POLYCHLORINATED BIPHENYLS IN *PERUMYTILUS PURPURATUS* (LAMARCK 1819) ALONG THE CHILEAN COAST REFLECTS LATITUDINAL CONCENTRATION GRADIENTS.

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Introduction

PCBs were widely used in Chile as dielectric fluids during the last 50 years, and up to day remains some still in use or stored[1], nowadays they are considered global pollutants. During the past decade Wania and Mackay[2] proposed a global fractionation hypothesis of POPs, explaining the theoretical basis for the trends of some POPs including PCBs to move towards higher latitudes. This hypothesis have been confirmed by several experimental data mainly gathered in the northern hemisphere[3], lacking some experimental evidence from the southern hemisphere. Chile is characterized by a long latitudinal gradient from 18º SL to 54º SL, therefore it can be suitable to test if there are concentration gradients independent of point sources located along the coast. In the marine environment mytillids have been use extensively as bioindicators of pollution. This invertebrates due to their sessile habitat are linked the entire life cycle to a specific location *P. purpuratus* is a widely distributed mytilid in the intertidal area along the entire Chilean coast [4].Distributed in the pacific ocean from the Ecuador until the Magellan Strait and the south Atlantic ocean in the Argentinean coast [5] it reach a maximum size of about 3-4 cm and rest by about three to four years in the intertidal zones. Lives in the rocky intertidal zone where it forms extense banks. They perform both aerobic and anaerobic respiration process, being able to consume oxygen from the air[4].

Previous reports on PCBs levels in mytilids in Chile were by other authors[6] in seven locations in Chile, results were very interesting because a clear concentration gradient were observed finding higher concentrations of PCBs near the harbour of Punta Arenas (southern Chile 54 SL). Also this study serves as an excellent archive for time series comparison for trace organics compound at the beginning of the 90's. This paper presents some data gathered in Chilean coastal areas using one species of bivalve widely distributed in order to gain more understanding of the cyling of these xenobiotics in the Chilean ecosystems and as part of a research effort searching for evidence of latitudinal fractionation considering the broad latitudinal gradient covered by the chilean coast.

Material and Methods

Samples of *P. purpuratus* were obtained in 13 localities along the Chilean Coast Figure 1 Shows the sampling sites. Selected sites were choosing according accessibility. At each site**,** 30-40 samples of individuals *P.purpuratus* were sampled,and stored in pre cleaned aluminum foil and transported to the labratory on ice.At the laboratory valves were removed and soft parts were pooled to make a single sample.

PCBs were analized by GC-ECD, briefly, samples were freeze dried, homogenized and subjected to a soxhlet extraction in hexane for 24 hours, then cleaned-up with powder copper followed by florisil column chromatography and concentrated sulphuric acid. Individual PCBs congeners (49) were used

for the identification. Chromatographic conditions were the following. GC PERKIN ELMER, Autosystem, Capillar column SPB5, Supelco 30m x 0,25 µm x 0,25 mm , Injection port temperature 200 ºC, Injection system split/splitless, Electron Capture Detector ^{63} Ni (ECD) Detector temperature 310 ºC, Oven initial temperature,100 ºC,3 min, Ramp rate, 5 ºC /min to 280 ºC. A calibration curve for each congener was determined in order to calculate concentrations of each congener within the sample, detections limits ranged from 1.51 to 11.95 ng/g on a lipid basis depending on the congener and detector response. Data quality was assessed for each batch of samples by the analysis of blanks and certified Standard Reference Materials (NRCC), recoveries higher than 60 % -Figure 3- were obtained using this procedure. In addition, duplicate samples were analized both at Siena and Concepción for comparative purposes and analytical quality assurance, differences were below 15 %, quantifying with different standard material

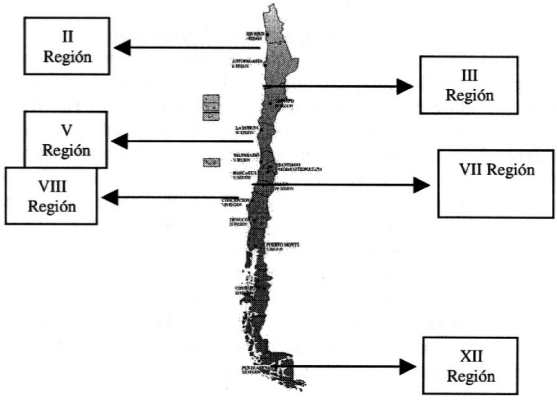

Figure 1. Sampling sites along the Chilean coast

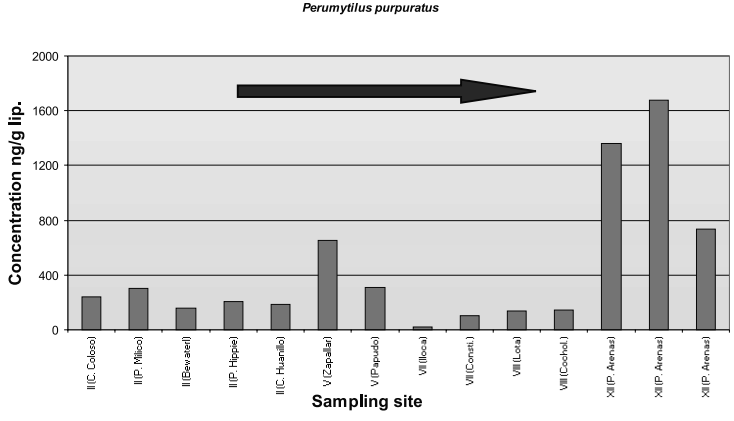

Figure 2. Total PCBs concentration in several localities along the Chilean coast

Results and Discussion

In general, levels of PCBs were detectable under our analytical conditions in almost all analized samples several congeners co elute under the experimental conditions utilised, then are expressed as the sum of the co eluting congeners .Concentrations of total PCBs, ranged from 1 ng g^{-1} to 323 ng g^{-1} dry weight, in Iloca (central Chile, 35 SL) and Punta Arenas (southern 54 SL) respectively. The Punta Arenas samples were colected near the harbour, Iloca is a site where no nearby sources could be identified. Total PCBs expressed as ng g-1 lipid basis showed a clear latitudinal trend towards higher concentrations of total PCBs in higher latitudes(r^2=0.5796) Figure 2

Four different zones were clearly identified considering the congener composition in each zone, being PCBs of lower molecular weight in higher concentrations at higher latitudes, and this effect associated to a sea superficial temperature gradient (r^2=0.6065, temperature v/s total. PCBs).

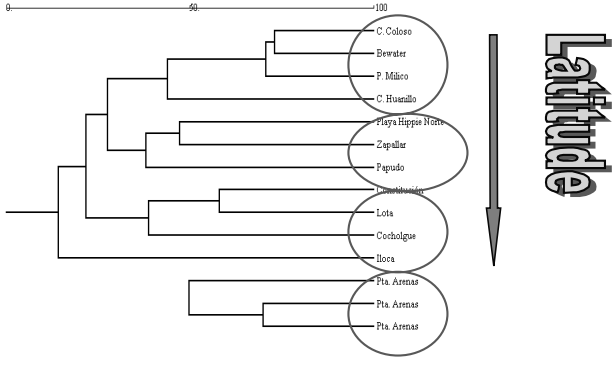

Figure 3. Definition of four zones of similarities considering congeneric composition of PCBs along the coast.

Congener specific analysis give us more insights in the understanding of PCBs behaviour in Chile, different congeners fingerprint were observed in the different locations reinforcing the idea of different patterns of accumulation. For example in northern Chile, levels of PCBs were very low and predominating PCBs congeners were PCB 118/149, 153 and 31/28/50, penta, hexa and hepta PCBs account for more of the70 % of total mass of PCBs in these samples, average percentage penta was 47 %, hexa 6.7 % and hepta 21 %, respectively. This pattern changes again in central north locations, where most of congeners were tetra, hexa and hepta substituted. Drastic changes were observed in southern Chile mainly in Punta Arenas area(54SL) where light congeners were found in high concentrations (PCBs 15 and 18).However it was not found a clear gradient for individual congeners, because of different congeneric composition in the samples.

Previous report from other authors[6] have indicated a similar concentration gradient between northern Chile and Southern Chile in mussel samples collected in the early 90´s, however congener composition of samples did no present such differences observed in this work, probably because they sampled different species of mussels.

Our results demonstrated that PCBs are widely distributed along the chilean coast, but congeneric composition results to be different as we move from north to south. These phenomena could be

explained by three factors, the first is related to PCBs contaminated areas near the sampling sites, but in that case probably we could not expect such differences in congeneric composition. The second factor could be related to a more global effect regarding atmospheric transport and deposition process considering the wide latitudinal gradient analized. A third factor explaining the observed results could be consequence of illegal dumping in southern Chile, since not major industrial settings with the exception of petrochemical complex and transport, nor population exist within the area. However, for demonstrating wich factor is predominating in the observed levels, more research is needed, probably involving the use of SPMDs or other environmental compartments as indicators for PCBs fractionation along the Chilean coast.

Ackowledgments

This research was supported by FONDECYT Nº 1010640.

References

1. CONAMA (2001) PCBs en Chile: Diagnóstico Nacional de Contaminantes Orgánicos Persistentes (COPs). Documento de trabajo Nº 2 .
2. Wania, F. And D.Mackay (1993) Ambio 22, 10.
3. Ockenden W.,Steinnes., Parker and KC Jones (1998) Environ Sci Technol 32, 2721.
4. Vial, M;, Simpfendörfen, R.; López, D., González, M & Oelcker, K. 1992. J. Exp. Biol. Ecol. 159: 191-201.
5. Lozada E. & P. Reyes. 1981 The Veliger 24 (2), 147.
6. Sericano JL., Wade TL., Jackson TJ.,Brooks JM., Tripp BW.,Farrington JW.,Mee LD.,Readmann JW., Villeneuve JP.and Goldberg ED (1995 Mar Poll Bull 31, 214.