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# Profiling and Spatial Variation Analysis of Persistent Organic Pollutants in South African Delphinids

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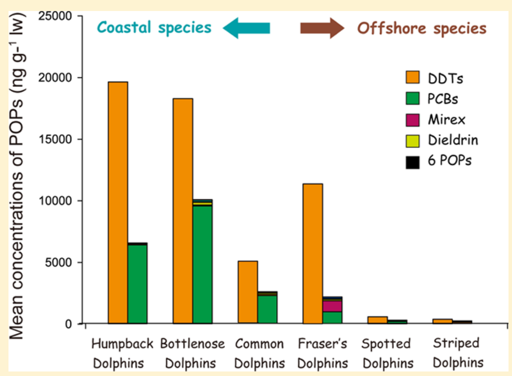
*Supporting Information*

**ABSTRACT:** The continuous disposal of persistent organic pollutants (POPs) in South Africa (SA) warrants concern about their detrimental effects on humans and wildlife. We surveyed six dolphin species ($n$ = 90) incidentally captured in shark net installations or stranded off the SA east and south coast from 2005 to 2009 to study the POP exposure. *Sousa plumbea*, an inshore and estuarine species, was found to be the most contaminated by total POPs (21 100 ng $g^{-1}$ lw) of all the dolphins off SA, followed by *Tursiops aduncus* (19 800 ng $g^{-1}$ lw), *Lagenodelphis hosei* (13 600 ng $g^{-1}$ lw), and *Delphinus capensis* (5500 ng $g^{-1}$ lw), whereas POP levels in the offshore or pelagic delphinids were much lower. In all delphinids, dominant pollutants were dichlorodiphenyltrichloroethanes (DDTs), which represented more than 60% of the total concentration of total POPs, followed by polychlorinated biphenyls (PCBs, 30%). Concentrations of DDTs in *S. plumbea* and *T. aduncus* off SA were among the highest levels reported in delphinids globally. Approximately half of the adult *T. aduncus* had PCB concentrations above the effect threshold for impairment of immune functions. The concentrations of Mirex and Dieldrin in SA delphinids were higher than those found in species from other regions of the Southern Hemisphere.




## INTRODUCTION

Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) are among the most toxic persistent organic pollutants (POPs), which are widely distributed in coastal marine ecosystems. After trophic transfer, these toxicants can eventually bioaccumulate to high levels in human tissue as well as bodies of marine predatory mammals, causing immune and reproductive dysfunction, birth defects, and certain cancers.[1,2] Given the prolonged persistence and long-range transport of POPs in marine ecosystems, no countries or regions are free from such ecotoxicological impact. International and intergovernmental cooperation in monitoring the spatial and temporal trends of POPs is therefore essential in tracing the source and fate of these contaminants, especially for developing countries such as South Africa (SA), where certain legacy POPs continue to be detected at concentrations that are among the highest globally (e.g., dichlorodiphenyltrichloroethane (DDT)[3] and hexachlorocyclohexanes (HCHs)[4]) and where new POPs (e.g., PFOS, dechlorane, PBDEs, etc.) have emerged due to recent industrialization.[5−7] Although there are indications that the concentrations of PCBs, DDTs, and HCHs in the SA environment have decreased or been constant since the mid-1980s,[8,9] the high POP levels found in the SA human population[10−13] and other biota[14−16] still raise serious concerns.

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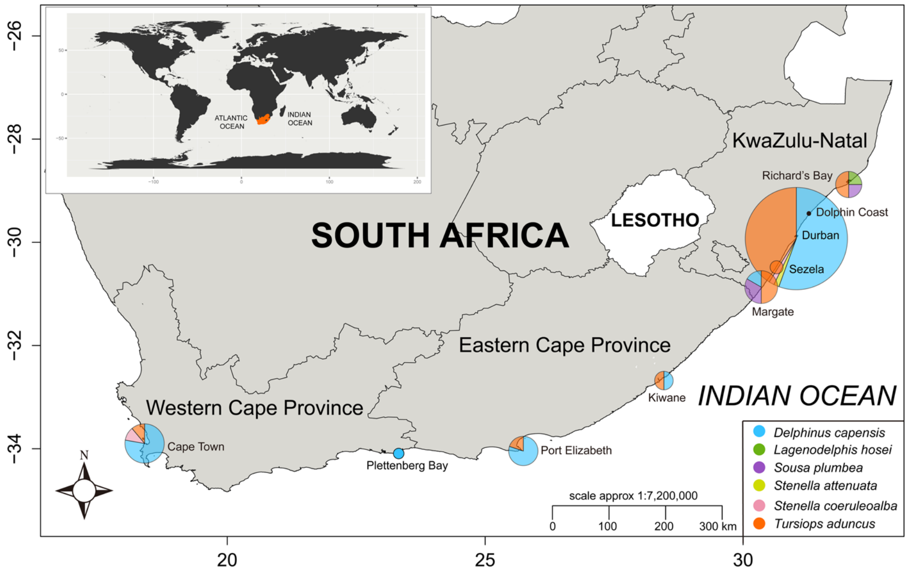


**Figure 1.** Sampling locations of six dolphin species along the east and south coast of South Africa. The size and color of the circles represent the sample size and species, respectively.

Considering the ocean is the ultimate sink for terrestrial pollutants, nearshore delphinids are prone to accumulate high levels of lipophilic POPs. As top predators with long lifespans and rich fats in body tissues, delphinids can serve as a model for studying a long-term POP bioaccumulation and can be regarded as bioindicators to profile the spatial and temporal trends of coastal pollutions.[17−19] However, monitoring of POP exposure in cetaceans in the Southern Hemisphere is scanty.[20] Recent studies revealed elevated levels of POPs in marine mammals from the Antarctic region,[21] while those off the Brazilian coast were reported to be stable or decrease slightly over a 10-year period (1994−2004).[22]

The east and south coast of SA (KwaZulu-Natal, hereafter KZN; the Eastern Cape and the southeast coast of the Western Cape Province) is washed by a strong warm southerly Agulhas Current. Several dolphin species are known to occur in this region, and most of them are designated under the IUCN criteria as "data deficient" because of the limited local and regional knowledge of their populations and ecology.[23,24] SA delphinids show varied niche width and trophic diversity, which are associated with their habitat selectivity off SA.[25] Indian Ocean humpback dolphins (*Sousa plumbea*) are strictly inshore. Indo-Pacific bottlenose dolphins (*Tursiops aduncus*) inhabit nearshore waters, and long-beaked common dolphins (*Delphinus capensis*) tend to inhabit nearshore or continental shelf waters, whereas striped dolphins (*Stenella coeruleoalba*), pantropical spotted dolphins (*Stenella attenuata*), and Fraser's dolphins (*Lagenodelphis hosei*) are pelagic species that prefer deeper waters further offshore.[26] A number of delphinids were caught in shark nets off KZN, which were set to protect bathers against shark attacks (for more information about the program, see http://www.shark.co.za/).[27−29] The most frequently caught are *T. aduncus*, *D. capensis*, and *S. plumbea*. Although much less frequently captured compared to *T. aduncus* and *D. capensis*, *S. plumbea* is of a particular concern due to their small population size (estimated 165 in KZN[30,31]) and high number of mother/calf pairs captured in the net installations.[27,32,33] Seasonal dietary shift and increased parasitic diseases have been reported in recent investigations of SA delphinids,[34,35] which showed correlation with recent global climate change and expanding fisheries,[36] although no obvious pathological symptoms nor epidemiological evidence on health effects of recent ecological changes were discovered. Trend analysis of POP concentrations in the SA delphinids would therefore help in the understanding of the potential involvement of pollutants in the overall negative environmental impacts.

A number of studies regarding the spatial and temporal trends of POP accumulation in SA delphinids were undertaken in the 1980s.[37−41] However, the last such study dates back to 1987, and the issue of POP exposure in SA coastal waters has not been comprehensively addressed since. Considering the continued input of legacy POPs in the environment, we hypothesize that SA dolphins might be exposed to elevated levels of POPs, and this magnitude of POP concentration may represent a health risk. In our study, we investigate the concentrations of 21 PCBs and 10 OCPs as biomarkers of recent POP exposure and determine concentrations of POPs in SA delphinids over time. A substantial number of dolphins were incidentally captured in shark nets, and dead carcasses were recovered off the east and south coast of SA during 2005−2009, which instigated this work. Furthermore, we investigate the major factors (e.g., the species, sex, age, and spatial variation) influencing the levels and profiles of POPs in SA delphinids, which may assist in future informed management decisions and help prioritize future studies of nearshore delphinids in SA and elsewhere.

## ■ MATERIALS AND METHODS

**Sample Collection.** A total of 90 blubber samples from six dolphin species, *S. plumbea* ($n = 3$), *T. aduncus* ($n = 32$), *D. capensis* ($n = 50$), *S. coeruleoalba* ($n = 2$), *S. attenuata* ($n = 2$), and *L. hosei* ($n = 1$), were collected between 2005 and 2009 in 9 locations on the east (from Richard's Bay to Kiwane, approximately 660 km in a straight line) and south (from Cape Town to Port Elizabeth, approximately 660 km in a straight line) coast of SA (Figure 1). Samples originated primarily from dolphins incidentally caught in shark nets off the coast of KZN and, in some cases, from stranded carcasses recovered along the south and east coast (1 for *S. attenuata*, 1 for *L. hosei*, 2 for *S. coeruleoalba*, and 2 for *T. aduncus*). Only


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freshly dead (code 2) or early moderately decomposed (code 3) animals were sampled to ensure the quality of the analysis.[42] The blubber in front of the dorsal fin was removed, packed in aluminum foil, and stored at −80 °C. Total body length was measured as a straight line from the tip of the upper jaw to the fluke notch.[43,44] Sex was determined by external or internal examination. Sexual maturity was determined on the basis of the total length, following the method of Best.[26] It was assumed that the animals were sexually mature when their body length reached 243 and 238 cm for male and female *T. aduncus*, 220 and 213 cm for male and female *D. capensis*, 210−220 and 220−222 cm for male and female *S. plumbea*, 215 and 200 cm for male and female *S. coeruleoalba*, 186 and 181 cm for male and female *S. attenuata*, and 220−240 and 210−220 cm for male and female *L. hosei*, respectively. The samples were coded according to their maturity and sex: adult male (AM), adult female (AF), juvenile male (JM), and juvenile female (JF).

**Laboratory Analyses.** Analyses of PCBs and OCPs in blubber samples were performed according to Gui et al.[45] All the standards of target analytes were purchased from the AccuStandard company, USA. The full procedure of extraction and cleanup of PCBs and OCPs can be found in the Supporting Information. Briefly, after the addition of anhydrous $Na_2SO_4$, approximately 0.5 g of blubber tissue was extracted with hexane/dichloromethane (DCM) by the Soxhlet apparatus. Spiked surrogate standard was $^{13}C$-chlorobiphenyl (CB) 141 (AccuStandard, USA). Extracts were cleaned using an S-X3 Biobeads packed gel-permeation chromatography (GPC) column and eluted with a 1:1 mixture of hexane/DCM. The fraction was further purified by two types of chromatography columns separately for PCBs and OCPs according to Gui et al.[45] A known amount of internal standards [$^{13}C$-PCB 138 (AccuStandard, USA) for PCB analysis; naphthalene-$d_8$, acenanaphthene-$d_{10}$, phenanthrene-$d_{10}$, chrysene-$d_{12}$, and perylene-$d_{12}$ (Ultra Scientific, USA) for OCP analysis] was added to the final extract prior to instrumental analysis.

We used a gas chromatograph (GC, Agilent 7890, USA) coupled with a capillary column (DB-5MS with dimensions 60 m × 0.25 mm × 0.25 $\mu$m) (J&W Scientific, USA) and a mass spectrometer (MS) detector (Agilent 5975, USA) in electronic ionization mode (EI) with a selected-ion monitoring (SIM) acquisition method. The same parameters of GC-MS-EI-SIM, as listed by Gui et al.,[45] were used. Quantification ions ($m/z$) for each target compound were shown in Table S2. Briefly, the GC was operated in the splitless injection mode using 1 $\mu$L injection volumes. The column oven temperature for the detection of OCPs was programmed as follows: 70 °C held for 2 min; increased at 3 °C per minute to 270 °C and held for 5 min; increased at 5 °C per minute to the final temperature of 300 °C and held for 10 min. The column oven temperature for the detection of PCBs was programmed as follows: 80 °C held for 2 min; increased at 4 °C per minute to 290 °C and held for 6 min; increased at 20 °C per minute to the final temperature of 310 °C and held for 5 min. The temperatures of the transfer line, injector interface, and ion source were set at 300, 290 and 230 °C, respectively. Helium was used as the carrier gas. The rate of flow was set at 1.0 mL min$^{-1}$.

The analyzed compounds were 21 PCB congeners (CB28, CB37, CB52, CB77, CB81, CB101, CB105, CB114, CB118, CB123, CB126, CB153, CB138, CB128, CB156, CB157, CB167, CB169, CB180, CB188, and CB209), DDTs (dichlorodiphenyltrichlorethanes, including *o,p′*-DDT, *p,p′*-DDT, *o,p′*-DDD, *p,p′*-DDD, *o,p′*-DDE, and *p,p′*-DDE), HCHs (hexachlorocyclohexanes, including $\alpha$-HCH, $\beta$-HCH, and $\gamma$-HCH), CHLs (chlordanes, including *cis*-chlordane and *trans*-chlordane), Mirex, HCB (hexachlorobenzene), heptachlor, aldrin, pentachlorobenzene, dieldrin, and endrin.

**Quality Assurance/Quality Control (QA/QC).** Quality assurance/quality control (QA/QC) procedures followed criteria established by Mai et al.[46] A method blank, a spiked blank with a known standard solution, a matrix spike (a known amount of target analyte standard solutions spiked into pre-extracted blubber), and a sample duplicate were analyzed and compared in each set of 18 samples. The concentrations in the procedural blanks never exceeded the 3-fold values of the method detection limit (MDL), which ranged from 0.33 ng g$^{-1}$ lipid weight (lw) to 1.42 ng g$^{-1}$ lw as shown in Table 1. The relative difference between duplicate samples was below 15% for all target analytes. The matrix spike recovery rates of the target analytes (PCBs and OCPs) ranged from 79.6% to 119%, with a relative significant difference (RSD) lower than 12%. For PCB analysis, recovery rates of surrogate standard ($^{13}C$-PCB 141) ranged from 91.5% to 112%, with a mean of 98.4% (standard deviation = 10.2%). For OCP analysis, the recoveries of $^{13}C$-PCB 141 ranged from 72.2% to 118%, with a mean of 83.9% (standard deviation = 24.3%). Concentrations of POP classes were not corrected for recoveries since recoveries were within an established acceptable range.

**Data Analysis.** Statistical analyses were all conducted using R (Ver 3.1.0).[47] The adult female dolphins were excluded in all the comparison analysis due to the well-described maternal transfer effects of POPs during gestation and lactation.[45] POP concentrations were lipid-normalized for comparison. To calculate the total POP concentration, all values below the detection limit were assigned as a value of zero. Nonparametric or permutation-based approaches were selected instead of traditional parametric statistics, since the former ones are more appropriate for the processing of data with small sample size and outliers. For example, a permutation-based one-way analysis of variances (ANOVAs) followed by Tukey's Honestly Significant Difference (HSD) tests was performed to determine the POP concentration difference in each blubber among different age and sex groups and among locations. For the comparison of POP levels between two putative *T. aduncus* populations, a nonparametric alternative of the two-sample $t$ test (Wilcoxon rank sum test) was undertaken, using Monte Carlo simulation to sample from all possible permutations. We set the $p$-value as 0.05 to reject the null hypothesis. The regression of POP concentrations with the body length of *T. aduncus* and *D. capensis* was analyzed after a log-transformation of the original data. A Pearson rank order correlation was performed to examine the possible significance of linear relationships between the dolphin body length and POP concentration. For all POP components, no significant linear relationship was observed ($p$ > 0.05). Consequently, a LOWESS smoother (locally weighted scatter plot using a weighted quadratic least-squares regression smoothing) was applied to extrapolate the complex relationships between dolphin body length and POP concentration. Toxic equivalents (TEQ) relative to 2,3,7,8-TCDD were calculated for dioxin-like PCBs (mono−ortho PCBs 105, 114, 156, 157, and 189) that had over 60% detection rate using toxic equivalency factors (TEFs) derived from Van den Berg et al.[48]


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**Table 1. Persistent Organic Pollutants (ng g$^{-1}$ Lipid Weight) in Six Delphinid Species from South Africa Sampled between 2005 and 2009**

| | *Delphinus capensis* | | | *Tursiops aduncus* | | | *Sousa plumbea* | | | *Stenella attenuata* | | | *Stenella attenuata* | | | *Lagenodelphis hosei* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *n* = 50 | | | *n* = 32 | | | *n* = 3 | | | *n* = 2 | | | *n* = 2 | | | *n* = 1 |
| | mean (median) | min | max | mean (median) | min | max | mean (median) | min | max | mean | min | max | mean | min | max | |
| lipid content (%) | 58.6 | 21.2 | 83.2 | 67.2 | 36.7 | 90.8 | 77.3 | 56.3 | 90.5 | 62.4 | 52.6 | 77.2 | 80 | 77 | 82 | 65 |
| DDTs (ng g$^{-1}$ lw) | 3630 (3690) | 127 | 10900 | 11900 (7530) | 282 | 85800 | 15300 (6520) | 2180 | 37100 | 598 | 379 | 816 | 392 | 208 | 576 | 11400 |
| PCBs (ng g$^{-1}$ lw) | 1600 (1280) | 78.5 | 10300 | 7470 (4990) | 307 | 28500 | 5690 (4220) | 2150 | 10700 | 222 | 105 | 340 | 141 | 23.2 | 259 | 938 |
| HCHs (ng g$^{-1}$ lw) | 26.9 (26) | <1.42 | 62.2 | 40.6 (31.6) | 3.07 | 162 | 18.1 (15.6) | 6.73 | 32.1 | 15.4 | 10.6 | 20.2 | <0.38 | <0.39 | <0.37 | 13.0 |
| Mirex (ng g$^{-1}$ lw) | 92.7 (51.3) | 9.00 | 1070 | 72.7 (53.5) | 2.07 | 365 | 63.1 (73.2) | 22.4 | 93.7 | 44.7 | 21.2 | 68.1 | 60.1 | 33.1 | 87.1 | 891 |
| HCB (ng g$^{-1}$ lw) | 24.7 (16.4) | <1.42 | 197 | 18.0 (13.1) | 0.95 | 46.9 | 12.3 (4.86) | 1.33 | 30.6 | 4.64 | 2.21 | 7.07 | 10.4 | 2.65 | 18.1 | 139 |
| CHLs (ng g$^{-1}$ lw) | 33.7 (30.5) | 2.14 | 147 | 125 (52.7) | 10.6 | 854 | 2.47 (2.83) | 0.32 | 4.26 | 10.9 | 4.51 | 17.5 | 7.49 | 6.32 | 8.67 | 50.9 |
| dieldrin (ng g$^{-1}$ lw) | 81.2 (53.9) | <1.42 | 371 | 186 (73.6) | 3.04 | 1280 | 82.5 (90.9) | 38.4 | 118 | 26.2 | 9.06 | 43.2 | 30.1 | 23.0 | 37.1 | 114 |
| heptachlor (ng g$^{-1}$ lw) | 0.07 (0) | <1.42 | 0.60 | <0.45 | <0.82 | <0.33 | 0.98 (1.08) | <0.53 | 1.86 | 6.94 | <0.57 | 13.9 | 0.73 | <0.39 | 1.46 | <0.45 |
| pentachlorobenzene (ng g$^{-1}$ lw) | 0.09 (0) | <1.42 | 1.24 | 0.04 (<0.45) | <0.82 | 0.98 | 0.25 (<0.67) | <0.53 | 0.75 | <0.48 | <0.57 | <0.67 | <0.38 | <0.39 | <0.37 | <0.67 |
| endrin (ng g$^{-1}$ lw) | 1.89 (0) | <1.42 | 32.5 | 12.9 (1.01) | <0.82 | 109 | 0.38 (<0.67) | <0.53 | 1.13 | 2.12 | <0.57 | 4.24 | <0.38 | <0.39 | <0.37 | 78.7 |
| sum (ng g$^{-1}$ lw) | 5500 | | | 19800 | | | 21100 | | | 931 | | | 642 | | | 13600 |

## RESULTS AND DISCUSSION

**Comparison of Blubber POP Levels among Six Dolphin Species.** Blubber POP concentrations in six dolphin species are presented in Table 1. All 21 PCB and 10 OCP residues were detected in at least one specimen of each investigated species, except aldrin. The residues of heptachlor, pentachlorobenzene, and endrin were detected in fewer than 30% of samples, whereas the other POPs were all detected in more than 90% of samples.

Of all the species analyzed, *S. plumbea*, *T. aduncus*, *L. hosei*, and *D. capensis* displayed the highest levels of contaminants, with a mean of total POP concentrations at 21 100, 19 800, 13 600, and 5500 ng g$^{-1}$ lw, respectively (Table 1), most likely due to the proximity of their habitats to coasts with high pollution loads. For the remaining species including *S. attenuata* (930 ng g$^{-1}$ lw) and *S. coeruleoalba* (642 ng g$^{-1}$ lw), which are regarded as offshore or pelagic species, the total POP levels were markedly lower. Lower contamination levels of organic pollutants in offshore delphinids from less contaminated open sea agree with several previous studies.[49,50] However, it is interesting to note that *L. hosei*, a species inhabiting offshore waters and thus rarely stranding on the SA coast, had considerably high POP levels (13600 ng g$^{-1}$ lw). *Lagenodelphis hosei* feeds mainly on midwater and deepwater fishes in mesopelagic waters[51] and likely has an elevated exposure to other contamination sources due to its wide distribution range.

**Comparison with Other Regions.** It is well-known that habitat, sex, and individual maturity can influence POP accumulation in dolphins's blubber.[52] Considering this, we compared our findings to what is known of delphinids elsewhere, using individuals of the same sex and maturity of congeneric species or species that inhabit similar habitats (e.g., *S. plumbea* and *Sotalia guianensis* both inhabit inshore and estuarine habitats).

Among all the analyzed POP components, DDTs were the predominant contaminants (Figure 2). The juvenile male (JM) *S. plumbea* presented the highest mean level of DDTs, which was slightly higher than that in the same age class of *S. chinensis* from the Pearl River Estuary, China[45] and approximately 2.3–

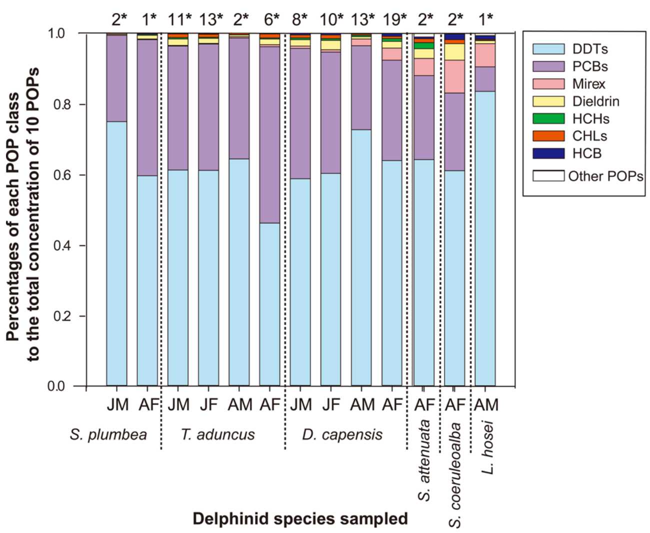


**Figure 2.** Percentage contributions of each POP class to the total POP concentration in juvenile male (JM) and female (JF) and adult male (AM) and female (AF) groups of six delphinids sampled in South Africa. *Sample size per group is shown above each bar.


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25 times higher than that in *Sotalia guianensis* off the northeastern[52] and southeastern[53] coast of Brazil (Supporting Information). *Sousa chinensis* and *S. guianensis* are currently known to accumulate DDTs at the highest levels in the Northern and Southern Hemisphere, respectively, due to their preference for nearshore habitats and the considerable DDT contamination of coastal waters off China and Brazil, two developing countries where DDTs are still in use.[45,53] In *T. aduncus*, the two dead dolphins stranded off Durban had the first and second highest concentration of DDTs among all samples analyzed in this study (mean = 64 600 ng $g^{-1}$ lw), indicating that the death of these dolphins could be associated with the potential sources of DDTs. DDT levels in all age/sex classes of *T. aduncus* from SA were slightly lower than those collected between 2000 and 2002 off Zanzibar, Tanzania, East Africa,[54] except for the juvenile male group (Table S1). This pattern indicates that DDTs are ubiquitously distributed at high levels in near-shore dolphins off the east coast of Africa. Compared with *D. capensis* from southeastern Brazil,[50] individuals off the SA coast represent 3.3-fold higher levels of DDTs in the juvenile female group but 4.9-fold lower in the adult male group (Table S1). DDT levels found in *L. hosei* off SA were 6.6−27-fold as high as those off Brazil.[50] However, the results for *D. capensis* and *L. hosei* were not robust due to the low sample size. In conclusion, the DDT levels in SA delphinids were notably higher than those reported from other geographic regions and should be considered as a warning of a potential threat to local dolphin populations.

Following DDTs, which accounted for around 65% of the total POP concentration, PCBs averaged 30% and represented the second most common POPs in SA delphinids (Figure 2). In this study, samples from adult male (AM) *T. aduncus* showed the highest mean concentration of PCBs, followed by the juvenile male (JM) group, JM of *S. plumbea*, and others. The total PCB concentrations obtained in this study were not directly comparable among the available dolphin studies due to the great differences in numbers and types of PCB congeners analyzed. Nevertheless, the highest residual level of PCB 153 in SA dolphins (7930 ng $g^{-1}$ lw) was 20.4-fold lower than that in Australian humpback dolphins (*Sousa sahulensis*) inhabiting an urbanized region (170 000 ng $g^{-1}$ lw[55]), which is among the highest recorded for marine mammals worldwide. For *T. truncatus* in the Southern Hemisphere, the highest concentration of PCB 153 was reported in AM individuals off southeastern Brazil (approximately 2010 ng $g^{-1}$ lw),[50] which was 1.50-fold lower than the values found in AM *T. aduncus* in this study (5180 ng $g^{-1}$ lw). Furthermore, a comparison of PCB concentrations of the same number and type of PCB congeners in inshore species between SA and other regions indicated that PCB concentrations in SA *S. plumbea* were 1.32- to 19.5-fold higher than the Pearl River Estuary's *S. chinensis* in China.[45]

The effect threshold on immune function of total PCBs provides a guide to determine what concentrations may have a deleterious influence on dolphin health.[57] In this study, the PCB levels in four AM and one AF *T. aduncus* collected in the urbanized region of Durban exceeded the approximate known threshold (17 000 ng $g^{-1}$ lw),[56] including the two stranded dead *T. aduncus*. The TEQs approach, based on the most recent TEFs reported by Van den Berg et al.[48] was adopted for the toxicity assessment of dioxin-like PCB congeners. PCB 126 was the main contributor to total TEQs in SA dolphins, which had over 90% detection rate, whereas PCB 81 and 169 were detected in less than 30% of samples. The highest mean TEQ concentration was found in *S. plumbea*, followed by *T. aduncus*, *D. capensis*, *S. attenuata*, *L. hosei*, and *S. coeruleoalba* (Table S3). By comparing with TEQs calculated for PCB 126 in corpses of diseased dolphins collected from various stranding events elsewhere (ranging from 7.02 to 43 ng $g^{-1}$ lw),[57−59] those in SA dolphins were notably lower (0−4.73 ng $g^{-1}$ lw). However, the overall PCB levels in the SA dolphins were relatively higher compared with those in delphinids worldwide,[45,50] which should be a cause for concerns, especially so for the inshore dolphin species off the SA coast.

The high concentrations of Mirex in AM *L. hosei* were comparable with the highest records reported in rough-toothed dolphins (*Steno bredanensis*) (829 ng $g^{-1}$ lw) from the Pacific.[49] The second highest Mirex concentration was found in AM *T. aduncus* followed by AM *D. capensis* (Table S1). Mirex is primarily used as an insecticide to control harvester termites (*Trinervitermes trinervoides*) in SA and fire ants (*Solenopsis invicta*) in the USA. Mirex is not registered for use in SA;[60] however, low levels of Mirex in bird eggs in central and southwestern SA have been reported recently.[61] Mirex levels in south polar skuas (*Catharacta maccormicki*)) from the Antarctic have also been shown to be among the highest recorded levels in birds.[62] Mirex is listed in the Stockholm Convention as one of the most persistent of current POPs.[63] The unknown sources of Mirex in delphinids and bird eggs in SA, as well as bird blood from the Antarctic, call for watchful monitoring of the contamination and its hazardous impacts in the Southern Hemisphere.

The highest dieldrin levels were found in JM *T. aduncus*, followed by AM *L. hosei* and AM *D. capensis*. Dieldrin levels in the juvenile *T. aduncus* off the SA coast were similar to levels reported in juvenile *T. truncatus* from two estuaries in the southeastern United States (356 ng $g^{-1}$ lw).[64] In comparison with *S. chinensis* from China's Pearl River Estuary,[45] dieldrin levels of *S. plumbea* in SA were 2-fold higher. Although field application of dieldrin has been banned for several decades in SA,[58] periodic use and high levels of this insecticide have been reported in southern Africa.[65] The relatively high level of this POP observed in delphinids from SA may indicate the high persistence and the possible continuing use of this chemical in this region.

The highest levels of HCHs, CHLs, HCB, heptachlor, and pentachlorobenzene were found in *T. aduncus*. Compared with congeneric or similar delphinids from other geographic regions,[45,52,54] delphinids in SA had lower levels of these chemicals, most likely because these POPs were less used than PCBs, DDTs, and other POPs in SA. However, heptachlor and pentachlorobenzene can be degraded to heptachloroepoxide and pentachloroanisole, respectively, which could also attribute to their low residue level detected in SA dolphins.

The highest levels of endrin were found in *L. hosei*. Levels in *S. plumbea* (0.38 ng $g^{-1}$ lw) were lower than those in *S. chinensis* from the Pearl River Estuary, China (26.5 ng $g^{-1}$ lw).[45] Endrin has been mainly used as an insecticide on field crops, although it was also used as rodent poison bait.[58] Its use has been banned in SA, and the level of endrin in the SA environment is generally low.[66]

**Congener Patterns for POPs.** Different composition patterns for POP congeners were observed between *T. aduncus* and *D. capensis* by the Nonmetric Multidimensional Scaling analysis (details about this method were shown in Figure S1), which could be due to their interspecific differences in diet composition or in metabolic capacity. However, POP profiles


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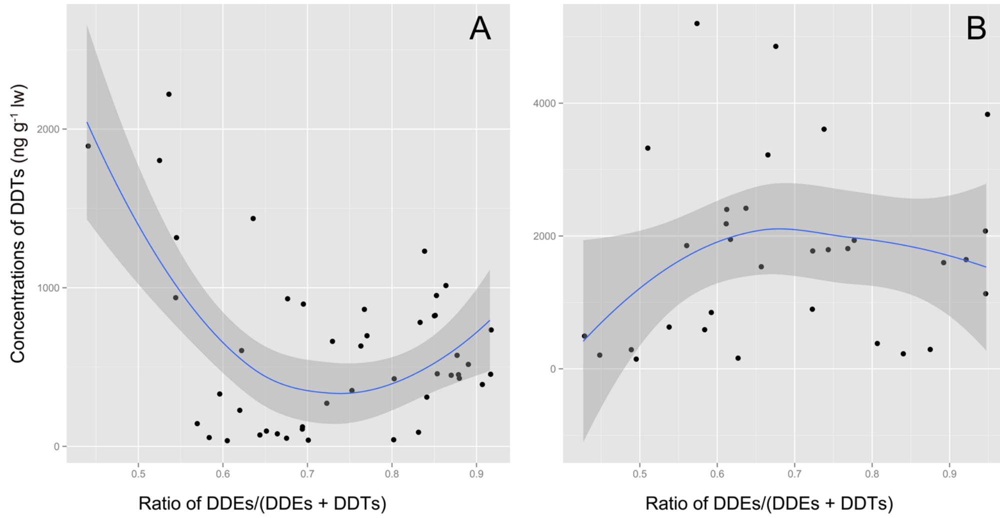


**Figure 3.** Relationships of DDEs/(DDEs + DDTs) ratio with the concentration of DDTs (*o,p′*-DDT + *p,p′*-DDT) in the blubber of *D. capensis* (A) and *T. aduncus* (B) in South Africa, respectively.

were not discriminated by other factors, such as spatial variation, maturity, and sex. Significant difference in diet composition between the two species was documented off the KZN coast; near-shore sardines and chub mackerel were the predominant prey items found in the stomach of stranded and shark-net entangled *D. capensis*, whereas *T. aduncus* feed on a wide variety of inshore and pelagic prey species.[25] Therefore, dolphin diet may represent different exposure pathways of pollutants for these two species. However, the residue patterns of POPs in the lipids of dolphins can also result from their species-specific ability to metabolize or excrete certain pollutants. A substantial interspecies difference in the capacity to metabolize POPs has been reported for several cetacean species.[67,68]

A typical technical DDT is composed primarily of *p,p′*-DDT (77.1%),[69] which can be metabolized by living organisms into *p,p′*-DDE (under oxidative conditions) or *p,p′*-DDD (under anaerobic conditions). The DDEs (*o,p′*-DDE + *p,p′*-DDE)/DDTs ratio may reveal the extent of degradation undergone by the precursor DDTs in the ecosystem.[70] The highest ratio of DDEs/DDTs among SA delphinids was observed in *S. plumbea* (0.96), whereas the lowest one was found in *S. attenuata* (0.48) (Table S2). *Sousa plumbea* is a shallow-water inshore species with high habitat selectivity and relatively limited ranging pattern,[71−73] while *S. attenuata* has a considerably wider distribution due to a greater physical ability to disperse.[26] Therefore, *S. attenuata* may have more exposure chance to pollutants from other regions, whereas the residual levels in *S. plumbea* represent more accurately the local coastal pollution status in SA. However, given the small sample size of *S. plumbea* and *S. attenuata*, the result had little statistical power. Metabolism rates and feeding habits can affect the ratio of DDEs/DDTs observed in the tissue of dolphins, which may or may not reflect recent DDT input to the ecosystem. Given the uncertainty, we have tested the correlation of the DDEs/(DDEs + DDTs) ratio with DDT (*o,p′*-DDT+*p,p′*-DDT) concentrations (Figure 3). For *D. capensis*, the DDT concentration decreased as the fraction of DDE in total DDTs increased, suggesting that DDTs were converted to DDEs given no continuous input of DDTs (Figure 3A). However, no clear trend was observed for *T. aduncus* (Figure 3B), which may be caused by a continuous exposure to DDTs. As *T. aduncus* inhabits waters closer to the coasts, compared to *D. capensis*, thus it is likely exposed to a more abundant source of DDTs discharged to the coastal waters by riverine input. Currently, DDTs are now no longer sprayed from aircraft in SA, but indoor residual spraying (IRS) with DDTs is practiced in SA for malaria control,[13] which might serve as a point source via river discharge. $\beta$-HCH was the predominant HCH isomer in SA delphinids, while *cis*-CHL was more abundant than *trans*-CHL, indicating the higher resistance of the compounds to metabolic degradation.

**Relationship of POP Levels with Body Length.** As shown in Figure S2, concentrations of DDTs, PCBs, and Mirex all had a contrasting pattern of distribution between males and females according to their body length. Their exposure levels were high in males with small body size but gradually decreased as the animals approached the size of sexual maturity, after which the concentrations started to increase with body length. Among females, small individuals had lower concentration levels of DDTs, PCBs, and Mirex than males, based on a small sample size of juvenile/neonate males. As females approached the size of sexual maturity, the concentrations increased and subsequently began to decline. In contrast to the pattern displayed by PCB, DDT, and Mirex, concentration levels of HCH, CHLs, HCB, and dieldrin did not increase with body length in males larger than the size at sexual maturity, while in females the concentrations also decreased after dolphins reached the size of sexual maturity.

This pattern can be explained as follows: high concentration levels in juveniles/neonates may be due to a high POP load received from maternal transfer and mother's milk during lactation, as evidenced in long-finned pilot whales (*Globicephala melas*)[74] and bottlenose dolphins (*Tursiops truncatus*).[75] As the body length increases rapidly in juveniles, POP concentrations may be diluted until the animals reach sexual maturity. OCP residues such as HCHs, which are less lipophilic and less stable than PCBs and DDTs, can be degraded or metabolized by adult animals, whereas highly lipophilic and stable contaminants including PCBs and DDTs continue to exhibit higher concentrations in male dolphins as their body size grows. For female *D. capensis* larger than 224 cm, an increasing POP concentration with increasing body size was noted. This profile may reflect a reduced reproductivity in older females, echoing


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similar reports by Muir et al.[76] and Ross et al.[77] However, these results had no statistic power due to the small sample size of *D. capensis* larger than 224 cm. No such pattern was observed in *T. aduncus* in this study.

**Spatial Variations and Temporal Trends for POPs.** As *D. capensis* caught in the shark nets off the KZN coast were presumably in pursuit of sardines (*Sardinops sagax*) moving from the far south,[78] *D. capensis* can not represent the ambient pollution levels around their sampling sites. Thus, *T. aduncus,* which exhibits stronger year-round residency off the coast of SA, was used for the spatial variation analysis. Since no significant difference was observed in POP concentrations among the JM, JF, and AM groups (ANOVA, $p > 0.05$), POP data from the three age and sex groups were pooled to obtain sufficient sample sizes (>3) for each site.

A statistically significant difference among locations was found for PCBs (ANOVA, $p < 0.05$). Concentrations of PCBs were significantly higher in *T. aduncus* from Sezela than those from Dolphin Coast [as indicated by (*) in Figure 4]. Cockcroft et al.[38] found that *T. aduncus* from Sezela and further north presented 2-fold higher mean concentrations of PCBs than those from Margate and further south, which corresponds with significant genetic differentiation ($p < 0.05$) between these two populations.[79] We also found that the mean levels of PCBs in *T. aduncus* from Sezela were approximately 3-fold as high as those from Magarate, which indicated the potential sources of PCB contamination off the coast of Sezela. No statistically significant difference among locations was found for OCPs, despite the highest mean levels of all OCPs were always found in *T. aduncus* from Durban (Figure S3). In addition, we found that one individual of *D. capensis* from the area off Port Elizabeth had 10-fold higher levels of Mirex (1070 ng $g^{-1}$ lw) than the second highest record in *T. aduncus* and *D. capensis*. Owing to small sample size from Port Elizabeth, however, this result has little statistical power and can not indicate a potential source of Mirex in Port Elizabeth.

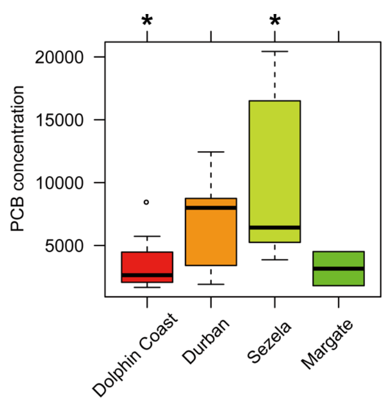


**Figure 4.** Site variations of the PCB levels (ng $g^{-1}$ lw) in *T. aduncus* along the east coast of South Africa. Groups (represented by box plots) labeled by (*) are significantly different.

By comparing earlier reports (1980−1985) of DDT, PCB, and dieldrin levels in *T. aduncus* off the coast of KZN[38] with those of the current study (2005−2009), different temporal changes were found among the three POP classes and among different age-sex groups, despite no significant difference was noted ($p > 0.05$, Wilcoxon rank sum test). DDTs showed an obvious increasing trend in adult males (Figure S4) and a moderate decrease in juvenile males and females. PCB levels apparently decreased in all age/sex groups from the 1980s to 2000s. Dieldrin also showed a decreasing trend in all the three groups in accordance with a global decline[20] (Figure S4).

The DDT residue results in dolphins from this study broadly corresponded with the contamination status in SA due to the continuous use of DDTs for malaria control after the 1980s.[64] In the same region and the same time period, a declining trend of PCBs and dieldrin was observed in all age and sex groups of *T. aduncus*, indicating the overall decrease of PCB and dieldrin levels in SA delphinids. From the perspective of food chain transfer, the detrimental effects and residue risk of DDTs in SA estuaries might have occurred not only in dolphins themselves but also in their prey, fish, and other seafood[80] used also for human consumption. Our study provides strong argument for further contamination control of DDT in the coastal ecosystem of South Africa. We suggest that the only effective approach to reduce the DDT contamination in this marine ecosystem is to discontinue the use of DDT for malaria control by finding a safer approach.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b06009.

Further details on the analytical methods, additional figures, and tables as noted in the text. (PDF)

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### Author Contributions

L.K. and Y.W. conceived and designed the research. Y.W. and L.K. managed the research project. S.P. and G.C. collected and provided the samples. L.C. supervised the experiments. Q.T. performed the experiments. D.G., R.-Q.Y., and Y.W. analyzed the data. D.G., R.-Q.Y., Y.W., and L.K. wrote the paper. D.G., R.-Q.Y., Y.W., L.K., S.P., and G.C. revised the manuscript. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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