

# PCDDs, PCDFs AND DIOXIN-LIKE PCBs IN BLOOD FROM KOREAN VIETNAM VETERANS WHO SERVED IN VIETNAM IN THE EARLY 70es

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### Introduction

Agent Orange, a phenoxyherbicide mixture of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 2,4-dichlorophenoxyacetic acid (2,4-D) was sprayed in large amounts of southern Vietnam during the Vietnam war between 1962-1971. 2,4,5-T was contaminated with the highly toxic and persistent 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in the low ppm-range (mg/kg). Previous studies have documented intake of TCDD from Agent Orange in among US war veterans and in Vietnamese (Kahn et al.<sup>1</sup>, Schecter et al.<sup>2</sup>, Michalek et al.<sup>3</sup>, Schecter<sup>4</sup> and Schecter et al.<sup>5,6,7</sup>). Samples collected between 1970 and 1973 documented elevated levels for TCDD from Agent Orange in milk samples from southern Vietnamese woman as well as in fish and shrimp samples from areas in this region (Baughman et al.<sup>8</sup>). Little is known regarding conditions of veterans from other countries serving in Vietnam. Approximately 320,000 Korean soldiers had participated in the Vietnam War from 1964 to 1973. Following the war, a series of demonstrations and appeals were made by the Korean veterans to demand medical care and compensation for their health damages. The Vietnam veterans issue became a serious public concern. As a result, a bill of medical care and compensation for the "Agent Orange Victims" was promulgated in 1993. About 4,000 veterans have been registered. However, there has been neither an extensive investigation on concentrations of dioxins in blood samples, nor an attempt to compare the Korean veterans with those from other countries using the same analytical protocols.

We collected blood samples from 6 Korean veterans who served from 12 to 36 months in Vietnam. In this paper we report on analytical data for dioxins and the dioxin like PCBs found in the Korean blood samples.

### Material and Methods

#### *Samples and Sampling*

The sampling was organized in cooperation with local health centers. Sampling was done in July 2001. All of participants were selected from the registry of Vietnam veterans "Agent Orange Victims" and were categorized as "mildly symptomatic" by the Korean Veteran's Administration. All participants were examined about their current health conditions during the interview with the physicians. Some background information for the individuals who donated the 6 Korean Blood samples is given below.

Samples were sent in frozen state by an international courier service to ERGO in Hamburg/Germany where they were stored below -18 °C until the beginning of the analyses.

# HUMAN EXPOSURE II

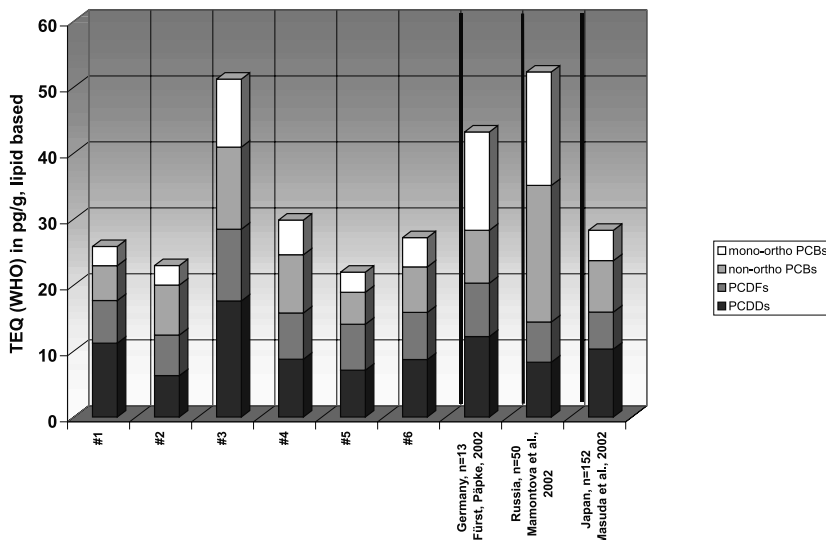
| Code | Age | Time of stay in Vietnam | Length of stay in Vietnam | Job description                              |
|------|-----|-------------------------|---------------------------|--|
| # 1  | 53  | 1969-1970               | 12 months                 | Infantry foot soldier                        |
| # 2  | 54  | 67-68, 69-71            | 36 months                 | Infantry foot soldier (involved in spraying) |
| # 3  | 54  | 70-71                   | 12 months                 | Infantry soldier (field communication)       |
| # 4  | 51  | 72-73                   | 12 months                 | Infantry foot soldier                        |
| # 5  | 52  | 72-73                   | 12 months                 | Infantry foot soldier                        |
| # 6  | 54  | 69-70                   | 12 months                 | Infantry foot soldier                        |

## Analysis

Before the extraction  $^{13}\text{C}$ -UL-labeled internal standards for all 17 PCDDs/Fs and 12 PCBs were added to the sample. After spiking, the samples were extracted with appropriate solvents using a solid/liquid extraction for blood. The cleanup was done on multicolumn systems involving carbon-on-glass fibre. The measurement was performed by means of high resolution gas chromatography and high resolution mass spectrometry (HRGC/HRMS) with VG-AutoSpec operating on a resolution of approximately 10,000 using DB-5 capillary column. For each substance 2 isotope masses were measured. The quantification was carried out with the use of internal and external standards (isotope dilution method). The analytical methods used are validated and successfully applied by participation at international quality control studies <sup>9,10</sup>.

## Results and Discussion

The results of this investigation are presented in Table 1. The total TEQ for the 6 samples ranges between 22 and 51 pg/g lipid.



**Figure 1.** TEQs for PCDDs, PCDFs, non-ortho and mono-ortho PCBs in blood from Korea and from other counties, values in pg/g, lipid based

For individuals possibly exposed to Agent Orange and its main product TCDD, the concentration for 2,3,7,8-TCDD is the most important value. The concentration found for TCDD in the 6 samples ranges between 1,7 and 4,2 pg/g lipid. These values are in the typical range for persons living in industrialized countries only being exposed to dioxins via dietary intake. They compare with levels in blood of some Vietnamese of up to 413 pg/g in blood and 1,850 pg/g TCDD in milk lipid from Agent Orange (Schechter et al<sup>2,5,6,7</sup>).

In Figure 1 we compare the TEQ-values for PCDDs, PCDFs, non-ortho-PCBs and mono-ortho-PCBs found in the 6 Korean samples with mean values for the general or background populations of Germany<sup>11</sup>, Japan<sup>12</sup> and Russia<sup>13</sup>. As can be seen from this figure, the individual values in the Korean samples are within the range of the general population of other industrialized countries.

Finally we note that the analysis of 6 individual blood samples of Korean Vietnam veterans is not an extensive investigation on concentrations of dioxins in Koreans or Korean Vietnam veterans. Although we believe this small investigation to be a first step in the right direction., a more detailed and representative investigation needs to be undertaken especially of highly exposed veterans.

### Acknowledgements

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**Table 1.** PCDDs/Fs and dioxin-like PCBs in blood of Korean veterans, values in pg/g, lipid based

| Code                        | TEFs    | Sample #1    |            | Sample #2    |           | Sample #3    |           | Sample #4    |           | Sample #5    |            | Sample #6    |           |
|-----------------------------|---------|--------------|------------|--------------|-----------|--------------|-----------|--------------|-----------|--------------|------------|--------------|-----------|
|                             |         | trations     | (WHO)      | trations     | (WHO)     | trations     | (WHO)     | trations     | (WHO)     | trations     | (WHO)      | trations     | (WHO)     |
| 2,3,7,8-Tetra-CDD           | 1       | 1,8          | 1,8        | n.d.(2)      | -         | 4,2          | 4,2       | 1,8          | 1,8       | n.d.(2)      | -          | 1,7          | 1,7       |
| 1,2,3,7,8-Penta-CDD         | 1       | 5,3          | 5,3        | 4,3          | 4,3       | 8,4          | 8,4       | 5,2          | 5,2       | 5,2          | 5,2        | 5,1          | 5,1       |
| 1,2,3,4,7,8-Hexa-CDD        | 0,1     | 2,8          | 0,28       | 3,9          | 0,39      | 6,5          | 0,65      | n.d.(2)      | -         | n.d.(3)      | -          | n.d.(3)      | -         |
| 1,2,3,6,7,8-Hexa-CDD        | 0,1     | 33           | 3,3        | 11           | 1,1       | 36           | 3,6       | 14           | 1,4       | 14           | 1,4        | 13           | 1,3       |
| 1,2,3,7,8,9-Hexa-CDD        | 0,1     | 3,6          | 0,36       | 2,9          | 0,29      | 4,6          | 0,46      | 3,5          | 0,35      | 3,9          | 0,39       | 2,8          | 0,28      |
| 1,2,3,4,6,7,8-Hepta-CDD     | 0,01    | 14           | 0,14       | 16           | 0,16      | 29           | 0,29      | 8,5          | 0,085     | 15           | 0,15       | 18           | 0,18      |
| OCDD                        | 0,0001  | 206          | 0,021      | 126          | 0,013     | 422          | 0,042     | 50           | 0,0050    | 107          | 0,011      | 144          | 0,014     |
| 2,3,7,8-Tetra-CDF           | 0,1     | n.d.(3)      | -          | 4,5*         | 0,45      | n.d.(3)      | -         | n.d.(3)      | -         | n.d.(3)      | -          | n.d.(3)      | -         |
| 1,2,3,7,8-Penta-CDF         | 0,05    | 3,1*         | 0,15       | n.d.(2)      | -         | n.d.(1)      | -         | 1,9*         | 0,095     | n.d.(2)      | -          | n.d.(2)      | -         |
| 2,3,4,7,8-Penta-CDF         | 0,5     | 8,6          | 4,3        | 6,2          | 3,1       | 16           | 8,0       | 9,8          | 4,9       | 8,9          | 4,5        | 9,5          | 4,7       |
| 1,2,3,4,7,8-Hexa-CDF        | 0,1     | 8,6          | 0,86       | 8,3          | 0,83      | 10           | 1,0       | 7,0          | 0,70      | 9,6          | 0,96       | 8,4          | 0,84      |
| 1,2,3,6,7,8-Hexa-CDF        | 0,1     | 6,7          | 0,67       | 8,1          | 0,81      | 9,3          | 0,93      | 7,3          | 0,73      | 8,3          | 0,83       | 7,6          | 0,76      |
| 1,2,3,7,8,9-Hexa-CDF        | 0,1     | n.d.(2)      | -          | n.d.(4)      | -         | n.d.(3)      | -         | n.d.(2)      | -         | n.d.(2)      | -          | n.d.(2)      | -         |
| 2,3,4,6,7,8-Hexa-CDF        | 0,1     | 4,5          | 0,45       | 8,3          | 0,88      | 8,4          | 0,84      | 3,9          | 0,39      | 6,5          | 0,65       | 7,5          | 0,75      |
| 1,2,3,4,6,7,8-Hepta-CDF     | 0,01    | 6,4          | 0,064      | 8,7          | 0,087     | 4,8          | 0,048     | 20           | 0,20      | 7,0          | 0,070      | 6,6          | 0,066     |
| 1,2,3,4,7,8,9-Hepta-CDF     | 0,01    | n.d.(2)      | -          | n.d.(2)      | -         | n.d.(2)      | -         | n.d.(2)      | -         | n.d.(2)      | -          | n.d.(2)      | -         |
| OCDF                        | 0,0001  | n.d.(16)     | -          | n.d.(21)     | -         | n.d.(18)     | -         | n.d.(20)     | -         | n.d.(21)     | -          | n.d.(17)     | -         |
| 3,3',4,4'-TCB (77)          | 0,0001  | n.d.(54)     | -          | n.d.(70)     | -         | n.d.(58)     | -         | n.d.(66)     | -         | n.d.(69)     | -          | n.d.(56)     | -         |
| 3,4,4',5-TCB (81)           | 0,0001  | n.d.(4)      | -          | n.d.(5)      | -         | n.d.(4)      | -         | n.d.(5)      | -         | n.d.(5)      | -          | n.d.(4)      | -         |
| 3,3',4,4',5-PeCB (126)      | 0,1     | 48           | 4,8        | 71           | 7,1       | 112          | 11        | 81           | 8,1       | 45           | 4,5        | 62           | 6,2       |
| 3,3',4,4',5,5'-HxCB (169)   | 0,01    | 46           | 0,46       | 41           | 0,41      | 122          | 1,2       | 68           | 0,68      | 39           | 0,39       | 75           | 0,75      |
| 2,3,3',4,4'-PeCB (105)      | 0,0001  | 1616         | 0,16       | 1814         | 0,18      | 5133         | 0,51      | 3901         | 0,39      | 1722         | 0,17       | 2288         | 0,23      |
| 2,3,4,4',5-PeCB (114)       | 0,0005  | 394          | 0,20       | 367          | 0,18      | 1539         | 0,77      | 782          | 0,39      | 424          | 0,21       | 519          | 0,26      |
| 2,3',4,4',5-PeCB (118)      | 0,0001  | 5902         | 0,59       | 6853         | 0,69      | 23691        | 2,4       | 15506        | 1,6       | 7459         | 0,75       | 9734         | 0,97      |
| 2',3,4,4',5-PeCB (123)      | 0,0001  | 192          | 0,019      | n.d.(286)    | -         | 449          | 0,045     | 911          | 0,091     | 202          | 0,020      | 465          | 0,046     |
| 2,3,3',4,4',5-HxCB (156)    | 0,0005  | 3066         | 1,5        | 3111         | 1,6       | 10255        | 5,1       | 4435         | 2,2       | 2973         | 1,5        | 4523         | 2,3       |
| 2,3,3',4,4',5'-HxCB (157)   | 0,0005  | 710          | 0,36       | 585          | 0,29      | 2590         | 1,3       | 1090         | 0,55      | 713          | 0,36       | 1129         | 0,56      |
| 2,3',4,4',5,5'-HxCB (167)   | 0,00001 | 855          | 0,0086     | 1260         | 0,013     | 4152         | 0,042     | 2137         | 0,021     | 1095         | 0,011      | 1808         | 0,018     |
| 2,3,3',4,4',5,5'-HpCB (189) | 0,0001  | 461          | 0,046      | 552          | 0,055     | 1350         | 0,13      | 646          | 0,065     | 414          | 0,041      | 760          | 0,076     |
| Total PCDD                  | -       | 266          | 11         | 164          | 6,3       | 511          | 18        | 83           | 8,8       | 145          | 7,1        | 185          | 8,7       |
| Total PCDF                  | -       | 38           | 6,5        | 45           | 6,2       | 49           | 11        | 50           | 7,0       | 40           | 7,0        | 40           | 7,1       |
| <b>Total PCDD/PCDF</b>      | -       | <b>304</b>   | <b>18</b>  | <b>209</b>   | <b>12</b> | <b>560</b>   | <b>28</b> | <b>132</b>   | <b>16</b> | <b>185</b>   | <b>14</b>  | <b>225</b>   | <b>16</b> |
| Total non-ortho-PCB         | -       | 94           | 5,3        | 113          | 7,6       | 234          | 12        | 149          | 8,8       | 84           | 4,9        | 136          | 6,9       |
| Total mono-ortho-PCB        | -       | 13197        | 2,9        | 14541        | 3,0       | 49158        | 10        | 29409        | 5,3       | 15002        | 3,0        | 21226        | 4,4       |
| <b>Total WHO-PCB</b>        | -       | <b>13291</b> | <b>8,2</b> | <b>14654</b> | <b>11</b> | <b>49392</b> | <b>23</b> | <b>29558</b> | <b>14</b> | <b>15086</b> | <b>7,9</b> | <b>21362</b> | <b>11</b> |

n.d. = not detected, detection limits in ( )

\* = possible influence of outside contamination