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Declining trends of PCDD/Fs in lichens over a decade in a Mediterranean area with multiple pollution sources

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HIGHLIGHTS

- We measured PCDD/F concentrations in lichens over a decade, from 2000 to 2011.
- PCDD/Fs in lichens have decreased approximately 70%.
- This decline couldn't be only explained by the reduction in industrial emissions.

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ABSTRACT

Lichens are one of the most useful environmental biomonitors, due to their ability to clearly reflect atmospheric deposition of pollutants. Dioxin and furan (PCDD/F) emissions have been reported to be decreasing in North European countries as a consequence of European regulations. This reduction has been perceptible across several environmental matrices, but it hasn't yet been shown in lichens as typical biomonitors of atmospheric pollution. In this work we compared concentrations of PCDD/Fs in two lichen species collected in a Mediterranean area with mixed land-uses, encompassing urban, industrial and natural areas, in 2009 and 2011 with the ones obtained in the same species collected in the same region in 2000. We found that PCDD/F concentrations in both lichen species have decreased approximately 70% since 2000 whereas industrial emissions have only decreased 25% for the same period. This substantial greater reduction observed in lichens may be due to several causes; after excluding fires as a possible explanation, we point out that possible causes could not only be the overall decrease in industrial emissions but also other causes such as traffic reduction and/or increase efficiency in the use of fuels.
Capsule: PCDD/F concentrations in lichens have decreased 70% over the last decade, whereas industrial emissions have only decreased 25%.

1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are toxic environmental pollutants generated during combustion processes, both of natural and anthropogenic origin. They were never intentionally manufactured; rather, they are byproducts of the synthesis and combustion of chlorinated organic chemicals such as chlorophenols and other chlorinated aromatic compounds. Thus, although the production of such chemicals is heavily regulated in most countries, these contaminants are ubiquitous and persistent in the environment (Rappe, 1993; Fiedler, 2003).

Global agreements to reduce PCDD/F emissions and introduction of strict emission limits for European industries during the last decade have reduced emission of PCDD/Fs from industrial facilities (LRTAP, 1979; Stockholm Convention, 2000; Directive 2000/76/EG, 2000; Bruckmann et al., 2013). A review of emission data reported under the LRTAP Convention and NEC Directive of 2012 has stated that PCDD/F emissions in European countries have decreased from 1990 to 2010, showing a declining trend that has been taking place due to regulations

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(Mareckova et al., 2012). Between 2000 and 2011 (the time scale of our study), an approximately 60 percent drop in PCDD/F emissions for the 27 countries of Europe was registered (EEA, 2013); whereas specifically for Portugal, a 25 percent drop in emissions from 2000 to 2011 was observed (PEA, 2013). These reductions were attributable to the introduction of strict emission limits for European waste incineration plants and for industrial installations (Directive 2000/76/EG, 2000) which seem to be effectively reducing industrial emission of PCDD/Fs (Bruckmann et al., 2013).

Most studies related to trends on PCDD/Fs have been carried out in countries where heavy industry was built specifically after World War II. During this period there was an extensive promotion of industrial activities, which have been responsible for wide spread contamination of the environment, including air, soil and biota that might still be reflected in sink compartments such as sediments (Chi et al., 2009; Yunuén et al., 2011). Only after many years technology was improved and adopted by these early industrialized countries, and emissions of pollutants were reduced. Portugal, because of political reasons, experienced a later and less widespread industrialization, and newborn industries have used most recent and improved technology. Because of this later and cleaner industrial development, we expect the country to have less historical accumulation of persistent pollutants in the environment and thus it's predictable that there was a lower drop on PCDD/F emissions than other European countries for the same period.

However, emission from other sources, such as vehicles, and fireplaces, is yet to be quantified and regulated. With the introduction of limits for industrial emissions, these other sources, as well as natural (e.g. forest fires) and probably unknown sources might become more relevant.

Though measures to reduce industrial emission of PCDD/Fs have been implemented, monitoring programs showing the impact of this reduction on the environment at deposition level have seldom been conducted, especially in the decade 2000–2010 and in Mediterranean countries where dry deposition is an important route of pollutant clearance from atmosphere. Most studies covered the time scale of the 1990s or measured a single time PCDD/F deposition in the environment (Alcock and Jones, 1996).

Measuring PCDD/F deposition to the environment directly is difficult; in fact, deposition is commonly estimated from concentrations measured in air, precipitation, and soil (Wagrowski and Hites, 2000). All of these have restrictions; for example, because air is sampled for short periods (usually 24 to 48 h), PCDD/F concentrations tend to be below detection limits of analytical equipment (Gusev et al., 2011). However, since PCDD/Fs are lipophilic compounds with tendency to bioaccumulate, even if not detectable in air, they can be found in biota and soil. Soil is considered a natural sink for persistent organic pollutants; PCDD/Fs absorb to soil organic carbon, and once absorbed, remain relatively immobile (Fiedler, 1999). For this reason, concentrations in soil accumulate the long-term deposition during decades and consequently are not helpful to assess the impact of the recent measures to reduce emissions that have been taking place.

Alternative methods consider PCDD/F concentrations in vegetation as a measure of deposition; in this case, accumulation is dependent on the phenology of the plant (duration of leaves), which may be a disadvantage when the main objective is to obtain temporal trends. Besides, as plants absorb nutrients from soil through roots, they don't represent an independent measure of the present-time atmospheric deposition.

Lichens (symbiosis of fungi and algae or cyanobacteria), on the other hand, have neither roots nor a cuticle to control uptake of elements from the external environment, and thus absorb pollutants directly from atmosphere and accumulate them inside their tissues over time. This characteristic is particularly useful to monitor PCDD/Fs that exist at low concentrations in the environment. Lichens respond quickly to atmospheric changes in pollutant levels, though they still keep a signal of past pollution events (Munzi et al., 2011). Several works showed that lichens can indicate deposition of most atmospheric pollutants, including PCDD/Fs. They've been used to characterize spatial and temporal patterns of a wide range of atmospheric pollutants, ranging from metals to persistent organic pollutants (Augusto, 2012; Schrlau et al., 2011; Usenko et al., 2010; Branquinho et al., 2008; Branquinho, 2001; Manning and Feder, 1980; Martin and Coughtrey, 1982; Puckett, 1988; Garty, 1993). Though a set of studies has been published regarding the use of lichens to monitor PCDD/Fs (Augusto et al., 2013), an insight on temporal trends of these compounds in lichens is still missing.

The main aim of this study was to compare concentrations of PCDD/Fs in two lichen species collected in four sampling periods over a decade (2000–2011) in a Mediterranean area with mixed land-uses, encompassing industrial, urban and natural areas. We hypothesize that PCDD/F concentrations in lichens will show a decrease trend over time that follows the general trend of decrease of Portuguese emissions.

2. Material and methods

2.1. Study area

The study was conducted in an industrial/urban Mediterranean area in Europe (Portugal, Setúbal region) (Fig. 1). This area includes the Serra da Arrábida Natural Park, which covers 108 km^2 and is one of the 30 areas which are officially under protection in the country; and it is surrounded by urban and industrial areas (ICNF, 2013).

Relevant industrial activities comprise cement manufacturing using alternative fuels, production of electricity (using fossil fuel), treatment and disposal of non-hazardous waste, manufacture of fabricated metal products, manufacture of pulp, collection of hazardous waste, manufacture of pesticides and other agrochemical products, repair and maintenance of ships and boats, sea port activities, manufacture of plastics in primary forms, recovery of sorted materials, manufacture of motor vehicles, and manufacture of food and beverages (E-PRTR, 2014).

Urban areas include small villages scattered in the region and the city of Setúbal, summing to 233,516 inhabitants in 2011 (12% more in relation to 2001) (INE, Censos, 2011). Facing partially the Atlantic Ocean and partially the Sado River, the study area also includes recreation and bathing areas and an industrial harbor which serves the cement manufacturing plant. The region is crossed by important motorways and several roads.

2.2. Sampling

Sampling took place in February 2009, October 2009 and March 2011. At each sampling period, 19 to 20 samples of the fruticose lichen *Ramalina canariensis* Steiner and 8 to 11 samples of the foliose lichen *Xanthoria parietina* (L.) Th.Fr. were collected at 29 sampling sites from the available phorophytes — *Pinus pinea*, *Pinus pinaster*, *Olea europaea*, *Quercus suber*, and *Quercus coccifera* (Fig. 1). Previous studies have shown that there are no significant differences in the accumulation of PCDD/Fs by lichens growing on different phorophytes (Augusto et al., 2009). Approximately, 12 g of lichens (whole thallus) was collected at each sampling site.

Due to the variety of land uses existent in the area it wasn't possible to collect the same lichen species over the whole sampling area. Both species that were collected are ubiquitous but occupy sites with different land uses. While *X. parietina* is a very tolerant species found in highly polluted sites, *R. canariensis* is mostly found in forests and natural areas.

After collection, lichens were stored in plastic bags and transported to the laboratory, where the unwashed samples were immediately dried at room temperature (as lichens are poikilohydric, they dry as quickly as 24 h when left in a dry environment) and sorted to remove extraneous material. The cleaned samples were then stored in brown glass bottles until PCDD/F chemical analysis.

In 2000 an environmental biomonitoring baseline study was carried out in the same region as the current study. The same lichen species