Science of the Total Environment 461–462 (2013) 612–617

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Biological monitoring of PCDD/Fs and PCBs in the City of Mataró. A population-based cohort study (1995–2012)

Jordi Parera [a], Mateu Serra-Prat [b], Elisabet Palomera [b], Lisa Mattioli [a], Manuela Abalos [a], Josep Rivera [a], Esteban Abad [a,*]

[a] Laboratory of Dioxins, Department of Environmental Chemistry, IDÆA-CSIC, Jordi Girona 18, 08034 Barcelona, Spain
[b] Research Unit, Hospital of Mataró, Consorci Sanitari del Maresme, Carretera de Cirera s/n, 08304 Mataró, Barcelona, Spain

HIGHLIGHTS

- A sixteen year study on PCDD/PCDF and PCB levels in Spain of people living nearby a SWI
- This study shows no significant differences between exposed and control.
- The findings suggest no impact coming from the plant, therefore diet is the main route for exposure.

ARTICLE INFO

Article history:
Received 3 December 2012
Received in revised form 29 April 2013
Accepted 29 April 2013
Available online 10 June 2013

Editor: Adrian Covaci

Keywords:
Dioxins
Furans
PCBs
Blood
Thermal waste management
Environment exposure

ABSTRACT

There is great concern about the exposure to PCDD/Fs in areas near solid waste incineration (SWI) plants as, in the past, thermal waste treatment was a major source of PCDD/Fs, affecting negatively the environment and the population living nearby the area of influence. The aim of the present study was to monitor PCDD/Fs and PCBs levels in blood samples in general population living nearby a modern SWI. Up to 7 different campaigns were performed between 1995 and 2012. Overall, 104 exposed subjects (living <1000 m from the incinerator plant) and 97 non-exposed subjects (living >3000 m from the incinerator plant) were randomly selected from the municipal census of the City of Mataró in 1995. In addition, workers of the SWI plant were included in the study. Moreover, in 1999, 100 non-exposed subjects living in the nearby City of Arenys de Mar were added to the project. Overall, this study represents the longest consecutive human biomonitoring study of dioxins, furans and PCBs ever conducted in Spain. Concentrations of PCDD/Fs and PCBs were determined according to age, sex and distance to the SWI exposure in whole blood sample pools. No relevant differences in PCDD/Fs and PCBs levels were observed between SWI exposure groups. It could be noted that since 1999 all groups experienced a slight decrease in the levels of PCDD/Fs and marker PCBs. Moreover, concentrations of PCDD/Fs and marker PCBs were higher in women than in men, and in older age group in comparison to the younger ones.

1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), commonly known as dioxins, are two series of anthropogenic compounds. They are formed as non-intentional subproducts resulting from combustion processes, as well as by-products at trace levels from the manufacturing of various chlorinated chemicals (Fiedler, 1996). In contrast to dioxins and furans, polychlorinated biphenyls (PCBs) are man-made products, which have been manufactured as technical formulations and used since the 1930s for many different industrial applications, such as dielectric fluids in capacitors and transformers or as additives in pesticides, paints and plasticizers, until their use was banned in open systems and restricted in closed systems, in most industrialized countries in the 1970s (Council Directive 76/769/EEC, Jensen, 1972; Zhang et al., 2007).

The high stability of dioxins and PCBs in terms of resistance to the chemical and biological degradation, combined with their lipophilic nature results in their persistency, bioaccumulation and biomagnification in the environment (Schecter et al., 2006). Today, there is evidence that dioxins and PCBs may adversely affect exposed organisms, including humans (Kogevinas, 2001). Among the variety of toxic effects derived from chronic exposure to dioxins and PCBs described in the literature, it is of relevance that two out of the 17 of the 2,3,7,8-chloro-substituted congeners are considered as carcinogenic to humans by the International Agency for Research on Cancer (IARC) (Baan et al., 2009; IARC, 2007). Releases of these pollutants to the environment have been of great concern for the general population, scientific community and health care

* Corresponding author. Tel.: +34 934006100; fax: +34 932045904.
E-mail addresses: mserra@csm.cat (M. Serra-Prat), esteban.abad@idaea.csic.es (E. Abad).

0048-9697/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.scitotenv.2013.04.094

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 (Quaβ et al., 2004; Reis et al., 2007).

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 (Ulaszewska et al., 2011), as well as no significant differences in levels of these compounds over time or in relation to non-exposed populations (Zubero et al., 2009, 2011). On the contrary, other studies have shown adverse health effects, such as an increased risk of non-Hodgkin lymphoma (Viel et al., 2011) and of developing a sarcoma (Zambon et al., 2007). In this regard, it is important to distinguish between old waste incinerators and modern installations in which releases of these contaminants are drastically lowered according to current European law.

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).

2. Materials and methods

2.1. Study design

The study was performed in Mataró (Catalonia, Spain), a Mediterranean city of approximately 120,000 inhabitants, 25 km north of Barcelona (Spain). Mataró is a residential–industrial area located in an urban environment with high traffic density. In the past, textile manufacturing was the main industrial activity. There are no other known industrial sources of dioxins rather than the before-mentioned environment and an urban waste treatment plant which was activated in 1995. At that time, there was no limit for dioxin emissions, and the plant configuration was in accordance with legislation applicable at that time. In 1998, a European guide value was established, and in 2005, a limit of 0.1 ng I-TEQ/m^3 for PCDD/Fs entered into force together to other new limits for the rest of emissions (Council Directive, 2000; Ajuntament Mataró, 2008). Consequently, the plant was modernized in 2004 in order to comply with the set limit for air emissions.

The studied SWI is located less than 1 km from Mataró in an industrial area. The plant is equipped with 2 incineration lines of 24 Gcal/h with heat recovery and electricity production through 2 steam turbines of 11.25 MW and 2.3 MW, with a capacity for about 150,000 t of waste per year. The flue gasses are cleaned and emitted through two 45-m-high stacks. Air pollution control system consists on a semi-dry scrubber, followed by a dry reactor, a fabric filter and a *selective catalytic reduction* system for NOx. Mean dioxin emissions from 2000 to 2012 were 0.011 ng I-TEQ/m^3 (n = 44; range = 0.0002–0.05) from stack 1 and 0.013 ng I-TEQ/m^3 (n = 44: range = 0.0002–0.1) from stack 2. Mean heavy metals emissions during the same period were 0.064 mg/Nm^3 (range = 0.018–0.16) for Sb + AS + Pb + Cr + Co + Cu + Mn + Ni + V. Currently, the SWI treats the refuse from a Mechanical–Biological Treatment (MBT) Plant located on the same site with a capacity of 190,000 t of waste per year, which treats the mixed waste collected in the municipalities of Maresme and other surrounding areas (around 700,000 inhabitants served).

Just after the plant was put into service a population based cohort study was designed and conducted in Mataró. For this purpose, from March to June 1995, 201 adults (100 males and 101 females), aged between 18 and 69 years, were randomly selected from the municipal census of inhabitants stratified by age, sex and distance to the SWI. The first group contained 104 individual subjects living less than 1 km from the incinerator plant and were considered as exposed, and the second group comprised by 97 individuals living more than 3 km from the incineration plant were considered as non-exposed. No socioeconomic differences were found between exposed and non-exposed groups (Gonzalez et al., 1998). Apart from the exposed and non-exposed groups, a third group consisting of 17 workers from different sections of the plant was also considered. In 1999, a second group of non-exposed individuals living in the nearby town of Arenys de Mar (approximately 11 km north of Mataró) was recruited following the same sampling procedure and added into the study with the aim to evaluate unexposed individuals living far away from the SWI plant. The exposed and non-exposed groups were divided by sex and age into three sub-groups for males (18 to 29, 30 to 49 and 50 to 69 years old) and two sub-groups for females (18 to 39 and 40 to 69 years old). All subjects in the study cohort were monitored until 2008, with control visits for blood sampling in 1995, 1997, 1999, 2002, 2005 and 2008. In 2005, after 10 years follow-up, approximately half of the individuals initially recruited were lost, and in 2008 another sampling process was conducted following the same initial methodology. In 2008, additionally to blood samples, breast milk samples were collected. Levels of PCDD/F and PCB in breast milk samples are accepted indicators of exposure to these contaminants. 46 women, aged between 18 and 40 years old from Mataró who nurse their child and gave their informed consent were consecutively recruited in the post delivery quarantine obstetric control. Women were stratified in four groups depending on the age (≤30 years old and >30 years old) and previous child (no or one).

Whole blood samples were obtained by an expert nurse in primary care facilities following routine venipuncture to determine concentrations and congener pattern of PCDD/Fs and PCBs. About 16 mL of blood from each individual were collected in two 25 mL glass bottles, in order to avoid cross contamination, and kept frozen at −70 °C until the analysis. Blood samples were sent to the laboratory for PCDD/F and PCB determination. About 10 mL of breast milk sample for each individual were obtained by an expert nurse in primary care facilities through breast-pumps during a control visit approximately 40 days after delivery. Human milk samples were collected in 25 mL glass vials, previously washed with acetone and dried and then kept frozen at −70 °C until the analysis. Breast milk samples were sent to the laboratory for PCDD/F and PCB determination. A brief questionnaire was administered to gather relevant socio-demographic and clinical data. The study protocol was approved by the local ethical committee, and all subjects signed an informed consent form before inclusion. Values of PCDD/PCDF and PCBs for the total exposed men, total exposed women, total exposed and total of unexposed groups were calculated as weighted geometrical means. The weight of each age and sex group was equivalent to its demographic weight in the population of Mataró according to official data (municipal census).

2.2. PCDD/F and PCB determination

About 40 g of blood pools were prepared by mixing together individual samples according to above mentioned age, sex and exposure groups. Next, samples were spiked with known amounts of mixtures of $^{13}C_{12}$–PCDD/Fs (EPA-1613LCS, Wellington Laboratories Inc., Guelph, Canada) and $^{13}C_{12}$-marker PCBs (MBP-MXE, Wellington Laboratories Inc., Guelph, Canada). Afterwards, sample extraction was performed using a chromatographic glass column packed with several layers of Chem-Elut (Varian, Palo Alto, CA, USA) and NaCl (De Felip et al., 2008). The extracts were kept at 105 °C overnight, prior to gravimetrical fat determination. Fat residues were then redissolved in 100 mL of n-hexane. Organic components, fat and other interfering substances were removed by treating the n-hexane extracts with silica gel modified with sulfuric acid (44%). The extracts were further cleaned with an automated system based on the use of multilayer silica, basic alumina and carbon adsorbents. Further information on the clean-up procedure has previously been reported in detail (Abad et al., 2000).

Breast milk pools were prepared by mixing together individual samples according to above mentioned age and parity groups. Next,