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Tracking the Spatial Fate of PCDD/F Emissions from a Cement Plant by Using Lichens as Environmental Biomonitors

Sofia Augusto,[†,⊥] Pedro Pinho,[†,‡] Artur Santos,[†] Maria João Botelho,[§] José Palma-Oliveira,[∥] and Cristina Branquinho*[,†]

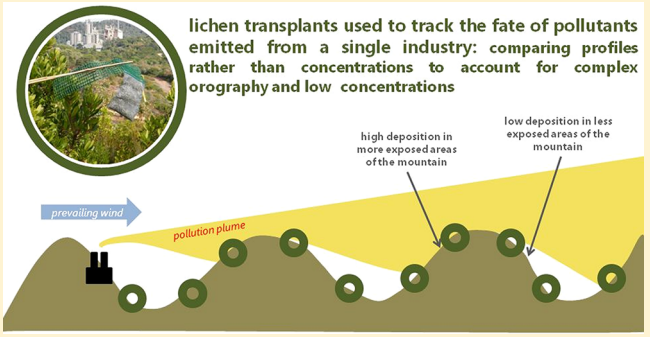
[†]cE3c, Centre for Ecology, Evolution and Environmental Changes, Faculdade de Ciências, Universidade de Lisboa, FCUL, Campo Grande, Bloco C2, Piso 5, 1749-016 Lisboa, Portugal

[‡]Centro de Recursos Naturais e Ambiente, Instituto Superior Técnico, Universidade de Lisboa (CERENA-IST-UL), Lisboa, 1649-004 Portugal

[§]Secil Companhia Geral de Cal e Cimento, Lisboa, 1600-079 Portugal

[∥]Faculdade de Psicologia, Universidade de Lisboa, Alameda da Universidade, Lisboa, 1649-013 Portugal

ABSTRACT: In an area with multiple sources of air pollution, it is difficult to evaluate the spatial impact of a minor source. Here, we describe the use of lichens to track minor sources of air pollution. The method was tested by transplanting lichens from a background area to the vicinity of a cement manufacturing plant that uses alternative fuel and is located in a Natural Park in an area surrounded by other important sources of pollution. After 7 months of exposure, the lichens were collected and analyzed for 17 PCDD/F congeners. The PCDD/F profiles of the exposed lichens were dominated by TCDF (50%) and OCDD (38%), which matched the profile of the emissions from the cement plant. The similarity in the profiles was greatest for lichens located northeast of the plant (i.e., in the direction of the prevailing winds during the study period), allowing us to evaluate the spatial impact of this source. The best match was found for sites located on the tops of mountains whose slopes faced the cement plant. Some of the sites with highest influence of the cement plant were the ones with the highest concentrations, whereas others were not. Thus, our newly developed lichen-based method provides a tool for tracking the spatial fate of industrially emitted PCDD/Fs regardless of their concentrations. The results showed that the method can be used to validate deposition models for PCDD/F industrial emissions in sites with several sources and characterized by complex orography.



1. INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/Fs) are a group of persistent, semivolatile and toxic organic pollutants that enter the environment from various combustion sources.[1,2] Although >200 congeners of PCDD/Fs have been described, only 17 (those with chlorine atoms at positions 2, 3, 7, and 8) are known to be toxic.[3] Because of the toxicity of PCDD/Fs and their persistence in the environment, European regulations and international treaties require that industries monitor their PCDD/F emissions and conduct environmental-impact assessment studies.[4−7]

However, in areas with multiple pollution sources, distinguishing the contribution of a given industry to the overall atmospheric deposition of PCDD/Fs is challenging, particularly when the source is a minor one. First, atmospheric deposition is fed not only by industrial sources but also by urban and natural (such as forest fires) sources. The latter are not monitored regularly, are difficult to control, and have yet to be regulated. Second, accurate monitoring of the atmospheric deposition of PCDD/Fs over large areas at high spatial resolution requires the installation of expensive equipment at numerous sites, which is not feasible from a financial standpoint.

As an alternative, dispersion models have been developed that predict the sites of environmental deposition of pollutants emitted by a given source. The accuracy of these predictions is increased by taking into account factors such as wind direction and intensity as well as the local orography. In recent years, the models have also included meteorological data. For example, AERMOD uses mesometeorological data provided by TAPM (The Air Pollution Model; CSIRO Atmospheric Research) to overcome the lack of detailed information on wind and local meteorological conditions. Because these models depend on modeled meteorological data, they need to be validated by deposition data, especially in areas with a complex orography

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and local winds. Moreover, deposition models rely solely on data from known pollution sources and therefore underestimate the contributions of unknown and unexpected sources as well as historical air pollution hot spots, where the soil is still contaminated and acts as a source of atmospheric deposition, through resuspended particles.

Deposition data may be obtained from several sources, ranging from air and soil to the local biota.[8] Air is usually monitored at air-quality monitoring stations using active samplers that collect the particulate and gas phase of air, in which PCDD/F concentrations are measured. However, as noted above, these stations are expensive to establish and maintain, such that it is not possible to install a sufficient number to obtain the desired spatial resolution. Also, in most installed stations, only the particulate phase of air is sampled, whereas the gas phase is neglected.[9] Passive air samplers have been used worldwide to measure atmospheric pollutants, including PCDD/Fs.[10] They can be placed in the field at as many sites as needed, do not require an energy supply, and can be exposed for longer periods than active samplers. These devices preferentially capture compounds present in the gas phase of air and thus underestimate environmental pollutant concentrations.[10]

Soil samples are also used to validate PCDD/F deposition models; however, PCDD/F concentrations in soils exhibit a high spatial variability because they are strongly influenced by the type of soil, its organic content, and land-use. Moreover, soils are sinks for PCDD/Fs, which remain adhered to the organic fraction of soil and thus reflect a historical contamination. Consequently, they do not provide a clear picture of the recent atmospheric deposition of PCDD/Fs.[11]

Biota samples, such as vegetation (pine needles, herbs, etc.), have also been used to determine PCDD/F deposition.[12−14] However, this approach is also problematic for the following reasons. First, the surfaces of plants are coated by a thin hydrophobic lipid layer, the cuticle (composed of biopolymers and cuticular waxes), which protects the plant and provides a waterproof coating that prevents water loss from its epidermal cells. Due to its lipophilic nature, the cuticle takes up PCDD/Fs, but it also act as a barrier to their internal penetration.[15] PCDD/Fs retained in the cuticle are likely to undergo photodegradation and revolatilization into the atmosphere, such that it is difficult to establish linear relationships with atmospheric concentrations. Second, because the growth rate of plants strongly varies, the concentration of PCDD/Fs will vary accordingly. For example, during the growing season, the growth rate of herbs increases, thus diluting PCDD/Fs within their tissues.[14]

In attempts to overcome these disadvantages, experiments on the suitability of lichens (symbioses of fungi and algae or cyanobacteria) to monitor the atmospheric deposition of PCDD/Fs were initiated in 2004.[16,17] Lichens are long-living, slow growing organisms.[18,19] Because they have neither roots nor a cuticle, their sole means of acquiring nutrients is through atmospheric deposition (either of nutrients or pollutants); they are therefore very efficient in intercepting pollutants from the atmosphere. In addition, their morphology remains constant throughout the year, such that they can be collected during any season; they are also widely distributed over the planet in biomes of almost every type.[20]

Recent studies have reported that lichens intercept and accumulate persistent organic pollutants present in the gas and particulate phases of air.[21−24] For example, polycyclic aromatic hydrocarbon (PAH) concentrations in the particulate phase (measured using active samplers) were shown to be significantly related to the concentrations in lichens collected in situ.[21,24] Significant relationships were also found for PAHs in the gas phase (measured using PASs) and in lichen transplants exposed for 2 months at the same locations.[22] PAHs are semivolatile organic compounds that share many characteristics with PCDD/Fs. By intercepting pollutants in both the gas and the particulate phase of air, lichens are a suitable biomonitor with which to complement data from active or passive air samplers and from other monitoring methods. The technique of transplanting lichens from a control area to another area can be used to pinpointing sources of pollution and to track temporal trends in pollutant uptake by lichens in the surroundings of pollution sources.[25] It is especially useful to assess pollution spatial impacts in areas where in situ lichens are absent. For example, a general decline in metal levels in lichens with increasing distances from the source has been reported.[25] In contrast, in situ lichens are long-living organisms surviving for decades, and together with their long-term pollution accumulation capacity, they are able to "store", for long periods of time, toxic elements in their thallus. Concentrations of pollutants measured in in situ lichens cannot be directly compared with the ones measured in transplanted lichens because the latter are exposed for a short period of time (months), and in situ lichens are usually exposed for years (long-term accumulators). Short-term transplants are expected to have lower pollutant concentrations than in situ lichens. Lichen transplants not only allow monitoring over precise time intervals but also avoid any substrate influence.[26]

Unlike standard physical methods, transplants are extremely cheap and simple to prepare, set up, and subsequently analyze. These advantages, together with the independence from an electrical power supply, allows their use in large numbers over wide geographical areas. Moreover, transplants are inconspicuous, require no maintenance during the exposure period and no protection from accidental damage or from weather.[26]

PCDD/F congener profiles (i.e. the relative contribution of each PCDD/F congener to the total concentration (as a percent)) have been used as signatures of specific emission sources[27] as different emission sources release PCDD/F congeners in different proportions.[28] However, other studies demonstrated the potential inaccuracy of relating a specific profile to a specific emission source.[29−31] Ames et al. (2012), in their analysis of >150 emission samples taken from different kilns of the same cement plant, concluded that different profiles were associated with different kilns, even those burning the same fuel.[29] Thus, to track the environmental fate of industrial PCDD/F, we first must determine the specific PCDD/F profile associated with each emission source within the same industry.[29−31] This is particularly important in areas with different sources of air pollution and if the pollutant of interest is a minor one.

Despite the features that recommend the use of lichens as PCDD/F biomonitors, there are no published studies comparing the PCDD/F profile of lichens with those measured in industrial emissions. Thus, the aims of the study described herein were: (i) to devise a method using PCDD/F profile variations in lichens to track the spatial fate of air pollution from a minor source within an area with multiple sources of air pollution and (ii) to confirm that the PCDD/F profiles in lichens reflect those of industrial emissions (in this case, from a cement plant).

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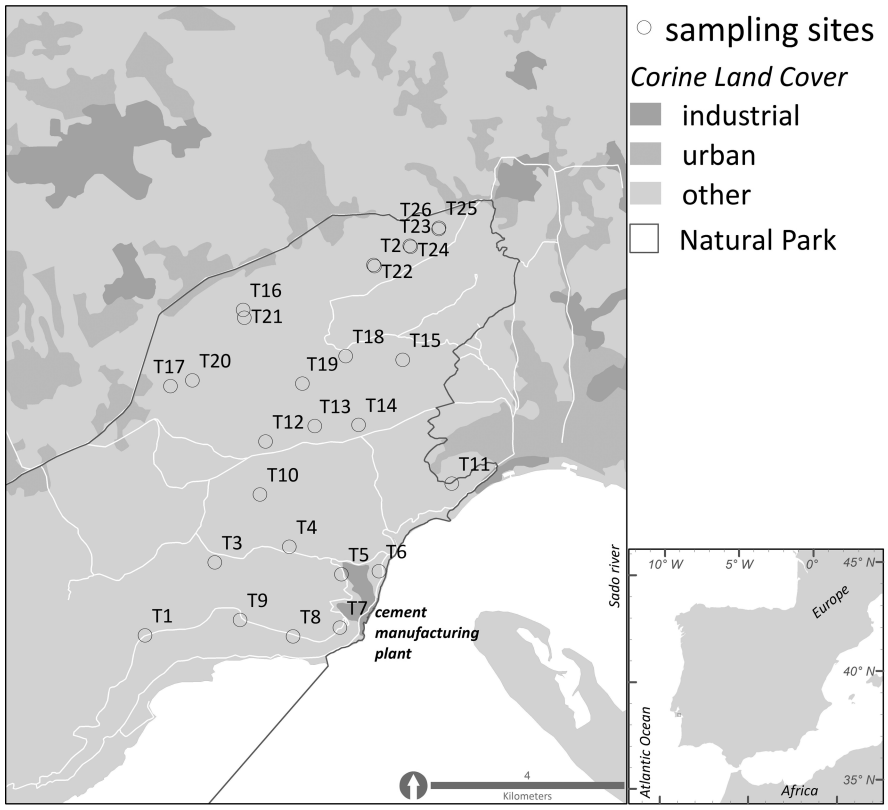

Figure 1. Location of the sampling sites in the study area. Lichen transplants were exposed for 7 months (n = 26) in locations in the vicinity of the cement manufacturing plant. Corine: the European Union's Coordination of Information on the Environment program.

2. EXPERIMENTAL SECTION

2.1. Study Area. The study was conducted in Portugal in an area of approximately 60 km^2 and located in the vicinity of a cement manufacturing plant that coincinerates hazardous waste using alternative fuel (Figure 1). The plant is located in Serra da Arrábida Natural Park, which covers 108 km^2 and is one of 30 areas under protection by the Portuguese government.[32]

2.2. Lichen Transplants. Lichens of the species *Ramalina canariensis* Steiner were collected in September 2012 in Comporta (~6 km south of the cement manufacturing plant), where previous studies conducted in the same region reported the lowest levels of pollutants (metals and PCDD/Fs).[16,17,25,33] This area faces the Atlantic Ocean and thus receives inputs of fresh air; industrial and urban pollution sources are absent. Healthy *R. canariensis* thalli 2−4 cm long were collected from pine trees (*Pinus* sp.) and transplanted within 48 h to 26 sites covering the entire study area (Figure 1).

The lichen transplants (~10 g each) were placed in 15 cm × 20 cm nylon bags and suspended from 1 m long wooden sticks. At each sampling site, the sticks were tied to available substrates (bushes, poles, and trees), avoiding placing them underneath a canopy and ensuring that they were >1.5 m above the ground.

After 7 months of exposure, the transplants were collected, stored in thermal boxes, and transported to the laboratory, where unwashed samples were immediately dried at room temperature and sorted to remove extraneous material. The exposure period was selected on the basis of previous experiments performed in our study area. These showed that 2 months was not long enough for the lichens to become enriched in PCDD/Fs (enrichments ~10%) close to the emission source, whereas after 12 months of exposure, they were enriched by >40%.[34] On the basis of this information, we determined that the exposure period selected for the current study was 7 months.

All samples (transplants after exposure and control samples) were then analyzed for PCDD/Fs.

2.3. Industrial Emissions. Data on the PCDD/F emissions of the cement manufacturing plant were obtained from published records.[29] During the 7 month lichen-exposure period, only one kiln (kiln 9) was in operation at the cement plant. Previous studies in which PCDD/F emissions from kiln 9 were analyzed over 6 years, from 2002 to 2008 and totaling 87 individual stack test runs, reported a consistent PCDD/F congener profile over time, independent of the fuel and waste used (a mixture of primary, special, and hazardous waste fuels).[29] This average profile was thus used for further comparisons with the lichen transplants.

Kiln 9 is a rotary kiln, 5.25 m in diameter and 83 m long. It is fitted with a preheating tower with four levels of cyclones and nine Unax coolers, has a nominal clinker production capacity of 3500 tons per day, and uses GRECO-type burners. Downstream from the preheater tower, kiln 9 uses an in-line extra air calciner for the initial decarbonization step (conversion of $CaCO_3$ into CaO). The primary fuel used to fire the kiln is petroleum coke. Special supplemental fuels include wood, animal meal, refuse-derived fuel, auto-shredder fluff, and tires. An additional special supplemental fuel is refinery distillation ends, which potentially contain toxic metals such as cadmium, mercury, and lead as well as toxic and environmentally persistent organic compounds. In Portugal, it is therefore designated as hazardous waste. Alternative fuels account for ~41% of the energy content. To ensure that the kiln meets the exhaust-gas concentration limits specified in European Union

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(EU) Directive 2010/75/EU,[6] the Secil Outão facilities have electrostatic precipitators and a baghouse collector that operate in series.

2.4. Analytical Procedure. PCDD/F analyses were carried out by a certified laboratory, Eurofins GfA Lab Service GmbH (Germany), which is accredited for determining dioxins (PCDDs) and furans (PCDFs) in plant matrices in accordance with DIN EN ISO/IEC 17025:2005. PCDD/F analyses in lichens followed the Internal Standard GLS DF 100, HRMS. The analytical steps were as follows: sample preparation (homogenization), addition of internal $^{13}C_{12}$-labeled PCDD/F standards of all PCDD/F components to be determined, extraction in Soxhlet, cleanup of the extract using column chromatography, analysis by means of high-resolution mass spectrometry (HRGC/HRMS), and quantification of the native PCDD/Fs via the internal $^{13}C_{12}$-labeled standards (isotope dilution method). A capillary gas chromatograph (HRGC, HP 5890) equipped with a PTV injector and connected to a high-resolution mass spectrometer (HRMS, VG-AutoSpec) was used. A HRMS tuning was performed to adjust the instrumental performance (at least once per analysis day, including mass axis calibration, adjustment of mass resolution, and sensitivity). All analyses were performed at a mass resolution of minimum 10000 @5% peak height. The instrument sensitivity was checked by means of native PCDD/F standards. A mixture of 16 $^{13}C_{12}$-labeled standards and of the 17 native standards was always injected to determine the relative retention times and the relative response factors for identification and quantification. During sample analysis, the stability of the mass focus was assured by means of perfluorokerosene lock masses. A total of 17 toxic PCDD/Fs (those with Cl at positions 2, 3, 7, and 8) were quantified in each sample. Compounds that were not detected (ND) were assumed to have a concentration equal to zero for data analysis only. Detection and quantification limits varied between 0.09 ng/kg (for TCDD) and 5.85 ng/kg (for OCDD) (see Table 1).

2.6. Data Analysis. During exposure, lichens will accumulate or lose pollutants according to the new local surrounding environment and will eventually reach equilibrium with the new atmospheric pollutant concentrations and microclimatic conditions after a certain period of time.

Enrichments (accumulations) in the ∑17PCDD/Fs and in each of the 17 congeners in each of the 26 sampling sites were calculated by subtracting the concentrations measured in the control lichens (before exposure) from those measured in the transplanted exposed lichens. The difference was defined as the amount accumulated by the lichens over the 7-month exposure period. These values for accumulation (enrichment) were used to determine their PCDD/F profiles.

An average PCDD/F profile, showing the relative contribution of each congener to ∑17PCDD/Fs, was established for the exposed lichens and compared with the PCDD/F profile reported for the cement-plant emissions.

To identify the sites best reflecting PCDD/F emissions from the cement plant, we compared the PCDD/F emission profile with the profiles obtained in the lichens after the 7-month exposure period. A cluster analysis was performed with Statistica using the profiles obtained from lichens exposed at each of the 26 sampling sites and the profile reported for the cement-plant emissions. A Euclidian distance was used. Cluster analysis calculates the distance between samples, taking into consideration the profile values: samples (sites) with a more similar profile are given smaller distance values between them, while sites with the most dissimilar profiles are given high distances. In this work, we were interested in the distances reported between the profile reported for the cement-plant emissions and each of the profiles obtained in each sampling site. Thus, after the analysis, these distances between the PCDD/F profiles of lichens exposed at each sampling site and the PCDD/F emissions profile were used in mapping. Mapping was done by interpolating the distances values using ordinary kriging after variogram analysis and modeling in GeoMS.[35] The variogram (500 m steps) was isotropic (i.e., without a preferential direction) and had a strong spatial structure, with a 0% nugget-to-sill ratio and a 2000 m range. It was then fitted with a spherical model, which fit well to the data. The model was then used to interpolate the distance to the emission data with ordinary kriging. Analyses and mapping were done with Statistica,[36] ArcGis,[37] and GeoMS[38] software.

Table 1. Concentrations (ng/kg) of Each of the 17 PCDD/Fs and of the ∑17PCDD/Fs [ng/kg and ng I-Toxic Equivalents (TEQ)/kg] Measured in the Control and Transplanted Lichens after 7 Months of Exposure[a]

	LOD/LOQ	control (n = 1)	transplants (n = 26)			
	(ng/kg)	(ng/kg)	mean	SD	min	max
2,3,7,8-tetraCDD	0.09	0.23	0.29	0.09	0.17	0.53
1,2,3,7,8-pentaCDD	0.25	1.01	1.13	0.20	0.72	1.54
1,2,3,4,7,8-hexaCDD	0.38	0.66	0.68	0.12	0.50	0.88
1,2,3,6,7,8-hexaCDD	0.90	1.42	1.33	0.24	0.94	1.81
1,2,3,7,8,9-hexaCDD	0.49	0.78	0.76	0.16	0.50	1.09
1,2,3,4,6,7,8-heptaCDD	0.50	5.92	4.82	0.89	3.52	6.72
octaCDD	5.85	10.20	9.50	2.26	6.11	17.10
2,3,7,8-tetraCDF	0.50	2.59	3.79	0.84	2.35	5.80
1,2,3,7,8-pentaCDF	0.50	3.10	3.41	0.66	2.16	5.09
2,3,4,7,8-pentaCDF	0.50	3.34	4.13	0.79	2.49	6.13
1,2,3,4,7,8-hexaCDF	0.50	3.73	3.27	0.64	2.26	4.72
1,2,3,6,7,8-hexaCDF	0.50	3.55	3.19	0.58	2.23	4.57
1,2,3,7,8,9-hexaCDF	0.88	<LOD	<LOD	n.a.	<LOD	<LOD
2,3,4,6,7,8-hexaCDF	0.50	2.32	2.29	0.43	1.65	3.38
1,2,3,4,6,7,8-heptaCDF	0.50	7.08	5.23	0.97	4.03	7.84
1,2,3,4,7,8,9-heptaCDF	0.17	0.43	0.39	0.09	0.23	0.70
octaCDF	0.82	1.49	1.39	0.23	1.04	2.08
Σ 17 PCDD/Fs (ng/kg)		47.85	45.59	7.71	34.83	64.08
Σ 17 PCDD/Fs (ng I-TEQ/kg)		4.21	4.73	0.88	3.03	6.95

[a]SD: standard deviation; min: minimum; max: maximum; <LOD: below the limit of detection; n.a: not applicable. LOD and LOQ are also displayed for each compound.

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3. RESULTS AND DISCUSSION

PCDD/F Concentrations in Transplanted Lichens. The lichens used in this study were transplanted from a control site (located in the Atlantic Coast) to 26 sites in the vicinity of a cement manufacturing plant that coincinerated alternative fuels to track pollution from this source. The cement plant is located in a natural park in an area surrounded by other, quantitatively more important sources of air pollution, such as the ones emitted by important and densely populated areas. For instance, the city of Setúbal is located less than 10 Km to the east of the cement plant; the urban-industrial areas of Barreiro and Montijo are located 20 km to the north of the study areas.

The descriptive statistics of the PCDD/F concentrations obtained in the control and in the transplanted lichens after 7 months of exposure in the study area are displayed in Table 1.

The ∑17 PCDD/F concentrations in the transplanted lichens varied between 34.83 and 64.08 ng/kg; the average concentration was 45.59 ng/kg (Table 1). With the exception of 1,2,3,7,8,9-HxCDF, all of the congeners were present in detectable concentrations in the lichen samples. Both concentration enrichments (accumulation in the lichen transplants after exposure) of the ∑17PCDDFs and of each congener were determined on the basis of comparisons with the pre-exposed control lichens (Table 1 and Figures 2 and 3). These enrichments are associated with the sources of pollution in the new location.

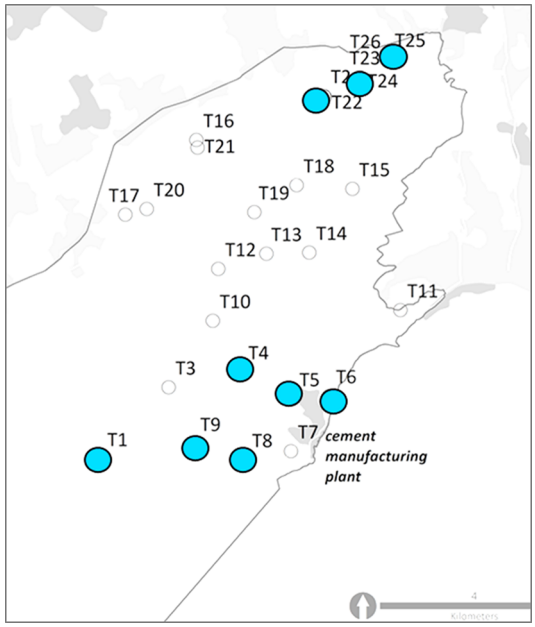

Figure 2. Sites with enrichment of the concentration of ∑17PCDD/Fs (ng/kg) in transplanted lichens after 7 months of exposure, as determined in comparisons with control lichens, in relation to the location of the cement manufacturing plant.

Figure 2 shows the location of the sites where lichen transplants become enriched for the ∑17PCDD/Fs. Enrichment occurred at sampling sites 1, 2, 4, 5, 6, 8, 9, 22, and 23; five were located <2 km from the cement plant (Figure 2). In the remaining sites, no enrichments were measured showing that for those locations the cement plant and the other local sources did not have a significant impact on air pollution deposition for the ∑17PCDD/Fs.

The cement plant is located in a mountain and thus, sampling sites not directly exposed to the emissions might be not impacted by this source. This is one of the reasons why modeling PCDD/F dispersion from sources and deposition is difficult in this specific area. Most differences found between samples are related not only to the distance to the cement plant but also to other factors. For example, altitude and exposition are important because the wind that blows with more intensity and which brings storms and rain is from the south; this implies that under this climate most southern exposed areas are subjected to the cement plant emissions, whereas the northern ones are protected. However, when the wind blows from north, it carries airborne contaminants from the urban−industrial areas located at the north of the study area, changing the deposition pattern to a signature that is not associated with the cement plant.

Further analyses of the 17 congeners individually showed variations in the degree of enrichment (Figure 3). The congeners with the highest average enrichment in the transplanted lichens were OCDD and TCDF (Figure 3). The concentrations of the most chlorinated OCDD varied greatly, with enrichment detected in only seven samples. This implied that the dispersion of OCDD was more localized than that of other, lighter compounds.

In contrast, TCDF was enriched in 25 samples and was thus present practically throughout the entire study area. In fact, overall, the lighter and less chlorinated congeners occurred at a greater number of sampling points than the heavier and more chlorinated congeners. For example, TCDD/Fs and PeCDD/Fs, with relative molecular masses of 305.97−356.41, were enriched in >50% of the samples, whereas OCDD/Fs and HpCDD/F, with molecular masses of 409.30−459.74, were enriched in <30% (Figure 3).

The results clearly show that there are two areas where lichen transplants become enriched in the ∑17PCDD/F. One of the areas is in the vicinity of the cement plant, where six sites revealed higher concentrations of PCDD/Fs than the ones observed in the control area, and another one was located to the northeast of the cement plant on the top of a mountain. For those sites, on the basis of only the PCDD/F concentrations, it is more difficult to track what pollutant sources might have been responsible for the enrichments and if the cement-plant emissions deposited in this area.

To evaluate the spatial impact of the cement plant emissions, it is necessary to look at the PCDD/F profiles measured in the lichen transplants and compare them with the profile reported for the emissions.

PCDD/F Profiles in Lichens versus Cement-Plant Emissions. A major challenge in working with pollutants such as PCDD/Fs is that they are released as a mixture of compounds. Because only 17 of the >200 PCDD/F congeners have toxic properties,[2,3] only the total concentration of these are typically reported. However, these values do not provide useful information to track pollution sources if the source of interest is not the dominant one in a multiple-source environment. Rather, to track sources, PCDD/F profiles (i.e., the relative contribution of each PCDD/F congener to the sum of the 17 PCDD/Fs) should be examined.

PCDD/F congener profiles have been used as signatures of specific emission sources.[27] Different emission sources release PCDD/F congeners in different proportions.[28] At the deposition level, PCDD/F profiles will be the consequence of several emission sources, each with a specific profile. For the

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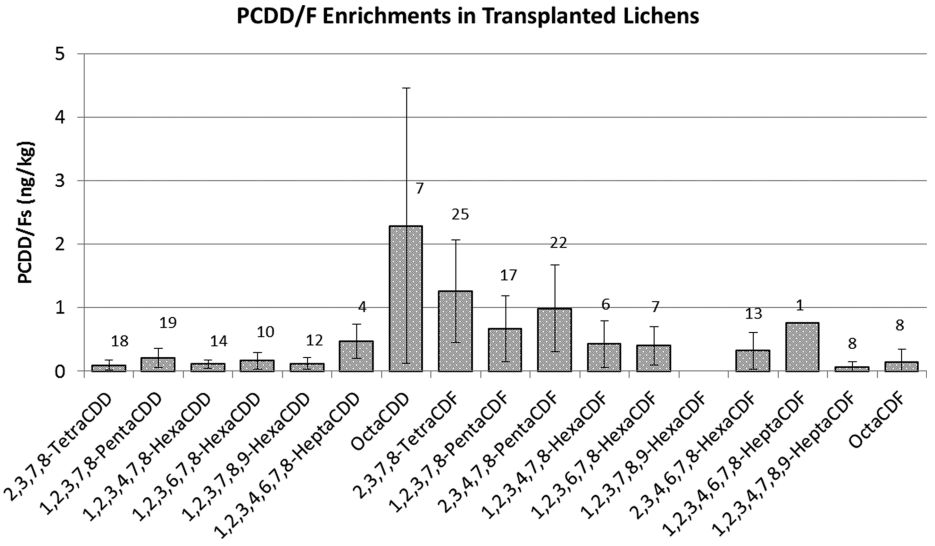

Figure 3. Average PCDD/F enrichment concentrations for each of the 17 congeners in the transplanted lichens. The concentrations in the nonexposed control were subtracted from those in the exposed lichens. Only values >0 were used to calculate the average (n displayed above each bar).

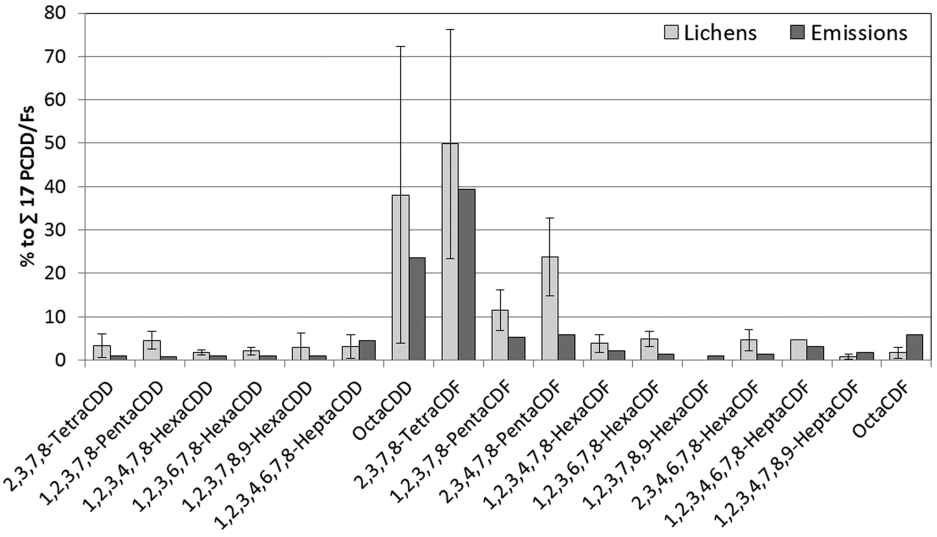

Figure 4. PCDD/F profile in transplanted lichens and in emissions from kiln 9 of the cement plant. In the lichen transplants assayed for each congener, n varied between 1 and 26 according to the number of samples with enrichment of PCDD/Fs after the control values were subtracted from the lichen values. Emissions data (n = 1) were obtained from published records.

detection of the contribution of industrial emissions, PCDD/F profiles measured in lichens must be compared with those reported for emissions. Accordingly, the PCDD/F congener profiles of the lichen transplants were calculated based on the enrichments of each congener after 7 months of exposure. Our study showed that the average PCDD/F congener profile in these lichens was dominated by TCDF (50%) and OCDD (38%) and matched the profile of the emissions from the cement manufacturing plant (Figure 4).

Emissions from the cement plant show a PCDD/F congener profile dominated by TCDF (40%) and OCDD (25%).[29] The emission profile seems to be widely reflected in the PCDD/F average profile of the exposed lichens, although the contributions of TCDF and OCDD to the latter were slightly larger. However, the lichens were exposed to the overall environment of the study area and therefore probably to other sources of PCDD/Fs, which could have additionally contributed to the total input of PCDD/Fs in the environment.

Studies directly comparing PCDD/F profiles in emissions from cement plants with profiles measured in lichens have not been published so far. We found two studies in which authors measured PCDD/F concentrations in herbage samples collected in the vicinity of Spanish cement plants.[39,40] In both studies, the PCDD/F profile in herbage was dominated by OCDD/Fs and 1234678-HpCDD/Fs, a similar profile to the one of lichens if the concentrations of the control sample had not been subtracted.[39,40] The advantage of using lichen transplants is that it allows obtaining temporal information. In our study we could obtain the PCDD/F profile characteristic of each sampling site during the 7 month period. This information can be directly correlated with PCDD/F profiles measured in the cement plant emissions.

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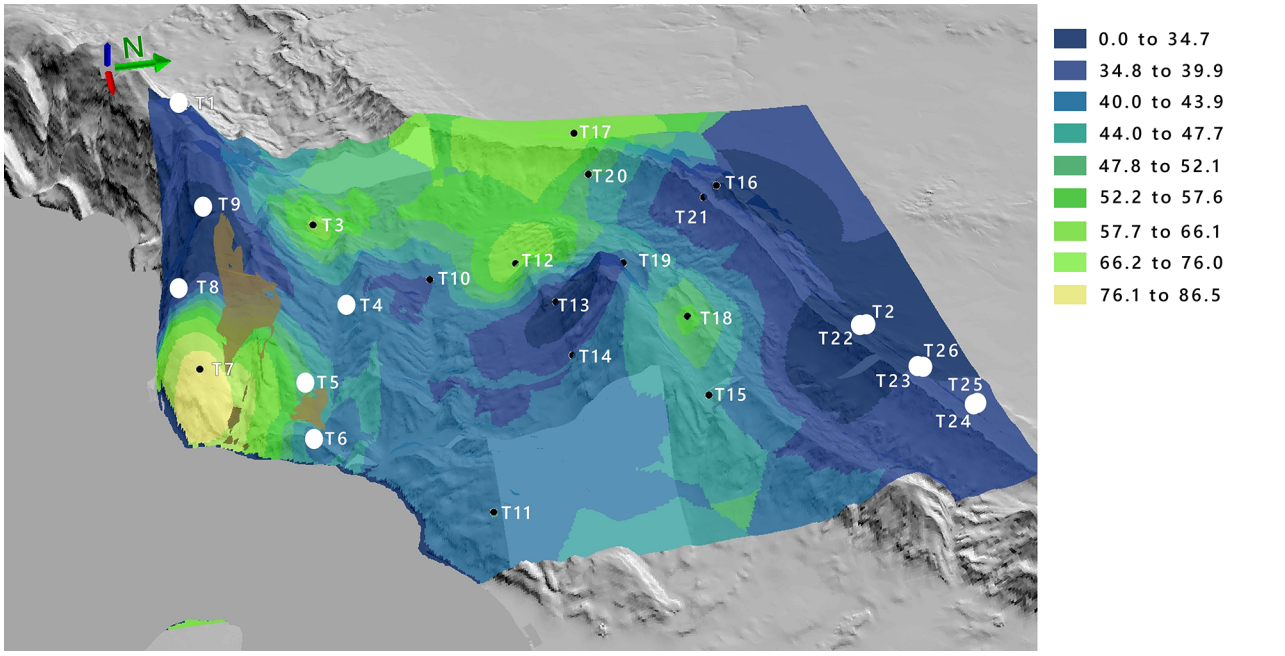

Figure 5. Interpolation of the distances between the PCDD/F emissions profile of the cement plant and the PCDD/F profiles of the lichens obtained at each sampling site. Smaller distance values reflect those sites where the lichen profiles were most similar to the profile of the cement industry. The distance values are presented overlapped to hill-shade (based on altitude with a vertical amplification = 4), and the numbers refer to the sampling sites. White circles correspond to transplants enriched in the ∑17PCDD/Fs. Gray areas to the left represent the cement industry facilities. For scale, please refer to Figure 1.

To determine which sites best reflected the industrial emissions from the cement manufacturing plant, we used a cluster analysis for all individual samples and mapped the dendogram distances to the emission profile (Figure 5). As shown in Figure 5, which represents an interpolation of these distances overlapped on a map showing elevation, the best matches between the PCDD/F profile of the lichen transplants and the emissions profile occurred at sites located on the tops of mountains whose slopes faced the cement plant. Some of these sites corresponded to the ones with the highest concentrations of PCDD/Fs, and others did not. This distinction is extremely important for validating dispersion and deposition models of industrial emissions in complex landscapes (several pollution sources and with complex orography).

Ours is the first study to compare PCDD/Fs in emissions from a specific industry with PCDD/Fs in lichens. Another study conducted in the same region as ours measured PCDD/Fs in lichens collected in situ and then compared the results with the values determined in multiple pollution sources (industrial, urban, forestry, etc.) based on land-use characterization.[16] The authors concluded that urban areas are important sources of PCDD/Fs and may be even more relevant than industrial ones.[16] During the last two decades, European regulations have set thresholds for PCDD/Fs in industrial emissions[41] but have not addressed other sources, such as urban ones. However, there has been an overall decline of PCDD/Fs in the environment, mostly in those associated with industrial areas.[41]

In this study, we used lichen transplants and examined the accumulation of PCDD/Fs over a period of 7 months. The data were compared with PCDD/F emissions released by a cement plant during the same period. The results confirmed the suitability of using lichen transplants as environmental monitors to measure PCDD/F emissions, even those that are low and do not represent an immediate risk to the environment or to human health, and to assess the impact of their sources. However, other sources in the region might have similar PCDD/F profiles and thus contribute to the profile determined in lichens. Thus, to improve the robustness of the lichen data, emissions from other industries in the region should be characterized as well.

AUTHOR INFORMATION

Present Address

[⊥]TECNATOX group, Chemical Engineering Department, Universitat Rovira i Virgili, C/Països Catalans, no. 26, 43007 Tarragona, Catalonia, Spain.

Notes

The authors declare no competing financial interest.

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