Comunicaciones

IV REUNIÓN NACIONAL DE DIOXINAS, FURANOS Y COMPUESTOS ORGÁNICOS PERSISTENTES RELACIONADOS

Alicante, 26-28 Junio 2013

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http://web.ua.es/dioxinas

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Ap. 99 E-03080 Alicante

Diseño de la portada: Mª Francisca Gómez-Rico

Impresión y encuadernación:
Imprenta Universidad de Alicante

Depósito Legal: A 286-2013

L22

SIXTEEN YEAR OF PCDD/FS AND PCBS BIOLOGICAL MONITORING IN MATARÓ. A POPULATION-BASED COHORT STUDY (1995-2012)

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Introduction

There is evidence that polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) may adversely affect the health of wildlife and humans[1]. Humans are daily exposed to complex mixtures of PCDD/Fs and PCBs mainly via trace amounts present in food[2]. A variety of toxic effects in experimental animals exposed to these chemicals, including immunologic, neurochemical, neurotoxic, carcinogenic and endocrine changes have been reported[3].

Releases of these pollutants to the environment have been of great concern for the general population, scientific community and health care administration. Particular attention has been focused on solid waste incinerators (SWI), which have been controversially questioned since these plants were historically a major source of PCDD/Fs emissions[4]. Different studies, with the objective to evaluate whether or not people living in the proximity of SWI installations are particularly exposed to dioxins and PCBs, have been undertaken within the last years. In the majority of the cases, reported data show no relationship between PCDD/Fs concentrations and health impairments in subjects living near a modern, well-controlled SWI[5], as well as no significant differences in levels of these compounds over time or in relation to non-exposed populations[6]. On the contrary, other studies have shown adverse health effects, such as an increased risk of non-Hodgkin lymphoma[7] and of developing a sarcoma[8].

The aim of the present study was to monitor (from 1995 to 2012) and compare PCDD/Fs and PCBs levels in blood samples from general populations considered exposed and non-exposed to a SWI in the city of Mataró (Spain).

Materials and Methods

The study was undertaken in Mataró, a Mediterranean city of approximately 125,000 inhabitants, 25 km North Barcelona, Spain. Mataró is a residential-industrial area located in an urban environment with high traffic density, where textile manufacture is the main industrial activity. In addition to that, there are no other known industrial sources of dioxins rather than the before-mentioned environment and an urban waste treatment plant (Figure 1). At the beginning of the study, in the period of March to June 1995, a total of 201 adults (100 males and 101 females), aged between 18 and 69 years, were randomly selected from the municipal list of inhabitants. Two groups were selected; the first was a group of potentially exposed individuals living in districts near the SWI plant. The second one was a group of unexposed individuals. Additionally, a third group formed by workers of the facility, was also considered. The exposed and unexposed groups were divided by sex and age in three sub-groups for males, from 18 to 29, 30 to 49 and 50 to 69 years old, respectively; and two sub-groups for females, from 18 to 39 and 40 to 69 years old, respectively. In 1999, a second group of unexposed individuals living in a vicinity town, Arenys de Mar (about 11 km away), was added with the aim to evaluate unexposed individuals living far away from the SWI plant. Whole blood samples were collected by Hospital of Mataró, following routine veinpuncture. From each individual, blood sample was collected in two conditioned 25 ml glass bottles and kept frozen at -30ºC until the time of analysis in the laboratory.

Individual samples were sent to the laboratory where pools were prepared by mixing, prior to the analysis. Samples were spiked with known amounts of mixtures of $^{13}C_{12}$-PCDD/Fs (EPA-1613LCS) and marker $^{13}C_{12}$-PCBs (MBP-MXE), both of them purchased from Wellington Laboratories Inc. (Guelph, Canada). After that, sample extraction was performed by a chromatographic glass column packed with several layers of Chem-Elut (Varian, Palo Alto, CA,

USA) and NaCl[6]. Next, a treatment with silica gel modified with sulphuric acid (44 %, w/w) was applied to remove organic components, fat and other interfering substances. Finally, the extracts were concentrated and transferred to n-hexane prior to the purification step. Details on the clean-up procedure based on the use of the Power PrepTM system (FMS Inc., MA, USA) are described elsewhere[9]. High resolution gas chromatography coupled to high resolution mass spectrometry (HRGC-HRMS) was used for the final instrumental analysis. All analyses were performed on a Trace GC ultra gas chromatograph (Thermo Fisher Scientific, Milan, IT) fitted with a 60 m x 0.25 mm i.d. x 0.25 µm film thickness DB-5ms fused silica column (J&W Scientific, CA, USA) coupled to a high resolution mass spectrometer (DFS, Thermo Fisher Scientific, Bremen, Germany) controlled by a Xcalibur data system. Positive electron ionization (EI+) operating in the MID mode at 10 000 resolving power was used. Quantification was carried out by the isotopic dilution method. Fat determination was performed by gravimetric methods. The criteria for ensuring the quality of dioxin analysis include the application of quality control (QC) and quality assurance (QA) measures, such as a continuous monitoring of laboratory contamination based on the determination of a blank sample covering the whole analytical procedure, including extraction, clean-up and quantification[10].

Results and Discussion

Table 1 shows the evolution of PCDD/Fs blood concentrations for all age, sex and exposure groups from 1995 to 2012. In addition to that, preliminary data reported by Gonzalez et al. (1998) have been included in the tables for comparative purposes, as they started this study in 1995[11]. Moreover, some parameters such as age, sex and place of residence are also given. As mentioned, the study included an exposed group from Mataró, two unexposed groups (Arenys de Mar and Mataró) as well as the group of workers from the facility.

In both exposed and non-exposed groups, PCDD/Fs concentrations were similar and experienced a slight increase from 1995 to 1999, followed by a slight decrease from 1999 to 2002 and stabilization afterwards, with no relevant differences between them. This is in accordance with a reduction of PCDD/Fs levels in plasma of non-occupationally exposed subjects from 1998 to 2002 described in the literature[12]. Concentrations of PCDD/Fs consistently increase with age in both sexes in all study determinations and were higher in women in comparison to men in nearly all cases. Table 2 shows the evolution of marker PCBs from 1995 to 2012 in the same age, sex and exposure study groups. A decrease in PCBs blood levels has been observed in all groups from 1997 on, with no relevant differences between exposed and non-exposed groups.

Our results contribute to the evidence indicating that exposure to PCDD/Fs and NDL-PCBs is not related with SWI closeness, suggesting that it might be mainly due to other sources such as diet, which is widely accepted as the major pathway for human dioxin exposure[13]. As expected, differences were found in relation to sex and age. Concentrations of PCDD/Fs and marker PCBs were higher in women than in men. Similar results have been observed by other authors[4].

It is remarkable that most of the studies described in the literature about SWI plants have shown no evidence that PCDD/F levels in the population living close to the facilities are greater than in the control populations, or that they increase over the time[4,14]. Blood levels of PCBs found in the general population of Mataró in this study are similar to those reported in the literature for population from unexposed geographical areas.

Conclusions

Results achieved from the study over the time showed that there are no differences in levels of PCDD/Fs and marker PCBs between the various zones, independently of the distance from the SWI plant. These results suggest, together with several other studies, that the main route of contamination of these compounds to humans is through other sources, mainly diet.

Acknowledgements

The authors want to thank to Consorci per al Tractament de Residus Sòlids Urbans del Maresme for their financial support. Special thanks to Mr. Carles Salesa for his encouragement in the development of this study.

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Figure 1.Sampling locations.

Table 1.Concentrations of PCDD/Fs (pg I-TEQ/g fat) in whole blood samples from exposed, unexposed and facility workers according to sex, age and place of residence.

	1995	1997	1999	2002	2005	2008	2012
Exposed							
Men 18-29	10.2	13.8	13.6	12.9	8.4	14.2	11.5
Men 30-49	12.9	15.5	22.5	17.7	12.7	12.1	13.7
Men 50-69	15.7	21.0	22.8	21.2	14.1	19.5	20.2
Women 18-39	11.0	13.3	13.3	11.8	9.4	12.7	8.3
Women 40-59	17.5	20.0	22.6	17.4	20.0	20.4	21.6
Control samples Mataró							
Men 18-29	9.8	11.6	14.9	14.8	9.9	8.3	12.0
Men 30-49	12.5	16.9	15.8	18.4	10.5	12.4	13.4
Men 50-69	14.5	19.2	18.4	18.9	13.2	14.3	14.1
Women 18-39	12.2	15.9	18.5	17.0	12.7	11.5	11.7
Women 40-59	17.9	19.9	24.5	24.4	17.4	22.6	17.4
Control samples Arenys de Mar							
Men 18-29	---	---	9.2	12.1	17.4	9.9	8.8
Men 30-49	---	---	18.2	14.9	17.4	16.0	14.6
Men 50-69	---	---	23.9	23.1	22.5	24.2	21.3
Women 18-39	---	---	20.3	12.2	15.1	14.0	9.6
Women 40-59	---	---	25.0	25.6	21.0	14.1	15.4
Facility Workers	13.9	15.7	14.8	13.4	12.8	15.3	12.8

Table 2. Total concentrations of marker-PCBs (µg/L), expressed as the sum of CB#138, CB#153 and CB#180 in whole blood samples from exposed, unexposed and facility workers according to sex, age and place of residence.

	1995	1997	1999	2002	2005	2008	2012
Exposed							
Men 18-29	1.39	1.36	1.42	0.87	0.55	1.05	0.35
Men 30-49	2.18	2.48	2.75	2.13	1.66	1.31	0.35
Men 50-69	2.49	2.83	2.48	1.95	1.94	1.81	1.85
Women 18-39	1.09	1.41	2.47	0.83	0.76	0.73	0.54
Women 40-59	1.74	2.13	1.61	1.81	1.51	0.78	0.56
Control samples Mataró							
Men 18-29	1.05	1.10	0.98	1.02	0.59	0.72	0.16
Men 30-49	1.85	2.10	2.45	1.85	0.88	1.05	0.70
Men 50-69	2.24	2.28	0.82	1.52	1.52	1.19	0.70
Women 18-39	1.34	1.61	1.30	0.75	1.04	0.69	0.98
Women 40-59	1.85	2.60	2.02	1.85	1.62	1.59	1.19
Control samples Arenys de Mar							
Men 18-29	---	---	2.04	0.90	0.53	0.72	0.92
Men 30-49	---	---	2.15	1.61	0.46	1.73	1.64
Men 50-69	---	---	1.39	3.20	2.11	3.69	3.90
Women 18-39	---	---	3.89	0.97	1.47	0.86	0.74
Women 40-59	---	---	1.22	2.11	1.99	1.60	1.42
Facility Workers	1.48	1.53	2.47	1.22	1.14	1.12	0.71