

Cod: 8.4005

COULD THE RATIO BETWEEN THE PCB-11 AND THE INDICATOR PCBS HELP TO DISTINGUISH BETWEEN LOCAL AND LONG-RANGE POLLUTION IN THE POLAR ENVIRONMENTS?

M. Vecchiato¹, A. Gambaro¹, C. Barbante², R. Piazza¹

¹*Department of Environmental Sciences, Informatics and Statistics (DAIS), Ca' Foscari University of Venice, Via Torino 155, 30172 Venezia-Mestre, Italy*

²*Institute for the Dynamics of Environmental Processes (IDPA-CNR), Via Torino 155, 30172 Venezia-Mestre, Italy*

Introduction

Polar environments are usually considered pristine environments, nevertheless these regions are influenced by POPs, mainly through long-range atmospheric transport and contamination from local sources, as for example research stations. One of the most important open question is to distinguish between these two kinds of sources, potentially contaminating the environment with the same pollutants. The congener PCB-11 (3,3'-dichlorobiphenyl) is a compound present in very small quantities in the original Aroclor mixtures, but it largely derives from consumer goods containing azo- and phthalocyanine pigments. The literature about this congener is absolutely scarce if compared to the other congeners, instead linked to Aroclor and the other commercial mixtures. Even less information is available about the occurrence of PCB-11 in the polar environments and it is limited to few zones: the region around Terra Nova Bay (BTN, East Antarctica) [1–3], King George Island (KGI) in the South Shetlands [4–8] and Ny Alesund in the Svalbard Islands [5,6,9,10].

Our hypothesis is that the comparison between the PCB-11 and the indicator PCBs (I-PCBs) typical of commercial mixtures, could help to distinguish between local and long-range pollution in the polar environments. The key point is that even if the PCB-11 and the indicator PCBs could have different original sources, the long-range transport will distribute the congeners mainly according to their chemical-physical properties. We hypothesized that in a given environment far from local inputs the ratio $\text{PCB-11}/\sum \text{I-PCBs}$ should be different in each compartment: e.g., in the aerosol the ratio should be higher than in the sediment, given the higher volatility of this dichlorobiphenyl. Consequently a significant deviation from the ratios expected from long-range transport in a series of environmental samples could indicate a local source of contamination.

Materials and methods

PCB-11 and I-PCBs were determined in different environmental compartments in the region around BTN. Gaseous and Total Suspended Particle (TSP) aerosol samples were collected during the austral summer of 2009–2010 using a high volume air sampler (AirFlowPUF, Analitica Strumenti) through quartz fiber filters (QFF) followed by polyurethane foam plugs (PUF). Other snow, water, sediment and soil samples were collected during the austral summer 2011–2012. Snow and water samples were collected in pre-cleaned airtight stainless steel containers and underwent continuous liquid-liquid extraction at Mario Zucchelli Station (MZS) in Antarctica. Solid samples were extracted by means of Pressurized Liquid Extractor (PLE, FMS, Fluid Management System) using dichloromethane/acetone (1:1 v/v) in presence of anhydrous sodium sulphate, diatomaceous earth and activated metallic copper. Clean-up was performed by injecting samples in an automated system (PowerPrep™, FMS) onto a disposable neutral silica column and by eluting it with 30 ml of n-hexane and 30 ml of 1:1 n-hexane:dichloromethane. A MAT 95XP (Thermo Finnigan) high-resolution mass spectrometer, coupled to a HP 6890 gas chromatograph with a 60-m HP-5MS column was used for instrumental analyses.

Results and discussion

The ratios $\text{PCB-11}/\sum \text{I-PCBs}$ reported in Figure 1 evidence how the various compartments in BTN are characterized by different values, supporting our initial hypothesis. In particular, in the aerosol samples the ratio resulted in general >1 and even >2 in the gaseous phase, while in the other environmental matrices it resulted in most cases ranging from 0.1 to 0.5, despite significant variabilities. Notably, the

only snow sample with a ratio >1 was collected near an aviation refuelling point, where containers and shelters are present, possibly highlighting local contamination.

Comparing with literature data, the ratio results much higher (PCB-11/ Σ I-PCBs: 20-71) in XAD-resin passive air samples from the Korean station in KGI [5], possibly reflecting local contamination from the base itself or from the upwind stations. PUF passive air samples deployed near the Chinese station in KGI during the austral summer (PCB-11/ Σ I-PCBs: 2.2-4.8) [8] resulted more similar to BTN aerosol values, while XAD year-round passive samples resulted lower (PCB-11/ Σ I-PCBs: 0.8-1.4) [7]. These latter values are comparable to the ratios of other XAD year-round passive samples collected in Ny Alesund [5] (PCB-11/ Σ I-PCBs: 0.2-1.5). Focusing on other matrices, the ratio of the mean values in sediments and soils from KGI (around 0.3) [4] is similar to those from BTN, while in the Arctic it resulted slightly lower (around 0.1) [10].

The number of observations is too limited to state definitive conclusions, however it provides interesting indications. The ratio PCB-11/ Σ I-PCBs could help to distinguish local inputs not only in the polar regions, but also in anthropized environments subjected to different pressures and polluting sources. The transport pathways of PCB-11 toward the remote environments are however still unclear and more detailed studies are needed to clarify the sources.

Acknowledgements

Funds were provided by the Italian National Program for Research in Antarctica PNRA2013/AZ2.05.

References

- [1] Piazza, R., Gambaro, A., Argiriadis, E., Vecchiato, M., Zambon, S., Cescon, P., Barbante, C. (2013) *Anal. Bioanal. Chem.* 405 (2-3), 917–932.
- [2] Vecchiato, M., Argiriadis, E., Zambon, S., Barbante, C., Toscano, G., Gambaro, A., Piazza, R. (2015) *Microchem. J.* 119, 75–82.
- [3] Vecchiato, M., Zambon, S., Argiriadis, E., Barbante, C., Gambaro, A., Piazza, R. (2015) *Microchem. J.* 120, 26–33.
- [4] Wang, P., Zhang, Q., Wang, T., Chen, W., Ren, D., Li, Y., Jiang, G. (2012) *RSC Adv.* 2 (4), 1350–1355.
- [5] Choi, S.-D., Baek, S.-Y., Chang, Y.-S., Wania, F., Ikonomou, M. G., Yoon, Y.-J., Park, B.-K., Hong, S. (2008) *Environ. Sci. Technol.* 42 (19), 7125–7131.
- [6] Baek, S., Choi, S., Chang, Y. (2011) *Environ. Sci. Technol.* 45, 4475–4482.
- [7] Li, Y., Geng, D., Hu, Y., Wang, P., Zhang, Q., Jiang, G. (2012) *Chinese Sci. Bull.* 57 (13), 1499–1503.
- [8] Li, Y., Geng, D., Liu, F., Wang, T., Wang, P., Zhang, Q., Jiang, G. (2012) *Atmos. Environ.* 51, 140–145.
- [9] Garmash, O., Hermanson, M. H., Isaksson, E., Schwikowski, M., Divine, D., Teixeira, C., Muir, D. C. G. (2013) *Environ. Sci. Technol.* 47, 12064–12072.
- [10] Zhu, C., Li, Y., Wang, P., Chen, Z., Ren, D., Ssebugere, P., Zhang, Q., Jiang, G. (2015) *Chemosphere* 126, 40–46.

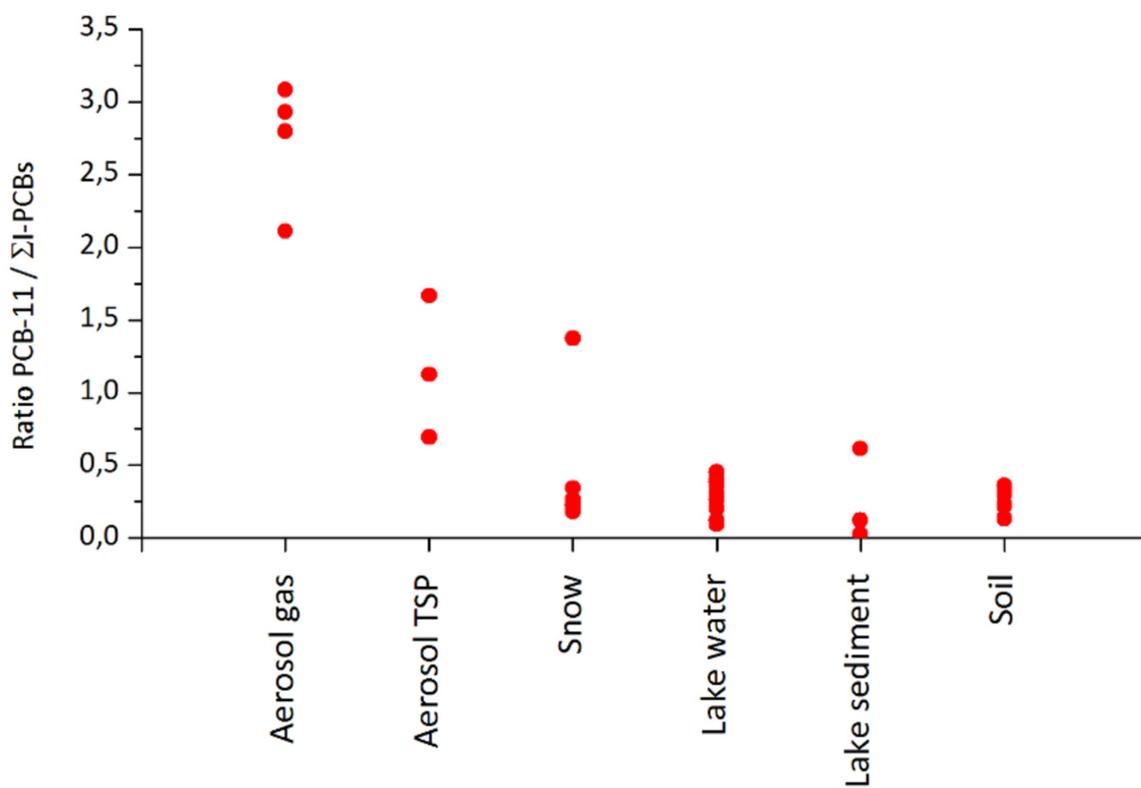


Figure 1: Ratios PCB-11/ Σ I-PCBs in different environmental compartments (BTN, Antarctica).

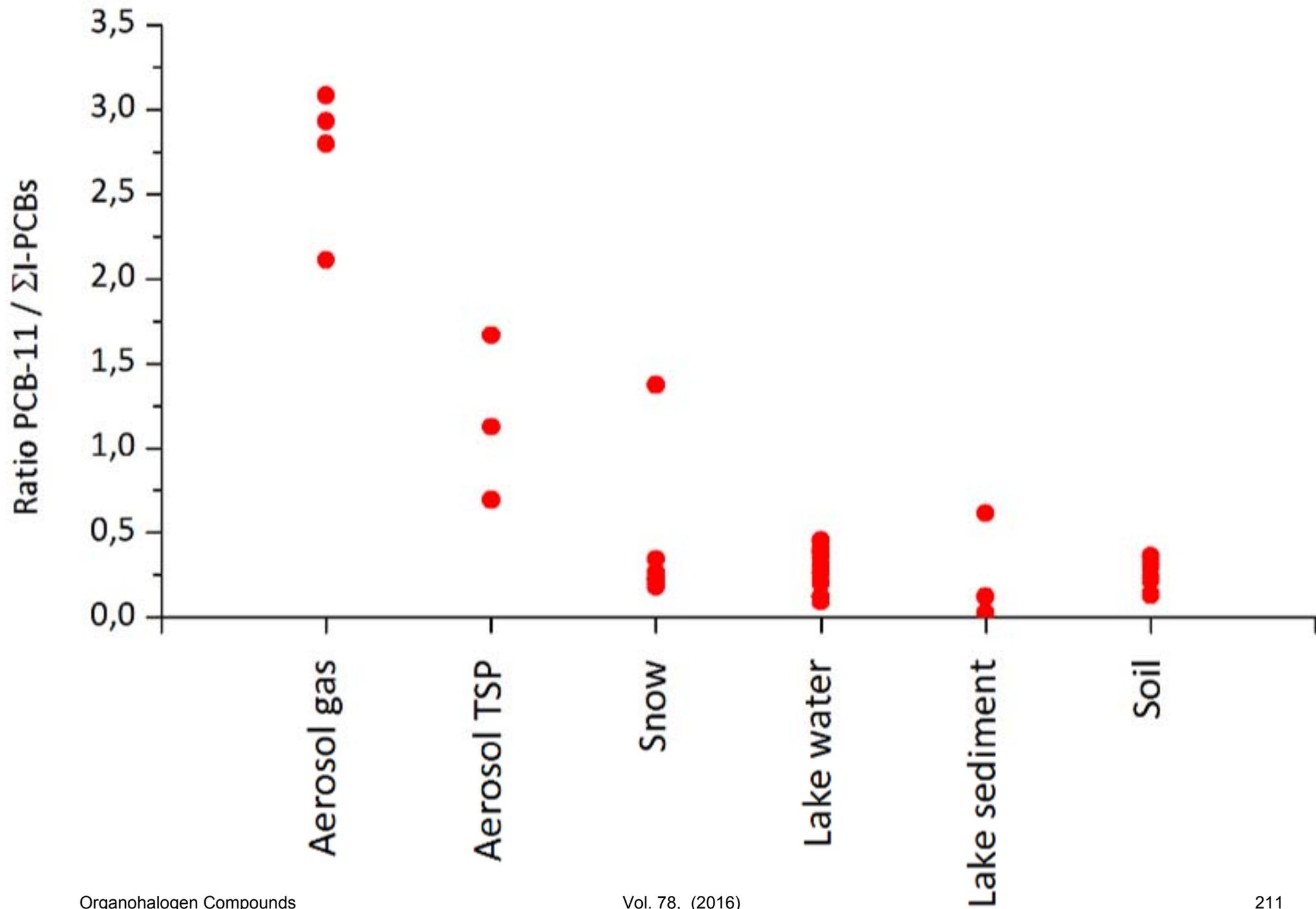


Figure 1: Ratios PCB-11/ΣI-PCBs in different environmental compartments (BTN, Antarctica).