Organohalogen Compounds, Volume 61, Pages 413-416 (2003)

ATMOSPHERIC INPUT OF POLYCHLORINATED BIPHENYLS TO THE EASTERN MEDITERRANEAN

Manolis Mandalakis[§], Euripides Stephanou

Environmental Chemical Processes Laboratory (ECPL), Department of Chemistry, University of Crete, GR-71409 Heraklion, Greece
[§]Present address: Institute of Applied Environmental Research (ITM), Stockholm University, SE-10405 Stockholm, Sweden

Introduction

Pollution throughout Mediterranean was always under special concern. The very high concentrations of PCBs and other xenobiotics in resident marine mammals[1] indicated that the pollution of western Mediterranean has reached alarming levels. Contaminants such as DDT and PCBs were regarded as responsible for the mass die-offs of monk seals[1] and striped dolphins[2] along the Mediterranean coasts.

Studies dealing with the mass balance of PCBs in the western Mediterranean Sea have shown that this region is continually acting as a reservoir of organochlorine compounds, while the atmospheric flux of PCBs due to dry and wet deposition account for most of the input[3]. However, the deposition fluxes calculated in these models were based on a limited number of field measurements[4]. Indeed, several chlorinated hydrocarbons including PCBs were formerly detected in a limited number of deposition samples, collected in south France[4].

Since PCBs are semivolatile compounds, they exist in both gas and particulate phases of the atmosphere[5]. Thus, both gaseous and particle-associated PCBs can be deposited on earth's surface through precipitation scavenging[5, 6]. In the absence of precipitation, particulate and gaseous PCBs can also be removed from the atmosphere due to dry deposition processes[5, 6].

Polychlorinated biphenyls were recently measured in dry and wet deposition samples collected from a marine, background station of northeastern Crete, Greece and the corresponding atmospheric fluxes were calculated. The flux of gaseous PCBs due to air-water exchange was also estimated by Liss and Slater model[7] based on previously reported atmospheric data[8, 9]. In the present study we investigate the contribution of each individual process to the atmospheric input of PCBs to eastern Mediterranean Sea. Furthermore, the washout ratio and the dry deposition velocity of PCBs were calculated and are also discussed.

Methods and Materials

Dry deposition (N=12) and wet deposition samples (N=6) were collected from the marine background sampling station of Finokalia (35^{o} 20' N, 25^{o} 40' E) between April 2000 and May 2001. A stainless steel funnels connected to an amber glass bottle was mounted at the roof of Finokalia sampling station in order to collect deposition samples. After sampling, particles remaining in the inner surface of the funnel were rinsed by using Milli-Q water. Samples were filtered through glass fiber filters to isolate particles from the dissolved phase. Subsequently, each phase was separately analyzed for PCBs. The extraction of the dissolved phase was performed using a liquid-liquid technique while particulate PCBs were extracted by sonication in an ultrasonic bath. A certain amount of surrogate standards (PCBs 54, 155, 185) were added in each sample prior the extraction.

The extracts was concentrated to 1 ml, applied onto a 1.5 g SiO_2 column and eluted with 12 ml of n-hexane. The eluted fraction was reduced to 1 ml and then passed through a disposable Pasteur pipette packed with 1cm of NaSO4, H_2SO_4 impregnated silica, KOH impregnated silica and deactivated silica in series. The final extract was evaporated to almost dryness and a certain amount of recovery standard (PCB 116) was added. A Finnigan GCQ gas chromatograph directly interfaced to a Finnigan GCQ ion trap mass spectrometer (GC-ITMS) operating in MS/MS mode was used for the quantification of PCBs. The GC was equipped with a 30 m x 0.25 mm, 0.25 μm film thickness, HP-5MS fused silica column. More information about the analysis and detection of PCBs has been reported in a previous study[10].

Results and Discussion

The average concentration of ΣPCB (sum of 54 PCB congeners) in precipitation samples collected from Finokalia station was 1.9±0.9 ng l^{-1}. In all cases, tri- and tetrachlorinated congeners accounted for more than 58% of ΣPCB in rainwater (Figure 1). The percentage of particle-bound PCBs ranged between 11 and 53% providing an average value of only 30±16%. On the basis of historical records (between 1995 and 2000), the annual precipitation rate in Finokalia is 438 mm $year^{-1}$. Based on these data, it was deduced that the annual wet deposition flux of PCBs should approach 832 ng m^{-2} $year^{-1}$. This flux is about one order of magnitude lower than the flux measured in western Mediterranean sixteen years ago[4].

The dry deposition flux of ΣPCB ranged between 39 and 394 ng m^{-2} $year^{-1}$ with an average value of 179±125 ng m^{-2} $year^{-1}$. The congeners containing three and four chlorine atoms were present in higher relative abundance for all analyzed samples (Figure 2). These congeners accounted for 65% of total PCBs measured in deposited material. Our results suggest that the annual dry deposition flux of particulate PCBs in eastern Mediterranean should be about 4.5 times lower than the wet deposition flux of these chemicals.

The fluxes of individual PCB congeners due to air-water exchange were calculated based on results of previous studies conducted in eastern Mediterranean[8, 9]. Figure 3 demonstrates that the PCBs congeners containing more than four chlorine atoms are absorbed into the surface waters of Mediterranean. On the contrary, the lighter PCB congeners (PCB 18, 28) exhibit the opposite direction and tend to volatilize from the surface waters to the atmosphere. Furthermore, it was estimated that the flux of total PCBs should be negative (gas absorption into surface waters) and it should approach 576 ng m^{-2} $year^{-1}$.

By taking into account the area of eastern Mediterranean Sea (about 2450000 km^2) it was estimated that approximately 1.9 tonnes of PCBs continue to enter the waters of eastern Mediterranean through atmospheric deposition processes. Moreover, it is suggested that the process of wet deposition (1.0 ton $year^{-1}$) should have a higher contribution than air-water gas exchange (0.7 ton $year^{-1}$) and/or dry deposition of particulate PCBs (0.2 ton $year^{-1}$).

Figure 1: Wet deposition fluxes of individual PCBs in Finokalia sampling station.

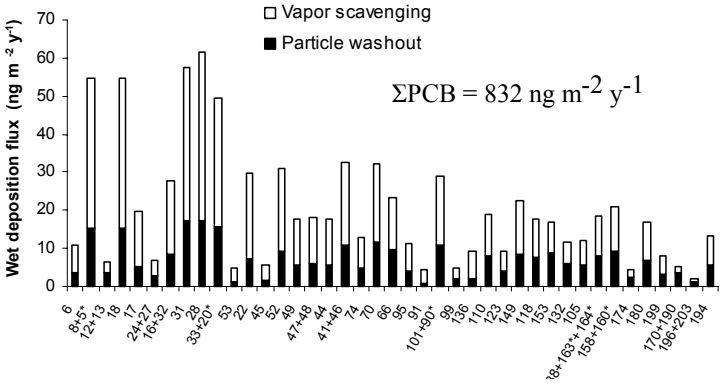


Figure 2: Dry deposition fluxes of individual PCBs in Finokalia sampling station.

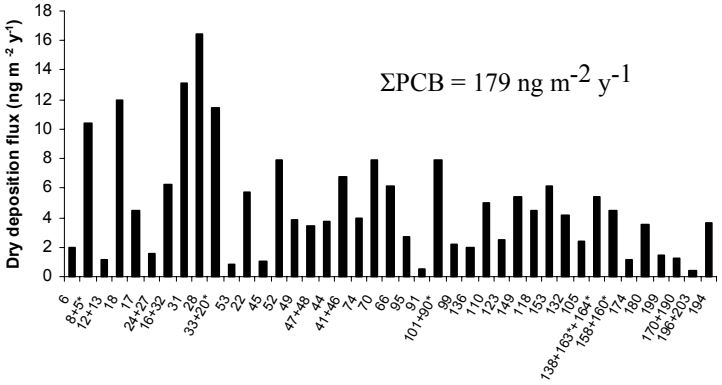
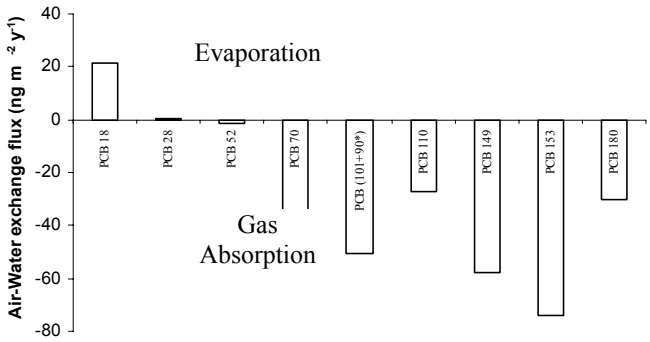


Figure 3: Gas exchange fluxes of PCBs in eastern Mediterranean. Negative fluxes denote gas absorption into surface waters.



References

1. Borrell, A., Aguilar, A., Pastor, T.; (1997) Marine Pollution Bulletin, 34, 505.
2. Borrell, A., Aguilar, A., Corsolini, S., Focardi, S.; (1996) Chemosphere, 32, 2359.
3. Tolosa, I., Readman, J.W., Fowler, S.W., Villeneuve, J.P., Dachs, J., Bayona, J.M., Albaiges, J.; (1997) Deep Sea Research II, 44, 907.
4. Villeneuve, J.P., Cattini, C.; (1986) Chemosphere, 15, 115.
5. Eisenreich, S.J., Looney, B.B., Thornton, J.D.; (1981) Environmental Science and Technology, 15, 30.
6. Seinfeld, J.H., Pandis S.N.; (1997) Atmospheric Chemistry and Physics, John Wiley & Sons, Incorporated.
7. Liss, P.S., Slater, P.G.; (1974) Nature, 47, 181.
8. Mandalakis, M., Stephanou, E.G.; (2002) Journal of Geophysical Research, 107, 1801.
9. Schulz, D.E., Petrick, G., Johannsen, H., Duinker, J.C.; (1997) Croatica Chemica Acta, 70, 309.
10. Mandalakis, M., Tsapakis, M., Stephanou, E.G.; (2001) Journal of Chromatography A, 925, 183.