MASS BUDGET AND DYNAMICS OF POLYCHLORINATED BIPHENYLS IN THE EASTERN MEDITERRANEAN SEA

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Introduction

Even though the production of polychlorinated biphenyls (PCBs) was banned two decades ago, they are still released into the atmosphere by primary and secondary emission sources. Atmospheric PCBs tend to partition between the gas and particulate phase of the atmosphere[1] and they are transported away from the release sources through the movement of air masses. Several studies have shown that atmospheric transport and deposition is a major mechanism by which PCBs and other semi-volatile organic compounds may enter the aquatic ecosystems[2] and contribute to biota contamination. In the aquatic environment, these compounds can be dissolved in the water phase or associated with particles depending on their hydrophobicity and organic

carbon-water partition coefficients. Particle-bound PCBs are subsequently removed from the water column by vertical transport of sinking particles[3].

Atmospheric dry particle deposition and settling of particles in the water column are two key processes that significantly affect the fate of organic pollutants in the environment. The fluxes arisen from these processes are difficult to be estimated for trace pollutants, such as PCBs, PCDD/Fs, etc., and in general there is a scarcity of field data. The objectives of the current study, were i) to assess the dry particle deposition and the settling flux of PCBs in the atmosphere and the water column of the eastern Mediterranean, respectively and ii) to synthesize the results of the present and previous studies in order to construct a mass balance which will describe the behavior of PCBs in this region.

Methods and Materials

Particle dry deposition samples (twelve samples) for PCB analysis were collected from the marine background sampling station of Finokalia (35° 20' N, 25° 40' E; Island of Crete, Greece) between April 2000 and October 2001. Samples were collected by using a stainless steel funnel (42 cm of diameter) connected directly to an amber glass bottle. Prior to sampling, both the funnel and the bottle were thoroughly rinsed with HPLC quality grade acetone and then with Milli-Q water. The sampler was horizontally exposed to the atmosphere during periods of no rain and the duration for the collection of each sample was on average 28 days. Each sample was separately analyzed for PCBs to obtain twelve single measurements. Settling particles within the water column were sampled from May to October 2001. Sediments traps were deployed at three different depths (186, 1426, 2837 m) in southern Ionian Sea (35° 10' N, 20° 51' E). Total mass fluxes were measured every 15 days, while PCBs were analyzed in two bulk samples from each water depth during the spring and summer period, Fifty-four PCB congeners (corresponding to 41 chromatographic peaks) were quantified during this study. More information about the analysis and detection of PCBs has been reported in previous studies[4].

Results and Discussion

For all three sediment traps, the total mass flux exhibited a clear seasonal variation with the maximum values occurring during spring and summer and the lowest ones during autumn and winter months. At the upper sediment trap (186 m water depth), the mass flux ranged between 8 and 220 mg m^{-2} day^{-1}, with an average value of 48 ± 65 mg m^{-2} day^{-1}. Although similar values were observed at 1426 (4 to 300 mg m^{-2} day^{-1}) and 2837 m water depth (6 to 259 mg m^{-2}

day^{-1}), the flux at the upper sediment trap was relatively higher throughout the spring.

The concentration of ΣPCB in settling solids varied between 3.3 and 19.0 ng g^{-1} (dry weight; dw) with an average value of 7.0 ± 5.5 ng g^{-1} dw. For all sediment traps, the levels of PCBs were generally higher during summer than spring samples. Congeners 18, 8+5, 28, 31 and 20+33 were the most abundant and the concentration of each one ranged between 0.2 and 1.8 ng g^{-1} dw.

For both sampling periods and especially during summer, the concentration of PCBs exhibited a decline with depth in the water column. In particular, the concentration of ΣPCB at the upper sediment trap ranged from 5.0 to 19.0 ng g^{-1} dw and it was substantially higher than those observed at the middle (4.5 to 7.4 ng g^{-1} dw) and near-bottom sediment trap (3.3 to 5.8 ng g^{-1} dw).

For all depths, tetra- and tri-chlorinated congeners dominated the PCB pattern and accounted for 38 ± 5% and 22% ± 5% of the total PCB, respectively. For all traps deployed, the derived depositional flux of ΣPCB varied between 0.18 and 1.04 ng m^{-2} day^{-1}, with the upper and near-bottom sediment traps providing the highest and the lowest values, respectively. The arithmetic average flux of PCBs was 0.63 ± 0.34 ng m^{-2} day^{-1}, while the corresponding time-weighted average flux approached 0.45 ng m^{-2} day^{-1}. The estimated annual settling flux of PCBs below the euphotic zone (186 m water depth) approached 214 ng m^{-2} yr^{-1}, while the corresponding fluxes at 1426 and 2837 m were 87 and 81 ng m^{-2} yr^{-1}, respectively. By taking into account the surface area of the eastern Mediterranean Sea (1.65 million km^2), it was roughly estimated that the annual export of PCBs out from the euphotic zone should be around 350 kg yr^{-1}, while only 40% of that amount (about 135 kg yr^{-1}) will finally reach deeper waters.

The dry deposition flux of PCBs was determined for each one of the twelve sampling periods. The flux of ΣPCB ranged from 0.1 to 1.1 ng m^{-2} day^{-1}, while the estimated annual dry deposition flux as 180± 110 ng m^{-2} yr^{-1}. Based on this result, the input of PCBs in the eastern Mediterranean due to dry deposition should be 0.3 t yr^{-1}.In consistence with the sediment traps samples collected from southern Ionian Sea and analyzed in the current study, PCBs 28, 31, 18 and 33+20 were also the predominant congeners in dry deposition samples. Tri- plus tetra-chlorobiphenyls constituted 50 to 70% of the total PCB mass, while congeners having seven or eight chlorines provided the minimum contributions (about 2% each). The average pattern of PCB homologues in dry particle deposition was very well correlated (R^2>0.97, p<0.001) with the corresponding pattern in the sediment traps and those previously observed in precipitation samples[5] and the atmospheric

particulate matter[1].

Wet deposition of PCBs is a process that has been poorly studied in the broader region of Mediterranean Sea. Recent results have been presented for the coastal background sampling station of Finokalia in the eastern part of the Mediterranean[5]. The concentration of ΣPCB in precipitation samples (particles plus dissolved phase) collected from Finokalia ranged between 1.0 and 3.6 ng l^{-1}, with an average value of 1.9 ± 0.9 ng l^{-1}. The volume-weighted mean (VWM) concentration of ΣPCB was 1.8 ± 0.4 ng l^{-1}. Based on the precipitation rate and the VWM concentration of PCBs in rainwater the estimated annual wet deposition flux of PCBs should approach 820 ng m^{-2} yr^{-1}. By taking into account the total surface area of eastern Mediterranean basin, the total input of PCBs in this area should be ca. 1.3 t yr^{-1}.

Diffusive gas exchange across the air-sea interface (volatilization/absorption) has been recognized as an import process for the delivery or the removal of PCBs from natural waters. In order to estimate the net vapor flux of PCBs (volatilization minus absorption) in the eastern Mediterranean Sea a modified two-film, gas exchange model was applied[7]. The atmospheric concentrations of gaseous PCBs have been monitored at the sampling station of Finokalia and these results have been previously reported[1]. The presence of PCBs in seawater of the Mediterranean basin has also been investigated[6]. The average values calculated from these results were subsequently used in our model. The fluxes of all individual congeners were positive (net volatilization) and ranged from +0.5 to +157 ng m^{-2} yr^{-1}. By summing up the fluxes of the congeners (18 chromatographic peaks) whose

concentrations were available in both seawater and air, the flux of PCBs was +940 ng m^{-2} yr^{-1}. Since, these congeners normally account for about 58% of ΣPCB (54 congeners) measured in different types of samples from the region of eastern Mediterranean (e.g. aerosols[1], precipitation[5], dry deposition and sediment trap samples), the gas-exchange flux of ΣPCB should approach +1600 ng m^{-2} yr^{-1}. By considering the surface area of the eastern Mediterranean Sea, we estimated that the annual evaporation of PCBs should be 3150 kg yr^{-1}. However, the estimated air-sea exchange flux should include a high uncertainty due to the assumptions used and thus this flux should be considered more as approximate estimation rather than exact value.

Based on laboratory-derived rate constants[7], Anderson and Hites suggested that the reaction with OH radicals should be the major permanent loss process of PCBs from the atmosphere. Some field measurements provided evidence for the occurrence of this reaction under real tropospheric conditions[8]. In the present study, the destruction of PCBs was assessed for each of the four seasons by using a one-box approach. Our results showed that the destruction of total PCBs (54 congeners) should be about 8 times higher in the summer (3300 kg) than in the winter (400 kg), while similar amounts of PCBs should be destructed during spring (1700 kg) and fall (1250 kg). Regardless of the season, the congeners having 2 to 4 chlorines accounted for 86% of the total destruction, with trichlorinated congeners exhibiting the highest contribution (about 40%) to this process. The estimated annual destruction of PCBs in the atmosphere overlying the eastern Mediterranean Sea should approach 6650 kg yr^{-1} and this loss process is remarkably higher than the corresponding fluxes of dry and wet deposition.

The mass balance is completed by assembling all of the fluxes reported above (Figure 1). The estimated pools of all PCBs in the atmosphere were clearly much lower than those in surface seawaters, and that was especially evident for the more chlorinated congeners. The atmospheric burden of ΣPCB approached 160 kg, while the corresponding burden in the euphotic zone should be 84 t. Particle-bound PCBs accounted for only 1% of the atmospheric pool, though about 97% of these chemicals in the euphotic zone should be associated with suspended particles. The atmospheric input of PCBs in the eastern Mediterranean Sea through dry and wet deposition was estimated to be 0.3 and 1.3 t yr^{-1}, respectively. The total atmospheric input estimated in the present study (1.6 t yr^{-1}) is about 8 times lower that the input previously reported for the western part of the Mediterranean (24 t yr^{-1})[2], which covers an area of 840000 km^2. The volatilization flux of ΣPCB from the eastern Mediterranean Sea due to air-sea exchange should be 3.15 t yr^{-1} and overall it should offset the input from wet and dry deposition (1.3 plus 0.3 t yr^{-1}). In general, the eastern Mediterranean Sea should act as a net source of PCBs to the atmosphere (volatilization minus wet and dry deposition) mainly due to the higher evaporation fluxes of the less chlorinated congeners (such as PCB 18 and 52). However, the opposite situation was apparent for some individual congeners such as PCB 28, 70, 110 and 180, whose evaporation fluxes were relatively lower than their inputs through atmospheric deposition. In addition, PCBs are removed from the euphotic zone with a settling flux of 350 kg yr^{-1}. Assuming steady-state conditions for the surface waters, an additional inflow of PCBs should be required. The discharge of urban and industrial sewage, riverine input and the transport of more polluted surface waters from western to eastern Mediterranean could justify such an inflow. The estimated destruction of ΣPCB by OH radicals (6.65 t yr^{-1}) was approximately four times higher than the export flux due to atmospheric deposition (wet plus dry deposition). By subtracting inflows (volatilization) from outflows (destruction and deposition), a net loss of 5.1 t yr^{-1} is predicted for ΣPCB, implying that the whole burden of these chemicals should be vanished from the atmosphere in 9 to 11 days. If a steady-state situation is assumed, a considerable continuous inflow is required to balance the net loss. We suggest that long or short range transport of PCBs from contaminated terrestrial surfaces is likely an additional pathway which introduces significant amounts of PCBs into the atmosphere of this region. The importance of atmospheric transport in this region has also been supported in a previous study[1].

The current mass budget indicates that the destruction by OH radicals is of major importance for the fate of PCBs in this region but further research effort is required to better understand and evaluate the precise magnitude of this loss process. In addition, our calculations for the air-sea exchange of PCBs indicated that this process may also play an important role. More accurate estimates for the air-sea exchange flux of PCBs should further improve our knowledge regarding the mobility of these contaminants between the atmospheric and aquatic compartments.

Figure 1: Mass balance of ΣPCB in the eastern Mediterranean Sea
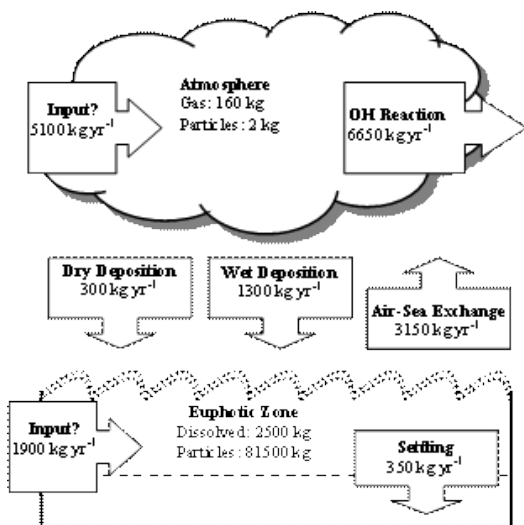
Acknowledgments

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