

PCDDs AND PCDFs IN VEHICLE EXHAUST PARTICLES

Yuichi Miyabara, Shunji Hashimoto, Masaru Sagai* and Masatoshi Morita

Regional Environment Division, National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305-0053, Japan

*Aomori University of Health and Welfare, 58-1 Mase, Hamadate, Aomori 030-8505, Japan (present address)

Introduction

Major sources of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are among other chemical synthetics, municipal incineration and chlorine bleaching. Although PCDDs/PCDFs mainly are emitted from municipal solid waste (MSW) incinerators in Japan, several reports have indicated that vehicle exhaust is also a PCDDs/PCDFs source (1-3). However, no report about emissions from cars in Japan is available which would allow to estimate the amount of dioxins released by car exhaust. In this paper, we inform about the PCDDs/PCDFs levels in vehicle exhaust particles (VEP). Based on these results, an attempt was made to estimate the contribution of vehicle exhaust to total amount of PCDDs/PCDFs found in ambient air.

Material and Method

Samples:

VEP was collected from electrostatic precipitators linked to the ventilators of a highway tunnel. After mixing, air-drying and grinding, the sample was sieved to 2 mm and homogenized. It was assigned as NIES certified reference material No. 8 "Vehicle Exhaust Particulates". It was stored at -20 °C until analysis.

Sample clean-up:

VEP sample was weighed and Soxhlet extracted with toluene for 18 hours. The extract was concentrated to about 0.5 mL on a rotary evaporator and washed into separation funnels with n-hexane. It was spiked with 50 pg each of (¹³C) 2,3,7,8-substituted PCDDs and PCDFs isomers as internal standards. The extract was cleaned-up by partitioning it at least twice with concentrated sulfuric acid for 60 minutes. The n-hexane layer was rinsed three times with water, and then dried by passing it through anhydrous sodium sulfate in a glass funnel. The solution was concentrated to 5 mL and sequentially subjected to silica gel, alumina and activated carbon column chromatography. 120 mL of n-hexane were used to collect the PCDDs/PCDFs fraction from a silica gel column (1.5 g Kieselgel 60, 70-230 mesh, activated at 130 °C for 3 hours, Merck). After concentration, the solution was transported to an alumina column (7.5 g of Aluminum oxide 90, basic, activity I, 70-230 mesh, Merck). Major PCBs were eluted with 60 mL of dichloromethane/n-hexane (2/98, v/v), and the PCDDs/PCDFs fraction was obtained in a volume of 120 mL of dichloromethane/n-hexane (60/40, v/v). It was cleaned-up further by an activated carbon-silica gel column (0.5 g of active carbon impregnated-silica gel, Wako Pure Chemical,

Osaka, Japan). Remaining PCBs were eluted with 50 mL of dichloromethane/n-hexane (25/75, v/v), and the PCDDs/PCDFs with 100 mL of toluene. The final eluate was concentrated to about 1 mL on a rotary evaporator under reduced pressure, and the solvent was blown off with a nitrogen gas stream. The residue was dissolved in 50 μ L of toluene (4).

Quantification:

The GC/MS analysis was performed in the selected ion mode on a JEOL JMS SX-102 high performance double focusing mass spectrometer. A mass resolution of $m/\Delta m$ of $>10,000$ was used in the EI mode. 2 μ L of the sample was injected into a Hewlett Packard 5890 II gas chromatograph equipped with a SP-2331 column for tetra to hepta chloro congeners (Supelco, PA, USA; 30 m x 0.25 mm i.d., film thickness 0.30 μ m) or a PTE-5 column for OCDD and OCDF (30 m x 0.25 mm i.d., film thickness 0.25 μ m). Data acquisition and processing of the mass spectrometer were controlled by a Hewlett Packard 98785 work station. The GC/MS operating conditions (SP-2331) were : injector temperature 260 $^{\circ}$ C, column temperature programmed from 100 $^{\circ}$ C (1 minute) to 180 $^{\circ}$ C (0 minute) at 20 $^{\circ}$ C/minute then to 260 $^{\circ}$ C (hold) at 3.0 $^{\circ}$ C/minute. The GC/MS operating conditions for the PTE-5 column was : injector temperature 270 $^{\circ}$ C, column temperature programmed from 120 $^{\circ}$ C (1 minute) to 270 $^{\circ}$ C (hold) at 30 $^{\circ}$ C/minute. Identification was based on the correct isotope ratio of M^{+} to $(M+2)^{+}$ or $(M+2)^{+}$ to $(M+4)^{+}$ ($\pm <15\%$), recoveries (50-120%) and retention time (± 4.0 sec) of the GC separation. The area of mass profile peaks of the quantification ions was used for the quantitative analysis of PCDDs and PCDFs (4).

Results and Discussion

The concentrations of PCDDs/PCDFs in SPM are shown in Table 1. SPM obtained from a highway tunnel was contained considerable amounts of PCDDs/PCDFs. It reflects the average emissions from various vehicles driving through the tunnel. The I-TEQs concentration in VEP was calculated to 242 pg/g. Urban ambient air contains approximately 40 μ g/m³ SPM in Japan (5). The SPM related I-TEQs level in ambient can be estimated to be at least 0.01 pg/m³. Compared to this, the average I-TEQs levels of urban air was 0.37 pg/m³ in Japan in 1994 (5). This would indicate that the contribution of vehicle emissions is about 2.8 % to the total amount of PCDDs/PCDFs in urban air. 4.5 millions and 68 millions of vehicle were existed in Tokyo and Japan in 1994, respectively, corresponding to an emission of 4,200 t and 64,000 t of VEP. On the basis of our data, the amounts of PCDDs/PCDFs emitted from vehicles are 1 and 17 g I-TEQs/year for Tokyo and Japan, respectively. This estimate amount of emission from vehicles is two orders of magnitude higher than that previously reported in Japan (0.07 g I-TEQs/year for Japan) (6). It is much lower than that on the total amount of PCDDs/PCDFs in urban air. In conclusion, the amount of PCDDs/PCDFs from vehicles is small, however the contribution ratio is relatively high in Japanese urban atmosphere.

The research described in this article has been funded in part by the Japan Environmental Agency with the National Institute for Environmental Studies. The manuscript has been reviewed in accordance with the Japan Environmental Agency policy and approved for publication; however it does not necessarily reflect the views of the agency.

Table 1. Levels of 2,3,7,8-chlorine substituted congeners, total PCDDs/PCDFs and TEQs in vehicle exhaust particles ^a.

PCDDs		PCDFs	
<i>Congeners</i>	Concentration (pg/g)	<i>Congeners</i>	Concentration (pg/g)
2,3,7,8-TCDD	<5.2 ^b	2,3,7,8-TCDF	108 ± 0.69 ^c
<i>Other TCDD</i>	4580 ± 1190	<i>Other TCDF</i>	2830 ± 194
1,2,3,7,8-PCDD	40.8 ± 10.6	1,2,3,7,8-PCDF	184 ± 1.65
		2,3,4,7,8-PCDF	107 ± 3.65
<i>Other PCDD</i>	1240 ± 259	<i>Other PCDF</i>	29700 ± 268
1,2,3,4,7,8-HCDD	42.3 ± 6.86	1,2,3,4,7,8-HCDF	243 ± 12.7
1,2,3,6,7,8-HCDD	96.7 ± 1.64	1,2,3,6,7,8-HCDF	231 ± 6.98
1,2,3,7,8,9-HCDD	71.0 ± 1.97	1,2,3,7,8,9-HCDF	38.6 ± 12.5
		2,3,4,6,7,8-HCDF	387 ± 15.5
<i>Other HCDD</i>	1100 ± 92.4	<i>Other HCDF</i>	1600 ± 44.6
1,2,3,4,6,7,8-HCDD	1700 ± 209	1,2,3,4,6,7,8-HCDF	1330 ± 198
		1,2,3,4,7,8,9-HCDF	143 ± 46.2
<i>Other HCDD</i>	1360 ± 144	<i>Other HCDF</i>	778 ± 119
OCDD	3650 ± 169	OCDF	1450 ± 254
Total PCDDs/PCDFs	26000 ± 1520		
I-TEQs	242 ± 6.44		

^a NIES certified reference material No. 8 “Vehicle Exhaust Particulates”.

^b not detected (<S/N=3)

^c (n=3, mean ± STD)

References

1. Hagenmaier H, Lindig C and She J; *Chemosphere*, **1994**, 29, 2163
2. Wenning R J, Paustenbach D J, Harris M A and Bedbury H; *Arch. Environ. Contam. Toxicol.*, **1993**, 24, 271
3. Douben P E T; *Chemosphere*, **1997**, 34, 1181
4. Hashimoto S, Yamamoto T, Yasuhara A and Morita M; *Chemosphere*, **1995**, 31, 4067
5. Japan Environmental Agency, p. 416-419, p. 423-424 in *Quality of the Environment in Japan 1998, 1998*: ISBN4-17-155417-9. (in Japanese)
6. Hiraoka M, *Abstract of the Kyoto conference on dioxin problem of MSW incineration 1991*, **1991**, 1