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A study on PCB, PCDD/PCDF industrial contamination in a mixed urban-agricultural area significantly affecting the food chain and the human exposure. Part I: Soil and feed

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Abstract

This study deals with a PCB, PCDD and PCDF contamination in Brescia, a city in the North-West of Italy, affecting an area with about 11 000 inhabitants. The area is close to an industrial plant that produced, in total, some 31 000 ton of PCB. A relevant part of the polluted area is agricultural soil, where cattle were fed with polluted forage and farmers were consuming their own products, so that contamination led eventually to human exposure.

Total levels of PCDD/Fs varied from 8 to 592 pgTE(WHO)/g for soil samples and when the dioxin-like PCBs (dl-PCBs) are included, the levels varied from 14.6 to 1033.7 pgTE(WHO)/g. In several cases, the legal limit was exceeded by more than one order of magnitude, with the highest contamination in some agricultural areas and in the surrounding zones. For the forage samples, total levels of PCDD/Fs varied from 0.29 to 2.04 pgTE(WHO)/g and, when dl-PCBs are included, this range increased from 2.04 to 4.75 pgTE(WHO)/g. PCB contamination of the forage through vapor condensation seemed to be relevant. The toxic contribution of dl-PCBs is always relevant and must be considered for risk management.

The main component of the contamination source is probably a heavy PCB mixture, such as Aroclor 1262.

The study dealt generally with the contamination transfer of PCBs, PCDDs and PCDFs from soil up to humans across the food chain. Results on soils and forages are shown, while measurements concerning the contamination of the animals fed with contaminated forage, and the exposure of the farmers (through human serum analyses), as compared to general population, will be reported in a dedicated paper.

Keywords: Toxicity equivalent; Contamination profile; Dioxin-like PCBs; Contamination source

1. Introduction

The Istituto Superiore di Sanità is involved in a study on the effects on food and human exposure of a large contamination of agricultural soil caused by industrial PCB mixtures.

The source was probably an industrial plant inside Brescia, a city in the North-West of Italy, where, from 1958 to 1983, about 31 000 ton of polychlorinated biphenyls (PCBs) were produced (Brievik et al., 2002). In 1994, 1996 and 1998 three monitoring programs, preliminary to the construction of a municipal waste incinerator near the industrial plant, were carried out (CTS, 2003). High PCB levels in soils were observed, 3000–6000 fold higher than the limit of 0.001 mg/kg allowed by the 1999 Italian

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law (GU, 1999), in an agricultural area where several small farms are located; the farmers had been consuming food, such as milk and meat, produced in their own farms for a long time.

Three different zones were present in the area around the industrial plant (Fig. 1), inside the city of Brescia: an agricultural zone, a built-up urban zone with apartment blocks and private vegetable gardens, and a mixed zone such as public park and 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 borders of private or public properties for the third zone. Inside the sampling units, three or five sampling spots were chosen and the sub-samples were pooled to produce a sample representative of the whole square.

This study deals with the contamination transfer of PCB, PCDD and PCDF from soil up to humans across the food chain, with the following aims:

1. to evaluate the agreement between new and old data on PCB and PCDD/PCDF levels in soils, particularly in 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 PCBs and PCDD/Fs in order to provide more information on the source of the contamination;
3. to give further elements for the risk management by determining, together with PCDD/Fs, the dioxin-like PCBs (dl-PCBs), which allows evaluation of the overall toxicity of contaminated samples and determination of the respective contribution to the toxicity equivalent;
4. to measure the PCB and PCDD/PCDF levels in the bovines from the small farms near the industrial area. These levels are possibly related to soil contamination (objective 1) on one side and cause exposure of consumers (objective 5) on the other;
5. to measure the PCB and PCDD/PCDF levels in pools of human serum of the farmers and to compare them with the values obtained for pools of various possibly environmentally exposed groups of population and with the general population of Brescia.

This paper presents in particular the results for objectives 1–3 relating to soil and forage, whilst results obtained on objectives 4 and 5, already partially reported for objective 4 (La Rocca et al., 2004), will be completely presented in a paper still in preparation.

The first requirement was to re-analyze some of the soil and forage samples already analyzed in order to confirm the data and to determine dioxin-like PCBs, on which no information was available.

To fulfil this, 10 soil samples and 5 forage samples were selected according to the following criteria:

- an aliquot of the previously analyzed pooled sample should be available to be re-analyzed;

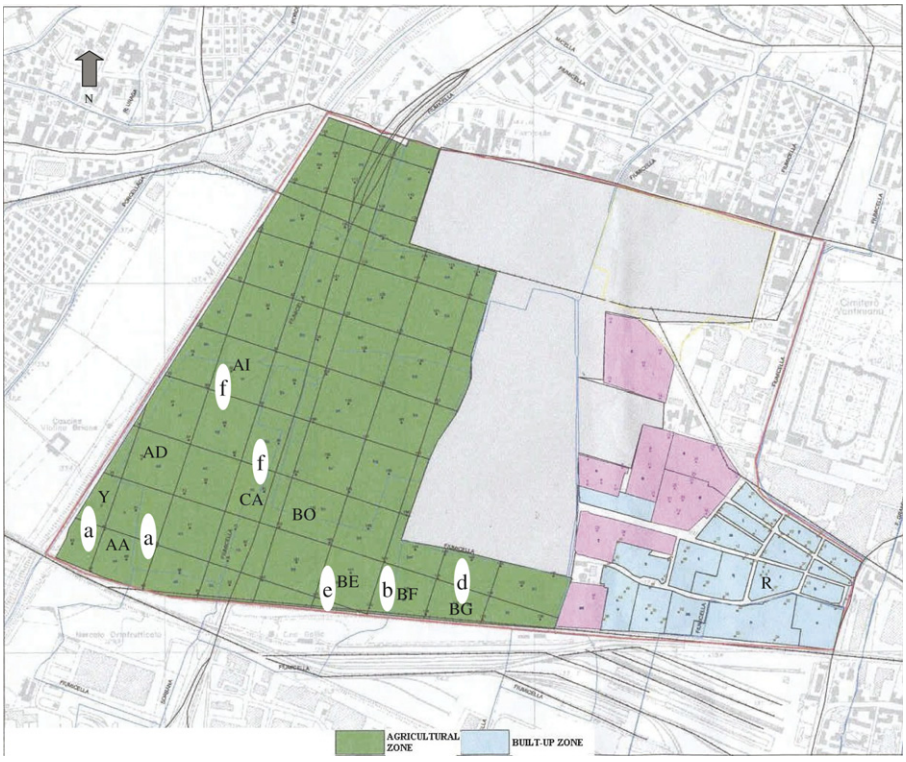


Fig. 1. Map of the area around the industrial plant inside Brescia city. In capital letters the soil samples and in small letters the forage samples analyzed in this study.

- the soil samples chosen should represent the whole range of the contamination levels previously found, such as two high level, three medium level and five low level samples;
- the samples should represent the soils where the forage used for feeding the animals of the farms was grown, which was the case for 7 out of 10 soil samples.

2. Methods

Fig. 1 shows the map of the area, where the farmable land is depicted in dark grey (green in the internet edition), the capital letters indicate the soil samples and the small letters the forage samples analyzed.

The forage "a" was grown on the soil squares AA and Y, "d" on BG, "e" on BE, and "f" on AI and CA; sample "b" is a pool from different soil squares (BF, BG and BE).

For its dimensions, this study should be considered as a pilot study. Further studies will be necessary for more detailed information.

2.1. Soil

Each soil sample (120 g) was homogenized and a 10 g subsample was taken. The detailed analytical procedure for PCDD/Fs and PCBs in soil has been described previously (Turrio-Baldassarri et al., 2004). Briefly, the extraction was carried out by ASE, two aliquots (I and II) of

Table 1
Levels of PCDD/Fs, dioxin-like PCB and HCB, DDE, DDD and DDT (pg/g dry weight) in soil samples

	Soil samples									
	AA	AD	AI	BE	BF	BG	BO	CA	R	Y
2,3,7,8-TCDD	<2.4	<6.2	<6.4	<17.9	<1.3	<1.6	<30.2	<6.7	<0.6	<0.8
1,2,3,7,8-PeCDD	<5.1	<16.6	<21.7	<57.8	<2.3	1.9	<36.0	<11.4	<1.1	<1.9
1,2,3,4,7,8-HxCDD	4.5	19.6	13.3	52.5	1.7	<1.6	65.2	12.3	<0.9	1.9
1,2,3,6,7,8-HxCDD	6.7	20.4	22.2	59.9	3.1	2.2	86.6	20.5	1.8	2.5
1,2,3,7,8,9-HxCDD	5.2	19.4	21.2	55.5	1.7	1.9	56.7	18.0	1.3	2.0
1,2,3,4,6,7,8-HpCDD	99	179	183	498	28	23	593	166	32	32
OCDD	5376	1095	1189	5918	390	162	3463	866	218	490
2,3,7,8-TCDF	210	1219	190	739	69	34	1039	220.3	7.6	121
1,2,3,7,8-PeCDF	105	711	121	357	44	21	441	118.1	4.4	74
2,3,4,7,8-PeCDF	76	376	97	311	33	20	505	99.3	5.5	43
1,2,3,4,7,8-HxCDF	141	477	203	549	54	33	822	199.0	8.0	104
1,2,3,6,7,8-HxCDF	27	94	39	121	11.4	7.7	143	38.4	3.2	21
1,2,3,7,8,9-HxCDF	<6.2	<1.5	<12.6	<4.0	<1.3	<1.6	<7.8	<1.6	<0.8	<0.4
2,3,4,6,7,8-HxCDF	19	52	22	87	9	8	108	27	4	11
1,2,3,4,6,7,8-HpCDF	97	265	141	538	48	37	847	156	18	60
1,2,3,4,7,8,9-HpCDF	36	119	62	217	14	10	291	56	3	26
OCDF	897	1791	792	4297	143	123	6624	874	31	293
Sum PCDD/F	7115	6461	3137	13878	855	490	15161	2891	341	1284
p5cb 105	6700	77000	24500	139900	7400	6200	255500	33200	1000	6900
p5cb 114	1700	25600	7600**	49300	3200	1500	83300*	1500	400	300
p5cb 118	15800	189700	63000	364400	19200	13400	642700	85300	2000	17100
p5cb 123	300	3200	1000	6100	<60	300	10100	1400	50	300
h6cb 156	3400	40500	11700	79800	3600	2900	128200	18400	700	3000
h6cb 157	700	7500	2100	14900	1100	500	23600	3400	100	700
h6cb 167	1700*	20500	5800	40200	1900*	1400*	64900	9000	400**	1500**
h7cb 189	700	7800	2200	13800	<80	600	24400	3500	200	500
Sum mono-*ortho*	31000	371800	117900	708400	36540	26800	1232700	155700	4850	30300
t4cb 77	960	9904	4399	19659	1041	736	33921	5432	95	883
t4cb 81	40	325	163	293	38	32	490	140	5	36
p5cb 126	158	584	339	953	272	210	2248	474	55	117
h6cb 169	27	67	41	109	40	32	190	57	12	17
Sum non-*ortho*	1185	10881	4942	21015	1391	1009	36850	6104	166	1052
HCB	701*	3491**	2136	12324*	1761*	289**	44646	2014**	564*	n.d.
DDE	25470	147143	76316	363985	<163	1815*	500878	62572	6433	10551*
DDD	2098	42939	7997	85432	31888	<70	52476	13323	974	2263
DDT	10165	39037	10171	178680	<1219	<113	206622	15211	2373	5559*

* Blank incidence range from 5% to 25% of the sample signal.
** Blank incidence range from 25% to 75%.

the extract were collected from each subsample; aliquot I was used for the determination of 17 dioxin and furan congeners (PCDD/PCDF) and of four coplanar PCBs, whilst aliquot II for the determination of 57 other PCB congeners ranging from 3 to 8 chlorine atoms (listed in Turrio-Baldassarri et al., 2005a), and of the chlorinated pesticides DDT, DDE, DDD, and HCB. Both aliquots were spiked with $^{13}C_{12}$ recovery standards. The clean-up was performed with an automated multi-column Power-prep system (Focant et al., 2001), and quantification was performed with high resolution gas chromatography high resolution mass spectrometry (HRGC–HRMS; for aliquot I) and high resolution gas chromatography low resolution mass spectrometry (HRGC–LRMS; for aliquot II).

2.2. Forage

From about 200 g of forage available for each sample, an homogeneous 50 g subsample was obtained. It was spiked with $^{13}C_{12}$ recovery standards (nine 2,3,7,8 substituted congeners of PCDD/PCDF and PCB 77, 126 and 169) and Soxhlet extracted using *n*-hexane as solvent. After elution over concentrated sulfuric acid coated on a column of inert support (Extrelut), two aliquots (I and II) were obtained from each extracted subsample as for soils. For aliquot I, purification was carried out by an automated multi-column Power-prep system, and quantification was performed by LRGC–HRMS. Aliquot II was spiked with a mixture of 14 labeled PCB and 3 labeled pesticides (DDT, DDE, and HCB) and directly injected in the GC–MS system.

A laboratory blank was also analyzed with each set of samples.

3. Results and discussion

3.1. Soils

Three different laboratories obtained aliquots of the pooled samples to determine PCB and PCDD/F congeners. The results allowed the mapping of the contamination levels of pollutants.

Based on these results, the mayor of the city prohibited any agricultural activity and advised the population that lived in the contaminated area (11 000 people) to avoid activities potentially leading to increased exposure such as: leaving children to play in gardens, touching earth or grass, playing outdoors.

However, the data elucidated by various laboratories using different analytical methods were often not

Table 2
PCDD/Fs and dioxin-like PCBs toxic equivalent levels in soil samples (pgTE(WHO)/g dry weight) and percentage contribution to the total TEQ (2a). PCDD/Fs and dioxin-like PCBs toxic equivalent levels in forage samples (pgTE(WHO)/g dry weight) and percentage contribution to the total TEQ (2b)

	Soil samples (2a)									
	AA	AD	AI	BE	BF	BG	BO	CA	R	Y
mono-*ortho* pgTE(WHO)/g	5.3	65	20	125	6.6	4.5	211	24	1.0	4.5
non-*ortho* pgTE(WHO)/g	16	60	35	98	28	21	230	49	5.6	12
TOT PCB dioxin-like pgTE(WHO)/g	21	125	55	223	34	26	442	73	6.6	16
PCDD pgTE(WHO)/g	11	31	36	98	4.6	4.4	93	25	2.4	3.7
PCDF pgTE(WHO)/g	85	412	103	331	34	20	499	106	5.6	52
PCDD + PCDF pgTE(WHO)/g	96	442	139	429	38	24	592	131	8	56
PCB + PCDD + PCDF pgTE(WHO)/g	117	567	194	653	73	50	1034	204	15	72
% mono-*ortho* TE(WHO)	4.5	11.4	10.3	19.1	9.1	9.0	20.5	11.8	6.6	6.3
% non-*ortho* TE(WHO)	13.7	10.6	17.9	15.1	38.1	42.6	22.3	23.8	38.5	16.6
% PCDD TE(WHO)	9.1	5.4	18.4	15.0	6.3	8.7	9.0	12.2	16.7	5.2
% PCDF TE(WHO)	72.7	72.6	53.4	50.8	46.4	39.7	48.3	52.2	38.3	72.0
% PCDD + PCDF TE(WHO)	81.8	78.0	71.8	65.8	52.7	48.4	57.3	64.4	54.9	77.2

	Forage samples (2b)					
	a	a′	d	e	f	b
mono-*ortho* pgTE(WHO)/g	0.44	0.26	0.64	0.23	0.24	0.43
non-*ortho* pgTE(WHO)/g	2.28	1.48	2.86	1.41	1.16	2.05
TOT PCB dioxin-like pgTE(WHO)/g	2.71	1.75	3.50	1.65	1.40	2.48
PCDD pgTE(WHO)/g	0.46	0.11	0.25	0.22	0.23	0.16
PCDF pgTE(WHO)/g	1.59	0.18	0.92	0.43	0.51	0.54
PCDD + PCDF pgTE(WHO)/g	2.04	0.29	1.16	0.64	0.74	0.70
PCB + PCDD + PCDF pgTE(WHO)/g	4.75	2.04	4.66	2.29	2.14	3.18
% mono-*ortho* TE(WHO)	9.2	12.9	13.7	10.2	11.2	13.6
% non-*ortho* TE(WHO)	47.9	72.8	61.3	61.8	54.1	64.3
% PCDD TE(WHO)	9.6	5.6	5.3	9.4	10.8	5.1
% PCDF TE(WHO)	33.4	8.7	19.6	18.6	23.8	16.9
% PCDD + PCDF TE(WHO)	43.0	14.3	25.0	28.0	34.6	22.0

comparable. In some cases, the analyses of PCBs were not congener-specific and the results expressed as Aroclor; one lab measured 18 congeners, but only on a limited number of sampling units; the PCDD and PCDF determinations were performed by low resolution MS.

No information was available on dl-PCBs, a most relevant issue in a case where PCBs are the contamination source.

Whilst the new soil data show a good agreement with the previous ones for PCB and PCDD/PCDF for the lower contaminated samples, the old data show an almost systematic overestimation of PCDD/F in the higher contaminated samples, possibly due to the use of low resolution MS.

The analytical levels of PCDD/F and dl-PCBs, total PCBs and DDE, DDD, DDT and HCB are reported in Table 1. The equivalent toxicity (TE) contribution, calculated using WHO-TEF (Van den Berg et al., 1998) values, are reported in Table 2a. If a signal of a target compound was detected in any blank sample, the result of the corresponding set of samples was treated according to the following procedure: it was corrected if the contribution of the blank signal was in the 5–75% range; if the contribution was >75%, the congener concentration was reported as "n.d.", not determined; one asterisk flags blank incidence up to 25% on analyte signal, two asterisks flag blank incidence up to 75%.

Total levels of PCDDs and PCDFs varied from 8 to 592 pgTE(WHO)/g. With the exception of sample R (7.7 pgTE(I)/g, 8 pgTE(WHO)/g), these levels were higher than the limits for public and private gardens (10 pgTE(I)/g; GU, 1999).

Table 3
Levels of PCDD/Fs, dioxin-like PCB and HCB, DDE, DDD and DDT (pg/g dry weight) in forage samples

	Forage samples					
	a	a′	d	e	f	b
2,3,7,8-TCDD	<0.09	<0.03	<0.06	<0.06	<0.06	<0.04
1,2,3,7,8-PeCDD	<0.09	<0.07	<0.14	<0.12	<0.13	<0.10
1,2,3,4,7,8-HxCDD	0.2	<0.1	<0.1	<0.1	<0.1	<0.1
1,2,3,6,7,8,-HxCDD	0.59	<0.05	0.17	<0.10	<0.11	<0.06
1,2,3,7,8,9-HxCDD	0.3	<0.1	0.1	<0.1	<0.1	<0.1
1,2,3,4,6,7,8-HpCDD	14.50	0.22	0.87	0.50	0.36	0.40
OCDD	122.0	0.5	10.6	2.1	2.0	3.3*
2,3,7,8-TCDF	1.31	0.50	2.14	1.32	1.51	1.91
1,2,3,7,8-PeCDF	0.58	0.16	0.77	0.31	0.45	0.54
2,3,4,7,8-PeCDF	0.8	0.2	1.0	0.4	0.5	0.5
1,2,3,4,7,8-HxCDF	1.11	0.12	0.70	0.19	0.40	0.54
1,2,3,6,7,8-HxCDF	2.55	0.08	0.40	0.13	0.15	0.15
1,2,3,7,8,9-HxCDF	<0.2	<0.04	<0.1	<0.1	<0.1	<0.1
2,3,4,6,7,8-HxCDF	2.67	0.07	0.46	0.12	<0.11	0.13
1,2,3,4,6,7,8-HpCDF	35.92	0.31	1.23	0.55	0.35	0.55
1,2,3,4,7,8,9-HpCDF	<0.26	<0.06	0.18	<0.12	<0.12	0.19
OCDF	7.6	0.4	1.9	0.4	0.9	0.9
Sum PCDD/F	190.7	2.9	20.9	6.9	7.6	9.4
p5cb 105	600	300	800	300	300	600
p5cb 114	200	100	300	100	95	200
p5cb 118	1900	1100	2400	1000	1000	1900
p5cb 123	<5	<5	<5	<5	<6	<6
h6cb 156	100	80	200	70	60	100
h6cb 157	30	20	80	30	50	50
h6cb 167	100	60	100	50	80	80
h7cb 189	<8	<7	<8	<7	<8	<9
Sum mono-*ortho*	2943	1672	3893	1500	1600	2945
t4cb 77	174.8	116.8	187.9	98.0	130.2	181.4
t4cb 81	5.8	3.9	6.9	3.2	4.0	6.8
p5cb 126	22.4	14.6	28.0	13.8	11.4	20.1
h6cb 169	1.7	1.3	3.1	2.1	1.0	1.6
Sum non-*ortho*	205	137	226	117	147	210
HCB	227	239	378	213	304	310
DDE	3830*	1783*	6372	1296*	1827*	2905*
DDD	356*	67**	404*	162**	40**	166*
DDT	6301*	1035**	8267*	666**	n.d.	1613**

* Blank incidence range from 5% to 25% of the sample signal.
** Blank incidence range from 25% to 75%.

In several cases, the legal limit was exceeded by much more than one order of magnitude. The highest contamination was located in some agricultural areas and in the surrounding zones. The lowest level of PCDD/F contamination (soil R), the only one lower than the legal limit, was found in one sample from the urban zone. When the dl-PCBs contribution to the toxicity equivalent (TEQ) was considered, all analyzed samples displayed higher values than the legal limit for PCDD/F (DM 471/99); it must be considered, however, that the legal limits are set in a different toxicity equivalent scale (I-TE) than the one considered in this study (WHO-TE), which includes dl-PCBs. It is relevant to point out that the dl-PCBs contribution to the toxicity equivalent ranges from 18.2% to 51.6% and it is then a critical point in the risk management of the area. The use of the WHO toxicity equivalence factors is in fact the only approach that allows assessment of the contribution of the dioxin-like PCBs to the carcinogenic risk: in fact the only soil sample (R) with a PCDD/F TEQ lower than the legal limit, exceeds this limit when dl-PCBs are considered.

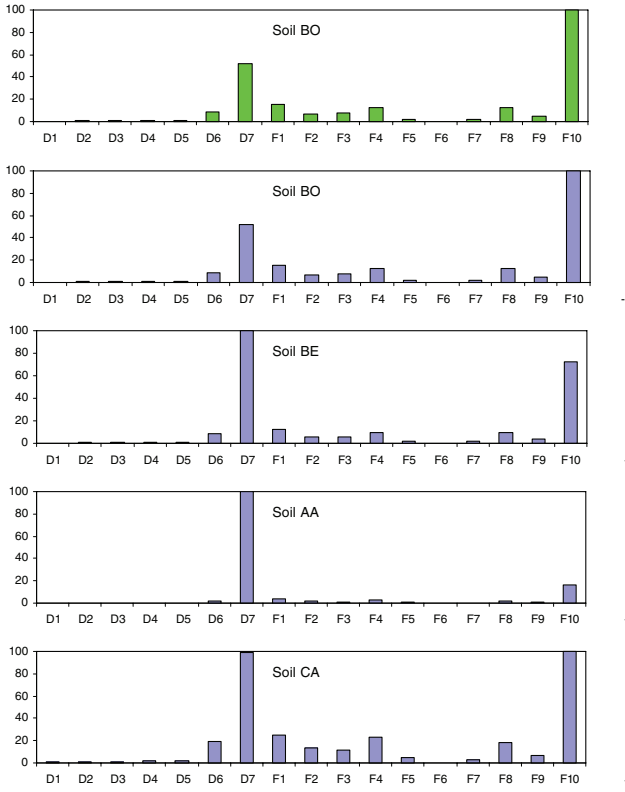
Total levels of PCBs varied from 81 ng/g to 18 700 ng/g. The levels were always higher than the legal limit (1 ng/g). All the soil samples with high PCDD/F values display also high PCB values. Again, the samples from the urban zone have much lower values than the agricultural ones.

Several elements indicate an industrial mixture of PCBs as the contamination source: first, the particularly high levels of both PCDFs and PCBs in some areas; PCB levels found in many soil samples were orders of magnitude higher than the background levels. As PCBs are not accidental products, the only sources of PCBs are industrial mixtures, and so high environmental levels over a wide area indicate that the contamination source is close; concentration gradients may help in identifying the source: a smaller scale sampling grid with non-pooled samples is, however, required to achieve this goal.

A second element is the large prevalence of PCDFs over PCDDs. The industrial mixtures of PCBs have up to ppm levels of PCDDs and PCDFs (De Felip et al., 1994), in which PCDFs are clearly prevailing, particularly for tetra-, penta- and hexa-CDFs (Bernard et al., 2002). These features were also observed in the present study.

Finally, the PCB contamination profile, which is the same for all samples, shows the presence of all kind of congeners, in the range from 3 to 8 chlorine atoms, and this indicates the presence of various mixtures with different chlorine content. However, the prevalence of congeners with 6 and 7 chlorine atoms indicates that the main components are heavy mixtures, such as Aroclor 1260 or Aroclor 1264 type mixtures (Schulz et al., 1989; Frame et al., 1996).

It is interesting that DDT concentrations in soil are apparently coherent with PCB and PCDD/F contamination values. The use of DDT in agriculture has not been allowed from at least the end of the 70s; however, its previous use as a pesticide would probably have produced



	Soil BO	Soil BE	Soil AA	Soil CA	Soil AI	Soil BG	Soil Y	Soil BF	Soil R
Corr D	1.000	0.997	0.990	1.000	1.000	1.000	0.995	0.996	1.000
Corr F	1.000	1.000	0.995	0.992	0.991	0.980	0.948	0.923	0.908
Corr tot	1.000	0.870	0.536	0.943	0.846	0.877	0.811	0.684	0.505
meanD F	1.000	0.998	0.993	0.996	0.995	0.990	0.972	0.960	0.954

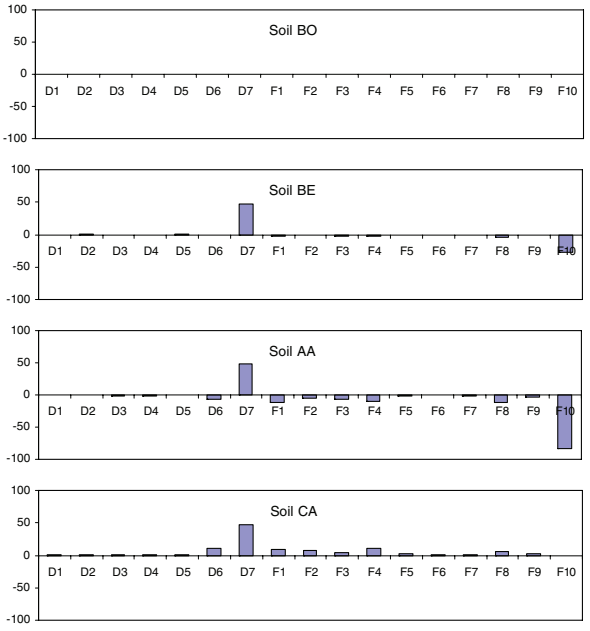


Fig. 2. PCCD + PCDF profiles of soil samples. In the table are reported the Pearson correlation coefficients for the dioxins (Corr. D) and for the furans (Corr. F), calculated with respect to profile of the BO sample. In the left side are shown the profiles of the four best fit samples, and in the right side, the profile differences among each profile and the BO sample.

more uniform contamination levels in the agricultural area. Unofficial information available at the moment indicates that the industrial plant, which produced a wide variety of organochlorine compounds during its long period of activity, did produce DDT.

3.2. Forage

Previous results were available for three of the same forage samples, for both the dioxin-like PCBs and the seven indicator PCBs. The maximum difference found between the two sets of data is within a factor 2, which may be regarded as acceptable, considering that the samples were far from being homogeneous and consequently different subsamples from the same sample were analyzed by the two laboratories.

The analytical levels of PCDD/F and dl-PCBs, total PCBs and DDE, DDD, DDT and HCB are reported in Table 3, and the toxicity equivalent (TE) contributions, calculated using WHO-TEF values, are given in Table 2b.

The PCDD/F levels in the forage samples varied from 0.29 to 2.04 pgTE(WHO)/g forage. Only the "a" and the "d" samples were higher than the legal limit of 0.75 pgTE(WHO)/g for vegetable feed (EC, 2001/102), whilst the "b", "e", and "f" samples were over the action level (0.50 pgTE(WHO)/g; EC, 2002/201). According to the above European laws, the first limit implies the elimination of the feed, and the second reveals significant contamination; investigations to find its source are needed. However, when the dl-PCBs are included, the toxicity equivalent of the same samples increases sharply, ranging from 1.4 to 3.5 pgTE(WHO)/g (all values higher than limits of regulation EC, 2001/102), with the contribution of PCCD/Fs in the interval 14.3–43%. It is worth noticing that the contribution to TEQ of the PeCB 126 alone is very high, being slightly lower than 50% for only one sample and higher for all the others.

The total PCB levels varied from 25 to 60 ng/g dry forage and indicate a diffuse and significant contamination. The contamination of forage by PCBs seemed to be fairly constant throughout the agricultural area, apparently not significantly influenced by the contamination of the soil where it was grown. This suggests that forage contamination by PCBs was determined mostly by an evaporative process. Forage is indeed a summer product and airborne PCBs are almost totally present as vapor in the warm seasons (Kaupp et al., 1996). However, more samples and more accurate information on forage sampling would be necessary to confirm this indication.

3.3. Considerations on contamination profiles

Objective 2 of the present work was to examine the contamination profiles of both PCBs and PCDD/Fs to gain

	Soil BO	Soil AI	Soil CA	Soil AA	Soil R
Corr tot	1.000	0.994	0.992	0.975	0.974
Corr 7 PCB	1.000	0.992	0.989	0.974	0.991
Corr 18 PCB	1.000	0.994	0.991	0.970	0.975

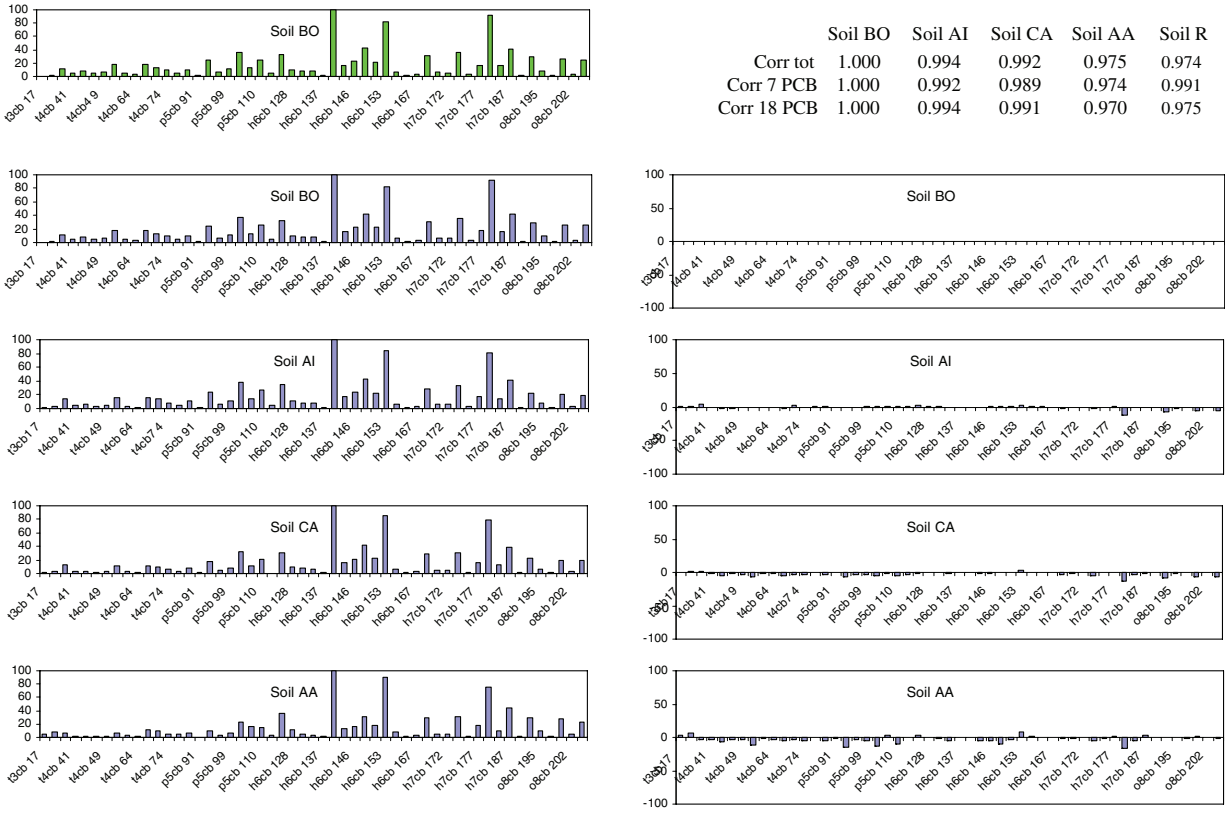


Fig. 3. PCB profiles of soil samples. In the table are reported the Pearson correlation coefficients for the 60 PCB congeners (Corr. tot), for the 7 indicator congeners (Corr. 7) and 18 congeners (Corr. 18) calculated with respect to profile of the BO sample. In the left side are shown the profiles of the four best fit samples, and in the right side, the profile differences among each profile and the BO sample.

	Soil BE	Soil AI	Soil BO	Soil AD	Soil CA	Soil Y
Corr tot	0.427	0.359	0.333	0.324	0.296	0.270
Corr 7 PCB	-0.549	-0.524	-0.497	-0.547	-0.545	-0.585
Corr 18 PCB	0.210	0.124	0.111	0.081	0.056	0.040

Fig. 4. PCB profiles of the forage sample in correlation with the soil samples. In the table are reported the Pearson correlation coefficients for the 60 PCB congeners (Corr. tot), for the 7 indicator congeners (Corr. 7) and 18 congeners (Corr. 18) calculated with respect to profile of the forage sample f. In the left side are shown the profiles of the four best fit samples, and in the right side, the right side, the profile differences among each profile and the forage sample f.

information on the source of contamination. Fig. 2 illustrates the correlation for the PCCD + PCDF profiles of the soil samples. This simple profile correlation was previously used to check source-related variations in the profile (Turrio-Baldassarri et al., 2005b). The Pearsson correlation coefficients for the 17 congeners (Corr. tot), for the dioxins (Corr. D) and for the furans (Corr. F) of the profile of each sample with respect to the one of the sample BO (the most contaminated) are reported in the table included in the figure, while the first four best fit profiles (ordered according to the dioxin correlation) are reported (left side) together with the profile difference (right). It is clearly visible that OCDD (D7) and OCDF (F10) display the highest differences in the profiles.

The application of this approach to the PCB profile complements the information provided by the PCDD/F profile analysis and helps to identify the contamination source.

In Fig. 3, the correlation coefficients for the 60 PCB congeners (Corr. tot), for the 7 indicator congeners (Corr. 7) and the 18 congeners (Corr. 18), monitored in the Italian National Residue Plan, are reported for the soil samples. The high correlation coefficients for all the profiles and the lack of significant peaks in the graphs of the profile differences indicate that all samples are probably contaminated by the same PCB mixture, suggesting that the source of the contamination was the same.

The results reported in Fig. 4 are obtained by correlating one of the forage samples profile with the soil profiles: the correlation coefficients are very low or negative, and the profile differences are very distinct. Generally, forage profiles are richer for lower chlorinated congeners and poorer for the higher chlorinated ones with respect to soil: it is reasonable to think that although some soil powder may be present on forage (sample were analyzed as received, assuming that cattle consumed it the same way), a consistent proportion of PCB present in the forage was condensed on it as a vapor after evaporating from the soil.

4. Conclusions

This study confirms the presence of a wide PCB, PCDD and PCDF contamination in an urban-agricultural area in the city of Brescia; some 11 000 people live in the contaminated area.

The source of the contamination is probably a heavy PCB mixture with a prevalence of hexa/hepta chlorinated congeners (such as an Aroclor 1262 or Aroclor 1264 type of mixture) with a minor component of lighter congeners. DDT was also present.

The determination of dl-PCBs in all the samples analyzed indicates that their contribution to the overall toxicity equivalent is significant, sometimes outweighing the

contribution of PCDD/F, and must be considered in terms of risk management.

Results on forages indicate that PCB contamination via evaporation from soil-condensation on vegetables may be relevant in the heavily contaminated area.

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