Interference of past soil contaminations on the biomonitoring of PCB emissions from an RDF co-powered cement plant

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Abstract: Although the intentional production of polychlorinated biphenyls (PCBs) has totally been banned, these pollutants are still released into the atmosphere by industrial and domestic burning processes and volatilization from soils locally contaminated by PCB spill-overs. The present work aims at identifying the PCB sources in a mixed land use area of NE Italy around a cement plant co-powered with Recovered Derived Fuels (RDFs) from 2018. Leaves of *Robinia pseudoacacia* trees were systematically sampled over c. 40 km^2 in 37 sites and analysed for 12 dioxin-like and 20 non-dioxin-like congeners. The samples of most sampling sites had a PCB content <LOD whereas those with higher content were located in urban sites. The spatial distribution of PCB leaf content was not centred on the purported emission sources. The samples of three spatially unrelated sites had high content of 2, 12 and 18 PCB congeners, the last two in combinations fully compatible with past commercial mixtures traded under different names. Comparison of these results with those of previous (bio-)monitoring surveys supports the hypothesis that the area has been subjected to punctiform PCB spill-overs, which overwhelm the contribution from present day industrial emissions, comprised those actually derived from the use of RDFs.

Keywords: biomonitoring, black locust, persistent organic pollutants, soil pollution, polychlorinated biphenyls, recovered derived fuels.

1. Introduction

Recovered Derived Fuels (RDFs) largely consist of non-recyclable plastics (PVC excluded), paper cardboard, and other corrugated materials. Shredded into a uniform grain size, or also pelletized in order to produce a homogeneous material, RDFs can be burned for thermal recovery as a valid alternative to traditional fossil fuels, reducing landfill storage of non-recyclable plastics[1]. With respect to hydrocarbon fuels, RDFs have higher calorific value and release less greenhouse gasses and pollutants, e.g., heavy metals, SO_x, and NO_x[2]. RDFs are thus increasingly used in cement kilns, thermo-to-energy plants, blast furnaces and foundries[3]. However, in sub-optimal conditions (e.g., in oxygen-depleted conditions and low temperatures), RDF combustion can lead to the formation of multi-chlorinated benzenes, whose radical dimerization lead to an unintentional, *de novo* synthesis of polychlorinated biphenyls (PCBs) and other persistent organic pollutants (POPs), such as polychlorinated dibenzo dioxins/furans[4]. For this reason, specific directives (e.g. the European directive 2000/76/EC) have been issued at national and/or international level to regulate the combustion process of RDF containing halogenated compounds. Furthermore, industrial plants authorized to use RDFs are subjected to severe emission controls, typically more rigid that those applied before the transformation of the combustion chambers for RDFs use (see European directive 2010/75/EC).

The potential dispersion of PCBs and other POPs in the environment remains one of the main public concerns limiting the use of RDFs in several countries. This argument is often raised by Not-In-My-BackYard (NIMBY) opponents afraid for the possible health consequences at local level. PCBs may actually cause serious damage to human health and ecosystems[5]. In particular, the non-ortho and mono-ortho substituted dioxin-like PCBs (DL-PCBs) cause toxic effects in humans and animals, interacting with the intercellular aryl hydrocarbon receptor[6]. Furthermore, PCBs accumulate in the food-webs through biomagnification[7], being highly resistant to biodegradation[8].

In the past, due to their chemical stability, PCBs were widely and commonly used as dielectrics in capacitors, coolant fluids in transformers, flame-retardants in plastics, plasticizers in paints and

cement, and additives in paper-based products[9], reaching a total production of c. 1-1.5 million tonnes in c. 70 years[10] before being banned[11]. Unfortunately, still 14 million tonnes of PCBs-contaminated oil and equipment exist worldwide[12], and only a small fraction is properly disposed of and eventually processed for thermal destruction[13].

Soil PCB spill-overs – old or recent, criminal or accidental, totally unknown or (un)voluntarily neglected – may be important sources of contamination, the volatilization from locally contaminated soils being recognized as a primary source of PCBs in the atmosphere and water bodies[14]. These spill-over sources can overlap – and obscure – those related to the activity of waste incineration, cement production, and foundry processes, i.e. the recognised, post-ban, industrial sources of PCB release in the atmosphere[15].

The correct assessment of the overall PCB load in a territory and the identification of past vs. current PCB emission sources are of paramount importance for making the use of RDFs at industrial level a common practice, if not acceptable also for NIMBY opponents. This goal can be obtained by applying biomonitoring techniques based on a rigorous spatially-based sampling design and on the direct comparison between the PCB composition of the environmental samples and the current source(s). Among environmental matrix(es), plant materials are undoubtedly the most convenient since their commonness allows high sampling density without raising ethical concern[16]. Leaf sampling has frequently been applied for fast, efficient biomonitoring of PCBs at small and large scales[17]. In fact, the PCB leaf content is a good proxy of the time-integrated PCBs deposition occurred between foliation and leaf sampling[18], although in some herbaceous plants (maize, cabbages, and carrots[19]; squash[20]; sunflower[21]) there may be a significant uptake and transportation of PCBs, dependent on the specific properties of the compound. In woody plants, however, PCBs remain blocked in the wood and are not translocated to the leaves of, *e.g.*, hybrid poplars[22] and willows[23]: for this reason they can profitably be used for PCB biomonitoring because the PCB concentration of their leaves is strictly related to that of the surrounding atmosphere[18].

Robinia pseudoacacia L. (blak locust) is a tree very common in agricultural and urban-industrial

areas of all temperate Europe, and is recognized as an efficient biomonitor of airborne persistent pollutants. The leaves of *R. pseudoacacia* are rather thin (130-190 μm in average), lack hard, sclerenchymatous tissues[24], and thus the plant exposes a larger intercepting leaf surface per leaf mass unit with respect to other deciduous trees[25]. Furthermore, the leaves have a thick layer of epicuticular waxes[26], self-maintained till the end of summer[27], in which airborne lipophilic substances, PCB included, are accumulated efficiently[17,28].

The present work aims at using the leaves of *R. pseudoacacia* as a matrix for monitoring PCBs in a mixed land use area of NE Italy. Here a cement plant, operating since 1950, has been authorized to use RDFs as co-fuel from 2014, becoming fully operative after 2017. The cement plant is a known local source of PCBs, which are released in fully compliance[29] to the threshold values set by the integrated environmental authorization[30]; notwithstanding this, it has been at the centre of harsh debates with local NIMBY opponents. The work hypothesis is that if the PCB fingerprint in the leaf samples collected in the study area is heterogeneous and no spatial trend centred on the cement plant is discernible, old pollution events or sources different from the plant must critically be taken into account. The results will critically be compared with those of previous PCB monitoring surveys carried out in the same area from 2016 onward[29,31-33] (Supplementary Table S1). New and old data will thoroughly discussed, with special attention to the added value offered by a correct biomonitoring approach.

2. Results

2.1 PCB concentrations and fingerprints in R. pseudoacacia *leaf samples*

Sampling of *Robinia pseudoacacia* leaves was carried out in 37 sites according to a systematic sampling design described elsewhere[34-36] (Fig. 1). Overall, 18 out of the 37 leaf samples had a PCB content lower than the limit of detection (Table 1), 15 contained only one or two congeners below or equal to 4.6 ng g^{-1}, one contained two congeners equal to 8.40 ng g^{-1} (i.e. the third highest PCB content in the study area), while three samples, i.e. 4C, 1E and 4A, had a mixture of 3, 12 and 18

congeners, respectively (Fig. 2), with a total content of 4.69, 80.20, and 99.85 ng g^{-1} PCBs. DL-PCBs were detected in 14 samples, NDL-PCBs in 9 samples; they were co-occurring in 4 cases (Table 1; Fig. 2). The average of the concentration sums of DL-PCB (Σ_{12} DL-PCB) was three times higher than that of NDL-PCB (Σ_{20} DL-PCB) (Table 1). Overall, 49% and 43% of the analysed samples had a concentration sum of all PCBs (Σ_{32} PCB) lower than the limit of detection (LOD=0.6 ng g^{-1}) or comprised between the LOD and the average value observed in the study area (6.48 ng g^{-1}), respectively. Nevertheless, the PCB concentrations in the samples 1E, 4A and 5E strongly deviated not only from the average (Table 1), but also in the high content of Σ_{12} DL-PCB in the former two samples and Σ_{20} NDL-PCB in the latter (Table 1; Fig. 2). The PCB fingerprint of these three samples was different: samples 1E and 4A shared 11 PCB, but the former contained PCB-52 while the latter contained PCB-44, -126, -128, -146, -149, -151 and -156 (Fig. 2). The fingerprint of the sample 5E, instead, was characterized by PCB-170 and -183 (Fig. 2).

2.2 Influence of land use strata and distance from the potential emission sources

To localize the potential sources of PCB emissions in the study area the concentration sums of PCBs (i.e. Σ_{12} DL-PCB, Σ_{20} NDL-PCB and Σ_{32} PCBs) were first compared as a function of the site-specific dominant land use strata using a non-parametric ANOVA (Kruskall Wallis Test). Following the Corine land cover classification[37], 20 sampling sites belonged to the agricultural land use stratum, 9 to the urban stratum, 4 to the industrial stratum and 4 to the forest stratum. Among the four samples collected within the forest stratum (i.e. 1A, 1B, 1C and 1D), only that sampled in the immediate proximity of the urban centre of Maniago (site 1A; Fig. 1) had a detectable content of two DL-PCBs (PCB-105 and -126; Fig. 3). On the contrary, more than half of the samples collected in the sites classified as agricultural accumulated DL- and/or NDL-PCB in amounts similar or higher than those collected in the industrial ones (Fig. 3). The highest PCB contents were observed in the samples from the urban sites, with a median value of Σ_{12} DL-PCB, Σ_{20} NDL-PCB, and Σ_{32} PCB one order of magnitude higher than those observed in the industrial sites (Fig. 3). Interestingly,

the samples from urban areas differed also in the percentage of PCB homologous group, i.e., group of congeners with the same number of chlorine atoms. If most of the samples collected throughout the study area had 1 to 3 penta- and/or epta-chlorinated congeners, only those collected in the urban stratum contained also tri-, tetra- and hexa-PCBs (Fig. 3d).

No statistically significant linear relationship was found between the concentration PCB sums and the distance of the sampling sites from the major potential emission sources, i.e. the cement plant and the industrial park (Supplementary Table S2). This suggests that the activity of the two potential emission sources was unrelated to the distribution pattern of PCB in the study area. In support of this, the distribution maps of Σ_{12} DL-PCB, Σ_{20} NDL-PCB, and Σ_{32} PCB values had an undefined pattern characterized by three extremely localized hot spots, i.e. sites 1E, 4A and 5E (Fig. 4).

2.3. Fingerprint comparison

In order to give an origin of the peculiar PCB content observed at the hot spots, the relative percentage of PCB homologous groups in the leaf samples were compared with those of (*i*) the stack emission of the cement plant available for February, July and October 2018 and May 2019[29] (Supplementary Table S3) and (*ii*) 21 past commercial PCB mixtures[38,39] (the sample 5E, having only two congeners, was excluded).

The leaf samples strongly differed from the stack emissions in terms of relative percentage of tri-, tetra-, penta-, hexa- and epta-chlorinated biphenyls. In particular, leaf samples had similar content of tetra-, penta- and hexa-chlorinated biphenyls, which were absent in the stack emissions of e.g. July 2018 (i.e. before the leaf sampling); the latter, on the contrary, were characterized by penta-chlorinated PCBs, absent in the leaf samples (Fig. 5a).

The comparison with the relative percentage of PCB homologous group of the 21 past commercial PCB mixtures was carried out through hierarchical clustering. The results (Fig. 5b) indicated that the relative percentage of PCB homologous groups in the leaf samples from sites 1E e 4A is very similar and, most importantly, highly compatible with PCB mixtures produced in the past, namely

Arochlor 1254 (U.S.A.), Sovol (former U.S.S.R.) and Kanechlor 500 (Japan).

3. Discussion

Robinia pseudoacacia has frequently been used in bioremediation processes of PCBs-contaminated soils[40] due to its nitrogen-fixing bacterioid symbionts, and as bioaccumulator of airborne trace elements[25,41] and PAHs[17]. To the best of our knowledge, this is the first study to use the leaves of *R. pseudoacacia* as a matrix for monitoring PCBs. Therefore, it is difficult to correctly evaluate the magnitude of the observed PCB concentration values from an environmental point of view. The comparison with data derived from other plants that will be given herein is merely indicative, because the composition of the epicuticular layer is species-specific[28], each plant has a different leaf-air partition coefficient for gaseous PCBs and thus accumulate airborne PCB differently[42]. As a first approximation, however, the range of the PCB content measured in this study is lower than those reported in other surveys based on deciduous and coniferous species sampled in close proximity to relevant PCB emissions sources such as electronic-waste incinerators[43], densely inhabited areas with industrial plants[44], and PCB contaminated soils[45]. It is similar to that observed in samples of deciduous plants collected in agricultural fields exposed to the emission of an electronic waste incinerator[46], or in evergreen plants from areas with contaminated streams[47] or hosting industrial plants[48]. Lower values are reported only for plant samples intended for human consumption[49] or collected in remote areas[50] (Supplementary Fig. S1).

Usually, in presence of an important pollutant source, an evident distribution pattern, compatible with wind regimes, geomorphology and chimney height, should be expected[51]. In this study, on the contrary, no evident trend emerged either from the analysis of the PCBs distribution maps (Fig. 4), or from the regression analysis between concentration values and distance of the sampling sites from the two purported sources, i.e. the cement plant and the industrial park (Supplementary Table S2). Only the land-use based comparison revealed that the environmental availability of NDL- and DL-PCB was significantly higher in urban sites rather than in agricultural or industrial ones (Fig.

3). Similar patterns were already observed in other PCB biomonitoring surveys carried out in China[44], France[52], and Poland[53], with pine needles as biological matrix. High PCB content in urban leaf samples has frequently been attributed to off-gassing from PCB-treated construction materials in old buildings, and leakage from closed systems such as old electrical equipment (e.g. capacitors and transformers that still contain large quantities of PCB fluids)[9]. However, a further important source of PCBs at local level might be the burning of old wood floors and furniture, with their PCBs-containing finishes, de-dusting agents, paints, and waterproofing compounds. This is reinforced by the fact that in the study area wood burning is a common practice for domestic heating, and causes an important local enrichment in e.g. 4-ring PAHs[34].

The aberrant, high concentration values observed in three sites only, i.e. 1E, 4A and 5E (Fig. 4), cannot be referred to any clear distribution pattern. These three sites were characterized by a peculiar PCB composition with respect to the other 34 sampling sites (Fig. 5a). The leaf PCB fingerprint from sites 1E and 4A was remarkably different from that of the cement plant stack emissions recorded immediately before leaf sampling (July 2018; Fig. 5a). A critical re-appraisal of the site cards, which were carefully compiled during the sampling, did not reveal any evident environmental anomaly and/or the presence of combustion activity linked to domestic heating. Thus, the most probable explanation is a very localized soil contamination, caused by a past release of PCBs or of PCBs-enriched materials. This hypothesis needs validation by direct assays of soil samples, but it is fully supported by the peculiar congener composition of the samples 1E and 4A, which is fully congruent with that of some commercial PCB mixtures. Notwithstanding their different trade names, these mixtures had very similar compositions[54] and were widely used in products distributed also in the Italian market[55].

The direct terrigenous contamination of the samples 1E and 4A must be excluded, because all the leaf samples processed in this study had been rinsed in distilled water before chemical analyses (see Sect. 5.2), specifically to remove the fraction of particulate matter deposited on the external leaf surface[56]. Since in trees PCBs are not translocated to the leaves[22,23], the PCB enrichment of samples

1E and 4A might be the direct consequence of the volatilization of the PCBs present in the upper soil layers, and absorbed by the leaves of the surrounding vegetation. Interestingly, this accumulation mechanism was demonstrated in azalea (*Rhododendron* sp.) potted plants exposed in mesocosms containing PCB contaminated soil[57].

Also previous (bio-)monitoring surveys (Supplementary Table S1) committed by a local organization of NIMBY opponents or, in response to them, by the regional environmental protection agency (ARPA-FVG), had pinpointed single hot spots of PCB contamination in the study area, referred to the use of RDF as co-fuel in the cement plant (the NIMBY ones) or by unknown sources (the ARPA-FVG ones). The analysed matrices were the most diverse: hen fat tissues[31], chicken eggs and hen fodder[33], soil[32], and air particulate matter[29]. Each survey adopted a different sampling strategy, with different numbers of sampling sites, possibly chosen for the availability of the selected matrix, and unfortunately never resampled from one study to the other. Interestingly, all the surveys based on animal and plant samples pinpointed single hot spots of PCB contamination, whose spatial distribution differed from study to study and was never constant in terms of PCB composition, and never fully compatible with the industrial processes known from the area. This contamination heterogeneity might depend on very localised past PCB spill-overs, caused by the aleatory dispersal of PCB-containing materials, occurred independently several times in different places. In fact, if leaves may accumulate soil PCBs through their volatilization (see above), the high PCB content observed in hens bred in open field conditions might derive from the ingestion of soil and soil organisms, such as worms and slugs[58], living in or nearby a contaminated site. Notoriously, PCBs can persist for many decades in the environment[8], are easily retained within the organism and are subjected to important biomagnification processes. Besides, humans have generally too a short memory to remember what occurred in a site only a few decades ago.

4. Conclusions

The use of *Robinia pseudoacacia* leaves allowed to monitor the distribution of airborne PCBs with

high spatial resolution in an area characterized by mixed land use. Thanks to the adoption of a systematic sampling design with high sampling density it was possible to trace back the differences in the PCB leaf content to the land use strata and exclude their spatial relationship with the geographical position of the main potential emission sources, i.e. the cement plant and the industrial park. The hierarchical clustering carried out on the PCB homologous group measured in the leaf samples and those of former commercial PCB mixtures supported the hypothesis that the unusual high PCB concentration values of three hot-spots derive from volatilization of occasional PCB spill-overs, excluding the present use of RDF as co-fuel in the cement plant.

5. Materials and methods

5.1 Study area

The study area (Fig. 1) is located at the foot of the Carnic Pre-Alps (NE Italy) and extends over 40 km^2 in the typical mixed land use of N Italy, where natural, agricultural, and urban-industrial land uses are strongly intermingled[34]. The main potential pollution sources are: i) an isolated medium-sized cement plant (clinker production 556,000 ton $year^{-1}$)[34], powered by petroleum coke and RDF[29]; ii) a large industrial park consisting of two steel works, several knife manufacturing factories and a chemical plant producing pesticides; iii) vehicular traffic, which is concentrated in the town of Maniago (c. 10,000 inhabitants), in the three municipalities of Fanna, Cavasso Nuovo and Arba, and along the national road which crosses the northern portion of the study area (Fig. 1). In the past, the cement plant also used alternative co-fuels, such as industrial and sewage sludge; bottom ash, slug and boiler dusts from industrial combustion process are used as raw materials. In the cement production process linings and refractories from non-metallurgical processes, clay, marl and carbonate rocks are processed. Stack emissions (summarized in Supplementary Table S3) are routinely checked by the local environmental protection agency and the company owing the cement plant.

5.2 Plant material sampling

Samples were collected on August 18th, 2018. Overall, 34 sampling sites were selected at the knots of a 700 m step grid and 3 further ones in the nearby centres of Arba, Cavasso and Maniago (Fig. 1). At each site, 10 to 20 leaves were sampled at 4-6 m above the ground from the canopies of three mature *R. pseudoacacia* trees, at a minimum distance of 20 m from linear and point emission sources (e.g. busy roads and house chimneys). Sampled leaves were stored in paper bags and immediately transported to the laboratory. The leaflets of each sample (10-12 g fresh weight) were excised from the rachis, washed in distilled water and then dried at 50 °C for 24 hours[59]. In this way, possible sample contamination derived from particulate matter on leaves surfaces was minimized. Afterwards, the samples were ground with a planetary mill equipped with zirconium oxide spheres and jars, cleaned with 20 mL of an acetone aqueous solution (1:1; v/v) after each grinding cycle. The pulverized samples were transferred to pre-labelled glass jars and kept at 4 °C until chemical analyses.

5.3 Chemical analyses

Chemical analyses were carried out following the EPA protocols 3546 e 8270. Briefly, 2 g of each sample were dispersed in 10 mL of an acetone/hexane mixture (1:1; v/v) which was heated at 140 °C for 15 min in a MAE microwave system (Ethos-TC, Milestone). The extracts were concentrated in hexane under nitrogen flow to a final volume of 2 mL. Extract purification was carried out through solid phase extraction using SPE LC-NH2 Supelco tube enriched with 100 mg of anhydrous sodium sulphate and 100 mg of Florisil®. Before adding the extract, the tubes were treated with 6 mL of dichloromethane and 3 mL of hexane. Afterwards, the extract was added and the tube wall was rinsed with 0.5 mL of hexane. The tube containing the extract was eluted twice using 2 mL of hexane/dichloromethane mixture (65:35; v/v). The eluate was recovered and concentrated under nitrogen flow. PCBs concentration was measured by injecting 0.5 mL of the concentrated eluate in a gas chromatographer equipped with a RXI-17SIL-MS Restek column and

coupled to a mass spectrometrer (Bruker, TQ300). Overall, the content of 12 dioxin-like (77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189) and 20 non-dioxin-like (18, 28+31, 44, 52, 95, 99, 101, 110, 128, 138, 146,149, 151, 153, 170, 177, 180, 183, 187 e 194) PCB congeners were measured with a limit of detection (LOD) of 0.6 µg kg^{-1} with the only exception of the congeners 28 and 31 whose sum (PCB-28+31) was measured with a LOD of 0.8 µg kg^{-1}. For the calibration of the GC-MS six working standard solutions were prepared at six concentrations from 1 to 200 µg L^{-1} diluting an inhouse primary standard of the congener 209 with a concentration of 100 µg L^{-1}.

Data availability

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

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Authors' contributions

L. F.: data curation; formal analysis; investigation; methodology; resources; software; visualization; writing - original draft. M. T.: conceptualization; funding acquisition; investigation; methodology; project administration; supervision; validation; writing - original draft, review & editing.

Additional Information

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Figure captions

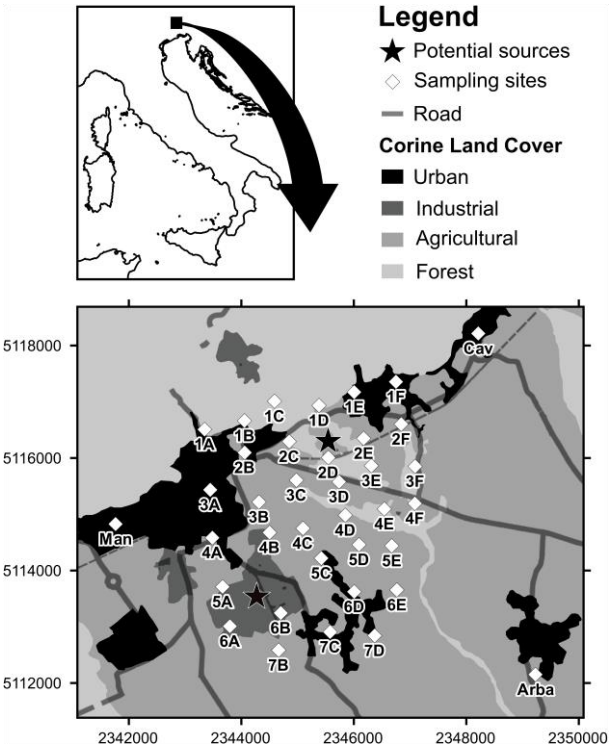

Fig. 1 Geographical localization of the study area with the 37 sampling sites (◇). Black stars near to sites 2D and 5A indicate the cement-plant and the industrial park, respectively.

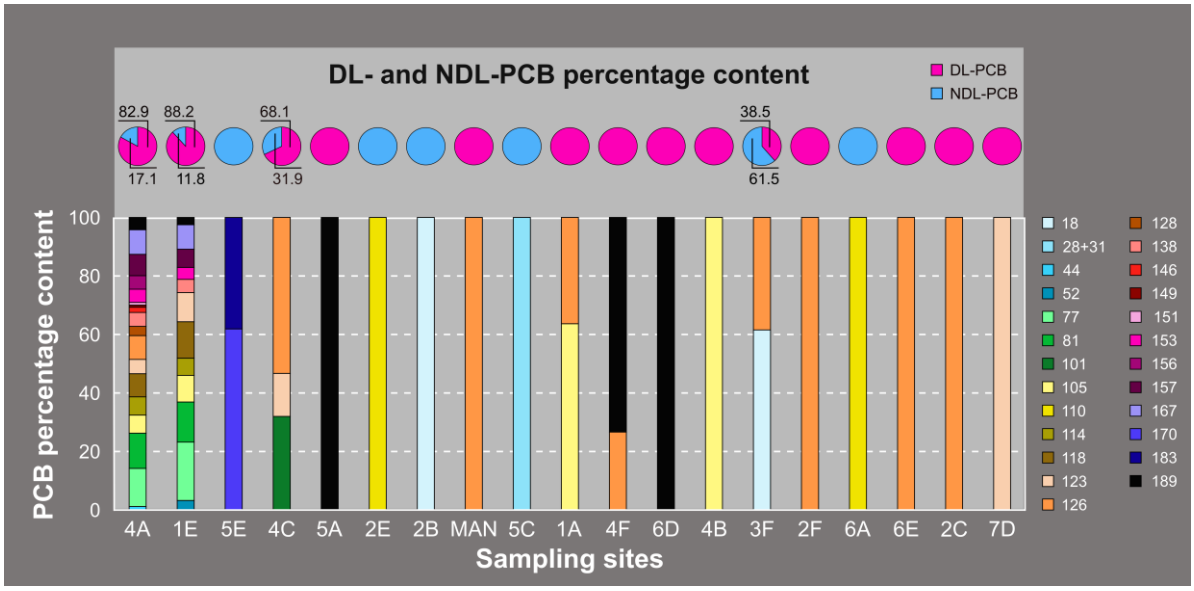

Fig. 2 Percentage content of PCB congeners measured in the 19 *Robinia pseudoacacia* leaf samples collected in the 32 sampling sites of Fig. 1 with PCB content > LOD. The samples are sorted along the abscissa in descending order according to the total content of all 32 PCBs. The upper circular graphs show the percentage content of dioxin-like (DL) and non-dioxin-like (NDL) PCBs.

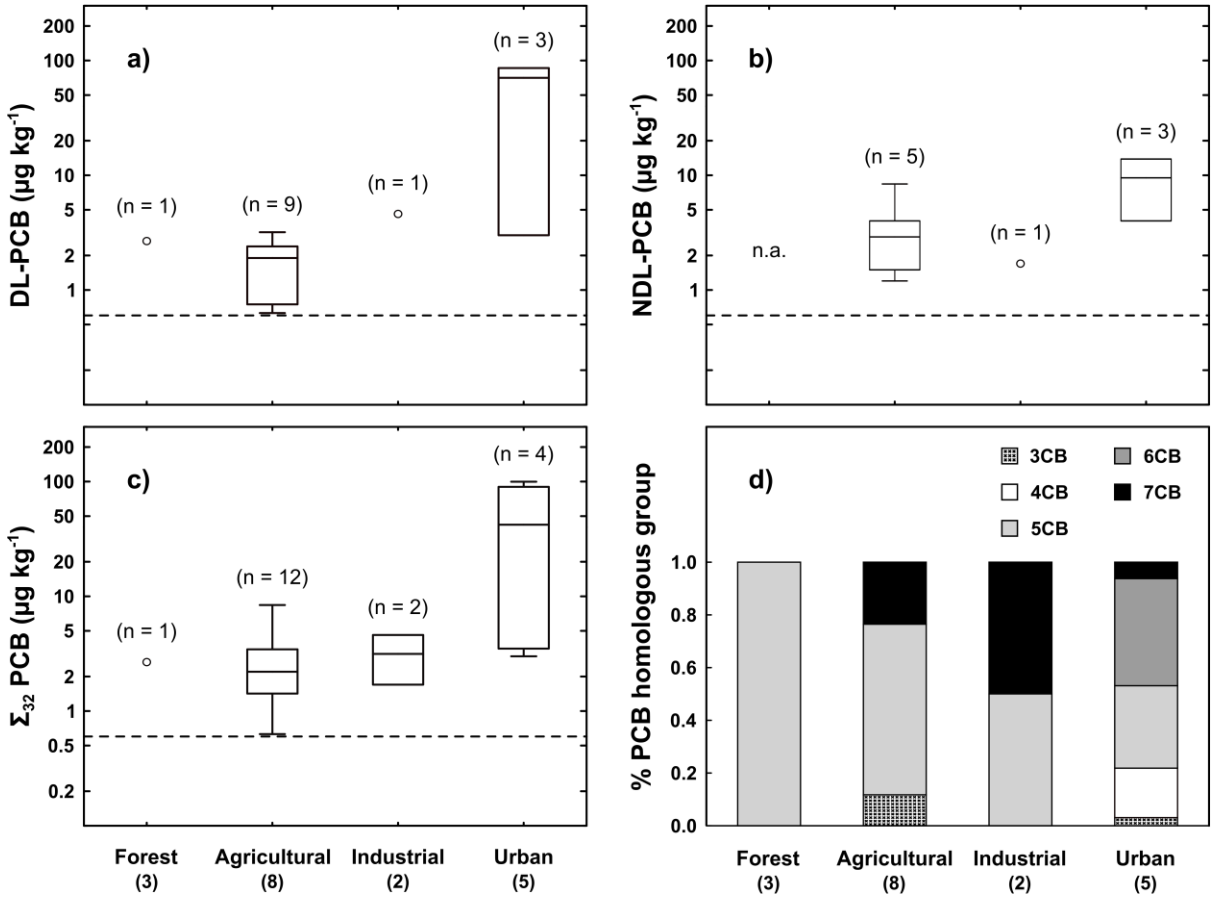

Fig. 3 Statistical comparison (Kruskal-Wallis Test) among the concentration sums of the 12 dioxin-like ($\sum_{12}$ DL-PCB) (a), 20 non-dioxin-like ($\sum_{20}$ NDL-PCB) (b), and all 32 PCB congeners ($\sum_{32}$ PCB) (c) measured in *Robinia pseudoacacia* leaf samples collected in forest, agricultural, industrial and urban strata of the study area of Fig. 1; the analysis was based on the 19 samples with PCB content > LOD (black dotted line). The average of the percentage of PCB homologous groups calculated for leaf samples collected in the strata is given in (d). The numbers in brackets below the labels of the x-axis corresponds to the samples with PCB content < LOD.

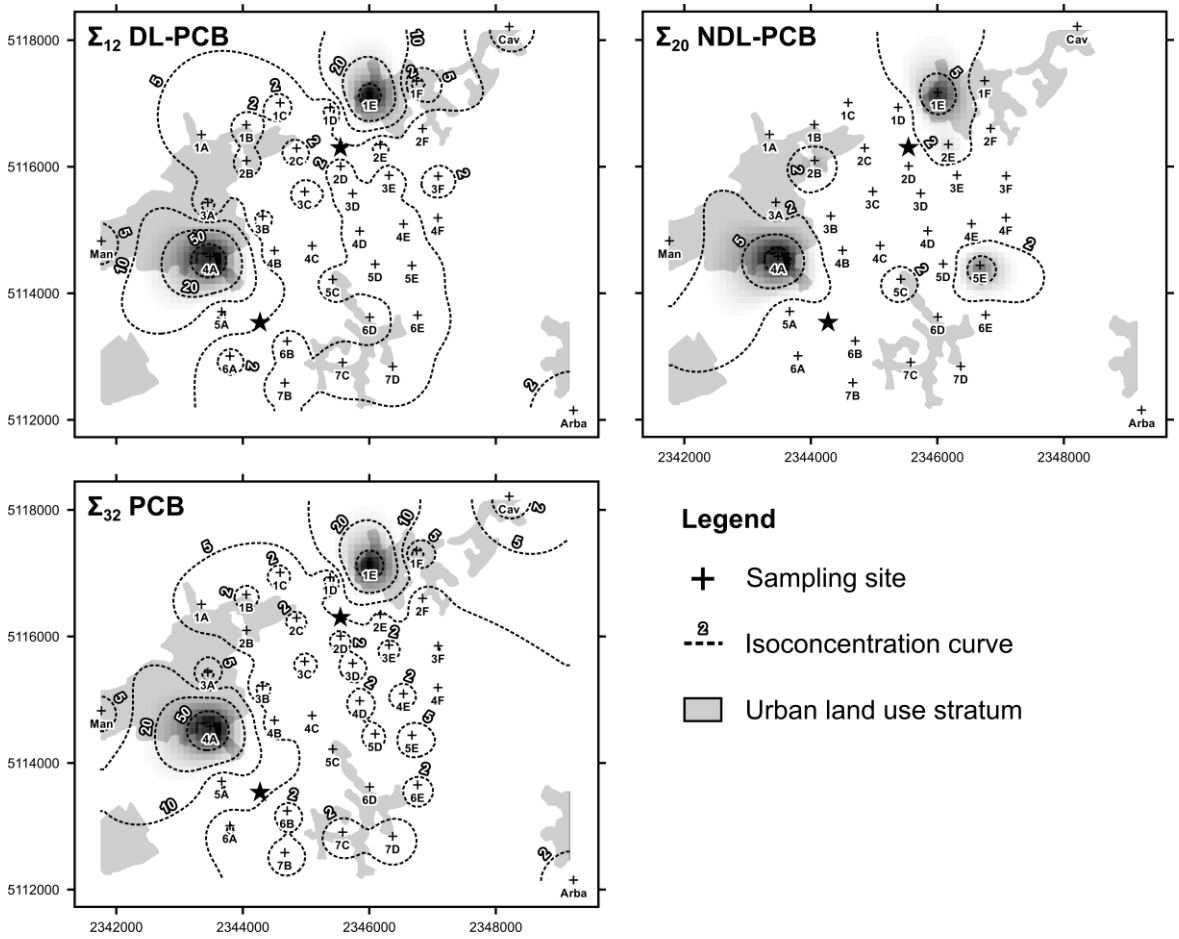

Fig. 4 Distribution pattern of the concentration sums of the 12 dioxin-like (Σ_{12} DL-PCB), 20 non-dioxin-like (Σ_{20} NDL-PCB), and all 32 PCB congeners (Σ_{32} PCB) measured in the *Robinia pseudoacacia* leaf samples of Fig. 1. For a list of measured PCBs, see the text.

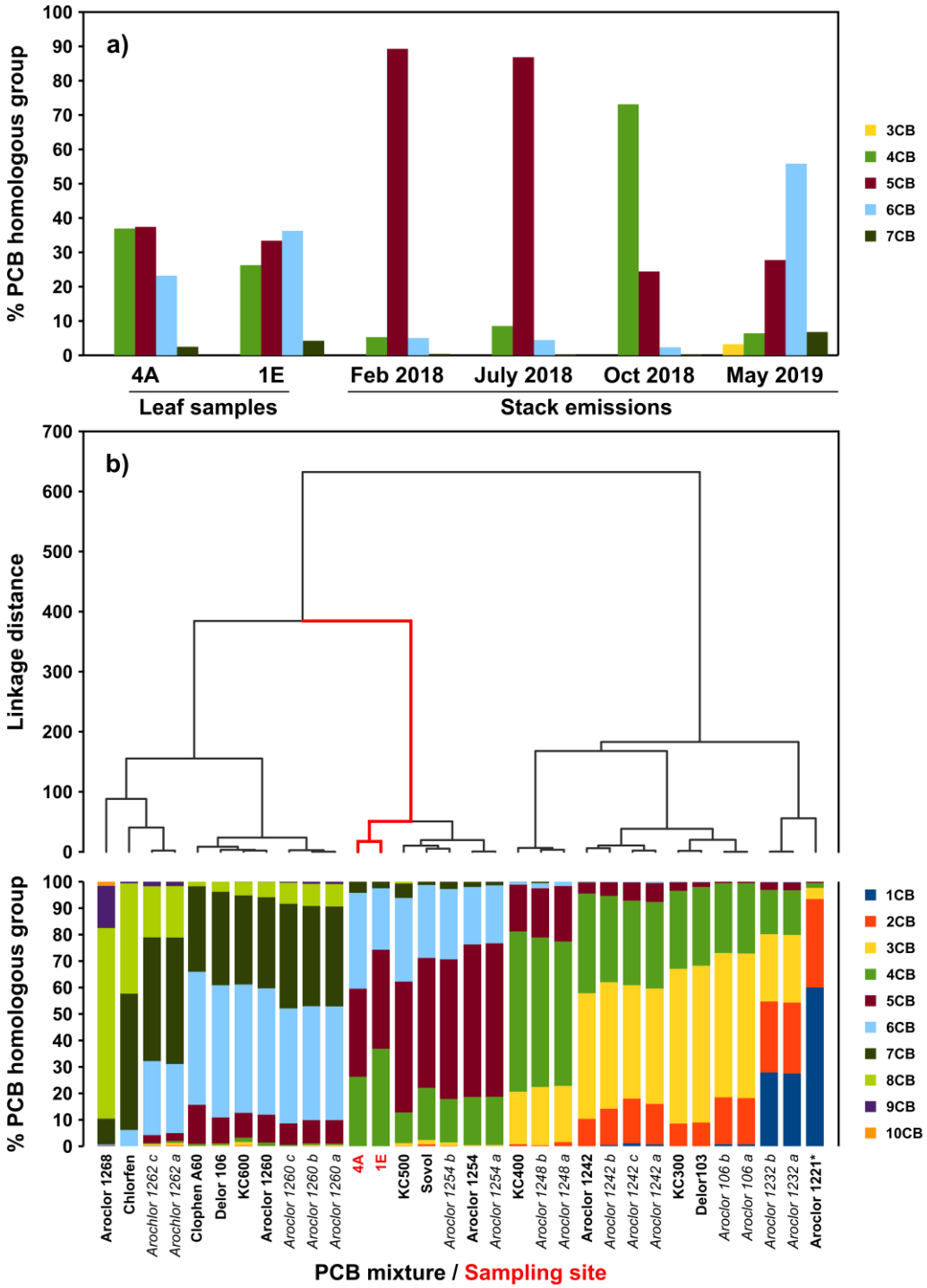

Fig. 5 Percentage of PCB homologous group (3CB-7CB) in leaf samples from sites 4A and 1E and in the stack emission of the cement plant in four periods [data from ARPA (2019b)] (a), and results of the hierarchical clustering (b), carried out on the percentage of PCB homologous groups (1CB-10CB) calculated for the same leaf samples and selected PCBs mixtures commercialized in the past. The lower histogram represents the percentage of PCB homologous groups (1CB-10CB) [data form Frame et al. (1996) (labels in italics) and Wyrzykowska et al. (2006)].

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Tables

Tab. 1: concentration sums of the 12 dioxin-like (Σ_{12} DL-PCB), 20 non-dioxin-like (Σ_{20} NDL-PCB), and all 32 PCB congeners (Σ_{32} PCB) calculated for the *Robinia pseudoacacia* leaf samples collected in the 37 sampling sites of Fig. 1. n PCBs: number of PCBs detected in each sample; LOD: limit of detection. Note that samples were sorted in descending order depending on the Σ_{32} PCB values.

Sampling site	n PCBs	$\sum_{12}$ DL-PCB	$\sum_{20}$ NDL-PCB	$\sum_{32}$ PCB
4A	18	86.00	13.85	99.85
1E	12	70.70	9.50	80.20
5E	2	*<LOD*	8.40	8.40
4C	3	3.19	1.50	4.69
5A	1	4.60	*<LOD*	4.60
2B	1	*<LOD*	4.00	4.00
2E	1	*<LOD*	4.00	4.00
MAN	1	3.00	*<LOD*	3.00
5C	1	*<LOD*	2.90	2.90
1A	2	2.67	*<LOD*	2.67
4F	2	2.59	*<LOD*	2.59
6D	1	2.40	*<LOD*	2.40
4B	1	2.00	*<LOD*	2.00
3F	2	0.75	1.20	1.95
2F	1	1.90	*<LOD*	1.90
6A	1	*<LOD*	1.70	1.70
6E	1	0.94	*<LOD*	0.94
2C	1	0.71	*<LOD*	0.71
7D	1	0.63	*<LOD*	0.63
1B	0	*<LOD*	*<LOD*	*<LOD*
1C	0	*<LOD*	*<LOD*	*<LOD*
1D	0	*<LOD*	*<LOD*	*<LOD*
1F	0	*<LOD*	*<LOD*	*<LOD*
2D	0	*<LOD*	*<LOD*	*<LOD*
3A	0	*<LOD*	*<LOD*	*<LOD*
3B	0	*<LOD*	*<LOD*	*<LOD*
3C	0	*<LOD*	*<LOD*	*<LOD*
3D	0	*<LOD*	*<LOD*	*<LOD*
3E	0	*<LOD*	*<LOD*	*<LOD*
4D	0	*<LOD*	*<LOD*	*<LOD*
4E	0	*<LOD*	*<LOD*	*<LOD*
5D	0	*<LOD*	*<LOD*	*<LOD*
6B	0	*<LOD*	*<LOD*	*<LOD*
7B	0	*<LOD*	*<LOD*	*<LOD*
7C	0	*<LOD*	*<LOD*	*<LOD*
Arba	0	*<LOD*	*<LOD*	*<LOD*
CAV	0	*<LOD*	*<LOD*	*<LOD*
Average		**5.29**	**1.73**	**6.48**
Minimum		**0.60**	**0.60**	**0.60**
Maximum		**86.00**	**13.85**	**99.85**