

Persistent organic pollutants and trace metals in selected marine organisms from the Akanda National Park, Gabon (Central Africa)

Fany Sardenne, François Le Loc'h, Nathalie Bodin, Jean-Hervé Mve-Beh, Jean-Marie Munaron, Jean-Daniel Mbega, Aimé Roger Nzigou, Oumar Sadio, Hélène Budzinski, Christophe Leboulanger

▶ To cite this version:

Fany Sardenne, François Le Loc'h, Nathalie Bodin, Jean-Hervé Mve-Beh, Jean-Marie Munaron, et al.. Persistent organic pollutants and trace metals in selected marine organisms from the Akanda National Park, Gabon (Central Africa). Marine Pollution Bulletin, 2024, 199, pp.116009. 10.1016/j.marpolbul.2023.116009. hal-04399286

HAL Id: hal-04399286 https://hal.univ-brest.fr/hal-04399286v1

Submitted on 18 Jan2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés. Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

Persistent organic pollutants and trace metals in selected marine organisms from the Akanda National Park, Gabon (Central Africa)

Fany Sardenne^{1*}, François Le Loc'h¹, Nathalie Bodin², Jean-Hervé Mve-Beh^{1,3}, Jean-Marie Munaron¹, Jean-Daniel Mbega³, Aimé Roger Nzigou⁴, Oumar Sadio⁵, Hélène Budzinski⁶, Christophe Leboulanger⁷

¹IRD, Univ Brest, CNRS, Ifremer, LEMAR, IUEM, F-29280 Plouzané, France

²Sustainable Ocean Seychelles, BeauBelle, Mahé, Seychelles

³Institut de Recherches Agronomiques et Forestières, CENAREST (Laboratoire d'Hydrobiologie et

d'Ichtyologie), BP 2246 Libreville, Gabon

⁴Université des sciences et techniques de Masuku, Franceville, Gabon

⁵IRD, Univ Brest, CNRS, Ifremer, LEMAR, Dakar, Sénégal

⁶Bordeaux University, EPOC-LPTC, UMR 5805 CNRS, Talence, France

⁷MARBEC, Univ Montpellier, IRD, Ifremer, CNRS, F-34200 Sète, France

^{*} Corresponding author. *E-mail address:* fany.sardenne@ird.fr (F. Sardenne).

Abstract

Akanda National Park (ANP) is composed of mangrove ecosystems bordering Libreville, Gabon's capital. The contamination of aquatic resources from the ANP by persistent organic pollutants (POPs) and trace metals (TMs) was never evaluated. To provide a basis for their monitoring in the ANP, five species (two fish, two mollusks, and one crustacean) were analyzed from three sampling sites in 2017. Contamination levels for POPs and TMs were below maximum acceptable limits for seafood, including Cd and Pb. No DDT was found in any sample. Inter-specific differences were more obvious than the differences among sites, although the results may be biased by an unbalanced sampling design. The oyster *Crassostrea gasar* was the most contaminated species, making this species a good candidate to assess environmental contamination in the area. The studied species also contained essential elements, such as Fe, Zn and Mn at interesting levels in a nutritional point of view.

Key words

Contaminants, Fish, Mangrove, Marine protected area, Mollusks

Highlights

- Levels of studied contaminants in organisms from Akanda national park are low
- Interspecific differences in contamination were stronger than inter sites differences
- Crassostrea gasar was the most contaminated species and could serve as a sentinel
- A monitoring program including more contaminants must be developed in the region

Akanda National Park (ANP), Gabon, covering an area of about 540 km² of which 46% is sea water (Aldous et al., 2021), extends northeast and east of the capital Libreville (ca. 1 million inhabitants in 2023). Most of the ANP is composed of mangrove forests of Avicennia nitida, Rhizophora harrisonii and Rhizophora racemosa (Lebigre, 1990), mudflats, seagrass beds, and underwater bedrock. ANP was created in 2002 and is a classified Ramsar wetland site since 2007 due to its importance for migratory shorebirds and marine turtles. In the context of ANP biodiversity protection regulations (e.g. restrictions on the harvesting and gathering of certain natural resources; Yobo and Ito, 2016), autochthonous communities are allowed to fish in the area and consume fish products (Gabonese people consume more than 30 kg of fish per year per person; FAO, 2022). However, the proximity to the capital city with a growing population and the important extractive industries of Gabon, such as offshore oil exploitation, manganese and gold mining, exposes the ANP to increasing anthropic pressures. Some of these pressures were recently documented at the microbiological level (Leboulanger et al., 2021) and there are no studies reported on the contamination of aquatic resources by persistent organic pollutants (POPs) and trace metals (TMs). These pollutants generally enter mangroves from urban and agricultural runoff, industrial effluents, navigation and recreational use of water bodies, chemical discharges, domestic sewage, landfill leaching and mining activities (Peters et al., 1997). As a result, pollution levels vary considerably from one mangrove ecosystem to another (Kulkarni et al., 2018; Zhang et al., 2014). POPs are compounds of anthropogenic origin that are persistent, bioaccumulative and toxic, and can travel far from emission sources. Regulated POPs are those included in the United Nations Stockholm Convention, which aims to protect human health and the environment from their effects. They include among others polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) such as dichlorodiphenyl-trichloroethane and its metabolites (DDTs) or hexachlorocyclohexanes (HCHs), and brominated flame retardants such as polybrominated diphenyl ethers (PBDEs). TMs are natural inorganic elements released into all environmental compartments by natural sources such as volcanism and by the aforementioned anthropogenic activities. Some TMs such as Cu, Mn and Zn are essentials for the proper functioning of organisms at a certain concentration, and become deficient or toxic at too low or too high concentrations. Others elements such as Cd, Pb and Hg are toxic for organisms at any concentration (Mason, 2013). Long-term exposure to POPs or TMs results in adverse health effects in organisms, including wildlife and humans (e.g. Dietz et al., 2019; Krönke et al., 2022; Vonderheide et al., 2008).

Studies in West and Central African countries have reported mixed results regarding mangrove contamination. Mangrove sediments of Cameroon contained polycyclic aromatic hydrocarbon, PCBs and OCPs including DDT and metabolites (Mbusnum et al., 2020). Mangrove water from an asphyxiated swamp of Nigeria also contained high levels of Zn, Ni and Pb (Essien et al., 2009). Levels of DDTs and HCHs above 10 ng/g were found in clams and crabs from a Nigerian's mangrove estuary (Oyo-Ita et al., 2014). In contrast, mollusks from Senegal's mangrove revealed low levels of OCPs, PCBs, PBDEs and TMs below the maximum permissible concentrations established for food contaminants to protect human health, except for Cd (Bodin et al., 2013, 2011; Sidoumou et al., 2006). Although in general trace organic and metal contamination was low, these mollusks were consistently 2-3 times more contaminated with POPs (particularly PCBs congeners CB-153, CB-138 and CB-18) at the end of the rainy season, due to higher accumulation of lipids during the pre-reproductive period and to leaching of pesticide residues from inland to the marine ecosystem (Bodin et al., 2011; Otchere, 2005). Several factors other than habitat or season are sources of variability in the contamination of biota. In particular trophic level, generally estimated though nitrogen isotopic compositions, is related to biomagnified compounds such as CB-153 and organic Hg (Bayen et al., 2005; Harmelin-Vivien et al., 2012; Souza et al., 2021), lipid content is associated with PCBs and OCPs (Bodin et al., 2014; Jørgensen et al., 1997), and age and metabolization capacities of the organisms determine the assimilation efficiency and elimination rate of many such contaminants (Gray, 2002; Le Croizier et al., 2018; Sussarellu et al., 2022).

The current status of contamination of marine biota from the ANP was never evaluated. The purpose of this study was therefore (i) to determine its levels of contamination for representative organisms with different feeding habits and positions in the food web, and (ii) to provide a basis for monitoring future trends in POPs and TMs contamination in the area. For this, POPs and TMs analyses of five species from three sites of the ANP were compared and complemented by analyses of carbon and nitrogen isotopic compositions and elemental ratio (δ^{13} C and δ^{15} N values, C:N ratio) to help interpreting the contamination data.

The following methodology was put in place to meet these objectives. To cover a representative area of the ANP, organisms were collected at three sites: (1) Babylone, a locality in the Ntisini channel 8 km upstream from Libreville, (2) Bambouchine, a fishing settlement located at the bottom of Mondah Bay at 10 km east of Libreville, and (3) Moka, an undisturbed site at 20 km north of Libreville and the closest to the ocean (Fig. 1). Sea surface temperature is globally higher and less variable at Babylone (circa 30°C) than at the two other sites (26.5°C and 27.5°C) and oxygen percent and salinity are similar at the three sites (Mve Beh et al., 2023). In order to be as conservative as possible in terms of contamination, organisms were collected at the end of the major rainy season, between May 17th and 22nd, 2017. Five species with different feeding modes and ecologies were considered: the oyster Crassostrea gasar (filter-feeder), the gastropod Pugilina morio (scavenger), the estuarine fishes Pseudotolithus elongatus and Ilisha africana (ichthyophagous and planktivorous species, respectively), and the crab Callinectes pallidus (opportunistic benthic predator). Organisms were collected by hand or bought from artisanal anglers a few hours after capture for fish, then determined using identification keys (Carpenter and De Angelis, 2002; FAO, 2016; Stiassny et al., 2007). After size measurement and tissue sampling (dorsal white muscle for fish, whole flesh for the other species), samples were freeze-dried for 72 h and homogenized with a ball grinder. For fish, the quantity of powder obtained allowed the analysis of TMs and POPs on the same individual. For the other species, composite samples of two to six individuals were made for one or the other analysis (Table 1).

Bulk compositions in carbon and nitrogen stable isotopes (δ^{13} C and δ^{15} N) and elemental ratio C:N (i.e. proxy for carbon storage in the form of lipids or glycogen) were analyzed on a Flash EA2000 coupled to

a Delta V Plus IRMS at the PSO, University of Brest, France. Analytical variability was $\pm 0.15\%$ for both δ^{13} C and δ^{15} N values. C:N ratio was determined from % element weight (**Table 1**).



Fig. 1. Location of the three sampling sites (Bambouchine, Babylone and Moka) for organisms of the Akanda National Park, Gabon. Green areas are under national park protection status, with buffer zone delimited by dashed green line. Marine protected areas are delimited by solid (core reserve) and dashed (buffer) blue lines. The current extent of Libreville agglomeration corresponds to the grey area.

Table 1. Sampling design for organisms of the Akanda national park, Gabon, analyzed for POPs and TMs,and bulk nitrogen and carbon isotopic values and C:N elemental ratio (median \pm interquartile range) atthe end of the major rainy season. N = number of pools and n = number of individuals per pool.

Species	Site	N (n) for N (n) for		Size	δ ¹⁵ N (‰)) δ ¹³ C(‰)	C:N
		POPs	TMs	(mm)		(_
Callinectes pallidus	Bambouchine	3 (1)	0	48–58	8.7 ± 1.0	-18.4 ± 1.5	3.3 ± 0.2
Crassostrea gasar	Babylone	1(3)	1(2)	46-61	9.4 ± 0.1	-31.6 ± 0.3	4.1 ± 0.1
	Bambouchine	1(3)	1(2)	45–55	9.2 ± 0.0	-30.1 ± 0.6	4.3 ± 0.3
	Moka	1(6)	3 (2)	60–80	7.5 ± 0.4	-23.2 ± 0.4	4.1 ± 0.1
Ilisha africana	Moka	6(1)	6(1)	195–215	11.3 ± 0.2	-21.7±0.6	3.2 ± 0.0
Pseudotolithus elongatus	Bambouchine	6(1)	6(1)	225-255	11.2 ± 0.5	-20.4 ± 1.5	3.2 ± 0.0
	Moka	3 (1)	3 (1)	314-365	10.1 ± 0.3	-22.0 ± 0.9	3.2 ± 0.0
Pugilina morio	Babylone	5 (1)	5 (1)	78–92	11.7 ± 0.5	-23.2 ± 0.7	3.5 ± 0.2

Persistent organic pollutants were analyzed according to the protocol of Tapie et al. (2008). Briefly, dried samples (0.5-3 g; n=23) spiked with internal standards (CB-30, CB-103, CB-155 and CB-198) were extracted using dichloromethane within a microwave-assisted extraction. The extract was filtered, concentrated and purified on a column of acidic silica gel column with activated copper, eluted with a pentane-dichloromethane mixture, then concentrated and transferred to isooctane, and spiked with an internal standard of octachloronaphthalene. Certified reference materials SRM-2977 and WM-F01 were analyzed together with samples. POPs analyses were performed on an HP 5890 series II GC coupled to a ⁶³Ni ECD, with a HP5-MS capillary column (60 m \times 0.25 mm \times 0.25 μ m) at the EPOC lab facility (Bodin et al., 2011; Tapie et al., 2008). Twenty-three POPs were analyzed (see the list below), of which 13 were below the limits of quantification (LOQ, based on a signal to noise ratio of 9) for all samples: BDE-28, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183, HCB, yHCH and p,p'-DDT (each LOQ = 0.2 ng/g), CB-28, o,p'-DDD and o,p'-DDT (each LOQ = 0.3 ng/g) and Mirex (LOQ = 1.4 ng/g). The 10 others (considered hereafter) were: BDE-47 (LOQ = 0.2 ng/g), CB-52 (LOQ = 1.4 ng/g), CB-101 (LOQ = 1.6 ng/g), CB-118 (LOQ = 1.0 ng/g), CB-153 (LOQ = 0.8 ng/g), CB-138 (LOQ = 1.2 ng), CB-180 (LOQ = 1.7 ng/g), p,p'-DDE (LOQ = 0.2 ng/g), o,p'-DDE and p,p'-DDD (both LOQ = 0.3 ng/g). All POPs concentrations were expressed in ng/g on a dry weight basis.

Trace metals were analyzed according to Idardare et al. (2008). Dried samples (~200 mg; n=28; no crab as the amount of material available was insufficient) were digested with a mixture of hydrochloric and nitric acids on a heating block following the procedure of, and re-diluted with milli-Q water when necessary before analyses. Ten TMs (As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were analyzed on an iCAP Q ICP-MS at the AETE-ISO platform, OSU-OREME/Université de Montpellier, France. Analytical performance was checked using the certified reference materials from the National Research Council of Canada SLRS6 and DORM2, which displayed mean element recoveries ranging from 98% to 135% and 82% to 120%, respectively. TMs concentrations were expressed in µg/g and ng/g on a dry weight basis.

Regarding statistical comparisons, log transformed concentrations of POPs and TMs were compared among sites and among species with no interaction due to the unbalanced sampling design. Parametric tests ANOVA or ANOVA for censored data, i.e. when some values were <LOQ (Helsel, 2006) were used when the normality of residuals was reached (Shapiro test > 0.05). Otherwise, nonparametric Kruskall-Wallis and post hoc Dunn tests, or Peto-Peto test with adjusted p-value for multiple comparisons for censored data (Helsel, 2006) were used. Data analyses were carried out with R software 3.5.0 (R Core Team, 2016) and *NADA2* package (Julian and Helsel, 2021). As most concentration data were not normally distributed, they were presented as median ± interquartile range (IQR, i.e. the difference between the 75th and 25th percentiles of the data). Where specified, these were Kaplan-Meier estimates of the median and the interquartile range for censored data (Helsel, 2006). The most frequently detected POPs were p-p'DDE (quantifiable in 96% of samples except one P. elongatus from Moka), CB-153 (quantifiable in 92% of samples except two P. elongatus from Moka and Bambouchine) and CB-138 (quantifiable in 65% of samples). PCBs congeners were higher than DDTs congeners in all samples, and CB-153 accounted for 17.4 to 89.2 % of all POPs in *P. morio* and *I. africana*, respectively. Regarding species, C. gasar had the most diverse POPs profile (eight POPs in more than two samples) and was the most contaminated species on average: Σ PCBs was higher in *C. gasar* $(19.5\pm3.2 \text{ ng/g})$ and lower in *P. elongatus* $(3.1\pm6.4 \text{ ng/g})$ and *P. morio* $(2.0\pm2.1 \text{ ng/g})$ $(\chi^2 = 10.3, \text{ df}=4, \text{ p})$ < 0.05) (Fig. 2A). In particular, concentration of CB-153 in C. gasar (8.7±0.5 ng/g) was similar to C. pallidus (4.2±1.8 ng/g) (p=0.085) and higher than in I. africana (2.7±1.0 ng/g), P. elongatus (2.4±2.1 ng/g) and *P. morio* (2.0±0.9 ng/g) (all p < 0.05), with no clear relationship to the average values of δ^{15} N (Fig. 3). Similarly, Σ DDTs was higher in *C. gasar* (3.3±2.2 ng/g) and lower in *P. morio* (0.3±0.0 ng/g) (χ^2 =11.8, df=4, p < 0.05). The same ranking as for CB-153 was observed for p-p'DDE. Regarding sites, Bambouchine had the most diverse profile (five POPs in more than two samples), no CB-118 was detected at Moka and no CB-180 was detected at Babylone. No difference in SPCBs and SDDTs concentrations was detected among the three sites (χ^2 = 0.16, df=2, p = 0.926 and χ^2 = 2.01, df=2, p = 0.366, respectively) (Fig. 2B). Regarding less frequently detected POPs, only one individual of P. morio from Babylone contained quantifiable levels of CB-52 (3.0 ng/g) and CB-101 (3.9 ng/g) and two C. gasar from Babylone and Bambouchine contained quantifiable levels of BDE-47 (both 0.6 ng/g).



Fig. 2. Persistent organic pollutants concentrations (median values) in ng/g dry weight for (A) five selected marine species and (B) three sampling sites from the Akanda National Park, Gabon, at the end of the major rainy season. Where specified, compounds were > LOQ in only one sample (n=1). c = censored data with at least one value < LOQ.



Fig. 3. Biplot of medians and interquartile ranges for δ^{15} N values and (A) CB-153 concentrations and (B) p,p'DDE concentrations for five species collected from the Akanda national park, Gabon. Species, from

top to bottom: *Pugilina morio, Ilisha africana, Pseudotolithus elongatus, Crassostrea gasar* and *Callinectes pallidus.* Images from Wikipedia, Ondřej Radosta and Dioniso de Souza Sampaio.

The 10 studied TMs could be quantified in all samples, except Cd for three samples and Pb for one sample. Zn was the most abundant, followed by Fe and Cu, and Cd the least abundant TM (**Fig. 4**). Regarding species, mollusks *C. gasar* and *P. morio* contained globally more TMs than the two fish species, with *C. gasar* containing the highest levels in all TMs except for As (highest in *P. morio* with 11.7±17.7 µg/g) (**Fig. 4A**). In particular, the levels of Cd and Pb in *C. gasar* (720±623 and 311±79 ng/g, respectively) were significantly higher than that in *P. morio* (34±8 and 146±96 ng/g), followed by that in *I. africana* (2±0 and 26±18 ng/g) and *P. elongatus* (<1 and 11±10 ng/g) (χ^2 = 44.8, df=4, p < 0.001 and χ^2 = 43.7, df=4, p < 0.001). Regarding sites, Cd was found in similar levels at the three sites (χ^2 = 5.3, df=2, p = 0.07) while Pb was higher at Babylone (171±101 ng/g) than at the two other sites (26±83 and 17±7 ng/g) (χ^2 = 8.8, df=2, p < 0.05) (**Fig. 4B**).



Fig4. Trace metals concentrations (median and IRQ) in μ g/g dry weight for (A) four selected marine species and (B) three sampling sites from the Akanda National Park, Gabon, at the end of the major rainy season. Elements in red are toxic for organisms at any concentration. c = censored data with at least one value < LOQ.

To initiate a monitoring of POPs and TMs contamination in Akanda National Park, Gabon, five species (two fish, two mollusks, and one crustacean) were analyzed at three sites in 2017. Contamination levels of both POPs and TMs were low for all species. Industrial POPs (PCBs, PBDEs) were higher than pesticide POPs (DDTs) in all samples. Inter-specific differences were more obvious than the differences among sites, the oyster being the most contaminated species.

The oyster C. gasar occupied the lowest trophic position and was the most contaminated species in both POPs and TMs, suggesting that the studied contaminants are mainly associated with suspended organic matter (which only oyster of the 5 studied species feed on). PCB levels of C. gasar from the ANP were roughly equivalent to those measured in the Sine-Saloum mangrove swamp (Senegal) during the wet season (e.g. CB-153 concentration of 3.2-10.5 vs 8.7±0.5 ng/g here) (Bodin et al., 2011). C. gasar was overall more contaminated by PCBs than P. morio while the opposite trend was highlighted in Senegal (e.g. CB-153 concentration in Senegal of 3.5–10.5 and 13.7–31.9 ng/g for C. gasar and P. morio, respectively ; Bodin et al., 2011), which could be explained by a higher PCB contamination of the suspended matter on which C. gasar feeds in Gabon than in Senegal or, more likely, by differences in lipid content of organisms among regions. Indeed, based on bulk C:N and Post et al. (2007) equation, the average % lipids in C. gasar and P. morio in our study were 9.9% and 4.8% respectively, while in Senegal they were 9.3% and 11.5% (Bodin et al., 2011). C. gasar from the ANP was about 10 times less contaminated by Cd and with similar levels in Pb than in Senegal (Bodin et al., 2013; Sidoumou et al., 2006; Table S1) and 5 times less contaminated by Cd than in a costal lagoon of lvory coast (Tuo et al., 2020; Table S1), where these contaminations seem to be mainly related to domestic and industrial discharges (Diop et al., 2015; Tuo et al., 2020). For other elements, C. gasar showed concentrations equivalent to neighboring countries (Table S1) and to other mangrove regions (which are highly variable). Zinc levels, for example, are quite variable, being highest at the Bambouchine site (8805 μ g/g dw): this is high compared with levels in bivalves from the Zhanjiang mangrove, China (< 75 µg/g dw; Zheng et al., 2023) but similar to levels in oysters from the Cleverland mangrove, Australia (8253 μ g/g dw; Jones et al., 2000) or those from the Sine-Saloum mangrove estuary, Senegal (up to 2100 μ g/g dw, Bodin et al., 2013).

The fish species *P. elongatus* and *I. africana* were also very low in contamination, despite their relatively high trophic level (between 3 and 4; Fishbase). In other Gulf of Guinea countries, similar observations of low contamination were obtained for per- and polyfluoroalkyl substances in *P. elongatus* (Ekperusi et al., 2023) and for As, Cd and Pb in *I. africana* (Eboh et al., 2006), suggesting that for the time being these fish species may have little exposure to the various contaminants in this region (but see Pb of *I. africana* in Douala, Cameroon; Table S1). No DDT was found in any sample, whatever the species or the sampling site. Considering a half-life of 8 months for *p*,*p*'-DDT in fish (Binelli and Provini, 2003), this suggested no recent inputs of DDT from agricultural or sanitary regulation measures (e.g. Malaria prevention) and that the ANP was more exposed to industrial organochlorinated than to agricultural contaminants in 2017. However, the presence of *p*,*p*'-DDE (half-life of about 7 years in fish; Binelli and Provini, 2003) in almost all samples implied ancient uses of DDT near the ANP.

Overall, all the studied contaminants were below the maximum permitted levels set by world regulatory agencies for seafood (compiled by De Witte et al., 2022). Thus, expressing obtained values in wet weight (ww) by assuming a water content of 80%, the maximum measured level of ΣPCBs was 4.2 ppb ww for oyster, when the maximum limit is 2000 ppb ww for seafood in USA (US Food and Drugs Administration, 2022) and Russia (Russia Customs Union, 2011). The maximum observed levels of Cd were 0.21 and <0.001 ppm ww for oyster and fishes, when the maximum limits are 1 ppm ww for bivalves in EU (European Commission Regulation, 2006) and 0.05 and 0.2 ppm ww for fish in EU and Russia (European Commission Regulation, 2006; Russia Customs Union, 2011). The maximum limits are 1.5 ppm ww for bivalves in EU (European Commission Regulation, 2015) and 0.3 ppm ww for fish in EU and for FAO (Codex Alimentarius, 1995; European Commission Regulation, 2015). On the other hand, the two fish species under study have high commercial value and contain some essential elements, such as Fe, Zn and Mn, although at lower levels than mollusks. They are also high in omega-3 fatty acids, especially *l. africana*

https://doi.org/10.1016/j.marpolbul.2023.116009

(Eboh et al., 2006; Njinkoue et al., 2016). In the current state of toxicological knowledge and from a nutritional point of view, their consumption by autochthonous populations allowed to fish in the ANP could be recommended.

Monitoring of environmental contamination in the ANP can be based on *C. gasar* since it concentrates POPs and TMs better than the other organisms from the present study. Sessile filter feeders are commonly used to monitor contamination of the marine environment (e.g. Aguirre-Rubí et al., 2018; Aminot et al., 2021; Santos et al., 2020) and in particular through the International Mussel Watch program (Farrington et al., 2016), partly because of their low capacity to metabolize contaminants. At the same time, the main species exploited for human consumption must also be monitored, especially fish, as results obtained on *C. gasar* cannot be extrapolated to other species.

Furthermore, no site was more contaminated than the others, excepted for Pb and POPs diversity which were slightly higher at Babylone, located downstream from Libreville, but this result could reflect a bias in the sampling design since only mollusks were caught at this site. Monitoring of biota contamination should therefore include a more robust sampling design than the one implemented in this study, allowing in particular to test the interactions between sites and species on contamination levels and seasonal variations in contaminations and therefore make stronger consumption recommendations. Difference in analyzed tissues (muscle for fish, whole body for the other species) as well as lipid content and lipid composition could also induce a bias in contaminant data (Elskus et al., 2005; Gray, 2002). Using similar tissues across trophic levels and expressing the POP contents in g of lipids may well help to reduce variabilities in contaminant data within organisms (although from a human consumption perspective, contents in g of fresh weight might be more appropriate).

Finally, although all the studied contaminants were found in low concentrations, the toxicological assessment was incomplete and these results should be taken with caution. For example, the content in emerging organic contaminants and Hg had not been evaluated, nor has the speciation of metals (proportion methylmercury, the most toxic forms of Hg). Hg in particular could contaminate the area

15

due to gold panning in Gabon and needs to be rapidly assessed. Indeed, although artisanal gold production is relatively small in Gabon, in Africa it uses proportionally more Hg than in other parts of the world (Seccatore et al., 2014). In addition, it would be interesting to monitor other micronutrients (e.g. omega-3 fatty acids, vitamins and selenium) in the marine resources consumed by local populations, in order to assess the benefit-risk balance for the consumption of these species in the ANP, and to monitor the abiotic compartments (water and sediment in particular) to identify the exposure sources of the marine organisms.

To conclude, the ANP's marine resources appeared fairly low in contamination in 2017 and they did not present any toxicity risk for human consumption associated with the studied contaminants. This seemingly low contamination must be moderated, however, because analyzing Hg and the emerging POPs could draw a different pattern of seafood contamination in the area. As environmental contamination also increases with anthropization, and considering the frantic pace of coastal urban extension, it is necessary to set up a monitoring of these contaminations possibly using oysters as sentinels.

Acknowledgments

We would like to thank the Gabonese Agence Nationale des Parcs Nationaux (ANPN), Gabon and the French Agence Française de Développement (AFD), France who funded this study under the "Arc d'Emeraude" project. We also thank the technicians of the LHI/IRAF/CENAREST laboratory who participated in the sampling campaigns and Rémi Freydier and Sophie Delpoux from the AETE-ISO platform for trace metals analysis. Finally, thanks to two anonymous reviewers for their comments and the editor for improving the quality of the final manuscript.

Data Availability

The data for this study are available on the repository DataSuds: <u>https://doi.org/10.23708/80UARI</u>.

References

- Aguirre-Rubí, J., Luna-Acosta, A., Ortiz-Zarragoitia, M., Zaldibar, B., Izagirre, U., Ahrens, M.J., Villamil, L., Marigómez, I., 2018. Assessment of ecosystem health disturbance in mangrove-lined Caribbean coastal systems using the oyster *Crassostrea rhizophorae* as sentinel species.
 Science of The Total Environment 618, 718–735. https://doi.org/10.1016/j.scitotenv.2017.08.098
- Aldous, A., Schill, S., Raber, G., Paiz, M.-C., Mambela, E., Stévart, T., 2021. Mapping complex coastal wetland mosaics in Gabon for informed ecosystem management: use of object-based classification. Remote Sensing in Ecology and Conservation 7, 64–79. https://doi.org/10.1002/rse2.161
- Aminot, Y., Munschy, C., Héas-Moisan, K., Pollono, C., Tixier, C., 2021. Levels and trends of synthetic musks in marine bivalves from French coastal areas. Chemosphere 268, 129312. https://doi.org/10.1016/j.chemosphere.2020.129312
- Bayen, S., Wurl, O., Karuppiah, S., Sivasothi, N., Lee, H.K., Obbard, J.P., 2005. Persistent organic pollutants in mangrove food webs in Singapore. Chemosphere 61, 303–313. https://doi.org/10.1016/j.chemosphere.2005.02.097
- Binelli, A., Provini, A., 2003. DDT is still a problem in developed countries: the heavy pollution of Lake Maggiore. Chemosphere 52, 717–723. https://doi.org/10.1016/S0045-6535(03)00188-7
- Bodin, N., N'Gom Ka, R., Le Loc'h, F., Raffray, J., Budzinski, H., Peluhet, L., Tito de Morais, L., 2011.
 Are exploited mangrove molluscs exposed to Persistent Organic Pollutant contamination in Senegal, West Africa? Chemosphere 84, 318–327.
 https://doi.org/10.1016/J.CHEMOSPHERE.2011.04.012
- Bodin, N., N'Gom-Kâ, R., Kâ, S., Thiaw, O.T., Tito de Morais, L., Le Loc'h, F., Rozuel-Chartier, E., Auger, D., Chiffoleau, J.-F., 2013. Assessment of trace metal contamination in mangrove ecosystems from Senegal, West Africa. Chemosphere 90, 150–157. https://doi.org/10.1016/J.CHEMOSPHERE.2012.06.019
- Bodin, N., Tapie, N., Le Ménach, K., Chassot, E., Elie, P., Rochard, E., Budzinski, H., 2014. PCB contamination in fish community from the Gironde Estuary (France): Blast from the past. Chemosphere 98, 66–72. https://doi.org/10.1016/j.chemosphere.2013.10.003
- Carpenter, K.E., De Angelis, N., 2002. The living marine resources of the Western Central Atlantic. Food and agriculture organization of the United Nations Rome.
- Codex Alimentarius, 1995. Codex general standard for contaminants and toxins in food and feed, Adopted 1995; Revised 1997, 2006, 2008, 2009; Amended 2009, 2010. Rome: FAO/WHO.
- De Witte, B., Coleman, B., Bekaert, K., Boitsov, S., Botelho, M.J., Castro-Jiménez, J., Duffy, C., Habedank, F., McGovern, E., Parmentier, K., Tornero, V., Viñas, L., Turner, A.D., 2022. Threshold values on environmental chemical contaminants in seafood in the European Economic Area. Food Control 138, 108978. https://doi.org/10.1016/j.foodcont.2022.108978
- Dietz, R., Letcher, R.J., Desforges, J.-P., Eulaers, I., Sonne, C., Wilson, S., Andersen-Ranberg, E., Basu, N., Barst, B.D., Bustnes, J.O., Bytingsvik, J., Ciesielski, T.M., Drevnick, P.E., Gabrielsen, G.W., Haarr, A., Hylland, K., Jenssen, B.M., Levin, M., McKinney, M.A., Nørregaard, R.D., Pedersen, K.E., Provencher, J., Styrishave, B., Tartu, S., Aars, J., Ackerman, J.T., Rosing-Asvid, A., Barrett, R., Bignert, A., Born, E.W., Branigan, M., Braune, B., Bryan, C.E., Dam, M., Eagles-Smith, C.A., Evans, M., Evans, T.J., Fisk, A.T., Gamberg, M., Gustavson, K., Hartman, C.A., Helander, B., Herzog, M.P., Hoekstra, P.F., Houde, M., Hoydal, K., Jackson, A.K., Kucklick, J., Lie, E., Loseto, L., Mallory, M.L., Miljeteig, C., Mosbech, A., Muir, D.C.G., Nielsen, S.T., Peacock, E., Pedro, S.,

Peterson, S.H., Polder, A., Rigét, F.F., Roach, P., Saunes, H., Sinding, M.-H.S., Skaare, J.U., Søndergaard, J., Stenson, G., Stern, G., Treu, G., Schuur, S.S., Víkingsson, G., 2019. Current state of knowledge on biological effects from contaminants on arctic wildlife and fish. Science of The Total Environment 696, 133792. https://doi.org/10.1016/j.scitotenv.2019.133792

- Diop, C., Dewaelé, D., Cazier, F., Diouf, A., Ouddane, B., 2015. Assessment of trace metals contamination level, bioavailability and toxicity in sediments from Dakar coast and Saint Louis estuary in Senegal, West Africa. Chemosphere 138, 980–987. https://doi.org/10.1016/J.CHEMOSPHERE.2014.12.041
- Eboh, L., Mepba, H.D., Ekpo, M.B., 2006. Heavy metal contaminants and processing effects on the composition, storage stability and fatty acid profiles of five common commercially available fish species in Oron Local Government, Nigeria. Food Chemistry 97, 490–497. https://doi.org/10.1016/j.foodchem.2005.05.041
- Ekperusi, A.O., Bely, N., Pollono, C., Mahé, K., Munschy, C., Aminot, Y., 2023. Prevalence of per- and polyfluoroalkyl substances (PFASs) in marine seafood from the Gulf of Guinea. Chemosphere 335, 139110. https://doi.org/10.1016/j.chemosphere.2023.139110
- Elskus, A.A., Collier, T.K., Monosson, E., 2005. Chapter 4 Interactions between lipids and persistent organic pollutants in fish, in: Mommsen, T.P., Moon, T.W. (Eds.), Biochemistry and Molecular Biology of Fishes, Environmental Toxicology. Elsevier, pp. 119–152. https://doi.org/10.1016/S1873-0140(05)80007-4
- Essien, J.P., Essien, V., Olajire, A.A., 2009. Heavy metal burdens in patches of asphyxiated swamp areas within the Qua Iboe estuary mangrove ecosystem. Environmental Research 109, 690– 696. https://doi.org/10.1016/j.envres.2009.04.005
- European Commission Regulation, 2015. Commission Regulation (EU) 2015/ 1005 of 25 June 2015 amending Regulation (EC) No 1881/ 2006 as regards maximum levels of lead in certain foodstuffs.
- European Commission Regulation, 2006. Commission Regulation (EC) 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs. Official Journal of the European Union. L364/ 5. [WWW Document]. URL https://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2006:364:0005:0024:EN:PDF (accessed 9.4.23).
- FAO, 2022. The State of World Fisheries and Aquaculture 2022: Towards Blue Transformation, The State of World Fisheries and Aquaculture (SOFIA). FAO, Rome, Italy. https://doi.org/10.4060/cc0461en
- FAO, 2016. The living marine resources of the Eastern Central Atlantic. Volume 4: Bony fishes part 2 (Perciformes), FAO Species Identification Guide for Fishery Purposes. FAO, Rome, Italy.
- Farrington, J.W., Tripp, B.W., Tanabe, S., Subramanian, A., Sericano, J.L., Wade, T.L., Knap, A.H., 2016. Edward D. Goldberg's proposal of "the Mussel Watch": Reflections after 40years. Marine Pollution Bulletin 110, 501–510. https://doi.org/10.1016/j.marpolbul.2016.05.074
- Gray, J.S., 2002. Biomagnification in marine systems: the perspective of an ecologist. Marine Pollution Bulletin 45, 46–52. https://doi.org/10.1016/S0025-326X(01)00323-X
- Harmelin-Vivien, M., Bodiguel, X., Charmasson, S., Loizeau, V., Mellon-Duval, C., Tronczyński, J.,
 Cossa, D., 2012. Differential biomagnification of PCB, PBDE, Hg and Radiocesium in the food web of the European hake from the NW Mediterranean. Marine Pollution Bulletin 64, 974–983. https://doi.org/10.1016/j.marpolbul.2012.02.014
- Helsel, D.R., 2006. Fabricating data: How substituting values for nondetects can ruin results, and what can be done about it. Chemosphere 65, 2434–2439. https://doi.org/10.1016/j.chemosphere.2006.04.051
- Jones, G.B., Mercurio, P., Olivier, F., 2000. Zinc in Fish, Crabs, Oysters, and Mangrove Flora and Fauna from Cleveland Bay. Marine Pollution Bulletin, Sources, Fates and Consequences of

Pollutants in the Great Barrier Reef 41, 345–352. https://doi.org/10.1016/S0025-326X(00)00132-6

Jørgensen, E.H., Burkow, I.C., Foshaug, H., Killie, B., Ingebrigtsen, K., 1997. Influence of lipid status on tissue distribution of the persistent organic pollutant octachlorostyrene in Arctic charr (*Salvelinus alpinus*). Comparative Biochemistry and Physiology Part C: Pharmacology, Toxicology and Endocrinology 118, 311–318. https://doi.org/10.1016/S0742-8413(97)00160-6

Julian, P., Helsel, D.R., 2021. NADA2: Data Analysis for Censored Environmental Data.

- Krönke, A.A., Jurkutat, A., Schlingmann, M., Poulain, T., Nüchter, M., Hilbert, A., Kiviranta, H., Körner, A., Vogel, M., Söder, O., Bornehag, C.G., Kiess, W., 2022. Persistent organic pollutants in pregnant women potentially affect child development and thyroid hormone status. Pediatr Res 91, 690–698. https://doi.org/10.1038/s41390-021-01488-5
- Kulkarni, R., Deobagkar, D., Zinjarde, S., 2018. Metals in mangrove ecosystems and associated biota: A global perspective. Ecotoxicology and Environmental Safety 153, 215–228. https://doi.org/10.1016/j.ecoenv.2018.02.021
- Le Croizier, G., Lacroix, C., Artigaud, S., Le Floch, S., Raffray, J., Penicaud, V., Coquillé, V., Autier, J., Rouget, M.-L., Le Bayon, N., Laë, R., Tito De Morais, L., 2018. Significance of metallothioneins in differential cadmium accumulation kinetics between two marine fish species. Environmental Pollution 236, 462–476. https://doi.org/10.1016/j.envpol.2018.01.002
- Lebigre, J.-M., 1990. Les marais maritimes du Gabon et de Madagascar : contribution géographique à l'étude d'un milieu naturel tropical (These de doctorat). Bordeaux 3.
- Leboulanger, C., Kolanou Biluka, L., Nzigou, A.-R., Djuidje Kenmogne, V., Happi, J.L.M., Ngohang, F.E., Eleng, A.S., Ondo Zue Abaga, N., Bouvy, M., 2021. Urban inputs of fecal bacteria to the coastal zone of Libreville, Gabon, Central Western Africa. Marine Pollution Bulletin 168, 112478. https://doi.org/10.1016/j.marpolbul.2021.112478
- Mason, R.P., 2013. Trace metals in aquatic systems. John Wiley & Sons.
- Mbusnum, K.G., Malleret, L., Deschamps, P., Khabouchi, I., Asia, L., Lebarillier, S., Menot, G., Onguene, R., Doumenq, P., 2020. Persistent organic pollutants in sediments of the Wouri Estuary Mangrove, Cameroon: Levels, patterns and ecotoxicological significance. Marine Pollution Bulletin 160, 111542. https://doi.org/10.1016/j.marpolbul.2020.111542
- Mve Beh, J.H., Sadio, O., Mbega, J.D., Tchinga, G., Tsinga, F., Leboulanger, C., Ben Rais Lasram, F., Tito de Morais, L., Le Loc'h, F., 2023. Spatial and temporal structure of the fish assemblage in Akanda National Park (Gabon), an equatorial mangrove estuary. Regional Studies in Marine Science 59, 102805. https://doi.org/10.1016/j.rsma.2022.102805
- Njinkoue, J.M., Gouado, I., Tchoumbougnang, F., Ngueguim, J.H.Y., Ndinteh, D.T., Fomogne-Fodjo, C.Y., Schweigert, F.J., 2016. Proximate composition, mineral content and fatty acid profile of two marine fishes from Cameroonian coast: *Pseudotolithus typus* (Bleeker, 1863) and *Pseudotolithus elongatus* (Bowdich, 1825). NFS Journal 4, 27–31. https://doi.org/10.1016/J.NFS.2016.07.002
- Otchere, F.A., 2005. Organochlorines (PCBs and pesticides) in the bivalves *Anadara (Senilia) senilis*, *Perna perna* and *Crassostrea tulipa* from the lagoons of Ghana. Science of The Total Environment 348, 102–114. https://doi.org/10.1016/J.SCITOTENV.2004.12.069
- Oyo-Ita, O.E., Ekpo, B.O., Adie, P.A., Offem, J.O., 2014. Organochlorine pesticides in sedimentdwelling animals from mangrove areas of the Calabar river, SE Nigeria. EP 3, p56. https://doi.org/10.5539/ep.v3n3p56
- Peters, E.C., Gassman, N.J., Firman, J.C., Richmond, R.H., Power, E.A., 1997. Ecotoxicology of tropical marine ecosystems. Environmental Toxicology and Chemistry 16, 12–40. https://doi.org/10.1002/etc.5620160103
- Post, D.M., Layman, C.A., Arrington, D.A., Takimoto, G., Quattrochi, J., Montaña, C.G., 2007. Getting to the fat of the matter: models, methods and assumptions for dealing with lipids in stable isotope analyses. Oecologia 152, 179–189. https://doi.org/10.1007/s00442-006-0630-x

- Russia Customs Union, 2011. Technical Regulation of the Customs Union 021/2011 concerning safety of food products.
- Santos, L.L., Miranda, D., Hatje, V., Albergaria-Barbosa, A.C.R., Leonel, J., 2020. PCBs occurrence in marine bivalves and fish from Todos os Santos Bay, Bahia, Brazil. Marine Pollution Bulletin 154, 111070. https://doi.org/10.1016/j.marpolbul.2020.111070
- Seccatore, J., Veiga, M., Origliasso, C., Marin, T., De Tomi, G., 2014. An estimation of the artisanal small-scale production of gold in the world. Science of The Total Environment 496, 662–667. https://doi.org/10.1016/j.scitotenv.2014.05.003
- Sidoumou, Z., Gnassia-Barelli, M., Siau, Y., Morton, V., Roméo, M., 2006. Heavy metal concentrations in molluscs from the Senegal coast. Environment International 32, 384–387. https://doi.org/10.1016/j.envint.2005.09.001
- Souza, I.C., Morozesk, M., Azevedo, V.C., Mendes, V.A.S., Duarte, I.D., Rocha, L.D., Matsumoto, S.T., Elliott, M., Baroni, M.V., Wunderlin, D.A., Monferrán, M.V., Fernandes, M.N., 2021. Trophic transfer of emerging metallic contaminants in a neotropical mangrove ecosystem food web. Journal of Hazardous Materials 408, 124424. https://doi.org/10.1016/j.jhazmat.2020.124424
- Stiassny, M.L.J., Teugels, G.G., Hopkins, C.D., 2007. Fresh and brackish water fishes of Lower Guinea, West-Central Africa. IRD Editions.
- Sussarellu, R., Chouvelon, T., Aminot, Y., Couteau, J., Loppion, G., Dégremont, L., Lamy, J.-B., Akcha,
 F., Rouxel, J., Berthelin, C., Briaudeau, T., Izagirre, U., Mauffret, A., Grouhel, A., Burgeot, T.,
 2022. Differences in chemical contaminants bioaccumulation and ecotoxicology biomarkers
 in *Mytilus edulis* and *Mytilus galloprovincialis* and their hybrids. Environmental Pollution 292,
 118328. https://doi.org/10.1016/j.envpol.2021.118328
- Tapie, N., Budzinski, H., Le Ménach, K., 2008. Fast and efficient extraction methods for the analysis of polychlorinated biphenyls and polybrominated diphenyl ethers in biological matrices. Anal Bioanal Chem 391, 2169–2177. https://doi.org/10.1007/s00216-008-2148-z
- Tuo, A.D., Soro, M.B., Trokourey, A., Bokra, Y., 2020. Seasonal variation in trace metal contents in oyster *Crassostrea gasar* from the Milliardaires Bay, Côte d'Ivoire. Int. J. Chem. Stud. 8, 624– 630. https://doi.org/10.22271/chemi.2020.v8.i2j.8838
- US Food and Drugs Administration, 2022. Fish and Fishery Products Hazards and Controls Guidance.
- Vonderheide, A.P., Mueller, K.E., Meija, J., Welsh, G.L., 2008. Polybrominated diphenyl ethers: Causes for concern and knowledge gaps regarding environmental distribution, fate and toxicity. Science of The Total Environment 400, 425–436. https://doi.org/10.1016/j.scitotenv.2008.05.003
- Yobo, C.M., Ito, K., 2016. Evolution of policies and legal frameworks governing the management of forest and National Parks resources in Gabon. IJBC 8, 41–54. https://doi.org/10.5897/IJBC2015.0834
- Zhang, Z.-W., Xu, X.-R., Sun, Y.-X., Yu, S., Chen, Y.-S., Peng, J.-X., 2014. Heavy metal and organic contaminants in mangrove ecosystems of China: a review. Environ Sci Pollut Res 21, 11938–11950. https://doi.org/10.1007/s11356-014-3100-8
- Zheng, R., Liu, Y., Zhang, Z., 2023. Trophic transfer of heavy metals through aquatic food web in the
- largest mangrove reserve of China. Science of The Total Environment 899, 165655.

https://doi.org/10.1016/j.scitotenv.2023.165655