ORGANIC POLLUTANTS IN HUMAN HAIR FROM BRAZILIAN AMAZON

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Abstract

Human hair, as a potentially additional tool for the public health surveillance, is providing a non-invasive sampling tool with additional merits, e.g. stable matrix, easy for collection, short and long-term exposure tracings and so forth. The aim of this study is to determine the concentrations of Organochlorine pesticides, Polychlorinated Biphenyls (PCBs) and Polycyclic Aromatic Hydrocarbons (PAHs) in human hair collected in the Madeira river Basin.

Introduction

Human monitoring of persistent organochlorine pollutants (POPs) has become increasingly important for exposure and risk assessment. Body fluids and tissues are commonly used to evaluate human exposure[1,2,3]. Due to its relatively high percentage of lipids (3.5–4%), hair has been identified as a suitable indicator for short- and long-term exposure to organochlorines[4].

In comparison to traditional matrices, hair has received little attention for the analysis of organochlorine compounds[5,6,7,8]. Because of easy and non-invasive sampling, hair can be an alternative matrix for the monitoring of endangered animal species or children. Moreover, hair analysis can be applied to any population group (when compared with human milk restricted to women in lactating period or adipose tissue available under surgery). However, there are some drawbacks of using hair for biomonitoring environmental organic pollutants[9]. It is not a homogeneous sample and there is still to learn about excretion and distribution of POPs in hair. Finally, there is a great uncertainty for the comparison of concentrations found by different studies in different matrices[10].

Material and Methods

Eighty five hair samples were collected from riverines communities of Madeira River, Amazon-Brazil (Figure 1). These communities have a historic use of DDT to control the Malaria vector – *Anopheles* sp. The samples (1-2 g), from the occipital region, were collected using scissors and wrapped in aluminum foil and stored in polyethylene bags until the moment of analyses.

Sample clean-up and extraction techniques were carried out as documented in the form of Standard Operation Procedures (SOPs) in the accredited Dioxin Laboratory at the Institute of Ecological Chemistry in the German Research Center for Environmental Health.

The extraction procedure used was Accelerated Solvent Extractor (ASE). The clean-up was realized in two steps: 1) mixed column: composed of an alumina oxide layer and a silica gel layer. This column eliminates non-polar halogenated aromatics such as PCB and polar contaminants. The silica layer removes also polar pollutants as well as lipids; 2) Solid Phase Extraction (SPE) column: The octadecyl (C_{18}) silica gel is composed of C_{18} hydrocarbon bounded to the silica gel support. This column retains in the hydrophobic stationary phase long chain hydrocarbons that can interfere in the posterior analysis.

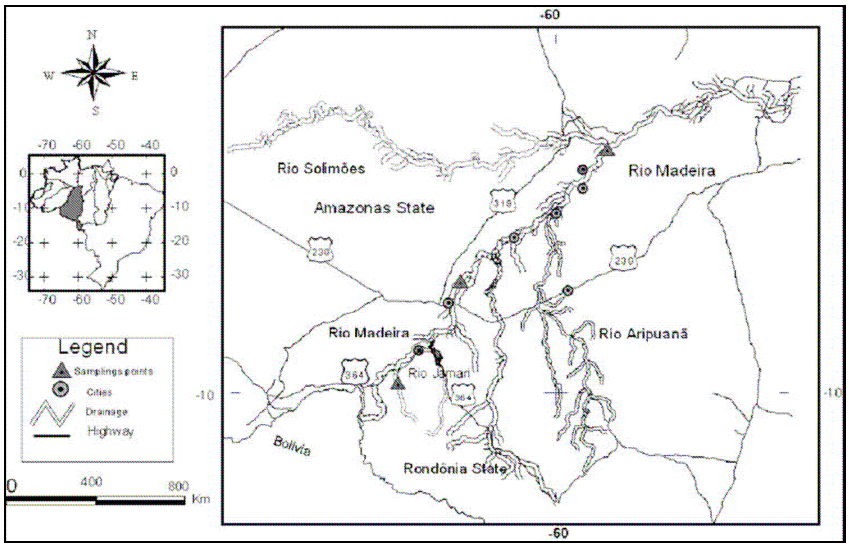

Figure 1: Study Area

The analytical determinations of POP are performed by a high-resolution mass spectrometer (HRMS) Finnigan MAT 95 (Thermo Electron GmbH, Bremen, Germany) coupled with a high resolution gas chromatograph Agilent GC 5890 (Agilent Technologies, Palo Alto, CA, USA). The chromatographic separation is achieved by splitless injection (cold injection system CIS3, Gerstel GmbH, Mülheim, Germany) on different columns (Restek GmbH, Sulzbach, Germany) depending on the family of compounds analysed. The mass spectrometer is operated in selected ion monitoring (SIM) mode at a resolution of 8000. The two most intense ions of the molecular ion cluster are monitored for the unlabelled and labelled standard isomers. The ^{13}C-labelled standards and the deuterated PAH standard mixtures are purchased from LGC Promochem (Wesel, Germany).

Results and Discussion

A total of 85 human hair samples were included in the study. All samples correspond to the female volunteers of 3 different communities from Amazon – Brazil (Table 1).

Table 1: Volunteers from 3 different communities from Brazilian Amazon and Percentage of Lipids in Hair Samples.

Communities	N	% Lipids *
Puruzinho Lake – Amazonas State /Brazil	52	3.99
Abunã – Rondônia State /Brazil	23	5.27
Vista Alegre - Rondônia State /Brazil	10	4

*Average in samples

The samples were quantified for 15 target OCP compounds (included isomers of DDT, DDE and DDD, isomers of HCH and others) , 16 target PAH compounds (included naphthalene, acenaphthylene, acenaphthene, fluorene and others) and PCBs (classified into three categories: indicator PCBs - consisted of six congeners that are predominantly present in most PCB mixtures in the environmental samples-, Non-ortho PCB - nos. 77, 81, 126, 169- and Mono-ortho PCB - nos. 105, 114, 118, 123, 156, 157, 167, 189.

For the organochlorine pesticides, DDT and its metabolites were the predominant contaminants found in all hair samples analyzed (95.29%). The DDTs profile consisted in 67% for isomers of

DDT (*o,p'*-DDT + *p,p'*-DDT), 31.87% for isomers of DDE (*o,p'*-DDE + *p,p'*-DDE) and only 1.07% for isomers of DDD (*o,p'*-DDD + *p,p'*-DDD). The results suggest recent exposure to fresh DDT and support the possibility of using hair as a suitable indicator for the assessment of long-term exposure organochlorine pesticides. For the concentrations of Σ-DDT (*o,p'*-DDT + *p,p'*-DDT + *o,p'*-DDE + *p,p'*-DDE + *o,p'*-DDD + *p,p'*-DDD) the maximum value found in the hair samples analyzed was 8141.58 $ng.g^{-1}$ and minimum 10.96 $ng.g^{-1}$ with median equal 760.26. The basic statistic for DDT and related compounds is showed in the table 2.

Table 2: Basic statistic for DDT and its metabolites finds in the samples analyzed ($ng.g^{-1}$).

Compound	N	Average	SD (±)	Median	Min	Max
p,p'-DDT	85	1017.90	1300.0	399.81	2.57	5,394.10
o,p'-DDT	85	76.23	124.4	38.84	0.70	870.80
p,p'-DDD	85	10.04	13.9	4.26	nd	108.58
o,p'-DDD	85	3.72	8.3	2.30	nd	74.27
p,p'-DDE	85	526.11	678.7	233.01	nd	3,177.37
o,p'-DDE	85	5.04	7.5	2.11	0.07	50.56

nd: not detectable

Further pesticides were quantified in the samples. The compound trans-Heptachloroepoxid was not detected among the samples analyzed. In the case of delta-Hexachlorocyclohexane, epsilon-Hexachlorocyclohexane, Pentachloroanisole, Octachlorstyrene and trans-Heptachloroepoxid just 2.35%, 1.17%, 8.23% and 1.17% of the samples presented some concentrations of these compounds, respectively.

PCBs were classified into three categories as follows: indicator PCBs - consisted of six congeners that are predominantly present in most PCB mixtures in the environmental samples and they included these six congeners, known as the indicator PCB nos. 28, 52, 101, 138, 153, 180. Non-orho PCBs consisted of non-ortho PCBs nos. 77, 81, 126, 169 whereas the third category included mono-ortho PCBs nos. 105, 114, 118, 123, 156, 157, 167, 189.

Between the categories, the indicator PCBs present 97.24% of total samples, majority found at super intensive systems, mono-ortho (were present in 2.49% of total samples) and non-ortho (0.27% of total samples). The major levels of PCB congeners found were in the following rank PCB 52 (20.02 $ng.g^{-1}$) > PCB 28 (18.89 $ng.g^{-1}$) > PCB 101 (8.75 $ng.g^{-1}$) > PCB 153 (4.17 $ng.g^{-1}$) > PCB 138 (2.77 $ng.g^{-1}$) > PCB 180 ($ng.g^{-1}$). The percentage of indicator PCBs analyzed in human hair form 3 communities of Brazilian Amazon was PCB 28 (40.87%), PCB 52 (40.4%), PCB 101(12.23%), PCB 153 (3.1%), PCB 138 (1.96%) and PCB 180 (1.43%).To the mono-ortho category the most present congeners were 118 (61.13% - average 0,23 $ng.g^{-1}$ and median equal 0.06 $ng.g^{-1}$) and PCB 105 (21.54% - average 0.08 $ng.g^{-1}$ and median equal 0.02 $ng.g^{-1}$).The major congener of non-ortho category is the PCB 77, present in 94.56% of total samples (max equal 0.33 $ng.g^{-1}$ and minimum 0.0052 $ng.g^{-1}$). The percent values were calculated using the dry mass of hair used for analysis.

All samples analyzed present some concentrations of polycyclic aromatic hydrocarbons. The most abundant compound found in the samples analyzed was Phenanthrene that occurred in 39% of the samples with minimum concentration equal to 20.4 $ng.g^{-1}$ and maximum 1,045.27 $ng.g^{-1}$. On the other hand: Acenaphthylene, Acenaphthene, Benzo(g,h,i)perylene and

Dibenzo(a,h)anthracene are present at 0.64%, 0.84%, 0.94% and 0.24% respectively. Figure 2 shows the percentage of all Polycyclic Aromatic Hydrocarbons analyzed.

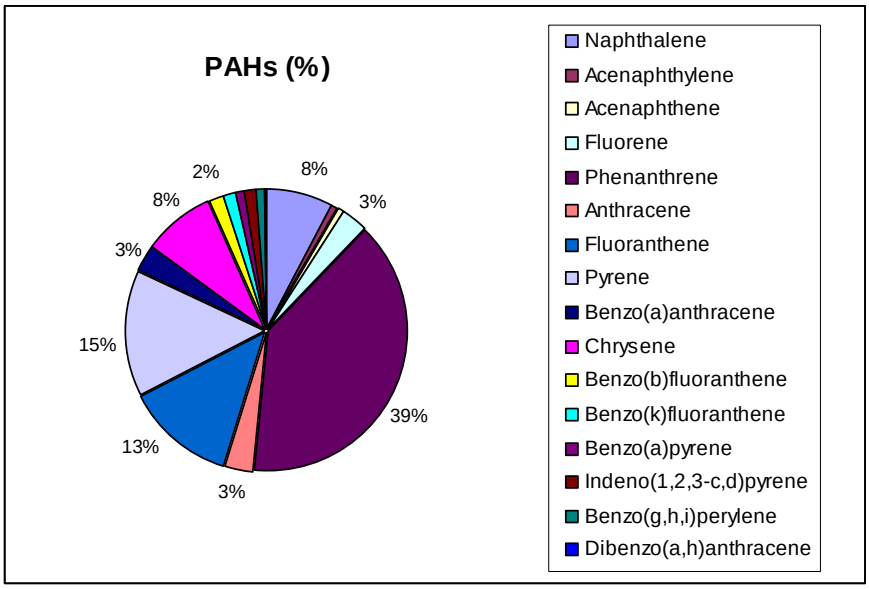

Figure 2: Percentage of Polycyclic Aromatic Hydrocarbons in human hair from Brazilian Amazon.

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