Water and sediment pesticide contamination on indigenous lands surrounded by oil palm plantations in the Brazilian Amazon

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A B S T R A C T

Large-scale oil palm cultivation with intensive pesticide use has been growing worldwide and reached the Brazilian Amazon. The rapid expansion of this crop over the last decade has reached vast areas, including the boundaries of different indigenous lands. This study aimed at assessing the occurrence of pesticide residues in surface and ground waters as well as drainage sediments in the Turé-Mariquita Indigenous Territory, in addition to other nearby indigenous villages in the northeastern state of Pará. Thirty-three (33) water samples were collected from streams, springs and from active and abandoned wells at 19 sampling points, as well as 16 sediment samples at 9 sampling sites both during dry and rainy seasons. In total, 49 environmental samples were taken during fieldworks and subsequently analyzed by means of liquid chromatography and mass-mass spectrometry. The analytical determination of pesticide residues showed the occurrence of three pesticides in the water both from streams and from wells, two of them knowingly used by the oil palm company: glyphosate-based herbicides (GBHs) and endosulfan insecticides. Although the highest glyphosate and endosulfan levels as well as the maximum concentration of glyphosate found in ground water are within the Brazilian environmental regulatory guidelines, all the values for human consumption found in the glyphosate-containing samples are well above the European Union regulatory standards. Our results draw the attention to the risks of biota contamination and human exposure to multiple-pesticide residues.

1. Introduction

Environmental contamination by pesticides is a global critical concern because of the important toxic risks to biodiversity and human health [1,2]. Intensive agriculture constitutes one of the most important sources of pesticides to the environment due to the use of significant amounts of these compounds in this commodity production mode [3].

The Amazon is known to hold the largest portion of the world's biodiversity and is home to more than 300 indigenous peoples and forest-based communities [4]. Over the last decades, it has been undergoing rapid land-use changes as a result of the expansion of agricultural frontiers from Midwestern Brazil, mainly for feedstock and for biodiesel (i.e., soybean and oil palm) [5,6]. Oil palm (*Elaeis guineensis*) is one of the growing commodities in the Amazon due to supportive development policies, edaphoclimatic aptitude and the

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international market search for arable areas to supply increasing world demands [7].

The state of Pará, the second largest in Brazil, concentrates 90% of the national palm oil production in its northeastern portion, whose planted area has grown around 200% between 2006 and 2014, reaching 219,000 ha [8]. The expansion of the biofuel agro-industry has been exposing the Amazon biodiversity and vulnerable human populations to significant environmental health risks (e.g., indigenous peoples, riparian villagers and other traditional populations) due to the occurrence of several pesticides in ecosystems previously free of these contaminants [9–11]. This expansion poses underlying water contamination risks that can lead to loss of water quality for human consumption and even to ecotoxicological effects on aquatic organisms, both locally and regionally [12,13].

Some studies carried out in Brazil and other South American countries have initially shown the potential for displacement and accumulation of pesticide residues in rural and urban areas close to chemical-intensive monocultures such as corn, soybean, cotton and sugarcane [14–16]. Intensively cultivated areas and their adjacent regions have presented a broad spectrum of pesticide residues, sometimes concomitant in a variety of environmental compartments (e.g., soil, sediments, surface and ground waters, rainwater and atmosphere) [17–20]. The occurrence of pesticide residues in the environment has the potential to reach non-target organisms in the aquatic biota and to cause acute and/or chronic human exposures to these compounds and/or their degradation byproducts [21].

At least seven herbicides and sixteen insecticides are used in oil palm plantations in Brazil and other producing countries in different combinations [22,23]. Glyphosate-based herbicides (GBHs) are listed among the pesticides used in this crop in the state of Pará and are the most widely used herbicides worldwide, being at the center of the debate in the world scientific community about pesticide toxic risks, including their potential carcinogenic effect [24]. Of enough concern, residues of endosulfan, an organochlorine insecticide banned in Brazil since 2010, were recently found in a sediment analysis from oil palm-producing areas in the northeastern region of Pará (R. Mendes, Personal communication, October 2021).

The ecotoxicological risks for aquatic environments from the intensive use of pesticides in large-scale crops have been mentioned as potential environmental impacts in Brazil and other producing countries [25]. However, empirical studies of environmental pollution from pesticides applied on oil palm plantations in the main producing countries are rather scarce [22,23]. In fact, to the best of our knowledge, there are no scientific studies reporting data on pesticides in or close to oil palm plantations in Brazil.

This paper contributes data of pesticide analyses in water bodies from indigenous villages and their surroundings under the influence of oil palm plantations in Tomé-Açu, a municipality that is part of the major Brazilian production hub located in the northeastern state of Pará. Our objective was to analyze pesticides in water bodies and sediments from small springs and streams, and from wells both under use and deactivated, which correspond to the only water supply sources to the Tembé people in the Turé-Mariquita Indigenous Land (IL) and other surrounding indigenous villages from the Brazilian Amazon.
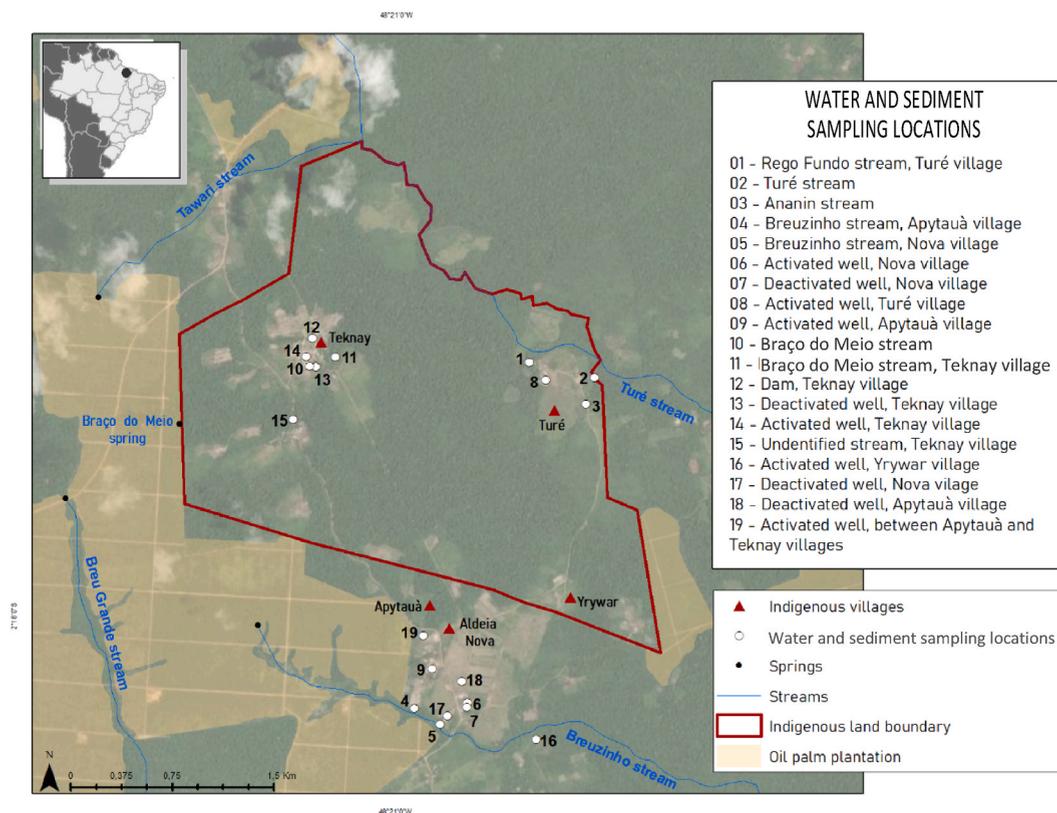

Fig. 1. Sampling points in Turé-Mariquita and surrounding indigenous villages in Tomé-Açú, Pará, Brazil. Sources: IBGE, INPE - Landsat 5 TM (2008, 2009 and 2010), Rapideye ETM+ (2011, 2012, 2013 and 2014) and INPE/Embrapa - Terraclass images (2004, 2008, 2010, 2012 and 2014).

2. Methods

2.1. Study area

The Turé-Mariquita Indigenous Land (IL) and two contiguous villages are located in the municipality of Tomé-Açu (2° 25′ 8″ S latitude, 48° 9′ 7″ W longitude), approximately 200 km from Belém, the capital city of Pará, in a region where cultivation of this oilseed is concentrated in Brazil. Around 130 Tembé indigenous people live in their protected area, a polygon of 734.8 ha with three inner villages (*Teknay*, *Turé* and *Yrywar*), and two surrounding villages (*Nova* and *Apytauà*), with 25 and 50 ha, respectively.

The surrounding area is characterized by forest remnants; vegetation in natural regeneration and an extensive oil palm crop, put in place between 2009 and 2010, when pesticide spraying was initiated in the IL boundaries and other surrounding indigenous villages. According to secondary data, around 6 L of glyphosate have been sprayed per hectare of oil palm planted area in a year to control weeds around palm trees, applied in association with other herbicides.

The monoculture area comprises 2287.8 ha within 5 km from the boundaries of the indigenous land. To put the crop in place, 333.8 ha of secondary forest in regeneration were suppressed [11], coherently with documented deforestation rates recently evidenced in eastern Amazon [28].

The water for human consumption and daily activities of these indigenous communities comes from small streams and artesian wells. Five streams traditionally used by the indigenous villagers (i.e., *Breuzinho*, *Turé*, *Breu Grande*, *Tawari* and *Braço do Meio*) have their springs within the crop upstream their protected land. The topography of both indigenous lands and their surroundings is predominantly flat with steep slope near the water courses. The soil in this basin has predominance of dystrophic yellow latosol and average annual rainfall of approximately 2500 mm [26].

2.2. Sampling

A total of 33 surface water samples were collected in streams and springs, as well as 16 underground water samples from active and abandoned wells at 19 sampling points (Fig. 1). In addition, 16 sediment samples were taken at 9 sampling points during the dry period in October 2016 and the rainy season between January and February 2017. Between the first and the second field campaigns, 5 new sampling points were added with the objective of expanding coverage of the study. The sampling sites were selected with the support of Tembé leaders, according to the importance of these water bodies for water supply and traditional use, and also considering the wide coverage of spatial distribution of water bodies in the region.

Surface and ground water samples were collected into 1-Liter sterilized amber glass bottles, identified on site and transported in coolers to the IEC laboratory, where they were stored under refrigeration until analysis. The sediment samples were collected with a

Table 1
Pesticides analyzed according to their toxicological classes, Limit of Detection (LoD) and Limit of Quantification (LoQ) for water (µg/L) and sediments (µg/kg).

Class	Pesticide	LoD	LoQ	LoD	LoQ
		(µg/L)		(µg/kg)	
Herbicide	Glyphosate + AMPA	10	50	–	–
	Molinate	0.001	0.01	0.2	2.0
	Alachlor	0.0005	0.001	0.2	1.0
	Atrazine	0.0002	0.001	0.1	0.5
	Pendimethalin	0.0001	0.005	0.05	0.1
	Metolachlor	0.0002	0.005	0.01	0.1
	Trifluralin	0.0001	0.005	0.05	0.1
Insecticide	Methyl parathion	0.001	0.005	0.01	0.1
	Ethyl parathion	0.001	0.005	0.01	0.1
	Methamidophos	0.0001	0.004	0.05	0.5
	DDT	0.0002	0.001	0.2	1.0
	DDE	0.0002	0.001	0.05	1.0
	DDD	0.0002	0.001	0.1	1.0
	Permethrin	0.2	1.0	0.05	0.2
	Lindane	0.0002	0.001	0.01	0.1
	Endrin	0.0002	0.001	0.1	0.5
	Dieldrin	0.0005	0.001	0.1	0.5
	Malation	0.005	0.01	0.01	0.1
	Acephate	0.005	0.02	0.05	0.2
	Aldrin	0.0005	0.001	–	–
	Chlorpyrifos	0.0005	0.001	–	–
	Endosulfan (α, β and salts)	0.0005	0.001	0.01	0.1
	Profenofos	0.005	0.01	–	–
Fungicide	Metalaxyl	0.001	0.01	0.15	1.0
	Tebuconazole	0.005	0.01	–	–

Glyphosate + AMPA: Ion chromatography.
Other pesticides: Gas chromatographer with a triple quadrupole mass spectrometer.

Van Veen dredge from 6 streams, along the water course and from the springs, where around 1 kg of each sample was stored in a chemically clean bag, identified and packed in polystyrene boxes until arrival at the laboratory. The samples were dried at room temperature and homogenization was obtained by using an agate grade. To obtain the fine fraction, around 100 g of the samples were disaggregated in ultrasound and then sieved through 200 μm mash with a stainless-steel sieve and stored in properly identified 30 mL acrylic tubes.

2.3. Chemical analyses

Selection of the pesticides to be determined was based on the list of compounds sprayed in oil palm plantations in Brazil and in other countries (Table SI1), and for which there were analytical protocols. The analyses also included part of the pesticides listed in Resolution No. 357/2005 of the Brazilian National Environmental Council (CONAMA), so as to broaden the coverage spectrum. In all, 25 active ingredients and their degradation by-products in water and 20 in sediments were determined in an IEC accredited laboratory (Table 1). For 7 of these compounds (i.e., Acephate, Aldrin, Chlorpyrifos, Metolachlor, Molinate, Profenofos and Tebuconazole), the analyses both in water and in sediments was only possible in the rainy season. Detection of GBHs was restricted to the water samples.

2.4. Analyses of water and sediment samples

The chemical analysis for GBHs in water was performed by means of Ion Chromatography in a Dionex Model ICS-3000 device, following the protocol developed by Ref. [27] and briefly described as follows: the samples were directly injected without pre-treatment within 48 h after field collection. The IC conditions were as follows: ION Pac AG19 column and AS19 analytical columns, ASRS-300 suppressor (2 mm); mobile phase: potassium hydroxide electronically generated with an EGC-KOH cartridge; gradient: 0–12 min: 8 mM KOH 12–16 min: 8–40 mM KOH 16–21 min: 40 mM KOH; Flow rate: 300 μL/min; and injection volume of 200 μL.

For the other herbicides and insecticides, a Gas Chromatographer with a Triple Quadrupole Mass Spectrometer (GC-MS/MS), model TSQ 8000 (Thermo Scientific) was used. The extraction was performed by means of a Solid Phase Extraction (SPE) system, which consisted in conditioning the SPE C18 column (1 g) with 10 mL of methanol followed by 10 mL of 30% methanol. In the preconditioned column, 1000 mL of the water sample were washed through the cartridge, washed with 2 mL of 30% methanol and followed by 2 mL of distilled water and vacuum-dried for 15 min. Elution was with 5 mL of ethyl acetate and storage in a centrifuge tube, proceeding to concentration in N_2 gas flow to 0.5 mL. After titration to 1 mL with ethyl acetate, a 1 μl aliquot was injected into GC-MS/MS.

Regarding the analysis of the sediment samples, a mass of 2 g of the fine fraction (P3) of each sample was conditioned into a 75 mL Teflon tube with 20 mL of 50% acetone/dichloromethane solution (organic extract). In a microwave device, the solution went through a heating ramp (30 °C–120 °C) for 30 min, with medium stirring and pressure of 800 w. The extract was cooled to room temperature and subjected to a clean-up procedure [28].

For the quantitative analysis, the GC-MS/MS Triple Quadrupole was equipped with a capillary column of 30 m × 0.25 mm of ID (Internal Diameter) and 0.25 μm of film thickness (DB-5). The oven temperature ramp for the column was programmed as follows: 80 °C for 1 min, 80 °C at 280 °C (13 °C/min) for 3.5 min. The carrier gas was He (99.999% purity) with flow of 1.5 mL min^{-1}. The injector was operated at 280 °C in splitless mode. The transfer line temperature was 275 °C and the ion source was at 260 °C, respectively.

Laboratory tests were performed with blanks to verify interference in the samples. Recovery tests were performed on fortified water and sediments. The recovery of pesticides in water was in the range of 78%–92% and in sediments it was between 83.2% and 94.6%, within the acceptable limit for chromatographic tests (i.e., 70%–120%). The calibration curves were made by external standardization with correlation coefficients (r) higher than 0.99. The method's limit of detection (LoD) was calculated from 3 times the signal produced by the signal-to-noise ratio obtained in the baseline of the chromatograms (Table 1).

2.5. Land use and cover 30 km around the IL

To examine the possible occurrence of additional commodities near the Indigenous Land, a 30 km buffer was employed along its boundaries. Within this designated area, the identification of other crops, apart from oil palm, was evaluated by using data gathered from the Mapbiomas collection 7.1 project and verified through analysis of available Landsat images specific to the region for 2014 and the present time.

Additionally, we visually inspected and adjusted the data to match them to the map scale to confirm that there was only oil palm planted around the IL. The data were downloaded by using the Google Earth Engine (GEE) app and the land use & cover classes were based on the collection legend table.

3. Results

The findings show the occurrence of three contaminants (glyphosate, DDT and endosulfan) both in water and in sediments at the Turé-Mariquita Indigenous Land and surrounding indigenous villages. Given the inexistence of other monocultures for any other pesticide-using commodities along a 30 km buffer of the studied indigenous lands, it is highly likely that all the pesticide residues reported in this study originally came from the surrounding oil palm plantations. The data analysis from the satellite images does indicate there are no large-scale plantations of other chemical-intensive monocultures (e.g., corn, soybean, cotton, rice and sugarcane) 30 km around the Indigenous Land (Fig. 2).

When considering the entire sample set, all six streams investigated in the indigenous areas and 40% of the wells showed residues of some contaminant in water and/or sediments in at least one of the seasons, which might constitute a risk factor for human exposure to these contaminants. The presence of residues in ground water is particularly worrying because this is the only alternative to direct water consumption from the streams.

Among the wide range of compounds, some contaminants were identified both in water and in sediments during the rainy and dry seasons, not only covering herbicide-based compounds of different generations but also organochlorine insecticides (Table 2). Despite some limitation related to the number of samples collected per sampling site in each season, it is worth noting that the sample design covered all the wells and the main streams under use by the indigenous villagers, as indicated by the Tembé leaders [11].

For the dry season, glyphosate presented a mean concentration of 29.4 ± 9.6 µg/L in water, and 30.5 ± 10.8 µg/kg for DDT in sediments. On the other hand, during rainy season we observed a mean concentration of 15.8 ± 4.4 µg/L for glyphosate in water, while for sediments DDT revealed a mean concentration of 26.5 ± 8.8 µg/kg.

Considering a total of 33 water samples from both seasons (surface and ground waters), 10 samples (30.3%) revealed residues for at least 1 contaminant. When all the samples were divided by season, a much higher percentage was observed for glyphosate in the dry season for water, reaching 50% of the samples (7), not observing any other contaminants. Furthermore, by stratifying all the water samples collected in the dry season (14) between ground water (6) and surface water (8), it can be seen that more than half of the ground water (66.6%) contained glyphosate, whereas 37.5% of the surface water samples contained residues of these herbicides.

In the rainy season, 19 water samples were collected in total (underground and surface), and pesticides were detected for at least 1 contaminant in 3 samples (15.7%). When stratifying the total samples of this season into underground (10) and surface (9) waters, a relatively lower number of glyphosate-containing samples were observed in surface waters (only 3 samples comprising 33.3%), in addition to 1 sample containing the endosulfan organochlorine insecticide (α, β and salts) (11.1%). No samples were found contaminated with any contaminant in ground water during this season.

Concerning the sediments, 12 samples corresponding to 75% of all (n = 16) for both seasons showed Dichlorodiphenyltrichloroethane (DDT) residues as well as of its degradation by-products: DDE and DDD. Endosulfan residues (α and sulfate) were also detected in 18.7% of the total sediment samples (3) and were only found in the rainy season. In the total set of water and sediment samples, opposite patterns of occurrence and residue concentrations were noticed among the insecticides. For instance, DDT and its derivatives were only found in sediments and had higher concentrations during the dry season, whereas endosulfan residues were detected in water and sediments only in the rainy season.

Glyphosate-contaminated water samples showed significant variation in their spatial distribution, according to the season (Fig. 3). During the dry season, the sampling points with glyphosate residues were distributed in water bodies and wells to the Northwest, South and Northeast areas of the indigenous territory, whereas in the rainy season the residues were only found in the Northeast portion. The
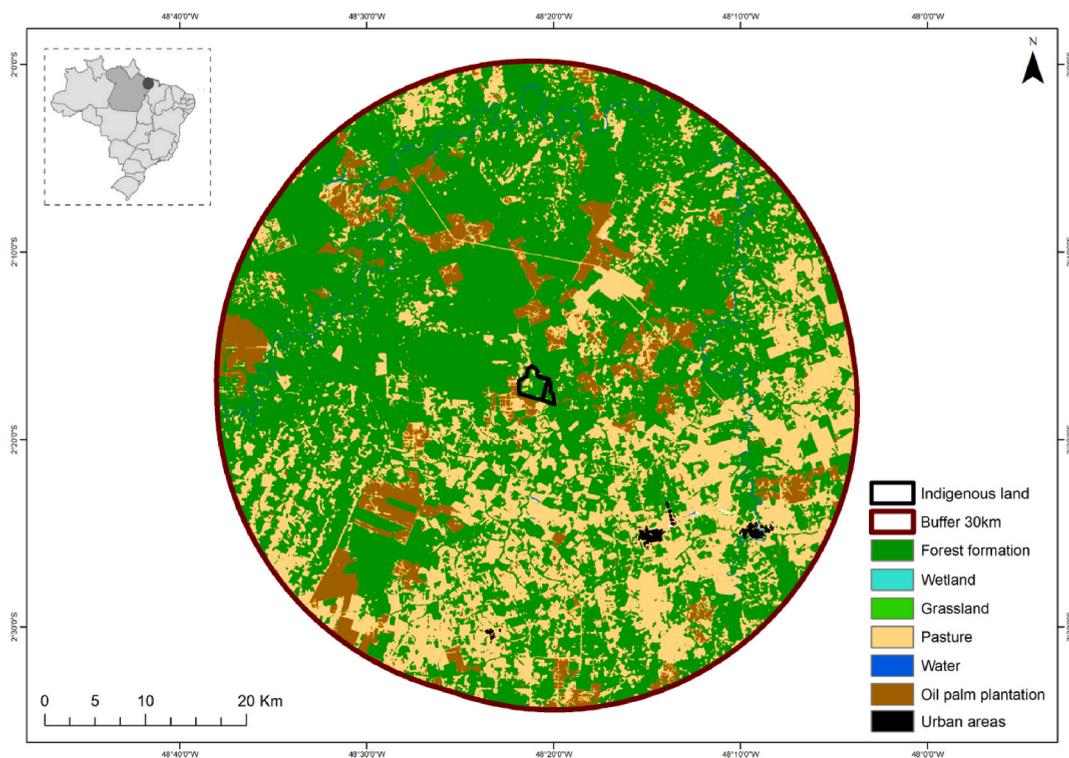

Fig. 2. Land use and cover within the buffer 30 km around the Turé Mariqurita indigenous land, Pará, Brazil. Sources: Mapbiomas col. 7.1 (2014), IBGE.

Table 2
Pesticide concentrations in surface waters, artesian wells (activated and deactivated) and sediments.

Sampling sites	DRY SEASON				RAINY SEASON						
	Water (µg/L)	Sediment (µg/kg)			Water (µg/L)		Sediment (µg/kg)				
	Glyphosate	DDT	DDE	DDD	Glyphosate	Endosulfan (α, β and salts)	DDT	DDE	DDD	α-endosulfan	Endosulfan sulfate
S1- Rego fundo stream, Turé village	<LoD	45.3	60.35	15.1	20.3	0.03	<LoD	<LoD	<LoD	<LoD	<LoD
S2 - Turé stream	<LoD	33.12	41.25	8.75	15.5	<LoD	29.94	6.12	17.13	<LoD	<LoD
S3 - Ananim stream	<LoD	22.45	19.5	<LoD	11.6	<LoD	<LoD	17	<LoD	<LoD	<LoD
S4 - Breuzinho stream, Apytauà village	45.5	<LoD	9.67	<LoD	<LoD	<LoD	13.35	9.85	6.43	5.44	<LoD
S5 - Breuzinho stream, Nova village	20.7	33.8	38.78	2.89	<LoD	<LoD	NC	NC	NC	NC	NC
AW1 - Nova village	25.1	NC	NC	NC	<LoD	<LoD	NC	NC	NC	NC	NC
DW1 - Nova village	18.8	NC	NC	NC	<LoD	<LoD	NC	NC	NC	NC	NC
AW1 - Turé village	29.9	NC	NC	NC	<LoD	<LoD	NC	NC	NC	NC	NC
AW2 - Apytauà village	27.1	NC	NC	NC	<LoD	<LoD	NC	NC	NC	NC	NC
S6 - Braço do meio stream	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	30.95	36.1	2.13	5.68	<LoD
S7 - Braço do meio stream, Teknay village	38.7	17.65	20.15	3.54	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD
D - Teknay village	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	31.62	6.5	1.66	<LoD	<LoD
DW2 - Teknay village	<LoD	NC	NC	NC	<LoD	<LoD	NC	NC	NC	NC	NC
AW3 - Teknay village	<LoD	NC	NC	NC	<LoD	<LoD	NC	NC	NC	NC	NC
S7 - Unidentified stream, Teknay village	NC	NC	NC	NC	<LoD	<LoD	<LoD	9.93	1.65	<LoD	20.68
AW4 - Yrywar village	NC	NC	NC	NC	<LoD	<LoD	NC	NC	NC	NC	NC
DW3 - Nova village	NC	NC	NC	NC	<LoD	<LoD	NC	NC	NC	NC	NC
DW4 - Apytauà village	NC	NC	NC	NC	<LoD	NC	NC	NC	NC	NC	NC
AW5 Between Apytauà and Teknay villages	NC	NC	NC	NC	<LoD	NC	NC	NC	NC	NC	NC

S – Stream; AW – Activated Well; DW – Deactivated Well; D – Dam; NC – Not Collected; <LoD – Below the Limit of Detection.
Only compounds for which positive samples were found are presented.

highest glyphosate concentration was found in the dry season, with a high value of 45.5 μg/L.

3.1. Spatial and time distribution patterns

The highest glyphosate concentration was expected during the rainy season due to more intense rainfall events favoring higher runoff but, instead, it was lower in this season as compared to the dry one. Additionally, in the rainy season the contaminated samples showed a diverse and more restricted occurrence pattern. Glyphosate residues in this season were detected in smaller number and only in streams from the Northeast zone of the indigenous land. In fact, the predominance of higher glyphosate concentrations in the dry season has been found in other studies in Mexico [29,30].

Two hypotheses have been raised to explain such pattern. First, during the rainy season, another herbicide might be used instead of glyphosate in some of the planting stretches at the boundaries of the indigenous land that showed no glyphosate in this season. Secondly, as it was not possible to obtain accurate information on the pesticide spraying date in the surrounding crops, another explanation would be the dilution of the pesticides by rainfall events prior to our sampling campaign. In such case, the second sampling could have been conducted after a greater dilution of the compounds carried by the soil during the rainy season before the samples were collected. According to Lupi et al. (2019) [20], 88.1% of the sprayed glyphosate is retained in the surface soil layer and dragged by runoff.

As for the other contaminants, organochlorine DDT revealed higher concentrations in sediments during the dry season (45.3 μg/kg), whereas another organochlorine, endosulfan, was detected in water and sediments only for the period of greatest rainfall, which suggests possible erosion and leaching to the water bodies with subsequent accumulation in the sediments of the streams.
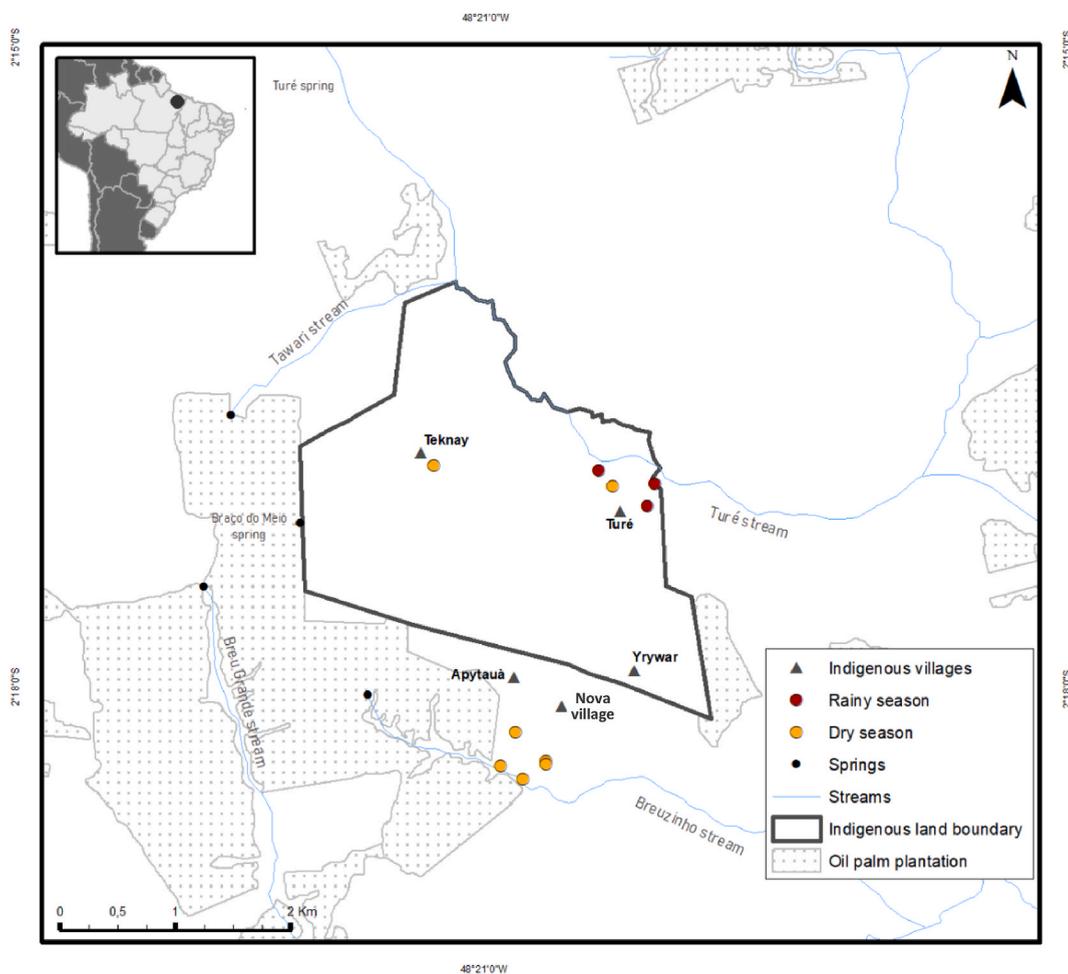

Fig. 3. Distribution of positive samples in water in the dry and rainy seasons. Sources: IBGE, INPE - Landsat 5 TM (2008, 2009 and 2010), Rapideye ETM+ (2011, 2012, 2013 and 2014) and INPE/Embrapa - Terraclass images (2004, 2008, 2010, 2012 and 2014).

4. Discussion

To the best of our knowledge, this is the very first study to determine the occurrence of pesticide residues in environmental samples from indigenous areas close to large-scale oil palm plantations in the Brazilian Amazon. There is limited research on pesticide pollution from this major crop that might pose a risk to surrounding indigenous settlements. Most of the current pesticide research is related to occupational exposures [31] and yet, environmental pollution from this crop is of international concern, as oil palm cultivation has been increasing in Africa, Asia and Latin America [32].

In fact, the most important finding of this study is identifying, for the very first time, glyphosate residues both in surface and in underground water samples on a law-protected indigenous land but heavily surrounded by oil palm plantations in the Amazon. In addition, our data show the presence of residues of other organic contaminants in the environment, not only in water but also in sediment samples collected in the same indigenous area.

Among the detected compounds, two are indicated to be used in oil palm crops: GBHs, which are systemic action organophosphorus compounds that have become the most used in the world; and the endosulfan organochlorine insecticide, which is also listed among those used in this crop (Table SI1). GBHs are used to control weeds around palm trees, with recommended spraying from three to five times a year depending on the crop development stage [33], although Mardegan et al. (2022) claim that such use would be made only twice a year [34]. On our end, during fieldwork we did observe this use would be made five times a year [11], clearly corroborating the findings of Gomes Junior (2010) [33]. Endosulfan is a product that has been banned in Brazil and gradually withdrawn from the market after Resolution No. 28/2010 issued by ANVISA - the Brazilian National Health Surveillance Agency.

Regarding organochlorine insecticide DDT, banned in the country between 1985 and 2009, in theory, its probable origin is the

Table 3
Examples of concentrations detected for GBHs, endosulfan and DDT in water (surface and underground) and sediments in previous studies in Brazil and other countries.

Location and environmental matrix	Crops	Product analyzed	Maximum concentration	Authors
Surface water				
Mexico	Not specified	GBH	510.46 µg/L (510.46 ppb)	Silva-Madera et al. (2021) [72]
Brazil	Citrus, coffee, corn, eucalyptus, soybean	GBH	11.33 µg/L	Correia et al. (2020) [73]
Brazil	Miscellanea	GBH	1.65 µg/L	Mendonça et al. (2020) [74]
Argentina	Soybean and corn	GBH	13.2 µg/L	Mas et al. (2020) [75]
Mexico	Miscellanea	GBH	4.33 µg/L	Reynoso et al. (2020) [30]
Brazil	Soybean	AMPA	1.93 µg/L	Passos et al. (2018) [16]
Colombia	Sugar cane	GBH	10.25 µg/L	Passos et al. (2018) [16]
Pará, Brazil	Palm oil	GBH	17.25 µg/L	Cruz and Farias (2018) [76]
Argentina	Soybean	GBH	1.600 µg/L	Avigliano and Schenone (2015) [40]
Mexico	Miscellanea	GBH	36.71 µg/L	Ruiz-Toledo et al. (2014) [29]
USA	Miscellanea	GBH	73 µg/L	Battaglin et al. (2014) [18]
Argentina	Miscellanea	GBH	7.60 µg/L	Aparício et al. (2013) [77]
USA	Miscellanea	GBH	430 µg/L	Coupe et al. (2012) [78]
Ethiopia	Miscellanea	Endosulfan	1.85 µg/L	Merga et al. (2021) [79]
Costa Rica	Melon and watermelon	Endosulfan	5.76 µg/L	Rodríguez-Rodriguez et al. (2021) [80]
South Korea	Miscellanea	Endosulfan	0.02 µg/L (2.1 ng/L)	Kim et al. (2020) [81]
Greece	Miscellanea	Endosulfan	0.241 µg/L	Kapsi et al. (2019) [82]
Costa Rica	Rice and sugar cane	Endosulfan	0.465 µg/L	Carazo-Rojas et al. (2018) [83]
Argentina	Soybean, corn and cotton	Endosulfan	0.10 µg/L (106 ng/L)	Bonansea et al. (2013) [84]
Mato Grosso, Brazil	Miscellanea	Endosulfan	0.94 µg/L	Moreira et al. (2012) [14]
Ecuador	Oil palm	Endosulfan	0.18 µg/L (0.00018 mg/L)	Núñez et al. (2009) [23]
Underground water				
Argentina	Soybean and corn	GBH	10.6 µg/L	Mas et al. (2020) [75]
Mexico	Miscellanea	GBH	1.18 µg/L	Reynoso et al. (2020) [30]
Mexico	Miscellanea	GBH	1.42 µg/L	Rendón-von Osten and Dzul-Caamal (2017) [85]
Colombia	Sugar cane	GBH	1.58 µg/L	Passos et al. (2018) [16]
Canada	–	GBH	0.66 µg/L (663 ng/L)	Van Stempvoort et al. (2016) [86]
Sri Lanka	Rice	GBH	3.5 µg/L	Jayasumana et al. (2015) [62]}
USA	Miscellanea	GBH	2.03 µg/L	Battaglin et al. (2014) [18]
Mexico	–	GBH	18.43 µg/L	Ruiz-Toledo et al. (2014) [29]
Sediment				
Pará, Brazil	Oil palm	Endosulfan	5.480 µg/kg (5.48 mg/kg)	R. Mendes (Personal communication, October 04, 2021)
South Korea	Miscellanea	Endosulfan	0.1 µg/kg (0.1 ng/g)	Kim et al. (2020) [81]
Costa Rica	Rice and sugar cane	Endosulfan	0.206 µg/kg	Carazo-Rojas et al. (2018) [83]
Pará, Brazil	Oil palm	DDT	65 µg/kg (0.065 mg/kg)	R. Mendes (Personal communication, October 04, 2021)

widespread use of this compound in the past for malaria control in the Amazon, when these compounds were not always properly stored [28]. Now classified as Persistent Organic Pollutants (POPs) by the Stockholm Convention [35], endosulfan and DDT are organochlorines with high toxicity and ability to bioaccumulate and persist for very extended periods of time in the environment.

In fact, DDT and its degradation byproducts (e.g., DDD and DDE) can persist for decades in the environment, and endosulfan (α, β and salts) can remain for up to two years in the soil [36–38]. GBHs have a longer half-life in soil than the one initially estimated, varying according to several factors (e.g., climate conditions, soil) from some days to almost one year [39]. A GBH degradation byproduct, Amino Methyl Phosphonic Acid (AMPA), has a half-life in soil with a similar variation to the compound of origin [18].

The maximum glyphosate concentration for surface waters in our study (45.5 μg/L) was much higher than the one obtained in previous analyses for areas under intensive soybean cultivation in the Brazilian Amazon, as well as from oil palm plantations in Ecuador [16,23], although surpassed by the levels of GBH residues recorded by Avigliano and Schenone (2015) in the San Antonio River in the highlands of the Argentinean province of Misiones (1600 μg/L) [40]. In contrast, the maximum concentration of these herbicides in ground water (29.9 μg/L) was higher than the one found in recent studies in Brazil and other countries (Table 3). This finding is supported by Góngora-Echeverría et al. (2019), who found evidence that glyphosate was prone to leaching, representing a threat for the ground waters in southeastern Mexico [41].

As for the insecticides, the maximum concentrations in water and sediments in our study were lower than the levels reported in recent studies. However, in neighboring municipalities of northeastern Pará, R. Mendes (Personal communication, October 2021) found residues of endosulfan and DDT and of their derivatives in sediments of palm-producing areas at levels much higher than those of the current analysis (Table 3).

Environmental characteristics (e.g., soil, topography, climate and hydrology) are factors that interfere with mobility of the contaminants [42]. According to field observations and satellite imagery, most of the water courses sampled upstream of the indigenous areas have their springs inside the corporate oil palm plantation, surrounded by and within few meters from the palm tree lines, little forest cover and slope towards the bed (Fig. 1). The high rainfall index of the area, proximity to the plantation and the slope towards the water bodies can favor surface runoff.

Pessoa et al. (2006) indicated yellow latosol, the type of soil predominant in our study area, among those with greater potential for ground water contamination because it favors leaching [43]. We highlight that the environmental characteristics of our study area along with the crops' location, i.e., in the boundaries of the indigenous land, are all favorable to the surface and underground dispersion of contaminants that should be the focus of further studies. Ground water monitoring should receive special attention because the community water supply wells had concentrations much higher than previous surveys in areas of agricultural influence in different countries (Table 3).

It is important to note that some indigenous families have started to spray small amounts of GBHs in pepper plantations, and their possible contribution to the presence of residues of these compounds within the indigenous land needs to be further studied. However, it is considered that this influence, if any, could possibly occur only in a small part of the samples, not explaining the overall scope of sampling sites with pesticide residues.

This assertion is corroborated by the fact that the presence of GBHs in wells and streams was found in areas within the indigenous territory without any use of this herbicide by the indigenous people. Other evidence is the complaints related to health problems (e.g., itchiness, headache, skin spots, rashes, vomiting) from the Tembé people after spraying pesticides in the large stretches of oil palm crop in the vicinities of the indigenous land and close to springs and streams traditionally used by them in the study locus [11].

The highest levels of pesticides found in surface water for glyphosate (45.5 μg/L) and endosulfan (0.03 μg/L), as well as the maximum glyphosate concentration found in groundwater (29.9 μg/L), are within the Brazilian environmental regulatory guidelines (i.e., CONAMA Resolution No. 357/2005), which establishes maximum values of 65 μg/L for glyphosate and of 0.056 μg/L for endosulfan residues in surface freshwater, suitable for human consumption with simplified water treatment and for recreational use, whereas CONAMA Resolution No. 396/2008 defines a maximum value of 500 μg/L for glyphosate residues in ground water.

The concentration of DDT and their degradation by-products found in sediments (DDT = 45.3 μg/kg; DDE = 60.35 μg/kg, and DDD = 17.13 μg/kg) far exceed the maximum permitted values of 4.77 μg/kg, 6.75 μg/kg and 8.51 μg/kg for dredged material, above which there is a higher probability of adverse effects on the biota (i.e., CONAMA Resolution No. 454/2012). For the endosulfan insecticide, there is no regulatory limit in the country for dredged material that can support critical discussions of the values found in our study area, at least from a regulatory perspective.

Although it is a reference source for the monitoring and legal protection policies, the wide discrepancy of regulatory limits across countries (e.g., glyphosate limits in water vary from 0.1 to 1000 μg/L) reveals the weakness of these regulations as exclusive guidelines of ecotoxicological and/or human health risk assessment [16]. If the most stringent European Community regulatory framework for GBHs (0.1 μg/L) was considered for comparison purposes, all glyphosate-contaminated waters from our study would be substantially above public health safety concentrations.

Synergistic, additive and antagonistic effects may occur in the interaction between multiple contaminants in the environment [39, 44,45]. Unexpected effects and damage to aquatic organisms have been identified when exposed to GBHs at doses below the lethality limit [46]. Herek et al. (2020) found that chronic exposure to GBHs in concentrations found in waters from Brazil can lead to death and malformations (e.g., shorter lengths and lower masses) on tadpoles from two South American native species: *Physalaemus cuvieri* and *P. gracilis* [47].

In addition, laboratory studies indicate higher toxicity for commercial formulations under use in agricultural areas when compared to the active ingredients alone [48]. Combined use of GBHs and methylsulfuron, two compounds knowingly used in oil palm plantations, in tests with sublethal concentrations (from 0.0097 to 160 mg) showed synergism in butyrylcholinesterase and acetylcholinesterase inhibition, as well as induction of genotoxic effects in *Rhinella arenarum* tadpoles [44].

The endosulfan insecticide is extremely toxic to aquatic communities, and toxic effects were indeed found in fish exposed to levels as low as 0.01 µg/L [49], that is, below the concentrations found in the waters analyzed in our study (0.03 µg/L). In addition, even sublethal doses suggest neurotoxic effects in fish [50] as well as alterations in growth and reproduction [51]. Concentrations below those tested in experimental studies may be toxic in smaller individuals living in water bodies with higher temperatures [52]. The Tembé people's perception is that fish became smaller and leaner in recent years [11].

According to Hernández et al. (2017) environmental or dietary sources can lead to human exposure to mixtures of pesticides in low doses, which can exert a long-term negative impact on health related to the increase in chronic and degenerative diseases, developmental neurotoxicity, and even cancer [45]. In addition to the risks of chronic exposure to low doses of multiple pesticides, both organochlorine insecticides detected in our study (i.e., endosulfan and DDT) have bioaccumulation properties in fat and animal and human tissues. All three pesticides found in waters and sediments are also endocrine disruptors [53,54].

A mix of pesticides in the environment may constitute a source of human exposure at concentrations that can reach levels higher than those of the environment because of magnification in wild animals consumed by the population. DDT and its degradation byproducts were already detected in dozens of Amazonian fish species that are part of the daily diet of traditional populations [55,56]. Miranda et al. (2008) found DDT, endosulfan and diuron residues, among other contaminants, in specimens of *Hoplias malabaricus* in natural environments, whose samples had liver lesions [57].

Ecotoxicological analyses conducted by Moreira et al. (2012) detected residues of up to 18 contaminants, including endosulfan and DDT, both with teratogenic potential, in blood plasma of *Rhinella schneideri* frogs and *Leptodactylus labyrinthicus* pepper frogs under environmental conditions, including individuals with appendicular malformations compatible with exposure to these pesticides [14]. Morphophysiological abnormalities in amphibians have been associated with GBHs at sublethal doses in laboratory studies [58].

Another aspect to be considered with possible implications for biota and/or human health in our study is the possible proliferation of cyanobacteria and the generation of cyanotoxins in streams, used for bathing, water supply and fish consumption. In fact, GBH concentrations from 5 to 10 µg/L served to modify the structure of phytoplankton communities [59], and studies in laboratory and shallow water bodies with GBHs showed repercussions both in terms of increase and reduction of different cyanobacterium species [60].

Regarding risks to human health, we highlight the occurrence of elevated concentrations of GBH residues in some of the ground water samples from wells that supply water for human consumption, with glyphosate values from 18.9 to 29.9 µg/L. Long-term laboratory toxicity studies in rats conducted by Mesnage et al. (2015) indicated that ultra-low doses (50 ng/L, equivalent to 0.05 µg/L) of GBHs in water can result in damage to the liver and kidneys, with potential implications for animal and human health [61]. High prevalence of renal problems among farmers in Sri Lanka has been associated with drinking water from wells containing metallic minerals and GBH residues, ranging from 0.7 to 3.5 µg/L, much lower than the concentrations found in most wells of our indigenous areas [62]. These research studies evidence the potential risks to human health associated with waters containing GBHs at low concentrations.

A number of studies indicate that oil palm production can be a reality with sustainable management, reducing or even eliminating dependence on the use of agrochemicals. Biological control of insects, manual trimming of understory vegetation and silvopastoral management practices with livestock integration are optional ways that oil palm growers can use to manage pests and weeds [34, 63–65].

In the conversion from conventional to organic plantations, chemical management of weeds is replaced by manual management, preventing agrochemicals from entering into the environment and human and animal exposure risks to these compounds. Mardegan et al. (2022) discovered that organic oil palm plantations in southeastern Amazon exerted an influence on the dynamics of the soil's organic matters, increasing carbon and nitrogen sequestration when compared to conventional farming [34].

Despite the benefits of adopting sustainable practices in the oil palm plantations close to the study locus, we acknowledge that there are several negative impacts perceived by the Tembé people related to the establishment of oil palm monocultures in the vicinities of the law-protected area that also need to be addressed, such as deforestation, degradation of springs, biodiversity loss, microclimate changes, proliferation of insects and snakes, and restriction of indigenous access to perform their traditional practices, as reported by Damiani et al. (2020) [11].

Oil palm production in biodiverse agroforestry systems with a chemical-free approach and combined with native vegetation is a feasible alternative to production and to preserve the provision of biodiversity and ecosystem services in degraded areas within buffer zones where conservationist production systems are allowed by law [66–68]. These measures for the sustainability of oil palm production might be viable management options in contrast to the intensive use of pesticides worldwide in oil palm plantations [69–71].

5. Conclusion

Our study shows the occurrence of pesticide residues in water and sediments from small streams within indigenous lands under the influence of surrounding oil palm monoculture, suggesting possible risks of ecotoxicological effects for the aquatic biota and human exposure of indigenous peoples living in their law-protected lands. Considering their traditional way of life in close relation with natural resources and their proximity to the oil palm plantations, these indigenous communities could be considered vulnerable to environmental exposure to multiple pesticides.

Given the current scientific framework on the possible risks associated with acute and/or chronic environmental exposure to pesticides, further ecotoxicological and human studies are advised. Our findings suggest that water resources used by other indigenous peoples neighboring oil palm monocultures should be investigated to better understand the dynamics of the contaminants in different areas with vulnerable populations.

Our results provide relevant information to address public policies related to the protection of indigenous lands and other vulnerable human settlements in the Amazon as well as other natural sensitive ecosystems in oil palm producing countries. Given the risks discussed in this paper, it would be recommendable to encourage productive activities not using agrochemicals in the buffer zone of law-protected areas and in the vicinities of traditional communities and peoples.

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Author contribution statement

Conceived and designed the experiments: Sandra Damiani and Carlos José Sousa Passos.

Performed the experiments: Sandra Damiani, Carlos José Sousa Passos, Maria Tereza Leite Montalvão; Rosivaldo de Alcântara Mendes and Amilton César Gomes da Costa.

Analyzed and interpreted the data: Sandra Damiani and Carlos José Sousa Passos.

Contributed reagents, materials, analysis tools or data: Maria Tereza Leite Montalvão; Rosivaldo de Alcântara Mendes and Amilton César Gomes da Costa.

Wrote the paper: Sandra Damiani and Carlos José Sousa Passos.

Data availability statement

Data will be made available on request.

Additional information

No additional information is available for this paper.

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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