

# ASSESSMENT OF PERSISTENT ORGANIC POLLUTANTS (POPs) IN SERUM FROM GUINEA-BISSAU, WESTERN AFRICA – A TIME TREND STUDY

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## Abstract

There is a lack of information on POPs in developing countries in general and specifically in Africa. This study aims to investigate the occurrence and possible time-trends of POPs in Guinea-Bissau. Pooled blood samples from 34 police officers taken at 4-5 occasions between 1990 and 2007 were analyzed in search for chlorinated pesticides, PCBs and PBDEs. Decreasing levels over time were seen for all investigated compounds except for the PBDEs that did not show a significant time trend. 4,4'-DDE was found at the highest concentration in all samples followed by 4,4'-DDT,  $\beta$ -HCH,  $\gamma$ -HCH and PCBs. The mean 4,4'-DDE concentration was 2400 ng/g fat and the mean 4,4'-DDT concentration was 630 ng/g fat. There was a distinct decrease (90%) of  $\gamma$ -HCH from the first time point (1990-1991) to the second point (1993-1995) thereafter it seems to reach a steady state. There was a decrease of  $\beta$ -HCH as well but not as fast. CB-153 was the major PCB congener followed by CB-180 and CB-138. The concentration of CB-153 was between 20 and 100 ng/g fat. PBDEs were found at low levels.

## Introduction

Levels and trends of various persistent organic pollutants (POPs) have been assessed in human samples from many industrialized countries as reviewed by for example Solomon and Weiss<sup>1</sup> and Hites<sup>2</sup>. But the information on POPs in developing countries, especially in Africa, is scarce. There are a few studies mainly on various chlorinated pesticides in human milk and serum samples from African countries<sup>3-9</sup>.

The aim of this study was to investigate levels and trends of POPs in a population living in a developing country in Africa. The concentration of 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (4,4'-DDT) and its metabolites, hexachlorocyclohexanes (HCHs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) were determined in pooled samples from male police officers from Guinea-Bissau sampled between 1990 and 2007. Guinea-Bissau is situated on the west coast of Africa and it is one of the 10th poorest countries in the world.

## Materials and Methods

**Samples:** Police officers in Guinea-Bissau have donated blood yearly for a HIV study since 1990. The cohort is described in more details elsewhere<sup>10</sup>. We received samples from 34 HIV negative men that had donated blood at 4-5 occasions between 1990 and 2007. The samples were pooled into six different pools.

**Method:** The pooled serum samples were extracted using a modified version of a liquid-liquid method described by Hovander et al<sup>11</sup>. In brief, internal standards (CB-200 and BDE-138) hydrochloric acid and 2-propanol were added to the serum before the extraction with cyclo-hexane:methyl *tert*-butyl ether (1:1). The lipid weight was determined gravimetrically. Potassium hydroxide was used to separate phenolic compounds from neutral compounds. The neutral fraction was cleaned-up with sulfuric acid and sulfuric acid treated silica gel columns. All solvents, acids and salts were of highest quality available. Silica gel, 200-400 mesh, 60 Å, was purchased from Aldrich, USA. The silica gel was baked at 300°C over night before use.

**Instruments:** DDTs, PCBs and HCHs were analyzed on a Varian CP-3800 gas chromatograph (GC) equipped with a CP-8400 autosampler and an electron capture detector (ECD). A large volume injector was used (the injection volume was 5  $\mu$ l) and the temperature program for the injector was: 80°C, 0.35 min; 200°/min to 300°. A non-polar column (CP-SIL 8CB 25 m  $\times$  0.15 mm  $\times$  0.12  $\mu$ m) was used. Helium was used as a carrier gas and

nitrogen as the make up gas. The column oven temperature was programmed from 80°C, 2.5 min; 20°/min to 300°; hold for 5 min. After GC/ECD analysis, the PBDEs were separated from the chlorinated compounds on a silica gel column before analysis on GC/MS-ECNI (SSQ 710, ThermoFinnigan). A septum equipped temperature programmable injector (SPI) was used together with a DB-5 HT capillary column (15 m × 0.25 mm × 0.1 μm). Helium was used as a carrier gas and selected ion monitoring (SIM) mode (isotopes m/z 79 and 81) were used for the analysis of PBDE congeners.

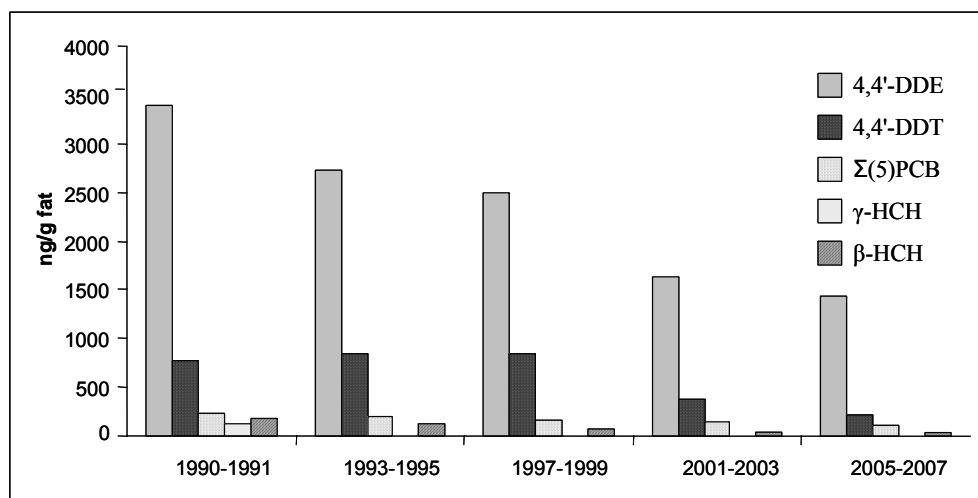
### Results and Discussion

Decreasing trends over time were seen for most of the POPs studied as seen in other parts of the world<sup>1,12-14</sup>. 4,4'-DDE was the major compound found in all samples followed by 4,4'-DDT, β-HCH, γ-HCH and PCBs. The time trends of the mean levels of these compounds in the six pooled samples are illustrated in Figure 1. The concentration of 4,4'-DDE in the pooled samples varied between 800-7700 ng/g fat over time whereas the concentration of 4,4'-DDT varied between 140-1600 ng/g fat. The DDT/DDE ratio was between 0.07-0.7. The high 4,4'-DDE/4,4'-DDT ratio indicates recent or ongoing use of DDT. 2,4'-DDT followed the same pattern as 4,4'-DDT at about 20% of the 4,4'-DDT concentration.

All pools showed a distinct decrease (90%) of γ-HCH from the first time point (1990-1991) to the second point (1993-1995) thereafter it seems to reach a steady state (see Figure 1). There is a decrease of β-HCH as well but it is much slower. The concentration of γ-HCH was between LOQ and 240 ng/g fat and 18-320 ng/g fat for β-HCH. The fast decrease of γ-HCH might be due to a total stop of the use of Lindane in the early 1990's. The other HCH isomers were not found neither was hexachlorobenzene (HCB).

Decreasing concentrations of the PCBs over time was seen as well (Figure 1). The concentration of PCBs in 2007 was 50% of the concentration in 1990. CB-153 was the major PCB congener followed by CB-180, CB-138, CB-170 and CB-187. CB-153 concentrations were between 20 and 100 ng/g fat. Higher concentrations of PCBs were seen in the pooled sample containing the oldest individuals compared to the pools containing younger individuals. No significant time trend was seen for the PBDEs. They were detected at low levels except for the deca brominated BDE-209 that was found in relatively high concentration compared to the other PBDE congeners. BDE-209 was quantifiable in two thirds of the samples with a mean concentration of 3.8 pmol/g fat (<LOQ-24 pmol/g fat). BDE-47 was found in most samples but all values were below the LOQ (three times the amount in the blank samples). BDE-153 was quantifiable in two out of thirds of the samples and BDE-154 in one third of the samples.

This study is unique since we have been able to analyze samples from the same individuals at several time points during seventeen years. These results gives a good picture on how the concentration of POPs has changed from the early 90's until today in people living in a developing country in western Africa.



**Figure 1.** Mean concentration (ng/g fat) of 4,4'-DDE, 4,4'-DDT, Σ(5)PCB, γ-HCH and β-HCH in six pooled serum samples from police officers from Guinea-Bissau.

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