compared to those measured in Aliaga region (Fig. 2). In general, POP concentrations measured in Hatay-Iskenderun region were high compared to rural and urban literature values while they were comparable to those measured in Aliaga (Table 2, Fig. 2). Minimum concentrations measured in this study were higher than those measured in Aliaga for all compound groups. PAH concentrations in the present study were significantly higher than those measured in Aliaga (two-tailed t test, p<0.01) while PCB concentrations were high and comparable in both regions. Average PCN concentrations in Hatay were 3.7 times lower. PBDE concentrations in Hatay were similar to those measured in Izmir area with the exception of the concentration (2,840 μg kg^{-1}) measured near an electronics industry (Fig. 2).

OCP concentrations in soil samples were also measured in the present study. Discussion on soil OCP levels in Hatay-Iskenderun region can be found in the Electronic Supplementary Material.

Trace elements and anions Several inorganic pollutants (SO_2, NO_x, HCl, HF, and trace elements) are also emitted from steel plants. It was shown that elements like Zn, Pb, and Cu are markers for steel plants with EAFs (IPPC 2001; Cetin et al. 2007).

Table 1 POP concentrations (microgram per kilogram dry weight) in soil samples (industrial sites, n=17)

PCB^{a}	AVG	SD	GM	PCN^{a}	AVG	SD	GM	PAH	AVG	SD	GM
PCB-18 (3)	0.8	0.7	0.6	PCN-19 (3)	0.012	0.008	0.009	ACY	45	70	12
PCB-17 (3)	0.3	0.3	0.2	PCN-24,14^{b} (3)	0.038	0.029	0.025	ACT	20	29	7
PCB-31 (3)	0.8	0.9	0.3	PCN-15 (3)	nd	nd	nd	FLN	36	41	14
PCB-28 (3)	1.2	1.5	0.6	PCN-16 (3)	nd	nd	nd	PHE	377	568	107
PCB-33 (3)	0.7	0.8	0.4	PCN-17,25^{b} (3)	nd	nd	nd	ANT	66	100	17
PCB-52 (4)	0.6	0.6	0.4	PCN-23 (3)	nd	nd	nd	CRB	22	35	6
PCB-49 (4)	0.5	0.5	0.3	PCN-42 (4)	0.005	0.004	0.003	FL	614	957	160
PCB-44 (4)	0.6	0.5	0.4	PCN-33,34,37 (4)	0.025	0.022	0.016	PY	486	750	128
PCB-74 (4)	0.5	0.5	0.3	PCN-47 (4)	0.008	0.007	0.006	BaA	309	476	81
PCB-70 (4)	0.9	1.0	0.5	PCN-36,45^{b} (4)	0.005	0.003	0.003	CHR	601	924	169
PCB-95 (5)	0.4	0.4	0.2	PCN-28,43 (4)	0.019	0.016	0.013	BbF	398	616	111
PCB-101 (5)	0.7	0.7	0.4	PCN-32 (4)	0.011	nd	0.011	BkF	298	453	84
PCB-99 (5)	0.4	0.3	0.2	PCN-35^{b} (4)	0.037	0.020	0.033	BaP	279	424	77
PCB-87 (5)	0.4	0.3	0.3	PCN-38,40 (4)	0.046	0.031	0.037	IcdP	222	334	67
PCB-110 (5)	0.8	0.7	0.4	PCN-46 (4)	0.043	0.008	0.043	DahA	183	277	53
PCB-82 (5)	0.3	0.2	0.2	PCN-52,60^{b} (5)	0.021	0.020	0.015	BghiP	236	346	77
PCB-151 (6)	0.2	0.3	0.1	PCN-58 (5)	nd	nd	nd	Σ_{16}PAH	4,192	6,309	1,213
PCB-149 (6)	0.8	1.0	0.3	PCN-61 (5)	0.040	0.015	0.038				
PCB-118 (5)	1.0	0.9	0.7	PCN-50^{b} (5)	0.007	0.006	0.005				
PCB-153 (6)	1.1	1.3	0.6	PCN-57 (5)	0.029	0.014	0.026				
PCB-132 (6)	0.4	0.4	0.3	PCN-62 (5)	0.050	0.018	0.049				
PCB-105 (5)	0.6	0.5	0.4	PCN-53 (5)	0.038	0.002	0.038				
PCB-138 (6)	1.4	1.5	0.8	PCN-59 (5)	0.054	0.012	0.053				
PCB-158 (6)	0.2	0.2	0.1	PCN-66,67^{b} (6)	0.006	0.008	0.004				
PCB-187 (7)	0.6	0.8	0.3	PCN-64,68 (6)	0.006	0.007	0.004				
PCB-183 (7)	0.3	0.3	0.2	PCN-69 (6)	0.010	0.012	0.006				
PCB-128 (6)	0.4	0.4	0.3	PCN-71,72 (6)	0.016	0.020	0.011				
PCB-177 (7)	0.4	0.4	0.3	PCN-63 (6)	0.006	0.006	0.004				
PCB-171 (7)	0.2	0.1	0.2	PCN-65 (6)	0.006	0.008	0.004				
PCB-156 (6)	0.2	0.1	0.2	PCN-73 (7)	0.005	0.004	0.004				
PCB-180 (7)	1.1	1.5	0.4	PCN-74 (7)	0.006	0.007	0.004				
PCB-191 (7)	0.1	0.01	0.1	PCN-75 (8)	0.005	0.003	0.004				
PCB-169 (6)	nd	nd	nd	Σ_{32}PCN	0.28	0.28	0.18				
PCB-170 (7)	0.6	0.8	0.3								
PCB-199 (8)	0.5	0.4	0.4	PBDE^{c}							
PCB-208 (9)	nd	nd	nd	PBDE 28 (3)	0.02	0.02	0.01				
PCB-195 (8)	0.3	0.1	0.3	PBDE 47 (4)	0.22	0.31	0.08				
PCB-194 (8)	0.6	0.4	0.5	PBDE 100 (5)	0.07	0.09	0.04				
PCB-205 (8)	nd	nd	nd	PBDE 99 (5)	0.40	0.51	0.17				
PCB-206 (9)	0.3	0.1	0.2	PBDE 154 (6)	0.11	0.18	0.05				
PCB-209 (10)	nd	nd	nd	PBDE 153 (6)	0.15	0.24	0.07				
Σ_{41}PCB	19.0	18.0	11.0	PBDE 209 (10)	36	63	17				
				Σ_{7}PBDE	37	64	17				

AVG average, *SD* standard deviation, *GM* geometric mean, *nd* not detected, *ACY* acenaphthylene, *ACT* acenaphthene, *FLN* fluorene, *PHE* phenanthrene, *ANT* anthracene, *CRB* carbazole, *FL* fluoranthene, *PY* pyrene, *BaA* benz[*a*]anthracene, *CHR* chrysene, *BbF* benzo[*b*]fluoranthene, *BkF* benzo[*k*]fluoranthene, *BaP* benzo[*a*]pyrene, *IcdP* indeno[*1,2,3-cd*]pyrene, *DahA* dibenzo[*a,h*]anthracene, *BghiP* benzo[*g,h,i*]perylene

[a] Number of chlorine atoms are shown in parenthesis

[b] Combustion marker PCNs

[c] Number of bromine atoms are shown in parentheses

Table 2 Soil POP concentrations (microgram per kilogram dry weight) reported in the literature

	Rural/ background/ agricultural	References	Urban/ suburban		Industrial	References
ΣPCBs	1.6–4.4	Armitage et al. (2006)	26–76	Wilcke et al. (2006)	0.7–68.4	Ruzickova et al. (2008)
	0.047–0.42	Wang et al. (2009)	1.8–20.1	Ruzickova et al. (2008)	42.5–3,085	Ruzickova et al. (2008)
	1.3–2.3	Ruzickova et al. (2008)	2.6–4.3	Backe et al. (2004)	85.4–342	Motelay-Massei et al. (2004)
	0.3–2.1	Nadal et al. (2007)	0.2–10.5	Nadal et al. (2007)	0.3–17.9	Nadal et al. (2007)
	1.1–5.0	Krauss and Wilcke (2003)	1.5–20.7	Krauss and Wilcke (2003)	2.3–70.2	Krauss and Wilcke (2003)
ΣPCNs	0.001	Nadal et al. (2007)	0.016–0.13	Nadal et al. (2007)	0.018–0.37	Nadal et al. (2007)
	0.07–0.82	Krauss and Wilcke (2003)	0.23–7.4	Krauss and Wilcke (2003)	0.67–15	Krauss and Wilcke (2003)
	0.039	Nadal et al. (2009)	0.15	Nadal et al. (2009)	0.09	Nadal et al. (2009)
ΣPBDEs	0.004–0.035	Wang et al. (2009)	0.016–211	Li et al. (2008)	0.03–1.7	Kumar et al. (2009)
	0.04–0.27	Kumar et al. (2009)	8.7–18.6	Cetin and Odabasi (2007)	5.1–207	Luo et al. (2009)
	0.065–2.4	Nam et al. (2008a)	0.54–3.9	Harrad and Hunter (2006)	50–81	Luo et al. (2009)
	3.8	Leung et al. (2007)			6–144	Li et al. (2008)
	0.07–0.29	Harrad and Hunter (2006)			28–122	Zou et al. (2007)
					48.2–3,570	Leung et al. (2007)
ΣPAHs	8.6–1,055	Nam et al. (2008b)	366–27,825	Tang et al. (2005)	152–983	Nadal et al. (2004)
	34.3	Zhang et al. (2006)	1,646–2,990	Motelay-Massei et al. (2004)	3,394–5,642	Motelay-Massei et al. (2004)
	37–503	Nadal et al. (2007)	169	Zhang et al. (2006)	34–6,056	Nadal et al. (2007)
	0.16–2.1	Krauss and Wilcke (2003)	42–1,472	Nadal et al. (2007)	2.4–48.9	Krauss and Wilcke (2003)
			0.3–186	Krauss and Wilcke (2003)		

There are several sources of SO_4^{2-}, NO_3^-, Cl^-, and F^- in soil. SO_2, NO_x, HCl, and HF are also transferred from air to soil by dry and wet deposition. Therefore, soil anion concentrations could be increased near the steel plants. Trace elemental and anionic concentrations measured in this study are presented and compared to those measured in Izmir, Turkey in Table 3. All elemental and anionic concentrations measured in the industrial region were 1.4 (F^-)–4.7 (Pb) times higher than those measured at urban/suburban sites with the exception of nitrate (Table 3). SO_4^{2-}, NO_3^-, and Cl^- concentrations measured in Izmir area were highly variable, and their spatial distribution could not be related to the influence of industrial sources (Table 3; Yatkin et al. 2008). Sulfate, nitrate, and chloride concentrations measured in the present study were significantly lower from those measured at several sites in Izmir while fluoride concentrations were comparable. Zn, Pb, Cr, and Cd concentrations in Izmir were generally higher in industrial sites compared to those measured at urban, rural/agricultural sites. Cd, Cu, Pb, and Zn concentrations in Hatay-Iskenderun were similar to those measured in industrial sites in Izmir. However, significantly higher Cr and Ni concentrations were measured in Hatay-Iskenderun area (Table 3).

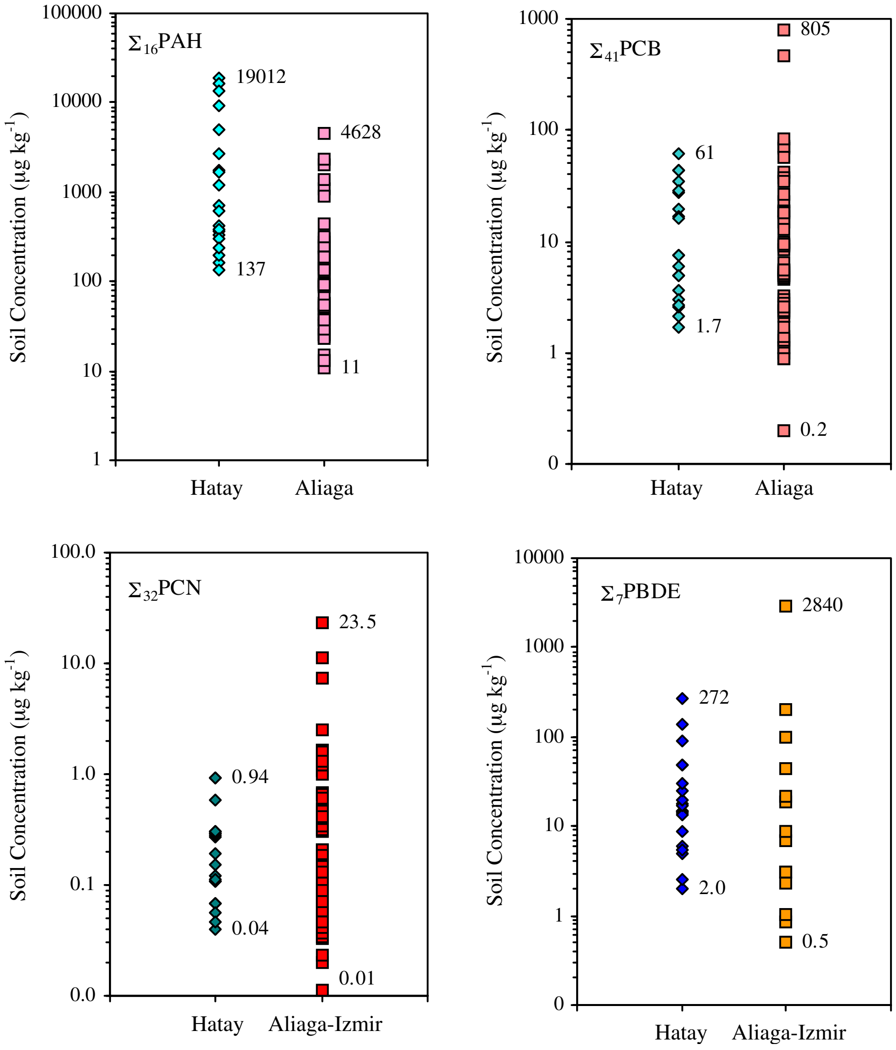

Fig. 2 Comparison of the soil POP concentrations measured at the study area with those measured recently in Izmir-Aliaga region (Cetin and Odabasi 2007; Bozlaker et al. 2008a, b; Odabasi 2009)

3.2 Sources and Spatial Distribution of Pollutants

Persistent organic pollutants Spatial distributions of soil POP concentrations are shown in Fig. 3. For all POPs, the highest concentrations were measured at sites located north of the iron–steel plants with EAFs and the integrated steel plant, where their emissions are transported by the prevailing southerly winds (Turkish State Meteorological Service 2009). Spatial variation of POP concentrations indicated that iron–steel plants in Hatay-Iskenderun area are important sources emitting these pollutants, similar to the plants located in Aliaga region. Payas county and iron–steel plant housings are among the sites with high soil POP concentrations. Payas is mainly affected by the emissions from the integrated steel plant while the steel plant housings are affected from the scrap processing steel plants with EAFs located south (Figs. 1 and 3). Soil POPs measured near Sincan village were lower than those measured at other sites. This was probably due to the location and distance of the village (east of steel plants) that are not affected significantly from the steel plant emissions being transported S–N axis (Fig. 3). There was not any significant difference between the sites affected by scrap or iron ore processing plants in terms of types and levels of pollutants. It was obvious that both types of plants emit significant amounts of PAHs, PCBs, PCNs, and PBDEs. However, PAH emissions of the integrated steel plant are higher probably due to the presence of coke ovens. PBDEs are not the characteristic pollutants for the integrated steel

Table 3 Soil concentrations (milligram per kilogram dry weight) of selected anions and trace elements

	Hatay-Iskenderun[a] (industrial, n=17)			Hatay-Iskenderun[a] (urban/suburban, n=3)			Izmir[b] (AVG ± SD)		
	AVG	SD	GM	AVG	SD	GM	Industrial	Urban	Rural/agricultural
F^-	13	6	10	10	3	9	31±25	16±19	12±11
Cl^-	37	36	27	25	21	17	68±48	230±346	330±1,030
NO_3^-	49	19	46	65	2	65	1,090±2,700	9,860±16,130	4,440±6,400
SO_4^{2-}	115	99	92	54	15	53	170±90	730±1,650	1,310±4,300
As	9	7	8	3	3	2			
Cd	2	3	2	1	0.5	1	2.4±0.6	1.8±0.3	1.9±0.6
Cr	798	411	685	322	175	292	151±163	117±61	97±39
Cu	61	24	57	33	9	32	45±11	49±40	38±22
Ni	1,154	736	925	501	380	394	62±29	63±59	54±29
Pb	109	162	73	23	19	14	87±60	40±24	43±25
Sn	7	3	7	3	2	2			
Zn	531	786	361	244	214	185	1,030±940	280±170	320±210

AVG average, *SD* standard deviation, *GM* geometric mean

[a] This study

[b] Yatkin et al. (2008), industrial sites in Aliaga region

plant that mainly uses iron ore for steel production. However, PBDE concentrations were also high at the sites near this plant. This could be attributed to the partial use of ferrous scrap in this plant during steel production.

The TOC content of the soil samples ranged between 1.0–10.7% (average ± SD, 5.3±2.9%). The relationship between the soil POP concentrations and TOC content was also investigated. The relationship between TOC and POP concentrations was statistically significant for PAHs ($p<0.05$) while it was insignificant for PCBs, PBDEs, and PCNs ($p>0.05$). TOC content explained only 10–22% variability in soil POP concentrations (Figure S2 in the Electronic Supplementary Material). This further suggested that the spatial variability in soil concentrations were mainly due to deposition/gas absorption of POPs emitted from their sources (i.e., iron–steel plants) rather than soil properties.

PCNs were produced and used in the past as technical mixtures consisting of several congeners (i.e., having commercial names like Halowax 1014). They are also formed during thermal processes. Some congeners are combustion markers (Table 1), and they could be used to assess PCN sources or formation mechanisms (IPPC 2001; Helm and Bidleman 2003). $\Sigma PCN_{Combustion}/\Sigma PCN$ ratio could be used to assess the contribution of thermal formation processes to PCN emissions. Combustion marker PCN congeners are also found in Halowax 1014, and the $\Sigma PCN_{Combustion}/\Sigma PCN$ ratio for this mixture is 0.13. Thus, ratios >0.13 may indicate that the contribution of thermal formation processes to measured PCN concentrations is important. $\Sigma PCN_{Combustion}/\Sigma PCN$ ratio measured in this study ranged between 0.10 and 0.52 (0.29±0.09, average ± SD), and it was >0.13 for most of the samples suggesting a significant contribution from thermal PCN formation mechanisms.

The sources of PAHs may also be identified using diagnostic ratios. It was reported that a phenathrene/anthracene ratio >15 and a fluoranthene/pyrene ratio <1 indicate crude oil while phenathrene/anthracene <10 and fluoranthene/pyrene >1 indicates combustion sources (Wang et al. 2004). In the present study, phenathrene/anthracene ratio was generally <10 (average 7.5) and fluoranthene/pyrene >1 (average 1.3) suggesting combustion was the dominating source.

Trace elements and anions Similar to POPs, the highest Zn and Pb concentrations were measured at sites close to steel plants (Fig. 4). Spatial variation of trace element concentrations indicates that iron–steel

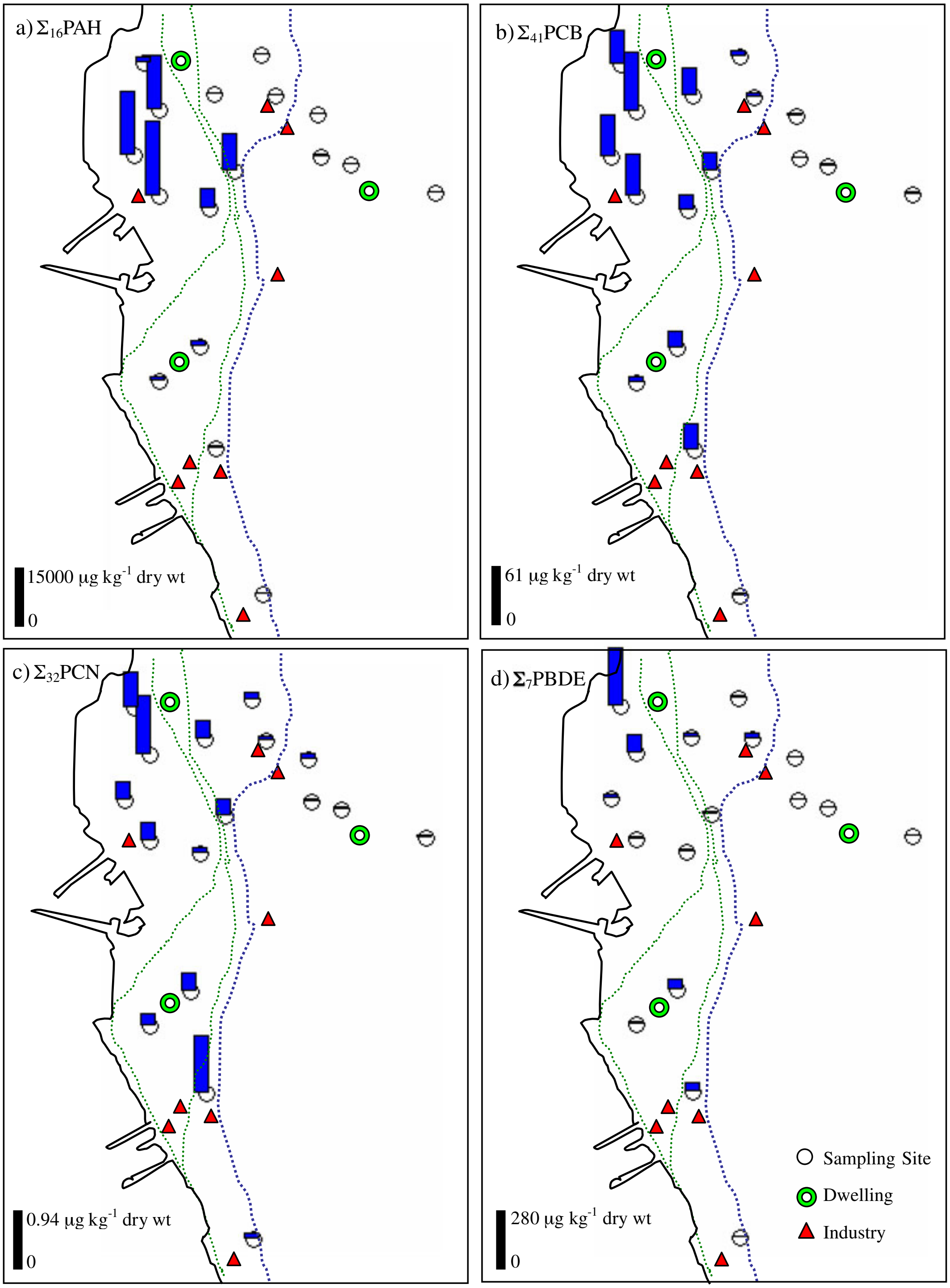

Fig. 3 Spatial variation of PAH, PCB, PCN, and PBDE concentrations in soil

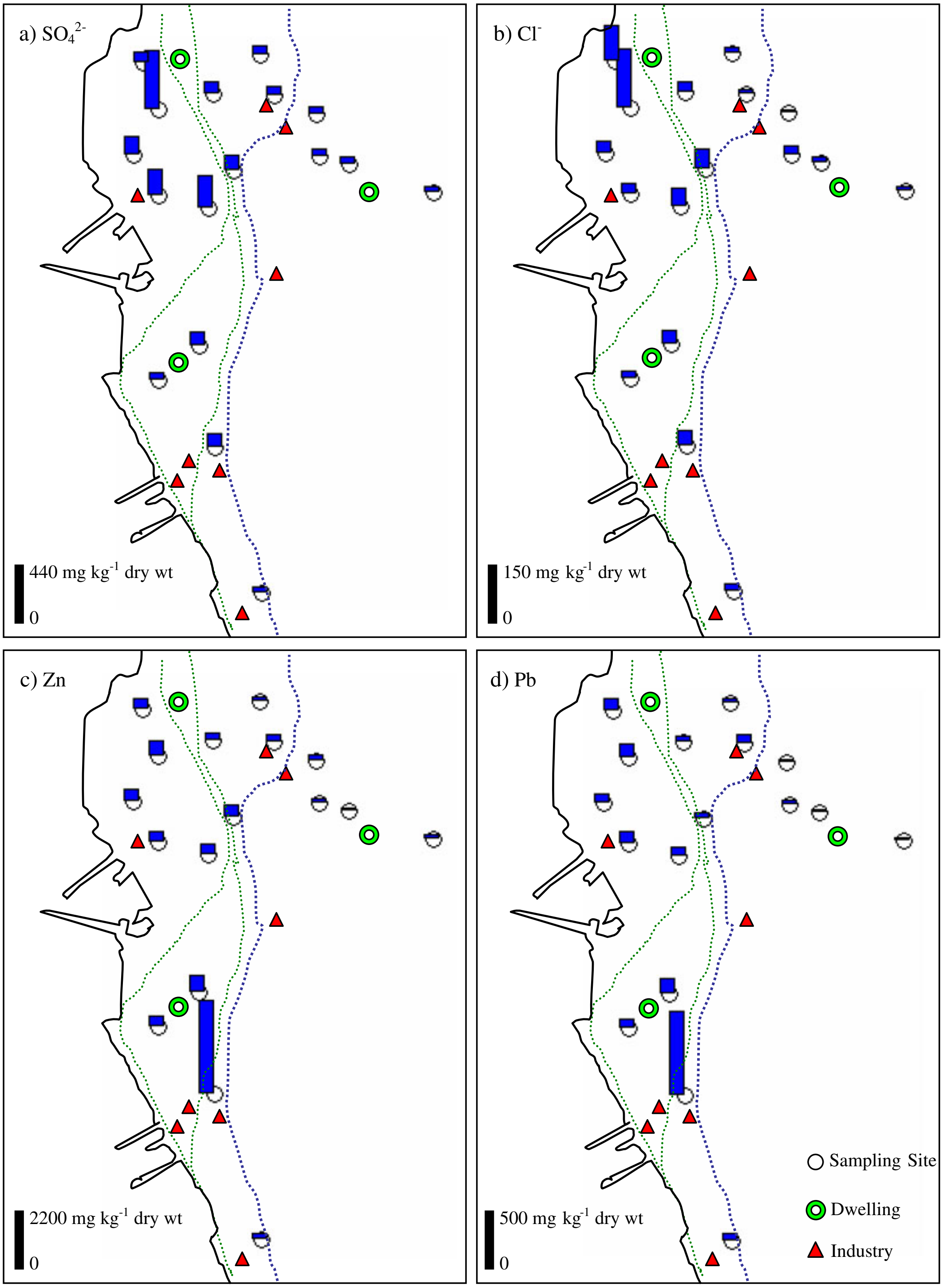

Fig. 4 Spatial variation of SO_4^{2-}, Cl^-, Zn, and Pb concentrations in soil

plants in Hatay-Iskenderun area are significant sources emitting these pollutants, similar to those located in Aliaga. Trace element concentrations measured in the present study were several times higher than those that were reported for rural/agricultural sites in Izmir, Turkey (Table 3). Elements like Zn and Pb are markers for scrap processing steel plants with EAFs (IPPC 2001; Cetin et al. 2007). In the present study, the highest Zn and Pb concentrations were measured around the scrap processing plants (sites 5 and 9). The highest anionic concentrations were also measured at sites close to steel plants (Fig. 4). Anions may naturally be present in soil, or they may have anthropogenic sources. However, spatial variations of anions in this study indicated that their soil concentrations are affected significantly from the steel plant emissions, especially from the integrated steel plant (Fig. 4).

The degree to which trace elements in the soil are enriched or depleted, relative to a specific source, can be assessed using enrichment factors (EF_{crust}; Odabasi et al. 2002). In general, an internationally accepted average crustal composition is used to calculate trace element EFs for local soils. Aluminum (reference crustal element) could be used to estimate the EFs relative to average crustal composition:

$$EF_{crust} = (Tr/Al)_{local}/(Tr/Al)_{crust} \quad (1)$$

where $(Tr/Al)_{local}$ is the concentration ratio of the trace element (Tr) to Al in the local soils and $(Tr/Al)_{crust}$ is the average ratio in average crustal soil (Odabasi et al. 2002). By convention, an arbitrary average EF_{crust} value of <10 is taken as an indication that a trace element in soil is not significantly enriched. In contrast, an EF_{crust} value of >10 is considered to indicate that a significant proportion of an element has a noncrustal source (i.e., anthropogenic). EFs in the present study were calculated using Al as the reference element and an average crustal composition (Sumner 2000). Cu, Cr, Hg, Zn, Pb, Ag, Co, Ni, and Cd were significantly enriched (EF_{crust}=10–120), suggesting their soil concentrations were mainly affected by anthropogenic sources while Na, Be, K, Ba, Sr, Sn, V, and Li were not enriched (EF_{crust}=0.3–3.5). As, Sb, Fe, and Mn had EF_{crust} values between 6 and 9, suggesting a slight enrichment (Figure S3 in the Electronic Supplementary Material).

The relationships between POPs, trace elements, and anions were investigated by constructing a correlation matrix (Table S3 in the Electronic Supplementary Material). The statistically significant correlations ($p<0.05$) between the several organic and inorganic parameters further indicated that they are emitted by common sources. No industrial activities (i.e., scrap metal/raw material storage, waste storage/dumping) directly affecting the soil were present at the sampling points. Therefore, the most likely sources affecting the soil concentrations are the iron–steel plant emissions.

4 Conclusions

Spatial distribution and levels of POPs in soil indicated that the iron–steel plants in Hatay-Iskenderun area are significant sources emitting these pollutants. In general, soil concentrations for all POPs were high relative to those reported previously for rural/urban areas around the world, and they were comparable to those measured in Aliaga region. It was reported that ambient air POP concentrations near the steel plants were also significantly high in Aliaga (Cetin et al. 2007; Cetin and Odabasi 2007; Bozlaker et al. 2008a, b). These results suggest that ambient air POP concentrations may also be high in Hatay-Iskenderun region. Although atmospheric POP concentrations were not measured, this hypothesis was supported by recent studies that measured ambient air PM_{10}, $PM_{2.5}$, NO_x, and SO_2 concentrations at several sites in Hatay-Iskenderun region (Ari et al. 2008; Yay et al. 2008). These studies have reported that air pollutant concentrations were appreciably higher at Payas indicating the effect of steel plant emissions. There are residential sites (Payas county and steel plant housings) among those having significantly high soil concentrations and possibly high ambient concentrations. Therefore, it is possible that a significant population living and working in the study area is exposed to high POP concentrations. We believe that ambient air POP concentrations in the area should also be measured to further assess the health risks associated with the steel plant emissions.

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