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Short Communication

Occupational exposure to PCDDs, PCDFs, and DL-PCBs in metallurgical plants of the Brescia (Lombardy Region, northern Italy) area

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HIGHLIGHTS

- PCDDs + PCDFs and PCBs serum levels of metallurgical workers were investigated.
- Professionally (PE) and Not professionally (NPE) exposed subjects were considered.
- The PE group was further subdivided in ferrous and not ferrous work environments.
- Difference between not ferrous and ferrous work environments was observed.
- The congener-specific difference appears to correspond to the work environments.

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ABSTRACT

The concentration values of polychlorodibenzodioxins (PCDDs), polychlorodibenzofurans (PCDFs), and dioxin-like polychlorobiphenyls (DL-PCBs) in blood serum samples (pools) of metallurgical workers in the area of the city of Brescia (northern Italy) were statistically processed. As to workers' exposure characteristics, pools were divided into 34 professionally exposed (PE) and 11 non-professionally exposed (NPE). A further subdivision of PE pools was according to workplaces in which ferrous ($N = 24$) and non-ferrous ($N = 10$) materials were handled. To evaluate the aforesaid differences we applied the age-adjusted Generalized Linear Models. We identified significant ($P \leq 0.05$) exposure models of the classification groups. The first subdivision was confirmed by the concentrations of 1,2,3,4,6,7,8-H_7CDF, DL-PCB 105, and DL-PCB 189; the second was confirmed by the concentrations of PCDF TEQ_{97}, PCDD + PCDF + DL-PCB (TEQ_{TOT}) TEQ_{97}, 2,3,4,7,8-P_5CDF, 1,2,3,6,7,8-H_6CDD, 1,2,3,4,6,7,8-H_7CDD, and PCB 189. Based on the literature, all mentioned congeners have been found in stack gas and fly ash samples of metallurgical plants: therefore, these indicators indicate the exposure to such work environments. Specifically, the concentrations measured in the workers' blood serum appear to depend on the type of material processed during work.

1. Introduction

In 2013, a first assessment was published on the occupational exposure to polychlorodibenzodioxins (PCDDs), polychlorodibenzofurans (PCDFs), and dioxin-like polychlorobiphenyls (DL-PCBs) of metallurgical workers in the Brescia area (Abballe et al., 2013). The assessment was carried out to meet the public concern also shared by the local health agency — Azienda Sanitaria Locale (ASL) — of the city of Brescia on specific exposure situations in local metallurgical plants: already in 1999 the Lombardy Region health authority had warned the regional health agencies about a relevant PCDD and PCDF presence detected in emission dusts from electrical iron smelters. Results showed that the contaminant cumulative concentrations were higher in the professionally exposed (PE) than in the non-professionally exposed (NPE) workers. Metallurgical workers could be exposed to PCDDs, PCDFs, and DL-PCBs more than the general population, in particular due to non-negligible contributions to exposure from workplace ambient air. An improvement of preventive measures may be required to avoid chemical overexposure in certain metallurgical workplaces.

In this study, a re-evaluation has been carried out of the same

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Table 1
Synopsis of the participating subjects and blood serum samples (pools) that were assayed for PCDDs, PCDFs, and DL-PCBs. Work types are only indicative. All subjects were males.

Pool number	Number of subjects	Identification	Material/Work type	Mean pool age (y)
Professionally exposed (PE)subjects				
01	10	Steel 1	Steel/Fusion	40.2
02	9	Steel 1	Steel/Fusion	45.1
03	10	Steel 1	Steel/Casting	46.3
04	10	Steel 1	Steel/Casting	42.7
05	10	Steel 1	Steel/Casting	46.3
06	12	Steel 1	Steel/Scrap handling	42.0
07	8	Steel 1	Steel/Maintenance	42.0
08	8	Steel 1	Steel/Maintenance	42.4
09	10	Steel 2	Steel/Casting	44.6
10	10	Steel 2	Steel/Casting	43.3
11	10	Steel 2	Steel/Casting	43.0
12	10	Steel 2	Steel/Fusion	41.3
13	10	Steel 2	Steel/Fusion	36.2
14	8	Steel 2	Steel/Maintenance	44.3
15	7	Steel 2	Steel/Maintenance	36.6
16	6	Steel 2	Steel/Scrap handling	46.3
17	6	Steel 2	Steel/Scrap handling	44.3
18	10	Steel 3	Steel/Fusion	47.6
19	9	Steel 3	Steel/Scrap handling	45.1
20	14	Steel 3	Steel/Casting	46.3
21	7	Steel 3	Steel/Maintenance	42.7
22	9	Aluminum 1	Aluminum/Fusion	46.3
23	10	Aluminum 1	Aluminum/Casting	42.0
24	6	Aluminum 1	Aluminum/Scrap handling	46.8
25	8	Aluminum 1	Aluminum/Maintenance	48.3
26	5	Aluminum 1	Aluminum/Scrap handling	41.2
27	6	Aluminum 1	Aluminum/Maintenance	47.3
28	10	Aluminum 1	Aluminum/mixed	44.6
29	9	Brass 1	Brass/Fusion	44.8
30	9	Brass 2	Brass/Fusion	44.6
31	9	Brass 3	Brass/Fusion	46.8
32	7	Cast iron 1	Cast iron/Fusion	42.9
33	10	Cast iron 2	Cast iron/Mixed	41.0
34	8	Cast iron 3	Cast iron/Mixed	46.3
Non-professionally exposed (NPE) subjects				
01	10	Industrial environment	Administrative employees	37.9
02	10	Industrial environment	Administrative employees	39.3
03	13	Urban environment	Brescia inhabitants	38.9
04	11	Urban environment	Brescia inhabitants	46.7
05	11	Urban environment	Brescia inhabitants	46.7
06	11	Urban environment	Brescia inhabitants	47.1
07	9	Rural environment	Remote subjects	35.3
08	10	Rural environment	Remote subjects	33.5
09	9	Rural environment	Remote subjects	39.7
10	9	Rural environment	Remote subjects	39.9
11	10	Rural environment	Remote subjects	39.0

database to determine which significant differences existed between the NPE and PE workers of ferrous and non-ferrous materials in addition to those already described by Abballe et al. (2013).

2. Materials and methods

Chemical concentrations were measured in 45 blood serum samples (pools) of PE and NPE subjects (Abballe et al., 2013). PCDDs, PCDFs, and DL-PCBs in serum samples were analyzed by high-resolution gas chromatography coupled with high-resolution mass spectrometry (HRGC-HRMS), with an in-house adaptation of US EPA Method 1613 (Abballe et al., 2013). Cumulative concentrations of PCDDs, PCDFs, and DL-PCBs were expressed as dioxin toxicity equivalents (TEQ) by using the 1997 WHO-TEF system (Van den Berg et al., 1998). However, results are also expressed with the 2005 WHO-TEF system (Van den Berg et al., 2006). Lipid-based (lb) congener limits of detection (LODs) were in the order of 1–2 pg/g for most PCDDs and PCDFs, in the 10–100 pg/g range for DL-PCBs. Repeatability standard deviation was better than |±10%| for individual congeners and cumulative values, while the expanded uncertainty of the method (coverage factor, $k = 2$) was less than |±25%| for individual congeners and less than |±20%| for cumulative values. This would permits to adopt three significant figures for pertinent data.

The differences between PE and NPE chemical concentrations were statistically processed with the Generalized Linear Models (GLMs) (Stata 12, Stata Corp). This approach gives the estimates of concern factors adjusted on the confounding influences. The ratio sample/variable was 10/2 and the estimated coefficients were adjusted on the average age of each pool. The significance level was set at $P \leq 0.05$. GLMs evaluations were carried out on the natural logarithms of the original data, but in Table 2 middle and lower sections concentration figures were converted back to linear form.

Two strategies were adopted to determine pool differences by GLMs: the first took into consideration the subdivision of NPE ($N = 11$) and PE ($N = 34$), while the second considered the NPE group and the subdivision of the PE group in pools deriving from workers of the ferrous (PE-1, $N = 24$) and non-ferrous (PE-2,

Table 2
Upper section: mean medium-bound WHO-TEQ_{97} and WHO-TEQ_{05} estimates for NPE, PE-1, and PE-2 exposure groups[a]. Middle section: significant results from GLMs evaluations applied to NPE and PE exposure groups (N = 11 and 34, respectively). Lower section: significant results of GLMs evaluations applied to NPE, PE-1 and PE-2 exposure groups[b].

Chemical	NPE pools (N = 11)	PE-1 pools (N = 24)	PE-2 pools (N = 10)
PCDDs, $pgTEQ_{97}\ g^{-1}$ lb	7.91	8.22	9.50
PCDDs, $pgTEQ_{05}\ g^{-1}$ lb	7.94	8.25	9.55
PCDFs, $pgTEQ_{97}\ g^{-1}$ lb	11.6	13.2	17.0
PCDFs, $pgTEQ_{05}\ g^{-1}$ lb	12.8	14.6	19.3
TEQ_{TOT}, $pgTEQ_{97}\ g^{-1}$ lb	43.1	46.8	51.5
TEQ_{TOT}, $pgTEQ_{05}\ g^{-1}$ lb	33.5	36.3	41.6

Chemical[c]	Coefficient	P	Lower limit[d]	Upper limit[d]
2,3,4,7,8-P_5CDF, pg g^{-1} lb	1.15	0.094	0.98	1.35
1,2,3,4,6,7,8-H_7CDF, pg g^{-1} lb	1.62	0.045	1.00	2.61
PCB 105, pg g^{-1} lb	1.32	0.022	1.04	1.66
PCB 189, pg g^{-1} lb	1.82	0.003	1.23	2.69
PCDFs, $pgTEQ_{97}\ g^{-1}$ lb	1.16	0.008	1.04	1.30
PCDDs + PCDFs, $pgTEQ_{97}\ g^{-1}$ lb	1.13	0.033	1.01	1.27
1,2,3,6,7,8-H_6CDD, pg g^{-1} lb	1.26	0.017	1.04	1.53
2,3,4,7,8-P_5CDF, pg g^{-1} lb	1.14	0.010	1.03	1.27
PCB 189, pg g^{-1} lb	1.25	0.040	1.01	1.56

[a] NPE, PE-1, and PE-2 identify non-exposed subjects and workers of the ferrous and non-ferrous metallurgic plants, respectively. The uncertainty characterizing the concentration values reported have been described under Materials and methods Section.
[b] GLMs evaluations were carried on ln-transformed data; results are shown in linear form.
[c] Concentration units reported from the original database.
[d] Confidence interval limits, P = 95%.

N = 10) metallurgical plants.

3. Results

A total of 413 individual serum specimens were collected from 300 PE and 113 NPE subjects. NPE subjects included industrial administrative employees, Brescia inhabitants, and remote rural people. On average, a pool was constituted of 9.2 ± 1.8 individuals reflecting their specific roles in the company and the metal materials processed. The individuals of each pool had approximately a similar employment age (not reported); in general, the mean age of pools was reasonably similar. Subjects' age was recorded to calculate the pertinent indexes of central tendency and dispersion (Table 1).

For this study, the PE data were further subdivided into groups PE-1 and PE-2 characterizing, respectively, the exposure of workers in ferrous and non-ferrous metallurgic plants. The previous observations on PCDFs and PCDDs + PCDFs were fully confirmed with a higher statistical significance ($P \leq 0.05$). Therefore an increased exposure was determined between PE and NPE pools, which characterizes specifically the non-ferrous workers. Table 2 summarizes the pertinent data of the three groups in $pgTEQ_{97}\ g^{-1}$ lb and $pgTEQ_{05}\ g^{-1}$ lb.

4. Discussion

Previous work estimated the mean values of the PE and NPE exposure groups (Abballe et al., 2013): PCDDs, 8.63 *vs.* 7.93 $pgTEQ_{97}\ g^{-1}$ lb; PCDFs, 16.0 *vs.* 12.9 $pgTEQ_{97}\ g^{-1}$ lb; PCDDs + PCDFs, 24.6 *vs.* 20.8 $pgTEQ_{97}\ g^{-1}$ lb; PCDDs + PCDFs + DL-PCBs (TEQ_{TOT}), 48.9 *vs.* 43.1 $pgTEQ_{97}\ g^{-1}$ lb. The application of Mann–Whitney *U* test showed a significant difference ($P \leq 0.05$) for PCDFs and a marginally significant one ($P \leq 0.1$) for the cumulative estimate of PCDDs + PCDFs. However, it did not show any statistically significant differences between PE and NPE for PCDDs and TEQ_{TOT} data.

PE and NPE groups were significantly different at $P \leq 0.05$ with the three congeners 1,2,3,4,6,7,8-H_7CDF, PCB 105, and PCB 189, and at $P \leq 0.1$ with the 2,3,4,7,8-P_5CDF congener (Table 2). The first three marked specifically the PE group. The mean 1,2,3,4,6,7,8-H_7CDF concentration measured in the PE group was 2.55 times the one determined in the NPE group. 1,2,3,4,6,7,8-H_7CDF and PCB 105 appear to be diffuse exposure factors in the metallurgical environments in that their concentrations in the NPE, PE-1, and PE-2 groups did not differ significantly, while PCB 189 was significantly different in both statistical approaches. However, 1,2,3,4,6,7,8-H_7CDF and PCB 105 were reported to characterize the external emissions of the non-ferrous foundries, although not exclusively (Antunes et al., 2012); PCB 189, on the contrary, appears to be an indicator of the iron-containing materials. In Table 2 more exposure indicators were identified in the three groups confirming that specific exposures exist in metallurgical environments (Antunes et al., 2012; Byeong-Woon et al., 2006): the most important markers were the PCDFs probably because they are specific of metallurgical industrial impact. In the table, 2,3,4,7,8-P_5CDF is the most significant indicator at congener level. In addition, this congener has the second most important toxicity equivalency factor (TEF) (Van den Berg et al., 1998, 2006). Its mean concentration is 1.3 times that in the NPE group. This congener is the most frequently detected in stack gas and fly ash samples of both ferrous and non-ferrous metallurgic plants (Byeong-Woon et al., 2006). An additional marker of toxicological concern of the PE-2 group is 1,2,3,6,7,8-H_6CDD whose average concentration is 1.9 times that in the NPE group. Congeners 2,3,4,7,8-P_5CDF and 1,2,3,6,7,8-H_6CDD are predominant among those that determine the internal human exposure (EFSA, 2004).

The highest exposure of workers of the non-ferrous metallurgic plants has been already observed (Sweetman et al., 2004), and appears to be due to the temperatures used in such plants, lower than those necessary for steel productions, as well as to the use of scraps containing organic impurities, and to the "de novo" synthesis of PCDFs (Davy, 2004; Lenoir et al., 2012).

Of remarkable interest is the comparison of the data reported by Abballe et al. (2013) with the human blood serum pool data of the general population recently determined in the Campania Region in Italy (De Felip et al., 2014). The sampling operations were carried out in the same period (2008–2009); the analyzed samples were normally pools of ten individuals of the same age range and sex. The NPE average TEQ_{TOT} estimation (43.1 $pgTEQ_{97}\ g^{-1}$ lb; age range, 34–47 y) was 1.82 times higher than the average TEQ_{TOT} estimation determined in the general male population (23.6 $pgTEQ_{97}\ g^{-1}$ lb, estimated by these authors; age range, 35–49 y), whereas the corresponding estimation for the non-ferrous group (51.5 $pgTEQ_{97}\ g^{-1}$ lb) was 2.18 times higher. This indicates that in the Brescia area the exposure to PCDDs, PCDFs, and DL-PCBs was relatively high, the professional exposure in metallurgical plants being even higher, in particular in the plants handling non-ferrous materials. EFSA (2004) reported that the exposure levels in human fat were approximately half of those detected in the 1980s: it may be inferred that the oldest metallurgical workers probably experienced quite higher exposures than those observed by Abballe et al. (2013).

5. Conclusions

NPE, PE-1 and PE-2 groups were significantly different but the workers of the non-ferrous metallurgic plants (PE-2) showed the highest concentrations. The most important markers were the PCDFs and the congeners 1,2,3,4,6,7,8-H_7CDF and 2,3,4,7,8-P_5CDF. Between the PCDDs, an additional marker of toxicological concern was determined in the PE-2 group: 1,2,3,6,7,8-H_6CDD. Based on the literature, the above-mentioned markers appear to be specific of the work environments. Probably, only a retrospective cohort study regarding the metallurgical workers could assess possible health effects at individual level.

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