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Franciscana dolphins, *Pontoporia blainvillei*, as environmental sentinels of the world's largest mining disaster: Temporal trends for organohalogen compounds and their consequences for an endangered population☆

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ABSTRACT

On November 5th, 2015, the Fundão dam collapsed in Minas Gerais, southeastern Brazil, releasing millions of cubic meters of mud containing mining residue into the Doce River. Two weeks later, the mud arrived to the marine environment, triggering changes in franciscana dolphin habitat, *Pontoporia blainvillei*, from Franciscana Management Area Ia. This is an isolated population of the most endangered cetacean species in the South Atlantic Ocean. Organohalogen compounds (OHCs) may pose a threat to this endangered population because of their endocrine disrupting properties. Hence, this study sought to determine if there were differences in the bioaccumulation profile of OHC (PCBs, DDTs, Mirex, HCB, HCHs, PBDEs, PBEB, HBBZ and MeO-BDEs) in franciscana dolphins before and after dam collapse and to build a temporal trend. Blubber of 33 stranded individuals was collected in Espírito Santo state for organohalogen assessment between 2003 and 2019. Differences were found between franciscana dolphins collected prior to and after the disaster. Additionally, significant temporal trends for organochlorine pesticides and natural and anthropogenic organobromine were detected. The increase in pesticide concentrations after 2015 is suggestive of their reavailability in the environment. The decline in organobromine over time could be due to their debromination in the marine environment and alterations in the composition of their natural producers. PCBs remained stable during the period of the study. Our findings show an increase in endocrine disruptor concentrations, which is of great concern for this endangered population.

1. Introduction

Persistent organic pollutants (POPs) are ubiquitous contaminants presenting physical-chemical features that ensure their persistence in the marine environment and bioaccumulation in the marine biota (UNEP, 2017). POPs are lipophilic, easily transported through air and recalcitrant compounds that can undergo biomagnification on trophic webs and are found at elevated levels in apex predators, such as cetaceans (Gray, 2002). Organohalogen compounds (OHCs), e.g., organochlorine pesticides (OCPs), and those of industrial use, e.g.,

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polychlorinated biphenyls (PCBs) and brominated flame retardants (BFRs), are among the POPs of primary interest listed in the Stockholm Convention (UNEP, 2017). Their use was restricted worldwide when their toxic effects on the biota and bioaccumulation potential were described (Jepson and Law, 2016; UNEP, 2017). Since then, concentrations of POPs in distinct matrices have slowly started to decline, including OCPs in cetaceans from the Brazilian coast (Anttila et al., 2016; Kong et al., 2014; Leonel et al., 2010). However, these compounds can still be detected in elevated concentrations in odontocetes (Lailson-Brito et al., 2012). The accumulation profile of POPs in cetaceans and their temporal trends are driven, in general, by biological features of the species, such as sex and age (Reijnders et al., 2009), and environmental parameters that can influence their bioavailability (Borgå et al., 2004; Dachs et al., 1997; Lalah et al., 2009).

On November 5th, 2015, the Fundão mining dam collapsed in Mariana, Minas Gerais state (MG), in southeastern Brazil, releasing 55–62 million m^3 of iron ore tailings into the Doce River (Fernandes et al., 2016; Ferreira et al., 2020) and characterizing one of the world's largest environmental disasters in recent history. The mud ran through the Doce River basin and reached the sea on the coast of Espírito Santo state (ES) on November 22nd, 2015 (Fernandes et al., 2016). The mud, containing residues from mining activities, and rich in iron and manganese, altered the elemental dynamics in the riverine, estuarine, and coastal areas influenced by the Doce River (Gabriel et al., 2020; Hatje et al., 2017; Longhini et al., 2020; Schettini and Hatje, 2020).

The increment of trace elements from the iron ore tailing and the mud in the marine environment caused major modifications in the water body, such as shifts in organic matter interactions and in fish ecological niches (Andrades et al., 2020; Longhini et al., 2020). Altogether, these environmental changes can influence the dynamics of organohalogen compounds in the environment, affecting their biomagnification in apex predators and, ultimately, the sustainability of an endangered population.

The coastal region affected by the mud included the area inhabited by franciscana dolphins, *Pontoporia blainvillei*, designated Franciscana Management Area Ia (FMA Ia) (Cunha et al., 2014), where the largest concentration of individuals from this population can be found (Sucunza et al., 2019). Franciscana dolphins are small odontocetes with coastal to estuarine habits and an endemic distribution between ES and the Gulf of San Matías in Argentina (Crespo et al., 1998; Jefferson et al., 2015; Siciliano et al., 2002). The species is classified as vulnerable along its range (Zerbini et al., 2017) and as critically endangered in Brazil (ICMBio, 2018). Individuals from FMA Ia constitute a genetically and geographically isolated population, increasing their risk of local extinction (Cunha et al., 2014; Oliveira et al., 2020). The current population estimate is 595 individuals, with a highly restricted area of use in the surroundings of the Doce River's mouth, and it is likely the smallest population of the species (Sucunza et al., 2019).

POPs may affect the immune and reproductive systems of marine mammals (Desforges et al., 2016; Helle et al., 1976), which can result in population-level consequences. PCBs were already related to predicted population collapse in other cetacean species (Desforges et al., 2018; Hall et al., 2018; Oliveira-Ferreira et al., 2021), while OCPs and BFRs present endocrine disrupting properties that may influence individual homeostasis and population dynamics (Das et al., 2006).

Franciscana dolphins can be used as sentinels due to their long life cycle, site fidelity, thick blubber layer and high trophic level in food webs, which provide a comprehensive overview of the system (Bossart, 2011; Ross, 2000; Vos et al., 2003). The bioaccumulation trends of POPs and biosynthesized OHC in franciscana dolphins are indicators of environmental health (Vetter, 2006; Vetter et al., 2002).

To provide an integrative environmental assessment of the impact of Fundão dam collapse in OHC and its consequences in franciscana dolphin bioaccumulation, the following compounds were analyzed: the OCPs dichlorodiphenyltrichloroethane (DDT) and its metabolites dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD), mirex, hexachlorobenzene (HCB) and hexachlorocyclohexane (HCH); the polychlorinated biphenyls (PCB); the BFRs polybrominated diphenyl ethers (PBDE), pentabromoethylbenzene (PBEB) and hexabromobenzene (HBBZ); and the naturally produced methoxylated brominated diphenyl ethers (MeO-BDE). Thus, the study aimed to investigate differences in the profile of OHCs in the blubber of franciscana dolphins from FMA Ia before and after the dam collapse, as well as to construct their temporal trends between 2003 and 2019.

2. Material and methods

2.1. Study site

The study site encompasses the coast of ES, in southeastern Brazil, the habitat of franciscana dolphins from FMA Ia (Sucunza et al., 2019), in the South Atlantic Ocean (Fig. 1). This population uses a small area of the ES coastline in the northern portion of the state between the municipalities of Conceição da Barra (18°35′S) and Aracruz (19°56′S) (Sucunza et al., 2019).

The region is influenced by the Abrolhos bank, a biodiversity hotspot for marine organisms (Dutra et al., 2005; Rodrigues et al., 2020), and receives a discharge from the Doce River, which runs through 228 municipalities, and its river basin supports 3.1 million inhabitants (Santolin et al., 2015). Moreover, it is subjected to the impact of agricultural and industrial activities (Hatje et al., 2017), characterizing a high anthropogenic pressure in this environment. The collapse of the Fundão mining dam in November 2015 and the arrival of mud rich in trace elements (Segura et al., 2016) pose a critical impact in this area (Gomes et al., 2017; Hatje et al., 2017).

2.2. Sampling

Stranded franciscana dolphin carcasses were collected with the permission of environmental agencies (Brazilian Environmental Agencies – IBAMA/MMA permission #11495-1 and ICMBio/MMA permission #64724-5) by the partner institutions Instituto Baleia Jubarte and Instituto ORCA. Blubber samples were collected during necropsy (Geraci and Lounsbury, 2005), frozen and sent to Laboratório de Mamíferos Aquáticos e Bioindicadores for OHC assessment. Only fresh carcasses (codes 2 and 3, Geraci and Lounsbury, 2005) were included in this study. A total of 33 individuals were obtained between 2003 and 2019 in ES (Fig. 1), where 23 were obtained before the dam collapse - 2003 to 2015- and 10 were obtained after the dam collapse -

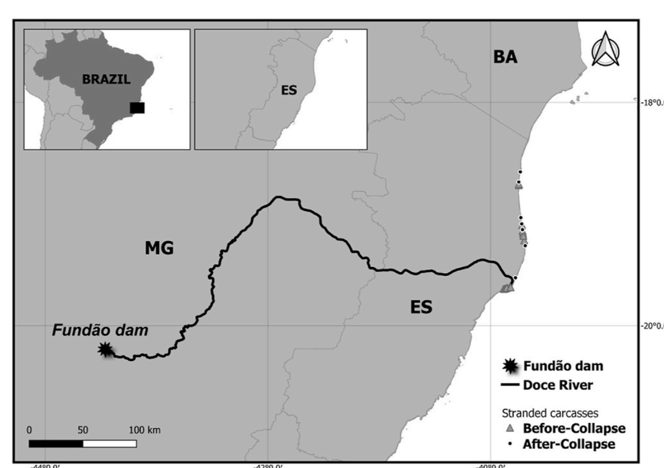

Fig. 1. Study site in the Espírito Santo state coast, where stranded carcasses of *Pontoporia blainvillei* were collected between 2003 and 2019. Star points out to the location of the Fundão Dam, in Minas Gerais state.

2016 to 2019 (Table S1, Supplementary Material). Sex and total length were determined during the necropsy. Teeth from the central section of the individuals' lower jaw were collected for age estimation by counting the growth layer groups in the cementum (Pinedo and Hohn, 2000) (Table S1, Supplementary Material). Sexual maturity was determined by histological evaluation of gonads, and when this evaluation was not possible, 2-year-old males and 3-year-old females were considered sexually mature as described in the literature for the FMA Ib population (Ramos et al., 2000) (Table S1, Supplementary Material).

2.3. Analyses of organohalogen compounds

Analyses of OHCs were adapted from methodologies previously described elsewhere (Dorneles et al., 2010; Oliveira-Ferreira et al., 2021) and are detailed in the Supplementary Material. In short, 0.5 g of blubber was homogenized with sodium sulfate and spiked with internal standards (ISTD; PCB 103 and PCB 198 for organochlorine analysis and PBDE 181 for organobromine analysis). The samples were extracted using Soxhlet with dichloromethane:n-hexane (1:1), and an aliquot was collected for gravimetric determination of lipid content. Then, the extract was cleaned up with sulfuric acid and eluted on an aluminum oxide column. The final extract volume was reduced in nitrogen flow.

The organochlorine assessment in samples received before 2018 was performed in a gas chromatograph (*Agilent Technologies 6890*) coupled to a ^{63}Ni electron capture detector (GC/ECD, *Agilent Technologies 7890*), while samples received between 2018 and 2020 were analyzed by GC coupled to a mass spectrometer (GC/MS, *Agilent Technologies 5975*).

For GC/ECD analyses, samples were not subjected to the last purification step on an aluminum oxide column. A total of 2 μL of the samples was injected using an autosampler (*Agilent Technologies 7683B*) in splitless mode at 280 °C and 13 psi with a detector at 320 °C. Hydrogen was chosen as the carrier gas, with nitrogen chosen as the auxiliary gas. A DB-5MS capillary column (30 m × 0.25 mm x 1 mm) was used. A peak confirmation step followed in GC/MS with an electron impact source (EI) was performed in scan mode.

For GC/MS analyses of organochlorine compounds, an EI source in selected ion monitoring (SIM) mode was used. The sample injection followed the same parameters described for GC/ECD, and an HP-5MS silica capillary column (30 m × 0.25 mm x 0.25 mm) was used.

The chromatographic run for organochlorine compound analyses lasted approximately 67 min and followed a temperature slope for compound separation of 70 °C for 1 min, 40 °C/min until 170 °C, 1.5 °C/min until 240 °C and 15 °C/min until 300 °C for both GC/ECD and GC/MS.

Analyses of organobromine compounds of natural and anthropogenic sources were performed in GC/MS, also using an HP5-MS capillary column (30 m x 0,25 mm x 0,25 mm), on negative chemical ionization (NCI), using ammonia as ionizing gas with a 3.0 mL/min flow. The chromatographic run lasted for approximately 82 min, and the temperature slope consisted of 110 °C for 1 min, increased 8 °C/min until 180 °C, increased 2 °C/min until 240 °C and increased 2 °C/min until 300 °C.

The data were analyzed in Ezchrom software (*Agilent Technologies*) for GC/ECD and Enhanced ChemStation (*Agilent Technologies*, MSD ChemStation E.02.02.1431) for GC/MS, and concentrations were calculated based on individual lipid content ($\mu g.g^{-1}$ lw).

2.4. Quality control

A total of 58 OHCs were analyzed in the present study. Among them, 32 PCB congeners (PCB-8, -28, -31, -33, -44, -49, -52, -70, PCB74, -97, -99, -101, -105, -118, -132, -138, -141, -151, -153, -158, -170, -174, -177, -180, -183, -187, -194, -195, -199, -203, -206 and -209); eight OCPs: the *p.p'* forms of DDT, DDE and DDD, the isomers α-HCH, β-HCH and γ-HCH, HCB, and mirex; the anthropogenic brominated flame retardants PBEB, HBBZ, and seven PBDE congeners (PBDE-28, -47, −99, −100, −153, −154 and −183); and eight congeners of the naturally produced MeO-BDEs (6-MeO-BDE 47, 2′-MeO-BDE 68, 5-MeO-BDE 47, 4′-MeO-BDE 49, 5′-MeO-BDE 100, 4′-MeO-BDE 103, 5′-MeO-BDE 99 and 4′-MeO-BDE 101).

All standards for organochlorine compounds and PBDEs of primary interest were purchased from *Accustandard Laboratories* (Connecticut, USA). PBEB and HBBZ were purchased from *Cambridge Isotope Laboratories* (Wisconsin, USA), and MeO-BDEs were purchased from *Wellington Laboratories* (Ontario, Canada).

Standard reference material (SRM® 1945) from the National Institute of Standards and Technology (NIST) from pilot-whale blubber was analyzed to certify the protocol, and compound certification followed a recovery between 65 and 135%. A ±30% variation of ISTD recovery in samples was accepted and reached 89.2% ± 15.5% (mean ± standard deviation) for organochlorine analyses and 100.8% ± 14.8% for organobromine analyses.

Limits of detection and of quantification (LOD and LOQ, respectively) were determined for all compounds (Tables S2 – S5, Supplementary Material). Analytical blanks were added to every batch to detect possible contaminations during the procedure. In the case of compound detection in blanks above the LOD, these were subtracted from samples of the batch. A calibration curve was used for each class of contaminants for quantification purposes.

2.5. Data analyses

The statistical analyses were performed using STATISTICA 7.0© and R software (R Core Team, 2019). Only OHCs found above the LOQ in at least 50% of the dataset were included in the statistical tests. Out of 58 compounds analyzed in the present study, 29 met the criteria.

The Kolmogorov–Smirnov test was performed to determine normality and revealed a nonnormal distribution of the dataset. A discriminant function analysis (DFA) was applied to detect alterations in the organohalogen contamination profile in franciscana dolphins before and after dam collapse. Among the 29 variables available for testing, 20 fitted the model (PCB-97, -118, −138, −141, −151, −153, −158, −170, −177, −180, −194, −195, HCB, *p.p'*-DDE, *p.p'*-DDD, *p.p'*-DDT, mirex, PBDE-47, 2′-MeO-BDE 68 and 6-MeO-BDE 47).

A Kruskal–Wallis test was used to determine the influence of sex and sexual maturity on the concentrations of OHCs. Spearman's correlation was applied to determine the relationship between the concentrations of OHCs in the blubber of male and female franciscana dolphins and the individuals' ages. To avoid bias of sampling year on the analyses, only samples collected after the dam collapse, between 2016 and 2019, were included in these analyses.

Finally, a generalized additive model (GAM) was fitted to the data to identify a temporal trend in the OHC concentrations found in the bubbler of franciscana dolphins between 2003 and 2019. The model was performed in R using the *mgcv* package (R Core Team, 2019), with a *gamma* distribution. The gamma value was set at 1.4, and a cubic spline was chosen to smooth the data (Jepson et al., 2016; Law et al., 2010). "Year of Sampling" and "Age of Individuals" were the most suitable covariables fitting the model for pesticides, whereas the two variables combined to "Sex" and "Sexual Maturity" presented a better fit for PCBs and natural and anthropogenic organobromine compounds, as tested to prevent overfitting of the data.

3. Results & discussion

3.1. Contamination profile of franciscana dolphins before and after the mining dam collapse

The concentrations of OHCs of anthropogenic and natural sources found in blubber of franciscana dolphins from FMA Ia are presented in Table 1 (see also Tables S6–S9, Supplementary Material).

A separation between individuals sampled before and after the dam

Table 1
Median, mean, standard deviation (SD), minimum (Min) and maximum (Max) of age and organohalogen concentrations found in blubber of franciscana dolphins, *Pontoporia blainvillei*, from FMA Ia. Samples collected before the collapse of Fundão mining dam (Before Dam-Collapse) were obtained between 2003 and 2015, whereas samples collected after the disaster (After Dam-Collapse) were obtained between 2016 and 2020. Age is expressed in years and concentrations in μg.g^{-1} lw.

	Age	∑PCBs	∑DDTs	Mirex	HCB	∑PBDEs	∑MeO-BDEs
Before Dam-Collapse (n= 23)							
Median	4.0	2.37	0.893	0.172	0.0180	0.0153	1.96
Mean ± SD	4.1 ± 3.7	2.49 ± 1.65	1.08 ± 0.75	0.235 ± 0.187	0.0247 ± 0.0173	0.0222 ± 0.0248	2.51 ± 1.44
Min – Max	0–11	0.312–6.60	0.117–2.99	0.0360–0.865	<0.0006–0.0678	<0.0002–0.113	0.780–6.11
After Dam-Collapse (n= 10)							
Median	1.0	1.12	1.13	0.0993	0.0230	0.00946	1.58
Mean ± SD	2.5 ± 3.6	2.36 ± 3.75	1.52 ± 1.49	0.189 ± 0.308	0.0269 ± 0.0190	0.0187 ± 0.0287	1.51 ± 0.59
Min – Max	0–11	0.266–12.8	0.205–5.36	0.0337–1.06	0.00646–0.0648	0.00233–0.0984	0.485–2.47

Legend: (ΣPCBs) Sum of PCB congeners; (ΣDDTs) Sum of *p.p'*-DDE, *p.p'*-DDD and *p.p'*-DDT; (ΣPBDEs) Sum of PBDE congeners; and (ΣMeO-BDEs) Sum of MeO-BDE congeners.

collapse was identified in the DFA (Wilks' Lambda: 0.15; F(20, 13) = 3.7; p < 0.009) and suggests alterations in the general contamination profile with a 97.1% correct classification. In fact, the profile of organochlorine compounds presented a change in compound dominance before and after dam collapse. The profile prior to the dam collapse was dominated by ΣPCBs (68%), followed by ΣDDTs (26%), mirex (5%) and HCB (1%). (Fig. 2). However, franciscana dolphins collected after the disaster presented a profile dominated by ΣDDTs (48%), followed by ΣPCBs (47%), mirex (4%) and HCB (1%) (Fig. 2). The organobromine general profile was not altered, and ΣMeO-BDEs predominated (>95%), followed by ΣPBDEs (Fig. 2). ΣHCHs and PBEB were detected in less than 50% of the samples, and HBBZ was not detected above the LOQ in any sample; therefore, they were not included in statistical analyses.

For ΣDDTs, *p.p'*-DDE was the most abundant, followed by *p.p'*-DDT and *p.p'*-DDD. The *p.p'*-DDE/ΣDDTs ratios before and after dam collapse were 0.65 and 0.74, respectively. These values reflect the historical use of DDT and, consequently, the degradation of *p.p'*-DDT in its most persistent metabolite, *p.p'*-DDE, since the latter was not present in relevant concentrations in commercialized DDT formulations (Borrell and Aguilar, 1987).

Among ΣPCBs, penta-, hexa- and hepta-PCBs were the most abundant before and after the disaster. This profile represents the technical mixtures commercialized in Brazil, such as Ascarel®, and was already seen in other coastal cetaceans from southeastern Brazil (Lailson-Brito et al., 2012, 2010).

The OHC profile in franciscana dolphins, especially before dam

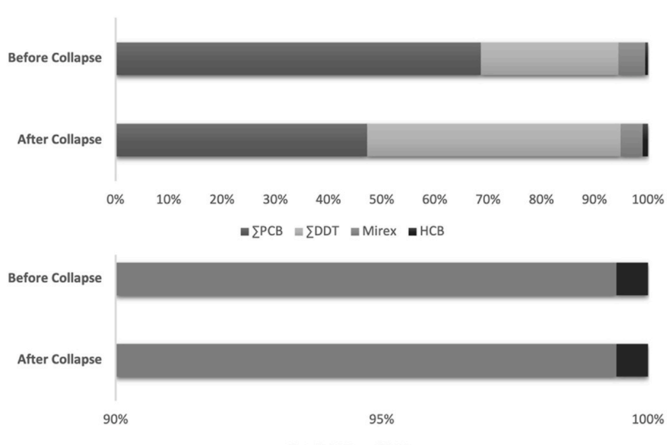

Fig. 2. General contamination profile of (A) organochlorine compounds (ΣPCBs, ΣDDTs, Mirex and HCB) and (B) organobromine compounds (ΣPBDEs and ΣMeO-BDEs) in franciscana dolphins, *Pontoporia blainvillei*, from FMA Ia. Samples collected before the collapse of the Fundão mining dam (Before Dam-Collapse) were obtained between 2003 and 2015 and samples collected after the disaster (After Dam-Collapse) were obtained between 2016 and 2020.

collapse, is consistent with coastal cetaceans foraging in highly urbanized areas, e.g., rough-toothed dolphins, *Steno bredanensis*, and Guiana dolphins, *Sotalia guianensis*, from southeastern Brazil (Lailson-Brito et al., 2010; Oliveira-Ferreira et al., 2021). Franciscana dolphins from FMA Ia can be found year-round along the coast of ES (Sucunza et al., 2019). This population feeds mainly on demersal sciaenid fish, such as *Isopisthus parvipinnis* and *Stellifer* sp., which are commonly associated with river runoff (Rupil et al., 2019).

For anthropogenic organobromine flame retardants, PBDE 47 was the main congener and was the only one detected in more than 50% of the dataset; it is also the main congener found in other cetacean species on the Brazilian coast (Alonso et al., 2012; Leonel et al., 2014). PBDE-28, -99, −100, −154 and PBEB were also detected above the LOQ in several samples but at a less relevant frequency. The dominance of PBDE-47 may reflect the environmental debromination of penta- and octa-BDE formulations (Stapleton et al., 2004) restricted by the Stockholm Convention in 2009, before the deca-BDE formulations, for example (UNEP, 2017). The debromination of heavier PBDE congeners seems to explain the mismatch between the most common congener profile in recent commercial mixtures and the contamination profile in sentinel species. Furthermore, it is noteworthy that while there are no records of PBDEs being produced in Brazil, these compounds are present in local trophic webs. BFRs are not chemically linked to the materials where they are applied (Kim et al., 2006). Their presence in household goods and technical equipment allows BFRs to leach to marine ecosystems when the products are discarded, while river runoff and atmospheric transport may also contribute to their global distribution.

For the natural compounds, 6-MeO-BDE 47 and 2′-MeO-BDE 68 were predominant in the profile before and after the collapse and may represent the influence of the Abrolhos bank in franciscana dolphin habitat (Alonso et al., 2012; Teuten et al., 2005; Vetter et al., 2002).

3.2. Temporal trend of organohalogen compounds in franciscana dolphins

Concentrations of OCPs such as *p.p'*-DDE, *p.p'*-DDD, *p.p'*-DDT, mirex and HCB presented statistically significant temporal trends (Fig. 3; Table S10, Supplementary Material). Additionally, the model pointed out that mirex was also influenced by the individuals' age.

The most persistent PCB congeners found in franciscana dolphins (PCB-153, -138 and −180) as well as ΣPCBs did not present a significant temporal trend, while biological parameters, such as age and/or sexual maturity, seem to have a more relevant effect on their bioaccumulation (Table S10, Supplementary Material).

PBDE-47, ΣPBDEs, 2′-MeO-BDE 68, and ΣMeO-BDEs presented significant declines over time, but sex and sexual maturity were also significant covariables (Fig. 4; Table S10, Supplementary Material).

While there is a recognition that the sample size is small and caution is advised when interpreting the results, it is particularly important to underscore the value of the long-term monitoring data for a threatened species.

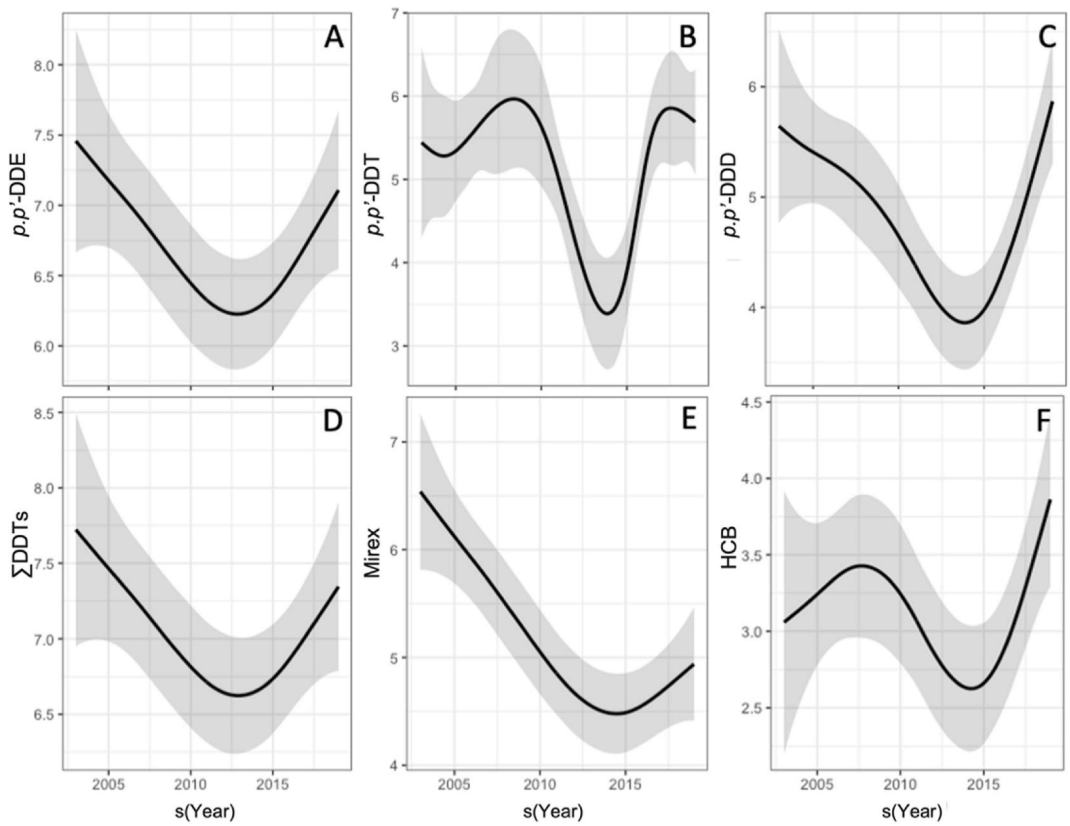

Fig. 3. Temporal-trend for organochlorine pesticides in franciscana dolphins, *Pontoporia blainvillei*, from FMA Ia collected between 2003 and 2019. Natural log-transformed concentrations of (A) *p.p'*-DDE; (B) *p.p'*-DDT; (C) *p.p'*-DDD; (D) ΣDDTs; (E) Mirex and (F) HCB across smoothed sampling period. The line represents the smoothed trend, and the shaded grey area represents the 95% confidence interval as estimated by fitting the data in a Generalized Additive Model (GAM).

3.2.1. *Organochlorine pesticides*

The FMA Ia population experienced two periods of increase in concentrations of OCPs. The first one was an increase in *p.p'*-DDT concentration between 2005 and 2008. Records indicate an increase in DDT usage as vector control in the Southern Hemisphere until 2008, decreasing again in 2009 (Van Den Berg, 2009; Van Den Berg et al., 2012) (Fig. 3). The increase in DDT use and, consequently, in its availability was also perceived in the endemic and endangered Galapagos sea lion, *Zalophus wollebaeki*, analyzed in 2005 and 2008 (Alava et al., 2011).

Following the decrease in OCPs, the concentrations of *p.p'*-DDT, *p.p'*-DDD and *p.p'*-DDE, mirex and HCB increased after dam collapse. This increase in OCP concentrations is probably related to the drag of Doce River's riverbed in a region characterized by agricultural activities such as coffee production, between MG and ES (Volsi et al., 2019), disturbance of sediment (Fernandes et al., 2016), and physical-chemical alterations in water condition (Hatje et al., 2017), leading to the reavailability of OCPs.

The predominance of DDTs in the blubber of franciscana dolphins after dam collapse is unlikely to be related to new entrances of this recalcitrant pesticide in the environment. The prevalent form in ΣDDTs was *p.p'*-DDE, and the ratio *p.p'*-DDE/ΣDDTs after collapse was higher than that before, altogether suggesting historical rather than recent contamination by DDT in southeastern Brazil (Borrell and Aguilar, 1987). Additionally, low concentrations of OCPs and PCBs were reported in recently deposited sediment from the Doce River mouth before collapse (de Souza et al., 2022). Hence, it is likely that old stocks of DDTs were disturbed by the mud drag and made available for bioaccumulation in franciscana dolphins.

Unusual events can be responsible for the remobilization of OCPs, as was observed in polar bears, *Ursus maritimus*. A study found that concentrations of *p.p'*-DDE decreased until 2011, with a posterior increase between 2012 and 2017 related to the release of immobilized pesticides due to fires in boreal forests (Lippold et al., 2019).

Pesticide leaching is strongly associated with its own properties and to environmental conditions such as sediment characteristics, trace element concentrations, organic matter and pH, which can influence the adsorption and desorption of organic compounds to soil and sediment (Lalah et al., 2009). The physical drag of the mud itself could act on its long-distance transport from the riverbed to the marine environment (Calvet, 1989). Nevertheless, the increase in some metal concentrations caused by iron ore tailings (Hatje et al., 2017) can decrease OCP adsorption to soil (Lalah et al., 2009). The remobilization of pesticides and desorption of compartments where they were previously immobilized ultimately impacts their bioavailability and input into trophic webs, where they can undergo biomagnification (Gray, 2002), explaining their increase in franciscana dolphins from FMA Ia after the disaster.

Although the sampling set after the environmental disaster was mostly composed of young individuals (Table 1), there was an increase in the bioaccumulation of OCPs following dam collapse. This increase was unexpected considering the known influence of biological parameters and indicates that this pattern was mainly influenced by the arrival of mud in the franciscana dolphin habitat. In addition, because the sampled dolphins were young, the bioaccumulation of pesticides reveals an important threat to individuals at a critical developmental stage (Das et al., 2006).

As observed in individuals from FMA Ia between 2008 and 2015, DDTs were also found to decline over time in the FMA IIIa population between 1994 and 2004 (Leonel et al., 2010), demonstrating the slow but active degradation of this legacy contaminant. However, the recent increase in the bioavailability of these endocrine disruptors in FMA Ia

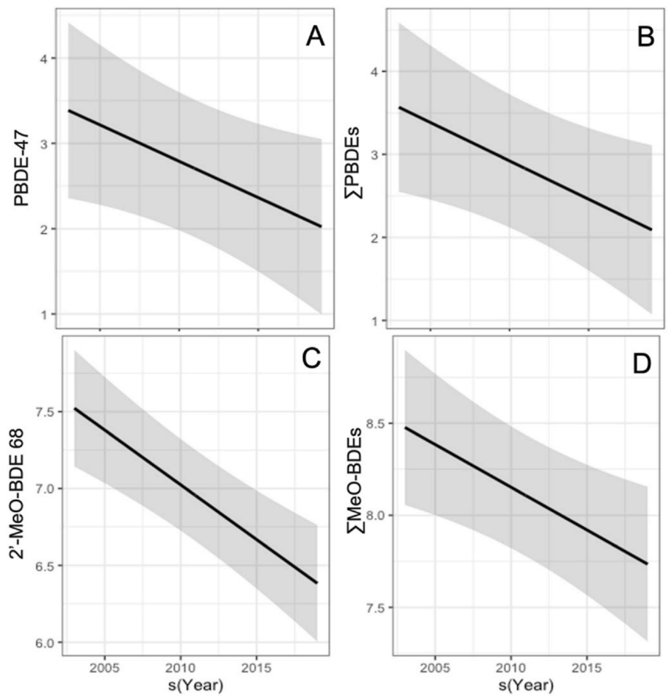

Fig. 4. Temporal-trend for organobromine of anthropogenic and natural sources in franciscana dolphins, *Pontoporia blainvillei*, from FMA Ia collected between 2003 and 2019. Natural log-transformed concentrations of (A) PBDE 47; (B) ΣPBDEs; (C) 2′-MeO-BDE 68; (D) ΣMeO-BDEs across smoothed sampling period. The line represents the smoothed trend, and the shaded grey area represents the 95% Confidence Interval as estimated by fitting the data in a Generalized Additive Model (GAM).

can trigger serious deleterious effects at the population level for this endangered species.

It is noteworthy that this population tends to use the coastal area more frequently during the rainfall season, probably due to an increase in productivity (Mayorga et al., 2020). It is also during this season that micropollutants tend to be remobilized and made available for incorporation into trophic webs as a consequence of an elevated discharge of the Doce River in the marine environment and increased disturbance of sediment influenced by waves (Andrades et al., 2021; Longhini et al., 2022).

Elevated concentrations of DDTs have the potential to interfere with the reproductive process of marine mammals. Examples are the induction of morphological impairments such as uterine stenosis in ringed seals, *Pusa hispida*, in combination with elevated concentrations of PCB (Helle et al., 1976), and disturbance of androgen homeostasis in bottlenose dolphins, *Tursiops truncatus* (Galligan et al., 2019). Furthermore, hormonal alterations triggered by DDTs are also related to corticosteroid hormones involved in several physiological processes associated with stress, and the immune response can also be affected (Galligan et al., 2019; Marsili and Fossi, 2003; Vos et al., 2003). Contaminant mixtures pose deleterious effects for cetaceans (Desforges et al., 2017, 2016), and the increase in OCP levels in addition to increased mercury concentrations post collapse in franciscana dolphins (Manhães et al., 2021) raises questions regarding the sustainability of the FMA Ia population.

The small size of this population and bycatch (Danilewicz et al., 2012; Netto and Di Beneditto, 2008; Secchi et al., 2003; Sucunza et al., 2019) increase the concern for one of the least known franciscana dolphin populations. The imbalance between removal and replacement rates due to anthropogenic activities was linked to the population decline of Guiana dolphins from Guanabara Bay on the southeastern Brazilian coast, which suffered a serious reduction (Azevedo et al., 2017). The negative impact of OCPs on survival and reproduction can be a harmful factor for a small, isolated, genetically impoverished and thus endangered population (Sucunza et al., 2019; Oliveira et al., 2020).

3.2.2. PCBs

The lack of a significant temporal trend for PCBs is consistent with patterns previously observed in other cetaceans from the Southern Hemisphere (Aono et al., 1997; Law, 2014; Leonel et al., 2010), while in the Northern Hemisphere, long-term monitoring studies point toward a decline in PCB concentrations (Kajiwara et al., 2008; Lebeuf et al., 2014). The temporal trend observed for organochlorine compounds in this population of franciscana dolphins supports the faster decline of OCPs when compared to PCBs (Leonel et al., 2010) until the interference of an unusual event such as the dam collapse. Stable concentrations of PCBs have been linked to their recalcitrant nature and elevated residence time in the water column, hence environmental persistence (Dachs et al., 1997; Jepson and Law, 2016), as well as to recurrent input in the marine environment via inappropriate disposal of PCB-containing equipment (Leonel et al., 2010).

While no temporal trends were identified for PCBs, the relative decrease in the median concentrations of PCBs after dam collapse can be related to biological parameters. The average age of individuals was lower after collapse, and age was a relevant covariant in the bioaccumulation of PCBs (Table S10, Supplementary Material).

PCB availability is also driven by local environmental characteristics and biogeochemical processes (Dachs et al., 1997). Despite the absence of clear temporal trends for this class of contaminants, the median concentrations of PCBs after the dam collapsed (1.1 μg g^{-1} lw) were half of what was found prior to collapse (2.4 μg g^{-1} lw). This decrease could be due to the physical-chemical alterations in water properties once organic matter and trace element composition in the water column changed (Hatje et al., 2017; Schettini and Hatje, 2020). In particular, hydrophobic compounds, such as highly chlorinated PCBs, tend to present high affinity to organic matter, reducing their residence time in the water column and, consequently, their bioavailability (Dachs et al., 2002; Lailson-Brito et al., 2010). In fact, pentachlorine PCBs presented a slight increase in contribution after collapse when compared to the other two major contributors, hexa- and heptachlorine congeners.

PCB concentrations in franciscana dolphins from FMA Ia were lower than threshold concentrations of 17 μg g^{-1} lw in blubber found to trigger immunosuppression and reproductive failure in adult cetaceans (Kannan et al., 2000). However, these values must be cautiously interpreted due to franciscana dolphins' smaller size and respective body burden (Murphy et al., 2018), and further research is required to understand the thresholds for this species. In fact, long-term exposure to concentrations lower than the known threshold still interferes with the health of the harbor porpoise (*Phocoena* phocoena) (Williams et al., 2020). The additive effects of the sudden increase in pesticide concentrations and chronic exposure to low, but stable, PCB concentrations may pose an important threat to the viability of this population.

3.2.3. Organobromine compounds of anthropogenic sources

The significant decrease over time of PBDEs in FMA Ia (Fig. 4) contrasts with the trend observed in the FMA IIIa population, where an exponential increase in PBDE concentration was detected between 1994 and 2004 (Leonel et al., 2014). The trend identified in the southern region suggested a recurring use of these compounds as BFRs in developing countries (Leonel et al., 2014). A positive correlation between PBDE liver concentration in Guiana dolphins and sampling year was also identified, suggesting an increase in such concentration between the years 1994 and 2006 (Dorneles et al., 2010). The declining trend observed in this study could be related to the timespan when compared to previous reports.

PBDEs appear to have peaked in the late 1990s and early 2000s in marine mammals from the Northern Hemisphere, whereas their concentrations now slowly start to decline or stabilize (Kajiwara et al., 2004; Lebeuf et al., 2014; Rotander et al., 2012; Simond et al., 2017), reflecting the regulation policies to control BFR. There have been no declining trends reported for PBDEs in the Southern Hemisphere thus far (Dorneles et al., 2010; Leonel et al., 2014; Markham et al., 2018). In Brazil, there are no records of PBDE production, no clear directives for the usage of such compounds, and recent reports on the importation of PBDEs are highly unspecific, making it difficult to trace it, despite the country being a signatory of the Stockholm Convention (Annunciação et al., 2018; Botaro and Torres, 2007; Sharkey et al., 2020). However, the trend observed in franciscana dolphins could reflect the decrease in the importation of PBDE-containing products given their replacement as flame retardants in several Northern Hemisphere countries.

Notwithstanding, the temporal trends of PBDE 47 and ΣPBDEs could also be explained by the biotransformation of these compounds into less brominated forms, such as other PBDE congeners or hydroxylated compounds, as often observed in marine biota (Bhavsar et al., 2008; Stapleton et al., 2009, 2004). Additionally, younger individuals can present higher concentrations of PBDEs due to their low metabolization capability and the biodilution effect in adults (Das et al., 2006; Hall et al., 2003; Weijs et al., 2013). Since the period after the dam collapse presented a higher number of immature individuals (lower median age; Table 1), it is unlikely that the dataset biased the downward trend of organobromine compounds.

3.2.4. Naturally produced organobromine compounds

Methoxylated bromine is biosynthesized by marine organisms such as algae, sponges and cyanobacteria (Teuten et al., 2005; Vetter et al., 2002, 2001), and the Abrolhos bank is likely to have a significant influence on the profile of MeO-BDEs in franciscana dolphins inhabiting the coast of ES. These compounds correspond to more than 95% of the organobromine profile, and 6-MeO-BDE 47 and 2′-MeO-BDE 68 were the main congeners detected in these dolphins.

While 6-MeO-BDE 47 remained stable during the 16 years of monitoring and its bioaccumulation in franciscana dolphins was not influenced by the year of sampling, 2′-MeO-BDE 68, synthesized mainly by sponges and associated organisms (Vetter, 2006), declined over time (Fig. 4).

Variations in natural product concentrations may be related to changes in the community composition of organisms responsible for their production. In the last few years, an increase in coral reef diseases potentially related to climate change was detected in the Abrolhos bank, and an increase in turf algae coverage was perceived (Francini-Filho et al., 2013, 2008), altering the ecological interactions of lower trophic level groups.

While differences in methoxylated compounds could be related to environmental processes and climate change, the introduction to the mud in the Abrolhos bank (Coimbra et al., 2020; Francini-Filho et al., 2019) also impacted local biodiversity and ecological relationships. Evaluation of macrofauna and analyses of stable isotopes in estuarine fish species evidenced decreased biodiversity and ecological niche shifts as a consequence of dam collapse (Andrades et al., 2020; Gomes et al., 2017), which may have had a bottom-up effect (Tarnecki and Patterson, 2015). Nevertheless, mud rich in iron was linked to an increase in phosphorous availability in the estuarine environment, which could trigger eutrophication (Queiroz et al., 2021) and influence the composition of producers and ecological relationships in the area. Alterations in the species composition at lower trophic levels can reflect prey availability for apex predators and influence the organobromine profile found in franciscana dolphins.

Altogether, these results highlight the importance of using marine mammals as sentinels of environmental health (Bossart, 2011). Data obtained from franciscana dolphins from FMA Ia provide valuable information on environmental alterations and can also be used to monitor local conditions, as these are long-lived, fat-rich species ideal for understanding the long-term dynamics of naturally produced compounds.

3.3. Influence of biological parameters on the bioaccumulation of organohalogen compounds

Because biological parameters such as age and sexual maturity were important covariants in the GAM, further investigation of their influence on the organohalogen profile was conducted. No significant relationships were found between biological parameters of franciscana dolphins from FMA Ia and the bioaccumulation profile of OHC, such as correlations with age (*Spearman* correlation, $p > 0.05$) or differences between sex and sexual maturity (*Kruskal–Wallis's* test, $p > 0.05$).

The lack of differences in the bioaccumulation profile attributed to biological variables could be biased by the small sampling set, since the number of individuals for these analyses was drastically reduced to avoid the influence of the year of sampling in the results, accounting for only individuals collected after the collapse ($n = 10$). However, it is also noteworthy that franciscana dolphins present a life cycle shorter than delphinid species, for example, reaching sexual maturity at the young age of 2 and 3 years old (Ramos et al., 2000), and the dynamics of OHC may differ from what is described in the literature for other species. Additionally, not all OHCs presented the same dynamics. While some organochlorine compounds tend to present clear associations with biological parameters in several cetacean species, the relationship of organobromine compounds to such variables could be harder to determine, especially because of their biotransformation process in marine biota (Alonso et al., 2012; Ross et al., 2000; Weijs et al., 2009).

Differences between size classes and the effect of age on the accumulation of OHC were already described for franciscana dolphins from other FMAs (Kajiwara et al., 2004; Leonel et al., 2010). Notwithstanding, age and sexual maturity had an important influence on PCB and organobromine concentrations in the blubber of franciscana dolphins from FMA Ia, as pointed out by GAM. It is known that biological parameters can influence the accumulation process because of maternal transfer of lipophilic compounds via lactation and placenta, which act as a depuration route for mature females and an important entrance via for the offspring, while males tend to continuously bioaccumulate these compounds throughout their life cycle (Kajiwara et al., 2008; Reijnders et al., 2009).

3.4. Comparison between franciscana dolphins from other FMAs

To the best of our knowledge, this is the first study reporting concentrations of OHCs in the blubber of franciscana dolphins from FMA Ia. This remains one of the most underexplored populations of the species, while comprehension of biological, ecological and ecotoxicological aspects is only starting to be elucidated (Alonso et al., 2012; Danilewicz et al., 2012; Rupil et al., 2019; Sucunza et al., 2019).

DDTs, HCB and mirex concentrations are similar to those found in populations from FMA II in southeastern Brazil and FMA III in southern Brazil (Kajiwara et al., 2004; Lailson-Brito et al., 2011; Leonel et al., 2010; Oliveira-Ferreira et al., *in prep*) and are one order of magnitude higher than FMA IVa in Argentinian waters (Romero et al., 2018). PCB levels in blubber are on the same order of magnitude as those in FMA II and FMA III (Kajiwara et al., 2004; Lailson-Brito et al., 2011; Leonel et al., 2010).

Concentrations of organochlorine contaminants in franciscana dolphins from FMA Ia are on the same order of magnitude as populations from highly urbanized areas and with great human population density as well as areas showing a strong influence of agricultural activities (Lailson-Brito et al., 2011; Leonel et al., 2010; Yogui et al., 2010), suggesting that FMA Ia is under great anthropogenic pressure.

Regarding PBDEs, the concentrations are at least fivefold lower than those presented by individuals from FMA II (Leonel et al., 2014; Yogui et al., 2011) and on the same order of magnitude as the population from FMA IIIa (Leonel et al., 2014). These differences could be influenced by the sampling period of the studies (Leonel et al., 2014; Yogui et al., 2011).

PCB and PBDE blubber concentrations in FMA Ia are lower than liver concentrations from the adjacent population in northern Rio de Janeiro state (Lavandier et al., 2016), and PBDE is lower than in the liver of franciscana dolphins from the FMA Ia (Alonso et al., 2012). Furthermore, dioxin-like PCBs, known for their toxicity, such as congeners 105 and 118, were detected in the blubber of franciscana dolphins in the present study (Table S7, Supplementary Material) as well as in the hepatic tissue of specimens from FMAs I, II and III (Dorneles et al., 2013).

For MeO-BDEs, concentrations in the liver of franciscana dolphins from FMAs I, II and III (Alonso et al., 2012) show that individuals from FMA Ia presented the highest concentrations (Alonso et al., 2012), similar to what was observed in the present study, indicating the strong influence of the Abrolhos bank in the natural profile of this population (Oliveira-Ferreira, *in prep.*). However, differences in the analyzed matrices may pose a confounding factor for these comparisons. The liver acts as an important biotransformation site for OHC, whereas blubber is the main storage tissue for these pollutants (Alonso et al., 2012; McKinney et al., 2006).

4. Conclusion

Franciscana dolphins are important sentinels of environmental health and provide a comprehensive scenario of the presence of OHCs in FMA Ia. The collapse of the Fundão dam had important consequences for an endangered population of franciscana dolphins. The arrival of the mud related to the collapse potentially led to an increase in the bioavailability and bioaccumulation of OCPs that were previously declining. This class of chemical pollutants is known to cause endocrine disruption in cetaceans and may pose a threat to this population's viability.

PCBs remained stable in franciscana dolphins, possibly because of their recalcitrant nature. Variations in these contaminants were related to the biological parameters of the populations.

PBDEs presented a declining trend over time in franciscana dolphins, suggesting either the effectiveness of prohibition measures for their application as flame retardants and/or the environmental debromination of these pollutants.

Naturally synthesized 2′-MeO-BDE 68 also presented a declining trend over time, underscoring changes in their producers' composition. This could be influenced by a decrease in species diversity and ecological niche shifts observed in the lower trophic levels postcollapse and climate change.

Along its distribution, franciscana dolphins have been exposed to anthropogenic pressure in the coastal environment, resulting in the high extinction risk the species faces today. In addition to the environmental alterations caused by the dam collapse possibly influencing the increase in the concentration of endocrine disruptors, the contamination profile and the order of magnitude of organohalogen concentrations found in the FMA Ia population are similar to populations inhabiting areas of high anthropogenic pressure. Although the present study relies on a small dataset, the temporal trends for franciscana dolphins show changes in the environment that could influence the population's sustainability.

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Authorship statements

Nara de Oliveira-Ferreira: Conceptualization; Data curation; Methodology; Validation; Formal analysis; Investigation; Visualization; Writing – original draft; Writing – review & editing. **Bárbara Manhães**: Conceptualization; Data curation; Methodology; Validation; Investigation; Visualization; Writing – review & editing. **Elitieri Santos-Neto**: Conceptualization; Data curation; Methodology; Validation; Investigation; Visualization; Writing – review & editing. **Yasmin Rocha**: Methodology; Investigation; Validation; Writing – review & editing. **Emi Brinatti Guari**: Methodology; Investigation. **Silvina Botta**: Methodology; Validation; Investigation; Writing – review & editing. **Adriana Castaldo Colosio**: Methodology; Resources; Writing – review & editing. **Hernani Gomes da Cunha Ramos**: Methodology; Resources; Writing – review & editing. **Lupércio Barbosa**: Methodology; Resources; Writing – review & editing. **Ian Augusto Gusman Cunha**: Methodology; Writing – review & editing. **Tatiana Lemos Bisi**: Resources; Visualization; Funding acquisition; Writing – review & editing. **Alexandre de Freitas Azevedo**: Resources; Project administration; Funding acquisition; Writing – review & editing. **Haydée Andrade Cunha**: Conceptualization; Resources; Visualization; Project administration; Funding acquisition; Writing – review & editing. **José; Lailson-Brito**: Conceptualization; Resources; Visualization; Supervision; Project administration; Funding acquisition; Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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