Formation of PCDD/F during drying process of sewage sludge

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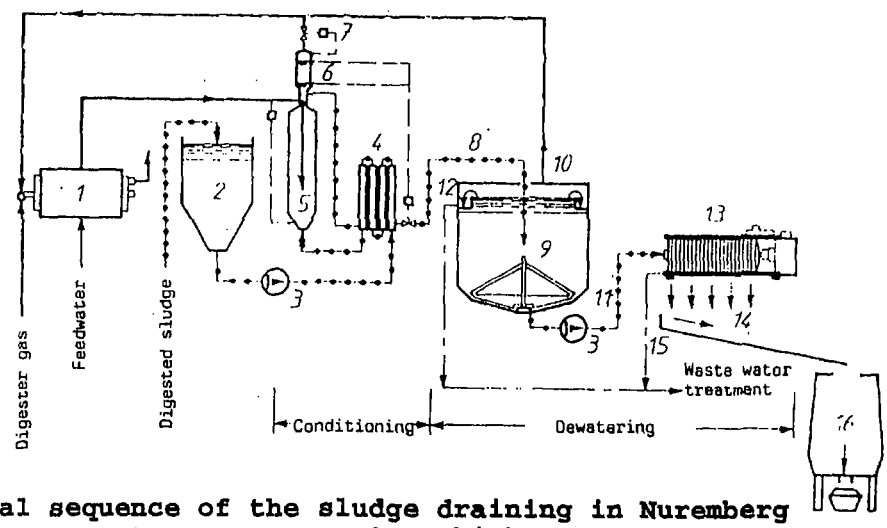
In the city of Nuremberg (Germany), each year about 25,000 tons (dry matter) of sewage sludge are created as a by-product of waste water treatment. The digested sludge consists of 96 % water and until 1992 was thermally stabilized using the Porteous procedure: the sludge was heated up in an autoclave to a temperature of 180 - 200 °C at a pressure of 28 bar. After relaxation, it was moved to a thickener where a substantial part of the liquid could be removed. After running through a chamber filter, the sludge contained only about 50 % dry matter. This treatment does not only remove water, but organic matter is also digested or evaporated.



Operational sequence of the sludge draining in Nuremberg

1	Steam generator	9	Thickener
2	Storeroom	10	De-aeration
3	Piston diaphragm pump	11	Thickened sludge
4	Heat exchanger	12	Waste water
5	Autoclaves	13	Chamber filter press
6	Gauge equipment	14	Press cake
7	Release of pressure	15	Filtrate
8	Conditioned sludge	16	Silo

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Between November 1991 and May 1992, the sludge was analysed four times before and after the drying process and examined for heavy metals (Pb, Cd, Cr, Cu, Ni, Hg, Zn), polychlorinated biphenyls (PCB) and PCDD/F. It was found that the concentration of heavy metals and PCB (related to dry matter) had increased by a factor of about 1.3 after the drying process (see table 1 and 2).

Table 1 Heavy metals in the sewage sludge before and after the drying process (concentrations in mg/kg dry matter)

	Pb	Cd	Cr	Cu	Ni	Hg	Zn
Nov. 91 before drying	120	3	160	520	64	4	1700
after drying	150	4	200	630	79	5	2000
Jan. 92 before drying	200	4	170	540	76	4	2100
after drying	270	5	210	700	96	5	2400
April 92 before drying	160	4	200	590	80	6	1900
after drying	190	3	250	730	91	8	2400
May 92 before drying	140	4	200	640	82	5	1900
after drying	180	5	270	780	100	6	2400
average factor	1,27	1,15	1,27	1,24	1,21	1,26	1,21

Table 2 PCB-concentrations in the sewage sludge before and after the drying process (concentrations in µg/kg dry matter)

	PCB 28	PCB 52	PCB 101	PCB 138	PCB 153	PCB 180	Σ PCB
Nov. 91 before drying	13,2	23,3	56,5	106,4	91,4	61,8	352,6
after drying	18,6	35,6	83,3	131,0	111,1	73,7	453,3
Jan. 92 before drying	12,6	19,7	58,3	78,0	67,7	52,9	289,2
after drying	22,2	30,4	58,6	119,3	89,1	65,6	385,2
April 92 before drying	14,1	19,3	34,2	73,4	61,7	46,1	248,8
after drying	20,6	28,8	44,8	85,3	69,0	53,0	301,5
May 92 before drying	32,8	22,2	43,6	87,0	71,3	53,0	309,9
after drying	33,4	44,4	70,2	125	104	74,2	451,2
average factor	1,41	1,63	1,36	1,34	1,28	1,25	

This effect may be explained by the decrease of organic matter during drying. In the case of PCDD/F, the ITQ was found to be increased by a factor of 3.2, for some congeners even by a factor of 8 (see table 3). This may only be explained by the fact that during thermal conditioning, PCDD/F ist formed from precursors like e. g. chlorophenols. This formation is probably catalyzed by metals like copper or nickel and considerably sped up by the higher temperatures.

Table 3: PCDD/F-concentrations in the sewage sludge before and after the drying process (in ng/kg dry matter)

Parameter	Nov. 1991			Jan. 1992			April 1992			May 1992			average factor
	before drying	after drying	factor	before drying	after drying	factor	before drying	after drying	factor	before drying	after drying	factor	
2,3,7,8- TCDD	0,47	1,1	2,34	0,67	1,9	2,82	0,54	1,39	2,57	0,63	1,32	2,10	2,46
1,2,3,7,8 PeCDD	4,7	18,9	4,02	4,2	14,5	3,50	3,68	17,5	4,75	4,96	15,6	3,15	3,86
1,2,3,4,7,8 HxCDD	9,5	22,8	2,40	6,6	21,4	3,24	3,48	22,1	6,35	5,96	22,1	3,71	3,93
1,2,3,6,7,8 Hx	95,6	306,0	3,20	61,3	232,7	3,80	44,0	273	6,2	67,9	283	3,87	4,27
1,2,3,7,8,9 Hx	44,8	152,3	3,40	29,0	118,8	4,10	18,9	136	7,20	29,9	142	4,75	4,86
1,2,3,4,6,7,8 Hp	1151	4028	3,50	938	3430,6	3,66	781	4100	5,25	1100	3320	3,02	3,86
OCDD	6375	12069	1,90	4978	8923	1,79	5320	13400	2,52	6530	11200	1,72	1,98
2,3,7,8 TCDF	9,9	20,7	2,10	9,1	13,2	1,45	10,0	16,8	1,68	10,6	11,5	1,10	1,58
1,2,3,7,8 PeTCDF	7,2	16,2	2,25	6,6	13,2	2,0	6,31	16,8	2,66	7,44	12,8	1,72	2,16
2,3,4,7,8 PeCDF	8,0	15,5	2,58	8,0	7,2	0,9	5,67	16,1	2,84	8,26	11,7	1,87	2,05
1,2,3,4,7,8 HxCDF	7,2	14,1	1,96	8,1	14,0	1,73	8,37	19,0	2,27	9,86	14,1	1,43	1,85
1,2,3,6,7,8 HxCDF	4,7	10,1	2,15	9,1	13,5	1,48	6,11	15,3	2,50	7,27	10,1	1,39	1,88
1,2,3,7,8,9 HxCDF	0,6	3,5	5,83	0,6	0,9	1,80	1,04	2,42	2,33	1,30	1,24	0,95	2,73
2,3,4,6,7,8 HxCDF	4,1	12,0	2,93	9,2	9,6	1,05	6,87	13,7	1,99	7,26	10,3	1,42	1,85
1,2,3,4,6,7,8 Hp	97,3	146	1,50	83,6	142	1,70	77,8	179	2,3	108	130	1,20	1,68
1,2,3,4,7,8,9 Hp	2,6	3,3	1,27	2,9	4,9	1,69	4,41	10,1	2,29	7,13	6,71	0,94	1,55
OCDF	141,9	83,3	0,59	135,7	124,4	0,92	228	394	1,73	223	258	1,16	1,10
∑ TCDD	124	634	5,11	76,8	406,3	5,36	47,2	527	11,17	77,6	507	6,53	7,04
∑ PeCDD	200	823	4,12	81,8	786,5	9,61	60,1	720	11,98	112	680	6,10	7,95
∑ HxCDD	745	1838	2,47	613	2427,5	3,96	378	2000	5,29	582	1922	3,30	3,08
∑ HpCDD	2260	7271	3,22	1710	5845,7	3,42	1610	7300	4,53	2080	5760	2,77	3,49
∑ TCDF	75,2	211	2,81	71,4	152,8	2,14	72,4	151	2,09	85,3	115	1,35	2,10
∑ PeCDF	122,2	307	2,51	57,6	260,8	4,53	61,3	148	2,41	65,5	160	2,44	2,97
∑ HxCDF	85,6	192	2,24	86,1	176,3	2,05	64,8	193	2,98	99,3	141	1,42	2,17
∑ HpCDF	170,0	245	1,44	149	221,8	1,49	144	316	2,19	212	230	1,08	1,55
ITQ	42,8	127	2,97	35,7	101	2,83	29,6	126	4,26	39,5	109	2,76	3,21