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Spatio-temporal trends and body size differences of OCPs and PCBs in *Laeonereis culveri* (Polychaeta: Nereididae) from Southwest Atlantic estuaries

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ABSTRACT

Southwest Atlantic (SWA) estuaries have been historically impacted by industrial and agricultural activities that represent an important source of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). Intraspecific differences in OCPs and PCBs levels were evaluated in the benthic polychaete *Laeonereis culveri* from SWA estuaries (Samborombón; Mar Chiquita; Quequén Grande and Bahía Blanca) at different spatio-temporal scales. Regarding inter- and intra-estuarine spatial comparisons polychaetes showed significant differences in OCPs/PCBs levels ($p < 0.05$) being DDTs, endosulfan, penta- and hexa-CBs homologues the most representative compounds. Intra-estuarine comparisons also showed significant differences in terms of seasonality and body size ($p < 0.05$). OCPs/PCBs concentrations were negatively correlated with animal weight, but this covariable was not relevant on differences observed. OCPs/PCBs levels in polychaetes showed strong relationships with those of sediments, being suitable for estuarine biomonitoring studies. Seasonal and body-size differences found in OCPs and PCBs levels in tissues reveal the importance of these factors for intra-estuarine monitoring.

1. Introduction

Persistent organic pollutants (POPs) had an extensive worldwide use in the last century until their prohibition. Many of them remain in several environmental matrices including coastal sediments. Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are POPs of environmental concern due to its persistence, toxicity and biomagnification along terrestrial and aquatic trophic webs (Bodin et al., 2008; Burreau et al., 2004; Li et al., 2017). Sediment inhabiting organisms would be exposed to legacy POPs over extended periods, making them useful for biomonitoring studies (Ruus et al., 2002; Nunes et al., 2011; Van Ael et al., 2012, 2013). Nereid polychaetes are common benthic species from soft-bottom sediments, which represent important food supply for estuarine food web and some species had been used as biomonitors of organic pollutants (Ruus et al., 2002; Nesto et al., 2010; Díaz-Jaramillo et al., 2015; Li et al., 2017). The estuarine polychaete *Laeonereis culveri* (formerly, *Laeonereis acuta*) is a key estuarine species from Southwest Atlantic (SWA) estuaries and they are used in many fields and laboratory toxicological studies (De Jesús-flores et al., 2016; Díaz-Jaramillo et al., 2016; Sardi et al., 2016).

Particularly, some estuaries in Argentina are located in many crowded and industrial areas, with their catchment area under extensive and intensive agricultural activities (Gonzalez et al., 2013). Besides, many of these coastal environments serve as nesting and feeding habitats for many species, among other ecosystem services, being protected natural areas of regional and global concern (Kopprio et al., 2015). Several studies reported the occurrence of PCBs and OCPs in sediment, water and vertebrate species from SWA estuaries (Colombo et al., 2005; Gonzalez et al., 2013; Tombesi et al., 2017). However, few studies have focused on benthic invertebrate species (Menone et al., 2001, 2006). Information about OCPs and PCBs levels in key benthic species, as nereids polychaetes, are necessary in order to compare impacted and non- impacted areas as well as the potential risk to other species associated in the estuarine food web.

Inter-estuarine differences in OCPs/PCBs levels of benthic species are expected upon the different anthropogenic pressure on each system. However, for infaunal species, intra-estuarine variability may also be considered. Spatial and temporal trends are important for studies that involve OCPs and PCBs tissue analysis and their intraspecific variability in benthic species (Olenycz et al., 2015; Li et al., 2017). Additionally, when evaluating the use of *L. culveri* as POPs biomonitor, is necessary to consider the influence of age or body size in the intra-estuarine variability, to obtain proper comparisons among sites or estuaries (Burreau et al., 2004; Milun et al., 2016; Viganò et al., 2007).

The aim of this study was to determine OCPs and PCBs levels in *L. culveri* tissues and sediments from Samborombón Bay, Mar Chiquita

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Table 1
SWA estuaries, *L. culveri* and sediment sampling site description. *Sampling sites for inter-estuarine spatial comparisons, **Sampling sites for intra-estuarine spatial comparisons, ***Sampling sites for intra-estuarine seasonal comparisons, ****Sampling sites for intra-estuarine body weight/size comparisons.

	Sites	Coordinates	Site Description	Comparisons
Samborombón	SAM 1	36°19′21″S 56°46′26″W	Tapera de López sector, recreational activities. Protected area.	*, **
Urban & Agricultural catchment basin	SAM 2	36°20′37″S 56°44′44″W	San Clemente del Tuyu Port, boat traffic. Protected area.	*, **, ***
Mar Chiquita	MCH 1	37°44′39″S 57°25′23″W	Mar Chiquita town, recreational activities. Protected area.	*, **, ***, ****
Agricultural catchment basin	MCH 2	37°44′22″S 57°25′37″W	Mar Chiquita town, small boat traffic and recreational activities. Protected area.	*, **
Quequén Grande	QQG 1	38°33′13″S 58°43′29″W	Necochea city, recreational activities	*, **, ***
Agricultural catchment basin	QQG 2	38°33′44″S 58°42′58″W	Quequén city, boat traffic and recreational activities.	*, **
Bahía Blanca	BBL 1	38°44′54″S 62°22′57″W	Cuatreros Port, boat traffic and industrial activities. Protected area.	*, **
Industrial & Agricultural catchment basin	BBL 2	38°44′15″S 62°18′49″W	Maldonado sector, recreational and industrial activities.	*, **, ***

coastal lagoon, Quequén Grande river and Bahía Blanca SWA estuaries. OCP and PCB residues in *L. culveri* tissues and sediments were analyzed in terms of intra and inter-estuarine differences related to spatio-temporal and size differences.

2. Material and methods

2.1. Study area

SWA estuaries located in the Pampean biome extends > 1000 km and are characterized by variable morphology and hydrography (Piccolo and Perillo, 1999) (Table 1). Samborombón estuary (SAM) is a microtidal estuary that corresponds to Samborombón-Salado system; its wetland area was declared a Ramsar site due to its importance for biodiversity conservation (Kopprio et al., 2015). Anthropogenic chemical impacts reported in SAM and adjacent areas are related to eutrophication, heavy metal and OCPs pollution (Colombo et al., 2005; Kopprio et al., 2015). Mar Chiquita estuary (MCH) is a microtidal coastal lagoon, which receives freshwater inputs from many streams of the wet Pampean region and was declared Man and the Biosphere Reserve by UNESCO (Beltrame et al., 2009). Agricultural and recreational activities in the lagoon and adjacent areas represent the main threats. POPs and heavy metals were observed in particulate material and sediments (Menone et al., 2001; Beltrame et al., 2009; Díaz-Jaramillo et al., 2016). The Quequén Grande estuary (QQG) is a partially mixed microtidal estuary surrounded by an important port area. QQG also receives important inputs of OCPs and other pesticides derived from extensive agricultural activities in its watershed and other compounds from Necochea and Quequén cities (Gonzalez et al., 2013; Kopprio et al., 2015; Silva Barni et al., 2014; Lupi et al., 2015). Bahía Blanca (BBL) is a mesotidal estuary located in the south of the study area. This larger estuarine system (3000 km^2) comprises different anthropogenic activities, in conjunction with preservation areas of regional and global concern (Kopprio et al., 2015). Urban activities, petrochemical industries, maritime traffic and sewage discharges represent the main pollution threats. OCPs, petroleum-related hydrocarbons, heavy metals and organotin compounds were reported in sediments and biota from this SWA estuarine environment (Marcovecchio and Ferrer, 2005; Menone et al., 2006; Delucchi et al., 2007; Tombesi et al., 2017).

2.2. Sampling

Two sites were sampled in each estuarine area during the warm season (December–January) according to the occurrence of *L. culveri* on intertidal sediments for inter-estuarine comparisons (Table 1). Intra-estuarine seasonal trends in the OCPs and PCBs levels in *L. culveri* were assessed by the additional sampling of one site from each estuarine system in cold seasons (June–July) (Table 1). For intra-estuarine comparisons, intraspecific size differences were performed by obtaining polychaetes from the same sampling site (Table 1). Three sizes were defined according to the wet weight of individuals: large (≈0,70 g/70 mm), medium (≈0,25 g/40 mm) and small (≈0,05 g/ < 20 mm). Three composite samples were obtained ($n = 3$) considering the most common size in each estuarine site. Polychaeta composites of 3,5 or 15 individuals were made from large, medium and small individual, respectively. Each individual of *L. culveri* was manually removed from the sediments and subject to 24 h purge in filtered, diluted seawater (20 PSU) to eliminate recently ingested sediments. Surface sediments (0–10 cm deep) were obtained in each sampling site ($n = 3$) using metallic core. Tissue composites and sediments were frozen at −20 °C, until chemical analysis. Samples of *L. culveri* individuals from estuarine preservation areas (Table 1) were taken with permission from OPDS 2145-12776/16 (Organismo Provincial de Desarrollo Sostenible, Buenos Aires, Argentina).

2.3. Sediment physico-chemical characterization

Total organic carbon in estuarine sediment was determined by the wet-oxidation method described by Mingorance et al. (2007).

2.4. OCPs and PCBs analysis

2.4.1. Sample preparation

Sediments (8–10 g) and polychaete tissues (0.5–1.5 g) were homogenized with sodium sulfate and Soxhlet extracted (8 h) with a mixture of hexane–DCM (1:1). All samples were spiked with 20 ng of PCB #103 as internal standard. Extracts were subsequently concentrated to 2 mL. Polychaete tissue extracts included a lipid removal step by gel permeation chromatography (GPC, Bio Beads S-X3, 200–400 mesh, Bio-Rads Laboratory, Hercules, USA) followed by the gravimetric calculation of lipid percentage (Metcalfe and Metcalfe, 1997). The cleanup of polychaete tissues and sediments was carried out using activated silica gel (200 °C, 24 h) conditioned with 10 mL of hexane and eluted with 10 mL of a mixture of hexane:DCM (1:1) (Gonzalez et al., 2013). Extracts were then evaporated with N_2 to incipient dryness and reconstituted in 500 μL of hexane prior to the analysis. Sulfurs impurities were eliminated from sediment extracts by reaction with pre-activated copper particles (Metcalfe and Metcalfe, 1997).

2.4.2. Analysis of OCPs/PCBs

OCPs and PCBs were analyzed using a gas chromatograph with an electron capture detector (GC-ECD, Shimadzu 17-A, Japan) using a SPB-