sustainability

MDPI

Article

Assessment of Pesticide, Dioxin-like Polychlorinated Biphenyl, and Polycyclic Aromatic Hydrocarbon Existence around Galindez Island, and Comparison with the Organic Pollution Bibliography of the Antarctic Peninsula

Halim Aytekin Ergül [1,*], Türkan Erdem [1], Ezgi Gizem Pelin [1], Arda M. Tonay [2,3], Serdar Aksan [1] and Bayram Öztürk [2,3]

[1] Department of Biology, Science and Arts Faculty, Kocaeli University, 41380 İzmit, Turkey; turkanerdem@gmail.com (T.E.); egpelin@gmail.com (E.G.P.); serdar.aksan@kocaeli.edu.tr (S.A.)
[2] Faculty of Aquatic Sciences, Istanbul University, 34134 Fatih, Turkey; atonay@istanbul.edu.tr (A.M.T.); ozturkb@istanbul.edu.tr (B.Ö.)
[3] Turkish Marine Research Foundation, 34820 Istanbul, Turkey
* Correspondence: halim.ergul@kocaeli.edu.tr

Abstract: Sediment, notothenioid fish, and moss samples were collected from the vicinity of Galindez Island, Antarctic Peninsula during the austral autumn of 2016 and 2017. Pesticide, Polycyclic Aromatic Hydrocarbon (PAH), and dioxin-like Polychlorinated Biphenyl (*dl*-PCB) concentrations were measured using High-Resolution Gas and Liquid Chromatography. Pollutant concentrations were below detection limits in sediment and moss samples. However, pesticides, PAH, and *dl*-PCB congeners were detected in the muscle tissue of fishes. Pesticide concentrations varied between 0.46 and 12.2 ng/g-dw, and Mecarbam was the dominant compound. Kresoxim-methyl, Mecarbam, Procymidone, Pyridaben, and Quinoxyfen were reported in the muscle tissue of the fishes, for the first time from the Antarctic. PCB-118, PCB-105, and PCB-156 were dominant *dl*-PCBs. The ∑12-*dl*-PCB concentration was 160,929 pg/g-dw, and WHO-TEQ-total *dl*-PCB was 8.30 pg/g-dw in *Trematomus bernachii*, over the consumable limit in fishes according to the European Commission. The PCB-126 concentration was 36 pg/g-dw in the muscle tissue of fish, the first reported from the Antarctic. Phenanthrene was the dominant PAH congener. The ∑16-PAH concentration was 22.5 ng/g-dw. PAH sources were local and petrogenic in the fishes, likely after long-term bioaccumulation. The flow rate is rather low around Galindez Island; accordingly, contaminant removal takes time and may demonstrate long-lasting effects including bioaccumulation in the marine food web.

Keywords: Antarctic Peninsula; notothenioid fishes; pesticides; *dl*-PCBs; PAHs; Turkish polar program

check for updates

Citation: Ergül, H.A.; Erdem, T.; Pelin, E.G.; Tonay, A.M.; Aksan, S.; Öztürk, B. Assessment of Pesticide, Dioxin-like Polychlorinated Biphenyl, and Polycyclic Aromatic Hydrocarbon Existence around Galindez Island, and Comparison with the Organic Pollution Bibliography of the Antarctic Peninsula. *Sustainability* **2022**, *14*, 3994. https://doi.org/10.3390/su14073994

Academic Editor: Just Tomàs Bayle-Sempere

Received: 16 February 2022
Accepted: 22 March 2022
Published: 28 March 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Both the Arctic and Antarctic are considered relatively non-polluted environments. The Antarctic continent, in particular, is further away from anthropogenic influences. However, in the last few decades, organic pollutants have started to show up in these environments [1–7]. Therefore, the level of existing pollutants in the continent, whether new ones are transported, and, if they are, the transportation pathways, are issues that need to be investigated.

Organic contaminants resistant to environmental degradation to a varying degree, which possess toxic features and a risk of causing adverse effects to biota and humans, are termed persistent organic pollutants (POPs) (e.g., *dl*-PCB's, DDT, Aldrin, Beta Hexachlorocyclohexane, Chlordane, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene [HCB], Lindane, Mirex, Toxaphene, etc.) [8]. POPs, such as dioxin-like Polychlorinated Biphenyls (*dl*-PCBs), and some pesticides can be used to understand the long-range transport of pollutants in regions such as the Antarctic, where local sources of pollution are almost absent [9]. Their

resistance to biological, chemical, and photolytic processes allows them to travel across intercontinental boundaries by water currents and air movements, which may deposit them far from where they originate [10,11].

Even though pesticides are considered useful for crop yield, some of them are highly toxic to living organisms, including humans. Indeed, 9 of the 12 initial POPs and 16 of all 30 listed POPs declared by the Stockholm Convention [10] are pesticides [12]. *dl*-PCBs, which are commercially used in capacitors, transformers, building sealants, etc., have generally high lipophilicity, a persistent nature, and toxicity [13,14]. *dl*-PCBs tend to spread into wide areas by binding to different vectors in air and fall on both land and sea surfaces as snowflakes or raindrops via precipitation in the Antarctic [15]. Although most of the listed POPs are no longer produced, their traces are still present worldwide due to global cross-border movements [16]. On the other hand, Polycyclic Aromatic Hydrocarbons (PAHs) are another one of the important toxic organic pollutant groups, due to the mutagenic and/or carcinogenic properties of some of their congeners on animals, as well as humans [17]. Different from the other chemicals investigated in the present study, PAHs are emitted locally into the atmosphere, particularly during fuel combustion for heating purposes in research bases established in the Antarctic [18].

After long-range transport or local accumulations, the pollutants can directly settle on the sea or be deposited through permanent conservation in the moss, soil, snow, ice, or firm-ice cover. Accumulated contaminants may be released from melting ice and snow that sink into oceanic waters and sediments [8] and then may join the marine food web [5,6].

The present study was conducted as a part of ecological research on the western Antarctic Peninsula [19,20] in the frame of the first Turkish polar program [21]. The study aims to better understand the contamination level and transportation pathway of some potentially dangerous organic pollutants for aquatic and terrestrial biota, including POPs, in living and non-living constituents in the Antarctic. Therefore, in the present study, we investigated 262 Pesticides', 12 *dl*-PCBs', and 16 PAHs' congener concentrations in the surface sediment, fish (to evaluate transport, in particular by marine water), and moss (to evaluate atmospheric deposition) samples, collected from the vicinity of Galindez Island (Antarctic Peninsula), and assessed their possible sources.

2. Material and Methods

2.1. Study Locations and Characterization of Samples

The Antarctic Peninsula is the part of Antarctica nearest to South America. Because of its location and milder climate, today, there are several permanent and seasonal research stations established throughout. The Ukrainian Vernadsky Research Base (formerly the British Faraday Station) is one of the oldest research bases in the Antarctic Peninsula and is located at Marina Point on Galindez Island, where the present study was conducted around its vicinity.

In the frame of the present study, fish, sediment, and moss samples were collected around Galindez Island (Antarctic Peninsula) to analyze 262 Pesticides', 12 *dl*-PCBs', and 16 PAHs' congener concentrations, including some POPs. The sediment and fish samples were collected during the first Turkish Joint Antarctic Expedition in April 2016, and the moss samples in April 2017 (Figure 1).

To trap fishes, a cone-type fyke net was anchored in two sites (Stations 2 and 3) at Galindez Island offshore. In total, nine adult fish, i.e., three *Trematomus bernacchii* Boulenger, 1902 (emerald rock-cod) and six *Notothenia coriiceps* Richardson, 1844 (black rock-cod), were trapped and used for analysis. Due to unfavorable weather conditions and difficulties with fishing, a limited number of fish could be caught. However, the number of samples taken was sufficient for analytical measurements and recovery procedures. Both fishes are benthic, typically live in shallow coastal waters, and feed on various organisms that live at the bottom. The total lipid contents of flesh were reported as 6.1% and 4.6% dw for *N. coriiceps* and *T. bernacchii*, respectively, and 23% dw in the liver for *N. coriiceps* [22]. Since the tissue structures are important in the bioaccumulation of lipophilic chemicals, both species that

have notable fatty tissue were used in the analysis. These species are also known as having restricted home ranges that may help to understand nearby contamination [22,23]. Surface sediment samples were collected from five sites (i.e., Stations 2, 3, 4, 5, and 6) using a Van Veen-type grab sampler thrown by hand from a boat, and the moss samples (*Polytrichum briedel* and *Andreaea regularis*) were collected manually in Station 1 from a rocky area located a hundred meters north of the Vernadsky Research Base (Figure 1).

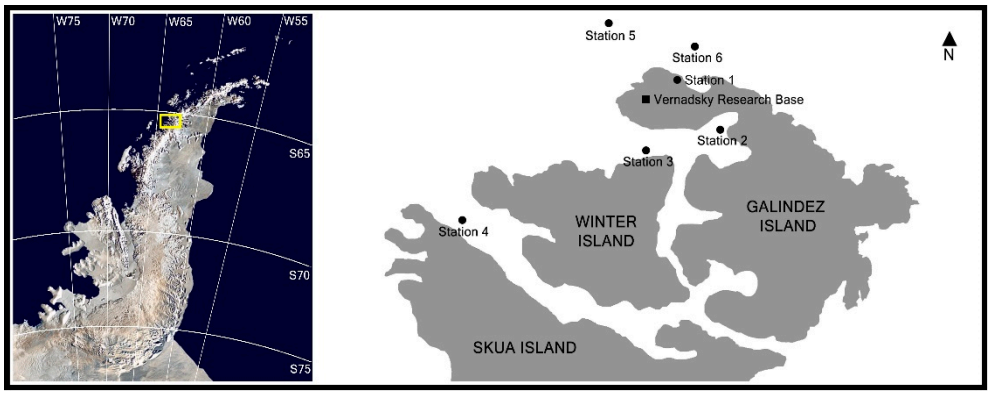

Figure 1. The study area and sampling stations around Galindez Island (Antarctic Peninsula).

2.2. Analytical Preparation of the Samples and Extraction

The muscle tissues of the fishes were filleted using a porcelain knife, divided into small pieces, and the tissues belonging to each fish species were mixed. Sediment samples were desalted three times using distilled water, and coarse particles (>1 mm) were removed using a stainless-steel sieve. Rhizoid and gametophyte parts of the moss samples were separated from each other. After pretreatment, all samples were weighed and freeze-dried at −55 °C for 72 h using Christ Alpha 1–2 LD+ equipped with RZ 2.5 Rotary vane pump. Before homogenization, the samples were transported to a desiccator to remove moisture and weighed. Dry samples were homogenized using a porcelain mortar and pestle and stored at −20 °C until analysis.

Preparations and extractions of all samples were carried out according to the methods US-EPA 429 [24], ISO 11338 [25], and IP 346 [26] for the fish, US-EPA 429 and modified STN EN 16619 [27] for the moss, and US-EPA 429 [24], ISO 11338 [28], and US-EPA 3540 [29] for the sediment samples to determine the PAH concentrations, whereas the methods used to determine the *dl*-PCB concentrations were modified US-EPA 1668 [30] for the fish, modified US-EPA 1668 and modified CSN P CEN/TS 16190 [31] for the moss, and JIS K0311 [32] for the sediment samples, using an isotope dilution technique via High-Resolution Gas Chromatography–High-Resolution Mass Spectrometry (HRGC-HRMS).

A modified AOAC 2007.01 [33] method was used for pesticide residue analysis in sediment by acetonitrile extraction and partitioning with magnesium sulfate, by gas and liquid chromatography–tandem mass spectrometers (GC-MS/MS and LC-MS/MS). A certain amount of the sediment sample (15 g) was homogenized by adding distilled water. Fifteen milliliters of 1% acetic acid (HOAc) and buffered acetonitrile (MeCN) were added to the sample and transferred to a centrifuge tube. Six grams of anhydrous magnesium sulfate and 1.5 g of sodium acetate ($MgSO_4$/NaOAc—4/1, *w*/*w*) were added and vortexed. The mixture was centrifuged for 2 min at 4000 rpm. The upper layer of the MeCN extract was added to the 15 mL centrifuge tube containing 250 mg $MgSO_4$ and 50 mg PSA (5/1, *w*/*w* per 1 mL extract) and was centrifuged again for 2 min at 4000 rpm. The final extract was transferred to autosampler vials after filtration through a 0.45 µm filter paper for analysis by GC-MSMS and LC-MSMS. For pesticide residue analysis in biota, a modified method, namely PAM Vol. 1-82-1 [34], was used. The biota samples (10 g) were mixed with 50 mL of petroleum ether and shaken vigorously. One milliliter of the extract was passed through a petroleum ether-conditioned florosil cartridge, then 5 mL of 6%, 15%, and 50% petroleum ether/diethyl ether (1:1, *w*/*w*) mixtures were passed through the cartridge. Collected

extracts were dried under a slow stream of high-purity nitrogen and then dissolved in 5 mL of acetone and injected into both GC-MSMS and LC-MSMS instruments.

To calculate recovery values, a 2000 mg/kg pesticide congener mix (Accustandard) stock solution was prepared (80 µg/g in 1% acetic acid) and added to the dried *N. coriiceps* tissue (10 g, separated from the extracted sample) and analyzed via GC-MSMS and LC-MSMS. According to compound specifications (e.g., solubility, volatility, polarity, etc.), LC-MS/MS or GC-MS/MS was used to quantify a total of 262 pesticide compounds, including organochlorine, organobromine, and organophosphates. The concentrations of detectable pesticides in the muscle tissue of the *T. bernacchii* and *N. coriiceps*, thallus of *P. briedel* and *A. regularis*, and five surface sediment samples were measured. The concentrations obtained from the samples were subtracted from the concentrations obtained from the samples with the congener mix, and recovery values were calculated (Table S1-1). The recovery values for pesticide compounds ranged between 41.6% and 112% with an average of 77% in the muscle tissue of *N. coriiceps*; however, their concentrations were below the detection limits for all other moss and sediment samples (i.e., <1.0 ng/g dw for that analyzed in GC MS/MS and <2.0 ng/g dw for that analyzed in LC-MS/MS; Tables S1-1, S1-2). The compound-specific spectrometer settings (i.e., ion rates, collision energies, polarities, and chromatography operating conditions) were given in the Supplementary Material (Tables S1-3, S1-4, S1-5, S1-6). To perform the external calibration, pesticide mix standards were used and correlation coefficients for calibration curves were calculated higher than 0.99 for all the congeners. In both the sediment and biota, 186 pesticide congeners were analyzed by GC-MS/MS, and 76 by LC-MS/MS (Tables S1-5, S1-6).

The dried sample was spiked after homogenization with an extraction containing $^{13}C_{12}$-labeled PCB congeners and $^{2}H_{x}$-labeled PAH congeners. The spiked sample was mixed with anhydrous sodium sulfate/silica (1/1) and transferred into an extraction thimble. Extraction with DCM/hexane (1/1, *v*/*v*) in a Soxhlet extractor took 20 h. Then, the remaining was concentrated in the rotary vacuum evaporator. For the cleanup of PAHs, the raw extract was pre-cleaned on the column containing silica-gel impregnated with NaOH solution. The DCM/hexane (2/1, *v*/*v*) fraction from the column was concentrated using the modified Kuderna–Danish concentrator up to 0.5–1 mL. For the cleanup of *dl*-PCBs, the final extract was transferred to an Erlenmeyer flask, diluted in hexane, and shaken with silica-gel impregnated with H_2SO_4. Then, the whole mixture was transferred to the top of a multi-layer silica-gel column and eluted with hexane/DCM (95/5, *v*/*v*). The extract was concentrated using the modified Kuderna–Danish concentrator up to 0.5–1 mL. For the fractionation florisil column and the combination of hexane and dichloromethane, the elution of two different PCBs fractions was used. The first hexane fraction contained mono-ortho PCBs and non-dioxin-like PCBs. The dichloromethane fraction contained non-ortho PCBs. Both fractions were concentrated using a Kuderna–Danish concentrator to a volume of approximately 0.5 mL. The final extract containing PAHs is spiked with a specific $^{2}H_{x}$-labeled injection standard, and 2–4 µL are injected into HRGC-HRMS. The final extract containing mono-ortho PCBs and non-dioxin-like PCBs is spiked with an injection standard containing specific $^{13}C_{12}$-labeled PCBs, and 2–4 µL are injected into HRGC-HRMS. The final extract containing non-ortho PCBs is concentrated up to dryness under a nitrogen stream and then spiked with an injection standard containing specific $^{13}C_{12}$-labeled PCBs, and 2–4 µL are injected into HRGC-HRMS. Some details (e.g., the sample amount, dry matter, final extract-injection volume, detection limits, etc.) regarding PAH and *dl*-PCB analysis are provided in the Supplementary Material (Tables S2-1, S2-2, S2-3, S2-4, S2-5, S2-6).

The measurement uncertainty was expressed as a double relative standard deviation (RSD%) and corresponded to a 95% confidence interval. The estimation of measurement uncertainty for each PAH and *dl*-PCB was 30%, while for WHO-TEQs, it was 20%. The sums of measured values were determined as ∑16-PAH and ∑12-*dl*-PCB. For *dl*-PCB-WHO-TEQ calculation in biota, the concentrations were multiplied with the toxic equivalency factor (TEF), which have been developed to compare the toxicity and assess the combined effect of PCDD/Fs and *dl*-PCBs [35], revised by WHO in 2005 [36], while the concentrations were

multiplied with TEFs according to Ahlborg et al. [37] for *dl*-PCB toxic equivalency (*dl*-PCB-TEQ) calculations in sediment samples. The limit of quantifications (LOQs) was defined on the base of the blank level and used for non-detectable PCBs to calculate WHO-TEQ and TEQ values (Tables S2-2a, S2-2b, S2-4a, S2-4b, S2-6a, S2-6b, S2-6c, S2-6d, S2-6e). Since the PAH and *dl*-PCB congener concentrations were measured below the detection limits in the thallus and rhizoid of *P. briedel* (i.e., ranged between <0.24 and <6.30 ng/g dw for PAHs, and <0.037 and <9.70 pg/g dw for *dl*-PCBs) and sediment (i.e., ranged between <0.00026 and <0.15 ng/g dw for PAHs, and <0.00071 and <2.6 ng/g dw for *dl*-PCBs) samples, measurement details are provided in the Supplementary Material (Tables S2-3, S2-4a, S2-4b, S2-5a, S2-5b, S2-5c).

2.3. PAH Source Estimation

Proportions between certain PAH congeners, referred to as the diagnostic PAH ratio, can be used to understand particular emission sources. Although these ratios are usually preferred for sediment, Guinan et al. [38] reported that the PAH profiles of sediment and mussels are often similar, and diagnostic PAH ratios in biota samples such as fish and pine needles as well as water, air, and dust samples can be used for the PAH source partitioning [39]. Therefore,

$$Flu/(Flu + Pyr) \text{ and } Ant/(Ant + Phe)$$

ratios were used to estimate PAH sources, considering certain PAH congener concentrations in the muscle tissue of fish. In the formulas, *Flu*, *Pyr*, *Ant*, and *Phe* represent fluoranthene, pyrene, anthracene, and phenanthrene, respectively.

2.4. Oceanographic Measurements

A data logger (Hydrolab DS-5) was used to measure the temperature, salinity, chlorophyll-*a* (Chl-*a*), dissolved oxygen (DO), and pH at Station 3 along a 20 m water column. The data logger was calibrated before deployment, waiting two minutes for it to warm up, and was then submerged at a constant speed (i.e., 0.2 m/s) in the water column. The device was adjusted for one measurement per second.

Pearson correlations (two-tailed) were used to determine linear correlations between two variables (e.g., congener concentrations in *T. bernacchii* and *N. coriiceps*) at 95% and 99% confidence levels where necessary.

3. Results

3.1. Oceanographic Conditions

The average values of water temperature (°C), salinity, DO (mg/L), Chl-*a* (µg/L), pH, and turbidity (NTU) through the water column were −0.68, 30.2, 11.4, 7.72, 0.47, and 0.005, respectively (Figure 2). The surface water temperature represented late autumn conditions with −0.8 °C, and slightly increased by depth. Salinity and DO concentrations have a similar increasing pattern by depth, while pH and turbidity were almost the same along the water column. In the vicinity of the stations, no ice cover was present during the study.

3.2. Pesticides in Biota and Sediment Samples

In total, 21 pesticide compounds were determined in the muscle tissue of fish. While two fungicides, two herbicides, and twelve insecticides were found in *T. bernacchii*, four fungicides, one herbicide, and eleven insecticides were found in *N. coriiceps*. Nineteen pesticide compounds were organochlorines and organophosphates, whereas two were organobromines. Sixteen pesticide compounds were detected in both fish species, of which ten of them were common (Table 1). The detectable concentration ranges varied between 0.99 ng/g dw (Trifluralin) and 8.50 ng/g dw (*p,p'*-DDT) in the muscle tissue of *T. bernacchii*. In *N. coriiceps*, Mecarbam had the highest concentration (12.2 ng/g dw). The ratios of ∑(DDD + DDE)/∑DDT were calculated as 0.86 for both fish species. Total pesticide concentrations were 57.9 ng/g dw and 75.5 ng/g dw in *T. bernacchii* and *N. coriiceps*, respectively (Table 1). On the other hand, those concentrations were below the detection

limits in the thallus of *P. briedel* and *A. regularis*, and sediment samples were collected from five stations in the vicinity of Galindez Island (Table S1-2).

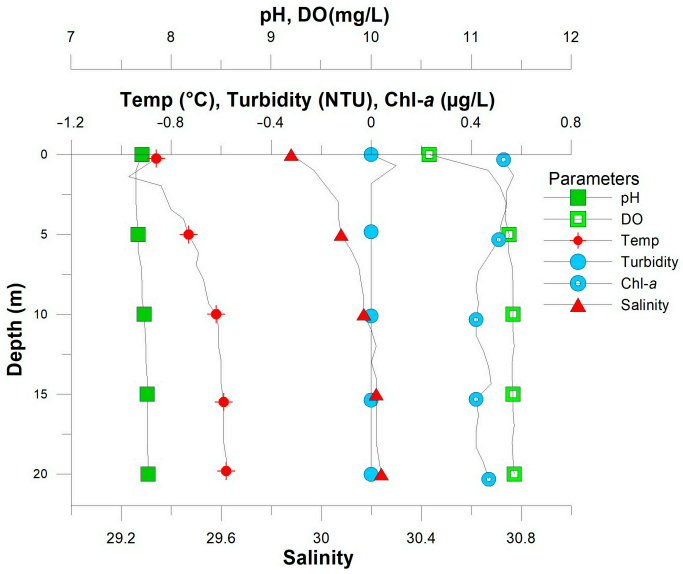

Figure 2. Temperature, salinity, dissolved oxygen, Chl-*a*, pH, and turbidity levels throughout the water column of Station 3.

Table 1. Pesticide concentrations (ng/g-dw) in the muscle tissue of *T. bernacchii* and *N. coriiceps*, gametophyte of *P. briedel* and *A. regularis*, and surface sediment samples collected from the vicinity of Galindez Island and Vernadsky Research Base.

Pesticide Congeners	Fish		Moss		Sediment [a]
	T. bernacchii	*N. coriiceps*	*P. briedel*	*A. regularis*	Sediment
Hexachlorobenzene (HCB) [f,#]	1.76	1.86	<1.0	<1.0	<1.0
Kresoxim-methyl [f,*]	-	5.80	<2.0	<2.0	<2.0
Procymidone [f,#]	6.03	6.09	<1.0	<1.0	<1.0
Quinoxyfen [f,#]	-	7.62	<1.0	<1.0	<1.0
Trifluralin [h,#]	0.99	1.32	<1.0	<1.0	<1.0
Lindane (δ-BHC) [h,#]	3.20	-	<1.0	<1.0	<1.0
Lindane (γ-HCH) [i,#]	1.46	-	<1.0	<1.0	<1.0
2,4′-DDD (*o*,*p*′-DDD) [i,#]	4.20	6.03	<1.0	<1.0	<1.0
2,4′-DDE (*o*,*p*′-DDE) [i]	3.90	6.07	<1.0	<1.0	<1.0
2,4′-DDT (*o*,*p*′-DDT) [i,#]	8.05	11.2	<1.0	<1.0	<1.0
4,4′-DDD (*p*,*p*′-DDD) [i,#]	7.08	-	<1.0	<1.0	<1.0
4,4′-DDE (*p*,*p*′-DDE) [i,#]	4.11	6.30	<1.0	<1.0	<1.0
4,4′-DDT (*p*,*p*′-DDT) [i,#]	8.50	4.70	<1.0	<1.0	<1.0
Bromophos methyl [i,#]	2.72	0.72	<1.0	<1.0	<1.0
Bromophos-ethyl [i,#]	1.97	1.96	<1.0	<1.0	<1.0
Chlordan gamma [i,#]	-	1.49	<1.0	<1.0	<1.0
Chlorpyrifos-ethyl [i,#]	1.14	-	<1.0	<1.0	<1.0
Heptachlor [i,#]	1.48	1.65	<1.0	<1.0	<1.0
Mecarbam [i,*]	-	12.2	<2.0	<2.0	<2.0
Methoxychlor [i,#]	1.35	-	<1.0	<1.0	<1.0
Pyridaben [i,*]	-	0.46	<2.0	<2.0	<2.0
TOTAL	57.9	75.5			

[f]: Fungicide, [h]: Herbicide, [i]: Insecticide, [#]: by GC-MS/MS, *: by LC-MS/MS, [a]: Since concentrations of pesticide compounds in the sediment samples were below the detection limit in all stations, only one column is used in the table.

3.3. dl-PCB and PAH Concentrations in Biota and Sediment Samples

Dioxin-like-PCBs were found in detectable levels merely in the muscle tissues of the fish species (Table 2) whereas all of the *dl*-PCB congeners were below detection limits in the moss and surface sediment samples (Tables S2-4a, S2-4b, S2-6a, S2-6b, S2-6c, S2-6d, S2-6e). Elevated levels of *dl*-PCBs were found in both fishes' muscle tissue. With a 30% measurement uncertainty, ∑12-*dl*-PCB was calculated as 160,929 pg/g dw and 26,593 pg/g dw in the muscle tissue of *T. bernacchii* and *N. coriiceps*, respectively. PCB 118, 105, and 156 were the dominant congeners with contributions of 56.4–68.4%, 19.9–20.7%, and 7.5–15.0%, respectively (Table 2). Lower-bound WHO-TEQ levels from quantified *dl*-PCB concentrations were calculated as 8.30 and 0.81 for *T. bernacchii* and *N. coriiceps*, respectively (Tables S2-2a, S2-2b). Ten of the twelve *dl*-PCB congeners were detected in the muscle tissue of the fishes. However, none of them were detected in thallus and rhizoide of *P. briedel* as well as surface sediment samples (Tables S2-4a, S2-4b, S2-6a, S2-6b, S2-6c, S2-6d, S2-6e).

Table 2. *dl*-PCB concentrations (±uncertainty) in the muscle tissue of fishes, gametophyte, and rhizoid of moss and sediment samples collected from the vicinity of Galindez Island (pg/g-dw).

***dl*-PCB Congeners**	**Fish Species**		**Bryophyta Species**		**Sediment**	**WHO 2005 TEFs**
	T. bernacchii	***N. coriiceps***	***P. briedel* (gametopyhte)**	***P. briedel* (Rhizoid)**	**Sediment [a]**	
PCB 77	83.0 ± 30%	<37.0	<3.20	<3.40	<88.0	0.0001
PCB 81	<8.80	<2.80	<0.31	<0.56	<0.83	0.0003
PCB 126	36.0 ± 30%	<4.50	<0.51	<0.48	<0.71	0.1
PCB 169	<0.58	<3.10	<0.04	<0.30	<1.10	0.03
PCB 105	32,000 ± 30%	5500 ± 30%	<5.80	<9.60	<1300	0.00003
PCB 114	680 ± 30%	<29.0	<0.04	<0.30	<29.0	0.00003
PCB 118	110,000 ± 30%	15,000 ± 30%	<9.20	<9.70	<2600	0.00003
PCB 123	600 ± 30%	<18.0	<0.44	<0.71	<39.0	0.00003
PCB 156	12,000 ± 30%	4000 ± 30%	<2.70	<5.10	<170	0.00003
PCB 157	1900 ± 30%	1000 ± 30%	<0.28	<1.20	<63.0	0.00003
PCB 167	3400 ± 30%	1000 ± 30%	<0.67	<3.00	<97.0	0.00003
PCB 189	230 ± 30%	93.0 ± 30%	<1.90	<0.33	<1.80	0.00003
WHO-TEQ (*dl*-PCB) Lowerbound	8.30 160,929 pg/g	0.81 26,593 pg/g	0	0	0	
WHO-TEQ (*dl*-PCB) Upperbound	8.30	1.40	0.053	0.058	0.0007	

[a]: Since concentrations of *dl*-PCB compounds in the sediment samples were below the detection limit in all stations, only one column is used in the table.

Among the analyzed PAH congeners, Phenanthrene Fluoranthene and Pyrene were found in detectable levels in the muscle tissue of *T. bernacchii* and *N. coriiceps*, while the other congeners were below the detection limits (Table 3). All of the PAH congeners were found to be below the detection limits in the moss and surface sediment samples (Tables S2-3, S2-5). In the muscle tissue of *T. bernacchii* and *N. coriiceps*, ∑16-PAH concentrations were calculated as 20.9 ng/g dw and 22.5 ng/g dw, respectively. Phenanthrene was the dominant congener, while fluoranthene had the lowest value among detectable PAH congeners in both fish species (Table 3).

Table 3. PAH concentrations (± uncertainty) in the muscle tissue of fishes, gametophyte, and rhizoid of moss and sediment samples were collected from the vicinity of Galindez Island (ng/g-dw).

PAH Congeners	**Fish**		**Moss**		**Sediment [a]**
	T. bernacchii	***N. coriiceps***	***P. briedel* (thallus)**	***P. briedel* (Rhizoide)**	**Sediment**
Naphthalene	<4.30	<4.60	<4.10	<5.30	<4.90
Acenaphthylene	<0.39	<0.62	<0.24	<0.33	<3.60 <0

Table 3. *Cont.*

PAH Congeners	Fish		Moss		Sediment [a]
	T. bernacchii	*N. coriiceps*	*P. briedel* (thallus)	*P. briedel* (Rhizoide)	Sediment
Acenaphthene	<0.85	<0.62	<0.27	<0.43	<4.90
Fluorene	<3.10	<3.10	<0.27	<1.40	<61.0
Phenanthrene (*Phe*)	9.80 ± 30%	10.0± 30%	<2.20	<6.30	<300
Anthracene (*Ant*)	<0.46	<0.46	<0.36	<1.00	<3.00
Fluoranthene (*Flu*)	3.40 ± 30%	4.70 ± 30%	<0.88	<2.33	<20.0
Pyrene (*Pyr*)	7.70 ± 30%	7.80 ± 30%	<0.90	<4.30	<18.0
Ant/(*Ant* + *Phe*)	0.06	0.04			
Flu/(*Flu* + *Pyr*)	0.31	0.38			
Benz[a]anthracene	<0.36	<0.46	<0.24	<0.38	<6.10
Chrysene	<0.21	<0.46	<0.36	<0.38	<7.30
Benzo[b]fluoranthene	<0.21	<0.31	<0.24	<0.38	<8.50
Benzo[k]fluoranthene	<0.21	<0.31	<0.24	<0.38	<6.70
Benzo[a]pyrene	<0.14	<0.31	<0.24	<0.25	<6.70
Indeno[1,2,3-cd]pyrene	<0.14	<0.31	<0.24	<0.25	<6.10
Dibenzo[a,h]anthracene	<0.14	<0.31	<0.24	<0.25	<2.40
Benzo[ghi]perylene	<0.21	<0.31	<0.24	<0.25	<5.10
∑16 PAH-Lowerbound	20.9	22.5	0	0	0
∑16 PAH-Upperbound	31.6	34.7	11.0	24.0	464

[a]: Since concentrations of PAH compounds in the sediment samples were below the detection limit in all stations, only one column is used in the table.

4. Discussion

The Antarctic, which is known as a pristine environment, receives pollutants from point sources and non-point sources in remote areas. Therefore, terrestrial mosses, surface sediment, and fish samples were analyzed in the present study to discriminate possible transport pathways of these chemicals, to understand whether they came via atmospheric deposition or water currents. Moreover, we measured some oceanographic parameters simultaneously with the samplings to understand the living conditions of the examined fish.

The measured oceanographic parameters represented convenient conditions for marine organisms around the island (Figure 2). The presence of Chl-*a* through the water column indicates primer productivity. Considerable living activity, including phytoplankton and zooplankton, was reported from the vicinity of Galindez Island on the same date as the sampling of the present study [20].

Results of the present study indicate that a significant amount of pesticides, *dl*-PCBs, and PAHs, including POPs, have contaminated the Antarctic marine environment, and new contaminants have been added to the list. In studies conducted around Elephant Island in 1987 and 1996, HCB concentrations in the liver of the same Notothenioid fish species were found to measure an average of 24 ng/g in Extracted Organic Material (EOM) and 19 ng/g in EOM, respectively [40], while in the same location, HCB concentrations were 17 ng/g in EOM and 30 ng/g in EOM during the same period in the muscle tissue of another Notothenioid fish species (Goerke et al., 2004). In the present study, measured HCB concentrations (i.e., 1.76 ng/g dw and 1.86 ng/g dw in the muscle tissue of *T. bernacchii* and *N. coriiceps*, respectively) were higher than the concentrations measured in the previous studies in the muscle tissue, whereas they were lower than the concentrations in the liver, considering a wet weight basis. The γ-HCH concentration was 3.44 ng/g lw in the muscle tissue of *N. coriiceps* between 2008 and 2011 in the Antarctic peninsula (Table 4) [41]. Its concentration was measured as 1.46 ng/g dw in 2016 in the present study for the same fish species and tissue; therefore, the γ-HCH concentration, measured in the present study, was higher than the previous study, on a wet weight basis. Chlordan-gamma, another highly poisonous banned insecticide, was 1.49 ng/g dw in *T. bernacchii* in the present study.

These data suggest that HCB, γ-HCH, and Chlordan-gamma maintain their presence in the Antarctic Peninsula and Notothenioid fish, despite their banning over time since 1985.

Despite being banned since the 1970s, DDT and its derivatives joined circulation in the world and maintained its existence due to its long half-life and environmental persistence [42]. Results of previous studies from the Antarctic Peninsula suggest that while the final degradation product of *p,p′*-DDT (i.e., *p,p′*-DDE) concentrations are increasing, *p,p′*-DDT levels in fish tissue have been relatively decreasing since 1985 [41,43–45] (Table 4). However, in the present study, *p,p′*-DDT, and ∑DDT levels were measured as 4.70 ng/g dw and 34.3 ng/g dw, respectively, whereas their concentrations were found to be 2.14 ng/g lw and 9.95 ng/g lw, respectively, in the muscle tissue of *N. coriiceps* during 2008–2011 in the Antarctic Peninsula [41] (Table 4). In the same study, *p,p′*-DDT and ∑DDT concentrations were also measured in a trematomus species' (i.e., *Trematomus newnesi*) muscle tissue as 4.70 ng/g lw, and 11.90 ng/g lw, respectively, while their concentrations were found to be 8.50 ng/g dw and 35.8 ng/g dw, respectively, in *Trematomus bernachii* muscle tissue in the present study (Table 4). Since the present *p,p′*-DDT and ∑DDT levels are higher than the previous studies (on a wet weight basis), it is thought that DDT is still transported outside of the continent. Eventually, transportation and deposition of contaminants by global distillation and cold condensation [5,46] and subsequent transport through the food chain still cause ∑DDT concentrations to increase in the muscle tissue of Antarctic fish. Besides DDT and its derivatives, the abovementioned compounds (i.e., HCB, γ-HCH, Chlordan isomers) were also reported from the Arctic fish [6,7], indicating the global impact of pesticide pollution.

Table 4. ∑16 PAH, ∑12 *dl*-PCB, and OCp concentrations detected in several moss, fish, and sediment samples around the Antarctic Peninsula (ng/g except for *dl*-∑PCBs, which is in pg/g).

Pollutant	Moss		Fish		Sediment	
	Conc. (ng/g)	Date [Site, Species], Reference	Conc. (ng/g)	Date [Site, Species (tissue)], Reference	Conc. (ng/g)	Date [Site], Reference
∑16 PAH	4.400–34.00	2009 [L.isl, Su], [45]	20.90–22.50 257.1 268.0 398.0–596.0	2016 [G.isl, Tb (muscle)-Nc (muscle), TS] 2004–05 [P.cov, Nc (liver)], [47] 1991–93 [D.bay, Nc (liver)], [48] 1991–93 [P.sta, Nc (liver)], [48]	32.70–1900 nd-14.49 200.0–1.650 14.00–280.0 nd-202.0 nd-252.8	2005 [P.cov], [47] 1989 [P.sta], [49] 1989 [P.sta], [50] 1988 [S.isl], [51] 2004 [A.bay], [18] 1997–00 [A.bay], [52]
∑12 *dl*-PCB (pg/g-dw)	10.40–812.0 8.000–79.00	2008 [F.pen, ns], [14] 2009 [L.isl, Su], [45]	26,593–160,929 21.180 32.200–191.00	2016 [G.isl, Tb (muscle)-Nc (muscle), TS] 2015 [KG.isl, Th (muscle)], [14] 2010 [KG.isl, Tb (muscle)], [53]	nad	
Hexachlorobenzene	0.021–0.120 0.300 0.450 0.800 0.680 0.139–0.663 0.779 1.06 0.811	2009 [L.isl, Su], [45] 1985 [PL, Ba], [44] 1985 [G.isl, Du], [44] 1985 [R.pt, Ar], [44] 1985 [La.isl, Du], [44] 2009–10 [KG.isl, ns], [43] 2004–05 [KG.isl, Bs], [54] 2004–05 [KG.isl, Sp], [54] 2004–05 [KG.isl, Su], [54]	1.760–1.860 17.00, 30.00 17.10, 15.50 26.00, 20.40 22.60, 18.60	2016 [G.isl, Tb (muscle)-Nc (muscle), TS] 1987, 1996 [E.isl, Te (muscle)], [55] 1987, 1996 [E.isl, Ca (liver)], [40] 1987, 1996 [E.isl, Cg (liver)], [40] 1987, 1996 [E.isl, Gg (liver)], [40]	16.70 14.90 3.400 0.300 0.400 0.058 0.950–4.000	2008 [SOoL.isl], [56] 2008 [OoP.sta], [56] 2008 [OoLv.isl], [56] 2008 [OoA.isl], [56] 2008 [SOoAP], [56] 2009–10 [KG.isl], [43] 2005 [JR.isl], [28]
2,4′-DDD (o,p′-DDD)		nad	4.20–6.03 <LOD <LOD <LOD	2016 [G.isl, Tb (muscle)-Nc (muscle), TS] 2008–11 [P.cov, Tn (muscle)], [41] 2008–11 [P.cov, Nc (muscle)], [41] 2008–11 [P.cov, Nr (muscle)], [41]	nad	
4,4′-DDD (p,p′-DDD)		nad	7.080 2.630 0.940 0.870	2016 [G.isl, Tb (muscle), TS] 2008–11 [P.cov, Tn (muscle)], [41] 2008–11 [P.cov, Nc (muscle)], [41] 2008–11 [P.cov, Nr (muscle)], [41]	nad	
4,4′-DDE (p,p′-DDE)	0.005–0.040 0.170 0.320 0.330 0.530 0.020–0.228	2009 [L.isl, Su], [45] 1985 [PL, Ba], [44] 1985 [G.isl, Du], [44] 1985 [R.pt, Ar], [44] 1985 [La.isl, Du], [44] 2009–10 [KG.isl, ns], [44]	4.110–6.300 4.200, 7.700 7.200, 14.50 4.000, 5.000 3.700, 7.500 4.590 6.860 7.310	2016 [G.isl, Tb (muscle)-Nc (muscle), TS] 1987, 1996 [E.isl, Te (muscle)], [55] 1987, 1996 [E.isl, Ca (liver)], [40] 1987, 1996 [E.isl, Cg (liver)], [40] 1987, 1996 [E.isl, Gg (liver)], [40] 2008–11 [P.cov, Tn (muscle)], [41] 2008–11 [P.cov, Nc (muscle)], [41] 2008–11 [P.cov, Nr (muscle)], [41]	1.400 2.800 1.600 38.10	2008 [SOoL.isl], [56] 2008 [OoP.sta], [56] 2008 [OoL.isl], [56] 2009–10 [KG.isl], [43]

Table 4. *Cont.*

Pollutant	Moss		Fish		Sediment	
	Conc. (ng/g)	Date [Site, Species], Reference	Conc. (ng/g)	Date [Site, Species (tissue)], Reference	Conc. (ng/g)	Date [Site], Reference
4,4′-DDT (p,p′-DDT)	<LOQ-0.014	2009 [L.isl, Su], [45]				
	0.300	1985 [PL, Ba], [44]	8.500–4.700	2016 [G.isl, Tb (muscle)-Nc (muscle), TS		
	0.250	1985 [G.isl, Du], [44]	4.700	2008–11 [P.cov, Tn (muscle)], [41]		
	0.440	1985 [R.pt, Ar], [44]	2.140	2008–11 [P.cov, Nc (muscle)], [41]	0.313	2009–10 [KG.isl], [43]
	0.550	1985 [La.isl, Du], [44]	3.610	2008–11 [P.cov, Nr (muscle)], [41]		
	nd-0.051	2009–10 [KG.isl, ns], [43]				
∑DDTs	0.020–0.324	2009–10 [KG.isl, ns], [43]	35.80–34.30	2016 [G.isl, Tb (muscle)-Nc (muscle), TS		
	1.220	2004–05 [KG.isl, Bs], [54]	11.90	2008–11 [P.cov, Tn (muscle)], [41]	0.577	2009–10 [KG.isl], [43]
	1.730	2004–05 [KG.isl, Sp], [54]	9.950	2008–11 [P.cov, Nc (muscle)], [41]	0.190–1.150	2005 [JR.isl], [28]
	1.620	2004–05 [KG.isl, Su], [54]	11.80	2008–11 [P.cov, Nr (muscle)], [41]		
Chlordan gamma	nad		1.490	2016 [G.isl, Nc (muscle), TS	3.600	2008 [OoP.sta], [56]
			nad	nad	1.000	2008 [OoL.isl], [56]
Lindane (γ-HCH)	0.400	1985 [PL, Ba], [44]	1.460	2016 [G.isl, Tb (muscle), TS		
	1.060	1985 [G.isl, Du], [44]	2.340	2008–11 [P.cov, Tn (muscle)], [41]		
	1.700	1985 [R.pt, Ar], [44]	3.440	2008–11 [P.cov, Nc (muscle)], [41]	nd	2009–10 [KG.isl], [43]
	1.160	1985 [La.isl, Du], [44]	3.900	2008–11 [P.cov, Nr (muscle)], [41]		
	nd-0.079	2009–10 [KG.isl, ns], [43]				

dw: Dry weight, ww: Wet weight, nd: Not detected, nad: No available data, LOD: Limit of Detection, TS: This study. Ar: *Andreaea regularis*, Ba: *Bryum algens*, Bs: *Brachitecyum* sp., Ca: *Chaenocephalus aceratus*, Cg: *Champsocephalus gunnari*, Du: *Drepanocladus uncinatus*, Gg: *Gobionotothen gibberifrons*, Nc: *Notothenia coriiceps*, Nr: *Notothenia rossii*, Su: *Sanionia uncinata*, Sp: *Syntrichia princeps*, Te: *Trematomus eulepidotus*, Tb: *Trematomus bernacchii*, Th: *Trematomus hansoni*, Tn: *Trematomus newnesi*, ns: Not specified A.bay: Admiralty bay, D.bay: Dalman bay, E.isl: Elephant island, F.pen: Fildes peninsula, G.isl: Galindez island, JR.isl: James Ross island, KG.isl: King George island, La.isl: Lagoon island, L.isl: Livingstone island, OoA.isl: Offshore of Adelaide island, OoLv.isl: Offshore of Lavosier island, OoP.sta: Offshore of Palmer station, P.cov: Potter cove, P.sta: Palmer station, PL: Port Lockroy, R.pt: Rothera point, S.isl: Signy island, SOoAP: Southern Offshore of Antarctic Peninsula, SOoL.isl: Southern offshore of Livingstone island,

Among the detected pesticides in the present study, *δ*-BHC, Trifularin, Bromophos-ethyl, Bromophos-methyl, Chlorpyrifos-ethyl, Heptachlor, and Metoxychlor have been reported previously from the Antarctic [57] but not the Antarctic Peninsula. Furthermore, no available data were found in open literature regarding residues of Kresoxim-methyl, Mecarbam, Procymidone, Pyridaben, and Quinoxyfen from the Antarctic Peninsula, and to our knowledge, these pesticides are reported from the Antarctic for the first time by the present study. These new pesticides are described as very toxic and hazardous to the aquatic environment, and among them, Kresoxim-methyl is suspected to cause cancer [58]. Since these compounds have low and/or moderate volatility, their transportation mechanism is presumably atmospheric after adsorption into the particles. However, concentrations of these pesticides were below the detection limits in the moss samples of the present study.

There were no available data in the open literature regarding *dl*-PCB contamination around Galindez Island. However, elevated *dl*-PCB congener concentrations (e.g., PCB 118, 105, 156, 167, 157, and 189) were found in the muscle tissue of *T. bernacchii* and *N. coriiceps* in the present study (Table 2). It is striking that the WHO-TEQ *dl*-PCB value (i.e., 8.30 pg/g) of the present study is over the consumable limit in fishes (i.e., 4.5 pg/g WHO-TEQ *dl*-PCB) according to the European Commission directive [59]. In another aspect, since the Scientific Committee on Food of the European Union established a tolerable weekly intake of 14 pg TEQ/kg body weight [35], the amount measured in the present study (i.e., 8.30 pg/g) is over the limit for an average (i.e., 70 kg) adult that consumes 120 g of fish weekly. Moreover, PCB 126, which has the highest toxicity among *dl*-PCBs (i.e., TEF = 0.1) [36], was found in the muscle tissue of *T. bernacchii* at a level of 36 pg/g dw. These concentrations are the highest *dl*-PCB concentrations in the muscle tissue of fish samples ever reported from the continent, and hundreds to thousands-fold higher than previous studies [14,53] carried out in the Antarctic Peninsula (Table 4). Significant positive correlations (in terms of detected common *dl*-PCB congener concentrations) between *T. bernacchii* and *N. coriiceps* muscle tissue ($r = 0.99$, $p < 0.01$, $n = 6$) indicate that both fish species were exposed to *dl*-PCB contamination via the same pathway. Since all *dl*-PCB congener concentrations were below detection limits both in the moss and the sediment samples, it is thought that the contaminants are not of airborne origin and are very likely from local contamination sources.

Diagnostic PAH ratios, i.e., *Flu*/(*Flu* + *Pyr*) and *Ant*/(*Ant* + *Phe*), obtained from fish tissues were used to estimate PAH sources. Both ratios in *T. bernacchii* (i.e., 0.31 and 0.06, respectively) and *N. coriiceps* (i.e., 0.38 and 0.04, respectively) indicate that PAHs around Galindez Island originated from petrogenic sources (Figure 3).

Since diesel PAHs mainly comprise low molecular PAHs (i.e., 2 and 3 ringed) and contain very low amounts of anthracenes due to refining processes [60], detected PAH congeners in the present study are very likely to be related to diesel contamination. In fact, the Ukrainian Vernadsky research base in Galindez Island is one of the oldest bases in the Antarctic and the oldest operational one in the Argentina Island archipelago in the Peninsula, operating year-round since 1934 [61]. Furthermore, the base host's non-governmental cruise vessels and thousands of tourists annually since 1996 [62], as well as unwanted leakages from small, motorized transportation vehicles or marine vessels may contribute to PAH contamination. Although insignificant ($p > 0.05$), the remarkable correlation ($r = 0.99$) calculated for three detectable PAH congener concentrations between *T. bernacchii* and *N. coriiceps* suggests that the fish were exposed to the same contamination sources.

In previous studies, besides atmospheric long-range transportation, numerous PAH contamination issues have been reported to be linked to fuel storage tanks, ship and boating activities or accidents, construction, station runoff, decommissioned dump sites, past disposal practices, etc., from the scientific bases [48,49]. Previous studies around the peninsula [47,50] have shown that PAHs reached elevated levels in the liver, while its concentrations did not present a detectable level in muscle, which needs a relatively long time for accumulation. In the present study, ∑16-PAH concentrations were 20.9 ng/g dw and 22.5 ng/g dw in the muscle tissue of *T. bernacchii* and *N. coriiceps*, respectively. There-

fore, the present results represent long-term PAH bioaccumulation because of previous contamination rather than a recent accident. It should be noted that, in the present study, phenanthrene was the dominant PAH congener (i.e., 9.80 ng/g dw, and 10.0 ng/g dw, in the muscle tissue of *T. bernacchii* and *N. coriiceps*, respectively), similar to mentioned studies. This result is probably related to the high adsorption capacity of phenanthrene on suspended particular matter and subsequent bioaccumulation by fish.

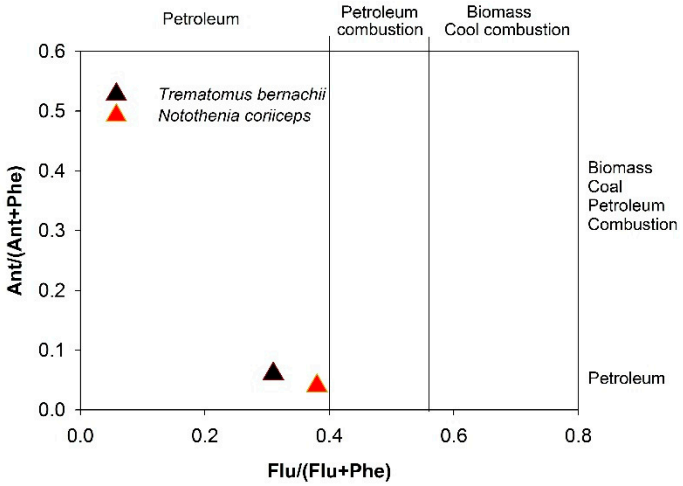

Figure 3. Source partitioning of PAHs around the vicinity of Galindez Island. Values < 0.5 of *Flu*/(*Flu* + *Pyr*) indicate that the major PAH input is from petrogenic sources [63], also values <0.1 of *Ant*/(*Ant* + *Phe*) are attributed to petrogenic sources [64].

Although POPs released to the atmosphere are mainly transported through air movements [5], water currents may play important roles in the fate of all the POPs on a local scale. It is reported that the movements around Galindez Island are in the northern direction in the surface zone and in the southern direction in the lower layer, the average current speed in both regions is 4 cm/sec, and the tidal currents are generally less than 10 cm/s [47,65,66]. Therefore, compared with open waters, removal of the contaminants may take a long time, and the increased retention time of the pollutants around the island makes it easier for marine organisms, including fish, to intake contaminants.

5. Conclusions

Comparisons between the present results and long-term data regarding persistent organic pollutant concentrations revealed that the Antarctic continent has lost its pristine features over time. The Argentina Island Archipelago and Galindez Island, in particular, are under the influence of environmental contaminants, and alongside nonpoint sources, increased human activities cause pollutant accumulation, including POPs, in living organisms. Since the renewal capacity of the surrounding water is rather low around the island, the intake of pollutants may increase. After their occurrence, some pollutants may show long-lasting effects around Galindez Island, including bioaccumulation and biomagnification stages in the marine food web. In addition, the availability of contaminants in fish tissue suggests that *T. bernacchii* and *N. coriiceps* are ideal bioindicators of local contamination because of their feeding habits and restricted home ranges. Consequently, the implementation of monitoring studies using appropriate bioindicator organisms to determine the pollution trend would be beneficial for Antarctic regions such as Galindez Island that are under the influence of human activities and the effect of contaminants.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/su14073994/s1, S1-Data for Pesticides; S2-QAQC Data for PAHs and dl-PCBs.

Author Contributions: All authors have made significant contributions (listed below) to this study. H.A.E.: Designing the study, sampling procedure, analysis details, and writing the manuscript. T.E.: Conducting laboratory analysis and interpretation of the data. E.G.P.: Conducting laboratory analysis and interpretation of the data. A.M.T.: Conducting field sampling and interpretation of the data. S.A.: Conducting laboratory analysis and interpretation of the data. B.Ö.: Designing the study, sampling procedure, and interpretation of the data. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Scientific Research Projects Coordination Unit of Kocaeli University, grant number 2016/026, and the Scientific Research Projects Coordination Unit of Istanbul University, grant number FOA-2016-20530. The APC was funded by ÇEVSİS R&D, grant number 2022/01. The authors thank the Rectorates of Istanbul and Kocaeli Universities, Turkish Marine Research Foundation (TUDAV), the captain and crew of M/V Ushuaia, and the Turkish and Ukrainian authorities for their valuable help and support.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Baek, S.Y.; Choi, S.D.; Chang, Y.S. Three-Year Atmospheric Monitoring of Organochlorine Pesticides and Polychlorinated Biphenyls in Polar Regions and the South Pacific. *Environ. Sci. Technol.* **2011**, *45*, 4475–4482. [CrossRef] [PubMed]
2. Bidleman, T.F.; Walla, M.D.; Roura, R.; Carr, E.; Schmidt, S. Organochlorine Pesticides in the Atmosphere of the Southern-Ocean and Antarctica, January March, 1990. *Mar. Pollut. Bull.* **1993**, *26*, 258–262. [CrossRef]
3. Khairy, M.A.; Luek, J.L.; Dickhut, R.; Lohmann, R. Levels, sources and chemical fate of persistent organic pollutants in the atmosphere and snow along the western Antarctic Peninsula. *Environ. Pollut.* **2016**, *216*, 304–313. [CrossRef] [PubMed]
4. Montone, R.C.; Taniguchi, S.; Weber, R.R. PCBs in the atmosphere of King George Island, Antarctica. *Sci. Total Environ.* **2003**, *308*, 167–173. [CrossRef]
5. Wania, F.; Mackay, D. Global Fractionation and Cold Condensation of Low Volatility Organochlorine Compounds in Polar-Regions. *Ambio* **1993**, *22*, 10–18.
6. Kylin, H.; Hammar, J.; Mowrer, J.; Bouwman, H.; Edelstam, C.; Olsson, M.; Jensen, S. Persistent organic pollutants in biota samples collected during the Ymer-80 expedition to the Arctic. *Polar. Res.* **2015**, *34*, 11. [CrossRef]
7. Hargrave, B.T.; Harding, G.C.; Vass, W.P.; Erickson, P.E.; Fowler, B.R.; Scott, V. Organochlorine Pesticides and Polychlorinated-Biphenyls in the Arctic-Ocean Food Web. *Arch. Environ. Contam. Toxicol.* **1992**, *22*, 41–54. [CrossRef]
8. Persistent Organic Pollutants an Assessment Report on: DDT-Aldrin-Dieldrin-Endrin-Chlordane Heptachlor-Hexachlorobenzene Mirex-Toxaphene Polychlorinated Biphenyls Dioxins and Furans. Available online: http://chm.pops.int/Portals/0/docs/from_old_website/documents/meetings/inc1/RITTER-En.html (accessed on 15 February 2022).
9. Trinh, M.M.; Chang, M.B. Review on occurrence and behavior of PCDD/Fs and dl-PCBs in atmosphere of East Asia. *Atmos. Environ.* **2018**, *180*, 23–36. [CrossRef]
10. UNEP. Stockholm Convention on Persistent Organic Pollutions (POPs). In Proceedings of the Secretariat of the Stockholm Convention, Geneva, Italy, 24 April–5 May 2017.
11. Weber, R.; Aliyeva, G.; Vijgen, J. The need for an integrated approach to the global challenge of POPs management. *Environ. Sci. Pollut. Res.* **2013**, *20*, 1901–1906. [CrossRef]
12. Gilden, R.C.; Huffling, K.; Sattler, B. Pesticides and Health Risks. *J. Obstet. Gynecol. Neonatal Nurs.* **2010**, *39*, 103–110. [CrossRef]
13. Alcock, R.E.; Behnisch, P.A.; Jones, K.C.; Hagenmaier, H. Dioxin-like PCBs in the environment-Human exposure and the significance of sources. *Chemosphere* **1998**, *37*, 1457–1472. [CrossRef]
14. Wang, Q.; Shi, Y.H.; Hu, J.X.; Yao, Z.W.; Fang, X.K.; Dong, Y.A. Determination of dioxin-like polychlorinated biphenyls in soil and moss from Fildes Peninsula, Antarctica. *Chin. Sci. Bull.* **2012**, *57*, 992–996. [CrossRef]
15. Fuoco, R.; Giannarelli, S.; Wei, Y.; Ceccarini, A.; Abete, C.; Francesconi, S.; Termine, M. Persistent organic pollutants (POPs) at Ross Sea (Antarctica). *Microchem. J.* **2009**, *92*, 44–48. [CrossRef]
16. Weber, R.; Bell, L.; Watson, A.; Petrlik, J.; Paun, M.C.; Vijgen, J. Assessment of pops contaminated sites and the need for stringent soil standards for food safety for the protection of human health. *Environ. Pollut.* **2019**, *249*, 703–715. [CrossRef] [PubMed]
17. Abdel-Shafy, H.I.; Mansour, M.S.M. A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egypt. J. Pet.* **2016**, *25*, 107–123. [CrossRef]
18. Bicego, M.C.; Zanardi-Lamardo, E.; Taniguchi, S.; Martins, C.C.; Da Silva, D.A.M.; Sasaki, S.T.; Albergaria-Barbosa, A.C.R.; Paol, F.S.; Weber, R.R.; Montone, R.C. Results from a 15-year study on hydrocarbon concentrations in water and sediment from Admiralty Bay, King George Island, Antarctica. *Antarct. Sci.* **2009**, *21*, 209–220. [CrossRef]
19. Ozturk, B.; Tonay, M.A.; Oz, M.I.; Yilmaz, I.N.; Ergul, H.A.; Ozturk, A.A. Sightings of cetaceans in the Western Antarctic Peninsula during the first joint Turkish-Ukrainian Antarctic Research Expedition, 2016. *Turk. J. Zool.* **2017**, *41*, 955–961. [CrossRef]
20. Yilmaz, I.N.; Ergul, H.A.; Mavruk, S.; Tas, S.; Aker, H.V.; Yildiz, M.; Ozturk, B. Coastal Plankton Assemblages in the Vicinity of Galindez Island and Neumayer Channel (Western Antarctic Peninsula) during the First Joint Turkish-Ukrainian Antarctic Research Expedition. *Turk. J. Fish. Aquat. Sci.* **2018**, *18*, 577–584. [CrossRef]

21. Öztürk, B.; Fach, B.A.; Çiçek, B.Ö.; Hüsrevoğlu, S.; Salihoğlu, B.; Ergül, H.A.; Aktaş, Ş.; Çotuk, B.; Çifçi, G.; Öztürk, A.A. Towards the Turkish Antarctic Science Programme. *J. Black Sea/Mediterr. Environ.* **2014**, *20*, 92–95.
22. Kamler, E.; Krasicka, B.; Rakusa-Suszczewski, S. Comparison of lipid content and fatty acid composition in muscle and liver of two notothenioid fishes from Admiralty Bay (Antarctica): An eco-physiological perspective. *Polar Biol.* **2001**, *24*, 735–743.
23. Cali, F.; Riginella, E.; La Mesa, M.; Mazzoldi, C. Life history traits of Notothenia rossii and N-coriiceps along the southern Scotia Arc. *Polar Biol.* **2017**, *40*, 1409–1423. [CrossRef]
24. *US-EPA 429*; California Environmental Protection Agency (CEPA) Method 429. Determination of Polycyclic Aromatic Hydrocarbons (PAH). California Air Resources Board: Sacramento, CA, USA, 1997.
25. *ISO 11388*; Stationary Source Emissions—Determination of Gas and Particle—Phase Polycyclic Aromatic Hydrocarbons—Sampling. International Organization for Standardization: Geneva, Switzerland, 2003.
26. *IP 346*; Determination of Polycyclic Aromatics in Unused Lubricating Base Oils and Asphaltene Free Petroleum Fractions-Dimethyl Sulphoxide Extraction Refractive Index Method. Standard Methods for Analysis and Testing of Petroleum and Related Products. John Wiley and Sons: Chichester, UK, 1992.
27. *CEN, EN 16619*; Food Analysis Determination of Benzo[a]pyrene, Benz[a]anthracene, Chrysene and Benzo[b]fluor Anthene in Foodstuffs by Gas Chromatography Mass Spectrometry (GC-MS). European Committee for Standardization: Brussels, Belgium, 2015.
28. Klánová, J.; Matykiewiczová, N.; Máčka, Z.; Prošek, P.; Láska, K.; Klán, P. Persistent organic pollutants in soils and sediments from James Ross Island, Antarctica. *Environ. Pollut.* **2008**, *152*, 416–423. [CrossRef] [PubMed]
29. *US-EPA 3540*; Test Methods for Evaluating Solid Waste-Soxhlet Extraction. The United States Environmental Protection Agency US GPO: Washington, DC, USA, 1995.
30. *US-EPA 1668*; Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS. EPA-821-R-00-002. United States Environmental Protection Agency: Washington, DC, USA, 1999.
31. *CSN 121 P CEN/TS 16190*; Footwear-Critical Substances Potentially Present in Footwear and Footwear Components. Test Method to Quantitatively Determine Polycyclic Aromatic Hydrocarbons (PAH) in Footwear Materials. International Organization for Standardization: Genova, Italy, 2013.
32. *JIS, K0311*; Method for Determination of Tetra-through Octachlorodibenzo-p-Dioxins, Tetrathrough Octachlorodibenzofurans and Dioxin-like Polychlorinated Biphenyls in Stationary Source Emissions. Japanese Standards Association: Tokyo, Japan, 2005.
33. Lehotay, S.J. Determination of pesticide residues in foods by acetonitrile extraction and partitioning with magnesium sulfate: Collaborative study. *J. AOAC Int.* **2007**, *90*, 485–520. [CrossRef] [PubMed]
34. US-FDA. Pesticide Analytical Manual (PAL). In *Methods Which Detect Multiple Residues*; Bernadette, M.M., Sawyer, L.D., Eds.; US Department of Health and Human Services Food and Drug Administration: Rockville, MD, USA, 1987; Volume 1-82-1, pp. 179–192.
35. Weber, R.; Herold, C.; Hollert, H.; Kamphues, J.; Ungemach, L.; Blepp, M.; Ballschmiter, K. The Life cycle of PCBs and contamination of the environment and of food products from animal origin. *Environ. Sci. Pollut. Res.* **2018**, *25*, 16325–16343. [CrossRef] [PubMed]
36. Van den Berg, M.; Birnbaum, L.S.; Denison, M.; De Vito, M.; Farland, W.; Feeley, M.; Fiedler, H.; Hakansson, H.; Hanberg, A.; Haws, L.; et al. The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicol. Sci.* **2006**, *93*, 223–241. [CrossRef]
37. Ahlborg, U.G.; Becking, G.C.; Birnbaum, L.S.; Brouwer, A.; Derks, H.; Feeley, M.; Golor, G.; Hanberg, A.; Larsen, J.C.; Liem, A.K.D.; et al. Toxic equivalency factors for dioxin-like PCBs: Report on WHO-ECEH and IPCS consultation, December 1993. *Chemosphere* **1994**, *28*, 1049–1067. [CrossRef]
38. Guinan, J.; Charlesworth, M.; Service, M.; Oliver, T. Sources and geochemical constraints of polycyclic aromatic hydrocarbons (PAHs) in sediments and mussels of two Northern Irish Sea-loughs. *Mar. Pollut. Bull.* **2001**, *42*, 1073–1081. [CrossRef]
39. Pinheiro, N.; Barreira, L.; Lopes, B.; Bebianno, M.J. Assessment of oil contamination in the bay of Porto Grande (Cape Verde) using the mullet Chelon bispinosus. *Afr. J. Environ. Sci. Technol.* **2013**, *7*, 657–670.
40. Weber, K.; Goerke, H. Persistent organic pollutants (POPs) in Antarctic fish: Levels, patterns, changes. *Chemosphere* **2003**, *53*, 667–678. [CrossRef]
41. Lana, N.B.; Berton, P.; Covaci, A.; Ciocco, N.F.; Barrera-Oro, E.; Atencio, A.; Altamirano, J.C. Fingerprint of persistent organic pollutants in tissues of Antarctic notothenioid fish. *Sci. Total Environ.* **2014**, *499*, 89–98. [CrossRef]
42. ATSDR. *Toxicological Profile for DDT, DDE, and DDD (Draft for Public Comment)*; Department of Health and Human Services, Public Health Service: Atlanta, GA, USA, 2019.
43. Zhang, Q.H.; Chen, Z.J.; Li, Y.M.; Wang, P.; Zhu, C.F.; Gao, G.J.; Xiao, K.; Sun, H.Z.; Zheng, S.C.; Liang, Y.; et al. Occurrence of organochlorine pesticides in the environmental matrices from King George Island, West Antarctica. *Environ. Pollut.* **2015**, *206*, 142–149. [CrossRef] [PubMed]
44. Bacci, E.; Calamari, D.; Gaggi, C.; Fanelli, R.; Focardi, S.; Morosini, M. Chlorinated Hydrocarbons in Lichen and Moss Samples From the Antarctic Peninsula. *Chemosphere* **1986**, *15*, 747–754. [CrossRef]
45. Cabrerizo, A.; Dachs, J.; Barcelo, D.; Jonest, K.C. Influence of Organic Matter Content and Human Activities on the Occurrence of Organic Pollutants in Antarctic Soils, Lichens, Grass, and Mosses. *Environ. Sci. Technol.* **2012**, *46*, 1396–1405. [CrossRef] [PubMed]

46. Wania, F.; Mackay, D. Tracking the distribution of persistent organic pollutants. *Environ. Sci. Technol.* **1996**, *30A*, 390–396. [CrossRef]
47. Curtosi, A.; Pelletier, E.; Vodopivez, C.L.; Mac Cormack, W.P. Distribution of PAHs in the water column, sediments and biota of Potter Cove, South Shetland Islands, Antarctica. *Antarct. Sci.* **2009**, *21*, 329–339. [CrossRef]
48. McDonald, S.J.; Kennicutt, M.C.; Liu, H.; Safe, S.H. Assessing Aromatic Hydrocarbon Exposure in Antarctic Fish Captured Near Palmer and Mcmurdo Stations, Antarctica. *Arch. Environ. Contam. Toxicol.* **1995**, *29*, 232–240. [CrossRef]
49. Kennicutt, M.C.; McDonald, T.J.; Denoux, G.J.; McDonald, S.J. Hydrocarbon contamination on the Antarctic Peninsula: I. Arthur harbor—Subtidal sediments. *Mar. Pollut. Bull.* **1992**, *24*, 499–506. [CrossRef]
50. Kennicutt, I.I.M. Oil spillage in Antarctica: Initial report of the National Science Foundation-sponsored Quick Response Team on the grounding of the Bahia Paraiso. *Environ. Sci. Technol.* **1990**, *24*, 620–624. [CrossRef]
51. Cripps, G.C. The Extent of Hydrocarbon Contamination in the Marine-Environment from a Research Station in the Antarctic. *Mar. Pollut. Bull.* **1992**, *25*, 288–292. [CrossRef]
52. Martins, C.C.; BÍCego, M.C.; Taniguchi, S.; Montone, R.C. Aliphatic and polycyclic aromatic hydrocarbons in surface sediments in Admiralty Bay, King George Island, Antarctica. *Antarct. Sci.* **2004**, *16*, 117–122. [CrossRef]
53. Wolschke, H.; Meng, X.Z.; Xie, Z.Y.; Ebinghaus, R.; Cai, M.H. Novel flame retardants (N-FRs), polybrominated diphenyl ethers (PBDEs) and dioxin-like polychlorinated biphenyls (DL-PCBs) in fish, penguin, and skua from King George Island, Antarctica. *Mar. Pollut. Bull.* **2015**, *96*, 513–518. [CrossRef] [PubMed]
54. Cipro, C.V.Z.; Yogui, G.T.; Bustamante, P.; Taniguchi, S.; Sericano, J.L.; Montone, R.C. Organic pollutants and their correlation with stable isotopes in vegetation from King George Island, Antarctica. *Chemosphere* **2011**, *85*, 393–398. [CrossRef] [PubMed]
55. Goerke, H.; Weber, K.; Bornemann, H.; Ramdohr, S.; Plötz, J. Increasing levels and biomagnification of persistent organic pollutants (POPs) in Antarctic biota. *Mar. Pollut. Bull.* **2004**, *48*, 295–302. [CrossRef] [PubMed]
56. Zhang, L.; Dickhut, R.; DeMaster, D.; Pohl, K.; Lohmann, R. Organochlorine Pollutants in Western Antarctic Peninsula Sediments and Benthic Deposit Feeders. *Environ. Sci. Technol.* **2013**, *47*, 5643–5651. [CrossRef]
57. Miranda, K.C.; Metcalfe, C.D.; Metcalfe, T.L.; Muelbert, M.M.C.; Robaldo, R.B.; Martinez, P.E.; Colares, E.P.; Bianchini, A. Lactational transfer of PCBs and chlorinated pesticides in pups of southern elephant seals (Mirounga leonina) from Antarctica. *Chemosphere* **2009**, *75*, 610–616. [CrossRef]
58. Chemicals Evaluated for Carcinogenic Potential Annual Cancer Report. Available online: https://apublica.org/wp-content/uploads/2020/05/chemicals-evaluated.pdf (accessed on 15 February 2022).
59. EU. *Commission Directive 2006/13/EC*; Official Journal of the European Union: Brussels, Belgium, 2006.
60. Wang, Z.D.; Fingas, M.; Sigouin, L. Characterization, and identification of a "mystery" oil spill from Quebec (1999). *J. Chromatogr. A* **2001**, *909*, 155–169. [CrossRef]
61. Bondar, S. Assessment of Load Influence of the Akademik Vernadsky Antarctic Station on the Quality of Adjacent Marine Area. *Ukr. Antarct. J.* **2003**, *1*, 143–145. [CrossRef]
62. Fedchuk, A. The development of tourism at Faraday/Vernadsky station: Changes in governance and visitor patterns. *Polar Rec.* **2013**, *49*, 286–290. [CrossRef]
63. De La Torre-Roche, R.J.; Lee, W.Y.; Campos-Diaz, S.I. Soil-borne polycyclic aromatic hydrocarbons in El Paso, Texas: Analysis of a potential problem in the United States/Mexico border region. *J. Hazard. Mater.* **2009**, *163*, 946–958. [CrossRef]
64. Pies, C.; Hoffmann, B.; Petrowsky, J.; Yang, Y.; Ternes, T.A.; Hofmann, T. Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in riverbank soils. *Chemosphere* **2008**, *72*, 1594–1601. [CrossRef]
65. Brion, D.; Pelletier, E. Modelling PAHs adsorption and sequestration in freshwater and marine sediments. *Chemosphere* **2005**, *61*, 867–876. [CrossRef] [PubMed]
66. Bondar, S.; Orlova, I.G.; Popov, Y.I.; Ukrainsky, V.V.; Usenko, V.P. Ecological Monitoring in the Region of Akademik Vernadsky Antarctic Station. *Ukr. Antarct. J.* **2003**, 139–142. [CrossRef]