

# High-Resolution Gas Chromatography-Tandem Mass Spectrometry: A Sensitive Analytical Technique Suitable for the Study of Atmospheric Processes of Polychlorinated Biphenyls and Dibenzo-*p*-Dioxins/Furans

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**Abstract:** The trace-level environmental determination of polychlorinated biphenyls (PCBs) and 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) requires the use of delicate fractionation and analytical techniques such as high-resolution gas chromatography coupled with high-resolution mass spectrometry. The analytical requirements are even higher if atmospheric physicochemical processes of these persistent organic compounds (POPs) are to be studied in remote areas, where concentrations are very low. The optimization of a fractionation method, and of the high-resolution gas chromatography/ion trap tandem mass spectrometry system instrumental parameters enabled us to establish the optimum conditions for the determination of atmospheric PCBs and PCDD/Fs at the low pg or even fg m<sup>-3</sup> level. By using this analytical procedure, we accomplished the reliable determination of ca. 54 PCBs and 17 PCDD/Fs individual congeners, of different chlorination level, in the gas and particulate phase of atmospheric aerosol samples collected from the Eastern Mediterranean basin. Furthermore, we were also able to study the atmospheric physicochemical and loss processes of PCBs, such as gas-particle partitioning, wet and dry deposition, and PCBs reaction with hydroxyl radicals.

**Keywords:** Dibenzo-*p*-dioxins · Eastern Mediterranean · Gas chromatography ion trap tandem mass spectrometry · Hydroxyl radicals · Polychlorinated biphenyls

## Introduction

Although the production and use of polychlorobiphenyls (PCBs) were banned by the mid-1970s, these chemicals are ubiquitous pollutants in nearly all environmental compartments [1]. Unlike PCBs, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) have never been deliber-

ately manufactured, instead it is generally accepted that they are unintentionally formed during a variety of anthropogenic combustion activities and industrial processes such as the manufacture and use of organochlorine chemicals.

In recent years, numerous laboratory and field studies [2][3] have focused on the presence and the gas/particle partitioning of these compounds in the atmosphere, since this process will determine the extent of their transportation and spread globally. However, the vast majority of the field studies have been conducted close to urban regions, where the levels of PCBs are relatively high. The scarcity of results from remote areas is due to difficulties in the determination of the low PCB concentrations in the gas phase and the even lower concentrations in the particulate phase.

Laboratory studies have indicated that the reaction with hydroxyl radicals might be the dominant loss process of PCBs in the atmosphere [4]. In fact, since the atmospheric concentration of OH radicals maximizes during daytime, a significant decrease of gas-phase PCBs should be expected during the same time period. Nevertheless, such a decrease should be mostly observable in remote areas where the sources of PCBs are negligible and the daytime volatilization of PCBs to the atmosphere is minimal.

The investigation of the diurnal cycle and gas/particle partitioning of PCBs in the atmosphere of remote areas are two examples where delicate and sensitive analytical methods have to be applied. Capillary HRGC coupled with electron capture detection (ECD), a still widely utilized ana-

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lytical technique for the trace analysis of PCB in various environmental matrices, is unable to differentiate between co-eluting PCBs and suffers from non-linear response behavior across relatively narrow amount ranges and wide variation in response within a PCB homologue group [5]. The main alternative mass spectrometry techniques currently used for analysis of PCBs at trace level are Negative Chemical Ionization–Mass Spectrometry (NCI-MS) [6] and High-Resolution Mass Spectrometry (HRMS) [7]. Both techniques provide higher sensitivity but also complexity of use. Recently, tandem mass spectrometry (MS/MS) analysis by Ion Trap Mass Spectrometers (ITMS) became a competitive technique for the determination of PCDD/Fs and PCBs [8][9].

Our aim was to establish an analytical method, including a clean-up procedure and the optimization of ion trap tandem mass spectrometry parameters, in order to attain the highest sensitivity for the determination of PCBs and PCDD/Fs in atmospheric aerosol and deposition samples. The optimization of a fractionation method, and of high-resolution gas chromatography/ion trap tandem mass spectrometry (GC/MS-MS) instrumental parameters allowed the optimum conditions to be achieved for the determination of atmospheric PCB and PCDD/F concentrations at the low pg or even fg m<sup>-3</sup> level [10].

By using this analytical technique we were able to measure the air concentration of PCBs and PCDD/Fs at very low levels [11–13], to study their gas-particle partitioning [11–13], to measure their atmospheric deposition processes [12] and also to determine *in situ* the rate constants of the atmospheric reaction of PCBs with OH radicals [14] in a remote site of the eastern Mediterranean. We were thus able to construct the mass balance of PCBs in the eastern Mediterranean and to determine that the PCB-OH radical reaction is the main loss mechanism of PCBs in this subtropical area.

## Experimental

Polychlorinated biphenyls and 2,3,7,8-substituted congeners of PCDD/Fs were analyzed on a Finnigan GCQ ion trap mass spectrometer operating in MS/MS mode. The mass spectrometer was directly coupled with a GC equipped with a 30 m × 0.25 mm, 0.25 μm film thickness, HP-5MS fused silica column. The operating parameters of the ion trap mass spectrometer during the analysis of PCBs were set at the optimum values, which have been specified in

previous studies [10][15]. Field and laboratory blank samples (polyurethane foam plus glass fiber filter) were routinely analyzed in order to evaluate analytical bias and precision. Blank levels of individual compounds were normally very low and in most cases not detectable. The method detection limit (MDL) for PCBs and PCDD/Fs is 0.01 pg m<sup>-3</sup> and 0.5 fg m<sup>-3</sup>, respectively.

Measurements of atmospheric gaseous and particulate PCBs and PCDD/Fs, and hydroxyl radical concentrations were performed at the marine background station of Finokalia (35° 19' N, 25° 40' E), a coastal site 70 km eastward of Heraklion (Island of Crete, Greece) at the top of a hilly elevation (130 m above sea level). The levels of PCDD/Fs and PCBs were determined by analyzing 24 h samples (850 m<sup>3</sup> of air per sample) collected by a high-volume sampler. The sampling frequency for PCBs for the study of PCBs-OH reaction was one sample/h during daytime (7:00–20:00; Eastern European Summer Time (EEST)) and every 2 h during the night-time (20:00–7:00 next morning; EEST). In the same study, atmospheric OH concentrations were measured based on methods previously developed and described in detail elsewhere [16]. The PCB-OH rate constants of different PCB congeners were determined from field data by applying the relative rate method [4].

Dry deposition and wet deposition samples were collected at the same marine background sampling station between April 2000 and May 2001. A stainless steel funnel connected to an amber glass bottle was mounted on the roof of the 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) was added to each sample prior to extraction. The same analytical method as above was used for the analysis of deposition samples. The complete procedures for the analysis of PCBs and PCDD/Fs in air samples or deposition samples have been described in detail elsewhere [10][12][13].

## Results and Discussion

### Study of PCB and PCDD/F Atmospheric Concentrations and Gas-Particle Partitioning

The average concentrations of total PCB congeners ( $\Sigma$ PCBs) in the gas and particulate phase of the atmosphere were  $68.1 \pm 28.8$  pg/m<sup>3</sup> and  $2.3 \pm 1.8$  pg/m<sup>3</sup>, respectively. The lack of seasonal variation for the atmospheric concentration of individual congeners and  $\Sigma$ PCBs, and the shallow slopes obtained from the Clausius-Clapeyron plots for several PCB congeners indicated that long-range transport is the main factor controlling the atmospheric levels of PCBs in the eastern Mediterranean area [11]. Most of the episodes with elevated concentrations of  $\Sigma$ PCBs concurred with air transport from Western and Central Europe [11]. Significant changes observed on the homologue group profile of PCBs were mostly related to the origin of air parcels sampled, and, during summer, most probably to the reaction of the lighter congeners with OH radicals. Partitioning of PCBs between gas and particulate phases was well correlated with the subcooled liquid vapor pressure  $P_L^0$  for 11 of the 37 samples. The slopes of  $\log K_p$  versus  $\log P_L^0$  ranged between  $-0.233$  and  $-0.445$  and are among the shallowest measured worldwide. This fact may indicate absorption of PCBs in particles covered by a polar film or non-equilibrium conditions [11][12][15].

The concentrations of total PCDD/Fs congeners in the gas and particulate phase of the atmosphere ranged from 42–44 fg/m<sup>3</sup> and 46–62 fg/m<sup>3</sup>, respectively [13]. Partitioning of PCDD/Fs between gas and particulate phases was well correlated with the subcooled liquid vapor pressure  $P_L^0$  only for few samples ( $R^2$ , 0.78–0.89) [13][15]. The average slopes of  $\log K_p$  versus  $\log P_L^0$  ranged between  $-0.78$  (PCDDs) and  $-0.75$  (PCDFs) [13][15].

### Study of PCB Deposition Processes

The average concentration of  $\Sigma$ PCBs (sum of 54 PCB congeners) in precipitation samples collected from the Finokalia station was  $1.9 \pm 0.9$  ng/l and in all cases, tri- and tetrachlorinated congeners accounted for more than 58% of  $\Sigma$ PCBs in rainwater. The percentage of particle-bound PCBs ranged between 11 and 53% providing an average value of only  $30 \pm 16\%$ . On the basis of previous reports (between 1995 and 2000), the annual precipitation rate in Finokalia is 438 mm year<sup>-1</sup>. Based on these data, it was deduced that the annual wet deposition flux of PCBs should approach 832 ng m<sup>-2</sup> year<sup>-1</sup> [12].

The dry deposition flux of  $\Sigma$ PCBs (sum of 54 PCB congeners) ranged between 39 and 394 ng m<sup>-2</sup> year<sup>-1</sup> with an average value of 179 ± 125 ng m<sup>-2</sup> year<sup>-1</sup>. The congeners containing three and four chlorine atoms were present in higher relative abundance for all analyzed samples. 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 [12].

### Study of PCBs-OH Radicals Reaction

Fig. 1a, b, and c present the diurnal variation of the total PCB concentration ( $\Sigma$ PCBs, sum of 27 congeners). The simultaneous variation of the OH radical concentration for each one of the three intensive sampling periods is also shown in the same figures. In all cases, the variation of  $\Sigma$ PCBs concentration showed a diurnal pattern inversely related to that of OH. In particular, the highest OH radical concentrations were observed approximately between 10:00 and 15:00 EEST (Eastern European Summer Time), while the lowest  $\Sigma$ PCBs concentrations were measured during the same daytime period (Figs 1a, b, c). Fig. 1d, e, and f show the corresponding diurnal variation of the ambient temperature. As for OH radical concentration, an opposite trend between ambient temperature and  $\Sigma$ PCBs concentration was observed. The diurnal variation of PCBs observed in our study, suggests that the volatilization/exchange of PCBs from contaminated surfaces was of minor importance [14].

Air mass back-trajectory analysis during the measurement period (18 to 21 August, 2001) showed that air masses reaching the sampling station of Finokalia were of similar origin, predominantly from north easterly directions. Consequently, observed diurnal changes in the concentration of PCBs could not be explained by significant changes in air mass origin. The meteorological conditions (*e.g.* intensive sunlight, high temperatures, elevated O<sub>3</sub> levels, *etc.*) dominating year round over the eastern Mediterranean [17], especially during summer, can enhance photochemistry in the atmosphere and result in relatively high OH concentrations. Since PCBs are present in the atmosphere primarily in the vapor phase [11], they may react with OH radicals at environmentally significant rates. By using the K<sub>OH</sub> value of the trichlorinated congener PCB 28 (1.1 10<sup>-12</sup> cm<sup>3</sup> s<sup>-1</sup> molecule<sup>-1</sup>) [4] and the average atmospheric concentration of OH radicals observed during daytime (1.3 × 10<sup>7</sup> molecules cm<sup>-3</sup>), we calculated (pseudo-first order kinetics) the decline that should be expected for the atmospheric concentration of this congener. The result of this calculation has shown that the atmospheric concentration of PCB 28 should decline by 27% after 6 h of reaction. This simple calculation provided further evidence that the daytime depletion observed for the PCBs (Fig. 1a, b, c), and especially of the less chlorinated ones, should be attributed to their reaction with OH radicals.

Based on the loss rates of atmospheric PCBs observed during daytime, we estimated the OH-PCB reaction rate constants (K<sub>OH</sub>) for several individual congeners and compared our results with those reported

from laboratory experiments. For this purpose, we applied the relative reaction rate method approach [4] using 2,4,4'-trichlorobiphenyl (PCB 28) as reference compound. The K<sub>OH</sub> values derived from our field measurements for nine PCB congeners of environmental significance and increasing degree of chlorination (2, 3, 4, and 5 Cl atoms), were notably coherent with those measured in the laboratory [4]. The relatively low overestimation trend observed for most congeners field-determined K<sub>OH</sub>, although acceptable when field results are compared to laboratory ones, suggests that in addition to the OH-PCB reaction, photolysis of some PCB congeners may also be an atmospheric loss process bearing special note [14].

The potential effect of the degree of chlorination on OH-PCB reaction rate constants was also considered in detail. Our field results confirmed that the OH-PCB reaction rate constants consistently decreased in sequence for those compounds showing an increasing degree of chlorination on the biphenyl group (Fig. 2). This observation was also in line with results of previous laboratory experiments [4].

### Mass Balance of PCBs in the Eastern Mediterranean

By taking into account the area of the eastern Mediterranean Sea (about 2450000 km<sup>2</sup>) it was estimated that approximately 1.9 tonnes of PCBs continue to enter the waters of the eastern Mediterranean through atmospheric deposition processes [12]. Moreover, we observed that the process of wet deposition (1.0 t y<sup>-1</sup>) should have a higher contribution than air-water gas exchange (0.7 t y<sup>-1</sup>) and/or dry deposi-

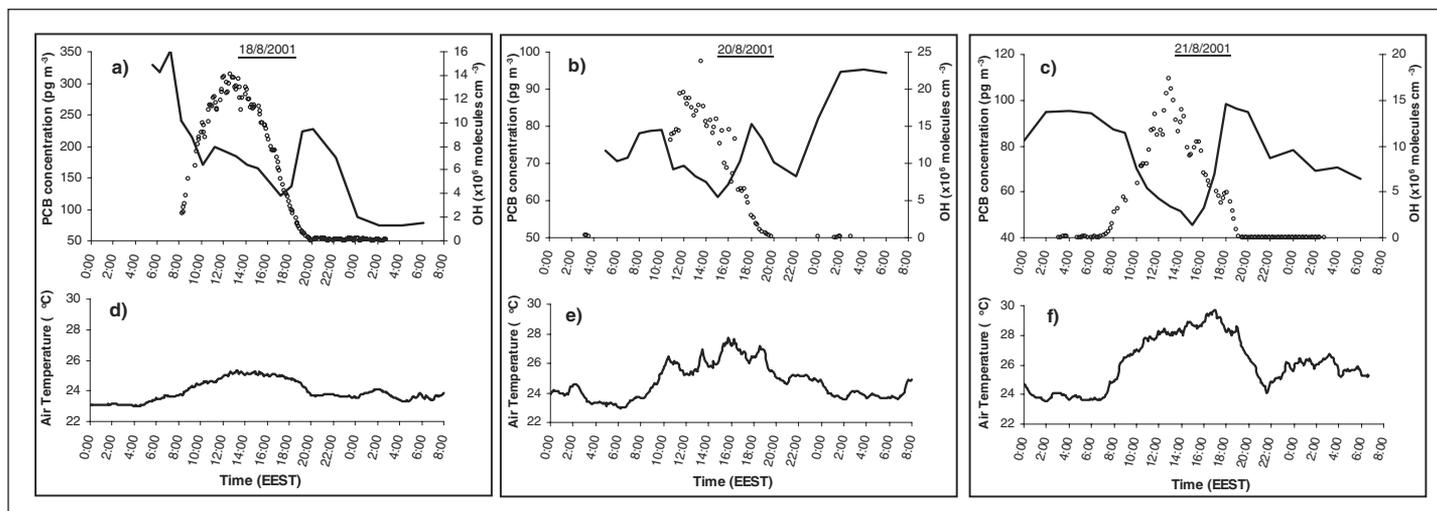


Fig. 1. Diurnal variation of the atmospheric concentration of  $\Sigma$ PCBs (solid line) and hydroxyl radicals (circles) (a,b,c), and of the ambient temperature (d,e,f) [14].

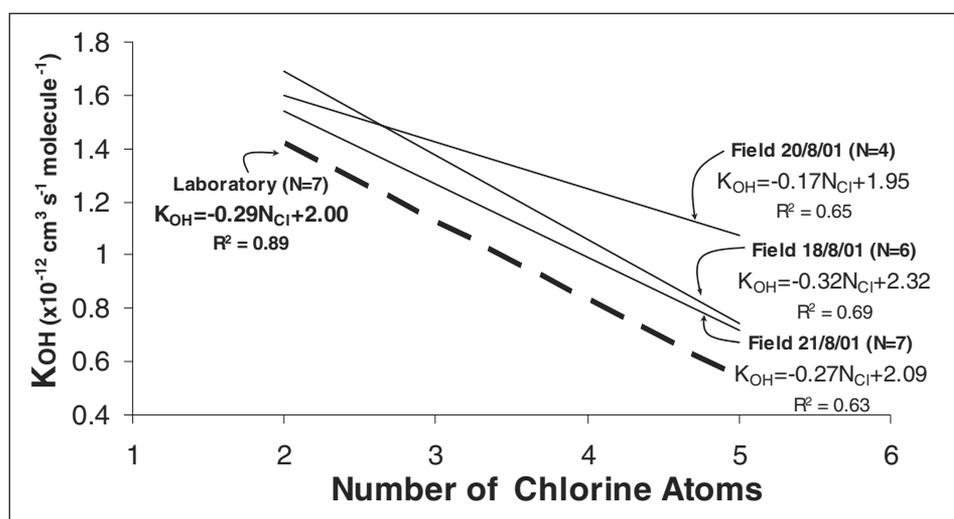


Fig. 2. Plots of the observed environmental rate constants for the OH-PCB reaction versus the number of chlorine atoms ( $N_{Cl}$ ). Each solid line is a linear regression fitted to environmental rate constants of PCBs observed during 18, 20 and 21 August 2001 [14]. The dashed line represents the PCB-OH rate constants (at 298 K) measured in laboratory [4].

tion of particulate PCBs ( $0.2 \text{ t y}^{-1}$ ). The fluxes of individual PCB congeners due to air-water exchange were calculated by using the Liss-Slater model [18], our results [11] and the results of a previous study [19] concerning the analysis of PCBs in seawater of eastern Mediterranean basin. We estimated that the flux of total PCBs should be negative (gas absorption into surface waters) and should approach  $576 \text{ ng m}^{-2} \text{ y}^{-1}$ . It means that air-sea exchange is responsible for the elimination of  $0.7 \text{ t y}^{-1}$ . Moreover, it was estimated that PCBs losses via hydroxyl radicals in the atmosphere may be responsible for the elimination of  $4.0 \text{ t y}^{-1}$  [12].

Our results offer direct evidence that the destruction of PCBs via hydroxyl radicals in the eastern Mediterranean atmosphere is probably the most important loss mechanism for these persistent organic pollutants.

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- [1] B.D. Rodan, D. Pennington, N. Eckley, R. Boethling, *Environ. Sci. Technol.* **1999**, *33*, 3482.  
 [2] F. Wania, D. Mackay, *Ambio* **1993**, *22*, 10.  
 [3] S.Y. Panshin, R.A. Hites *Environ. Sci. Technol.* **1996**, *28*, 2001.  
 [4] P.N. Anderson, R.A. Hites, *Environ. Sci. Technol.* **1996**, *30*, 1756.  
 [5] J.W. Cochran, G.M. Frame, *J. Chromatogr. A* **1999**, *843*, 323.  
 [6] R. Chaler, R. Vilanova, M. Santiago-Silva, P. Fernandez, J.O. Grimalt, *J. Chromatogr. A* **1998**, *823*, 73.  
 [7] J. Ferrario, C. Byrne, A.E. Dupuy, *Chemosphere* **1997**, *34*, 2451.  
 [8] T. Kuchler, H. Brzezinski, *Chemosphere* **2000**, *40*, 213.

- [9] P.E.G. Leonards, U.A.T. Brinkman, W.P. Cofino, *Chemosphere* **1996**, *32*, 2381.  
 [10] M. Mandalakis, M. Tsapakis, E.G. Stephanou, *J. Chromatogr. A* **2001**, *925*, 183.  
 [11] M. Mandalakis, E. G. Stephanou, *J. Geophys. Res.* **2002**, *107*, 1801.  
 [12] M. Mandalakis, 'Study of the fate of PCBs in the atmosphere of Eastern Mediterranean', Ph. D. Dissertation, University of Crete, **2002**.  
 [13] A. Tsoga, 'Optimization of GC/MS-MS for the analysis of PCDD/Fs in air samples at low concentration', M.Sc. Dissertation, University of Crete, **2001**.  
 [14] M. Mandalakis, H. Berresheim, E.G. Stephanou, *Environ. Sci. Technol.* **2003**, *37*, 542.  
 [15] M. Mandalakis, M. Tsapakis, A. Tsoga, E.G. Stephanou, *Atmospheric Environment* **2002**, *36*, 4023.  
 [16] H. Berresheim, T. Elste, C. Plass-Dülmer, F.L. Eisele, D.J. Tanner, *Int. J. Mass Spectrom.* **2000**, *202*, 91.  
 [17] G. Kouvarakis, K. Tsigaridis, M. Kanakidou, N. Mihalopoulos, *J. Geophys. Res.* **2000**, *105*, 4399.  
 [18] P.S. Liss, P.G. Slater, *Nature* **1974**, *47*, 181.  
 [19] D.E. Schulz, G. Petrick, H. Johannsen, J.C. Duinker, *Croatica Chemica Acta* **1997**, *70*, 309.