The potential influence of forests and climate change on the environmental fates of organic compounds in tropical watersheds

Abstract

Several organic compounds are under global scrutiny because of their widespread distribution and potential for adverse health impacts. Among these are poly-brominated diphenyl ethers (PBDEs), dioxins and furans, as well as current-use pesticides. PBDEs and current-use pesticides are produced for their beneficial services as flame retardants and pest controls, respectively, whereas dioxins and furans are the by-products of combustion events involving many organic compounds. These organics distribute to various environmental media and are associated with adverse health effects, including neurotoxicity. The temperate and boreal forests have been shown to impact the environmental fates of select organic chemicals by transferring them from the atmosphere to the soils. Changing climate variables, such as temperature change, are also expected to be important in the environmental distribution of organic contaminants. However, the effect of these factors, forests and climate change, on the environmental fates of organic pollutants in tropical watersheds have not been adequately examined. This review synthesizes current knowledge on the use, exposures and environmental fates of PBDEs, dioxins and dioxin-like chemicals, and current-use pesticides, as well as purports the potential for forests and climate change to affect their fates at the catchment scale in tropical regions.

Keywords: climate change, environmental fates, forests, organic pollutants, tropical watersheds

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1.1 Introduction

Many organic compounds used have caused tremendous concern, due to their global distribution, as well as potential for adverse environmental and health effects [1]. Among these are polybrominated diphenyl ethers (PBDEs), dioxins and dioxin-like compounds, such as furans, as well as pesticides. They are among the ubiquitous environmental pollutants [2].

The pollutants differ by their sources and release media [3] and display varying environmental distribution behaviors, patterns and fates. The differences are controlled by the intrinsic physicochemical properties of the chemical [4]. Such properties include partition coefficients, media-specific half-lives, aqueous solubility and vapor pressure [5]. These intrinsic properties dictate the persistence, long range transport potential, bioaccumulation and environmental state, among others. Contaminants that display unfavorable attributes – persistence, bioaccumulation potential, long range transport potential and toxicity – are recommended for regulation, management or bans [6]. In fact, the possession of these four attributes is a criterion applied by the United Nations Environment Programme for the regulation of persistent organic pollutants (POPs) [7]. For example, PBDEs, dioxins and furans display high octanol-air partition coefficients and long environmental half-lives and, consequently, they bioaccumulate, bio-magnify, and persist in the environment. They are also toxic. Hence, they are classified as POPs [5].

Properties relating to the environment or landscape govern the environmental fates and behavior of organic compounds. Precipitation provides a key mechanism via wet deposition for the transfer of chemicals from the atmosphere to terrestrial and aquatic compartments [8, 9]. Also, processes such as volatilization and evaporation, which increase atmospheric concentrations, are often positively influenced by ambient temperatures. Vegetative covers, such as forests, have been shown to influence the environmental distribution of some organic compounds, whether by enhanced uptake from the atmosphere and subsequent transfer to soils or via re-volatilization from leaf surfaces [10, 11]. Therefore, climatic conditions and vegetation influence the fates of organics [12].

Once in the environment, these organic compounds may cause adverse health effects ranging from skin disorders to neurological dysfunction, endocrine disruption and immuno-toxicity [2, 13-16]. Therefore, understanding all the factors and mechanisms governing the environmental fates of these organics, as well as their impacts is critical.

This review first synthesizes current information on the use, exposures, health effects and environmental fates of select organic contaminants – PBDEs, dioxins, furans and current-use pesticides. Subsequently, the potential for tropical forests and climate change to affect the environmental fates of the chemicals in watersheds is examined.

1.2 Use, exposures and health effects – PBDEs, PCDDs and PCDFs

Polybrominated diphenyl ethers (PBDEs) are semi-volatile organic compounds and are among the cheapest flame retardants, whose purpose in items or materials is to interfere with combustion [17, 18]. There are 209 congeners of PBDEs, with 1 to 10 bromine atoms possibly attached to the diphenyl ether molecule. Commercial mixtures of the PBDEs include pentabrominated BDE (pentaBDE), octabrominated BDE(octaBDE) and decabrominated BDE (decaBDE) [19]. PentaBDE and octaBDE have been banned in select states in the US and in

Europe [19]. The main constituents of the pentaBDE formulation are PBDE- 47, 99, 100, 153 and 154, whereas PBDE- 153, 154, 183, 196, 197, 203, 207 and 208 are the components of the octaBDE mixture [20]. Commercial decaBDE is the most globally used and its main constituent congener is PBDE-209 (also called decaBDE). The extensive use of PBDEs in recent years has led to global distribution and, as such, they are now ubiquitous [21, 22]. These organic compounds are not only persistent, but they also bio-accumulate, bio-magnify and cause adverse human and ecosystem health. A number of manufacturers in the US had committed to gradually stop the use and production of decaBDE [23].

OctaBDE and decaBDE are mainly used in electronic housings, whereas foams and textile materials typically contain pentaBDE [22]. As a result, PBDEs are found in furniture, clothing, our homes and other indoor environments, vehicles and electronic devices. PBDEs are dissolved in the polymers of the material, and the lack of chemical bonding means that PBDEs are constantly being emitted, from the material to which they have been added, during use and disposal. Point sources of PBDEs include manufacturing, recycling and waste disposal facilities. Other sources include back-yard burning [22].

Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzo-furans (PCDFs) are semi-volatile organic compounds, that are the unintentional by-products of waste incineration, paper and pulp bleaching, pesticide manufacture and industrial combustion processes [2, 24]. They are also impurities in chlorinated products/materials. Natural events, such as volcanic eruptions and forest burning, are among the point sources of PCDDs and PCDFs. There are 75 PCDDs and 135 PCDFs, of which only seven (7) PCDDs and ten (10) PCDFs are of interest, because they have been found to be toxic [25, 26]. These 17 dioxins and furans have chlorine atoms on the second, third, seventh and/or eighth positions on the dibenzo-p-dioxin or dibenzofuran parent molecule, respectively. PCDDs and PCDFs adsorb onto particulate matter and are soluble in octanol and lipids, with their solubility positively correlated with their chlorine-atom content [27]. PCDDs and PCDFs are subject to long range atmospheric transport and this, in combination with them being by-products of common events, has resulted in global distribution and ubiquitousness [28].

Atmospheric and aqueous concentrations appear to be high for the pentaBDE, whereas higher concentrations of decaBDE are often found in soils and sediments. PBDEs in the atmosphere and sediment have been extensively assessed, but less is known about concentrations in the soil and aquatic media, although soil appears to be a major sink [22]. In the environment, PBDEs degrade to form lower congeners. Humans are not only exposed to PBDEs via the abiotic environment, but also through diet [29], with fish being the major dietary contributor [30] – this is because PBDEs are lipophilic. Although decaBDE is not well absorbed and is quickly eliminated from animals [31], the lower PBDE congeners bioaccumulate in lipids and bio-magnify as the distance up the food chain increases.

In the environment, PCDDs and PCDFs are deposited from the atmosphere to the water and terrestrial compartments. However, they more readily partition to soils and sediments than water, mainly due to their high octanol-water partition coefficient (K_{ow}) [27]. These organic compounds are persistent, accumulate in lipids, biomagnify in the food web and cause adverse environmental and human health. Higher order PCDDs and PCDFs degrade to the more toxic, lower order PCDDs and PCDFs, respectively.

Upon exposure, PBDEs may cause several health effects. They have been associated with thyroid hormone disruption and developmental neurotoxicity, and decaBDE has carcinogenic potential [16, 20].

PCDDs and PCDFs are among the most toxic organic chemicals, achieving status amongst the United Nations Environment Programme's (UNEP's) 'Dirty Dozen' [24]. The most toxic is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). The toxicities of the 17 PCDDs and PCDFs of interest are compared to that of TCDD, via the World Health Organization's (WHO's) 2005 toxicity equivalence factors (TEFs), using half-order increments on a logarithmic scale (0.03, 0.1, 0.3, etc.) [32]. The TEFs are used to calculate toxicity equivalence quotients (TEQs), which are compared to a tolerable daily intake of 1-4 pg TEQ/kg-bw. PCDDs and PCDFs have been associated with a variety of effects on humans and animals, not limited to skin lesions, disrupted liver function, disrupted metabolism, behavioral and developmental disorders, immunotoxicity and neurotoxicity. TCDD has also been found to be teratogenic and carcinogenic [2, 13].

1.3 Use, exposures and health effects – current-use pesticides

The negative health and environmental effects associated with many currently used organic pesticides have placed pesticides under much scrutiny. Major classes include organochlorine insecticides, organophosphate insecticides, pyrethroids, fungicides, rodenticides, carbamates and herbicides [33]. Organochlorine (halogenated) insecticides are considered to be POPs [34], and many such pesticides are banned from use in a number of developed countries. There is instead a global shift towards non-halogenated pesticides, including organophosphate insecticides and herbicides [35]. These increasingly popular non-halogenated pesticides will herein be referred to as current-use pesticides (CUPs). In this review, the focus will be on select categories of current-use pesticides: pyrethroids; carbamates; organophosphate insecticides; and herbicides.

Pyrethroids are neuro-toxic insecticides, affecting the sodium and chloride channels of the nerves, and are also associated with respiratory, dermal and gastrointestinal disorders [36]. Organophosphate pesticides are also neuro-toxic insecticides. However, they inhibit the cholinesterase enzyme, resulting in elevated levels of acetylcholine at the nerve-muscle junctions, causing muscular spasms [37, 38]. Carbamate insecticides operate in a similar fashion to organophosphate insecticides by inhibiting acetylcholinesterase, and are therefore also neurotoxic [39]. They have caused endocrine disruption, muscular disorders, respiratory distress, and some are potentially carcinogenic [40]. Herbicides control weeds primarily through the inhibition of photosystem I, photosystem II, acetyl-CoA carboxylase enzyme, EPSP synthase or the acetolactate synthase enzymes [41]. Glyphosate-based herbicides are among the first used herbicides, and are still globally used [42], despite concerns being raised about probable carcinogenicity [43]. These herbicides have been found to cause adverse liver and kidney effects in animal studies [44].

Human exposures to the pesticides are primarily occupational, with some environmental exposure. Whereas acute exposures to pyrethroids, organophosphate and carbamate insecticides causes the typical symptoms of pesticide exposure, such as muscle weakness, sweating and gastrointestinal upset, chronic exposures have been associated with nausea, vomiting, blurred vision, among other symptoms [45]. Although, there is limited data on the health effects of exposure to herbicides, exposures to some herbicides, such as phenoxy herbicides, have been

associated with chloracne [14], whereas acute ingestion of glyphosate herbicides may cause gastrointestinal erosion, hemorrhaging, as well as sore throats [46].

1.4 Forests effects on environmental fates

Environmental fates and distribution studies about organic pollutants give information on the short- and long-term environmental concentrations, exposure media, time period during which the hazard potential is greatest, as well as the factors affecting their respective fates. Further understanding of pollutants and their behavior in the environment comes from physiochemical studies of the organic compounds, field measurements of environmental concentrations/distribution and from transport models.

It is well known that climate affects land cover. However, it is being recognized that land cover also influences climatic conditions. Increasing the vegetative density has been shown to increase albedo and total latent heat flux, while simultaneously decreasing sensible heat flux, thereby resulting in cooler and wetter climatic conditions [47]. The vegetative cover and soil distribution in ecosystems affect climate through changes in the balance of water, momentum and energy, and grasslands and pastures display lowered humidity, lowered precipitation and higher surface temperatures [48]. Tropical deforestation has been associated with climatic changes, such as increased temperatures and albedo, as well as with decreased evaporation, cooling and precipitation rates [49, 50]. There is clearly a feedback system between climate and land cover. Since climate affects the fates of organic compounds, it was reasonably hypothesized that land cover also influences the fates of these chemicals.

Land use/cover influences the fates of organics in the environment because the retention capacity of the surface for the chemicals is determined by conditions such as vegetative cover [51]. There are studies that correlate land use/cover with either pollutant fates or some influential factors of their fates. For instance, the contamination of surface waters depends on land use [52]. The uptake by vegetation is more important in reducing atmospheric concentrations than uptake by soil for organics with log $K_{OA} > 6$ [53]. Also, land use/cover influences the volatilization fluxes of POPs to the atmosphere [54] whereas plant cover controls run-off [55]. Hence, contaminant fates depend on land use/cover.

There are a few studies assessing the influence of specific land covers, such as forests, on the fates of organic contaminants. Temperate forests are thought to reduce the atmospheric concentrations of a subset of organics, specifically semi-volatile organic compounds with $7 < \log K_{OA} < 11$ and $\log K_{AW} > -6$, by transferring these to forests soils [56]. With reduced atmospheric concentrations of these semi-volatile organic compounds, there is the resultant reduction in atmospheric deposition to surface waters. However, there is increased delivery to the surface waters via forest soil run-off, although to a lesser degree [11]. In examining the role of forests in a Canadian watershed, the vegetative cover was alternated between forested and urban coverage, and it was found that forests soils may be reservoirs for semi-volatile organic compounds [57]. Therefore, these forests are filters of many organic contaminants and their soils the reservoirs.

First, the forest canopy uptakes the chemicals from the atmosphere via gaseous diffusion, wet gaseous deposition, as well as wet and dry particle-bound deposition [58]. The uptake rates are controlled by the deposition velocities of particles and gases, with gaseous deposition velocities typically exceeding particle-bound deposition velocities. Thereafter, the canopy transfers the

organics to the soil primarily through canopy drip, cuticular-wax erosion and litterfall [58]. This process of chemical uptake and transfer to soils by forest canopies is classified as the forest 'filter effect'. This filter effect has been described for those organic pollutants that are hydrophobic, persistent and with $7 < \log K_{oa} < 11$ and $\log K_{aw} > -6$. Chemicals such as these are considered to fall within the forest 'filter window'.

The type of forest is thought to be important in the filter effect for the organic pollutants. Atmospheric deposition fluxes to deciduous forests were higher than to coniferous forests [11, 58]. The boreal forests, especially those that are deciduous, may be more effective at capturing some atmospheric organic pollutants than tropical rainforests [11]. Globally, boreal forests, especially deciduous boreal forests, reduce the atmospheric and ocean concentrations of organic pollutants, but increase the environmental persistence of these chemicals by delivery to forest soils where they are stored [59]. It had been previously suggested that the filter effect may be absent for some organics, such as polychlorinated biphenyls (PCBs) in tropical forests [56]. It was proposed that temperature affects the partition coefficients K_{oa} and K_{aw} and that the filter factor, which is a function of deposition velocities, which in turn are governed by these partition coefficients, is then also temperature dependent and appeared to be reduced at higher temperatures [56]. Also, the uptake ability from the atmosphere of forests is reduced during higher temperatures, with mass transfer coefficients displaying lower median values during periods with higher temperatures [60]. These suggest that the higher temperatures of tropical regions may inhibit the filtering effect of forests within.

However, many tropical regions display high precipitation rates. Wet deposition, an important process influencing the forest uptake of organic compounds, is positively associated with precipitation rates and is therefore a key transport mechanism [9], especially for the more polar organics. In some tropical regions, the higher temperatures may inhibit whereas the higher precipitation rates may enhance the forest filter effect for organic contaminants, especially the more polar current-use pesticides. It is yet unexplored whether the combined high temperatures and precipitation rates of some tropical regions allow for organic contaminants to be filtered from the atmosphere. A recent study demonstrated that tropical forests exhibit a filter effect for PBDEs [61]. However, it is not known how the probable filtering effect of tropical forests may vary with forest structure and coverage, as well as climatic conditions.

Although vegetative compartments affect the atmospheric concentrations of organic contaminants, by uptake from the atmosphere [53], re-emissions to the atmosphere are expected under select conditions. Organics with higher K_{oa} values ($8 \leq \log K_{oa} \leq 10.7$) can be re-emitted during seasons with higher temperatures [10]. Therefore, forests may act as secondary sources of organic pollutants at the local or regional scale. The role of tropical forests in acting as secondary sources of organic pollutants has not been adequately explored [12]. To add to considerations forests' influences on environmental fates, changes to agrochemical use, due to changes in land use, such as shifts from arable to forested land, were found to influence environmental distribution of pesticides with reductions in atmospheric concentrations associated with increased forested acreage [62]. Therefore, despite a potentially smaller filter effect, tropical forests may use other processes to control the fates of organic contaminants, including those that are less persistent.

Many current-use pesticides, such as organophosphates and carbamates are more polar (with low air-water and octanol-water partition coefficients) and less persistent [63]. Some possess partition coefficients outside of the forest 'filter window'. While as yet unknown, it is possible

that the filter effect extends to these products, especially since the forest filter effect is expected to vary widely because the filter factor is dependent on a number of parameters including deposition velocities, temperature, the canopy storage capacity for lipophilic organic contaminants, as well as particle-air partitioning [56]. Whereas it is internationally accepted that tropical forests provide critical environmental and economic services, such as habitat, biodiversity conservation, timber production and carbon sequestration [64, 65], these biomes may also provide the additional benefits of human and ecosystem health preservation as they regulate organic contaminants.

Hazard assessment end-points, such as overall persistence and long-range transport potential, as well as steady state concentrations, are often used for the purpose of evaluating or predicting environmental impact [11, 66-71]. The long-range transport potential (LRTP) of organic contaminants speaks to the ability of the locally emitted contaminants to be transported over large distances [72] via air ($LRTP_A$) or water ($LRTP_w$), and is therefore indicative of the capacity to cause adverse effects on larger scales – regional, continental or global [7, 73-75]. Quantified metrics that allow for the evaluation of long-range transport potentials include those that are transport based, such as the characteristic travel distance, as well as those that are target oriented, such as the arctic contamination potential [75]. The characteristic travel distance is defined as the distance over which the contaminant is transported such that its concentration is 1/e (37%) of its original [74]. For an organic contaminant evaluated using the characteristic travel distance (CTD) and travelling at a height of 1000 m in the atmosphere at 25 ºC, employed classifications for the contaminant are as follows: Class 1 – atmospheric CTD of greater than 2000 km; Class 2 – atmospheric CTD of 700 to 2000 km; and Class 3 – atmospheric CTD of less than 700 km [7].

The overall persistence at its simplest is a measure of the tendency or ability to maintain presence in the given environmental system [76]. Whereas single media persistence considers contaminant presence in an individual medium (air, water, among others), overall persistence assumes total presence, given a set of linked environmental media. Overall persistence is measured using half-lives [76] or steady-state residence times [75]. The residence time is the time taken for the contaminant to be degraded to 1/e of its original concentration. Therefore, overall persistence depends primarily on degradation losses from the entire environment [76, 77].

It is recommended that hazard assessments focusing on hazard end-points, such as overall persistence and long-range transport potential, be conducted prior to toxicological assessments [77]. The overall persistence and long-range transport potential of a few persistent pollutants have been assessed [7, 70]. Also, some current-use pesticides, which tend to be more polar than their halogenated counterparts, have been found to display regional transport potential [78]. There is little information about the way forests affect the above hazard assessment end-points and any associated health effects of the organic pollutants. In a study on the contribution of forests to the fates of select organic compounds, the observed reduced atmospheric concentrations led the authors to suggest that forests may be important in reducing the long range transport potential of many organic contaminants [11]. In a global study, forests reduced atmospheric and aquatic (oceanic and freshwater) concentrations of the studied organic compounds [59]. Therefore, in reducing media-specific concentrations, forests alleviated media-specific health risks. However, the overall global persistence/residence times due to delivery to forest soils was increased [59], with potentially enhanced risk via this medium.

Therefore, with the potential decreases to long range transport potential and persistence in the atmosphere in temperate regions and globally, in addition to observed global increase in overall

persistence, it is possible that tropical forests may exhibit similar effects on these variables for organic pollutants – persistent and less persistent. One important question that comes to mind is, "Are tropical forests among those that can influence the fates of a chosen subset of organics?" This area of research has been little explored. Also, studies assessing the fates and health effects of POPs and current-use pesticides in tropical regions, given the presence of forests at a site with other co-existing land uses, such as agriculture or urban centers, have not been identified.

To summarize, the impact of tropical forests on the environmental fates of some organic pollutants, such as PBDEs, dioxins, furans and current-use pesticides, especially at the watershed scale with co-existing land uses, is yet unknown.

1.5 Climate change effects

The major determinants of climate are precipitation and atmospheric temperature [79]. These variables influence parameters responsible for the environmental distribution of organic pollutants. For example, partition and transport coefficients are functions of temperature and/or precipitation rate. The mobility of persistent organic pollutants is dependent on climatic conditions, such as temperature, wind and precipitation distribution [80]. Increasing temperatures result in increases in the primary volatilization of select organic contaminants [80-83]. For each 10 ^{o}C increase in temperature, the half-life of pesticides in soils is expected to decrease by as much as 60% [84]. Increased precipitation is associated with increased wet deposition and delivery to terrestrial and aquatic surfaces [8]. Therefore, changes to the climate variables, temperature and precipitation rate, are expected to alter the environmental fates of organic chemicals. These are the direct impacts of climate change on the fates of organic contaminants.

The indirect impacts of climate change on the fates of organic contaminants are difficult to quantify and assess [83]. Agrochemicals will herein be used for elucidation. Regional changes in climate are expected to result in subsequent shifts in the types and size of pest populations. For instance, insect proliferation is expected with rising temperatures [84]. Also, as the climate changes, geographical shifts in the types and quantity of crops produced are expected [51]. To add to this, pesticide losses may occur from processes such as volatilization, degradation, erosion or run-off with consequential increased applications to compensate for the losses [8]. Since pesticide use influences the fates of these chemicals, climate change may indirectly affect their fates, by governing their use patterns.

All these studies [62, 71, 80, 82-84] demonstrate that it may be difficult to predict the exact impact of climate change on environmental fates, because of the complex nature of climate processes. Nevertheless, efforts to quantify the potential impacts of climate change on the fates of organic pollutants, under a limited number of climate change scenarios, are on the rise. It has also been shown that pesticide leaching was dependent on the specific climatic conditions [85]. For example, they found that leaching was generally higher when pesticides were applied in the autumn than in the spring. In another study, the atmospheric concentration records, since the 1990s, of select organic chemicals, were compared with arctic variables, such as surface air temperature and sea-ice extent, and it was found that the increasing atmospheric concentrations of these compounds as the arctic warms were due primarily to revolatilization [81]. In yet another study using the multimedia model EVn-BETR, climate change scenarios included changes to land cover, precipitation and temperature, in the time periods 1991-2020, 2021-2050, 2051-2080 and 2071-2100, to assess the resultant impacts on the fates of poly-chlorinated

biphenyls (PCBs) and PBDEs [82]. It was found that temperature was the major determinant for atmospheric fates, with reduced concentrations due to increased degradation and volatilization rates when the temperatures increased. To show that temperature most strongly affected the global atmospheric fates of some organic contaminants, BETR Global was used to create two climate change scenarios (for the periods 1981-2000 and 2080-2099) by varying select climate variables, such as temperature fields, wind fields, ocean current fields and precipitation rates [80]. Using BETR Research, a global-scaled seven compartment (upper air, lower air, sediment, soil, fresh water, ocean water and vegetation) multimedia model, to compare emissions with climate change scenarios, it was observed that increased temperature was the chief determinant of increases in arctic ocean and atmospheric concentrations of α-hexachlorocyclohexane (α-HCH), due to atmospheric transport to the arctic [62].

On the horizon are studies comparing climate and land use change effects on the fates of organic compounds. Shifts from arable land to forests reduced volatilization fluxes from soils, whereas temperature rises increased volatilization fluxes from soils [54]. This suggests that land use/cover may counteract or temper some direct effects of climate change.

The assessments described above were primarily conducted for the arctic region, or otherwise at a global scale. Watershed scaled assessments of climate change effects on the environmental fates of organic contaminants, in tropical regions, have not been identified. The studies involving climate change impacts are predictive and, as such, require the use of multimedia models. Some of these models, such as G-CIEMS [86], BasinBox [87], and SESAMe [88], are site-specific and not applicable in other places. In other models, such as GIM3 [89] and MUM [67], only one vegetative cover is incorporated, with the application of weighted parameters, limiting their application in multi-use tropical watersheds. Finally, there are watershed models, like LOIS [90] or even GREAT-ER [91]; however, these are specifically for evaluating water quality and not environmental distribution. Consequently, the influence of any vegetative cover, especially tropical forests, in the regional environmental fates of organic pollutants in a watershed with co-existing land uses/covers has not been adequately examined using multimedia modeling. In addition to this, assessments on the impacts of climate change on the long-term fates and associated health impacts of select organic contaminants in such watersheds, as well as on the roles played by tropical forests in governing these fates and health impacts, are limited.

1.6 Conclusion

PBDEs, dioxins, furans and current-use pesticides are among those organic compounds that are now ubiquitous, associated with adverse effects and, therefore, have raised global concern. The design and implementation of control or mitigation measures requires understanding the emission-fate-effect relationships of these chemicals, and such information is limited. The identified knowledge gaps include:

- the influence of tropical forests on the long-term environmental fates and health impacts of the select organic contaminants in a multi-use watershed;
- the effects of climate change on the long-term environmental fates of the organic chemicals in a tropical region;
- the effects of climate change on the influence of tropical forests on the environmental fates and hazard potential of the contaminants;

It is recommended that studies, aimed at filling the identified knowledge gaps, be conducted.

References

1. Su C, Zhang H, Cridge C, Liang R. A review of multimedia transport and fate models for chemicals: Principles, features and applicability. Sci Total Environ. 2019;668:881-92. doi:https://doi.org/10.1016/j.scitotenv.2019.02.456
2. Kanan S, Samara F. Dioxins and furans: A review from chemical and environmental perspectives. Trends Environ Anal Chem. 2018;17:1-13. doi:https://doi.org/10.1016/j.teac.2017.12.001
3. Lohmann R, Breivik K, Dachs J, Muir D. Global fate of POPs: Current and future research directions. Environ Pollut. 2007;150(1):150-65. doi:http://dx.doi.org/10.1016/j.envpol.2007.06.051
4. Nizzetto L, Butterfield D, Futter M, Lin Y, Allan I, Larssen T. Assessment of contaminant fate in catchments using a novel integrated hydrobiogeochemical-multimedia fate model. Sci Total Environ. 2016;544:553-63. doi:https://doi.org/10.1016/j.scitotenv.2015.11.087
5. Jones KC, de Voogt P. Persistent organic pollutants (POPs): state of the science. Environ Pollut. 1999;100(1–3):209-21. doi:http://dx.doi.org/10.1016/S0269-7491(99)00098-6
6. Mackay D, McCarty LS, MacLeod M. On the validity of classifying chemicals for persistence, bioaccumulation, toxicity, and potential for long-range transport. Environmental Toxicology and Chemistry: An International Journal. 2001;20(7):1491-98.
7. Beyer A, Mackay D, Matthies M, Wania F, Webster E. Assessing long-range transport potential of persistent organic pollutants. Environ Sci Technol. 2000;34(4):699-703.
8. Walcott KC, Erwin KN, Levin ED. The toxicology of climate change: Environmental contaminants in a warming world. Environ Int. 2009;35:971-86.
9. Noyes PD, McElwee MK, Miller HD, Clark BW, Van Tiem LA, Walcott KC, et al. The toxicology of climate change: Environmental contaminants in a warming world. Environ Int. 2009;35(6):971-86. doi:https://doi.org/10.1016/j.envint.2009.02.006
10. Nizzetto L, Perlinger JA. Climatic, Biological, and Land Cover Controls on the Exchange of Gas-Phase Semivolatile Chemical Pollutants between Forest Canopies and the Atmosphere. Environ Sci Technol. 2012;46(5):2699-707. doi:10.1021/es2036527
11. Wania F, McLachlan MS. Estimating the Influence of Forests on the Overall Fate of Semivolatile Organic Compounds Using a Multimedia Fate Model. Environ Sci Technol. 2000;35(3):582-90. doi:10.1021/es0011919
12. Kallenborn R, Halsall C, Dellong M, Carlsson P. The influence of climate change on the global distribution and fate processes of anthropogenic persistent organic pollutants. J Environ Monit. 2012;14(11):2854-69. doi:10.1039/C2EM30519D
13. Fiedler H. Dioxins and furans (PCDD/PCDF). Persistent Organic Pollutants: Springer; 2003. p. 123-201.
14. Sterling TD, Arundel AV. Health effects of phenoxy herbicides: A review. Scand J Work Environ Health. 1986;12(3):161-73. doi:10.2307/40965305
15. Dabrowski JM, Shadung JM, Wepener V. Prioritizing agricultural pesticides used in South Africa based on their environmental mobility and potential human health effects. Environ Int. 2014;62:31-40. doi:https://doi.org/10.1016/j.envint.2013.10.001
16. Linares V, Bellés M, Domingo JL. Human exposure to PBDE and critical evaluation of health hazards. Arch Toxicol. 2015;89(3):335-56. doi:10.1007/s00204-015-1457-1
17. Rahman F, Langford KH, Scrimshaw MD, Lester JN. Polybrominated diphenyl ether (PBDE) flame retardants. Sci Total Environ. 2001;275(1):1-17.

18. Gibson EA, Siegel EL, Eniola F, Herbstman JB, Factor-Litvak P. Effects of Polybrominated Diphenyl Ethers on Child Cognitive, Behavioral, and Motor Development. Int J Environ Res Public Health. 2018;15(8):1636. doi:10.3390/ijerph15081636
19. Costa LG, Giordano G, Tagliaferri S, Caglieri A. Polybrominated diphenyl ether (PBDE) flame retardants: environmental contamination, human body burden and potentialadverse health effects. Acta Bio Medica Atenei Parmensis. 2009;79(3):172-83.
20. EPA U, editor Recommended toxicity equivalence factors (TEFs) for human health risk assessments of 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin and dioxin-like compounds2010: Risk Assessment Forum Washington, DC.
21. Allen JG, Gale S, Zoeller RT, Spengler JD, Birnbaum L, McNeely E. PBDE flame retardants, thyroid disease, and menopausal status in U.S. women. Environ Health. 2016;15(1):60-60. doi:10.1186/s12940-016-0141-0
22. Vonderheide AP, Mueller KE, Meija J, Welsh GL. Polybrominated diphenyl ethers: causes for concern and knowledge gaps regarding environmental distribution, fate and toxicity. Sci Total Environ. 2008;400(1):425-36.
23. Fromme H, Hilger B, Kopp E, Miserok M, Völkel W. Polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) and “novel” brominated flame retardants in house dust in Germany. Environ Int. 2014;64:61-68. doi:https://doi.org/10.1016/j.envint.2013.11.017
24. Srogi K. Levels and congener distributions of PCDDs, PCDFs and dioxin-like PCBs in environmental and human samples: a review. Environ Chem Lett. 2008;6(1):1-28.
25. Schecter A, Birnbaum L, Ryan JJ, Constable JD. Dioxins: an overview. Environ Res. 2006;101(3):419-28. doi:10.1016/j.envres.2005.12.003
26. Mukherjee A, Debnath B, Ghosh SK. A review on technologies of removal of dioxins and furans from incinerator flue gas. Procedia Environ Sci. 2016;35:528-40.
27. Lohmann R, Jones KC. Dioxins and furans in air and deposition: a review of levels, behaviour and processes. Sci Total Environ. 1998;219(1):53-81.
28. Ueno D, Watanabe M, Subramanian A, Tanaka H, Fillmann G, Lam PKS, et al. Global pollution monitoring of polychlorinated dibenzo-p-dioxins (PCDDs), furans (PCDFs) and coplanar polychlorinated biphenyls (coplanar PCBs) using skipjack tuna as bioindicator. Environ Pollut. 2005;136(2):303-13. doi:https://doi.org/10.1016/j.envpol.2004.12.036
29. Consonni D, Sindaco R, Bertazzi PA. Blood levels of dioxins, furans, dioxin-like PCBs, and TEQs in general populations: A review, 1989–2010. Environ Int. 2012;44:151-62. doi:https://doi.org/10.1016/j.envint.2012.01.004
30. Frederiksen M, Vorkamp K, Thomsen M, Knudsen LE. Human internal and external exposure to PBDEs–a review of levels and sources. Int J Hyg Environ Health. 2009;212(2):109-34.
31. McDonald TA. A perspective on the potential health risks of PBDEs. Chemosphere. 2002;46(5):745-55.
32. Van den Berg M, Birnbaum LS, Denison M, De Vito M, Farland W, Feeley M, et al. The 2005 World Health Organization Reevaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-Like Compounds. Toxicol Sci. 2006;93(2):223-41. doi:10.1093/toxsci/kfl055
33. Kim K-H, Kabir E, Jahan SA. Exposure to pesticides and the associated human health effects. Sci Total Environ. 2017;575:525-35. doi:https://doi.org/10.1016/j.scitotenv.2016.09.009

34. Dehn PF, Allen-Mocherie S, Karek J, Thenappan A. Organochlorine insecticides: impacts on human HepG2 cytochrome P4501A, 2B activities and glutathione levels. Toxicol In Vitro. 2005;19(2):261-73. doi:DOI: 10.1016/j.tiv.2004.10.002
35. Yao Y, Tuduri L, Harner T, Blanchard P, Waite D, Poissant L, et al. Spatial and temporal distribution of pesticide air concentrations in Canadian agricultural regions. Atmos Environ. 2006;40(23):4339-51. doi:10.1016/j.atmosenv.2006.03.039
36. Saillenfait A-M, Ndiaye D, Sabaté J-P. Pyrethroids: Exposure and health effects – An update. Int J Hyg Environ Health. 2015;218(3):281-92. doi:https://doi.org/10.1016/j.ijheh.2015.01.002
37. Muñoz-Quezada MT, Lucero BA, Barr DB, Steenland K, Levy K, Ryan PB, et al. Neurodevelopmental effects in children associated with exposure to organophosphate pesticides: a systematic review. Neurotoxicology. 2013;39:158-68. doi:10.1016/j.neuro.2013.09.003
38. Costa LG. Current issues in organophosphate toxicology. Clin Chim Acta. 2006;366(1-2):1-13.
39. Fukuto TR. Mechanism of action of organophosphorus and carbamate insecticides. Environ Health Perspect. 1990;87:245-54.
40. Morais S, Dias E, Pereira M. Carbamates: human exposure and health effects. The impact of pesticides. 2012:21-38.
41. Kudsk P, Streibig JC. Herbicides – a two-edged sword*. Weed Res. 2003;43(2):90-102. doi:10.1046/j.1365-3180.2003.00328.x
42. Gasnier C, Dumont C, Benachour N, Clair E, Chagnon M-C, Séralini G-E. Glyphosate-based herbicides are toxic and endocrine disruptors in human cell lines. Toxicology. 2009;262(3):184-91. doi:http://dx.doi.org/10.1016/j.tox.2009.06.006
43. Van Bruggen A, He M, Shin K, Mai V, Jeong K, Finckh M, et al. Environmental and health effects of the herbicide glyphosate. Sci Total Environ. 2018;616:255-68.
44. Myers JP, Antoniou MN, Blumberg B, Carroll L, Colborn T, Everett LG, et al. Concerns over use of glyphosate-based herbicides and risks associated with exposures: a consensus statement. Environ Health. 2016;15(1):1-13.
45. Jaga K, Dharmani C. Sources of exposure to and public health implications of organophosphate pesticides. Rev Panam Salud Publica. 2003;14(3):171-85.
46. Talbot AR, Shiaw M-H, Huang J-S, Yang S-F, Goo T-S, Wang S-H, et al. Acute Poisoning with a Glyphosate-Surfactant Herbicide ('Roundup'): A Review of 93 Cases. Hum Exp Toxicol. 1991;10(1):1-8. doi:10.1177/096032719101000101
47. Bounoua L, Collatz G, Los S, Sellers P, Dazlich D, Tucker C, et al. Sensitivity of climate to changes in NDVI. J Clim. 2000;13(13):2277-92.
48. Foley JA, Costa MH, Delire C, Ramankutty N, Snyder P. Green Surprise? How Terrestrial Ecosystems Could Affect Earth's Climate. Front Ecol Environ. 2003;1(1):38-44. doi:10.2307/3867963
49. Costa M, Bonell M, Bruijnzeel L, editors. Large-scale hydrological impacts of tropical forest conversion. The joint UNESCO International Hydrological Programme (IHP)-International Union of Forestry Research Organizations (IUFRO) symposium and workshop, Forest-water-people in the humid tropics: past, present and future hydrological research for integrated land and water management, Universiti Kebangsaan Malaysia, 30 July-4 August 2000.; 2004: Cambridge University Press.
50. Costa MH, Foley JA. Combined Effects of Deforestation and Doubled Atmospheric CO2 Concentrations on the Climate of Amazonia. J Clim. 2000;13(1):18-34. doi:10.1175/1520-0442(2000)013<0018:ceodad>2.0.co;2

51. Schiedek D, Sundelin B, Readman JW, Macdonald RW. Interactions between climate change and contaminants. Mar Pollut Bull. 2007;54(12):1845-56. doi:http://dx.doi.org/10.1016/j.marpolbul.2007.09.020
52. Holvoet KMA, Seuntjens P, Vanrolleghem PA. Monitoring and modeling pesticide fate in surface waters at the catchment scale. Ecol Modell. 2007;209(1):53-64. doi:DOI: 10.1016/j.ecolmodel.2007.07.030
53. Nizzetto L, Pastore C, Liu X, Camporini P, Stroppiana D, Herbert B, et al. Accumulation Parameters and Seasonal Trends for PCBs in Temperate and Boreal Forest Plant Species. Environ Sci Technol. 2008;42(16):5911-16. doi:10.1021/es800217m
54. Komprda J, Komprdová K, Sáňka M, Možný M, Nizzetto L. Influence of Climate and Land Use Change on Spatially Resolved Volatilization of Persistent Organic Pollutants (POPs) from Background Soils. Environ Sci Technol. 2013;47(13):7052-59. doi:10.1021/es3048784
55. Garmouma M, Teil MJ, Blanchard M, Chevreuil M. Spatial and temporal variations of herbicide (triazines and phenylureas) concentrations in the catchment basin of the Marne river (France). Sci Total Environ. 1998;224(1–3):93-107. doi:10.1016/s0048-9697(98)00326-x
56. McLachlan MS, Horstmann M. Forests as Filters of Airborne Organic Pollutants: A Model. Environ Sci Technol. 1998;32(3):413-20. doi:10.1021/es970592u
57. Priemer DA, Diamond ML. Application of the Multimedia Urban Model To Compare the Fate of SOCs in an Urban and Forested Watershed. Environ Sci Technol. 2002;36(5):1004-13. doi:10.1021/es001397+
58. Horstmann M, McLachlan MS. Atmospheric deposition of semivolatile organic compounds to two forest canopies. Atmos Environ. 1998;32(10):1799-809. doi:http://dx.doi.org/10.1016/S1352-2310(97)00477-9
59. Su Y, Wania F. Does the Forest Filter Effect Prevent Semivolatile Organic Compounds from Reaching the Arctic? Environ Sci Technol. 2005;39(18):7185-93. doi:10.1021/es0481979
60. Nizzetto L, Stroppiana D, Brivio PA, Boschetti M, Di Guardo A. Tracing the fate of PCBs in forest ecosystems. J Environ Monit. 2007;9(6):542-49.
61. Barrett KSC, Jaward FM, Stuart AL. Forest filter effect for polybrominated diphenyl ethers in a tropical watershed. J Environ Manage. 2019;248:109279. doi:https://doi.org/10.1016/j.jenvman.2019.109279
62. Wöhrnschimmel H, MacLeod M, Hungerbuhler K. Emissions, Fate and Transport of Persistent Organic Pollutants to the Arctic in a Changing Global Climate. Environ Sci Technol. 2013;47(5):2323-30. doi:10.1021/es304646n
63. Zacharia JT. Identity, physical and chemical properties of pesticides. Pesticides in the modern world-trends in pesticides analysis. 2011:1-18.
64. Chomitz KM, Kumari K. The domestic benefits of tropical forests: a critical review. World Bank Res Obs. 1998;13(1):13-35.
65. Kalácska M, Sánchez-Azofeifa GA, Rivard B, Calvo-Alvarado JC, Journet ARP, Arroyo-Mora JP, et al. Leaf area index measurements in a tropical moist forest: A case study from Costa Rica. Remote Sens Environ. 2004;91(2):134-52. doi:http://dx.doi.org/10.1016/j.rse.2004.02.011
66. Bennett DH, Scheringer M, McKone TE, Hungerbühler K. Predicting Long-Range Transport: A Systematic Evaluation of Two Multimedia Transport Models. Environ Sci Technol. 2001;35(6):1181-89. doi:10.1021/es001278u
67. Diamond ML, Priemer DA, Law NL. Developing a multimedia model of chemical dynamics in an urban area. Chemosphere. 2001;44(7):1655-67. doi:http://dx.doi.org/10.1016/S0045-6535(00)00509-9

68. Fenner K, Scheringer M, Hungerbühler K. Persistence of Parent Compounds and Transformation Products in a Level IV Multimedia Model. Environ Sci Technol. 2000;34(17):3809-17. doi:10.1021/es0000347
69. Fenner K, Scheringer M, MacLeod M, Matthies M, McKone T, Stroebe M, et al. Comparing Estimates of Persistence and Long-Range Transport Potential among Multimedia Models. Environ Sci Technol. 2005;39(7):1932-42. doi:10.1021/es048917b
70. Leip A, Lammel G. Indicators for persistence and long-range transport potential as derived from multicompartment chemistry–transport modelling. Environ Pollut. 2004;128(1–2):205-21. doi:10.1016/j.envpol.2003.08.035
71. Gouin T, Armitage JM, Cousins IT, Muir DCG, Ng CA, Reid L, et al. Influence of global climate change on chemical fate and bioaccumulation: the role of multimedia models. Environ Toxicol Chem. 2013;32(1):20-31. doi:10.1002/etc.2044
72. Scheringer M, Jones KC, Matthies M, Simonich S, Van De Meent D. Multimedia partitioning, overall persistence, and long-range transport potential in the context of POPs and PBT chemical assessments. Integrated Environmental Assessment and Management: An International Journal. 2009;5(4):557-76.
73. Scheringer M. Persistence and spatial range as endpoints of an exposure-based assessment of organic chemicals. Environ Sci Technol. 1996;30(5):1652-59.
74. Bennett DH, McKone TE, Matthies M, Kastenberg WE. General Formulation of Characteristic Travel Distance for Semivolatile Organic Chemicals in a Multimedia Environment. Environ Sci Technol. 1998;32(24):4023-30. doi:10.1021/es980328g
75. Scheringer M. Long-range transport of organic chemicals in the environment. Environmental Toxicology and Chemistry: An International Journal. 2009;28(4):677-90.
76. Webster E, Mackay D, Wania F. Evaluating environmental persistence. Environmental Toxicology and Chemistry: An International Journal. 1998;17(11):2148-58.
77. Wegmann F, Cavin L, MacLeod M, Scheringer M, Hungerbühler K. The OECD software tool for screening chemicals for persistence and long-range transport potential. Environmental Modelling & Software. 2009;24(2):228-37. doi:10.1016/j.envsoft.2008.06.014
78. Matthies M, Klasmeier Jr, Beyer A, Ehling C. Assessing Persistence and Long-Range Transport Potential of Current-Use Pesticides. Environ Sci Technol. 2009;43(24):9223-29. doi:10.1021/es900773u
79. Granger OE. Caribbean climates. Prog Phys Geogr. 1985;9(1):16-43. doi:10.1177/030913338500900102
80. Lamon L, von Waldow H, MacLeod M, Scheringer M, Marcomini A, Hungerbühler K. Modeling the global levels and distribution of polychlorinated biphenyls in air under a climate change scenario. Environ Sci Technol. 2009;43(15):5818-24.
81. Ma J, Hung H, Tian C, Kallenborn R. Revolatilization of persistent organic pollutants in the Arctic induced by climate change. Nat Clim Chang. 2011;1(5):255-60.
82. Paul AG, Hammen VC, Hickler T, Karlson UG, Jones KC, Sweetman AJ. Potential implications of future climate and land-cover changes for the fate and distribution of persistent organic pollutants in Europe. Global Ecol Biogeogr. 2012;21(1):64-74. doi:10.1111/j.1466-8238.2010.00547.x
83. Hansen KM, Christensen JH, Geels C, Silver JD, Brandt J. Modelling the impact of climate change on the atmospheric transport and the fate of persistent organic pollutants in the Arctic. Atmos Chem Phys. 2015;15:6549.

84. Bloomfield JP, Williams RJ, Gooddy DC, Cape JN, Guha P. Impacts of climate change on the fate and behaviour of pesticides in surface and groundwater—a UK perspective. Sci Total Environ. 2006;369(1–3):163-77. doi:http://dx.doi.org/10.1016/j.scitotenv.2006.05.019
85. Steffens K, Larsbo M, Moeys J, Jarvis NJ, Kjellström E, Lewan E, editors. Assessing pesticide leaching under climate change: The role of climate input uncertainty. EGU General Assembly Conference Abstracts; 2013.
86. Suzuki N, Murasawa K, Sakurai T, Nansai K, Matsuhashi K, Moriguchi Y, et al. Geo-referenced multimedia environmental fate model (G-CIEMS): Model formulation and comparison to the generic model and monitoring approaches. Environ Sci Technol. 2004;38(21):5682-93.
87. Hollander A, Huijbregts M, Ragas A, Van de Meent D. BasinBox: a generic multimedia fate model for predicting the fate of chemicals in river catchments. Living Rivers: Trends and Challenges in Science and Management: Springer; 2006. p. 21-38.
88. Zhu Y, Price OR, Tao S, Jones KC, Sweetman AJ. A new multimedia contaminant fate model for China: How important are environmental parameters in influencing chemical persistence and long-range transport potential? Environ Int. 2014;69:18-27. doi:https://doi.org/10.1016/j.envint.2014.03.020
89. Luo Y, Gao Q, Yang X. Dynamic modeling of chemical fate and transport in multimedia environments at watershed scale—I: Theoretical considerations and model implementation. J Environ Manage. 2007;83(1):44-55. doi:10.1016/j.jenvman.2006.01.017
90. Boorman DB. LOIS in-stream water quality modelling. Part 1. Catchments and methods. Sci Total Environ. 2003;314-316:379-95. doi:https://doi.org/10.1016/S0048-9697(03)00064-0
91. Schowanek D, Fox K, Holt M, Schroeder F, Koch V, Cassani G, et al. GREAT-ER: a new tool for management and risk assessment of chemicals in river basins Contribution to GREAT-ER No. 10. Water Sci Technol. 2001;43(2):179-85.