PCDD, PCDF AND PCB LEVELS IN STACK EMISSIONS FROM CZECHO-SLOVAK WASTE INCINERATORS

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ABSTRACT

PCDDs, PCDFs and PCBs were detected (total concentration ranged from tens to thousands ng/m³) in stack emissions from all investigated Czecho-Slovak incineration plants burning municipal or industrial waste. In all samples 2,3,7,8-TCDD equivalent concentrations exceeded 0.1 ng/m³. No apparent correlation was observed between the content of hydrogen chloride and free chlorine and PCDD/F levels in flue gases.

INTRODUCTION

After the presence of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) was uncovered in fly ash from municipal waste incinerators in the Netherlands [1], many researchers and authorities have paid considerable attention to the PCDD/PCDF occurrence and formation mechanism in combustion processes [2-4]. At present stack emissions from the waste incinerators are considered to be one of the significant sources of direct pollution of the atmosphere and gradually additional parts of the biosphere [5,6].

Although waste incineration is not today a major way of waste treatment in Czecho-Slovakia (waste dumps are prevailing), however, its importance is raising because a greater number of municipal and industrial incineration facilities have been built in this country. Since there is a general effort to know the range of PCDD/PCDF/PCB amounts emitted by the waste incinerators we have analyzed flue gases from some Czecho-Slovak municipal and industrial incinerators.

EXPERIMENTAL

Stack-gas samples as described in Table I were collected between the electrostatic precipitator (when present) and the stack using an isokinetic sampling techniques known as a "standard train" which consists of a heated filter, a condenser and impingers filled with ethylene glycol or methoxyethanol [7,8]. The stack-gas sampling volumes were between 10 and 20 m^3.

The components of the sample train were analyzed separately. Every sample, before extraction, was fortified with six ^{13}C-labelled standards (2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD and OCDD). The sample extraction and sample clean-up were done in accordance with the procedures described in detail elsewhere [9,10]. The method includes 24 hr Soxhlet extraction of the filter with toluene and a shaking of the condensate and the absorbent with toluene and n-hexane. The extracts are cleaned-up using a combined modified silica column (H_2SO_4, NaOH and $AgNO_3$ on silica) and fractionated on a ICN Alumina B Super I column. The 1st fraction (n-hexane-dichloromethane 98:2) was used for PCB determination after an additional clean-up step on a florisil column. The 2nd fraction (n-hexane-dichloromethane 50:50) containing PCDDs and PCDFs was analyzed by GC/MS.

All PCDD, PCDF and PCB quantifications were performed using high resolution gas chromatography and low resolution mass spectrometry in SIM mode. For PCB separation a PONA capillary column (Hewlett-Packard Co.) coupled through an open-split interface with a mass spectrometer (Hewlett-Packard 5985A) was used. For PCDD/PCDF separation either a HP-17 (Hewlett-Packard Co.) capillary column or a SP-2331 (Supelco Inc.) one connected directly to a mass selective detector (Hewlett-Packard 5970B) was used. Sample injections were carried out in splitless mode. At least two molecular ions were monitored for each PCDD/PCDF/PCB congener. PCDD/PCDF quantification was done using the ^{13}C-surrogates added to the samples as internal standards. A mixture of Aroclor 1242/1260 (1:1) was used for PCB quantification.

RESULTS AND DISCUSSION

PCDD, PCDF and PCB levels have been determinated within the framework of a complex investigation of Czecho-Slovak waste burning facilities. More detailed information on the facilities are presented in Table I. Moreover, Table I contains additional data on oxygen, free chlorine, hydrogen chloride content in stack-gases, kind of fuel, and combustion temperature. None of the incinerators was equipped with a 2nd step of flue gas cleaning, i.e. scrubbers, fabric filters, etc.

PCDD, PCDF and PCB concentrations found in analyzed samples are given in Table II. It is evident that the presence of PCDDs, PCDFs and PCBs was confirmed in stack-gases of all the investigated facilities. Increased concentrations of PCDDs+PCDFs (>1000ng/m^3) were determinated in the sample No. 2d (MSW combustion at decreased oxygen surplus), in some measurements of the sample No. 4 (low combustion temperature) and in the sample No. 5 (the combustion of plastics, incl. PVC - elevated PCDF levels are remarkable). On the other hand decreased PCDD+PCDF concentrations (<100ng/m^3) were observed in the stack emissions from the plants burning coal and/or some kinds of non-municipal waste

(the samples Nos. 6 and 7). PCB levels were approximately constant in all the samples (hundreds of ng/m³). It seems that there is no unambiguous correlation between the content of O_2, Cl_2, HCl and PCDDs, PCDFs, PCBs in the stack-gases. It is necessary to mention that fuel composition entering the combustion process was unknown during the stack-gas sampling.

Table III contains 2,3,7,8-TCDD equivalent values from several measurements (those where PCDD/F isomer-specific analysis was carried out) calculated using different toxicity equivalence factors (TEFs). The application of a model created by U.S. EPA gave the lowest values while proposed international TEFs gave the highest ones (approximately 2-times higher). It is noteworthy that in all the analyzed samples 2,3,7,8-TCDD equivalent concentration exceeded 0.1 ng/m³ which is the recommended value in several countries.

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Table I. Characteristics of investigated Czecho-Slovak waste incineration facilities

Sample	Sampl.time	Facility	Description	Fuel	Combust.temp.
1 (6 measurements)	Oct.1989	MWI Bratislava	Furnace with cylindrical grates, boiler, ESP, $@O_2$=11.5-15.4% $@Cl_2$=ND-21 @HCl=45-171	MSW 110.000 t/yr.	730-950°C
2 a (1 measurement)	July 1989	MWI Brno	Furnace with cylindrical grates, boiler, ESP, $@O_2$=11.0% $@Cl_2$=0.5 @HCl=37.6	MSW (11.5 t/hr.) current work.conditions	1150°C
b (1 measurement)	"	"	" $@O_2$=14.0% $@Cl_2$=1.0 @HCl=30.7	MSW (14.1 t/hr.) increased O_2 surplus	1110°C
c (1 measurement)	"	"	" $@O_2$=11.5% $@Cl_2$=1.8 @HCl=15.7	MSW (17.4 t/hr.) max.boiler capacity	1140°C
d (1 measurement)	"	"	" $@O_2$=8.0% $@Cl_2$=3.0 @HCl=31.5	MSW (15.4 t/hr.) decreased O_2 surplus	1110°C
e (1 measurement)	"	"	" $@O_2$=10.0% $@Cl_2$=ND @HCl=85.0	MSW+textiles (incl. plastics) 2:1 (9 t/hr.)	1150°C
3 a (1 measurement)	Nov 1989	MWI Brno	Furnace with cylindrical grates, boiler, ESP, $@O_2$=12.9% $@Cl_2$=58 @HCl=35	MSW 100.000 t/yr.	910°C
b (1 measurement)	"	"	" $@O_2$=12.1% $@Cl_2$=58 @HCl=26	MSW+plastics (polyethylen)	850°C
4 (5 measurements)	May 1989	STS Velké Meziříčí	Rotary kiln+post-combustion chamber, cyclone separator $@O_2$=16.4% $@Cl_2$=12-453	Sludge+grease +w.oil+sawdust 1.500 t/yr. @HCl=NM	320-660°C
5 (3 measurements)	Sept.1989	Technoplast Chropyně	Rotary kiln+post-combustion chamber $@O_2$=17.5% $@Cl_2$=ND @HCl=11.4-14.7	Plastics+wood w. +textiles+paper +leather cloth 5.000 t/yr.	980-1000°C
6 (4 measurements)	Sept.1989	Kaučuk Kralupy	Rotary kiln+post-combustion chamber, cyclone separator $@O_2$=14.0-20.6% $@Cl_2$=2.0 @HCl=14.3-18.0	Sludges f. sewage disposal+distillation &pyrolytic residues 20.000 t/yr.	640-960°C
7 a (1 measurement)	Dec.1989	SONP Kladno	Steam-boiler plant $@O_2$=14.2-16.4% $@Cl_2$=ND @HCl=61.5	"Salty" black coal 400.000 t/yr.	890-1100°C
b (2 measurements)	"	"	" $@O_2$=12.0-14.0% $@Cl_2$=ND @HCl=70.3-91.0	"Salty" black coal +non-metallic waste from scrap-metal collecting plants (4:1)	800-1200°C

Abbr.: MSW - municipal solid waste MWI - municipal waste incinerator
ESP - electrostatic precipitator $@O_2$ - oxygen concentration (vol.%) in stack-gas
$@Cl_2$ - concentration of free chlorine (mg/m^3) in stack-gas
@HCl - hydrogen chloride concentration (mg/m^3) in stack-gas
NM - not measured ND - not detected

Table II. Levels [ng/m^3] of PCDDs, PCDFs and PCBs in stack emissions from Czecho-Slovak waste incineration plants (sample numbering according to Table I)

Sample		PCDDs	PCDFs	PCDDs+PCDFs	PCBs
1	[average (min-max)]	78 (44-95)	239 (125-302)	317 (170-385)	91 (60-208)
2a		260	410	670	365
2b		130	180	310	380
2c		380	570	950	230
2d		1260	1850	3080	420
2e		290	430	720	400
3a		132	270	402	965
3b		126	270	396	344
4	[average (min-max)]	445 (66-1056)	520 (87-1200)	965 (153-2256)	450 (245-662)
5	[average (min-max)]	335 (270-380)	1630 (1135-2060)	1965 (1405-2415)	170 (108-282)
6	[average (min-max)]	16 (11-23)	24 (15-30)	40 (26-46)	310 (46-669)
7a		27	60	87	274
7b	[min-max]	7.1-13	19-36	26-49	312-2113

Table III. Comparison of 2,3,7,8-TCDD equivalent levels based on different TEF-values (sample numbering according to Table I).

Sample		2,3,7,8-TCDD equivalents [ng/m^3]				
		EPA (USA)	Eadon (NY)	BGA (FRG)	Nordic model (Scandinavia)	International TEFs
1	[average (min-max)]	3.9 (1.5-4.3)	6.2 (3.1-8.7)	5.1 (2.2-6.7)	7.5 (3.3-10.8)	7.7 (3.4-11.0)
3a		3.5	5.8	5.2	6.8	7.0
3b		3.5	7.0	5.0	6.9	7.2
7a		0.70	1.49	1.18	1.55	1.62
7b	[min-max]	0.27-0.32	0.57-0.73	0.38-0.57	0.55-0.80	0.57-0.83