Levels and congener pattern of PCDD/PCDF in fly and bottom ash from waste wood and natural wood burned in small to medium sized wood firing facilities in Switzerland

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Introduction

In Switzerland the annual per capita consumation of wood amounts to about 320 kg [1)]. A total of 380'000 t of waste wood are produced annually [5)]. A more intensive use of different kind of wood to produce energy is an aspect of todays Swiss energy policy. Potentially about 6 % of the heat energy production of Switzerland could be delivered by wood combustion [6,9)]. In 1993 the combustion of $2.1*10^6$ m^3 of wood resulted in an estimated amount of 24'000 t of ash.
The solid residues from wood combustion can either be used in industry as supplementary material, in agriculture as fertilizers or must be disposed in environmentally compatible waste dumps. Research work is in progress to get more information about the range of concentrations and the type of chemicals which are part of such residues [9)]. Dioxins and some heavy metals which are ubiquitous in nearly all types of ashes from wood burning are the targets of most relevance [2,3,5,9)].
Three classes of wood [7)] and two types of solid residues have been investigated:
Urban **waste wood** (**Altholz** , painted, glued, wood waste from construction and demolition and furniture, except PVC coated waste and pressure treated wood.), **residual wood** products (**Restholz** , all types of wood products which have been processed such as: chipboard, wood dust from machining), **natural wood** or native wood (**Holz naturbelassen** , natural wood without any treatment, includes also saw dust, shavings and bark). This classification differs from that of other countries (e.g.Germany). The solid residues are classified as **fly ash**, which includes all solid material beeing separated from the flue gas stream by cyclones, electrostatic precipitators (ESP), fabric filters, ceramic filters and **bottom ash**, which includes those solid residues, which are commonly known as wood ash and which are separated as the so called bottom ash from the burning volume by falling through a moving grate or left over in the oven compartment depending on the construction of the incinerator. The bottom ash could sometimes be partially formed into slag. From some incinerators only a mix of cyclone ash and the ash from grate separation was accessible for analysis. Such a mix was then classified as fly ash likewise.

Methods

Extraction, cleanup and detection were performed according to a method described in [8]. A short hand description is given: Acid treatment of the air dried ash. Soxhlet extraction for 24 h using toluene. Semiautomatic low pressure chromatography (Fluid management system, FMS, Watertown MA, U.S.A.) for the multistage cleanup of the extract with a combined silica column (acid/base), alumina (ICN super B) column and carbon celite (PX 21) column. For each sample a whole set of new columns was used. Ultimately the PCDD/PCDF were backflushed from the carbon column with toluene. Separation and detection was achieved with a J&W DB-Dioxin column (length 60 m, inner diameter 0.25 mm, film thickness 0.25 µm). Helium at 10 psi head pressure was used as carriergas. Gas chromatographic separation was carried out on a Varian 3400 after automatic splitless injection of 2-3 µl of sample volume at 260 °C. The GC was programmed from 140°C at 1 min, to 220 °C at 8 min, 260°C at 18 min, 260°C at 80 min. The mass spectrometric resolution was 10'000 (10% valley definition). Electron ionization EI+ at 70 eV was used. The two most abundant ions of the molecular cluster were monitored with multiple ion detection (MID) at 0.8s cycletime. In the first three mass windows (18 masses per window monitored) the dwelltime was 31 ms for each mass and 75 ms in the forth mass window (10 masses monitored). Native standards from BCR (Geel, Belgium) were used to calculate the response factors for the $^{13}C_{12}$-labelled isotope standards (from CIL, Cambridge Isotope Laboratories, MA, U.S.A.) used for isotope dilution analysis. The whole method was tested in several certification exercises conducted by BCR (today: Measurements and Testing, Brussels) for the analysis of PCDD/PCDF congeners in different materials. The reference material used was CRM 429 (BCR fly ash extract).

Results and discussion

A total of 30 samples were quantitatively analysed for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. The following TEQ values [ng/kg] were found:

Residue	Waste wood			Residual wood			Natural wood		
type	min	max	mean (n)	min	max	mean (n)	min	max	mean (n)
Fly ash	730	21000	5800 (9)	18	6300	2800 (3)	1.5	4.0	2.5 (6)
Bottom	4.2	3300	820 (4)	---	---	--- (0)	0.60	8.6	5.3 (8)

Typical patterns are given for a sample of fly ash from waste wood and bottom ash, as well as from the burning of natural wood (cf. Figures for sample Nr. 4, 19, 11, 28). The TEQ-level of bottom ash (Nr. 28) from natural wood is comparabel to that of the fly ash from natural wood (Nr. 19), in contrast to the pattern, which is not similar. OCDD is usually the most abundant congener. The concentrations increase with the degree of chlorination for the dibenzo-p-dioxins, whereas the concentrations of the PCDFs are elevated for the lower and higher chlorinated congeners.

Conclusions

It is shown, that the TEQ-values of all analysed incineration residues from natural wood are below 10 ng/kg. TEQ-values of ashes from the combustion of residual wood are not different from those of waste wood. If the carbon burnout ot the ashes is incomplete (cf. sample Nr. 13; urban waste wood), the grate ash too can be heavily loaded with PCDD/PCDF up to 3300 ng/kg in our case. Considerably lower values, usually 4 to 10 ng/kg are found in urban waste wood bottom ashes.

References:

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6) VHe Vereinigung für Holzenergie, (1991), Mit Holz heizen / modern und umweltgerecht, Zürich. Michael Oehme, Markus Müller, (1995), Levels and congener pattern of polychlorinated dibenzo-p-dioxins and dibenzofurans in solid residues from wood fired boilers. Influence of combustion conditions and fuel type, Chemosphere, 30(8), 1527-1539.
7) Luftreinhalte-Verordnung (LRV), (1985), from 16th December 1985, update July 1993, Switzerland.
8) Ivan Samuel Dolezal, Klaus Peter Segebarth, Markus Zennegg, Samuel Wunderli (1995), Comparison between supercritical fluid extraction (SFE) using carbon dioxide/acetone and conventional soxhlet extraction with toluene for the subsequent determination of PCDD/PCDF in a single electrofilter ash sample, Chemosphere 31(9), 4013-4024.
9) Verwertung und Beseitigung von Holzaschen (1996), Bundesamt für Umwelt, Wald und Landschaft (BUWAL), Bern, Switzerland, Schriftenreihe Umwelt (in press).

SOUR (po)

Residue type	Residue from	Waste wood Power of the heating system, type of incinerated wood	TEQ [ng/kg]
1 Fly ash	Cyclone	1800 kW, mix of contaminated wood, house demolition and construction	930
2 Fly ash	ESP	1800 kW, mix of contaminated wood, house demolition and construction	1200
3 Fly ash	Cyclone	2 x 850 kW, contaminated waste wood including 15 % chips from green wood	730
4 Fly ash	ESP	2 x 850 kW, contaminated waste wood including 15 % chips from green wood	3600
5 Fly ash	Cyclone	1800 kW grate firing, waste wood (on/off operation)	2300
6 Fly ash	ESP	1800 kW grate firing, waste wood	21000
7 Fly ash	Fabric filter	850 kW grate firing, waste wood (sorbalite used for PCDD/PCDF ceapture)	17000
8 Fly ash	Cyclone	850 kW grate firing, waste wood (low carbon burnout)	3700
9 Fly ash	Fabric filter	800 kW grate firing, waste wood	1700
10 Bottom	Grate ash	2 x 850 kW, mix of contaminated wood, demolition and construction waste wood	4.2
11 Bottom	Grate ash	1800 kW, contaminated waste wood including 15 % green wood chips	10
12 Bottom	Grate ash	1800 kW grate firing, waste wood	7.9
13 Bottom	Grate ash	850 kW grate firing, waste wood, bad incineration, low carbon burnout	3300

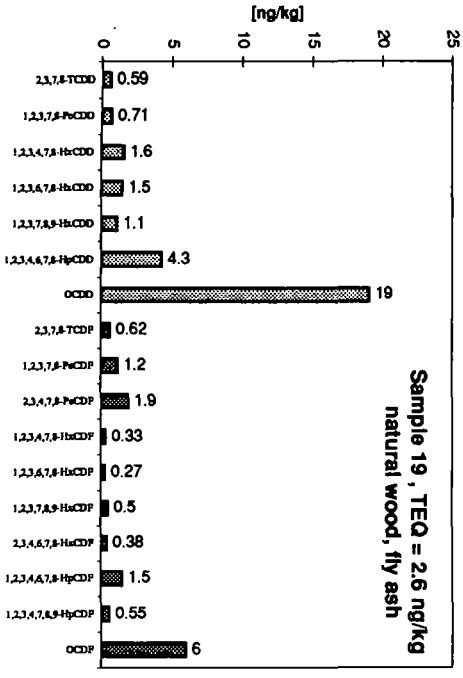
Residue type	Residue from	Residual wood Power of the heating system, type or origin of incinerated wood	TEQ [ng/kg]
14 Fly ash	Cyclone	150 kW, carpentry, builing sites, reconstruction, wood dust from abrade	2000
15 Fly ash	Cyclone	450 kW, chipboard	6300
16 Fly ash	Cyclone	1 MW, furniture construction, partially varnished beech 60 %, chipboard 40 %	18

Residue type	Residue from	Natural wood Power of the heating system, type of incinerated wood	TEQ [ng/kg]
17 Fly ash	Cyclone	300 kW, sawmill, 90 % bark, 10 % saw dust	3.2
18 Fly ash	Cyclone	1.8 MW, chips of wood, mix	1.5
19 Fly ash	Cyclone/Grate	750 kW, chips of wood, mix	2.6
20 Fly ash	Cyclone	450 kW, wood lumps (ash with 1.6 ‰ Cu, 1.3 ‰ Zn)	4.0
21 Fly ash	Cyclone/Grate	900/430 kW, chips of wood, mix	2.3
22 Fly ash	Cyclone/Furnace	180 kW, chips of wood, mix, 95 % spruce, shavings, natural wood dust	1.4
23 Bottom	Furnace	900 kW, chips of wood, leaf wood	0.59
24 Bottom	Furnace	40 kW, chips of wood, leaf wood	5.0
25 Bottom	Grate	20 kW, wood lumps from leaf trees, few residual wood	8.5
26 Bottom	Furnace	110 kW, wood chips	4.7
27 Bottom	Grate	450 kW, wood lumps (ash with 1.6 ‰ Cu, 1.3 ‰ Zn)	4.9
28 Bottom	Furnace	450 kW, wood from spruce trees, few leaf trees	6.6
29 Bottom	Grate	35 kW, wood lumps, leaf trees	7.1
30 Bottom	Grate	49 kW, wood lumps, 75 % leaf trees, 25 % spruce trees	4.4

Concentrations [ng/kg] of all 2,3,7,8-substituted PCDD/PCDF congeners and sums of isomers:

Nr.	2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF	1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF	1,2,3,7,8,9-HxCDF	2,3,4,6,7,8-HxCDF	1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF	OCDF	ΣTCDD	ΣPeCDD	ΣHxCDD	ΣHpCDD	ΣTCDF	ΣPeCDF	ΣHxCDF	ΣHpCDF
1	51	410	150	370	280	960	1200	340	690	860	250	260	39	180	570	140	220	2800	3600	4100	1800	9800	10000	2300	960
2	61	520	250	390	400	2300	7500	360	1000	1000	570	500	70	270	1700	500	1200	2100	3200	4800	4500	7700	11000	4400	3000
3	70	170	390	550	530	1900	2300	200	770	570	170	210	16	190	740	180	260	2900	4700	9100	4200	5400	7200	2600	1400
4	320	1100	1200	2100	4900	9000	10000	1200	3600	2500	670	700	220	770	2700	1100	1900	4500	15000	29000	15000	9700	20000	4800	6200
5	350	450	350	560	590	200	1300	1600	3500	2100	770	730	61	380	1200	310	270	7000	5600	9700	4400	29000	25000	4300	2100
6	1100	2700	4100	4600	4700	26000	29000	7900	33000	22000	12000	10000	590	7300	28000	5900	13000	28000	34000	60000	51000	200000	270000	95000	41000
7	460	3000	4900	7200	5800	32000	38000	6300	17000	18000	6300	7300	560	6400	18000	5700	8400	24000	39000	81000	97000	130000	140000	40000	32000
8	830	670	820	1400	1100	5000	5300	1300	3700	2900	1200	1000	160	790	2500	1000	1300	6100	11000	16000	9800	36000	33000	6900	5100
9	76	360	250	750	600	5300	16000	780	1900	1700	760	680	87	560	2000	510	860	2700	3800	8400	10200	11000	15000	4400	3600
10	0.44	1.1	0.78	1.9	1.8	24	104	2.3	5.5	2.9	1.2	1.1	0.51	1.0	8.5	2.4	5.6	18	31	29	54	43	44	18	32
11	0.41	1.9	6.7	9.9	3.2	44	96	2.7	13	9.2	3.6	3.8	1.4	4.2	19	2.8	4.7	39	83	172	94	91	123	63	2.9
12	0.85	1.2	1.9	2.9	1.8	17	71	4.1	10	7.4	3.4	2.3	2.8	0.30	5.8	1.2	5.1	27	28	54	46	110	98	27	15
13	120	720	910	1500	1200	6500	8600	940	2400	3400	1300	1200	120	1100	3800	1200	1600	1800	6500	16000	13000	8200	21000	8000	6700
14	380	770	380	690	490	1500	1100	1600	1600	1400	320	300	47	170	430	140	91	7900	7000	6600	3100	14000	11000	2100	900
15	570	2600	1600	4200	2200	11000	8800	2400	4600	5200	1600	1500	140	880	2700	710	540	38000	53000	58000	21000	56000	64000	12000	4400
16	3.0	4.8	1.8	3.4	3.2	14	19	9.5	14	16	7.9	6.3	1.5	5.2	14	7.2	7.8	66	45	57	40	180	190	55	37
17	0.53	1.9	0.94	0.56	1.1	18	14	1.2	1.0	1.8	0.34	0.39	0.93	0.90	2.1	0.72	10	29	39	57	46	14	24	13	34
18	0.41	0.33	0.45	0.28	0.41	10	38	0.92	0.66	0.79	0.43	0.32	0.27	0.47	0.89	0.14	6.0	21	26	26	22	16	18	11	1.4
19	0.59	0.71	1.6	1.5	1.1	4.3	19	0.62	1.2	1.9	0.33	0.27	0.50	0.38	1.5	0.55	6.0	18	20	26	41	13	14	8.8	14
20	0.19	1.1	0.40	0.91	0.49	10	27	4.0	4.8	3.7	1.1	1.3	0.54	1.1	2.8	0.030	5.4	14	15	28	19	63	47	14	2.8
21	0.40	0.79	1.2	2.3	1.2	7.2	19	0.54	1.2	1.1	1.2	0.52	0.39	1.1	2.0	0.62	6.4	7.6	11	19	18	6.4	9.8	6.7	14
22	0.53	0.36	0.25	0.63	0.80	2.8	5.0	0.68	0.53	0.52	0.60	0.26	0.28	0.61	0.71	0.19	2.9	7.3	6.5	10	7.7	6.5	7.7	3.3	3.9
23	0.10	0.13	0.66	0.85	0.56	0.88	4.5	0.11	0.15	0.13	0.38	0.16	0.25	0.41	0.50	0.26	1.2	2.4	4.6	5.1	2.1	3.4	5.4	6.1	2.4
24	0.55	0.84	1.2	1.3	1.2	5.3	19	4.3	4.2	4.8	2.1	1.4	0.36	1.3	9.0	1.8	7.1	22	27	26	20	48	69	43	27
25	1.7	2.7	2.0	4.5	3.4	23	43	3.6	6.4	5.8	2.2	2.1	0.57	1.5	5.3	0.9	3.8	60	58	87	57	76	80	24	16
26	0.86	1.9	0.70	0.82	0.91	5.3	13	1.9	3.6	3.4	1.4	1.3	1.1	1.6	3.1	1.6	4.9	14	22	57	22	41	38	24	47
27	0.12	1.2	2.3	3.9	7.0	5.3	24	0.41	3.1	4.0	1.3	1.4	1.9	1.3	1.1	0.92	11	1.2	19	74	17	21	32	21	3.4
28	0.81	1.9	3.6	3.4	1.8	5.3	22	4.1	20	3.8	1.1	1.1	1.5	1.2	6.8	2.5	9.4	130	120	180	13	130	98	51	290
29	0.88	1.6	0.79	1.3	1.4	8.3	39	4.9	7.5	6.5	2.6	2.5	0.70	1.6	7.0	2.2	11	58	37	34	42	140	130	45	23
30	1.7	0.40	1.3	1.6	1.4	2.8	16	6.7	3.1	1.7	0.58	0.49	0.77	1.6	3.1	1.2	8.4	35	20	38	29	40	28	37	30

SOUR (po)


[ng/kg]
0
5
10
15
20
25
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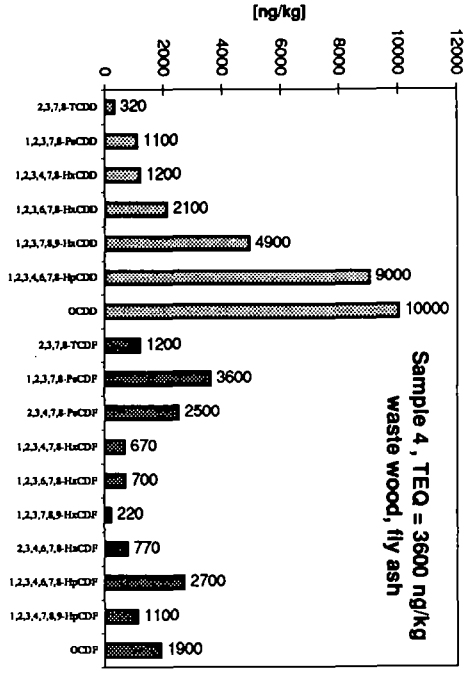
1,2,3,4,7,8-HxCDD 1.6
1,2,3,6,7,8-HxCDD 1.5
1,2,3,7,8,9-HxCDD 1.1
1,2,3,4,6,7,8-HpCDD 4.3
OCDD 19
2,3,7,8-TCDF 0.62
1,2,3,7,8-PeCDF 1.2
2,3,4,7,8-PeCDF 1.9
1,2,3,4,7,8-HxCDF 0.33
1,2,3,6,7,8-HxCDF 0.27
1,2,3,7,8,9-HxCDF 0.5
2,3,4,6,7,8-HxCDF 0.38
1,2,3,4,6,7,8-HpCDF 1.5
1,2,3,4,7,8,9-HpCDF 0.55
OCDF 6
Sample 19 , TEQ = 2.6 ng/kg
natural wood, fly ash


[ng/kg]
0
2000
4000
6000
8000
10000
12000
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1,2,3,7,8-PeCDD 1100
1,2,3,4,7,8-HxCDD 1200
1,2,3,6,7,8-HxCDD 2100
1,2,3,7,8,9-HxCDD 4900
1,2,3,4,6,7,8-HpCDD 9000
OCDD 10000
2,3,7,8-TCDF 1200
1,2,3,7,8-PeCDF 3600
2,3,4,7,8-PeCDF 2500
1,2,3,4,7,8-HxCDF 670
1,2,3,6,7,8-HxCDF 700
1,2,3,7,8,9-HxCDF 220
2,3,4,6,7,8-HxCDF 770
1,2,3,4,6,7,8-HpCDF 2700
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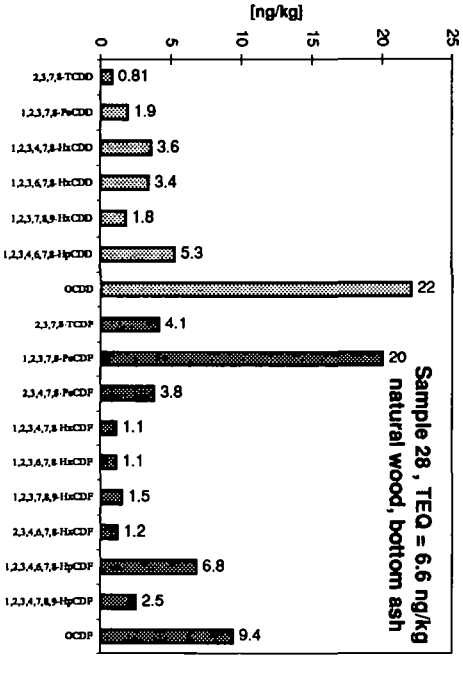
OCDF 1900
Sample 4 , TEQ = 3600 ng/kg
waste wood, fly ash


[ng/kg]
0
5
10
15
20
25
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1,2,3,7,8-PeCDD 1.9
1,2,3,4,7,8-HxCDD 3.6
1,2,3,6,7,8-HxCDD 3.4
1,2,3,7,8,9-HxCDD 1.8
1,2,3,4,6,7,8-HpCDD 5.3
OCDD 22
2,3,7,8-TCDF 4.1
1,2,3,7,8-PeCDF 20
2,3,4,7,8-PeCDF 3.8
1,2,3,4,7,8-HxCDF 1.1
1,2,3,6,7,8-HxCDF 1.1
1,2,3,7,8,9-HxCDF 1.5
2,3,4,6,7,8-HxCDF 1.2
1,2,3,4,6,7,8-HpCDF 6.8
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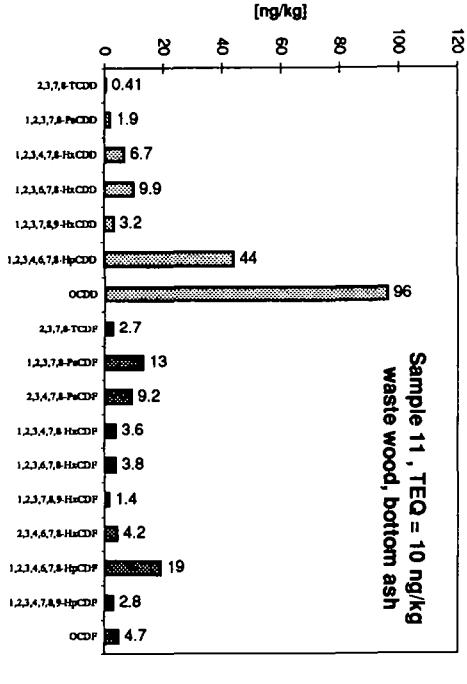
OCDF 9.4
Sample 28 , TEQ = 6.6 ng/kg
natural wood, bottom ash


[ng/kg]
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20
40
60
80
100
120
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1,2,3,4,7,8-HxCDD 6.7
1,2,3,6,7,8-HxCDD 9.9
1,2,3,7,8,9-HxCDD 3.2
1,2,3,4,6,7,8-HpCDD 44
OCDD 96
2,3,7,8-TCDF 2.7
1,2,3,7,8-PeCDF 13
2,3,4,7,8-PeCDF 9.2
1,2,3,4,7,8-HxCDF 3.6
1,2,3,6,7,8-HxCDF 3.8
1,2,3,7,8,9-HxCDF 1.4
2,3,4,6,7,8-HxCDF 4.2
1,2,3,4,6,7,8-HpCDF 19
1,2,3,4,7,8,9-HpCDF 2.8
OCDF 4.7
Sample 11 , TEQ = 10 ng/kg
waste wood, bottom ash