Indirect emissions from organophosphite antioxidants result in significant organophosphate ester contamination in China

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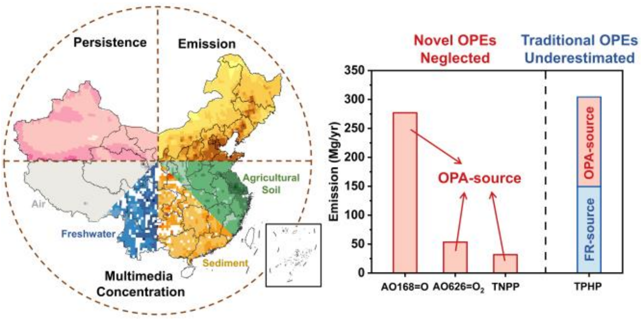
Abstract

Organophosphite antioxidants (OPAs) have been seriously neglected as potential sources of organophosphate esters (OPEs) in environments. This study utilizes a modeling approach to quantify - for the first time national emissions and multimedia distributions of triphenyl phosphate (TPHP) - a well-known flame retardant - and three novel OPEs: tris(2,4-di-tert-butylphenyl) phosphate (AO168=O), bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphate (AO626=O_2), and trisnonylphenol phosphate

(TNPP). Emphasis is on quantitative assessment of OPA source contributions in China. TPHP has 1.1–9.7 times higher emission (300 Mg/yr in 2019 with half from OPA sources) than AO168=O (278 Mg/yr), AO626=O_2 (53 Mg/yr) and TNPP (32 Mg/yr), but AO168=O is predominant in environments (63–79%) except freshwaters. About 72–99% of the studied OPEs are emitted via air, with 88-99% ultimately distributed into soils as the major sink. OPA-source emissions contribute 9.5-57% and 4.7-56% of TPHP masses and concentrations (except in sediments) in different media, respectively. Both AO168=O and AO626=O_2 exhibit high overall persistence ranging between 2–11 years. Source emissions and environmental concentrations are elevated in economically developed areas, while persistence is higher in northern areas where precipitation and temperature are lower. The study shows significance of OPA sources to OPE contamination, which supports chemical management of these substances.



Synopsis: Significance of indirect emissions of organophosphite antioxidant precursors to organophosphate ester contamination in multimedia environments is evaluated for the first time.

Keywords: organophosphate esters, organophosphite antioxidants, emission, multimedia environmental fate modeling.

Introduction

Organophosphate esters (OPEs) have received considerable international attention as extensively used flame retardants (FRs), plasticizers or other direct additives in diverse industrial and household products.[1-3] As replacements of legacy polybrominated diphenyl ethers (PBDEs), they are ubiquitously detected in various environmental matrices and biosystems, often at levels higher than peak PBDE concentrations, due to their high consumption volumes (~6.8×10^4 Mg in 2015).[3-5] Evidence suggests that OPEs may exhibit endocrine disruption effects, neurotoxicity, reproductive and developmental toxicity at environmental levels, and be detrimental to various living creatures including humans.[6-10] Under the circumstances, related agencies in the EU, Canada and the United States (US) have enforced regulations to investigate or restrict the use of several widely used OPEs, but only as FRs.[11, 12]

Important recent research has identified organophosphite antioxidants (OPAs) a poorly recognized indirect source of OPEs to the environment.[13, 14] Commonly used as auxiliary antioxidants in production of plastics and rubber, OPAs have high global consumption (~4.0×10^4 Mg in 2013), comparable to that of OPEs.[15] OPAs retard oxidation reactions of polymers via decomposing hydroperoxides and trapping peroxyl radicals, and are transformed to OPAs=O (i.e. OPEs) as their major oxidation derivatives.[16, 17] OPAs=O include both novel OPEs (NOPEs) which have no known direct sources (e.g. Tris(2,4-di-tert-butylphenyl) phosphate (AO168=O, also known as TDtBPP) and bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphate (AO626=O_2))

and traditional OPEs widely used and studied as FRs (e.g. triphenyl phosphate (TPHP)). OPAs have been detected at varying levels in product materials (e.g. food contact materials, face masks and baby products) and environments extremely close to emission sources, such as indoor or e-waste dusts and farmland soils covered by mulch films.[5, 13-15, 18-21] Outdoor field studies detected the presence of low or absent OPAs in environments, but identified NOPEs - likely converted from OPAs, with even higher levels and abundance than widely used traditional OPEs (e.g. AO168=O *versus* TPHP).[22-25] This suggests i. the extremely poor stability of OPAs under environmental oxidative (including thermo-, photo- and ozone-oxidative) conditions, which makes evaluating OPA impact on OPE environmental contamination difficult by laboratory observations (especially for the OPEs concurrently having strong direct sources), and ii. the potentially important role of OPAs as an indirect source of environmental OPEs.

A bottom-up modelling approach linking emissions to environmental contamination should prompt understanding of OPA contribution. To the best of our knowledge, current research on emission inventories and environmental fate modelling of OPEs failed to (1) capture indirect emissions of OPAs, resulting in underestimation of OPE emissions, and (2) include emission pathways such as freshwaters and soils, just focusing on the atmosphere.[26-28] Emissions of OPEs from wastewater treatment plants (WWTPs) to water systems and soils merits attention, as in previous studies.[29-32] The large uncertainties have hampered assessment of ecological or human health risks of OPE related chemicals.

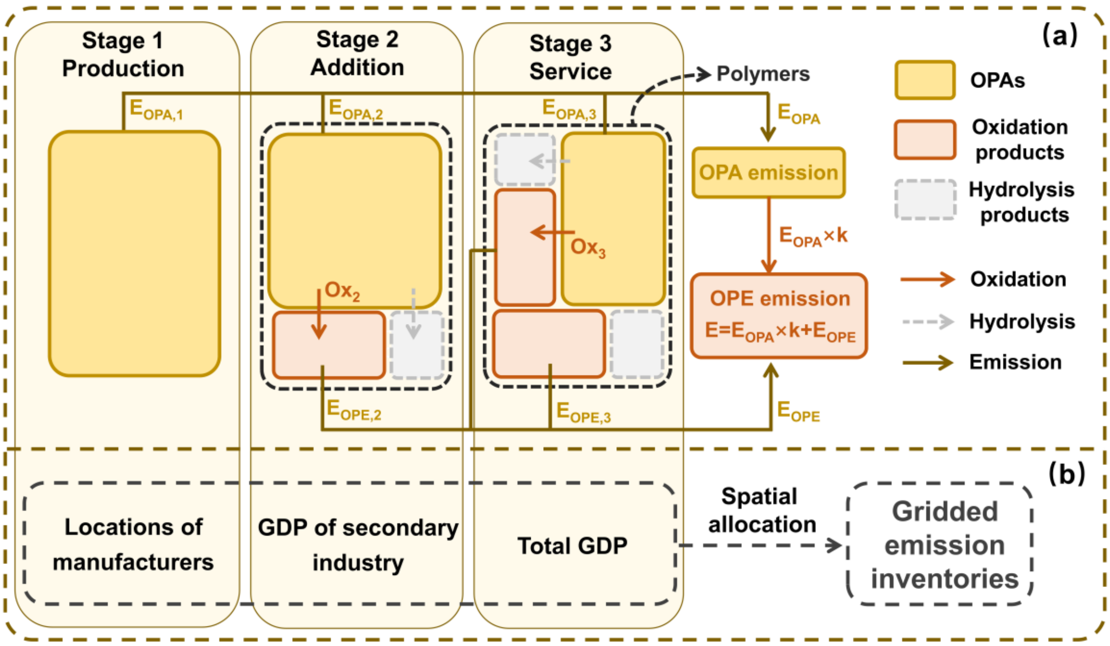
China is the world's largest producer of plastics and chemicals.[33, 34] The potential production or use of OPAs must be high in China. Here, we set up gridded emission inventories of OPEs to consider transformation of the most used OPAs in China. Multiple environmental emission pathways were considered. A well developed and verified spatially explicit multimedia environmental fate model for the Chinese Mainland - the Sino Evaluative Simplebox-MAMI Model (SESAMe v3.4 model, 0.5°) was utilized to predict concentrations, multimedia distribution and persistence of OPEs in Chinese environments. This is the first study to quantify the contribution of OPAs to OPE emissions and environmental contamination across China. We also highlight the potential eco-environmental health risk of OPEs arising from OPA use. The results help formulate more effective and efficient regulations regarding the safety management of these chemicals by policy makers.

Methods

Selected OPAs and oxidation derivatives

Four OPAs with the highest annual production volumes, cumulatively accounting for > 90% of the total OPA production in China, were selected after a preliminary screening, namely tris(2,4-di-tert-butylphenyl) phosphite (AO168), bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphate (AO626), trisnonylphenol phosphite (TNPPi) and triphenyl phosphite (TPHPi). The annual production of these four OPAs in China in 2019 was 5.6×10^4, 1.5×10^4, 9.1×10^3, and 4.3×10^4 Mg, respectively.[35-40] The first three can be oxidized to AO168=O, AO626=O_2 and trisnonylphenol phosphate (TNPP), which are NOPEs with almost no production in China as direct additives incorporated in commercial products, so far as we know. The last one has an oxidation derivative—TPHP, which is also a traditional OPE having direct emissions as FRs or plasticizers. Hence, the selection includes both situations for a full consideration of previously overlooked OPE contamination and potential risks derived from indirect sources. Detailed information of these substances is given in Table S1 and Figure S1 in the Supporting Information (SI).

Emission estimation



Scheme 1 Flowchart of methodology for developing emission inventories of OPEs derived from OPAs. (a) Estimation of total emissions of OPEs in China in different stages and (b) the method for spatial allocation of emissions in 2019; $E_{OPA,i}$ and $E_{OPE,i}$ (i = 1, 2, 3) are emissions in the stages 1 to 3; Ox_i (i = 2, 3) is the amount of OPA oxidized during Stage 2 and 3 in polymers; k is the molar mass ratio of OPEs and corresponding precursor OPAs (M_{OPE}/M_{OPA}). Hydrolysis processes and products are

present in the flowchart to show their existence, but are not specifically investigated in this study.

Scheme 1 illustrates the methodology for estimating emissions of OPA-derived OPEs - Stage 1. synthesis of OPAs, Stage 2. addition of OPAs to materials for commercial product manufacture and Stage 3. service life of commercial products. OPAs will be released into environments in all three stages. Moreover, in both Stage 2 and 3, OPAs can be oxidized to corresponding OPEs in polymer materials, which will be released from polymers to environments together with OPAs. Figure S2 illustrates the potential transformation pathways of OPAs in materials and the environment, with particular emphasis on the process of direct oxidation to form the target OPEs, as investigated in this study. Previous studies have found that 70-100% of the target OPAs can be transformed to corresponding OPEs within 80 minutes under natural light and oxidation conditions, while 47.0-98.5% can be transformed within 12 hours under dark conditions when exposed to air.[15, 41] Given the rapid oxidation kinetics in natural environments, the emission rate of OPAs from materials will likely governs the rate of transformation from OPAs to OPEs.[41] This study investigates annual emissions and subsequent spatial and across-media distribution patterns at the steady state in China, of which the timescale is much longer than the transformation period. Therefore, emission inventories were established exclusively for the target OPEs, assuming immediate transformation of OPA to OPEs upon emission into environments. Hydrolysis processes of OPAs in polymer materials and environments are not contributing to the generation of any OPEs relevant to the present research aims (Figure S2).[16] Hence, hydrolysis processes and products were not investigated in this study, but only appear in the Scheme 1 to show their existence.

Based on the above facts and assumptions, the emission (E) of OPA-source OPEs can be estimated as below:

$$E_{OPA}=E_{OPA,1}+E_{OPA,2}+E_{OPA,3} \quad (1)$$

$$E_{OPE}=E_{OPE,2}+E_{OPE,3} \quad (2)$$

$$k=M_{OPE}/M_{OPA} \quad (3)$$

$$E=E_{OPA}\times k+E_{OPE} \quad (4)$$

where E_{OPA} and E_{OPE} are the amount of OPAs and OPEs released directly from polymers, respectively; k is the molar mass ratio of OPEs and corresponding precursor OPAs (M_{OPE}/M_{OPA}). The subscripts 1, 2 and 3 indicate parameters for Stage 1, 2 and 3. Detailed methods of each stage are described below.

Stage 1. OPAs emitted to air during synthesis processes were estimated as the product of OPA production volumes (P) and the emission factor ($f_{OPA,1}$) during this stage, as shown in equation (5) (Eq. 5).

$$E_{OPA,1}=P\times f_{OPA,1} \quad (5)$$

Stage 2. Emissions during additive processes are mainly through air and freshwater,[42] which were calculated as Eqs. 6-8:

$$E_{OPA,2}=\alpha\times P\times f_{OPA,2} \quad (6)$$

$$E_{OPE,2}=Ox_2\times k\times f_{OPE,2,air}+Ox_2\times k\times f_{OPE,2,water}\times\beta \quad (7)$$

$$Ox_2=\alpha\times P\times f_{Ox,2} \quad (8)$$

where α is a coefficient reflecting international trade of OPAs for calculating national use from production in China; $f_{OPA,2}$ is the emission factor of OPAs in Stage 2; Ox_2 and $f_{Ox,2}$ are the amount and ratio of OPAs oxidized, respectively; $f_{OPE,2,air}$ and $f_{OPE,2,water}$ are the emission factors of OPEs released to air and water; β is the removal efficiency of OPEs in WWTPs. Here it is assumed that all industrial wastewater is connected to WWTPs. Different OPA oxidation ratios in plastics and rubber ($f_{Ox,2,plastic}$ and $f_{Ox,2,rubber}$) were considered in the calculation of $f_{Ox,2}$ (Eq. 9)

$$f_{Ox,2}=k_2\times(f_{Ox,2,plastic}\times p_{plastic}+f_{Ox,2,rubber}\times p_{rubber}) \quad (9)$$

where k_2 is the total conversion ratio of OPA in Stage 2; $p_{plastic}$ and p_{rubber} indicate the proportion of OPA used on plastics and rubber, respectively, out of all nationally used OPAs.

Stage 3. Emissions in this stage include the diffusive release of chemicals from product materials to air and from mulch films to agricultural soils.[5, 42]

$$E_{OPA,3}=(\alpha\times P-Ox_2)\times f_{OPA,3,air}+P_{mf}\times C_{OPA}\times f_{OPA,3,farmland} \quad (10)$$

$$E_{OPE,3}=(Ox_2+Ox_3)\times k\times f_{OPE,3,air}+P_{mf}\times C_{OPE}\times f_{OPE,3,farmland} \quad (11)$$

$$Ox_3=(\alpha\times P-Ox_2)\times p_{indoor}\times f_{Ox,3,indoor}+(\alpha\times P-Ox_2)\times p_{outdoor}\times f_{Ox,3,outdoor} \quad (12)$$

where $f_{OPA,3,air}$, $f_{OPE,3,air}$, $f_{OPA,3,farmland}$ and $f_{OPE,3,farmland}$ respectively denote the emission factors of OPAs and OPEs into the air and farmlands, released from polymers during product use; P_{mf} is the annual production volume of mulch films; C_{OPA} and C_{OPE} are the inclusion levels of OPAs and OPEs in mulch films, respectively; Ox_3 is the amount of

OPA oxidized in polymer materials during Stage 3; $f_{Ox,3,indoor}$ and $f_{Ox,3,outdoor}$ are the ratio of OPA oxidized in materials in indoor and outdoor environments, respectively, considering varying oxidative rates in indoor and outdoor conditions; p_{indoor} and $p_{outdoor}$ are the percentages of OPAs used in indoor and outdoor products/materials, respectively. Values of parameters in Eqs. 1-12 and their sources are shown in Table S2 in the SI.

The direct emission of TPHP used as FRs in China was estimated based on a total emission inventory of organophosphate FRs (OPFRs) developed by Ma *et al.*[27] The emission factors of TPHP released to air and water during its addition to materials were both 2.08×10^{-4}.[42] The land application of sludge from WWTPs was considered as soil discharge for all four OPEs. The relevant data and calculation methods are given in SI (Table S3). The production data for the selected OPAs from 2010 to 2021 in China were obtained from industry database, national statistical data and securities research institute reports.[35-40]

OPE emissions have to be distributed within a 0.5°×0.5° latitude-longitude grid to fit the SESAMe v3.4 model. As shown in Scheme 1b, locations of individual manufacturers (Figure S3a) were found to allocate the emissions in Stage 1. The secondary industry and total Gross Domestic Product (GDP) shown in Figure S3b,c were applied to allocate the emission in Stage 2 and Stage 3, respectively.

Model and validation

SESAMe v3.4 is adopted to simulate multimedia concentrations of OPEs, as it is able to capture multiple emission pathways and relatively complete advective and diffusive transport processes at interfaces at a relatively high resolution in the Chinese mainland.[9, 43, 44] The physicochemical parameters of the four OPEs were collected from the literature for measured data or predicted by EPI Suite (half-lives) and COSMOtherm (version 21.0) (the vapor pressure, solubility and octanol-water partition coefficient (K_{OW})) (Table S4). COSMOtherm is a robust software package rooted in quantum chemistry and thermodynamics principles following the COSMO-RS theory. It employs first-principle ab initio calculations, requiring little empirical calibration.[45-47] The SESAMe v3.4 model has been well validated in previous studies on organics with a range of physicochemical properties.[9, 43, 44, 48] The external validation using different chemicals shows good model performance. This study primarily verified the model with TPHP, as it has been better studied with substantial observations available in the literature, compared to the three NOPEs. Observations of TPHP sampled between 2014 and 2022 were comprehensively collected from the literature to cover the different environmental compartments and areas for a better model validation (Table S5). Based on the limited monitoring data, a preliminary validation of the three novel OPEs was also been conducted, with the details summarized in Table S6. Uncertainty analysis was performed by Monte Carlo simulation by running SESAMe v3.4 10,000 times. Values of environmental parameters were randomly taken from the environmental parameter pool of SESAMe v3.4.

Persistence assessment

Chemical persistence (P_{OV}) is defined as the average time (yr) that a chemical resides in the environment. The P_{OV} of individual OPEs in the multimedia environmental system of each grid cell is calculated as Eq.13 using SESAMe v3.4:

$$P_{OV} = M_{total} / E \tag{13}$$

where M_{total} is the total amount of a chemical (mol) in the system at the steady state; E indicates the emission rate (mol/yr).[49] P_{OV} is an integrative index of a chemical's overall persistence in the multimedia environment, which is the result of both chemical and physical processes in the target system.[1, 50]

Results and discussion

Emissions

Emissions of TPHP increased from 122 to 360 Mg/yr during 2010-2021 in China, and were relatively high compared to the other three NOPEs (Figure 1). However, our calculations show that half of this is from indirect emissions of its precursor—TPHPi (79–181 Mg/yr), implying a substantial under-estimate of OPA sources in previous publications.[27, 28, 51] Of the three NOPEs, AO168=O exhibits the highest emission (169–283 Mg/yr), comparable to TPHP especially in early years. Emissions of AO626=O_2 and TNPP are relatively low, but still reach 31–67 Mg/yr and 17–39 Mg/yr, respectively. Among the four OPEs, TPHP had the most rapid growth rate of emissions at ca. 10% per annum on average with a sharp rise in 2016 (24%), probably attributed to the gradual restriction on PBDEs in China since 2014 and a subsequent demand for substitutes.[52] Emissions of the three NOPEs increase more steadily at a rate of 4.9–8.1% per annum. The emission of AO168=O during Stage 3 accounts for 47% of the total emissions, significantly surpassing the other three OPEs (18% at the same stage). This disparity arises from the extensive addition of AO168 in mulch films and its substantial release into the farmlands. As for the other three OPEs, over 80% of the total emission occurs during the manufacture with >70% in Stage 1 and nearly 8% in Stage 2, indicating a potentially elevated occupational and residential exposure in or around manufacturing sites.

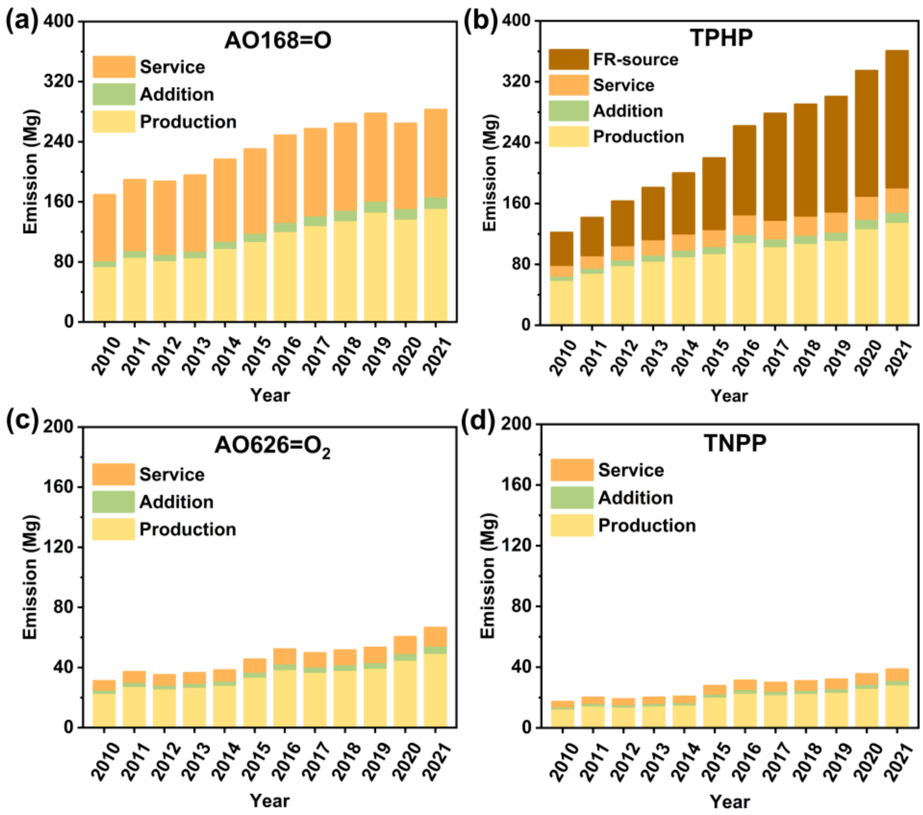


Figure 1 Annual OPE emissions from 2010 to 2021 in China.

The 5th–95th percentile ranges (median in brackets) of emissions for the 0.5° grid cells are 0.004–62 (1.3) kg for AO168=O, 0.001–10 (0.2) kg for AO626=O_2, 0.0006–5.9 (0.1) kg for TNPP and 0.01–113 (1.4) kg for TPHP across China taking 2019 as the case year (Figures 2 and S4). Generally, higher emissions appear in economically developed regions in eastern and southern China, such as the Beijing-Tianjin-Hebei region, the Yangtze River Delta (YRD), eastern Sichuan, the coastal area in Guangdong and Fujian and the urban areas of some provincial capitals. Regions with high adoption rates of mulch film, such as Ningxia, Shandong, Jiangsu and Henan, have also emerged as hotspots for AO168=O emissions. Although TPHP emission derived from TPHPi is comparable to FR-source emissions, it shows a more skewed geographical distribution (Figure 2a–b). This is because OPA manufacturers only cluster in locations in central and southern Shandong, southern Liaoning, western Ningxia, southern Hubei and central Jilin (Figure S3a), compared to the more scattered and numerous manufacturers of OPFRs.

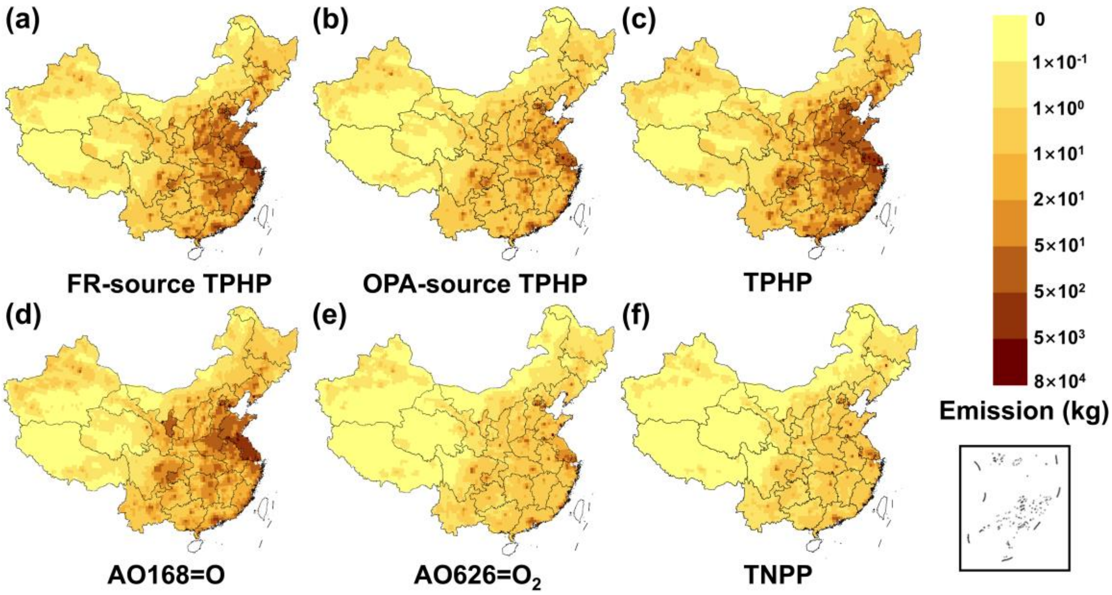


Figure 2 Gridded OPE emissions in 2019. (a) FR-source TPHP emission, (b)OPA-source TPHP emission, total emissions of (c) TPHP, (d) AO168=O, (e) AO626=O_2 and (f) TNPP.

OPE budget

Emission to air was assumed to be the sole environmental emission pathway of

OPEs (only as FRs) in previous modelling studies as above mentioned.[2, 27, 28, 53] An updated estimation in this study indicates that 72–99% of the target OPEs are emitted via atmosphere, which primarily occurs in chemical synthesis processes. Accounting for the OPA source, TPHP emission to air is ca. 278 Mg/yr in China. Its near-ground deposition is 146 Mg/yr to soils and 10 Mg/yr to freshwaters, mainly driven by precipitation (Figure 3a). Approximately 45% (to soils) and 82% (to freshwaters) of the total deposition occurs in Jiangsu and Shanghai, due to the combined effect of higher emissions and higher precipitation. Deposition is the primary input of TPHP to land and makes soils the major sink, retaining 99% (93 Mg) of TPHP at steady state. The land application of WWTP sludge only releases 4.9 Mg TPHP to agricultural soils per annum, accounting for about 1.6% of the total TPHP emission. WWTP discharges and soil surface runoff deliver 17 Mg and 2.2 Mg TPHP to the freshwater system per annum, which contributes a net input to sediments at 0.18 Mg/yr. This makes sediments the secondary sink, holding 0.31 Mg (0.36%) of TPHP in China. Approximately 0.13 Mg (0.21%) TPHP remains in freshwaters. Irrigation is an important anthropogenic pathway, allocating 0.76 Mg TPHP from freshwaters to agricultural soils per annum. The fluxes of TPHP from freshwaters and soils to air are only 0.03 kg/yr and 1.1 kg/yr across China, which are negligible.

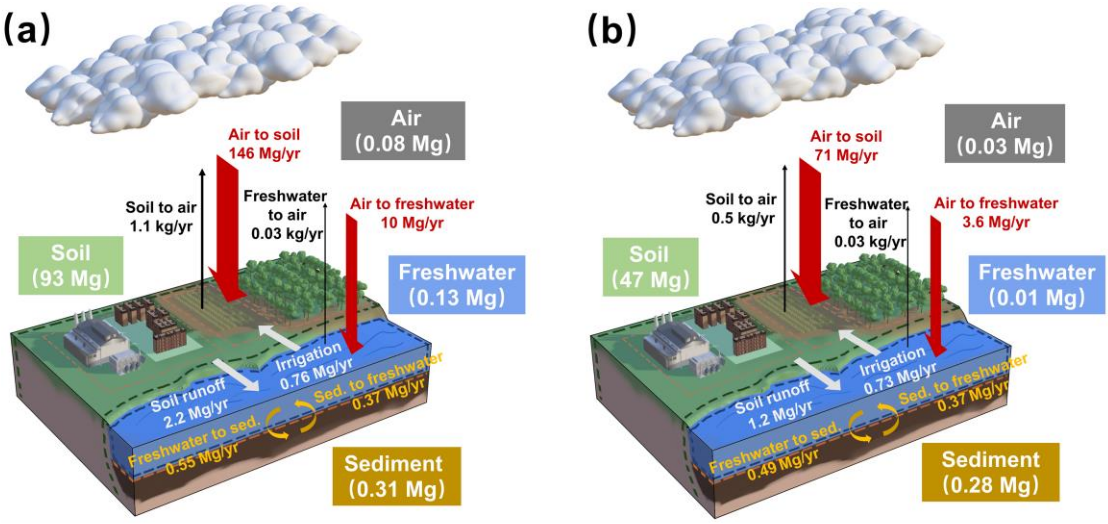


Figure 3 Budget of TPHP derived from (a) FR and OPA sources and (b) only FR sources at the steady state

Emission to air of the three NOPEs is calculated to be 32–202 Mg/yr. Near-ground atmospheric deposition is their major input to soils (27–117 Mg/yr) and freshwaters (1.1–6.1 Mg/yr) (Table S7). This also makes soils and sediments the primary sinks of the three NOPEs with a steady-state mass ranging between 20–827 Mg (88–95%) in soils and 2.5–42 Mg (4.3–11%) in sediments. Despite TPHP having an air emission rate that is 2.1–8.7 times higher than the three NOPEs, its atmospheric deposition rate is only 1.2–5.4 times that of NOPEs. Meanwhile, the mass of AO168=O and AO626=O_2 is 2–9 times that of TPHP in soils, and the mass of the three NOPEs is 8–135 times that of TPHP in sediments. The rationale behind this is that the three NOPEs have water solubilities that are 2–13 orders of magnitude lower than that of TPHP, a K_{OW} that is 4–14 orders of magnitude higher than that of TPHP, and lower degradation rates in sediments and soils compared to TPHP. This makes them more prone to attaching to solids and partitioning in particulate matter, sediments, and soils. For AO168=O, the emissions to farmlands through mulch film can reach 80 Mg/yr, constituting another significant reason in the substantial presence of AO168=O in soils. The emission of the three NOPEs to water and soils via WWTP discharges is minimal.

OPE concentrations and contribution of freshwater/soil emissions

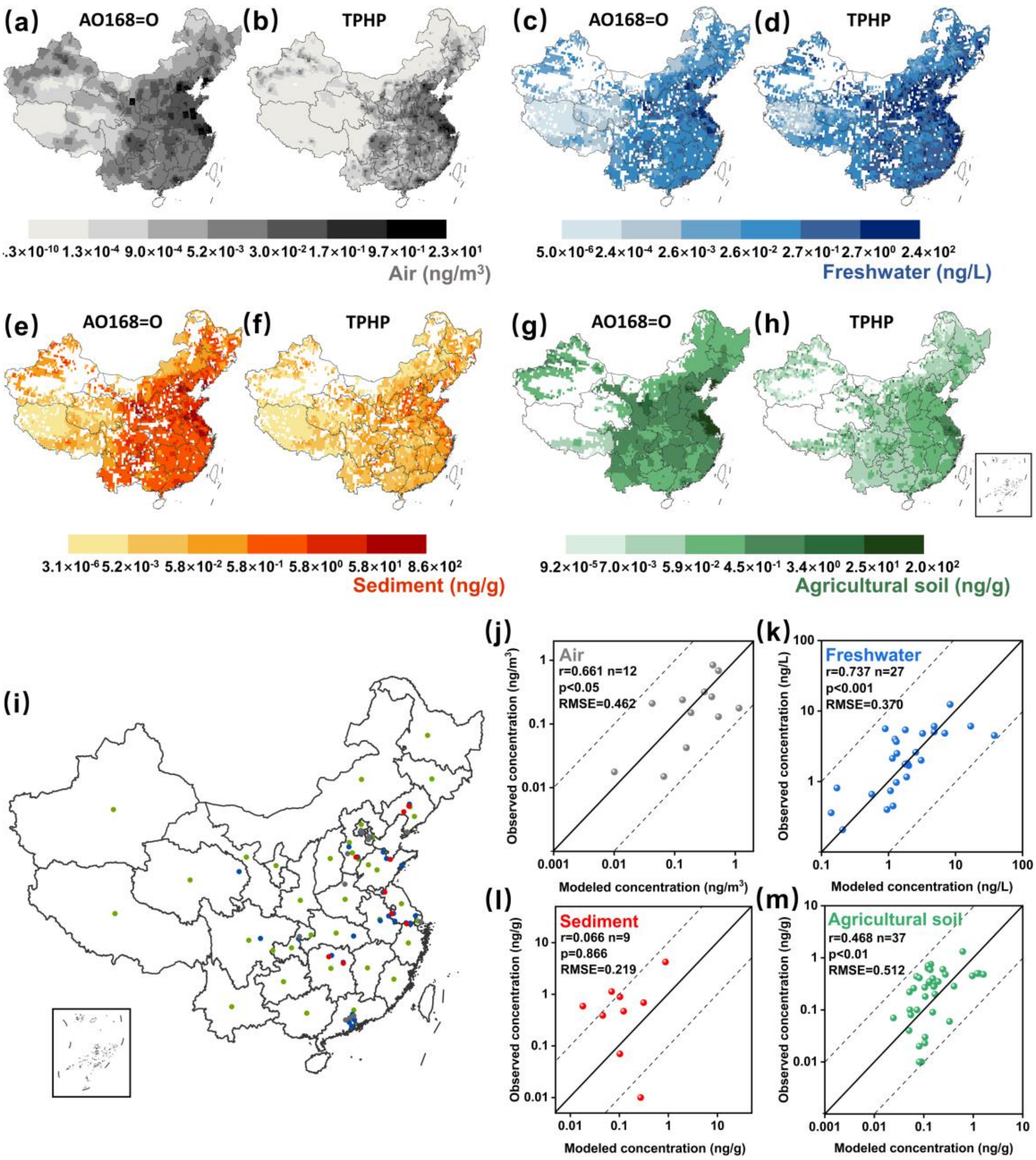


Figure 4 Spatial distribution of predicted TPHP and AO168=O concentrations in (a, b) air, (c, d) freshwaters, (e, f) sediments and (g, h) agricultural soils in 2019. (i) Location and results of model verification on TPHP in (j) air, (k) freshwaters, (l) sediments and

(m) agricultural soils. The solid line is 1:1. The dashed lines are 10:1 and 1:10 lines. The root mean square error (RMSE) is logarithmic scaled.

Predicted concentrations generally have consistent geographical patterns with emissions (Figures 4 and S5). Despite having relatively higher emissions, TPHP only shows higher concentrations in freshwaters, with lower or comparable concentrations in air, sediments and agricultural soils, compared to the other OPEs (Table 1 and Figure S6). This is a result of intermedia transport and partitioning, driven by physico-chemical properties, as stated above. Additionally, release to freshwaters is considered as a pathway for synthesis of TPHP used as FRs; OPAs are more likely to be hydrolyzed after being released to freshwater without the generation of OPE derivatives (Stage 1).[17] This is a major cause of the 1–2 orders of magnitude higher concentrations of TPHP simulated in freshwaters than the NOPEs. Of the four OPEs, AO168=O is the predominant component (except in freshwaters), with 1–2 orders of magnitude higher concentrations than TPHP in air, sediments and agricultural soils. This aligns with the observation in airborne particulate matter, sediments and agricultural soils in China, as well as in the sediment of the Chicago Sanitary and Ship Canal and the atmospheric particles in Chicago, US.[5, 22, 23] The contamination of NOPEs, especially AO168=O, in multiple compartments warrants further attention.

Figures 4i-m and S7 illustrate a generally strong performance of the model on OPEs. TPHP has more measured data across different media and larger areas of China than the NOPEs. Most observation-prediction points of TPHP cluster around the 1:1

line. Root Mean Square Error (RMSE) falls between 0.22 and 0.51, with significant correlation between predictions and observations, except for sediments ($p < 0.05$). Extremely limited measurements have been found for NOPEs, with often lacking location details and concentrations for individual sampling sites (Figure S7). However, best attempts have been made to conduct a preliminary validation on the three NOPEs in air, sediments and agricultural soils. The modeled values also exhibit a satisfactory agreement with the observed values, with differences mostly within 58%. A few cases display greater discrepancies between predictions and observations, such as TPHP in sediments, AO168=O in agricultural soils and TNPP in air. This primarily stems from limitations in amount and coverage domains of available measured data, so observations usually cannot represent an average level in 0.5° grid cells and throughout one year. However, the deviation is acceptable for this type of mechanistic model. The model performance is therefore considered to be reliable, also given its previous external validation with other organic compounds across a range of chemical properties.[43, 44, 54, 55] Uncertainty analysis was conducted by performing a Monte Carlo simulation (Figure S8).

Table 1 Modeled concentration ranges (5th-95th percentiles), medians and means.

		AO168=O	AO626=O_2	TNPP	TPHP
Air (ng/m^3)	Range	4.9×10^{-5}-0.099	8.9×10^{-6}-0.024	7.9×10^{-6}-0.015	1.0×10^{-6}-0.032
	Median	0.0036	0.00093	0.00059	0.00015
	Mean	0.079	0.025	0.013	0.016

Freshwater (ng/L)	Range	4.6×10^{-5}-0.72	1.2×10^{-5}-0.12	4.6×10^{-6}-0.027	7.7×10^{-4}-6.13
	Median	0.033	0.0054	0.0014	0.18
	Mean	0.30	0.11	0.013	1.48
Sediment (ng/g)	Range	1.1×10^{-3}-16	2.5×10^{-4}-2.3	1.0×10^{-4}-0.48	7.1×10^{-5}-0.68
	Median	0.75	0.12	0.026	0.021
	Mean	6.7	1.67	0.23	0.16
Agricultural soil (ng/g)	Range	0.054-2.1	0.0065-0.59	9.9×10^{-4}-0.10	0.0049-0.52
	Median	0.42	0.036	0.0049	0.041
	Mean	1.7	0.44	0.057	0.22

Although comprising only 0.1%–5.7% (37–17224 kg/yr) of total emissions for individual target OPEs, freshwater emissions are dispersed widely across regions where commercial products are produced in China. Contrarily, air emissions derived from the OPA source mostly affect more localized regions, as they primarily occur in Stage 1 from 23 manufacturers, which are only located in 20 grid cells. As above mentioned, the freshwater emission is particularly critical for TPHP. Taking it into account, the average concentrations of TPHP rises one order of magnitude in both freshwaters and sediments from 0.19 to 1.5 ng/L and 0.021 to 0.11 ng/g, compared to when only air emission is considered. A consequent enhanced flux through irrigation results in the transfer of six times more TPHP mass from freshwaters to soils. Influence of freshwater emissions on air concentrations are negligible, due to the low fluxes from freshwaters to air. The soil emission is mainly significant for AO168=O (80 Mg/yr, 28% of total emissions), especially in regions such as eastern Ningxia. This is a relatively economically underdeveloped region in economy without any OPA manufacturers, but has a high rate of mulch film usage. Upon considering soil emissions additional to air and freshwater emissions, the average concentrations in air, freshwater and soil concentrations have increased by around 1.5, 28 and 62 times, respectively.

Contribution of indirect sources

In 2019, OPA-source and FR-source TPHP emissions are comparable (149 *vs* 151 Mg) (Figure 1d). A dominating percentage of OPA-source TPHP is emitted to atmosphere (about 99.9%). This contributes 65% and 51% of total TPHP atmospheric deposition to freshwaters and soils, respectively. If only the FR source was considered, the total TPHP masses in air, soils, freshwaters and sediments would be underestimated by 57%, 49%, 24% and 9.5%, respectively (Figure 3b). As a consequence, the average concentration in air, agricultural soils and freshwaters would be underestimated by 56%, 36% and 4.7%. The impact on sediment is minimal. The greater effect on air and soil masses and concentrations can be explained by the overwhelming emissions to atmosphere.

The OPA source makes a significantly higher contribution to TPHP concentrations, especially in Shandong Peninsula, Jiangsu and Shanghai, eastern Sichuan and Chongqing (Figure S9). The presence of TPHPi manufacturers contributes 28%–99% of air concentrations and 21%–99% of agricultural soil concentrations in Shandong Peninsula, and 42%–92% of air concentrations and 48%–94% of agricultural soil concentrations in Jiangsu and Shanghai for TPHP. In areas without TPHPi manufacturers, such as southern Sichuan and Chongqing, OPA-source emissions in Stage 2–3 contribute ca. 50% of TPHP concentrations in the air and agricultural soil (0.0079 *vs*. 0.016 ng/m^3 in air; 0.0051 *vs.* 0.011 ng/g in agricultural soil) (Figure S9c).

Persistence and risks

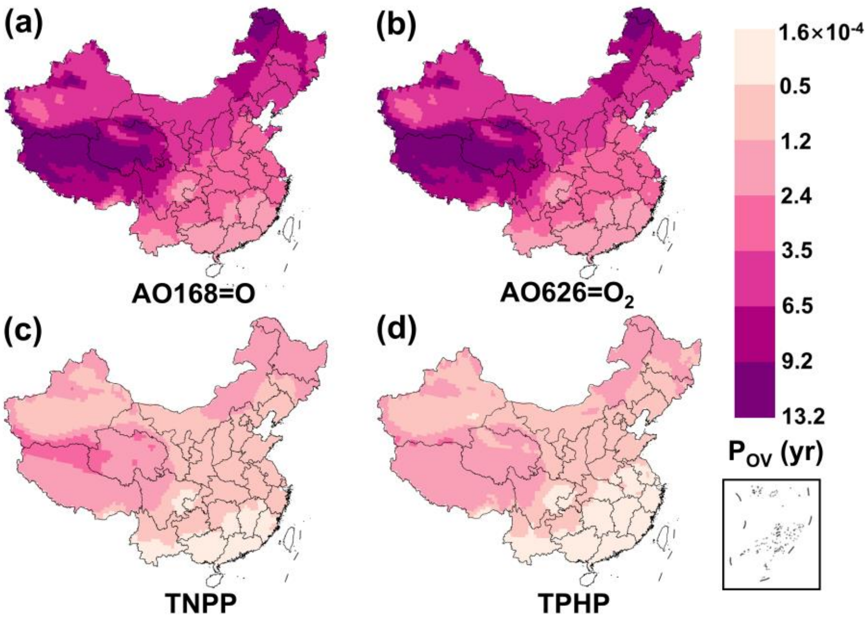


Figure 5 P_{OV} distribution of (a) AO168=O, (b) AO626=O_2, (c) TNPP and (d) TPHP.

Persistence is a key parameter for chemicals under many eco-environmental risk assessment schemes. It stands at the first place of PBT (persistent, bioaccumulative and toxic) as the assessment criteria under the Stockholm Convention on Persistent Organic Pollutants. High persistence indicates the potential for durable environmental and human exposure to a substance which is difficult to control or remove, and has even been suggested as a major cause of concern alone.[50] AO168=O and AO626=O_2 both have a high P_{OV} ranging between 2–11 yrs (5^{th}-95^{th} percentile range), with an average around 5.8 yrs in China (Figures 5 and S10). This is significantly higher than the P_{OV}

of TNPP and TPHP, which range between 0.4–2.1, with an average of 1.1 yr. P_{OV} is significantly higher (at 7.0 yrs) for AO168=O and AO626=O_2 and 1.3 yrs for TNPP and TPHP in the north and west of China (e.g., Qinghai, Tibet and northeast of Inner Mongolia), compared to 2.5 yrs and 0.5 yrs in the south and east of China (e.g., YRD and the Pearl River Delta (PRD)), which is very different from the distribution pattern of emissions and concentrations.

As previously stated, the three NOPEs are more readily distributed in soils and sediments than TPHP. The degradation rate in soils is regarded as the most sensitive parameter influencing P_{OV}, considering the large area of soils and the mass of chemical stored within it.[49] Meanwhile, chemical degradation rates in sediments and soils are normally lower than those in air and freshwaters. Thus, AO168=O and AO626=O_2 exhibit greater environmental persistence with a longer soil half-life (360 d) than TNPP and TPHP (both 75d). They can also be classified as "very persistent" (vP) substances under the EU chemicals regulation, REACH.[56] The geographical distribution of P_{OV} is essentially driven by environmental factors, such as precipitation, temperature and fraction of soil organic carbon contents (f_{OC}).[49] Precipitation is the dominant environmental parameter influencing P_{OV} through air scavenging and soil leaching. Higher temperatures increase degradation rates of substances in the environment. The southeastern regions have more abundant precipitation than the northwest, which is in agreement with the geographical distribution of P_{OV}. Higher f_{OC} levels are present in Qinghai, southern Xinjiang, southern Tibet, northeastern Inner Mongolia and northern

Heilongjiang, which slightly increases persistence of OPEs in these regions.[49] Taking contamination levels into account, it is imperative to pay close attention to areas such as Heilongjiang, northern Xinjiang, southern Tibet, central Inner Mongolia and eastern Qinghai, where AO168=O exhibit both higher concentrations and higher persistence (Figure S11).

Toxicity studies on NOPEs are scarce. However, the structure of AO168=O and AO626=O_2 closely resembles that of TPHP (Figure S1), which has noted neurotoxicity, hepatotoxicity, developmental toxicity and cardiotoxicity.[10, 57-61] Existing studies indicate that these NOPEs are equally or more hazardous than traditional OPEs, such as (but not limited to) TPHP. For example, AO168=O has been found to be more cytotoxic than TPHP, tris(2-butoxyethyl) phosphate (TBOEP), tris(1,3,-dichloro-propyl) phosphate (TDCIPP) and tris(methylphenyl) phosphate (TMPP), and one congener of banned PBDEs, i.e. BDE-47.[62] In addition, AO168=O represents a potentially higher toxicity than 2,4-di-tert-butylphenol (2,4-DtBP)—a hydrolysis product of AO168 and AO168=O, which is better investigated with respect to its hepatic and renal toxicity and other endocrine disruption effects.[63-65] Furthermore, AO168=O and TNPP can be potentially further transformed to more toxic compounds, such as bis(2,4-di-tert-butylphenyl) phosphate (B2,4DtBPP) and bis(4-nonylphenyl) hydrogen phosphate (BNPP).[15, 22] Certain metabolic products resulting from hydroxylation, dealkylation, methylation, and hydrolysis of OPA compounds or their corresponding NOPEs may exhibit increased toxicity compared to the parent compounds.[15] Each of the above reveals noteworthy hazards of NOPEs.

Taking account of the potentially higher environmental exposure level of NOPEs than traditional OPEs in soils and air, as predicted in the present study, eco-environmental health risks of NOPEs are considerable relative to traditional OPEs via exposure by inhalation and soil/dust ingestion. This is empirically demonstrated in previous studies. An occupational exposure assessment in an e-waste disposal area showed that hand-to-mouth contact led to the estimated daily intake (EDI) of AO626=O_2, TNPP and AO168=O comparable with or over four times that of TPHP.[14] Indoor dust ingestion was clarified to cause higher EDI of AO168=O than the total EDI of 19 traditional OPEs in a large scale study across China.[15] Cai et al. delineated two orders of magnitude higher EDI of AO168=O than that of 2,4-DtBP through inhalation exposure to $PM_{2.5}$.[66]

Uncertainties and limitations

Limitations remain due to the lack of data, which causes uncertainties. An identical value was taken for emission factors of all four OPAs from OECD documents in this study, which may result in uncertainties. More refined data better differentiating chemical properties will improve the accuracy of emission estimates. In addition, as mentioned above, release to freshwater in Stage 3 (service) was not considered, which may lead to an underestimation of total emissions to freshwater. Some physicochemical properties, such as half-life, K_{OW} and water solubility, are simulated by models, which may bring uncertainties to predicted environmental concentrations. Experimental data of these properties, especially half-life, is needed to refine the simulation. Finally, the SESAMe v3.4 model only simulates chemical exchange between regional-scale cells and the surrounding area in the air and freshwater, but has not incorporated long-range transport processes. This may introduce uncertainties in concentration simulation especially for remote areas. However, the uncertainty could be minimal for most regions, as the current model setting can capture the most important physical processes and contamination characteristics of the target OPEs in China. Future incorporation of long-range transport will further improve the model accuracy. Nevertheless, this is the first study on OPA-source emissions and contamination across China. It has provided the best assessment to date of the contribution of the indirect emission to contamination and risks of traditional and novel OPEs, based on current knowledge and available data.

Implications

This study identifies a substantial unrecognized emission of traditional and novel OPEs from OPA sources. The simulation in this study illuminates risks of NOPEs in China and their higher persistence properties in environments compared to traditional OPEs. With regard to the high and growing global production of plastics and rubber, OPA source contamination should be a worldwide issue but has been overlooked so far.[23] Meanwhile, other potential OPAs with lower production volumes in China could be investigated to cover OPEs with a broader range of properties and toxicity, while similar research could also be expanded globally to explore the discrepancies between countries in the future research. Incremental toxicity studies should be conducted to grant a better knowledge on risks of NOPEs, as the current available information only provides indirect proof of their high hazards. At the level of policy formulation, current regulations only target FR management, for instance, mandatory statements of FR usage and inclusion levels on product packaging especially those for children's use, and restriction of three traditional chlorinated OPEs used as FRs in EU.[3] This study has revealed the significance of use supervision of OPAs, given the substantial contribution to contamination and risks of OPEs and potential derivatives.

Supporting Information

The Supporting Information is available at https://pubs.acs.org

Information of the target chemicals; parameters for emission estimation; distribution of measured data and validation results for target OPEs; transformation pathways; spatial distribution of OPA manufacturers and economic data for spatial allocation; illustration of chemical emissions, budget, concentrations with spatial information; distribution of areas with both high Pov and environmental concentrations.

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