2,3,6,7-TETRACHLORINATED BIPHENYLENE (2,3,6,7-TeCBP): A KEY ROLE COMPOUND IN FIRES OF ELECTRICAL SYSTEMS

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Introduction

Polychlorinated aromatic compounds as polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) have a significant history of environmental monitoring[1]. It is known that when fires or explosions involve electrical systems, together with PCDDs and PCDFs, polychlorinated biphenylenes (PCBPs) are also produced. These chlorinated tricyclic aromatic pollutants were object of interest in the mid-80s when their formation process and their physical, chemical and structural properties were studied[2-6]. They were noticed in the rubble of an office building fire in 1981[4] and after the destruction of the World Trade Center[8,] however the absence of the corresponding standards, associated with the analytical difficulties in developing an efficient method[2,7], have limited the knowledge of the environmental distribution of PCBPs and the possibility of their monitoring. Today, especially in the light of the toxicological findings, 2,3,6,7-TeCBP was found to be equipotent with 2,3,7,8-TeCDD[8,9], PCBPs call for more accurate investigations. Here, for the first time, a study entirely focused on 2,3,6,7-TeCBP concentration, distribution and persistence in the air matrix is reported. In detail, 2,3,6,7-TeCBP concentration was investigated after a fire broke out in an extended industrial building (site A) by using a robust analytical method previously developed by our group[10].

Materials and methods

Site location

The site A is an extended two-story industrial building. The fire broke out on the first floor and, in order to have an accurate monitoring, the sampling sites were located in different points. In detail, as schematized in Figure 1, site A1 is the closest to the source of the fire, the A2 and A3 sites are at the same floor of the fire but further from it. A4 and A5 sites are at the ground floor and A6 is an outdoor site immediately adjacent to the entrance of the building.

Sample collection and extraction

The 3-day sampling campaigns were carried out, according to the EPA methods[11,12]. Each sample was spiked with a mixture of standard labeled compounds (^{13}C-2,3,6,7-TeCBP, EN1948-ES and WP-LCS) before the 36-h Soxhlet-extraction with toluene from the PUF and the filter. The organic extracts were purified and fractionated as previously described[10].

Instrumental analysis

The gas chromatography/mass spectrometry (GC/MS) analyses were run on a Trace GC Ultra gas chromatograph equipped with a TriPlus autosampler and coupled by a heated transfer line to a TSQ Quantum Triple Quadrupole GC-MS/MS spectrometer (Thermo Scientific). The analyses were executed according to the method previously developed for 2,3,6,7- TeCBP[10].

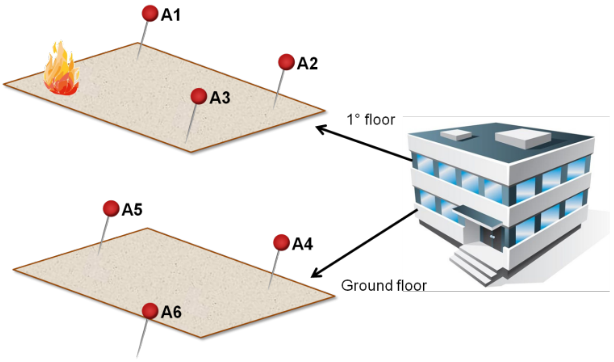

Figure 1. Schematization of the site A.

Results and discussion:

2,3,6,7-TeCBP concentration measured at site A

The first sampling campaign at site A was carried out immediately after the fire and, despite the confinement of the blaze, due to the building's extension, sampling sites were located in different areas (A1, A2, A3, A4, A5 and A6), including sites quite far from the fire's source (refer to the Figure 1). Sites were chosen as to have an accurate and complete monitoring of the place. In figure 2 are reported the concentrations measured for 2,3,6,7-TeCBP (blue columns) compared with the values of 2,3,7,8-TeCDD (red columns), the most toxic dioxin catalogued by WHO, both expressed in fg/m^3. On the basis of the equipotence of the two analytes, these values correspond also to the fg TEQ/m^3 concentrations. As expected, the highest concentration was measured in corrispondence to the fire (site A1) and the levels of 2,3,6,7-TeCBP decrease with increasing distance from the source.

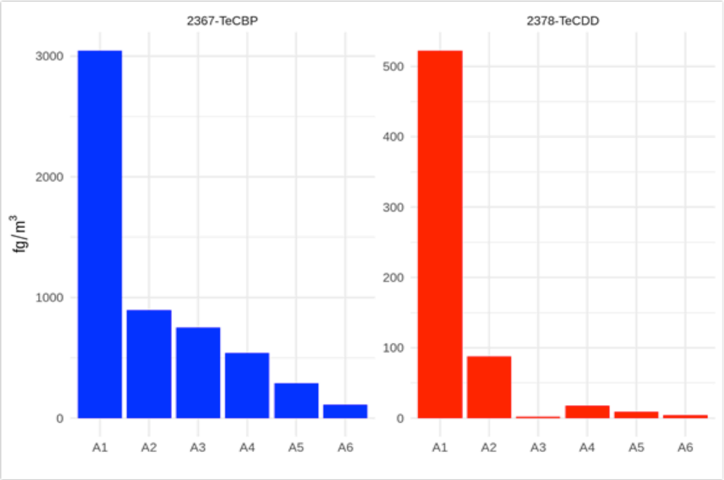

Figure 2. 2,3,6,7-TeCBP (blue columns) and 2,3,7,8-TCDD (red columns) concentrations expressed in fg/m^3 in the six different sites of area A immediately after the fire.

These findings are in agreement with previous reports concerning the formation of PCBPs, and they are of environmental importance given the toxicity of these analytes. As shown in the figure 2, at each site the concentrations measured for 2,3,6,7-TeCBP are significantly higher than the corresponding tetra-chlorinated dibenzo-p-dioxin, in some cases also more than two orders of magnitude. In detail, considering the first floor of the building, where the fire broke out, the 2,3,6,7-TeCBP levels at sites A1, A2 and A3 were respectively 3045.5 fg/m^3, 895.6 fg/m^3 and 753.0 fg/m^3 while the corresponding values of 2,3,7,8-TeCDD were 522.4 fg/m^3, 88.1 fg/m^3 and 2.2 fg/m^3, respectively. At the ground floor the concentrations of the analytes were significantly lower but still alarming. By analyzing the PUF and the filter collected by the high-volume sampler located outside (site A6) it is evident that the fire bring a significant impact to the surrounding atmosphere in terms of 2,3,6,7-TeCBP concentration (112.6 fg/m^3). The correspondent value of the tetra-chlorinated dibenzo-p-dioxin was pretty low and it is not matter of concern.

Further evidence for the significance of 2,3,6,7-TeCBP congener in the evaluation of the health effects correlated to these "advents of fire" are reported in figure 3 where a comparison among the fg TEQ/m^3 concentration of 2,3,6,7-TeCBP and the total fg TEQ/m^3 concentrations of PCDD/Fs and dioxin-like PCBs is showed. It is important to highlight that, despite the comparison was made between a single analyte (2,3,6,7-TeCBP, blue columns) and entire classes of analytes (PCDD/Fs, orange columns, and PCBs, green columns), the percentages of contribution of 2,3,6,7-TeCBP at the six sites is extremely relevant being respectively 26.6 at site A1, 28.0 at A2 site, 21.3 for A3, 39.4 for A4, 34.4 for A5 and 31.8 for A6.

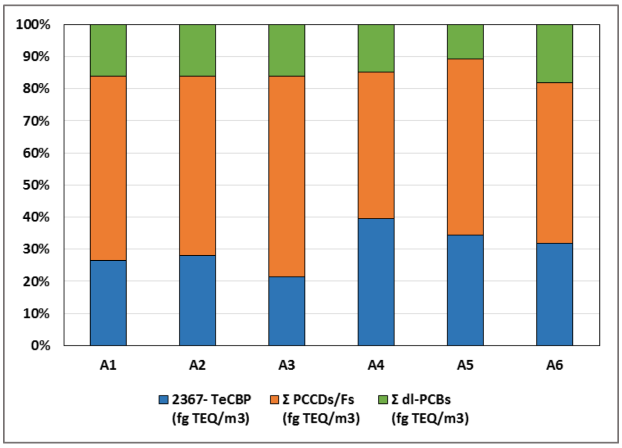

Figure 3. Percentage of contribution of 2,3,6,7-TeCBP (expressed in fg TEQ/m^3) respect to the total concentrations of PCDD/Fs and dioxin-like PCBs (fg TEQ/m^3).

Temporal trend of 2,3,6,7-TeCBP at sites A1and A2

In light of the alarming findings summarized in the previous section the level of 2,3,6,7-TeCBP at sites A1 and A2 has been monitored in order to define its time trend. To the authors' knowledge it is the first time that a similar investigation has been executed. The impossibility to make a comparison with literature, on the one hand, and the equitoxicity with 2,3,7,8-TeCDD (which has been widely studied) on the other hand, induced us to maintain the comparison between 2,3,6,7-TeCBP and 2,3,7,8-TeCDD also in this analysis of persistence. The temporal monitoring plan was set up on the basis of the results obtained at each timepoint and, consequently, it results in more frequent samplings in the very first period (during the two months after the fire, eight 3-days samplings were executed). The levels of the two analytes were monitored for two years until the tetrachloro-biphenylene was not detectable anymore. In figures 4 the temporal trends of 2,3,6,7-TeCBP (blue line) and 2,3,7,8-TeCDD (red line) at sites A1 and A2 are reported and it is evident that the analytes show the same evolution in time. However, it is important to observe that at both site A1 and site A2 temporal trends are represented with a double axes of concentration. This is also true for figure 2, consequently, despite showing the same trend, the compounds maintain a significant difference of concentration. The first month's campaigns reveal stable levels of both 2,3,6,7-TeCBP and 2,3,7,8-TeCDD at both sites. These results can be explained by considering the persistent nature of the two pollutants on one hand, and, on the other hand, the confinement of the building and the fact that any decontamination activities have yet to be executed at that point in time.

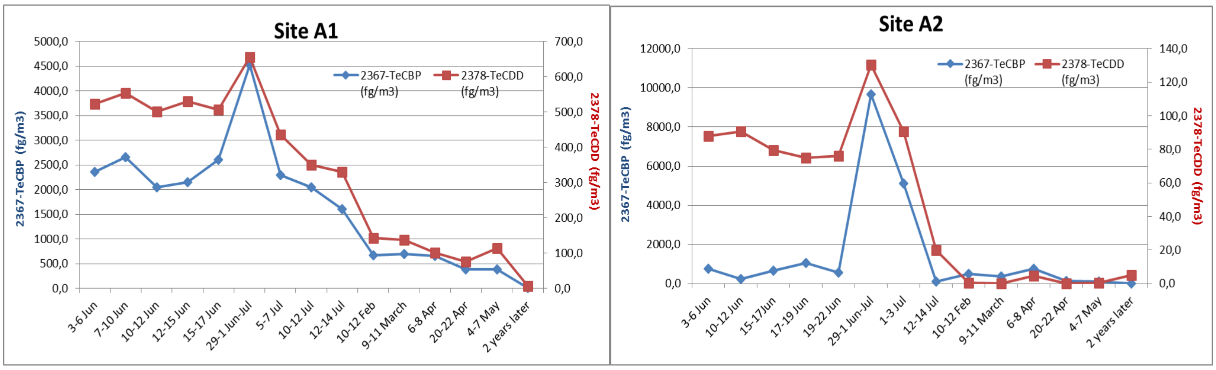

Figure 4. Temporal trend of 2,3,6,7 TeCBP (blue line) 2,3,7,8-TeCDD (red lines) and at sites A1and A2

In fact, the peaks of concentration of 2,3,6,7-TeCBP (respectively 4533.3 fg/m^3 at site A1 and 9661.9 fg/m^3 at A2) and 2,3,7,8-TeCDD (656.7 fg/m^3 and 130 fg/m^3) measured during the experimental campaign for 29th June -1st July are the results of the decontamination effort. In detail, the remedial measures were based on the removal of particulate and condensed matter on the surface of the entire building, which justifies the concentration peaks, and on a subsequent sealing of particularly exposed areas. Moreover, the air conditioning systems were completely substituted and temporary additional ventilation systems were used. These changes of air circulation could explain, also on the basis of the semi-volatile nature of the pollutants analyzed, the fact that immediately after these measures the highest values of 2,3,6,7-TeCBP and 2,3,7,8-TeCDD were revealed at the

A2 site. Despite this initial normal increase, the next experimental campaigns showed a progressive reduction at site A1, which was faster at A2, of the content of the monitored analytes, demonstrating the efficiency of the decontamination plan. The last decontamination effort was executed one year after the fire by removing the contaminated material which was then taken to a landfill as special waste. This operation corresponded to an increase of the concentration of the two analytes at both sites (6-8th April experimental campaign) and thereafter that the levels of the pollutants of interest steadily decreased.

Conclusion

The data collected in this study clearly show how 2,3,6,7-TeCBP plays a key role, on the basis of its acute toxicity, concentration and persistence, in the determination of the risk assessment correlated with cases of fire involving electrical systems. The comparison with 2,3,7,8-TeCDD levels further highlights the significance of 2,3,6,7-TeCBP: the most toxic dioxin represents only the 4-8% of the total content of PCCDs/Fs and, on the other hand, is about the 20% of the 2,3,6,7-TeCBP. Consequently, it is our opinion that the WHO should consider this persistant organic analyte to be investigated and monitored in case of fires.

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