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Results of dioxins emission measurements from thermal processes in Poland 1996-2002

In Poland since 1996 until the June 2002 stack gases released to the atmosphere from incinerators for hospital waste incineration, municipal and industrial power plants, industrial waste incinerators and cement kilns where co-incineration of hazardous and industrial wastes are performed were measured for dioxins concentration using the methods based on the EN-1948 European standard. The purpose of these measurements was to collect data about emission of dioxins in Poland from industrial sources as well as to adjust the laboratory methods and instrumentation for routine analysis prior to introduction the Polish requirements concerning dioxin emission control.

From thes installations, only 11 are equipped with modern systems of dry/wet stack gas cleaning technology of combustion gases, which do not dispose liquid effluents. 13 industrial and hospital waste incinerators dispose the effluents to industrial wastewater treatment plants whereas 12 dispose waste waters to municipal collectors. In non-sewage solutions, wet systems of combustion gases purification are also applied but the excess of used, recirculating absorbing solution is evaporated, what leads to cooling the hot stack gas stream (quenching process). In all cases we have serious problems with disposal of residues from incinerators. Mostly with fly and bottom ashes. Accordingly to the new polish regulations – established by Polish Ministry for Environmental Protection in July 2001 these residues should not be landfilled.

Our dioxin mesurements shown, that only a few newly constructed incinerators emitted stack gases of dioxins concentration below 0,1 ng-TEQ/m^3. Mostly, for older plants high emission values were obtained. Even in some cases 105 ng-TEQ/m^3 were measured! Average emission factors was in the level of 200 μg-TEQ/t of incinerated hospital wastes, however, 990μg-TEQ/t was also measured.

It will be also presented data for dioxin concentartion released from cement kilns during co-incinerated of hazardous industrial wastes for exaple from car shredding, petrochemical wastes and animal meal. In July 2001 measurements of hazardous substances emission were conducted during co-incineration of time-exposed, not used chlorinated pesticides in selected cement kiln. However, even then, data from measurement indicates that dioxins concentartion in stack gases which are released to atmosphere from cement kilns not exceeded 0,5 ng-TEQ/m^3 in any cases. The problem is in releasing of huge volumes of stack gases which are mostly 1 million of m^3/h.

Dioxin emissions from hard coal burning were also measured in 2000-2002. We have shown, that polish big power stations burning over 50 tons of coal/h – mostly in fluidised bed emit gases containing very low dioxins concentration eg. lower than 0,01 ng-TEQ/m^3. In the other cases dioxins concentration rises up even to 10 ng-TEQ/m^3 if polish hard coal is burned in small plants (50 – 200 kg/h). We have shown, that emission from houses heated with coal

may be in some cases even 77 ng-TEQ/m^3. In Poland most cities are heated with small power stations so far.
Stack gas dioxin concentration measured from house-hold waste incineration showed values from 0,5 up-to 77 ng-TEQ/m^3 of higly contaminated stack gases released from house chimneys.
However, when grass is fired in Spring and Autumn in Poland (very often and typical in Poland in rural areas) the dioxins in ambient air concentration has to be found on a level of 50 pg-TEQ/m^3 about 1 km from fire area. In this case the fire took place on 0,5 ha area and wind velocity was about 5m/s. In Cracow suburbia we have shown in one case 0,3 ng-TEQ/m^3 of air when large grass fire had took place in late autumn 2001.
In the period of 1996-2001 dioxins concentration was also determined in ambient air from Krakow (Cracow) city and the suburbian area. Due to the incineration of house-hold wastes in houses in winter time the average dioxin concentration in the air rised–up to 10 pg-TEQ/m^3.
In 2001 the air dioxin concentration was higher in winter than in 1999 and 2000. Possibly, people get rid of their house hold refuses in theit stoves more often than in last years. This is caused from economical reason. In last years waste disposal costs in Poland increased significantly.
In summer time air dioxins concentration was on the level of 0,2-0,5 pg-TEQ/m^3.
The measured dioxins emissions indicated that apart from needs of the upgrading of incineration technology for waste thermal utilisation it also should be forced not to incinerate a house-hold wastes in houses as well as grass should not be fired on large open areas.
The education of polish society should be the most important in this case.

Preliminary measurements of dioxins concentration in air in Cracow (Kraków) – the second largest city in Poland of above of one million of inhabitants were carried out in 1996.
As a result, it was revealed that, the basic source of the emission of PCDD/F into the air over Cracow were uncontrolled processes of burning of wastes. Burning of fuels in engines with spark ignition is another source of this emission, however, less important.
Moreover, soot which was taken from chimneys of houses which were coal-fired, contained a significant concentration of dioxins. It could testify that burning of wastes is very common in Cracow. The process of dioxin formation, under these conditions, has been thoroughly worked out. Tests were made on a number of randomly chosen samples (mainly because of the fact that analyses were very expensive). Having had only a small number of samples it was impossible to draw any univocal conclusions which made it possible to define main sources of the increase in dioxin content in air during winter months.

Measurements of dioxin content in air in Cracow which were carried out in period of 1996 - 2001, were aimed not only at defining of potential threads on health of Cracow's citizens but also at indicating of basic sources of emission of dioxins into the atmosphere. Because of strong adsorption of dioxins to surface-active particles of the s.p.m. (*suspended particulate matter*) they are present in air mostly in the form of adsorbed compounds onto surface of solid particles.
Selection of sampling points was made on the basis of earlier preliminary measurements of PCDDs/PCDFs (the largest city crossing),observations of traffic and observations in which

quarters of Cracow coal heating of houses was the most intensive in winter and early spring months (South part and Center of Cracow) [1].
To those measurements were subjected samples of suspended particulate matter in air, of dimensions less than 10 μm, which were taken from monitoring points in four major quarters of Cracow: Centrum, Nowa Huta, Podgorze and Krowodrza

In Nowa Huta – the East part of the City, the majority of contamination was formed in processes of steel production at steel factory - Huta Sendzimira. Sampling of the suspended particulate matter (s.p.m.), which then were subjected to analysis of PCDDs and PCDFs was performed using highly efficient samplers PM10 of type MFC-HVPM10 produced by ANDERSEN Samplers Inc. USA. These samplers are used by monitoring stations in Cracow, which are controlled by local Inspectorate for Environmental Pollution Controll in Cracow. Each time, 1600 m^3 of air was sampled. Each sampling took 24 hours. Samples were taken during winter months from the beginning of 1996-1998. In January, February and March, there were taken 2 samples from the same measurement point (about every 14 days) and comparatively 2 samples in June. There were taken 8 samples from each monitoring point, what meant that, in total, 32 samples were taken every year. Samplings were performed in not windy days and then, when it was not raining. Average Air temperature in January and February were about -10^0C. In March, temperature of air was about 0^0C whereas in June it was about 20^0C. The results presented in Figure 1 show that the level of PCDD/F content in air in winter months in Cracow is much higher, with comparison to, their content in air in other big cities in Western Europe. It is reported by Moche and Thanner [2,3] that in Western cities ambient air dioxin concentration was about 0.3 pg-TEQ/m^3. When one compares the results of analysis of PCDD/F content in Austrian air during the years 1992-1993, which are cited by Wolfgang Moche, to results of measurements of air in Cracow, it is seen that the distribution of groups of congeners PCDD/F are very similar. Measurements in Austria were made on samples from Linz and Vienna. In samples taken in Cracow, tetrachlorodibenzofurans were detected as dominating PCDD/F congeners.PCDDFs ration to PCDDs expressed as TEQ value is 1.6. As a result, it was revealed that, perhaps, the basic sources of the emission of PCDDs/Fs into the air over Cracow were uncontrolled processes of burning of wastes realised mainly in hard coal heating stoves in houses by many inhabitants as a household refuse disposal method. Burning of fuels in engines with spark ignition is another source of this emission, however, less important.
Results of analytical investigations of sources of dioxins from uncontrolled incineration of house-hold wastes are presented in Fig. 2 and 3.
Interesting data was obtained for ambient air dioxins concentration caused by grass fires. In Figures 4 and 5 it is presented the result of the determination of contaminated air.

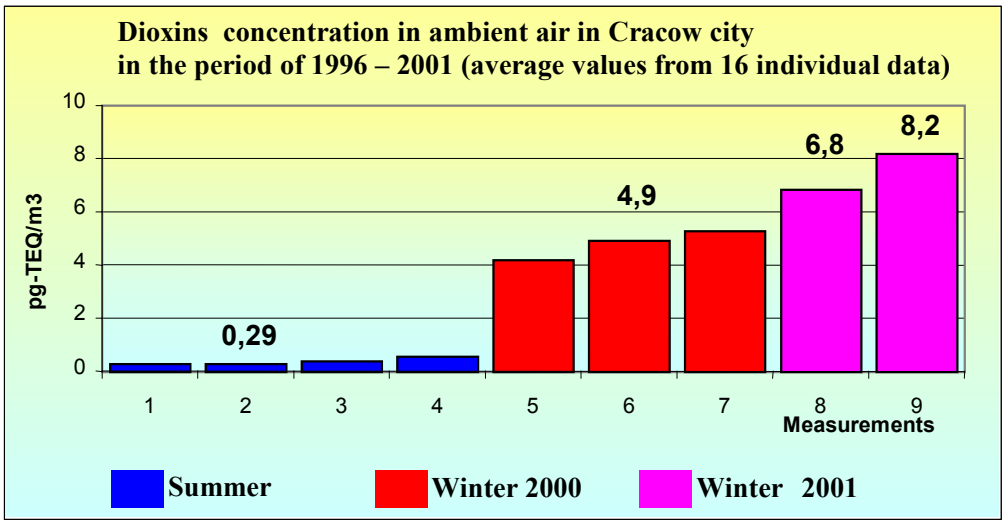

Figure 1

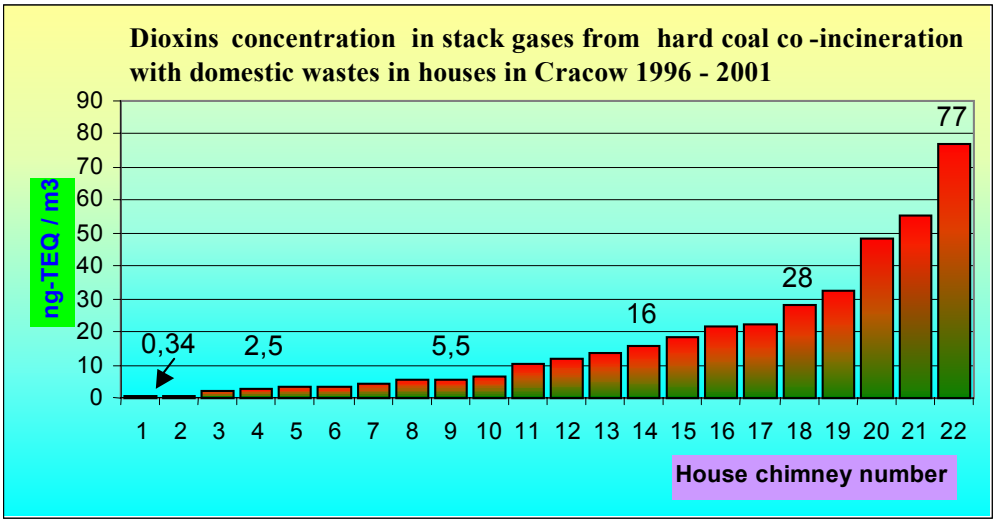

Figure 2

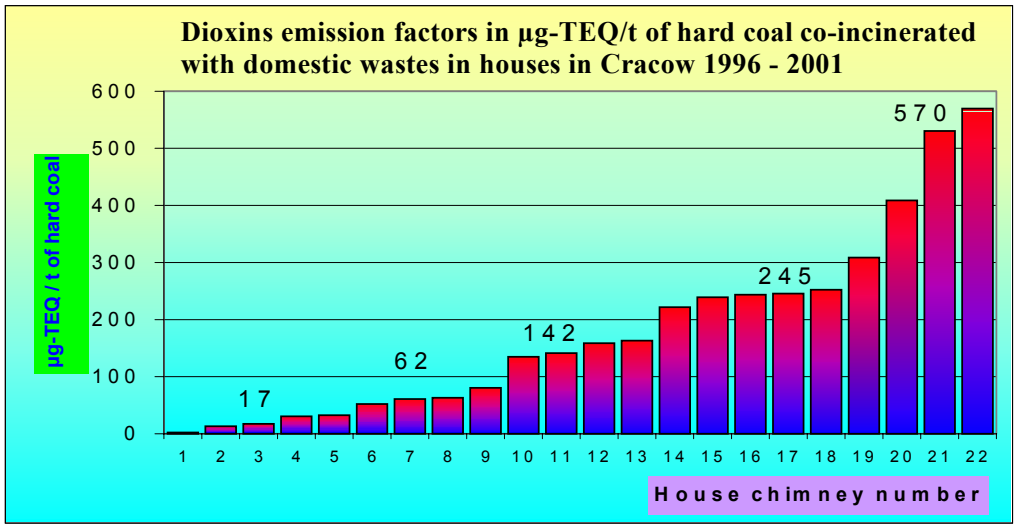

Figure 3

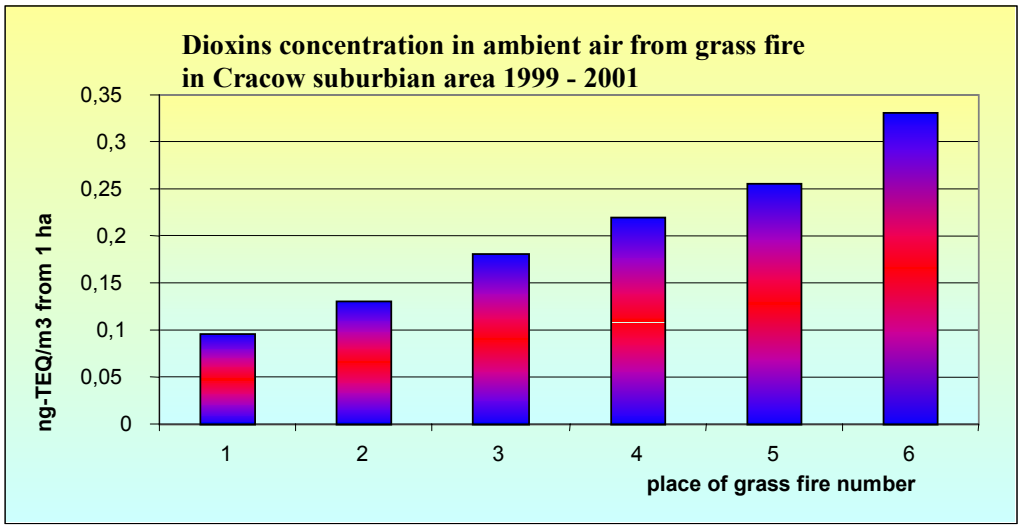

Figure 4

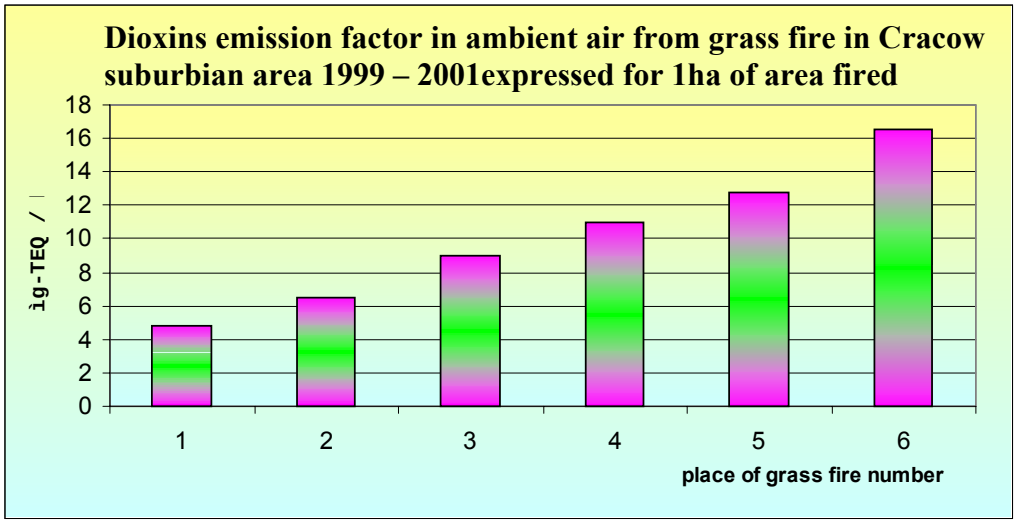

Figure 5

Interesting results were obtained when the above mentioned results were re-calculated with reference to mass unit of s.p.m. in the air. These data much better characterized of local contamination because they eliminate of influences from unstable atmospheric conditions within 24 hours of sampling. The most toxic s.p.m. was observed on January in Rynek Podgórski - 23,5 ng-TEQ/g. On the same day, the level in Aleje Krasińskiego was 17 ng-TEQ/g, whereas in Nowa Huta, where there is a big steel factory, the level was unexpectedly low - 7 ng-TEQ/g. During summer months, that level in s.p.m. was of one order lower - about 2 ng-TEQ/g of ash. It might suggest that steel industry is not the main source of contamination in Cracow in winter months. Analysis of s.p.m. showed that it contained polychlorinated dibenzofurans, mainly tetrachlorodibenzofurans. Among them, 2,3,7,8-T_4CDF, 2,3,4,7,8-P_5CDF, 1,2,3,4,7,8-H_6CDF and 1,2,3,4,6,7,8-H_7CDF were dominated. Each sample showed higher content of OCDD than OCDF. The average level was calculated of about 0.5 pg/m^3 (5 ng/g ash). These results can lead to the conclusion that in winter months s.p.m. is much more toxic.

Dioxins emission from incineration of wastes and co-incineration in power plants and cement kilns.

Since 1996 in many Polish hospitals wastes are burning in local power stations which are fired with hard coal. These plants are not designed for waste incineration nor equipped with appropriate devices for stack gas cleaning [4]. Until December 2000, in Poland have been built and commissioned 34 new, hospital waste incinerators, mostly based on pyrolysis processes and dry/wet stack gas cleaning. Based on actual needs and analysis performed by Ministry of Health and Ministry of Social Welfare in Poland and on the base of guidelines of WHO, it was considered a new list of central incineration plants for hospital wastes. The Project has started in 1994 and is funded mainly by Polish National Foundation for Environmental Protection. So far, there are realised 34 new hospital waste incinerators. Most of them are designed and constructed also in Poland [5].21 new incineration plants and respectively 11 older ones were subjects for the determination of dioxins in stack gases. This is curiousal, that most of the incinerators are equipped with ineffective devices for cleaning of combustion gases or even do not have them at all.From these 32 installations, only 9 are equipped with combined dry and wet systems of stack gas cleaning, which do not cause disposal of liquid effluents. Among 23 installations, 12 dispose the effluents to industrial wastewater treatment plants whereas the other 11 dispose liqud effluents to municipal collectors. Only a few newly constructed incinerators release stack gases of dioxins concentration below 0,1 ng-TEQ/m^3 (see figure 6). Mostly, for incinerators equipped with ineffective devices for stack gas cleaning, high emission values were obtained. Even in some cases 80 ng-TEQ/m^3 were measured. Average emission factors was in the level of 200 μg-TEQ/t of incinerated hospital wastes, however, 940 μg-TEQ/t was also measured [6]. In figures 7 is presented data for dioxin concentartion released from cement kilns during co-incineration of hazardous industrial wastes. For exaple, co-incinerated wastes origin is: *car shreddings, petrochemical wastes and animal powdered material*. Data from these measurement indicates that dioxins concentartion in stack gases from cement kilns not exceeded 0,5 ng-TEQ/m^3 in any cases. There is no corelation between co-incineration of industrial wastes and dioxins stack gas concentration. In Figure 8 the result from the determination of the PCDDs and PCDFs in the Polish power plant in Tarnów town (80,000 inhabitants) fired with hard coal as a primary fuel is presented. In this case the liquid and gaseous industrial wastes from PVC production in local chemical factory are co-incinerated. In this case about 1-2% of fuel input was substituted with industrial wastes containing 30 – 60% of organic chlorine. Although the dioxins concentration does not rise up significantly in stack gases if compared to emission from primary fuel firing, total emission of dioxins is relatively high; because of the stack gas emission is of 10^6 m^3/h.
SO_2 concentration was between 100 and 300 mg/m^3.

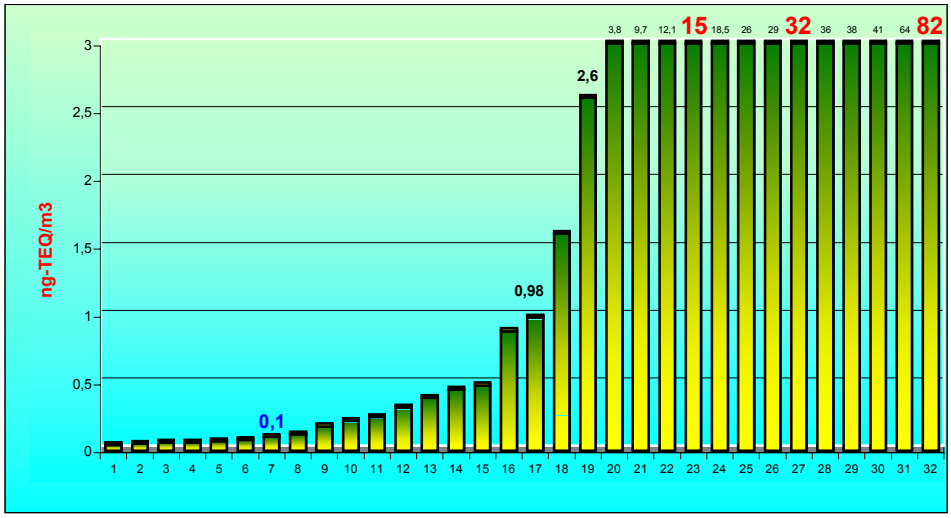

Figure 6: Dioxins concentration in stack gases from 32 hazardous waste incinerators in Poland 1997-2000

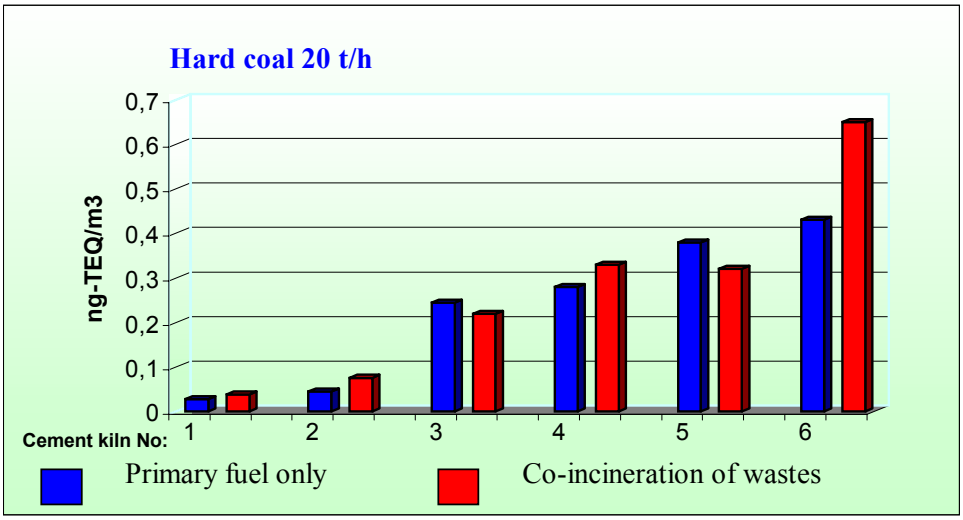

Figure 7: Comparison of dioxins concentration in stack gas during standard cement production and co-incineration of industrial wastes in cement kiln**.**

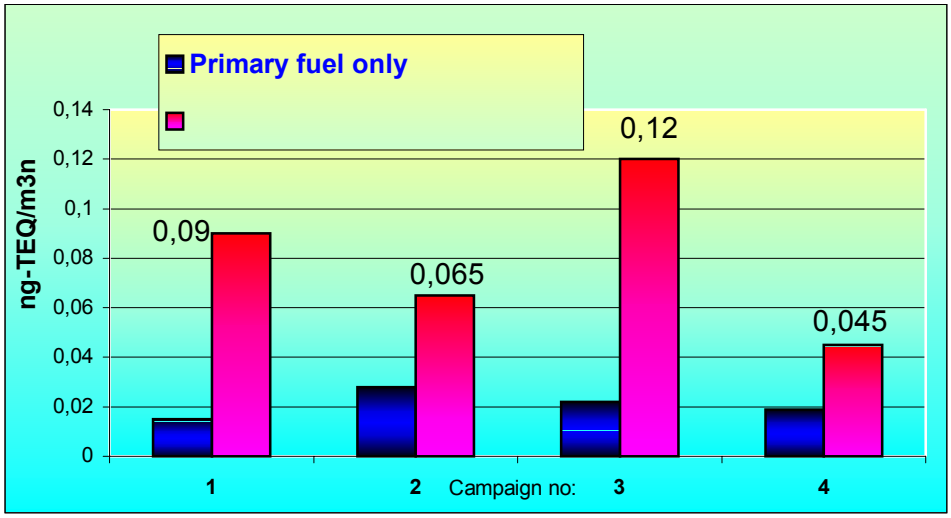

Figure 8: PCDDs and PCDFs stack gas concentration in power plant in Tarnow, Poland during co-incineration of PVC waste gases 1997-2000

DIOXIND EMISSION
FROM HARD COAL BURNING IN POLISH POWER PLANTS

FLUIDIZED BED COMBUSTION

Dioxins in stack gases ng-TEQ/m^3	Coal mass combusted t/h	Stack gas emission m^3/h	Emission factor µgTEQ/t of coal
0,0012	16	330000	0,025
0,0015	9	200000	0,033

Average emission factor 0,029 µg-TEQ/t. Relative error ± 20%

COAL SPRAY DUST COMBUSTION

Dioxins in stack gases ng-TEQ/m^3	Coal mass combusted t/h	Stack gas emission m^3/h	Emission factor µgTEQ/t of coal
0,0012	28	400000	0,017
0,002	35	750000	0,043
0,0025	20	385000	0,048
0,0032	85	900000	0,034

Average emission factor 0,036 µg-TEQ/t. Relative error ± 10%

GRID FURNACE COMBUSTION

Dioxins in stack gases ng-TEQ/m^3	Coal mass combusted t/h	Stack gas emission m^3/h	Emission factor µgTEQ/t of coal
0,001	17	388000	0,023
0,0014	30	650000	0,030
0,0022	12	360000	0,066
0,0042	5	120000	0,101

Average emission factor 0,055 µg-TEQ/t. Relative error ± 10%

Data from measurements in 1998-2001

DIOXIND EMISSION FROM HARD COAL BURNING IN POLISH INDUSTRIAL AND LOCAL SMALL POWER PLANTS

OLD, SMALL GRID FURNACE for local house heating

Dioxins in stack gases ng-TEQ/m^3	Coal mass combusted t/h	Stack gas emission m^3/h	Emission factor µgTEQ/t of coal
9,2	0,05	1500	276
4,1	0,02	700	144

Average emission factor 210µg-TEQ/t. Relative error ± 50%
Possibly, some wastes were co-incinerated

OLD GRID FURNACE (Built in 1950)

Dioxins in stack gases ng-TEQ/m^3	Coal mass combusted t/h	Stack gas emission m^3/h	Emission factor µgTEQ/t of coal
0,125	0,3	8700	3,625
0,080	0,5	13500	2,160

Average emission factor 2,893 µg-TEQ/t. Relative error ± 20%

GRID FURNACE (Built in 1985)

Dioxins in stack gases ng-TEQ/m^3	Coal mass combusted t/h	Stack gas emission m^3/h	Emission factor µgTEQ/t of coal
0,024	2,2	26000	0,284
0,090	0,86	11250	1,177

Average emission factor 0,731 µg-TEQ/t. Relative error ± 20%

INDUSTRIAL FLUIDIZED BED

Dioxins in stack gases ng-TEQ/m^3	Coal mass combusted t/h	Stack gas emission m^3/h	Emission factor µgTEQ/t of coal
0,074	8,4	285000	2,510
0,166	3,9	154500	6,580

Average emission factor 4,55 µg-TEQ/t. Relative error ± 50% from only two measurements

Data from measurements in 2000-2002

2. Experimental

2a. Ambient air sampling

Sampling of the suspended particulate matter (s.p.m.), which then were subjected to analysis of PCDDs and PCDFs was performed using highly efficient samplers PM10 of type MFC-HVPM10 produced by ANDERSEN Samplers Inc. USA. These samplers are used by monitoring stations in Cracow, which are controlled by local Inspectorate for Environmental Pollution Controll. Each time, 1600 m^3 of air was sampled. Each sampling took 24 hours. Samples were taken during winter months from the beginning of 1996. In January, February and March, there were taken 2 samples from the same measurement point (about every 14 days) and comparatively 2 samples in June 1996. There were taken 8 samples from each monitoring point, what meant that, in total, 32 samples were taken.. Sampling was made in windless days and in days without rainfalls. Temperatures of air in January and February were about -10^0C. In March, temperature of air was about 0^0C whereas in June it was about 20^0C.
Selection of sampling points was made on the basis of earlier preliminary measurements of PCDDs/PCDFs (Mateczny crossing), observations of traffic (Aleje), and observations in which quarters of Cracow coal heating of houses was the most intensive in winter and early spring months (Rynek Podgórski and Śródmieście). In the Nowa Huta region, the majority of contamination was formed in processes of steel processing at Huta T. Sendzimira (former Huta im. Lenina).

2b. Stack gas sampling

Sampling methodology was determined by the complexity of PCDFs and PCDDs formation in flue gas. First of all, large volumes of flue gas were sampled as 10 – 20 m^3 because it was assumed that concentrations of PCDFs and PCDDs would be at ng/m^3 or even pg/m^3 level. Samples of fly ash (if present) were taken using glass fibre filters of pore size of 0,2 μm placed in EMIOTEST 9265 sampling apparatus (Wrocław, Poland). This instrument was specially designed for isokinetic sampling of industrial gas samples for the determination of trace organic compounds. Sampling probe and nozzles were made of titanium. Inside the probe quartz tube was inserted as a sampling gas duct. The sampling train is designed for filter/condenser method as it is described in EN-1948 European Standard and VDI 3499 P.2. PCDDs and PCDFs present in vapour form in cooled flue gas stream were sorbed on PU-foam plug or XAD-2, placed in a cartridge. In addition, at high humidity of flue gas a condensate containing dissolved PCDFs and PCDDs and other organic compounds were also taken. Sampling line consisted of heated filter holder with glass fibre filter, gas cooler, container with PU or XAD-2 sorbent, borosilicate glass condenser for condensed water and impingers filled with ethylene glycol.
Samples of fly ash collected on glass fibre filters, sorbents and water condensate were immediately delivered to laboratory. After standard addition samples were extracted with toluene according to procedures recommended by EN-1948. This procedure guarantees 95% collection efficiency of PCDFs and PCDDs from flue gas and determination limit of PCDFs/PCDDs at 0.001 ng-TEQ/m^3 in gas sample.

2c. analysis

Filters made of quartz fibres of dimension 25.4 cmX20.3 cm, with adsorbed s.p.m., were subjected to PCDDs/PCDFs mixture (precision and recovery standard, CIL EDF-957). Then, they were extracted with toluene during 24 hours in Soxhlet apparatus. Extract clean-up was performed using standard procedure based on acidic/base silica chromatography and planar compounds separation on activated carbon. Samples were analyzed using GC-MS/MS technique on ThermoQuest GCQplus instrument equipped with DB-5MS and DB-17 60m columns.

3. References

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