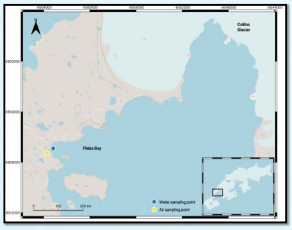
Occurrence and diffusive air-seawater exchanges of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in Fildes Bay, King George Island, Antarctica

Thais Luarte[1,2,3]; Andrea Hirmas-Olivares[2,3,4]; Juan Höfer[12,13]; Ricardo Giesecke [11,12]; Andrés Pérez-Parada; Gustavo Chiang[14]; Rainier Lohmann[5]; Jordi Dachs[6], Susan Bengtson Nash[7]; José Pulgar[4]; Karla Pozo7[8,9], Petra P Přibylová[9], Jakub Martiník[9] ; Cristóbal Galbán-Malagón[2,3,10]*

[1]Programa de Doctorado en Medicina de la Conservación, Facultad Ciencias de La Vida, Universidad Andrés Bello, Santiago, 8370251, Chile; [2]GEMA, Center for Genomics, Ecology & Environment, Universidad Mayor, Camino La Pirámide, 5750 Huechuraba, Santiago, 8580745, Chile; [3]Anillo en Ciencia y Tecnología Antártica POLARIX, Universidad Mayor, Camino La Pirámide, 5750 Huechuraba, Santiago, 8580745, Chile; [4]Department of Ecology and Biodiversity, Faculty of Life Sciences, Universidad Andres Bello, Santiago, 8370251, Chile; [5]Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode Island, 02882, USA; [6]Department of Environmental Chemistry, IDAEA-CSIC, c/Jordi Girona 18-26, Barcelona, Catalunya 08034, Spain; [7]Southern Ocean Persistent Organic Pollutants Program, Centre for Planetary Health and Food Security, School of Environment and Science, Griffith University, Nathan, QLD, 4111, Australia; [8]Facultad de Ingeniería y Tecnología, Universidad San Sebastián, Lientur 1457, Concepción, Chile; [9]Masaryk University, Faculty of Science, RECETOX, Kotlářská 2, 611 37, Brno, Czech Republic; [11] Instituto de Ciencias Marinas y Limnológicas, Universidad Austral de Chile, Valdivia, Chile, ; [12] Centro FONDAP de Investigación en Dinámica de Ecosistemas Marinos de Altas Latitudes (IDEAL), Valdivia, Chile,; [13] Escuela de Ciencias del Mar, Pontificia Universidad Católica de Valparaíso, Valparaíso, Chile,; [14]Centro de Investigacion para Sustentabilidad & Depertamento de Ecologia y Biodiversidad, facultad de Ciencias de la Vida, Universidad Andres Bello. Santiago, Chile

Introduction

Persistent Organic Pollutants (POPs) are transported to Antarctica primarily through long-range atmospheric transport (LRAT). These pollutants tend to accumulate in the polar zone, with deposition being more prevalent than volatilization. However, climate change may reverse this pattern as rising temperatures cause POPs that have been trapped in water, ice, and soil for decades to volatilize, creating a secondary source of these harmful compounds. Therefore, updated studies are essential to document the behavior of POPs in polar regions. The objective of this study was to determine the levels of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in seawater and air, estimate the air-sea dynamics through diffusive exchange analysis, and evaluate the physical and biological factors driving the recorded dynamics of POPs. Samples of air and seawater were collected from Fildes Bay, King George Island, Antarctica, between November 2019 and January 30, 2020.



Fugacity ratio and air-water flux estimation

Fugacity ratio reflects the tendency of a substance to prefer one phase (liquid, solid, or gas) over another, and can be literally defined as "the tendency to flee or escape". It could be estimated as follows.

$$f_w = C_{TD} \cdot H'$$

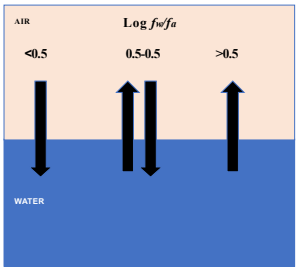
$$f_a = C_G \cdot R \cdot T$$

$$f_w/f_a = C_{TD} \cdot H' / C_G$$

Net fluxes of air–water gas exchange (F_{AW}) were estimated using the Whitman two-film model

$$f_{AW} = K_{AW} (C_{TD} - C_G \cdot R \cdot T / H)$$

$$1/K_{AW} = (RT / k_A \cdot H') + (1 / k_W)$$



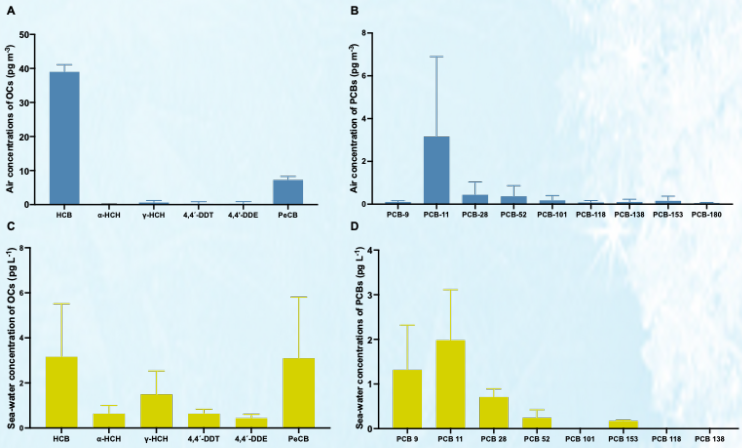
Where C_G, C_{TD}, represents air and trully dissolved water concentractions respectively, R is the ideal gas constant, T is the temperature in K, H' is the temperature and corrected dimensionless Henry's Law Constant, f_a and f_w represents air and water fugacities respectively and f_w/f_a is the air-water fugacity ratios. f_{AW} is the air–water gas exchange fluxes , K_{AW} (m d^{-1}) is the global air-water mass transfer coefficient, k_A and k_W are the mass transfer coefficients (m d^{-1}) across the air and water layers, respectively, calculated according to previous studies[1,2].

Final Remarks

The air-seawater fugacity dynamics recorded in this study demonstrate the importance of certain biotic and abiotic factors on the biogeochemistry and environmental fate of POPs. For example, the deposition documented for most of the OCs is likely due to the possible biodegradation of these compounds in surface waters. Concerning Log $f_w f_a^{-1}$ results for PCBs, these showed differences between congeners. For example, for less hydrophobic compounds, such as PCB-9, extending compounds to snow and ice melt from receding glaciers is essential in increasing air-seawater fugacity, with volatilization predominating over deposition. On the other hand, as hydrophobicity increases, the biological carbon pump begins to act by decreasing the concentrations of PCBs present in seawater, with a substantial effect on PCBs exceeding a Log K_{OW} >6.5, as evidenced in this study with the atmospheric deposition of PCB-180. This. study highlight the effect that glacial melting has, because of climate change[3,4], on the biogeochemistry of POPs, where snow/ice melting may likely cause the re-emission of compounds previously kept in the ice

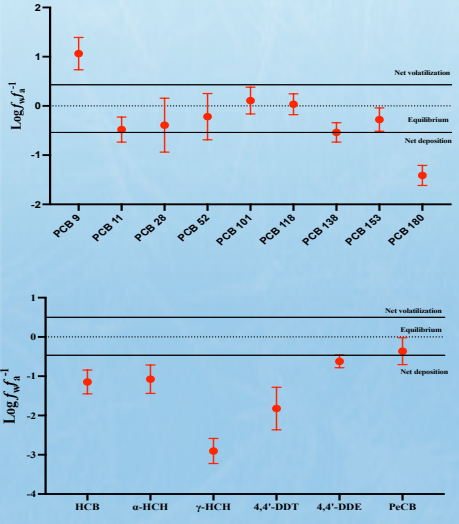
Results & Discussion

Air and Water levels at Fildes Bay, Antarctica



Hexachlorobenzene (HCB) was the most abundant isomer recorded in this study, with a mean of 39 ± 2.1 pg m-3 and 3.2 ± 2.4 pg L-1 in air and seawater, respectively. The most abundant PCB congener was PCB 11, with a mean of 3.16 ± 3.7 pg m-3 in air and 2.0 ± 1.1 pg L-1 in seawater.

Air-Seawater exchange



The fugacity gradient estimated for the OCP isomers indicate a predominance of net atmospheric deposition for HCB, α-HCH, γ-HCH, 4,4'-DDT, 4,4'-DDE isomers, and close to equilibrium for the PeCB compound. The observed deposition of most OCs may be due to high biodegradation rates and settling fluxes contributing to the decrease of these compounds in surface water. The estimated fugacity gradients for PCBs showed differences between congeners, with net volatilization predominating for PCB-9, a trend close to equilibrium for PCB congeners 28, 52, 101, 118, 138, and 153, and deposition predominating for PCB 180. Snow amplification plays an important role for less hydrophobic PCBs, with volatilization predominating after snow/glacier melting.

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Acknowledgement

The authors acknowledge the support of the Research Infrastructures RECETOX RI (No LM2018121, LM2023069) and the projects CETOCOEN EXCELLENCE (No. CZ.02.1.01/0.0/0.0/17_043/0009632) financed by the Ministry of Education, Youth and Sports of the Czech Republic. The support from the "Instituto Antártico Chileno Ref: Dg_02_21 and RT_12_17. The support of the ANID by means of FONDECYT 1210946 and ANID-PIA-INACh_192057. Also Thais Luarte akckoledges the funding from Vicerrectoria de Investigación y Doctorados Universidad Andrés Bello for their PhD grant funding program.