A STUDY ON PCB, PCDD/PCDF INDUSTRIAL CONTAMINATION IN AN URBAN/AGRICOLTURAL AREA. PART I: SOIL

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Introduction

The Istituto Superiore di Sanità is involved in a study on the impact of existing and past industrial activities as possible sources of contamination on the surrounding environment.

The study will focus on an industrial plant inside Brescia, a city in the north-west of Italy, where, from 1938 to 1984, 150 tons of polychlorinated biphenyls (PCBs) were produced. In 1994, 1996 and 1998 three monitoring programs, preliminary to the construction of a municipal waste incinerator near the industrial plant, were carried out[1]. High PCBs levels in soils were observed, namely 3000-6000 fold higher than the limits (0,001mg/Kg) allowed by the 1999 Italian law[2], in an agricultural area where several small farms are located; the farmers have been consuming for a long time food, such as milk and meat, produced in their own farms.

This study has different aims: confirming and enriching previous data; helping determining the contamination source; measuring the contamination of the animals living in the area or fed with contaminated forage; evaluate the exposure of the farmers as compared to general population.

Moreover, this study is interested in studying the PCB and PCDD/PCDF transfer from soils to humans across the food chain. The objectives of the work are the following:

1. to evaluate the agreement between new data and the previously reported PCB and PCDD/PCDF levels in soils, with particular attention to the areas where the small farms are located in order get information useful for objectives 3 and 4;
2. to examine the contamination profiles of both PCB and PCDD/F in order to provide more information on the source of the contamination;
3. to measure the PCB and PCDD/PCDF levels in the bovines, in particular perirenal fat, liver and milk[3]. These levels are probably related to soil contamination (objective 1) on one side and cause exposure of consumers (objective 4)

4. to measure the PCB and PCDD/PCDF levels in the human serum and in the breast milk of the farmers and to compare them with the values obtained for the possibly occupationally exposed population and the general population of Brescia.

For its dimensions, this study should be considered as a pilot study. Further studies could be necessary for more detailed information.
In particular in this paper we briefly present the methods and preliminary results for objectives 1 and 2, whilst in another paper we present preliminary results obtained on objective 3.

Materials and Methods

Previous data

Three different zones were identified in the area around the industrial plant, inside the city of Brescia: an agricultural zone, a built-up urban zone, with apartment blocks and private vegetable gardens, and a mixed zone made of public and big private gardens. Each zone was divided in sampling units coincident with squares (150 m * 150 m) for the agricultural zone, with the blocks for the built-up urban zone and with the private or public properties for the third zone. Inside the sampling units, three or five sampling spots (georeferenziati) were chosen and the sub-samples were pooled to produce a sample representative of the whole square.
Three different laboratories obtained aliquots of the pooled samples to determine PCB and PCDD/F congeners. The results allowed to map the contamination levels of pollutants. However the data produced by various laboratories using different analytical methods are not comparable: in some case the analyses of PCBs are not congener-specific and the results are espressed as Aroclor; one lab measured 18 congeners, but only on a limited number of sampling units; the PCDD and PCDF determination were performed by low resolution MS.

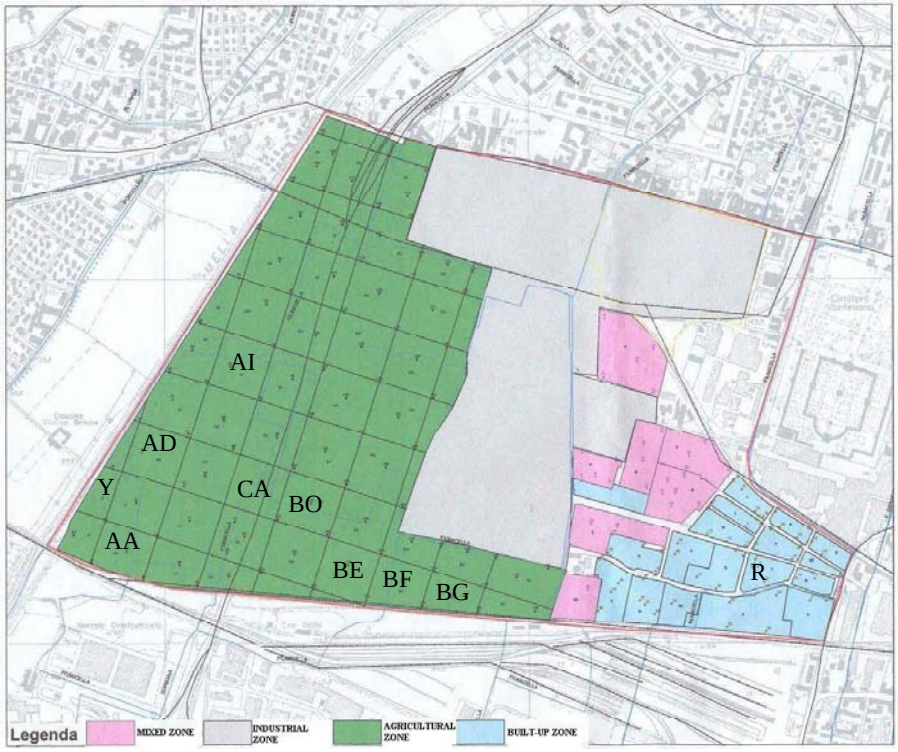
This study

So, the first need was to re-analyse some of the samples already analysed to possibly confirm the data and eventually establish a correlation with results obtained with different analytical methods.
To fulfil this need we selected 10 soil samples using the following criteria:

- an aliquot of the previously analysed pooled sample must be available for re-analysis;
- the samples chosen should represent the whole range of the contamination levels previously found: namely, two high level, three medium level and five low level samples;
- seven out of the ten samples chosen represent the contamination of the soil where the forage for feeding the animals of the farms was grown.

In Figure 1 the map of the area is represented: the farmable land is in green, the soil samples chosen to be re-analysed are indicated by capital letters.

Figure 1: Map of the area around the industrial plant inside the Brescia city . In capital letters the samples analyzed in this study.



For each soil sample, up to 120 grams of humid soil were available; so it was necessary to homogenize each sample, then to spread it, collect and pool several subsamples until about 10g were obtained. These pooled samples were thoroughly mixed-up and air dried to constant weight. Two aliquots (I and II) were collected from each pooled sample; the first one was used for the determination of 17 dioxin and furans congeners (PCDD/PCDF) and 4 coplanar PCB, while the second one other 57 PCB congeners were determined. The aliquot I was mixed with copper, transferred in ASE extraction thimbles and spiked with labeled $^{13}C_{12}$ recovery standards (nine 2,3,7,8 substituted congeners of PCDD/PCDF and PCB 77, 126 and 169). The extraction, purification and quantification method is reported elsewhere[4]. The automated multi-column Power-prep system[5], was modified for the elution volumes, *n*-hexane:dichloromethane (98:2): 140 ml, *n*-hexane:dichloromethane (50:50): 190 ml, Toluene: 70 ml.

The aliquot II was also mixed with copper, transferred in SFE steel thimbles and spiked with a mixture of 14 labeled PCB and 3 labeled pesticides. The extraction was performed using supercritical fluid CO_2 extractor (SFE Hewlett-Packard 7680T) with the same extraction condition reported elsewhere[6], except for a 20 minute static step to allow the reaction between copper and the sulphur possibly present.

Results and Discussion

So far, only 5 soil samples were reanalyzed. Data on the seven 2,3,7,8 substituted PCDD, ten 2,3,7,8 substituted PCDFs and 61 PCB congeners are available. Objective 2 of the present work was to examine the contamination profiles of both PCBs and PCDD/F to gain information on the source of the contamination. Figure 2 illustrates the correlation for the PCCD+PCDF profiles of the five samples. Generally, with this simple profile correlation we are able to rank source-related variations in the profile[7]. In the Table included in Figure 2 are reported the Pearson correlation coefficients for the 17 congeners, for the dioxins (Corr.D) and for the furans (Corr.F); each correlation is calculated with respect to profile of the Y sample. In the left side of the figure are shown the profiles of the five samples, in the right side are shown the profile differences among each profile and the Y sample, the lowest contaminated one. It is apparent, looking at the graphs and at the correlation of dioxins (Corr.D) and furans (Corr.F) that the main differences are related to the OCDD (D7), OCDF (F10) and to the ratio dioxins/furans. The application of this approach to the PCB profile will complement the information provided by the PCDD/F profile analysis and hopefully help in the identification of the contamination source.

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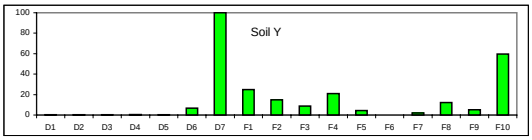
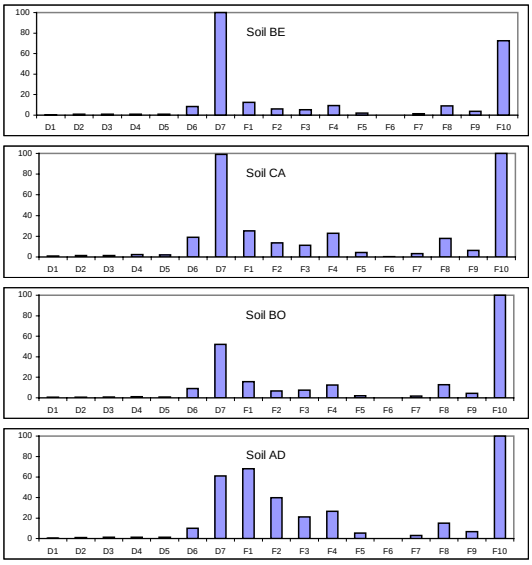


Correlation				
	Soil BE	Soil CA	Soil BO	Soil AD
Corr	0,979	0,955	0,811	0,794
Corr D	1,000	0,993	0,995	0,996
Corr F	0,953	0,979	0,948	0,947



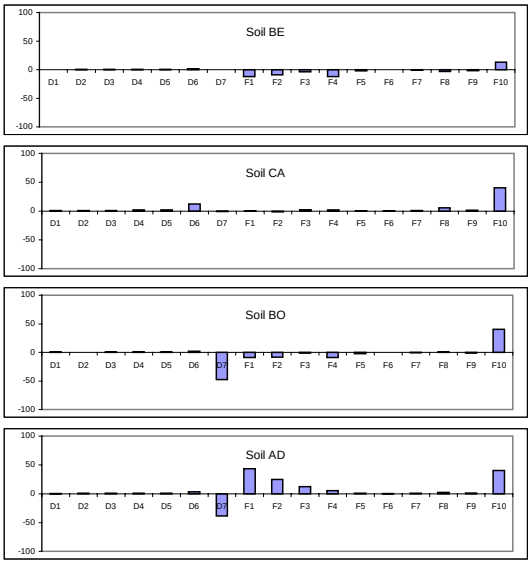


Figure 2: PCCD+PCDF profiles of the five soil samples. In the table are reported the Pearson correlation coefficients for the dioxins (Corr.D) and for the furans (Corr.F), calculated with respect to profile of the Y sample. In the left side are shown the profiles of the five samples, in the right side are shown the profile differences among each profile and the Y sample, the lowest contaminated one.