Determination of concentrations of Dioxins and Polychlorinated Biphenyls in canned mackerel (*S. japonicus*) from Peruvian industry and evaluation of their safety status

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Introduction

Persistent Organic Pollutants (POPs) are organic chemicals that have a particular set of physical and chemical properties that when released into the environment: (i) remain intact for exceptionally long periods, (ii) are widely distributed into the environment as a result of natural processes, (iii) accumulate in the fatty tissue of living organisms, including humans, as it introduced into the food chain, (iv) are toxic to humans and wildlife [1].

Foods are the main route of exposure to these compounds [2], among these, animal-derived foods are the main contributors, because PCDDs, PCDFs, PCBs can bioaccumulate in the fatty tissue of animals and humans [3]. Regarding the efficiency of the absorption of these compounds in the mammalian organism, a 90% absorption of 2,3,7,8-TCDD has been observed by oral administration [4]. On the other hand, regarding its bioaccumulation in the human organism, minimal decreases in the concentrations of these contaminants in human blood serum have been reported at a rate of 20 pg TEQ/g fat per year [5].

There is evidence hydrobiological food products (i.e. fish and seafood), such as those derived from some species of fish, has considerable concentrations of these compounds [6][7]. Likewise, there is evidence that the bioaccumulation of PCDD/Fs is particularly important in fish predators with high fat content [8]. For this reason, these criteria should be taken into account for the selection of species with a higher probability of contamination.

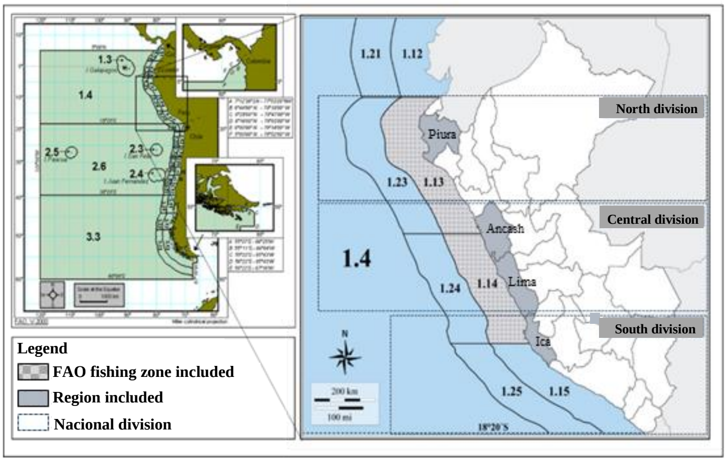
According to the latest inventory published by the National Environmental Council of Peru [9], the total dioxin and furan generation estimated for Peru was 424,09 g TEQ/year for the year 2003. Likewise, this concentration corresponds to a demographic rate of 29,92 µg TEQ/person year and a regional distribution and rate of 0,3 mg TEQ/ km^2.year. In these reports, it was concluded that the major contributions were towards air (46%), waste (39%), and soil (14%).

The objective of this research is to determine the safety status of canned mackerel (*Scomber japonicus peruanus*) of Peruvian industry produced during the year 2016 in relation to contamination by dioxins and PCBs and to carry out a sanitary evaluation regarding the maximum permissible limits (MPLs) established by the national and international legislation, with the purpose of contributing information and scientific knowledge to the evaluation of the exposure of POPs by ingestion of Peruvian hydrobiological products. Also we aim to promote the conduct of future studies of risk analysis for human health, contributing to the safeguard the public health of national and international consumers.

Materials and methods

Samples were taken from batches of canned mackerel from companies throughout the country in accordance to the guidelines of the Peruvian Technical Standard NTP 700.002-2012. It was established to select 1 pool of 5 units from each batch to perform a single laboratory test. Likewise, the population was identified as the 52 plants that produce canned hydrobiological products from around Peru, specifically located in the coastal regions (departments) of Piura, Ancash, Lima and Ica. According to the classification of FAO's fishing zones [10] these were the fishing zones from which mackerel, the raw material, was harvested.

Fig 1. Department and FAO's fishery zone included in the scope of the research sampling program.



Finally, the sampling program included 60 global samples (300 cans) of mackerel canning from the 23 qualified companies with the highest production capacity located in four coastal regions of Peru. These samples were sent to Canada for testing in a laboratory according to accredited methods (Pacific Rim Laboratories Inc. Surrey, British Columbia)

Thirty-five congeners of PCDDs, PCDFs, dioxin-like PCBs (dl) and non-dioxin-like PCBs (non dl) were designated to analyze, based on their toxic potential and the likelihood of food contamination. The analytical methods were: (i) Dioxin (PCDD/PCDFs) congeners in Animal Tissue, Fish: *EPA Method 1613 Tetra-through Octa-Chlorinated Dioxins and Furans by Isotope Dilution by HRGC/HRMS* [11]. Modifications proposed by Hope *et al* [12] were applied to the method; (ii) Congeners of dioxin-like PCBs and non-dioxin-like PCBs in animal tissue, Fish: *EPA Method 1668 Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS* [13]. Modifications proposed by Pond *et al* [14] were applied to the method.

Results and discussion

Three results are shown: (i) Table 1 shows the averages of pollutants concentrations determined in the samples, grouped into the categories considered for this research (Fig. 1), highlighting concentrations with the highest recorded value.

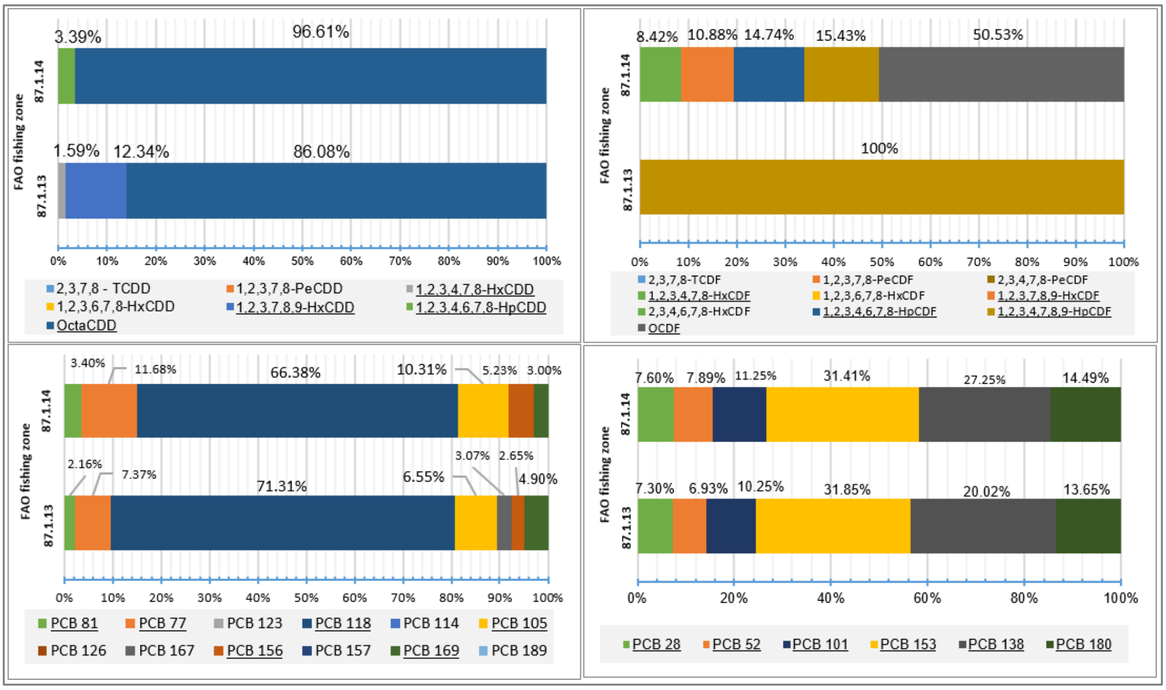
Table 1. Summary of mean concentrations of PCDDs, PCDFs and PCBs in samples

				PCDD/PCDF WHO-TEQ´s 2015 (ng TEQ/kg)		PCB´s dl WHO-TEQ´s 2015 (ng TEQ/kg)		PCDD/PCDF/PCB´s dl WHO-TEQ´s 2015 (ng TEQ/kg)		PCB non dl (ng/kg)
Division	**Dept.**	**87 FAO's fishing Zones**	**N° of samples**	**Lower bound**	**Upper bound**	**Lower bound**	**Upper bound**	**Lower bound**	**Upper bound**	**Total**
North	Piura	87.1.13 Zone	2	ND	0.16125	0.00013	0.13120	0.00013	0.29245	63.60000
Total – division			**2**	**ND**	**0.16125**	**0.00013**	**0.13120**	**0.00013**	**0.29245**	**63.60000**
Central	Ancash	87.1.13 Zone	36	0.00454	0.16517	0.01875	0.14725	0.02329	0.31241	72.29167
		87.1.14 Zone	10	0.00752	0.16612	0.01449	0.14243	0.02200	0.30855	96.80000
	General - region		46	0.00518	0.16537	0.01782	0.14620	0.02301	0.31157	77.61957
	Lima/ Callao	87.1.13 Zone	6	ND	0.16125	0.00019	0.13122	0.00019	0.29247	65.20000
		87.1.14 Zone	1	ND	0.16125	0.00026	0.13129	0.00026	0.29254	52.40000
	General - region		7	ND	0.16125	0.00020	0.13123	0.00020	0.29248	63.37143
Total – division			**53**	**0.00450**	**0.16483**	**0.01550**	**0.14422**	**0.01999**	**0.30905**	**75.73774**
South	Ica	87.1.13 Zone	4	ND	0.16125	0.00034	0.13132	0.00034	0.29257	87.47500
		87.1.14 Zone	1	ND	0.16125	ND	0.13112	ND	0.29237	28.70000
Total - division			**5**	**ND**	**0.16125**	**0.00027**	**0.13128**	**0.00027**	**0.29253**	**75.72000**
Total 87.1.13 fishing zone			**48**	0.00340	0.16419	0.01412	0.14325	0.01752	0.30743	72.30833
Total 87.1.14 fishing zone			**12**	0.00626	0.16531	0.01209	0.14056	0.01836	0.30587	87.42500
NATIONAL TOTAL			**60**	**0.00397**	**0.16441**	**0.01371**	**0.14271**	**0.01769**	**0.30712**	**75.33167**

The concentrations of the contaminants obtained in the samples expressed in national average ranges were: (i) PCDD/PCDF $0{,}00397<x<0{,}16441_{\text{WHO-EQT 2015 (ng-TEQ/kg)}}$; (ii) dl-PCBs: $0{,}01371<x<0{,}14271_{\text{WHO-TEQ's 2015 (ng TEQ/kg)}}$; (iii) PCDD/PCDF/dl-PCBs $0{,}01769<x<0{,}30712_{\text{WHO-TEQ's 2015 (ng TEQ / kg)}}$; and (iv) PCB-non dl $26{,}92<75{,}33<246{,}34_{\text{(ng/kg)}}$.

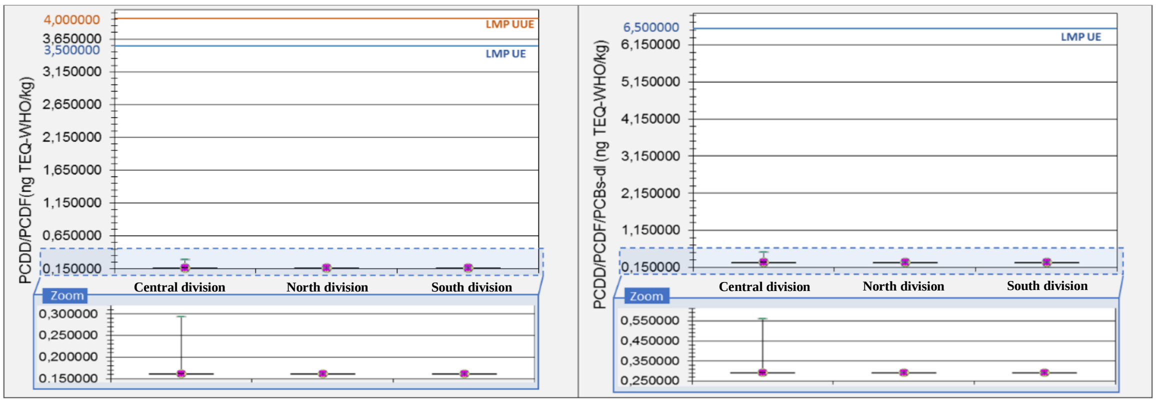
(ii) Fig. 2 depicts the congeners identified during the analyses of the samples grouped by the FAO catch area where the mackerel was caught and the percentage that was found relative to the total concentration of each group of contaminant.

Fig 2. Percentage of concentrations of PCDDs, PCDFs, dl-PCBs and non dl-PCBs congeners in samples by FAO fishing zones.



These results show the presence of these compounds in very low concentrations: (i) PCDDs: *1,2,3,4,7,8-HxCDD*; *1,2,3,7,8,9-HxCDD*; *1,2,3,4,6,7,8-HpCDD* and *OctaCDD* were detected; the most abundant congener was *OctaCDD*; (ii) PCDFs: *1,2,3,4,7,8-HxCDF*; *1,2,3,7,8,9-HxCDF*; *1,2,3,4,6,7,8-HpCDF*; *1,2,3,4,7,8,9-HpCDF* and *OctaCDD* were detected; the most abundant congener was *OctaCDF*; (iii) dl-PCBs: *PCBs 81*; *PCB 77*; *PCB 118*; *PCB 105*, *PCB 167*, *PCB 156* and *PCB 169* were detected; the most common congener was *PCB 118*; (iv) non dl-PCBs: *PCBs 28*; *PCB 52*; *PCB 101*; *PCB 153*, *PCB 138* and *PCB 180* were detected, the most common congener was *PCB 153*.

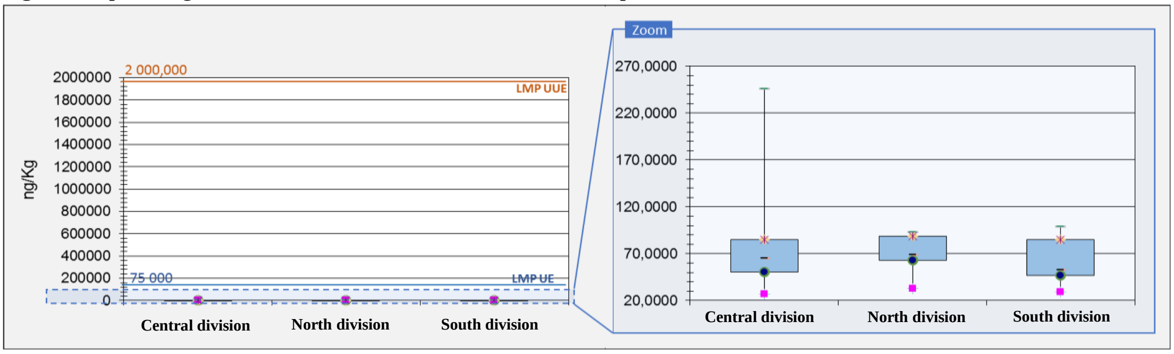
Fig 3. Box plot diagrams of PCDD/PCDF and PCDD/PCDF/dl-PCBs concentration and comparison to EU and EUE LMPs.



(iii) In figs 3 and 4: box plot diagrams of the concentrations of PCDDs/PCDFs, PCDDs/PCDFs/PCBs-dl and PCB-non dl found in the samples grouped by national divisions in order to observe the dispersion of the data with respect to its arithmetic mean. LMPs for foodstuffs are also marked by European Union legislation (LMP UE) (PCDD/Fs 3.5 pg/g FW; PCDD/Fs + dl-PCBs 6,5 pg/g FW; non dl-PCBs 75 ng/g) and Eurasian Economic Union (LMP EEU)

(Dioxins 0,000004 mg/kg, PCBs 2,0 mg/kg) for the purpose of comparing the samples to determining their safety. Consequently, we have demonstrated that the samples had concentrations of contaminants far below the MPL used for the comparison. Therefore, we conclude that the samples were safe.

Fig 4. Box plot diagrams of non dl-PCBs concentration and comparison to EU and EUE LMPs.



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