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Polycyclic Aromatic Hydrocarbons (PAHs) and Organochlorinated Pesticides (OCPs) in Yellowtail (*Seriola lalandi*) from three Spatially Distinct Locations along the Coast of South Africa: Levels, Sources and Fish Size Effect

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) and organochlorinated pesticides (OCPs) such as dichlorodiphenyltrichloroethane (DDT), endosulfan and benzenehexachloride (BHC) were evaluated in yellowtail (*Seriola lalandi*) fish species. These hardous compounds were studied in fish sampled from three locations: Port Elizabeth, Yzerfontein and Struis Bay. The aim of the study was to investigate the profiles, levels and sources of PAHs and pesticides in yellowtail from the selected locations in relation to fish size and lipid content. Significant variations ($p<0.05$) were observed in the levels of PAHs measured in fish sampled from the three locations. Fish from Port Elizabeth had the highest PAHs concentrations (533.95 ± 34.36), followed by Yzerfontein (221.40 ± 33.03) and Struis Bay (88.97 ± 2.83) µg/kg wet weight. Benzo(*a*)pyrene (as PAHs biomarker) exceeded the recommended EU limit (2 µg/kg) in samples from Port Elizabeth and Yzerfontein whereas samples from Struis Bay did not exceed. DDT was detected only in samples from Port Elizabeth and Yzerfontein with mean total concentrations (7.48 ± 5.18 and 11.14 ± 1.44 respectively) not significantly different. Fish size (weight) correlated positively with lipid content (0.65; $p<0.01$) and a stronger positive correlation with ΣPAHs (0.83; $p<0.01$). PAHs input source in fish from Port Elizabeth reflected a mixture of petrogenic and pyrogenic whereas, Yzerfontein and Struis Bay showed input source as petrogenic. In conclusion, consumption of large sized fish in locations with high PAHs burden can predispose consumers to health risk. Further investigation into human dietary exposure with the species is recommended.

Highlights

a. Organic contaminants (OCs) PAHs and organochlorine pesticides were investigated in yellowtail (*S. lalandi*).

b. Variation in levels and profiles of OCs were evidenced across study locations.

c. Fish size, lipid content and locational inputs were contributory variation factors.

Keywords: *Seriola lalandi*; Organic contaminants; Fish size; Fish fat; Health-hazard

Introduction

Sequel to the Stockholm convention on persistent organic pollutants (POPs) in 2002, some hazardous compounds have been identified for global control or ban based on their persistence, ubiquity, toxicity and carcinogenicity [1-3]. These hazardous compounds remain in the environment due to their low degradation, spatial transferability and lipophilicity which promotes their accumulation in fatty tissues and thus biomagnify in the food web [4-6]. Such hazardous compounds considered in this study include polycyclic aromatic hydrocarbons (PAHs) and organochlorinated pesticides (OCPs). PAHs are a group of compounds formed by the fusion of two or more benzene rings with napthalene (2 benzene rings) as the simplest [7]. Though more than 100 PAHs have been isolated from various matrices, the 16 PAHs US EPA priority PAHs were considered. In addition to the PAHs, OCPs such as dichlorodiphenyltrichloroethane (DDT), benzenehexachloride (BHC), endosulfan, aldrin, eldrin and dieldrin among others were also evaluated in *S. lalandi*. In line with the US EPA recommendations for choice of contaminants to be studied [4]; the target contaminants (PAHs and OCPs) were selected based on their prevalence and use within the country [8-10]. These compounds hither to be referred to as organic contaminants (OCs) except where otherwise stated.

Organochlorine contaminants accumulates in fish mainly through contaminated diet and water in polluted aquatic environment with oily fish accumulating higher levels [11]. A number of biological factors such as fish sex, age, feeding habit and lipid content (among others) can affect the accumulation of contaminants in fish [12]. Once the contaminants are ingested into the fish, redistribution into different tissues portions occurs based on binding affinity. For example, the lipophilic ones can be trapped in more fatty tissues such as liver [13]. Furthermore, enzymatic biotransformation of these contaminants can lead to their breakdown into by-products that can be stored in the fish or eliminated [14,15]. However, no conclusive trend had been reported with these factors with respect to accumulation of contaminants for they are interwoven but fish species as well as contaminant type were reported as major determining factors. Frequent consumption of fish contaminated with OCs may hamper the associated health benefits from fish particularly the dietary contribution of omega 3 and 6 fatty acids. Human dietary exposure to the OCs were reported to be significantly higher via fish and sea foods [15-17], hence the relevance to assess

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the OCs levels and sources in one of the South African commonly consumed marine species (*S. lalandi*). Yellowtail is an important commercial and recreational marine linefish species and is among the most commonly consumed fish species in South Africa [18,19]. It is pelagic as well as demersal species (benthopelagic) and widely distributed in places such as the Atlantic, Pacific and Indian temperate waters [18], whilst distribution within South Africa include KwaZulu-Natal, Western and Eastern Cape Provinces. Its current status is being over fished and annual catch was reported to have declined from 700 tonnes (1995) to 400 tonnes in 2011 [20]. Currently information on concentration of OCs in yellowtail species is scarce globally and South Africa in particular. The study was therefore aimed at evaluating the concentrations and profiles of OCs in yellowtail (*Seriola lalandi*) marine fish harvested from Yzerfontein, Port Elizabeth and Struis bay, on the coast of South Africa. In addition the size, lipid content and locational distribution of OCs in yellowtail species from the three study locations were compared.

Materials and Methods

Sample collection and preparation

Ten yellowtail fish were harvested from each of the three different locations namely Port Elizabeth (33.9581°S, 25.6000°E) in the Eastern Cape Province and Yzerfontein (33.3330°S, 18.1620°E) and Struis Bay (34.8044°S, 20.0575°E) both in the Western Cape Province. Fish samples were harvested by local line fishermen in collaboration with the Department of Agriculture, Fisheries and Forestry (DAFF), which were sampled from these locations on different dates. Harvested fish were transported in crates covered with ice to the Stellenbosch University laboratory and fish biometric data; total length (cm) and weight (g), were recorded (Table 1). Fish samples were rinsed under clean tap water and thereafter eviscerated, beheaded, skinned and filleted. Finally samples were homogenized on an individual basis, vacuum packed and stored at -20°C until further chemical analysis.

Experimental analysis

Chemicals and standards: Acetonitrile of analytical grade (purity > 98%) purchased from Stargate Science, South Africa was used as extraction solvent. High purity analytical calibration standards (≥ 99.9%) used for instrumental calibration were purchased from Sigma Aldrich (USA) (with catalogue number M-610). These include Accustandard polynuclear aromatic hydrocarbon (PAH) mix comprised of 16 US EPA priority PAHs (acenaphthene, acenaphthylene, anthracene, benz(*a*) anthracene, benzo(*a*)pyrene, benzo(*b*)fluoranthene, benzo(*g,h,i*) perylene, benzo(*k*)fluoranthene, chrysene, dibenzo(*a,h*) anthracene, fluoranthene, fluorene, indeno(*1,2,3-cd*)pyrene, naphthalene, phenanthrene and pyrene), and EPA Pesticide mix (4,4′-DDT, 4,4′-DDE, 4,4′-DDD, aldrin, chlordane, endrin, endosulfan 1 and 2, heptachlor, benzenehexachloride (BHC-alpha, beta, delta and gamma analogues), eldrin aldehyde, endosulfan sulfate). Internal standards used were deuterated 4,4′-DDT-d8, naphthalene d8, acenaphthene d10, chrysene d12 and perylene d12. Certified reference material (CRM) of fish origin could not be purchased due to logistical restrictions; therefore, a soil certified reference material (CRM 141.50G) PAH-Loamy clay was used. QuEChERS pre-packed extraction kits (50 mL Teflon centrifuge/extraction tube and 15 mL Teflon centrifuge/clean-up tube containing extraction salts and clean-up agents, respectively) were used. All standard stock solutions were prepared in acetonitrile then diluted to the desired concentrations. A 7-point GC calibration of mix standard solutions was made at concentration levels: 10 µg/L, 20 µg/L, 40 µg/L, 60 µg/L, 100 µg/L, 200 µg/L and 300 µg/L. To each calibration solution, the internal standards mixture (50 µg/L) was added. The extraction solvent acetonitrile containing the internal standards mixture (50 µg/L) was freshly prepared before extraction.

Location	Sample size (n)	Weight (g)	Length (cm)	Lipid (%)
Port Elizabeth	10	13925.00 ± 321.48	123.75 ± 1.81	3.605 ± 0.22
Yzerfontein	10	3236.30 ± 131.61	72.48 ± 1.01	2.771 ± 0.06
Struis Bay	10	6955.00 ± 415.56	98.18 ± 2.59	Missing data

Table 1: Average (± Std. Error) weight, length and lipid content of yellowtail (*Seriola lalandi*) sampled from Port Elizabeth, Yzerfontein and Struis Bay assessed for organic contaminants OCs (PAHs and OCPs).

Total lipid determination: Total lipid (crude fat) was determined according to Lee et al. [21] by using 5 g of homogenized fish, (ten per location in duplicates) extracted with 50 mL of chloroform methanol in the ratio of 1:2 v/v. A hand held mixer (bamix) was used to mix the fish and solvent thoroughly for 1 min, which was then filtered into a separating funnel and with the addition of 20 mL of 5% salt solution, the polar and non-polar phases were separated after standing for 60 min. The polar phase was decanted into an Erlenmeyer flask and 5 mL extract transferred into a pre-weighed fat beaker which was dried in a sand bath to a constant weight (45 min) and the percentage lipid gravimetrically calculated.

Extraction and instrumental analysis of OCs: The target OCs (16 US EPA PAHs, DDT and other OCPs) were extracted from fish samples on individual basis according to AOAC [22] and Anasstasaides et al. [23] quick, easy, cheap, efficient, rugged and safe (QuEChERS) method (with modification). Briefly described thus, 5 gram of each individual fish homogenate was weighed into a 50 mL QuEChERS Teflon centrifuge tube. Milli-Q-water (5 mL) was added; shaken (1 min) to mix thoroughly, 10 mL acetonitrile containing 50 µg/L mixed internal standards was added. Each tube was allowed to stand for 15 min, then QuEChERS pre-mix salt (6 g $MgSO_4$ and 1.5 g NaCl) was added, vigorously shaken for 1 min (for quick dispersion of the salts into the fish homogenate), vortexed (3 min) and centrifuged (4 min) at 4000 revolution per minute (rpm). The vortex and centrifuge increased the separation and clarification of the lipid and aqueous phases. An aliquot of 6 mL from the supernatant was transferred into the (QuEChERS) 15 mL dispersive solid phase (dSP) clean-up Teflon centrifuge tube containing 900 mg $MgSO_4$, 300 mg PSA (primary secondary amine) and 150 mg C_{18} (sorbent). Then the individual tubes and content were again shaken and vortexed (1 min) and centrifuged as above. Finally, 1 mL of the purified extract was transferred into a GC labelled vial, corked and analysed with GC-MS/MS.

Simultaneous analysis of OCs from purified fish extract was carried out according to a modified method described by Kalachova et al. [24] with a GC Thermo Scientific TRACE™ 1310 (USA) automated injection, coupled to TSQ 8000 Mass Spectrometer detector (MSD) (USA). The GC column length was 15 m, with an internal diameter (ID) of 0.25 mm and thickness of 0.25 µm (P/N 13620-127). Initial oven temperature was 75°C, held for 3 min, where after it was increased by 10°C/min to 200°C, held for 10 min at this temperature before being heated to 320°C and held for 2 min with a total run time of 34 min. The injector temperature was 275°C and the injector line temperature was 250°C. The injection was set to splitless mode with flow rate of 50 ml/min while the carrier gas was helium with a flow rate of 1.15 ml/min. The GC/MSD was operated with a programmable temperature vaporizer (PTV) and the mass spectrometer was set in electron ionization (EI) mode. The ionization source temperature was set at 250°C and the emission current was 75 µA and Argon as collision gas.

Identification of target analytes were based on the matching of sample peak area and the retention time (RT) to that of reference standard, allowing a RT tolerance intervals of 2.5% to 4% (of the reference standard) within same analytical batch. While quantification (µg/L wet weight) was based on the response ratio of the sample peak area against concentration of the analyte to that of the internal standard. The concentration of the contaminant in fish was expressed as µg/kg wet weight (ww).

Quality control: The target analytes peaks were monitored from other interferences using procedural blank samples which were analysed in each batch of 20 samples. Validation of method was achieved with certified reference material (CRM) PAH–loamy clay [25,26] obtained from Sigma-Aldrich (USA). The CRM was extracted in the same manner as the fish samples with percentage recoveries calculated for each analyte. Multiple internal standards were necessary to ensure that internal standard with retention time (RT) close to the target analytes was used for identification. Limits of detection (LOD) and quantitation (LOQ) of the analytes were calculated based on calibration standards (n=7) signal to noise ratio of 3:1 and 10:1 respectively [27]. Blank sample values (particularly for naphthalene) were usually subtracted from sample values and carry-over of analytes was checked by running solvent blanks after each batch of 10 samples.

Statistical analysis

All data were checked for normality and homogeneity with Kolmogorov-Smirnov and Levene's F tests respectively. Differences in contaminants concentrations in fish sampled from the three locations were compared using analysis of variance (one way-ANOVA). But where the equality test failed, non-parametric tests (Mann Whitney *U* test or Kruskal Wallis) were used. A post hoc test was further carried out to establish significant variation of means**.** Correlations of fish weight with lipid content and OCs were established using both Pearson and Spearman's correlation which showed similar result. However, Pearson's correlation with stronger positive values was presented. As some PAHs were below detection limit they were not statistically assessed. In addition, ANOVA evaluation was limited, where only PAHs common (detected) in at least two locations were considered for statistical analysis. Significant differences and correlations were established at 95% confidence limit ($p<0.05$) and all statistics was done using Statistica version 12.3 (Statsoft Inc., USA, in 2012).

Results and Discussion

PAHs in *S. lalandi*

Of the 16 PAHs analysed in yellowtail fish from Port Elizabeth, Yzerfontein and Struis Bay, two (acenaphthene and benzo(*k*) fluoranthene), five (benzo(*k*)fluoranthene, chrysene, benzo(*a*) anthracene, benzo(*b*)fluoranthene and indeno(*1,2,3-cd*) pyrene) and seven (acenaphthene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, indeno (*1,2,3-cd*) perylene, dibenz (*a,h*) anthracene and benzo (*g,h,i*) perylene) PAHs were not detected respectively. Most of the non-detected PAHs (in fish from Yzerfontein and Struis Bay) were predominantly HMW PAHs which usually emanate from incomplete combustion of organic substances. This trend in low detection of HMW and high detection of LMW PAHs in fish has been observed in previous published studies [28-31] and may be due to uptake pathways and longevity in the body [32]. HMW PAHs are taken up predominantly through diet whilst LMW PAHs are mostly accumulated through water [33]. Furthermore, HMW PAHs can be metabolized by some large fish and be excreted [14] thereby reducing accumulation and concentration (retention) in the fish body. A summary of yellowtail PAHs concentrations (mean, S.E and range) from the three study location were given in Table 2.

The most abundant PAHs were naphthalene, phenanthrene and anthracene (in descending order), where the highest concentration of naphthalene (137.33 ± 15.17 µg/kg) was found in fish sampled from Port Elizabeth. The dominance of naphthalene in fish tissue could be a reflection of its relative abundance as revealed in a study on global PAHs emission which observed that naphthalene was the overall dominant PAH, often present at up to 50% more than other PAHs present [34]. Naphthalene is predominantly derived from anthropogenic sources such as oil and gas drilling, crude oil, petroleum refining and bitumen among others [16,21]. Therefore, the high abundance of naphthalene relative to other PAHs may be due to its high input into the environment through industrial and domestic emissions [34], in particular petroleum sources [35]. In addition, the higher concentrations of LMW PAHs such naphthalene,

Location	Yzerfontein		Port Elizabeth		Struis Bay	
Compound	**Mean ± S.E**	**Range**	**Mean ± S.E**	**Range**	**Mean ± S.E**	**Range**
Naphthalene	137.33^{a} ± 15.17	55.75 - 244.09	132.47^{a} ± 8.41	93.98 - 163.87	84.59^{b} ± 3.41	68.21 - 100.63
Acenaphthylene	3.05^{a} ± 0.13	2.30 - 3.77	17.84^{b} ± 0.53	16.44 - 21.21	0.74^{c} ± 0.07	0.18 - 1.03
Fluorene	10.40^{b} ± 2.36	5.01 - 30.97	29.33^{a} ± 2.18	24.31 - 42.31	0.05^{c} ± 0.03	<dl - 0.31
Phenanthrene	16.02^{b} ± 3.44	9.70 - 45.08	52.54^{a} ± 2.27	48.56 - 72.15	0.24^{c} ± 0.15	<dl - 0.45
Anthracene	10.09^{b} ±0.24	8.99 - 11.56	32.68^{a} ± 0.7	31.01 - 37.90	2.95^{c} ± 2.02	<dl - 17.90
Fluoranthene	10.66^{a} ± 0.06	10.44 - 10.89	7.21^{b} ± 2.02	<dl - 24.59	0.09^{c} ± 0.05	<dl - 0.41
Pyrene	23.60^{b} ± 16.77	5.70 - 174.51	28.42^{a} ± 2.07	26.09 - 47.04	0.05^{c} ± 0.03	<dl - 0.25
Benz(*a*)pyrene	6.16 ± 0.92	4.10 - 10.10	29.35 ± 2.38	17.33 - 38.04	0.25^{c} ± 0.07	<dl - 0.62
Dibenz(*a,h*)anthracene	1.69 ± 0.70	<dl - 4.97	24.13 ± 4.58	<dl - 49.59	ND	ND
Benz (*g,h,i*)perylene	2.39 ± 0.98	<dl - 6.05	5.13 ± 5.13	<dl - 51.32	ND	ND
DDT	11.14 ± 1.44	2.03 - 16.55	7.48 ± 5.18	0.45 - 53.93	ND	-
BHC beta	0.26 ± 0.14	<dl - 1.22	1.08 ± 0.31	<dl - 2.54	ND	-
BHC gamma	0.28 ± 0.19	<dl - 1.68	1.94 ± 0.23	<dl - 2.86	ND	-
Endrin	0.40 ± 0.11	<dl - 1.01	1.29 ± 0.52	<dl - 5.30	ND	-
ND - Not Detected; Values: Mean ± Standard Error of Mean.						

Table 2: Concentration (mean and range) in µg/kg wet weight of organic contaminants (OCs): polycyclic aromatic hydrocarbons (PAHs), dichlorodiphenyltrichloroethane (DDT) and organochlorine pesticides (OCPs) detected in yellowtail species (*Seriola lalandi*) sampled from Yzerfontein, Port Elizabeth and Struis Bay, coast of South Africa. Different alphabet letter(s) on the same row denote significant difference ($p<0.05$).

acenaphthylene, phenanthrene, fluorene and anthracene in fish may also be attributed to their higher solubility in water compared to HMW PAHs [36]. Therefore, LMW PAHs are readily bioavailable through fish gill and skin diffusion whereas the HMW PAHs attach to particles and sediment and must be consumed through diet [32,35,36].

In general, significant variations were observed in the mean concentration of total PAHs in fish from the three locations where yellowtail fish from Port Elizabeth had higher ($p<0.05$) PAHs concentration (533.95 ± 34.36 µg/kg) compared to Yzerfontein (221.40 ± 33.03 µg/kg) and Struis Bay (52.54 ± 2.27 µg/kg). In view of the associated toxic and carcinogenic effects of PAHs caused by binding of PAHs (breakdown products) to human genetic cells, the elevated PAHs burden in fish particularly from Port Elizabeth is of health interest and need further investigation. The fish sampled from Port Elizabeth, which is considered an industrial area [37], had slightly higher percentage of HMW PAHs (50.39%) in comparison to LMW PAHs (49.61%) (Figure 1) but not significantly different (Figure 2) in terms of concentration.

The ratio of LMW/HMW being <1, suggests pyrogenic sources as the main PAHs contributors [35]. The significant differences observed between the total LMW PAHs and total HMW PAHs (Yzerfontein and Struis Bay) shown in Figure 3, reflects the dominance of LMW over the HMW in these locations. However, fish sampled from Port Elizabeth had an average ratio of LMW/HMW as 0.984 whilst some individual fish had a ratio >1 which suggested a mixed contamination from both petroleum and combustion inputs with a slight dominance of pyrogenic sources. Thus the PAHs input sources from Port Elizabeth were both petrogenic as well as pyrogenic which may be a reflection of activities at the harbours, ports and the accumulation of fumes into the marine environment from automobile industries within location. According to Zhang and Tao [34], the spatial variations in PAHs concentrations as observed in fish sampled from these study locations is a reflection of emission source and quantity. In a previous study on PAHs along the coast of South Africa by Degger et al. [8] using brown mussel (*Perna perna*) and semi permeable membrane device (SPMD)

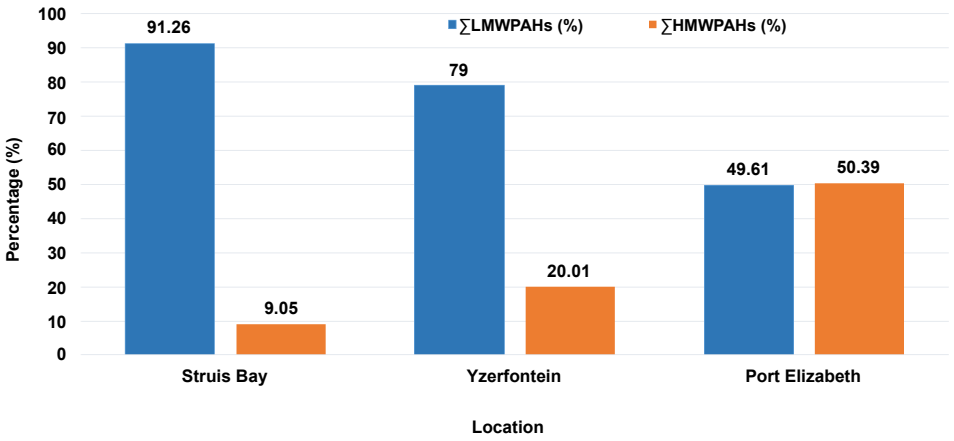

Figure 1: Percentage distribution of low molecular weight (LMW) and high molecular weight (HMW) PAHs in yellowtail (*Seriola lalandi*) fish species from Struis Bay, Yzerfontein and Port Elizabeth along the coast of South Africa.

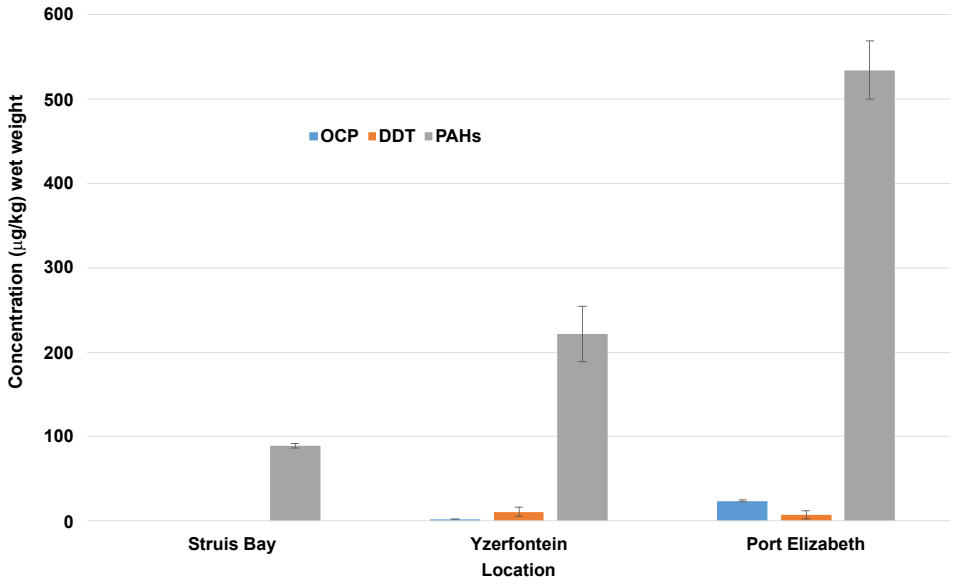

Figure 2: Total concentration (mean ± SE) of persistent organic contaminants (ΣOCPs, ΣDDT and ΣPAHs) in yellowtail (*Seriola lalandi*) from Struis Bay, Yzerfontein and Port Elizabeth along the coast of South Africa.

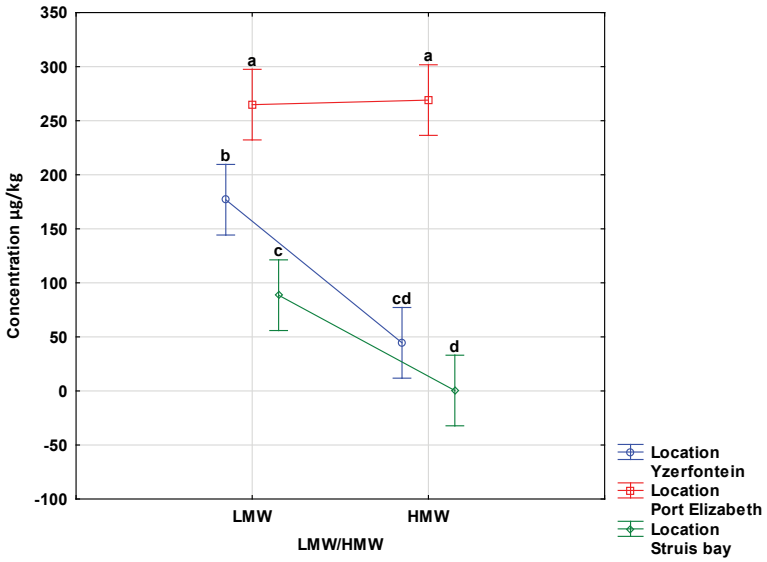

Figure 3: Distribution of Low molecular weight and high molecular weight PAHs in yellowtail across three study locations highlighting significant differences ($p<0.05$) with different alphabets letters.

transplanted at five different harbours, Port Elizabeth was reported as the most contaminated based on the SPMD. The non-biological SPMD in contrast to the biological transplanted object (mussel) accumulated more HMW PAHs such as chrysene, benzo(*b*) fluoranthene and benzo (*k*) fluoranthene which except for benzo(*k*) fluoranthene were also amongst the PAHs detected in fish sampled from Port Elizabeth (in this study). Benz(*a*)pyrene the PAHs acceptability indicator was found to exceed the EU maximum limit of 2 µg/kg ww in all the samples from Port Elizabeth and Yzerfontein (28.42 ± 2.07 and 6.16 ± 0.92 respectively). Fish sampled from Struis Bay, (rarely contaminated with the assessed OCs) had benz(*a*)pyrene concentration of 0.25 ± 0.07 µg/kg ww which was less than the EU limit. Though consumption risk was not determined, however, due to benz(*a*)pyrene level found to exceed EU limit in fish from 2 locations, as the study was baseline, further investigation to generate enough evidence for advisory purposes would be necessary. Similar reports in excess of the EU limit with benzo(*a*) pyrene were also observed in marine fish species sampled from Ghana [38], Nigeria [39] and Egypt [40]. The metabolites of carcinogenic PAHs such as benzo(*a*)pyrene can form complexes by binding with cellular DNA and can alter genetic sequence and consequently can promote cancer [41]. Owing to the associated carcinogenic effects of benzo(*a*)pyrene considered as one of the most potent PAHs [16], there is need to protect fish consumers from dietary exposure of fish with increased benzo(*a*)pyrene burden by avoiding fish species identified as benzo(*a*)pyrene accumulators. Contamination of fish with PAHs according to Baumard et al. [42] can be classified based on measured concentrations into: low contamination (0-100); moderately contaminated (100-1000); highly contaminated (1000-5000) and very highly contaminated if greater than 5000 ng/g. Thus based on this classification the fish sampled from Port Elizabeth and Yzerfontein could be said to be moderately contaminated (100-1000 µg/kg) with PAHs while fish from Struis Bay had low contamination with PAHs. The uptake of PAHs and distribution of PAHs in fish can be affected by a number of factors such as fish anatomical section [25], species [13], size [17], gender and biotransformation ability [43]. Therefore choice of fish portion, size and species among other factors can increase or reduce human dietary exposure to PAHs.

DDTs and OCPs in *S. lalandi*

DDT was detected in Yzerfontein and Port Elizabeth and not detected in all samples from Struis Bay. Struis Bay an old fishing harbour in Western Cape, South Africa [44] is a settlement for peasant dwellers [45] and not with dense population and industrial activities as Yzerfontein and Port Elizabeth probably do not have application of DDT in the area. DDT can be introduced into the environment other than for malaria control such as from its use as anti-fouling agent in paint used for undecked boat maintenance [34,46] also in Dicofol pesticides, synthesised from DDT. These may explain the low level of OCs and in particular the non-detection of DDT in the fish sampled from Struis Bay where agricultural and harbour activities are not comparatively high as the other locations. The more stable DDT analogues (DDE and DDD) were below detection limit in all the sampled fish from all the three locations which indicated their low concentrations and the non-degradation of the fresh DDT input. Overall, the total concentration of 4,4'-DDT (the only analogue detected) was significantly higher ($p<0.05$) in Yzerfontein compared to Port Elizabeth (Figure 3). The predominance of DDT (4,4'-DDT analogue) was an indication of fresh input or current DDT usage in the environment [47], where a greater usage of DDT may have occurred in Yzerfontein than the other locations. The higher concentration of DDT in fish from Yzerfontein (an indication of higher DDT pollution) may be a reflection of increased application of antifouling DDT containing paints in the care of undecked fishing boats. Yzerfontein has more fishing activities than other locations and is reported to provide about 60% of line fishes in the western coast [48].

The spatial transferability of OCs such as DDT can result to detection even in places/matrices remote from points of production, use or emission. For instance in a study by Channa et al. [49] on prenatal exposure to DDT in malaria and non-malaria regions of South Africa, DDT was equally detected among women from the non-malaria zone though at a lower concentrations than the malaria endemic regions. Again, the detection of DDT in fish especially non-resident species may not provide actual environmental pollution history. Despite the presence of DDT in yellowtail from Yzerfontein and Port

Elizabeth, the concentrations were considerably lower than the Food and Drug Administration (FDA) action level of 5000 µg/kg (legal level of confiscation) [4]. This suggests that yellowtail caught in the three study locations are considered acceptable for human consumption with respect to DDT. Other pesticides detected in the studied fish from the locations are as shown in Table 2. The concentrations of all detected pesticides excluding DDT were summed up as total OCPs (∑OCPs) where the concentration of ∑OCPs in fish from Port Elizabeth was ($p<0.5$) higher than fish from Yzerfontein. The detection of these pesticides, except for DDT which is currently being used in the country, may reflect their persistence, illegal application and possibly as metabolites from industrial incineration [50]. A list of banned pesticides in South Africa include aldrin, endrin, mirex, chlordane and heptachlor, therefore the detection of endosulfan and BHCs though on global list of banned pesticides but not included in banned list in South Africa and could still be in use. This calls for further investigation in order to conform to the Stockholm treaty of which South Africa is a signatory. Nevertheless the levels of the studied pesticides in all the sampled fish from the locations under investigation were below the EU maximum residue levels (MRLs) for pesticides in the range of 50-300 µg/kg [4].

Relationship between fish size (weight), lipid content and OCs concentrations

Yellowtail (n=20) size (weight) had a strong positive correlation with lipid content ($r=0.65$); $p<0.01$ (Table 3). The increased lipid content with body weight could be a reflection of growth variation where older fish accumulate more lipid as energy reserve for migration and reproduction [51]. Thus larger fish with increased surface area (intracellular and extracellular muscles which contribute to overall weight) would be expected to have more oil than smaller sized fish. Thus lipid content in fish could be associated with growth rate (a function of age, weight and length) [52]. A strong negative correlation ($r=0.67$; $p<0.001$) between lipid content of fish and size (length) was observed in fish species (e.g. *Carasius auratus gibelio* and *Abramis brama*) from Romania, though the study did not determine relationship with weight [52]. However, information regarding the relationship between fish size (weight) and lipid content is limited for extensive comparison.

In this study, a strong positive correlation was observed with fish weight and total PAHs ($r=0.83$; $p<0.01$) as well as some individual carcinogenic PAHs benzo(*a*)pyrene, ($r=0.81$; $p<0.01$), anthracene ($r=0.78$; $p<0.01$) dibenz(*a,h*)anthracene ($r=0.77$; $p<0.01$) (Table 3).

Variable 1	Variable 2	Correlation value (Pearson)	p - value
Fish weight	Lipid content	0.65	<0.01
Fish weight	Acenaphthylene	0.87	<0.01
Fish weight	Fluorene	0.69	<0.01
Fish weight	Phenanthrene	0.74	<0.01
Fish weight	Anthracene	0.78	<0.01
Fish weight	Benz(*a*)pyrene	0.81	<0.01
Fish weight	Dibenz(*a*)anthracene	0.77	<0.01
Fish weight	Total PAHs	0.83	<0.01
Fish weight	BHC beta	0.51	<0.01
Fish weight	BHC gamma	0.80	<0.01
Fish weight	∑BHC	0.71	<0.01
Fish weight	∑OCPs	0.64	<0.01

Table 3: Significant correlations (positive) of fish weight to fish lipid content, organic contaminants (Polycyclic aromatic hydrocarbons and organochlorinated pesticides) detected in yellowtail fish (*Seriola lalandi*).

Similar to increased lipid content in older fish, the lipophilic nature of PAHs leads to their binding and accumulating in fatty matrices. Thus higher lipid content of investigated species will imply increase in the accumulation of PAHs particularly the carcinogenic PAHs. The positive correlation existing between these PAHs and fish weight may be as a function of prolonged exposure spanning over period of juvenile to adult stage (maturity) and in addition to larger surface area in adult fish. Similar result of positive correlation ($r=0.99$; $P<0.05$) with total PAHs and fish weight was observed in *Siganus rivulatus* from Lebanon [53], with chub and horse mackerel. In any case fish species effect, cannot be ruled out as playing significant role to these interactions of fish parameters and contaminant. As different species vary in their degree of enzymatic breakdown which may give rise to products that be excreted and consequently affect the residual level of contaminant. In view of this, the observed relationship was not definitive and may require further investigation and comparison with different species may be a misleading interpretation. For instance, Perugini et al. [31] observed no significant correlation with total PAHs and weight, length and trophic levels of evaluated marine species (e.g. *Merluccius merluccuius* and *Scomber scombrus*).

Conclusion

The variations in concentrations of evaluated contaminants in the fish sampled from the three locations (Yzerfontein, Port Elizabeth and Struis Bay) were attributed to fish size, lipid content and locational effects. The study revealed that fish from Port Elizabeth (despite the size and lipid content) had the highest contamination of PAHs and pesticides. This was followed by Yzerfontein whilst fish from Struis Bay had the least contamination. The pollution input sources of PAHs from Port Elizabeth showed a mixture of petrogenic and pyrogenic possibly due to industrial and harbour activities. Whilst from Yzerfontein and Struis Bay both locations revealed input as predominantly petrogenic sources which may be due to refineries and shipping activities within the province. The bioconcentration of OCs particularly the carcinogenic (HMW) PAHs and OCPs (DDT and BHCs) revealed increased concentration with fish size. This implication may need further investigation for development of a possible fish weight-OCs predictable model which will be beneficial in determining the critical size of yellowtail above which consumption might be harmful.

Overall, all detected OCPs (DDT and BHCs) were below the EU limits and therefore designated acceptable for human consumption in all sites sampled; however, Benz(*a*)pyrene the PAH acceptable marker was found to exceed the EU maximum limit of 2 µg/kg ww for yellowtail sampled in Port Elizabeth and Yzerfontein. Therefore, fish consumers in particular, food (fish) regulatory agencies and those in fish business (fishing & industries) need an increased awareness of current prevalence and composition of these chemical contaminants in these locally consumed and commercially important fish species. Owing to the prevalence of some of the banned pesticides, a greater monitoring and control of product distribution and use is needed to prevent further environmental contamination.

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