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Combined field/modelling approaches to represent the air-vegetation distribution of benzo[a]pyrene using different vegetation species

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HIGHLIGHTS

- Pine needles are biomonitors of BaP air levels when coupled with CTM strategies.
- Modelling results depend more strongly on the location than on the pine species.
- Modelling of BaP canopy levels was successfully validated with pine needles data.
- Comparison with biomonitoring data showed the best results in the warmer months.

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ABSTRACT

A strategy designed to combine the features of field-based experiments and modelling approaches is presented in this work to assess air-vegetation distribution of benzo(a)pyrene (BaP) in the Iberian Peninsula (IP). Given the lack of simultaneous data in both environmental matrices, a methodology with two main steps was employed. First, evaluating the simulations with the chemistry transport model (CTM) WRF (Weather Research and Forecasting) + CHIMERE data against the European Monitoring and Evaluation Programme (EMEP) network, to test the aptitude of the CTM to replicate the respective atmospheric levels. Then, using modelled concentrations and a method to estimate air levels of BaP from biomonitoring data to compare the performance of different pine species (*Pinus pinea*, *Pinus pinaster*, *Pinus nigra* and *Pinus halepensis*) to describe the atmospheric evidences. The comparison of modelling vs. biomonitoring has a higher dependence on the location of the sampling points, rather than on the pine species, as some tend to overestimate and others to underestimate BaP concentrations, in most cases regardless of the season. The climatology of the canopy levels of BaP was successfully validated with the concentrations in pine needles (most biases below 26%), however, the model was unable to distinguish between species. This should be taken into consideration in future studies, as biases can rise up to 48%, especially in summer and autumn, the. The comparison with biomonitoring data showed a similar pattern, but with the best results in the warmer months.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are atmospheric pollutants originated from several natural (forest fires, volcanoes) and anthropogenic (traffic, industry) sources, via the combustion of fossil fuels, wood or other organic materials. But their release into the environment as a consequence of human activities is increasing continuously (Lapviboonsuk and Loganathan, 2007). The noticeable differences in their physical–chemical properties have a decisive influence on their emission, transport and deposition behaviour (Ravindra et al., 2008). Both gaseous and particulate PAHs can undergo atmospheric transport over long distances (Baek et al., 1991), carrying potentially high toxicity towards organisms worldwide (Solé, 2000).

Several chemistry transport model (CTM) approaches tried to describe the levels and patterns of PAHs (Sehili and Lammel, 2007; Matthias et al., 2009; Bieser et al., 2012; Friedman and Selin, 2012; San José et al., 2013). In particular benzo(a)pyrene (BaP), predominantly found in the particulate fraction of the atmosphere and the reference for the existing air quality standards for PAHs (European

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Commission, 2008). However, CTMs still cannot provide a full understanding of the processes involved in their atmospheric fate (Galarneau et al., 2013), being the lack of field data reporting atmospheric concentrations a major reason for this fact. For instance, the measuring stations of the European Monitoring and Evaluation Programme (EMEP) network cover the whole European territory, but those monitoring semi-volatile organic compounds (SVOCs) like PAHs are located essentially in the Scandinavian countries and almost absent from the southern European countries (Bieser et al., 2012; Torseth et al., 2012). This is why the use of alternative ways to include field sampling data in the validation of the models has to be considered.

One valid option is performing monitoring studies employing vegetation species, which have been used for some time in the assessment of PAHs levels. Coniferous species, in particular the lipid-rich cuticle of their needles, is likely to accumulate such contaminants (Simonich and Hites, 1995) and are favoured due to their ubiquity, which allows the establishment of trans-boundary studies (Lehndorff and Schwark, 2004). According to McLachlan (1999), PAHs can reach the needles by equilibrium partitioning between the vegetation and the gas phase, kinetically-limited gaseous deposition, or wet and dry particle-bound deposition. A few studies proved the ability of coniferous needles to establish levels and spatio-temporal patterns of PAHs (Lehndorff and Schwark, 2009; Augusto et al., 2010; Ratola et al., 2010a, 2010b, 2012; Amigo et al., 2011), but only a very limited number of literature is available regarding the air-vegetation distribution, in controlled systems (Zhu et al., 2008) or in field-based studies (St Amand et al., 2009a, 2009b). However, the strong potential of biomonitoring data and CTMs can be used in concomitance to obtain reliable estimates of the air-vegetation partition of PAHs. Differences between the uptake capacity of the needles of several pine species and the dissimilar levels depending on the land use have been reported in biomonitoring schemes (Librando et al., 2002; Piccardo et al., 2005; Ratola et al., 2011), and it would be very important that CTMs could represent those differences adequately, especially in areas where data regarding persistent atmospheric pollutants is scarce, such as the western Mediterranean (Bernalte et al., 2012).

As such, an innovative approach using the Weather Research and Forecasting (WRF) + CHIMERE modelling system, coupled to emission data from EMEP and compared to data from 70 pine needles sampling sites is presented in this work. The main objective is to evaluate the presence of BaP in the Iberian Peninsula, in order to verify if models and field data can represent accurately their atmospheric concentrations, and at the same time unveil possible differences between pine species (in this case *Pinus pinea*, *Pinus pinaster*, *Pinus nigra* and *Pinus halepensis*).

2. Experimental section

2.1. Pine needles sampling and analysis

Details on the sampling campaigns taken in consideration for the pine needles can be found elsewhere (Ratola et al., 2010a, 2012). A brief description can be found in Supporting Information.

2.2. Estimation of BaP air concentrations from pine needles

An estimation of atmospheric concentrations of BaP in the sampling sites chosen for this study was performed using the levels found in pine needles. This indirect calculation was necessary to face the scarce information on the atmospheric presence of BaP in the area of study. The methodology employed is based on the studies by St. Amand et al. (2007, 2009a, 2009b), who determined levels of gas-phase and particulate PAHs (and PBDEs) in vegetation and in the nearby atmosphere. They reported an approach to estimate the air concentrations from those found in vegetation, consisting briefly in the following calculations:

$$Ca = Cp + Cg \quad (1)$$

with

$$Cp = (Cvp*m)/(A*v_p*t) \quad (2)$$

and

$$Cg = (Cvg*m)/(A*v_{gt}*t) \quad (3)$$

where Ca, Cp, Cg – total, particulate and gas-phase (respectively) concentrations of the target compound in air (ng m^{-3}); Cvp, Cvg – contribution of particle-bound and gaseous deposition (respectively) to the total concentration in vegetation (defined as Cvp + Cvg, ng g^{-1}); m – dry weight of pine needles (g); A – total surface area of pine needles (m^2); v_p – particle-bound deposition velocity (m h^{-1}); v_{gt} – net gaseous transfer velocity (m h^{-1}); t – environmental exposure time of pine needles (h). For BaP, the gas-phase contribution is strongly predominant (ASTDR, 1995; Friedman and Selin, 2012), so the gas-phase contribution is considered negligible (St. Amand et al., 2009a), meaning Cg ≈ 0 and Ca ≈ Cp. This way, v_p can be calculated by Equation (2), if the concentrations in air (Ca) and vegetation (Cvp) are known. However, due to the lack of atmospheric measurements, it was impossible to calculate v_p for our samples. So, given that the value reached by St. Amand et al. (2009a) was for Norway spruce (*Picea abies*) needles, it was decided to use the deposition velocity estimated for BaP over a coniferous forest canopy by Horstmann and McLachlan (1998): 2.196 m h^{-1}. This way, it is possible that the differences in the PAHs uptake by different pine species found in literature (Librando et al., 2002; Piccardo et al., 2005; Ratola et al., 2011) were somehow compensated in this first approximation. Table S1 (Supporting Information) presents the mass and total surface area for the pine needles species considered in this work. The exposure time (in hours) was estimated from April 15th (considered as the day the needles sprung out) to the sampling day.

2.3. Modelling experiment

In this study, the modelling system consists on the Advanced Research Weather Research and Forecasting (WRF-ARW) Model v3.1.1 (Klemp et al., 2007; Skamarock et al., 2008) coupled off-line to the CHIMERE chemistry transport model (Menut et al., 2013). Details are presented in Supporting Information.

2.4. Model evaluation

For the evaluation of canopy deposition and atmospheric concentrations, the spatial correlation coefficient (*r*), root mean square error (RMSE) and mean bias (MB) values were selected after Pay et al. (2010). Annual and seasonal mean statistics are computed, with seasons corresponding to December, January and February (DJF, winter), March, April and May (MAM, spring), June, July and August (JJA, summer) and September, October and November (SON, autumn). Also, the mean fractional bias (MFB) and the mean fractional error (MFE) will be used instead of the mean normalised bias error (MNBE), since Boylan and Russell (2006) reported that the latter may not be appropriate for evaluating particulate materials. This is due to the fact that the concentrations of these components can be considerably low, leading sometimes to very large