PCDD/F levels in suspended particulate matter in ambient air from the Krakow city, Poland

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1. Introduction.

Contamination of the atmosphere by polychlorinated dibenzodioxins and dibenzofurans is caused by a number of thermal processes, which take place naturally in the environment. Volcanoes eruptions, forest fires, atmospheric discharges are among reasons for that dioxins have been present in the environment for millions of years. During that time, a dynamic equilibrium between formation and destruction of these compounds has been established in the environment. Since the middle of 20th century, there has been seen an increase in the presence of dioxins in the ecosphere. Air is a medium in which spreading of gaseous contaminants and ashes takes place in the quickest way. Similarly, penetration of contaminants into human body is a huge source of poisoning.
Measurements of dioxin content in air in Krakow (the second largest city in Poland of one million of inhabitants), which were carried out in 1996, were aimed not only at defining of potential threads on health of Krakow'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., they are present in air in the form of adsorbed compounds onto surface of solid particles.
As a result, it was revealed that, perhaps, the basic source of the emission of PCDD/F into the air over Krakow were uncontrolled processes of burning of wastes. Burning of fuels in engines with spark ignition is another source of this emission, however, less important.
Problem of contamination of air in Krakow by dioxins was pointed out, for the first time, after preliminary measurements which had been done in 1994/1995. Results of those measurements were presented[1)] at the Dioxin'95. Those measurements showed that air contamination by dioxins was the highest around the Mateczny crossing during winter months.
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 Krakow. 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.
In 1996, thorough measurements of PCDDs and PCDFs content in s.p.m. in air in Krakow during winter months were undertaken. In order to make comparison, similar measurements were carried out in June 1996.
To those measurements were subjected samples of suspended particulate matter in air, of dimensions less than10 μm, which were taken from monitoring points in four quarters of Krakow:
Śródmieście - point at Al. Krasińskiego (Krakow Centrum)
Podgórze - point at Rynek Podgórski (Krakow South)
Nowa Huta - point at Szpital im. S.Zeromskiego (Krakow East)
Krowodrza - point at Szpital im. J.Pawła II (Krakow North/West)

2. Experimental.

a. 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 Krakow, which are controlled by Wojewódzki Inspektorat Ochrony Środowiska in Krakow. 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^{0}C. In March, temperature of air was about 0^{0}C whereas in June it was about 20^{0}C.
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 Krakow 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).

b. 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. After standard procedures of purification were applied (column chromatography on Bio-Sil SX-3, Al_2O_3, alkali-acidic gels and activated carbon) samples were analyzed using GC-MS technique (HP-MSD 5972 non-standard system with higher sensitivity; capillary columns 60m, type RTX-5 MS and DB-Dioxin).

3. Results and discussion.

The results show that the level of PCDD/F content in air in Krakow is much higher, with comparison to, their content in air in other big cities in Western Europe. It is reported[2,3,4,5,6,7] that in Western cities this content is 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[6,7] , to results of measurements of air in Krakow, 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 those samples, tetrachlorodibenzofurans were detected as dominating PCDD/F congeners. Only for samples from Graz, the distribution was different. In Krakow, during winter months, the level of dioxin content was over 5 pg-TEQ/m^3 The levels of dioxin content were as follows: Aleje Krasińskiego 5.74 pg TEQ/m^3, Rynek Podgórski 5.45 pg - TEQ/m^3, Nowa Huta 2.58 pg- TEQ/m^3, Krowodrza 3.34 pg- TEQ/m^3. In other samples from winter months, the average content of dioxins in air from January to March were about 2 pg- TEQ/m^3. Analysis of samples from June showed that the level of dioxin content was very low and it was in the range 0.06-0.12 pg- TEQ/m^3. Fig. 1 shows the results of the analysis of PCDD/F content in air from Krakow Center, the most polluted area.

In figure 2 there are presented the results from analysis of PCDD/F in ambient air from Krakow East quarter.
The East part of Krakow was not so heavy polluted during sampling season.

Fig. 1: PCDD/F concentration in ambient air in Krakow CENTER (Aleje Krasinskiego)

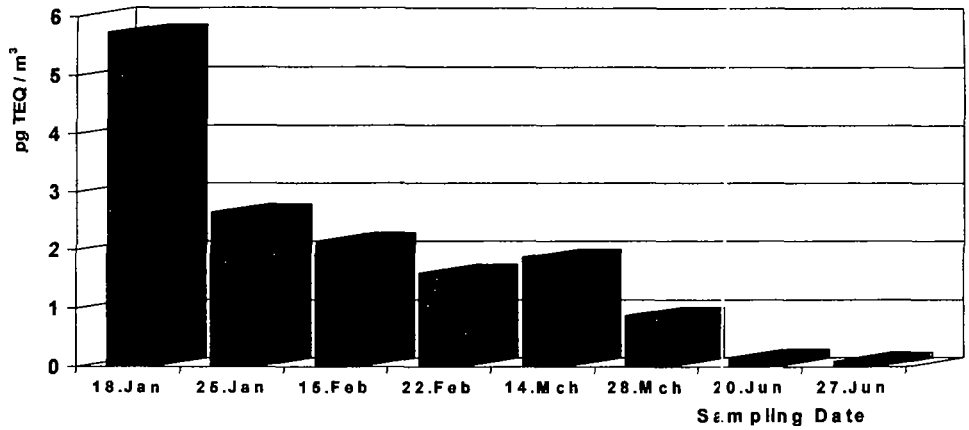
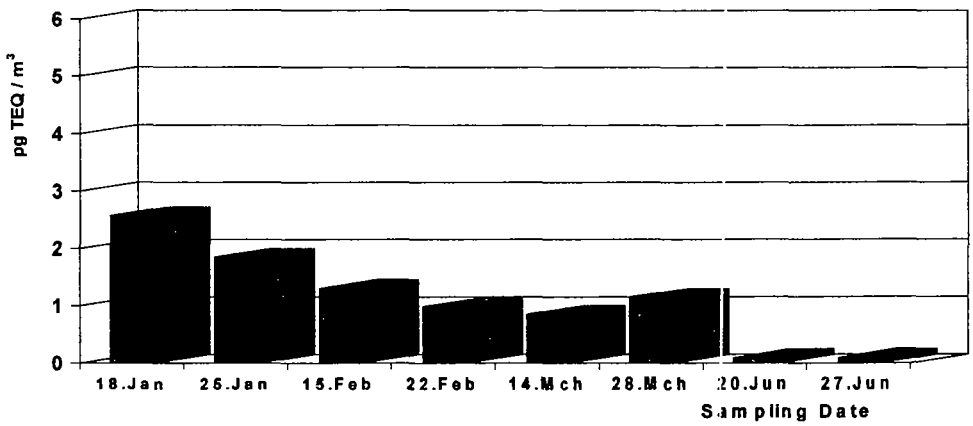
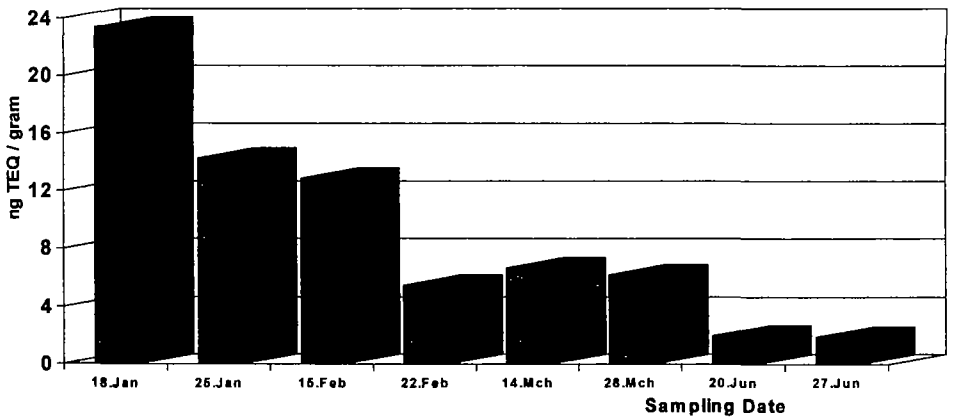


Fig. 2: PCDD/F concentration in ambient air in Krakow EAST (Nowa Huta)



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. Results of analysis of s.p.m. are shown in Fig. 3. The most toxic s.p.m. was observed on 18th 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 Krakow in winter months.

Fig. 3: PCDD/F concentration in suspended particulate matter filtered from ambient air from Krakow SOUTH quarter (Rynek Podgórski)



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. Fig. 4 shows the distribution of PCDD/F congeners in s.p.m. in January 1996 in Rynek Podgórski. The average level of s.p.m. in air in winter months was about 100 μg / m^3, although, on January 18, the level was about 3 times higher (over 300 μg / m^3).

It was observed decrease in toxicity of s.p.m. during summer months. Then, the level of dioxin content decreased 10 times. This was particularly seen in Krakow Centre and Krakow East quarters. It leads to the conclusion that the basic source of emission of dioxins into the atmosphere might be burning processes which occur in furnaces. Houses in these quarters are, in large extend, heated by coal furnaces, in which it is possible for people to burn household wastes. This is supported by similar results of distribution of groups of PCDD/F congeners in soot samples, which were also taken in winter from chimneys, when they were compared to samples from incineration plant.

Despite the presence of SO_2 in combustion gases, with the concentration of about 100 mg/m^3, burning of coal in furnaces with stationery grids occurs under conditions which are ideal for formation of dioxins, if there are chloroorganic compounds, such as PVC, present in wastes subjected to burning. Despite official ban on burning of wastes in open air in Krakow, there have been build concrete structures in which wastes from commercial activity and organic wastes are burnt in afternoons or at nights.

Measurements of the emission of PCDD/F present in combustion gases from Polish power stations, which were performed in 1995-96, revealed that those gases contained small amounts of dioxins (about 0.005-0.01 ng-TEQ/m^3).

Burning of coal, which takes place in furnaces in Krakow, occurs under totally different conditions. These conditions are much worse regarding total after-burning and energy of this process. The level of dioxin content in combustion gases which was measured in Krakow was higher than in power stations and was about 0.01-0.2 ng-TEQ/m^3. It is caused by improper burning conditions such as oxygen deficiency, lower temperatures of burning, lack of after-

burning and slower cooling of combustion gases in chimneys. . Furnaces are, in most cases, equipped with stationery grids which can burn about 2-5 kg of coal at the same time.
If, apart from coal, in furnaces are burnt such wastes as polyethylene, polypropylene, polystyrene, poly(ethylene terephthalate), wet organic wastes, leather, rubber, etc. then, burning occurs with very low efficiency. It is smoldering rather than burning.
Such conditions as oxygen deficiency, low temperatures, significant amounts of CO and soot, are ideal for dioxin synthesis. It was shown by the results of the measurement of PCDD/F content in soot from chimneys, which carry away of combustion gases from furnaces in which wastes from household activity are burnt.
Car exhausts show much lower influence on the contamination of air in Krakow. It is concluded from comparison of dioxin content in samples of air, which were taken in winter and summer months, when there were not observed big seasonal differences in traffic.

4. Conclusion

Those analyses led to the conclusion that the main sources of PCDDs and PCDFs emitted into air are processes of uncontrolled burning. It mainly refers to burning of wastes in coal-fired furnaces.
In conclusion, it should be stated that the content of dioxins in air in Krakow, during winter months, was one order higher than in other big cities in Western Europe. For instance, the level of PCDD/F content in Hamburg, Berlin, Graz, Linz and others[4,5,6,7], is about 0.3 pgTEQ/m^3. Higher level of PCDD/F content and the danger of dioxin accumulation in urban areas, indicate that it is necessary to undertake actions aimed at decreasing of dioxin content in s.p.m.. To do it, it is necessary to issue of regulations refer to waste management. However, as far as households are concerned, it is possible to do it by informing people about harmful effects of burning of wastes in household furnaces. Moreover, it is necessary to undertake firmly actions aimed at ban of burning of grass, burning of organic wastes on allotments and markets inside the administration area of Krakow. Another solution is to replace individual coal furnaces with gas-fired furnaces and solve traffic problems, specially in central areas of Krakow.

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5. References

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