

POPs IN THE AMAZON: CONTAMINATION OF MAN AND THE ENVIRONMENT

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Abstract

The organochlorine insecticide DDT was extensively used in Brazil since 1945, both for agricultural purposes and for vector control measures. In 1986 its uses were forbidden in agriculture and in 1997 it was phased-out also in vector controls programs. However, the presence of DDT in urban and forested soils, breast milk and aquatic biota is still common especially at the Amazon. The results gathered since the middle of the 90s indicate that the environmental contamination with this pesticide is still relatively high. Due to the high fish consumption by riverside traditional populations, the human breast milk may represent an important source of DDT exposure to newborns. New results on DDT and PCBs in the red dolphin (*Inia geoffrensis*), an endemic aquatic mammal of the Amazon region, is also reported.

The Intoxication of the Amazon, Brazil's University Actions and the IPCP initiative

Our compromise is to provide reliable scientific information in order to subsidize the government with information regarding the overall aspects of chemical pollution. The problem of pollution is often mistreated in developing countries because large parts of the population are not aware of the risks associated with the use of chemicals. Brazil's Universities can deal with different aspects of pollution, especially in the Amazonian Terrestrial as well as Aquatic Environments. Estimation of heavy metal burdens and of the presence of different POPS (Persistent Organic Pollutants) in human beings and biotic and abiotic materials are important actions relative to two classes of substances whose measurements and related educative topics may exert influence on the future discussion of the IPCP initiative. Brazil stopped to use DDT against malaria and other disease vectors in 1997¹. However, malaria cases are around 500.000 per year with 99% of cases in the Amazon Region. To face these problems we need to cooperate to combat the detrimental impact over the environmental health of past and present land uses in the last largest rainforest of the world. The importance of this endeavor is clear and we ought to struggle and help to change this situation, working together in a cooperative and friendly basis. There is need for modernization in several laboratories and acquisition of new equipment is a very important issue for Brazilian Laboratories (e.g.: GC-MS/MS and Isotopic Dilution Techniques). We will need resources to buy modern chromatographs and there is huge necessity to train skilled people in this machines operation. The exchange of people and researchers may help to diminish the effects of some of these problems. The most urgent needs are for funds for fellowships that must be supplied without too much paperwork, besides being able to buy new equipments. We think that we ought to invest in human resources formation and combat the brain drain. Taking this in account, we must to make easier for researchers of different parts of the world to maintain and cooperate with our Brazilian Institutions.

Energy and Politic related issues related to Environmental Pollution in the Near Future of the Amazon in Brazil (Dam the Rivers, Damn the People and the Environment)

In July of 2007 the Brazilian Environmental Authorities, after a long and rather confuse process, has decided to liberate the permission for the construction of two new Hydroelectric Power Plants in the Madeira River at Rondonia State². The Madeira River is the main tributary of the Amazon River in its right margin and represents 15% of the water and 50% of the sediments that are discharged by the Amazon River at its mouth on the Atlantic Ocean. This new projects will generate together 6.450 MW of Electricity (8% of Brazil annual needs). These enterprises will be constructed over one of the oldest gold mining areas of the Brazilian Amazon where mercury was intensely used for decades. They also represent a threat against the reproductive migration of 40 species of giant catfishes. This energy will be used to expand the exploration of metallic ores of this state, especially for Sn enriched minerals. This approach aims to develop and industrialize the southern part of the Amazon where deforestation for soybean plantation, timber production and cattle grazing has completely destroyed almost 30% of the whole

Amazon region. Besides CO₂, the burning of the forest may be also releasing PAHs to the atmosphere. Taking in account that our country, although having a good set of environmental laws, we lack almost completely an efficient law enforcement and do not have enough trained people nor have enough equipped laboratories to cope with this huge challenge of protecting and controlling the overall impact of this enterprises over the last large rainforest of our planet. Brazil needs to grow, but we have to act now in order to mitigate the impacts over nature in order to protect the rights of the next generations to have available the environmental services offered by the forest in controlling the climate by releasing condensation nuclei for the formation of tropical rains and gendering moisture to a great extend of South-American atmosphere

Material and Methods

Abiotic materials (e.g.: soils and river sediments) and biotic samples were collected at different parts of the Amazon, especially at the Madeira River basin. The initial collection of fishes and hair samples started in the beginning of the 90's in order to access Hg contamination in a fruitful academic cooperation whit the Rondonia Federal University, which is maintained 'freeze-dried' over the last 20 years. The studies with DDT and PCBs started around 1998 and were supported in part by The Mount Sinai School of Medicine (New York – USA). Huge hydroelectric power plant man-made lakes located at three different Amazonian States (Amazonas – Balbina reservoir, Para – Tucuruí reservoir and Rondonia – Samuel reservoir) facilities were also visited between 1995 and 2005. The following certified materials were used (NIST- SR1588, Cod Liver Oil). The Radioisotopes Laboratory participated with good Z scores in IAEA inter-comparison using IAEA435 (Tuna fish). For the analyses of organochlorine pesticides and PCB congeners, conventional and modified Soxhlet extraction using non-polar solvents were employed. For abiotic materials, especially for river bottom sediment samples and desulphurization method based on the Jensen reaction was developed after Japenga et al³. Milk samples were extracted using C-18 SPE and Florisil cartridges using a SUPELCO vacuum manifold. The extracts were submitted to an acid clean-up using concentrated sulfuric acid. We used a Shimadzu CG-14B with 60 m capillary DB-5 column coupled to a ⁶³Ni Electron Capture Detector (ECD). Identification was based in the relative retention times using octachloronaphthalene – OCN as an Internal Standard, that was also used for quantification based on calculated standard solutions response factors.

Results

Soils: The concentrations of Σ DDT (*o,p'*-DDE + *p,p'*-DDE + *p,p'*-DDD + *o,p'*-DDT + *p,p'*-DDT) on house soils varied from 2.0 a 55.4 ng g⁻¹ while forest soils the obtained values were between 1.6 e 13.3 ng.g⁻¹. The *p,p'*-DDD / *p,p'*-DDE ratio in house soils (mean= 3,85) and for forest soils (mean= 1,87) were high when we compared this results to a previous work⁴ at a location with a known history of DDT utilization. In this work, surface soils were collected at rural areas of Jacarepagua, located at Rio de Janeiro city were 0,06 (1997) and 0,09 (1999). Our study confirms the previous work of Parr and Smith⁵ and Ramesh *et al*⁶ that had demonstrated that the DDT degradation to DDD is mediated by anaerobic bacteria and fungi working in reductive environments, that may be the case of the Amazon soils during the rainy season. The DDT/DDE ratio can be used as an estimative of the time trend of DDT application. The present study of the Puruzinho Lake we have found mean ratios of 1,86 for the house soils and 0,85 for the forest soils. The mean value for the soil of the houses is similar to the one found by Vieira and co-workers⁴, 1.91 in 1997 and 1.19 in 1999. However these results are higher than the previous ratios reported by Torres *et al*⁷, in a study urban soils collected in some towns along the Madeira river. These high ratios may be due do recent reported uses of DDT against termites that commonly attack the local wooden houses. The DDT concentrations at both forest and house soils are irregularly distributed showing a somewhat erratic distribution and behavior of pesticide in the study area.

DDT in Amazon Fish (1990-2005): As the fish samples come from very different locations and may have different food habits, the average exercise presented here must be interpreted with caution. However, such kind of approach may be considered as 'eye-opening'⁸, since a somewhat decreasing time trend was observed. This is an indicative of DDT clearance in the Amazon fish biota. As all samples were freeze-dried, the results are in µg g⁻¹ (dry weight). The average and standard deviations of total DDT levels are: 1990 = 49.9 ± 17.4; 1991= 54.4 ± 108.8; 1992= 20.3 ± 17.9; 1993= 23.19 ± 54; 1996= 10.1 ± 64.3; 2000= 3.9 ± 40.2; 2002= 6.15 ± 2.5. The declining trend can be seen at Figure 1.

DDT in Amazon breast milk: All of the chromatograms of the breast milk samples showed residues of DDT and its metabolites in all analysed samples. The concentration ranged from 10.7 to 7272 ng g⁻¹ of lipid for *p,p'*-DDE, from near limit of quantification to 400.7 ng/g of lipid for *p,p'*-DDD, from 3.0 to 2534 for *p,p'*-DDT, and 25 to 9362 for total DDT. The Figure 2 shows the distribution of average and geometric mean of the total DDT values in the different studied localities. The obtained geometric mean of the total DDT in the different studied localities ranged from 118.3 in Santa Rosa to 1005 ng of total

DDT/g of lipid in Cachoeirinha. Geometric mean of total DDT/g of lipid of the localities showed a good correlation ($r = 0.993$) with the average values. The geometric mean/average ratio was 0.76. The overall results on breast milk contamination are expressed in Figure 2.

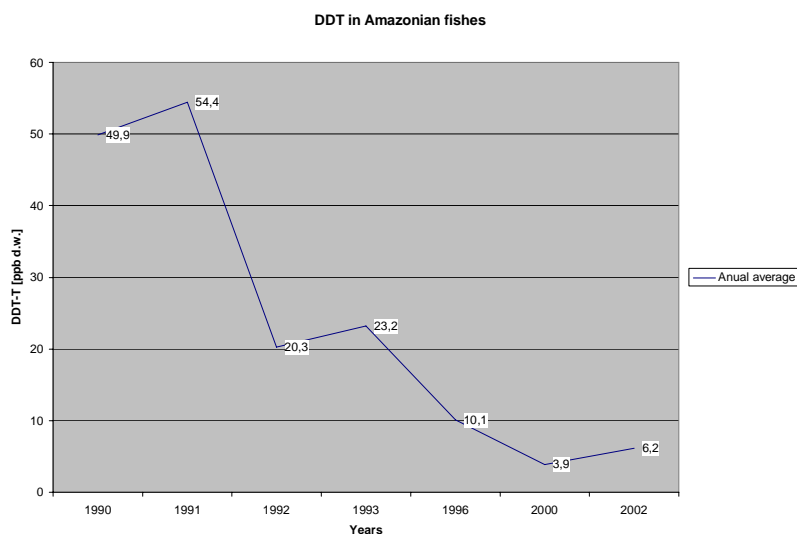


Figure 1: DDT in Fishes from the Amazon in Brazil 1990 - 2002

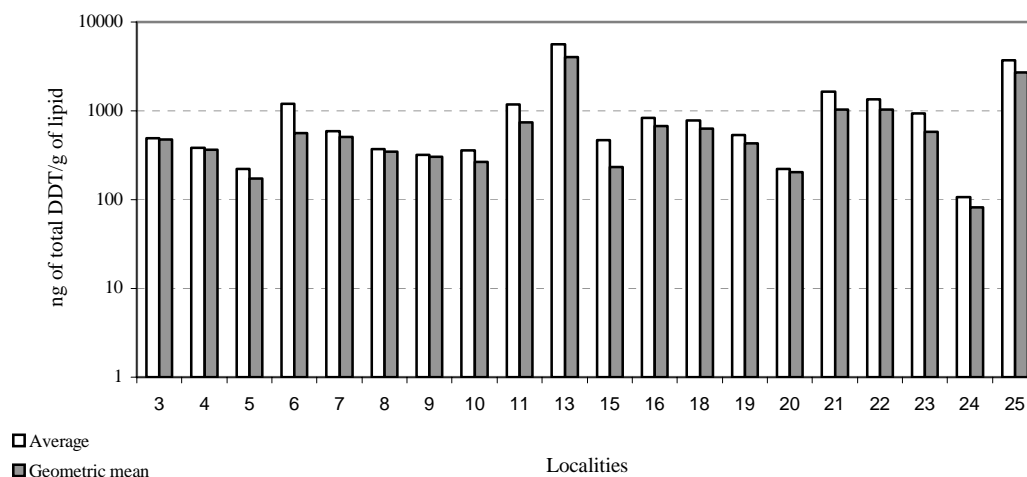


Figure 2: Total DDT in breast milk of different localities of the Madeira River.

HCb, DDTs and PCBs in the red dolphin (*Inia geoffrensis*): These four last results are a complementary indication of the overall contamination of this region. The specimen collected at the Madeira River is a juvenile. Table 1 presents these results in $\mu\text{g g}^{-1}$ (lipid basis).

Table 1: Organochlorines in aquatic mammals from the Amazon in Brazil ($\mu\text{g g}^{-1}$ lipid)

<u>Rio Solimões (Mamirauá)</u>	ΣDDT	ΣPCB	HCb
<i>Inia geoffrensis</i> (In1)	3176	1314	36
<i>Inia geoffrensis</i> (In2)	698	463	9
<i>Inia geoffrensis</i> (In3)	190	151	3
<u>Rio Madeira</u>			
<i>Inia geoffrensis</i> (In4)	2430	3216	6

Discussion

All over the world, there are limits for the presence of DDT residues in food items. Most of this legislation follows recommendations developed decades ago, when DDT was considered an innocuous substance setting the limits up to 5 mg g^{-1} wet weight. Today, new recommendations set 0.3 mg g^{-1} for poultry meat, keeping the 5 mg g^{-1} level to other kinds of meat⁸. The acceptable daily intake of DDT is <

0.025-mg/kg bw/day⁹. But since DDT is stored in the fat, the most correct attitude should be to settle limits using fat corrected data. However, in this case, if the fish has a very low fat content, this correction would gender a larger result. What can be said in this first effort to understand the DDT levels in fish from the Amazon, we can see that the poor people in the Amazon, that eat fish every day, was probably eating more DDT in the 80's than is eating today, but pregnant women nowadays were certainly born when DDT was on use for vector control. The highest value of total DDT (9361.9 ng of total DDT/g of lipid) was obtained of a *primiparae* mother aging 27 years old. Parity is pointed as a factor in the organochlorine amounts in breast milk⁹. Lactation is potentially the most significant activity in the reduction of the stored organochlorine in the human body, once it was observed the decrease of these compounds during its course¹⁰⁻¹⁴. Age has been noted as one of the most significant contributors of organochlorine pesticides in breast milk. The increase of the concentrations of DDT in breast milk with age was observed by previous studies¹⁵⁻¹⁶. The average of p,p'-DDE/ p,p'-DDT ratio was 6.3. This means a non-recent use of the insecticide DDT in most places. There is sufficient evidence that the presence of the DDT and its metabolites in the analysed milk samples is due to diet rich in fish, once considered the statement that the consumption of contaminated food represents an important source of organochlorine pesticides to humans⁹. The population living in the Madeira River region is characterised by high consumption of fish meat in their diet. The presence of DDT observed in previous works⁸ and its high consumption can be the source of DDT in the studied human milk samples. In 19 of the 20 localities presented total DDT contamination ranging from 118 to 771.4 ng of total DDT/g of lipid. Just one locality (Cachoeirinha) presented geometric mean for total DDT higher than 1000 ng of total DDT/g of lipid.

Conclusion

Our data as well as those gathered from the scientific literature supports that the overall *per capita* consumption of fish can surpass 550 g of fish per day and this is the main explanation for the high level of residues in breast milk. Viewing from an urban point of view and even according to the Brazilian standards, the general conditions of this kind of populations, is clearly poor and is most of them may eat basically three fish meals with cassava flour per day. Locally collected native fruits may complement this diet. None of the riverine communities has a sanitary system and the houses are no more than a hut constructed on wood and straw. Treated potable water do not exist in any part of Amazon rural settlements and most of this people drink the water of the river after the suspended material is deposited in the bottom of big plastic or clay canisters. The average DDT levels in fish are decreasing and the human exposure to this compound is declining. However, chronic exposure to low concentration of organochlorines as well as to other persistent pollutants may represent a particular risk. Due to the long half-lives in the organism, exposure for long periods may result in bioaccumulation and occurrence of uncontrolled adverse effects.

Acknowledgements

CNPq-PPG7, CNPq-PRONEX 0877 supported this work. Claudio Eduardo and Claudio D'Amato, M. Sc. received a Ph. D fellowships of CNPq/MCT and CAPES/MEC. Dr. Torres is Selikoff Advance Fellow at Mount Sinai/Queens College International Training Program of Environmental and Occupational Health and is partly funded by the Fogarty - NIH Grant 1 D43 TW00640.

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