DIOXIN CONTAMINATION OF FOOD PRODUCTS IN THE VICINITY OF A MUNICIPAL LANDFILL AFTER A FIRE

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Abstract
In this study we report a case of food contamination after a fire in the municipal landfill of Tagarades, in the wider area of Thessaloniki in northern Greece. Food samples of meat, eggs and dairy products as well as vegetables were collected from sources up to 4 km away from the landfill. Soil samples were taken from various sites at distances up to 5 km from the landfill. All the samples were analyzed for dioxin and dioxin-like PCB contamination. Some food samples were found above the limits specified by the EU, while all food samples were above the usual levels of Greek food. The results of the soil samples indicate, for dioxins, a reverse correlation between dioxin contamination and distance from the contamination source.

Introduction
The use of public landfills is one of the main ways of waste disposal in Greece[1,2]. Intentional or incidental open-fire burning, which often takes place in landfills, is a common source of dioxin and dioxin-like PCB contamination of soil[3]. Although, for safety reasons, landfills are not situated near densely populated areas, this contamination is often transferred to humans through the consumption of contaminated food, due to the inevitable transport of contaminated soil and fly-ash through the air and water to areas of agricultural production and animal rearing[4]. We report here a study of food contamination after a fire in the public landfill of Tagarades, which is situated southeast of Thessaloniki, and has been used for the disposal of domestic waste (organic, plastic, paper, etc) from the wider area of Thessaloniki for the last 30 years. In July 2006 a fire broke up in the landfill, causing the precipitation of contaminated fly ash in the surrounding area. Food samples of meat, eggs and dairy products from animals grazing near the affected area, and vegetables growing in nearby orchards were collected, as well as soil samples from various sites at a distance up to 5 km from the landfill, and analyzed for dioxin and dioxin-like PCB contamination. Concentrations and isomeric patterns of polychlorinated dioxins and furans are examined.

Methods and Materials
Collection of samples. Meat/milk/egg/vegetable samples and soil samples, were collected by the Department of Veterinary, the Department of Agricultural Development and the Department of Environmental Protection of the Prefecture of Thessaloniki, respectively.

Lipid extraction and cleanup. The lipid extraction and cleanup method applied has been described in detail elsewhere[5]. In brief, lipid extraction took place by the Soxhlet method in the case of meat, egg, dairy products and vegetable samples, and by a liquid-liquid method in the case of milk. In each case, the organic layer was evaporated, dried and weighed to calculate the lipid content. The quantification standards used were ^{13}C-labelled solutions of dioxins and PCBs in toluene and were added to each sample prior to extraction.
The extracted lipid was then dissolved in dichloromethane and brought onto the top of a Carbosphere column, which was placed in a reflux unit and refluxed for 2 h with dichloromethane. This fraction, including residual fat amounts, was discarded. Next, the column was rinsed with toluene and refluxed with 40 ml of toluene for 1 hour. This fraction contained the dioxin-like PCBs and was evaporated to dryness. The Carbosphere column was then inverted in the reflux unit and the PCDD/F fraction was eluted from the column by refluxing with 40 ml of toluene for 16 h. This fraction was evaporated to dryness.
The PCB fraction was dissolved in hexane and the mixture was brought onto a column containing 0.5 g of 44 % H_2SO_4-silicagel, and 5 g of alumina. The alumina column was rinsed twice with hexane and then washed with a hexane/dichloromethane mixture (1:1 v/v). This eluate was evaporated to dryness and re-dissolved in toluene containing injection standard $^{13}C_{12}$ PCB-80.
The fraction containing PCDD/Fs, was dissolved in hexane and the mixture was brought onto a column containing 0.5 g of 44 % H_2SO_4-silicagel, and 5 g of alumina. The alumina column was rinsed twice with hexane

and then washed with a hexane/dichloromethane mixture (93:7 v/v). This eluate was discarded. PCDDs and PCDFs were eluted with a hexane/dichloromethane mixture (60:40 v/v). Finally, the eluate was evaporated to dryness and re-dissolved in toluene containing injection standard $^{13}C_{12}$ 1,2,3,4-TCDD.

Instrumental analysis. The quantification of PCDD/Fs was performed on a DB5-MS column (30m, 0.25mm, 0.1μm, J&W) by HRGC-HRMS (EI) in MID mode on a Trace GC mass chromatograph (ThermoFinnigan) coupled to a MAT-95 XP mass spectrometer (ThermoFinnigan) equipped with a CTC A 200S autosampler at 10000 resolving power (10% valley definition). The quantification was carried out by the isotopic dilution method.

Quality control. A method blank and a quantitative control sample (reference) were included in the study. As reference sample, olive oil spiked with PCDD/Fs (TEQ value 3.0 pg/g) was used. It should be added that the laboratory has been participating successfully in international interlaboratory studies since 2003 and is accredited according to ISO/IEC 17025/2005.

Results and discussion

Twenty food products (including milk, meat, eggs and vegetables as well as olives intended for olive oil production) as well as 12 soil samples were taken from locations up to 7 km from the affected area, during a time period beginning immediately after the fire, and ending one month later. The details concerning the location of each sample, as well as the measured dioxin data, expressed as WHO TEQ values[6], are listed in the following tables:

Table 1. Food Samples

Sample	Distance and orientation relative to landfill	Dioxins pg/g fat TEQ WHO 1997	Maximum levels defined by EU Directive 13/2003 (pg/g)
Goat/sheep milk	0.5 km N	**11.00**	3
	2 km NE	1.65	3
	2.5 km NW	**3.84**	3
	4 km SE	**8.98**	3
	4 km SW	**3.72**	3
	6 km N (control)	0.45	3
	6 km E (control)	0.80	3
Eggs	2.5 km NW	0.63	3
Goat meat	0.5 km N	**8.82**	3
Chicken	2 km NE	**2.20**	2
Tomatoes*	2 km NE	Non detected	Non defined
Zucchini*	2 km NE	Non detected	Non defined
Aubergines*	2 km NE	Non detected	Non defined

*The results are expressed as dioxins pg/g fresh weight TEQ

Table 2. Olive samples (no maximum levels are defined by the EU)

Location	Dioxins pg/g fat TEQ WHO 1997
0.5 km N	67.30
2 km NW	13.08
4 km SW	7.14
4 km SE	2.81
4 km E	2.45
6 km N	3.60
7 km E	1.64

Table 3. Soil samples

Location	Dioxins ng/kg TEQ WHO 1997
Landfill	**7.91**
0,5 km N	0.17
1 km N	0.19
1,5 km NE	0.18
2 km N	0.17
3 km N	0.21
4 km S	0.29
4 km SE	0.22
4 km E	0.19
5 km W	0.17
7 km (control)	0.17
7 km (control)	0.17

The levels of dioxins in all lipid containing food samples are higher than those normally found in respective products randomly collected from the Greek market and production, and in some cases, above the maximum dioxin levels accepted according to the EU requirements (regulation 1881/2006/EC). The normal levels usually found in Greek food are 0.5-0.7 pg/g fat TEQ for sheep and goat milk, 0.2-0.8 pg/g fat TEQ for sheep and goat meat, 0.2-0.5 pg/g fat TEQ for chicken, and 0.3-0.7 pg/g fat TEQ for eggs[7]. As expected, no dioxins were detected in vegetables, due to the very low lipid content. Food samples collected more than 5 km away from the affected area, showed no sign of contamination.

In contrast to other samples of vegetal origin, olives have a relatively high lipid content, which means that they have the ability to absorb dioxins and dioxin-like compounds which are transferred by contaminated fly-ash in cases of fire. Therefore, olives are considered an indicator of dioxin contamination. In the present case, the highest contamination was observed in olive samples taken from sites near the fire, while dioxin concentrations diminished in samples taken from remoter sites. Therefore, taking into account the direction and intensity of winds, dioxin contamination in general diminishes with the distance from the contaminated site.

In the case of milk samples, the congener profile revealed that the most dominant congeners were 1,2,3,7,8-PCDD and 2,3,4,7,8-PCDF. OCDF and OCDD, which are often high in biological samples after long-term exposure, and are produced by metabolic conversion of other dioxin congeners, were very low in these samples probably due to the short time between exposure and collection of samples. In the case of olives, 2,3,7,8-TCDF was the highest congener and 1,2,3,4,6,7,8-HpCDD and 2,3,4,7,8-PCDF were elevated (Figures 1, 2). The difference in the isomeric distribution between milk and olives can be attributed to the different accumulation mechanism (bioacumulation through the stomach vs. absorption from the olive surface).

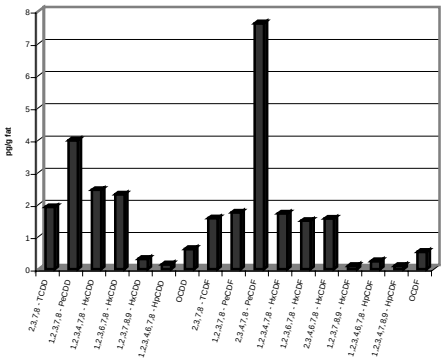

Figure 1. Congener profile of the most contaminated milk sample (concentration pg/g fat)

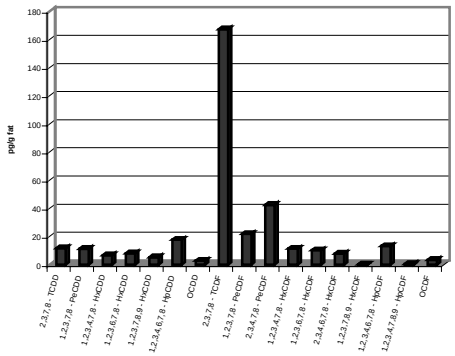

Figure 2. Congener profile of the most contaminated olive sample (concentration pg/g fat)

Concerning soil samples, the sample taken inside the landfill, had a high burden of dioxin contamination (7.91 ng/kg TEQ). Most of the samples taken 0.5 km and up to 5 km away from the landfill showed no signs of contamination, which is in agreement with previous studies reporting that no contamination is detected in soil samples at a distance of 200 m from the source of contamination[8]. The congener profile of a highly burdened soil sample, showing a high content in 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TCDF, 2,3,4,7,8-PCDF and 1,2,3,4,6,7,8-HpCDF is shown in Figure 3. The formation and isomeric distribution of PCDD/F depends on the burning conditions and the waste composition.[9]

It should be noted that PCB levels were normal in all analyzed samples.

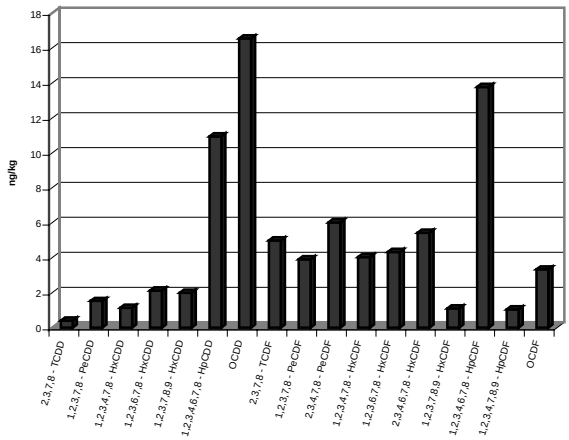

Figure 3. Congener profile of the most contaminated soil sample (concentration pg/g fat)

The consumption of food products originating from the contaminated area was prohibited, till the restoration of normal levels of all dioxin congeners. For this purpose, further determinations of food and soil samples in different time intervals are planned.

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