COMBINED APPROACHES TO ASSESS THE IMPACT OF A FIREWOOD ON THE ENVIRONMENTAL CONTAMINATION IN PCDD/F AND PCB

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Introduction

Fires might be the source of persistent organic pollutant (POP) such as dioxins, furans (PCDD/F) and/or polychlorobiphenyls (PCBs) in the environment. Once emitted, these molecules tend to accumulate in the food chain and are subject to long-range transport[1]. In addition, they are toxic to Humans at very low concentrations[2]. Because of these characteristics, the impacts of such an acute event might have significant consequences in terms of Human chronic exposures and should therefore be thoroughly assessed. A pre-requisite for such an exposure assessment is to delineate the extension of the environmental impact. In particular, one crucial question is what the contribution of the event to the environmental background of contaminants is. Recently, different methods including isotopic, chemical or statistical methods have been developed to discriminate environmental samples according to their congener distribution profiles or chemical properties, such as chirality. However in the context of an accidental event such as a fire, the initial characteristics of the sources are not known and these methods have to be completed by other approaches such as modeling or experimental characterization of the emission. In this case, a combination of different investigation levels, ranging from the laboratory to field scale experiments seems to be necessary. An illustration of such approach is given here to delineate the environmental impacts of firewood that took place between August and December 2008, on a former pyralene-transformers disposal site in the area of Saint-Etienne (Loire, France). The fire led to the combustion of an estimated volume of 25 000 m^3 of wood stocked over soils potentially contaminated with PCBs. Firewood is known to generate atmospheric pollutants among which are CO, CO_2, polycyclic aromatic hydrocarbons (PAH) and persistent organic pollutants such as PCDD/F and PCBs[3]. In addition, at the site in question, PCBs were also probably emitted through the heating of the underlying contaminated soils due to the volatility of these molecules[4]. However, in terms of signature and identification of legal responsibilities, a single focus on the soil concentrations of the contaminants is not sufficient to trace the impact of firewood in the environment, as soils integrate deposits of POPs from several diffuse sources. Moreover, a dilution of the contamination within the soil profile might occur due to anthropic activities (ploughing, etc…). In this case, a specific tracer of the event should be identified. A better insight into PCDD/F and PCB emission should be carried out through a combination of complementary field, laboratory and modeling efforts[1]. The objective of this work was to illustrate such an approach to show how appropriate modeling, field and experimental investigations can be useful to identify a tracer of PCDD/F and PCB contamination and, consequently, the extension of the contamination.

Materials and methods

The impact of the firewood was assessed using field surveys, modeling and laboratory experiments.

Fire impact modeling

The general methodology was based on an empirical description of the fire by the rescue team following their intervention. The volume of the initial wood stock was estimated around 25 000 m^3. To facilitate fire extinction, the stock was divided in two piles by the firemen. Volumes and heights of each pile were estimated. All over the fire, three states were described: intense, moderate and smoldering. For each of these steps, temperatures were empirically assigned.

On site soils and lichens survey

The model allowed for designing the soil and bioindicators (lichen) sampling strategy. 32 soils were sampled within a radius of 5 km from the burnt down parcel. Soil sampling was conducted on the surface soils (0-5 cm) using a shavel. Lichens (*Xanthoria parietina*) naturally developed on the site were sampled in addition to the soils. The sampling method consists of collecting lichens that were naturally developed on the site according to a transept, in agreement with the major wind directions. Nine zones were selected and the distance of each zone from the plot that burnt down is given below within a 10 km radius from the burn down parcel. For each zone, a composite sample of lichen was combined.

Combustion experiments

In addition to the field work, combustion of wood was done in combustion chambers allowing for determination of emission factor for PCB-I, PCB-dl and PCDD/F from wood was sampled from the test site and dried at 20°C for 24 hours. The combustion experiments were carried out in an 80 m^3 open-chamber. The burnt material was placed on a balance and loss of weight was measured throughout the experiment. Continuous sampling of the emissions of PCDD/F and PCBs was possible via an extractive tube placed just above the combustion area. The extraction flow rate was set at 2700 Nm3 h^{-1} leading to an hourly air-renewal value of 33.8. The oxygen concentration in the smokes was very close to the O_2 concentration in the air showing that the simulated fire was equivalent to an outdoor fire. A blank was carried out prior to any combustion experiments. Two materials were burnt: 20 kg of wood (modality 1) and a mix of 2 kg of wood and contaminated soils sampled on the burnt down parcel (modality two). From the measurement of PCDD/F and PCB concentrations in the air, emission factors were calculated as the air: wood concentration ratio of each pollutant.

Analysis of PCDD/F and PCB-I and PCB-dl

Analysis of PCDD/F and PCB-dl were done using a gas chromatography / high resolution mass spectrometry (GC/HRMS) technique. Analyses were carried out by CARSO (Lyon, France). The quality control was insured by the accreditation process for this laboratory regarding the analysis of PCDD/F and PCB in soils, lichens and in air samples. Results are expressed both for each congener and in toxic equivalent factor (I-TEQ) or total concentration of the congeners.

Statistical analysis

The correlation matrix of the chemical concentrations in soil samples was determined using the R statistical environment. Soil samples were ordered by hierarchical clustering according to the concentrations of PCB, PCDD and PCDF. Hierarchical clustering was performed using the complete-linkage Euclidean distance metrics after log-transformation of the concentrations values. The concentrations in PCDD/F and PCB of each area were scaled (i.e. dividing by standard deviation) to prevent a "size" effect between soil samples (row normalization). Consequently, the hierarchical clustering analysis was only based on the pattern of chemicals measured in soil samples from the different areas (concentration did not impact the classification). Clusters are defined by cutting branches of the dendrogram at a threshold height equal to 2.

Results and discussion

Modeling

The geographic extension of the possible impact of the fire as modeled by ADMS 4 was modeled (PM 10) over the 3 months of the fire. The maximal impact was obtained along an axial transept of 7 km from the site in the NW/SE direction that matches to the major wind direction.

Soil survey

On the burnt down plot, the soil PCDD/F concentrations varied between 980 and 7 000 ng I-TEQ kg-1. To our knowledge, these concentrations are among the highest ever published in the literature concerning the soil matrix in France or across Europe[5,6]. The pattern of soil PCDD/F concentration was a significant decrease with increasing distance from the burning place. Compared to the reference background value of 4.7 ng ITEQ kg^{-1} in soils from equivalent areas[4], the soil concentrations were largely higher within 500 m from the burnt down plot and decreased to be of the same order of magnitude beyond 2 km than the background value. The hierarchical clustering of the values shows that the soil samples can be gathered according to the distance to the burnt down plot. In this case, the clusters were spatially structured. Similarly to PCDD/F, concentrations of PCB-dl and PCB-I on the burnt down plot are extremely high, ranging between 356 ng I-TEQ kg^{-1} and 5200 ng I-TEQ kg^{-1} for PCB-dl and 3 mg kg^{-1} and 158 mg kg^{-1} for PCB-I. A concentration of 0.05 mg kg^{-1} might be used as an indicative background concentration for PCB-I[7]. Soil concentrations measured in this case largely exceeded this background value for the soils sampled at a distance of less than 500 m from the burnt down plot. The concentrations measured beyond 500 m dramatically decreased to values of the same order of magnitude as the suggested background concentration. For PCB-dl, the UK Environment Agency (2008) published a survey that allows for a calculation of an indicative background concentration of 0.9 ng ITEQ kg^{-1} for surface soils. If compared to this value, very high concentrations are measured on the burnt down plot in this study. Concentrations in soils sampled within a 1 km radius from the burnt down plot still elevated beyond, the background level defined by the UK Environment Agency. Contrary to the PCDD/F concentrations and even if a general decrease of PCB concentrations is observed with the distance from the burnt down plot, the clusters were not spatially structured.

Lichen survey

In lichens, the overall pattern of PCDD/F and PCB concentrations decreased with an increasing distance from the burnt down plot. The PCDD/F concentrations in lichens varied between 2.2 ng I-TEQ kg^{-1} and 230 g I-TEQ kg^{-1}, with the concentration of PCB-dl ranging between 0.5 ng I-TEQ kg^{-1} and 60 ng I-TEQ kg^{-1} and PCB-I between 2 000 ng kg $^{-1}$ to 173 000 ng kg $^{-1}$. These measures confirm the impact of the firewood on the atmospheric contamination and have to be linked to the results mentioned above on the soil samples. The concentrations of PCB and PCDD/F beyond 2 km do not continue to decrease, suggesting that the background level was reached at this marker. The results obtained from lichen analysis confirm the relatively recent contamination of the atmosphere from a point located on the burnt down plot and that was mostly noticeable within 2 km of this source point. For PCB and PCDD/F, the pattern of the concentration follows that of the soil contamination, supporting the hypothesis of an atmospheric origin to the soil contamination. At this stage, further evidence that the PCDD/F and PCB were emitted during the fire is needed as atmospheric contamination could be linked to other sources, from either local or long-range events for molecules such as PCB.

Experimental combustion

From the combustion experiments, the emission of PCDD/F is almost similar for the two modalities, being 1 µg ITEQ kg^{-1} for modality 1 (wood only) and 1.6 µg ITEQ kg^{-1} for modality 2 (mix between wood and contaminated soil). Whatever the modality, furans dominate the distribution of PCDD/F in the smokes. This suggests than furans might be considered as a potential tracer of the emissions from the combustion that occurred on the plot. For PCBs, the emission factor of PCB-I is 5667 µg kg^{-1} for modality 2, and equal to 2612 µg kg^{-1} for the first modality. Again, these results suggest that the emission of PCB is enhanced when contaminated soils burn confirming that the PCB-contaminated soils are an additional source of PCB emission into the atmosphere.

General discussion

Furans appear as a potential tracer for the combustion that took place on the burned plot. These categories of PCDD/F have already been shown to be characteristic of low temperature wood combustion process. If the above hypothesis concerning the impact of the fire of the contamination of the soils and lichens are verified, then furans could be a common tracer of combustion.

Indeed, within the 1 km radius zone, the furans dominate the overall PCDD/F distribution profiles (between 95 % and 54 %). Beyond this radius, dioxins dominate the overall PCDD/F distribution profile (between 50% and 75%). On the burnt down plot, a noticeable low contribution from heptachlorodibenzodioxin (HpCDD) and octachlorodibenzodioxin (OCDD) (Figure 1) can be seen, whereas the literature shows a higher contribution of these two heavy dioxins congeners appear in soils[4].

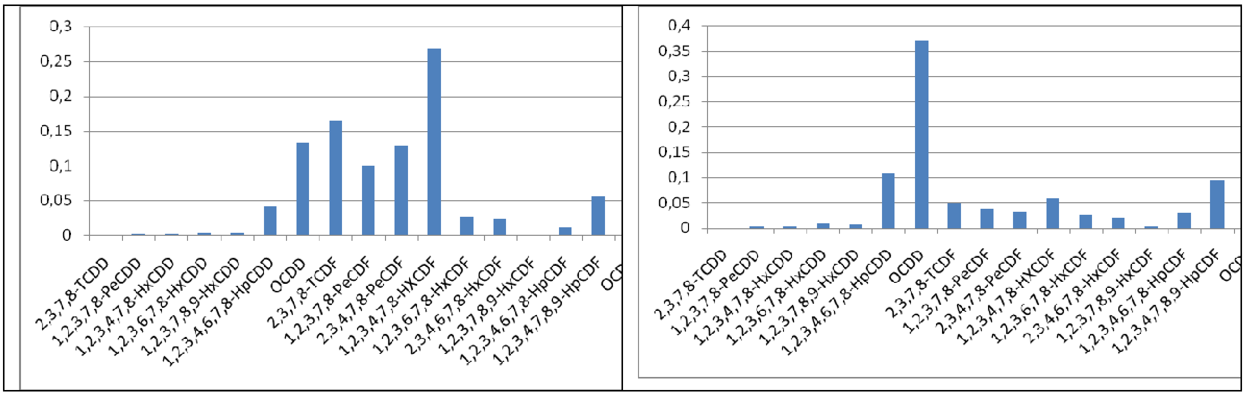

Figure 1 : Distribution profile of PCDD/F on different areas (burnt plot on the left and beyond 2 km on the right)

The contribution of these congeners increases with distance from the burnt down plot where they reach similar congener distribution profiles to those described in the literature. The same analysis in the lichens shows a dominant contribution from the furans within the 2 km radius zone (between 34 and 80% of the PCDD/F distribution). For the PCBs, no distinct difference could be seen in terms of profile distribution among the different samples. All of these observations on soil PCDD/F concentrations, related to the furan/dioxin ratio and compared to the examination of the total concentration of these molecules allow for the identification of three groups: the massively impacted soils directly affected by the fire, the soils between 1 and 2 km, which appear to be slightly impacted and the soils over 2 km from which both the total concentrations are close to the local background level and the congeners distribution profiles similar to the background pattern. For PCDD/F, the identification of a specific tracer, i.e. predominance of the furans, allows verification that the impact of the fire is limited to a 2 km radius and that within this zone, the PCDD/F were mostly emitted by the fire. For the PCB, the total concentrations and their comparison to the background allowed for delineation of the empirical impact of the fire. However, it was not possible to identify a specific tracer for these compounds. Thus the distance over which the fire had no impact in terms of PCB contamination could not be addressed precisely.

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