Environmental Toxicology and Chemistry

Environmental Chemistry

BTS, PAHS, OCPS AND PCBS IN SEDIMENTS AND BIVALVE MOLLUSKS IN A MID-LATITUDE ENVIRONMENT FROM THE PATAGONIAN COASTAL ZONE

MARTA G. COMMENDATORE, MARCOS A. FRANCO, PATRICIA GOMES COSTA, ITALO B. CASTRO, GILBERTO FILLMANN, GREGORIO BIGATTI, JOSÉ L. ESTEVES, AND MARINA L. NIEVAS

Environ Toxicol Chem., **Accepted Article** • DOI: 10.1002/etc.3134

Environmental Chemistry **Environmental Toxicology and Chemistry**
DOI 10.1002/etc.3134

BTS, PAHS, OCPS AND PCBS IN SEDIMENTS AND BIVALVE MOLLUSKS IN A MID-LATITUDE ENVIRONMENT FROM THE PATAGONIAN COASTAL ZONE

Running title: Organic pollutants in sediments and bivalves from Patagonia

MARTA G. COMMENDATORE, *† MARCOS A. FRANCO, †‡ PATRICIA GOMES COSTA, § ITALO B. CASTRO, §‖ GILBERTO FILLMANN, § GREGORIO BIGATTI, # JOSÉ L. ESTEVES, † AND MARINA L. NIEVAS †‡

† LOQYCA, Centro Nacional Patagónico (CONICET), Puerto Madryn, Chubut, Argentina

‡Universidad Tecnológica Nacional-Facultad Regional Chubut (UTN-FRCH), Puerto Madryn, Chubut, Argentina

§Universidade Federal do Rio Grande (FURG), Río Grande, Brazil

‖Universidade Federal do São Paulo (USP), São Paulo, Brazil

LARBIM, Centro Nacional Patagónico (CONICET), Puerto Madryn, Argentina

* Address correspondence to commenda@cenpat-conicet.gob.ar

Additional Supporting Information may be found in the online version of this article.

Submitted 17 November 2014; Returned for Revision 19 February2015; Accepted 26 June 2015

Abstract: BTs, PAHs, OCPs and PCBs were assessed in a mid-latitude environment of the Patagonian coast, distant from important pollutant sources. Bioaccumulation processes through bottom sediment re-suspension were suggested by BTs level found in surface sediment (<LOD-166.5 ng (Sn) g^{-1}dw) and bivalve mollusks (29.4-206.0 ng (Sn) g^{-1} dw); while imposex incidence was only 15% in the gastropod *P. plumbea* collected near a harbor. Low hydrocarbon pollution was found in sediments and bivalves with ∑PAHs(16) ranging from<LOD to 94.9 and from<LOD to 54.9 ng g^{-1}dw, respectively. Values were typical of locations distant from pollutant sources and showed different compositional patterns for both substrates. However, concentrations for some individual PAHs in sediments were found over the threshold effect level (TEL).On average ΣPCB not exceed the SQGs being 0.57 ± 0.88 ng g^{-1} dw in sediments and 0.41 ± 0.26 ng g^{-1} dw in bivalves. Average ΣOCPs in sediments were 0.53 ± 0.34 ng g^{-1} dw and ranged from <LOD to 0.22 ng g^{-1}dw in bivalves, showing a different pattern and suggesting a different accumulation pathway as it was found for PAHs. While both discrete and atmospheric sources can be considered for PAHs, OCs pollution was clearly related to atmospheric global transport, indicating that in the studied area, OCPs and PCBs suffer permanent or temporal deposition during their migration to southern zones.

Keywords: Butyltins, PAHs, Organochlorines, Pollutant sources, sediment quality

INTRODUCTION

Stockholm Convention (2009) [1] includes many organochlorine pesticides (OCPs) and all polychlorinated biphenyls (PCBs) as persistent organic pollutants (POPs). Both, OCPs and PCBs, exert adverse effects on humans and ecosystems and are highly resistant to degradation. Due to their hydrophobic nature they accumulate in sediments [2], being able to be transferred through the food web reaching significant levels in top predators. Industrial and agricultural sources have contributed significant amounts of organochlorines to the environment through leakage, disposal, and evaporation [3]. Although numerous countries withdrew the registered usage of OCPs many years ago, these man-made chemicals still persist at considerable levels worldwide [2]. Actually, some countries in the Southern Hemisphere continue to use these compounds [4]. Butyltins (BTs) and polyaromatic hydrocarbons (PAHs) are lipophilic, noxious on marine biota, and relatively persistent pollutants found in the marine environment. TBT used in antifouling paints has been detected since the 80s in coastal areas around the world associated with intense maritime activities [5]; it is easily transferred to the biota mainly through the sediment-water interfacial contact and harmful effects have been reported [6]. PAHs are ubiquitous contaminants, present in complex mixtures and introduced into the environment via natural processes and/or anthropogenic activities [7]. Due to their environmental concern, they have been studied in regards to their origin, distribution, and destination in the environment [8].

Most of POPs are susceptible to long-range transport, being conveyed to polar regions primarily via air masses, according to the global distillation and fractionation processes [9]. Volatilization/deposition cycles may be repeated many times and the most volatile compounds such as HCHs, HCB and low-chlorinated PCBs can redistribute globally [9]. In recent years, POPs have been increasingly documented in the Northern Hemisphere [10] and in Arctic and Antarctic animals remote from points of their uses or emissions [11, 4, 12, 13]. Despite of POPs are a global issue, the existing research and monitoring efforts are mainly concentrated in the Northern Hemisphere. Hence, a global

bias exists in data distribution limiting a comprehensive global assessment. In addition, the information is generally aggregated in densely populated areas along the extensive hydrographic basins of major rivers. In spite of the large development of coastal marine areas along the Atlantic and Pacific Oceans, they have received proportionally less attention than fresh water environments [14]. The monitoring of legacy and emerging POPs is considered a valuable tool to detect trends of POPs and improve the understanding of their sources, occurrence and fate [15]. Studies on long range transport in South Hemisphere (SH) practically do not exist; only a few works have been conducted in the region, where several POPs have been detected in remote areas showing the relevance of atmospheric and ocean transport [16, 17, 14,10]. Remote environments, removed from local sources influences are required to assess global POP trends sites [15]. The study of mid-latitude environments in the SH can help to elucidate the fate of POPs in its probable global transport to lower latitudes. Coastal areas are highly relevant in terms of POP cycling since they are highly populated and at the interface between open oceans and continents [15]. In the coastline of Patagonia, contamination research on lipophilic pollutants has been mainly focused on hydrocarbons (e.g. [18, 7]), being the assessment of POPs very scarce. The goal of this study is to determine the level, probable sources, age, and distribution patterns of a broad range of compounds including OCPs, PCBs, PAHs, and BTs in sediments and bivalve mollusks from North Zone of the San Jorge Gulf (NZ-SJG, Patagonia), a mid-latitude environment with great biodiversity and little anthropic influence. In addition, imposex in gastropods and a comparison with sediment quality guidelines (SQGs) to estimate sediment health is reported.

MATERIALS AND METHODS

Study area

The San Jorge gulf is located between 44° 55´ S and 47° 07´ S in Patagonia (Argentina) (Figure 1). The north zone of the gulf (NZ-SJG) is characterized by a high biodiversity including marine birds, marine mammals, fishes, and benthic communities with big seaweeds and marine invertebrates whose diversity is valuable for feeding of resident and migratory birds. It extends along 100 km of coast with

diverse environments including more than 40 islands and islets. For its preservation NZ-SJG was designed Patagonian Austral Inter-jurisdictional Marine Costal Park in 2009, being the first national marine park in Argentine. Recently, it was designated Biosphere Reserve in the frame of the Man and Biosphere Program of UNESCO (Jun 2015). Anthropic activities are scarce and principally focused in recreational and artisanal fishing, sheep farms and rural tourism. A single small human settlement, Camarones town with nearly 1300 inhabitants, located at the northern edge of the park has a little harbor for commercial activities.

Sample collection

Samples of bivalve mollusks (7 sites) were collected in April 2010, while surface sediments (7 sites), bivalve mollusks (5 sites), and three species of gastropods (*Pareuthria plumbea*, *Trophon geversianus*, and *Buccinanops globulosus*) (5 sites) were sampled in October 2010 (Table 1, Figure 1).Samples were designed by a lower case *s* o *b* denoting sediment or bivalve, respectively, and for bivalves by *S* (spring sampled in October) or A (autumn sampled in April) following the sample site. (e.g. S2(b, A) meant bivalve sampled in Autumn in site S2 while S3(s) meant sediments sampled in October in site S3). Sampling stations were located close to sites with some probable anthropogenic influence (S1, S2, and S3), and areas without direct exposure to human influence (S4, S5, S6, and S7) (Table 1). Sediment was obtained close to mussel beds using ten acrylic corers (4.5 cm i.d. x 30 cm length) per station and covering a surface of around 50 m^2. The superficial sediment layers (5 cm) of each corer were mixed and homogenized in a composite sample. Bivalve mollusks (*Mytilus edulis* or *Aulacomya atra atra*, depending on the site) were removed by hand from the rocky substrate bordering to the soft sediment (~100 individuals per site). The soft tissue of 30-40 individuals of similar size (~5 cm) was blended to form a composite sample. Samples were stored in glass flasks at –20°C until its analysis. Specimens of gastropods were taken and kept alive in the laboratory until imposex measurements.

Sediment and organism characterization

Sediment sub samples were used to determine moisture, organic matter and granulometry. Dry sediment was sieved (20 min) into gravel (>2 mm), sand (2-0.063 mm), and fine fractions (silt-clay, <0.063 mm). Moisture was obtained by weighting the sediment before and after dried for 48 h at 105 °C, and organic matter by ignition loss of dry sediment (4 h at 450 °C) in a muffle furnace. Total lipid content (TLC) and condition index (CI) were measured in bivalve mollusks. TLC was analyzed as it was described in Niencheski and Fillmann [19] and expressed as a percentage of tissue weight. CI was determined according to the formula: CI = weight of soft parts (g)/valves lenght^3 x 100 [20]. Imposex in gastropods was calculated as: %imposex = (number of females with imposex/number of total females) x 100 [21].

Sample analysis

Butyltins (TBT, DBT, and MBT) extraction, derivatization, clean-up, and chromatographic analysis were performed according to Castro et al. [22].

Identification and quantification of analytes was conducted in a Perkin Elmer Clarus 500MS gas chromatographer equipped with a mass spectrometer detector, auto sampler, and an Elite-5MS (5% diphenyl- 95% dimethylpolysiloxane) capillary column (30 m x 0.25 mm x 0.25 µm film thickness). Gas carrier was helium ultra-pure at 1.7 mL min^{-1} flow. Oven program was as follows: 80ºC (2 min) and a rate of 11 °C min^{-1} increasing to 300 °C (10 min). Injector (split mode) temperature was maintained at 280ºC. MS operating conditions were: interface 280 °C, ion source 200 °C, and electron energy 70 eV. Identification of compounds was based on its mass spectra and retention times in comparing to NIST library and authentic standards. Quantification was made using the single ion monitoring (SIM) mode. Tripropyltin was used as surrogate standard and tetrabutyltin as internal standard. Biodegradation Butyltin Index (BDI), which gives information about age pollution, was calculated as (DBT+MBT)/TBT. The predominance of TBT over its metabolites indicates a recent input of TBT through the water column, while the predominance of DBT and MBT indicates a past discharge [23].In addition, the degradation rate defined as %BTsdegr= [1-(TBT/TBT+DBT+MBT)] x

100, was used to estimate the amount of TBT being degraded in the environment. Polyaromatic hydrocarbons and organochlorine analysis in sediment and biota including extraction, clean-up, fractionation, and chromatographic analysis were performed as described in Niencheski and Fillmann [19]. PAHs identification and quantification was performed in a gas chromatograph/mass spectrometer (Perkin Elmer®Clarus 500 – GC-MS) supplied with an Elite-5MS silica capillary column (5% diphenyl-95% dimethylpolysiloxane; 30 m x 0.25 mm x 0.25 µm film thickness).The injector was kept at 280 °C in splitless mode. The oven temperature program started at 40°C, increasing at 10°C min^{-1} until 60°C and then at 5°C min^{-1} to 290°C (5 min); finally, at 10°C min^{-1}until 300°C (10 min). Helium was used as carrier gas (1.5 mL min^{-1}).MS operating conditions were: interface 290 °C, ion source 200 °C, and electron energy 70 eV.

The following PAHs were analyzed: Naphthalene (Naph), 1-Methyl Naphthalene (1-MNaph), 2-Methyl Naphthalene (2-MNaph), 2,6-DiMethyl Naphthalene (2,6-DMNaph), 1,7-DiMethyl Naphthalene (1,7-DMNaph), Acenaphthylene (Acl), Biphenyl (Bph), Acenaphthene (Ace), Fluorene (Fl), Dibenzothiophene (DBT),Phenanthrene (Phe), Anthracene(Ant), Fluoranthene (Flt), Pyrene (Pyr), Benzo[a]anthracene (BaA), Chrsene (Chr), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[e]pyrene (BeP), Benzo[a]pyrene (BaP); Perylene (Pe), Indeno[1,2,3cd]pyrene (IP), Dibenz[a,h]anthracene (DBA), Benzo[ghi]perylene (BP). Results were expressed as the sum of the 16 USEPA priority PAHs (ΣPAHs (16)) and sum of 24 PAHs (ΣPAHs (24)). Parental PAHs included the two to six ring polycyclic aromatic hydrocarbons m/z: 128 (Naph), 178 (Phe/Ant),166 (Fl), 202 (Pyr/Flt), 228 (Chr/BaA), 252 (BbF, BeP, BaP), and 276 (IP, BP). Compounds identification was based on individual mass spectra and retention times in comparison to NIST library and authentic standards. *p*-Terphenyl-d_{14} was used as surrogate standards and naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, Chrsene-d_{12} , and perylene-d_{12} as internal standards. Organochlorines identification and quantification was conducted on a Perkin Elmer Clarus 500 gas chromatograph equipped with a ^{63}Ni electron capture detector (ECD), an autosampler, and an Elite 5 - Perkin Elmer® capillary column (5%

diphenyl 95% dimethylpolisiloxane; 30 m x 0.25 mm x 0.25 μm film thickness) capillary column. The oven temperature program started in 40 °C increasing at 5 °C min^{-1} to 290 °C (10 min) and at 10 °C min^{-1} until 300 °C (10 min). The injector and detector temperatures were 280 °C and 300 °C, respectively. The oven temperature program started at 40°C, increasing at 10°C min^{-1} until 60°C and then at 5°C min^{-1} to 290°C (5 min); finally, at 10°C min^{-1} until 300°C (10 min). Helium was used as carrier gas (1.5 mL min^{-1}) and N_2 as make-up gas (30 mL min^{-1}). Splitless mode was used, and after a minute was changed to split flow (50:1).

The OCPs determined were: HCHs (α-, β-, γ-, and δ-hexachlorocyclohexane); HCB (hexachlorobenzene); cyclodienes group (aldrin, endrin, dieldrin, endrin ketone, heptachlor, heptachlor epoxide, α- and γ-chlordane, trans- and cis-nonachlor); DDTs (dichlorodiphenyltrichloroethane, DDT; dichlorodiphenyldichloroethylene, DDE; dichlorodiphenyldichloroethane, DDD); Endosulphans (endosulphan I, endosulphan II, endosulphansulphate); and Mirex. PCBs congeners analyzed were: 17, 18, 31, 28, 33, 52, 49, 44, 74, 70, 95, 101, 99, 87, 110, 82+151, 118+149, 153+105+132, 138+158, 187, 183, 128, 177, 171, 156, 180, 191, 169, 170, 199, 208+195, 194, 205, and 206.Compounds identification was based on GC retention times in comparison to authentic standards, while its confirmation was done on a gas chromatograph Perkin Elmer Clarus 500 with mass spectrometry detector (GC-MS). In the present work seven PCB congeners were selected as indicator PCBs according to Baars et al.[24]: 28, 52, 101, 118, 138, 153, and 180. PCBs 28 and 118 are mono-ortho PCBs, while the others have two chlorine atoms on the ortho-positions.

Quality Assurance and Quality Control

The quality assurance and quality control for BTs, PAHs and organochlorine analyses was based on regular analyses of method blanks, spiked matrices and, whenever available, reference material (RM) and certified reference material (CRM) processed with the samples [25]. The laboratory at which the samples were analyzed participates semiannually in an inter-laboratorial comparison exercise promoted by the Canadian Association for Laboratory Accreditation Inc. (CALA) and has

obtained satisfactory results for PAHs and PCB analyses in sediment samples. In addition, analytical procedures were previously validated according to SANCO [26]. The limits of detection (LOD) for each procedure were calculated based on the parameters of the analytical curve of seven sediment or tissue samples containing the target compounds at a level of one to five times the expected LOD[27].Concentrations found in the procedural blanks were never greater than three times the detection limit and were subtracted from respective samples.

Butyltins. For sediment and tissue analyses, the analytical curves were made using the matrix addition technique and LODs were 0.2, 0.7, and 0.9 ng (Sn) g^{-1} for TBT, DBT and MBT in sediment, and 1.0, 1.0, and 1.5 ng (Sn) g^{-1} for TBT, DBT and MBT in tissue, respectively. The matrices recoveries ranged between 78% and 107% and RSD were below 20% [28]. Results obtained for the CRM of marine sediment PACS-2/ National Research Council of Canada, Ottawa, Canada (TBT - 852 ± 47 ng (Sn) g^{-1}; DBT - 1035 ± 35ng (Sn) g^{-1} and MBT - 557 ± 38 ng (Sn) g^{-1}) were in good agreement with the certified (TBT – 890 ± 105 ng (Sn) g^{-1} and DBT - 1047 ± 64 ng (Sn) g^{-1}) and reported values (MBT - 600 ng (Sn) g^{-1}) (based on 5 independent analysis). All concentrations are reported as ng (Sn) g^{-1} on a dry weight basis (dw).

PAHs. Limits of detection (LOD) for the individual compounds varied between 0.003-0.013 and 0.02-0.10 ng g^{-1} for sediments and tissues, respectively. The matrices recoveries varied between 72% and 118% for sediments and 71% and 111% for tissues. Results in the RM of marine sediment IAEA-417 (International Atomic Energy Agency, Viena, Austria) and RM of fish homogenate IAEA-406 (International Atomic Energy Agency, Viena, Austria) were in good agreement with the certified values and recoveries varied between 71 and 112% and 72 and 117%, respectively (n = 5). Concentrations are expressed as ng g^{-1} on a dry weight basis (dw).

Organochlorines. LODs varied between 0.0005 and 0.0006 ng g^{-1} for OCPs and 0.0005 and 0.0010 ng g^{-1}PCB for sediments; while for organisms LODs varied between 0.004 and 0.005 ng g^{-1} for OCPs and 0.004 to 0.008 ng g^{-1} for PCBs. Spiked matrices recoveries varied between 69% and 119%

for sediment and tissue. Results in RM IAEA-417 (marine sediment) and IAEA-406 (fish homogenate) were in good agreement with the certified values with recoveries between 74 and 107% for OCPs and 76 and 98% for PCBs in sediments; and between 71 and 111% for OCPs and 70 and 96% for PCBs in fish homogenate (n = 5). Concentrations are expressed as ng g^{-1} on a dry weight basis (dw).

Principal Components Analysis (PCA)

The concentration of organic pollutants in sediment and organisms were analyzed separately by type of compounds in the PCA: For BTs, a data matrix comprising 17 rows (sampling sites) and 5 column variables (TBT, DBT, and MBT concentration and BDI and %BTsdeg indices) was used (Table 2). For samples with DBT and/or MBT concentration below LOD, BDI and %BTsdeg indices were calculated using LOD/2 for PCA analysis. For PAHs, the data matrix was constructed with 14rows (sampling sites with at least one compound determined above the LOD, Table 3) and 16column variables containing compounds that were found in more than 10% of the cases [29]:Methyl-naphthalenes (MNaphs = 1-MNaph+2-MNaph+2,6-DMNaph+1,7-DMNaph) and the individual concentrations of Acl, Bph, Ace, Fl, Phe, Ant, Flt, Pyr, Chr, BbF, BkF, BeP, BaP, Pe, and DBA. PCBs were analyzed grouping concentration by the number of chlorine substituents being the data matrix comprise by 19 rows (sampling sites)and 5 column variables with concentrations of: trichloro-; tetrachloro-; pentachloro+hexachloro-; heptachloro-; and octachloro+nonachloro-PCBs (Table S4). OCPs were analyzed grouping the concentrations by compound families being the data matrix comprise by 16 rows (sampling sites) and 7 column variables with concentrations of: HCHs, HCB, DDTs, Chlordanes, DRINs, Endosulfans, and Mirex (Table 4). The sites in which all compounds concentrations were non-detectable were eliminated from the PCA. The data were standardized to unit variance prior to PCA analysis. Concentrations detected below the LOD were assumed to be equal to half of the LOD of the corresponding analyte, for both sediments and organisms samples [7, 30]. PCA analyses were performed using the Multi-Variate Statistical Package version 3.13b (MVSP®, Kovach Computing Services, USA).

RESULTS AND DISCUSSION

Sample Characterization

Sediment granulometry showed predominance of sand particles (76.4 ± 10.3%, n = 7) with lower contribution of fine material (21.1 ± 9.7%, n = 7) and gravel (2.5 ± 3.7%, n = 7) (Table 1). OM ranged from 0.6 to 4.5% (Table 1) and correlated positively with fine sediment particles (r^2 = 0.861, $p<0.05$, n = 7). The TLC varied according to the month in which the bivalves were sampled, being significantly higher ($p <0.01$) in autumn (2.0 ± 0.2%, n = 7) than in spring (1.1 ± 0.2%, n = 5). Instead CI was not significantly different in autumn (0.34 ± 0.05; n = 7) and in spring (0.39 ± 0.05; n = 5). No significant differences were found in CI nor in TLC between species ($p>0.05$). Massara Paletto et al. [31], reported similar lipid (0.9 ± 0.17%, n = 6) and CI (0.32) values, for *Aulacomya atra atra* sampled in November (spring) in Nueva bay (42.75° S-65.00° W), than those found in the present study for bivalves of the NZ-SJG. The TLC decrease found between autumn and spring samples, close to 1%, may be associated to lipid loss by bivalves' partial spawning [31]. The correlations between CI and TLC for both seasons were r^2 = 0.968 (n = 7) and r^2 = 0.849 (n = 5), respectively; indicating the same behavior for all the bivalve mollusks sampled along the NZ-SJG.

Butyltins

BT levels in surface sediment and in bivalve mollusks varied between <LOD and 166.5 and between 29.4 and 206.0 ng (Sn) g^{-1}, respectively, with presence of TBT in all but one sampled site (Table 2). MBT, which concentration ranged from <LOD to 132 ng (Sn) g^{-1}, was the most abundant metabolite in sediments contributing 76% to total butyltins (ΣBTs) denoting degradation processes of TBT, whereas DBT levels were <LOD for all sediment samples. The highest level of BTs was found in S1, the port of Camarones town, in agreement with BTs increased concentrations reported with ports and traffic maritime proximity [21].TBT levels, excluding S1, were positively associated with the sediment fine material (r^2=0.775, $p<0.05$, n=6); while, r^2 value was 0.066 when S1 was included indicating that fishing and port activities are TBT point sources coming from ships' antifouling paints.

In addition, TBT levels were relatively high in bivalves from S1, both in autumn and spring, which was the only place where imposex (15% of incidence) was found in the gastropod *P. plumbea.* In the other assessed species, *Trophon geversianus* and *Buccinanops globulosu*s, imposex was not detected probably due to the relatively low level of TBT. In fact, Bigatti et al. (2009) [21] reported that *Trophon geversianus* only presents imposex in high TBT polluted areas while *Buccinanops globulosus* is an indicator of medium TBT pollution[32]. BTs discrete pollution was also reflected in S3(s) (Sara creek), where small fishing boats operate. PCA analysis for BTs concentration and degradation indices showed that the first three principal components (PC) explained 94.9% of the total variance (Figure 2A). The PC1 may be interpreted as the fresh-old BT inputs: fresh inputs associated with positive values on the PC1 axis (0.53 TBT loading) and metabolite presence with negative values on the PC1 axis (-0.59 %BTsdegr loading, Figure 2A). PC2 had a positive association with BTs concentrations, thus samples were distributed from lower BT levels at negative values to higher levels at positive values along PC2. Most sediment, besides some of them with low concentrations, distribute along the negative axis of PC2 according to its more degraded BT composition (Figure 2). S1(s), S3(s) and S2(b,A) (indicated in a circle in Figure 2A), samples with the highest degradation indices (79-88% %BTsdegr), were taken from sites with human activity (two little harbors and a bivalve culture). In general, values of BDI and %BTsdegr for sediments in the rest of the sites indicated a past discharge of TBT (Figure 2A), except for S6(s), where TBT was only detected in sediments, suggesting a recent input of this compound probably associated to small boats operating in this zone. In general, bivalves were grouped at the positive PC1 axis, according to its fresher BTs content in all sites and %BTsdegr relatively low, denoting fresh TBT inputs, except for S2(b,A) and S4(b,A) (autumn) (Table 2). These sites showed the lowest BTs concentration and the higher %BTsdegr (88 and 59%), suggesting that the organisms of these sites suffered an old and relative low exposition to BT compounds and accumulated the pollutant by filter feeding.

Despite anthropic activities developed in the NZ-SJG coastal zone are scarce, TBT and its metabolites were found in all sampled sites. In S1 and S3, the occurrence of BTs may be related to port activities; while in the other sites could be associated to commercial and industrial fishery fleets that operate along the gulf. Since, TBT has low volatility [33] point or relatively point sources may be expected. TBT levels were relatively low in sediments, while in bivalves they were at least one order of magnitude higher than in sediments of the same site, except for S1 (Table 2). This fact indicated bioaccumulation in organisms through the intake of re-suspended bottom sediments and/or suspended particles from the water column. MBT and DBT predominated in sediments, while TBT was most prevalent in bivalves, probably associated to metabolism of this compound. Shim et al. [34] found higher levels of TBT than DBT and MBT in bivalves. These authors reported that the composition of TBT, DBT, and MBT in biota results from the extent of fresh input of TBT into receiving waters, the distribution of these chemicals in the uptake sources including surrounding water and food of organisms, the metabolic capacity of the organisms, and the fate of TBT and its degradation products in the study area. Horiguchi et al. [35], reported for bivalves mollusk from Vancouver and Victoria (Canada) that TBT was the most predominant in almost all bivalve specimens surveyed, suggesting a low rate of metabolism of TBT in these bivalve species. In addition, Wade et al. [36] indicated that once the mussel takes up TBT it may take months to depurate back to background levels and that in general, the order of body burden of the Butyltin species is TBT > DBT > MBT. Bivalves, unlike fish and other species, are generally deficient in degradative enzymes such as microsomal oxidases and mixed-function oxidases which are responsible for the degradation of organic contaminants. Therefore, bivalves can serve as integrators and bio monitors of pollutants [37]. Chandrinou et al. [38] reported that TBT was predominated among Butyltin species in Mediterranean mussels and scallops, reaching 47% and 48% of BTs, respectively, implying low metabolic activity toward TBT in these species. These values confirm the presence of TBT as dominant species in scallops and mussel tissues [39-41],

as well as that *Mytilus galloprovincialis* has a limited ability to metabolize TBT to DBT and MBT [42-44].

Presence of TBT in sediments and organisms of the coastal zone indicated the current use of antifouling paints based on Butyltin, despite the ban of use that exists in Argentina and worldwide. Information on BT levels in sediments is scarce in the Argentinean coast (>5000 km), and even more in marine organisms. Delucchi et al. [45] reported TBT and DBT levels in sediment from the inner zone of Bahía Blanca estuary, a heavily industrial zone with port activities, ranging from *nd* to 170.3 and from *nd* to 75.2, respectively, while the highest concentration (3,288 and 1,645 ng (Sn) g^{-1} for TBT and DBT, respectively) was found close to a dry dock port (Puerto Belgrano). Bigatti et al. [21] reported TBT levels ranging from *nd* to 1370 ng (Sn) g^{-1} along the Argentinian shoreline. These authors found 1.5 ng (Sn) g^{-1} of TBT in Camarones harbor in 2008 (41% of imposex in *P. Plumbea*) and 5.6 ng (Sn) g^{-1} in Sara creek (8% of imposex in *P. Plumbea*). In the current study, TBT levels were in general lower than those reported in Bahía Blanca estuary and the Argentinian shoreline, reflecting scarce anthropic influence in the NZ-SJG, although in S1 the concentration was slightly higher than those found by Bigatti et al. [21]. In general, BT levels reported in this study were in a similar order of magnitude compared to values reported by other authors worldwide (Table S1).

Polyaromatic Hydrocarbons

In sediments, total PAHs (∑PAHs(24)) ranged from <LOD to 157.7 ng g^{-1}, while USEPA priority PAHs (∑PAHs (16)) ranged from <LOD to 94.9 ng g^{-1}. PAHs were not present only in S7. Naphthalene was not detected in any sample, while its alkyl derivatives were found in bivalves and sediments (Table 3). All target PAHs were found in S1 (Camarones harbor), generally with a higher level for each compound than those determined in the other sites (Figure 3, Table 3). No correlation between PAH levels and OM or sediment fine particles were found. In bivalve mollusks, ∑PAHs(16) ranged from <LOD to 54.9 ng g^{-1} and from <LOD to 12.5 ng g^{-1} in individuals collected in autumn and spring, respectively; while for ∑PAHs(24) values ranged from <LOD to 83.0 ng g^{-1} and from <LOD to

27.2 ng g^{-1} (Table 3). Bivalves taken in different seasons showed different compositions of PAHs. In autumn, 1- and 2-MNaph, 1,7-DMNaph, Biph, Fl, Phe, Ant, Pyr, Chr, BbF, BkF, BeP, BaP, and Pe were found and highest concentration of ∑PAHs(16) was registered in S5(b, A), followed by S1(b,A) and S2(b,A) sites. In spring, Fl and Pe were the only present compounds in two sampling points and in levels lower than in autumn (Table 3). Compositional indices in sediments such us the high to low molecular weight PAHs content HMW/LMW (HMW, four to six rings, LMW, two to three rings); Phe/Ant ratio, Flt/Pyr ratio, and IP/IP+BP has been used to discriminated sources related to fuel-combustion (pyrolitic) or crude oil (petrogenic) contamination, respectively (e.g. [46, 47]). Compositional indices calculated for NZ-SJG sediments and bivalves and their references values are given in Supplemental data (Table S2). The PCA of PAHs concentration in sediments and bivalves is shown in Figure 2B. The first three PC explained 80.8% of the total variance. PC1 (42.0%) showed a positive association with MNaphs and the LMW PAHs (Biph, Acl, Ace, DBT, and Phe), and also with the HMW BaA, IP, BP, and in a minor extent with Chr, BbF, BkF, and DBA, denoting an association with petrogenic and pyrolitic PAHs along the positive axis of PC1. PC2 (25.8 %) showed a positive association with Fl, Pe, and the HMW BbF, BkF, BeP, and BaP and a negative association with Phe, Ant, Pyr and Chr. Thus, PC2 represent pyrolitic and diagenetic PAHs at positive values and petrogenic PAHs at negative values. Sediments and bivalves with low PAH contents (ranging from <LOD-37 ng g^{-1}) were grouped near zero in the PC1 vs. PC2 graph (see circle in Figure 2B). This group includes: S3(s)-S6(s) sediments and S1(b,A), S3(b,A), S4(b,A), and S6(b,A) bivalves with a mix of PAHs sources; pyrogenic and petrogenic supported by the compositional indices (Table S2). Sediment at Camarones harbor (S1(s)), and from S2(s) to a minor extent, separated from other sites on the PC1 axis, indicating increasing petrogenic and pyrogenic content. Compositional PAHs ratios were in agreement with the PCA analysis. In S1, MNaphs contribute 26% of the total PAHs (Figure 3) suggesting relatively fresh petrogenic input associated with port activities. S5(b,A) separate at positive values in PC2 due to HMW content, indicating pyrogenic hydrocarbon input in mollusks from Melo and the

highest Pe content that was found for S5(b,A) and S3(b,S) bivalves. Perylene contributed to the sediment un-substituted PAHs with a nearly constant level (2 to 3 ng g^{-1}) in all the sites, except for S7 (Table 3). Correlation between Pe and total PAHs was not found, indicating quite different distribution probably due to a biogenic terrigenous source for this compound. An abundance of Pe>10% of parent PAHs in S3(s), S4(s), S5(s), and S6(s), and particularly in S5(b,A)(19%) and S3(b,S) (55%), is indicative of diagenetic process [48]. The *in situ* diagenetic perylene formation from terrigenous precursors seem to be suitable, such us from *Salcocornia* sp. and *Spartina alterniflora,* which constitute large coastal grassland. S2(b,A), at the negative PC2 axis (Figure 2), showed a mixed origin as it was found in sediments.

For PAHs (∑PAHs(16)), according to sediment pollution levels assigned by Baumard et al. [49], stations S2(s), S3(s), S4(s,) S5(s), and S6(s) were slightly polluted (less than 100 ng g^{-1}), while S1(s) (Camarones, 95 ng g^{-1}) was close to the lower limit assigned for moderately contaminated sites (100 to 1000 ng g^{-1}). A comparison of individual PAH levels found in sediments from NZ-SJG with Sediment Quality Guidelines (SQGs) [50-52] (Table S3), showed that Acl in S1(s) and Ace and DBA in S2(s) were found over the TEL, representing a toxicological health concern to aquatic organisms. However, none of the compounds presented values close to the probable effects level (PEL); therefore, biological toxic effects to aquatic organisms are not expected. In addition, ΣPAHs(16) were below TEL values. Levels of ∑PAHs (16) in bivalve tissues reached up to 54.9 ng g^{-1} (S5(b,A), Melo bay), considered low polluted (parent ∑PAH <100 ng g^{-1} [49]); and typical for locations distant from contaminant sources. In general, the compositional PAHs pattern was different in sediments and bivalves from the same site (Table 3), suggesting that bivalves were not directly exposed to pollutants adsorbed onto bottom sediment, but they may incorporate hydrocarbons through suspended particles from the water column by filtering feeding. In addition, different patterns may result from biodegradation processes in sediment and metabolism in bivalves. PAH levels in sediments and

organisms reported in this study were generally lower or of similar magnitude than values reported by others locations in South America (Table S5).

Organochlorinated compounds

OCPs. In sediments, ΣOCP values ranged from 0.20 to 1.23 ng g^{-1} (average 0.53 ± 0.34 ng g^{-1}; n = 7). In organisms, ∑OCPs ranged from <LOD to 0.21 ng g^{-1} in autumn bivalves (average 0.06 ± 0.09; n = 7) and between <LOD and 0.22 ng g^{-1} (average 0.12 ± 0.08; n = 5) for those sampled on spring, being the total pesticide levels not significantly different in both months. The OCP compounds in bivalve mollusks and sediments showed different patterns (Figure 4), and no correlation between sediments OCP concentrations and OM was evident. PCA carried out when analyzing the concentrations of the families of compounds in sediment and organism showed three differentiated groups: S1 Camarones sediments, others sediment sites, and organism sites (Figure 2). The first three components of PCA explained 82.6% of the total variance (PC1 37.9%; PC2 25.2%; and PC3 19.5%). Camarones sediments were more strongly associated with cyclodienes and DDTs content, the others sediments were associated with HCHs, HCBs, and mirex, while bivalves mollusks were associated mainly with CHLs (Figure 2). This fact may be due to different input pathways such as OCPs incorporation in organisms directly from the water column suspended particles while being transformed in sediments. DDT and HCH families occupied the largest percentage of OCPs in sediments. This agrees with their extensive use worldwide [53]. P-p' DDT was only found at S4(s) (10 pg g^{-1}), together with its metabolites o,p-DDE and p,p'-DDD (70 and 10 pg g^{-1}, respectively). P-p'-DDD was present in five of the seven sediment stations constituting 96% of the total DDTs (Table 4). Thus, the DDTs contribution likely entered sediments via atmospheric transport, taking into account that DDT was withdrawn in Argentina since 1990, agricultural areas are at least 1000 km distant away from the studied zone, and that the under-representation of DDT vs its metabolites is indicative of historical contributions rather than a recent inputs [54]. The dominance of DDD respect DDE metabolite is an indicative of anaerobic conditions in sediments, except for S6(s), since the degradation pathway of

DDT in sediments is redox potential dependent, and a predominant reductive dechlorination of DDT to DDD happen under redox anaerobic conditions, while DDE is the main metabolite under oxic conditions [55]. In addition, the p,p'DDT presence and the DDD/DDE ratio likely reflect poor degradation of DDT more than a fresh input of DDT in S4. HCHs (α, β, γ, and δ isomers) constituted 26% of total OCPs with a distribution of 38.9% β-HCH, 29.2% γ-HCH, 19.9% δ-HCH, and 12.0% α-HCH. Therefore, the dominant isomer was β-HCH, which is the HCH isomer with the lowest water solubility and vapor pressure, and the most stable and resistant to microbial degradation. These properties may account for higher levels of this isomer in some sediment [56]. Technically HCH, used for agricultural purposes, generally contains α-HCH 55-80%, β-HCH 5-14%, γ-HCH 8-15%, and δ-HCH 2-16% [57].β-HCH may come from environmental transformation of the α-HCH isomer after this suffered air partition and long transport, principally in the atmosphere. In fact, α-HCH has higher values of Henry's law constant and vapor pressure than β-HCH and γ-HCH, indicating a greater efficiency by atmospheric transport of α-isomer than others [58]. In NZ-SJG, the largest contribution of β-HCH in sediment suggested that HCH input is not recent. As in the case of the DDT family, only in S4 did the α-HCH isomer have a greater concentration value than in the other sites, suggesting poor transformation of α in the β isomer or a fresh input of HCHs in this area. According to Kim and Smith [59], the α-HCH/γ-HCH ratio, whose value is between 4 and 7 in commercial grade HCH, is relatively stable and can be used as an indicator of degradation rate or current use of commercial HCHs. In this study, values for this ratio were between 0.0 and 0.8 (S3 to S7) indicating weathering processes of α-HCH in other HCH isomers. Although the γ-isomer was not present in S1 and S2, β- and δ-isomers had greater concentrations than the α-isomer, confirming aged input of HCHs in these two sites. Lindane levels ranged from <LOD to 110 pg g^{-1} (S4, Table 4), not exceeding the threshold effect level of 320 pg g^{-1} [60]. Other light OCPs such as HCB were measured at S4, reaching the highest level of 190 pg g^{-1}. The sum of HCHs and HCB reached 39.6% of OCPs in sediments, compounds strongly associated with atmospheric transport. Among cyclodienes, aldrin was the most abundant with ~50% of the total

corresponding to this group (Figure 4). Aldrin had higher concentration in S1 (170 pg g^{-1}) than in the other stations (20±2.2 pg g^{-1}). Endrin was found in two sites (Table 4), while dieldrin and endrin ketona were not detected at any station. Endosulfan I was found in three locations (S1, S2, and S3), while their derivatives, endosulfan II and endosulfan sulphate were not detected. In commercial endosulfan, the isomers I and II are normally present in a ratio 7:3 which could explain the absence or lack of detection of the II isomer. In addition, the absence of endosulfan sulphate suggested a recent incorporation of the insecticide endosulfan. Mirex, a widespread insecticide and flame retardant additive, contributed with 15.3% to ∑OCPs, and it was found in five of the seven stations, reaching a maxim value of 180 pg g^{-1} at S5(s). This compound, banned in Argentina in 1999, has half-life in soils up to 10 years, thus it is possible a recent entry of this pesticide in the NZ-SJG. Other pesticides, heptachlor, heptachlor epoxide, γ- and α-chlordane, and trans-nonachlor, were detected in very low levels, therefore representing little environmental concern in the study area (Table 4). The OCP distribution in organisms showed a greater contribution of heptachlor both in autumn and spring (44.8 and 63.6%, respectively), followed by Endosulfan I (21.3 and 24.7%, respectively). Another contribution to ∑OCPs was done in April by δ-HCH (13.6%), endrin ketona (11.1%), mirex (5.8%), and p,p-DDE/o,p-DDD (3.9%), while in October dieldrin (6.4%), p,p-DDE/o,p-DDD (1%), and endrin ketona (1%) (Figure 4) were found. The HCH family was represented only by δ-HCH (60 pg g^{-1}) in S2 in April. P,p-DDE/o,p-DDD were present in both sampled months but in different sites: S2 on autumn and S7 on spring. DDT was not detected in bivalve mollusks, indicating the metabolization of this compound by organisms or a preferential accumulation of DDE and DDD. Cyclodienes were represented by endosulfan I, dieldrin, and endrin ketona. Levels in bivalve mollusks were lower than those found in sediments, suggesting no OCPs accumulation. A comparison of OCP levels with other sites in South America and Antarctica has shown that sediments from NZ-SJG had little contamination while organisms had low levels of these POPs (Table S5).

PCBs

The ΣPCB average in sediments and bivalves was 0.58±0.88 ng g^{-1} (n=7) and 0.42±0.26 ng g^{-1} (n=12), respectively (Table 4). PCB is a family with 209 congeners, from which 12 of them are considered "dioxin-like" compounds (DL-PCBs). These compounds were widely studied due to their toxic effects, mostly related to their binding and activation of the aryl hydrocarbon receptor (AhR) signal transduction pathway [61]. In sediments, ΣPCBs ranged between 0.08 and 2.56 ng g^{-1} (n=7), and the highest concentration was found at Camarones harbor(S1) (Table 4). For the other sites, the average value was 0.25±0.14 (n=6) ng g^{-1}. The largest contribution to total PCBs was done by congeners 138+158 (19.5%), 153+105+132 (14.5%), and 87 (14.5%) (see individual PCBs composition in Table S4). No correlation between ΣPCBs vs. OM% or between ΣPCBs vs. fine sediment content was found, even excluding the S1 station. Not significantly differences were found between the average level of ΣPCBs in organisms (0.42±0.26 ng g^{-1}) and sediments (0.58±0.88 ng g^{-1}), nor between autumn (0.53±0.27 ng g^{-1}; n=7) and spring (0.27±0.17 ng g^{-1}, n=5) bivalves. These results indicated that there was not a bioaccumulation process taking place in sampled biota. In both seasons, the predominant congener was PCB-87, which contributed with 47 and 50%; respectively, to the ΣPCBs. PCA was performed in order to observe PCBs distribution considering its concentrations grouped by the degree of chlorination (Figure 2 and 5). The first three PCs explained 85.5% of the total variance. PC1, accounting for 41.3% of the total variance, was negatively associated with the five to seven chlorinated PCBs, while the positive axis was weakly associated with the lower chlorinated PCB congeners content (tri- and tetra-chlorobiphenyls). Thus, the PC1 may be interpreted as the volatile – less volatile PCBs content for sites that are distributed from right to left along the PC1 axis. PC2 (30.6%) was negatively associated with octa-+nona-chlorinated PCBs and positively associated with the tri- and tetra-chlorinated congeners. Then PC2 also describes the volatile to less volatile PCBs from top to bottom in the PC1 vs. PC2 space. As can be seen in Figure 2, samples are separated in three groups: Camarones harbor sediments (S1), where the highest PCB concentration with penta- to hepta- congeners dominance was found; S4 and S5 sediments, with low total PCB content (0.32-0.48 ng g^{-1}), with

dominance of the lower chlorinated congeners; and a third group generally characterized by sediments and organisms with low ΣPCB content (0.10-0.81 ng g^{-1}), with penta- to heptachloro-congeners dominance and octa-+nona-chlorinated PCBs presence, but in very low concentrations (<LOD-0.03 ng g^{-1}). From the 4 DL-PCBs assessed in this study (156, 169, 105, and 118), PCB-169 was not detected either in sediment nor in organism samples; PCBs-156 was only detected at low levels in Camarones harbor (0.02 ng g^{-1}) and in S5(b,A), S7(b,A) and S2(b,S) ranging from 0.01 to 0.11 ng g^{-1} (Table S4). While the presence of PCB-105 in S1(s) and S5(b,S) and PCB-118 S1(s), S1(b) and S2(s) was only suspected due to the congeners co-elution in the CG-ECD analysis.

In summary, PCB levels in the NZ-SJG were fairly low by global standards for near-shore sediments and organisms (Table S5), and even the maximum concentration found in S1(s) (2.6 ng g^{-1}) was near one order of magnitude lower than the SQG TEL value of 21.6 ng g^{-1} [50]. Therefore, biological toxic effects to aquatic organisms are not expected. The low PCB level found together with the large distances from the studied sites to point PCB sources suggested that the main contribution of these compounds was through global transport. Only at Camarones harbor (S1(s)) a different point input was suggested by PCBs dissimilar pattern in comparison with the other places. Low levels found in this mid-latitude environment of the southern hemisphere were similar to those found in remote sites as Antarctica (Table S5). Moreover, the chlorinated distribution found in the current study site agrees with possible Arochlor 1242, 1254, and 1260 mixtures (Figure 5). The general dominance of congeners with five to seven chlorination degrees found is consistent with the expected volatility and preferential deposition and accumulation of PCBs at mid-latitude [9].

OCP, PCB, AND PAH LEVELS IN COASTAL SEDIMENT FROM SOUTHERN HEMISPHERE

Despite POPs have been assessed for decades, most available information allows the obtaining of relatively reliable POP inventories and temporal trends of their concentrations in the North Hemisphere, mainly in Europe and USA, as well as in polar regions [15]. However, very few works

have been reported in the Southern Hemisphere, and even less in South America. In consequence, great uncertainties exist in POP concentrations in this region in spite the migration of POPs from source emission zones to the poles have been extensively documented [64].Table S5 (Supplemental data) summarizes levels of OCP, PCB, and PAH in coastal sediments from South America and Antarctica obtained between 1999 (Corsolini et al., 2002) and 2011 (Yoshimine et al., 2012) (see complete references in Supplemental data). The comparison between studies should be considered cautiously, as information was obtained in different years and assessed with different methodologies and research groups. However, it is possible to highlight some points related particularly with HCH and DDT organochlorines.

Lowest reported values for HCHs in coastal sites located within 23º 67' to 63º 51' south latitude were near the LOD of the respective assessment techniques, and the mean highest value was 0.61 ± 0.30 ng g^{-1} (n=5) (Supplemental data, Figure S6). This data were assessed at different times in a near ten-year period in sites considered with low direct anthropic impact (NZ-SJG Patagonia and Antarctica) and sites heavily impacted by industrial and urban activities (San Pablo and Florianopolis in Brazil and Bahía Blanca in Argentina). However, there was no obvious trend at these sites, which suggests that HCH levels in sediments may be quite homogeneous. This fact may be explained by a uniform distribution of these compounds in the atmosphere. In relation to the POPs spatial distribution along the north (52º N)-south (72º S) transect, Dachs et al. (2002) [16] reported that, as expected, the less chlorinated PCBs did not show a decrease in concentration at high latitudes but displayed uniform atmospheric concentrations over the Atlantic Ocean. This could be the case for the HCHs reported in West Atlantic Ocean coastal sediments, which could act as a sink for these compounds coming from the atmosphere. Moreover, HCHs are classified as *swimmer* compounds defined by their partition properties log K_{AW} and log K_{OA}, which means that HCHs have affinity to be transported by oceanic current [65]. However, further research on air and ocean water HCH concentrations is needed to confirm this hypothesis.

DDTs in sediments tended to decrease with increasing latitude, probably due to the different exposure to these compounds, which is greater close main agricultural sources located at tropical sites and lower in distant areas with fewer agricultural activities (Supplemental data, Figure S7). This gradient could be associated to the relatively high value of log Kow (6.91). According to Dachs et al. (2002) [16] concerning the spatial distribution along the north-south transect, the more hydrophobic POPs show higher concentrations at low latitudes than at mid to high latitudes, and higher concentrations in the northern hemisphere, consistent with emission distribution.

PAH concentrations were very variable, so it was not possible to compare among localities. This may be the consequence of the existence of multiple sources for these compounds, which include point, relatively discrete, and remote sources, as reported in Table S5 (Supplemental data). For PCBs, the different number of congeners analyzed in each case difficult the comparison of data. In addition, it was not possible to establish a trend for organisms because of the few reported data and its high variability (Supplemental data, Table S5).

Further research is needed on POP contents in South American marine sediments and organisms to help identify sources and fate of these compounds. The present study reports the first data set on organochlorines, PAHs, and TBTs in a mid-latitude coastal area of great environmental value included in a marine park and recently designated as a biosphere reserve ("Patagonia Azul"; UNESCO, 2015).

CONCLUSIONS

The spatial distribution of BTs, PAHs, OCPs and PCBs was assessed in a mid-latitude environment of the Southern South Atlantic coasts (NZ-SJG). In general, pollutant levels were low comparing with other places worldwide, except for BTs, which showed moderate concentration associated to local sources. PAHs had a predominant pyrogenic origin excluding Camarones harbor, where petrogenic hydrocarbons were found. As crude oil exploitation in the San Jorge gulf is expected to increase, these results will be useful to check the future sediments health. Organochlorinated pollution was clearly related to atmospheric global transport, suggesting that in the studied area, OCPs

and PCBs suffer deposition during their migration to the southern zones. In summary, in the present study, a remote place with very low human settlement showed a low level of organic pollution, likely related with global migration of contaminants. In addition, it constitutes the first assessment of POPs in a Maritime National Park located in a south mid-latitude environment from the Patagonian coastal zone.

SUPPLEMENTAL DATA

Tables S1–S5.

Figures S1–S2. (87 KB DOCX).

Acknowledgment—We are grateful to our workmate H. Ocariz for his valuable assistance in the campaigns and to M. Soriano for their contribution to the logistics in the fieldwork. Financial support was provided by the National Agency for Scientific and Technological Promotion (ANPCyT) - Project PICT 0441 and MINCyT-CAPES bilateral project Argentine-Brazil BR/09/03. Í.B. Castro was sponsored by CAPES (802-16/2012) and FAPERGS (0885/12-1), P. G. Costa by FAPERGS (12/1426-8) and CAPES (23038.028239/2009-69) and G. Fillmann by CNPq (PQ 312341/2013-0). We dedicate this work to H. Ocariz memory.

Data availability— For data please contact Marta Commendatore at commenda@cenpat-conicet.gob.ar.

REFERENCES

1. Convenio de Estocolmo sobre contaminantes orgánicos persistentes. 2009. Secretaría del Convenio de Estocolmo. Programa de las Naciones Unidas para el Medio Ambiente (PNUMA). Pp 60.
2. Pazi I, Kucuksezgin F, Gonul LT. 2011. Distribution and sources of organochlorinated contaminants in sediments from Izmir Bay (Eastern Aegean Sea). *Mar Pollut Bull* 62: 1115-1119.
3. Tolosa I, Mesa-Albernas M, Alonso-Hernandez CM. 2010. Organochlorine contamination (PCBs, DDTs, HCB, HCHs) in sediments from Cienfuegos bay, Cuba. *Mar Pollut Bull* 60: 1619-1624.
4. Cincinelli A, Martellini T, Del Bubba M, Lepri L, Corsolini S, Borghesi N, King MD, Dickhut RM. 2009. Organochlorine pesticide air–water exchange and bioconcentration in krill in the Ross Sea. *Environ Pollut* 157: 2153-2158.
5. Evans SM. 1999. Tributyltin Pollution: the Catastrophe that Never Happened. *Mar Pollut Bull* 38 (8): 629-636.
6. Meador JP, Sommers F, Cooper KA, Yanagida G. 2011. Tributyltin and the obesogen metabolic syndrome in a salmonid. *Environ Res* 111 (1): 50-56.
7. Commendatore MG, Nievas ML, Amin O, Esteves JL. 2012. Sources and distribution of aliphatic and polyaromatic hydrocarbons in coastal sediments from the Ushuaia Bay (Tierra del Fuego, Patagonia, Argentina). *Mar Environ Res* 74: 20-31.
8. Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S. 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry* 33 (4): 489-515.
9. Wania F, Mackay D. 1996. Tracking the Distribution of Persistent Organic Pollutants. Control strategies for these contaminants will require a better understanding of how they move around the globe. *Environ Sci Technol/ News* 30 (9).

10. Lavandier R, Quinete N, Hauser-Davis RA, Dias PS, Taniguchi S, Montone R, Moreira I. 2013. Polychlorinated biphenyls (PCBs) and Polybrominated Diphenyl ethers (PBDEs) in three fish species from an estuary in the southeastern coast of Brazil. *Chemosphere* 90(9):2435-2443.
11. Zhang L, Dickhut R, DeMaster D, Pohl K, Lohmann R. 2013.Organochlorine Pollutants in Western Antarctic Peninsula Sediments and Benthic Deposit Feeders. *Environ Sci Technol* 47: 5643−5651.
12. Arctic Monitoring and Assessment Program (AMAP). 2010. Assessment 2009 - Persistent Organic Pollutants (POPs) in the Arctic. *Sci Total Environ* 408:2851-3051.
13. Bargagli R. 2008. Environmental contamination in Antarctic ecosystems. *Sci Total Environ* 400 (1-3): 212-226.
14. Barra R, Colombo JC, Eguren G, Gamboa N, Jardim WF, Mendoza G. 2006. Persistent Organic Pollutants (POPs) in Eastern and Western South American Countries. *Rev Environ Contam Toxicol* 185:1-3.
15. Lohmann R, Breivik K, Dachs J, Muir D. 2007. Global fate of POPs: Current and future research directions. *Environ Pollut* 150: 150-165.
16. Dachs J, Lohmann R, Ockenden WA, Mèjanelle L, Eisenreich SJ, Jones KC. 2002. Oceanic Biogeochemical Controls on Global Dynamics of Persistent Organic Pollutants. *Environ Sci Technol* 36: 4229-4237.
17. Borghini F, Grimalt JO, Sanchez-Hernandez JC, Barra R, Torres García CJ, Focardi S. 2005. Organochlorine compounds in soils and sediments of the mountain Andean Lakes. *Environ Pollut*136: 253-266.
18. Commendatore MG, Esteves JL, Colombo JC. 2000. Hydrocarbons in coastal sediments of Patagonia, Argentina: Levels and probable sources. *Mar Pollut Bull* 40: 989-998.
19. Niencheski LF, Fillmann G. Contaminantes: Metais, Hidrocarbonetos e Organoclorados. In.: Lana, P.C., Bianchini, A., Ribeiro, C.A.O., Niencheski, L.F.H., Fillmann, G., and Santos, C.S.G. (Ed).

Avaliação Ambiental de Estuários Brasileiros: Diretrizes Metodológicas. Museu Nacional, Rio de Janeiro, RJ. 2006; Cap. 4, P63-118.

20. De Wilde PAWJ. 1975. Influence of temperatura on behaviour, energy metabolism, and growth of *Macoma balthica* (L.). Proc. 9th European Mar. Biol. Symp.: 239-256. Aberdeen Univ. Press.
21. Bigatti G, Primost M, Cledón M, Averbuj A, Theobald N, Gerwinski W, Arntz W, Morriconi E, Penchaszadeh PE. 2009. Contamination by TBT and imposex biomonitoring along 4700 km of Argentinean shoreline (SW Atlantic: from 36ºS to 54ºS). *Mar Pollut Bull* 58: 695-701.
22. Castro I, Arroyo M, Costa P, Fillmann G. 2012. Butyltin compounds and imposex levels in Ecuador. *Arch Environ Contam Toxicol* 62: 68–77.
23. Díez S, Abalos M, Bayona JM. 2002. Organotin contamination in sediments from the Western Mediterranean enclosures following 10 years of TBT regulation. *Water Research* 36: 905–918.
24. Baars AJ, Bakker MI, Baumann RA, Boon PE, Freijer JI, Hoogenboom LAP. 2004. Dioxins, dioxin-like PCBs and non-dioxin-like PCBs in foodstuffs: occurrence and dietary intake in The Netherlands. *Toxicol Letters* 151: 51–61.
25. Wade TL, Cantillo AY. Use of standards and reference materials in the measurement of chlorinated hydrocarbon residues. Chemistry workbook. NOAA technical memorandum. Maryland: Silver Spring; 1994.
26. SANCO. 2009. Method validation and quality control procedures for pesticide residues analyses in food and feed. Document No. SANCO/10684/2009, European Commission. 53 p.
27. Ribani M. 2004. Validação em métodos cromatográficos e eletroforéticos. *Quim Nova*27 (5): 771-780.
28. IUPAC. International Union of Pure and Applied Chemistry (IUPAC technical report). 2002. Prepared for publication by Thompson M., Stephen L., Ellison R., Wood R. Harmonized guidelines for single-laboratory validation of methods of analysis Pure *Appl Chem* 74 (5): 835-855.

29. Liberda EN, Tsuji LJS, Martin ID, Cote S, Ayotte P, Dewaill E, Nieboer E. 2014. Plasma concentrations of persistent organic pollutants in the Cree of northern Quebec, Canada: Results from the multi-community environment-and-health study. *Sci of the Total Environ* 470–471(0): 818-828.
30. Gauthier TD, Hawley ME. 2007. Statistical Methods. In: Introduction to Environmental Forensics, Chap 5 (Second Edition), Murphy BL, Morrison RD (Eds.), Academic Press, Burlington, Pages 129-183,II-III, ISBN 9780123695222.
31. Massara Paletto V, Commendatore MG, Esteves JL. 2008. Hydrocarbon levels in sediments and bivalve mollusks from Bahía Nueva (Patagonia, Argentina): An assessment of probable origin and bioaccumulation factors. *Baseline / Mar Pollut Bull* 56: 2082-2105.
32. Primost MA. 2014. Ecotoxicología y alteraciones morfo-funcionales en gasterópodos marinos expuestos a contaminación por metales y organometales. Ph.DThesis. Facultad de Ciencias Naturales y Museo (UNLP).
33. Fent K. Ecotoxicology of organotin compounds. 1996. *Critical Reviews in Toxicology* 26: 1-117.
34. Shim WJ, Yim UH, Kim NS, Hong SH, Oh JR, Jeon JK, Okamura H. 2005. Accumulation of butyl- and phenyltin compounds in starfish and bivalves from the coastal environment of Korea. *Environm Pollut* 133: 489–499.
35. Horiguchi T, Li Z, Uno S, Shimizu M, Shiraishi H, Morita M, Thompson JAJ, Levings CD. 2003. Contamination of organotin compounds and imposex in molluscs from Vancouver, Canada. *Mar Environ Res* 57: 75-88.
36. Wade TL, Garcia-Romero B, Brooks JM. 1988. Tributyltin Contamination in Bivalves from United States Coastal Estuaries. *Environ Sci Technol* 22 (12):1488-1493.
37. Pereira WE, Wade TL, Hostettler FD, Parchaso F. 1999. Accumulation of Butyltins in Sediments and Lipid Tissues of the Asian Clam, *Potamocorbula amurensis*, Near Mare Island Naval Shipyard, San Francisco Bay. *Mar Pollut Bull* 38 (11): 1005-1010.

38. Chandrinou S, Stasinakis AS, Thomaidis NS, Nikolaou A, Wegener JW. 2007. Distribution of organotin compounds in the bivalves of the Aegean Sea, Greece. *Environ International* 33: 226-232.

39. Harino H, Fukushima M, Yamamoto Y, Kawai S, Miyazaki N. 1998. Contamination of butyltin and phenyltin compounds in the marine environment of Otsuchi Bay, Japan. *Environ Pollut* 101: 209-214.

40. Harino H, O'Hara SCM, Burt GR, Chesman BS, Langston WJ. 2005. Accumulation of butyltin compounds in benthic biota of the Mersey Estuary. Baseline / *Mar Pollut Bull* 50: 208-236.

41. Albalat A, Potrykus J, Pempkowiak J, Porte C. 2002. Assessment of organotin pollution along the Polish coast (Baltic Sea) by using mussels and fish as sentinel organisms. *Chemosphere* 47: 165-171.

42. Lee RF. 1996. Metabolism of Tributyltin by aquatic organisms. In: Organotin. Eds Champ MA, Seligman PF. Chap.18: 369-382. ISBN 978-94-010-7174-1.

43. Barroso CM, Mendo S, Moreira MH. 2004. Organotin contamination in the mussel *Mytilus galloprovincialis* from Portuguese coastal waters. Baseline / *Mar Pollut Bull* 48: 1145-1167.

44. Diez S, Lacorte S, Viana P, Barceló D, Bayona JM. 2005. Survey of organotin compounds in rivers and coastal environments in Portugal 1999-2000. *Environ Pollut* 136: 525-536.

45. Delucchi F, Tombesi N, Freije R, Marcovecchio J. 2006. Butyltin Compounds in Sediments of the Bahía Blanca Estuary, Argentina. *Environ Monitor Assess* 132: 445-451.

46. Yan W, Chi J, Wang Z, Huang W, Zhang G. 2009. Spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs) in sediments from Daya Bay, South China. *Environ Pollut* 157:1823-1830.

47. Cardellicchio N, Buccolieri A, Giandomenico S, Lopez L, Pizzulli F, Spada L. 2007. Organic pollutants (PAHs, PCBs) in sediments from the Mar Piccolo in Taranto (Ionian Sea, Southern Italy). *Mar Pollut Bull* 55: 451-458.

48. Tissier MJ, Saliot A. 1981. In: Advances in Organic Geochemistry. Bjoroy, M., Ed.; John Wiley & Sons: NewYork, Pp: 268-278.

49. Baumard P, Budzinski GH, Michon Q, Garrigues P, Burgeot T, Bellocq J. 1998. Origin and Bioavailability of PAHs in the Mediterranean Sea from Mussel and Sediment Records. *Estuarine Coastal Shelf Sci* 47: 77-90.

50. Long ER, MacDonald DD, Smith S., Calder FD. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environ Management* 19: 81-97.

51. FDEP. Florida Department of Environmental Protection, 1994. Approach to the Assessment of Sediment Quality in Florida Coastal Waters. Volume 1 - Development and Evaluation of Sediment Quality Assessment Guidelines. Prepared by: D.D. MacDonald. MacDonald Environmental Sciences Ltd. Pp: 126

52. Aldarondo-Torres JX, Samara F, Mansilla-Rivera I, Aga DS, Rodríguez-Sierra CJ. 2010. Trace metals, PAHs, and PCBs in sediments from the Jobos Bay area in Puerto Rico. *Mar Pollut Bull* 60: 1350-1358.

53. de Carvalho Oliveira R, Santelli RE. 2010. Occurrence and chemical speciation analysis of organotin compounds in the environment: A review *Talanta* 82: 9-24.

54. Arias AH, Pereyra MT, Marcovecchio JE. 2011. Multi-year monitoring of estuarine sediments as ultimate sink for DDT, HCH, and other organochlorinated pesticides in Argentina. *Environ Monit Assess* 172:17-32.

55. Tolosa I, Bayona JM, Albaigés J. 1995. Spatial and temporal distribution, fluxes, and budgets of organochlorinated compounds in northwest Mediterranean sediments. *Environ Sci Technol* 29: 2519-2527.

56. Ramesh A, Tanabe S, Murase H, Subramanian AN, Tatsukawa R. 1991. Distribution and behavior of persistent organochlorine insecticides in paddy soil and sediments in the tropical environment: A case study in South India. *Environ Pollut* 74 (4): 293-307.

57. Lee KT, Tanabe S, Koh CH. 2001. Distribution of organochlorine pesticides in sediments from Kyeongii Bay and nearby areas, Korea. *Environ Pollut* 114: 207-213.

58. Iwata H, Tanabe S, Sakai N, Nishimura A, Tatsukawa R. 1994. Geographical distribution of persistent organochlorines in air, water and sediments from Asia and Oceania, and their implications for global redistribution from lower latitudes. *Environm Pollut* 85 (1): 15-33.

59. Kim JH, Smith A. 2001. Distribution of organochlorine pesticides in soils of South Korea. *Chemosphere* 43: 137-140.

60. CCME. Canadian Council of Ministers of the Environment. 2001. Canadian sediment quality guidelines for the protection of aquatic life: Summary tables. Updated. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

61. Elnar AA, Diesel B, Desor F, Feidt C, Bouayed J, Kiemer AK, Soulimani R. 2012. Neurodevelopmental and behavioral toxicity via lactational exposure to the sum of six indicator non-dioxin-like-polychlorinated biphenyls (6 NDL-PCBs) in mice. *Toxicology* 299: 44-54.

62. Nizzetto L, Lohmann R, Gioia R, Jahnke A, Temme C, Dachs J, Herckes P, Diguardo A, Jones KC. 2008. PAHs in Air and Seawater along a North–South Atlantic Transect: Trends, Processes and Possible Sources. *Environ Sci Technol* 42: 1580-1585.

63. Gioia R, Nizzetto L, Lohmann R, Dachs J, Temme C, Jones KC. 2008. Polychlorinated Biphenyls (PCBs) in Air and Seawater of the Atlantic Ocean: Sources, Trends and Processes. *Environ Sci Technol* 42: 1416-1422.

64. Sadler R, Connell D. 2012. Global Distillation in an Era of Climate Change, Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update, Dr. Tomasz Puzyn (Ed.), ISBN: 978-953-307-917-2, InTech, Available from:

http://www.intechopen.com/books/organic-pollutants-ten-yearsafter- the-stockholm-convention-environmental-and-analytical-update/global-distillation-in-an-era-of-climate change.

65. Wania F. 2003. Assessing the Potential of Persistent Organic Chemicals for Long-Range Transport and Accumulation in Polar Regions. *Environ. Sci. Technol* 37: 1344-1351.

Table 1.Sampling sites and characteristics of sampled sediments and bivalves mollusks

Station	Name	Geographic position		Sediments				Organisms*				
				Granulometry			OM	Specie	TLC (%)		CI	
		S latitude	W longitude	% gravel	% sand	% fine	%		A	S	A	S
S1	Camarones bay	44°48'08"	65°42'38"	10.2	65.3	24.5	3.4	*A. atra atra*	2.2	1.3	30	35
S2	Bivalves culture	44°53'27"	65°37'24"	1.0	96.7	2.3	0.6	*M. edulis*	1.9	-	26	-
S3	Sara creek	44°54'17"	65°34'27"	2.1	75.3	22.6	2.7	*A. atra atra*	2.2	1.4	42	47
S4	Hornoscreek	45°01'53"	65°40'48"	0.0	74.3	25.7	4.5	*A. atra atra*	2.0	-	38	-
S5	Melo bay	45°00'53"	65°53'41"	4.3	81.3	14.4	1.1	*A. atra atra*	1.8	0.9	32	36
S6	Malaspina creek north	45°08'37"	66°34'48"	0.0	69.4	30.6	4.2	*M. edulis*	1.7	1.0	34	37
S7	Malaspina creek south	45°10'48"	66°32'11"	0.0	72.3	27.7	3.8	*M. edulis*	1.9	1.0	35	40

* *A. atra atra, Aulacomya atra atra; M. edulis, Mytilus edulis ;*A, autumn; S, spring; OM: organic matter; TLC: total lipid content; CI: condition index

Table 2.BTs in sediments and bivalves mollusks as ng (Sn) g^{-1} dw, Biodegradation Index (BDI), and percentage of biodegradation (%BTsdeg)

	S1	S2	S3	S4	S5	S6	S7
Sediment							
TBT	34.7	<LOD	3.8	2.6	3.2	4.6	3.8
DBT	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
MBT	131.9	<LOD	20.2	2.8	3.5	<LOD	8.1
∑ BTS	166.5	<LOD	24.0	5.4	6.7	4.6	11.8
BDI*	3.8	-	5.3-5.5	1.1-1.3	1.1-1.3	0.0-0.4	2.2-2.3
% Btsdeg*	79	-	84-85	52-57	52-57	0-26	68-70
BivalvesAutumn							
TBT	134.0	3.5	110.0	21.0	86.0	120.0	nd
DBT	15.3	12.2	<LOD	11.0	<LOD	6.0	nd
MBT	56.7	13.7	27.8	19.0	20.0	14.0	nd
∑ BTS	206.0	29.4	137.8	51.0	106.0	140.0	nd
BDI*	0.5	7.4	0.3	1.4	0.2	0.2	-
% Btsdeg*	35	88	20-21	59	19-20	14	-
Bivalves Spring							
TBT	123.0	ns	177.0	ns	40.0	100.0	98.0
DBT	10.0	ns	12.0	ns	<LOD	7.0	9.0
MBT	14.0	ns	17.0	ns	12.0	20.0	13.0
∑ BTS	147.0	ns	206.0	ns	52.0	127.0	120.0
BDI	0.2	ns	0.2	ns	0.3	0.3	0.2
% BTsdeg	16	ns	14	ns	23-25	21	18

* Ranges calculated with the limit values 0 ng (Sn) g^{-1}dw and LOD for sites with concentrations <LOD.
ns: not sampled
nd: not determined

Table 3. PAHs concentration (ng g^{-1} dw) in sediments and bivalves mollusks from NZ-SJG

Compound*	S1	S2	S3	S4	S5	S6	S7	S1	S2	S3	S4	S5	S6	S7	S1	S3	S5	S6	S7
	Sediments							***BivalvesAutumn***							***Bivalves Spring***				
Naph	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
2-MNaph	3.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.60	<LOD	<LOD	0.28	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
1-MNaph	14.35	<LOD	<LOD	<LOD	<LOD	0.69	<LOD	<LOD	<LOD	0.44	<LOD	<LOD	0.26	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
2,6 DMNaph	17.84	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
1,7 DMNaph	4.33	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.33	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Biph	5.68	0.98	<LOD	<LOD	1.16	<LOD	<LOD	<LOD	<LOD	0.28	<LOD	<LOD	0.24	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Acl	17.44	3.89	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ace	5.67	8.73	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fl	3.20	2.28	2.02	<LOD	<LOD	2.28	<LOD	19.81	<LOD	<LOD	<LOD	17.70	<LOD	<LOD	12.46	12.19	<LOD	<LOD	<LOD
DBT	9.09	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Phe	10.49	3.11	2.81	1.65	1.62	1.69	<LOD	8.26	9.15	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ant	8.99	1.95	1.85	1.67	1.74	1.72	<LOD	9.20	10.18	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Flt	2.09	5.13	0.79	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pyr	1.53	6.50	5.70	2.62	2.61	3.58	<LOD	<LOD	9.12	<LOD	10.19	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BaA	4.55	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chr	8.55	1.07	1.07	1.12	<LOD	1.46	<LOD	<LOD	8.66	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BbF	9.61	3.61	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.27	<LOD	11.21	0.31	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BkF	5.94	1.82	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	9.09	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BeP	4.74	1.88	1.80	<LOD	<LOD	1.73	<LOD	<LOD	<LOD	<LOD	<LOD	12.16	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BaP	6.88	2.97	2.59	<LOD	2.58	2.88	<LOD	<LOD	<LOD	<LOD	<LOD	16.93	0.29	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pe	2.86	3.43	2.43	2.29	2.51	2.38	<LOD	<LOD	<LOD	<LOD	<LOD	15.95	0.09	<LOD	<LOD	14.99	<LOD	<LOD	<LOD
IP	2.58	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
DBA	4.77	6.75	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BP	2.59	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
∑ PAHs(24)	157.71	54.10	21.06	9.35	12.22	18.41	<LOD	37.27	37.11	1.59	10.19	83.04	1.80	<LOD	12.46	27.18	<LOD	<LOD	<LOD
∑ PAHs(16)	94.88	47.81	16.83	7.06	8.55	13.61	<LOD	37.27	37.11	0.27	10.19	54.93	0.60	<LOD	12.46	12.19	<LOD	<LOD	<LOD

LOD, Limit of Detection: LOD < 0.013ng. g^{-1}dw for sediments; LOD < 0.10 ng g^{-1} dw for bivalve mollusks.
* ∑ PAHs(16) is the sum of 16 US EPA priority pollutant PAHs, which are marked in bold type letter.

Table 4. OCs concentration (ng g^{-1}dw) in sediments and bivalve mollusks from NZ-SJG.

	S1	S2	S3	S4	S5	S6	S7	S1	S2	S3	S4	S5	S6	S7	S1	S3	S5	S6	S7
OCPs	*Sediment*							*BivalvesAutumn*							*Bivalves Spring*				
HCHs																			
α-HCH	<LOD	0.01	0.02	0.09	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
β-HCH	0.06	0.10	0.14	<LOD	0.05	0.02	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
γ-HCH	<LOD	<LOD	0.06	0.11	0.04	0.01	0.06	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
δ-HCH	0.08	0.02	<LOD	0.01	0.06	0.03	<LOD	<LOD	0.06	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
HCB	<LOD	0.02	0.17	0.19	0.01	0.01	0.05	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
DDTs																			
p,p-DDT	<LOD	<LOD	<LOD	0.01	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
p,p-DDD	0.90	<LOD	0.01	0.07	0.01	<LOD	0.05	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
o,p-DDE	<LOD	<LOD	<LOD	0.01	0.01	0.01	0.01	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
p,p-DDE/o,p-DDD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.02	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.01
Chlordanes																			
α-chlordane	<LOD	0.02	<LOD	0.01	0.02	0.01	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
γ-chlordane	0.01	<LOD	<LOD	0.01	0.01	<LOD	0.01	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
t-nonachlore	<LOD	0.01	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heptachlor	<LOD	<LOD	<LOD	0.02	<LOD	<LOD	<LOD	<LOD	0.08	0.12	<LOD	<LOD	<LOD	<LOD	0.10	<LOD	0.08	0.14	0.08
HeptachorEpoxide	<LOD	<LOD	<LOD	<LOD	0.01	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
DRINs																			
Aldrin	0.17	0.06	0.03	0.02	0.02	0.01	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Dieldrin	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.01	0.02	0.01
Endrin	<LOD	<LOD	<LOD	0.01	<LOD	<LOD	0.04	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EndrinKetone	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.04	<LOD	<LOD	<LOD	0.01	0.01	<LOD	0.01	<LOD	<LOD	<LOD	<LOD
Endosulphan I	0.01	0.01	0.09	<LOD	<LOD	<LOD	<LOD	<LOD	0.03	0.07	<LOD	<LOD	<LOD	<LOD	0.02	<LOD	0.04	0.06	0.04
Mirex	<LOD	0.14	0.08	<LOD	0.18	0.10	0.07	<LOD	<LOD	0.02	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
∑ OCPs	1.23	0.39	0.60	0.56	0.42	0.20	0.29	0.04	0.19	0.21	<LOD	0.01	0.01	<LOD	0.13	<LOD	0.13	0.22	0.14
∑PCBs	2.56	0.08	0.26	0.48	0.32	0.10	0.26	0.77	0.63	0.11	0.72	0.31	0.34	0.81	0.10	0.54	0.23	0.19	0.28
∑IndPCBs*	0.09-1.57	<LOD--0.03	0.01-0.04	0.11-0.13	0.03-0.04	0.01	0.01-0.04	0.02-0.07	0.01	0.03	0.01	0.02-0.04	<LOD-0.01	0.02	0.05	<LOD	0.02	<LOD	0.02
∑ OCs	3.79	0.47	0.86	1.04	0.74	0.30	0.55	0.81	0.82	0.32	0.72	0.32	0.35	0.81	0.23	0.54	0.36	0.41	0.42

OCPs Limit of Detection (LOD) range: 0.0005-0.0006 and 0.004-0.005ng g^{-1} for sediments and organisms, respectively.
PCBs Limit of Detection (LOD) range: 0.0005-0.0010 and 0.004-0.008ng g^{-1} for sediments and organisms, respectively.

* Estimation of ∑IndPCBs (28, 52, 101, 118, 138, 153, 180): range minimum value (sum of PCBs-28, 52, 101, 180); range maximum value (minimum value + [118+149] + [138+158] + [153+105+132]) due to PCBs congeners co-elution indicated in brackets.
c-nonachlore/o,p-DDT, Endosulphan II and Endosulphan sulphate concentration were <LOD for all samples.

Figure 1

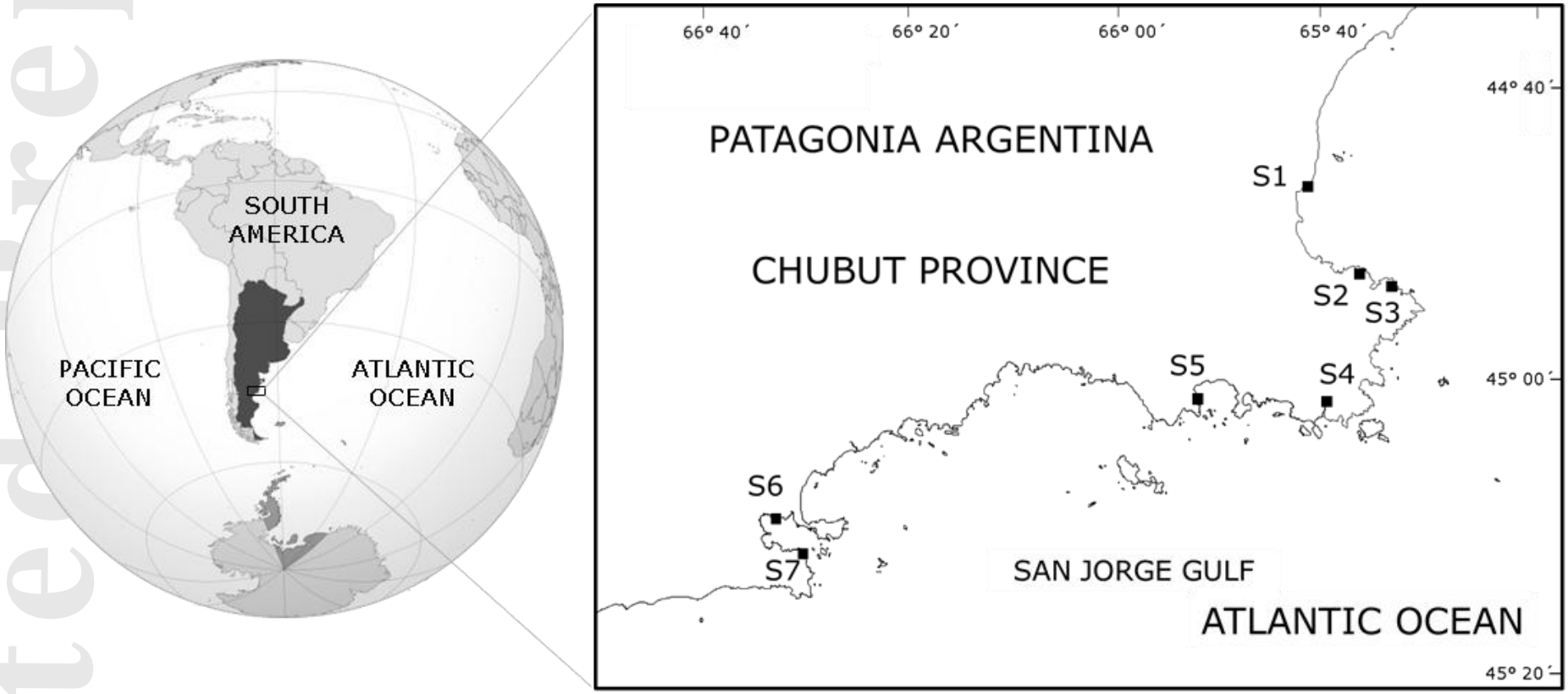


Figure 2

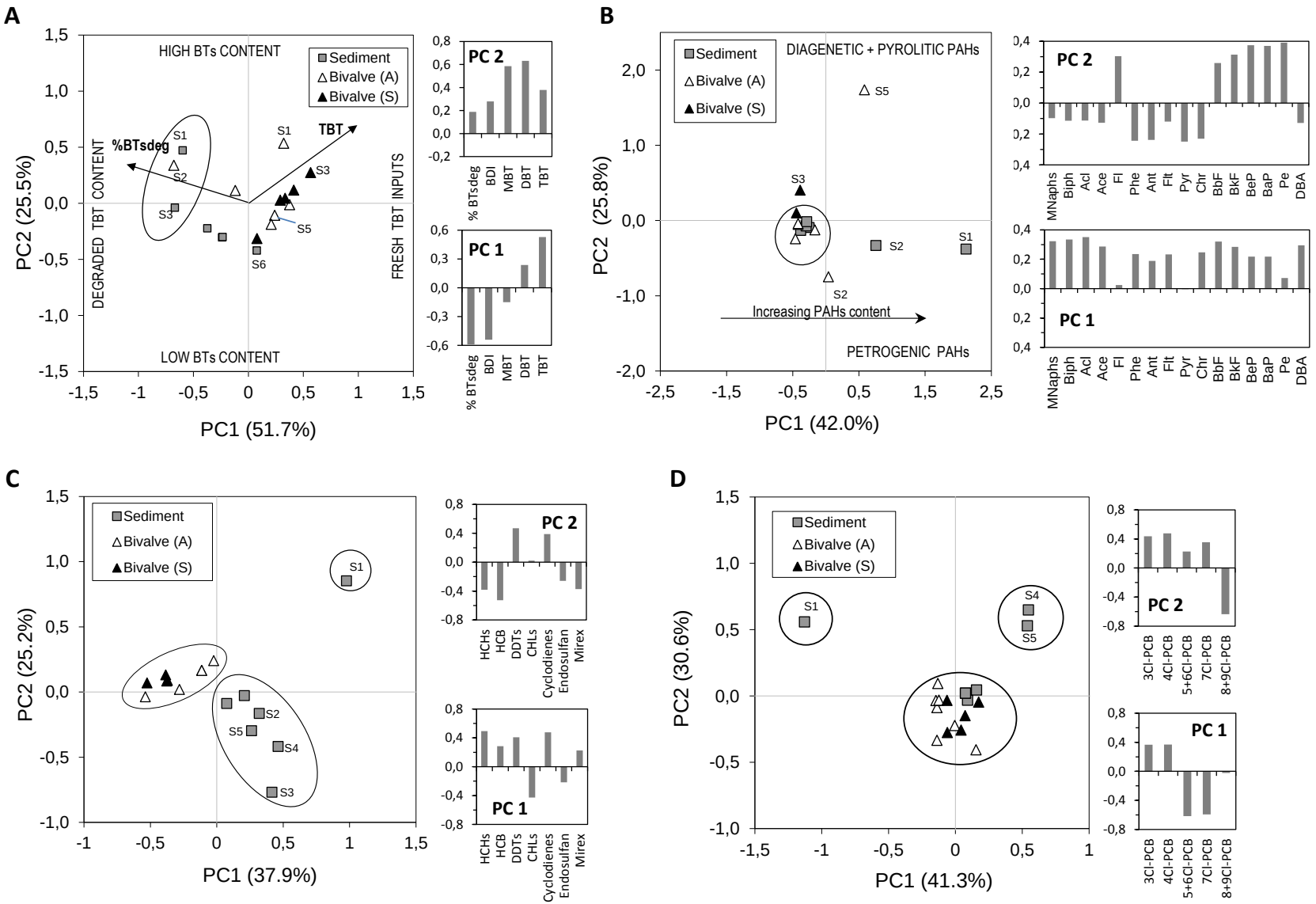


Figure 3

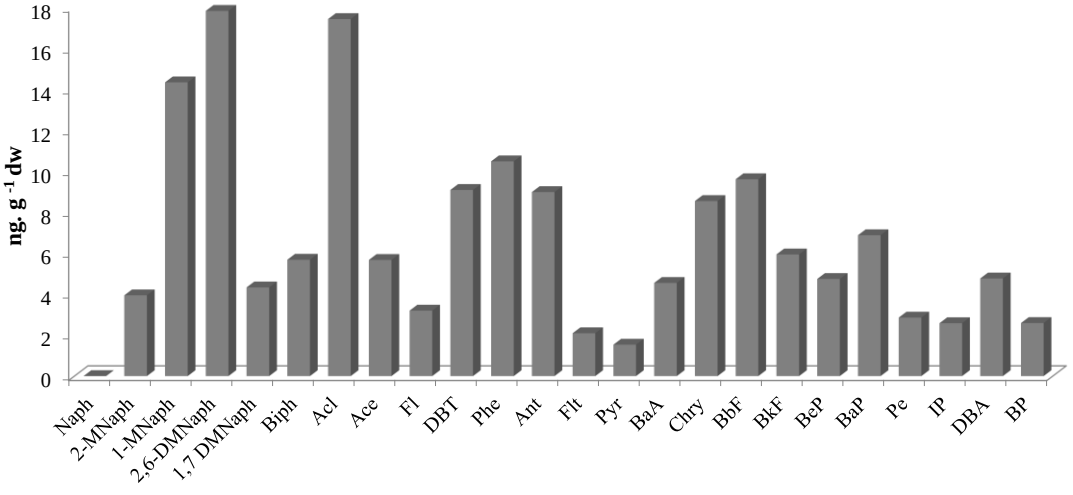
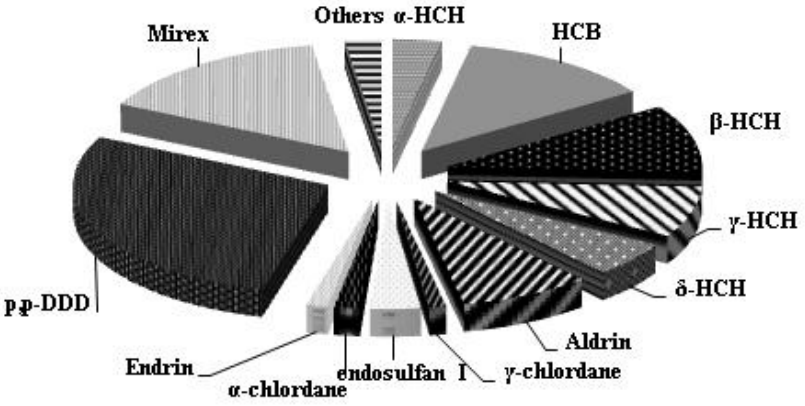
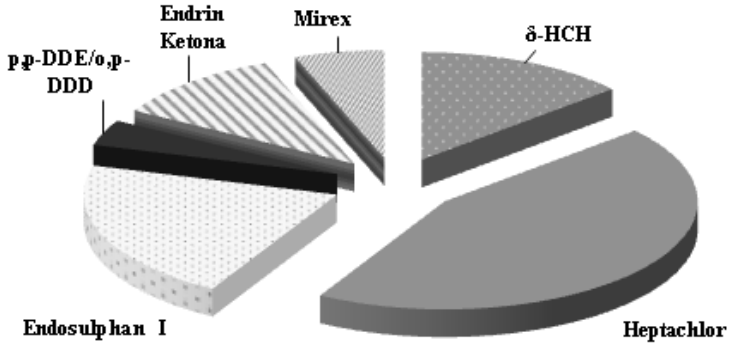


Figure 4

A SEDIMENTS



B AUTUMN BIVALVES



C SPRING BIVALVES

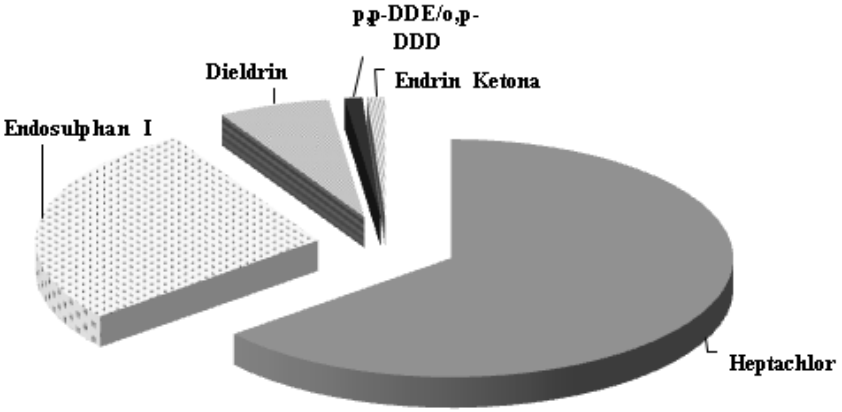


Figure 5