THE EFFECT OF COOKING FOOD ON FIRES FROM SOLID FUELS VS ELECTRICITY, GAS AND PARAFFIN ON LEVELS OF DIOXINS AND PCBs IN A SOUTH AFRICAN POPULATION

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Introduction
South Africa ratified the Stockholm Convention on Persistent Organic Pollutants (SC POPs) September 20021 and by doing so became obliged to limit and reduce the classes of persistent organic pollutants listed in SC POPs. Compared to the amounts of data on POPs in the environment, biota, and human populations from countries in the northern hemisphere, little was known about POPs in the South African environment and human population by the time of ratification. Most publications focussed on pesticide POPs2-5. A few studies were published on polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) and other POPs in the environment6-9 and basically three studies on POPs levels in humans10-12.

Since a large part of the South African population still has to rely on solid biomass fuels for household cooking, and heating, they would be exposed to amongst other pollutants, PCDD/Fs and dioxin-like polychlorinated biphenyls (DL-PCBs)13,14 as this is a known source. Half of the energy sources for cooking in the rural areas of the province, in which this study took place, is wood15. The aim of this study was to compare the levels of PCDD/F, DL-PCBs and selected non-DL PCBs (NDL-PCBs) (28, 52, 101, 138, 153, and 180) in the serum of people that uses electricity, gas and paraffin (kerosene) on the one hand to those who burn biomass such as wood, household waste and agricultural residues to cook food and heat their houses. Other factors that might influence the levels of these compounds were also considered: gender, age, employment and if a female breastfed during her lifetime (Table 1).

Materials and methods

Chemicals, sample collection and storage
All data concerning the quality and potential pre-treatment of the entire chemical used for those analyses are available in a previous report16. Quality control (QC) samples consisted in a home-made pool of non-fortified human serum. All QA/QC criteria are similar to those we routinely use for food control under EU regulation17. The human subjects were from rural and urban regions in the North-West Province, South Africa. They were part of the Prospective Urban Rural Epidemiology (PURE) study, which is a large-scale epidemiological study that recruited individuals from 600 communities in 17 low-, middle-, and high-income countries around the world. The PURE study is coordinated from the Population Health Research Institute, Ontario. The overarching aim of the PURE study was to examine the relationship of societal influences on human lifestyle behaviours, cardiovascular risk factors, and incidence of chronic non-communicable diseases18. In addition to the samples collected for the PURE study in 2010, serum samples were collected from 693 Tswana adults for this study. Samples were pooled according to the factors in Table 1. All samples were collected, stored at 4°C until they reached the sampling laboratory, then frozen and stored at -20°C.

Analytical procedure
The samples were received frozen at CART analytical laboratory of the University of Liège. All samples were processed in series of routinely analyzed samples (one method blank, one instrumental blank, one QC and 10 unknown) in an ISO17025 BELAC accredited laboratory. Sample sizes ranged between 10 and 20 g. Each pool was extracted by SPE carried out using 2 g/15 ml non-endcapped [Si(Me3)] octadecyl SPE disposable cartridges. The lipid content was determined enzymatically. The automated clean-up and fractionation in subgroups of analytes was performed by automated multi-sorbent (silica, alumina and carbon-based) liquid chromatography (LC) using the Power-Prep System (Power-Prep™, Fluid Management Systems Inc., Waltham, MA, USA)19. Sizes of PTFE disposable columns were 4 g (2 g acid, 1 g basic and 1 g neutral) for silica, 4 g for
basic alumina and 0.35 g of carbon dispersed on Celite for the carbon column. Measurements of MO-PCBs and NDL-PCBs were carried out on a MAT95 XL (ThermoFinniganMAT, Bremen, Germany). The GC column was an HT-8 (25 m x 0.22 mm ID x 0.25 µm df) (SGE, Villebon, France). 1.2 µl of the final extract in nonane (95 µl) were injected into a split/splitless injector held at 275°C in splitless mode. Measurements of PCDDs, PCDFs, and NO-PCBs were carried out on an Autospec Ultima (Micromass, Manchester, United Kingdom) The GC column was a VF-5MS (50 m x 0.2 mm ID x 0.33 µm df) (Varian Inc., Sint-Katelijne-Waver, Belgium). 5 µl of the final extract in nonane (10 µl) were injected into programmable temperature vaporization (PTV) injector (Agilent Technologies, Diegem, Belgium). Additional GC and HRMS parameters were described previously. All TEQ values were based on middle bound data.

**Data treatment**

The means of the following groups were compared for statistical significant differences:
- Burning solid fuel vs electricity, gas and paraffin across genders, breastfeeding and employment status and age group;
- Breastfeeding vs non-breastfeeding females across both fuel classes
- Females vs males; within both fuel classes
- Younger age group vs the older age group; within the burning fuel class
- Employed vs unemployed people; within the electricity, gas and paraffin fuel class

The above comparisons were repeated for different concentration formats in which the data can be presented, i.e. concentration in pg/L, in pg/g lipid, and in pg WHO-TEQ/L and pg WHO-TEQ/g lipid for the PCDD/Fs, and DL-PCBs. The compound groups that were compared were the PCDDs, PCDFs, DL-PCBs, and NDL-PCBs. Between the four compound classes and the various concentration formats, 14 types of compound classes and concentration format combinations were compared. The T-tests for independent samples for parametric data and the Mann-Whitney U test for non-parametric data were used for comparison between two groups. The sample size however, dictated that the non-parametric test results are reported. The SPSS Inc. (2011) software was used for all of the tests.

**Results and discussion**

For the sake of brevity only the WHO-TEQ/g lipid values of the PCDD/F and DL-PCBs and the pg/g lipid concentrations of the NDL-PCBs are reported here. Statistically significant differences (p<0.05) were observed for some of the categories of data (as described in the materials and methods):
- People using electricity, gas and paraffin as a fuel source, had higher levels of PCDD/Fs than those using solid fuel combustion, but lower levels of the DL-PCBs and NDL-PCBs (Figure 1);
- Females had higher levels of PCDD/Fs than males when both fuel classes were included, but both the DL-PCB and NDL-PCB levels in the males were higher. When considering the solid biofuel separately from the electricity, gas, and paraffin class the levels of all pollutant classes were higher in the males than in the females. However, the levels were higher in the females for the electricity, gas, and paraffin fuel class (for the DL-PCBs is was not significant);
- Non-breastfeeding females had higher levels of all pollutants than the breastfeeding females across both fuel classes;
- The older aged people had higher levels of all pollutant groups and concentration formats than the younger people across both fuel classes as well as within the electricity, gas & paraffin fuel class. The older people had higher levels for the burning solid biofuels, but the PCDD (WHO-TEQ) formats were not significantly so.
- The effect of employment on the levels was not as distinct as the previous factors. Of the 14 possible compound classes and concentration formats, 11 showed that unemployed people had higher levels. Only 7 of these were statistically significant. In 3 cases employed people seemed to have higher levels and only one of these, NDL-PCB (pg/g lipid) was statistically significant.

The hypothesis that people who use solid biofuels for cooking and heating have higher PCDD/F and PCB levels than people who have access to electricity, gas and paraffin only holds true for PCDD/Fs but not the PCBs for the population in this study. At a first glance it seems as if the PCDD/Fs and PCBs have different sources, with more of the PCBs coming from combustion of solid biofuels. The higher levels of PCDDs and PCDFs in females
than in males coincide with international trends and might be due to a greater percentage of body fat. Women had a significantly higher waist circumference than the men in the same population. It is still unresolved why.

Table 1: PCDD/F and PCB levels of the various human serum pools.

<table>
<thead>
<tr>
<th>Age (years)</th>
<th>Gender</th>
<th>Breastfed?</th>
<th>Employed?</th>
<th>n</th>
<th>( \sum \text{PCDD/Fs &amp; DL-PCBs} ) (pg WHO-TEQ/g lipid)</th>
<th>( \sum \text{NDL-PCBs} ) (ng/g lipid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37-60</td>
<td>Male</td>
<td>✔</td>
<td></td>
<td>87</td>
<td>4.4</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td>Male</td>
<td></td>
<td>✔</td>
<td>26</td>
<td>4.0</td>
<td>10.7</td>
</tr>
<tr>
<td>61-84</td>
<td>Male</td>
<td>✔</td>
<td></td>
<td>3</td>
<td>1.8</td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td>Male</td>
<td></td>
<td>✔</td>
<td>57</td>
<td>9.4</td>
<td>62.5</td>
</tr>
<tr>
<td></td>
<td>Female</td>
<td>✔</td>
<td></td>
<td>10</td>
<td>6.9</td>
<td>54.0</td>
</tr>
<tr>
<td></td>
<td>Female</td>
<td>✔</td>
<td></td>
<td>56</td>
<td>56.9</td>
<td>219.1</td>
</tr>
<tr>
<td>Electrici</td>
<td>Male</td>
<td>✔</td>
<td></td>
<td>4.6</td>
<td>27.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Male</td>
<td></td>
<td>✔</td>
<td>2</td>
<td>4.6</td>
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<tr>
<td></td>
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<td>20</td>
<td>6.7</td>
<td>54.9</td>
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<tr>
<td></td>
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<td></td>
<td>50</td>
<td>11.5</td>
<td>67.1</td>
</tr>
<tr>
<td></td>
<td>Female</td>
<td>✔</td>
<td></td>
<td>15</td>
<td>16.6</td>
<td>94.7</td>
</tr>
</tbody>
</table>

*Answer to the question if the females breastfed their children or not. #Answer to the question if people were employed or not.
Figure 1: Comparing the means between the two fuel classes for the different concentration formats and compounds groups (\* p<0.05).

The males would have higher PCB levels. The higher levels in non-breastfeeding females compared to breastfeeding females agree with other studies\textsuperscript{24} as well as the tendency for older people to have higher levels than younger people\textsuperscript{22, 24}. There is no clear message as to influence of employment on the pollutant levels.

Globally, compared to Central European background levels, the South African Tswana population of the present study exhibited significantly lower levels for PCDD/Fs, DL-PCBs, and NDL-PCBs. Such findings were already highlighted in the early nineties\textsuperscript{10}. TEQ levels appeared to be three times lower for the South African population (8.4 pg/TEQ/g fat vs. 27.3 pg/TEQ/g fat for n=1000 in France).

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References: