Journal of Environmental Management 156 (2015) 52–61

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Relationship between levels of polycyclic aromatic hydrocarbons in pine needles and socio-geographic parameters

Raquel Fernández-Varela [a], Nuno Ratola [b, c, *], Arminda Alves [c], José Manuel Amigo [d]

[a] Department of Plant and Environmental Sciences, Faculty of Science, University of Copenhagen, Thorvaldsensvej 40, 1871 Frederiksberg C, Denmark
[b] Physics of the Earth, Regional Campus of International Excellence "Campus Mare Nostrum", University of Murcia, Edificio CIOyN, Campus de Espinardo, 30100 Murcia, Spain
[c] LEPABE, Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[d] Department of Food Science, Spectroscopy and Chemometrics, Faculty of Sciences, University of Copenhagen, Rolighedsvej 30, DK-1958 Frederiksberg C, Denmark

ARTICLE INFO

Article history:
Received 23 July 2014
Received in revised form
10 February 2015
Accepted 12 March 2015
Available online 17 March 2015

Keywords:
Canonical correlation
Environmental pollution
PAHs
Pinus pinaster
Pinus pinea

ABSTRACT

The ability of pine needles to capture polycyclic aromatic hydrocarbons (PAHs) from the surrounding air is well known. In this work the current knowledge of this affinity will be enhanced, investigating the plausible links between the concentrations of PAHs found in pine needles collected in different sites in Portugal, and several socio-geographic variables with environmental relevance. Canonical correlation analysis (CCA) has proven to be a suitable and innovative technique to look for relationships within environmental datasets. In the current work, CCA will simultaneously include chemical information (concentration of PAHs found in pine needles) and socio-geographic information associated to the sampling areas. In order to be more robust in these conclusions, *Pinus pinea* and *Pinus pinaster* species were considered separately, allowing an accurate direct comparison between them. The information concerning the different seasons and land occupation was also taken into account. Our results demonstrate how CCA can be a useful tool in environmental impact assessment, and highlight the importance of pine needles as trustful biomonitors of the influence of socio-geographic parameters on the levels of PAHs in a given area.

1. Introduction

Although petroleum-related sources are a major cause of the environmental presence of anthropogenic PAHs, another important contribution comes from processes such as biomass burning, volcanic eruptions and diagenesis (Wang et al., 2007). Consequently, these chemicals can be ranked as petrogenic, pyrogenic or biogenic (Dahle et al., 2003). Petrogenic PAHs are related to combusted oil, coal and their by-products (da Silva and Bícego, 2010), and mainly comprised by 2 and 3-aromatic ring structures (Baumard et al., 1998), whereas in pyrogenic PAHs the "heavier" 4–6 ring molecules predominate, and their sources are primarily anthropogenic combustion processes (e.g. car exhaust, local heating facilities, industrial-related activities), forest fires, or tar use in asphalt (Bjørseth and Ramdahl, 1983; Guillon et al., 2013; Jensen et al., 2007). Biogenic PAHs are linked to biological material or early diagenetic processes, and are characterised by a strong presence of perylene (Gocht et al., 2001).

In many recent studies, vegetation has been used as a biomonitor of atmospheric contamination to identify point sources of pollution and to determine regional and global contamination patterns. Deciduous tree leaves, lichens, mosses and coniferous needles are the most used matrices (Alfani et al., 2001; Augusto et al., 2010; Desalme et al., 2013; Holoubek et al., 2000; Piccardo et al., 2005). In particular, pine needles of several species yielded good performances in biomonitoring studies of PAHs worldwide, due to their unique morphology and waxy content, leading to a successful uptake of semi-volatile organic compounds (Amigo et al., 2011; Ratola et al., 2010a, 2010b, 2011; Simonich and Hites, 1995). A useful characteristic of pine needles is that it is relatively easy to establish their age. They can grow up to several years old, depending on the species and the environmental conditions. Therefore, it has been demonstrated that pine needles contain

* Corresponding author. Physics of the Earth, Regional Campus of International Excellence "Campus Mare Nostrum", University of Murcia, Edificio CIOyN, Campus de Espinardo, 30100 Murcia, Spain.
E-mail address: nrneto@um.es (N. Ratola).

http://dx.doi.org/10.1016/j.jenvman.2015.03.019
0301-4797/

complementary monitoring information, such as a trustworthy time-integrated pollution dataset able to produce a comprehensive assessment of levels, sources and spatio-temporal patterns of PAHs (Amigo et al., 2011; Lehndorff and Schwark, 2009a, 2009b; Navarro-Ortega et al., 2012; Noth et al., 2013; Ratola et al., 2010b; Tremolada et al., 1996). There are major difficulties in obtaining accurate estimations of the origin of the PAHs, due to the complex mixtures of individual PAHs released to the environment from different sources of emission that may be localized within a specific geographical area. This makes the quantification and the linkage of the PAHs with a given source particularly challenging (Mostert et al., 2010), although some methods like molecular ratios assessment were proposed (Yunker et al., 2002).

To overcome these barriers and improve the accuracy of source apportionment studies, chemometric tools have been widely used (Gredilla et al., 2013; Mas et al., 2010). Chemometric methods in analytics is the discipline that uses mathematical and statistical methods to obtain the maximum chemical information when analysing chemical data. Methods such as principal component analysis (PCA), widely employed in several environmental areas (Rojo-Nieto et al., 2013; Terrado et al., 2006), partial least squares-discriminant analysis (PLS-DA), artificial neural networks (ANNs) (Álvarez-Guerra et al., 2010), cluster analysis (Chen et al., 2012) or positive matrix factorisation (PMF) (Jang et al., 2013) are presented in the literature as a complement to classic univariate statistics, often unveiling concealed environmental information (Álvarez-Guerra et al., 2010; Chen et al., 2012; Gredilla et al., 2013; Jang et al., 2013; Navarro et al., 2006). Canonical correlation analysis (CCA) is an exploratory method designed to study the relationship between data matrices containing different information within the same samples, which make it especially attractive in the field of environmental monitoring (Amigo et al., 2012; Galloway et al., 2002). This allows one to link the behaviour of variables of different nature that, otherwise, would be very difficult to assess (e.g. relating metal content in water with physico-chemical variables (Amigo et al., 2012).

The objective of this study, thus, is to examine the suitability of using pine needles as biomonitors of PAH levels, relating them with several socio-geographic parameters. We consider needles of different ages in different pine species and different sampling sites, and examine parameters such as population, population density, urban waste, petroleum and gas consumption, water consumption or elevation. We use CCA to establish these coordinates and identify behavioural patterns and potential sources for the presence of PAHs.

2. Material and methods

2.1. Sampling and sample analysis

The samples were collected in different locations distributed throughout mainland Portugal, covering major industrial areas, large and small cities, rural areas and also two remote mountainous sites. Since each new shoot of needles blooming each spring is easily separated in the branch from the previous ones, it was possible to separate the needles by year of exposure, which varied according to the pine species and the site. A total of 29 sampling sites (14 urban, 5 industrial, 8 rural, 2 remote) and four sampling campaigns (one per season) yielded a field dataset of 670 samples divided into two clearly differentiated blocks: 294 samples from *Pinus pinaster* (including duplicates of each sample) and 376 samples from *Pinus pinea* (with duplicates), as reported previously (Ratola et al., 2010b). This high amount of samples was obtained since it was possible to collect needles from different ages (in our case, life spans of two to four years depending on the species and the tree). The sampling strategy, maps and the methodology for sample analysis and quantification were described in detail elsewhere (Ratola et al., 2006, 2009, 2010a, 2010b). In brief, the needles were collected from the bottom branches (1.5–2 m above the ground), always from the same trees in all four campaigns, and properly conditioned until analysis. This procedure consisted firstly of an extraction by sonication for 10 min with 30 mL hexane/dichloromethane (1:1), repeated twice using fresh solvent. The extracts were combined and evaporated to almost dryness (0.5 mL, approximately) in a rotary evaporator (Flawil, Switzerland) before being further purified using a clean-up procedure with polypropylene SPE alumina cartridges (5 g, 25 mL). After conditioning the cartridges with 50 mL hexane/dichloromethane (1:1), the extract was added to the column and eluted with 50 mL hexane/dichloromethane (1:1) and 50 mL dichloromethane into a pear-shaped flask, pre-concentrated in a rotary evaporator to 0.5 mL and transferred to 2 mL amber glass vials. Extracts were then blown down under nitrogen at room temperature, and reconstituted in 1 mL of hexane into the GC–MS injection vials. Chromatographic analysis of PAHs was done with a Varian CP-3800 gas chromatograph (Lake Forest, CA, USA) coupled to a Varian 4000 mass spectrometer in electron impact mode (70 eV) and a CP-8400 autosampler. Injection was in splitless mode (2 μL) and the GC column was a FactorFour VF-5MS (30 m × 0.25 mm ID × 0.25 μm film thickness) from Varian. Overall recoveries were between 65 and 110% and repeatabilities below 10%.

This methodology involving a classic approach such as sonication has been used successfully in many other related studies (Augusto et al., 2010; Capuano et al., 2005; Holoubek et al., 2000; Librando et al., 2002; Piccardo et al., 2005; Tian et al., 2008), similar to the performances shown by the more recent accelerated solvent extraction (ASE). Although two studies from one group show the latter with better recoveries that the former, the opposite was seen by Ratola et al. (2006). These differences may be due to the use of different pine species by both groups (*Pinus sylvestris* and *P. pinea*, respectively) and the still existing gaps and uncertainties pointed out by two reviews (Barber et al., 2004; Desalme et al., 2013) in the understanding of the air-vegetation partition of PAHs, despite the number of different models attempted for its description. Since the intention of the current work is to make a comparison between samples, the key concern is to have all of them passing through the same handling/extraction/quantification procedure, to avoid differences in the systematic errors associated.

Six geo-social-economic parameters with an expected environmental impact on the concentrations of PAHs, namely population (number of inhabitants), population density (people/km^2), elevation (above sea level, m), urban waste produced (t – tonnes), water consumption (m^3) and petroleum and gas consumption (t – tonnes) were obtained for the areas of concern from the databases of the Portuguese National Statistics Institute (INE, 2013). The last four are calculated as the production/consumption of the population of the areas of each sampling site. The variables were chosen considering their availability in the database, the complete information for the chosen areas and, as mentioned above, their expected relevance concerning the generation of different PAHs.

2.2. Data treatment

The PAH concentrations obtained for all the samples were collected in a matrix **X** ($M \times 16$) with as many rows as samples (M) and as many columns as number of PAHs (16). In the same way, the socio-geographical parameters were collected in a second matrix **Y** ($M \times 6$) with the same number of rows as **X**, but with as many columns as the socio-geographical variables considered. Both matrices were independently normalized prior to the analysis. In