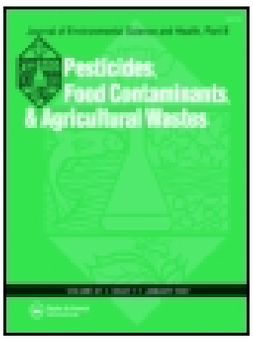

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REVIEW ARTICLE

Assessment of DDT and mercury levels in fish and sediments in the Iriri River, Brazil: Distribution and ecological risk

Rosivaldo A. Mendes[a], Marcelo O. Lima[a], Ricardo J.A. de Deus[b], Adaelson C. Medeiros[a], Kelson C.F. Faial[a], Iracina M. Jesus[a], Kleber R. F. Faial[a], and Lourivaldo S. Santos[b]

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ABSTRACT

In order to assess the risk of exposure of human populations to dichlorodiphenyltrichloroethane (DDT) and mercury, muscles of five fish species were analysed, along with the surface sediment of 14 Iriri River sampling sites. The fish specimens were sacrificed by the spinal section, prior to sex identification, body weight determination and total length. Considering the fish specimens studied, 11% of them showed concentrations of mercury higher than the maximum established by the World Health Organization for safe human consumption. A positive correlation between fish body weight and mercury concentration was observed, besides a positive correlation between the fish size and Hg concentration. Significant differences ($P < 0.05$) were found between mean concentrations of DDT and metabolites among species of fish studied. In the *Plagioscion squamossissimus* species, the highest concentration of total DDT (151.4 ng/g) was found, while in *Eugerres Brasilianus* species, the lowest. However, the DDT levels in fish muscle of studied species are below the maximum set by FAO-Alimentarius CODEX. In the sediments, total DDT ranged from 11.58 ng/g to 48.4 ng/g, which is associated with the historical DDT use in the Amazon. According to sediment quality guidelines, these levels have a moderate toxic effect in almost all of the studied region.

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KEYWORDS
Amazon; ecological risk; fish; Iriri River; sediment

Introduction

The advancement of the human population into the Amazon over the past years, has mainly occurred in more remote areas, and is the results of activities such as cattle production, wood exploitation, mining activity, hydroelectric construction and road opening. This has generated an increase in human exposure to endemic diseases such as malaria and environmental contamination via chemical pollutant emissions, originated by anthropogenic activities, which has led to contamination of soils, rivers, air and biota.[1] Against this backdrop, mercury (Hg) and dichlorodiphenyltrichloroethane (DDT) was widely used in the Amazon region for many years. In gold mines, Hg was used for the extraction of gold[2], and DDT was intensively used in the dispute against malaria, since this disease has always been a public health problem of great concern in Brazil, owing to the favourable conditions for the development of the disease, mainly in the Amazon region. Because of that, it is estimated that, in Brazil, thousands of tons of DDT were applied over several years.[3]

The prohibition of DDT in Brazil in 1985 for use in agriculture, and in 1997, in public health campaigns,[4] left a huge environmental liability, with a large amount of product residues without a suitable destination. All of this, because DDT belongs to a group of banned chemical compounds, called persistent organic pollutants, that have high environmental persistence, a long half-life, and the ability to be transported over long distances.[5,6]

On the other hand, Hg contamination in the Amazon region has been the subject of several studies owing to the intense activity of gold exploration, with the introduction of 2000 tons during the 1980s and 1990s, as well as the release of Hg by natural sources, such as forest fires, which has caused contamination and toxic effects on aquatic biota and humans.[7,8] In addition, a number of studies of Hg in fish have been carried out in the Amazon region, including in the Tapajós River Basin,[9–15] Madeira River[16–20] and Negro River.[21–24]

The main source of human contamination by these substances is the ingestion of contaminated foods, such as fish.[25] Fish are considered an important indicator of environmental pollution and the present bioaccumulation and biomagnification process in the food chain.[25–27] In aquatic environments, DDT is distributed in the most diverse systems, such as in the water, particulate matter, sediment, and aquatic biota,[28] and presents high toxicity with its accumulation capacity in sediments and biological tissues.[29]

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Sediments are considered an important reservoir and a potential source of contaminants and act through a series of biochemical processes. The DDT concentrations in sediments may be affected by various input sources, such as agricultural runoff, wastewater and sewage discharge, and atmospheric deposition.[26]

The data on the presence and distribution of DDT in edible fish species are therefore important from ecological and human health perspectives.[30] Thus, in the Amazon region, fish are the main source of food and subsistence of the traditional populations living on the riverbanks, such as the Indians and riverine, and is being exposed to high concentrations of Hg.[11,22,31]

The objectives of this study were to evaluate (1) the patterns of distribution and occurrence of DDT and Hg in sediment and fish samples from the Iriri River; (2) the ecological risks associated with the sediment quality of the aquatic ecosystem of the study area and (3) to analyse the potential risk to human health through consumption of contaminated fish from the river Iriri.

Materials and methods

Study area

The Iriri River with an extension of more than 1000 km starts in the Serra do Cachimbo on the border of Pará State and the Mato Grosso State, being a tributary of the Xingu River, adding in its trajectory other rivers of great water volume, such as the Catete and Curuá Rivers. It has an extensive drainage network and is characterized by a geological formation where the existence of countless waterfalls, along its entire course, makes it difficult to navigate, especially during periods of low rainfall (usually from July to December). The Iriri River surrounds an area where there is great deforestation, owed to the livestock production and agriculture. Besides that, there are several indigenous villages along the river and gold-digging in distant and remote areas on the border with Mato Grosso State, in Brazil's Central West.

In the section of the Iriri River sampled in the present study, almost all of the river bank has well preserved riparian forests, which highlights the existence of preservation areas, such as the Xingu National Forest and indigenous reserves of various ethnic groups, all of which are controlled by the National Indian Foundation and the National Foundation of Health. Within Iriri river waters exists an abundance of numerous species of fish that have varied eating habits, besides an enormous flora and fauna diversity, with some animals that are considered rare in this region.

Sampling

The fish samples were collected from 14 sampling sites, shown in Figure 1. There were 54 fish samples collected, which represents the most frequent species of the region: *Serrasalmus rhombeus* ($n = 17$), *Phractocephalus hemioliopterus* ($n = 3$), *Plagioscion squamosissimus* ($n = 18$), *Cichla* sp. ($n = 5$), *Eugerres brasilianus* ($n = 4$) and *Serrasalmus manueli* ($n = 7$). The fish samples were collected by direct fishing at sampling sites designated by the identification P01, P02, P05, P06, P10, P12, P13 and P14 and not being collected at other points. The applied methodology required approximately 100 g of muscle tissue, which were removed from each specimen. The samples were then packed in plastic bags, carefully identified to avoid mis-identification, and then frozen and transported in thermic containers, containing dry ice, to the laboratory. Subsequently, the samples were homogenized and conditioned in amber glass, then stored in a freezer at −20 °C until chemical analysis.

The sediment samples (1 kg) were collected from each site using a stainless steel sampler. The equipment used for sediment sample collection was rinsed with hexane and acetone. Samples were packed in chemically clean polyethylene bags and transported to the laboratory, where they were immediately air dried, sieved through 270 mesh stainless steel sieves, and packed and stored in amber glass vials at 4 °C, until laboratory analysis.

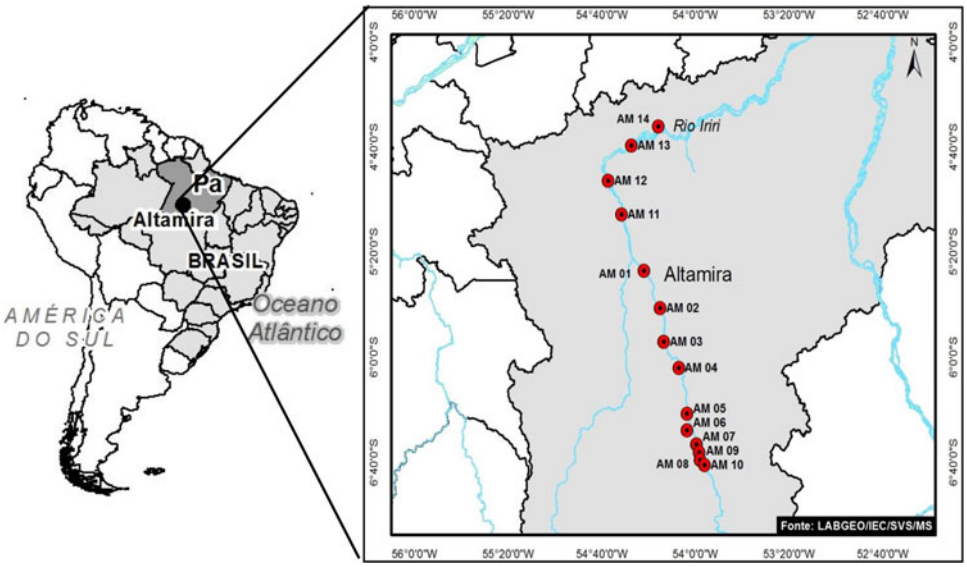

Figure 1. Localization of the study area in the Iriri River, Brazil. Source: Geoprocessing Sector of Evandro Chagas Institute.

Extraction and analysis

Analytical standards for pp′-DDT, pp′-DDE, pp′DDD, op′-DDE, op′-DDD and op′-DDT were obtained through ChemService (West Chester, USA). Reagents and high purity solvents were supplied by Mallinckrodt. (St. Louis, USA).

For the analysis of DDT in fish and sediment, the samples were extracted by a microwave assisted extraction system (Mars Xprees Xtraction; CEM, Matthews Corporation, North Carolina, USA). In the sediment, approximately 2.0 g of a sample in dry mass (d.w.) was added to 20 mL of the 8:2 n-hexane/acetone solution (v.v). The extraction occurred under medium agitation, with 800 W power and an initial temperature ramp of 30 °C for 2 min, increased to 120 °C (10 °C/min^{-1}) for 30 min. After extraction, the sediment samples were purified on SPE cartridges packed with 2.0 g of deactivated silica gel and 1.0 g of dehydrated anhydrous sodium sulphate, with portions of n-hexane and n-hexane/dichloromethane 1: 1 (v/v), concentrated to 0.2 mL in N_2, in a flow rate of 5 mL/min^{-1}, eluted to 1.0 mL in hexane for gas chromatography (GC) injection. For the extraction in fish, 5.0 g of the wet mass sample (wet weight, w.w) was added to 20 mL of the 20% n-hexane/acetone solution and washed via microwave assisted extraction under the same operating conditions as for the sediment extraction. For purification of the organic extract, the samples were subjected to an acid treatment, with the addition of 98% sulphuric acid to remove excess fat in the organic extract and filtered with anhydrous sodium sulphate to remove moisture. Then, the samples were concentrated to 2 mL on a rotary evaporator under vacuum, dissolved in 10 mL with n-hexane, and passed through a SPE-containing SPF column deactivated at 400 °C at a rate of 5 mL/min^{-1}. The analyte trapped in the cartridge was eluted with 5 mL aliquots of 2 mL n-hexane for recovery of the analytes and concentrated to a volume of 1 mL, in neat N_2 with a flow rate of 5 mL/min^{-1}, at 40 °C, for gas chromatography (GC) injection. The identification and quantification of the samples were performed by comparing the analytical standards.

A GC 3800 gas chromatograph (Varian, Palo Alto, MA, USA) equipped with an electron capture detector (GC-ECD) and the Workstation 5.0 software program were used for processing of the chromatographic data. A 30 m × 0.32 mm fused silica capillary column of internal diameter [i.d.] and 0.25 μm film thickness (OV-5; OHIO VALLEY Specialty Chemical, OHIO, USA) was used. The column oven temperatures were 150 °C for 1 min and 150–250 °C (6 °C/min^{-1}) for 5 min. The carrier gas was N_2 (99.999% purity) with a flow rate of 1.2 mL/min^{-1}. The injector was operated at 250 °C in the splitless mode and the detector temperature was 300 °C. The qualitative analysis for the confirmation of identified analytes was performed on a Mass Spectrometer TSQ 8000 (Thermo Scientific, Waltham, MA, USA) with a triploquadrupolo mass analyzer. It was operated in the full sweep, in the selected reaction monitoring (SRM) mode, and as equipped with ChromQuest 5.0 software program for data processing. A Silica capillary column of 30 m × 0.32 mm internal diameter [i.d.], 0.25 μM film thickness, TG 5MS, Thermo Scientific (Waltham, MA, USA) was used at 80 °C (1 min), 80–280 °C (13 °C/min^{-1}, 3.5 min). The carrier gas was helium (99.999% purity) at a flow rate of 1.0 ml/min^{-1}. The injector was operated at 280 °C in the split mode. The transfer line temperature was 275 °C, and the ion source was 260 °C.

The determination of HgT in fish muscles was determined based on the method described by Akagi et al.[32], where 2 mL of HNO_3 + $HClO_4$ (1:1), 5 ml of H_2SO_4, and 1 mL of deionized water were added to 0.5 g of sample and heated at 230 °C for 20 min, cooled to room temperature, diluted to 50 mL with deionized water, and analysed by atomic absorption spectrophotometry, with cold vapour generation, using mercury analyser Hg 201 (Sanso Seisskucho, Co. Ltd.).

Quality control

For analytical control, we performed blank analyses to test for interference in the samples and carried out recovery tests in triplicate on fortified samples and standard reference material (SRM 1944 NIST, SRM 1947 NIST, Gaithersburg, MD, USA), according to the method described above. Sediment was fortified at 50 μg/g, and fish were fortified at 100 ng/g of the pesticide mixture (op′- and pp′-DDT, DDE, DDD). The results for the fortified samples and standard reference materials ranged from 83.2% to 94.6% and 73.5% to 88.7% (sediment) and 89% to 112% and 80% to 102% (fish), respectively, which was within the acceptable limit for chromatographic tests (70–120%). We calculated calibration curves by external standardization with correlation coefficient (r) $\geq$0.99. The limits of detection and quantification of the method were calculated from three to five times the signal produced by the signal-to-noise ratio obtained at the baseline of the chromatograms and ranged from 0.01 to 0.05 μg/kg dry mass (dw) in the sediment samples and between 0.2 and 0.7 μg/kg wet weight (ww) in fish. For HgT in fish, the reference material DORM-2 (NRC-CNRC, Montreal, CAN) had an average recovery of 85% and the limit of quantification was 0.1 μg/g.

Ecological risk

To evaluate the ecological risk in the present study, the Canadian quality guideline values for sediments in aquatic environments were used.[33] This guideline recommends the use of the interim sediment quality guideline (ISQG) values and the probable level of effect (PEL). The ISQG represents the level below which adverse biological effects are expected to rarely occur, and the PEL sets the level above which adverse effects occur frequently. The guideline established where the ERL (low range effects) and ERM (mid-range effects) values were compared.[34]

Statistical analysis

Principal component analysis (PCA) was performed with the Minitab 17 software program, and differences in DDT concentrations among different fish species and sediment

samples were evaluated by analysis of variance (ANOVA), followed by the Tukey's post-hoc test using Statistica 7.0 vsoftware program, with the significance level at 0.05 ($P < 0.05$).

Results and discussion

DDT's distribution in sediments

In the Iriri River, total DDT levels in sediments varied between 11.58 and 48.43 ng/g, with a mean concentration of 23.82 ng/g (Table 1). The pp′-DDE, op′-DDT, pp′-DDT and op′-DDT metabolites were detected in 100% of the samples, whereas pp′-DDD and op′-DDD were only detected in 71% and 50% of the samples, respectively. The pp′-DDE metabolite had the highest contribution among DDTs (Fig. 2), due to its higher mean contribution (8.24 ng/g), followed by op′-DDE (6.21 ng/g), suggesting persistence and accumulation of this metabolite in the environment. The persistence of these hydrophobic contaminants in the surface sediments of the Iriri River, although they were banned in Brazil in 1997, indicates that these contaminants are still present in the river basin, which can be attributed to the DDT's slow degradation. DDT levels were higher in the present study than the limits established by Crommentuijn et al.[35], together with the Dutch government, for sediment quality assessment of 150 organic substances, including some pesticides, in soil, water and sediment, used to verify the maximum allowable concentrations, which were negligible in these matrices. In this case, the maximum allowable concentrations for pp′-DDE and pp′-DDT were 1.5 ng/g and 9.4 ng/g, respectively. In Brazil, the Brazilian National Environmental Council (CONAMA, 2012), the maximum values for sediment and two concentration levels were DDT (1.19–4.77 ng/g), DDD (3.54–8.51 ng/g) and DDE (1.42–6.75 ng/g). In the Iriri River, the DDE and DDT levels found were higher than the maximum allowable in 100% of samples, and the same occurred in 57% of DDD samples. These high levels may cause adverse effects on aquatic biota due to the toxic effects of DDT and metabolites on human health and environment.

The values reported in the present study were higher than those found by Wasswa et al.[36] with studied sediments from Lake Victoria, Uganda, where the levels of 16 organochlorine pesticides were monitored, taking into account the region's seasonality, and Li et al.[37] monitored the levels of DDT and other organochlorine pesticides in the Yangtze Statuary, China at different times, taking into account the seasonality of the region.

Table 1. Dichlorodiphenyltrichloroethane levels and metabolites in sediments (ng/g, d.w).

Sites	pp′-DDE	pp′-DDT	pp′-DDD	op′-DDE	op′-DDT	op′-DDD	DDT total
P01	6.72	1.72	n.d	2.31	1.77	n.d	12.52
P02	7.41	2.26	n.d	6.27	2.38	n.d	18.32
P03	7.83	2.34	1.14	2.80	2.16	2.03	18.30
P04	4.96	2.25	1.89	10.40	5.60	1.82	26.92
P05	13.96	3.82	4.70	4.58	4.80	n.d	31.86
P06	4.66	5.29	1.64	4.69	2.33	n.d	18.61
P07	15.59	9.96	5.23	11.42	4.58	1.64	48,42
P08	7.53	2.26	1.15	1.84	0.76	n.d	13.54
P09	2.68	1.83	n.d	4.96	2.11	n.d	11.58
P10	6.12	3.15	2.13	7.59	5.59	3.20	27.78
P11	6.88	2.64	n.d	2.80	2.82	1.08	16.22
P12	8.70	4.08	1.98	13.64	3.93	1.89	34.22
P13	16.38	4.41	1.96	5.60	2.65	1.33	32.33
P14	5.95	2.49	1.18	8.11	1.79	n.d	19.52
X ± SD	8.24 ± 4.14	3.46 ± 2.14	2.30 ± 1.45	6.21 ± 3.06	3.09 ± 1.53	1.85 ± 0.67	23.58 ± 10.46

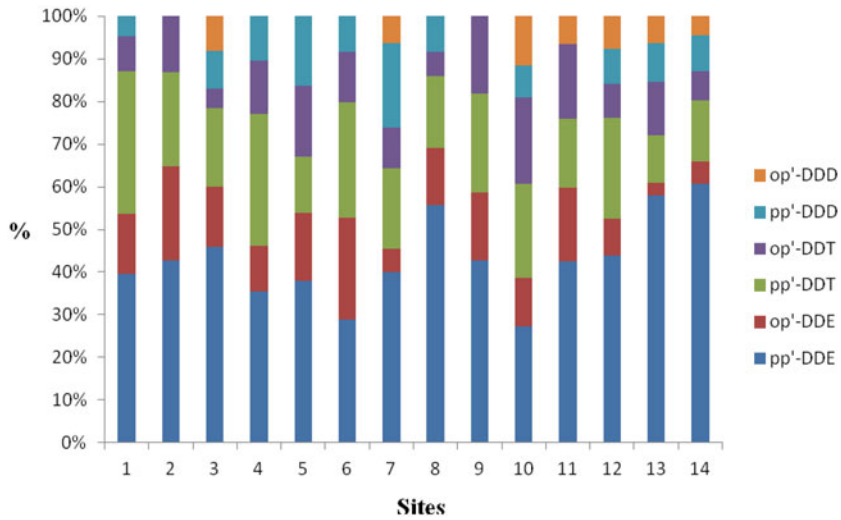

Figure 2. Contribution (%) of DDTs in sediment samples.

Table 2. Ecological risk assessment of Iriri River sediments using sediment quality guidelines.

OCPs	Faixa (ng g^{-1})	ISQG	↑ISQG (%)	PEL	↑ PEL (%)	ERL	↑ERL (%)	ERM	↑ERM (%)
DDE	9.35–27.01	1.42	100	6.75	100	2.2	100	27	7
DDD	0.00–6.80	3.54	36	8.51	0	–	–	–	–
DDT	3.49–14.54	1.19	100	4.77	50	–	–	–	–
∑DDT	11.58–48.42	–	–	–	–	1.58	100	46.1	7

In the Pearl River Delta, China, DDT and metabolites were monitored in several matrices for 20 years after the DDT ban, with a gradual decrease found over the years.[26] The values determined in the present study were lower than the values reported in rivers in an ecological savanna area in Nigeria.[38] Cal et al. [39] in Rio Cica, Spain found total DDT values between 9.0 ng/g and 93.9 ng/g. Silva et al.[40] studied the sediments of the Piracicaba River, Brazil, with maximum levels of total DDT being 20 ng/g.

In the Amazon region, a study conducted in the Tapajós River Basin at seven sampling sites found DDT sediment levels ranging from 3.2 ng/g to 61.5 ng/g in soil with higher levels (281 μg/kg to 1224 μg/kg), in an area of malaria control in the Amazon region, where DDT was used.[41] During the same study, sediments were analysed at seven sampling sites in the Madeira River Basin, Rondônia, with much lower levels (0.01 ng/g–1.1 ng/g) than the levels reported in the Tapajós River Basin. The distribution of total DDT in sediments at all sampling sites showed that the highest concentration was found at site 07 (48.42 ng/g). Several other points had high concentrations and the lowest value was found at site 09 (11.58 ng/g). In general, DDT levels increased from sites 01 to 05, and then variations occurred in the upstream direction of the river. This variation also occurred in the downstream direction of the river at sites 11 to 14. Several sampling site where concentrations were relatively high were close to areas that contained livestock and agriculture activities and were influenced by anthropogenic activities, and site 14 is located on the shores of an indigenous village.

The DDE + DDD/ΣDDT total ratio shows information on the identification of sources of pollution and is an indicator of the entry of DDT into the environment. A ratio of total DDE + DDD/ΣDDT greater than 0.5 indicates the long-term degradation of DDT to DDE and DDD, suggesting an earlier entry of DDT into the environment, whereas a ratio less than 0.5 might indicate recent DDT application.[42] In this study, the ratios varied between 0.59 and 0.80, indicating that there was no recent DDT entry at the sampling sites. Alonzo-Hernandez et al.[6] found DDE + DDD/ΣDDT greater than 0.5 at all sampling sites in the Gulf of Batanabó, Cuba. Lu et al. [43] also found high values of this ratio, indicating an ancient DDT entry in Lake Poyang, China.

Dichlorodiphenyltrichloroethane is degraded over time to DDE in aerobic conditions and DDD in anaerobic conditions.[44] Thus, the high proportions of DDE in the sediments of the Iriri River could arise from an aerobic form of DDT degradation. Oliveira et al. [45] also found that DDE was abundant in sediments of the Jaguaribe River, in the same aerobic conditions, in the semi-arid tropical region of Brazil.

Table 3. Total DDT levels found in each fish species from the Rio Iriri (ng/g, w.w).

Fish	pp′-DDT	pp′-DDE	pp′-DDD	DDT total
S. rhombeus	21.9 ± 9.7 (10.1–47.5)	28.5 ± 6.7 (15.3–38.1)	2.9 ± 1.8 (n.d–7.2)	53.3 ± 15.4 (28.2–83.1)
P. squamossissimus	41.4 ± 56.7 (5.2-228.2)	100.7 ± 81.0 (24.7-287.1)	9.3 ± 11.1 (0.5-35.4)	151.5 ± 141.7 (41.4-550.5)
Cichla sp	5.0 ± 11.3 (n.d–25.3)	18.3 ± 29.2 (2.2–70.5)	1.5 ± 3.3 (n.d–7.5)	24.8 ± 43.9 (2.2–103.3)
Serrasalmus sp	5.2 ± 6.3 (n.d–12.5)	11.1 ± 7.0 (6.4–23.3)	n.d	16.3 ± 11.5 (6.4–32.9)
P. hemiolioptemus	24.8 ± 9.5 (n.d–9.0)	80.6 ± 78.2 (44.2–170.3)	6.1 ± 8.1 (n.d–15.3)	111.5 ± 95.5 (43.4–220.7)
E. brasilianus	n.d	7.8 ± 2.6 (5.0–10.9)	n.d	7.8 ± 2. (5.0–10.9)

Ecological risk

As shown in Table 2, DDE and DDT exceeded the ISQG, PEL and ERL values in all samples except for the PEL, for DDT that was exceeded in half of the samples. For DDD, the PEL value was not exceeded in any samples. Thus, DDT and DDE were the contaminants that presented the greatest potential ecotoxicological risk in the region. Only sampling site 07 was above the ERM for total DDT; therefore, there is a moderate toxic effect on sediments in almost all of the studied region. In Brazil, the only official guideline to assess the risks associated with contamination with toxic substances is Resolution N° 454/2012 of the National Council for the Environment,[46] which provides the maximum values for DDT, DDE and DDD in freshwater sediments as being the same values for ISQG and PEL as the Canadian guidelines on sediment quality in aquatic environments.[45]

Levels of DDT in fish

The results of the DDT concentrations from all samples are shown in Table 3. The metabolites pp′-DDT, pp′-DDE and pp′-DDD were detected in 73%, 100% and 61% of the samples, respectively. The pp′-DDE metabolite is a pp′-DDT biotransformation product, has high chemical stability and environmental persistence, and was the most abundant metabolite found in the fish species in the present study, reinforcing the persistence of DDT in aquatic species. The order of concentration of DDT in fish was similar to the sediment samples with the pp′-DDE metabolite having the highest contribution (53.4–100%), followed by pp-DDT (22.2–41.1%) and pp′-DDD (5.4–6.1%). *Plagioscion squamossissimus* had a higher concentration of ΣDDT than that in the other fish species and is a highly consumed carnivorous species in the Amazon region. The species with the lowest concentration was *E. brasilianus* which is an herbivorous species.

The concentrations of total DDT in the studied fish muscles presented high variability in some species, such as

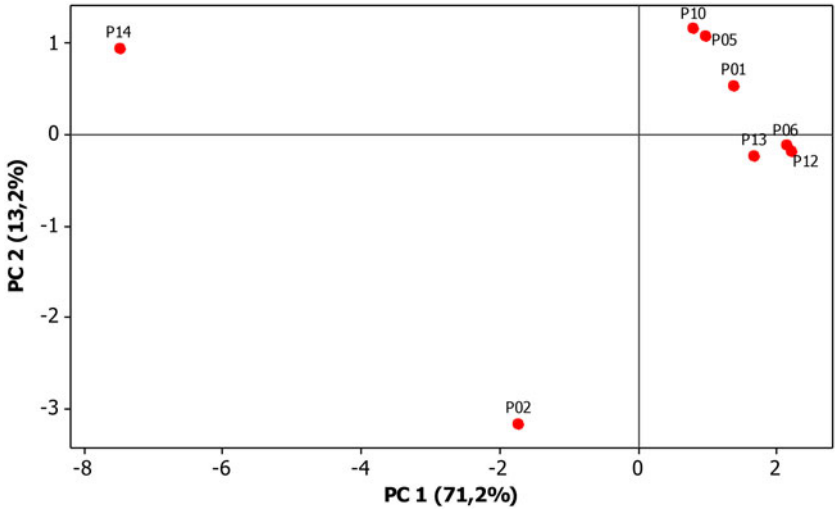

Figure 3. PCA relating the mean concentration of total DDT in fish of the Iriri River with the sampling points.

P. squamossissimus and *Cichla* sp., and a smaller variation in the species *E. brasilianus, Serrasalmus* sp., *P. squamossissimus,* and *P. hemiolioptemus,* which are at the top of the food chain and had the highest levels of ΣDDT, which indicated a possible accumulation of DDT along the food chain in these species.

Significant differences ($P < 0.05$) were found among the mean concentrations in *P. squamossissimus* and the other species studied. The concentration differences among the species studied might be related to age and migration of species. For example, although both species belong to the same genus, and have the same size and feeding habits, *Serrasalmus* sp. had concentrations of total DDT three times smaller than *S. rhombeus,* which might be related to the age of the analysed species. The geographical variation can be an important factor in determining the differences in concentration among species at different sampling sites, which might influence the accumulation of compounds studied. To verify if there were significant correlations between the concentrations of DDT among the different fish species at the different sampling sites, a PCA was performed as shown in Figure 3. Being a multivariate statistical technique, PCA analyses a set of quantitative data, allowing the reduction of the number of variables for a new and smaller set of variables, and shows any correlations with the original variable.[47] The matrices' correlation included concentrations of DDT and metabolites with eight variables corresponding to the sampling sites, where the fish and sediment samples were collected. We verified that in the present study the sampling site was an important factor for the determination of DDT concentrations, since there was a similarity among the concentrations of DDT at fish in 6 sampling sites (P01, P05, P06, P10, P12 and P13). The PC1 factor was the most important, corresponding to 71.2% of the data variation, which can be explained by the negative contribution of the pp′-DDE metabolite in the sediments at these 6 sampling sites. There was no similarity among the concentrations of DDT in fish and sediments at sites P02 and P14 with the other sampling sites. The second PC2 factor corresponded to 13.2% of the data variation, which was due to the higher concentration of pp′-DDE in the sediments and consequently in the fish at these two sampling sites. There were significant differences ($P < 0.05$) among mean concentrations of DDT and metabolites in fish at sites 02 and 14 with fish collected at the other sampling sites. These sites are distant from each other, with point 02 located at an isolated area with a dense forest vegetation and site 14 located in the nearby of an indigenous village.

This variation among sites displayed different levels of DDT based on spatial variation, and coincided with the highest levels of total DDT in fish collected at this sampling point (P14). In similar studies, Szlinder-Richert et al. [48] did not find significant differences among concentrations of organochlorine pesticides (DDTs, HCHs and HCB) in fish at six different sampling sites, with nine variables collected in the Baltic Sea. Yun et al.[49] indicated that most of the sampling sites (88%) in the study area in their study had the same potential source of organochlorine pesticides, with the historical input of use being the main potential source of organochlorine pesticides.

The ratio of DDE/DDT that established the recent arrival of DDT in the environment was high among the species and ranged from 1.12 to 3.22, suggesting an ancient contamination of DDT in all species studied. This ancient contamination could be related to the intense use of agrochemicals in the region in public health campaigns for years, which has contaminated most of the Amazonian environment.

The values of DDT and metabolites found in the Iriri River are lower than those found in the Tapajós River in the Brazilian Amazon.[50] Kalyoncu et al.[27] analysed 18 fish species in Konya, Turkey, and DDT levels ranged from 0.08 μg/kg to 71.7 μg/kg, with pp′-DDT levels higher than pp′-DDE levels. In addition, these authors detected the presence of other organochlorines such as HCH and isomers, dieldrin, aldrin, heptachlor and endosulfan and isomers. Dhananjayan et al.[51] found low levels of DDT when analysing 156 samples distributed in nine fish species in India, where DDT was banned in agriculture in 1985 but continued to be used for the control of malaria. Ondarza et al.[52] analysed the muscle and liver tissues of nine trout samples

Table 4. Weight, height and concentration (μg/g, w.w) of HgT in fish from the Iriri River.

Fish	*S. rhombeus*	*P. squamossissimus*	*Cichla* ssp.	*Serrasalmus* sp.	*P. hemiolioptera*	*G. altifrans*
Weight (g)	1003.81 ± 415.75 (180–2000)	803.52 ± 243.38 (500–1500)	846.66 ± 571.80 (150–2100)	650 ± 337.88 (300–1300)	20220 ± 11825 (3100–30000)	136.25 ± 43.4 (90–200)
Height (cm)	33.66 ± 5.28 (18.5–42.5)	38.28 ± 3.81 (33–50)	34.56 ± 9.01 (21–51.5)	29.57 ± 4.63 (24–38)	93.2 ± 22 (61–117)	16.93 ± 2.37 (14–21.5)
HgT	0.39 ± 0.23 (0.11–0.97)	0.22 ± 0.06 (0.12–0.37)	0.18 ± 0.09 (0.08–0.35	0.18 ± 0.09 (0.10–0.39)	1.82 ± 1.62 (0.15–3.76)	0.06 ± 0.02 (0.05–0.10)

in Patagonia, Argentina, with total DDT levels of 131 μg/kg and 139 μg/kg. The levels of DDT and metabolites found in fish species in the Iriri River are within the maximum residue limits established by national and international legislation.

Levels of total Hg in fish

The mean concentrations of HgT in all analysed samples of the six species that were studied showed great variation (0.06–1.82 μg g). The levels of HgT in fish muscle and their biometric data are shown in Table 4.

The species *S. rhombeus* and *Serrasalmus* sp., popularly known as "piranha preta" and "piranha camari", respectively, are very common species in the Iriri River. These carnivorous species have higher Hg levels than non-predatory species.[12] *S. rhombeus* had higher levels of HgT than *Serrasalmus* sp. The greater weight and length of *S. rhombeus* might have contributed to the higher concentration of HgT found in this species [17,53]. This species had mean values of HgT greater than the species in Amazonia, i.e., *Cichla* sp. and *P. squamossissimus*. Fish species that meet at the top of the food chain, such as piscivorous and carnivorous species, have higher Hg concentrations than species with another alimentary dietary habit. Bastos et al.[20] concluded that biomagnification was probably occurring in the food chain in the Madeira river.

The determination of Hg concentrations in fish muscle is important, considering that this is the edible part of the fish consumed by humans.[54] The omnivorous *P. hemioliopteus* species, although not at the top of the food chain like the piscivorous and carnivorous species are, had the highest average concentrations of HgT (1.82 ± 1.62 μg/g) and was also the largest fish collected. Larger fish have the ability to bioaccumulate levels of Hg in their muscles.[55] The mean concentration of HgT for *S. rhombeus* (0.39 μg/g), in this study, was higher than the mean concentration found in the Madeira River[20] and lower than the levels found in the Bacajá River.[56] In this latter study, HgT levels of *P. hemioliopteus* were lower than in the present study; however, the study contained a larger number of samples ($n = 31$) and covered a shorter average length. Although the Iriri River is distant from gold mines, was observed the presence of HgT in all analysed samples. Other studies have found high levels of Hg in fish in rivers distant from anthropogenic activities.[57,58] In the Amazon region, high levels of Hg have been found in the soils and their release into rivers is an important source of natural origin.[59,60]

Positive correlations were found between weight and HgT concentration ($r = 0.47$–0.93, $P < 0.05$) and between HgT size and concentration ($r = 0.41$–0.90, $P < 0.05$). Several studies have indicated that the concentration of HgT increases with increasing size,[61–63] whereas other studies did not find a positive correlation.[21,64] The length might suggest the age of the fish, with older fish having the highest concentrations of Hg, whereas the younger fish have the lowest.[53] Shao et al.[65] found a positive relationship between concentrations of HgT and fish weight, indicating that the weight in part influenced the HgT concentrations in the fish. Dos Santos et al.[66] found a positive correlation between Hg concentration and weight in two species of fish in the Amazon.

The mean concentration (0.47 μg/g) of Hg in all the samples studied in this study was below the limit for human consumption recommended by the World Health Organization, which is 0.5 μg/g.[67] Among the samples analysed, in this study, 11% were above the limit established by the World Health Organization.

Conclusions

This study evaluated the levels of contamination of HgT, DDT, and metabolites in fish and sediments in the Iriri River, which is located in the Brazilian Amazon region. To the best of our knowledge, this is the first study on the contamination of environmental pollutants in this study area. ΣDDT and HgT were found in significant concentrations in some samples at higher levels than what has been found previously in similar studies. Among DDTs, the metabolite pp′-DDE was the most predominant in the two matrices studied, which indicates the persistence of these compounds in the environment. The relationship between DDE + DDD/ΣDDT in sediments showed an ancient entry of DDT into the environment, which is associated with the historical use of DDT in the Amazon region. Based on the criteria of environmental quality in sediments, a low toxic effect was observed in almost all of the studied region.

Dichlorodiphenyltrichloroethane levels in fish are within the maximum residue limits established by national and international legislation. Positive correlations were found among weight, height, and HgT concentrations in fish samples, and only 01 species (*P. hemioliopteus*) presented a mean high concentration and one that was higher than the maximum levels required for human consumption by the World Health Organization.

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