

Emerging and Legacy Organic Halogenated Pollutants in Indoor Dusts [†]

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Abstract: In indoor environments, the concentration of halogenated organic pollutants in dust can be high due to the presence of products treated with these chemicals. In this study, we monitored emerging organic pollutants, such as novel brominated flame retardants (NBFRs) and some perfluoroalkyl substances (PFAS), together with legacy polychlorinated biphenyls (PCB) and polybrominated diphenyl ethers (PBDEs) in settled dust collected in five (domestic and occupational) different environments. In workplaces a high incidence of PCBs PBDEs and NBFRs occurred. Dust collection represents a simple, fast and cost-effective sampling and dust contamination level can be a useful indicator of environment healthiness.

Keywords: multiclass; priority; settled dust; environment monitoring; preventive measure

1. Introduction

In indoor environments such as houses and workplaces, the concentration of organic pollutants in dust can be high, due to the presence of textile, electronic, building materials and furniture treated with these chemicals. Among them, we focused on different classes of halogenated compounds, mostly used as flame retardants (FRs), such as novel brominated flame retardants (NBFRs) and some perfluoroalkyl substances (PFAS), together with legacy polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs). PCBs were used in thousands of consumer products. Some of them, called dioxin-like, have chemical-physical characteristics that make them similar to dioxins and furans, causing therefore the same toxicological effects. In addition, PBDEs, due to structural similarity with thyroxine, the main thyroid hormone, may interfere with the endocrine system. The association between high concentrations of some PBDEs in adipose tissues and the onset of cancer was also found. Another potential adverse effect has been shown in the neurological development of exposed children [1].

Due to the ban [2,3] on using the aforementioned PCBs and PBDEs, but owing to their essential role, new brominated flame retardants (NBFR) have been placed on the market. For these alternative chemicals, little or no toxicity data exist, therefore there is no scientific evidence that these products are safer than the banned ones. Hence, these compounds are of health concern because it would be expected behaviour similar to legacy ones, such as bioaccumulative and toxicity properties, including endocrine toxicity and carcinogenicity. Among them, tetrabromobisphenol A (TBBPA) is the most

highly produced brominated flame retardant in the world, broadly added to printed circuit boards and to several types of polymers. Nevertheless, an environmental risk was identified and legislative restrictions were applied in Europe through the IPPC (Integrated Pollution Prevention and Control) Directive, since 1995 [4]. To date, effects on reproductive and nervous system development, including brain and thyroid function were recorded. TBECH is used in construction materials, electric cables, polystyrene-based insulation panels, plastics and adhesives. In vitro studies have shown the ability to bind and activate the androgen receptor (hAR) with high affinity. Even low-level exposure may cause behavioural, functional and developmental disorders [5].

Perfluorinated alkylated substances (PFAS) are analogously added to many materials to increase their resistance. In particular, perfluorooctane acid (PFOA) and perfluorooctane sulfonic acid (PFOS) were extensively produced and used. Many in vivo and in vitro studies have suggested that exposure to PFOS may lead to adverse effects on human health, such as hepatotoxicity, neurotoxicity, reproductive toxicity, immunotoxicity, thyroid disruption, cardiovascular toxicity, pulmonary toxicity, and renal toxicity [6–8].

Electronic and electric components, insulation wires, cables, and computers, televisions, electronic equipment, small and large domestic appliances, furniture, upholstery, mattresses, carpets and furniture can be sources of the above mentioned compounds in indoor environments such as houses, offices and mechanical and electronic workshops. Especially during processing of old and new devices and furniture, particles containing legacy and emerging halogenated pollutants can be released in the environment [9]. Hence, a simple, fast and cost-effective chemical characterization of indoor dust can be a useful indicator of environmental unhealthiness.

In this study, we monitored selected emerging organic pollutants, 13 nBFRs and 5 PFAS, together with 21 PCBs and 12 PBDEs in settled dusts in different indoor environments. Both domestic and workplace dusts were analysed, in order to investigate where the potential major exposure occurs.

2. Methods

The dust samples were collected during Summer 2019 in five different sampling sites, in two domestic environments (D1, D2), an office (D3), in an electronic workshop (D4) and in a mechanical (D5) one, by using a household vacuum cleaner. Starting from previous our works focused on FRs occurrence in air and dust of an electrical and electronic waste treatment facility [10,11], we improved the analytical method to extend the investigation to new compounds. After sampling, dusts were sieved at 63 μm and extracted by accelerated solvent extraction. The chromatographic mass spectrometric analyses were performed with both reversed phase high performance liquid chromatography (RP-HPLC) and gaschromatography (GC) equipped with a methylphenyl (5%) silicone column. In particular an HPLC 1260 Infinity II system (Agilent Technologies Italia S.p.A., Cernusco sul Naviglio MI, Italy), coupled to a triple quadrupole mass spectrometer API 2000 (AB SCIEX S.r.l. Forster City, CA) was used. HPLC-MS/MS was fitted with both ESI (electrospray ionization) and APCI (atmospheric pressure chemical ionization) sources. For GC-MS analyses, an HP 7890 B gas chromatograph fitted with an HP 5977B single quadrupole mass-selective detector (Agilent Technologies, Palo Alto, CA) was used in Negative Chemical Ionization (NCI).

Determination of method performances and quantitative analyses were carried out as described in Buiarelli al. [10].

3. Results and Discussion

Thanks to the optimized sample preparation for the analytical determination of this broad and heterogeneous group of compounds, we obtained extraction recoveries of about 88%.

After the analyses of D1, D2, D3, D4 and D5 dusts, the results highlighted that in the electronic and mechanical workshops (D4 and D5), besides a high incidence of PCBs PBDEs and nBFRs, PFOA was also detected. By contrast, the total contribution of the investigated pollutants was lower in house (D1 and D2) and in office (D3) dusts except for few nBFRs.

The total contamination obtained by summing the contribution of each analyte showed the following pattern: D4>D5>D2>D3>D1 (data not shown); hence, D4 and D5 were the most contaminated environments.

For each sampling site, the sum of the compound concentration belonging to the same class (Σ PCBs, Σ PBDEs and Σ nBFRs), was calculated and reported in the histograms of Figure 1.

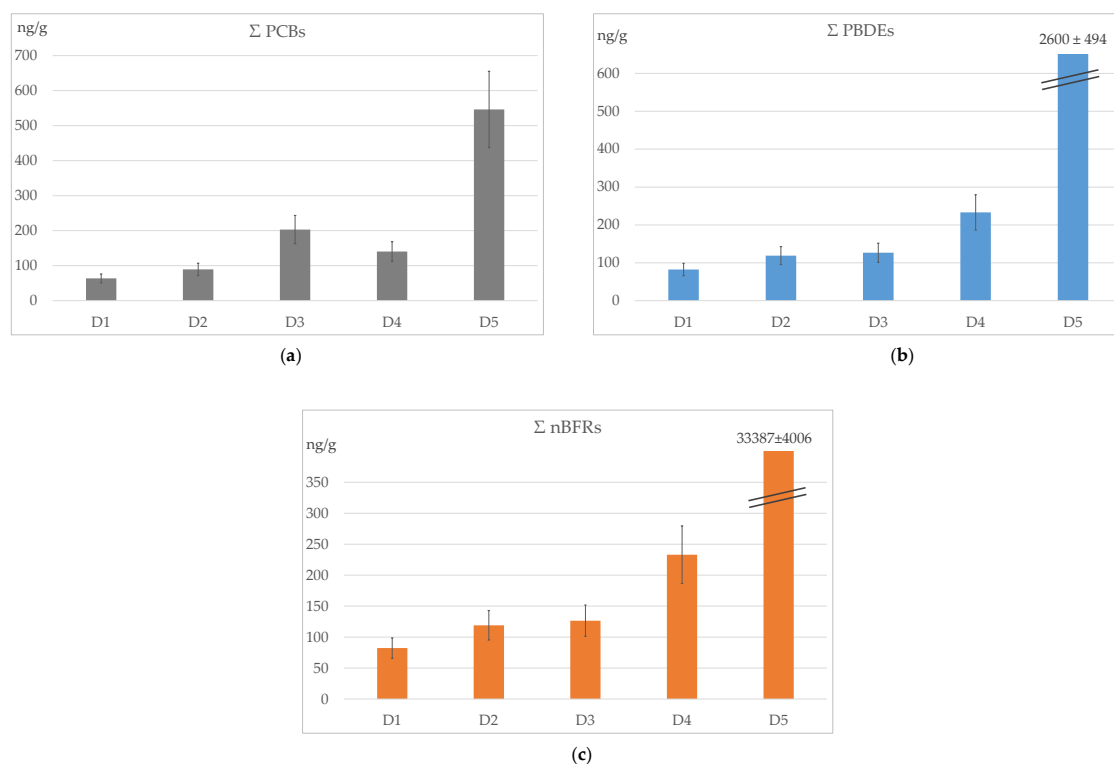


Figure 1. Σ PCBs (a), Σ PBDEs (b), and Σ nBFRs (c) in ng/g detected in each dust sample.

The higher concentration of Σ PCBs (Fig. 1a) was found in workplace dusts in the following order: D5>D3>D4, with D5 value about 4 times higher than D4, due to the larger size and the old age of D5 workplace, where there is a prevalence of a great number of old electronic devices [12].

In absence of a specific limit Σ PCBs in dust, we compared the obtained concentrations with the value related to the soil, presented in Regional Screening Level Tables calculated from EPA to prevent carcinogenic risk resulting from long term exposure to PCBs [13], equal to 0.22 $\mu\text{g/g}$. In D5, the PCB concentration of 0.55 $\mu\text{g/g}$ exceeded more than twice the EPA value, proving to be the only alarming result. Furthermore, we monitored 8 dioxin-like PCBs (DL PCBs), due to the health concern about these substances. The Σ DL PCBs was calculated, and their percentage versus Σ PCBs was above 50% for all samples except for D4.

Our findings about Σ PBDEs were summarized in Figure 1(b). Similarly to PCBs, Σ PBDEs was higher in D4 e D5, with D4 result more than twice those in D1, D2 and D3. It is noteworthy the Σ PBDE value in D5, strongly affected by the PBDE 209, detected in the highest concentration among the PBDEs. PBDE 209 is the most widespread PBDE, found in high concentration in several studies [14–16].

The Σ nBFRs was reported in Figure 1(c); in this study, we investigated 13 nBFRs, including TBBPA that was the most concentrated pollutant detected. The D4 contamination was characterized by the prevalence of TBBPA, with a concentration of 32,320 ng/g, perhaps due to the worker practise to remove the dust stored inside the devices, before repairing them. High TBBPA concentrations were in agreement with other studies carried out in similar workplaces [17], as expected for its widespread

use instead of octaBDE formulation [18, 19]. Except D4, the Σ nBFRs was comparable in all sampling sites, with a high value detected in a domestic dust (D2).

Regards the five PFAS investigated in this study, PFOA was the only detected with a concentration less than LOQ (119 ng/g) in both D4 and D5 samples, whilst PFBS, PFOS, PFTeDA and FOSA were not detected in any samples. Because of the PFOS and PFOA phase out, analysis of other PFAS, used alternatively, will be the next step in our scientific investigation.

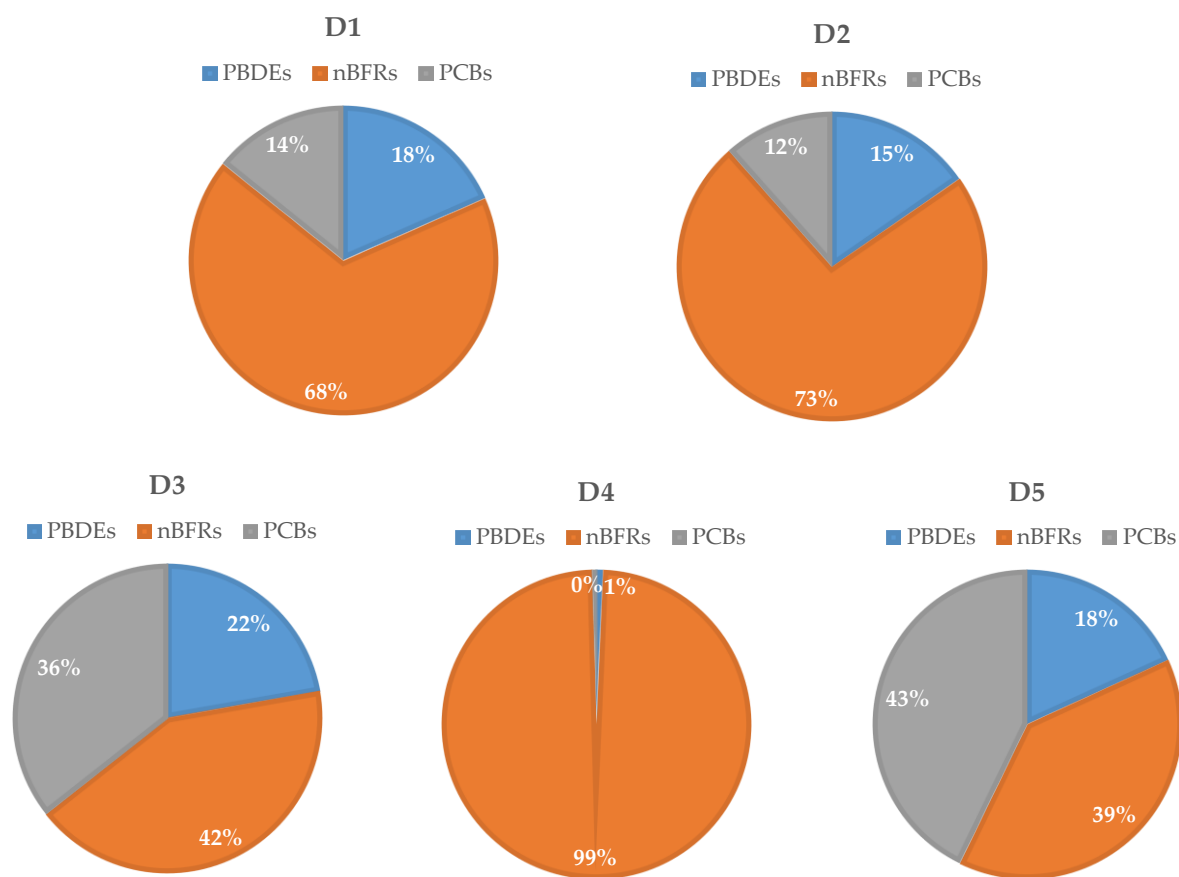


Figure 2. Percentage pie chart for the distribution of Σ PCBs; Σ PBDEs and Σ nBFRs for each dust sample.

In order to compare the contamination profile in the different indoor environments, pie charts were reported in Figure 2. They show the percentage distribution for the Σ PCBs; Σ PBDEs and Σ nBFRs in each site.

Domestic dust D1 and D2 show a similar compound distribution, with a predominance of nBFRs. All pollutant categories contribute, almost in equal measure, to D3 and D5 contamination. The relative abundance of PCBs may be due to the presence of old electric and electronic devices and furniture. The relevant concentration of TBBPA in D4 yields a percentage of 99% Σ nBFR, 1% Σ PCBs and 0% Σ PDBEs. However, the same percentage calculated without TBBPA concentration was slightly different, yielding 82% Σ nBFR, 11% Σ PCBs and 7% Σ DBEs. The very peculiar concentration profile in D4 is due to the modern devices stored and repaired in the workplace. Finally, the results obtained in all sites highlight the importance to monitor the nBFR.

4. Conclusions

Since dust contamination level can be a useful indicator of environmental healthiness, we applied an analytical method for the determination of 51 legacy and emerging pollutants, belonging to different chemical classes, in indoor dust from life and work places. The mechanical and electronic

workshops showed to be the more contaminated indoor environments, high concentrations of PCBs, PBDEs and nBFRs occurred. The Σ PCBs contamination in D5 resulted above the ESA Regional Screening Level to prevent carcinogenic risk. Moreover, TBBPA and PBDE 209, found in D4 and D5 respectively, were the most concentrated compounds detected in this study. The results suggest the need to still monitor the legacy PCBs and PBDEs, especially in workplaces where aged devices are handled, and the high occurrence of nBFRs due to the modern electronic equipment highlight the wide spreading of these emerging contaminants. The results obtained can be a basis for exposure estimation and risk assessment studies.

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Conflicts of Interest: The authors declare no conflict of interest.

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