AVERAGE METHOD BLANK QUANTITIES OF DIOXIN-LIKE CONGENERS AND THEIR RELATIONSHIP TO THE DETECTION LIMITS OF THE U.S. EPA's NATIONAL DIOXIN AIR MONITORING NETWORK (NDAMN)

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Introduction

The U.S. EPA established a National Dioxin Air Monitoring Network (NDAMN) to determine the temporal and geographical variability of atmospheric CDDs, CDFs and coplanar PCBs throughout the United States[1].. Currently operating at 33 sampling stations , NDAMN has, as one of its tasks, the determination of atmospheric levels of dioxin-like compounds at rural and non-impacted locations of the U.S. As was mentioned by Ferrario et al[2], at the extremely low levels of detection needed to achieve congener-specific detection limits of 0.1 fg m^{-3} for 2,3,7,8-TCDD and 10 fg m^{-3} for OCDD, a number of analytical issues have been raised. One of these issues is the quantity of congeners to be expected in the laboratory method blanks[3].. This paper presents the average, standard deviation, median, range, and detects of the quantities of the congeners from 52 laboratory sample sets. These values enable the accurate determination of the dioxin-like compounds at extraordinarily low levels.

Methods

The analytes of interest in this monitoring program are the PCDDs; PCDFs substituted in the 2,3,7,8 positions on the molecule, and the coplanar PCBs (IUPAC PCB-77; PCB-105; PCB-118; PCB-126; PCB-156; PCB-157 and PCB-169). Thirty-three stations are now operational within the contiguous United States. After collection of the air samples as previously described by Cleverly et al.[1], the air samples were shipped to the EPA's Environmental Chemistry Laboratory for extraction, clean-up and analysis with High Resolution Gas Chromatography coupled with High Resolution Mass Spectrometry (HRGC/HRMS) in accordance with a modification of EPA Method 1613[4] The air samples are grouped in sample sets consisting of a method blank, laboratory control, spike, and a maximum of ten field samples for analysis. The method blank consists of 200 ml of the extracting solvent which is processed in the same manner as the field samples.

The fifty-two sample set method blanks were examined for quality control adherence to ion ratio limitations and laboratory conditions (i.e., events that could result in excessive contamination) and the presence of outliers at the 5 % level. These sample set method blanks were removed from the final

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calculations. Many of the congeners were often not detected in any of the method blanks. The average background method blank quantities were from only the detected amounts. This resulted in a true arithmetric mean with a calculated value larger than if zeros or 0.5 x LOD for the non-detects (N.D.s) in the calculation of the mean. Initial limits of detection (LODs) for the NDAMN analytical procedure expressed as total picograms for each congener group are presented in Table 1[5].. The method detection are calculated by dividing the calculated amounts of each congener by the volume of air sampled.

Results

The results of the fifty-two method blanks analyzed with air samples collected for NDAMN during 1998-2000 are presented (Table 2). In the case of the PCDDs and PCDFs, all fifty-two sample sets were used to calculate the associated average, standard deviation, median, ranges, and detections of the concentrations for the method blanks. The 2,3,7,8-TCDD/-TCDF were never measured above the limit of detection (LOD)[0.5 pg]; 1,2,3,7,8-PeCDF/-PeCDD and 2,3,4,7,8-PeCDF were measured only once above the LOD [1.5 pg]; and, of the HxCDDs/CDFs, only 2,3,4,6,7,8-HxCDF was measured more than twice above the LOD [1.5 pg]. 1,2,34,7,89-HpCDF was measured three times above the LOD [1.5 pg], while 1,2,3,4,6,7,8-HpCDF/CDD were measured more than fifteen times [1.5/2.5 pg], respectively. OCDD and OCDF were often present above their LODs [20 and 4 pg].

With respect to the coplanar PCBs, the presence of these PCBs were more frequent and generally higher due to the presence of background levels in laboratory spaces. There were only fifty-one sample sets examined as one of the sets failed quality control limitations. Additional sample sets revealed PCB contamination due to uncontrollable laboratory conditions. Thus, between forty four and forty-nine sample sets were used in calculating the values for the method blanks for the co-planar PCBs. PCBs 77, 105, 118, 156, and 157 were measured in all of the method blanks. PCB 126 were measured in more than half of the sample sets above the LOD [2 pg] and PCB 169 in only four sets above the LOD [1 pg].

The preliminary limits of detection (LODs) for NDAMN that were based on an evaluation of the instrumental detection limits and method blanks generated during the Demonstration of Capabilities phase compare very favorably with the average background method blank quantities of the project to date.

Table 1. Limits of Detection (LOD:pg)

Congener	Quantity (pg)	Congener	Quantity (pg)
TCDD/CDF	0.5	PCB 77	20
PeCDD/CDF & HxCDD/CDF	1.5	PCB 118	500
HpCDF	1.5	PCB 105	300
HpCDD	2.5	PCB 126	2.0
OCDF	4.0	PCB 156	80.0
OCDD	20.0	PCB 157	20.0
		PCB 169	1.0

Table 2. Background Method Blank Quantities (pg)

Congener	Average	Standard	Median	Range	Detect/Total
2,3,7,8-TCDD	ND	-	-	-	0/52
1,2,3,7,8-PeCDD	ND	-	-	-	1/52

1,2,3,4,7,8-HxCDD	ND	-	-	-	1/52
1,2,3,6,7,8-HxCDD	ND	-	-	-	2/52
1,2,3,7,8,9-HxCDD	ND	-	-	-	2/52
1,2,3,4,6,7,8-HpCDD	1.8	1.2	1.8	0.5-6.1	43/52
1,2,3,4,6,7,8,9-OCDD	10.5	5.1	20	2.6-24	52/52
2,3,7,8-TCDF	ND	-	-	-	0/52
1,2,3,7,8-PeCDF	ND	-	-	-	1/52
2,3,4,7,8-PeCDF	ND	-	-	-	1/52
1,2,3,4,7,8-HxCDF	ND	-	-	-	2/52
1,2,3,6,7,8-HxCDF	ND	-	-	-	1/52
2,3,4,6,7,8-HxCDF	1.1	0.5	1.5	0.5-2.6	22/52
1,2,3,7,8,9-HxCDF	ND	-	-	-	1/52
1,2,3,4,6,7,8-HpCDF	1.4	0.8	1.5	0.2-3.1	18/52
1,2,3,4,7,8,9-HpCDF	ND	-	-	-	1/52
1,2,3,4,6,7,8,9-OCDF	3.2	3.6	2.1	0.4-18	36/52
PCB 77	13.1	8.2	10.1	6.2-32	51/51
PCB 126	1.9	1.5	2	0.6-5.4	24/51
PCB 169	1.0	-	-	-	4/51
PCB 105	176	73	165	0.7-334	51/51
PCB 118	358	125	326	167-677	51/51
PCB156	46	20	40	16-87	51/51
PCB 157	14	12	9.9	3.3-33	51/51

ND - Not Detected

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