DDT AND METABOLITES IN SOILS OF PURUZINHO LAKE, AMAZON, BRAZIL

Torres, JPM [1]; Saldanha, GC [1,2]; Bastos, WR[2]; Meire, RO; Silva, CEA; Fonseca, MF[1]; Rebelo, MF[1]; Claudio, L[3]; Steven Markowitz[4] and Malm, O[1].

[1] Laboratório de Radioisótopos Eduardo Penna Franca, Instituto de Biofísica Carlos Chagas Filho – Universidade Federal do Rio de Janeiro. Avenida Pau Brasil, s n. Centro de Ciências da Saúde, bloco G, Subsolo sala 61. Ilha do Fundão, Rio de Janeiro, RJ – Brasil. jptorres@biof.ufrj.br.
[2] Laboratório de Biogeoquímica Ambiental – Universidade Federal de Rondônia. Br 364 Km 9,5. Sentido Acre. Porto Velho, Rondônia – Brasil.
[3] Community and Preventive Department, The Mount Sinai School of Medicine, New York, NY – USA.
[4] Center for Biology of the Natural Systems, Queens College, New York, NY – USA.

Introduction

Attention must be paid to the negative impacts upon health and the environment of the synthetic insecticides and this includes an estimative of more than 1 million human poisoning cases with approximately 20.000 deaths per year, thousands of cases of chronicle illness, sterility and cancer[1]

Dichlorodiphenyltriclhoroetane (DDT) is the most famous among the organochlorine group, and due to this fame rendered from its large usage in agriculture and disease vector control, the verb: to 'dedetize' was coined in Brazil[2].

DDT was first synthesized by Zeidler in 1874, but its insecticide properties were discovered by the Swiss chemist Paul Muller in 1939. It is considered one of the most used and studied molecules of the XX century, having two main metabolites dichlorodyphenilethylene (DDE) and dichlorodyphenyldichloroethane (DDD). This compounds bioaccumulate in body fat and biomagnifies along the food chain[3].

Organochlorine residues have contaminated practically all of the ecosystems and they are often found in the most varied environmental matrices. Researchers recently found the organic pollutants moving through the atmosphere from its sources located in warmer areas of the globe and they may condense when the air masses reach the colder regions, leading the pollutant to precipitation over soils, vegetation and water courses[4].

The transport of DDT in soils may occur by colloidal transportation, via solvents and by biosorption. However the mobility of DDT is low due to its lack of solubility in water and high affinity to clay and silt and other mineral surfaces, especially when covered by organic matter films[5].

In the tropics the permanence of DDT is expected to be shorter, rendering to high evaporating and degradation rates by microorganisms. DDT can disappear more rapidly during floods, but this escape also occurs in dry conditions. Soil type and pH seems to govern such phenomena. In contrary in temperate soils the half life can be more than 5 years or more[6].

Material and methods

Study area- The Puruzinho lake is located at Humaitá municipality in the utmost south region of the Amazonas State in Brazil (Fig. 1). It is formed by the Puruzinho river and it is located around 5 km from its mouth at the left margin of the Madeira River, one of the most important tributaries of the right margin of the Amazon River. The lake's area corresponds to 38 km^2 and its perimeter was calculated in 23.195 m [7].

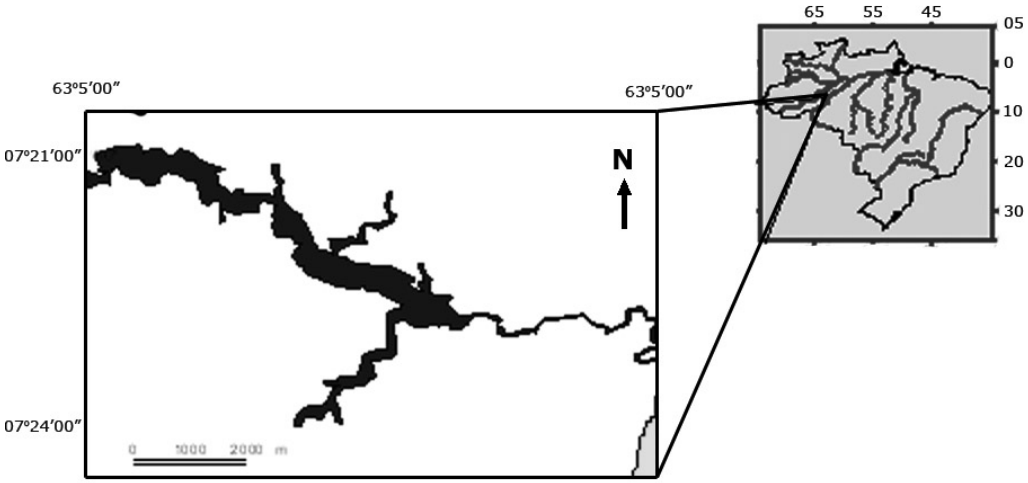

Figure 1: Study area**:** Puruzinho Lake – Humaitá /AM.

The samples were collected at 20 points along the Puruzinho lake shore line, all of them where georeferenced using GPS (Garmin 48). Half of the samples comprises soils under or around the older houses of the community. The other 10 samples where collect inside the forest that are located near this houses. All of the samples correspond to the A soil horizon, using acetone rinsed metallic devices and where stored in acetone washed wide mouth glass jars closed with metal caps over an aluminum foil protection.

The determination of the persistent organic pollutants in the soil samples followed the method described by Japenga and coi-workers[8], modified by Torres[9], consisting of four distinct consecutive steps: extraction (ultrasonic device using a solvent mixture – acetone, hexane and isooctane), clean-up (desulphurization using sodium sulphite adsorbed to alkaline alumina), fractionation (dry silica gel column) and automatic injection of 2µl (Shimadzu AOC-17, split less) high resolution gas chromatography coupled to an electron capture detector (Shimadzu GC-14B).

We used ultra-pure hydrogen (35 ml/min) trough the SE-30/SE-52 capillary columns (25 m; 0,2 mm ID; 0,25 µ film thickness) and ultra-pure N_2 was the make-up gas. The injector and the detector temperatures were set in 300°C and 310°C, respectively.

For quantification, an internal standard OCN (octachloronaphtalene) was added prior injection and the results were statistically evaluated and graphically described by box-plots using the software STATISTICA (version 6.0). The Shapiro-Wilk's test was used to check the results for normality and the comparison of the distribution of the compounds between the house and forest soils was determined using the U test of Mann-Withney.

Results and Discussion

The concentrations of ΣDDT (*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 result of the descriptive analysis is shown on table 1.

Table 1: DDT and its metabolites concentrations ($ng.g^{-1}$) in house and forest soils of the Puruzinho Lake, Amazon - 2005

			House soils	**n=10**		
	N	**Average**	**Mean**	**Min**	**Max**	**Std dv.**
***o,p'*-DDE**	10	7,48	3,48	0,85	31,02	9,56
***p,p'*-DDE**	10	1,01	0,12	<DL	6,23	1,96
***p,p'*-DDD**	10	6,96	0,38	<DL	55,79	17,30
***o,p'*-DDT**	10	7,26	1,88	<DL	38,12	12,06
***p,p'*-DDT**	10	8,39	0,23	<DL	70,80	22,04
			Forest soils	**n=10**		
	N	**Average**	**Mean**	**Min**	**Max**	**Std dv.**
***o,p'*-DDE**	10	3,09	2,84	0,71	7,18	1,75
***p,p'*-DDE**	10	0,702	0,26	0,02	2,19	0,84
***p,p'*-DDD**	10	0,471	0,44	0,22	0,81	0,20
***o,p'*-DDT**	10	0,435	<DL	<DL	2,37	0,92
***p,p'*-DDT**	10	0,431	0,45	<DL	1,28	0,40

<DL: below the detection limits of the method

The *Shapiro-Wilk* test showed that the distribution was not normal for both the results of the soil of the houses ($p<0,001$) as well as for the forest soils ($p< 0,007$). The U test of *Mann-Whitney* reveled that there were no significant difference between the results obtained for both houses and forest soils ($p>0,290$).

The *p,p'*-DDD / *p,p'*-DDE ration in house soils (mean= 3,85) and for forest soils (mean= 1,87) were high when we compared this results to the previous work of Vieira[10] 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). This results were expected since our sampling occurred during the rainy season, and since the high index of heavy rains in this region, our study confirms the previous work of Parr e Smith[11] and Ramesh *et al*[12] that had demonstrate that the DDT degradation to DDD is mediated by anaerobic bacteria and fungus working in reductive environments, that may be the case of the Amazon soils during the rainy season.

The DDT/DDE ration 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-workers[9], 1,91 in 1997 and 1,19 in 1999. However these results are higher than the previous ratios reported by Torres et al[10], 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.

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References

1. WHO. The World Health Report. Geneva, Switzerland, 1996.
2. D'AMATO C.; TORRES, J. P. M. e MALM. O. DDT (Dicloro Difenil Tricloroetano): Toxicidade e Contaminação Ambiental – Uma Revisão.Química Nova 2002:25; 995:1002.
3. VIEIRA, E. D. R.; TORRES, J. P. M. e MALM, O. Environmental Persistence from Its Use in a Vector Control Program: a Case Study. Environmental Research 2001:86; 174:182.
4. SIMONICH, S. L. e HITES, R. A. Global Distribution of Persistent Organochlorine Compounds. Science 1995: 269; 1851:1854.
5. MORRISON, R.D. e NEWELL, A. E. The cosolvation transport of DDT and toxaphene in xylene at a pesticide formulation facility. Journal Soil Contamination 1999: 8,63:80.
6. ATSDR. Toxicological, Profile for DDT, DDE and DDD. U.S. Department of Health and Human Services. Public Health Service 2002:497.
7. ALMEIDA, R. de. Distribuição espacial dos níveis de Hg no sedimento de fundo em um ambiente lacustre formado pelo Rio Puruzinho-Amazonas. 2006. Dissertação (Mestrado em Desenvolvimento Regional). Universidade Federal de Rondônia.
8. JAPENGA, J,; WAGENAAR, W. J.; SMEDES, F. e SALOMONS, W. A new, rapid clean-up procedure for the simultaneous determination of different groups of organic micro pollutants in sediment: application in two estuarine sediment samples. Environmental Technology Letters, 1987: 8;9:20.
9. VIEIRA, E. D. R. Persistência ambiental e biológica do DDT: estudo de um caso em área tropical. Rio de Janeiro, 2000. Dissertação (Mestrado em Biofísica). Universidade Federal do Rio de Janeiro.
10. TORRES, J. P. M. Ocorrência de Micropoluentes Orgânicos (organoclorados e hidrocarbonetos policíclicos aromáticos) em sedimentos fluviais e solos tropicais. Rio de Janeiro, 1998. Tese (Doutorado em Biofísica). Universidade Federal do Rio de Janeiro.
11. PARR, J.F. e SMITH, S. Degradation of DDT in an Everglades muck as affected by lime, ferrous, iron and anaerobiosis. Soil science, 1974:118; 45:52.
12. RAMESH A.; TANABE, S. e TATSUKAWA, R. Seasonal variations of organochlorine insecticide residues in air from Porto Novo, South India. Environmental Pollution, 1989:62; 213:222.