# Dioxin and Dibenzofuran Congeners in 2,4-Dichlorophenoxyacetic acid, 2,4,5-Trichlorophenoxyacetic acid, and Agent Orange

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## Introduction

Agent Orange, a herbicide used for forest defoliation and food crop destruction by American armed forces in Vietnam between 1962 and 1971, was a mixture of equal parts of esters of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). Previous analyses of Agent Orange found an average of 2-3 parts per million of TCDD, contributing to concern in Vietnam and among US veterans about the long-term health consequences of Agent Orange exposure (1,2). Until recently it was not known that 2,4-D contained toxic 2,3,7,8 chlorine substituted dioxin and dibenzofuran congeners. It also was assumed that 2,4,5-T and its esters contained only one toxic dioxin congener, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). We recently reported analyses of 2,4-D samples from Russia, Palestinian areas (manufactured in Austria and packaged in Israel) and the United States, demonstrating the presence of 2,3,7,8 chlorine substituted PCDD/F congeners in all samples (3).

During the past year, we have obtained old stored samples of 2,4-D and 2,4,5-T and Agent Orange, the latter collected in 1968. Decades-old samples of 2,4-D and 2,4,5-T were taken from farms in upstate New York as part of a project to remove and dispose of toxic agricultural chemicals in rural areas. A sample of Agent Orange was received in 1998 from stored material donated by a veteran to the US Air Force Research Laboratory. It was collected by the veteran in 1968 during his service in Vietnam. The sample has been sent to ERGO laboratory for analysis. Using the more sensitive congener specific analytic methods

available today, congeners other than 2,3,7,8-TCDD presumably present in the samples can be measured at lower levels than was previously possible.

In this study, we provide data on levels of dioxin and dibenzofuran congeners in the Russian and Palestinian 2,4-D samples, several recently purchased U.S. 2,4-D samples, and data from decades old samples of 2,4-D, 2,4,5-T, and Agent Orange.

## Materials and Methods

Samples of 2,4-D were collected from the Ufa Chimprom agrochemical plant in Russia from archived materials and from commercially available supplies in Palestinian areas. Several American samples of 2,4-D were purchased from garden and agricultural chemicals suppliers and the other phenoxyherbicide samples were collected in 1997 from a barn in upstate New York. Samples were purchased in the US and the Middle East between 1992 and 1996, and the sample from Ufa, Russia was obtained in 1992. The Agent Orange sample was originally obtained in Vietnam in 1968.

The high resolution gas chromatography-mass spectrometry analytic techniques have been described previously and will not be repeated here (3).

## Results and Discussion

Table 1 presents the results of selected analyses from our series of 2,4-D results. TEQ is calculated assuming zero levels of congeners not detected, and levels of detection are indicated. Dilution of 2,4-D in the purchased commercial samples varied, so that the levels shown should not be interpreted as reflecting dioxin concentration in 2,4-D itself.

The levels of PCDDs, PCDFs, and total TEQ vary considerably in these samples, with TEQ from 1.9 to 828 ppt. Some of the congeners reported here are among those we and others reported in food and human tissues (5-8).

Based on these findings consideration should be given to the contributions of phenoxyherbicides to total dioxins and dibenzofurans in the environment in the United States and elsewhere. 2,4-D is commonly used as a weedkiller on lawns in the United States at the present time. Exposure to the dioxin contaminants can occur potentially during manufacture, packaging, and application, and children and animals including household pets can be exposed when walking or playing on sprayed lawns.

Measurement of the levels of dioxin and dibenzofuran congeners in the old samples of 2,4-D and 2,4,5-T originally purchased decades ago, as was the Agent Orange mixture that was used in Vietnam, can serve as a basis for conducting exposure assessment of human tissues in continuing studies of health effects from wartime or agricultural exposures. Elevated levels of some dioxin and dibenzofuran congeners with relatively short half lives in human tissues may no longer be found in US veterans. But further congener-specific exposure assessment would be feasible among people in some areas of Vietnam who may

continue to be exposed to dioxin congeners that remain in soil and sediment and which might enter the food chain.

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**Table 1. Measured Levels of Dioxin and Dibenzofuran Congeners and Total Dioxin TEQ* in 2,4-D Herbicides from Different Countries**

pg/g (ppt)

| Country of Origin | USA | | Palestine/Israel | | | Russia |
|---|---|---|---|---|---|---|
| Measured Level | Brand A | Brand B | Brand C | Brand D | Brand E | Chimprom factory, Ufa |
| 2,3,7,8-TCDD | n.d. (1.0) | n.d. (2.0) | n.d. (100) | n.d. (100) | n.d. (100) | n.d. (20) |
| **Total TCDD TEQ** | **0** | **0** | **0** | **0** | **0** | **0** |
| 1,2,3,7,8-PeCDD | 1.4 | n.d. (2.0) | 100 | n.d. (100) | 1166 | 30 |
| **Total PeCDD TEQ** | **0.7** | **0** | **50** | **0** | **583** | **15** |
| 1,2,3,4,7,8-HxCDD | n.d. (1.0) | n.d. (2.0) | n.d. (100) | n.d. (100) | n.d. (100) | 20 |
| 1,2,3,6,7,8-HxCDD | 2.4 | n.d. (2.0) | n.d. (100) | 160 | 580 | 50 |
| 1,2,3,7,8,9-HxCDD | 1.0 | n.d. (2.0) | n.d. (100) | n.d. (100) | 350 | n.d. (20) |
| **Total HxCDD TEQ** | **0.3** | **0** | **0** | **16** | **93** | **7** |
| 1,2,3,4,6,7,8-HpCDD | 1.7 | 3.8 | 100 | 1200 | 300 | 230 |
| **Total HpCDD TEQ** | **0.0** | **0.0** | **1** | **12** | **3** | **2.3** |
| OCDD | 6.3 | 18.4 | 100 | 2600 | 100 | 850 |
| **OCDD TEQ** | **0.0** | **0.0** | **0.1** | **2.6** | **0.1** | **0.9** |
| 2,3,7,8-TCDF | 3.6. | 15.6 | 300 | n.d. (100) | n.d. (100) | n.d. (100) |
| **Total TCDF TEQ** | **0.4** | **1.6** | **30** | **30** | **0** | **0** |
| 1,2,3,7,8-PeCDF | 1.0 | n.d. (2.0) | n.d. (100) | 200 | 700 | 1200 |
| 2,3,4,7,8-PeCDF | 1.1 | n.d. (2.0) | n.d. (100) | n.d. (100) | 100 | 60 |
| **Total PeCDF TEQ** | **0.6** | **0** | **0** | **10** | **85** | **90** |
| 1,2,3,4,7,8-HxCDF | 1.3 | 2.1 | n.d. (100) | 140 | 380 | 80 |
| 1,2,3,6,7,8-HxCDF | n.d. (1.0) | n.d. (2.0) | n.d. (100) | n.d. (100) | 120 | 110 |
| 1,2,3,7,8,9-HxCDF | n.d. (1.0) | n.d. (2.0) | n.d. (100) | n.d. (100) | n.d. (100) | n.d. (20) |
| 2,3,4,6,7,8-HxCDF | 1.1 | n.d. (2.0) | n.d. (100) | n.d. (100) | 120 | 50 |
| **Total HxCDF TEQ** | **0.3** | **0.2** | **0** | **14** | **62** | **24** |
| 1,2,3,4,6,7,8-HpCDF | 1.6 | 4.6 | 100 | 800 | 100 | 240 |
| 1,2,3,4,7,8,9-HpCDF | n.d. | 2.4 | n.d. (100) | n.d. (100) | n.d. (100) | 20 |
| **Total HpCDF TEQ** | **0.0** | **0.1** | **1.0** | **8** | **1.0** | **2.6** |
| OCDF | 3.9 | 12.9 | 200 | 3800 | 400 | 460 |
| **OCDF TEQ** | **0.0** | **0.0** | **0.2** | **3.8** | **0.4** | **0.5** |
| Total PCDD TEQ | 1.0 | 0.1 | 51.1 | 30.6 | 679.1 | 25.2 |
| Total PCDF TEQ | 1.3 | 1.9 | 31.2 | 65.8 | 148.4 | 117.1 |
| **Total PCDD/F TEQ** | **2.4** | **1.9** | **82.3** | **96.4** | **828** | **142** |

*Calculated with n.d. = 0

n.d. not detected, detection limit in parentheses

n.a. not analyzed because of interference

discrepancies in totals due to rounding