Peruvian marine ecosystems under metal contamination : first insights for marine species consumption and sustainable management

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Abstract

Scientific research addressing environmental conditions of aquatic ecosystems has high priority in Peru. Nevertheless, there is a lack of knowledge on environmental contamination of Peruvian marine ecosystems. To address this knowledge gap, this review article summarizes the available information in order to estimate the environmental health status (EHS) of Peruvian marine ecosystems. In this study, none of the studied Peruvian marine ecosystems could be rated as EHS-good, and the southernmost locations showed the most degraded conditions and a low EHS. Freshwater and brackish ecosystems contribute to the overall metal concentrations in Peruvian marine ecosystems. Environmental contamination and stressors are also reaching the

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Peruvian Marine Protected Areas (MPAs). The management of coastal marine areas and MPAs in Peru should be urgently re-formulated. This study also identifies the optimal bio-monitoring approach in the current economic situation in Peru, and how marine research studies can support adjacent fields, e.g. nutrition and human health.

Keywords: Environmental health status; metal contamination; marine; malnutrition; future foods; Peru

1. Introduction

The environmental or ecosystem health status (EHS) is an integrated approach that could help to determine the degree of degradation of a specific ecosystem (EEA, 2019) and translate it into useful information for the local population and policy makers from Peru. EHS is not simple to define because it integrates the complexity of human-environment interactions. Moreover, the current diverse environmental problems (e.g. pollution; El Niño events,…) makes EHS even more difficult to address (EEA, 2019; WHO; 2019). In marine areas, humans have been operating with and within aquatic ecosystems for millennia, causing changes through often complex interactions (Lavallée & Michèle, 2012). The consequences of human activities on marine ecosystems around the globe have mostly been negative (EEA, 2019). A healthy ecosystem implies that adverse or possible negative conditions are minimal or absent for the ecosystems' organisms (ODPHP, 2019). Different international institutions or agencies aim to maintain ecosystems in a healthy, uncontaminated, productive and resilient condition, so that they provide services and benefits to humans (EEA, 2019; WHO; 2019). Within Europe for instance, the Marine Strategy Framework Directive (MSFD) defines a good environmental status to marine waters that provide ecologically diverse and dynamic oceans and seas, which are clean, healthy and productive (MSFD, 2021).

In Peru, studies with an ecosystem-based approach are lacking, with the exception of some recent trophodynamic and modelling studies in either pelagic or benthic ecosystems (Kluger et al. 2016; Espinoza et al. 2017; Loaiza et al. 2021). Peruvian marine ecosystems were described as unit, such as the northern Humboldt Current System (NHCS) by Chavez, 2008. At the same time, the latter study mentioned the importance of an ecosystem based-management approach. The main reason for the lack of benthic-pelagic or ecosystem-based studies are that most studies in Peru focus on a single species related to their economically and individually importance, therefore never interconnected, e.g. numerous oceanographic 'pelagic' studies on *Engraulis ringens*, vs. numerous studies on *Argopecten purpuratus* ecology (Mendo et al. 2016; Moron et al. 2019). The recent Chilean study in nearby waters of Peru remarked that benthic-pelagic trophic interactions are highly important in the NHCS ecosystems, due to the upwelling-governed marine system (Docmac et al. 2017).

An ecosystem-based approach was also taken into account to study the seafood valuing in Peru. The Peruvian anchovy *E. ringens* and other marine commercial species were modelled in order to determine the contribution of each species or group of species to the national Gross domestic product (GDP) and employment in Peru. Unexpectedly, the study found that Peruvian anchovy accounts for only 31% of the sector contribution to GDP and for only 23% of the employment in Peru (Christensen et al. 2014). With a more eco-toxicology approach, EHS's were also addressed using different research methods in Loaiza et al. (2018; 2020a; b; c). These studies led to a consistent pattern for the EHS analysis in Peruvian marine ecosystems, showing that the southern locations (e.g. Paracas Bay - Ica and Punta San Juan – Marcona) were more degraded and metal enriched than locations in the North (Sechura Bay). Metal contamination is currently a serious concern in Peru, especially in the southern part of Peru that has been characterized as "naturally metal-rich", as stated by the government to explain the elevated concentrations of harmful metals, e.g. Cd, Pb (Barriga-Sánchez and Pariasca, 2018; SANIPES, 2019).

Peru is a mining country, being the first in gold and second in cadmium production in Latin America, and the second in copper, silver and zinc production worldwide (MINEM, 2019). The southern region has a high concentration of mining activities from Shougang down to Pucamarca at the border with Chile (e.g. up to 15 concessions in Arequipa), which could lead to substantially increased metal levels and low EHS in the southern marine and coastal environments (MINEM, 2019). Agriculture is also an economical activity that could contribute considerably to the high metal concentrations found along the coast of Peru (MINAM, 2019). This activity is poorly regulated and pesticides and other chemicals (i.e. metal derived-compounds) are indiscriminately used, thus discharge in coastal marine areas can occur (Yucra et al. 2006).

Peruvian marine ecosystems are still rich and abundant in living and non-living resources. This positive aspect could be also a threat for the conservation of these ecosystems. Over-exploitation of Peruvian domain resources are highly possible to happen when no precautionary management plan is considered. Previous experiences on Peruvian anchovy and Peruvian scallop are *"lesson-learnt"* of the high and non-planned exploitation of marine resources (Chavez, 2008; Mendo et al. 2016). In the meantime, these species were also highly impacted by the 1972 El Niño: Peruvian anchovy, and by El Niño 82/83 and 97/98: Peruvian scallop, where both fisheries collapsed. This complex NHCS productive ecosystem is well known because it is strongly affected by climate variabilities (e.g. ENSO) (Chavez, 2008; Mendo et al. 2016). Therefore, scientific ecosystem-based research is urgently needed in this changing and unpredictable ecosystems.

Peruvian marine ecosystems have been monitored since 1954 by the Consejo de Investigaciones Hidrobiológicas (CIH) (Chavez et al. 2008). So far, oceanographic and sanitary measurements have been reported in Peru, however a more research-based and improved approach should be implemented (IMARPE, 2019; SANIPES, 2019). In developing countries such as Peru, *in-situ* studies (or field monitoring) are a priority due to the lack of baseline information in marine ecosystems. Therefore, scientific knowledge on marine ecosystems is increasing in Peru, especially in oceanography due to the threats to the Peruvian anchovy industry, e.g. El Niño and ongoing Climate Change (IMARPE, 2019). This process is accelerated by extra funding from the Consejo Nacional De Ciencia y Tecnologia (Concytec) of Peru, which provides substantial funding for research serving the development of Peru (Melgar-Sasieta et al. 2018), including the present study.

Different methods have been developed to study marine ecosystems as a unit, including new models to study trophic interactions and contaminants distribution (e.g., Ecosim model, Ecotracer; which are part of Ecopath with Ecosim (EwE) software), in order to integrate the different compartments (incl. contaminants) of the ecosystem under study (Walters and Christensen, 2018; Booth et al. 2020). These models helped to simulate, estimate and analyze the environmental status to understand its functioning for a proper management as an unit. The EwE software package can be used for multiple purposes, such as: 1) to address ecological questions; 2) to evaluate ecosystem effects of fishing; 3) to explore management policy options; 4) to analyze impact and placement of marine protected areas; 5) to model effect of environmental changes; 6) to facilitate end-to-end model construction; 7) to predict movement and accumulation of contaminants and tracers (Ecotracer) (Booth et al. 2020).

The use of a large data set and Geoecological Information-Modeling System (GIMS) was performed to model the status of marine ecosystems (e.g. Okhotsk Sea). It is based on existing monitoring data from a marine ecosystem to predict its status, including its complex and nonlinear biological structure (biocomplexity) and its ability to remain alive or continue to exist (survivability) (Varotsos et al. 2018; 2019). The dependence of energy exchange processes on environmental factors is modeled with a minimum level of uncertainty. The biological components are modeled using traditional trophic balance equations, whose coefficients are determined from observational data. The Sea Ecosystem Model showed that the Okhotsk Sea could have a critical status, when the biocomplexity and survivability of this ecosystem reach dangerous levels due to Climate change after the 2075 year, the total production of Okhotsk Sea will begin to decline after that year (Varotsos et al. 2019).

The present study assesses the metal contamination of Peruvian coastal ecosystems in Sechura Bay (incl. Illescas Reserved Zone), Paracas Bay and Punta San Juan. This study used the actual values of metals (As, Cd, Cu, Ni, Pb and Zn) and beneficial compounds (fatty acids) from previous studies, from different environmental compartments (i.e. from food sources to predators) and aquatic ecosystems, e.g. marine, brackish and freshwater ecosystems. The following research questions were addressed in this study: 1) how is the sediment and seston quality?; 2) is there an influx of contaminants from freshwater-brackish resources?; 3) how much is the degree of metal contamination in marine reserves or protected areas (MPAs)?; and 4) how much is the content of beneficial elements/compounds and contamination in seafood? Additionally, the present study addresses the use of different approaches and designs for EHS monitoring and how to provide information on the proper consumption of marine species in Peru, specifically for human use e.g. food safety and nutritional approaches.

2. Methods

2.1 Data analyses

2.1.1 Environmental health status (EHS)

Data on metal concentrations and estimated EHS of the following Peruvian ecosystems were taken from Loaiza et al. (2018; 2020a; b; c): Sechura Bay (southern location SL, northern location NL, incl. Illescas Reserved Zone IRZ), Paracas Bay (PL1, PL2) and Punta San Juan (PSJ, SHO) (Fig 1). Briefly, frozen tissues and the environmental compartments (POM; *sensu lato*, seston and sediments) were dried for at least 72 h at 60°C. The dried tissues were weighed and sorted into small (<0.06 g) and large (>0.06 g) tissues. Small and large tissues were digested overnight with respectively 1 or 2.5 ml of highly purified concentrated 69% nitric acid (HNO_3). For filters (POM; *sensu lato* and seston) and sediments, 4 ml of highly purified concentrated (69%) HNO_3 was used. Subsequently, all samples were heated to 110°C during 30 min in the digester. After cooling (~10 min), 0.1, 0.25, 0.5 ml of hydrogen peroxide (H_2O_2) was added for small tissues, large tissues and the environmental compartiments (POM; *sensu lato*, seston and sediments), respectively. The samples were heated again during 30 min at 110°C to complete the total digestion. The digested samples were diluted up to 5 (small), 10 (large) and 40 (filters and sediments) ml with Milli-Q grade for the metal analysis using inductively coupled plasma mass spectrometry (ICP-MS ; 7700×, Agilent Technologies). For samples below the detection limit (BDL) of the ICP, an extra analysis with the high resolution inductive coupled plasma mass spectrometry (HR-ICP-MS; Element XR, Thermo Scientific, Finnigan element 2, Bremen, Germany) was performed. The quality controls for metal analysis consisted of standard reference material (SRM) for mussel tissues (2976, National Institute of Standards and Technology, NIST). The recovery ranges were 98.9–113.5% (n=71) for each metal. For filters and sediment, the certified reference materials were the Channel Sediment BCR-320R and the Estuarine Sediment BCR-277R, which exhibited recoveries from 70.3% to 121.1% (n=23, per metal).

Metal and metalloid concentrations (As, Cd, Cu, Ni, Pb and Zn) in sediments and seston (also considered as re-suspended sediments) were compared with the different international limits (Long et al. 1995; U.S. EPA, 2019). Firstly, sediment and seston concentrations (µg/g dwt.) were compared to the estimated indices: Effects Range-Low (ERL) and Effects Range-Median (ERM) to determine adverse biological effects due to chemical sediment concentrations. The ERL values are the lowest concentration of a metal in sediment that produce adverse effects in 10% of the data reviewed. Similarly, the ERM designates the level at which half of the studies reported harmful effects. Metal sediment and seston concentrations below the ERL value are not expected to cause adverse effects, while levels above the ERM value are likely to be very toxic. Locations were rated as "good" EHS when the concentrations of all measured metals in sediments and seston were below the ERL limit. An "intermediate" EHS rating applied if one metal exceeded an ERL limit, and a "poor" EHS rating refers to an exceedance of the ERM limit for at least one metal (Long et al. 1995; U.S. EPA, 2019). Secondly, a similar approach was applied using the Interim Sediment Quality Guideline (ISQG) and the Probable effect level (PEL) from the Canadian Council of Ministers of the Environment (1999). When the contaminant in sediments and seston is ≤ ISQG, up to 9% of adverse biological effects can be expected, while the probability for adverse effects is 13-27% when the concentration is between ISQG and PEL and it is up to 71% when the contaminant level is > PEL.

Basal resources (e.g. particulate organic matter or POM; *sensu lato*) were compared in relation to their origin, e.g. freshwater-brackish environments vs. marine environments, which gives an indication of the metal influx (i.e. As, Cd, Ni, Pb) from the freshwater-brackish ecosystems to the coastal marine ecosystems. The comparison was performed using statistical analysis (i.e. one-way ANOVA and post-hoc Tukey multiple comparison) in order to determine how significant ($p < 0.05$) and different are the environments in metal concentrations, and the possible metal contribution from one environment to the other one. To evaluate the EHS of ecosystems in the vicinity of the marine reserves or protected areas (MPAs) of Peru, POM *sensu lato* and sediment metal concentrations (µg/g dwt.) in different proximities (i.e. in front, near, far) to the MPAs were compared. The northern MPA is Illescas Reserved Zone, the center MPA is the Paracas National Reserve and the southern MPA is the Punta San Juan Reserve (i.e. part of the Peruvian Guano Islands, Isles and Capes National Reserve (RNSIIPG)). In front, near and at far distances refer to 1-5, 10-12 to up to 25 miles from the MPA, respectively.

2.1.2 Human health and nutrition

The maximum amount (limited by the most toxic metalloid and metal, e.g. inorganic As and Cd) that could be consumed of each species was based on results from Loaiza et al. (2018; 2020b), while the nutritional and beneficial (EPA+DHA+ARA) intakes (mg/day) were taken from Loaiza et al. (2020b). Briefly, fatty acids (FAs) of tissues were extracted and methylated to FA methyl esters (FAMEs) by a modified 1-step derivatization method following Abdulkadir and Tsuchiya (2008) as in De Troch et al. (2012). Samples were freeze-dried for at least 48 h and weighed and placed in glass tubes of 7 ml. Subsequently 2 ml of 2.5 % sulfuric acid (H_2SO_4)-methanol solution (in a proportion of 1:4) was added. An internal standard (1 mg/ml of methylnonadecanoate C19:0) was added and the solution was vortexed for 10 s, prior to placing them in a water bath at 80°C for 90 min. Samples were cooled down to room temperature (~5 min) and 1 ml of hexane and 1 ml of sodium chloride (NaCl) (0.98%) were added, followed by stirring again for 10 s. Samples were placed in a centrifuge 5810 R (Eppendorf) at 160 g speed for 10 min. Then, the extracted samples in hexane (upper layer) were transferred to small vials with sodium sulfate (Na_2SO_4) for absorption of the last remaining water for at least 1 h, and subsequently placed in a micro insert spring of 1 ml for FA analysis.

The extracted FAMEs obtained were analyzed using a gas chromatograph (HP 6890N) coupled to a mass spectrometer (HP 5973). The samples were run in split10 mode injecting 1 µl at an injector temperature of 250 °C using an HP88 column (Agilent J&W; Agilent Co., Santa Clara, CA, USA). The FAME were identified by comparing the retention times and mass spectra with authentic standards and mass spectral libraries (WILEY, NIST, FAME, own libraries) and analyzed with MSD ChemStation software (Agilent Technologies). The FAME quantification was calculated by linear regression of the chromatographic peak areas and corresponding concentrations of the external standards, ranging from 100 to 1000 µg/ml. Control samples (n=30) were treated and analyzed in the same way as the samples to test the applied analytical procedure accuracy. Internal standard (1 mg/ml of methylnonadecanoate C19:0) was also added in order to ensure precision control for the extraction procedure. All FA concentrations were calculated on mg/100g wet weight basis (wwt.). These units were selected in view of the relevance of the obtained data for the nutrition and food safety and industry approach (Loaiza et al. 2020b).

2.2. Statistical and numerical analyses

2.2.1 Statistical analysis

One-way ANOVA and post-hoc Tukey multiple comparison were performed to compare metal concentrations in freshwater-brackish and marine basal resources, as well as for the metal concentrations between different proximities to the MPAs. For non-parametric data, an extension of Kruskall-Wallis test was used with the post hoc non-parametric Kruskalmc test function. Results were statistical significant when $p < 0.05$.

2.2.2 Numerical analysis

The cost-benefit to conduct different EHS approaches

Three different EHS approaches were applied to determine the cost-benefit of these potential monitoring strategies (Loaiza et al. 2018; 2020a; b; c): 1) single species approach, 2) multi-species approach and 3) ecosystem-based approach. Budgets (€ · area · yr) were calculated per sampling area and year based on the analysis of metals (e.g. potentially harmful), micro-nutrients and fatty acids (non-harmful or beneficial), and stable isotopes as chemical analysis costs.

The budget was estimated using the following equation:

$$\text{Budget}\ (€\ \cdot \text{area}\ \cdot \text{yr}) = \text{n x (environ. compart) x n x } \left(\text{t}_{\text{species}}\right) \text{ x R x C. C. A x T. L}_{(\text{f})} + ((\text{n})\text{xS}_{\text{Cam}}))$$

where:

environ. compart: environmental compartments (species and/or food sources);

$t_{species}$: tissues of species;

S_{Cam}: sampling campaigns; considering 150 € per sampling campaign (incl. materials, fuel,…);

n: number of environ. compart, or $t_{species}$ or S_{Cam};

R: number of replicates;

C.C.A: cost per chemical analysis: Digestion + first metal analysis is 14 €, additional metals are 2 € per metal (based on UAntwerpen facilities: https://www.uantwerpen.be/en/research-groups/sphere/); 10 € for stable isotope analysis (based on UC-DAVIS: https://stableisotopefacility.ucdavis.edu/); and 50 € per fatty acid profiling (based on UGent facilities: http://www.assembleplus.eu/TA_UGent);

$T.L_{(f)}$: time-lapse factor, 12 for monthly; 4 for seasonal; 1 for inter-annual evaluations.

3. Results and discussion

3.1 Environmental health status (EHS)

Based on the comparison between metal concentrations (µg/g dwt.) in sediment and seston and the ERL (for As (8.2); Cd (1.2); Cu (34); Ni (21); Pb (47); Zn (150)) and ERM (for As (70); Cd (9.6); Cu (270); Ni (52); Pb (220); Zn (410)), there is no single location in this study that could be rated as "good". The sites PL1, PL2 and PSJ could be rated as intermediate (Fig 1). IRZ, SL, NL and SHO were considered to be the poorest in terms of environmental conditions, they exceeded the ERM-limits for Cu, Ni and Zn (Fig 1). When the ISQC ((for As (7.24); Cd (0.7); Cu (18.7); Pb (30.2); Zn (124)) and PEL ((for As (41.6); Cd (4.2); Cu (108); Pb (112); Zn

(271)) are used, the highest % incidence of adverse conditions was found for SHO, this location exceeded the ISQC for As and Pb and the PEL for Cd, Cu and Zn. IRZ, SL, and PL2 also exceeded PEL for Cd, so this means that there is a 71% chance that living organisms from these four locations could be affected by the Cd concentrations measured in sediment and/or seston (see Fig 1). Sediment contaminant levels also reflected the EHS determined by Loaiza et al. (2018; 2020a; b; c), with the sediment of the southern Punta San Juan' location (SHO) having the poorest environmental condition. This location showed the highest % incidence of adverse biological effects and the highest metal concentrations. IRZ and SL, the southernmost locations of Sechura Bay also exhibited degraded conditions as indicated by the metal contamination in the sediment and seston.

Oceanographic conditions (incl. El Niño effect) could also explain the EHS spatial and temporal variation in the Peruvian coastal waters. The important Northern Humboldt Current System (NHCS) flows northward from Chile to the north of Peru. Despite the fact that it is oceanic, this strong current probably washed contaminants from the south to the north, and distributed them along the way (center-south of Peru: Paracas and Punta San Juan) (Cabarcos et al. 2014). As this is a strong upwelling system, the sunken nutrients, minerals and possible contaminants are probably also brought to the surface and distributed along the water column, and as such will be distributed over the entire ecosystem. Peruvian Coastal Currents also play a crucial role in particulate matter distribution (i.e. chemicals), and reinforce what is brought up by the NHCS (Huyer et al. 1991; Cabarcos et al. 2014).

During the strong-El Niño of 2017, river flow capacities reached their maximum in Peru due to the strong rains. Their discharges (incl. contaminants) were extremely high along the Peruvian coast, which substantially changed the environmental conditions (and thus health) of the marine ecosystems (Loaiza et al. 2018; 2020a; 2020b). Fig 3 shows the metal contribution of freshwater and brackish environments to the marine environment. Metal levels (e.g. As, Ni) for the POM (or 'input') from the Sechura River, Virrila Estuary and San Pedro Mangrove were mostly higher than the concentrations in the marine ecosystems, and significantly different for the concentrations of As, Ni and Pb in sediments. The input from river and mangrove was also significantly higher in As and Ni concentrations than those in marine compartments (with the exception of Ni-seston). High variability was found for Cd in both environments, similar concentrations (up to ~5 μg/g) and non-significant differences were observed for the freshwater-brackish and marine basal resources (Fig 3).

The metal contamination at different distances from the MPAs shows that the highest POM and sediment metal concentration (e.g. As, Pb) were measured near the southern MPA, followed by the location in front of the northern MPA (Fig 4). Overall, in front of (1-5 miles) and in the vicinity of (up to 12 miles) the MPAs a similar degree of metal contamination was observed, with slightly lower levels in the sampling locations further away. This pattern means that environmental contamination and stressors are reaching the MPAs and their surrounding areas. MPA management in Peru should therefore be re-formulated in terms of possible direct and indirect environmental impacts in their vicinity, from the south to the north. We suggest a proper marine monitoring program (incl. vigilance) along the coast and marine vicinity of the MPAs, to identify the main stressors and metal-driven activities. It is noteworthy to mention that the Peruvian government considered mainly the land area as the protected or reserved area for Illescas Reserved Zone and for Punta San Juan Reserve. It covers 4 miles without a proper maritime control from the government, which can explain the lack of control of these marine ecosystems. Therefore, when the northern MPA was evaluated, we could see that the major industrial activities were situated around that Illescas Reserved Zone and during water collection, oil traces were observed along the water surface and sub-surface of the sampling locations (pers. obs.).

Overall, the metal concentrations in environmental compartments, e.g. POM, sediment and seston strengthen the consistent pattern, e.g. the southernmost locations (i.e. SHO, IRZ, southern MPA) have a poor EHS, as shown in Loaiza et al. (2018; 2020a; b; c) previous EHS analyses, which were mainly based on organism specific-tissue metal accumulation that reflects the environmental current status. We emphasise that metal contamination is a serious concern in Peru, this is reflected in 1) the elevated sediment and seston concentrations that exceeded the international limits (e.g. ERM, PEL) being more pronounced in the southern locations; 2) the possible effect of metal (e.g. As, Ni) exchange between freshwater-brackish environments and marine coastal environments, and being intensive during El Niño events and 3) the level of degradation in the proximity of the MPAs, with the MPA in the South being the most metal enriched. As previously mentioned, mining (incl. illegal mining) and agriculture could be most important source of metal contamination, however more studies must be conducted to determine the activity contributing most to the metal levels in Peruvian aquatic systems.

Further studies that multi-integrate the environmental compartments could play a key role to estimate the EHS into a ‘big picture’ using methods, such as: Ecotracer model, GIMS data and other complementary data; which could strength the insights of the study. Environmental metal concentrations is only one part of the stressors for aquatic ecosystems in Peru, the inclusion of Climate change and ENSO as driven variables in the model could give a more dynamic analysis that provides information for a better ecosystem-based management of Peruvian ecosystems. Varotsos et al. (2019) could determine that the Okhotsk Sea will decrease its productivity in ~55 years due to Climate change. The same conclusion can also be made for Peruvian ecosystems using a large data set (i.e. GIMS) combined with anthropogenic (e.g. metal contamination) factors. Two trophic model studies indicated that Sechura Bay Ecosystem is a relatively inefficient system from a community energetics point of view, likely due to the periodic perturbations of ENSO. These studies also found that the environmental driver variables, i.e. riverine inputs played a crucial role on the scallop survival and ecosystem dynamics, information that could also be integrated to the present study for ENSO scenario predictions, which is highly relevant for the management of marine ecosystems in Peru (Taylor et al. 2008; Loaiza et al. 2021).

3.2. Designing strategies for EHS monitoring

In determined time-frame studies, it is crucial to set priorities. Generally, research questions are determined first, and then a possible way to tackle these questions and find answers is designed. It is essential to take into account procedures that are economically, logistically and analytically feasible. This also partly explains why different approaches can be performed for EHS analyses (Long et al. 1995; Breitwieser et al. 2018). Different approaches for EHS or monitoring program design are always related to the cost-benefit of the involved activities. In terms of cost-efficiency, a research-question approach prior to analysis is ideal for EHS. It is not always feasible to measure an enormous amount of biotic and abiotic environmental compartments to estimate EHS. Therefore, a summarizing analysis of the cost-benefit of the different approaches was made (Fig 5).

The single species use is the economically most optimal approach (2 760 € · area · yr), but a substantial ecological knowledge of the species under study (e.g. potential bioindicator; *A. purpuratus*; Loaiza et al. 2020a) is required. The species could be analysed by using its different compartments (e.g. 5 tissues: gills, digestive gland,…) to give a wide spectrum of tissue-specific contaminant accumulation for each season (T.L$_{(f)}$: 4) (Fig 5). It is noteworthy to mention that only relevant and specific contaminants (number of samples; n=3) must be considered including potentially harmful metals (Cd, As,…; 6 replicates per tissue) due to their high persistence and for the food safety approach. Study areas should be separated by enough distance (not just a few miles) to disentangle population mixing. These distances will allow to compare different environmental conditions and pressure from anthropogenic activities (Loaiza et al. 2020a).

A multi-species (number of samples; n=6) approach based on ecologically and economically important species requires a medium budget (~ 9 570 € · area · yr) (Fig 5). The budget is mainly related to the measurement costs of biomarkers such as fatty acids (~ 50 € per sample; 3 replicates per species), but also numerous metals (n=7; As, Cd, Cu, Fe, Ni, Pb and Zn; 6 replicates per species). The advantage of measuring fatty acids and micro-nutrients (e.g. Fe, Zn,...) is its dual use as tracer and biomarker, and as beneficial compound for nutritional approaches. Seasons but also low-and-high rain periods (T.L$_{(f)}$: 5; 4 seasons + 1 extra sampling in summer (i.e. high-raining period)) are considered in this approach based on the impact of the river discharges (incl. other environmental factors) on the seafood safety and quality (Loaiza et al. 2018).

An ecosystem-based approach requires a large budget (~ 16 296 € · area · yr) because of the high number of environmental compartments to be sampled, and the number of sampling (~ 6) expeditions in order to collect all samples per region (Fig 5). In order to have a robust picture of the ecosystem tropho-dynamics and functionality in Peruvian marine ecosystems, a minimum number of species (or trophic levels) is required for the analysis (n= ~23; 20 marine species and at least 3 food sources i.e. POM, seston,…). This number of species is related to the high biodiversity (and abundance) found in the study locations along the Peruvian coast (Loaiza et al. 2020b; c). The budget of 16 296 € · area · yr is only considering metals (n=3; As, Cd, Pb,…) and stable isotopes ($\delta^{15}N$ and $\delta^{13}C$) to be analyzed. In case of the nutritional approach, e.g. to search for new marine foods, the amount would reach up to a ~2-fold higher cost due to the fatty acid analysis (Loaiza et al. 2020b). Regional and seasonal samplings are a priority for numerous species approaches (i.e. multi-species or ecosystem) due to the high budget per sampling action. This sampling method has the advantage that it can answer additional research questions related to the effect of climate and oceanographic characteristics (i.e. ongoing Climate Change, El Niño event), which is stronger at the regional level.

4. Future perspectives for marine contamination research in Peru

4.1 Improving feeding practices and nutrition of Peruvians

Health risk assessments could be part of an EHS monitoring when the human component is included, e.g. the analysis of beneficial and risk elements (or compounds) of commercial (~edible) species for humans; which gives insights and useful information to estimate the health status, risks and habits of certain populations (Oremus et al. 2011). Fig 6 shows preliminary guidelines for seafood consumption based on the results obtained in Loaiza et al. (2018; 2020b). Both studies used risk indices to estimate the possible adverse effects of metal ingestion through the consumption of edible, potentially-edible and non-edible species. In human health, a very precautionary approach must be considered in order to give preventive information to the decision makers (Lipfert et al. 2005).

Loaiza et al. (2018) used the maximum level (MAL) of metal in edible species for index calculations, instead of average values as was the case in Loaiza et al. (2020b). For example, the safe amount (per week) that can be consumed of the snail *Bursa ventricosa* was a rate of 0.02 kg/week in Loaiza et al. (2018), a 10-fold lower value than the calculated amount (0.21 kg/week) with the average metal concentrations of Loaiza et al. (2020b) (Fig 6). It is noteworthy to mention that Loaiza et al. (2020b) also included more precise ingestion rates in the analysis per study area, based on the frequency feeding questionnaires (FFQ; incl. anthropometrics), while the other study used ingestion rates estimated from the seafood (item) available for a Peruvian person from Food Balance Sheets (FBS) (FAO, 2019).

When the estimated ingestion rates based on FFQ and FBS were compared, we found considerably differences: mollusks are ingested (or supplied) in up to 35 times larger quantities (in accordance to the FBS) than the ~0.4 g/day estimated value for snail consumption using the FFQ. An over-estimation could also be observed for crustaceans, up to 7-fold higer ingestion rates (i.e. 2.8 g/day) were calculated using FBS. However, octopus (i.e. cephalopods) consumption was under-estimated using FBS, with 0.8 g/day compared to an average of 5.0 g/day, based on FFQ. For fish consumption, the FFQ results in a range of 36-42 g/day were comparable with the national estimated consumption (~14.5 kg/yr or 39.7 g/day; PRODUCE, 2019) from the Peruvian goverment. It is worth noting that FBS estimations and national estimated consumptions are based on the entire Peruvian (population) regions, while the FFQ were conducted in coastal populations in the North and South, partially explaining some of the differences.

In conclusion, a good preliminary analysis is required to properly address actual risks. In this case MAL values would give the most protective advise to the Peruvian authorities or decision makers, i.e. SANIPES, PRODUCE, among others (see Fig 6). However, this risk could be over-estimated when FBS data (i.e. food item supply or availability) are used. Individual intake levels (incl. anthropometrics) from nutritional and social surveys (e.g. FFQ) for specific populations give the most accurate information to determine the actual risks for seafood consumption in Peru. A probabilistic model (e.g. Monte Carlo simulation) that integrates the specific-individual intake and seafood nutrient/contaminant could be also an interesting methodology to determine the risk and benefit for Peruvian seafood consumption and was already suggested to be used in future studies (Sioen et al. 2007).

Further studies and interventions on improving feeding practices and nutrition of the local population on the long term are needed in Peru. Chronic malnutrition in children (< 5 year) and chronic diseases in adults are still severe problems in Peru (Majluf et al. 2017). Risk estimations are valuable information but *posteriori* actions are the important steps to tackle and attenuate the real problem. This can be realized 1) by providing education on seafood quality to researchers, doctors, fishermen and teachers at the local scale, and 2) by increasing awareness on food safety and food quality for seafood through guidelines at the national level. The combined work of public health experts and marine biologists could lead to actions (e.g. human health evaluations) at different levels of organization and interactions (Fig 7).

Affordability and access of seafood, and people's feeding habits, perceptions of seafood quality and perceived benefits over health (e.g., malnutrition and chronic diseases) are factors that could contribute to the acceptance and consumption of seafood (Laraia et al. 2013). We suggest the use of a socioecological perspective for understanding the range of factors and actors that influence health and seafood consumption (Peters et al, 2008). The socio-ecological model proposes that behaviour is influenced by five levels of social environments which include intrapersonal, interpersonal, institutional, community and public policy: i) at personal level, e.g. with issues related to knowledge and skills, ii) at interpersonal level e.g. factors influencing the social network or the interaction between community members, and family, iii) at community level, e.g. information available at a health care level or from programme promoters, iv) at institutional level, e.g. availability of actors and programmes and delivered interventions in the study area and v) at policy level, e.g. general mandates or governmental sectoral policies (incl. human health care projects) (Fig 7). As a result, all actors will be involved in the development of guidelines for seafood consumption in Peruvian populations.

To improve feeding practices and nutrition of the local population in Peru on the long term, we proposed to design an intervention study over a 4-year period. Data collection will include repeated observations of the same variables at two moments, at the baseline (before the intervention) and at the end of the study (after the intervention). Participants will include children under 5 years, and men and women from specific locations in Peru. The following data could be collected at the baseline and the end of the study: 1) Socio-economic status (SES) and livelihoods questionnaire: socio-economic information will include demographic characteristics, households' material endowments, education and income. Questions will be adapted from the National Demographic and Health Survey (INEI, 2021; ENDES, 2020). Additionally, the questionnaire will collect information regarding the five capitals of the Sustainable Livelihoods Framework: financial, human, social, physical and natural (Lax & Krug, 2013). All this information will be used to determine the changes that improving seafood consumption can have over those capitals providing a score, which can subsequently be translated to poverty reduction, well-being and capabilities as well as livelihoods adaptation, vulnerability and resilience (Fig 7) (Commodore et al. 2013);

2) Food security and feeding practices assessments: This will be carried out in a food frequency questionnaire (FFQ) to estimate dietary intake and through direct observation on a subset of participants as in Loaiza et al. (2020b) (Fig 7);

3) Health assessments: For children under 5 years old, anthropometric measurements will be conducted to determine the prevalence of stunting, wasting, and the use finger pricking to determine anemia prevalence in these populations. In case of men and women, they will undergo a health evaluation that includes: anthropometric measurements, blood pressure, and a lipid and glucose profile using a point of care system. These measures will allow the diagnosis of metabolic syndrome, hypertension and diabetes (Fig 7) (Sanchez-Samaniego et al. 2019);

4) Elaborate and implement an education food safety guideline/educational materials: The seafood composition and properties, estimates of dietary intake and health assessments at the beginning and after the intervention will provide an insight of the required changes to improve the feeding habits. Food safety and food quality guidelines will be developed in cooperation with the local population (incl. teachers, doctors, fishers and government functionaries) in workshops. Awareness of possible consequences of seafood consumption for human health will also be discussed during these activities. Finally, this will provide the basic information to establish policies for socio-environmental and human health care at the national government level (Fig 7).

All actors will be informed about seafood biochemical properties and the benefits and risks of seafood consumption, in terms of human health conditions. So far, local population and authorities are not aware about the consequences of consuming contaminated seafood, and what frequency and amount of consumption is possible according to risk assessments. On the other hand, micronutrients and fatty acids (e.g. omega-3 fatty acids) from seafood can contribute to a good nutrition of children and the local population in general. At the same time, to know which species are the richest in nutrients and properties and how this varies according to individual size, season, location, etc., is required for a sustainable use of marine resources on the long term.

4.2 New marine foods for alternative diets

Peruvian marine species exhibited high average amounts of 180, 100 and 40 mg/100g for EPA, DHA and ARA, respectively along the Peruvian coast (Loaiza et al. 2020b). Some of the highest concentrations were found in marine species that are characterized as potentially-edible or non-edible species for Peruvian consumers, suggesting that consumption of at least these species considered as potentially-edible could be promoted.

Food resources from land or sea ecosystems are getting depleted worldwide (Assadourian, 2010). The food industry has exponentially increased in recent decades because of the need to produce enormous amounts of food (Parodi et al. 2018). The overexploitation of marine-based resources is also the reason of the abrupt decline of the biomass of some species (Morato et al. 2006). The over-fishing of a few marine species as food sources and under-utilization (e.g. discards) of others is the cause of environmental degradation, as has been registered in fisheries historical records (e.g. Peruvian anchovy *Engraulis ringens*) (Boerema & Gulland 1973). Because of this non-sustainable scenario the use of alternative diets must be considered (Parodi et al. 2018).

New marine foods, perceived as potentially edible or even when considered non-edible by Peruvians, offer possibilities to be used as alternative diets (Loaiza et al. 2020b). However, attention has to be paid to food processing of different marine species (i.e. sea urchin, crabs, algae…) to make them an attractive food for human consumption, as this will determine their potentiality as nutritive commercial products. Physical and chemical processes could be applied to change texture and taste, and simultaneously to reduce their content of any toxic or harmful elements (e.g. metals, viruses, or other contaminants/patogens) (Hajeb et al. 2014; Piras et al. 2016). A scientific approach should be applied to find the most suitable process to minimize, for example, the metal contamination in these new marine foods. In addition, it is necessary to try to give them the best sensorial properties for human consumption.

Next to their shape and best properties, the method of preparation/cooking will be important as well. Increasing temperature by baking and steaming could considerable decreased the Pb and Cd concentration in fish (Atta et al. 1997). Cooking and boiling of algae could eliminate As up to 95% and 50%, respectively (Hajeb et al. 2014). Preparation and proper cleaning of edible tissues (e.g. remove of kidney, hepatopancreas) also considerably reduced the metal contents in mollusk bivalves (Bach et al. 2014). On the other hand, ethylenediaminetetraacetic acid (EDTA) and cysteine are chemicals (i.e. chelating agents) with the highest potential application of the industrial removal of toxic elements (Hajeb and Jinap 2012; Hajeb et al. 2014). By using response surface methodology (RSM), dipping raw mackerel fish fillets in a mixed solution of i.e. cysteine, EDTA, hydrochloric acid, sodium hydroxide and salt, the optimum conditions resulted in up to 91% Hg reduction (Hajeb and Jinap 2012).

Loaiza et al. (2020b) confirmed that the most promising new marine foods were the crabs *Cycloxanthops sexdecimdentatus* and *Cancer plebejus*, because of their beneficial chemical profile and low levels of potentially harmful (e.g. As, Cd) metals. The sea urchin *Tetrapigus niger*, the crab *Inachoides lambriformis*, the mussel *Semimytilus algosus*, the mantis shrimp *Squilla* sp. and the highly abundant squat lobster *Pleuroncodes monodon* contained high LC-

PUFA (EPA + DHA + ARA) concentrations but also Cd concentrations, which makes it more complex to select them as suitable food.

When these new marine foods are compared to land-based foods (meat), the EPA + DHA concentrations are up to ~190-fold higher (see Fig 8). Their use as edible species could be possible after testing by an appropriate process for metal depuration and/or sequestration. It is worth to mention that the previous physical (e.g. thermal treatment) and chemical processes could also alter the beneficial compounds, e.g. PUFAs (Piras et al. 2016). Subsequently the new marine foods could be tested as safe and acceptable (i.e. certified) for human consumption. Ecosystem-based management studies must be conducted prior to their exploitation in order to avoid and repeat previous experiences of intensive resource exploitation (e.g. as most large fisheries from the last decades).

5. Conclusions

Based on ERL and ERM comparisons, none of the studied Peruvian marine ecosystems could be rated as EHS-good. The southern location SHO was the poorest in terms of environmental conditions, exceeding metal sediment/seston limits for all studied metals (As, Cd, Cu, Ni and Zn). The southernmost locations (IRZ and SL) of Sechura Bay exhibited also degraded conditions and a low EHS, reflected in the metal sediment/seston contamination. Freshwater and brackish ecosystems could contribute to the overall metal concentrations in Peruvian marine ecosystems, this by different input pathways (e.g. food sources such as POM *sensu lato*) of As, Ni and Pb, which could be more pronounced during El Niño event. Environmental contamination and stressors are even reaching the Peruvian MPAs. The management of coastal marine areas and MPAs in Peru should be re-formulated in terms of possible direct and indirect environmental impacts in their vicinity. For a proper EHS monitoring, we suggest to consider the single-species approach with a previously studied species (or genus), this approach could be optimal in terms of cost-benefits (budget: 2 760 € · area · yr), while give interesting insights of the current EHS. Adjacent fields (e.g. human health, nutrition) could be covered when EHS monitoring are performed, whether the beneficial compounds (e.g. PUFAs) and elements (e.g. Fe, Zn) for humans are considered in the analysis. Safe amounts of seafood for human consumption are more reliable when FFQ data is used, estimations indicated that amounts are species-specific according to the metal load per species, and from 130 to 680 g are allowed for consumption per week. The beneficial intake as consequence of the consumption of Peruvian seafood at these safe amounts could reach about 200 mg PUFA, which could substantially help to improve the health of Peruvians in a sustainable way. For future marine research in Peru, the human component should be always considered in order to talckle current concerns in Peru, e.g. malnutrition and anaemia which could be addressed by providing new knowledge of nutritive marine foods.

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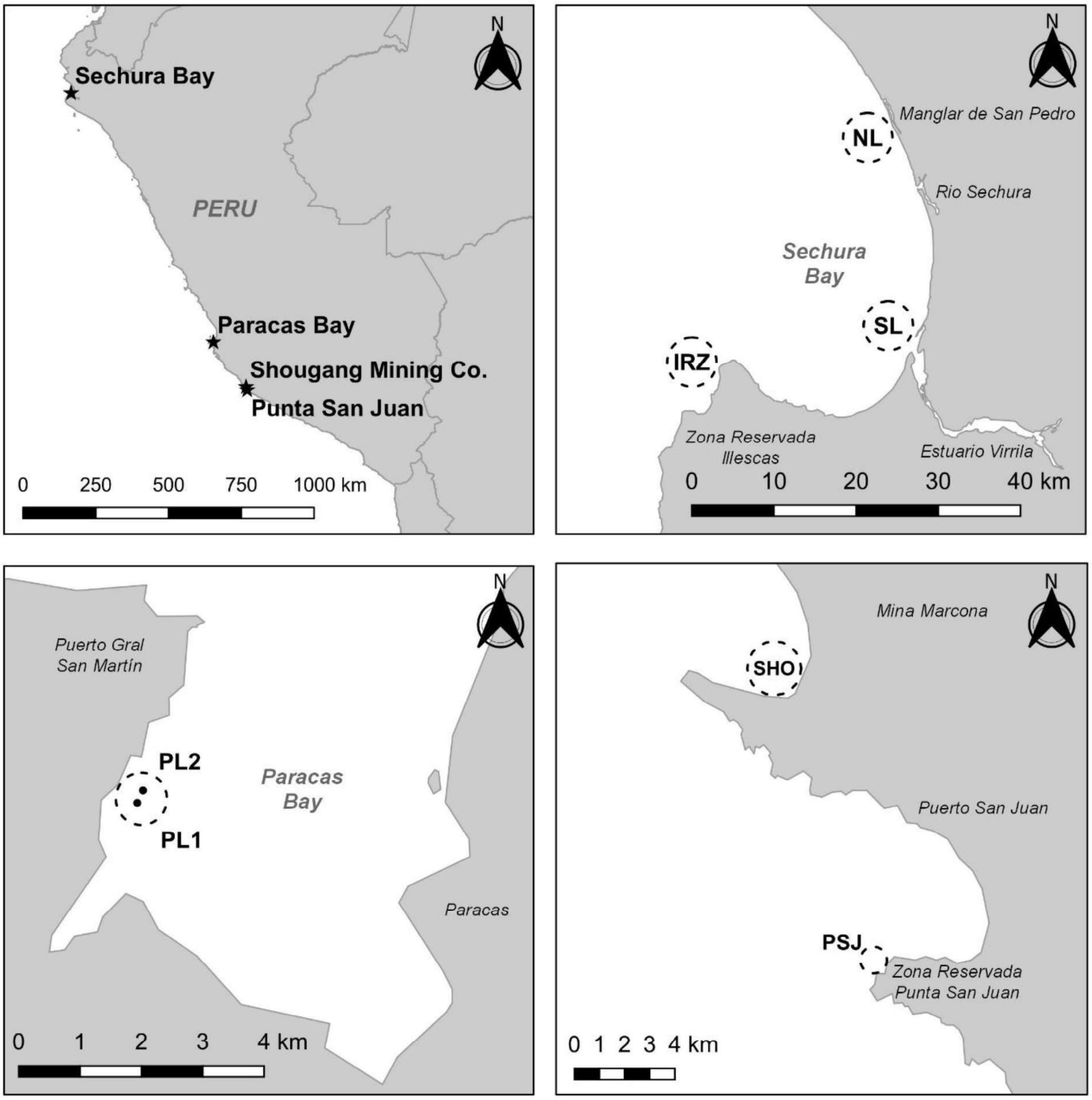
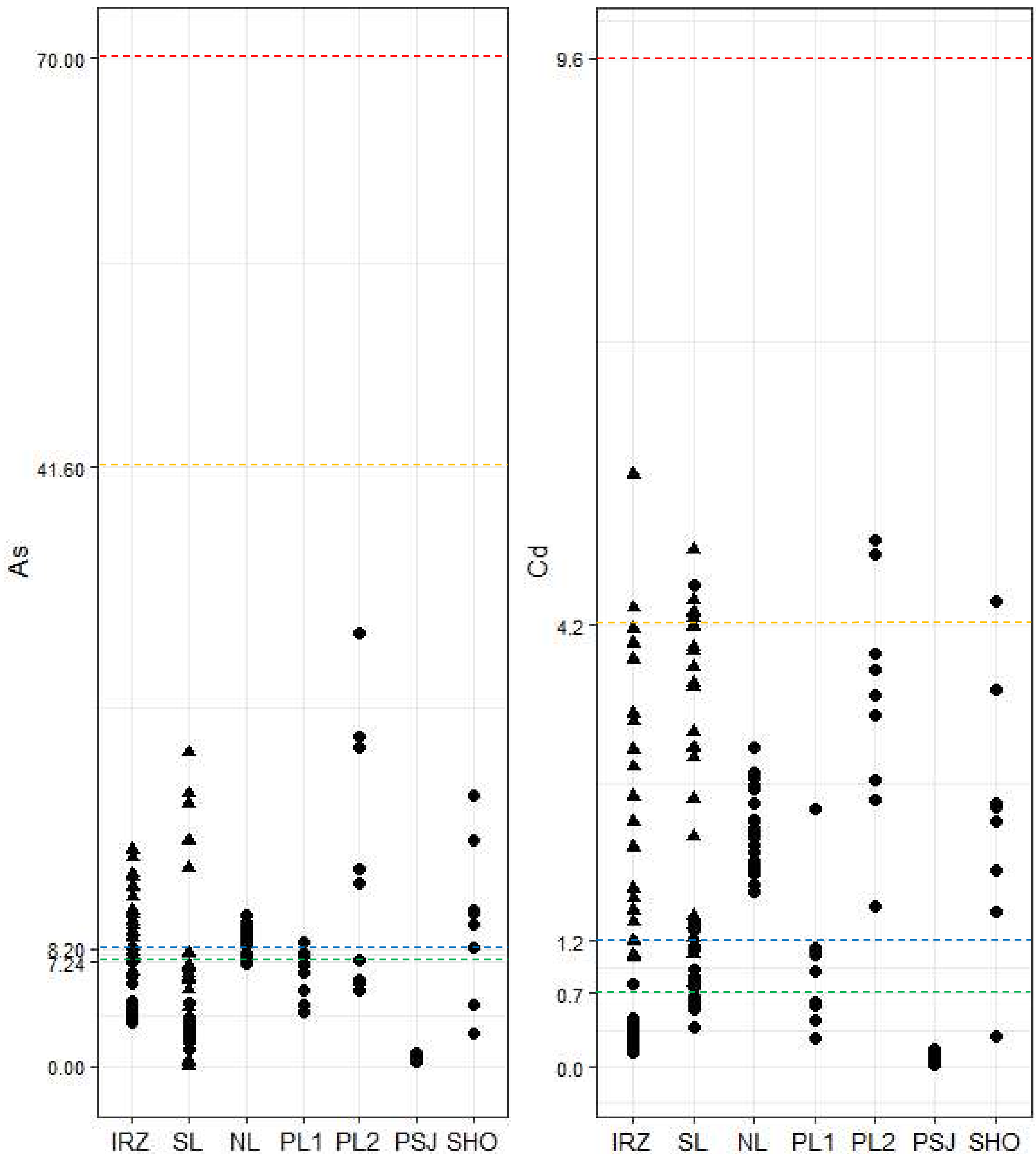
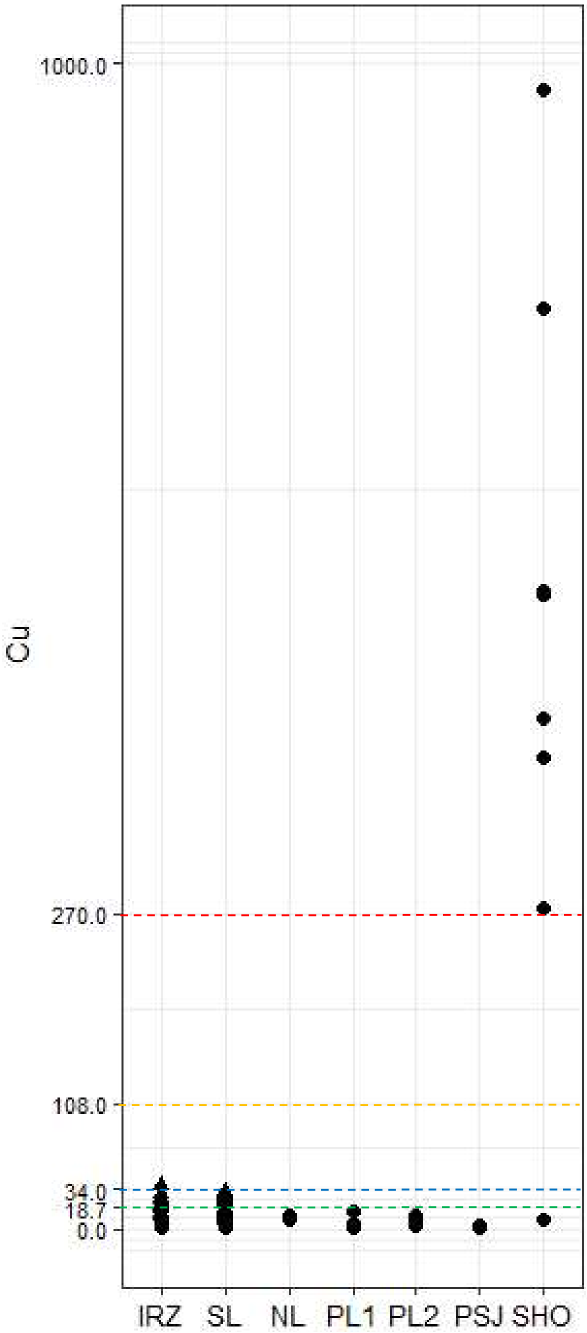


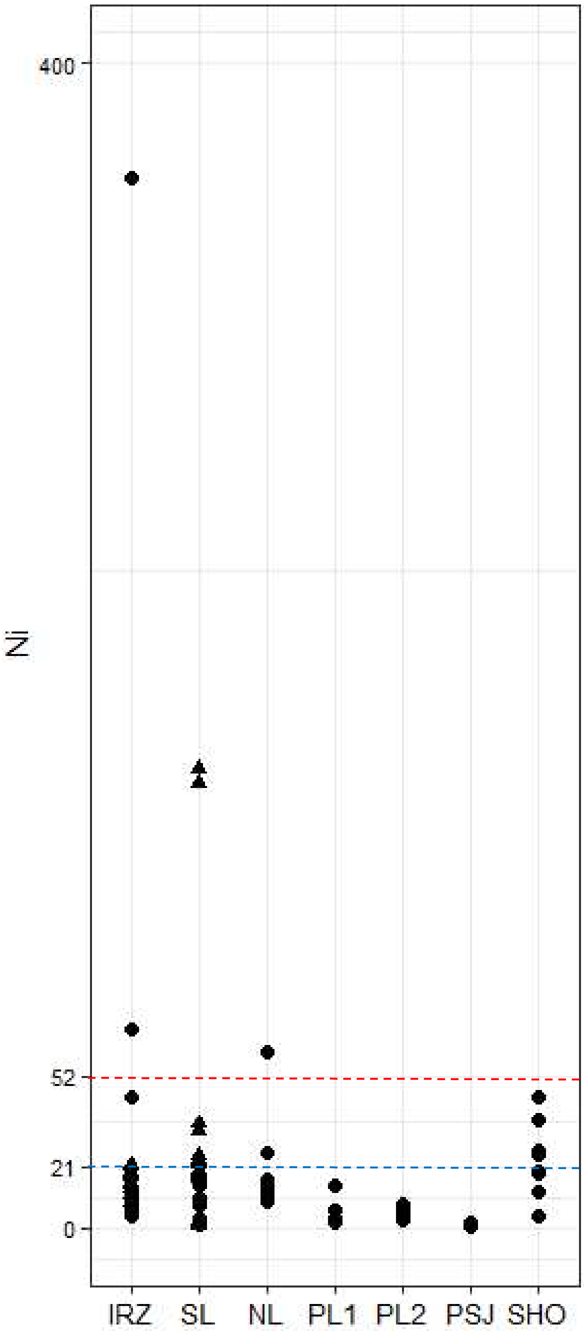
Fig 1. Location of the sampling areas in Sechura Bay (incl. Zona Reservada Illescas), Paracas Bay and Marcona. Southern (SL) and Northern (NL) locations in Sechura Bay; one location in front of the Illescas Reserved Zone (IRZ); PL1 and PL2 locations in Paracas Bay; and PSJ in front the Zona Reservada Punta San Juan, and SHO in front of the Shougang iron mining company.



70.00
41.60
As
8.20
7.24
0.00
IRZ SL NL PL1 PL2 PSJ SHO
9.6
Cd
4.2
1.2
0.7
0.0
IRZ SL NL PL1 PL2 PSJ SHO



Cu
1000.0
270.0
108.0
34.0
18.7
0.0
IRZ
SL
NL
PL1
PL2
PSJ
SHO



Ni
400
52
21
0
IRZ
SL
NL
PL1
PL2
PSJ
SHO

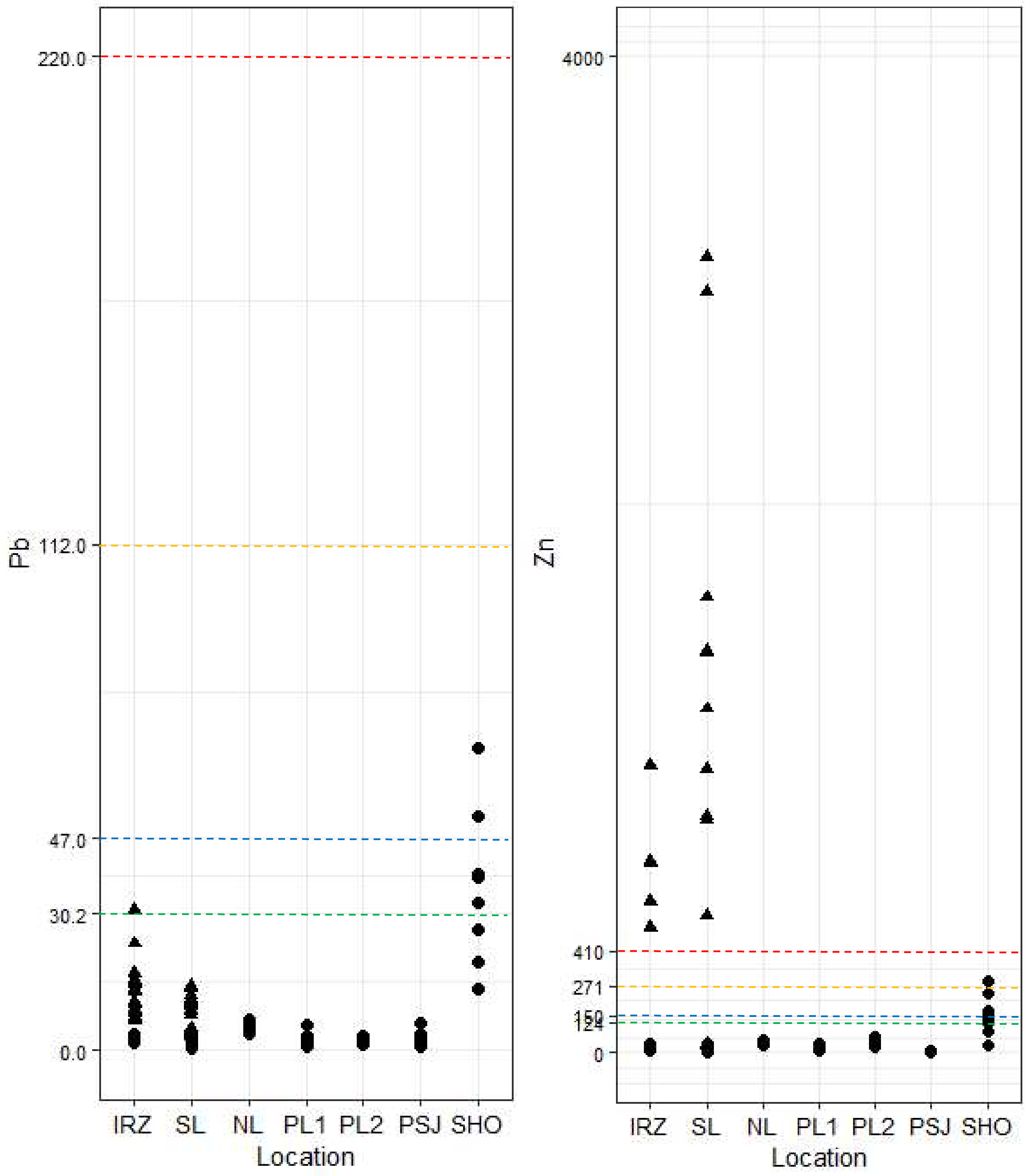
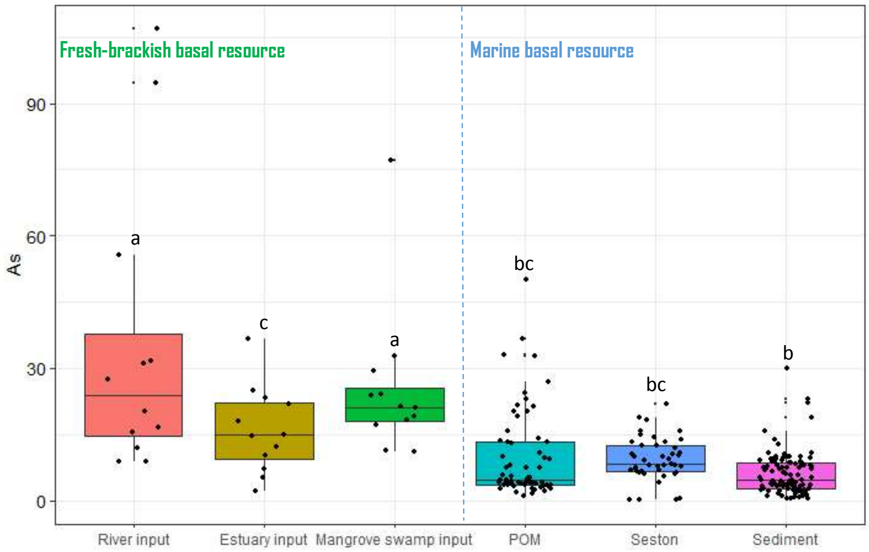
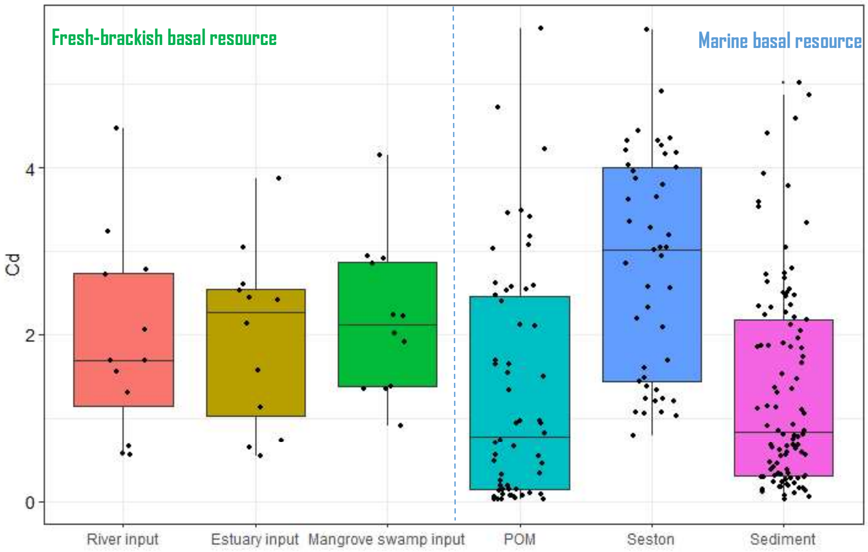
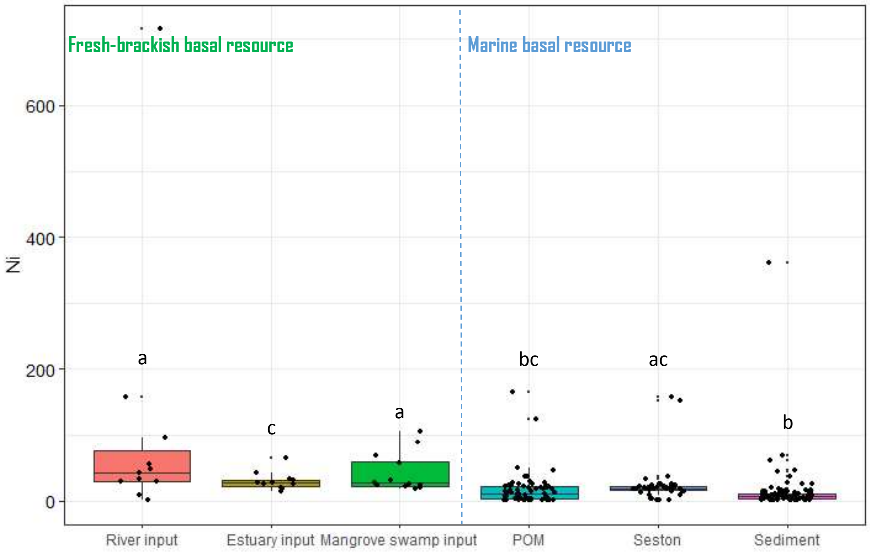


Fig 2. Metal concentrations (µg/g dwt.) of sediment (circle) and seston (triangle) per location compared to the Effects Range-Low (ERL) (- -) and Effects Rage-Median (ERM) (- -) limits from Long (1995), and Interim Sediment Quality Guideline (ISQG) (- -) and the Probable effect level (PEL) (- -) from the Canadian Council of Ministers of the Environment (1999).


Fresh-brackish basal resource
Marine basal resource
As
a
c
a
bc
bc
b
River input
Estuary input
Mangrove swamp input
POM
Seston
Sediment


Fresh-brackish basal resource
Marine basal resource
Cd
River input
Estuary input
Mangrove swamp input
POM
Seston
Sediment


Fresh-brackish basal resource
Marine basal resource
Ni
a
c
a
bc
ac
b
River input
Estuary input
Mangrove swamp input
POM
Seston
Sediment

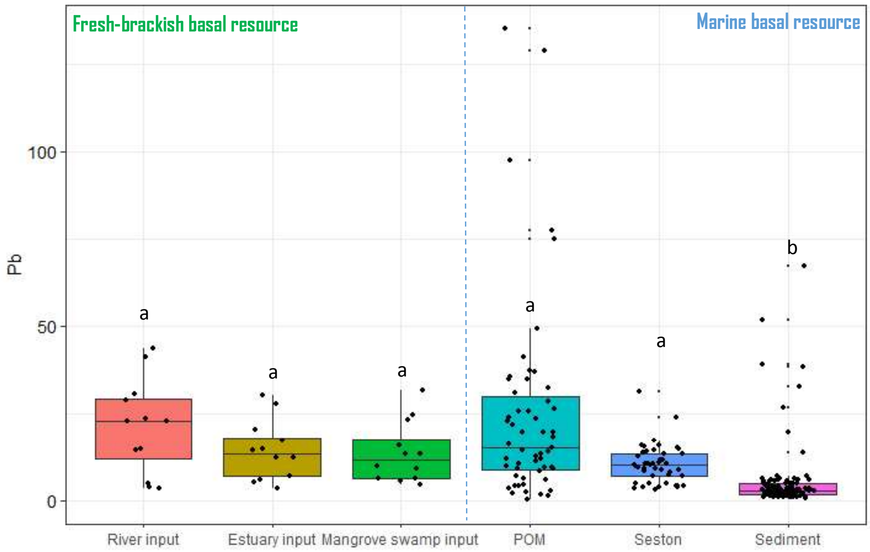


Fig 3. Metal concentrations (µg/g dwt.) in environmental compartments from the freshwater-brackish and marine water environments. Different letters indicate significant ($p<0.05$) differences between freshwater-brackish and marine basal resources.

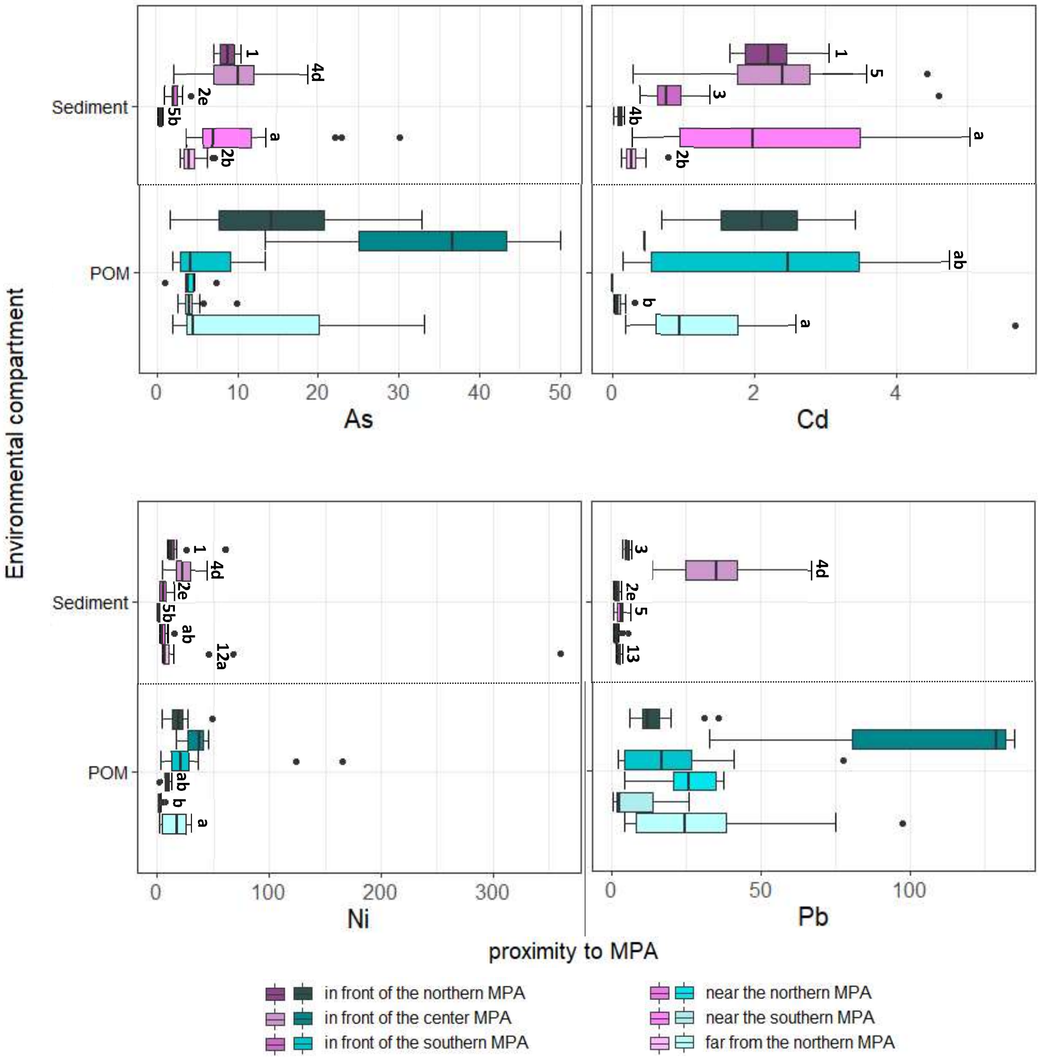
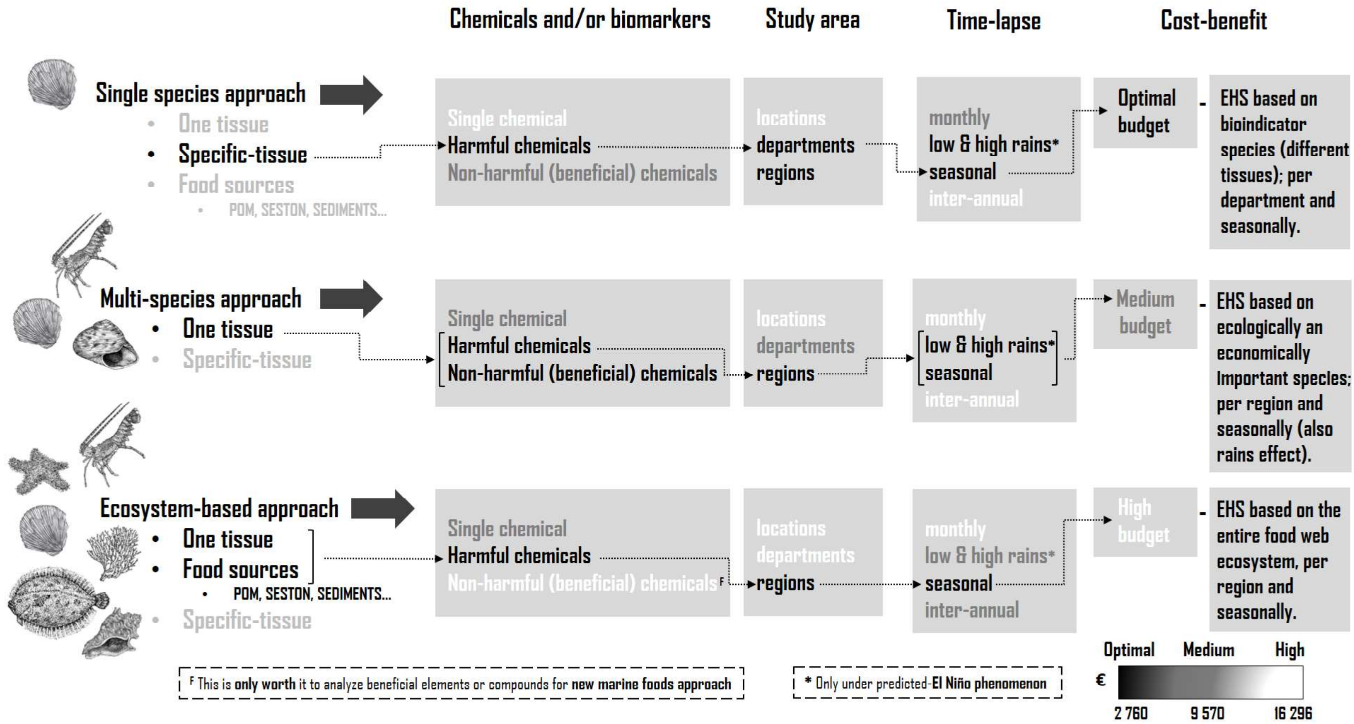
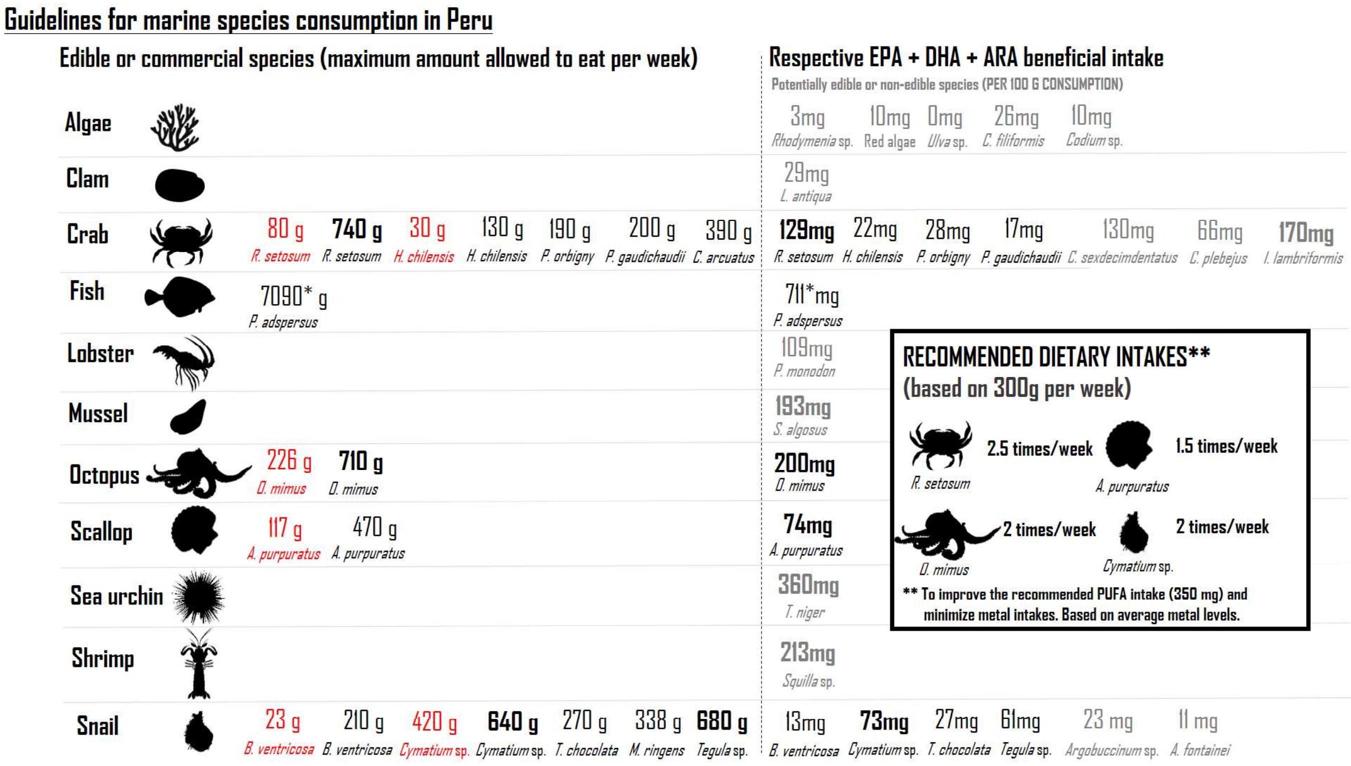


Fig 4. Metal concentrations (µg/g dwt.) in sediment and POM in the proximity to the MPAs. The northern MPA is Illescas Reserved Zone, the center MPA is the Paracas National Reserve and the southern MPA is the Punta San Juan Reserve. In front, near and far distances refer to 1-5, 10-12 to up to 25 miles, respectively from the MPA. Different numbers indicate significant ($p<0.05$) differences within distances in the north (1,2,3) and in the south (4,5), and different letters for significant differences between regions within front (a,b,c) and near (d,e) locations.



Note.- to our knowledge, the most (financially) feasible pathway is printed in black, and toward the lighter attenuation up to white as the least (financially) feasible.

Fig 5. Cost-benefit analysis based on the different approaches to estimate environmental health status (EHS) in marine studies (Loaiza et al. 2018; 2020a; 2020b). Budgets (€ · area · yr) were calculated using: metals (e.g. potentially harmful), micro-nutrients and fatty acids (non-harmful or beneficial) and stable isotopes as chemical analysis costs; and per sampling area and per year. Marine species drawings were made by the Peruvian artist Samantha Scavino, 2018.



Species and maximum allowed amounts to eat per week that are printed in red were calculated using maximum metal levels (MAL), while the printed in black were calculated with average metal levels (Loaiza et al. 2018; 2020b). Potentially edible and non-edible species and their respective EPA + DHA + ARA intakes that are printed in grey are based on the consumption of 100 g. (*) The flatfish *P. adspersus*' maximum amount to eat per week and respective beneficial intake were only based on inorganic-As concentrations, Cd was BDL for this species. The highest calculated values (i.e. maximum allowed amount and/or respective intake) were printed in bold.

Fig 6. Guidelines for consumption of seafood from Peruvian marine sources

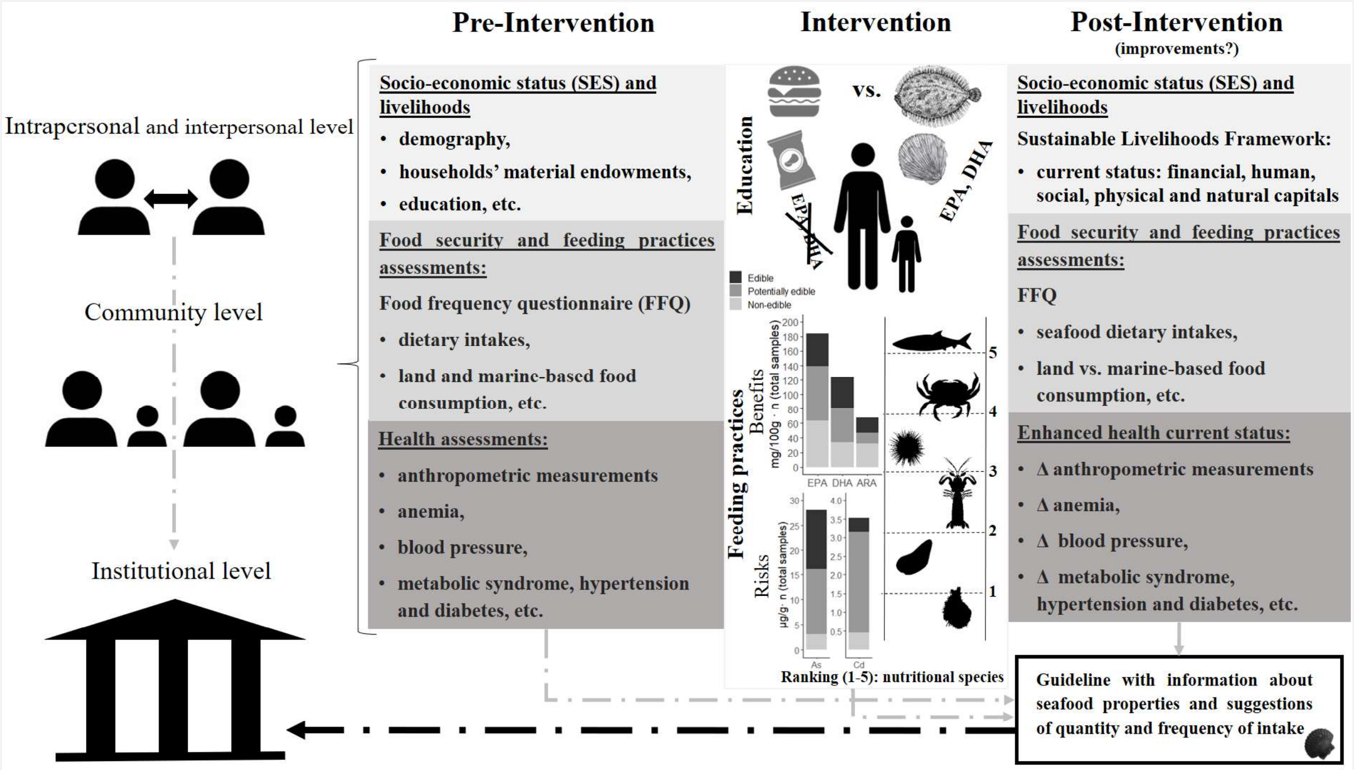


Fig 7. Scheme of interventions for improving feeding practices and nutrition for Peruvians.

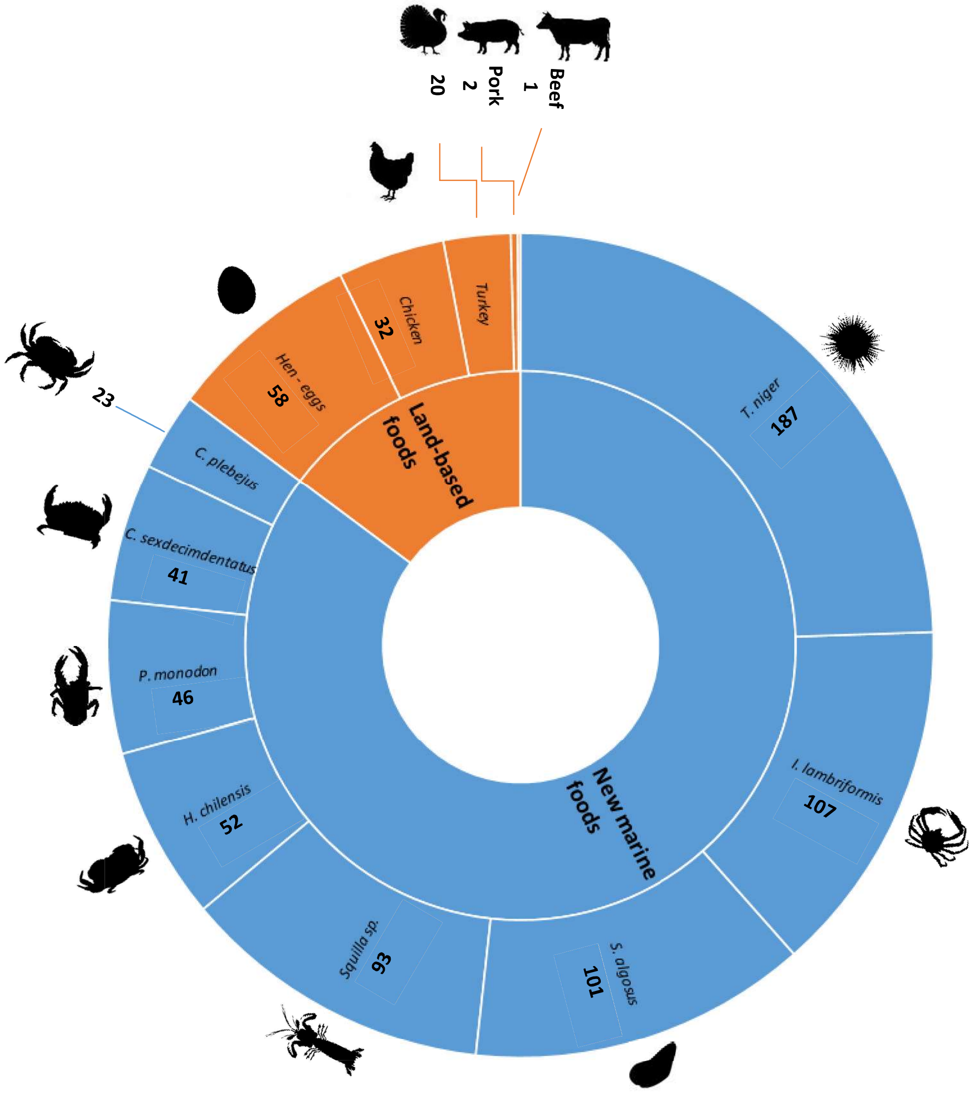


Fig 8. EPA + DHA concentrations (mg/100g wwt.) for the new marine foods and land-based foods. Land-based EPA and DHA concentrations were based on Tacon & Metian, (2013).