

Global Occurrence of Non-Dioxin Organochlorines in the Marine Atmosphere: PCBs

Karlheinz Ballschmiter, Jörn Schreitmüller*

Department of Analytical and Environmental Chemistry, University of Ulm
D-89069 Ulm, Germany

* Institut für Spektrochemie und Angewandte Spektroskopie, D-12489 Berlin, Germany

1. INTRODUCTION

The role of chemistry in our soon-to-be global industrial society requires a global perspective for the discussion of the uptake, transport, and conversion of chemical compounds in the environment. The fate of stable chlorinated organic compounds in the volume flow of the atmosphere and hydrosphere can be categorized into transport pathways and adjustments of equilibria in the multiphase system atmosphere - oceans - land and plant surfaces - biota. The global transport in the atmosphere (wind, areas of high and low pressure) and in the hydrosphere (rivers, circulation of water in lakes, ocean currents) alone would account for the spreading of organic compounds if they were indefinitely stable and molecularly distributed in air and water. For most organic compounds, complex adsorption/desorption processes on finely dispersed particle phases in the air and water environment as well as abiotic and biotic transformations determine however the transport behavior.

The complexity arising from the mixing and separation processes that are possible in the environment is further compounded by the wide range of physico-chemical and chemical properties of the many compounds that can be regarded as chlorinated xenobiotics. These range from the halomethanes to the C₂₅ chlorinated paraffins. Classical tracers in terms of a global distribution are among others the chlorinated ethanes and ethenes¹⁾, the hexachlorocyclohexanes isomers²⁻⁴⁾, and the polychlorinated biphenyls^{5,6)}, respectively.

2. EXPERIMENTAL

High volume sampling of air samples

Air samples were collected on the research vessel "Polarstern" on her South-North cruises to and from the Antarctic through the Atlantic Ocean. Samples of 500-1000 m³ of air

were collected windward on the upper-most deck of the ship about 25 m above sea level by a Ströhlein high-volume air sampler (Ströhlein, Kaarst, Germany) at a flow rate of 30-35 m³/h using an adsorption technique on pre-cleaned silica gel. The silica gel was transported prior to and after sampling in modified 250 ml Erlenmeyer flasks closed by melting the added glass tube. This technique effectively excludes any contamination during transport and storage.

Sample preparation

All sample preparation steps were accomplished under stringent control using a "metal/glass only" clean-bench with charcoal air filters to minimize any possible contamination of the sample from the laboratory environment. All glassware used has been pre-cleaned by heating to 350 oC in a stream of clean nitrogen.

The silica gel used for air sampling was packed in a glass column (length 20 cm, diameter 4 cm) and was eluted with 350 ml dichloromethane. The analytes were pre-separated on a column of 4.5 g silica gel 60, 35 - 70 mesh, (3% H₂O). The first fraction (LC 1), eluted with 30 ml hexane, contains the weakly polar substances (polychlorinated benzenes, polychlorinated biphenyls, part of the polychlorinated naphthalenes, 4,4'-DDE). The second fraction (LC 2), eluted with 40 ml hexane/dichloromethane (3:1), contains more polar substances like the hexachlorocyclohexanes, endosulfane, dieldrin, part of the polychlorinated naphthalenes and camphenes, part of the chlordane group, and the main part of the chlorinated anisoles.

The absolute amount handled per PCB congener was in the range of 0.2 to 35 nanogram.

High resolution gas chromatography

The gas chromatographic separation and identification of the substances was accomplished by capillary gas chromatography using capillary columns of different polarity: Column 1: CP-Sil 8 + 10% Me-C 18 (Methyl-5%-phenyl-polysiloxane plus 10%-octadecyl-polysiloxane) (Chrompack, Middelburg, Netherlands); Column 2: DB 1701 (7%-Cyanopropyl-7%-phenyl-methyl-polysiloxane) (J & W, Folsom, CA, USA);

3. RESULTS AND DISCUSSION

We assume that we are basically dealing with source-distant quasi-stationary conditions at least for the open sea. We pointed out before that the quantification of the polychlorinated biphenyls as the sum of PCB congeners or as an approximation to a technical mixture, e.g. Arochlor 1242 or Arochlor 1254, suppresses valuable information about their function as markers for a regional input and about their environmental fate with respect to the individual

physical and chemical properties. From the numerous PCB congeners detectable in the air samples we selected for a quantitation fourteen major congeners: the trichlorobiphenyls 2,4,4'-Cl₃B (PCB 28), 2,4',5'-Cl₃B (PCB 31), the tetrachlorobiphenyls 2,2',3,5'-Cl₄B (PCB 44), 2,2',4,5'-Cl₄B (PCB 49), 2,2',5,5'-Cl₄B (PCB 52), the pentachlorobiphenyls 2,2',3,4,5'-Cl₅B (PCB 87), 2,2',4,5,5'-Cl₅B (PCB 101), 2,3,3',4',6-Cl₅B (PCB 110), 2,3',4,4',5-Cl₅B (PCB 118), the hexachlorobiphenyls 2,2',3,4,4',5'-Cl₆B (PCB 138), 2,2',3,4',5',6-Cl₆B (PCB 149), 2,2',3,5,5',6-Cl₆B (PCB 151), 2,2',4,4',5,5'-Cl₆B (PCB 153) and the heptachlorobiphenyl 2,2',3,4,4',5,5'-Cl₇B (PCB 180). In all air samples all the PCB congeners were found at > 99% in the gaseous state.

Values for the sum of PCB were 48 pg/m³ (PCB 28: 1.3; PCB 52: 5.0; PCB 101: 3.0; PCB 118: 0.5; PCB 138: 1; PCB 153: 1; PCB 180: < 0.2) in the eastern North Atlantic, 22 pg/m³ (PCB 28: 2.3; PCB 52: 3.4; PCB 101: 0.5; PCB 118: < 0.2; PCB 138: < 0.2; PCB 153: < 0.2; PCB 180: < 0.2) in the Westwind Belt of the central South Atlantic, and up to 385 pg/m³ (PCB 28: 2.6; PCB 52: 11.7; PCB 101: 28.4; PCB 118: 9; PCB 138: 21; PCB 153: 18; PCB 180: 5.5) before the coast of South Patagonia, respectively. A difference depending on latitude and on terrestrial influenced air masses between the lower and the higher chlorinated congeners was observed. The levels of three- and tetrachlorinated congeners were highest in the Trade Wind regions. The contents of the higher chlorinated congeners had maxima in samples influenced by continental air masses⁷).

Congener specific North-South distribution of PCBs

The trichlorinated and tetrachlorinated congeners (vapour pressure > 1 x 10⁻² Pa) represented by the trichlorobiphenyl PCB 28 and the tetrachlorobiphenyl PCB 52 show a North/South profile, which is characterized by an increase of the concentrations towards the ITCZ in both the trade wind regions. This increase reflects partly the increase of the surface water temperatures and thus the temperature dependence of the K_{GW} partition constant. There is a slight increase at 46°N 12°W and a substantial break near the region 15° North within the Northern Trades.

The hexachlorinated and heptachlorinated congeners (vapour pressure > 1 x 10⁻³ Pa) - represented by the hexachlorobiphenyl PCB 153 and heptachlorobiphenyl PCB 180 - show an increase towards the ITCZ and a rather homogenous level without a perceptible interhemispheric difference. Distinct local maxima are observed however at 46°N 12°W, 27°S 40°W and 46°S 60°W. In the West Wind Belt of the central South Atlantic (50°S 3°W) the levels of the higher chlorinated PCBs in the atmosphere fall near or below the quantification limit of 0.2 pg/m³.

The pentachlorinated congeners exemplified by 2,2',4,5,5'-Cl₅B (PCB 101) lay between these two extremes: they also follow the profile of the lower chlorinated congeners, but on the other hand the concentrations are elevated at 46°N 12°W, 27°S 40°W and 46°S 60°W.

Air/sea exchange of PCBs

If we assume an air/sea exchange as a relevant source of PCBs in air of the open ocean a decline to higher latitudes should be given as the result of the temperature dependence of the K_{GW} value. Such a correlation between the levels of the lower chlorinated congeners in air over the South Atlantic and the water temperature and thus on the temperature dependance of the gas/water partition coefficient K_{GW} was observed.

The levels of the trichlorobiphenyls 28 and 31 in air decrease from a sample in the tropics (9°S 31°W) to a sample in the colder regions of the Westwinddrift (50°S 3°W) by one order of magnitude. The decrease in water temperature is nearly 25°C leading to a decrease of K_{GW} by a factor of ten. The measured reduction of the PCBs in air is in this range.

4. CONCLUSIONS

The correspondence of PCB levels in the marine boundary layer at 40°N and 40°S together with the occurrence of a defined marine clean air pattern support our conclusion of a general equilibrium of PCBs in the marine boundary layer based on a global sea/air exchange, which is driven by the PCB content in the surface water. Similar conclusions have to be drawn for the hexachlorocyclohexanes.

The occurrence of PCBs in shore distant marine air is not a remainder of an incomplete air to sea deposition but reflects the temperature regulated equilibrium with the PCB levels in the marine surface water. The equilibrium of PCBs between surface water and the deeper water layer of the oceans and the fallout by adsorption onto the marine detritus and/or marine snow will supplement the long term fate of PCBs in the global system of oceans.

5. REFERENCES

- 1) Th. Class, and K. Ballschmiter, (1987) *Fresenius Z. Anal. Chem.*, 327, 198-204.
- 2) R.C. Fischer, W. Krämer, and K. Ballschmiter, (1991) *Chemosphere*, 23, 889-900.
- 3) T. F. Bidleman, M. D. Walla, R. Roura, E. Carr, and S. Schmidt, (1993) *Mar. Poll. Bull.*, 26, 258-262
- 4) J. Schreitmüller, and K. Ballschmiter (1994), *Environ. Sci. Technol.*, 29, 207-215.
- 5) H. Iwata, S. Tanabe, N. Sakai, and R. Tatsukawa, (1993) *Environ. Sci. Technol.* 27, 1080-1098,
- 6) J. Schreitmüller, and Karlheinz Ballschmiter, (1994) *Fresenius J. Anal. Chem.*, 348, 226 - 239
- 7) J. Schreitmüller, M. Vigneron, R. Bacher, and K. Ballschmiter, (1994) *Int. J. Environ. Anal. Chem.*, 57, 33-52.