La Medicina del Lavoro

Med Lav 2017; 108, 3: 174-186
DOI: 10.23749/mdl.v108i3.5907

Assessment of residual exposure to PCBs in metallurgy

Jacopo Fostinelli, Simona Catalani, Alice Gaia, Giuseppe De Palma, Pietro Apostoli
Unit of Occupational Health and Industrial Hygiene, Department of Medical and Surgical Specialties, Radiological Sciences and Public Health, University of Brescia, Italy

Key words: PCB congeners; metallurgical factories; occupational exposure; environmental monitoring; biological monitoring

Parole chiave: Congeneri PCB; industrie metallurgiche; esposizione occupazionale; monitoraggio ambientale; monitoraggio biologico

Summary

Objective: *To evaluate the occupational exposure to polychlorinated biphenyls (PCBs) in 56 workers employed in 6 electric arc furnace steelmaking plants and 2 secondary aluminum smelting plants located in the highly industrialized area of Brescia, Northern Italy.* **Methods:** *Thirty-four PCB congeners were found in both environmental and biological samples from workers engaged in scrap yards, electric arc furnaces, casting and maintenance departments.* **Results:** *The highest airborne PCB levels were found in the aluminum plant, even 100 times those detected in the steelwork plants. Dioxin-like PCB congeners (DL-PCBs) were poorly represented in all biological samples, whereas non Dioxin-Like PCB congeners (noDL-PCBs), in particular environmentally widespread congeners (PCB 153, 138, 180), could be detected in almost all samples. The mean total PCB serum level was 3.9 ng/ml, with a range of 1.3-10.3 ng/ml, while the geometric mean for airborne PCBs levels was 9305 pg/m*^{3}*, with a range of 1138-217806 pg/m*^{3}*.* **Conclusions:** *Despite the higher PCB values recorded in some metallurgical plant workplaces, we failed to find any significant difference between serum concentrations in workers from steel or aluminum production, even in consideration of different tasks or different job seniority, while positive association was found only according to the age of the workers. A possible explanation may be identified in the effectiveness of the individual and collective preventive measures adopted in the workplace. Assessment of the occupational exposure to such compounds, in consideration of the recent classifications as carcinogenic to humans, should be encouraged.*

Riassunto

«Stima dell'esposizione residuale a PCB nella metallurgia»**.** **Obiettivi:** *Scopo del lavoro è la caratterizzazione dell'esposizione occupazionale a policlorobifenili (PCB), in un gruppo di 56 lavoratori addetti in imprese metallurgiche (6 acciaierie e 2 fonderie di alluminio) site nell'area densamente industrializzata della provincia di Brescia.* **Metodi:** *La valutazione è stata condotta attraverso un approccio combinato di monitoraggio ambientale e monitoraggio biologico, dosando 34 congeneri PCB.* **Risultati:** *Per quanto riguarda i campionamenti ambientali, le concentrazioni più elevate sono state registrate nella fusione dell'alluminio (fino a 100 volte superiori rispetto alla fusione dell'ac-*

Pervenuto il 7.11.2016 - Revisione pervenuta il 27.3.2017 - Accettato il 17.5.2017
Corrispondenza: Dr. Jacopo Fostinelli, Unit of Occupational Health and Industrial Hygiene, Department of Medical and Surgical Specialties, Radiological Sciences and Public Health, University of Brescia, Italy, P.le Spedali Civili 1, 25123 Brescia, Italy
Tel. +39-030-3995661 - Fax +39-030-3996046 - E-mail: j.fostinelli@unibs.it

Una parte dei dati riportati nel presente elaborato è stata oggetto di comunicazione orale al 76° congresso nazionale SIMLII di Bologna in data 16 ottobre 2014.

ciaio). I congeneri diossino-simili sono risultati poco rappresentati mentre i congeneri non diossino-simili, presenti anche nell'ambiente generale (PCB 153, 138, 180), sono risultati prevalenti. Il valore medio della sommatoria dei PCB nel siero dei lavoratori è risultato 3.9 ng/ml (range 1.3-10.3 ng/ml) mentre la media geometrica dei livelli ambientali è risultata pari a 9305 pg/m^3 (range 1138-217806 pg/m^3). **Conclusioni:** *Nonostante le differenze in termini di concentrazioni di PCB risultanti dai monitoraggi ambientali, i dosaggi effettuati sui lavoratori non hanno evidenziato differenze statisticamente significative, anche considerando la mansione e l'anzianità lavorativa, mentre l'unica associazione significativa è risultata con l'età anagrafica dei lavoratori. Una possibile spiegazione può essere ricercata nell'efficacia delle misure di prevenzione collettiva individuale e collettiva adottate. In considerazione della recente riclassificazione dei PCB come cancerogeni certi per l'uomo, si sottolinea la necessità di ulteriori studi che valutino l'entità dell'esposizione in ambito lavorativo.*

Introduction

The emission of unintentionally produced Persistent Organic Pollutants (POPs) from industrial processes is currently of great interest in terms of the health implications for workers and the general population. The recycling of dross and scrap is nowadays the main method of metal alloy production in developed countries due to economic and energy saving reasons. Ferrous and non-ferrous materials re usually melted down in Electric Arc Furnaces (EAFs) that typically consist of a refractory-lined steel vessel in which scrap is charged and melted by electrodes powered by alternating current. During the melting process, the formation of POPs, in particular polychlorinated dibenzo-p-dioxins (PCDDs), furans (PCDFs) and polychlorinated biphenyls (PCBs), may occur, mainly because dross and scrap materials may contain organic and chloro-organic impurities formed during the smelting processes. Indeed, it has been reported that melting dross and scrap yielded much higher concentrations of POPs than ingot smelters, due to the large percentage of waste or recycled material used. This could be a result of the incorrect preparation of raw materials, giving rise, among others, to organochlorine compounds (21, 22) during the recombination of organic and chlorine atoms in the furnace. PCB mixtures may consist of up to 209 possible congeners, differing from each other in number and position of chlorine atoms on the two basic benzene rings. From a toxicological point of view, PCBs can be divided into two categories: dioxin-like PCBs (DL-PCBs) whose toxic effects are comparable to those of PCDD/Fs, and non-dioxin-like PCBs (noDL-PCBs), which do not share a toxicological mechanism with PCDD/Fs. For DL-PCBs the World Health Organization (WHO) has established Toxicity Equivalent Factors (TEFs) (25). The Toxic Equivalency (TEQ) can be obtained by multiplying the DL-PCB concentrations by the respective TEF and the TEQ of a mixture is obtained by adding up the TEQs of individual compounds. The concept of toxic equivalency (TEQ) is based on a common action mechanism (mediated through AhR activation) of persistent organic pollutants. It uses the relative effective potencies of individual compounds to activate the AhR, and AhR-dependent toxic or biological effects relative to the reference toxicant, tetrachlorodibenzo-p-dioxin (TCDD). Regarding the carcinogenicity of such compounds, the association between occupational exposure to PCBs and the risk of cancer is still an active area of epidemiological research today, as confirmed by the several mortality studies conducted among large groups of PCB exposed capacitor workers (16). The International Agency for Research on Cancer (IARC) has recently classified PCBs as Group 1 carcinogens (carcinogenic to humans) (14) on the basis of their association with melanoma, whereas less consistent association has been found for Hodgkin's lymphoma and breast cancer (18). In agreement with the IARC evaluation, the Italian List of Occupational Diseases has been recently updated, approving the mandatory recognition of melanoma in workers occupationally exposed to PCBs as an occupational disease (10).

Several studies have investigated environmental emissions of PCDD/Fs and PCBs from metallurgical plants (2, 7, 20) but only a few have investigated both environmental emissions and workplace air levels, mainly in secondary aluminum smelting and steelmaking plants and mostly in EAF areas (12, 19). To the best of our knowledge, no studies have been undertaken to investigate the occupational exposure to PCBs in scrap yard areas of metallurgical plants, where PCBs can be present as contaminants. There is little information available about occupational exposure assessment in steelmaking and non-ferrous plants via biological monitoring, i.e. the determination of organochlorines in workers' serum levels. In a recent biomonitoring study carried out in the area of Brescia (northern Italy), which has seen the large-scale development of metallurgical, mechanical and chemical plants since the last century and is now home to an estimated 470 metallurgical companies and 17,500 workers (17), the levels of serum PCDD/Fs and PCBs in metallurgical workers have been found to be not significantly higher than those of a control group of people living in rural areas (1).

Thus, we planned to investigate the occupational exposure to PCBs in different areas of selected ferrous and non-ferrous plants, focusing on scrap yard departments, through a combined approach of environmental and biological monitoring. Although PCB exposure in humans occurs mostly via ingestion of contaminated food and, possibly, via dermal absorption, in the type of working environment in question, PCBs are mostly associated with the particulate matter, therefore we considered inhalation as the primary route of exposure.

Methods

Air sampling

PCB air sampling was performed in accordance with the NIOSH 5503 method, using a combination of a cassette filter (25 mm glass fiber) and a Florisil adsorbent tube (100 mg/50 mg) to sample, the particulate and the gaseous fraction respectively. The vacuum pumps were calibrated to a flow rate of 1 liter per minute for a sampling period of about 20 hours. The pumps were placed in the center of the sampling area of each factory; the cassette filters were positioned at 1.8 meters above the ground. Both air and biological sampling were carried out on the same day.

Regarding health and safety practices, during the sampling period, fume extraction systems were operated in the furnace areas in all the factories under investigation. In addition, according to the mandatory requirements, all workers wore full protective clothing to cover all potential dermal exposure routes and were also equipped with a mask protecting against airborne particles when operating in maintenance and in the melting areas.

Subjects and biological samples

Twenty ml of whole blood samples were drawn into tubes without anticoagulants and under fasting conditions from 56 workers from 8 metallurgical plants producing steel (n=6) and aluminum (n=2), in the area of Brescia. The resulting data is presented in table 1. Blood samples were collected during the work-shift from workers who have been assigned to specific departments for several years (scrap yards, EAF, melting and maintenance) and carry out the specific related tasks; serum was separated by centrifugation at 3500 rpm (5 min) and samples were stored at -20°C until analysis. With the collaboration of occupational health physicians, we also obtained the employment history of each participant, with particular focus on work undertaken in metallurgical plants, and information on potential environmental, in particular dietary, sources of exposure. Both biological and environmental samples were analyzed at the Laboratory of Occupational and Industrial Hygiene of the University of Brescia. The groups of participant workers were comparable in terms of residential area, dietary habits and compliance with the use of personal protective equipment in the workplace.

Analytical methods

Air samples. Filters and adsorbent tubes extracted in 5 ml of n-exane, the solution was centrifuged (3000 rpm, 5min), concentrated under vacuum and injected in GC-MS.

Biological samples. Serum PCBs were measured using the previously reported method, with slight modifications (3). After taking back the samples to R.T., 1 ml of serum was transferred to a glass tube,

Table 1 - Basic features of the investigated metallurgical plants, including air sampling areas and internal distribution of participant workers

Factories/Production	Air sampling areas (No.)	Work departments of participant workers (No.)
Steel (A)	• Scrap yard (1)	• Fusion/casting (3) • Scrap yard (2)
Steel (B)	• Scrap yard (1)	• Fusion/casting (3) • Scrap yard (2)
Steel (C)	• Scrap yard (1)	• Scrap yard (4)
Steel (D)	• Scrap yard (1)	• Scrap yard (4)
Steel (E)	• Scrap yard (1)	• Fusion/casting (1) • Scrap yard (6)
Steel (F)		• Fusion/casting (5) • Scrap yard (2) • Maintenance (2)
Aluminum (A)	• Scrap yard, crane cabin (1) • Scrap crusher entrance door (1) • Scrap dump (1) • Scrap yard, control cabin (1)	• Fusion/casting (3) • Scrap yard (3) • Maintenance (2)
Aluminum (B)		• Fusion/casting (5) • Scrap yard (3) • Maintenance (2)

spiked with internal standard and mixed for a few seconds by vortex. Methanol was added to the samples and mixed completely by vortex to precipitate the proteins, then extracted using n-hexane:diethyl ether (1:1 v/v) by rotary mixer. The upper layer was transferred to a new glass tube, concentrated under vacuum, purified in SPE and injected into GC–MS (as previously described) (8).

GC analysis

We identified 12 DL-PCBs (PCB congeners 81, 77, 123, 118, 114, 105, 126, 167, 156, 157, 169, 189) and 22 noDL-PCBs (PCB congeners 28, 31, 52, 74, 99, 101, 128, 138, 146, 153, 170, 172, 177 180, 183, 187, 194, 201, 206, 209, 196, 203) in both air and serum samples.

The LOQ was 0.05 ng/ml for each congener, in both serum and air samples.

The accuracy assessment and validation of serum measures of congeners 28, 52, 101, 138, 153 and 180, were undertaken via participation in an intercomparison program for toxicological analysis of biological materials (Institute for Occupational and Social Medicine of the University of Erlangen–Nuremberg, D-91054 Erlangen, Germany. External Quality Control according to the Guidelines of the German Medical Society), and fulfilled the requirements for the aforementioned parameters in the field of occupational medicine.

Concentrations of both serum and air PCBs were also expressed as the Toxic Equivalency (TEQ) established by the World Health Organization (WHO) in 2005 (WHO_{2005}-TEQ) (25). When the concentration of PCB congeners (in both biological and air samples) was lower than the LOQ, we considered half the LOQ for the congener for statistical analysis, and consequently for the calculation of the total WHO-TEQ (8).

Statistical analysis

Statistical analysis was carried out using IBM SPSS ver.20© software. First, we ran a descriptive analysis of airborne and serum PCB concentrations [including as a sum of DL-PCBs (Σ DL-PCBs), noDL-PCBs (Σ noDL-PCBs) all identified PCBs (Σ PCBs) and considering the degree of chlorination] and analyzed data distributions using the non-parametric Kolmogorov-Smirnov test. We used parametric (Student's t and ANOVA) or non-parametric (Mann-Whitney and Kruskal-Wallis) tests to assess differences between two or more groups, depending on normal or non-normal data distributions, respectively. Pearson's correlation analysis was performed to evaluate the relationship between age and job seniority of the workers, between air and serum PCB levels in scrap yards and scrap yard workers, respectively and the relationships between age and job seniority. As previously reported, for the identified values <LOQ, we used half of the LOQ value. Simple and stepwise multiple linear regression analysis was used to assess the relationship between Σ PCB serum levels and workers' age and job seniority.

In all cases, analysis was considered statistically significant for p values < 0.05.

Results

Air monitoring

Air PCB concentrations in different plants are summarized in table 2. Air monitoring was carried out in scrap yards in 5 out of 6 steel foundries, and in 4 areas in 1 aluminum plant. The scrap yard areas

Table 2: Air PCB levels of investigated polychlorinated biphenyl (PCB) congeners expressed as the sum of all the congeners (Σ PCBs), dioxin-like congeners (Σ DL-PCBs), non dioxin-like congeners (nonDL-PCBs), sum of Toxic Equivalency for DL-PCBs (Σ WHO-$_{2005}$ TEQ) , sum of lower chlorinated congeners (Σ Lower Cl PCBs) and sum of higher chlorinated congeners (Σ Higher Cl PCBs). Geometric means (GMs) and geometric standard deviations (GSDs) of the concentrations measured in the different steel factories and in the different locations of aluminum plant A are shown. Σ Lower Cl PCB=sum of PCB 28, 31. Σ Higher Cl PCBs=sum of all other congeners

	Steelworks						Aluminum plant A				
	A	B	C	D	E	GM (GSD)	Crane cabin	Scrap crusher	Scrap discharge	Control cabin	GM (GSD)
Σ PCBs pg/m^3	1138	28388	26969	7954	10065	9305.0 (3.22)	217806	57830	78619	76475	93286.4 (1.66)
Σ noDL PCBs pg/m^3	959	26105	25941	7214	9405	8848.2 (3.35)	212567	54231	75858	73480	89532.3 (1.68)
Σ DL PCBs pg/m^3	179	2283	1028	740	660	728.6 (2.28)	5239	3476	2761	2995	3533.7 (1.28)
Σ DL PCB pg WHO-TEQ$_{2005}$ /m^3	1.83	1.52	2.19	2.06	2.43	1.98 (1.18)	4.93	2.65	2.88	2.12	2.9 (1.36)
Σ Lower Cl PCBs pg/m^3	452	11306	18151	2592	5272	4174.4 (3.65)	155488	36124	56246	54372	64378.4 (1.71)
Σ Higher Cl PCBs pg/m^3	686	17082	8818	5362	4793	4839.9 (2.93)	62318	21706	22373	22103	28598.4 (1.57)

were representative of occupational PCB exposure for the majority of participant workers, in particular maintenance and furnace operators.

The Σ PCB concentrations (34 congeners) in steel production ranged from 1138 pg/m^3 (steel A) to 28388 pg/m^3 (steel B); the concentrations in aluminum plants were, on average, more than six times higher, ranging from 57830 pg/m^3 (scrap crusher aluminum A) to 217806 pg/m^3 (crane cabin, aluminum A). In aluminum plants, we observed the highest concentrations of both Σ DL- and Σ noDL-PCBs (5239 pg/m^3 and 212567 pg/m^3 respectively), the average values being around three and seven times higher than in steel foundries, respectively. A statistical analysis of PCB airborne concentrations in the factories investigated was not carried out, due to lack of available data.

The Σ DL-PCB levels expressed as WHO_{2005}-TEQ ranged, for steel factories, from 1.83 (steel A) to 2.43 (steel E) and, for aluminum samples, from 2.12 (control cabin) to 4.93 (crane cabin); the concentrations being about 50% higher in the aluminum plant, on average.

Figure 1 shows the geometric mean of the (%) concentrations of each PCB congener in relation to the air Σ DL- and Σ noDL-PCB concentrations.

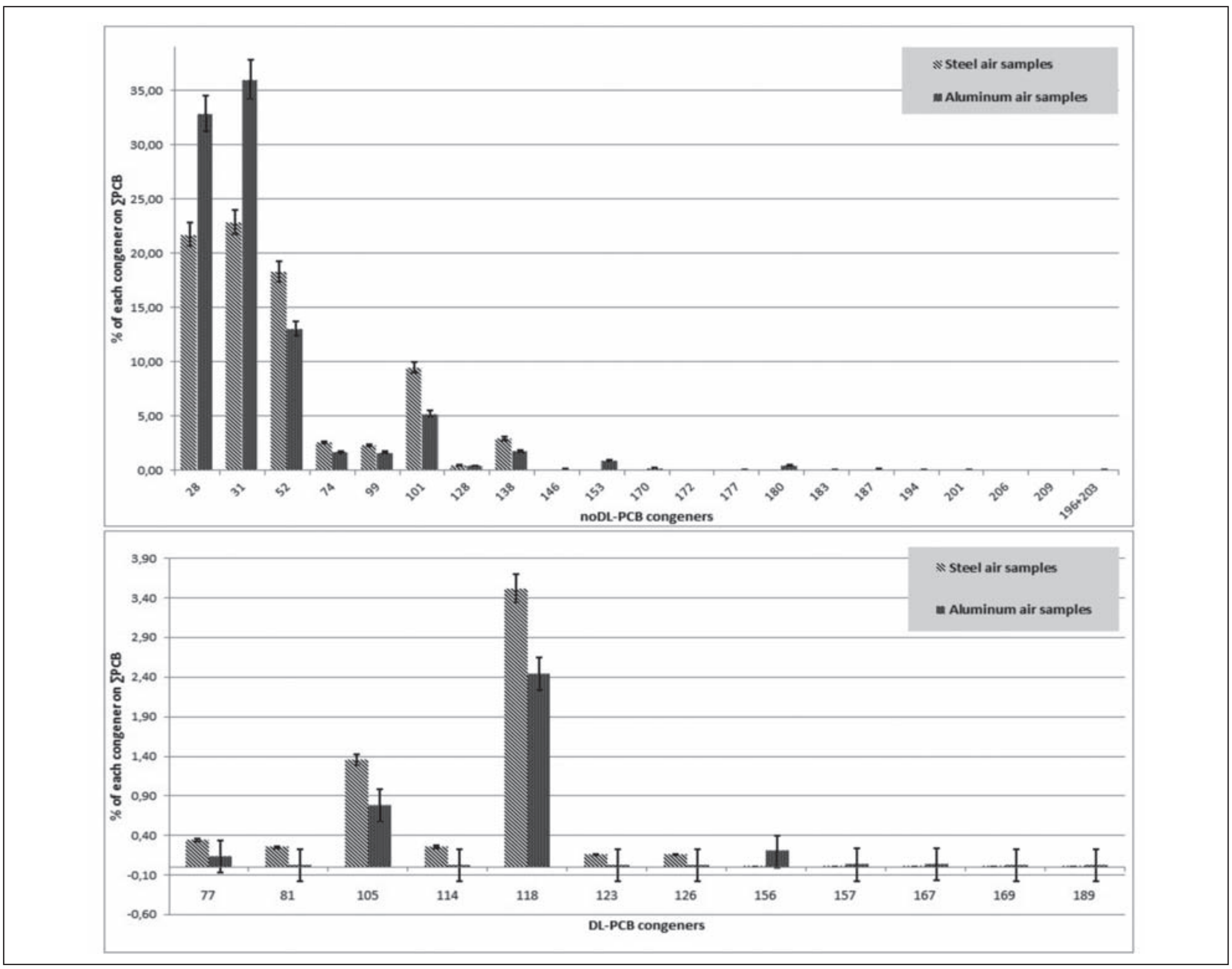

Figure 1 - Analytical profiles of air levels of DL-PCBs and noDL-PCBs sampled in workplace environments of steel and aluminum factories. Values are expressed as ratio between geometric mean of each congener and geometric mean of total PCB concentrations

Among DL-PCBs, the most frequently detected congeners were PCB 118 (from 2.19% to 4.84% of Σ PCB concentration in each sample) and PCB 105 (from 0.69% to 2.34%), whereas four congeners (PCB 123, 126, 169 and 189) were below the LOQ in every sample. PCB 118, the most common DL-PCB congener, ranged in concentration from 39 pg/m^3 to 593 pg/m^3 in steel factories and from 1784 pg/m^3 to 3439 pg/m^3 in the aluminum plant; PCB 105 ranged from 14 pg/m^3 to 473 pg/m^3 in steel factories A and B, respectively, whereas concentrations in the aluminum plant ranged from 614 pg/m^3 (scrap dump) to 962 pg/m^3 (crane cabin) pg/m^3.

Among noDL-PCBs, the most represented congeners were low chlorinated congeners PCB 28 (13-35% of Σ PCB concentrations), PCB 31 (16-35% of Σ PCB concentrations). In steel factories, PCB 28 concentrations ranged from 173 to 9174 pg/m^3, PCB 31 ranged from 279 pg/m^3 to 8677 pg/m^3. The same congeners also showed high concentrations alo in the aluminum plant: PCB 28 ranged from 16858 to 82820 pg/m^3; PCB 31 from 19266 to 72668 pg/m^3. Among noDL-PCBS, PCB 206 and 209 resulted below the LOQ in every collected sample.

Biological monitoring

The participant workers had a mean age of 43.3±10.1 years (range 22-60 years) and job seniority in metallurgical plants ranging from 1 to 35 years (mean 14.3±9.2 years). These variables were closely correlated (Pearson's r=0.54; $p<0.001$).

Among noDL-PCBs, PCBs 153, 138 and 180 were detectable in almost every sample (100%, 96% and 93% respectively), whereas PCBs 128 and 206 could not be identified in any sample. Figure 2 shows the amounts (%) of PCB congeners in relation to Σ PCB concentrations, as well as undetectable congeners. Furthermore, Table 3 shows the detectability percentages of each congener. In correspondence with the degree of chlorination, the most commonly identified congeners proved to be the higher chlorinated congeners, as compared to the lower chlorinated congeners.

Table 4 summarizes the descriptive statistics of serum PCB values as a proportion of Σ PCBs, Σ DL-PCBs and Σ noDL-PCBs.

Serum values of DL-PCBs ranged from 0.6 to 1.9 ng/ml (mean value 0.78, median 0.70), the most common being PCB 118 and PCB 156 (3.7% and 2.5% of Σ PCBs, respectively). PCB 118 and 156 could be detected in most of the samples (62% and 55% of samples, respectively), whereas PCB 77, 81, 114, 126, 169 and 189 could not be identified in any sample. Serum values of noDL-PCBs ranged from 0.65 to 8.35 ng/ml (mean value 3.22, median 2.93), the most common being PCBs 153 and 180 (18.8% and 18.4% of Σ PCBs, respectively).

The serum PCB concentrations expressed as WHO$_{2005}$-TEQ ranged from 6.53 to 6.57 ng/ml x 10^{-3}, the low variability possibly explained by the high rate of DL-PCB congeners falling below the LOQ.

Table 5 shows the distributions of serum Σ PCB, Σ DL-PCB and Σ noDL-PCB in workers classi-

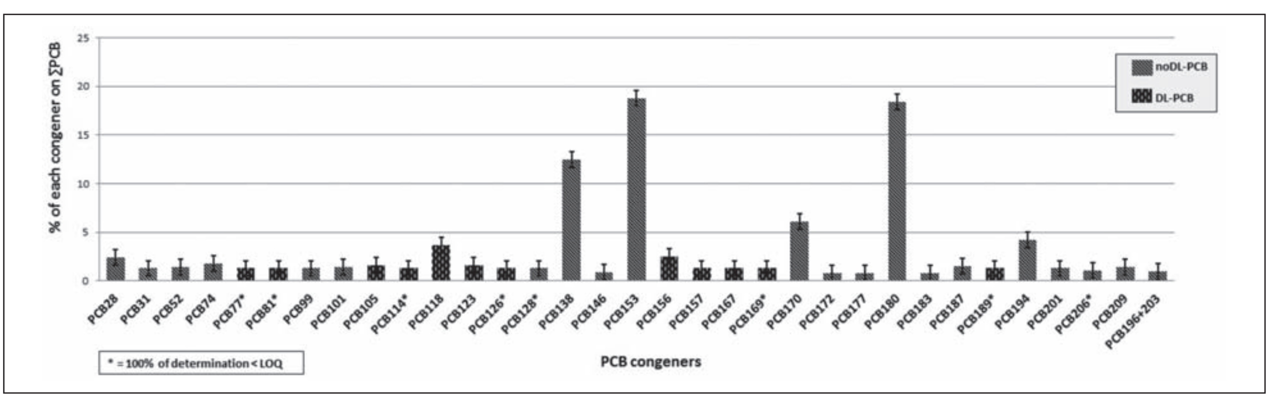

Figure 2 - Distribution of DL-PCB and noDL- PCB congeners and relative amounts (as percentage on Σ PCB concentration) in serum samples of all metallurgical workers. The values lower than the Limit of Quantification are marked as *

Table 3 - Serum PCB levels: percentages of DL-PCBs and nonDL-PCBs congeners below the limit of quantification (LOQ) in all samples

DL PCB Congeners	%<LOQ	Congener as % of total PCB concentrations	noDL PCB Congeners	%< LOQ	Congener as % of total PCB concentrations
77	100	1.3	28	79	2.4
81	100	1.3	31	96	1.3
105	88	1.6	52	89	1.4
114	100	1.3	74	29	1.8
118	38	3.7	99	46	1.3
123	82	1.6	101	93	1.4
126	100	1.3	128	100	1.3
156	45	2.5	138	4	12.5
157	98	1.3	146	43	0.9
167	96	1.3	153	0	18.8
169	100	1.3	170	21	6.1
189	100	1.3	172	54	0.8
			177	57	0.8
			180	7	18.4
			183	52	0.8
			187	30	1.5
			194	50	4.2
			201	41	1.1
			206	100	1.3
			209	86	1.4
			196+203	45	1.0

Table 4 - Distribution of the concentrations (ng/ml) of levels of serum polychlorinated biphenyl (PCB) congeners in the worker sample (No.=56) expressed as the sum of all the congeners (Σ PCBs), dioxin-like congeners **(**Σ DL-PCBs), non dioxin-like congeners (nonDL-PCBs), the sum of Toxic Equivalency for DL-PCBs (Σ WHO - $_{2005}$ TEQ), sum of lower chlorinated congeners (Σ Lower Cl PCBs) and sum of higher chlorinated congeners (Σ Higher Cl PCBs). Σ Lower Cl PCB=sum of PCB 28, 31. Σ Higher Cl PCBs=sum of all other congeners

	Mean (Std. Deviation)	Median	Min.	Max.
Σ PCBs	3.99 (1.9)	3.8	1.3	10.3
Σ DL-PCBs	0.78 (0.26)	0.7	0.6	1.9
Σ noDL - PCBs	3.22 (1.78)	2.93	0.65	8.35
Σ WHO – $_{2005}$ TEQ x 10^$^{-3}$	6.54 (0.008)	6.54	6.53	6.57
Σ Lower Cl PCBs	0.15 (0.12)	0.10	0.10	0.75
Σ Higher Cl PCBs	3.48 (1.82)	3.18	1.15	8.35

fied according to by metallurgical sector, tasks, job seniority and age. On average, higher values were found in aluminum workers, in those performing maintenance operations and in those with higher job seniority, never reaching, however, statistical significance. The Σ PCBs and Σ noDL-PCB values were significantly higher in older workers (aged ≥46 years, median of subjects' age) (p<0.001), who also displayed higher, but not statistically significant, Σ DL-PCB levels.

In simple regression analysis, both the Σ PCB and Σ noDL-PCB levels [Σ PCB=0,084 Age (years)

Table 5 - Distribution of the concentrations (ng/ml) of investigated levels of serum polychlorinated biphenyl (PCB) congeners expressed as the sum of all the congeners [Σ PCBs; means (standard deviations)], of dioxin-like congeners [Σ DL-PCBs; medians (25°-75° percentiles)], non dioxin-like congeners [Σ nonDL-PCBs; means (standard deviations)], of Lower chlorinated PCBs [Σ Lower Cl PCBs; medians (25°-75° percentiles)] and of higher chlorinated PCBs [Σ Higher Cl PCBs; means (standard deviations)] of congeners in the worker samples classified according to type of production, role, job seniority and age.**p<0.001, Student's t test. Σ Lower Cl PCB=sum of PCB 28, 31. Σ Higher Cl PCBs=sum of all other congeners

Variables	Production		Work areas			Job seniority		Age	
	Steel	Aluminum	Scrap yard	EAFs	Maintenance	<=13	>13	<=46	>46
N°	34	22	26	24	6	28	28	28	28
ΣPCBs	3.73 (1.97)	4.39 (1.91)	3.88 (1.72)	3.90 (2.00)	4.85 (2.84)	3.60 (1.84)	4.27 (2.02)	2.74 (1.59)	4.64** (1.83)
Σ DL PCBs	0.65 (0.60-0.80)	0.74 (0.64-0.95)	0.67 (0.60-0.80)	0.70 (0.60-0.84)	0.95 (0.63-1.34)	0.65 (0.60-0.84)	0.70 (0.64-0.91)	0.60 (0.60-0.94)	0.70 (0.65-0.80)
Σ non-DL PCBs	3.01 (1.83)	3.54 (1.66)	3.12 (1.56)	3.15 (1.87)	3.88 (2.38)	2.87 (1.72)	3.46 (1.78)	1.98 (1.34)	3.85** (1.63)
Σ Lower Cl PCBs	0.1 (0.1-0.1)	0.1 (0.1-0.35)	0.1 (0.1-0.1)	0.1 (0.1-0.1)	0.1 (0.1-0.27)	0.1 (0.1-0.1)	0.1 (0.1-0.1)	0.1 (0.1-0.25)	0.1 (0.1-0.1)
Σ Higher Cl PCBs	3.46 (1.98)	3.51 (1.57)	3.39 (1.65)	3.42 (1.92)	4.14 (2.31)	3.17 (1.73)	3.70 (1.87)	2.2 (1.28)	4.10** (1.76)

- 0,372; p=0.001); Σ noDL-PCB=0,083 Age (years) - 0,383; p<0.001)] were significantly affected by the workers' age. In a multiple linear regression model, setting the Σ PCB concentration as dependent variable and age and job seniority as covariates, only the worker's age (p=0.001; r^2=0,18) significantly affected the Σ PCB concentration.

The Pearson's correlation analysis between air (scrap yards) and serum Σ PCB concentrations (scrap workers) showed a positive but not statistically significant relationship between variables (data not shown).

Discussion

Occupational exposure to POPs, in particular PCBs, in metallurgical plants has seldom been investigated combining air and biological monitoring. Most of the studies have focused on the characterization of the emissions assessing concentrations of POPs (PCDD/F and PCBs) (15) in raw and stack gas and fly ash in the surrounding environment. In particular, to the best of our knowledge, there are no reports concerning the occupational exposure to PCBs of workers from the scrap yards in metallurgical factories. A further strength of our study is the large number of PCB congeners we could assess both in air and serum samples.

We looked for possible differences between airborne and serum PCB concentrations in the scrap yards of steel and aluminum plants. Moreover, we evaluated serum PCB concentrations in workers from different factory departments, as well as with different roles, ages and job seniority.

The PCB air levels we were able to identify resulted lower than the MAK of Deutsche Forschungsgemeinschaft (DFG) of 0.003 mg/m^3 (Σ 28, 52, 101, 138, 153, 180) (11) and lower than TLV of 0.5 mg/m^3 of ACGIH for 2017. Furthermore, in comparison with other measurements in similar workplaces, levels resulted higher than in previous assessments (4) in an EAF steelmaking plant in UK (0.02 pg WHO_{2005}-TEQ m^3 in the furnace control cabin and 0.46 pg WHO_{2005}-TEQ m^3 in the furnace tapping pit). These differences may be explained by the different type of production or different sampling areas considered. In our study, the airborne DL-PCB levels were also higher than in previous assessments in secondary nonferrous metallurgical facilities (copper, aluminum and lead smelting plants) in China (12) where DL-PCB samples ranged from 15.5 pg/m^3 to 770 pg/m^3 and TEQ ranged from 0.07 to 5.07 pg WHO_{1998}-TEQ m^3. Consideration must be made of the possible influence by the environmental PCB air contamination in the area of Brescia, which has been classified as a National Site of Priority Interest for PCB pollution, despite the fact that PCB mixtures are not exactly comparable. This pollution may be due to the existence in the past (from 1930 to 1984) of a chemical factory producing PCBs and to the high density of metallurgical plants, as reported in the introduction. It has been reported recently (9) that Σ DL-PCB air concentrations in different areas of the town range from 11.6 to 708.4 pg/m^3 (0.01-0.13 pg WHO_{2005}-TEQ m^3), the highest values (range 103.6-708.4 pg/m^3) being measured in areas once polluted by the chemical factory producing PCBs. Figure 3 shows the average relative contribution of PCB congeners to the Σ PCB values in airborne and serum samples. Overlapping spikes were apparent only for the most environmentally widespread congeners (PCB 118, 138, 153) but not for the congeners most commonly identified in the air samples of our survey (PCB 28, 31, 52, 101). The lower chlorinated congeners (PCB 28 and 31) proved to be most common in air samples in all the factories investigated, in particular in the two aluminum plants; however, these congeners were not the most common in biological samples of the workers. The biological results instead showed a prevalence of higher chlorinated congeners. In our opinion, this behavior would support the hypothesis that environmental air PCB contamination could be a determinant of the measured PCB air concentrations and PCB serum levels in our survey. Such a hypothesis is also supported by two findings: the lack of any significant relationship between air and serum PCB levels in scrap yard workers, as well as the lack of correlation between PCB levels and age, but not age seniority, despite the fact that the latter two variables were related, and the range of PCB elimination half-life in human (approximately 5 to 15 years), which leads to the exclusion of significant occupational exposure in the past.

As concerns the results of biological monitoring, we did not find significant differences in serum PCB levels among workers of steel or aluminum factories, or performing different jobs or with different job seniority. Thus, differences in airborne PCB levels between aluminum and steel plants were not associated with different physical burdens in workers of the two sectors. As a limitation to our investigation, it must be pointed out that comparison among serum airborne PCB levels was not possible

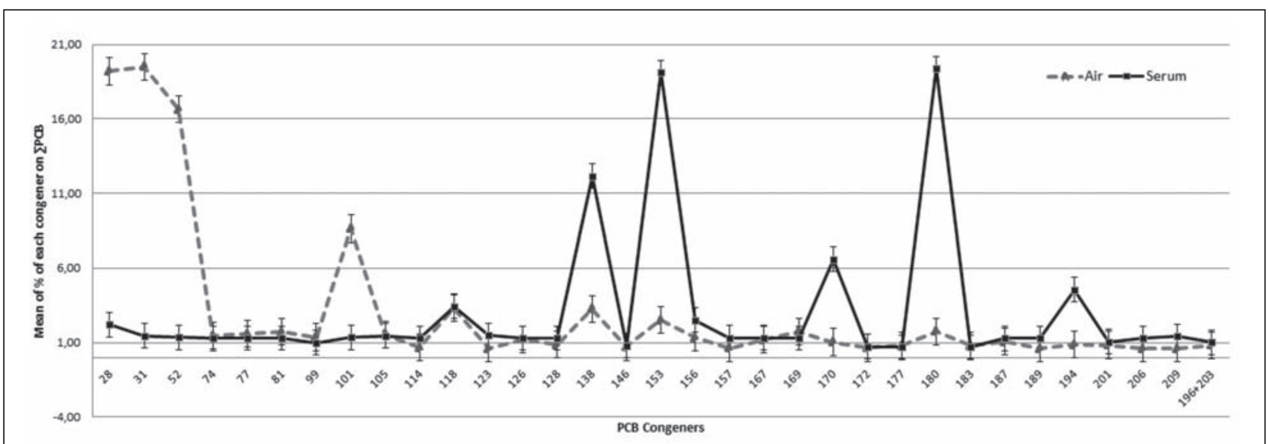

Figure 3 - Distribution of air and serum PCB congeners reported as mean of all determinations for both air and serum samples. For each congener, the levels are referred on Σ total PCB concentration

for one of the two aluminum factories. Nevertheless, the low variability of worker serum levels allows us to hypothesize a lack of correlation with airborne levels. The higher levels we observed in workers in EAF and maintenance workers are in partial agreement with a recent investigation carried out in our area (1) showing higher serum PCB levels among fusion and maintenance workers, as compared to other roles. In agreement with previous studies on the general population, the PCB congeners 153 and 118 (the most persistent) were the most commonly identified in workers' serum (13). Consistent with the aforementioned investigation (1), the most common congeners among DL-PCBs were PCB 118 and 156, whereas the congeners 180, 170, 153, 138 prevailed among noDL-PCBs. We could not compare single congeners in biological samples with these previous findings, since the serum values are normalized by total serum lipid (TSL) levels (ng/g lipids).

We compared our biological results with a recent survey carried out in an occupationally exposed population of workers in a transformer recycling company in Germany (24); among DL congeners, we found lower median values for PCB 118 and 105, while for other congeners the median resulted comparable (PCB 167, 156, 157 and 189). Among noDL congeners, our results showed lower median levels for PCB 28, 138 and 153, and comparable results for PCB 52, 101 and 180. The congeners with lower median levels were comparable with the serum levels measured in the control group of the study. A previous study by our group (3) showed mean Σ PCB (24 congeners) serum levels of 5.15 ng/ml in the general population from the area of Brescia. Two surveys have been carried out by the local health unit (5, 6) to assess PCB serum levels in people living in polluted and unpolluted areas. In the former, the average PCB serum levels in non-residents in polluted areas were 1.99 and 5.55 in the age groups 20-39 and 40-59 years, respectively. Ten years later, the same groups showed lower mean values of 0.65 and 2.62, respectively. The mean PCB value (3.79 ng/ml) in our workers falls within this described range, despite the air PCB levels we measured being higher than those identified in environmental samples from Brescia, further supporting evidence of PCB intake being more an environmental than occupational issue. A possible explanation for these finding may be the effectiveness of collective (fume extraction systems) or individual (personal protective equipment) preventive measures.

Our bio-monitoring results show higher levels of both DL-PCBs and noDL-PCBs as compared to that recently reported by people working in a building with materials containing PCBs (23). PCB exposure in metallurgical industries are of great interest in terms of the health implications for the workers involved, despite the fact that there is little investigative data available.

In our investigation, 7 PCB congeners (180, 153, 138, 170, 194, 118 and 156) including those more chlorinated, were identified in more than 30% of the subjects and contributed to 99% of Σ PCB levels, with a modest role played by DL congeners. Such data is comparable with the aforementioned studies performed in the area of Brescia.

As expected (3, 13, 27), a positive relationship was found between Σ PCB serum levels and age, due to the well-known bioaccumulation tendency of these compounds.

The PCB 126 congener is by far the greatest contributor to the TEQ in both air and serum (TEF 0.1) and accounts for about 52% of the environmental DL-PCBs contribution to the TEQ (26). In our study, it accounted for about 86.1% of the TEQ for air samples, and 76.5% for biological samples; notwithstanding it was undetectable both in environmental and biological samples. This clear overestimation relied on the method that we adopted to express undetectable PCB levels, as half of the LOQ for the congener, creating artificial discrete values.

Serum PCB levels were also compared with the BAT proposed by (DFG) for 2015 (11): the mean value of Σ PCB serum levels of our investigation (3.79 ng/ml) resulted below the BAT proposed for Σ 28, 52, 101, 138, 153, 180 (15 ng/ml). However, comparing our findings with the reference value proposed (0.02 ng/ml) for low chlorinated congener (PCB 28), we found higher mean levels in all the samples; a possible explanation for this finding could be the LOQ of our analysis (0.05 ng/ml), which is not sensitive enough to determine the limit value proposed.

Conclusions

Our research evaluated occupational exposure to PCBs in metallurgical factories by means of environmental and biological monitoring carried out in different plant departments, in particular scrap yards. Despite the airborne levels of DL-PCBs resulting higher than in previous studies in similar plants and in the urban environment of our city, the serum levels were seemingly unaffected and fit the range of temporal variability of PCB serum levels of the general population living in our area. In agreement with previous literature, the only factor affecting the serum PCB levels was the workers' age. The very low estimated intake of PCBs at the workplace was supported by the absence in the serum of PCB congeners found in high concentrations in the workplace air samples, the lack of relationship between air and serum PCB levels in scrap yard workers and the relationship of serum PCB levels with workers' age but not with job seniority. A possible explanation may be identified in the effectiveness of the individual and collective preventive measures adopted in the workplace. In consideration of the recent classifications of PCBs as carcinogenic to humans, more case studies are needed so that exposure in the workplace and the consequent health effects can be systematically and scientifically evaluated.

No potential conflict of interest relevant to this article was reported by the authors

Ethical Approval: All the workers participated under informed and verbal consent. Ethical approval was not required because all the procedures reported were part of mandatory occupational health risk assessments. All procedures were performed in accordance with the ethical standards of the institutional research committee and with the 1964 Helsinki declarations, and subsequent amendments, or comparable ethical standards.

References

1. Abballe A, Barbieri PG, di Domenico A, et al: Occupational exposure to PCDDs, PCDFs, and PCBs of metallurgical workers in some industrial plants of the Brescia area, Northern Italy. Chemosphere 2013; 90: 49-56
2. Antunes P, Viana P, Vinhas T, et al: Emission profiles of polychlorinated dibenzodioxins, polychlorinated dibenzofurans (PCDD/Fs), dioxin-like PCBs and hexachlorobenzene (HCB) from secondary metallurgy industries in Portugal. Chemosphere 2012; 88: 1332-1339
3. Apostoli P, Magoni M, Bergonzi R, et al: Assessment of reference values for polychlorinated biphenyl concentration in human blood. Chemosphere 2005; 61: 413-421
4. Aries E, Anderson DR, Fisher R: Exposure assessment of workers to airborne PCDD/Fs, PCBs and PAHs at an electric arc furnace steelmaking plant in the UK. Ann Occup Hyg 2008; 52: 213-225
5. ATS. Agenzia per la tutela della salute di Brescia (Local Health Unit of Brescia). Indagine sull'esposizione a PCB nella popolazione generale di Brescia, 2003. https://www.ats-brescia.it/media/pdf/Relazione-esposizione-a-PCB.pdf (last access 20 March 2017)
6. ATS. Agenzia per la tutela della salute di Brescia (Local Health Unit of Brescia). PCB sierici nella popolazione del comune di Brescia e in alcune aree limitrofe dei comuni di Castelmella e Capriano del Colle nel 2013. https://www.ats-brescia.it/bin/index.php?id=753&lng= (last access 20 March 2017)
7. Ba T, Zheng M, Zhang B, et al: Estimation and characterization of PCDD/Fs and dioxin-like PCBs from secondary copper and aluminum metallurgies in China. Chemosphere 2009; 75: 1173-1178
8. Bergonzi R, Specchia C, Dinolfo M, et al: Distribution of persistent organochlorine pollutants in maternal and fetal tissues: data from an Italian polluted urban area. Chemosphere 2009; 76: 747-754
9. Colombo A, Benfenati E, Bugatti SG, et al: PCCD/Fs and PCBs in ambient air in a highly industrialized city in northern Italy. Chemosphere 2013; 90: 2352-2357
10. Decree of 10 June 2014, Approval of updating of the list of occupational diseases for which notice is mandatory, according to the Decree 1124/1965. http://www.lavoro.gov.it/AreaPrevidenza/PrimoPiano/Documents/DM%20elenco%20malattie%20professionali.pdf (last access 20 March 2017)
11. Deutsche Forschungsgemeinschaft. List of MAK and BAT values, 2016
12. Hu J, Zheng M, Liu Wk, et al: Occupational exposure to polychlorinated dibenzo-p-dioxins and dibenzofurans, dioxin-like polychlorinated biphenyls, and polychlorinated naphthalenes in workplaces of secondary nonferrous metallurgical facilities in China. Environ Sci Technol 2013; 47: 7773-7779
13. Huetos O, Bartolomé M, Aragonés N, et al: Serum PCB levels in a representative sample of the SPANISH adult population: the BIOAMBIENT.ES project. Sci Total Environ 2014; 493: 834-844
14. International Agency for Research on Cancer. IARC Monographs on the evaluation of carcinogenic risks to

humans; Volume 107 Polychlorinated biphenyls and polybrominated biphenyls (2013, Lyon France)
15. Jackson K, Aries E, Fisher R, et al: Assessment of exposure to PCDD/F, PCB, and PAH at a basic oxygen Steelmaking (BOS) and an iron ore sintering plant in the UK. Ann Occup Hyg 2012; 56: 37-48
16. Kimbrough RD, Krouskas CA, Xu W, Shields PG: Mortality among capacitor workers exposed to polychlorinated biphenyls (PCBs), a long-term update. Int Arch Occup Environ Health 2015; 88: 85-101
17. Italian Institute of Statistics (ISTAT). 9th Industry and services census (2011). http://dati-censimentoindustriaeservizi.istat.it/ (last access 20 March 2017)
18. Lauby-Secretan B, Loomis D, Grosse Y, et al: Carcinogenicity of polychlorinated biphenyls and polybrominated biphenyls. The Lancet Oncology 2013; 14: 287-288
19. Lee CC, Shih TS, Chen HL: Distribution of air and serum PCDD/F levels of electric arc furnaces and secondary aluminum and copper smelters. J Hazard Mater 2009; 172: 1351-1356
20. Li S, Zheng M, Liu W, et al: Estimation and characterization of unintentionally produced persistent organic pollutant emission from converter steelmaking processes. Environ Sci Pollut Res Int 2014; 21: 7361-7368
21. Nie Z, Zheng M, Liu G, et al: A preliminary investigation of unintentional POP emissions from thermal wire reclamation at industrial scrap metal recycling parks in China. J Hazard Mater 2012; 215-216: 259-265
22. Odabasi M, Bayram A, Elbir T, et al: Electric arc furnaces for steel-making: hot spots for persistent organic pollutants. Environ Sci Technol 2009; 43: 5205-5211
23. Pedersen EB, Ebbehøj NE, Göen T, et al: Exposure to 27 polychlorinated biphenyls in the indoor environment of a workplace: a controlled bio-monitoring study. Int Arch Occup Environ Health, 17 April 2015
24. Schettgen T, Gube M, Esser A, et al: Plasma polychlorinated biphenyls (PCB) levels of workers in a transformer recycling company, their family members, and employees of surrounding companies. J Toxicol Environ Health A 2012; 75: 414-422
25. Van den Berg M, Birnbaum LS, Denison M, et al: The 2005 world health Organization Reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. Toxicol Sci 2006; 93: 223-241
26. Weiss J, Papke O, Bergman A: A worldwide survey of polychlorinated dibenzo-p-dioxins, dibenzofurans, and related contaminants in butter. Ambio Dec 2005; 34: 589-597
27. Wong LY, Uddin MS, Turner W, et al: Serum PCB concentrations in residents of Calcasieu and Lafayette Parishes, Louisiana with comparison to the U.S. population. Chemosphere 2015; 118: 156-162