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Polychlorinated biphenyls, dibenzo-*p*-dioxins and dibenzofurans in soil samples from airport areas of Croatia

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POLYCHLORINATED BIPHENYLS, DIBENZO-*P*-DIOXINS AND DIBENZOFURANS IN SOIL SAMPLES FROM AIRPORT AREAS OF CROATIA

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Levels and patterns of polychlorinated biphenyls (PCBs) were studied in surface soil samples collected in the coastal part of Croatia within and surrounding four different airports and in the vicinity of two partially devastated electrical transformer stations. The compounds accumulated from air-dried soil samples by multiple ultrasonic extraction with an *n*-hexane:acetone 1:1 mixture were analysed by capillary gas chromatography with electron capture and ion-trap detection. PCBs were quantified against a standard Aroclor 1242/Aroclor 1260 mixture and a standard mixture of 17 individual PCB congeners (IUPAC No.: 28, 52, 60, 74, 101, 105, 114, 118, 123, 138, 153, 156, 157, 167, 170, 180, and 189). The mass fractions of total PCBs in 18 soil samples collected within the airport premises ranged from 3 to 41 327 µg/kg dry weight (dw) (median: 533 µg/kg dw), and those in 21 samples collected at a distance ranging from several metres to 5 km away from the airport fence, from <1 to 39 µg/kg dw (median: 5 µg/kg dw). The highest PCB levels were determined in soils along the airport aprons where the aircrafts were serviced and refuelled. The PCB pattern was very similar to technical Aroclor 1260 in all airport soils. The PCB pattern in 22 soils collected in the vicinity of electrical transformer stations was dominated by congeners contained in Aroclor 1242. These soils contained 7 to > 400 µg/kg dw of total PCBs. One highly PCB-contaminated airport soil sample was analysed for polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs). With an international toxic equivalent (I-TEQ) of 9.7 ng/kg dw, the airport soil contamination was within values typical for urban and rural areas, and the congener patterns gave no clear indication for PCBs as the only source of PCDDs/PCDFs.

Keywords: Polychlorinated biphenyls; PCB congeners; Polychlorinated dibenzo-*p*-dioxins; Polychlorinated dibenzofurans; Airport soil

INTRODUCTION

Polychlorinated biphenyls (PCBs) belong to the widespread semi-volatile, non-polar, highly lipophilic and persistent environmental micropollutants with a high tendency

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to bioconcentration [1–3]. The commercial PCB mixtures were extensively used until the early 1970s in the so-called closed (e.g. in electrical transformers and capacitors) and open systems (e.g. additives in plasticizers, carbonless copy paper, paints, fire retardants etc.). In the late 1970s, their production and use ceased or were severely restricted in many countries, reflecting the concern for harmful effects of increasing residues in the environment.

PCB residues have been identified worldwide in air, waters, soils/sediments, and biota not only as a consequence of local contamination sources but also as the result of the global environmental contamination due to efficient long-distance transport via air and water circulation. PCBs have been found far from emission sites and in remote regions where they were never used, e.g. in Antarctica [4], Subarctic Finland [5], or European high mountain regions [6–8]. The global recycling of PCBs is substantially influenced and retarded by strong sorption of these pollutants in most soils. Despite restrictions introduced three decades ago, the bulk of PCB soil inventory is still close to primary sources, i.e. in urban areas within a few kilometres and in rural areas 10–100 km from sites where they were originally used [3].

The usage of PCBs in Croatia is today limited to still existing closed systems in older electricity facilities until their final substitution. Over the last 30 years, the occurrence and levels of PCBs were studied in Croatian river, ground, and drinking waters [9–12], eastern Adriatic coastal sea water [13], marine sediment [14], wet deposition [15], ambient air [16,17], and vegetation samples [18]. In most of these samples, the concentrations were at background levels reported in the literature as characteristic of the global environmental pollution. Increased levels of PCBs were found in some river and groundwaters as a consequence of improper disposal of industrial waste and uncontrolled discharge of PCB containing transformer oils [9–12]. Extremely high PCB mass fractions (> 2000 mg/kg) were determined in several soils collected in the Croatian coastal karst region in the vicinity of electrical transformer stations damaged during the 1991–1995 war [19].

Contamination of karst soils as a consequence of PCBs dispersion in the environment is a matter of special concern because of the possible leaching and migration of pollutants through a network of karst surface and groundwater streams. Investigating the soil contamination in the coastal part of Croatia, we determined the increased PCB levels in soils collected within the airport areas [20]. In a previous study, a highly contaminated airport soil was used in experiments for microcosm enrichment of biphenyl-degrading microbial communities [21]. The aim was to develop effective long-term inocula for PCB bioremediation. The soil contained 60 mg/kg of PCBs and originated from an airport in Berlin, Germany. To the best of our knowledge, that is the only published information concerning PCB levels in an airport soil, but still, it lacks information about the possible contamination sources.

The aim of the work presented in this article was to investigate the levels and patterns of PCBs in surface soils collected within and surrounding four different airports located in the Croatian coastal region and to compare them with those in soils adjacent to two electrical transformer stations from the same area. The soils were collected in the 1993–2002 period. In addition to PCBs, polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were determined in one airport soil sample containing more than 5 mg/kg dry weight (dw) of total PCBs.

MATERIALS AND METHODS

Soil Samples

Thirty-nine surface soil samples (0–10 cm) were collected within or in the vicinity of four airports: 18 samples along the airport aprons and runways, and 21 samples outside the airport premises at various distances (1–5000 m) from the airport fence. Surface soils from the area of electrical transformer stations (22 samples) were collected at a distance of 0.1–6.0 m from the damaged electrical equipment (capacitors).

All soil samples were dried at room temperature for 7–10 days. During drying, they were covered with soft paper tissue to minimize sample contamination from indoor air. Before analysis, the samples were sieved to < 1 mm.

PCB Standards

The PCB mixtures Aroclor 1242 and Aroclor 1260 were obtained as standard reference compounds from the U.S. Environmental Protection Agency Repository (Research Triangle Park, NC). Isooctane solutions of 17 single PCB congeners (IUPAC numbers 28, 52, 60, 74, 101, 105, 114, 118, 123, 138, 153, 156, 157, 167, 170, 180, 189; congener concentration 35 µg/mL, purity 99–100%) were purchased from Campro Scientific (Netherlands), as products of AccuStandard (New Haven, CT). A PCB set of six single PCB congener isooctane solutions (PCB-set OEKANAL[®], IUPAC No. 28, 52, 101, 138, 153, 180; congener concentration 10 µg/mL) was purchased from Riedl-de Haën, Seelze, Germany. The standards for gas chromatographic analysis were prepared in *n*-hexane.

Certified Reference Soil

The certified reference material CRM 481, purchased from the former European Community Bureau of Reference (Brussels), was used to validate the performance of the applied analytical method for determination of PCB congeners in soil. CRM 481 is an industrial soil with certified mass fractions of eight and indicative mass fractions of four PCB congeners at the mg/kg level.

Analysis of PCBs

PCBs were accumulated from the soil samples by sonicated multiple extraction with a 1:1 *n*-hexane:acetone mixture, as described previously [22]. In summary, the 10-g soil sample was extracted with 5 × 15 mL of *n*-hexane:acetone 1:1 mixture (four times for 3 min and the last time for 15 min) and finally washed with an additional 5 mL of solvent mixture. The combined extracts were evaporated under a stream of nitrogen to 10 mL. To remove the sulphur, the extract was stirred with 0.5 g of copper powder and 0.5 g of mercury for 2 h. The decanted liquid phase was evaporated to dryness under a stream of nitrogen. The residue was redissolved in 1.0 mL of *n*-hexane and washed with 1.0 mL of concentrated sulphuric acid by mixing the sample for 30 s. The organic layer was separated and analysed by capillary gas chromatography.

For analysis of PCB congeners in the certified reference material, the 0.3-g sample of CRM 481 was extracted with 5 × 1 mL of *n*-hexane:acetone 1:1 mixture and washed

out with an additional 1 mL of extracting solvent. After evaporation of the combined extracts under a stream of nitrogen, the dry residue was redissolved in 1.0 mL of *n*-hexane and treated with concentrated sulphuric acid as described above.

The gas-chromatographic analysis was performed on a Varian 3400 gas chromatograph fitted with either a 30- or 60-m-long SPB-5 (Supelco, Bellefonte, PA) fused silica capillary column of 0.25 mm i.d. and 0.25 µm film thickness, and with an ⁶³Ni electron capture detector (ECD). Helium was used as the carrier gas at the column head pressure of 137.9 kPa (30-m-long SPB-5 column) and of 172.4 kPa (60-m-long SPB-5 column). The 30-m-long SPB-5 column temperature was programmed from 40°C (for 1 min) to 165°C at 50°C/min (held isothermally for 1 min), then to 225°C at 2°C/min (held isothermally for 20 min) and then to 250°C at 40°C/min. The 60 m long SPB-5 column temperature was programmed from 60°C (for 1 min) to 180°C at 40°C/min (held isothermally for 1 min), then to 240°C at 2°C/min (held isothermally for 20 min), and finally to 260°C at 5°C/min. The injector and detector temperatures were 270 and 350°C, respectively. The injection mode was splitless for 45 s, and the injection volume was 2 µL.

Total PCBs were quantified against a standard mixture consisting of Aroclor 1242 and Aroclor 1260 in 2.5:1 ratio. The concentration of individual congeners in the standard was calculated by multiplying the mass fraction (%) of a given congener in Aroclor 1242 and Aroclor 1260 [23] by the concentration of that Aroclor and then by summing up the contributions from either Aroclors. The total PCBs in the analysed samples were calculated by summing the individual congener mass fractions (µg/kg dw) measured in that sample.

Two airport soil samples containing more than 2 mg/kg dw of total PCBs, and five soil samples collected adjacent to an electrical transformer station, were also analysed for 17 individual PCB congeners against the standard solutions prepared by dilution and mixing of original single isooctane solutions with *n*-hexane.

The results obtained by determination of total PCBs and individual PCB congeners were corrected for analytical solvent and reagent blanks which were prepared and analysed with each set of five samples.

The identity of PCBs in airport soil samples was confirmed by gas chromatographic-mass spectrometric (GC/MS) analysis of *n*-hexane extracts using a Varian Saturn II GC/MS system (ion-trap detector) equipped with a septum-equipped programmable injector (SPI) and a DB-5 fused silica column (J&W Scientific, CA), 30 m × 0.25 mm. i.d., film thickness 0.1 µm. The SPI temperature was programmed from 40 to 330°C at 200°C/min, then kept for 2 min at 330°C. The column temperature was programmed from 40°C (for 1 min) to 160°C at 15°C/min and then to 310°C at 5°C/min (held isothermally for 20 min). The carrier gas was helium, with a linear velocity of 0.46 m/s. The injection volume was 1 µL. The ion-trap detector operating conditions were: transferline temperature 260°C; electron impact ionization mode at 70 eV; full scale acquisition mode; scan range 50–500 amu.

Analysis of PCDDs and PCDFs

The HRGC/HRMS analysis of PCDDs and PCDFs in one airport soil sample was done by MWC-Michael Wilken UmweltConsulting, Berlin and MPU GmbH, Dep. Analytical Laboratory (Berlin). The PCDDs/PCDFs determination was performed in accordance with German VDI 3498 and AbfKlärV. The soil samples were extracted

with toluene in a Soxhlet extractor for 24 h after adding a mixture of $^{13}\text{C}_{12}$ -labelled PCDD- and PCDF-standard for each chlorination degree. The raw extract was purified by eluting over a silicagel column (mixture of silicagel/silicagel- H_2SO_4 /silicagel- NaOH) with *n*-hexane and finally fractionated over an aluminium oxide column (ultraactive basic alumina) by eluting the sample with different solvent mixtures of increasing polarity. The PCDDs/PCDFs containing fraction was concentrated and analysed by HRGC/HRMS (AutoSpec Ultima) on two different gas chromatographic columns (DB-5 and CP-Sil 88).

In addition to the quantification, the toxic equivalents of the analysed PCDDs/PCDFs were calculated according to the international NATO/CCMS system (international toxic equivalents, I-TEQ).

RESULTS AND DISCUSSION

Results of PCB Analysis

The analytical procedure applied for determination of PCBs in the investigated surface soil samples was validated through analysis of the certified reference industrial soil CRM 481 with a PCB content at the mg/kg level. Eight 0.3-g samples of the reference soil were analysed for six PCB marker congeners (IUPAC No. 28, 52, 101, 138, 153, and 180) most frequently found in environmental samples. Table I shows the certified/indicative and measured PCB congener mass fractions, percentage of certified/indicative values determined in this work, and the corresponding relative standard deviations. All results were within the range of plus/minus two standard deviations of the certified/indicative mass fraction mean values and within the 95% tolerance interval. The measured compound mass fractions were higher than 90% of certified/indicative values for all compounds except for PCB-28, which was present in the lowest mass fraction. The relative standard deviations of the repeatability of the results ranged from 10% for PCB-101 to 42% for PCB-28. An previous evaluation of the efficiency and reproducibility of the same method by analysis of spiked soils differing in their sorption controlling properties is discussed elsewhere [22].

The analytical blanks contained no substantial concentrations of PCBs or interferences at the retention times of the congeners analysed. Precautions were taken to minimize the possibility of sample contamination and the losses of analysed compounds

TABLE I Certified/indicative and found mass fractions of six PCB marker congeners in certified reference material (industrial soil CRM 481)

PCB congener	Mass fraction (mg/kg dw)		Found ^c (%)	R.S.D. (%)
	Certified/indicative mean \pm SD	Found ^c		
PCB-28	0.34 \pm 0.06 ^a	0.24	71	42
PCB-52	2.9 \pm 0.5 ^a	2.7	93	12
PCB-101	37 \pm 5	36	97	10
PCB-153	137 \pm 13 ^b	145	106	34
PCB-138	92 \pm 14 ^a	106	115	11
PCB-180	124 \pm 11 ^b	119	96	34

^aIndicative values reported by BCR.

^bCertified values reported by BCR.

^cMean of six to eight determinations.

TABLE II Mass fractions of total PCBs (expressed as Aroclor 1242/Aroclor 1260 mixture) in soil samples collected within and surrounding airports and in the vicinity of an electrical transformer station

Sampling location	Number of samples	Mass fractions ($\mu\text{g}/\text{kg dw}$)	
		Range	Median
Along the airport aprons	7	7–41 327	2603
Along the airport runways	11	3–2704	273
Airport surroundings	21	< 1–39	5
Electrical transformer station area	17	7–166	34

through volatilization during the air-drying of soils. Under the drying conditions applied in this work, no substantial losses of PCBs are expected, but for congeners with less than three chlorine atoms, they cannot be ruled out. Krauss *et al.* [24] have shown that air-drying of soils under conditions comparable with those applied in our work has no or little effect on the original composition of PCBs. They compared the mass fractions of 12 PCB congeners in one soil sample, which was extracted without drying, with those in the same soil sample, which was air-dried at room temperature for 8 days. The differences they found were in the range of determination error except for the most volatile congener in their PCB mixture, dichlorobiphenyl PCB-8. It was lost for about 45%.

Table II summarizes the results of total PCB analysis in different soil samples. The results are not corrected for recoveries. The PCB mass fractions in soils collected along the airport aprons and runways covered a wide range of values. Eight of the 18 airport soil samples showed a PCB contamination (expressed as Aroclor 1242/Aroclor 1260 mixture) above 1.5 mg/kg dw. The three highest PCB mass fractions (5314–41 327 $\mu\text{g}/\text{kg dw}$) were determined in samples collected along the airport aprons where the aircrafts were serviced and refuelled. The maximum and median PCB mass fraction values in samples collected along the airport runways were one order of magnitude lower than those in soils taken close to the aprons.

Figure 1 compares a typical GC-ECD chromatogram of PCBs extracted from the airport soil with the chromatogram of the Aroclor 1242/1260 standard mixture. PCB pattern in soil extracts showed a high similarity with the technical Aroclor 1260, a mixture of higher chlorinated PCB congeners often used in transformers. The identity of the compounds in the airport soil extracts was confirmed by the GC/MS analysis. The distribution of individual PCB congeners in two representative airport soil samples, collected at two different airports and containing more than 2 mg/kg dw of total PCBs, was determined by analysis of soil extracts against a standard mixture of 17 individual PCB congeners comprising tri- to heptachlorobiphenyls (Fig. 2). The three most prominent PCB congeners in both samples were PCB-138, PCB-153, and PCB-180. These congeners are prevalent also in a commercial Aroclor 1260 mixture. The PCB mass fractions in two airport soils expressed as the Aroclor 1242/Aroclor 1260 mixture and as the sums of 17 individual and seven marker (IUPAC No. 28, 52, 101, 118, 138, 153, and 180) PCB congeners are compared in Table III. The mass fraction of total PCBs, calculated against the Aroclor standard, was higher in both samples than the sum of the 17 congeners for about 30%. The ratio of the total PCBs and the sum of seven marker congeners was 2.1 in the first (AS 1) and 2.8 in the second (AS 2) airport soil sample.

The PCB mass fractions in airport soils lower than 1 mg/kg dw were in the range of those reported for soils collected in some industrial and urban areas, e.g. at industrial

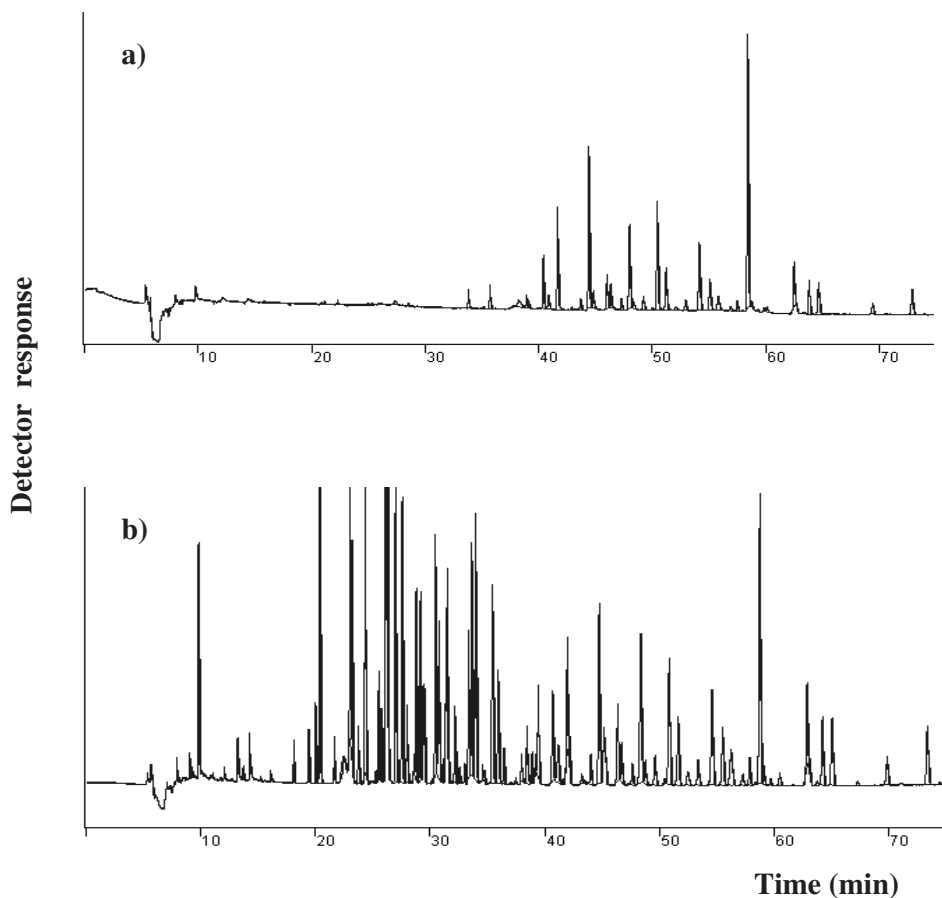


FIGURE 1 GC-ECD chromatograms of (a) PCBs extracted from the airport soil sample containing $2210 \mu\text{g}/\text{kg}$ of PCBs measured against the standard mixture of Aroclor 1242/1260 and (b) a standard solution of Aroclor 1242 ($485.25 \text{ ng}/\text{mL}$) and Aroclor 1260 ($213.60 \text{ ng}/\text{mL}$) mixture.

sites in the Seine river basin in France (up to $342 \mu\text{g}/\text{kg}$, sum of 22 PCB congeners) [25] and at urban sites in northern Italy ($6\text{--}98 \mu\text{g}/\text{kg}$, the sum of six PCB congeners) [7], northern Bavaria in Germany (up to $158 \mu\text{g}/\text{kg}$, the sum of 12 PCB congeners) [26], and Romania ($57.3 \pm 41.0 \mu\text{g}/\text{kg}$, the sum of 19 PCB congeners) [27]. In sandy soils rich in organic matter at a site located on the west coast of southern Sweden, PCBs were determined at mass fractions (sum of 44 congeners) ranging from 237 to $986 \mu\text{g}/\text{kg}$, with a median value of $332 \mu\text{g}/\text{kg}$ [28]. These soils contained large fractions of heavy PCB congeners possibly originating from the leakage of transformer fluid oil used within the lighthouse located at that site. The PCB composition in airport soils analysed in the present work was also dominated by penta- to heptachlorobiphenyls.

The maximum mass fraction of total PCBs determined in airport soils ($> 41 \text{ mg}/\text{kg}$ dw) was in agreement with the high PCB level reported for the airport soil sample collected in Berlin [21]. High PCB levels comparable with those in the airport samples were observed also in industrial soils taken in the vicinity of the asphalt/gravel mixing plants ($3.9\text{--}38 \text{ mg}/\text{kg}$) and near an industrial waste disposal site ($0.4\text{--}5.8 \text{ mg}/\text{kg}$) in the area of the former manufacture of PCBs in Slovakia [29]. Soil samples taken

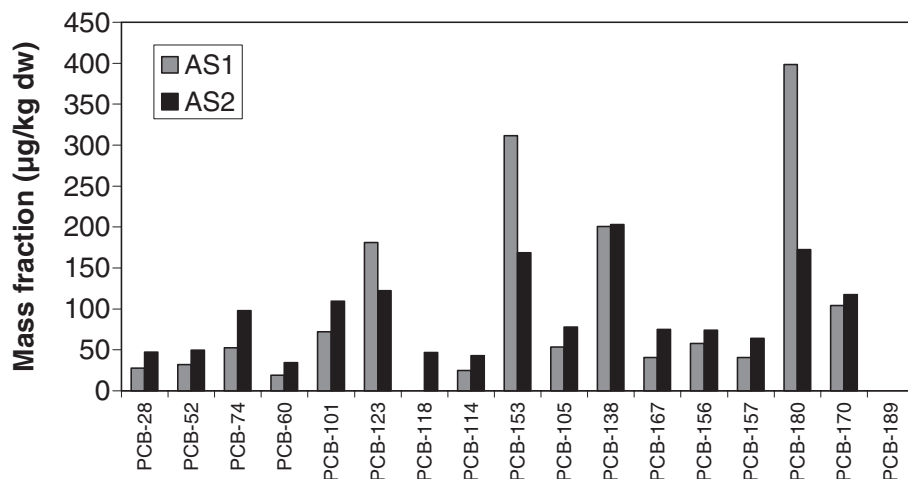


FIGURE 2 Distribution of individual PCB congeners in two airport soil samples (AS 1 and AS 2) collected at two different airports.

TABLE III PCB mass fractions in soil samples AS 1 and AS 2 from two different airports and in five soil samples (ETS 1–5) from the area of a devastated electrical transformer station^a

	Mass fraction (µg/kg dw)		
	AS 1	AS 2	ETS 1–5
Total PCB as Aroclor 1242/Aroclor 1260	2210	2250	Not determined
∑ 17 PCB congeners	1617	1503	101–354
∑ seven PCB marker congeners	1042	797	51–171

^aMass fractions are expressed as Aroclor 1242/Aroclor 1260, sum of the 17 individual PCB congeners, and sum of the seven PCB marker congeners.

near a factory producing organochlorines in Romania contained 722 µg/kg of PCBs (sum of nine PCB congeners) [27]. High PCB levels were found also in soils associated with radar stations located across the Canadian Arctic and Labrador [30]. The average PCB mass fractions ranged from 0.001 mg/kg in soils collected at background locations to 10 mg/kg in soils at different radar sites, and the maximum value reached 320 mg/kg.

The airport results pointed to a local source of PCBs in the airport soils, presumably being the uncontrolled spills and release from the airport electrical facilities or aircraft electric and hydraulic systems in the past. In soils collected in the surroundings of the airports, a distinct decrease in PCB levels was observed, in most samples approaching the values characteristic for global pollution of the environment (Table II).

PCB levels and pattern in the airport soils were compared with the levels and pattern found in surface soil samples collected in the area of two partially damaged electrical transformer stations. As shown in Table II in most of the soil samples, collected close to the capacitors of the first transformer station, the mass fractions of total PCBs were much lower than those determined in airport soils. At the moment of destruction, the electrical facilities at that station contained no PCBs, and the soil contamination was therefore attributed to the uncontrolled spills of PCB containing oils

used in the past. In contrast to airport soils, the PCB pattern in soil samples taken in the vicinity of the transformer station was dominated by congeners contained in the Aroclor 1242 mixture. Almost the same PCB profile was obtained by analysis of five soil samples collected at the location of another damaged electrical transformer station (Table III). In these soil samples, PCB congeners contained in Aroclor 1242 accounted for 69–76% of the total PCBs determined as the sum of 17 individual congeners. According to available information, capacitors destroyed at that location contained some PCB-containing oils at the moment of destruction. This might possibly explain the higher PCB levels found in the adjacent soils (Table III) compared with those found in the vicinity of the first transformer station (Table II).

Results of PCDD/PCDF Analysis

Commercial PCB mixtures, assumed to be the contamination sources of airport soils, are normally contaminated by various PCDFs at considerably varying levels, while the concentrations of PCDDs in those products are negligible [31,32]. To gain a preliminary insight into the composition of PCDD/PCDF mixture in an airport soil, we determined the mass fractions of PCDD/PCDF congeners in the soil sample which contained 5314 $\mu\text{g}/\text{kg dw}$ of PCBs. With a PCDD/PCDF mass fraction of 843.4 $\text{ng}/\text{kg dw}$ and an I-TEQ of 9.7 $\text{ng}/\text{kg dw}$, the soil was within values typical for urban and rural areas [33–35]. The congener patterns gave no clear indication for PCBs as the only source of PCDDs/PCDFs. The soil contained roughly equal mass fractions of total PCDDs (464.8 $\text{ng}/\text{kg dw}$) and PCDFs (378.6 $\text{ng}/\text{kg dw}$). The PCDF profile, presented in Fig. 3, showed an almost uniform distribution of tetra- to octa-CDFs, with mass fractions ranging from 63.7 $\text{ng}/\text{kg dw}$ for octa-CDF to 86.5 $\text{ng}/\text{kg dw}$

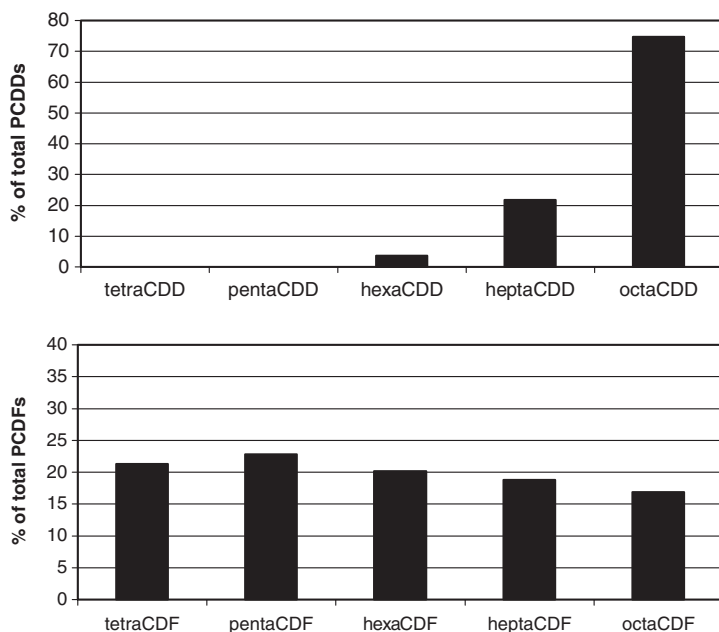


FIGURE 3 Profiles of PCDDs and PCDFs in the airport soil sample collected along the airport apron.

for penta-CDFs. However, the PCDD pattern was dominated by octa- (347 ng/kg dw) and hepta-CDDs (101 ng/kg dw), while tetra- and penta-CDDs were below the determination limit (Fig. 3). A similar distribution was found by determination of PCDD background levels in many soils. This agrees with the increased lipophilicity of the higher chlorinated PCDDs, which favours their sorption in the soil. The main pathway of PCDDs/PCDFs to enter the surface soil, which is an accumulating matrix, is atmospheric deposition. Analyses of background levels in air, soil, and sediment samples indicated various combustion and incineration processes as the major sources of PCDDs/PCDFs [32,34].

CONCLUSIONS

Data concerning persistent organochlorine pollutants in Croatian soils are generally lacking, although they are of great importance for evaluating environmental pollution, identifying possible past or present local contamination sources, and generating data for risk assessment. Significantly increased PCB levels determined in airport soil samples pointed to a local source of contamination within the airports. Outside the airport area, although still in its immediate vicinity, the soil contamination was reduced to levels characteristic for the global environmental pollution. Taking into account the present restricted use of PCBs, their origin in airport soils may mainly be attributed to the widespread use of PCB-containing materials in the past. Contamination of an airport soil with PCBs was not followed by an increase in levels of PCDDs/PCDFs above the background values typical for rural/urban areas in other European countries. As a conclusion, the results demonstrated that further studies are needed to identify the contaminated soil locations, especially in areas damaged by the war, and to clarify the sources of PCB, PCDD, and PCDF soil contaminants.

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