LEVELS OF DIOXINS IN MILK AND CHICKEN EGGS IN MOST INDUSTRIALIZED CITY OF TURKEY:KOCAELI

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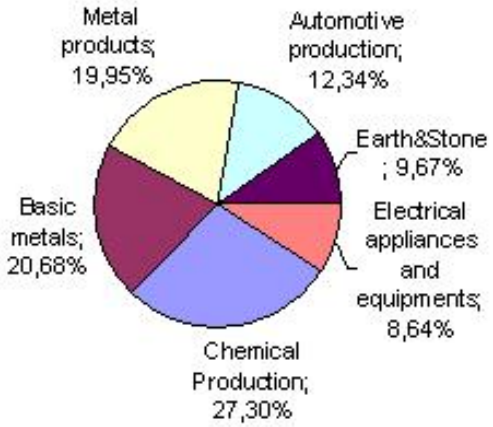
Introduction

Dioxins are among the most harmful "man-made" carcinogens ever studied and they are released to the environment from industrisal activities. Izmit Clinical and Hazardous Waste Incinerator has started to operate in 1997. Altough several metal and chemistry facilities are located in İzmit, environmental considerations, especially dioxin emissions, have become the major subject of public discussion since that time.

Kocaeli remains one of the fastest developing manufacturing regions of Turkey and takes 13-14% share in Turkey's manufacturing industry productivity. According to statistics of Kocaeli Chambers of Industry, there are almost 1300 manufacturing enterprises registered and active in Kocaeli.



Sector	Number of firms
Plastic&PVC	129
Stone and earth prod.	74
Chemical production	70
Food products	69
Metal production	51
Pharmaceuticals	50
Petroleum prod.	42
Wooden products	41
Automotive	41

Figure 1. The share of industry in Kocaeli

Kocaeli is located at the crossroads of Turkey, as a gateway from Asia to Europe. In addition to the D100 (appr. 90 km) and TEM (Trans European Motorway-appr. 95 km) highways, main railway also cross in Kocaeli. There are a total of 15 organised industrial zones which 6 of them are active, 2 free trade zones and 3 techno parks are also located in Kocaeli.

Materials and Methods

Sampling

The results of the PCDD/F concentrations in 10 food samples from Izmit city are presented in this study. The study included the analyses of cow milk and chicken eggs collected different locations around the city in April, 2005. The sampling locations and general map of the Kocaeli is shown in Figure 2.

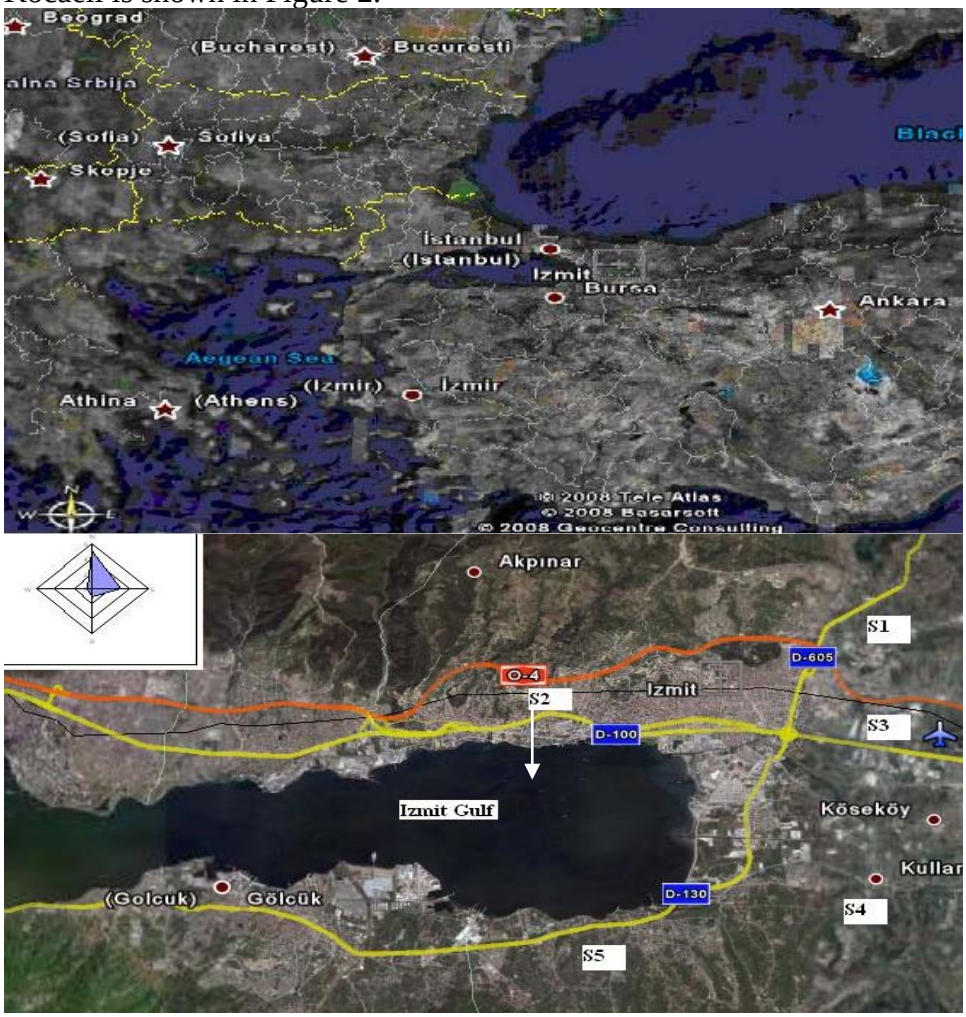


Figure 2. Kocaeli and sampling locations

All food items were collected and properly transported to the TUBITAK MRC Laboratories within one day and samples were kept at -20 ^{0}C until they were processed.
All chemicals used were HPLC grade and were purchased from Merck (Germany). The ^{13}C isotope labelled internal standard solutions were purchased from Wellington Laboratories. Egg samples boiled in 90 ^{0}C until they reached solid form and oily portion has grounded manually. Next, all the sample was mixed with anhydrous sodium sulphate and extracted with toluene in Soxhlet extractor. Milk samples were prepared by liquid-liquid extraction by

pentane. After soxhlet extraction, the solvent was evaporated in rotary evaporator and the lipid content was determined gravimetrically. 1 gr oil extracts were cleaned up on a layered silica gel (acidic-neural-basic), alumina and florisil, and then analysed by high resolution gas chromatography/mass spectrometry according to instructions given in EN 1948 protocol.

The prepared samples were spiked with a mixture of ^{13}C labelled internal PCDD/F standards before extraction and syringe.

Analytical Conditions

Micromass (Waters) Autospec Premier coupled with an Agilent 6890 Gas Chromatgoraph with Agilent Autsampler used for sample analysis. Data system was OPUS software. The quantification of PCDD/Fs was performed by GC-HRMS on EI(+) mode, equipped with HP 6890 GC without autosampler and coupled to a Micromass Zabspec mass spectrometer performing at 10000 resolution (%10 valley definition). A DB-5MS (30 m x 0,25 mm ID x 250 um film thickness) was installed into the split/splitless injector of the GC.
GC Oven Temperature program was used as follows;
140 ^{0}C (1 min) ;12 ^{0}C/min to 200 ^{0}C; 3 ^{0}C/min to 235 ^{0}C; 4 ^{0}C/min to 300 ^{0}C (12 mins wait)
Constant flow mode (1 ml/min) ; 280 ^{0}C Injector temperature; 1 μl splitless injection

Results and Discussion

During sampling, totaly 10 samples were analysed for PCDDs and PCDFs. As might be expected for industrialized city, some of the samples show that higher concentrations (6-14 pg/g lipid) regard to limit values in the EU Regulation 2375/2001/EC. The average concentration values for individual congeners, as well as the average concentration sums calculated as upperbound values and the average upperbound WHO-TEQ values for PCDD/Fs are given in Table 1 and 2.

The contamination was calculated as the TEQ values by multiplying the concentrations with corresponding WHO-TEFs for each congener (WHO-ECHS,IPCS, 1998). TEQ values of all compounds are reported on a fat basis (pg/g fat). Non-detected PCDD/F congeners assumed that are zero.

References:

1. European Council Regulation ’Maximum levels of certain contaminants in foodstuffs’’ (EC) No. 2375/2001 of 29 November 2001.
2. A.Papadopoulos et al., ‘’Levels of dioxins and dioxin-like PCBs in food samples on the Greek Market’’Chemosphere 2004; 57: 413-419
3. Kocaeli Chamber of Industry Statistical Book 2007
4. The Inventory of Sources of Dioxins and Dioxin-like Compounds in US, EPA 1996; 28-91
5. Christopher Rappe et al. ‘’Levels of PCDD and PCDDFs in MilkCartons and in Comercial Milks’’, Chemosphere 1990; 20: 1649-1656

Table 1. Average PCDD/Fs results of milk samples (TEQ $_{WHO\ 1998}$, pg/g lipid)

Congeners	S1	S2	S3	S4	S5
2378 TCDD	1,5249	1,1200	<0,083	<0,012	<0,011
12378 PeCDD	0,8423	0,7611	1,1098	<0,021	<0,018
123478 HxCDD	0,1149	0,2309	0,1954	0,1951	0,4116
123678 HxCDD	0,3433	0,1322	0,1550	0,1653	0,2292
123789 HxCDD	0,1247	0,0821	0,0810	0,1398	0,3674
1234678HpCDD	0,0275	0,0222	0,0603	0,0279	0,0110
OCDD	0,0072	0,0057	0,0189	0,0079	0,0072
2378 TCDF	0,3729	<0,015	0,1057	0,1210	<0,013
12378 PeCDF	0,1019	0,0200	0,0317	0,0579	0,0427
23478 PeCDF	1,9722	0,5150	0,2833	0,5261	0,1869
123478(9)HxCDF	0,1974	0,1022	0,2120	0,4644	0,1553
123678 HxCDF	0,2142	0,1117	0,3015	0,2670	0,0508
123789 HxCDF	0,0783	0,0399	0,1082	0,1486	0,1865
234678 HxCDF	0,0448	0,1342	0,0208	0,0457	0,0864
1234678 HpCDF	0,0320	0,0117	0,0253	0,0107	<0,0021
1234789 HpCDF	0,0125	0,0118	0,0101	0,0055	<0,0022
OCDF	0,0052	0,0074	0,0025	0,0027	0,0044
Sum PCDD	***2,985***	***2,354***	***1,620***	***0,536***	***1,026***
Sum PCDF	***3,031***	***0,954***	***1,100***	***1,650***	***0,713***
Total PCDD/F	***6,016***	***3,308***	***2,720***	***2,185***	***1,739***
EC Limit Value	3	3	3	3	3

Table 2. Average PCDD/Fs results of egg samples (TEQ $_{WHO\ 1998}$, pg/g lipid)

Congeners	S1	S2	S3	S4	S5
2378 TCDD	<0,079	1,8400	1,1176	<0,073	<0,067
12378 PeCDD	0,9659	3,0330	0,9596	2,5227	<0,0811
123478 HxCDD	0,7404	0,4690	0,3202	0,1733	0,6098
123678 HxCDD	1,2231	0,2059	0,1728	0,3197	1,4794
123789 HxCDD	0,6052	0,3124	0,2911	0,3178	0,4497
1234678HpCDD	0,3307	0,0270	0,0512	0,0372	0,0998
OCDD	0,0432	0,0072	0,0100	0,0051	0,0058
2378 TCDF	0,6453	0,6808	0,1841	0,4307	1,2359
12378 PeCDF	0,3578	0,0961	0,2274	0,0986	0,3802
23478 PeCDF	<0,0267	<0,040	<0,025	1,5873	3,7104
123478(9)HxCDF	0,9623	0,3533	0,2569	0,1524	<0,022
123678 HxCDF	<0,0152	0,1040	0,1897	0,2162	<0,021
123789 HxCDF	1,1415	0,2367	0,0369	0,1993	<0,018
234678 HxCDF	0,3468	0,1175	0,1358	0,1257	<0,019
1234678 HpCDF	0,4675	0,0399	0,0240	<0,0011	0,3250
1234789 HpCDF	0,0424	<0,0019	0,0070	<0,0009	0,0134
OCDF	0,0097	0,0021	0,0016	<0,0001	0,0043
Sum PCDD	***3,908***	***5,894***	***2,923***	***3,376***	***1,026***
Sum PCDF	***3,973***	***1,630***	***1,063***	***2,810***	***0,713***
Total PCDD/F	***7,881***	***7,524***	***3,986***	***6,186***	***1,739***
EC Limit Value	3	3	3	3	3