Levels of polychlorinated byphenils (PCBs) were monitored continuously in Zagreb between June 1999 and February 2000 and analysed qualitatively and quantitatively using high resolution gas chromatography (HRGC). Total PCBs were determined with respect to Aroclor 1260, which was used as the standard reference. The concentrations of PCBs ranged from 1.6 to 136 pg/m$^3$ and were higher in warmer seasons (temperatures above 10 $^\circ$C; 5.1-136 pg/m$^3$) than in colder seasons (temperatures from -10 $^\circ$C to about 10 $^\circ$C; PCB range: 1.6-23.5 pg/m$^3$). The increase in PCBs concentration with temperature followed an exponential curve.

**KEY WORDS:** levels in air, organochlorine compounds, persistent pollutants, POPs

Polychlorinated biphenyls (PCBs) make a group of 209 synthetic aromatic compounds differing by the number and the position of chlorine atoms ($C_{12}H_{10-n}Cl_n$; $n$ is the number of chlorine atoms). They are non-polar lipophilic compounds, stable in the environment in either alkaline or acid conditions. Due to their physical and chemical properties they were used widely in open systems as additives to cement, paints, or copy paper, as well as in closed systems such as transformers, condensers, and vacuum pumps (1).

The atmosphere is an important environment compartment under direct influence of PCBs. Because of their persistence and toxic influence on environment and humans, PCBs have limited application today. They are still found in such sources as waste, certain transformers and condensers, and they also evaporate from natural sorbents (such as sediments and biota). In ambient air, PCB compounds are present in the gas phase or are adsorbed on particulate matter. Higher chlorinated PCBs (with more than five chlorine atoms) are more lipophilic and therefore tend to adsorb on particles while PCBs with the lower chlorine content are mainly found in the gaseous phase. The evaporation from the sorbent's surface and long-range transboundary air transport of PCBs depend on the temperature and other meteorological conditions (2, 3). As PCB levels in ambient air tend to be higher at higher temperatures, seasonal variations are expected, with peaks in the summer (4).

The aim of this study was to monitor PCB levels in samples of ambient air collected in Zagreb, Croatia and establish their seasonal variations. One of the reasons for this study is that data on PCB levels in ambient air in Croatia are quite scarce (5), and seasonal monitoring had never been undertaken before.
MATERIAL AND METHOD

Total PCBs in the analysed ambient air samples were determined with respect to the reference Aroclor 1260 mixture, which has the most similar pattern to that of PCB. Samples (about 1,000 m³ air) were collected on polyurethane foam and quartz filters. From June 1999 to February 2000, 48 samples had been collected in the northern part of Zagreb around the clock. Data about air pressure and temperature were obtained from the Croatian Meteorological and Hydrological Service, and the volumes of sampled air were recalculated to standard temperature and air pressure. Polyurethane foam and quartz filters were extracted in Soxhlet (12 hrs, 4 cycles/h) with 5% diethyl ether in n-hexane. Extracts were evaporated to about 5 ml, cleaned with concentrated sulphuric acid and evaporated to dryness in a gentle stream of nitrogen. The samples were then analysed qualitatively and quantitatively using high-resolution gas chromatography with 63Ni electron capture detector and a 60-m long capillary column with inner diameter of 0.25 mm and SPB-5 stationary phase of 0.25 µm film thickness (5).

RESULTS AND DISCUSSION

PCBs were present in all 48 analysed samples and their levels ranged from 1.6 to 136 pg/m³ (Figure 1). It is evident from Figure 1 that PCB levels gradually increase with temperature. At temperatures below 0 °C concentrations are low (range: 1.6-2.7 pg/m³). Markedly higher levels were determined in samples collected when the average temperatures were above 10 °C. This increase with temperature is not linear, but follows an exponential equation: \( y = 4.46 e^{0.126x} \); where \( y \) is PCB concentration and \( x \) is the temperature. This equation also includes concentrations from three samples which for unknown reason contained PCBs at considerably higher levels than other samples collected at the same temperature (Figure 1). This might be the result of long-range transport of PCBs through the air.

Table 1 gives a summary of all results; concentrations and temperatures are expressed as monthly median and mean values, respectively. PCB levels were two or more times higher in the months with average temperatures ranging between 19.0 °C and 21.5 °C than in the months when average temperatures ranged from -1.4 °C to 11.5 °C.

According to Oehme and co-workers (6), higher PCB levels in ambient air can be observed when ambient temperatures keep above 10 °C over a longer period, necessary for PCBs to evaporate from the sorbent’s surface (6). Our results corroborate this finding. It seems that PCB levels in ambient air do not vary noticeably at low temperatures (7). Seasonal variations of PCB levels in ambient air were also determined in samples collected in Augsburg, Germany (8), as well as in Manchester, Cardiff, London, and Stevenage in the United Kingdom (9). According
to Kaupp and co-workers (8), PCB levels in ambient air vary because of temperature-dependent partition of PCBs between sorbents on the Earth’s surface (soil, water, biota) and air (8).

PCBs can be determined as individual congeners or can be compared to commercial mixtures which always contain numerous PCB congeners. Commercial mixtures differ by their chlorine content, that is, by the number and type of congeners. Different abilities and performance of laboratories and the differences in the approach to PCB measurement, measurement in various biological matrices make the comparison of published results difficult. To facilitate their comparison, it is necessary to state whether PCBs were determined as individual congeners or in comparison to a commercial reference mixture, as well as to indicate its content and type. When PCBs are determined as individual congeners, concentrations can be expressed as levels of each congener, as a sum of all congeners analysed, or as a sum of congeners within a group of homologues. To express concentrations as the sum of all congeners means to list all congeners included in their sum.

Granier and co-workers (10) reported that total PCB levels in ambient air samples collected in Paris in 1986 determined with reference to mixtures Aroclor 1242 : Aroclor 1254 : Aroclor 1268 (1:1:1) were relatively high (range: 5.0-19.0 ng/m$^3$), while in 1990 those levels were somewhat lower (range: 2.0-6.0 ng/m$^3$) (10). PCB levels in samples of ambient air collected on eleven locations in the southern Sweden (expressed as sum of levels of 51 congeners) ranged from 7.0 to 983 pg/m$^3$ (4). If our results are compared to those cited above, it is evident that total PCB levels determined in samples of ambient air collected in Zagreb keep within the range reported in other European countries.

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Sažetak

SEZONSKE VARIJACIJE POLIKLORIRANIH BIFENILA U ZRAKU GRADA ZAGREBA

Kontinuirano su praćene razine polikloriranih bifenila (PCB) u zraku skupljenom u sjevernom dijelu Zagreba tijekom devetomjesečnog razdoblja (lipanj 1999. - veljača 2000.). Kvalitativna i kvantitativna analiza provedena je plinskom kromatografijom visokog razlučivanja. Određivani su ukupni PCB-i prema smjesi Aroclor 1260. Koncentracije PCB-a bile su u rasponu 1,6 - 136 pg/m³. U razdoblju s višim temperaturama (iznad 10 °C) izmjerene su više koncentracije PCB-a (raspon: 25,1 pg/m³ - 136 pg/m³) nego u razdoblju s nižim temperaturama kada je raspon temperatura bio od -10 °C do +10 °C (raspon: 1,6 pg/m³ - 23,5 pg/m³). Porast razina ukupnih PCB-a s temperaturom zraka nije linearan, nego slijedi eksponencijalnu krivulju. Razine ukupnih PCB-a u uzorcima zraka skupljenim u Zagrebu unutar su raspona razina izmjereni u uzorcima zraka iz drugih europskih zemalja.

KLJUČNE RIJEČI: organoklorov spojevi, perzistentna zagađivala, POP, razine u zraku

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