Atmospheric Environment 140 (2016) 514–518

Contents lists available at ScienceDirect

Atmospheric Environment

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

Short communication

A preliminary investigation into the use of Red Pine (*Pinus Resinosa*) tree cores as historic passive samplers of POPs in outdoor air

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HIGHLIGHTS

- Red Pine trees provided historic concentration profiles for various POPs groups.
- A preliminary uptake model for transport from air through the bark was developed.
- A bark infiltration factor was determined at 2%.
- Areas for more intensive future research are highlighted.

ARTICLE INFO

Article history:
Received 27 January 2016
Received in revised form
7 June 2016
Accepted 8 June 2016
Available online 9 June 2016

Keywords:
Tree cores
POPs
PAHs
BFRs
Historic trends

ABSTRACT

The suitability of Red Pine trees (*Pinus Resinosa)* to act as passive samplers for persistent organic pollutants (POPs) in outdoor air and to provide historic information on air concentration trends was demonstrated in this preliminary investigation. Red Pine tree cores from Toronto, Canada, were tested for polycyclic aromatic hydrocarbon (PAHs), alkylated-PAHs, nitro and oxy-PAHs, polybrominated diphenyl ethers (PBDEs) and novel brominated flame retardants (novel BFRs). The PBDEs and novel BFRs demonstrated a similar relative contribution in cores representing 30 years of tree growth, to that reported in contemporary air samples. Analysis of tree ring segments of 5–15 years resulted in detectable concentrations of some PAHs and alk-PAHs and demonstrated a transition from petrogenic sources to pyrogenic sources over the period 1960–2015. A simple uptake model was developed that treats the tree rings as linear-phase passive air samplers. The bark infiltration factor, IF_{BARK}, is a key parameter of the model that reflects the permeability of the bark to allow chemicals to be transferred from ambient air to the outer tree layer (cambium). An IF_{BARK} of about 2% was derived for the Red Pine trees based on tree core and air monitoring data.

1. Introduction

Tree components (e.g. bark, leaves and stem) have been used extensively as natural passive samplers for measuring environmental concentrations of contaminants. Pine tree bark and needles in particular, are excellent samplers for measuring air concentrations of persistent organic pollutants (POPs) (Meredith and Hites, 1987; Salamova and Hites, 2010) such as the polycyclic aromatic hydrocarbons (PAHs) (Lehndorff and Schwark, 2004; Tremolada et al., 1996; Ratola et al., 2006; Chun, 2014; Amigo et al., 2011; Navarro-Ortega et al., 2012; Abril et al., 2014) and more recently the polybrominated diphenyl ethers (PBDEs) (Zhu and Hites, 2006; Wen et al., 2009; Ratola et al., 2011; Fu et al., 2014). POPs can enter plants through exchange between foliage and air (Paterson and Mackay, 1994; Simonich and Hites, 1994a; Terzaghi et al., 2015; Hassanin et al., 2005) with mass balance models determining vegetation removes up to 44% of PAHs emitted to the atmosphere (Simonich and Hites, 1994b). Uptake of POPs from soil to the root system (and hence translocation through the tree) is considered to be limited due to the hydrophobic nature of these compounds (Odabasi et al., 2015; Yin et al., 2011a). Bark as a passive sampler captures both the particle bound and vapour phase compounds (Chun, 2014; Salamova and Hites, 2013; Odabasi et al., 2015), although the capacity for capturing particle bound POPs is dependent on morphological characteristics of the bark such as surface area and roughness (Chun, 2014). Bark with a greater coarseness allows the capture of air bound particulates, along with vapour

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http://dx.doi.org/10.1016/j.atmosenv.2016.06.024

phase compounds, facilitating diffusion into the thin layer of wood next to the bark (the cambium, Fig. SI-1). Thus Red Pine trees are ideal for sampling of POPs present in both gaseous and particle phases of air.

Using tree components as samplers of POPs in air is advantageous as they are ubiquitous, have no cost or maintenance requirements and can be used to reconstruct historic trends. The primary uptake pathway of PAHs into trees is suggested to be via air through gaseous and particle-bound deposition onto foliage (Yin et al., 2011a). Yin et al. (Yin et al., 2011b) used a Burken's Donut model of uptake of PAHs in gingo trees to demonstrate that PAHs entering a tree through deposition in tree foliage would undergo vertical translocation through the tree (via xylem in the cambium, Fig. SI-1) yet radial diffusion into a tree trunk would be negligible, i.e. PAHs entering the tree should primarily stay in the 'newest' section of the trunk, or within that particular years growth ring. Thus, analysis of tree rings should provide information on historic trends of POP in air. A second mechanism proposed here for accumulation of compounds is by direct mass-transfer through the tree bark onto the underlying wood layer (cambium), which has been demonstrated previously for heavy metals (Watmough and Hutchinson, 2003). This would involve a combination of diffusion of the chemical through the bark layer and/or infiltration of vapour-phase and particle-bound compounds through the coarse bark layer with direct deposition to wood.

Few studies have analysed wood in selected trees for assessing levels and historic trends of POPs. Kuang et al. (Kuang et al., 2011) analysed Mason Pine (*Pinus massoniana* L.*)* samples from two industrial sites for PAHs, analysing segments representing five year growth intervals. The PAH pattern at both sites showed primarily pyrogenic sources (combustion) to air, with the 4-ring PAHs (sources: vehicular exhaust and industrial coal burning) peaking around 1976–1980. More recently, Odabasi et al. (Odabasi et al., 2015) analysed pine trees in Turkey for a range of POPs including PAHs, polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs) and PBDEs with tree cores divided into 5 year growth intervals. POP concentrations in cores increased from 1980 to 1995, corresponding with an increase in major industries in the area.

In the current study we develop and test a method for the analysis of four classes of POPs, the polycyclic aromatic hydrocarbons (PAHs) and alkylated-PAHs, nitro and oxy-PAHs, PBDEs and the novel brominated flame retardants (novel BFRs), from Red Pine (*Pinus Resinosa*) tree cores. Cores were segmented into sections representing between 5 and 15 years of tree growth to determine historical trends of POPs in Toronto air. Finally, theoretical sampling rates were calculated, assuming the uptake of POPs to the cambium layer is via mass-transfer through tree bark only. Air concentrations were derived and compared with measured air concentrations of POPs.

2. Materials and methods

2.1. Sampling

Red Pine tree core samples were collected from the Environment Canada (Downsview) field site in Toronto, Ontario (43°46′56″ N 79°27′56″ W), which was selected as air concentrations of POPs were already characterised from previous sampling campaigns (Shoeib et al., 2014; Eng et al., 2014). The sampling site is also adjacent to a park and not influenced by just a single emission source, and thus representative of a larger footprint of sources from across the city. Cores were obtained from 6 trees, sampled with a handheld stainless steel borer (14 inch, 0.2 inch diameter, 3 thread, Forestry Suppliers Inc, Jackson, MS, USA), cleaned with acetone between sampling. Cores were stored in pre-cleaned 15 mL polypropylene tubes, at 4 °C, before extraction. Four of the cores were sectioned into two parts separating at the point marking the last 30 years of growth of the tree (as represented by counting tree rings). The most recent 30 years of growth were then extracted to determine indigenous concentrations in the core whereas the second section of the core (representing ~30–50 years of tree growth) was used for matrix spike recovery experiments.

A further two cores were collected and separated into growth segments representing between 5 and 15 years, by counting tree rings. Target analytes are listed in Tables SI-1 to 3 and cover four POP analyte groups: the PAHs including the alkylated PAHs (alk-PAHs), nitro and oxy-PAHs, PBDEs and novel BFRs. Extraction, cleanup and analysis details are provided in the supplementary information, along with QA/QC data including information on blank and MDL calculations.

3. Results and discussion

3.1. Analyte concentrations in pine trees

Concentrations of POPs are reported here as ng/g (wet weight) as poor correlations have been reported in previous studies between POP concentrations in bark or tree cores and lipid content (Chun, 2014; Odabasi et al., 2015). In the core representing most recent 30 years of tree growth, few PAHs were detected (mean concentrations of 0.2–4.7 ng/g) however the alk-PAHs were detected more frequently and in higher concentrations than their PAH counterparts (0.2–35 ng/g), Table SI-5. The oxy-PAH, 1,4-naphthoquinone, was detected at concentrations 10 fold higher (mean of 5.7 ng/g) than the other nitro or oxy-PAHs which were all close to detection limits, Table SI-6.

The PBDEs present in the PentaBDE formulation (primarily BDE 47, 99, 100) dominated in the 30 year core samples with a mean concentration of Sum 47, 99 and 100 (ΣPentaBDEs) at 12 ng/g whilst BDEs 85, 153 and 154 (primarily in the OctaBDE formulation) were detected at ~0.6 ng/g in the cores, Table SI-7. The higher molecular weight BDEs (183 and 209) were not detected in cores above MDLs. The novel BFRs, which are mainly particle-bound in air (Shoeib et al., 2014), were all detected in the cores (except beta1,2,5,6Tetrabromocyclooctane (β-TBECO) which was <MDL) with mean core concentrations of 0.3–0.95 ng/g, suggesting the pine trees captured both particle bound POPs and those located primarily in the vapour phase. Toronto air concentrations of these flame retardants have previously been published by Shoeib et al. (Shoeib et al., 2014) from a high volume active air sampling campaign conducted throughout 2010 at the same sampling site. The higher molecular weight PBDEs (BDE 183 and 209) were collected in air yet these congeners were not detected in the tree cores. BDE-209 was present in air at concentrations ~30 times lower than the ΣPentaBDE congeners so the detection limits of the tree core method may be too high for BDE-183 and 209 detection at these concentrations.

A comparison of the flame retardant profiles in both air (mean of samples from 2010) and the tree cores (30 year mean) show similar profiles, with the PentaBDEs dominating over the other flame retardants, Fig. 1.

In the reported air samples (Shoeib et al., 2014), the novel BFRs that primarily occur in the vapour phase (Ally-2,4,6-tribromophenyl ether (ATE) and Beta tetrabromoethylcyclohexane (TBECH)) had higher relative contributions to the ΣnovelBFRs than the particle bound compounds, yet in the tree core the relative contributions were more consistent between the particle bound and vapour phase compounds. These differences between relative contributions in air vs tree trunk segments may reflect differences in the relative proportions of the FRs in ambient air at this site