

Derivation of Indicators for PCDD/PCDF concentration in MSWI Ashes

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Introduction

Both changes in combustion parameters (“t, t, t”: temperature, time, turbulence) and advances in air pollution control allow modern municipal solid waste incinerators (MSWI) to keep dioxin (PCDD+PCDF) concentrations in the stack gas below low limits such as 0.1 ng/m³ (I-)TEQ. However, the dioxin load of solid residues still is too high to fulfil stringent limits of total dioxin emission such as the Japanese limit of 5 µg TEQ/Mg of waste burned. Apart from APC residues, fly and boiler ashes account for the largest part of total dioxins emitted. Consequently, thermal treatment of the fly ash is implemented in several MSWI plants, most of them situated in Japan.

However, thermal ash treatment is expensive both considering costs and energy. Dioxin concentrations in solid residues were found to vary by 2 orders of magnitude¹. Although variation between different plants is larger than between different samples from the same plant, it should be possible to reduce residual PCDD/PCDF load substantially treating only the higher loaded fraction of the ashes if it is possible to select these on-line.

Aim of the research work was to derive on-line detectable indicators for the PCDD/PCDF load of boiler ash and ESP dust of MSWI plants.

Methods and Materials

Flue gas, boiler ash and fly ash were sampled over extended periods of time at three modern MSWI plants situated in Bavaria. Direct sampling of the fly ash from the ESP could be performed only on two of the plants (A and B). The plants were made from different suppliers and hence the grate systems, combustion chamber and boiler designs differed. Although the combustion lines were of similar nominal size (approximately 10 Mg/h), the plants were operated at different conditions e.g.

regarding burn-out versus residual oxygen excess. During the sampling campaigns normal changes in operation conditions were considered such as partial load operation, changes in lambda, and fouling (status in the inspection cycle). At plant A, we additionally investigated a start-up process. On several sampling dates at plant C temporarily disturbed combustion conditions causing CO-peaks were provoked to investigate the influence of such phases on the ash quality. Figure 1 shows the sampling points on one of the plants.

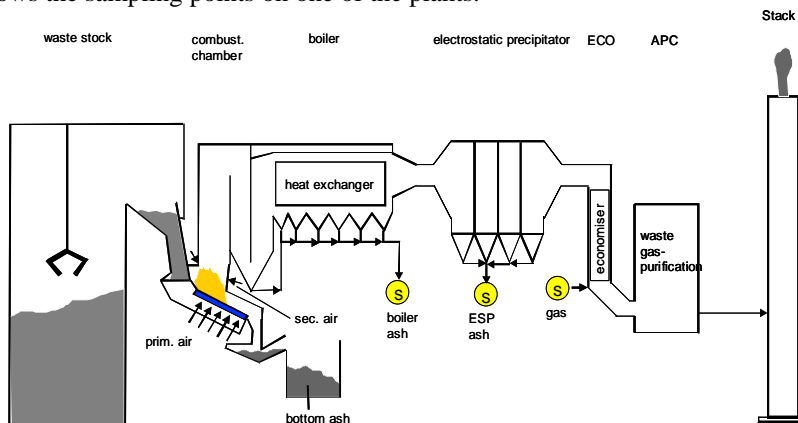


Figure 1: Sampling points at MSWI A

Samples were analysed on PCDD/PCDF according to DIN EN 1948. PAH (16 compounds according to EPA610, perylene, coronene and benzo(e)pyrene), chlorobenzenes (C12-C16) and chlorophenols (C11-C15) were analysed from aliquots of the extracts made for dioxin analysis. With respect to the volatility of some PAH, chlorobenzenes and chlorophenols, extraction was done in two steps with dichloromethane and toluene being concentrated separately.

Additionally, flue gas composition (O_2 , H_2O , CO , SO_2 , HCl) was measured either by continuous monitors available at the plants or by a flue gas analyser (TESTO 360) and discontinuous measurement of HCl . Plant operation parameters such as temperatures, steam parameters, feed rate and air flow rates were taken from the plant operation data logging systems.

The results from the test runs under impaired combustion conditions were evaluated separately from the data acquired at conditions which occur at normal operation. For data evaluation the concentrations of the organic trace components were transformed to a logarithmic base. All statistic calculations were performed with Statsoft's "Statistica" package.

Results and Discussion

Range of PCDD/PCDF concentrations in the samples

The PCDD/PCDF concentrations observed in the ashes from plants A and C were in the same range of concentrations as reported some years ago¹. The few boiler ashes sampled at plant B were lower on PCDD/PCDF. The ashes sampled at plant C during and after CO peaks caused by throddling the air supply or overcharging the grate showed PCDD/PCDF concentrations up to 9000 ng I-TEQ/kg. Equally the ashes from the start-up process at plant A showed much higher values than observed at normal combustion conditions².

Figure 1 gives a graphical presentation of the concentration ranges (mean, minimum and maximum values)

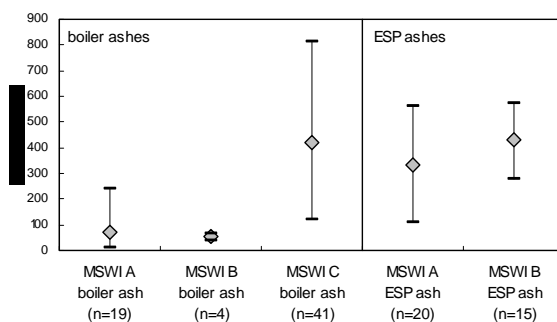


Figure 1: PCDD/PCDF concentration ranges of the boiler and ESP ashes sampled

Univariate Correlation Analysis

From different researchers several compounds in MSWI flue gas were found to be sufficiently correlated to PCDD/PCDF flue gas concentration to serve as dioxin surrogates, e.g. for process control³. In contrast to the flue gas PCDD/PCDF concentrations, there was almost no positive correlation of the ashes PCDD/PCDF concentrations to the compounds usually proposed as indicators or surrogates (test runs at impaired combustion conditions excluded). Also, flue gas and ashes PCDD/PCDF concentrations were not correlated to each other. Table 1 shows the results of correlation analysis between PCDD/PCDF in the ashes and flue gas, other trace compounds, flue gas composition and operational parameters.

Weak to significant negative correlation (descending slope) can be found between PAH concentrations in the flue gas and the ashes PCDD/PCDF content of all three plants. This is most pronounced at plant B, which is operated under CO minimising conditions with quite high oxygen excess (CO concentrations below the detection limit of the equipment installed)

Table 1: Selected results of correlation analysis

	Plant A						Plant B						Plant C					
	PCDD/PCDF						PCDD/PCDF						PCDD/PCDF					
	flue gas		boiler ash		ESP ash		flue gas		ESP ash				flue gas		boiler ash			
	r	n	r	n	r	n	r	n	r	n			r	n	r	n		
PCDD/PCDF_FLUE GAS			-0,11	15	0,05	15			-0,08	15					-0,33	16		
S_PAK_EPA	-0,2	15	-0,01	15	-0,46	15	0,68	8	-0,53	7			0,27	19	-0,64	14		
S_PAK_<200	-0,19	15	-0,01	15	-0,46	15	0,67	8	-0,47	7			0,24	19	-0,61	14		
S_PAK_>200	-0,23	15	-0,27	15	-0,25	15	0,74	8	-0,71	7			0,16	19	-0,23	14		
S_PCBZ	0,2	15	-0,02	15	-0,56	15	0,64	8	-0,22	7			0,69	19	-0,67	14		
S_PCPH	0,26	15	0,02	15	-0,16	15	n.a.	0	n.a.				0,37	19	0,21	14		
S_C2BZ	0,51	15	0,02	15	-0,46	15	0,64	8	-0,36	7			0,47	19	-0,07	14		
S_C3BZ	0,59	15	-0,02	15	-0,47	15	0,37	8	-0,3	7			0,73	19	-0,18	14		
S_C4BZ	0,64	15	-0,02	15	-0,45	15	0,3	8	-0,33	7			0,89	19	-0,45	14		
C5BZ	0,74	15	-0,05	15	-0,34	15	0,12	8	-0,34	7			0,87	19	-0,57	14		
C6BZ	0,73	15	0,04	15	-0,21	15	-0,04	8	-0,32	7			0,65	19	-0,35	14		
S_C1PH	0,04	15	0,07	15	-0,25	15	n.a.	0	n.a.				0,7	19	-0,13	14		
S_C2PH	0,19	15	0,1	15	-0,24	15	n.a.	0	n.a.				0,45	19	0,47	14		
S_C3PH	0,4	15	0,09	15	-0,18	15	n.a.	0	n.a.				0,52	19	0,45	14		
S_C4PH	0,11	15	-0,11	15	0,01	15	n.a.	0	n.a.				0,52	19	0,52	14		
C5PH	0,58	14	-0,1	14	-0,06	14	n.a.	0	n.a.				0,81	19	-0,06	14		

Table 1 (continued)

	Plant A						Plant B						Plant C					
	PCDD/PCDF						PCDD/PCDF						PCDD/PCDF					
	flue gas		boiler ash		ESP ash		flue gas		ESP ash				flue gas		boiler ash			
	r	n	r	n	r	n	r	n	r	n			r	n	r	n		
HCL_FLUE GAS	-0,34	8	-0,1	8	0,54	8	0,32	16	-0,32	15			0,28	20	0,27	16		
O ₂ _FLUE GAS	-0,38	15	-0,43	15	-0,18	15	0,44	16	-0,11	15			0,44	22	-0,63	16		
CO_FLUE GAS	0,11	15	-0,14	15	-0,1	15	n.a.		n.a.				-0,26	22	0,05	16		
SO ₂ _FLUE GAS	-0,34	8	-0,1	8	0,39	8	0,2	5	-0,62	5			0,35	22	-0,29	16		
NOx_FLUE GAS	0,04	8	-0,66	8	0,15	8	-0,05	15	-0,11	14			0,08	22	0,12	16		
FLOW PRIM AIR	0,37	15	0,22	15	0,13	15	0,29	16	0,49	15			0,6	22	-0,7	16		
FLOW SEC. AIR	-0,18	15	-0,28	15	0,52	15	-0,28	16	0,35	15			0,41	22	-0,72	16		
TEMP_CC	0,16	15	-0,52	15	0,05	15	-0,09	16	0,29	15			-0,45	22	0,5	16		
TEMP 2nd FLUE	-0,24	15	0,03	15	-0,22	15	-0,2	16	0,25	15			-0,43	22	0,76	16		
TEMP 3rd FLUE	-0,24	15	0,03	15	-0,22	15	n.a.		n.a.				n.a.		n.a.			
TEMP_BL END	-0,33	15	-0,22	15	0,12	15	-0,05	16	0,6	15			-0,32	22	0,34	16		

r: Pearson's correlation coefficient, n: number of data sets

At all three plants the correlations of operational parameters to the ashes PCDD/PCDF concentrations were stronger than to the flue gas PCDD/PCDF concentrations. Especially at plant C, there was a clear correlation between air

management, oxygen excess and the ashes PCDD/PCDF load. Plant C is operated “energy optimized” at a low air excess.

However, at none of the plants, one single parameter could give an satisfactory estimation of the PCDD/PCDF concentration in the ashes for the selection of highly loaded fractions.

Multivariate Correlation Analysis

After fitting of a correlation equation the residual variation of the data set can either be caused by other parameters having an influence on the target parameter or by mere stochastic errors. In the first case multidimensional fitting choosing appropriate parameters can reduce the residual variation. Parameters for multidimensional fitting were chosen either starting from those parameters giving the best results in the univariate calculations or from parameters chosen from principal component analysis. Tables 2 and 3 give examples of some results from multidimensional fitting. Obviously different parameter sets are best fitting for boiler ashes and ESP ashes and the selection of parameters is different for different plants. Common for all for sets of data is the importance of temperatures, either in the combustion chamber, the high gas temperature part of the boilers (2nd respectively 3rd flue) or at the boiler end. Oxygen supply (combustion air flow rates or excess oxygen concentration), showed to be important as well as HCl and SO₂ concentrations or the concentrations of selected PICs.

In all cases it has been possible to find parameter sets reaching correlation coefficients of 0.8 or more with combinations of 3 or 4 different parameters. Correlation coefficients of a minimum of 0.8 are considered to allow a rough estimation of the PCDD/PCDF load of the ashes.

Basing on the results of the correlation calculations it will be possible to merge the individual signals in a “senor array” to a single signal which can be processed by the plant’s control system.

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Table 2: Selected results of multivariate correlation analysis (boiler ashes)

Plant A, boiler ash			Plant C, boiler ash		
Number of parameters	Parameters chosen	Correlation-coefficient r	Number of parameters	Parameters chosen	Correlation-coefficient r
2	Temp. CC Temp. 3 rd flue	0.59	2	Temp. boiler end PAH > 200 m/z in flue gas	0.77
2	NOx in flue gas O ₂ in flue gas	0.73	2	Temp. boiler end CO in flue gas	0.80
3	Temp. CC NOx in flue gas CO in flue gas	0.76	3	Temp. boiler end CO in flue gas PAH > 200 m/z in flue gas.	0.82
3	O ₂ in flue gas SO ₂ in flue gas NOx in flue gas	0.76	3	Temp. boiler end SO ₂ in flue gas CO in flue gas	0.83
4	Temp. CC Temp. 3 rd flue O ₂ in flue gas CO in flue gas	0.78	4	Temp. boiler end SO ₂ in flue gas CO in flue gas HCl in flue gas	0.84
4	O ₂ in flue gas SO ₂ in flue gas NOx in flue gas PAH > 200 m/z in flue gas	0.80	4	Temp. boiler end SO ₂ in flue gas CO in flue gas PAH > 200 m/z in flue gas	0.85

Table 3: Selected results of multivariate correlation analysis (ESP ashes)

Plant A, ESP ash			Plant B, ESP ash		
Number of parameters	Parameters chosen	Correlation-coefficient r	Number of parameters	Parameters chosen	Correlation-coefficient r
2	Flow sec. air HCl in flue gas	0.62	2	HCl in flue gas Temp. boiler end	0.60
2	S_PCBz HCl in flue gas	0.66	2	PAH > 200 m/z in flue gas Temp. boiler end	0.79
3	S_PCBz HCl in flue gas SO ₂ in flue gas	0.70	3	PAH > 200 m/z in flue gas HCl in flue gas Temp. boiler end	0.79
3	Flow sec. air HCl in flue gas SO ₂ in flue gas	0.72	3	PAH > 200 m/z in flue gas Flow prim. air HCl in flue gas	0.82
4	Temp CC Temp 3 rd flue O ₂ in flue gas CO in flue gas	0.78	3	O ₂ in flue gas PAH > 200 m/z in flue gas Flow prim. air	0.89
4	Flow sec. air HCl in flue gas O ₂ in flue gas SO ₂ in flue gas	0.80	3	PAH > 200 m/z in flue gas Flow prim. air Temp. boiler end	0.90

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References

- 1 Riedel H., Hentschel B. and Thoma H. (1999) Organohalogen Compounds 40, 465-468.
- 2 Nordsieck H.O., Neuer-Etscheidt K. and Zimmermann R. (2003) Organohalogen Compounds 63, 33-36.
- 3 Öberg T, Neuer-Etscheidt K., Nordsieck H.O. and Zimmermann R. (2002) Organohalogen Compounds