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THE LEGACY OF PERSISTENT ORGANIC POLLUTANTS AT THE YANOMAMI INDIGENOUS PEOPLE LAND, BRAZILIAN AMAZON

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INTRODUCTION

During the twentieth century, a growing demand and supply of new chemicals has led to significant increases in the concentrations of these compounds in the environment, mainly through potentially polluting human activities (Almeida et al., 2007). Due to their low reactivity with the environment and high dispersion capacity, these substances are broadly distributed and found in all terrestrial and aquatic environments (Torres et al., 2002).

Among these chemicals, which affect ecosystems and cause negative impacts, are Persistent Toxic Substances (PTSs), characterized by high hydrophobicity, low reactivity in the environment and tendency to bioaccumulate in the tissues of organisms (Almeida et al., 2007). An important subcategory of PTSs are the Persistent Organic Pollutants (POPs), for they have having toxic properties, low reactivity in the environment, making them resistant to degradation, and prone to be bioaccumulative with high biomagnification potential along the food chain, as the proposed definition by the Stockholm Convention in May 2001 (UNEP, 2001).

Regarding POPs, the best known compound is Dichlorodiphenyltrichloroethane (DDT), which is considered one of the most used and studied synthetic substances in the twentieth century (D'Amato et al., 2002). This compound was widely used against pests in agriculture and farming, and to prevent endemic diseases around the world. In 1998, the Brazilian Ministry of Health stated that the use of this compound in the country was no longer allowed, but total ban only took place in 2009. The production of pesticides in industrial scales made Brazil one of the main exporters in South America (Almeida et al., 2007).

Although information about PTS contamination sources is considered scarce and generally is not available to the public, it is known that the massive use of DDT against the malaria vector had a great impact on the incidence of this disease in Brazil. However, in the Amazon region, this type of control, based solely on spraying pesticide directly on houses, was not as effective as in other regions of the country.

The Yanomami indigenous people are nomadic people who depend on hunting and occasionally fishing for subsistence. They inhabit the tropical rain forests of southern Venezuela and the Brazilian north of the Negro River, as well as the northwest part of Roraima State.

MATERIALS AND METHODS

Our study area was chosen due to a behavior change of Yanomami People in recent decades. Many settled in the Ariabu and Maturacá communities, both growing on the border of the municipalities of Santa Isabel do Rio Negro and São Gabriel da Cachoeira, in the state of Amazonas, Brazil.

Topsoil (n=5) and fluvial sediment (n=5) samples were collected at the Yanomami territory, in Ariabu and Maturacá (Table 1). The samples were collected using a metal spoon, cleaned using acetone and stored in glass jars previously cleaned at the laboratory. Extraction was done in a Soxhlet system using 3g dry weight, particle size <0.0212 mm, using 120 ml of dichloromethane for 12h. The extract was concentrated in a rotary evaporator to about 1 mL before being purified, in order to remove interfering substances, such as elemental sulfur and humic material, mainly present in anaerobic media, such as sediment samples. It was held in open chromatographic columns filled with 7g of a desulfurizer agent eluted with 15 ml of n-hexane to clean it (discarded). The concentrated sample was transferred to the top of the column, where it stayed for 15 minutes before being eluted with 20 ml of n-hexane. Finally, the samples were concentrated to 0.5 ml by rotary evaporation and nitrogen stream, respectively, and swelled to 1 ml with 0.5 ml internal standard solution (TCMX).

All analyses were performed in a gas chromatograph coupled with an electron capture detector (GC-ECD, Shimadzu – 2010, 63Ni). The injections of 1µl were applied with the gun operating without flow divider (splitless) for 60 seconds, at 270 °C. The carrier gas used was ultrapure hydrogen, with purge flow of the septum equal to 10 ml/ min. The temperature of the detector was kept at 310 °C and the auxiliary gas (make-up) used was ultrapure nitrogen (99.999%) with a flow of 45 ml/min. The program used started at 80 ºC, remaining for 1 minute. Then, temperature was raised to 5°C/min up to 205 °C, and kept constant for 15 minutes. After this period, temperature was raised again to 240°C at a rate of 2 °C/min, and then to 290°C, increasing at 25 °C/min, and held for 10 minutes. The total programming time was 70.50 minutes.
To ensure the reliability of our results, recovery patterns (PCB 103 and PCB 198) were added to each sample analysis in the beginning. Recoveries ranged from 78% to 112%. Furthermore, blanks were used in each analytical batch for contamination control; quantification limit was the mean of blanks and three times the respective standard deviations for each compound.

RESULTS AND DISCUSSION

Preliminary results, concerning 5 samples of soil and 5 samples of sediments, demonstrate that the most prevalent compound in contamination in all matrices is still DDT, and that it is present at higher total concentrations in soil samples (0.19 to 770.30 ng/g) than in sediment (0.10 to 871.29 ng/g). The same proportion was observed for soil and sediment from riverine communities of the Rio Negro and Puruzinho in a previous study (Guida et al., 2013). However, when grouped together, the sum of pesticides has a higher contribution to contamination in these matrices than the sum of DDT and PCB isolated (Figure 1).
"Sed C" was the sampling point with the highest concentrations of organochlorine pesticides. It was followed by "Soil 1" and "Soil 2", which were collected near houses, confirming the use of pesticides, applied directly on walls, as the main source of soil contamination, as reported by Mendez at al (2015). The main component of the commercial DDT formula (p,p' DDT) is still the most commonly form found in soils of the Yanomami territory, indicating that, due to its massive use and difficult degradation, these soils have become hot spots and secondary sources of pollutant emission into the environment (Figures 2 and 3)
As to other particular pesticides, compounds found in higher concentrations were Heptachlor (1.66 to 61.70 ng/g) and Methoxychlor (0.31 to 30.04 ng/g), respectively. They are mostly found in sediment samples. PCBs were present in concentrations ranging from 0.12 to 101.03 ng/g, and the lighter congeners, or with fewer chlorides, prevailed in the total contamination.
At Rio Ariabu ("Sed C"), the closest point to the communities, high concentrations of chlorinated pollutants in sediments (Figure 1), and especially p,p' DDT (Figure 2), were also found, indicating a possible soil leaching process from nearby houses to the river.
"Sed E", a sediment point collected from a small river inlet near the community, had lower organochlorine concentrations. This point lies at an elevation of 30 meters above the point where soils were collected in the village, which may corroborate the hypothesis of the effect of the bleaching process in the transport of pollutants from the community to the river, since Ariabu River is located on a topographic level below the points where soils were collected.
DDT is the compound found in greater concentrations, thus demonstrating that the Yanomami community is exposed to this contaminant from various sources, even today. Moreover, it is possible to see the difficult degradation of this compound, due to the greater presence of p,p' DDT (Figure 2), or, as shown in a recent study, it is possible that DDT has been used recently, after its ban, in the Brazilian Amazon (Mendez et al., 2015).
The analyses of abiotic samples from the Yanomami territory in the Brazilian Amazon proves that, even today are probably sprayed with insecticides to combat vectors of endemic diseases exposing people to contaminants through various sources, with levels in the same order of magnitude observed in the literature (Table 2).
More studies are needed to understand the behavior of DDT in this environment and its consequences for the local population. The continuation of this work is critical to understand and monitor the health of the Yanomami Indigenous people and their environment.

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Table 1: Sampling points and their coordinates

Sampling Points	Coordinates
Soil 1	00°37'40.7'' N 66°08'06.0'' W
Soil 2	00°37'41.4'' N 66°08'07.1'' W
Soil 3	00°37'40.9'' N 66°08'05.1'' W
Soil 4	00°37'40.8'' N 66°08'05.2'' W
Soil 5	00°37'39.6'' N 66°08'17.9'' W
Sed A/Sed B	-
Sed C	00°37'47.5'' N 66°08'04.3'' W
Sed D	00°35'43.9'' N 66°00'30.6'' W
Sed E	00°37'28.5'' N 66°08'32.4'' W

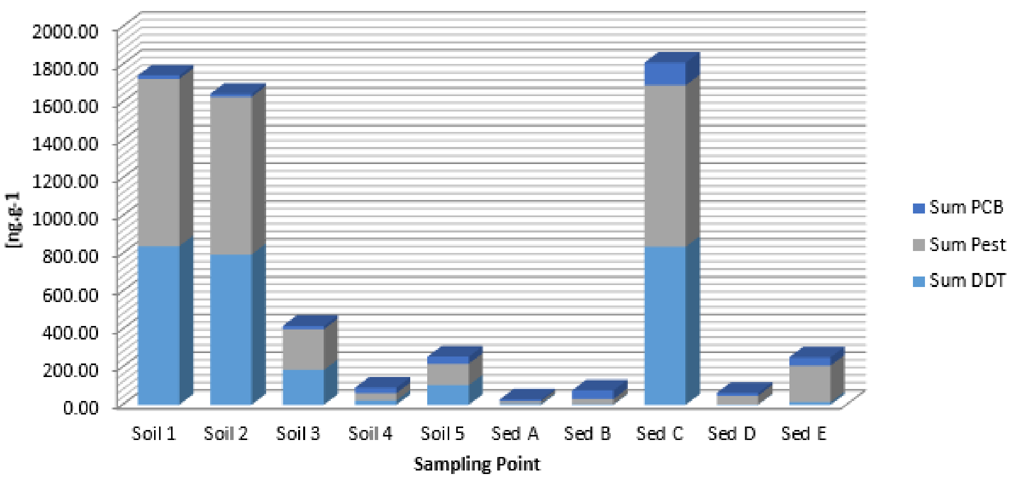

Figure 1: Contribution of PCB, DDT and other pesticides to overall contamination.

Figure 2: Concentration of each DDT congener DDT found in soil and sediment samples

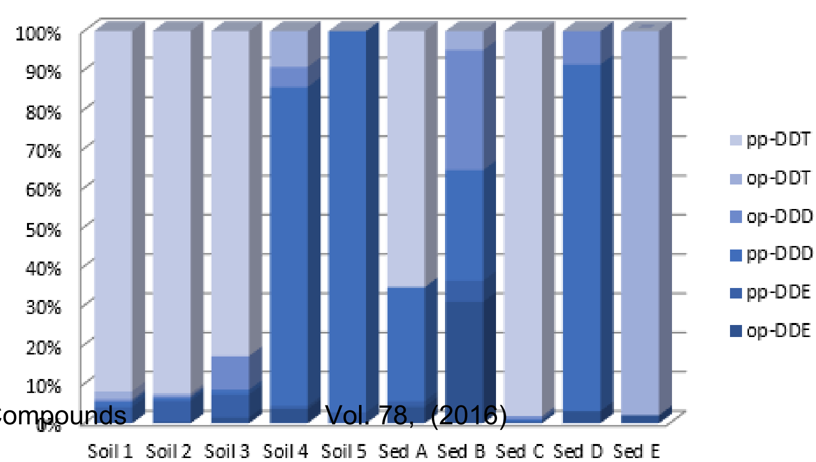

Figure 3: Contribution of each congener to total DDT

Table 2: Comparison of levels (ng/g) of DDTs in soil and sediment samples from different countries

Sediment			o, p DDE (ppb)		p, p DDE (ppb)		o, p DDD (ppb)		p, p DDD (ppb)		o, p DDT		p, p DDT (ppb)		ΣDDT (ppb)		N. Samples	Location
Author	Type	Year	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range		
Tolosa et al.	Soil	2005			1.21	0.16 - 3.72			0.48	0.09 - 1.60			0.87	0.01 - 9.58	2.57	0.25 - 12.79	17	*Cienfuegos bay, Cuba*
Yang et al.	Soil	2008	29.19	0.005 - 600.35			3.19	0.005 - 185.96			13.18	0.010 - 322.31	22.07	0.010 - 521.24	68.14	0.030 - 1282.58	8	*Beijing, China*
Mishra et al.	Soil	2010	13.9	0 - 31.7	89.55	4.35 - 388.5			26	0 - 131.85	48	0 - 196	137.5	9.2 - 472.5	315	70.8 - 742.5	68	*North-East India*
Marc S. Humphries	Soil	2012	13.83	0 - 42.8			27.46	0.8 - 74.1			1.86	0 - 6.2			43.19	0.8 - 123	11	*Lake Sibaya, South Africa*
Torres et al.	Soil	2015	0.77	0.26 - 2.00	0.61	0 - 2.80	1.7	0 - 7.0	1.77	0 - 3.11	2.8	0 - 13.85	165.17	0 - 821.79	172.87	3.95 - 836.76	5	*This Study*
Booij et al.	Sediment	2005			67.66	4.22 - 409.36			15.59	2.5 - 78.96			264.28	4.8 - 2640.26	347.55	17.24 - 2640.26	10	*Northern Oman*
Muñoz-Arnanz et al.	Sediment	2007	0.03	0 - 0.25	1.17	0.02 - 8.7	0.12	0 - 2	0.11	0 - 2.57	0.04	0 - 0.44	0.32	0.01 - 2.18	1.79	0.08 - 11.1	32	*South-western Spain*
Yi et al.	Sediment	2009	0.052	0 - 0.30	0.13	0.010 - 0.74	0.049	0 - 0.15	0.17	0.016 - 0.76	0.45	0.070 - 1.4	0.16	0.017 - 0.45	1	0.24 - 2.8	20	Fujian, China
Wang et al.	Sediment	2011	0.0095	0 - 0.097	0.728	0 - 17.1	0.029	0 - 0.091			0.305	0 - 4.56	6.65	0 - 21.3	1.36	0 - 41.6	60	*Tibetan Plateau, China*
Torres et al.	Sediment	2015	1.7	0 - 3.19	17.98	0.19 - 42.37	5.16	0 - 15.88	27.85	2.17 - 100.94	4.83	0 - 17.21	331.48	0 - 734.62	389.03	23.43 - 838.65	5	*This Study*

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