

LEVELS, SPATIAL DISTRIBUTION AND SOURCES OF ATMOSPHERIC OCPs, PCBs AND PBDEs IN A SVALBARD-SAO TOMÉ TRANSECT

Nuno Ratola^{1,2,3,*}, Carola Graf¹, Sonia Montesinos², Adrián Garrido², Pedro Jiménez-Guerrero², Knut Breivik⁴, Silvia Lacorte⁵, Arminda Alves³, Andrew J. Sweetman¹ and Kevin C. Jones¹

¹Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, U.K.; ²Physics of the Earth, University of Murcia, Edificio CIOyN, Campus de Espinardo, Murcia, Spain; ³LEPABE-DEQ, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, Porto, Portugal; ⁴Norwegian Institute for Air Research, Box 100, NO-2027 Kjeller, Norway; ⁵Department of Environmental Chemistry, IDAEA-CSIC, Jordi Girona 18-26, 08034 Barcelona, Catalonia, Spain

*corresponding author e-mail: nrneto@fe.up.pt

Introduction

Organochlorine pesticides (OCPs) have been intensively used in industry and agriculture, mostly between 1950 and 1970, but in some developing countries are still employed to this day¹. They are still found in the atmosphere and revolatilisation from the soils is now considered one of the most important sources to the environment². PCBs and PBDEs are anthropogenic compounds, widely used amongst other applications, as flame retardants in numerous applications such as vehicles, electronic devices, furniture or building materials³. Main sources of pollution include volatilization from materials and atmospheric transport. Although found in the environment at low concentrations, all these persistent organic pollutants (POPs) are generated by a multitude of processes with some substances defined as carcinogens⁴, and others as ecotoxicants partly due to their persistence in different environmental matrices (air, soil, water, living organisms). Semi-volatile POPs are transported in the atmosphere over long distances (LRAT) in gaseous form or sorbed onto particulate matter⁵. With the atmosphere being a key route of transport, it is important to measure the levels of the target contaminants in the air. Given the low maintenance costs and easy set-up, several types of passive air samplers (PAS) have been recently used at regional, continental and global scales with their feasibility demonstrated in deployments across large areas^{6,7}. PAS have been shown to be useful in recording changes along environmental gradients, to assess source-sink relationships, but also with the possibility of producing datasets for chemical fate and transport models^{8,9}. Polyurethane foam (PUF) disks were chosen for this study as they have been demonstrated in field studies to be suitable for legacy POPs⁶. This study covers a large latitudinal transect in the northern hemisphere (from Svalbard to São Tomé) and provides valuable data on background concentrations of “legacy” atmospheric pollutants through passive air sampling. Data is presented from one 6 month campaign and compares the findings with databases gathered and reported previously in similar continental and transect studies^{3,6,7,10}. The ultimate aim is to provide further knowledge on the processes controlling underlying atmospheric trends and help inform future control strategies.

Materials and methods

Passive air sampling

Pre-cleaned PUF disks (14 cm diameter; 1.35 cm thick; surface area, 365 cm²; mass, 4.40 g; volume, 207 cm³; density, 0.0213 g cm⁻³) were sent to the sampling sites in solvent rinsed airtight containers. Two PUF disks were placed at each site (duplicates), and another acted as a field blank at the moment of the deployment. A total of 38 samplers were successfully deployed over a period of approximately 6 months, in 17 background and 2 urban sites, described in Table 1. At the end of the deployment period, the samplers were retrieved by the volunteers, re-sealed in their original containers, and returned by courier to Lancaster University.

Table 1. Information on the passive air sampling sites along the transect.

Site	Country	Location	GPS Coordinates	Elevation(m)
1	Norway	Zeppelin (Svalbard)	78° 54 N; 11° 53 E	475
2		Tromsø	69° 45 N; 18° 30 E	25
3		Osen	61° 15 N; 11° 53 E	570
4		Birkenes	58° 23 N; 8° 15 E	190
5	Faroe Islands	Skoradalur	62° 04 N; 6° 58 W	360
6	United Kingdom	Ullapool (Scotland)	58° 01 N; 5° 04 W	245
7		Hazelrigg (England)	54° 00 N; 2° 46 W	92
8		Aberystwyth (Wales)	52° 25 N; 4° 03 W	31
9		North Wyke (England)	50° 45 N; 3° 28 W	178
10	Spain	Das	42° 22 N; 1° 51 E	1095
11		Barcelona	41° 23 N; 2° 06 E	180
12		Carrascoy	37° 54 N; 1° 00 W	455
13		Izaña (Tenerife)	28° 18 N; 16° 30 W	2390
14	Portugal	Porto	41° 11 N; 8° 36 W	124
15		Midões	40° 22 N; 7° 57 W	255
16		Arade	37° 14 N; 8° 22 W	70
17		Tronqueira (Azores)	37° 46 N; 25° 12 W	482
18		Fanal (Madeira)	32° 48 N; 17° 08 W	1159
19	S. Tomé and Príncipe	S. Tomé	0° 23 N; 6° 43 W	12

Analytical methodology

PUF disks were stored at -20 °C until extraction. Handling and extraction was conducted in a dedicated clean laboratory, where the samples were spiked with a range of ¹³C¹²-labeled PCBs and PBDEs and extracted for 16 h with hexane in a Soxhlet extraction unit. The extract was rotary evaporated and transferred with hexane to a 15 mL amber vial. This was blown down under a gentle stream of nitrogen to about 0.5 mL and cleaned on a 9 mm i.d. chromatography column packed with a slurry of 2 g activated silica (Merck Silica Gel 60), 1 g of activated alumina (Merck Aluminium oxide 90) and 1 cm of baked sodium sulfate (all baked at 450 °C overnight). This was followed by acid digestion with concentrated sulphuric acid and finally passed through a gel permeation chromatography (GPC) column containing 6 g of Biobeads SX 3. Samples were reduced to a final volume of 25 µL, which included three labelled PCB congeners and two PBDEs as internal standards. The samples were analyzed for by GC-MS on a Fisons MD800 operated in electron ionization mode using selected ion monitoring. The capillary column used was a Varian CP-SIL 8CB (50 m x 0.25 mm x 0.12 i.d.) with a retention gap for pesticides. The GC temperature program and monitored ions have been reported previously^{11,12}. A total of 40 PCB congeners, 21 PBDE congeners and 13 OC pesticides were monitored and quantified. All analytical procedures were monitored using strict QA/QC measures.

Data significance tests were done using the Pearson correlation coefficients, with a level of significance of 95% (p<0.05).

Results and discussion

Total concentrations of PCBs, OCPs and PBDEs found along the transect are shown in Figure 1. It is clear that São Tomé stands out from the rest of the sites, particularly owing to the extremely high OCPs concentrations. These chemicals are still commonly utilized in Africa, so not only local uses but also transport from mainland Africa may be responsible for this observation. For the rest of the sites, Barcelona has the second highest concentrations, along with the highest concentrations of total PAHs, which is in line with its urban nature. PBDEs were found at the lowest concentrations of the studied chemicals. It is interesting to note that the urban sites (Barcelona and Porto) and the most elevated site (Tenerife) showed the highest PBDE concentrations, with the latter being likely due to transport along the altitudinal gradient which rises to over 2000 m. All the other sites (all background) contained levels of the total pollutants lower than 200 pg m⁻³.

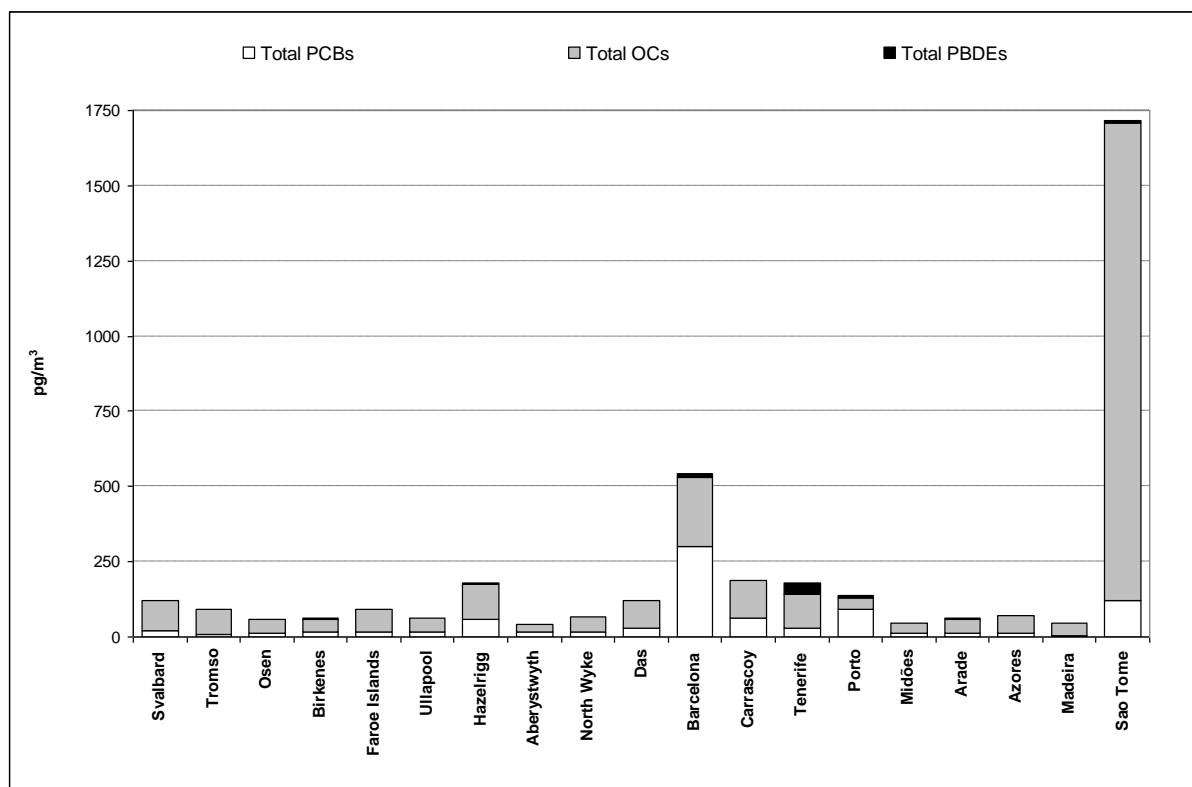


Figure 2. Cumulative concentrations of total PCBs, total OCPs and total PBDEs for the sampling sites in study.

Searching for possible correlations with relevant environmental parameters, it could be seen that total PCBs had a positive significant relationship with population density and atmospheric temperature, OCPs a negative correlation with latitude (clearly influenced by the São Tomé values, near the equator) and total PBDEs with elevation. Results are contained in Table 2.

Table 2. Pearson test correlations for total PCBs, OCPs and PBDEs and some geo-meteorological parameters. Significant results ($p < 0.05$) presented in bold.

Compounds	Elevation	Latitude	Population density	Temperature
Total PCBs	-0.1811	-0.3203	0.9189	0.4671
Total OCPs	-0.1614	-0.6466	0.0321	0.4122
Total PBDEs	0.7177	-0.3730	0.1704	0.3756

The results provide an important contribution to the knowledge of these contaminants on a global scale. Some of the levels found on background sites are quite similar or even higher than one of the urban sites considered in this study (Porto, in Portugal). Further analysis of back-trajectories will allow a more accurate assessment of the most likely sources for this site. For now, São Tomé is a hotspot needing additional investigation, as to the authors' knowledge, no relevant information was available on the incidence of these chemicals up to this point in time.

Acknowledgements

This work has been partially funded by the European Union Seventh Framework Programme-Marie Curie COFUND (FP7/2007-2013) under UMU Incoming Mobility Programme ACTION (U-IMPACT) Grant Agreement 267143. The Lancaster group is grateful to the UK Department of Environment, Food and Rural Affairs (Defra) for funding research on persistent organic pollutants. The Fundação para a Ciência e a

Tecnologia (FCT-Portugal) is thanked for funding Nuno Ratola's residence in the Lancaster Environment Centre and for projects PTDC/AGR-CFL/102597/2008 and EXPL/AAG-MAA/0981/2013. Dr. Pedro Jiménez-Guerrero acknowledges the Ramón y Cajal programme. Finally, we would like to thank the site owners and all the volunteers who took part in the deployment, supervision, collection and shipping of the passive air samplers for their kind cooperation.

References:

1. Scheyer A, Graeff C, Morville S, Mirabel P, Millet M. (2005); *Chemosphere* 58, 1517–1524.
2. Genualdi S, Simonich SLM, Primbs T, Bidleman T, Jantunen L, Ryyo K-S, Zhu T. (2009); *Environ. Sci. Technol.* 43: 2806-2811.
3. Schuster, J. K, Gioia, R, Breivik, K, Steinnes, E, Scheringer, M, Jones, K. C. (2010); *Environ. Sci. Technol.* 44: 6760-6766.
4. Baussant T, Sanni S, Jonsson G, Skadsheim A, Børseth JF. (2001); *Environ. Toxicol. Chem.* 20: 1175-1184.
5. Gioia R, Steinnes E, Thomas GO, Meijer SN, Jones KC. (2006); *J. Environ. Monitor.* 8: 700–710.
6. Jaward FM, Farrar NJ, Harner T, Sweetman AJ, Jones KC. (2004); *Environ. Sci. Technol.* 38: 34–41.
7. Pozo K, Harner T, Wania F, Muir D, Jones KC, Barrie LA. (2006); *Environ. Sci. Technol.* 40: 4867–4873.
8. Moeckel C., MacLeod M., Hungerbühler K., Jones KC. (2008); *Environ. Sci. Technol.* 42: 3219–3225.
9. Halse AK, Schlabach M, Eckhardt S, Sweetman A, Jones KC, Breivik K. (2001); *Atmos. Chem. Phys.* 11: 1549–1564.
10. Birgul A, Katsoyiannis A, Gioia R, Crosse J, Earnshaw M, Ratola N, Jones KC, Sweetman AJ. (2012); *Environ. Pollut.* 169: 105-111.
11. Thomas GO, Sweetman AJ, Parker CA, Kreibich H, Jones KC. (1998); *Chemosphere* 36: 2447–2459.
12. Gouin T, Thomas GO, Cousins I, Barber J, Mackay D, Jones KC. (2002); *Environ. Sci. Technol.* 36: 1426–1434.