Distribution and variation of organophosphate esters in the tree rings of arbor

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Research Article

Keywords: Organophosphate esters, Emerging pollutants, Arbor, Tree rings, Pollution characteristics, Inter-annual variation

Posted Date: June 13th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1659674/v1

Abstract

Organophosphate esters (OPEs) are a kind of emerging pollutants. Tree trunks are long-lasting reservoirs of OPEs in the environment. Using tree rings to study the temporal and spatial distribution characteristics of emerging pollutants - OPEs has a good indication of the use of OPEs in the region, and provides scientific support for the prevention and control of emerging pollutants such as OPEs. At present, the research on OPEs in tree rings is almost blank. In this study, gas chromatography-tandem mass spectrometry (GC-MS) was used to quantitatively analyze 6 kinds of OPEs in tree rings of 5 tree species from Sichuan Province, China. Its distribution characteristics and inter-annual variation were discussed and the pollution process of OPEs in this area was inferred. The results showed that Σ_6OPEs concentration in tree rings ranged from 189.79 (Fir) to 341.23 ng/g (Toona sinensis), with an average of 284.77 ± 46.66 ng/g. There was no significant difference in the distribution of OPEs among the 5 kinds of trees and the dominant monomer was TBEP resulting that arbor could be seen as a good passive sampler to show the historical changes of OPEs in the regional environment. Interestingly, the absorption and accumulation of arbors to OPEs was quite different from that to inorganic elements reported by other studies. Concentrations of TEHP and TnBP in each ring sample of the 5 arbor species were stable, while concentrations of the other 4 monomers fluctuated significantly.

Introduction

Organophosphate esters (OPEs) are a kind of emerging persistent organic pollutants. As the brominated flame retardants being gradually banned in many countries, OPEs have become the main substitute of brominated flame retardants because of its high flame retardant efficiency and economic availability. OPEs are widely used in different industries and consumer products such as textile, construction, electronic equipment, etc (Pantelaki et al. 2020; Wang et al. 2015). However, some OPEs have been proved to have reproductive toxicity, neurotoxicity, carcinogenicity and other health risks (Xu et al. 2018; Reemtsma et al. 2008). At present, OPEs have been detected in various environmental matrixes such as water (Ren et al. 2019; Yin et al. 2021), sediment (Castro-Jiménez et al. 2016), atmosphere (Yin et al. 2020), dust (Saito et al. 2007), soil (Wang et al. 2019), human urine (Schindler et al. 2009) and breast milk (Sundkvist et al. 2010), even in remote Arctic and Antarctic regions (Fu et al. 2021). In this paper, tri-n-butyl phosphate (TnBP), tris-(2-ethylhexyl) phosphate (TEHP), tris-(2-butoxyethyl) phosphate (TBEP), triphenyl phosphate (TPhP), tris-(2-chloroethyl)-phosphate (TCEP) and trichloropropyl phosphate (TCPP) were selected because they are common in literature reports (Bacaloni et al. 2008; Shi et al. 2016), and covers three classes of OPEs: alkyl OPEs (TnBP, TBEP, TEHP), chlorinated OPEs (TCEP and TCPP) and phenyl OPEs (TPhP). OPEs with different substituents have different physical and chemical properties (Table 1), so there are great differences in their bioaccumulation capacity (Wang et al. 2016; Chen et al. 2019).

Many studies have shown that tree rings can serve as a useful passive air sampler to monitor the long-term trends of pollutants such as inorganic pollutants, heavy metals and PAHs, and reveal the historical changes in the bioavailability level of polluting elements in the environment (Wang et al. 2021). Contaminants can enter tree rings in many ways (Wen et al. 2004), and tree rings in different ages can truly reflect the environmental information in that year (Yang et al. 2011). Therefore, the study of tree rings can reproduce the high-resolution history of environmental pollution, and determine the source and spatial path of pollutants entering the environment as well (Scanlon et al. 2020). Compared with shrub growth rings, arbor growth rings are generally wider with clear boundaries and easy to distinguish; compared with other plants commonly used in biological monitoring (such as lichens and mosses), arbor growth rings have a clear temporal trend. Therefore, this study chose arbor as the research object. However, large number of studies have focused on heavy metals in tree rings (Xu et al. 2005; He et al. 2021; Yin et al. 2011), while the research on trace organic pollutants - OPEs is almost blank. OPEs only have anthropogenic sources and no natural sources, therefore, monitoring the pollution level and distribution characteristics of OPEs in arbor is conducive to infer the pollution degree and profile of OPEs as well as provide basic data for the study of organic pollution in this area.

Leaves, bark and tree rings are good passive samplers for persistent organic pollutants (POPs), which can accurately reflect the large-scale and long-term pollution of POPs (Yin et al. 2011). Tree trunks are long-term reservoirs of atmospheric OPEs, and tree rings can reproduce historical changes in atmospheric OPEs pollution levels. Therefore, tree rings over 5 years can fully provide the information of the use and pollution history of OPEs in the region. In this study, 5 arbor species were selected and the objectives are to: (a) compare the concentration level and pollution characteristics of OPEs in tree rings among different tree species; (b) understand the distribution and correlation of 6 OPEs in 5 kinds of arbor trees; and (c) obtain the inter-annual variation of OPEs among different tree species and infer its pollution history in the study area.

Table 1
Physicochemical properties of common OPEs

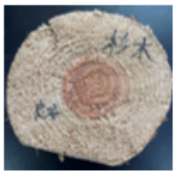
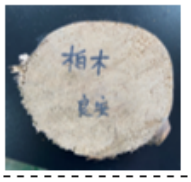
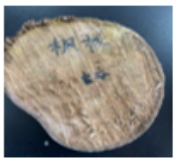
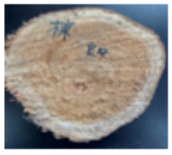
classification	abbreviation	CAS	molecular weight	Molecular formula	logKow	logKoc	BCF	Water solubility
Alkyl phosphates	TnBP	126-73-8	266	$C_{12}H_{27}O_4P$	4	3.28	1.03×10^3	0.04%(20℃)
	TBEP	78-51-3	398	$C_{18}H_{39}O_7P$	3.75	4.38	1.08×10^3	< 2g/L
	TEHP	78-42-2	434	$C_{24}H_{51}O_4P$	9.49	6.87	1×10^6	< 1g/L
Phenyl phosphates	TPhP	115-86-6	326	$C_{18}H_{15}O_4P$	4.59	3.72	113	insoluble
Chlorinated phosphates	TCEP	115-96-8	285.5	$C_6H_{12}C_{l3}O_4P$	1.44	2.48	1.37	7g/L(20℃)
	TCPP	13674-84-5	327.5	$C_9H_{18}C_{l3}O_4P$	2.59	2.21	8.51	1.6g/L(20℃)

Materials And Methods

Sample collection

Liang'an Town is located in Ziyang City, Sichuan Province, China which is in a temperate region, 46 km away from the county seat and 110 km away from Chengdu. The trees here grow faster in spring and summer to form loose xylem (earlywood), and slower in autumn and winter to form dense xylem (latewood). The alternate distribution of loose and dense ring makes it easy to distinguish tree-rings. At the same time, Liang'an town is a typical traditional agricultural town dominated by agriculture, animal husbandry and aquaculture activities. There is no industrial facilities, so the impact of OPEs point source pollution could be neglected. Therefore, the forest farm in Liang'an town (30°30'28.35"N 104°56'34.43"E) was selected as the sampling site, and 5 common perennial tree species: Toona sinensis, Cypress, Fir, Pterocarya stenoptera and Dongmu were selected as the research objects. They were in good growth condition, with similar tree ages. All of them were 8–10 years old, and the number of tree rings could meet the analysis needs of the latest eight years.

After the collected wooden piles being air-dried, the bark was removed and the rough surface of the tree disk was polished smoothly to distinguish the growth rings. By taking a complete circle of earlywood and latewood near the outermost layer as the first ring (the samples were collected in 2020, so the latest ring was formed in 2019). Every two growth rings from sapwood to heartwood were segmented for one study period, and the samples were numbered from 1 to 4 by year. More details of sampling were illustrated in Table 2.

Tree species	Introduction	Ring year	Sample number
Toona sinensis 	Arbor, the bark is rough, dark brown and flaky. Leaves long stalked. Even pinnate compound leaves, 30-50 cm long	2012-2013	XC1
		2014-2015	XC2
		2016-2017	XC3
		2018-2019	XC4
Fir 	Arbor, bark grayish brown, split long strip off, endothelial light red. Leaves firm and lanceolate or striped lanceolate, 2-6 cm long and 3-5 mm wide	2012-2013	SM1
		2014-2015	SM2
		2016-2017	SM3
		2018-2019	SM4
Cypress 	Arbor, bark light brownish gray, divided into narrow strips, Scaly leaves 2 - shaped, 1-1.5 mm long, apex acute	2012-2013	BM1
		2014-2015	BM2
		2016-2017	BM3
		2018-2019	BM4
Pterocarya stenoptera 	Arbor, bark smooth, light gray when young, deep longitudinal split when old. Leaves often even or rare pinnately compound, 8-16 cm long, petiole 2-5 cm long	2012-2013	FY1
		2014-2015	FY2
		2016-2017	FY3
		2018-2019	FY4
Dongmu 	Arbor, bark dark brown, longitudinal crack, lenticel more obvious. Leaves alternate, leaflets ovate to elliptic, 2-3 odd pinnate compound leaves	2012-2013	DM1
		2014-2015	DM2
		2016-2017	DM3
		2018-2019	DM4

Instruments and reagents

The main instruments included gas chromatography-mass spectrometry (Shimadzu, Japan, GC-MS 2010 plus) and vacuum concentrator (Buchi, Switzerland, R-215/v-700). The main reagents, such as ethyl acetate, acetone, hexane and acetonitrile, were high-performance liquid chromatography (HPLC) grade (Kelon Chemical Corp., China). The standard solution (Sigma Aldrich Corp., U.S.A.) included tri-n-butyl phosphate (TnBP), tris-(2-butoxyethyl) phosphate (TBEP), tris-(2-ethylhexyl) phosphate (TEHP), triphenyl phosphate (TPhP), tris-(2-chloroisopropyl) phosphate (TCPP) and tris-(2-chloroethyl) phosphate (TCEP). Copper, aluminium oxide, silica gel, Na_2SO_4 and other chemicals were purchased from Kelon Chemical Corp., China. The surrogate standard was triphenyl phosphate-d15 (TPhP-d15). Ultrapure water was obtained from Milli-Q equipment.

Sample pretreatment and clean up

In the process of sample preparation, the circular wooden pile was divided into fan-shaped areas with an electric saw. Considering the difference in growth speed between the north and south sides of the tree, a fan-shaped area of the same size was taken from the sparse surface (sunny surface) and dense surface (shady surface), respectively, so as to ensure the preciseness. The divided piles were mixed and crushed with an electric grinder and screened through 100 mesh, then the samples were wrapped in tin foil paper and labeled.

1.0000 g sample was accurately weighed and added into the test tube, soaked in 20 mL ethyl acetate: acetone (3:2 V/V) for 12 h, and then ultrasonic extracted for 30 min twice. The extraction solution was combined and centrifuged at 3000 r/min. The supernatant was transferred to a concentration bottle and concentrated to about 1 mL with a vacuum concentrator. 5–10 mL n-hexane was added for solvent conversion, and the supernatant continued concentrating to about 1 mL again. Then, it was separated and purified by silica gel/alumina/anhydrous sodium sulfate chromatography column activated with n-hexane. After 10 mL of n-hexane was added for removing the co-extracts, the target compounds were eluted with 20 mL of ethyl acetate: acetone (3:2 V/V), and the eluent was concentrated to 200 µL.

Instrumental analysis

The GC was equipped with a capillary column Rti-5MS (30 m × 0.25 mm× 0.25 µm), with a 280 °C inlet temperature using splitless injection. The MS source was electron impact (EI) and operated in selected ion monitoring (SIM) mode. Helium was used as a carrier gas with a flow rate of 1.00 mL/min. The GC oven temperature was held at 50 °C for 1 min, increased to 200 °C at 15 °C/min and held for 1 min, increased to 250 °C at 4.00 °C/min, and then increased to 260 °C at 20 °C/min and held for 4 min. The interface temperature was 280 °C, and the ion source temperature was 200 °C.

Quality assurance and Quality control (QA / QC)

The external standard method was used for quantification. The R^2 of the standard curve of each OPEs component was greater than 0.99. Surrogate standard (TPhP-d15: 100 ng) was added to each sample to determine the recoveries, and the recoveries ranged from 64–83%. The limits of detection (LOD) (Signal-to-noise ratio = 3) ranged from 0.02 ng to 0.4 ng. The instrument precision ranged from 1.9–8.3%. Only TBEP was detected in the blank experiment, and its maximum concentration was lower than 5% of the sample concentration.

The pictures in this paper were drawn by Origin 2017. Statistical analysis was performed with SPSS Statistics version 25 for Windows. Correlations between OPEs monomers concentrations in 5 tree species were analyzed by Pearson correlation coefficients. Non-parametric test was used to analyze the difference between Σ_6OPEs concentrations of 5 tree species. In order to explore the distribution differences of each monomer in 5 tree species, Friedman test was used for multiple comparison.

Results And Discussion

concentration of OPEs in tree rings

As shown in Fig. 1 (see Table 2 for more sample number details), the detection rate of 6 OPEs monomers in all samples was 100%, indicating that OPEs pollution was widespread in trees in the sampling area. High potential of long-range atmospheric transport and persistence of OPEs would be responsible for their presence in areas where there are few pollution sources (Wang et al. 2018). In addition, Even though their reported half-lives were short at atmosphere (< 21.3 h), OPEs could bind with air particles, which greatly enhance their persistence in the environment (Wei et al. 2015). This can explain the high detected frequencies of each individual OPEs in present study. Σ_6OPEs concentration in the tree-rings ranged from 189.79 to 341.23 ng/g, with an average of 284.77 ± 46.66 ng/g. The order of Σ_6OPEs concentration in various tree species was: Toona sinensis (320.64 ± 13.63 ng/g) > Cypress (301.46 ± 33.28 ng/g) > Pterocarya stenoptera (275.26 ± 48.53 ng/g) > Dongmu (274.12 ± 40.44 ng/g) > Fir (264.70 ± 50.82 ng/g). In terms of the average concentration of Σ_6OPEs over the last eight years, the Toona sinensis had the highest Σ_6OPEs concentration which was 1.2 times that of the Fir with the lowest concentration. This may be because stomata and lenticels are the main ways for organic pollutants to enter the xylem. The larger the leaf size and the more the number of stomata and lenticels, the easier it is for organic matter to accumulate in the growth rings (Kuang et al. 2011). SPSS software was used to conduct significant difference analysis between Σ_6OPEs concentration of 5 tree species. The results showed that $P = 0.433 > 0.05$, indicating that there was no significant difference in OPEs accumulation ability of various trees. Odabasi et al. (2015) reported that the concentration of

POPs in tree-rings in industrial areas (Σ_{16}PAHs: 2526 ng/g, Σ_{41}PCBs: 15.6 ng/g, Σ_{32}PCNs: 2.35 ng/g, Σ_{7}PBDEs: 16.65 ng/g) was higher than that in background areas (Σ_{16}PAHs: 1767 ng/g, Σ_{41}PCBs: 6.7 ng/g, Σ_{32}PCNs: 1.31 ng/g, Σ_{7}PBDEs: 6.51 ng/g) in Aliaga, Turkey. Compared with this paper, the concentration of OPEs was higher than many POPs (PCBs, PBDEs, PCNs, etc.), suggesting that OPEs pollution should be paid attention to. Compared with other literatures, Xu et al. (2005) studied the accumulation of 12 inorganic elements in 5 trees in Xiangshan, Beijing, and found that there were significant differences in the absorption and accumulation of inorganic elements among different tree species. Wu et al. (2017) found that a single tree species had different absorption capacities for different heavy metal elements by comparing the concentration of 8 heavy metal elements in 5 tree-rings, and the ability of 5 trees absorbing the same heavy metal element was also different. Xue et al. (2016) measured the accumulation of Zn, Cu, Pb, Cd, Hg and As in the trunk of seven plantations in Harbin and found that there were differences in the comprehensive accumulation ability of different plantations to heavy metals. Therefore, the absorption and accumulation of arbors to inorganic elements was inconsistent with that of organic pollutants in this paper. Compared with OPEs concentrations in leaves reported by other studies, the pollution degree of Σ_{6}OPEs in tree-rings in this study could not be ignored. For example, Santos et al. (2020) reported OPEs concentration in leaves of Bitter orange in Seville (TPhP: 47.5–265 ng/g, TCPP: 321–1058 ng/g) and Chen et al. (2019) reported that the concentration of Σ_{7}OPEs in leaves of Magnolia and Loquat were 191.3 ng/g and 83.1 ng/g, respectively. Therefore, the tree-rings are an important storage medium of OPEs in the environment.

Distribution and correlation of OPEs

The distribution of OPEs monomers in 20 samples from 5 tree species was shown in Fig. 2. In the distribution profile of OPEs, the concentration of TBEP in each sample was the highest, accounting for 31.60%-61.33% of Σ_{6}OPEs, followed by TCEP, TCPP, TPhP and TnBP, respectively, and TEHP was the lowest covering 2.11%-6.12% of Σ_{6}OPEs. In order to explore the distribution differences of each monomer in 5 tree species, Friedman test of SPSS Statistics version 25 was used for multiple comparison of 6 OPEs in 20 samples. $P = 0.1027 > 0.05$ indicated that there was no significant difference in OPEs composition distribution among 5 tree species. Therefore, the trunk rings of different tree species collected in this study have no obvious selectivity to the accumulation of OPEs, indicating that different types of tree species can be used as a good passive sampler to show the historical changes of emerging pollutants with similar physicochemical properties to OPEs in the regional environment.

According to current studies, the primary OPEs in atmospheric particulates in the suburbs of Chengdu were TBEP, followed by TCEP. The concentration of this two OPEs accounted for 57.44% of ΣOPEs, and the lowest TEHP accounted for 8.21% of ΣOPEs (Yin et al. 2015). The highest concentration of TBEP in Chengdu soil covered 52%-92% of ΣOPEs (Yin et al. 2016). For hydrophobic semi-volatile organic chemicals (SVOCs), atmospheric uptake was the primary mechanism and then accumulated in the new inner wood growth layer (the cambium), also known as the new tree-ring (Rauert et al. 2020). Compared with the distribution of OPEs in atmospheric particulate matter and soil in Chengdu, the concentration distribution characteristics of OPEs monomers in tree rings sample were similar to them to some extent, so tree rings could reflect the distribution of regional pollutants. In addition, Σ_{6}OPEs concentration in each annual ring was about 2–3 times that of Σ_{6}OPEs (99.9 ± 43.0 ng/g) in soil of Chengdu, suggesting that the trunk was an important sink of OPEs.

Pearson correlation analysis was used to analyze the correlation of OPEs in 20 samples of 5 tree species. As shown in Table 3, the correlation of TPhP and TCPP, TEHP and TCPP at 0.01 level was 0.689 and 0.714, respectively, while the correlation between other components was low, indicating that TPhP and TCPP, TEHP and TCPP in tree-rings samples in this area had homology.

Table 3
Correlation between different OPEs monomers in annual ring samples

	TnBP	TCEP	TCPP	TPhP	TBEP	TEHP
TnBP	1.000	0.363	0.175	0.187	-0.252	0.480*
TCEP	0.363	1.000	0.429	0.429	0.210	0.350
TCPP	0.175	0.429	1.000	0.689**	-0.073	0.714**
TPhP	0.187	0.429	0.689**	1.000	0.180	0.410
TBEP	-0.250	0.210	-0.070	0.180	1.000	-0.375
TEHP	0.480*	0.350	0.714**	0.410	-0.375	1.000
1)*. At level 0.05 (double-tailed), the correlation was significant.						
2)**. At level 0.01 (double-tailed), the correlation was significant.						

According to different substituents, the 6 OPEs monomers can be divided into alkyl phosphate (TnBP, TBEP, TEHP), chlorinated phosphate (TCEP and TCPP) and phenyl phosphate (TPhP). The proportion of different kinds of OPEs in this 5 tree species was alkyl phosphate (680.03 ± 89.00 ng/g) > chlorinated Phosphate (337.49 ± 42.13 ng/g) > phenyl phosphate (129.26 ± 34.98 ng/g) (Fig. 3). The accumulation ability of all kinds of tree species to alkyl phosphate was the highest which presented that the alkyl phosphate was the dominant OPEs in this area. The profile of OPEs in Fir was alkyl phosphate: chlorinated phosphate: phenyl phosphate ≈ 5:4:1 while the general profile of OPEs in the other 4 tree rings was alkyl phosphate: chlorinated Phosphate: phenyl phosphate ≈ 6:3:1, and the concentration of chlorinated phosphate in Fir (396.20 ng/g) was also higher than that in the other 4 tree species (Toona sinensis: 349.04 ng/g > Cypress: 340.55 ng/g > Pterocarya stenoptera: 321.10 ng/g > Dongmu: 280.56 ng/g). It showed that among the various tree species, the Fir had higher enrichment ability for chlorinated phosphate.

Inter-annual variation characteristics of OPEs in tree rings

Inter-annual variation of Σ_6OPEs in tree rings

In all kinds of trees, the variation trend of Σ_6OPEs concentration with years was different (Fig. 1). Among them, The concentration of Σ_6OPEs in Toona sinensis and Dongmu decreased year by year, and there was an obvious linear relationship between Σ_6OPEs concentration and year (Toona sinensis: $R^2 = 0.9882$, Dongmu: $R^2 = 0.9173$). The difference was that the Σ_6OPEs concentration decreased faster in Dongmu than in Toona sinensis. However, the Σ_6OPEs concentration in Cypress basically showed a slowly increasing trend while Σ_6OPEs concentration in Fir and Pterocarya stenoptera fluctuated greatly which showed no obvious unidirectional trend. For Fir, the concentration of Σ_6OPEs increased year by year in the first three groups, and reached the highest value (341.23 ng/g) in the third group (2015–2016), then decreased by about 1/3 in the fourth group (2017–2018). For Pterocarya stenoptera, the concentration of Σ_6OPEs in the first three groups fluctuated greatly, with a fluctuation range of 189.79-314.82 ng/g (inter-group variation: 9.9%-66.1%). For Cypress, the concentration of Σ_6OPEs fluctuated in the range of 254.00-329.30 ng/g (inter-group variation: 4.4%-23.6%), and the maximum value (329.33 ng/g) appeared at the second group (2014–2015), while the fourth group had a significant decline, which was 23.6% lower than that in the third group. The results showed that the sensitivity of different tree species to OPEs in the same area was different.

Inter-annual variation characteristics of OPEs monomer in each tree specie

The variation characteristics of OPEs monomer in different tree species varied greatly with the growth of rings (Fig. 4). Among them, the concentrations of TCPP and TPhP in Fir fluctuated greatly, and the highest concentration was 2.6 and 3.5 times of the lowest concentration, respectively. TCPP, TPhP, TEHP and TBEP showed an upward trend with the year, and reached the highest value in the third group. There was no significant change in TnBP concentration among annual rings and the fluctuation range of TCEP in each year was 9.8%-28.6%. As for Toona sinensis, the concentration of OPEs monomer changed little with years, and the fluctuation range of TBEP with the highest concentration was < 10%. For Cypress, the concentration of TBEP fluctuated from 144.54 to 184.57 ng/g (inter-group variation ~ 20%) and TPhP changed the most between the second group and the third group. The concentration of TCEP in the second group was 77% higher than that in the first group. For Pterocarya stenoptera, the variation of TPhP was the largest from the second group to the third group and the TPhP concentration in the third group was twice higher than that in the second group. The largest change of TBEP concentration was from the first group to the second group and the concentration of TCEP fluctuated between 32-63.74 ng/g. For Dongmu, except for the concentration of TCEP and TPhP, the other four OPEs monomers showed a downward trend year by year. Compared with the concentration in the first group, the concentration of TnBP, TCPP, TBEP and TEHP in the fourth group decreased by 13.8%, 43.1%, 27.3% and 43.2%.

In general, TBEP concentration showed the greatest influence on the variation of Σ_6OPEs in different tree species. The concentrations of TEHP and TnBP were relatively stable, while the concentrations of the other 4 monomers fluctuated significantly. Among different OPE components, TnBP has a short half-life (< 1d) and cannot exist for a long time in the environment (Li et al. 2018), so its interannual variation characteristics might indicate that there is continuous and stable pollution input in the local area. In addition, TnBP is often added as a plasticizer and additive in varnishes, concrete and plastics, and is widely used in construction and agricultural production (Wang et al. 2022). The study area in this paper mainly relies on agricultural development, so sewage irrigation and plastic film application in agricultural activities may be an important source of local OPEs pollution. As mentioned above, the accumulation of OPEs did not differ significantly among the five arbor species. However, the fluctuation of each monomer in Fir was relatively obvious, indicating that Fir was more sensitive to the change of OPEs monomer. Therefore, the adaptability of tree species should be considered when selecting trees to reflect the bioavailability and historical changes of pollutants in the environment. According to other studies, Conifer xylem has a high concentration of organic matter (such as Turpentine and Rosin), which showed the strong ability to absorb organic matter from the atmosphere and preserved them over time (Kuang et al. 2011).

Conclusions

There was no significant difference in the total concentration and distribution of OPEs in 5 kinds of arbor species indicating that arbor could be used as a good passive sampler to show the historical changes of emerging pollutants with similar physicochemical properties to OPEs in the regional environment. Therefore, it is suggested that the concentration and distribution of OPEs in the annual rings of whatever kind of local arbor species all over the world could be used to be roughly compared in a wide range. This could an effective scientific means to provide the usage and the pollution history of OPEs in different countries. If more detailed comparison is required, further study should be carried out. Among 5 kinds of arbor species, Fir was more sensitive to the change of OPEs monomer.

Declarations

Acknowledgements This work was financially supported by the National Natural Science Fundation of China. (No.41773072)

Ethical Approval Not applicable

consent to participate Not applicable

Consent to publish Not applicable

Authors' contributions Hongling Yin and Shuhong Fang contributed to the study conception and design. Methodology, material preparation, data analysis and writing were performed by Jiaojiao Song and Xiaoyu Xiong. Experiments were carried out by Xiaoyu Xiong, Jiaojiao Song and Yuanming Xiong. Writing-review was performed by Hongling Yin and Shuhong Fang. All authors commented on the previous versions of the manuscript. All authors read and approved the final manuscript.

Funding: This work was supported by National Natural Science Fundation of China (Grant numbers No.41773072).

Competing interests The authors declare that they have no competing interests

Availability of data and materials The datasets used and analysed during the current study are available from the corresponding author on reasonable request.

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Figures

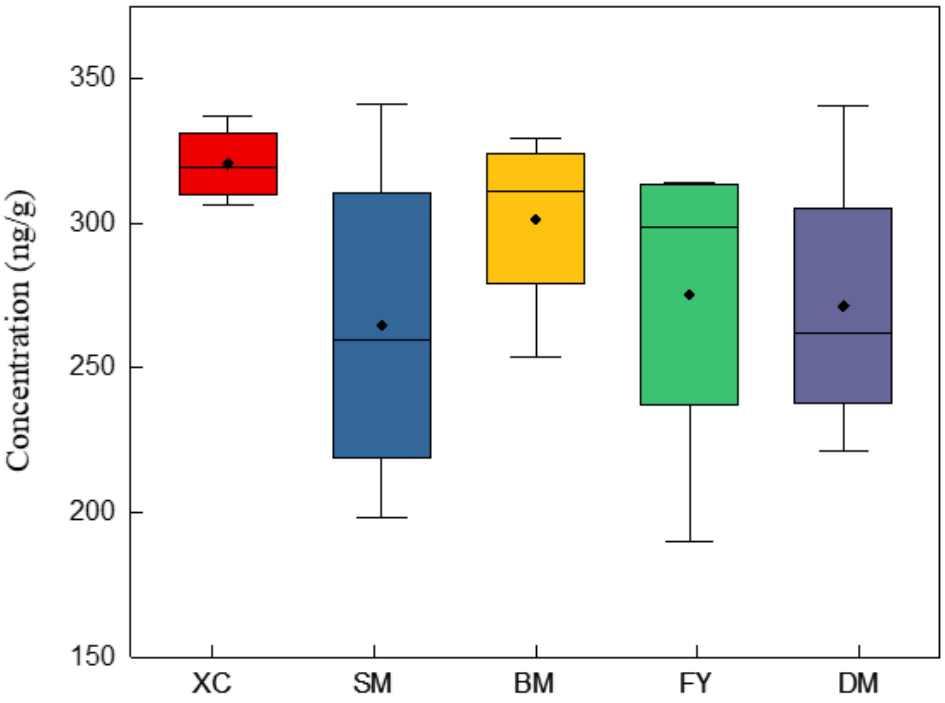

Figure 1

Concentrations (ng/g) of Σ_6OPEs in each annual ring sample from 5 kinds of trees. The black horizontal line inside each box represents the median, the boxes represent the 25th and 75th percentiles of concentrations, whiskers represent value of 1.5*IQR (Inter Quartile Range).

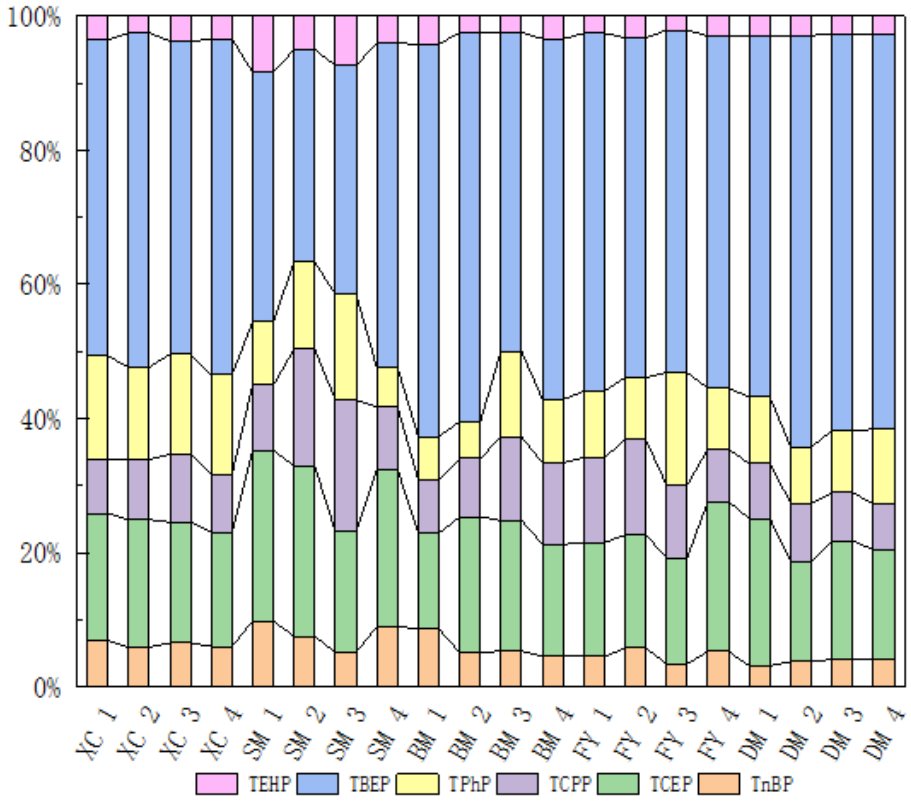

Figure 2

Distribution of OPEs in samples

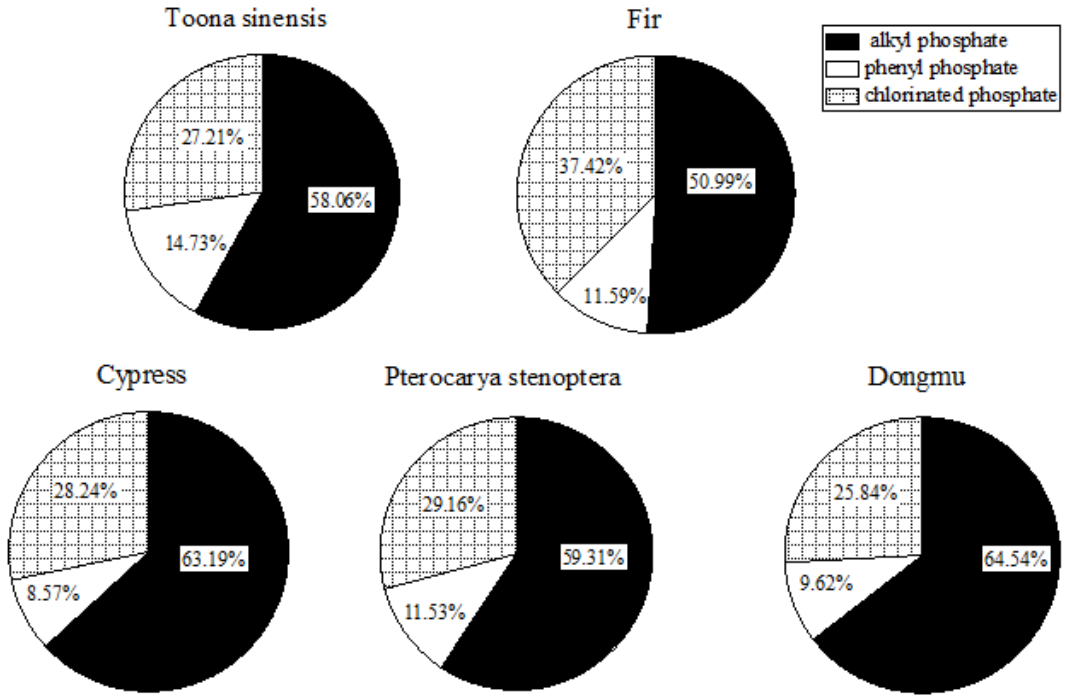

Figure 3

Proportion of three types of phosphate esters in different tree species

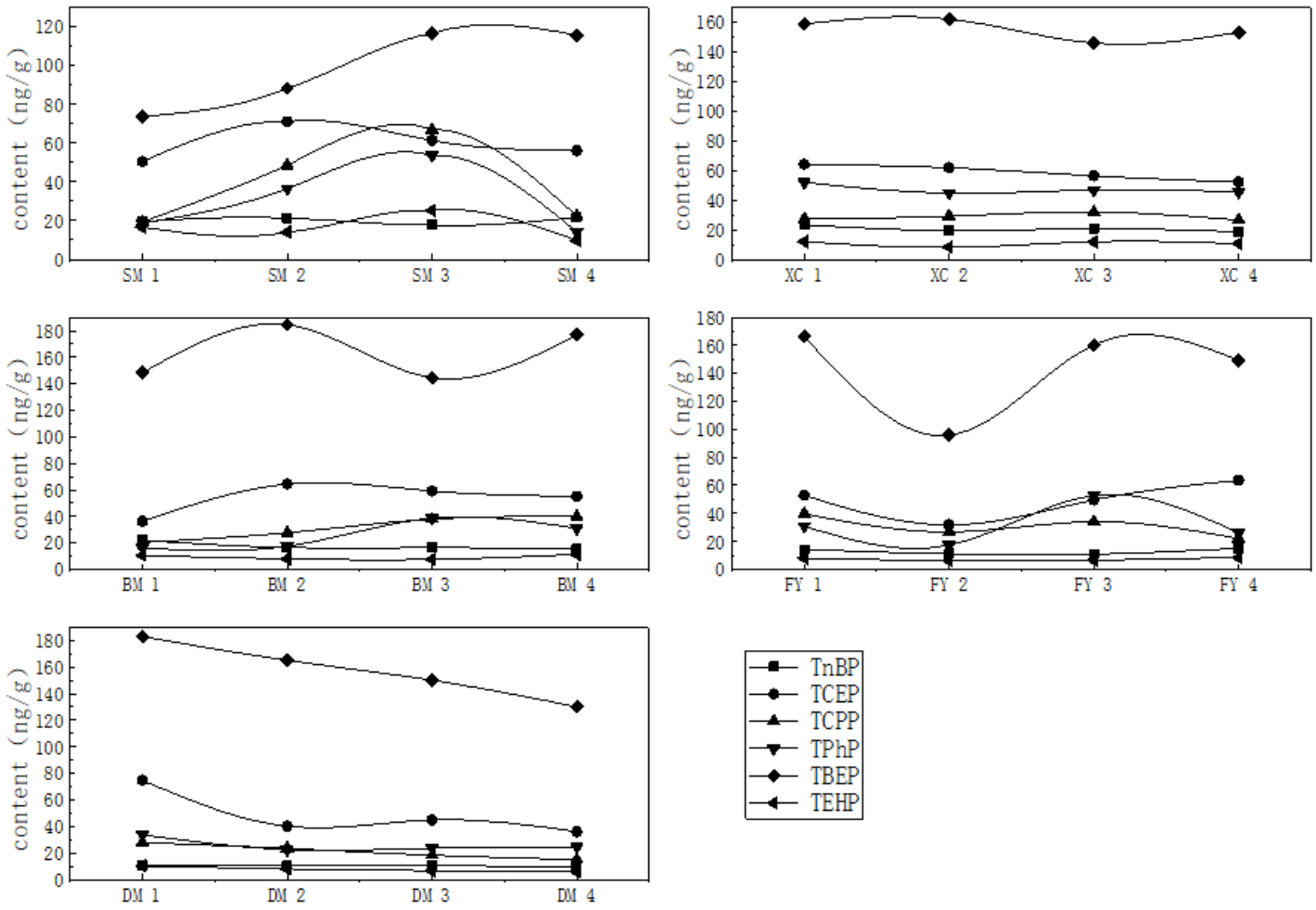

Figure 4

Inter-annual variation of OPEs monomer concentration in different trees