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Kayon Barrett
University of South Florida, kaydamibarrett@yahoo.com

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The Influence of Tropical Forests and Climate Change on the Fates of Select Organic Pollutants in a Jamaican Watershed

by

Kayon S. C. Barrett

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
Department of Environmental and Occupational Health
College of Public Health
University of South Florida

Co-Major Professor: Foday M. Jaward, Ph.D.
Co-Major Professor: Amy L. Stuart, Ph.D.
Jeffrey A. Cunningham, Ph.D.
Steven P. Mlynarek, Ph.D.
Ira S. Richards, Ph.D.

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b) polychlorinated dibenzo-p-dioxins (PCDDs) – tetra-chlorinated dibenzo-p-dioxin (TCDD) and octa-chlorinated dibenzo-p-dioxin (OCDD); and

c) polychlorinated dibenzofurans (PCDFs) – 2,3,4,7,8-Penta-chlorinated dibenzofuran (PeCDF) and 1,2,3,4,7,8-Hexa-chlorinated dibenzofuran (HxCDF).

Current-use pesticides

a) pyrethroids – cypermethrin and lambda-cyhalothrin;

b) organophosphate insecticides – diazinon and dimethoate;

c) carbamates – carbaryl and methomyl;

d) herbicides – diuron and glyphosate.

Abstract

Many organic compounds, although beneficial, are associated with negative health and ecological impacts. It is therefore imperative to understand the environmental fates of these contaminants. Whereas the fates and health impacts of many persistent organic pollutants have been extensively examined, there is limited research characterizing the fates of these and the less persistent organic compounds in tropical multi-use watersheds. This study therefore aimed to evaluate the roles of forests and climate change on the environmental fates and health impacts of select organic chemicals in the Rio Cobre watershed, a tropical river basin in Jamaica. A total of 16 organic compounds were selected for this assessment, including some polybrominated diphenyl ethers (PBDEs), dioxins, furans and current-use pesticides. In the first portion of the assessment, field measurements of the concentrations of select PBDEs (PBDE-28, -47, -99, -100, -153, -154, -183 and -209) in the deposition, soil, litterfall and atmosphere of a forest and nearby clearing in the aforementioned watershed were evaluated. The mean air and litterfall concentrations of the PBDEs were lower in the forest than in the clearing, whereas the deposition flux rate and soil concentrations were higher in the forest. It was therefore concluded that the tropical forest filtered the PBDEs by transferring them from the atmosphere to the soil. In the next segment of the assessment, a multimedia environmental model of contaminant fate and transport, reflective of a region with three vegetative covers – urban, agricultural/grassland and forests – was developed to assist with the evaluations. This model, RioShed, was used to compute and compare fate metrics, including persistence and long range transport potential, for the aforementioned 16 organic compounds given varying forest parameters and climatic conditions. The atmospheric long range transport potentials and overall persistence of the organics were generally lower in the forested tropical watershed than in the un-forested tropical watershed, especially when the forests were fully evergreen. In this tropical watershed, the fate metrics were particularly responsive to precipitation rates. The atmospheric long range transport potentials and overall persistence of the evaluated organics increased and decreased, respectively, under the climate change condition of decreased precipitation rates. However, the effects of precipitation on the atmospheric long range transport potentials and overall persistence were more varied for the current-use pesticides. It was therefore concluded that the fates of the evaluated chemicals differed in forested versus un-forested tropical watersheds and that such differences were influenced by forest parameters, climate drivers and the chemical properties of the organics. The results and methods described in this dissertation are applicable in environmental multi-media model development and can be used to inform land management practices, as well as assist in decision-making for environmental sustainability in tropical developing countries.

Chapter 1

Introduction

1.1 Problem statement

A number of organic compounds are under global scrutiny, because they are ubiquitous, as well as associated with human and environmental toxicity. Among these are the polybrominated diphenyl ethers, dioxins and furans, as well as pesticides. Many of these compounds serve a variety of essential functions. The polybrominated diphenyl ethers are manufactured for global use as flame retardants, preventing fire propagation in the materials to which they have been added (Alaee, Arias, Sjödin, & Bergman, 2003), whereas pesticides are used extensively to control pests, which are organisms that negatively impact humans or their property (Moore, 2007). However, dioxins and furans are the by-products of combustion processes (Fiedler, 2003), including those involved in the manufacture of these and other essential/beneficial organic compounds. These chemicals are of current interest because their extensive use or by-production status has resulted in them being ubiquitous, with the ensuing probability of human and environmental harm.

Upon emission or release, these organic contaminants are distributed among environmental compartments, from which they may exert varied adverse effects. For example, exposure to polybrominated diphenyl ethers has been found to cause endocrine disruption and neurotoxicity. In fact, decabrominated diphenyl ether has carcinogenic potential (US Environmental Protection Agency, 2010). Therefore, a keen understanding of the emission-fate-effect relationship for these organic contaminants is critical to formulate and implement appropriate control and/or remediation measures.

Many environmental fates and distribution studies, as well as impact assessments aim to evaluate the role of physicochemical, climatic and environmental factors in the environmental distribution of the chemicals and/or their consequential effects (Fiedler, 2003; Lohmann et al., 2007; Nizzetto & Perlinger, 2012; Sterling & Arundel, 1986; Walcott et al., 2009; Wania, 2006). One environmental factor that has not received as much attention in its influence on the fates of organic compounds is forest coverage.

Although, it has long been accepted that forests provide essential environmental services, such as carbon sequestration, biodiversity preservation and water quality enhancement (Chomitz & Kumari, 1998; Kalácska et al., 2004), one beneficial role that is being explored is the regulation/sequestration of organic compounds (McLachlan & Horstmann, 1998; Nizzetto et al., 2007; Su & Wania, 2005; Wania & McLachlan, 2000). Boreal and temperate forests have been shown to regulate the environmental fates of some semi-volatile organic compounds by transferring them from the atmosphere to forest soils through a process described as the 'filter effect' of forests (McLachlan & Horstmann, 1998; Wania & McLachlan, 2000). However, it has been suggested that tropical rainforests may not be as effective as these forests in capturing some atmospheric organic pollutants (Wania & McLachlan, 2000), and that the filter effect may even be absent in tropical forests for some persistent organic pollutants, such as polychlorinated biphenyls (PCBs) (McLachlan & Horstmann, 1998). In fact, the filter factor and uptake ability of forests are influenced by temperature-dependent variables, such as partition coefficients, and are reduced at higher temperatures. Despite the indications, it has not been determined whether tropical forests also exhibit the filter effect.

Some tropical regions display high precipitation rates, thereby providing a key mechanism – via wet deposition, especially of particle-adsorbed organic compounds – for the enhanced transfer of organic contaminants from the atmosphere to terrestrial compartments. Forest vegetation has been shown to be efficient at capturing select particle-adsorbed organic pollutants and releasing them to lower biomass and the soil (Terzaghi et al., 2013). In addition, vegetative cover influences terrestrial volatilization fluxes, surface run-off and local climate, all of which are factors that influence contaminant fates (Bounoua et al., 2000; Foley, Costa, Delire, Ramankutty, & Snyder, 2003; Garmouma, Teil, Blanchard, & Chevreuil, 1998; Komprda, Komprdová, Sáňka, Možný, & Nizzetto, 2013). Therefore, tropical forests can be expected to influence the environmental fates of organic contaminants, thereby also influencing associated health impacts, even if not via a filter effect. The mechanism, by which tropical forests may influence environmental fates, has not been fully explored.

Long-term fate metrics, such as overall persistence and long range transport potential, are hazard end-point indicators, which inform on the propensity of pollutants to cause adverse environmental and health effects. Overall persistence is indicative of longevity in a given environmental system, whereas long range transport potential indicates the ability to be transported distances from the source and the capacity to cause adverse effects at various scales – local, regional, continental or global (Bennett et al., 1998; Beyer et al., 2000; Scheringer et al., 2009; Webster et al., 1998). The desired outcome is reduction in these metrics.

In one study, temperate forests were shown to reduce the atmospheric concentrations of some organic pollutants, causing the authors to purport that they may reduce the atmospheric long range transport potential of the chemicals (Wania & McLachlan, 2000). In a global assessment, forests reduced the atmospheric and oceanic concentrations of the evaluated organics, but increased overall persistence due to enhanced delivery of the pollutants to forest soils, which are environmental sinks (Su & Wania, 2005). However, it is not known whether tropical forests, specifically, reduce the long term fate metrics, such as long range transport potential or overall persistence, of organic contaminants, and whether the organics are limited to those which are persistent, or may include more polar organics, such as some current-use pesticides.

The climate is expected to change, whether through increased precipitation, altered wind speeds or directions, among others (Dalla Valle, Codato & Marcomini, 2007). Changing climate conditions affect the environmental fates of organic chemicals (Lamon et al., 2009; Ma et al., 2011; Paul et al., 2012; Walcott et al., 2009). Although it is difficult to predict the actual impact of climate change on the environmental fates of organics, due to the complex nature of the climate processes (Bloomfield et al., 2006), quantification of the potential impacts has been accomplished in a number of temperate, as well as global assessments (Lamon et al., 2009; Ma et al., 2011; Paul et al., 2012; Steffens et al., 2013; Wöhrnschimmel et al., 2013). However, little is known about: 1) how climate change may affect the long-term fate metrics of organics (persistent and more polar) in tropical regions; 2) under which climate change scenarios are the fate metrics increased, which are undesirable outcomes; and 3) whether the presence of tropical forests can temper any negative effect of climate change on the environmental fates.

Shifting from agricultural land to forests saw reductions in volatilization fluxes, in a modeling study conducted in the Czech Republic (Komprda et al., 2013), with the possibility to also reduce atmospheric long range transport potential. This implies that land use or landscape architecture may affect the environmental fates of organic compounds. However, that which has not been well established for tropical regions includes: 1) the effect of land use on the environmental fates of select organics; 2) whether shifts from other land uses to forests would also be beneficial; and 3) if the effect of changing the forested portion in landscapes of the environmental fates of the organics depends on the land use benefitting from the change.

Effective management strategies are guided by local-scale assessments (Cash & Moser, 2000). Tropical watersheds are habitats and sources of food, income, aesthetic appeal and recreation. Therefore, maintaining ecosystems and human health in these environmental units is critical. At the watershed scale, tropical forests are particularly known to not only provide the aforementioned typical forest services, but to also enhance vegetative yield and to stabilize soils (Pattanayak, 2004). However, they may also play the vital role of protecting watersheds by regulating/sequestering organic pollutants.

The aforementioned filter effect is quantifiable using field measurements. However, such assessments are typically impractical in developing countries, which often lack the financial resources and analytical facilities to conduct the analyses of environmental samples. The use of multimedia environmental models to provide reasonable estimates/predictions of fates and impacts is a practical alternative. Additionally, some long-term fate end-points, such as overall persistence and long range transport potential, are not measurable and are solely computed using multimedia environmental models (Bennett et al., 2001; Fenner et al., 2005; Leip & Lammel, 2004; Matthies et al., 2009). Many environmental multimedia models that are publicly available, relatively easy to use, with quick output, and, hence, typically used for evaluative or predictive purposes, often include only one vegetative cover (Fenner et al., 2005; Rong-Rong et al., 2012). Environmental models with single vegetative compartments are considered too simplistic for the regional assessment of environmental fates (Cousins & Mackay, 2001), and those without a forest canopy may not adequately represent environmental fates in forested regions (Wania &

McLachlan, 2000). Adding to this, many of these available predictive models are steady-state models (Fenner et al., 2005; Rong-Rong et al., 2012). These are deficiencies that can impede their use in watersheds, especially given the fact that many watersheds have multiple land uses or vegetative covers and that pollutant inputs, as well as compartmental fates, are often dynamic. The management of such watersheds is considered better guided by models capable of performing dynamic evaluations. No publicly-available, predictive/evaluative and dynamic environmental multi-media model, with at least three vegetative compartments (forest being one of them), was identified.

The assessments in this dissertation were geared towards filling the identified knowledge gaps and developing the relevant tools to accomplish such.

1.2 Aim and objectives

This dissertation aims to contribute to the understanding of the influence of tropical forests and climate change on the environmental fates of select persistent organic pollutants and current-use pesticides at the watershed scale. For the purpose of this research, the Rio Cobre watershed in Jamaica was the case study. The selection criteria for the assessed organic compounds were that they be ubiquitous, associated with adverse health and/or environmental impacts, as well as be under current global scrutiny. Eight (8) known persistent organic pollutants, as well as eight (8) pesticides currently in use in Jamaica were selected for assessment. The persistent pollutants included the following:

a) polybrominated diphenyl ethers (PBDEs) – PBDE-47, PBDE-99, PBDE-153 and PBDE-209;

b) polychlorinated dibenzo-p-dioxins (PCDDs) – tetra-chlorinated dibenzo-p-dioxin (TCDD) and octa-chlorinated dibenzo-p-dioxin (OCDD); and

c) polychlorinated dibenzofurans (PCDFs) – 2,3,4,7,8-Penta-chlorinated dibenzofuran (PeCDF) and 1,2,3,4,7,8-Hexa-chlorinated dibenzofuran (HxCDF).

The pesticides assessed included:

e) pyrethroids – cypermethrin and lambda-cyhalothrin;

f) organophosphate insecticides – diazinon and dimethoate;

g) carbamates – carbaryl and methomyl;

h) herbicides – diuron and glyphosate.

The objectives of this dissertation are detailed below.

Objective 1: To determine whether tropical forests exhibit a filter effect for select persistent organic pollutants in the Rio Cobre watershed

Among the specific research questions to be answered by this objective are:

- Are depositions of some PBDEs greater in tropical forests than in clearings?
- Do tropical forests soils accumulate select PBDEs more than the soils in clearings?
- Do tropical forests reduce the atmospheric concentrations of select PBDEs in comparison to clearings?

To assist in answering these questions, samples of bulk deposition, litterfall, soil and ambient air were simultaneously obtained for a forest and adjacent clearing in the Rio Cobre watershed for a period of 15 weeks. These were used to compute filter, depletion and accumulation factors to quantify the effect of forests on the presence of the organic pollutants.

Objective 2: To determine the effects of tropical forests on the long-term fate metrics for select persistent organic pollutants and current-use pesticides in the Rio Cobre watershed

Some specific research questions to be addressed by this objective are as follows:

- Do tropical forests reduce the long-term fate metrics of both persistent and the more polar organic pollutants?
- Does the degree of the effect of tropical forests on long term fate metrics depend on the nature of the pollutant – persistent or more polar?
- How does the composition of the tropical forest affect its influence on the fate metrics for the evaluated pollutants?

It was hypothesized that tropical forests reduce the atmospheric concentrations and long range transport potentials of select organic pollutants at the expense of forest soils, but increase overall persistence. Therefore, to execute this objective, a multi-media model was first developed by modifying CalTOX 1.5 to include forest and urban covers. The model was then used to compute some long-term fate end-points – overall persistence, atmospheric long range transport potential, as well as steady state and average annual concentrations – for each of the 16 organic compounds in a forested and an un-forested scenario for the Rio Cobre watershed. Changes were evaluated by comparing the metrics in the forested scenario to that in the un-forested scenario.

Objective 3: To ascertain the influence of climate change and land use on the environmental fates of select persistent organic pollutants and current-use pesticides in the Rio Cobre watershed

For this objective, specific research questions include:

- Under which tropical climate change scenarios are the fate metrics of the evaluated organics increased?
- What are the climate change scenarios for which the negative effects of climate change on environmental fates are tempered by the presence of tropical forests?
- What land use distributions provide for increases in the long-term fate metrics of the organics in the tropical watershed?
- When forested proportions of the tropical landscape are altered, do the ensuing effects on environmental fates also depend on the land use benefitting from the changes?
- Do the climate change effects on environmental fates vary according to landscape architecture in the tropical watershed?

It was hypothesized that tropical forests exhibit different impacts on the environmental fates of select organic compounds, depending on the properties of the chemicals and the climatic conditions. Therefore, the multi-media model developed in objective 2 was used to quantify long-term fate metrics for varying forest coverage applied to the Rio Cobre watershed under four (4) climate change scenarios. A total of 20 assessment scenarios were generated and compared to control scenarios for the 16 organic compounds.

In this dissertation, current knowledge is first reviewed and the knowledge gaps are presented in Chapter 2. The methods used and the results of this evaluation are detailed in Chapters 3 to 5, whereas summary is provided in Chapter 6.

1.3 Significance

Long-term environmental fates, as well as exposures to organic pollutants at the watershed scale, may be regulated and/or mitigated by the presence of tropical forests. As a result, evaluating the relationship between these vegetative covers and the fate metrics of the contaminants may provide critical information for planning and environmental monitoring agencies, as well as health assessors, as they seek to formulate measures/methods to ensure human and environmental health. This dissertation seeks to contribute such information.

The organic compounds selected for assessment in this dissertation are polybrominated diphenyl ethers (PBDEs), dioxins, furans and some current-use pesticides, many of which provide essential functions. However, high environmental levels of these organics may cause adverse human and ecosystem health. This is deleterious at the watershed scale, with the co-existing potential for similar adverse effects on neighboring regions. Tropical forests may assist in this regard by controlling levels in exposure media. Additionally, climate change and land use are expected to affect not only the fates of the organic pollutants, but also any influence of forests on their fates and health impacts in a tropical region – hence the need for the assessments in this study.

Chapter 2
Literature Review

2.1 Introduction

Many organic compounds are the current source of tremendous concern, due to their global distribution, as well as potential for adverse environmental and health effects. Among these are polybrominated diphenyl ethers (PBDEs), dioxins, furans and pesticides. Some of these organic compounds are manufactured for their beneficial functions. For instance, PBDEs are flame retardants, which are produced and added to textile materials, foams and plastics to interfere with the initial stage of fire development, thereby restricting its propagation (Sjödin, Patterson, & Bergman, 2003). Pesticides are manufactured and applied to control pests (Moore, 2007). However, other organic compounds are unintentionally produced. Examples of these are dioxins and furans, which are the by-products of combustion processes or the manufacture of other chlorinated organic compounds (Jones & de Voogt, 1999). Nevertheless, they are all ubiquitous environmental pollutants.

The pollutants differ by their sources and release media (Lohmann, Breivik, Dachs, & Muir, 2007). PBDEs are chemical additives and, consequently, are released during all phases of their life cycle – manufacture, use and disposal. They are primarily emitted into the atmosphere. However, chemicals such as pesticides may be emitted directly into the atmosphere, soil or on vegetation typically during application (Ragnarsdottir, 2000).

Organic pollutants also display varying environmental distribution behaviors, patterns and fates. These are controlled by the intrinsic physicochemical properties of the chemical. Such properties include partition coefficients, media-specific half-lives, aqueous solubility and vapor pressure (Jones & de Voogt, 1999). 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 (Don Mackay, McCarty, & MacLeod, 2001). 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) (Beyer, Mackay, Matthies, Wania, & Webster, 2000). 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 persistent organic pollutants (POPs) (Jones & de Voogt, 1999).

In terms of environmental behavior, the organic compounds can also be differentially classified according to their mode of transport from their sources, as well as their potential to reach the Arctic environment. Some chemicals, especially those with octanol-air and air-water partition coefficients (K_{oa} and K_{aw}, respectively) such that $6.5 \leq \log K_{oa} < 10$ or $\log K_{oa} < 6.5$ with $-4 < \log K_{aw} < 0$, are transported to the polar region in a series of depositions and evaporations (depending on temperature changes) known as grass-hopping, and are considered ‘multiple hoppers’ (Wania, 2006). On the other hand, those with $\log K_{oa} > 10$ are the ‘single hoppers’, with limited potential to reach the Arctic, having been previously irreversibly deposited to the earth’s surface. ‘Swimmers’ are typically those with $\log K_{aw} < -2$ and traverse primarily via the oceans. However, there are the ‘fliers’, often with $\log K_{oa} < 6.5$ and $\log K_{aw} > 0$, which are very volatile and are not usually deposited (Wania, 2006). Some organics are both ‘multiple hoppers’ and ‘swimmers’. PBDEs, because of their high octanol-air partition coefficients, are among the ‘single-hoppers’ and as such they move from their region of emission to their final destination in a ‘single hop’ (Lohmann et al., 2007).

Other properties relating to the environment or landscape also 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 (Walcott, Erwin, & Levin, 2009). 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 (Nizzetto & Perlinger, 2012; Wania & McLachlan, 2000). Therefore climatic conditions and vegetation influence the fates of organics.

Once in the environment, these organic compounds may cause adverse health effects ranging from skin disorders to neurological dysfunction, endocrine disruption and immuno-toxicity (Fiedler, 2003; Sterling & Arundel, 1986). Therefore, understanding all the factors and mechanisms governing the environmental fates of these organics, as well as their impacts is critical. The evaluation of environmental fates and health impacts are accomplished using field measurements and/or multimedia environmental models.

With this in mind, this dissertation 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 contributions of tropical forests and climate change to the environmental fates of the chemicals in watersheds are examined. Finally, environmental management measures, such as fate assessment tools, specifically multi-media models, are considered.

2.2 Persistent organic pollutants

2.2.1 Use, exposures and health effects – poly-brominated diphenyl ethers

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 (Rahman, Langford, Scrimshaw, & Lester, 2001). 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) (Costa, Giordano, Tagliaferri, & Caglieri, 2009). PentaBDE and octaBDE have recently been banned in select states in the US and in Europe (Costa et al., 2009). 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 (USEPA, 2010). 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. These organic compounds are not only persistent, but they also bio-accumulate, bio-magnify and cause adverse human and ecosystem health. They are labeled as persistent organic pollutants (POPs).

OctaBDE and decaBDE are mainly used in electronic housings, whereas foams and textile materials typically contain pentaBDE (Vonderheide, Mueller, Meija, & Welsh, 2008). As a result, PBDEs are found in furniture, clothing, our homes and other indoor environment, vehicles and electronic devices. The 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 (Vonderheide et al., 2008).

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 (Vonderheide et al., 2008). In the environment, PBDEs degrade to form lower congeners. During incineration, PBDEs produce dioxins and furans.

Humans are not only exposed to PBDEs via the abiotic environment, but also through diet, with fish being the major dietary contributor (Frederiksen, Vorkamp, Thomsen, & Knudsen, 2009) – this is because PBDEs are lipophilic. Although decaBDE is not well absorbed and is quickly eliminated from animals (McDonald, 2002), the lower PBDE congeners bioaccumulate in lipids and bio-magnify as the distance up the food chain increases. Upon exposure, PBDEs may cause a number of health effects. They have been associated with thyroid hormone disruption and developmental neurotoxicity, and PBDE-209 has carcinogenic potential (US Environmental Protection Agency, 2010).

2.2.2 Use, exposures and health effects – dioxins and furans

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 (Srogi, 2008). 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, as they have been found to be toxic (Schecter, Birnbaum, Ryan & Constable, 2006). These 17 toxic dioxins and furans have chlorine atoms on the second, third, seventh and/or eighth positions on the dibenzo-p-dioxin or dibenzofuran parent molecule. PCDDs and PCDFs adsorb onto particulate matter and are soluble in octanol and lipids, with solubility positively correlated with chlorine-atom content (Lohmann & Jones, 1998). PCDDs and PCDFs are subject to long range atmospheric transport and this, in combination with their by-production from common events, has resulted in global distribution and the ensuing ubiquitousness.

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}) (Lohmann & Jones, 1998). 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.

PCDDs and PCDFs are among the most toxic organic chemicals, achieving status amongst the United Nations Environment Programme's (UNEP's) 'Dirty Dozen' (Srogi, 2008).

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.) (Van den Berg et al., 2006). 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 (Fiedler, 2003).

2.2.3 Environmental fates – PBDEs, PCDDs and PCDFs

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.

Persistent organic pollutants are organic compounds that not only reside in the environment for a long time, but also bio-accumulate, bio-magnify and cause adverse effects (Wania & MacKay, 1996). They are characteristically lipophilic and resistant to metabolism. Their distribution and movement through the environment are dependent on environmental properties, such as temperature and precipitation. For example, higher ambient temperatures facilitate evaporation into the atmosphere and migration, whereas lower temperatures facilitate deposition from the atmosphere to soils and aqueous media. Also, lower temperatures enhance partitioning from the gaseous to non-gaseous phase (as in condensation to aqueous media or adsorption on particles) and retard degradation – both facilitating persistence. Due to their persistent nature, these organic pollutants are also typically subject to long range transport (Lohmann et al., 2007).

Although some persistent organic pollutants display the traditional negative concentration gradient in non-gaseous media with respect to distance from emission sources, many of the more mobile and volatile display a positive correlation between concentration and distance from the source (Wania & MacKay, 1996). Therefore, it can be seen that significant properties influencing the environmental fates of these chemicals include their partition coefficients. Other key indicators of environmental fates are half-lives, vapor pressure, aqueous solubility and migration velocity (Jones & de Voogt, 1999; Wania & MacKay, 1996). For example, the more volatile persistent pollutants, those with lower octanol-air partition coefficients, are often airborne and tend to move faster from one location to the next, thereby displaying higher migration velocities (Wania & MacKay, 1996). The half-live of an organic is the time taken for its concentration to decrease to, or by, half of the original amount. This variable is a typical metric used to determine single-medium persistence, as well as overall persistence (which is calculated for a number of connected environmental media) (Webster, Mackay, & Wania, 1998). Therefore, organics that retreat to environmental media in which they display high half-lives or persistence, may contaminate the given media, persist, as well as cause adverse effects.

Persistent organic pollutants can also be categorized by the mode of production. Some are intentionally produced, such as PBDEs, whereas some are process by-products, such as PCDDs and PCDFs.

Sources generally emit directly to the atmosphere. Soils then receive these organic pollutants primarily from atmospheric deposition (Hassanin et al., 2004). However, some contaminants, such as PBDEs, can leach directly from sources, such as electronic waste recycling facilities, into the soils (Leung, Luksemburg, Wong, & Wong, 2007). Unintentionally produced organic pollutants, such as PCDDs and PCDFs, can also be formed directly in the soils, when the soils are contaminated with chlorinated organic compounds, and especially when the soils are alkaline (Sokolovich, 1994). Concentrations of persistent organic pollutants in soils are often balances of inputs and outputs because of long half-lives. Chemical concentrations in this medium are functions of the distance from the source, climatic drivers (temperature and precipitation), vegetative cover, soil organic carbon content, soil type and the long range atmospheric transport potential (LRAT) of the compound. For some persistent organic pollutants, such as PBDEs, soils retain the higher congeners more efficiently than the lower congeners (Hassanin et al., 2004). The lower congeners often experience 'hopping', due to their lower octanol-air partition coefficients, whereas the higher order congeners do not.

Many persistent organic pollutants are delivered to surface waters via atmospheric deposition. However, other inputs include surface run-off and direct discharges (Castro-Jiménez et al., 2008; Sepúlveda et al., 2010). Once in the aquatic media, these organic contaminants typically migrate to sediments and aquatic biota (Moon, Choi, Yu, Jung, & Choi, 2012).

Although the toxicities of some persistent organic pollutants, such as PBDEs, PCDDs and PCDFs, have been well characterized, identifying the sources of most was previously difficult because of their widespread use or unintentional production (Jones & de Voogt, 1999). However, methods have been developed to aid in such assessments, and the current focus is to identify and better characterize sources, as well as the environmental concentrations of many. In China, major sources of PCDDs and PCDFs were the impurities used in the production of many chlorinated organics (Zheng, Leung, Jiao, & Wong, 2008). Metal smelting operations and organochlorine chemical production were the major sources of PCDDs and PCDFs in the drainage areas of the Taiza River and Hun River, respectively, in China (Zhang et al., 2008). Fish is the major dietary source of PBDEs, with a mean observed concentration of 4200 pg/g bw (Frederiksen et al., 2009). Average soil and sediment PBDE concentrations decreased as progress was made downstream from the Shiawassee River in Michigan (Yun et al., 2008). Decreasing soil and sediment concentrations of PBDEs were also observed along the river flow gradient in Argentina, with concentrations associated with the presence of facilities such as hydroelectric power plants (Miglioranza et al., 2013). Waste electronic recycling plants are significant sources of PCDDs and PCDFs in China and India (Sepúlveda et al., 2010). Vehicle and house dust are significant sources of PBDEs in urban regions (Jones-Otazo et al., 2005; Lagalante, Oswald, & Calvosa, 2009). Although it has been possible to quantify environmental concentrations and identify the sources, emissions are still largely estimated (USEPA, 2010).

Despite the growing work demonstrated above, studies involving the role of many environmental factors, such as vegetative cover, on the fates of these select persistent organic pollutants are relatively few.

2.3 Current-use pesticides

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

The negative health and environmental effects associated with many currently used organic pesticides have placed them under much scrutiny. Major classes include organochlorine insecticides, organophosphate insecticides, pyrethroids, fungicides, rodenticides, carbamates and herbicides. Organochlorine (halogenated) insecticides are considered to be persistent organic pollutants (Dehn, Allen-Mocherie, Karek, & Thenappan, 2005), 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 (Yao et al., 2006). Even in a small developing country such as Jamaica, the Pesticides Control Authority of Jamaica (2011) estimated that, during 2010-2011, herbicides and other non-halogenated insecticides represented 55% and 32%, respectively, of imported pesticides, with 35.9% of all imported pesticides being directly imported by the agricultural sector and 32.4% as raw material for manufacture. Therefore, for the remainder of this dissertation, these increasingly popular non-halogenated pesticides will be referred to as current-use pesticides (CUPs). However, the focus will be on select current-use pesticides – pyrethroids, carbamates, organophosphate insecticides and herbicides.

Pyrethroids are insecticides, first identified in 1949. They are neuro-toxic, affecting the sodium and chloride channels of the nerves. Human exposures are primarily occupational. Environmental exposure is rare. As is common with many pesticides, acute ingestion can cause vomiting, headaches, coma and convulsions (Bradberry, Cage, Proudfoot, & Vale, 2005).

Organophosphate pesticides are also insecticides, which were first identified in 1938. Exposures are generally occupational, with some environmental exposures. Organophosphates are also neurotoxic and inhibit the cholinesterase enzyme, resulting in elevated levels of acetylcholine at the nerve-muscle junctions, causing muscular spasms. Acute exposure causes the typical symptoms of pesticide exposure, such as muscle weakness, sweating and gastrointestinal upset, whereas chronic exposure causes nausea, vomiting, blurred vision, among other symptoms (Jaga & Dharmani, 2003).

The evaluation of carbamates as insecticides was initiated in 1949 (Metcalf & Fukuto, 1965). These insecticides operate in a similar fashion to organophosphate insecticides by inhibiting acetylcholinesterase, and are therefore also neurotoxic (Fukuto, 1990). As a result, human exposures to these esters cause similar health effects to the organophosphates, such as muscular spasms, vomiting, headache, muscle weakness, blurred vision, among others.

Selective herbicides were introduced in the 1940s. Herbicides control weeds primarily through the inhibition of photosystem I, photosystem II, acetyl-CoA carboxylase enzyme, EPSP synthase or the acetolactate synthase enzymes (Kudsk & Streibig, 2003). Glyphosate-based herbicides are among the first used herbicides, and are still globally used (Gasnier et al., 2009). There is limited data on the health effects of exposure to herbicides. However, exposures to some herbicides, such as phenoxy herbicides, are associated with chloracne (Sterling & Arundel, 1986), whereas acute ingestion of glyphosate herbicides may cause gastrointestinal erosion, hemorrhaging, as well as sore throats (Talbot et al., 1991).

2.3.2 Environmental fates – current-use pesticides

Much research has been directed towards characterizing the fates of pesticides. It is known that pesticides typically enter the atmosphere via spraying, volatilization from soil and suspension of soil particles to which they are adsorbed (Scheyer, Morville, Mirabel, & Millet, 2007). These chemicals are then atmospherically transported varying distances from their application and emission sites (Sanusi, Millet, Mirabel, & Wortham, 2000).

Pesticides reside in the atmosphere as vapor, aerosols or adsorbed on soil particles (Sadiki & Poissant, 2008). The atmospheric state of the chemical is a function of its gas-particle partition coefficient, determined by its octanol-air coefficient, as well as vapor pressure (Sanusi, Millet, Mirabel, & Wortham, 1999). Variables such as air-water coefficients influence the removal processes for these organics from the atmosphere. For example, pesticides with low air-water partition coefficients (K_{aw}) are more easily removed by deposition. Those pesticides with higher K_{aw} exhibit longer atmospheric residence times, and hence are more likely to exhibit long range atmospheric transport, because they are less likely to be removed via wet or dry deposition (Scheyer, Morville, Mirabel, & Millet, 2008). Otherwise, pesticides are removed from the atmosphere via photo-degradation and reactions with radicals and oxidizing agents, such as ozone (Bossan, Wortham, & Masclet, 1995).

Contamination of surface waters by pesticides is a function of the physicochemical properties of the pesticide, such as octanol-water partition coefficient (K_{ow}) and aqueous solubility, as well as landscape properties, such as topography and location of waters with respect to the site of application (Dabrowski et al., 2002). Other factors that also influence pesticide concentrations in surface waters include the quantity of applied pesticide, the percentage available for run-off, application rate, precipitation rate, land use and loss to organic matter en route to surface waters. The most common source of surface water contamination is agricultural run-off. Direct releases from manufacturing plants also contribute tremendously to surface water contamination. The pesticide burden in surface waters includes the solute concentrations, concentrations adsorbed to settled and suspended particles, as well as concentrations in aquatic biota (Holvoet, Seuntjens & Vanrolleghem, 2007).

Pesticides may migrate to groundwater via leaching through soil. The concentration of these contaminants in ground-water is a function of quantity applied, the vertical distance between the surface application site and the water-table, soil properties, and recharge properties of the groundwater (Pionke & Glotfelty, 1989).

Soils are considered to be reservoirs for many organic compounds, such as pesticides, due to their high organic content. Contamination of this environmental medium occurs via atmospheric deposition, transfers from vegetation and direct application/spray. The main factors influencing the concentration of pesticides in this medium are the physicochemical properties of the pesticides, climatic conditions such as temperature and precipitation rate, application rate and quantity, as well as landscape properties. Also, soil characteristics play major roles in soil concentrations. These characteristics include organic content, porosity and air/water content, as these often influence sorption of the chemical to the soil colloids (van der Werf, 1996), and hence residence time. Pesticides may remain in the soil bound to soil particles, undergo degradation or be removed by non-degradation processes such as leaching, run-off among others. Sorption to soil colloids enhances persistence and determines the reservoir nature of the soil for the particular pesticide.

Much of the current field research includes regional studies aimed at determining media-specific concentrations. These studies are especially important because contaminants with elevated levels in given media, such as the atmospheric or aquatic media, may be subject to long range transport, with potential adverse effects in the immediate and distant environs. Also, re-volatilization may be an issue when levels are elevated in soils.

A recent trend is to characterize the environmental and climatic factors influencing the fates of pesticides, primarily the halogenated insecticides. For example, the seasonal variations in the atmospheric concentrations of some organochlorine pesticides have been assessed, with observed elevated concentrations in the summer over the winter. A major finding is that not only is primary emission significant for elevated atmospheric levels, but so also is re-volatilization from surfaces (Wu, Tao, Zhang, Lan, & Zuo, 2005; Yao et al., 2006; Yeo, Choi, Chun, & Sunwoo, 2003; Yeo, Choi, & Sunwoo, 2004). In many of these studies, the fates were assessed in single media (primarily the atmosphere) and the chemicals of interest were the known persistent organochlorines.

There is a growing number of field studies assessing climate-based changes/seasonal trends in the fates of current-use pesticides (Field, Reed, Sawyer, Griffith, & Wigington, 2003; Garmouma et al., 1998; Holvoet, Seuntjens, & Vanrolleghem, 2007), some of which have been found to be relatively persistent (Field et al., 2003). For instance, there are suggestions that dissipation half-lives for current-use pesticides are shorter in tropical soils than temperate soils (Laabs, Amelung, Pinto, & Zech, 2002) and the dissipation half-lives in tropical aquatic systems are similar to those in temperate aquatic systems, during the summer period (Laabs, Wehrhan, Pinto, Dores, & Amelung, 2007). Therefore, higher temperatures facilitate faster dissipitation. However, sorption behavior does not not depend on whether the soil is located in a tropical or temperate region (Oliver, Kookana, & Quintana, 2005), but instead depends on whether the soil is located in a wet or dry zone (Liyanage, Watawala, Aravinna, Smith, & Kookana, 2006). The time lapse between pesticide application and a rainy event influences the residence time of the chemicals in soils and the concentrations in surface waters in France (Garmouma et al., 1998).

Although substantial work has been conducted on assessing the role of climatic and environmental factors on the fates of pesticides, studies involving the role of vegetation are still limited.

2.4 Forests effects

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 (Bounoua et al., 2000). The vegetative cover and soil distribution in ecosystems affect climate through changes in the balance of water, momentum and energy (Foley et al., 2003). According to Foley (2003), grasslands and pastures display lowered humidity, lowered precipitation and higher surface temperatures. Tropical deforestation has been associated with climatic changes, such as increased temperatures and albedo, as well as decreased evaporation cooling and precipitation rates (Costa, Bonell, & Bruijnzeel, 2004; Costa & Foley, 2000). 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 (Schiedek, Sundelin, Readman, & Macdonald, 2007). 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 (Holvoet et al., 2007). The uptake by vegetation is more important in reducing atmospheric concentrations than uptake by soil for organics with lg $K_{OA} > 6$ (Nizzetto et al., 2008). It has been shown that land use/cover influences the volatilization fluxes of persistent organic pollutants to the atmosphere (Komprda et al., 2013). Plant cover controls run-off (Garmouma et al., 1998) and, hence, contaminant fate.

There are a number of 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 (McLachlan & Horstmann, 1998). 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 (Wania & McLachlan, 2000). 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 (Priemer & Diamond, 2002). Therefore, these forests are considered to be 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 (Horstmann & McLachlan, 1998). 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 (Horstmann & McLachlan, 1998). 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 (Horstmann & McLachlan, 1998; Wania & McLachlan, 2000). The boreal forests, especially those that are deciduous, may be more effective at capturing some atmospheric organic pollutants than tropical rainforests (Wania & McLachlan, 2000). 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 (Su & Wania, 2005). It has been suggested that the filter effect may be absent for some organics, such as polychlorinated biphenyls (PCBs) in tropical forests (McLachlan & Horstmann, 1998). Temperature affects the partition coefficients K_{oa} and K_{aw}. 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 appears to be reduced at higher temperatures. 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 (Nizzetto, Stroppiana, Brivio, Boschetti, & Di Guardo, 2007). These suggest that the higher temperatures of tropical regions may inhibit the filtering effect of forests.

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, especially for the more polar organics. In some tropical regions, the higher temperatures may inhibit while the higher precipitation rates may enhance the forest filter effect for organic contaminants, especially the more polar current-use pesticides. It is as yet unknown whether the combined high temperatures and precipitation rates of some tropical regions allow for organic contaminants to be filtered from the atmosphere. Also, it is not known how any filtering effect of tropical forests may vary with forest structure and coverage.

It has been shown above that vegetative compartments affect the atmospheric concentrations of organic contaminants, by enhanced uptake from the atmosphere. However, enhanced 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 (Nizzetto & Perlinger, 2012). Therefore, forests may act as secondary sources of organic pollutants at the local or regional scale. 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, given increased forested acreage (Wöhrnschimmel, MacLeod, & Hungerbuhler, 2013). Therefore, despite the suggestions that the filter effect of tropical forests may be reduced, these biomes may otherwise control the fates of organic contaminants, including those that are less persistent.

Although many current-use pesticides are organic contaminants, they are typically more polar (with low air-water and octanol-water partition coefficients) and less persistent. 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 (McLachlan & Horstmann, 1998).

It is internationally accepted that tropical forests provide critical environmental and economic services, such as habitat, biodiversity conservation, timber production and carbon sequestration (Chomitz & Kumari, 1998; Kalácska et al., 2004). These biomes may then also provide additional benefits such as 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 (Bennett, Scheringer, McKone, & Hungerbühler, 2001; Diamond, Priemer, & Law, 2001; Fenner, Scheringer, & Hungerbühler, 2000; Fenner et al., 2005; Leip & Lammel, 2004; Wania & McLachlan, 2000). The long range transport potential (LRTP) of organic contaminants speaks to the ability of the locally emitted contaminants to be transported over large distances (Scheringer, Jones, Matthies, Simonich, & van de Meent, 2009) 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 (Bennett, McKone, Matthies, & Kastenberg, 1998; Beyer et al., 2000; Scheringer, 1996, 2009). 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 (Scheringer, 2009). 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 (Bennett et al., 1998). For an organic contaminant evaluated using the characteristic travel distance (CTD) and travelling at a height of 1000 m in the atmosphere at 25 ^{o}C, recommended 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.

The overall persistence (P_{ov}) at its simplest is a measure of the tendency or ability to maintain presence in the given environmental system (Webster et al., 1998). 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 (Webster et al., 1998) or steady-state residence times (Scheringer et al., 2009). 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 (Webster et al., 1998; Wegmann, Cavin, MacLeod, Scheringer, & Hungerbühler, 2009a).

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 (Wegmann et al., 2009a). The overall persistence and long range transport potential of a few persistent pollutants have been assessed (Beyer et al., 2000; Leip & Lammel, 2004). Some current-use pesticides, which tend to be more polar than their halogenated counterparts, have been found to display regional transport potential (Matthies, Klasmeier, Beyer, & Ehling, 2009). There is little information on the manner in which 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 (Wania & McLachlan, 2000). In a global study, forests reduced atmospheric and aquatic (oceanic and freshwater) concentrations of the studied organic compounds. 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 (Su & Wania, 2005), with potentially enhanced risk via this medium.

Therefore, with the potential decreases to long range transport potential and persistence in the atmosphere at the regional scale in temperate areas, as well as 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 persistent organic pollutants 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 select persistent organic pollutants and current-use pesticides at the watershed scale with co-existing land uses is yet unknown.

2.5 Climate change effects

The major indicators of climate are precipitation and atmospheric temperature (Granger 1985). 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 (Lamon et al., 2009).

Increasing temperatures result in increases in the primary volatilization of organic contaminants (Lamon et al., 2009; Ma, Hung, Tian, & Kallenborn, 2011; Paul et al., 2012). For each 10 ^{o}C increase in temperature, the half-life of pesticides in soils is expected to decrease by as much as 60% (Bloomfield, Williams, Gooddy, Cape, & Guha, 2006b). Increased precipitation is associated with increased wet deposition and delivery to terrestrial and aquatic surfaces (Walcott et al., 2009).Therefore, changes to the climate variables, temperature and precipitation rate, are expected to alter the environmental fates of organic chemicals. These are considered to be 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. 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 (Bloomfield, Williams, Gooddy, Cape, & Guha, 2006a). Also, as the climate changes, geographical shifts in the types and quantity of crops produced are expected (Schiedek et al., 2007). 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 (Walcott et al., 2009). Since pesticide use influences the fates of these chemicals, climate change may indirectly affect their fates, by governing their use patterns.

An analysis by Bloomfield et al. (2006) suggests 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. Steffens et al. 2013 showed that pesticide leaching was dependent on the specific climatic conditions. 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 (Ma et al., 2011). 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 (Paul et al., 2012). 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. Lamon et al. (2009) also found that temperature most strongly affected the global atmospheric fates of some organic contaminants. They had used BETR Global 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. 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 (Wöhrnschimmel et al., 2013).

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 (Komprda et al., 2013). This suggests that land use/cover may counteract or temper some direct effects of climate change.

The assessments described above were primarily conduced for the arctic region, or otherwise at a global scale. Watershed scaled assessments of climate change effects on the environmental fates of organic contaminants have not been identified. The studies involving climate change impacts are predictive and, as such, require the use of multimedia models. Typically, only one vegetative cover is incorporated, with the application of weighted parameters. Consequently, the influence of any vegetative cover in the regional environmental fates of organic pollutants in a watershed with co-existing land uses/covers has not been adequately examined. 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.

2.6 Environmental assessment tools - multimedia modeling

Multimedia models are often used to quantify the environmental fates and health impacts of pollutants in the absence of monitoring or field data. Also, for select long term fate metrics, such as overall persistence and long range transport potential, computation is accomplished solely via multi-media models (Bennett et al., 2001; Fenner et al., 2005; Leip & Lammel, 2004; Matthies et al., 2009). Multimedia modeling is therefore key to assessing the chemistry and transport across environmental compartments (Semeena et al. 2006). A number of private and publicly available multimedia models exist, including CalTOX, ELPOS, SimpleBox, Globo-Pop, ChemRange, CliMoChem, The Tool, ECHAM5, CozMo-POP, among others (Fenner et al., 2005; Götz, Scheringer, MacLeod, Roth, & Hungerbühler, 2007; Wania & McLachlan, 2000; Wegmann, Cavin, MacLeod, Scheringer, & Hungerbühler, 2009b). The models differ by the scale of transport assessment (local/regional/continental/global), complexity of transport equations, the number and types of compartment combinations, as well as the various sources and loss mechanisms considered. The metrics defining terms, such as long range transport potential, differ depending on the goals of the different models (Fenner et al., 2005).

Multimedia environmental models are mass balance models that predict the fates of chemicals in the environment. For such models, the chemical properties, use patterns and quantities are the inputs used to estimate fates, exposures and health impacts (Donald Mackay & MacLeod, 2002). Multimedia environmental models consider transport and transformation processes including chemical reactions, diffusive transfer between phases (within and between environmental compartments/media) as well advective transport (Mackay & MacLeod, 2002). Also included in these models are sources to and sinks from the given environmental system. The multimedia environmental model can be classified as compartmental models, integrated-spatial-multimedia compartmental models or linked spatial single-media models (Rong-Rong, Che-Sheng, Zhong-Peng, & Xiao-Meng, 2012). Compartment models simulate the distribution of contaminants among several environmental compartments/media, all of which are assumed to be homogenous (i.e. well-mixed). As a result, these models typically do not display spatial dimension for chemical transport within any given compartment. In linked spatial single-media models, the spatially-explicit concentration in a single media is first calculated, which, using intermedia transport terms, serves as inputs into other relevant compartments for the sequential calculation of concentrations (Rong-Rong et al., 2012). These types of models can therefore exhibit fine spatial and temporal resolution. The integrated-spatial-multimedia compartmental model is a hybrid of both the compartmental and the linked spatial single-media models. It achieves an intermediate spatial and temporal resolution.

Compartmental models can be classified according to four levels: level I assumes a closed system, with a fixed amount of non-reacting chemical mass, with equilibrium established between compartments; level II assumes an open system at steady state, with inputs balanced by outputs and reaction losses, with equilibrium maintained between compartments; level III relaxes the equilibrium requirement, and instead uses intermedia transport rates while still assuming steady-state (inputs balanced by outputs and reaction losses); whereas level IV allows for dynamicity (unsteady-state) and non-equilibrium (Mackay & Paterson, 1982; Rong-Rong et al., 2012).

Many compartmental models are used primarily for evaluative/predictive purposes (Rong-Rong et al., 2012). The application of these models, due to their country of origin, is often in temperate developed countries. The modeled landscape is often delineated into compartments including air, soil, water, sediments and vegetation. Vertical layers or sub-compartments may be described for the soil, sediment and water compartments. The terrestrial and aquatic compartments often interact simultaneously with one atmospheric compartment spanning the combined surface area of these compartments.

Terrestrial landscapes are heterogeneous, often with a variety of co-existing land covers in any given region. This feature of the terrestrial environment is not well characterized in many compartmental models. It is known, for instance, that forests interact differently with the atmosphere above than do grasslands (Costa et al., 2004; Foley et al., 2003). Therefore, compartmentalizing the landscape according to vegetative cover may be a useful technique to employ in multimedia modeling.

Techniques, such as sub-grid scale parameterization, to account for the heterogeneous quality of landscapes, have been introduced in general circulation models (Avissar & Pielke, 1989; Entekhabi & Eagleson, 1989; Giorgi, Francisco, & Pal, 2003). In other words, the recognition that land cover affects climate and vice versa has resulted in the need to model according to land cover. This is accomplished by delineating the terrestrial compartment according to the various topographical features/ land use and describing individual land-atmosphere interactions for each feature/use (Giorgi et al., 2003). For example, the land surface can be gridded such that forests, grasslands, agricultural lands and urban locales interact independently with the atmosphere and surface waters. These models are often defined as spatially explicit and, although detailed in their description of contaminant transport, they often lack transparency and require substantial computational resources (Pistocchi, Sarigiannis, & Vizcaino, 2010). Therefore, for evaluative or predictive purposes, especially for hypothesis testing, simpler models are recommended.

For the purpose of this dissertation, a compartmental multimedia model with vegetation was considered most suitable. It has been suggested that many fate and transport models do not include a forest canopy and, as such, may not accurately describe chemical fate in significantly forested regions (Wania & McLachlan, 2000). As a result, forest canopy has already been included in a global contaminant fate model (Su & Wania, 2005).

Multimedia models with one vegetative cover are considered too simplistic for regional-scaled assessments (Cousins & Mackay, 2001). Indeed, many watersheds possess co-existing forests, grasslands, croplands and urban centers, and the adequate representation of such landscapes is crucial for informative evaluations. However, no compartmental model with adequate vegetative resolution was identified. Close contenders were: 1) CalTOX, which models one (1) vegetative compartment with three (3) associated soil compartments, in addition to non-vegetative compartments, such as the atmosphere and surface waters; 2) GIM3, which operates similarly to CalTOX, but links a number of adjacent watersheds; 3) CoZMoPOP, which models one (1) vegetative cover and two (2) soil types, in addition to other non-vegetative compartments, such as the atmosphere; 4) SimpleBox, which models vegetation above natural and agricultural soils, in addition to other non-vegetative compartments. Only CozMoPOP was found to have been employed to demonstrate that temperate forests affect the environmental behavior of some semi-volatile organic compounds. Therefore, for the purpose of this dissertation, a level IV compartmental model with three (3) vegetative compartments, one of which is a forest canopy, was developed for the improved assessment of the fates and health impacts of contaminants at the watershed or regional scale.

2.7 Summary

The 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. To assist in this capacity, this review presented current knowledge on the use, environmental distribution and fates, as well as exposures and health effects of these organic compounds. The known influences of specific factors such as forests and climate change on the fates and potential impacts of the chemicals were also examined. Hazard indicators such as long range transport potential were explained. Finally, fate and impact measurement tools such as multimedia environmental models were described.

A number of knowledge gaps were identified and include the following:

- the influence of tropical forests on the long-term environmental fates 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 of the contaminants;
- the existence of an evaluative watershed multimedia model with adequate heterogeneity in the terrestrial compartment, to aid in evaluating the fates and health impacts of organic chemicals in a multi-use watershed.

This dissertation is directed towards filling these knowledge gaps.

Chapter 3

The filter effect of forests on organic pollutants in a tropical watershed

3.1 Introduction

Polybrominated diphenyl ethers (PBDEs) are flame retardants added to the polymers of foams, textile and plastic materials (Rahman et al., 2001). They are simply dissolved into these materials with no chemical bonding occurring. As a result, they are constantly being emitted from the materials during use and disposal. Once released, these organics distribute among environmental compartments, in which they are potentially associated with adverse human and environmental health, such as neurotoxicity and thyroid hormone dysfunction.

Although there are 209 PBDE congeners, only a select few are included in commercial formulations. Technical mixtures are disseminated as pentabrominated BDE (PentaBDE), octabrominated BDE(OctaBDE) and decabrominated BDE (DecaBDE) (Costa et al., 2009). Commercial DecaBDE is the most globally used and its main constituent congener is PBDE-209 (also called decaBDE). However, the production and use of both pentaBDE and octaBDE have been banned in select states in the US and Europe (Costa et al., 2009).

In the environment, higher order (greater bromination) PBDE congeners degrade to the lower order congeners (Vonderheide et al., 2008). Adsorption to particles increases with bromination. Therefore, the apparent affinities of the PBDEs for the various environmental media differ. For example, higher order PBDEs, such as decaBDE, appear to have a high affinity for soils and sediments, whereas the lower order congeners, such as pentaBDEs, are more often found in high concentrations in the atmospheric and aqueous media (Vonderheide et al., 2008). The lower order congeners are therefore subject to long range transport. The greater affinity of the larger (greater molar mass) congeners for soils and sediment is expected given that octanol-air and octanol-water partition coefficients increase with bromination (Gouin & Harner, 2003; Vonderheide et al., 2008). Most PBDEs display limited mobility in soils, where they often persist, due to long residence times in these media. PBDEs are expected to also display a high affinity for vegetation, due to the organic carbon content of this environmental compartment. However, little is known about their persistence in the vegetative compartment (Gouin & Harner, 2003).

The PBDEs are not only toxic and persistent, but they also bio-accumulate and bio-magnify (Frederiksen et al., 2009). Therefore, they are classified as persistent organic pollutants, with the most toxic being PBDE-209, which is also a known potential carcinogen. PBDEs are now ubiquitous (Vonderheide et al., 2008), due to extensive global use and/or production.

Forests may be able to reduce the atmospheric concentrations of these pollutants by transferring them to forests soils, thereby reducing the amount available for partitioning to agricultural crops and surface waters, as well as direct exposures. The transfer process from the atmosphere to the forest soil is termed the forest filter effect and has been shown to be a function performed by boreal and temperate forests on select organic compounds with octanol-air (K_{oa}) and air-water (K_{aw}) partition coefficients such that $7 < \log K_{oa} < 11$ and $\log K_{aw} > -6$ (McLachlan & Horstmann, 1998). The forest filter effect is governed by a number of temperature dependent variables, such as chemical partition coefficients and half-lives, and, as such, is also temperature dependent. Also, the uptake abilities of forests have been shown to be temperature dependent (Nizzetto et al., 2007). The net conclusion is that the forest filter effect may be reduced at elevated temperatures, which are often experienced in tropical climates. However, since wet deposition also transfers atmospheric contaminants to other environmental media such as vegetation, the elevated precipitation rates of some tropical regions may facilitate the forest filter effect. In one study, the inclusion of a vegetation compartment, in the modeling of the environmental fate of PBDE-47, was shown to influence the atmospheric concentrations of this chemical, leading the authors to conclude that vegetation may play a role in the fates of PBDEs by augmenting air-surface exchange (Gouin & Harner, 2003).

There is limited information on the role of tropical forests in the environmental fates of the PBDEs. Therefore, the primary goal of this section of the study was to use field measured concentrations of select PBDEs in the soils, bulk deposition, litterfall and local atmospheres of a forest and nearby clearing to determine whether forests in tropical watersheds filter select PBDEs. Routinely detected PBDEs include PBDE -28, -47, -99, -100, -153, -154, -183 and -209, which are common constituents in the commercial products. These were selected for the assessment.

3.2 Methods

3.2.1 Study area

Jamaica is a tropical island located at approximately 77ºW and 18ºN. Despite a hundred-year mean annual rainfall of 1895 mm, this region displays distinct wet periods during May-July and August-November (Taylor, Enfield & Chen, 2002). Driest months occur during December to March. Temperatures are typically consistent, with average maxima ranging from 22.0 ºC to 30.3 ºC. Sunshine hours are also consistent, with maximum hours in June (up to 13.2 hours) and minimum hours in December (11 hours). However, daylight hours may be as low as six (6) hours in montane regions. Approximately 45% of this island is covered in forests, of which there are five (5) main types – limestone, shale, alluvial, wetland and anthropogenic forests.

Jamaica is approximately 11,244 km^2 and is delineated into ten (10) drainage basins, which are further divided into 26 watershed management zones. The Rio Cobre River drainage basin, also a watershed management unit, is the third largest watershed management unit in Jamaica with a drainage area of 1,249 km^2 (Forestry Department of Jamaica, 2015). As seen in Figure 3.1, it is further sub-divided into two sub-basins – the Upper and Lower Rio Cobre basins. The basin drains into the Rio Cobre River, which is the third longest river in Jamaica, with a length of 52.5 km and an average daily stream flow of 9.8 m^3.s^{-1} (Setegn et al., 2014). The annual average ambient temperature and precipitation rate for the 1986-2005 period were 302.79 K and 1953 m/y, respectively (Meteorological Service of Jamaica, 2015).

This watershed is home to many communities and urban pockets. Figure 3.2 shows that a variety of land covers exists in this area, including forests, farmlands, grasslands, wetlands and urban centers. It is a source of income from activities such as farming. Agricultural use includes sugar-cane and banana plantations as well as intensive and extensive mixed farming. The Rural Agricultural Development Agency (2015), a government body with responsibility for farming activities in rural Jamaica, indicated that there are approximately 16062 farmers conducting activities on 552.11 km^2 in St. Catherine.

In rural areas of Jamaica, such as the Rio Cobre River watershed, residents obtain their waters from ground and surface waters, including streams and rivers. A dam, the Rio Cobre Diversion Dam, is located along the junction between the Upper and Lower Rio Cobre Basins. The water is then diverted into canals to provide domestic water and for irrigation. Otherwise, the waters of this watershed are used for recreational activities, not limited to swimming. Mangroves, forests, swamps and other nature preserves are features within this watershed.

Backyard burning is widely practiced and waste disposal is relatively unmonitored. Pesticides are used extensively for agricultural, household and public protection. As a result, there exists the potential for widespread contamination within the watershed. In fact, this watershed is currently highly polluted, causing the local environmental agency, the National Environmental and Planning Agency (NEPA), to develop a strategic action plan (SAP) to ensure the proper management of this unit. It is therefore critical to characterize the probable fates and impacts of organic contaminants emitted/applied in this watershed.

Approximately 60% of the watershed is considered occupied by deciduous and evergreen forests, whereas approximately 25% and 15% are considered to be occupied by agriculture and urban areas, respectively, with surface waters occupying the negligible remaining portion. Figure 3.2 shows the sampling sites, which were established in a forest and nearby clearing in the Hellshire region of the Rio Cobre watershed.

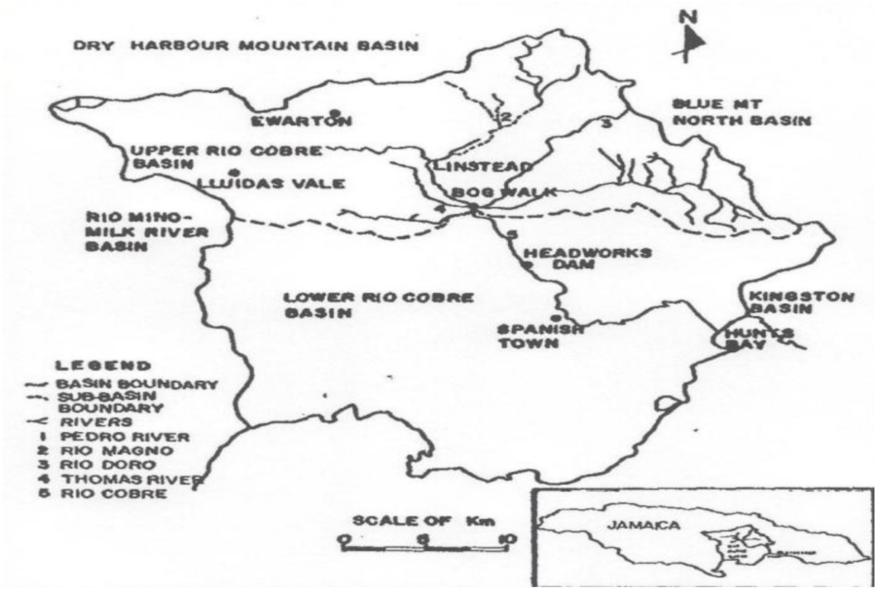


Figure 3.1: The Rio Cobre Watershed Management Unit.
Extracted with permission: Unpublished Report, 1995 (Water Resources Authority, Jamaica, 2014).

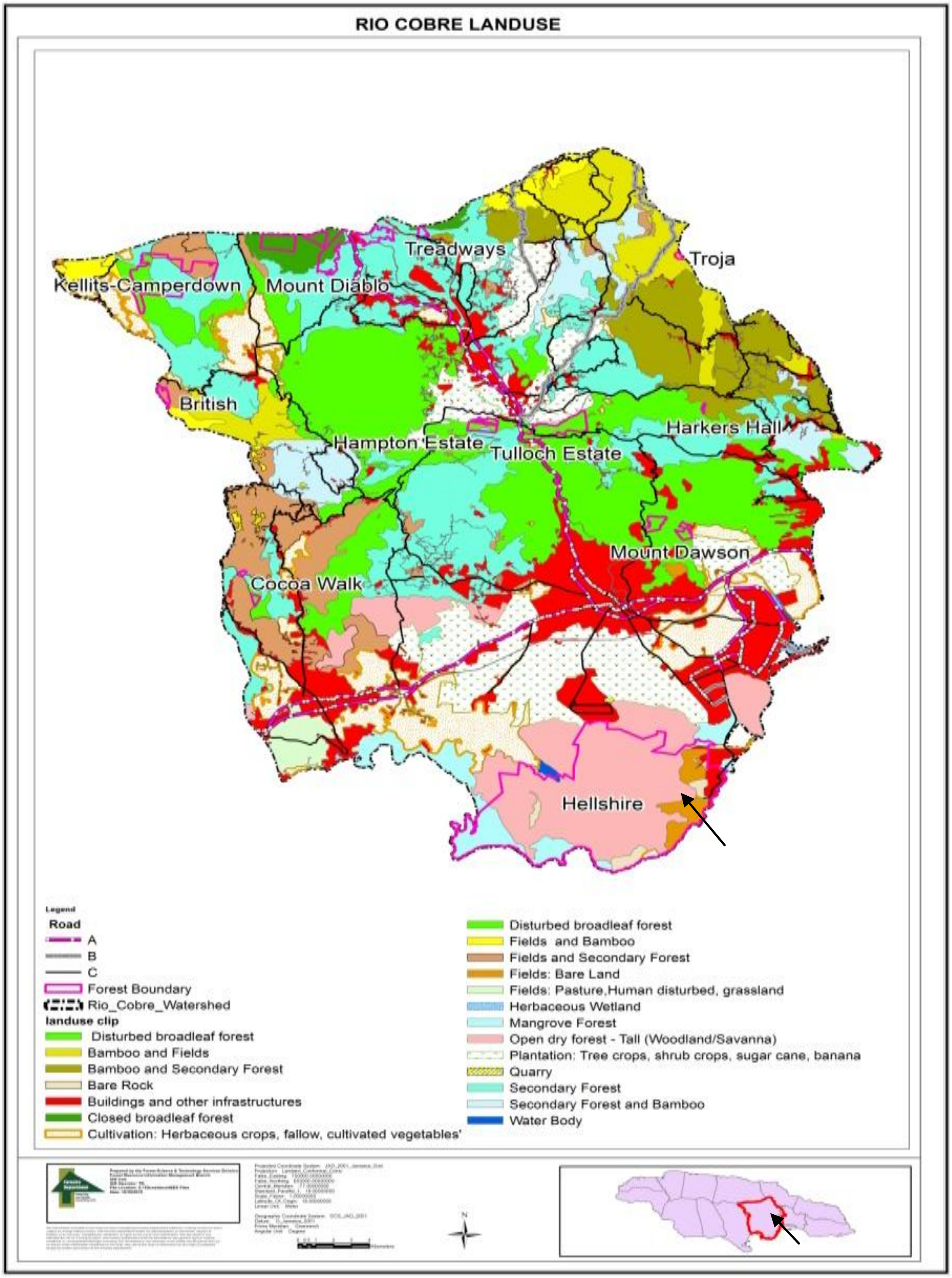


Figure 3.2: Land-use map of the Rio Cobre watershed.
Provided by the Forestry Department, Jamaica (2015).

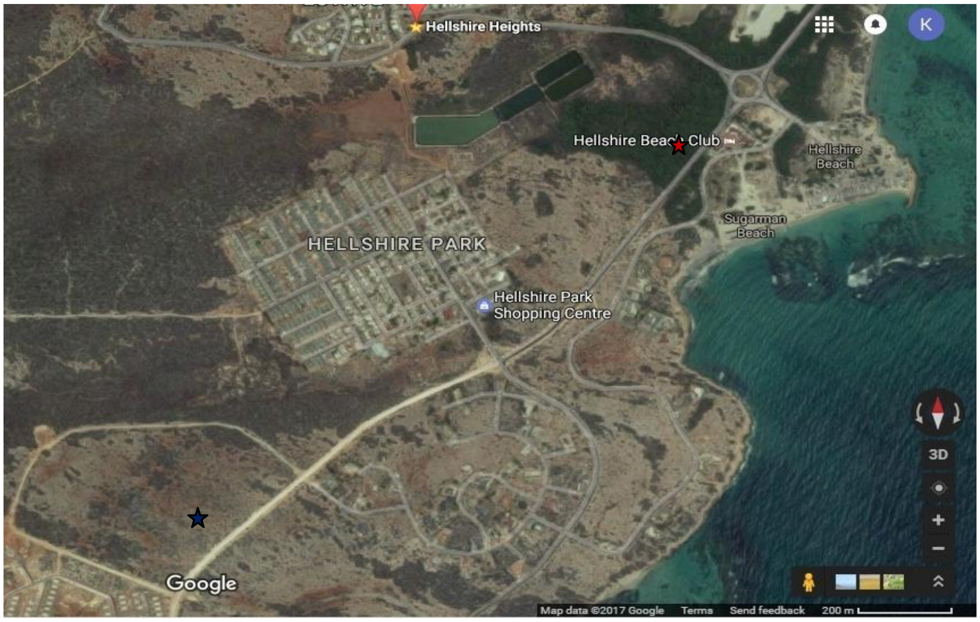


Figure 3.3: Satellite image of the sampling sites.
Extracted from Google Maps.
★ Sampling site in the forest.
★ Sampling site in the clearing.

At the forested site, the canopy was dense. The soil was extremely moist and was covered by a thick layer of plant litter. However, within the clearing, the vegetation was sparse, and the few plants present were either cacti or possessed few leaves. The land surface was rocky and the soil was dry and hardened, as seen in Figure 3.4 and Figure 3.5.

3.2.2 Sampling

Air, bulk deposition, litterfall and soil samples were collected from the two (2) monitoring sites described above. As seen in Figure 3.3, a monitoring site was established within a forest in the Hellshire dry forest region with a second site in a nearby clearing (open field), more than 150 m from the edge of the forest and 300m from the forest sampling site, as done by Horstmann and McLachlan (1998). Sampling began November 4, 2015 and extended for a period of 105 days.

Polyurethane foam passive air samplers (PUF-PAS) were used in this study. They have been found to provide reasonably good estimates of organic compounds when used in tropical environments (Gouin, Wania, Ruepert, & E. Castillo, 2008). Each monitoring site was equipped with five (5) polyurethane foam passive air samplers (PUF-PAS) mounted at approximately 2 m above ground, as shown in Figure 3.4. The foil-wrapped absorbents were transferred to the sampling sites at the beginning of the sample period in sealed solvent-cleaned zipper bags, unwrapped and inserted into the samplers on site. The polyurethane foam (PUF) absorbents were retrieved after 105 days and transported to the laboratory, where they remained frozen (< 4 ^{o}C) until extraction.

Figure 3.4: Polyurethane foam passive air sampler mounted in the forest

Bulk deposition is the sum of the wet deposition and sedimenting particles, with the inherent possibility of additional deposition of aerosols and gases, to a continuously open sampler (Dämmgen, Erisman, Cape, Grünhage, & Fowler, 2005). To collect bulk deposition, four (4) posts, were erected such that together they formed a square with sides of approximately 20 ft. Glass jars, with diametric openings of 8.5 cm, were mounted on each post at a height of 2 m. Also, on each post, one stainless steel drainage basket was mounted at a height of 50 cm to collect litterfall, as seen in Figure 3.5. This is a slight variation of previously employed methods (Horstmann, Bopp, & McLachlan, 1997; Horstmann & McLachlan, 1998). The bulk deposition and litterfall samples were both retrieved at weeks 4 (after 30 days in the field) and 15 (after 21 days in the field) and stored frozen at the laboratory until extraction.

Figure 3.5: Deposition and litterfall collectors in the clearing

Random grab soil samples were collected three (3) times, at each site, during the sampling period, as shown in Figure 3.6. In the forest, all overlying litter and debris were brushed aside to expose the soil below. This was not necessary in the clearing, which was free of overlying matter. To collect soil samples at both sites, the soil surface was skimmed within 2 cm using a steel trowel. The samples were wrapped in solvent-rinsed foil papers and subsequently transported to the laboratory, where they were stored frozen (< 4 °C) until extraction. The soil samples were collected on December 4, 2015, January 27, 2016 and February 17, 2016.

Figure 3.6: Soil sampling in the clearing

3.2.3 Sample extraction and clean-up

Only analytical-grade reagents were used in this study, including Baker-analyzed silica gel (100-200 mesh), alumina and sodium sulfate, as well as hexane and dichloromethane. They were purchased either through VWR Scientific, USA, or Fisher Scientific, USA.

Each sample was spiked with the recovery standards PBDE-35 and PBDE-181 prior to extraction. The soil, deposition and litterfall samples were extracted and cleaned in Jamaica, whereas the PUF samples were shipped to, extracted and cleaned in the US. The extraction methods for the different sample matrices are described below.

The soil samples, in 10 g batches, were mixed with 2 g of anhydrous sodium sulfate in extraction thimbles. The mixtures were soxhlet extracted for 24 hours using hexane: dichloromethane in a 1:1 ratio. The litterfall samples were ground, similarly blended with anhydrous sodium sulfate in extraction thimbles, and then soxhlet extracted for 24 hours, with 1:1 hexane: dichloromethane. Each poly-urethane foam (PUF) disk was also soxhlet extracted, using 1:1 hexane: dichloromethane, for 24 hours. The glass jars containing the bulk deposition were rinsed and the contents liquid-liquid extracted (using separatory funnels), using a 1:1 hexane: dichloromethane mix. Copper granules, activated with dilute nitric acid, were added to each extract to remove excess sulfur. The extracts were then transferred to fresh vials.

Each PUF extract was reduced to 1 mL, using a rotary evaporator, and then transferred to a fresh vial, which was capped with a foil-lined lid and sealed with paraffin film to prevent contamination and further evaporation. The 1 mL extracts were refrigerated until clean-up.

Prior to clean-up, the PUF extracts were all allowed to achieve room temperature. For the clean-up, specialty silica gel columns were used as specified by a modified AccuStandard/EPA method 1614. The columns were packed with the following: glass wool; 1 g silica; 4 g basic silica (33% w/w sodium hydroxide); 1 g silica; 8 g acidic silica (40% w/w sulfuric acid); 2 g silica; and 4 g anhydrous sodium sulfate. All silica reagents were slurry-packed using 1:1 hexane: dichloromethane whereas the sodium sulfate was dry-packed. Excess solvent was then drained from the column to a level about 1 cm above the reagents. Each extract was added to a prepared column, followed by the addition of 100 mL of 1:1 hexane: dichloromethane in 50 mL increments. Sample blanks were treated in the same manner. Each sample was then drained into a labeled flask, stoppered and sealed with paraffin wrap and stored in the refrigerator until instrumental analysis.

In Jamaica, the soil, litterfall and bulk deposition extracts were rotary evaporated to 30 mL. Extract columns were prepared with glass wool, as well as 10 g silica gel/anhydrous sodium sulfate. The columns were wetted with hexane and then drained of the excess solvent. Each sample was added to a column, followed by elution with 25 mL of hexane. The extracts were each collected, reduced to 1.5 mL using a gentle stream of nitrogen and transferred to gas chromatography-mass spectrometer (GC/MS) vials, sealed with paraffin wrap. The same method was applied to the sample blanks. The extracts were refrigerated until shipment to the US. The shipping agency was requested to refrigerate the samples in-between transport. Once delivered to the analytical laboratory in the US, the samples were again refrigerated until analysis.

3.2.4 Instrumental Analysis

For instrumental analysis, all cleaned samples (including sample blanks) were individually reduced to 1 mL using the rotary evaporator, transferred to fresh amber vials and placed in the nitrogen turbo-evaporator for further concentration. The samples were each transferred to labeled amber GC/MS vials, to which 50 µL of dodecane was added, and reduced again to 50 µL in the nitrogen turbo-evaporator. To each vial, 10 µL of Mirex (100 pg.µL^{-1}) was added as the internal standard. The vials were re-capped and placed in the GC-MS for analysis.

Analysis was conducted using an Agilent GC 7890A, which employs splitless injection with a pulse pressure of 25 psi for one (1) minute and then a purge flow-to-split vent of 50 mL.min^{-1}. The carrier gas was helium with a flow rate of 1.2 mL.min^{-1}.

A DB5-ms UI analytical capillary column, with length 20 m, film thickness 0.36 µm and a diameter of 0.18 mm, was used. Given an injection temperature of 300 ^{o}C, the oven temperature program included the following: initiation and holding at 80 ^{o}C for two (2) minutes; ramping at 25 ^{o}C.min^{-1} up to 210 ^{o}C; holding at 210 ^{o}C for two (2) minutes; ramping at 5 ^{o}C.min^{-1} up to 315 ^{o}C; and finally holding at 315 ^{o}C for ten (10) minutes.

The Agilent GC 7890A was coupled to an Agilent 5975C Mass Selective Detector. The detector was operated in the electron capture negative chemical ionization (ECNCI) mode, using methane as the reagent gas. To operate the detector, the transfer line, quadrupole and ion source were set at 315 ^{o}C, 150 ^{o}C and 300 ^{o}C, respectively.

For the identification and quantification of PBDE -28, -47, -99, -100, -153, -154, -183 and -209, five (5) calibration standards of known concentrations (5, 10, 25, 50 and 100 pg.µL^{-1}), with mirex as the internal standard, were used. The ion fragments with m/z 79 and 81 were monitored for the PBDEs, whereas those with m/z 402/404 were monitored for mirex. The eight (8) PBDEs were analyzed and quantified using calibration curves for each analyte.

3.2.5 Quality Assurance/Quality Control

Strict quality assurance/quality control measures were employed in all analytical procedures. All samples were treated in the same manner and using the same procedures. Two (2) field blanks were included for every five (5) atmospheric samples. Also, one (1) laboratory blank was analyzed per six (6) samples. The field and laboratory blanks were treated as samples. There were no discernable differences between field and laboratory blanks, indicating minimal contamination during transportation, storage and analysis. A test sample with known concentration of PBDE-47 was analyzed to monitor the recovery method. All quantified concentrations were blank-corrected by first subtracting the mean masses of each analyte in the appropriate blanks from those in the samples. However, reported values were not recovery corrected.

The peaks were positively identified if they were within ±0.05 min. of the retention time in the calibration standard. Also, the standard noise ratio of ≥ 3 was applied, such that any signal peak less than three (3) times the background signal was not quantified and was recorded as non-detectable. In the air field blanks, concentrations of the PBDEs ranged from 0.1 to 1.6 pg.m^{-3}. Therefore, the limit of detection for the GC/MS was set at either 2 pg.m^{-3} or the three times the standard deviations of the means of the analytes in the blank samples – whichever was higher. The analysis adhered to the recommended EPA Method 8270D.

The surrogates, PBDE-35 and PBDE-181, exhibited recoveries of 70 ± 12 % and 84 ± 8 %, respectively. For the entire method, external recovery analysis involved spiking six (6) polyurethane foam disks with a working standard containing the eight (8) PBDE congeners. All extraction and work-up procedures were the same as for the actual samples. Amber vials were used to minimize photodegradation, whereas foil-lined caps and paraffin film were used to restrict evaporative loss. Recoveries were 90 ± 12 % for the eight (8) congeners.

3.2.6 Quantification of the effect of forests

Bulk atmospheric deposition fluxes in ng.m^{-2}.d^{-1}, which is the mass deposited daily per unit area, was calculated for each PBDE at each site from collected bulk deposition. To compute deposition flux, the mass of each analyte in the glass jars was divided by both the cross-sectional area of the jar opening and the sampling time period. A forest filter factor, F, was subsequently calculated for each analyte, which is simply the ratio of the bulk deposition fluxes to the forest and to the clearing (McLachlan & Horstmann, 1998):

$$F = \frac{bulk\ \ deposition\ \ flux\ \ to\ forest\ \ canopy}{bulk\ \ deposition\ \ flux\ \ to\ clearing} \qquad \text{(i)}$$

A filter factor greater than 1 describes a filter effect (McLachlan & Horstmann, 1998).

Another factor that was also calculated was the depletion factor (DF). This factor speaks to the ability of the forest to deplete air concentrations and helps to express the filter effect of forests (Jaward et al., 2005). The DF, for each analyte, is the ratio of air concentrations in the forests and in the clearing.

$$DF = \frac{atmosp\ heric\ \ concentration\ \ \ in\ the\ forest}{atmosp\ heric\ \ concentration\ \ \ in\ the\ clearing} \qquad \text{(ii)}$$

A depletion factor less than 1 is indicative of a filter effect (Jaward et al., 2005).

In computing atmospheric concentrations, the quantified masses from the GC/MS were divided by the product of the number of sampling days (105 days) and the sampling/uptake rate of the passive samplers. Passive samplers typically have uptake rates for organics in the range 2 to 4 m^3.d^{-1} (Markovic, Prokop, Staebler, Liggio, & Harner, 2015). In this dissertation, an uptake rate of 3 m^3.d^{-1} was assumed for the selected PBDEs.

Forest soils have been shown to display higher concentrations of organic compounds than nearby non-forested soils (Su & Wania, 2005). Using the concepts employed for the derivations of filter and depletion factors, a new comparison factor for soils is being defined in this study and is called an accumulation factor (AF). This is considered to express the ability of forest soils to accumulate organics. For each analyte, the AF is the ratio of the forested soil concentration and soil concentrations in the clearing such that

$$AF = \frac{soil\ concentration\ \ in\ the\ forest}{soil\ concentration\ \ in\ the\ clearing} \qquad \text{(iii)}$$

It is being proposed that an accumulation factor greater than 1 aids in describing a filter effect. Since measured amounts of soil were analyzed, the soil concentrations were simply the ratios of the GC/MS quantified masses and the masses of soil analyzed.

3.3 Results & Discussion

PBDE -28, -47, -99, -100, -153, -154, -183 and -209 were detected in all sample matrices, as discussed below.

3.3.1 PBDEs in the atmosphere

As seen in Table 3.1, the congener with the highest atmospheric concentrations was PBDE-99, with mean values of 5.51 $pg.m^{-3}$ and 5.95 $pg.m^{-3}$ in the forest and clearing, respectively. PBDE-47 was the congener with the second-highest atmospheric concentrations in both the forest and clearing. Therefore, these two congeners dominated the atmospheres in both the forest and clearing. Both PBDE-47 and PBDE-99 are among the lighter and more volatile congeners and are less likely to be deposited than the higher brominated congeners. In one study, urban air was found to be dominated by PBDE- 47, -99 and -209 (T. Gouin et al., 2005). PBDE-

209 is the main constituent of the most globally used technical PBDE – decaBDE (USEPA, 2010). This congener degrades to lower molecular weight congeners, especially PBDE -28, -47 and -99. Therefore, the high atmospheric concentrations of PBDE-47 and PBDE-99 are to be expected. Although the study sites in this dissertation were not near to urban centers, they were relatively close to residential areas where activities, such as backyard burning and dumping, are often practiced.

In the forest air, the congeners with the lowest concentrations were PBDE- 28 and 154. However, in the clearing, PBDE-153 and 183 displayed the lowest atmospheric concentrations. Total atmospheric concentrations for the eight (8) congeners ranged from 8.11 pg.m^{-3} to 31.68 pg.m^{-3}. In the literature, reported values for summed atmospheric concentrations of PBDEs typically range from 0.78 pg.m^{-3} to 106.71 pg.m^{-3} (Hayakawa et al., 2004; Mariani et al., 2008; Su et al., 2009; Su, Hung, Sverko, Fellin, & Li, 2007). However, mean total atmospheric concentrations of the PBDEs have been found to be as high as 980 pg.m^{-3} (Hoh & Hites, 2005). The reporting of the total congeners differed in the various studies with some analyzing as few as seven (7) congeners and others as many as 15 congeners. Despite this, the values reported in this present study are within the range of the cited literature (see Table A.1 in Appendix A for the atmospheric masses of the contaminants in the forest and clearing).

3.3.2 PBDEs in bulk deposition

Table 3.1: Mean atmospheric concentrations and deposition fluxes for the PBDE congeners

PBDE congener	Atmosphere ($pg.m^{-3}$)		Deposition ($ng.m^{-2}.d^{-1}$)			
	Forest	**Clearing**	**Forest**		**Clearing**	
			Period 1 (11/4/2015 – 12/4/2015)	***Period 2*** (1/27/2016 – 2/17/2016)	***Period 1*** (11/4/2015 – 12/4/2015)	***Period 2*** (1/27/2016 – 2/17/2016)
28	0.91	1.17	1.58	2.24	2.59	2.44
47	2.17	4.16	2.80	2.57	2.03	2.40
99	5.51	5.95	2.74	2.51	1.87	2.31
100	1.09	1.22	1.77	2.57	1.59	2.21
153	1.02	1.11	3.68	2.27	1.66	2.27
154	0.96	1.70	9.55	2.20	1.56	2.20
183	1.21	0.98	10.6	2.40	1.76	2.28
209	1.47	3.28	43.8	3.74	2.97	3.65
$\sum_8 PBDE$	**14.34**	**19.57**	**76.52**	**20.50**	**16.03**	**19.76**

Examination of Table 3.1 shows that the higher congeners (PBDE- 153 to 209) were most likely to be deposited from the forested air. In fact, PBDE-209 experienced a mean deposition flux in the forest of 43.8 $ng.m^{-2}.d^{-1}$ and 3.74 $ng.m^{-2}.d^{-1}$ in the first and second sampling periods, respectively, compared to 1.58 $ng.m^{-2}.d^{-1}$ and 2.24 $ng.m^{-2}.d^{-1}$ for PBDE-28 in the first and second sampling periods, respectively. In the clearing, PBDE-209 observed the greatest deposition fluxes, with a greater deposition in the first sampling period. This congener is considered to be mostly associated with atmospheric particles (USEPA, 2010). As a result, the high deposition flux is expected. Also, both PBDE-28 and PBDE-47 were well deposited from the atmosphere in the clearing, whereas the remaining congeners were similarly less deposited. Total bulk deposition flux for the eight (8) congeners range from 16.03 $ng.m^{-2}.d^{-1}$ to 76.52 $ng.m^{-2}.d^{-1}$. Bulk deposition flux values in the literature ranged from 11 $ng.m^{-2}.d^{-1}$ to 1600 $ng.m^{-2}.d^{-1}$ (Hayakawa et al., 2004; Mariani et al., 2008; Moon, Kannan, Lee, & Choi, 2007). As with atmospheric concentrations, the ranges for the bulk deposition in the present study were well within the range of those found in other studies.

As seen in Table 3.1 (see Table A.2 in Appendix A for the PBDE masses in the depositions in the forest and clearing), the higher molecular weight congeners (PBDE-153 to PBDE-209) all experienced greater deposition fluxes in the forest during the first sampling period than in the second. However, in the clearing, all congeners, with the exception of PBDE-28, were deposited more in the second than the first sampling period. In this watershed, high precipitation rates are typical for November, with low precipitation rates often experienced in January and February. Given that adsorption to particles increases with bromination and particle deposition is affected by precipitation rate, then the higher deposition fluxes in the forest of the higher molecular weight congeners, which also display higher octanol-air partition coefficients, during the first sampling period is reasonable.

3.3.3 PBDEs in litterfall

In the litterfall, as seen in Figure 3.4 (see Table A.3 in Appendix A for the absolute mass concentrations of the PBDEs in the various samples), the congener with the greatest mean concentration was PBDE-209 with 109.53 pg.g^{-1} and 434.22 pg.g^{-1} in the forest and clearing litterfall, respectively. In the forest litterfall, both PBDE-47 and PBDE-99 displayed relatively higher concentrations than the remaining five congeners. In this particular compartment, the remaining five congeners (PBDE- 28, 100, 153, 154 and 183) displayed similar concentrations, albeit the lowest being that of PBDE-154. In the litterfall of the clearing, the lowest concentrations were of PBDE-153 and PBDE-154.

Congener concentrations were vastly higher in the litterfall of the clearing. It is probable that the plants in the clearing are among those that are more efficient in capturing organic compounds or more efficient in retaining uptaken organics than those in the forest. On the other hand, clearings typically display lower leaf area indices, and hence smaller plant compartment volumes, than forests. This could then lead to higher concentrations of captured organic contaminants, especially if the capture/uptake rates are similar.

Information on PBDE concentrations in litterfall is limited. However, PBDE concentrations in leaves have been reported in the range of 0.16 ng.g^{-1} dw to 34.1 ng.g^{-1} dw (Qin, Ni, Liu, Shi, & Zeng, 2011; St-Amand, Mayer, & Blais, 2007). In this current dissertation study, the total mean PBDE concentrations in the litterfall of the forest and clearing were approximately 0.62 ng.g^{-1} dw and 2.65 ng.g^{-1} dw, respectively.

3.3.4 PBDEs in surface soil

Soil concentrations for the PBDEs, excluding PBDE-153, ranged from 26 pg.g^{-1} to 46 pg.g^{-1} (see Table A.4 in Appendix A for the absolute mass concentrations of the PBDEs in the different soil samples). In the forest soil, PBDE-153 had concentrations ranging from 43 pg.g^{-1} to 162 pg.g^{-1} to yield a mean of approximately 113 pg.g^{-1}, thereby rendering this congener the dominant one in forest soils. However, Figure 3.7 shows that this PBDE congener was among those with the lowest levels in the soils of the clearing, where the dominant congener was PBDE-209. It has been previously shown that PBDE-209 tends to dominate urban soils (Cetin & Odabasi, 2008). Given that the study site is close to residential areas, the observations in this study are within reason.

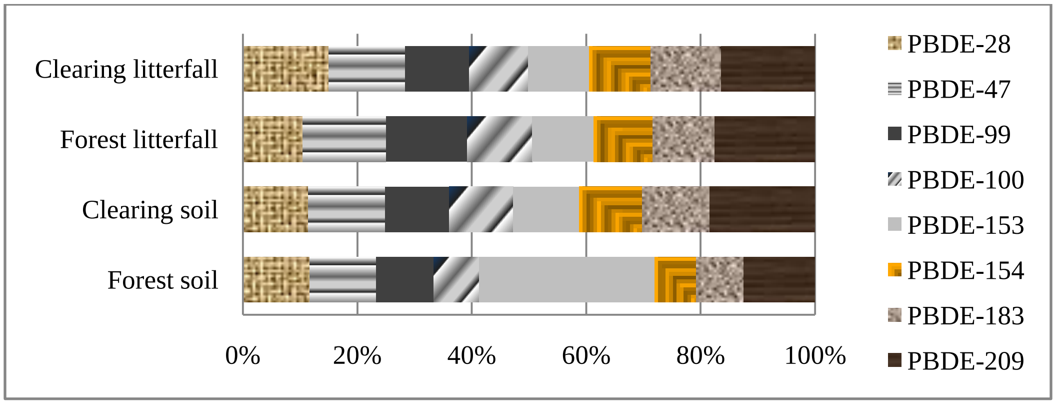


Figure 3.7: Percentage contribution of each congener in the given compartment

3.3.5 Forest filter effect

To assess the difference between the PBDE contaminants in the clearing and the forest, filter, depletion and accumulation factors were computed, as described in the methods section, and are displayed in Table 3.2. Accumulation and filter factors greater than one (> 1) and depletion factors less than one (< 1) are considered indicative of a filter effect. When these factors were computed for all the PBDEs together, a filter effect was clearly observed.

Table 3.2: Forest filter effect factors

PBDE congener	**Depletion factor**	**Filter factor**	**Accumulation factor**
28	0.78	0.80	1.58
47	0.52	1.22	1.33
99	0.93	1.26	1.40
100	0.90	1.14	1.09
153	0.92	1.44	4.14
154	0.56	2.56	1.02
183	1.23	2.61	1.09
209	0.45	5.28	1.05
$\sum_{8} PBDE$	***0.73***	***2.23***	***1.55***

All congeners, with the exception of PBDE-183, observed lower atmospheric concentrations in the forest than in the clearing. The remaining seven (7) congeners were therefore more efficiently depleted from the atmosphere by the forest than PBDE-183. This congener displayed mid-range mean atmospheric concentrations of all congeners in the forest but had the lowest mean atmospheric concentration in the clearing. Deposition fluxes for PBDE-183 were mid-range. However, concentrations of this chemical were amongst the highest and lowest in the litterfall of the clearing and of the forest, respectively.

The filter factor was higher for the higher-order congeners. This indicates that these congeners are more efficiently deposited from the atmosphere of the forest than the clearing. It appears then that deposition to vegetation is a significant pathway for the removal of PBDEs from the atmosphere, especially the higher molecular weight congeners.

The soil concentrations of all congeners were greater in the forest than in the clearing, leading to accumulation factors greater than 1. The lower-order congeners were typically more greatly accumulated in the forest soil than in the clearing soil, as shown by the higher accumulation factors (1.33 to 1.58). However, PBDE-153 displayed a substantially higher accumulation factor than the remaining congeners – a value of 4.14. This congener had amongst the lowest atmospheric concentrations. In one study, total PBDE background concentrations in forest soils have been found to exceed those in grasslands (Hassanin et al., 2004). The burden of select persistent pollutants tends to be higher in forest soils (Su & Wania, 2005). All these findings were for temperate regions. Therefore, the observations in this dissertation are consistent with those in the literature, despite the tropical nature of the study site.

3.4 Conclusions

Studies have been conducted to evaluate and compare the concentrations of select organic compounds in the soils, atmosphere and deposition of forests and clearings (or grasslands) (Horstmann et al., 1997; Horstmann & McLachlan, 1998; Jaward et al., 2005; McLachlan & Horstmann, 1998; Su & Wania, 2005). However, the assessments have been restricted to temperate regions. Studies performing similar evaluations in tropical regions have not been identified. This dissertation work is considered among the first to perform such comparisons in a tropical environment, especially in a developing country.

The goals were to determine whether there was a difference in the concentrations of PBDEs in the atmosphere, soils, litterfall and bulk deposition of a clearing versus a forest in a tropical region, as well as to conclude whether such differences led to a ‘filter effect’ for the PBDEs. A quantitative evaluation method was employed.

This dissertation showed that the bulk deposition fluxes and soil concentrations of the PBDEs were higher in the forested environment than in the clearing. These were quantitatively demonstrated by filter and accumulation factors greater than 1. Also, it was found that the atmospheric concentrations of the PBDEs were typically lower in the atmosphere of the forest than in the adjacent clearing. Computed depletion factors less than 1 supported this finding.

Studies comparing the concentrations of these select PBDEs in the litterfalls of clearings/grasslands and forests are limited. This dissertation is among the first to do so, especially in a tropical developing country. It was found that the litterfall of the clearing contained higher concentrations of the PBDEs than those in the forest.

These results therefore support this dissertation’s hypothesis that tropical forests filter PBDEs by transferring them from the atmosphere to the soils. The tropical forests therefore perform this role similar to their temperate counterparts.

The current work should be extended to determining how atmospheric and soil concentrations of the PBDEs vary with distance from the forest in the tropical region. Attempts should be made to identify the sources of the PBDEs in the watershed. Additional research is recommended to examine how the various tropical plants or trees contribute to the filtering effect of the forest. Quantifying the environmental concentrations of the congeners according to land use in such tropical developing nations would also provide useful information. These would all assist in identifying long-term control measures to reduce/prevent contamination. To date, such studies in developing tropical countries are limited.

Conducting this section of the dissertation was associated with a number of challenges. Only one laboratory was found that was equipped enough to conduct the extraction and clean-up of the samples. However, the associated cost was exorbitant. Shipping the soil, litterfall and deposition samples to the US, where the extraction and clean-up would be cheaper, was difficult. As a result, to conserve costs, the air samples were shipped to the US for extraction and clean-up, whereas the remaining samples were extracted in Jamaica. All samples were instrumentally analyzed in the US, as the cost to do so in Jamaica was astronomical. Although shipping the samples to the US required that they be in and out of refrigeration during transport, this was considered acceptable, only because the samples were expected to have maintained a low temperature. Also, negligible degradation was expected in the short time out of the refrigerator, because of the known long half-lives of the analytes. Challenges such as these are common in developing countries like Jamaica wherein analytical facilities and financial resources are limited. However, knowledge regarding the fates and distribution of organic contaminants is critical, especially in developing regions as Jamaica, where products are often overused and abused, and their disposals are largely unmonitored. Until the conduct of field monitoring and assessments become more practical, environmental multi-media models are critical tools that can be employed to serve as reasonable alternatives. Therefore, in this dissertation, such a representative model, able to assist with fate and health impact assessments, has been developed for employment in tropical developing countries. It is recommended for interim use in the research/assessments suggested above. This model is described and applied in Chapters 4 and 5.

Chapter 4

The effect of forests on the fates and distribution of organic contaminants in a tropical watershed

4.1 Introduction

A number of organic compounds are associated with adverse human and ecosystem health. Many are ubiquitous, having entered the environment from a variety of sources. Their propensity to cause adverse effects is reflected by hazard end-point indicators, such as long range transport potential and overall persistence (Fenner et al., 2005; Wegmann et al., 2009).

The assessment of the long term fates and health impacts of organic contaminants at the watershed scale is critical. Watersheds provide income, aesthetic appeal, recreational facilities and habitats for its human and non-human inhabitants. They are often delineated into combinations of land uses including urban regions, agricultural zones, grasslands, forests, among others. Forests, especially in tropical regions, provide beneficial functions such as water quality enhancement, yield promotion and soil stabilization (Pattanayak, 2004). However, their potentially beneficial role in controlling the long term fates, and resultant health impacts of environmental contaminants, has not been sufficiently explored. Such information would clearly be valuable for the formulation and implementation of watershed management strategies, policies and controls. Therefore, this chapter aims to examine the role of forests in influencing the fates of select organic pollutants in a tropical watershed.

Evaluations of the trends in the fates and distribution of environmental contaminants are considered to be best obtained from field monitoring and measurements. However, field assessments are typically challenging in many developing countries, which often lack the financial resources and analytical facilities to perform such tasks. An excellent alternative is the use of multimedia environmental models. These can provide reasonable estimates of these fates and health impacts of the organic contaminants, under various scenarios, in such tropical watersheds/catchments.

Long-term fate metrics are typically unmeasurable and are instead computed using multimedia fate models, which range from simple to complex. Simple compartmental models assume well-mixed compartments, with no spatially explicit transport. They are characteristically used for evaluative or predictive purposes, due to ease of use and quick output of information (Rong-Rong et al., 2012). More complex models provide spatially explicit representation of transport through the landscape. However, such complex models are often resource intensive, difficult to use, and not necessarily accurate or transparent (Pistocchi et al., 2010).

Examples of current compartmental multimedia environmental models, with assessment scales from regional to global, include CalTOX, ELPOS, SimpleBox, ChemRange, CliMoChem, ECHAM5, The Tool and CozMo-POP (Fenner et al., 2005; Götz et al., 2007; Wania & McLachlan, 2000; Wegmann et al., 2009b). Many compartmental models incorporate only one vegetative cover. Models with single vegetative compartments are considered too simplistic for local/regional scaled assessments (Cousins & Mackay, 2001). Also, many of these models do not include a forest compartment and may not accurately assess contaminant fate, especially in a forested region (Wania & McLachlan, 2000).

Additionally, many multimedia environmental models are not dynamic. While the use of steady state models is suitable for the assessment of long-term or average fates, their applicability may be limited when attempting to assess time-variant behaviors and processes

(Pistocchi et al., 2010) or when the environment experiences constant perturbations, such as variations in weather patterns over a given period. In such cases, a dynamic multimedia model is expected to give a more realistic representation of the changes to the fates of chemicals over time.

A limited number of multimedia models capable of assessing chemical distribution at the catchment scale have been developed, including G-CIEMS, BasinBox and GIM3 (Hollander, Huijbregts, Ragas, & Van de Meent, 2006; Luo, Gao, & Yang, 2007; Suzuki et al., 2004). However, these models are either site-specific for very small watersheds, steady state or lack the spatial heterogeneity in the vegetative/terrestrial compartments that is characteristic of many watersheds. Also, most current catchment models typically focus on water quality in lieu of chemical distribution among environmental media.

Therefore, another major goal of this dissertation was to develop a regional dynamic (level IV) multimedia model that provided the spatial heterogeneity, in the landscape, typical of many watersheds, and that could represent the fates of organics under both steady state and dynamic conditions. This was achieved by combining elements from three existing multimedia models – CalTOX 1.5 (California Environmental Protection Agency, 1993), GIM3 (Luo et al., 2007) and Multimedia Urban Model (MUM) (Diamond et al., 2001). A 16-compartmental model with three (3) vegetative surfaces – forests/grasslands, urban centers and cropland – was the result. The new model, named RioShed, was used in this dissertation to examine the association between tropical forests and the fates of select organic compounds at the watershed scale.

The chosen organic contaminants are among those that are under current global scrutiny due to their ubiquitous nature and potential to cause adverse health impacts. They include polybrominated diphenyl ethers (PBDEs), dioxins, furans and non-halogenated current-use pesticides (CUPs). The PBDEs, dioxins and furans are known persistent organic pollutants (POPs), that have been associated with endocrine disruption, immunological and neurological disorders, and some (PBDE-209 and tetrachlorinated dibenzo-p-dioxin (TCDD)) are classified as potentially carcinogenic. However, the current-use pesticides are typically more polar, less persistent and have been associated with headaches, comas, convulsions, muscular spasms and skin disorders (Bradberry et al., 2005; Fukuto, 1990; Jaga & Dharmani, 2003; Mitrou, Dimitriadis, & Raptis, 2001; Sterling & Arundel, 1986; Vonderheide et al., 2008).

To summarize, this study is among the first to characterize the effects of tropical forests on the fates of the above organic contaminants, using a newly developed, dynamic and spatially heterogeneous evaluative multimedia model. The study site is the Rio Cobre watershed in Jamaica.

4.2 Methods

4.2.1 Model Development - RioShed

4.2.1.1 Compartments

To develop RioShed, elements from select multimedia environmental models were combined. The selection criteria for the models were as follows: 1) they should be publicly and/or readily accessible; 2) when combined, they should allow for assessment across multiple vegetative covers and their respective soil compartments; and 3) they should be applicable to organic compounds, not limited to those of a persistent nature. The multimedia environmental models selected were CalTOX 1.5 (California Environmental Protection Agency, 1993), GIM3 (Luo et al., 2007) and the Multimedia Urban Model (MUM) (Diamond et al., 2001).

CalTOX 1.5 was used as the base model, due to its established good environmental fate predicting capabilities, as well as the fact that the required input data were obtainable or estimable. The existing vegetative cover in the base model was represented as agricultural vegetation. A second vegetative compartment was introduced for the forest canopy. The associated forest soil compartment was delineated into surface, root-zone and vadose-zone soils. Further to this, an impervious surface and co-existing urban vegetation, as modeled in the Multimedia Urban Model (MUM) (Diamond et al., 2001), were together also introduced into the model as an urban compartment. To ensure compatability, the associated soil for the urban compartment was also delineated into surface, root-zone and vadose-zone soil compartments. Whereas the base model (CalTOX 1.5) was pseudo-steady state, with the root-zone and vadose-zone soils at steady state with respect to the remaining compartments, RioShed is fully dynamic.

With the described modifications to CalTOX 1.5, the ensuing RioShed has a total of 16 compartments, which are: sediment (d); surface water (w); atmosphere (A); agricultural vegetation (c_a); agricultural surface soil (s_a); agricultural root-zone soil (r_a); agricultural vadose-zone soil (v_a); urban vegetation (c_u); urban impervious surface (i_u); urban surface soil (s_u); urban root-zone soil (r_u); urban vadose-zone soil (v_u); forest canopy (c_f); forest surface soil (s_f); forest root-zone soil (r_f); forest vadose-zone soil (v_f). A diagram representing the model is given in Figure 4.1.

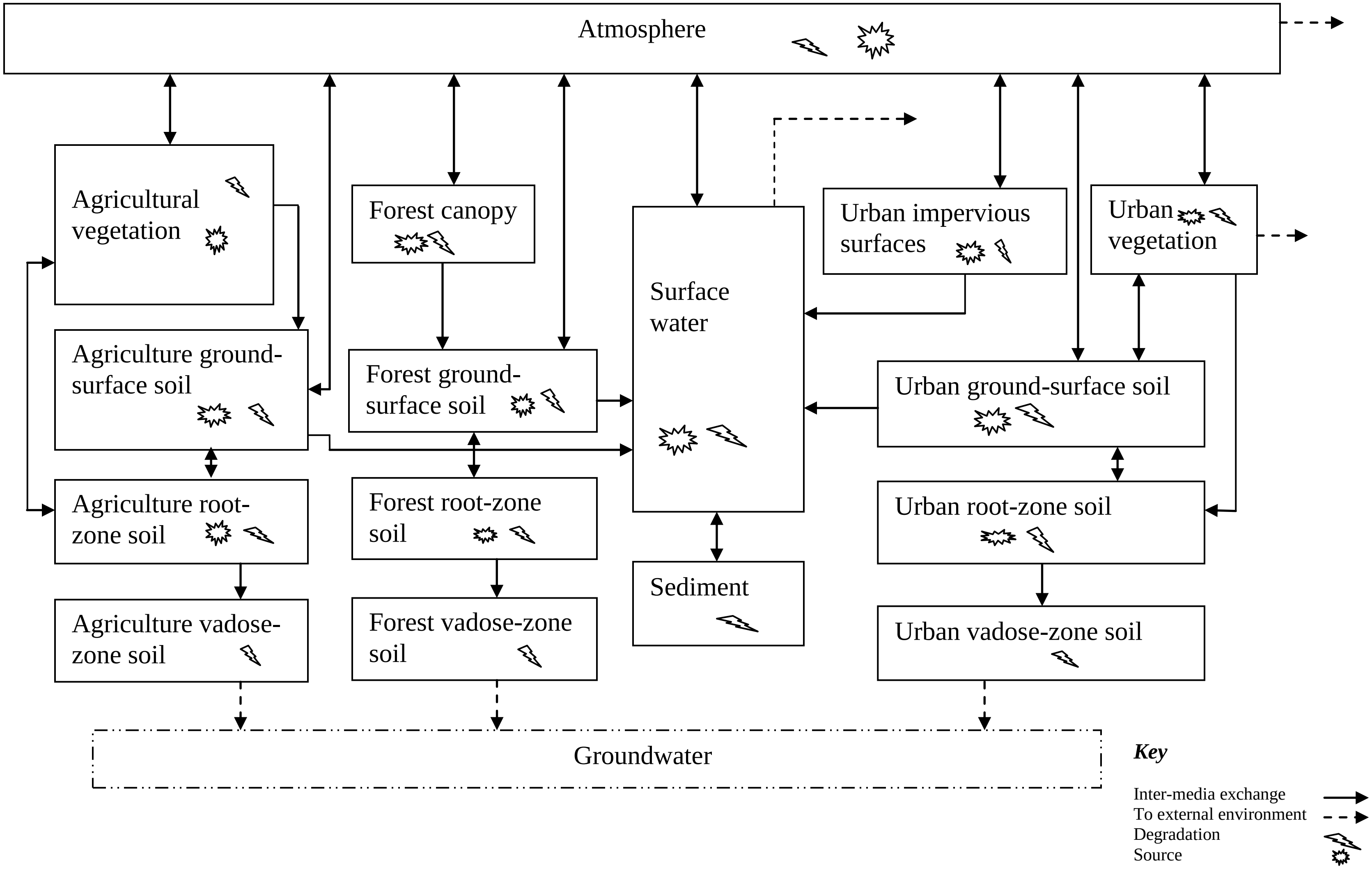


Figure 4.1: Illustration of Rioshed

The atmosphere compartment spans the area of the modeled region and is considered well-mixed and homogeneous. This compartment is modeled to extend from the top of the troposphere down to the top of the surface soil layer, and includes only particles and pure (free of other impurities) air. The surface water compartment is considered to include only suspended particles, aquatic biota and pure (free of other impurities) water, and consumes less than 10% of the modeled landscape. The sediment compartment lies below the water compartment and displays the same surface area. Only the top 2-5 cm of the sediment layer is modeled, since this section typically engages in exchange with the surface water above (Santschi et al., 1990; Wang et al., 2003). The sediment layer consists of particles and pure water in the pores. The soil has a thin surface layer (0.1-1 cm), a thick root-zone layer below and a base vadose-zone layer. All soil layers are considered to consist of particles, pure air and pure water. The vadose-zone layer is the layer of soil between the root-zone layer and the water table. Only vertical mass exchange is modeled between soil layers. The vegetative compartments (agriculture, forest and urban) include the above-ground portion of the plants (the leaves with associated cuticles and stoma), as well as the plant-roots. In their study, Diamond et al. (2001) considered the impervious surface to be coated with urban film, which constitutes of pure or organic film (30%) and particulate matter (70%). The organic film was assumed to have organic matter as its sole constituent and, hence, was modeled using the organic carbon fraction (f_{oc}) of octanol (0.74). This approach for representing the urban film was employed in RioShed.

4.2.1.2 Model equations in RioShed

In RioShed, the total mass entering the system is conserved, and each compartment is assumed homogenous and completely mixed. The transport processes considered are advective, diffusive and otherwise physical non-advective/diffusive, such as wind re-suspension (see Table B.1 in Appendix B for all considered compartment gains and losses). The fugacity approach is employed to calculate the transport rate constants (the equations for the relevant fugacity capacities are presented in Table B.3 in Appendix B; the formulations necessary to estimate the transport rate constants for the 16 compartments are presented in Table B.4 in Appendix B; and a description of the fugacity approach to intermedia transfer is also given in Appendix B).

The transport and transformation equations used are of the following general form –

$$\frac{d}{dt} N_i(t) = -R_i N_i(t) - \sum_{j=1, j\neq i}^{m} T_{ij} N_i(t) + \sum_{j=1, j\neq i}^{m} T_{ji} N_j(t) + S_i(t) - T_{io} N_i(t) , \qquad \text{(i)}$$

where $N_i(t)$ is the inventory of the contaminant in compartment *i*, mol; $N_j(t)$ is the inventory of the contaminant in compartment *j*, mol; R_i is the first-order removal constant from compartment *i*, d^{-1}; T_{ij} is the first order transfer rate constant for transport from compartment *i* to *j*, d^{-1}; T_{ji} is the first order transfer rate constant for transport from compartment *j* to *i*, d^{-1}; T_{io} is the first order transfer rate constant for transport from compartment *i* to a point outside the modeled domain, d^{-1}; S_i is the source input rate into compartment *i*, $mol.d^{-1}$; and m is the total number of compartments in the defined system.

Table 4.1 includes the mass balance equations for the 16 compartments.

Table 4.1: Mass balance equations for RioShed

Compartment	**Mass Balance Equation**
Atmosphere (A)	$\frac{dN_A}{dt} = -L_A N_A + S_A + T_{ca,A} N_{ca} + T_{cu,A} N_{cu} + T_{cf,A} N_{cf} + T_{sa,A} N_{sa} + T_{su,A} N_{su} + T_{sf,A} N_{sf} + T_{w,A} N_w + T_{iu,A} N_{iu}$
Surface Water (w)	$\frac{dN_w}{dt} = -L_w N_w + S_w + T_{A,w} N_A + T_{d,w} N_d + T_{sa,w} N_{sa} + T_{su,w} N_{su} + T_{sf,w} N_{sf} + T_{iu,w} N_{iu}$
Sediment (d)	$\frac{dN_d}{dt} = -L_d N_d + T_{wd} N_w$
Impervious Surface (iu)	$\frac{dN_{iu}}{dt} = -L_{iu} N_{iu} + T_{A,iu} N_A + S_{iu}$
Agricultural Canopy (ca)	$\frac{dN_{ca}}{dt} = -L_{ca} N_{ca} + T_{A,ca} N_A + T_{ra,ca} N_{ra} + S_{ca}$
Forest Canopy (Chapin et al.)	$\frac{dN_{cf}}{dt} = -L_{cf} N_{cf} + T_{A,cf} N_A + T_{rf,cf} N_{rf} + S_{cf}$
Urban Canopy (cu)	$\frac{dN_{cu}}{dt} = -L_{cu} N_{cu} + T_{A,cu} N_A + T_{ru,cu} N_{ru} + S_{cu}$
Agricultural Ground-surface Soil (sa)	$\frac{dN_{sa}}{dt} = -L_{sa} N_{sa} + S_{sa} + T_{A,sa} N_A + T_{ra,sa} N_{ra} + T_{ca,sa} N_{ca}$
Forest Ground-surface Soil (Berrisford et al.)	$\frac{dN_{sf}}{dt} = -L_{sf} N_{sf} + S_{sf} + T_{A,sf} N_A + T_{rf,sf} N_{rf} + T_{cf,sf} N_{cf}$
Urban Ground-surface Soil (su)	$\frac{dN_{su}}{dt} = -L_{su} N_{su} + S_{su} + T_{A,su} N_A + T_{ru,su} N_{ru} + T_{cu,su} N_{cu}$
Agricultural Root-zone Soil (ra)	$\frac{dN_{ra}}{dt} = -L_{ra} N_{ra} + T_{ca,ra} N_{ca} + T_{sa,ra} N_{sa} + S_{ra}$
Forest Root-zone Soil (Berrisford et al.)	$\frac{dN_{rf}}{dt} = -L_{rf} N_{rf} + T_{cf,rf} N_{cf} + T_{sf,rf} N_{sf} + S_{rf}$
Urban Root-zone Soil (su)	$\frac{dN_{ru}}{dt} = -L_{ru} N_{ru} + T_{cu,ru} N_{cu} + T_{su,ru} N_{su} + S_{ru}$
Agricultural Vadose-zone Soil (va)	$\frac{dN_{va}}{dt} = -L_{va} N_{va} + T_{ra,va} N_{ra}$
Forest Vadose-zone Soil (vf)	$\frac{dN_{vf}}{dt} = -L_{vf} N_{vf} + T_{rf,vf} N_{rf}$
Urban Vadose-zone Soil (vu)	$\frac{dN_{vu}}{dt} = -L_{vu} N_{vu} + T_{ru,vu} N_{ru}$

L_i is the loss rate constant for compartment i (which includes constants for reaction losses, as well as transport to other compartments and the external environment), d^{-1}; N_i is the i^{th} compartmental inventory, mol; $T_{i,j}$ is the transport rate constant for transport from compartment i to j, d^{-1}; and S_i is the source input rate for compartment i, mol.d^{-1}.

Bulk diffusivity in compartment i (j), $D_{i(j)}$, as well as the thickness of the boundary layer for compartment *i* (or *j*), $\delta_{i(\text{or } j)}$, and/or their ratios, were estimated as in CalTOX 1.5 (California Environmental Protection Agency, 1993) (see Table B.4 in Appendix B for the formulae used).

For the equations in Table 4.1, fully implicit solutions were obtained using the Backward Euler method such that

$$N_i(t+dt) = N_i(t) + dt\,\frac{dN_i}{dt}\Big|_{t+dt} \qquad \text{(ii)}$$

Substituting $\frac{dN_i}{dt}$ with the equations in Table 4.1 and solving for $N_i\,(t+dt)$ resulted in a system of equation that were solved to give the inventory values at each time step (see Figure S.1 in the Supporting Information for the matrix solution employed). The transport terms in the model depend on properties inherent to the landscape, such as ambient temperature, leaf area index (LAI), precipitation rate and compartment areas, as well as chemical data such as Henry's constant, partition coefficients, molecular weight, among others. Therefore, such landscape and chemical properties are inputs into the model.

Scripts were created in Matlab to accept these input data and to use them to calculate the model parameters (fugacity capacities and the associated transport coefficients). Matlab was also coded to use the matrix equation to give the simultaneous solution of media inventories at a specified time. For the calculation of inventories at steady state, the differential terms in the 16 differential equations were equated to zero with the resultant linear equations put in matrix form such that

$$\vec{n}_{ss} = -T^{-1}\vec{s}\,, \qquad \text{(iii)}$$

where T is the 16 by 16 matrix of transport coefficients, d^{-1}; $\vec{n}_{ss}$ is the column array of the steady state inventory in each compartment *i*, mol; and $\vec{s}$ is the column array of source input rates into each compartment *i*, mol.d^{-1}. Codes were generated in Matlab to use this matrix equation to generate simultaneous steady state compartment outputs (the matrix solution is given in Figure B.2 in Appendix B and the codes to generate the outputs are presented in Appendix E).

Outputs of RioShed include inventories (in moles), long term fate metrics, health impact metrics, as well as compartmental chemical losses and gains. These outputs can be obtained for steady state conditions or at a specified time after the chemical has been introduced into the modeled landscape.

4.2.1.3 Long –term fate metrics formulations in RioShed

Long-term fate metrics give information on the propensity of environmental contaminants to cause localized, as well as distant health and environmental effects. Examples of such metrics include overall persistence (P_{ov}) and long range transport potential (LRTP) (Bennett et al., 2001; Fenner et al., 2005; Leip & Lammel, 2004; MacLeod, Scheringer, McKone, & Hungerbuhler, 2010). Multimedia models are typically used to calculate these metrics, since direct measurements are not possible (Fenner et al., 2005). RioShed was employed for this purpose in this study. The computational methods are explained below.

Overall persistence, P_{ov}, is defined as the total residence time of a chemical in a system under steady state conditions (Fenner et al., 2000; Leip & Lammel, 2004; Wegmann et al., 2009b), and can be considered to be the time for degradation from the environment (Wegmann et al., 2009b). In RioShed, it is calculated as the ratio of the total steady state inventory of the chemical in the system, N_t (mol), and the sum of the products of the inventory in each medium *i*, N_i (mol), as well as the degradation rate for the chemical in the given medium *i*, k_i (d^{-1}) (Matthies et al., 2009; Stroebe, Scheringer, & Hungerbühler, 2004; Wania & Mackay, 2000), such that

$$P_{ov} = \frac{N_t}{\sum N_i k_i} \qquad \text{(iv)}$$

The long range transport potential (LRTP) of any chemical can be expressed by its characteristic travel distance (CTD) in a transporting fluid, often in air (CTD_A) or water (CTD_w).

For the purpose of this study, the CTD_i is the distance the *ith* transporting fluid, moving as a Lagrangian cell, travels before the concentration of the chemical in the medium is reduced to 1/e (or 37%) of the original concentration (Bennett et al., 1998).

CTD_i, and hence $LRTP_i$, is the product of the *i*th medium's advection velocity, u_i, and the residence time of the chemical in the medium i, τ_i, (Matthies et al., 2009), such that

$$LRTP_i = CTD_i = u_i \tau_i. \qquad \text{(v)}$$

The long range transport potential (or characteristic travel distance) is a steady state variable, since the residence times assume steady state. Medium-specific residence time τ_i was calculated as in CalTOX, such that

$$\tau_i = \frac{1}{L_i} \qquad \text{(vi)}$$

where L_i is the loss rate constant for the medium i, d^{-1}.

The annual average concentrations for each chemical in the *i*th compartment, $C_{iave,}$ similar to the average concentrations employed by Wania and McLachlan (2001), were computed by generating daily media concentrations for 365 days, given a dynamic solution, and averaging these over the period. Therefore, the annual average concentration for compartment *i* was computed using the following equation:

$$C_{iave} = \frac{1}{365} \sum_{n=1}^{365} C_{in} \qquad \text{(vii)}$$

It must be noted that for a system achieving steady state within days or weeks, the annual average concentrations approximate the steady state concentrations.

4.2.1.4 Formulation of health impact metrics in RioShed

A few health impact metrics can be estimated using RioShed. Among these is the non-cancer hazard quotient for consumption of surface water ($HQ_{nc,w}$), expressed as

$$HQ_{nc,w} = \frac{C_w \times EF \times ED(\frac{IR_w}{RfD_o} + \frac{IR_A \times K}{RfD_i})}{BW \times AT}$$ (US Environmental Protection Agency (USEPA), 1991), (viii)

where C_w is the concentration of the chemical in the surface water, mg.m^{-3}; IR_w and IR_A are the individual's intake rate of surface water and air, respectively, m^3.d^{-1}; RfD_o and RfD_i are the respective oral and inhalation reference doses, mg.kg^{-1}.d^{-1}; K is the volatilization factor; EF is the exposure frequency, d.y^{-1}; ED is the exposure duration, y; BW is the individual's body weight, kg; and AT is the averaging time, d.

Similarly, the non-cancer hazard quotient for inhalation of air ($HQ_{nc,A}$) is calculated using

$$HQ_{nc,A} = \frac{C_A \times EF \times ED \times IR_A}{RfD_i \times BW \times AT}$$ (USEPA, 2016b), (ix)

where C_A is the concentration of the chemical in the atmosphere, mg.m^{-3}; and the remaining terms are as previously defined.

Cancer risks for the consumption of surface water (CR_w) and inhalation of air (CR_A) are calculated using the following respective equations:

$$CR_w = \frac{C_w \times EF \times ED(SF_o \times IR_w + SF_i \times IR_A \times K)}{BW \times AT}$$ and (x)

$$CR_A = \frac{C_A \times EF \times ED \times SF_i \times IR_A)}{BW \times AT},$$ (xi)

where SF_o and SF_i are the oral and inhalation cancer slope factors, respectively, (mg.kg^{-1}.d^{-1})$^{-1}$; and the remaining terms are as previously defined.

Among the outputs of RioShed are the compartmental concentrations over a given period, as well as steady state concentrations for the given 16 compartments. RioShed is programmed to calculate risk using the average annual concentration, in the atmosphere or surface water, generated over the period specified by the user. Recommended default values for the terms in the risk equations are used such that: the averaging time is set to 70 years (25550 d) for carcinogenic risk and 30 years (10950 d) for non-cancer risk; the exposure duration used is 30 years (10950 d); the exposure frequency is 350 $d.y^{-1}$; the inhalation and ingestion rates are 15 $m^3.d^{-1}$ and 2e-3 $m^3.d^{-1}$, respectively; the body weight is set at 70 kg; and the volatilization factor is 0.5 (USEPA, 1991).

Health impacts are also evaluated in life cycle assessments. However, life cycle assessment differs from risk assessment in that the former is comparative. In life cycle impact assessments, the impacts of a given compound or product are compared with others, whereas in risk assessment, absolute risk is classified (Olsen et al., 2001). Life cycle analysts often evaluate health impacts, using metrics such as the human toxicity potential, HTP. The human toxicity potential is the resultant number of disease cases per kilogram of pollutant emitted. It is dependent on population density, and uses benchmark measures such as ED_{10} or ED_{50}, which are effect doses resulting in toxicity in 10% and 50% of the exposed population, respectively (Rosenbaum et al., 2011).

In RioShed, the non-cancer human toxicity potentials for exposures via intake route k ($HTP_{nc,k}$), whether ingestion or inhalation, is calculated using the general formula

$$HTP_{nc,k} = \frac{IF_k \times \alpha}{ED_{50\_nc,k}}, \qquad \text{(x)}$$

whereas the cancer human toxicity potentials for exposures via intake route k ($HTP_{c,k}$), whether ingestion or inhalation, is calculated using

$$HTP_{c,k} = \frac{IF_k \times \alpha}{ED_{50\_c,k}}, \qquad \text{(xi)}$$

where $HTP_{nc,k}$ and $HTP_{c,k}$ are the respective number of potential non-cancer and cancer disease cases via direct intake route k (ingestion or inhalation) per kilogram of the emitted pollutant, persons.kg^{-1}; IF_k is the fraction of the agent emitted that is taken in via route *k*; α is the slope factor relating the probability of cancer to the inverse of the ED_{50}; $ED_{50\_nc,k}$ and $ED_{50\_c,k}$ are the lifetime effect doses for intake route *k* resulting in increases in non-cancer and cancer probabilities, respectively, by 50%, kg.person^{-1} per lifetime.

For intake route k, the intake fraction is calculated as

$$IF_k = \frac{\tau_i \times IR_{k,i} \times P}{\rho_i \times V_i} \text{ (Margni et al., 2002; Rosenbaum et al., 2011),} \qquad \text{(xii)}$$

where τ_i is the residence time of the chemical in medium *i*, d; $IR_{k,i}$ is the intake rate via intake route *k* of medium *i*, kg.d^{-1}.person^{-1}; P is the population exposed, person; ρ_i is the bulk density of medium *i*, kg.m^{-3}; and V_i is the volume of medium *i*, m^3. The intake fraction calculated is actually the portion of the medium that is taken in by the exposed individual, during the residence time of the chemical in that medium. This is equivalent to the intake fraction of any pollutant via the medium. The total human toxicity potential is the sum of all calculated cancer and non-cancer human toxicity potentials for all intake routes.

Among the outputs of RioShed are the compartmental residence times for the pollutants, which are used in equation xii for the calculation of human toxicity potentials. The effect measure ED_{50}, which is the estimated lifetime dose that increases the probability of disease by 50% in the exposed population via the exposure route, is not known for many chemicals, including those assessed in this dissertation. However, the ED_{50} values for chemicals with no evidence of carcinogenicity can be estimated from no observed effect levels (NOELs), by multiplying the NOELs by a conversion factor of 9 (Rosenbaum et al., 2011). When a lowest observed effect level is instead used, a conversion factor of 2.25 can be employed. In the calculation of human toxicity potential using RioShed, the default slope factor (α) of 0.5, used by Rosenbaum et al. (2011), was employed. This value for the slope factor assumes linearity between the dose and the probability of effect, such that there is an additional 50% chance of having an effect, given consumption of a pollutant at a lifetime dose equal to the ED_{50}.

4.2.2 Model application

4.2.2.1 Study Site

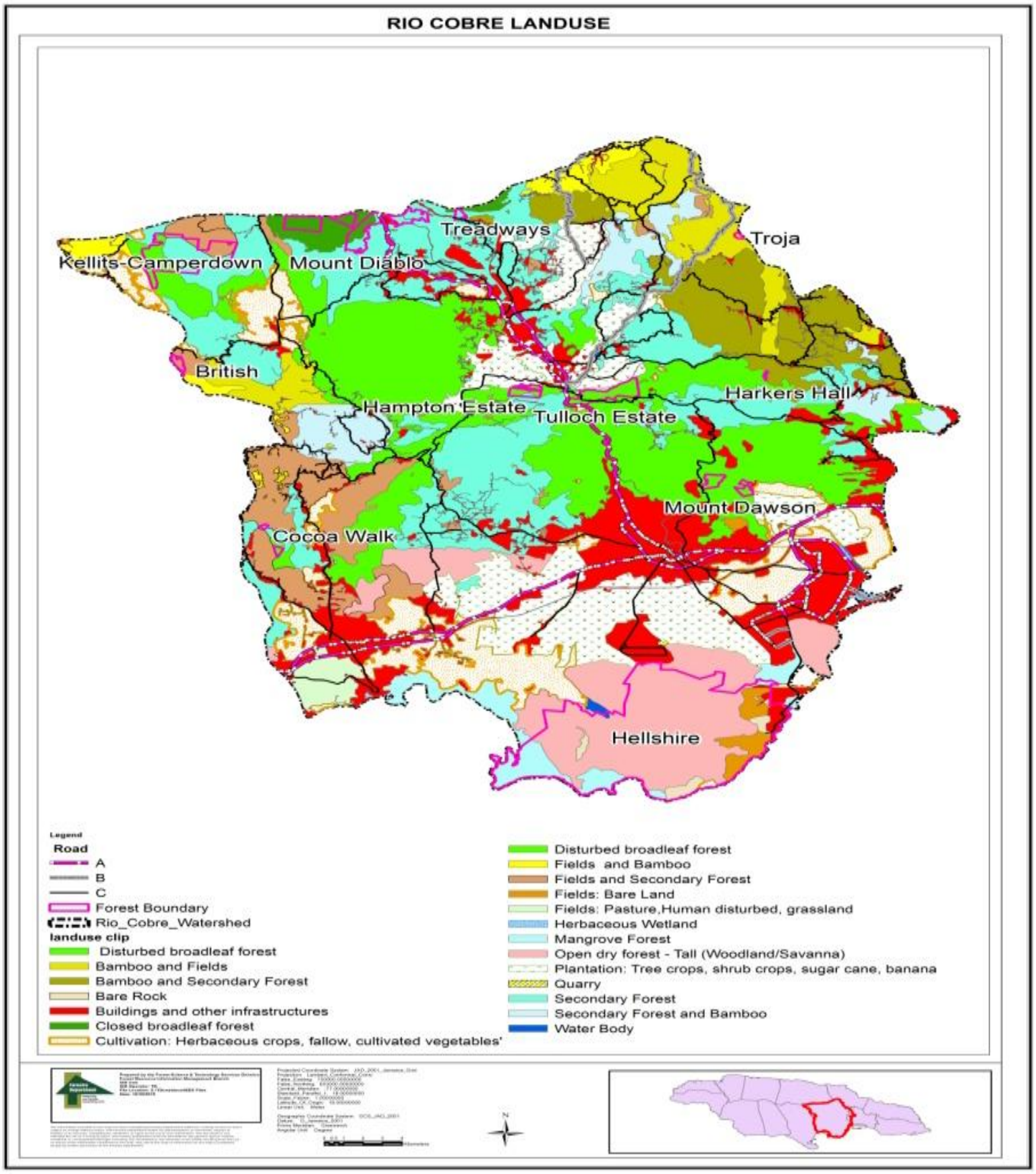


Figure 4.2: Land-use in the Rio Cobre watershed in Jamaica.
Povided by the Forestry Department of Jamaica (2015).

For this section of the dissertation, the main objective was to evaluate the effect of forests on the fates of select organic contaminants in a tropical watershed. The Rio Cobre watershed in Jamaica was chosen as the study site. The landscape properties of this watershed and the physicochemical properties of the evaluated contaminants were applied, with the physicochemical properties estimated based on the climatic conditions of the area.

Jamaica displays a bi-modal precipitation pattern, with wet seasons in May-July and August-November (Taylor, Enfield, & Chen, 2002). Average annual precipitation was 1953 mm, whereas average ambient temperature was 302.79 K, for the period 1986 to 2005 (Meteorological Service of Jamaica, 2015). The watershed drains into the 52.5 km long Rio Cobre River and occupies an area of 1249 km^2 (Forestry Department of Jamaica, 2015). A map of the area, Figure 4.2, shows that the watershed occupies the SSE section of Jamaica and that it is comprised of surface water, forests, fields, bare land, buildings and other infrastructure, and croplands (agriculture). For the purpose of this dissertation, the watershed was classified into three major vegetative covers – forests (60.15%), agricultural lands (25.19%) and an urban zone (14.48%) – and surface waters (0.18%).

4.2.2.2 Input data estimations – landscape and chemical properties

All fate metrics were computed using either the annually averaged or monthly averaged meteorological parameters (precipitation rate and ambient temperature), for the 1986-2005 period, for the Rio Cobre watershed, which were obtained from the Meteorological Service of Jamaica (2015). Landscape properties required included air and water content of the soils, lipid fraction in vegetation, density of particles in soil and sediment, fraction of surface water that is sediment, among others. For these, the properties specific to the Rio Cobre watershed were used when available. However, when lacking, estimates were either obtained from the literature or computed from accepted equations. Table 4.2 provides some examples of the data values and/or estimation methods for select input landscape properties (detailed landscape inputs are provided in Table D.1 in Appendix D).

Table 4.2: Select landscape parameters for the Rio Cobre watershed

Landscape Parameter	**Value Used/Estimating Equation**	**Source**
Area - Agricultural vegetation (m^2)	3.15E+08	Forestry Department of Jamaica (FDJ), 2015
Area - Forest vegetation (m^2)	7.51E+08	FDJ, 2015
Area - Urban region (m^2)	1.81E+08	FDJ, 2015
Area - Surface water (m^2)	2.20E+06	FDJ, 2015
Area - Atmosphere (m^2)	1.25E+09	FDJ, 2015
Average Ambient Temperature, T (K)	3.03E+02	Meteorological Service of Jamaica (MOJ), 2015
Average precipitation rate ($m.d^{-1}$)	5.35E-03	MOJ, 2015
Density of soil particles ($kg.m^{-3}$)	2650	CalTOX 2.3
Density of plants ($kg.m^{-3}$)	830	CalTOX 2.3
Lipid density in plants ($kg.m^{-3}$)	850	Multimedia Urban Model
Forest fractions: deciduous/evergreen	0.55/0.45	FDJ, 2015
Organic carbon fraction in urban film	0.74	Diamond et al., 2001
Organic carbon fraction in soil	0.036	Hennemann & Mantel, 1995
Fractions in foliage: Air, water, lipid	0.18, 0.8, 0.02	Cousins and MacKay, 2000
Leaf Area Index (LAI): deciduous forest, evergreen forest, agricultural vegetation, urban vegetation	3.9, 4.8, 3.6, 1.2	Asner et al., 2003; Diamond et al., 2001
Surface water outflow rate ($m.d^{-1}$)	2.46E-03	Setegn et al., 2014
Groundwater recharge rate ($m.d^{-1}$)	1.09E-03	Setegn et al., 2014
Transpiration rate ($m.d^{-1}$)	4.8E-03*LAI	GIM3
Run-off rate ($m.d^{-1}$)	2.82E-04	Setegn et al., 2014
Erosion rate ($m.d^{-1}$)	usrunoff/3E+04	GIM3

Table 4.3: Select chemical properties - Carbaryl

Chemical Parameter	**Value Used/Estimating Equation**	**Source**
Henry's Constant, H ($Pa.m^3.mol^{-1}$)	4.48E-05	Mackay et al., 2006
Melting Point (K)	418.15	Mackay et al., 2006
Vapor Pressure (Pa)	1.60E-04	Mackay et al., 2006
Octanol-Water partition coefficient, K_{ow}	229.09	Mackay et al. 2006
Air-Water partition coefficient, K_{aw}	H/RT or $10^{\wedge}(\log10(K_{ow}/K_{oa})-0.1+(0.3*\log10(K_{ow})-1.20))$ when $K_{ow}>1E4$ and $10^{\wedge}((\log10(K_{ow}/K_{aw})-0.1)$ when $K_{ow}<1E4$	Mackay et al., 2006
Octanol-air partition coefficient, K_{oa}	$10^{\wedge}(\log10(K_{ow}/K_{aw})-0.1+(0.3*\log10(K_{ow})-1.20))$	Mackay et al., 2006
Plant-air particle partition coefficient ($m^3.kg^{-1}$)	3000	CalTOX 2.3
Molecular weight ($g.mol^{-1}$)	201.221	Mackay et al., 2006
Atmospheric half-life (d)	5.25E-01	Mackay et al., 2006
Surface water half-life (d)	9	Mackay et al., 2006
Soil half-life, HLs (d)	10	Mackay et al., 2006
Vegetation half-life (d)	HLs/4	(Juraske, 2008 #889)
Urban film half-life (d)	HLs	*

* In the absence of measured values, the half-lives in soil were used for the half-lives in urban film.

For each chemical assessed, the intrinsic properties required included, as previously mentioned, partition coefficients (air-water, octanol-water, octanol-air, air-aerosol particle), vapor pressure, aqueous solubility, half-lives in each compartment, among others. Such data were retrieved from the literature, using values measured at temperatures close to the annual average temperature of the Rio Cobre watershed (302.79 K), or at 298.15 K when otherwise unavailable. In the absence of site-specific values, estimates were computed from accepted equations. Alternatively, representative values from the literature were used. For example, the estimated average global leaf area index for tropical deciduous forests was used, since none was available for such a forest in the Rio Cobre watershed. To provide an illustration of the types and data sources of the chemical properties used, those for Carbaryl are presented in Table 4.3 (see figure C.1 and Table C.1, Table C.2 and Table C.3 in Appendix C for the chemical structures and properties for all considered/evaluated contaminants).

4.2.2.3 Model testing & evaluation

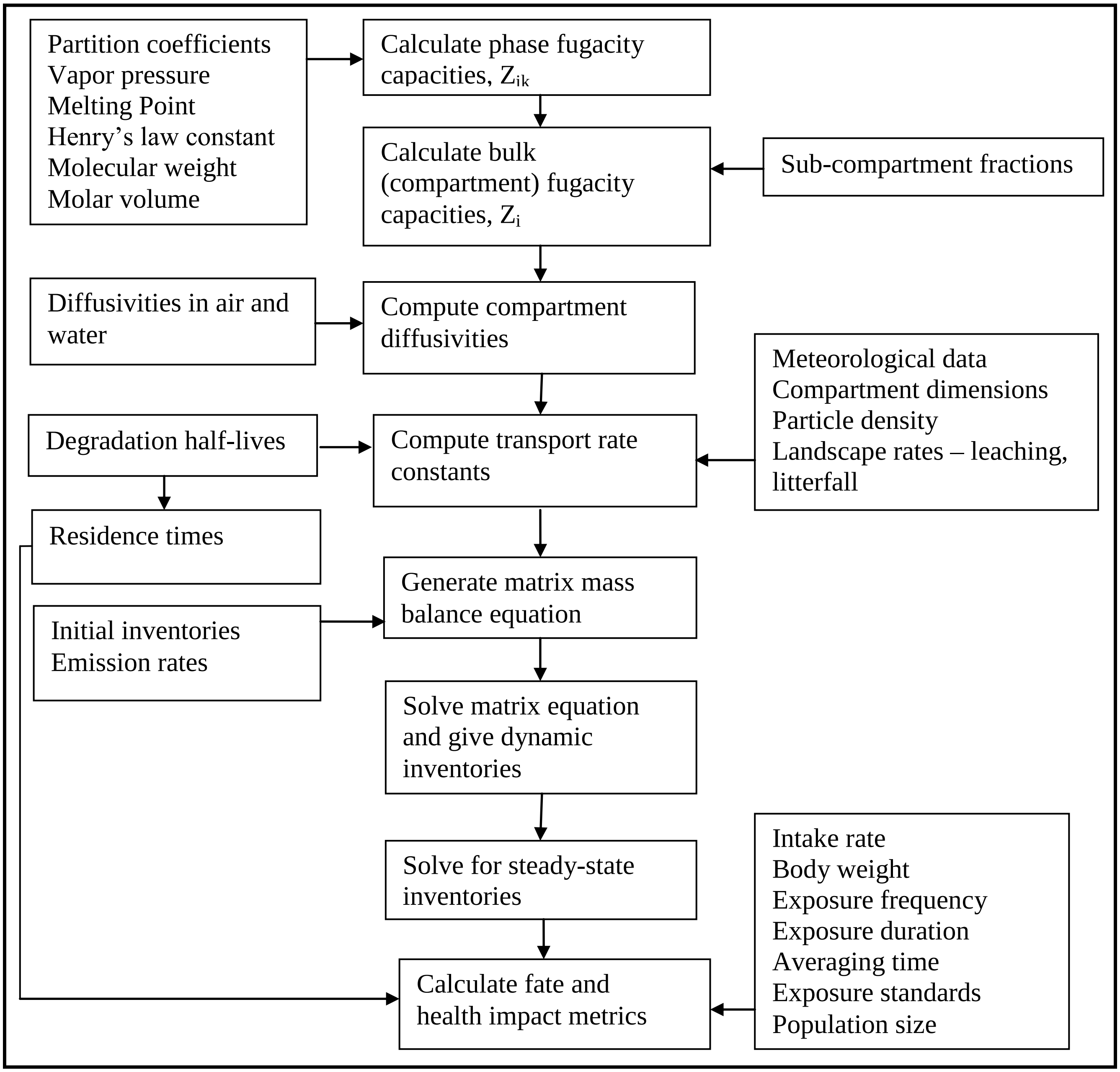


Figure 4.3: Simulation process in RioShed

A schematic diagram, summarizing the simulation process in RioShed, is presented in Figure 4.3. For ease of use of the developed model, input landscape values representative of a tropical region are supplied with the model. The simulation process was employed throughout all modeling aspects in this dissertation, including for model evaluation.

The performance of RioShed was benchmarked by comparing calculated fugacity capacities, transport rates, compartmental residence times and annual average concentrations to those calculated using CalTOX 2.3 and/or GIM3. Despite the fact that CalTOX 1.5 was the base model for RioShed, CalTOX 2.3 was used in the benchmarking exercise since this was the available version. CalTOX 1.5, CalTOX 2.3 and RioShed all differ from each other in the modeling of the plant and root-zone soil compartments.

In this exercise, the landscape properties of the Rio Cobre watershed were used and a hypothetical atmospheric emission rate of 10 g.d^{-1} was applied, using PBDE-47 as the test chemical. In 2007, it was estimated that 32.2 metric tons of deca-BDE was released into the US (USEPA, 2010), yielding a flux rate of 8.96 ng.m^{-2}.d^{-1}, given that the surface area of the US is approximately 9.86 Mkm^2. When this flux rate was applied to Rio Cobre watershed, an emission rate of 11.2 g.d^{-1} was obtained. As a result, a hypothetical emission rate of 10 g.d^{-1} was applied for the contaminant, given the absence of such data for the watershed. In this evaluation, only the seven mutual compartments for the three models were left active in RioShed. Once relevant data were inputted into the three models having the same active seven compartments, the computed fugacity capacities, transport rate constants and compartment residence times were compared using a percent bias (PBIAS) as follows:

$$\text{PBIAS} = \left[\frac{\sum_{i=1}^{n}\left(Y_i^{obs} - Y_i^{sim}\right) \times (100\%)}{\sum_{i=1}^{n}\left(Y_i^{obs}\right)}\right] \qquad \text{(Moriasi et al., 2007)} \qquad \text{(xiii)}$$

where Y_i^{obs} is the observed *i*th fugacity capacity, transport rate constant or residence time, generated using CalTOX 2.3 or GIM3; and Y_i^{sim} is the simulated *i*th fugacity capacity, transport rate constant, residence time or average annual compartmental concentrations, from RioShed. RioShed was considered to perform well for PBIAS values, for the fugacity capacity, transport rate constant, residence times or average annual compartmental concentrations, of or close to 0 for all compartments in which the inputs and losses were represented as in CalTOX 2.3 and/or GIM3.

Table 4.4: Comparison of fugacity capacities

Model	**Fugacity capacity of plant compartment (Z_{cm}), mol/m^3/Pa**	**Equation**	**Affected Transport Terms**
CalTOX 2.3	1.84e4	$Z_{cm} = K_{pa}\rho_p Z_{air} + K_{pa}^{p} Z_{ap}\rho_p \beta_A \rho_{smp}^{-1}$	T_{cmrm}, T_{cmsm}, T_{cmA}, T_{Acm}
RioShed	4.44e4	$Z_{cm} = f_{pw} Z_{water} + f_{pa} Z_{air} + f_{pl} Z_l$	

Z_{cm} is the fugacity capacity of plants, mol.m^{-3}.Pa^{-1}; f_{pw}, f_{pa}, f_{pl} are the respective fractions of water, air and lipids in vegetation; Z_{ap} is the fugacity capacity of atmospheric particles, mol.m^{-3}.Pa^{-1};Z_{water} is the fugacity capacity of water, mol.m^{-3}.Pa^{-1}; Z_{air} is the fugacity capacity of air, mol.m^{-3}.Pa^{-1}; Z_l is the fugacity capacity of lipids, mol.m^{-3}.Pa^{-1}; ρ_p is the density of plant, kg.m^{-3}; ρ_{smp} is the density of particles in surface soil, kg.m^{-3}; β_A is the atmospheric dust load, kg.m^{-3}; K_{pa} is the plant/air-vapor partition ratio; and K_{pa}^{p} is the plant/air-particle partition ratio; T_{cmrm} is the transport constant for movement from plant to root soil, d^{-1}; T_{cmsm} is the transport constant for movement from plant to surface soil, d^{-1}; T_{cmA} is the transport constant for movement from plants to atmosphere, d^{-1}; T_{Acm} is the transport constant for movement from atmosphere to plants, d^{-1}.

Table 4.5: Rate constant equations for comparison

Model	**Advective Transport rate constant (d^{-1})**	**Transport rate constant for transport via atmospheric particles (d^{-1})**	**Transport rate constant for transport via particles (d^{-1})**	**Reaction rate constant (d^{-1})**
CalTOX 2.3	$T_{Aij} = A_{ij} Z_{ic} u_i Z_i^{-1} V_i^{-1}$	$T_{Nij} = A_{ij} Z_{ip} u_i f_{ip} Z_i^{-1} V_i^{-1}$	$T_{Nij} = A_{ij} Z_{ic} u_{ic} Z_i^{-1} V_i^{-1}$	$R_{(d,r,v)} = \frac{0.693 Z_{water} f_{(d,r,v)w}}{Z_{(d,r,v)}}$
GIM3	$T_{Aij} = A_{ij} Z_{ic} u_i Z_i^{-1} V_i^{-1}$	$T_{Nij} = A_{ij} Z_{ip} u_i f_{ip} Z_i^{-1} V_i^{-1}$	$T_{Nij} = A_{ij} Z_{ip} u_{ip} f_{ip} Z_i^{-1} V_i^{-1}$	$R_{(d,r,v)} = \frac{0.693 Z_{water} f_{(d,r,v)w}}{Z_{(d,r,v)}}$
RioShed	$T_{Aij} = A_{ij} Z_{ic} u_i Z_i^{-1} V_i^{-1}$	$T_{Nij} = A_{ij} Z_{ip} u_i f_{ip} Z_i^{-1} V_i^{-1}$	$T_{Nij} = A_{ij} Z_{ip} u_{ip} f_{ip} Z_i^{-1} V_i^{-1}$	$R_{(d,r,v)} = \frac{0.693 Z_{water} f_{(d,r,v)w}}{Z_{(d,r,v)}}$

Highlights illustrate differences in modeled parameters

T_{Aij} is the advective transport rate constant for movement from medium *i* to *j*, d^{-1}; A_{ij} is the area of the interface between media *i* and *j*, m^2; u_{ic} and u_{ip} are the velocities of the carrying medium and particles, respectively, $m.d^{-1}$; Z_i the fugacity capacity of medium *i*, $mol.m^{-3}.Pa^{-1}$; Z_{water} is the fugacity capacity of water, $mol.m^{-3}.Pa^{-1}$; $Z_{(d,r,v)}$ is the fugacity capacity of sediment, root-soil or vadose-zone soil, $mol.m^{-3}.Pa^{-1}$; Z_d is the fugacity capacity of sediment, $mol.m^{-3}.Pa^{-1}$; Z_{ip} the fugacity capacity of particles in medium *i*, $mol.m^{-3}.Pa^{-1}$; Z_{ic} is the fugacity capacity of the carrying medium *c* in medium *i*, $mol.m^{-3}.Pa^{-1}$; V_i is the volume of medium *i*, m^3; T_{Nij} is the transport rate constant for transport on particles, d^{-1}; f_{ip} is the fraction of particles in medium *i*; $f_{(d,r,v)w}$ is the fraction of water in the sediment, root-zone soil and vadose-zone soil, respectively; $R_{(d,r,v)}$ is the reaction rate constant in the sediment, root-zone soil and vadose-zone soil, respectively, d^{-1}; R_d is the reaction rate constant in the sediment, d^{-1}.

Table 4.4 gives the different formulae used in RioShed and CalTOX 2.3 to calculate the fugacity capacity of the plants in the vegetation compartment. The formula used by RioShed was obtained from Mackay and Cousins (2000), who suggested the equation for the incorporation of a plant compartment into environmental models. As a result, the residence time in plants calculated by RioShed differs from those calculated using CalTOX 2.3 and GIM3. Consequently, the rate constants, for transport to and from the vegetation/canopy, are different in RioShed.

In RioShed, all diffusive and some advective transport rate constants are calculated the same as in CalTOX 2.3. The remaining advective terms for transport via particles in the atmosphere, soils and sediments are calculated as in GIM3, as seen in column 3 of Table 4.5. In RioShed, advective transport from the canopy/vegetation uses the canopy model employed by the Multimedia Urban Model (MUM).

For the sediment, root-zone and vadose-zone soils, reaction rate constants are calculated in RioShed, as also in both CalTOX 2.3 and GIM3, using the equation

$$R_i = \frac{0.693}{HL_i} \frac{Z_{water}}{Z_i} f_{iw} \qquad \text{(xxvii)}$$

where R_i is the reaction rate constant, d^{-1}; Z_{water} is the fugacity capacity of water, $mol.m^{-3}.Pa^{-1}$; HL_i is the half-life of the contaminant in medium *i* (sediment, root- or vadose-zone soil), d; Z_i is the fugacity capacity of medium *i* (sediment, root- or vadose-zone soil), $mol.m^{-3}.Pa^{-1}$; and f_{iw} is the fraction of water in medium *i* (sediment, root- or vadose-zone soil). For the remaining compartments, reaction rate constants are calculated using the known formula:

$$R_i = \frac{0.693}{HL_i} \qquad \text{(xxviii)}$$

with R_i and HL_i as the respective reaction rate constant, d^{-1}, and half-life, d, in medium *i*. RioShed also offers the option to calculate reaction rates in the root and vadose soils using this same formula.

RioShed was tested for sensitivity to select model input parameters – chemical, emission and landscape. This analysis indicated the dependence of the model's outputs on select inputs, under the hypothetical emission scenario used. The inputted chemical properties included media-specific half-lives, partition coefficients and molecular weight whereas the landscape properties included meteorological data (precipitation rate and ambient temperature), atmospheric dust load and compartment dimensions, among others. Also, the emission properties included the quantity released and the source compartment. The test chemical was 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and the hypothetical atmospheric emission rate of 3.65 kg.y^{-1} (10 g.d^{-1}) was used. As has been done in previous studies (Wania, Breivik, Persson, & McLachlan, 2006; Wania & McLachlan, 2001), the effect was analysed using an initial application of inputs in a control scenario. The current land-use distribution for the Rio Cobre watershed (agriculture: forest: urban – 25 %: 60 %: 15%), labeled as land-use distribution scenario I, was employed as the control scenario. In general, the parameters to be assessed were individually halved and the outputs compared to the initial output. However, where halving was unrealistic, the properties were doubled.

To evaluate the predictive capabilities of RioShed, some predicted outputs of the model were compared to the field measurements from Chapter 3. The field measurements included concentrations of some PBDEs in the soils, atmosphere, deposition and litterfall of a forest versus a nearby clearing, in the Rio Cobre watershed. However, the outputs of Rioshed were the concentrations of the same PBDEs in all of its 16 compartments for the forested versus un-forested version of the Rio Cobre watershed. The differences in the scope of the field monitoring and that employed in using RioShed allowed only a simple evaluation of whether RioShed could accurately predict an impact of forests on the fates of the PBDEs in the Rio Cobre watershed, given the findings of the field monitoring exercise.

4.2.2.4 Determination of forest effects

The goal of this assessment was to evaluate the effects of tropical forests on the fates of select organic contaminants in the Rio Cobre watershed. Since emission data for the chemicals in the given watershed were lacking and given the comparative nature of the assessment, an atmospheric emission rate of 3.65 $kg.y^{-1}$ was applied throughout. In 2007, deca-BDE was the only technical PBDE mixture produced and used in the USA, with an estimated release of 32.2 metric tons in that year (USEPA, 2010). Given a surface area of approximately 9.86 Mkm^2 for the USA, this equated to a release flux of 8.96 $ng.m^{-2}.d^{-1}$. Applying this flux to the Rio Cobre watershed, which exhibits a surface area of 1249 km^2, produced an equivalent release/emission rate of 11.2 $g.d^{-1}$. As a result, a hypothetical emission rate of 3.65 $kg.y^{-1}$ (10.0 $g.d^{-1}$) was used for each chemical, with the assumption that emission was solely into the atmosphere.

This evaluation was divided into segments – dynamic and steady state. Depending on the specific objective of any given segment, one of two control scenarios was employed. The current landscape of the Rio Cobre watershed was labeled land-use distribution scenario I and employed as control scenario I. For control scenario II, also labeled as land-use distribution scenario II, the forested area of the Rio Cobre watershed was instead modeled as grassland, with agricultural lands, urban zone and surface waters remaining as before, as seen in table 4.8. Figure 4.2 shows that, in the Rio Cobre watershed, fields occupy a far larger portion of the landscape (6.31%) than bare rocks (0.91%) (Forestry Department of Jamaica, 2015). Therefore, grasslands are more likely than bare rock. As a result, grassland was chosen in lieu of bare rock to replace forests in control scenario II (land-use distribution scenario II). In order to model the forested area as grassland, select forest parameters, such as litterfall rate, biomass production and leaf area index, were altered to representative grassland values.

Table 4.6: Physicochemical properties for PBDE-47 and dimethoate

Physicochemical properties	**PBDE-47**	**Dimethoate**
Henry's constant (Pa.m^3/mol)	1.107	1.15E-04
Henry's constant (Pa.m^3/mol) - 30^{o}C	1.78	-
Melting Point (K)	357.15	325.15
Vapor Pressure (Pa)	2.15E-04	3.63E-02
K_{oc}, Organic carbon partition coefficient (L/kg)	1.26E+06	15.85
K_{ow}, Octanol-water partition coefficient	2.46E+06	6.03
K_{aw}, Air-water partition coefficient	4.47E-04	4.57E-08
K_{oa}, Octanol-air partition coefficient	2.75E+10	1.13E+07
K_{paap}, Plant-air particle partition coefficient (m^3/kg)	3.00E+03	3.00E+03
K_{ps}, Plant root-soil partition coefficient (kg/kg)	5.38E-01	5.38E-01
Molecular Weight (g/mol)	485.791	229.258
Molecular Volume (cm^3/mol)	288.8	205.6
Bioconcentration factor fish/water (m^3/kg)	0	100
Atmospheric half-life (d)	1.07E+01	1.95E-01
Half-life in surface water (d)	150	29
Half-life in sediment (d)	600	7
Average half-life in vegetation (d)	Half-life in surface soil/4	2.95
Half-life in agricultural vegetation (d)	37.5	as above
Half-life in forest vegetation (d)	37.5	as above
Half-life in urban vegetation (d)	37.5	as above
Half-life in surface soil (d)	150	7
Half-life in agricultural surface soil (d)	as above	as above
Half-life in forest surface soil (d)	as above	as above
Half-life in urban surface soil (d)	as above	as above
Half-life in root-zone soil (d)	as above	as above
Half-life in agricultural root-zone soil (d)	as above	as above
Half-life in forest root-zone soil (d)	as above	as above
Half-life in urban root-zone soil (d)	as above	as above
Half-life in vadose-zone soil (d)	150	as above
Half-life in agricultural vadose-zone soil (d)	150	as above
Half-life in forest vadose-zone soil (d)	150	as above
Half-life in urban vadose-zone soil (d)	150	as above
Half-life in urban organic film (d)	150	as above
Half-life in biota (d)	30.1 - carp	2.95 - cabbage

In the first segment of the evaluation, a dynamic assessment was conducted of the environmental fates, of only dimethoate and PBDE-47, in a forested and un-forested landscape.

Two categories of organic pollutants are being examined in this dissertation – a few persistent pollutants and some polar current-use pesticides. PBDE-47 is a member of the more persistent group of pollutants, whereas dimethoate is from the current-use pesticides category. Both were arbitrarily selected from their respective groups for this evaluation exercise. The physicochemical properties used for these two organics are presented in Table 4.6. The outputs of this evaluation were the monthly compartmental concentrations using: 1) the average annual precipitation rate and ambient temperature for the 1986-2005 period, and 2) average monthly precipitation rates and ambient temperatures for the same 1986-2005 period.

Table 4.7: Monthly averaged climate variables for the Rio Cobre watershed for the 1986-2005 period

Month number	**Month**	**Temperature (K)**	**Precipitation rate ($\times10^{-3}$ m.d^{-1})**
1	January	300.82	2.74
2	February	301.26	2.32
3	March	302.19	2.32
4	April	302.82	4.35
5	May	303.16	8.72
6	June	303.91	5.03
7	July	304.23	5.91
8	August	304.30	6.20
9	September	304.18	9.87
10	October	303.34	7.63
11	November	302.20	5.84
12	December	301.23	3.14

Meteorological data was obtained from the Meteorological Service of Jamaica, 2015

To calculate the average annual temperature and precipitation rate, such data for the 1986-2005 period, was obtained from the Meteorological Service of Jamaica (MOJ) and averaged. The annually averaged temperature and precipitation rate for this period were 302.79 K and 5.35e-3 m.d^{-1}, respectively. To calculate the average monthly temperature and precipitation rate, the same data from the Meteorological Service of Jamaica (MOJ) was used, but instead the values, for each calendar month of the year, were averaged over the same 1986-2005 period. The monthly average climate values used are given in Table 4.7.

In the first part of the dynamic section, an initially pristine environment, with compartments void of the contaminants, was assumed. The hypothetical emission rate of 3.65 kg.y^{-1} was then applied for the two contaminants (PBDE-47 and dimethoate). The average annual climate data were input at the beginning of the model run, for each PBDE-47 and dimethoate, and remained unchanged thereafter. For each chemical, the model was run for both forested and un-forested scenarios. Control scenario I (land-use distribution scenario I) was employed to provide forested conditions, whereas control scenario II (land-use distribution scenario II) was used as the un-forested landscape. The system was evaluated to determine if and/or when steady state concentration was achieved in each compartment, in both the forested and un-forested scenarios.

In the second part of the dynamic assessment, two conditions were initiated: 1) a pristine environment and 2) an environment with compartmental concentrations set at the steady state values, previously calculated for an environment that was initially pristine, and thereafter receiving the contaminants only into its atmosphere, at a rate of 3.65kg.y^{-1}. At the beginning of each set of model runs, the averaged temperature and precipitation rate for January for the 1986-2005 period were the meteorological inputs. The model was then run for the 31 days of January and the end-of-month compartmental inventories obtained, as well as the next month's climate data, were the inputs for the model run for the following month. This procedure was employed for the months February to December, whereby the compartmental inventory outputs, from the previous month, were the initial compartmental inventories for the current month, and the meteorological inputs were the averaged temperature and precipitation rate for the current month, for the 1986-2005 period. The model was then run for the number of days typically associated with the given month. As before, this assessment was performed using both control scenarios I and II (land-use distribution scenarios I and II, respectively) to provide the forested and un-forested landscapes, respectively.

In the non-dynamic (steady state) segment of the evaluation, the effects of forests, on the long-term fates of the aforementioned 16 organic contaminants (four (4) PBDEs, four (4) dioxins and furans, as well as eight (8) current-use pesticides), were examined for varying forested landscapes, by comparing the long-term fate metrics calculated in forested scenarios with those calculated assuming grassland conditions. Control scenario II (land-use distribution scenario II) was employed as the control. Figure 4.4 illustrates the assessment process.

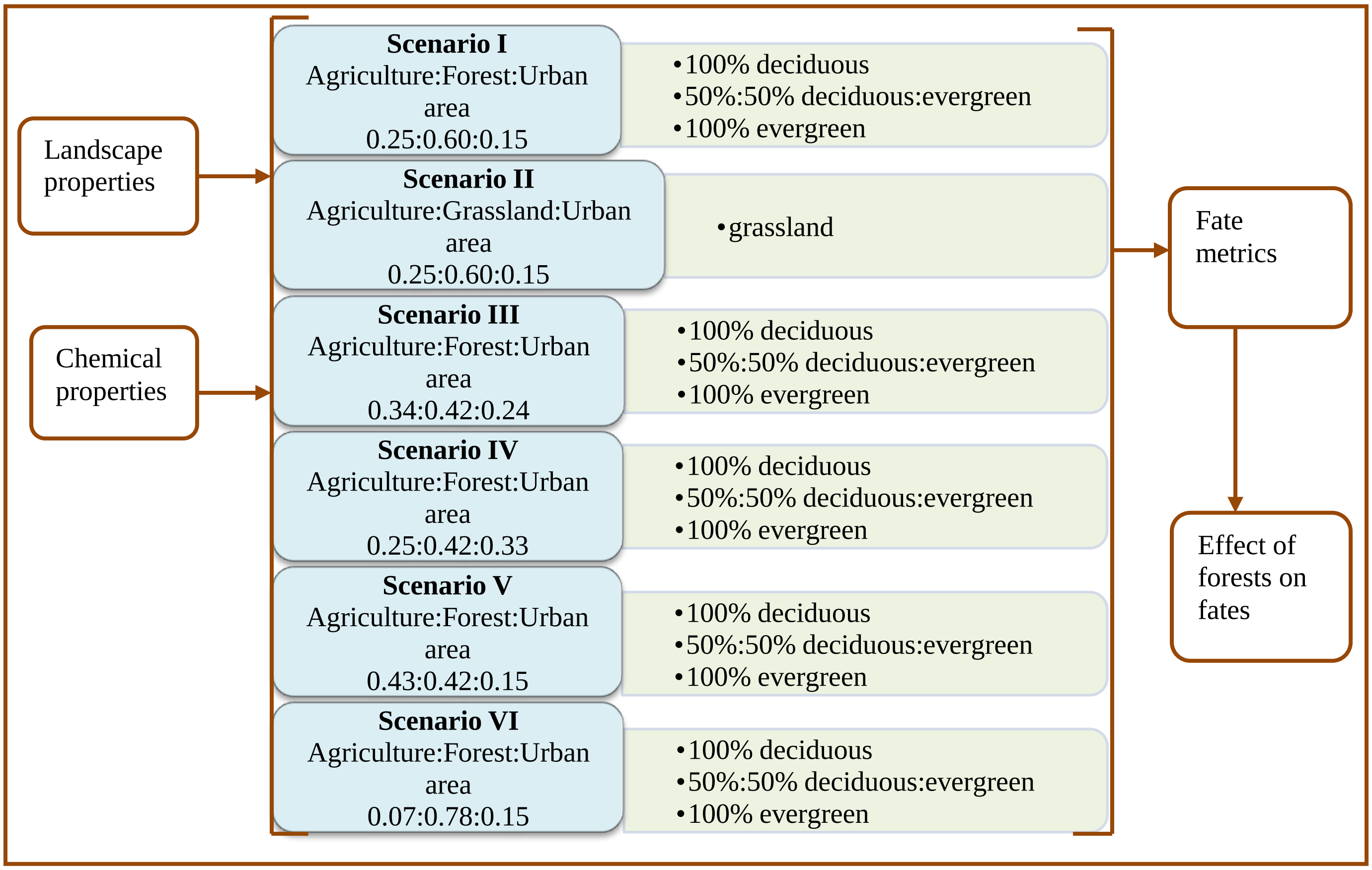


Figure 4.4: Schematic representation of the assessment process

Table 4.8: Land-use distribution scenarios

Scenarios	**Land-use percentage distribution (%)**		
	Agriculture	**Forest/Grassland**	**Urban**
I	25	60 (forest)	15
II	25	60 (grassland)	15
III	34	42 (forest)	24
IV	25	42 (forest)	33
V	43	42 (forest)	15
VI	7	78 (forest)	15

In this steady state assessment, control scenario I was employed as one of the forested landscapes and was labeled land-use distribution scenario I, whereas control scenario II was labeled land-use distribution scenario II. The remaining four (4) forested landscapes for comparison were generated by applying the following algorithms to the existing landscape of the Rio Cobre watershed (control/land-use distribution scenario I), such that there was a: a) 30% decrease in forest coverage, assuming equal distribution of the difference to the urban and agricultural compartments (agriculture:forest:urban area at 34%:42%:24%); b) 30% decrease in forest coverage, strictly due to urban expansion (agriculture:forest:urban area at 25%:42%:43%); c) 30% decrease in forest coverage, strictly due to agricultural expansion (agriculture:forest:urban area at 43%:42%:15%) and; d) 30% increase in coverage, through afforestation of agricultural lands (agriculture:forest:urban area at 7%:78%:15%). These comparison scenarios were labeled land-use distribution scenarios III to VI. The details of the generated land-use distribution scenarios are given in Table 4.8.

Three tropical forest compositions were considered: a) 100% deciduous; b) 50%:50% deciduous: evergreen; and c) 100% evergreen. These three compositions were applied to the five (5) forested land-use scenarios in Table 4.8. Therefore, for each of these 15 assessment scenarios generated, forest parameters were weighted according to the selected forest compositions, and representative values applied. Landscape and chemical properties were input into the model and the fate metrics obtained for each of the 16 scenarios. As indicated before, the fate metrics for the forested scenarios were assessed with respect to those obtained for control scenario II. As a further step in this evaluation of forest effects on the long-term fates, the fate metrics, obtained when the three (3) forest compositions (deciduous, evergreen and semi-evergreen) were applied to land-use distribution scenarios III to VI, were evaluated with respect to those obtained when the aforementioned three (3) forest compositions were applied to control scenario I (also labeled land-use distribution scenario I).

Daily compartmental concentrations for both dimethoate and PBDE-47 were generated for 365 days, using the annual average climate data for the 1986-2005 period, inputted at the beginning of the 365-day model run, with the assumption of an initially pristine environment (free of the select chemical). This allowed for the examination of how both the contaminant and the model behaved under such condition, as well as to confirm that steady state could be achieved. The daily compartmental concentration outputs were averaged over the 365 days to give representative annual average compartmental concentrations. This was done for both land-use distribution scenarios I (forested landscape) and II (un-forested landscape). The annual average concentrations were compared. Also, steady state concentrations were generated under these conditions. The steady state concentrations were used to compute the overall persistence and atmospheric long range transport potential. This allowed for the evaluation of the effect of forests on the long-term fate metrics for these two (2) chemicals. This evaluative method was also performed for the remaining 14 chemicals. The arithmetic means and ranges of the fate metrics for the eight (8) persistent pollutants and the eight (8) current-use pesticides in both land-use distribution scenarios were compared to determine the general effect of forests on the two groups of pollutants evaluated.

4.2.2.5 Determining the effects of forest parameters

A number of forest parameters influence the transport of organics between the atmosphere and soil, via the canopy. These include canopy drip, leaf area index, biomass, epicuticular wax erosion and litterfall. To assist with understanding how these parameters influence the effects of forests on the long-term fates of the assessed contaminants, the forest parameters were varied and the associated long-term fate metrics calculated and compared. The control in this segment of the evaluation was the current landscape architecture of the Rio Cobre watershed.

Canopy drip is the wet deposition of contaminants from the leaves of plants. The efficiency of this removal process is characterized by a canopy drip parameter (Diamond et al., 2001). In the application of their model MUM to the Don River Watershed in Canada, where the rainfall rate was approximately 815 mm.y^{-1}, Diamond et al. (2001) used a canopy drip parameter of 8.7×10^{-4}. This is expected to be larger in areas with higher precipitation rates. However, in the absence of actual values, this canopy drip parameter was applied to the Rio Cobre watershed. This section of the assessment then involved calculating and comparing output fate metrics generated by altering this parameter by factors of 0 to 2, in increments of 0.5.

The leaf area index (LAI) influences the deposition of contaminants from the atmosphere to the leaf, as well as diffusion between the atmosphere and the leaf. Global leaf area indices for various biomes have been found to range from 1.3 to 8.7, with a range of 2.6 to 8.7 for forests (Asner, Scurlock, & A. Hicke, 2003). The global mean for tropical deciduous and evergreen forests were given as 3.9 and 4.9, respectively. The output fate metrics were then computed and compared for leaf area indices in the range of 1 through to 9, varied in increments of 2.

Dry deposition interception is a function of biomass, which therefore impacts the direct transport of chemicals from the atmosphere to soils. Above ground biomass for tropical forests were found in the range 28.2-507.8 $Mg.ha^{-1}$, approximately 9.31-167 $\mu m.d^{-1}$ (Cairns, Olmsted, Granados, & Argaez, 2003; Malhi, Baldocchi, & Jarvis, 1999; Mani & Parthasarathy, 2007; Martinez-Yrizar et al., 1992; Yamakura, Hagihara, Sukardjo, & Ogawa, 1986). Biomass inventories were varied between 5 $kg.m^{-2}$ to 55 $kg.m^{-2}$, in increments of 10 $kg.m^{-2}$.

The influence of epicuticular wax erosion on contaminant fate is still little understood. It is known though that epicuticular wax morphology is a function of environmental conditions, such as temperature and irradiance (Baker & Hunt, 1986). Also, epicuticular wax production and wax erosion are dependent on the presence of atmospheric pollutants. Epicuticular wax has been found to be abraded by pollutants (Huttunen & Laine, 1983; Rogge, Hildemann, Mazurek, Cass, & Simoneit, 1993) and the structure altered by exposure to pollutants, such as vehicular exhaust (Honour, Bell, Ashenden, Cape, & Power, 2009) and pesticides (Baker & Hunt, 1986). However, the effect of wax erosion on the transport and transfer of contaminants has not been well characterized. In the application of MUM to the Don River watershed in Canada, Diamond et al. (2001) used a wax erosion transfer coefficient of 1.932×10^{-6} $m.d^{-1}$. Therefore, the wax erosion transfer coefficient was varied from 0 $m.d^{-1}$ and increased up to 200% of the quoted 1.932×10^{-6} $m.d^{-1}$, in increments of 50%. The long-term fate metrics, previously described, were calculated at each incremental change and compared.

Forest litterfall dynamics have been evaluated over the years. Litterfall rate is one dynamic found to influence contaminant transport from canopy to soil. Measured values for tropical leaf and total litterfall fluxes ranged from 2.1-9.6 $t.ha^{-1}.y^{-1}$ and 2.4-13.5 $t.ha^{-1}.y^{-1}$, respectively (Pragasan & Parthasarathy, 2005). Given a plant density of 830 $kg.m^{-3}$, this parameter was varied from 0.66 $\mu m.d^{-1}$ to 4.62 $\mu m.d^{-1}$.

4.3 Results & Discussion

4.3.1 Model testing and evaluation

4.3.1.1 Benchmarking

For this evaluation, the fugacity capacities, transport rate constants and compartmental residence times for PBDE-47 under select conditions were calculated, using RioShed, GIM3 and CalTOX 2.3, and compared. These outputs are given in Table 4.9, Table 4.10 and Table 4.11. The average compartmental concentrations, over a one (1) year period, generated using RioShed, were also assessed against those generated using CalTOX 2.3, as seen in Table 4.12.

Table 4.9: Fugacity capacities for PBDE-47 calculated using CalTOX 2.3, GIM3 and RioShed

	Fugacity Capacity ($mol.m^{-3}.Pa^{-1}$)		
Compartment	**CalTOX 2.3**	**GIM3**	**RioShed**
Pure air	4.0E+4	4.0E+4	4.0E+4
Atmosphere	4.3E+4	4.3E+4	4.3E+4
Pure water	9.0E-1	9.0E-1	9.0E-1
Surface water particle	6.0E+4	6.0E+4	6.0E+4
Surface water	2.9E+0	2.9E+0	2.9E+0
Sediment particle	6.0E+4	6.0E+4	6.0E+4
Sediment	4.8E+4	4.8E+4	4.8E+4
Plant	1.8E+4	4.4E+4	2.2E+4
Plant root	5.3E+1	2.2E+4	5.3E+1
Surface soil particle	1.1E+5	1.1E+5	1.1E+5
Root soil particle	1.1E+5	1.1E+5	1.1E+5
Vadose soil particle	1.1E+5	1.1E+5	1.1E+5
Surface soil	6.4E+4	6.4E+4	6.4E+4
Root soil	6.4E+4	6.4E+4	6.4E+4
Vadose soil	6.4E+4	6.4E+4	6.4E+4
Aquifer particle	1.1E+5	-	-
Aquifer	8.7E+4	-	-

Table 4.10: Transport rate constants for PBDE-47 calculated using CalTOX 2.3, GIM3 and RioShed

		Transport rate, T_{ij}, from medium *i* to *j* (d^{-1})		
Delivering Compartment, i	***Receiving Compartment, j***	***CalTOX 2.3***	***GIM3***	***RioShed***
Atmosphere	Surface water	3.4E-3	3.5E-3	3.4 E-3
Atmosphere	Plants	1.1E-1	3.3E-2	2.0E-1
Atmosphere	Surface soil	1.4E-1	3.6E-2	1.4E-1
Atmosphere	External environment	2.2E+0	2.3E+0	2.2E+0
Surface water	Atmosphere	4.3E-3	4.5E-3	4.3E-3
Surface water	Sediment	1.6E+1	1.1E-3	6.1E-4
Surface water	External environment	5.0E-2	5.0E-4	5.0E-2
Sediment	Surface water	9.9E-2	7.9E-2	7.9E-2
Sediment	N/A (burial)	2.5E-5	1.6E-1	2.0E-5
Plants	Atmosphere	2.4E-4	1.9E-4	6.1E-5
Plants	Surface soil	5.6E-3	5.6E-3	1.6E-2
Plants	Root soil	1.0E-5	8.3E-6	4.2E-6
Surface soil	Atmosphere	6.7E-6	1.3E-5	3.0E-6
Surface soil	Surface water	2.0E-6	1.3E-6	1.3E-6
Surface soil	Root soil	5.5E-6	5.5E-6	5.5E-6
Root soil	Plants	2.5E-7	2.4E-7	2.4E-7
Root soil	Surface soil	4.0E-8	4.0E-8	4.0E-8
Root soil	Vadose soil	1.6E-8	1.5E-8	1.5E-8
Vadose soil	External environment/Ground-water	4.5E-10	4.5E-10	4.5E-10

Table 4.11: Compartmental residence times for PBDE-47calculated using CalTOX 2.3, GIM3 & RioShed

Compartments	**Residence time (d)**			
	CalTOX 2.3	***GIM3***	***RioShed***	***RioShed (alternative)***
Air	3.89E-01	4.18E-01	3.75E-01	3.75E-01
Water	6.06E-02	9.39E+01	1.68E+01	1.68E+01
Sediment	1.01E+01	6.31E+00	1.26E+01	1.26E+01
Plant	1.72E+02	3.48E+01	2.57E+01	2.57E+01
Surface soil	2.16E+02	2.16E+02	2.16E+02	2.16E+02
Root-zone soil	3.09E+06	3.13E+06	3.13E+06	2.16E+02
Vadose-zone soil	4.46E+07	4.46E+07	4.46E+07	2.17E+02

Table 4.12: Annual average compartmental concentrations for PBDE-47 calculated using CalTOX 2.3 and RioShed

Compartment	**Concentration (mol.m^{-3})**	
	CalTOX 2.3	***RioShed***
Atmosphere	8.5E-15	8.2E-15
Surface water	6.7E-12	6.5E-12
Sediment	1.1E-7	4.8E-12
Vegetation	1.5E-8	1.0E-9
Surface soil	3.2E-8	1.4E-8
Root soil	5.1E-12	1.2E-13
Vadose soil	4.3E-18	5.5E-21

Table 4.9 reveals that all three models obtain the same values for the fugacity capacitites of all compartments, with the exception of the plant/vegetation compartment. This was expected given the different modeling of the vegetation compartment, as explained in section 4.2.2.3. This same difference in modeling technique also contributed to the different rate constants, involving transport to and from vegetation, seen in Table 4.10.

The different methods employed in both RioShed and GIM3, compared to that employed in CalTOX 2.3, to calculate advection via particles in the soils and sediment, led to the observed different transport rate constants, in Table 4.10, involving these compartments.

The higher rate constant for transport from vegetation to surface soils, observed in RioShed, is expected given the inclusion of transport via canopy drip, wax erosion and litterfall.

From Table 4.11, it can be garnered that RioShed performs similar to CalTOX 2.3 and/or GIM3 in some compartments. The marked difference in the residence times in the vegetative compartments are expected, as previously explained. However, the significant differences in the residence times in the water and sediment compartments originate from differences in calculating transport via particles, as shown in Table 4.5. For the compartments, except the atmospheric compartment, where the residence times calculated using RioShed differ from those using CalTOX 2.3 and GIM, those calculated with RioShed are the intermediate of those by CalTOX

2.3 and GIM3. The final column in Table 4.11 simply gives the residence times calculated by RioShed when the equation $R_i = \frac{0.693}{HL_i}$ is applied to each compartment *i*, except the sediment compartment, as explained in section 2.2.2.3.

It can be seen, in Table 4.12, that compartmental concentration distribution is predicted similarly by CalTOX 2.3 and RioShed. Therefore, both models predict higher annual average concentrations of PBDE-47 in vegetation and surface soils, whereas lowest concentrations are expected in the atmosphere and vadose soils. However, the distinct difference in the predictions for concentrations in the sediment is due to the significantly lower transport rate constant for transport from surface water to sediment, calculated by RioShed versus CalTOX 2.3. Other than direct input, surface water is the source of contaminants for the sediment. Consequently, the modeling method in RioShed for advection via particles resulted in the lower transport rate constant from surface water to sediment and, hence, the lower sediment concentration.

4.3.1.2 Sensitivity analysis

It was found that the long range transport potential via surface waters was unresponsive to most properties (see Table F.1a and Table F.1b in Appendix F for absolute results). However, this parameter was negligibly responsive to the half-life in water, but positively responsive to the water outflow current and modeled water depth. It can therefore be expected that the long range transport potential via surface water will remain constant unless these properties are altered. The atmospheric long range transport potential was notably sensitive to changes in wind speed, atmospheric area and depth. It was most sensitive to the atmospheric area, decreasing by approximately 27% when this parameter was halved. When atmospheric half-life was halved, atmospheric long range transport potential decreased by 8%. The overall persistence was highly sensitive to the halving of the following parameters, with the respective bracketed changes: air-water partition coefficient (increased by 52%); half-life in soil (decreased by 40%); wind speed (increased by 75%); atmospheric depth (increased by 89%).

The annual average concentrations in all compartments, except in the atmosphere, decreased appreciably when ambient temperature was halved. Consequently, overall persistence decreased by 12%. However, atmospheric concentration and long range transport potential negligibly increased. Similar changes, albeit more notable, were observed when precipitation rate was halved. Chemical concentration in the urban vegetation decreased less notably, in comparison to concentrations in the remaining compartments, when the ambient temperature was halved.

Canopy concentrations for all vegetative covers decreased by approximately 100% when log K_{oa} was halved. All compartment concentrations increased by 60% to 75% when wind speed was halved. Overall persistence increased when the wind speed was halved, and atmospheric long range transport potential decreased moderately by 12%. Although atmospheric concentrations and long range transport potential as well as urban vegetation concentration increased almost imperceptibly when the precipitation rate was halved, all other compartment concentrations and, hence, overall persistence decreased notably by 5% to 50%.

Doubling the atmospheric emission rate doubled the average compartment concentrations without affecting persistence or long range transport potential. Changing the receiving compartment from the atmosphere to agricultural surface soil resulted in exorbitant increases in contaminant concentrations in only the agricultural soils, whereas concentrations in all other compartments decreased by 75% to 100%. Notably, the overall persistence skyrocketed by more than 3000%, although atmospheric long range transport potential was not affected. When the agricultural soil compartment was added as a source compartment, with the same application rate as for the atmosphere, cropland soil concentrations increased substantially, whereas many of the other compartments observed negligible increases in concentrations. Surface waters saw an appreciable increase in contaminant concentrations, of about 22%, when agricultural soil was added as a source compartment.

4.3.1.3 Field monitoring versus RioShed

A simple evaluation of RioShed was done by comparing some results from the field monitoring, detailed in Chapter 3, to predicted outputs of the model for PBDE -47, -99, -153 and -209, as shown in Table 4.13.

Table 4.13: Field and modeled outputs for comparison – for PBDE-47, -99, -153 and -209

Field data	**Modeled data**
Ratio of concentrations in atmosphere of a forest and nearby clearing	Ratio of steady state concentrations in atmosphere of a forest and grassland
Ratio of concentrations in soil of a forest and nearby clearing	Ratio of steady state concentrations in surface soil of a forest and grassland
Ratio of concentrations in litterfall of a forest and nearby clearing	Ratio of steady state concentrations in vegetation of a forest and grassland

It must be noted that field measurements were accomplished by analyzing and comparing samples of the chemicals in a forest and nearby clearing. However, the outputs of RioShed for the same contaminants were obtained by comparing the steady state concentrations in the forest of a forested landscape with those obtained when the forest was replaced with grassland in an un-forested scenario, given the previously explained hypothetical emission scenario. Although the assessment criteria for the field work clearly differ from those for RioShed in this section of the dissertation, such a comparison was considered suitable to evaluate RioShed's ability to identify trends or make qualitatively accurate predictions.

Employing the previously described hypothetical emission scenario, RioShed predicted that the ratio of the atmospheric steady-state concentrations in the forest and grassland for PBDE – 47, -99, -153 and -209 should range from 0.95 to 0.98, as seen in Table 4.14. However, field monitoring yielded atmospheric concentration ratios for the forest and clearing, portrayed as depletion factors, as low as 0.45 for PBDE-209 and as high as 0.93 for PBDE-99.

Table 4.14: Atmospheric concentration ratios for select PBDEs

Contaminant	**Atmospheric Concentration Ratio**	
	Field measurements – forest/clearing	Modeled results using RioShed – forest/grassland
PBDE-47	0.52	0.98
PBDE-99	0.93	0.96
PBDE-153	0.92	0.97
PBDE-209	0.45	0.95

Specifically for PBDE-47, the ratio of the steady state concentrations in the vegetation of the forest and that in the vegetation of grassland was predicted, by the model, to be 0.31. However, the ratio of the mean concentration of PBDE-47 in the litterfall of the forest and that in the litterfall of the clearing was 0.26. Also, for this same organic, the model predicted that the ratio of the steady state concentrations in the surface soil of the forest and the grassland should be 1.09. However, field monitoring produced a value of 1.33 for the ratio of the mean concentrations of PBDE-47 in the forest and clearing.

Based on the above, it was concluded that the model accurately predicted that the presence of a forest should reduce atmospheric concentrations, but increase soil concentrations. It also accurately predicted that the concentrations in the vegetation of the forest should be lower than that in a more limited vegetative cover, such as grassland.

Quantitative accuracy was not expected of the model given that: 1) a hypothetical emission scenario was employed and 2) the forest was replaced by grassland in lieu of comparing concentrations in adjacent vegetative covers. However, accurate qualitative predictions were desired, despite the different assessment criteria, and these were obtained.

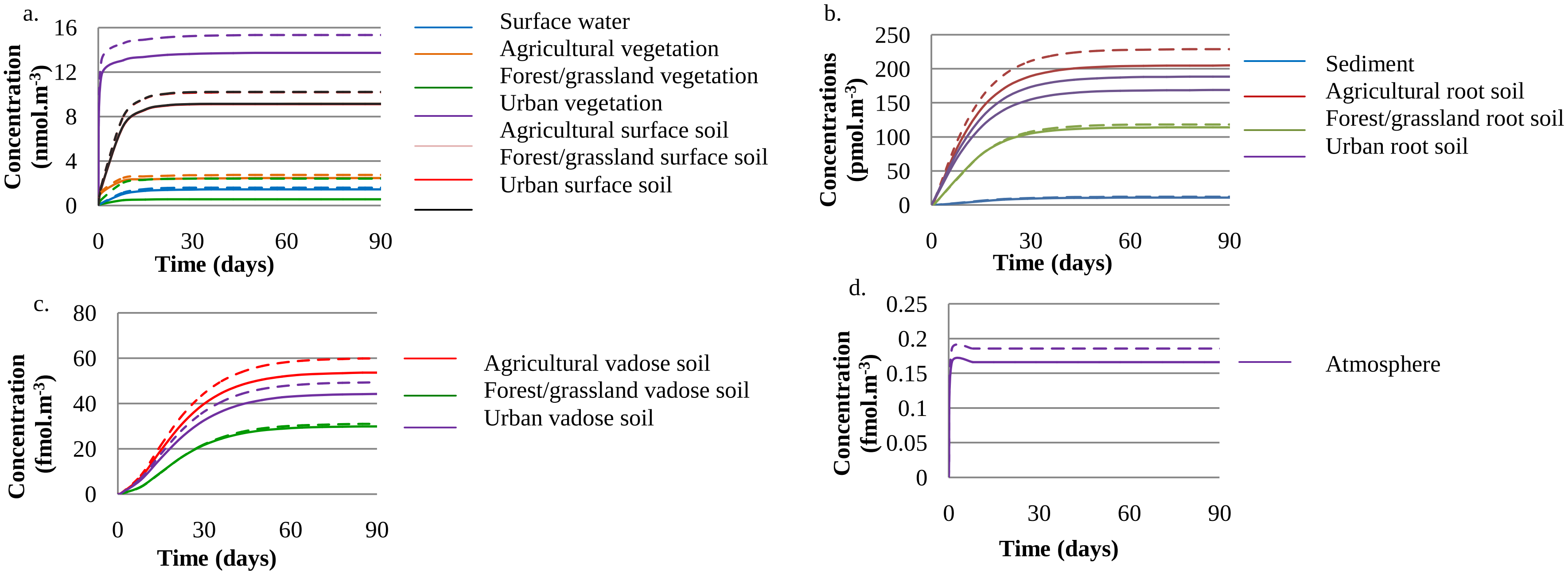
4.3.2 Dynamic evaluation of forest effects on PBDE-47 and dimethoate

To examine the impact of forests on fates in a dynamic system, only two chemicals were chosen – dimethoate and PBDE-47. Dimethoate was chosen from the more polar current-use pesticides, whereas PBDE-47 was from the more persistent pollutants.

Table 4.15: Percentage fraction of steady-state concentrations as at 29 and 365 days

	Percent fraction of steady-state concentration at the end of day 29 or 365 (%)							
Compartment	**Dimethoate**				**PBDE-47**			
	Grassland		**Forest**		**Grassland**		**Forest**	
	29 days	***365 days***	***29 days***	***365 days***	***29 days***	***365 days***	***29 days***	***365 days***
Atmosphere	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Water	99.4	100.0	99.4	100.0	99.5	99.9	99.5	99.9
Sediment	82.9	100.0	82.9	100.0	83.9	99.9	83.9	99.9
Imperv	100	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Agricultural vegetation	98.6	100.0	98.6	100.0	96.8	100.0	96.8	100.0
Forest vegetation	99.1	100.0	98.7	100.0	25.4	100.0	52.8	100.0
Urban vegetation	99.3	100.0	99.3	100.0	100.0	100.0	100.0	100.0
Agricultural surface soil	99.6	100.0	99.6	100.0	10.7	81.1	10.7	81.1
Forest surface soil	99.6	100.0	99.6	100.0	9.8	80.6	9.6	80.2
Urban surface soil	99.6	100.0	99.6	100.0	12.3	81.4	12.3	81.4
Agricultural root soil	91.6	100.0	91.6	100.0	1.2	51.6	1.2	51.6
Forest root soil	89.9	100.0	91.2	100.0	0.7	49.7	0.8	49.8
Urban root soil	91.1	100.0	91.1	100.0	1.2	51.2	1.2	51,2
Agricultural vadose soil	72.3	100.0	72.3	100.0	0.1	25.0	0.1	25.0
Forest vadose soil	68.7	100.0	70.4	100.0	0.0	23.5	0.0	23.6
Urban vadose soil	71.8	100.0	71.8	100.0	0.1	24.7	0.1	24.7

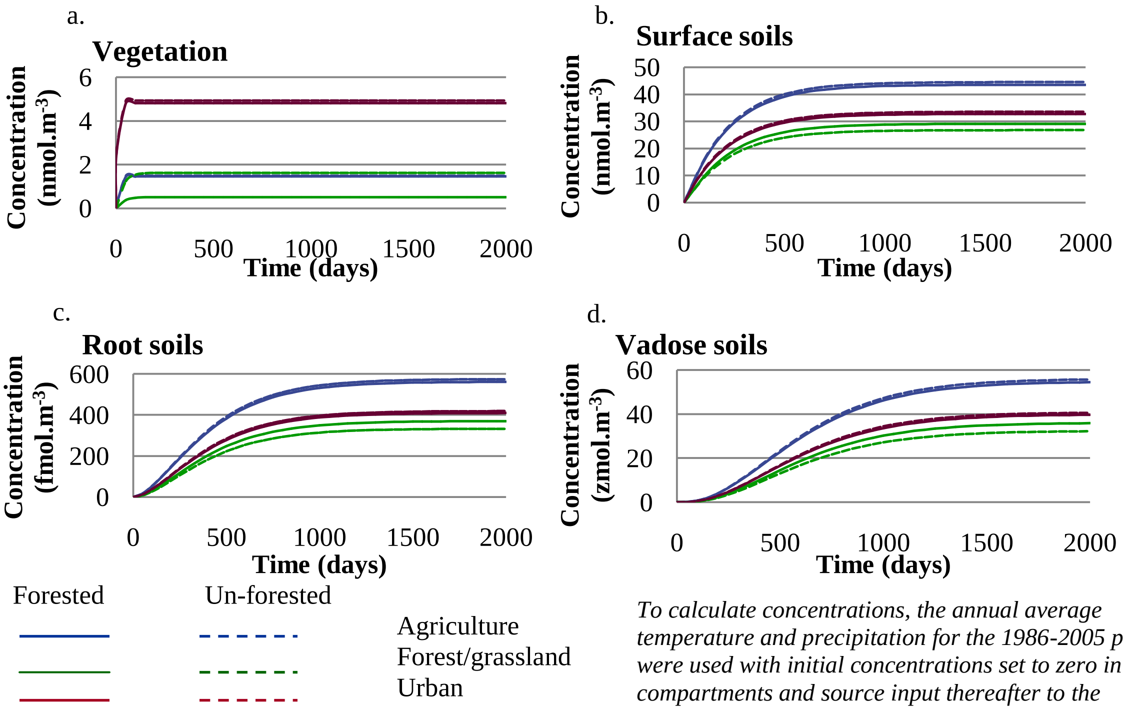
The physicochemical properties of these two contaminants, given in Table 4.6, were input into RioShed, which was then run to generate daily dynamic outputs for 365 days, for forested and un-forested landscapes, using the 1986-2005 annual average climate, as previously described in section 4.2.2.4.



Solid line – forested scenario
Dashed line – un-forested scenario

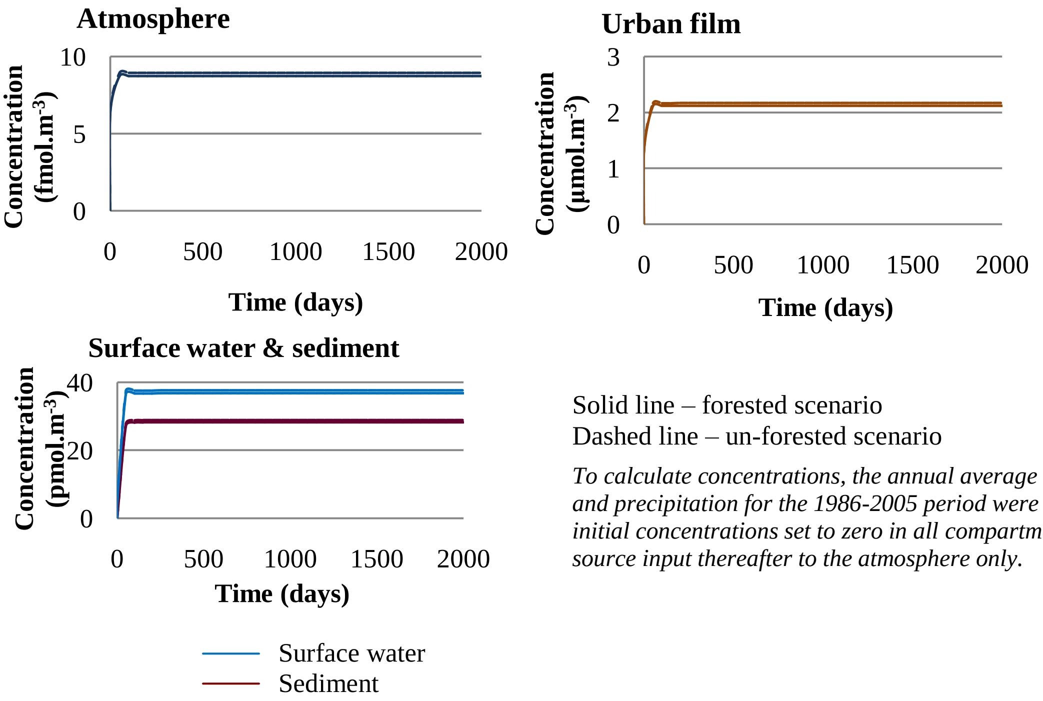
To calculate concentrations, the annual average temperature and precipitation for the 1986-2005 period were used with initial concentrations set to zero in all compartments and source input thereafter to the atmosphere only.

Figure 4.5: Time trend of dimethoate concentrations in given compartments (1986-2005 climate conditions)



To calculate concentrations, the annual average temperature and precipitation for the 1986-2005 period were used with initial concentrations set to zero in all compartments and source input thereafter to the atmosphere only.

Figure 4.6- A: PBDE-47 concentrations in the vegetation and soils (1986-2005 climate conditions)



Solid line – forested scenario
Dashed line – un-forested scenario

To calculate concentrations, the annual average temperature and precipitation for the 1986-2005 period were used with initial concentrations set to zero in all compartments and source input thereafter to the atmosphere only.

Figure 4.6- B: PBDE-47 concentrations in remaining compartments (1986-2005 climate conditions)

Within the first 29 days of introducing the source, steady state was achieved by dimethoate in the air and on impervious surfaces, irrespective of whether the landscape was forested or not. Table 4.15 and Figure 4.6 show that dimethoate achieved steady state at similar rates in all corresponding compartments of the forested and grassland scenarios, except in the canopies, root soils and vadose soils of the forests versus grassland vegetative covers, in which steady state was achieved at a marginally faster rate in the forested than un-forested landscape. For this organic, as revealed in Figure 4.5, steady state was achieved in all compartments within 90 days, irrespective of whether the landscape was forested or not. Also, steady state concentrations were typically higher in the un-forested landscape.

For PBDE-47, as seen in Table 4.15, steady state was achieved within the atmosphere, on impervious surfaces and in the urban canopies, in both the forested and un-forested landscapes, within the first 29 days of introducing the source. However, even after 365 days, concentrations were only within 20%-55% of steady state values in all root and vadose soils, and approximately 80% in the surface soils. As seen in Figure 4.6-A, steady state concentrations of PBDE-47 were achieved within 50 months in the root and vadose soils. Steady state was achieved at similar rates in all compartments of the un-forested landscape as in the corresponding compartments of the forested landscape. For this organic, steady state concentrations in the compartments of forested landscape were typically lower than in the un-forested landscape, except in the soils (surface, root and vadose).

For chemicals such as PBDE-47, which exhibit higher octanol-air partition coefficients and lower degradation rates in soils and sediments with respect to other compartments, the assumption of steady state may produce erroneous results in assessments in the range of weeks to months. However, such an assumption may be more reasonable for chemicals with properties similar to dimethoate.

Monthly compartmental inventories for both PBDE-47 and dimethoate were obtained over a one (1) year period, using the averaged monthly climate variables for the 1986-2005 period, for the forested and un-forested landscapes. The inventories of PBDE-47 and dimethoate were obtained, assuming both an initially pristine environment and an environment with initial conditions set at steady state, as explained in section 4.2.2.4.

In the current forested landscape under initially pristine conditions, most of PBDE-47 could be found in the forest surface soil after the first 3 months. Generally though, the main compartments to which this organic appeared to be disseminated included the surface soils of all vegetative covers, the forest canopy and the atmosphere. Therefore, a high affinity for surface soils and the forest canopy in a forested landscape is noted for this chemical. Although most of PBDE-47 did eventually retreat to the grassland surface soil in the un-forested landscape, it took 8 months. During the first 8 months, the highest inventory of the chemical, in this landscape, was recorded for the plant material of the grassland. Otherwise, the chemical was mostly observed in the agricultural and urban surface soils, as well as the atmosphere. It is apparent that vegetative covers do transfer some contaminants from the atmosphere to associated surface soils, with forests more quickly achieving this outcome.

When the steady state values from the previous results were instead used to initiate a model run, with monthly varying climate conditions, inventory distribution remained as at the start. The compartments with the highest inventories were the same as observed under initially pristine conditions – the surface soils for all vegetative covers and forest canopy. However, fluctuations occurred within the compartments, throughout the modeling year, depending on the climatic conditions. Lowest inventories in these compartments occurred in the months of March and April, displaying a one month delay in response precipitation rates, given that precipitation rates were lowest in February and March. However, highest inventories were observed in October, following the month that displayed the highest precipitation rate – September.

Dimethoate inventories observed a different pattern. Inventories were highest in the forest root soil and forest surface soil, followed by the agricultural root soil, in the forested landscape, irrespective of the initial conditions – pristine or steady state. When the landscape was devoid of forests, dimethoate was primarily in the plant material of the grassland. In this un-forested landscape, dimethoate inventories were also high in the grassland and agricultural root soils, as well as the grassland surface soil. Therefore, forests appear more effective than grassland vegetation at transferring dimethoate to the soils, irrespective of the initial conditions.

Comparing the results for PBDE-47 and dimethoate revealed that dimethoate, which has the lower air-water partition coefficient, displayed the greater affinity for surface water, irrespective of whether the landscape was forested or not.

4.3.3 Forest effects on long-term fates

There were two types of assessments conducted for the effects of forests on the fate metrics of the contaminants: 1) replacing an un-forested landscape with varying forested landscapes and 2) replacing a forested landscape with other forested landscapes, which were modifications of the original. In the first section of the evaluation, control scenario II (land-use distribution scenario II) was employed as the control, with the Rio Cobre watershed occupied by agricultural vegetation (25%), grasslands in lieu of forests (60%), and urban areas (15%). The comparison scenarios included the existing forest coverage (agriculture:forest:urban area –

25%:60%:15%), as well as other land use conversions of the forests, as described in section 4.2.2.4. The meteorological data included those annually averaged over the 1986-2005 period. The fate metrics of two chemicals – polybrominated diphenyl ether-47 (PBDE-47) and dimethoate were computed and compared for land-use distribution scenarios I and II, the results for which are provided in Table 4.16. It can be seen that the presence of the forest reduced the overall persistence of dimethoate, by 5.1%, and of PBDE-47, by as much as 6.2%. Both typically observed reductions in the average annual compartmental concentrations. However, the forest soil concentrations of PBDE-47 were higher than the grassland soil concentrations of this organic, by as much as 11.6%.

Table 4.16: Percent changes in the fate metrics for PBDE-47 and dimethoate when the grassland is replaced by forest

Fate Metric	**Percent change (%)**	
	PBDE-47	**Dimethoate**
Overall Persistence	-6.16	-5.13
Atmospheric long range transport potential	-2.27	-10.43
Atmospheric concentration	-2.27	-10.43
Surface water concentration	-2.26	-10.42
Sediment concentration	-2.26	-10.42
Impervious surface concentration	-2.27	-10.43
Agricultural vegetation concentration	-2.27	-10.43
Forest canopy concentration	-68.96	-76.57
Urban vegetation concentration	-2.27	-10.43
Agricultural surface soil concentration	-2.27	-10.43
Forest surface soil concentration	7.04	-10.39
Urban surface soil concentration	-2.27	-10.43
Agricultural root-zone soil concentration	-2.26	-10.43
Forest root-zone soil concentration	11.51	-3.48
Urban root-zone soil concentration	-2.26	-10.43
Agricultural vadose-zone soil concentration	-2.26	-10.43
Forest vadose-zone soil concentration	11.60	-3.47
Urban vadose-zone soil concentration	-2.26	-10.43

Table 4.17: Percent change in given fate metrics for the persistent chemicals in forested landscape versus un-forested landscape

	Percent change (%)								
Fate Metrics	PBDE-47	PBDE-99	PBDE-153	PBDE-209	TCDD	OCDD	PeCDF	HxCDF	Average
Overall persistence	-6.16	-1.49	-7.58	-6.29	13.79	-5.13	-4.39	-9.50	-3.34
Atmospheric long range transport potential	-2.27	-3.46	-3.39	-5.42	-1.72	-4.26	-1.92	-2.11	-3.07
Atmospheric concentration	-2.26	-3.46	-3.39	-5.42	-1.72	-4.25	-1.92	-2.10	-3.06
Surface water concentration	-2.25	-3.41	-3.39	-5.42	-1.71	-4.25	-1.91	-2.10	-3.05
Sediment concentration	-2.25	-3.41	-3.39	-5.42	-1.71	-4.25	-1.91	-2.10	-3.06
Impervious surface concentration	-2.26	-3.46	-3.39	-5.42	-1.72	-4.25	-1.92	-2.10	-3.06
Agricultural vegetation concentration	-2.26	-3.46	-3.39	-5.42	-1.72	-4.25	-1.92	-2.10	-3.06
Forest canopy concentration	-68.96	-69.21	-75.03	-77.71	-61.65	-76.57	-65.68	-69.29	-70.51
Urban vegetation concentration	-2.26	-3.46	-3.39	-5.42	-1.72	-4.25	-1.92	-2.10	-3.06
Agricultural surface soil concentration	-2.26	-3.46	-3.39	-5.42	-1.72	-4.25	-1.92	-2.10	-3.06
Forest surface soil concentration	7.04	12.15	-2.34	-5.33	4.73	-3.79	5.48	0.89	2.35
Urban surface soil concentration	-2.26	-3.46	-3.39	-5.42	-1.72	-4.25	-1.92	-2.10	-3.06
Agricultural root-zone soil concentration	-2.26	-3.45	-3.39	-5.41	-1.72	-4.25	-1.92	-2.10	-3.06
Forest root-zone soil concentration	11.50	12.62	0.36	-4.64	46.28	39.46	84.08	66.03	31.96
Urban root-zone soil concentration	-2.26	-3.45	-3.39	-5.41	-1.72	-4.25	-1.92	-2.10	-3.06
Agricultural vadose-zone soil concentration	-2.26	-3.45	-3.38	-5.41	-1.71	-4.25	-1.91	-2.10	-3.06
Forest vadose-zone soil concentration	11.59	12.42	0.57	-4.58	46.39	39.38	84.46	66.36	32.07
Urban vadose-zone soil concentration	-2.26	-3.45	-3.38	-5.41	-1.71	-4.25	-1.91	-2.10	-3.06

Positive changes to the fate metrics are highlighted

Table 4.18: Percent change in given fate metrics for the current-use pesticides in forested landscape versus un-forested landscape

	Percent change (%)								
Fate Metrics	Diazinon	Dimethoate	Carbaryl	Methomyl	Cyhalothrin	Cypermethrin	Diuron	Glyphosate	Average
Overall persistence	1.15	-5.13	-6.99	-9.65	0.09	-3.04	-2.07	0.28	-3.17
Atmospheric long range transport potential	-2.58	-10.43	-10.58	-10.59	-3.18	-4.65	-9.35	-10.60	-7.74
Atmospheric concentration	-2.58	-10.43	-10.58	-10.59	-3.18	-4.66	-9.36	-10.59	-7.75
Surface water concentration	-2.54	-10.42	-10.58	-10.57	-3.17	-4.65	-7.10	-10.59	-7.45
Sediment concentration	-2.54	-10.42	-10.58	-10.57	-3.17	-4.65	-7.10	-10.59	-7.45
Impervious surface concentration	-2.58	-10.43	-10.58	-10.59	-3.18	-4.66	-9.36	-10.59	-7.75
Agricultural vegetation concentration	-2.58	-10.43	-10.58	-10.59	-3.18	-4.66	-9.36	-10.59	-7.75
Forest canopy concentration	-73.80	-76.57	-77.31	-76.54	-74.84	-74.91	-71.95	-78.21	-75.52
Urban vegetation concentration	-2.58	-10.43	-10.58	-10.59	-3.18	-4.66	-9.36	-10.59	-7.75
Agricultural surface soil concentration	-2.58	-10.43	-10.58	-10.59	-3.18	-4.66	-9.36	-10.59	-7.75
Forest surface soil concentration	-2.41	-10.40	-10.55	-10.55	0.18	-0.96	1.24	-10.53	-5.50
Urban surface soil concentration	-2.58	-10.43	-10.58	-10.59	-3.18	-4.66	-9.36	-10.59	-7.75
Agricultural root-zone soil concentration	-2.58	-10.43	-10.58	-10.59	-3.18	-4.66	-9.36	-10.59	-7.75
Forest root-zone soil concentration	-5.26	-3.48	0.99	-5.52	0.26	2.09	4.26	33.69	3.38
Urban root-zone soil concentration	-2.58	-10.43	-10.58	-10.59	-3.18	-4.66	-9.36	-10.59	-7.75
Agricultural vadose-zone soil concentration	-2.58	-10.43	-10.58	-10.59	-3.18	-4.66	-9.36	-10.59	-7.75
Forest vadose-zone soil concentration	-5.08	-3.47	1.01	-5.31	0.24	15.09	4.35	33.95	3.48
Urban vadose-zone soil concentration	-2.58	-10.43	-10.58	-10.59	-3.18	-15.40	-9.36	-10.59	-7.75

Positive changes to the fate metrics are highlighted

For a more generalizable analysis, percent changes in the fate metrics, when the forest replaced the grassland, were also computed for all 16 evaluated organics, and are presented in Table 4.17 and Table 4.18 (see Table G.1, Table G.2, Table G.3 and Table G.4 in Appendix G for the absolute values for the 16 chemicals in each landscape). When the grassland was replaced by forests, annual average concentrations of the persistent organics were reduced in all compartments of the forested landscape, except in the forest soils. For those compartments observing concentration reductions, the change was approximately 3%, with the exception of the canopy, in which the change was about 71%. The surface, root-zone and vadose-zone soils for the forested region saw increases, in the average concentrations of the persistent pollutants, of 2%, 26% and 26%, respectively. As a result, for these persistent chemicals, both mean atmospheric long range transport potential and overall persistence decreased by aapproximately 3%.

Scrutiny of Table 4.18 revealed that most of the persistent pollutants, with TCDD as the exception, observed reduced overall persistences, in the range of 1.5%-9.5%, when forests replaced grassland. However, all observed reduced atmospheric concentrations and long range transport potentials (ranging from 2.1% to 5.4%) in the forested versus un-forested landscapes. All of the persistent chemicals had reduced concentrations in the agricultural, as well as urban root- and vadose- soils. Other than PBDE-209, the persistent chemicals observed greater concentrations, even as high as by 84%, in the forest root- and vadose- soils, compared to in the grassland equivalents. Only PBDE-153, PBDE-209 and OCDD observed decreased concentrations in the forest surface soil compared to the grassland surface soil.

Examination of Table 4.18 revealed that most of the current-use pesticides had decreased overall persistences (from 2.07% to 9.65%) in the forested (land-use distribution scenario I) versus un-forested (land-use distribution scenario II) landscapes. However, the atmospheric concentrations and long range transport potentials of all the current-use pesticides were lower in the forested landscape than the un-forested landscape, by as much as 11%. For these contaminants, whereas the forest surface soil concentrations were generally lower than the grassland counterpart, forest root-zone and vadose-zone soil concentrations were typically greater than the grassland root-zone and vadose soil concentrations, respectively.

This effect has been previously described as the ‘filter effect’ of forests, whereby the forests transfer persistent organic pollutants from the atmosphere to the forest soils (McLachlan & Horstmann, 1998; Su & Wania, 2005; Wania & McLachlan, 2000). However, in these studies, the soil compartment was not delineated so as to distinguish the soil layer(s) to which the pollutants commonly retreated.

The observations in this evaluation are less striking than those in the study by Wania and McLachlan (2000). There are a few probable reasons for this. In their study, Wania and McLachlan (2000) considered boreal and temperate forests, whereas tropical forests were the focus of this dissertation. The filter effect is possibly tempered for tropical forests, compared to temperate and boreal forests, due to processes such as increased volatilization, re-volatilization and the reduced uptake ability of forests when ambient temperatures are high. Also, the study by Wania and McLachlan (2000) considered bare soil as the control, compared to grasslands used in this dissertation. Grassland is vegetation that is expected to also uptake the organic contaminants from the atmosphere, albeit to a lesser degree than forests. Therefore, comparisons with grassland as the control are expected to be less notable than comparisons with bare soil as the control. This dissertation considered grasslands as the controls since such covers are more likely to exist in fertile/productive tropical countries such as Jamaica.

As also seen in Table 4.17 and Table 4.18, there were slight differences in the outcomes for the more polar current-use pesticides and the persistent pollutants. Compartmental concentrations of all evaluated contaminants, except in the forest or grassland soil compartments, were typically reduced when forests replaced grassland. However, the concentrations of the persistent chemicals in the forested landscape over the un-forested landscape were reduced in the range of 1.7%-77.7%, compared to similar reductions for the current-use pesticides with a range of 2.6%-78.2%. The reductions, in the atmospheric concentrations of the current-use pesticides, were as high as 11%, compared to the highest of 5% for the persistent pollutants. The consequence was that the mean atmospheric long range transport potential for the more polar organics was reduced by almost 8%, compared to 3% for the more persistent chemicals. Nevertheless, the overall persistences of most of the examined organics were reduced, with arithmetic means in the region of 3% (an arithmetic mean of 3.17%, with a range of -9.65% to 1.15%, for the current-use pesticides; and an arithmetic mean of 3.34%, with a range of -9.50% to 13.79%, for the persistent chemicals).

Concentrations in the forest root- and vadose- zone soils were typically higher than in the grassland counterparts. However, the concentrations of the pesticides in the forest root- and vadose- zone soils were at most 34% higher than in grassland root- and vadose- zone soils, whereas the persistent pollutants were at most 84% more concentrated in forest versus grassland root- and vadose- zone soils.

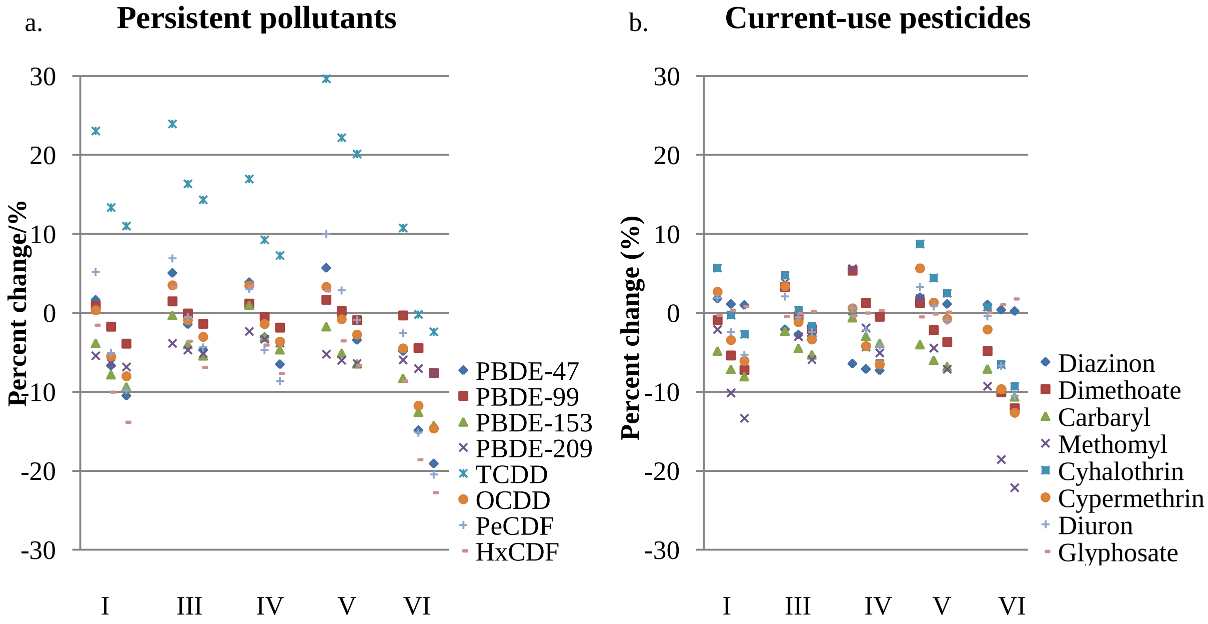
It appears that forests are more efficient at removing the current-use pesticides from the atmosphere than the less polar and more persistent pollutants. The reduced overall persistences when forests replace grasslands indicates that the tropical forests enhance the removal of these examined chemicals possibly through efficient degradation in the canopy.

For the persistent pollutants, the arithemetic mean of the annual average surface water concentrations were reduced by roughly 3%, whereas for the more polar current-use pesticides, these metrics were reduced by almost 7.5% when the forest replaced the grassland. Since drinking water health impacts are dependent on water concentrations, it can be concluded that tropical forests may reduce drinking water risks, especially for polar current-use pesticides.

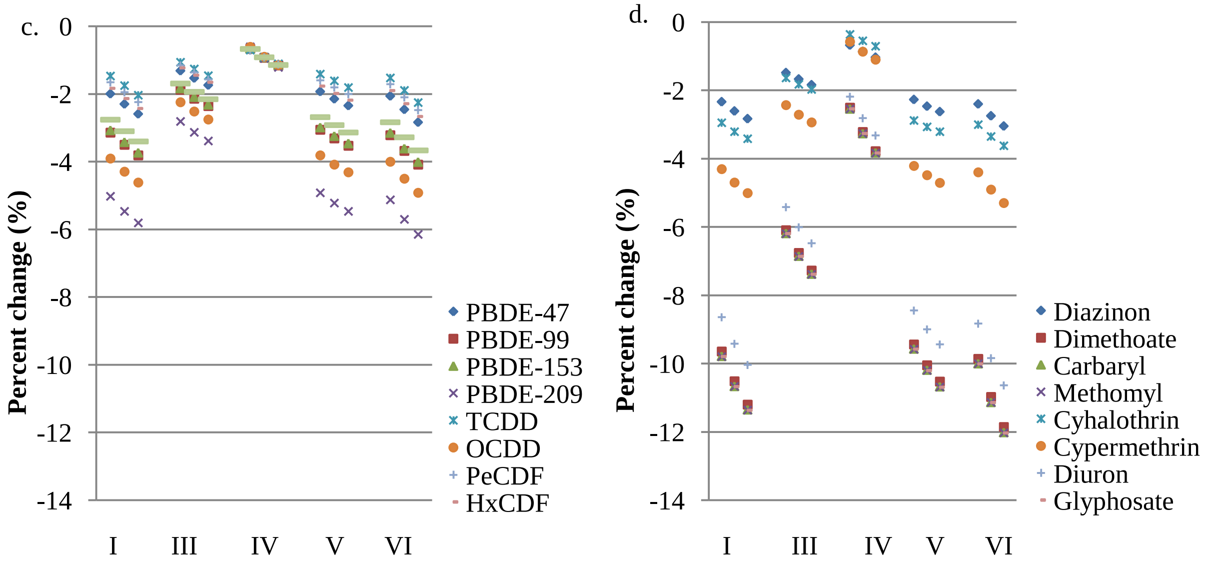
Figure 4.7 also shows that for the persistent organic pollutants, the general decrease in overall persistence, whenever forests are included in the landscape, is more striking when the forest composition includes only evergreen trees. The assessed persistent pollutants have high octanol-air partition coefficients. These types of organics are typically efficiently up-taken by vegetation and it is expected that forests should be more efficient at this task than grasslands. Given that evergreen trees retain their foliage and that degradation rates in vegetation are often higher than in compartments such as soils or sediments, the observed general reductions in overall persistences in the landscape, forested with evergreen trees, is reasonable.

In Figure 4.7, it can be seen that TCDD observed a distinctly higher increase in overall persistence than the remaining persistent pollutants when forests replaced the grasslands, except when the forest composition was small (7%). However, among the current-use pesticides, diazinon, cyhalothrin and cypermethrin experienced markedly smaller decreases in atmospheric long range transport potential than the remaining pesticides, when the un-forested landscape was replaced by forested landscapes.

Overall Persistence



Atmospheric long range transport



Land distribution scenarios
I – Agriculture:forest:urban composition of 25%:60%:15%
III – Agriculture:forest:urban composition of 34%:42%:24%
IV – Agriculture:forest:urban composition of 25%:42%:33%
V – Agriculture:forest:urban composition of 43%:42%:15%
VI – Agriculture:forest:urban composition of 7%:78%:15%

*In each scenario:
First column – 100% deciduous forest
Second column – 50%:50% deciduous:evergreen forest
Third column – 100% evergreen forest

Figure 4.7: Changes in the long-term fate metrics for the selected contaminants for various forested scenarios replacing the grassland scenario

Wania and McLachlan (2000) showed that the overall persistence of select persistent pollutants substantially increased when temperate forests replaced bare soils, due to enhanced transfers of these chemicals from the atmosphere to soils, which are the organic sinks. However, since the model simulation incorporated only one vegetative cover, the effect of the forests with co-existing land uses was not assessed. It can be seen in Figure 4.7 that the overall persistence of most of the examined persistent pollutants decreased when grasslands were replaced by forests of similar or greater acreage, as much as 22%. The observed decrease in overall persistence was positively correlated with the presence of evergreen trees. Some of these pollutants displayed increased overall persistence, up to 30%, when the forest acreage in the forested landscape was smaller than that of the grassland in the un-forested landscape. However, irrespective of the size of the forest, under all scenarios where forests were introduced into the landscape, the overall persistence was increasingly lower as the evergreen tree composition increased, than when the forests were strictly deciduous. Deciduous tropical forests possess trees that tend to lose their leaves at select times throughout the year, especially in the dry periods. This mechanism may be enhancing the transfer of the organics to the forests' soils, where degradation rates are typically slow. Therefore, this could explain the observed higher overall persistences in the landscape forested with deciduous trees.

In examining the conditions in which the forested landscape replaced the un-forested landscape, such that the forest acreage was less than the grassland acreage in the un-forested landscape (42% of the forested landscape under forests compared to 60% of the un-forested landscape as grassland), the overall persistences of the pollutants were reduced more when the urban area occupied 33% of the landscape than when the urban area was 15% of the landscape. It is expected that, given their high octanol-air partition coefficients, these organics should possess a high affinity for forest vegetation as well as the urban film over impervious surfaces. Forest vegetation appears to efficiently uptake the contaminants, thereafter facilitating dissipation and/or degradation. The reduced overall persistence when forests of similar or larger size replace the grasslands is therefore reasonable. Also, organic contaminants that are deposited to urban areas are often transferred to surface waters via wash-off. Organic chemicals typically exhibit shorter dissipation half-lives or residence times in surface waters than in soils. As a result, in a region such as the Rio Cobre watershed, which exhibits a relatively high precipitation rate, the observed decreased overall persistences of these chemicals, when the urban area is large, is also reasonable. The overall persistences of the contaminants were greater when the cropland acreage was larger. However, such increases in overall persistence were retarded by the presence of co-existing evergreen forests.

Figure 4.7 reveals that the current-use pesticides displayed a similar pattern for the overall persistence. Most of the pesticides experienced reduced overall persistence when an equally sized or larger forest replaced the grassland. This was enhanced as more evergreen trees were introduced into the forest compositions. It is possible that these polar current-use pesticides are also efficiently up-taken from the atmosphere by forests. However, their transfer to the soils may be retarded by efficient degradation in the canopy, leading to decreased overall persistence. The size of the agricultural land had a similar effect on the overall persistence of these current-use pesticides as on the more persistent chemicals.

The 16 evaluated organics displayed atmospheric characteristic travel distances less than 700 km under all evaluated conditions, rendering them as class III chemicals, with regional-scaled atmospheric long range transport potential. The atmospheric long range transport potentials of all assessed pollutants decreased whenever forests replaced at least some portion of the grasslands. In Figure 4.7, it can be seen that not only are the evergreen forests more likely to cause this decrease, but also that the current-use pesticides exhibit this favorable response to a greater degree, with a maximum decrease of 12%, compared to a maximum of 6% for the persistent organics.

The decreases in atmospheric long range transport potential were more notable for larger forested acreages. When the atmospheric long range transport potentials of the organic contaminants, in the landscape architectures exhibiting the same forest coverage (42%), were further examined and compared, it was found that the smallest decrease occurred when 30% of the forest had been converted to urban area – as it would be in urban expansion. When temperatures are elevated, as is characteristic of a tropical region, re-volatilization is promoted (Nizzetto & Perlinger, 2012). Therefore, atmospheric uptake by forests may be off-set by re-volatilization from urban surfaces. When the urban area is maintained, reduced atmospheric long range transport potential is associated with increased forest coverage.

The changes to atmospheric transport potential were generally larger for the current-use pesticides than the persistent pollutants. Atmospheric long range transport potential is a function of the partition coefficients. The organic chemicals used in this study have similarly high octanol-air partition coefficients. However, the current-use pesticides have lower air-water partition coefficients than the more persistent chemicals evaluated, and are considered more polar. Polar organics tend to be swimmers, whereas the less polar organic compounds, with both high octanol-air and air-water partition coefficients, tend to be hoppers (Lohmann et al., 2007). The hoppers are subject to re-volatilization. Since environmental surfaces, including forests re-volatilize when temperatures are elevated, it can be expected that in this tropical region, the select persistent pollutants assessed are more likely to be re-volatilized than the assessed current-use pesticides. Furthermore, the current-use pesticides often display shorter half-lives in the vegetation than the assessed persistent chemicals. This could facilitate a faster uptake of the current-use pesticides, by the forests, thereby reducing atmospheric concentrations. Therefore, forests in tropical regions can be expected to exhibit greater capabilities at reducing the atmospheric long range transport potentials of many current-use pesticides, than those of the more persistent pollutants.

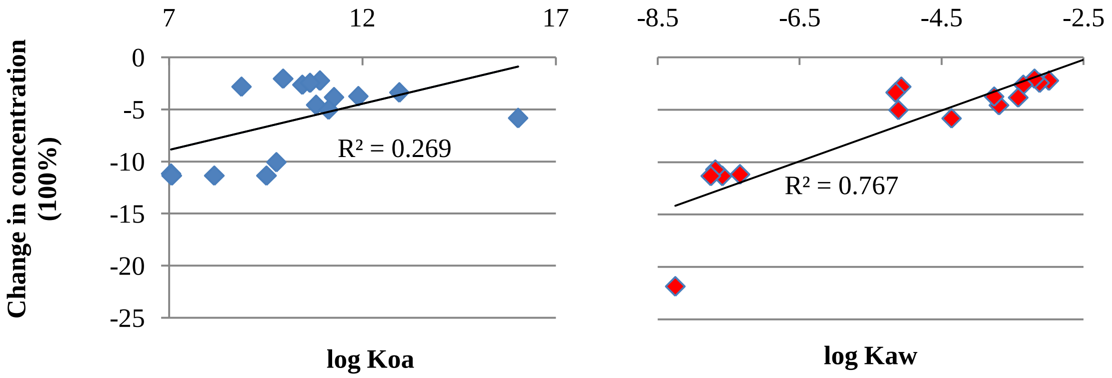


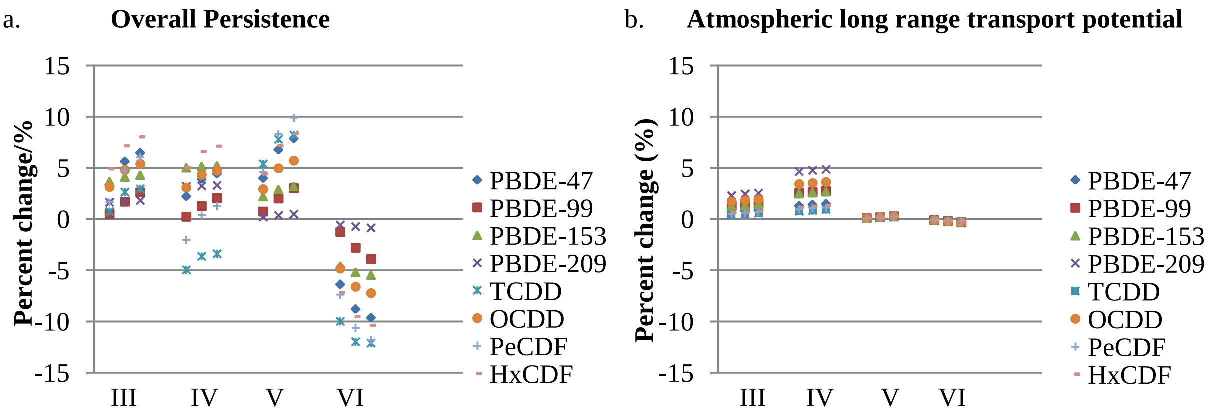
Figure 4.8: Changes in annual average atmospheric concentrations for given chemical properties in a landscape with a 100% evergreen forest

The changes to annual average atmospheric concentrations, when a 60% evergreen forest coverage replaced a similarly sized grassland, were examined with respect to select chemical properties – molecular weight, octanol-air partition coefficient and air-water partition coefficient. The reductions in atmospheric concentration associated with the evergreen forests were not correlated with molecular weight or octanol-air partition coefficient (K_{oa}), as illustrated in Figure 4.8. However, there was a reasonable correlation ($R^2 = 0.767$) between the reductions in atmospheric concentrations and air-water partition coefficient. Therefore, the more polar organic compounds, those with lower air-water partition coefficients (K_{aw}), observed greater reductions in atmospheric concentrations, in the forested evergreen landscape. This trend was also noted for deciduous and semi-evergreen forests, albeit to lesser degrees.

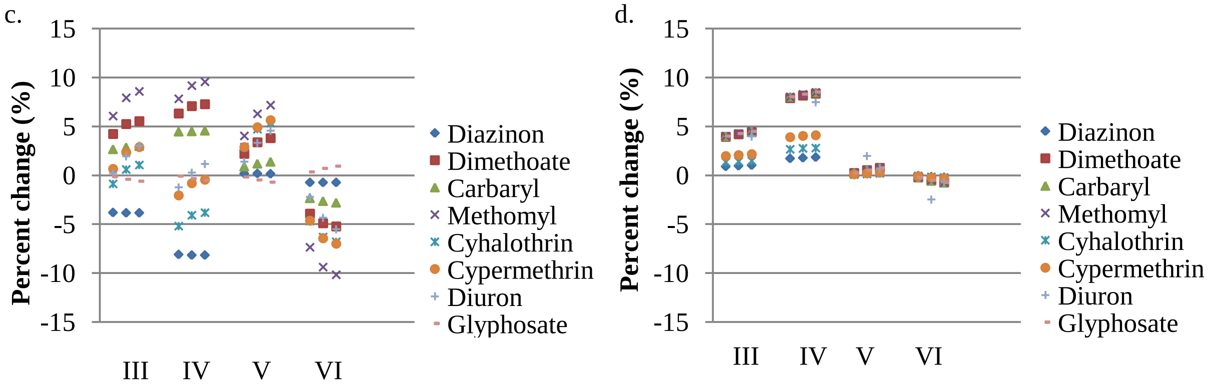
It has previously been shown that temperate forests reduce the atmospheric concentrations of select organic compounds, especially those with $7 < \log K_{oa} < 11$ and $\log K_{aw} > -6$. The organic contaminants, evaluated in this dissertation, exhibited $7 < \log K_{oa} < 17$ and $-9 < \log K_{aw} < -2$. This study shows that tropical forests are more apt at reducing the atmospheric concentrations, and, consequently, the long range transport potential of the more polar organics.

In another assessment, control scenario I, which is also the current land-use distribution of the Rio Cobre watershed (agriculture:forest:urban area at 25%:60%:15% - land-use distribution scenario I) was employed as the control. The land-use distribution was altered as described in section 4.2.2.4 and land-use scenarios III to VI were utilized as comparison scenarios. The forest composition was also altered between deciduous, evergreen and semi-evergreen, as before. As illustrated in Figure 4.9, the overall persistences of both the persistent organic pollutants and current-use pesticides generally increased when forested acreage decreased. Such increases were retarded as deciduous trees increased. For the current-use pesticides, the greatest increase in overall persistence, up to 10%, occurred during deforestation for urban expansion. However, the persistent pollutants generally observed the greatest increases in overall persistence during agricultural expansion, as much as 10%, when the co-existing forest was evergreen. The evaluated organics experienced reduced overall persistence during afforestation at the expense of agricultural land. These observed reductions in overall persistence, during afforestation, occurred to a greater degree and with greater variability for the persistent pollutants, ranging from less than 1% up to 13%.

Persistent pollutants



Current-use pesticides



Land distribution scenarios
III – Agriculture:forest:urban composition of 34%:42%:24%
IV – Agriculture:forest:urban composition of 25%:42%:33%
V – Agriculture:forest:urban composition of 43%:42%:15%
VI – Agriculture:forest:urban composition of 7%:78%:15%

*In each scenario:
First column – 100% deciduous forest
Second column – 50%:50% deciduous:evergreen forest
Third column – 100% evergreen forest

***Control scenario I was the control*
(Agriculture:forest:urban composition of 25%:60%:15%)

Figure 4.9: Changes in the long-term fate metrics for the selected contaminants for various forested scenarios replacing the current forested landscape

Table 4.19: Mean percent change in concentrations in the forest canopies, surface and root soils compartments when select forested landscapes replaced the un-forested landscape

		Mean percent change in concentration (%)					
		Persistent Organic Pollutants			Current-use Pesticides		
Land Distribution	**Forest Composition**	**Forest canopy**	**Forest surface soil**	**Forest root soil**	**Forest Canopy**	**Forest surface soil**	**Forest root soil**
A:F:U 0.25:0.60:0.15	D	-40.1	11.0	61.7	-55.5	-1.5	19.3
	E	-83.3	-1.8	8.9	-85.1	-8.6	-6.2
	D/E	-73.1	-1.6	23.3	-76.9	-6.1	1.2
A:F:U 0.34:0.42:0.24	D	-23.7	18.1	83.3	-46.5	3.0	31.1
	E	-76.8	3.0	26.4	-80.1	-3.7	3.6
	D/E	-63.5	6.8	42.3	-70.1	-1.3	11.9
A:F:U 0.25:0.42:0.33	D	-22.8	19.4	85.5	-44.9	6.0	34.7
	E	-76.6	4.1	27.8	-79.5	-1.0	6.4
	D/E	-63.1	8.0	44.0	-69.2	1.5	14.9
A:F:U 0.43:0.42:0.15	D	-24.5	16.8	81.0	-48.1	0.2	27.8
	E	-77.1	1.9	25.0	-80.6	-6.3	0.9
	D/E	-63.9	5.7	40.7	-70.9	-4.0	8.9
A:F:U 0.07:0.78:0.15	D	-50.4	7.4	47.9	-61.1	-2.8	13.1
	E	-86.8	-4.1	-1.8	-87.9	-10.3	-11.0
	D/E	-78.6	-1.1	11.5	-80.9	-7.7	-4.1

A – agriculture; F – forest; U – urban; D – deciduous; E – evergreen; D/E – 0.5:0.5 deciduous:evergreen

Therefore, for the evaluated organic contaminants, most observed increases in overall persistence during deforestation, when at least some portion was allocated for agricultural expansion, especially if the forest lost had been 100% evergreen. However, with the exception of glyphosate, the contaminants saw decreases in overall persistence, as much as 13%, during afforestation at the expense of agriculture.

In analyzing the changes to the atmospheric long range transport potential, the greatest increase, which was more distinct for the current-use pesticides, was observed when urban areas were expanded at the expense of forests. The observations for both types of contaminants examined are shown in Figure 4.9. The changes to the atmospheric long range transport potential displayed greater variability for the current-use pesticides than the persistent chemicals. For both the persistent organics and the current-use pesticides, negligible increases in atmospheric long range transport potential occurred during deforestation for agriculture, less observable for deciduous forests. On the other hand, negligible decreases in this metric were experienced during afforestation of croplands, with the changes even less notable if the forest was totally deciduous. Tropical forests and agricultural lands appear to impact atmospheric long range transport potentials similarly. Leaf area index appears to display notable impact on contaminant transport between vegetation and the atmosphere. Since croplands and deciduous forests display similar leaf area indices (3.6 and 3.9, respectively), the observed negligible changes to the atmospheric long range transport potential is reasonable.

The assessments demonstrated that increasing forest coverage, especially with a 100% evergreen composition, has the positive effect of not only reducing atmospheric long range transport potential, but also overall persistence.

As shown in Table 4.19, when forested landscapes replaced the un-forested landscape, mean concentrations in the forest vegetations were always lower than in the vegetation of the grassland. This is quite likely a response to the higher leaf area index and, consequently, the canopy area of the forests. However, for the persistent contaminants, the mean forest surface soil concentrations were generally higher than the grassland surface soil, and to a greater degree when the forests were deciduous. There were select conditions under which this was not observed – such as when the forest surface soil area, especially given an evergreen or semi-evergreen canopy, was the same or exceeded that of the grassland. For these chemicals, once a forest canopy existed, the forest root-zone soils exhibited higher mean concentrations than the grassland root-zone soils, by as much as 86%. This was more likely to occur when the forests were deciduous.

In comparing the observations for the persistent organics and the current-use pesticides in Table 4.19, it was also noted that in general, the forests more efficiently transferred the persistent contaminants to the soils below than the less persistent. Again, the impact was greater for the root-zone soil than the surface soil, especially for deciduous forests. This is similar to findings by Wania and McLachlan (2001), in which the uptake and subsequent transfer of contaminants from the atmosphere to forest soils by forests was reduced for the less persistent contaminants, due to competition between degradation processes and uptake.

4.3.4 The effects of forest parameters on long-term fates

This analysis was another comparative evaluation, in which the changes to the long term fate metrics, as consequences of changes in forest parameters, were examined. The control was the current forest coverage and composition of the Rio Cobre watershed, control scenario I (land-use distribution scenario I). Forest parameters were altered individually, as explained in section 4.2.2.5.

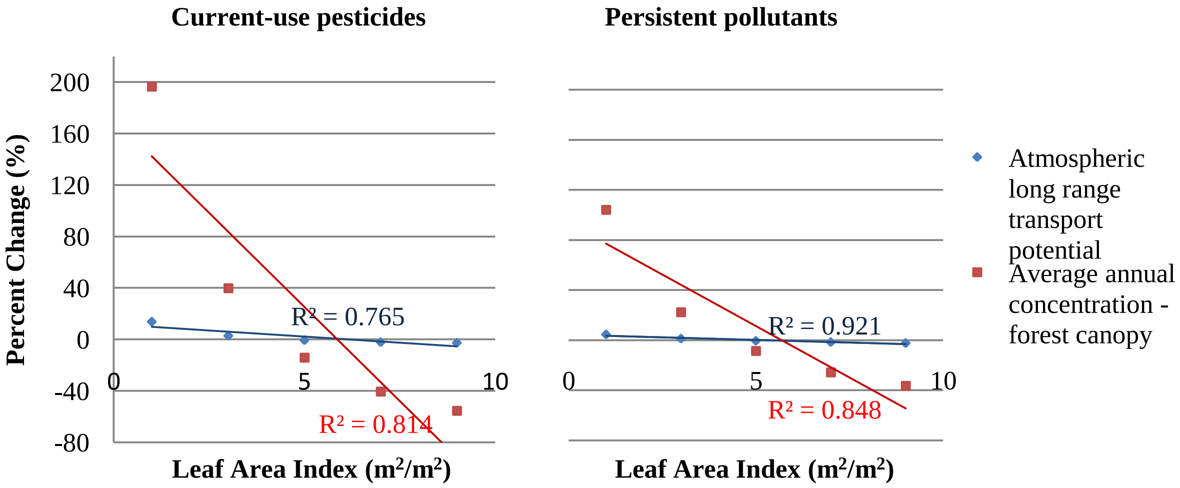


Figure 4.10: Leaf area index impact on mean fate metrics

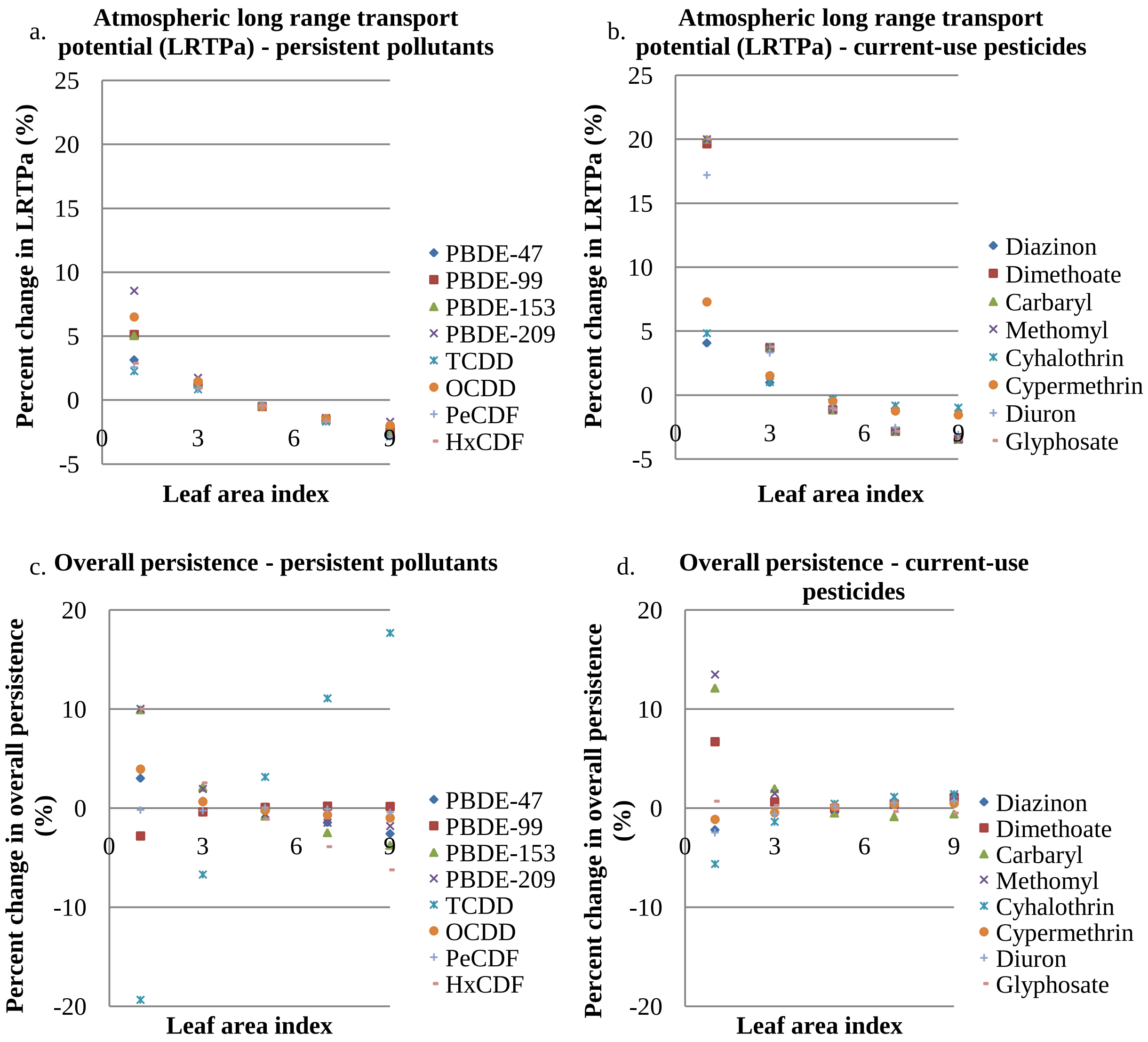


Figure 4.11: Percent changes in long-term fate metrics for the organic contaminants given varied leaf area indices

There were negligible changes in the long term fate metrics as biomass was varied. However, a negative association (R^2 value of 0.921) was observed between the mean atmospheric long range transport potentials of the persistent organics and the leaf area indices. The current-use pesticides exhibited a moderate negative correlation between the same two variables with a R^2 value of 0.765, illustrated in Figure 4.10. The leaf area index is a canopy surface area dimension, which dictates the uptake potential of the forest canopy. Therefore, increasing the leaf area index increases the atmospheric uptake potential of the forest, which is reflected as decreased atmospheric concentrations and, consequently, long range transport potential, as seen in Figure 4.11.

When the changes in the mean annual average concentrations in the forest canopy were assessed with respect to leaf area index, similar correlations were noted for the persistent organics and current-use pesticides. The leaf area index is reflective of the surface area occupied by the vegetation. Increases in this variable are associated with increases in the volume of the canopy. As a result, the decreasing annual average canopy concentrations with increasing leaf area indices were expected.

However, a general relationship between leaf area index and overall persistence was not readily apparent. As seen in Figure 4.11, for some organics such as TCDD and cyhalothrin, increasing the leaf area index caused increases in their overall persistence. This particular observation was distinct for TCDD, compared to other similarly reacting chemicals. Alternately, for other organics such as OCDD and dimethoate, increases in leaf area index were associated with decreases in overall persistence.

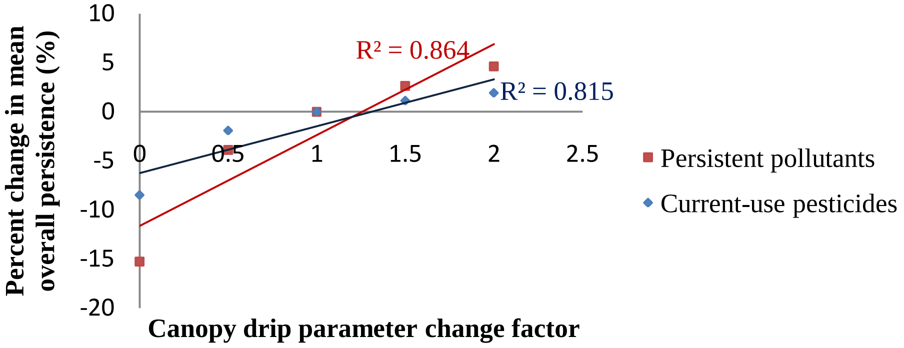


Figure 4.12: Changes in mean overall persistence given variations in canopy drip parameter

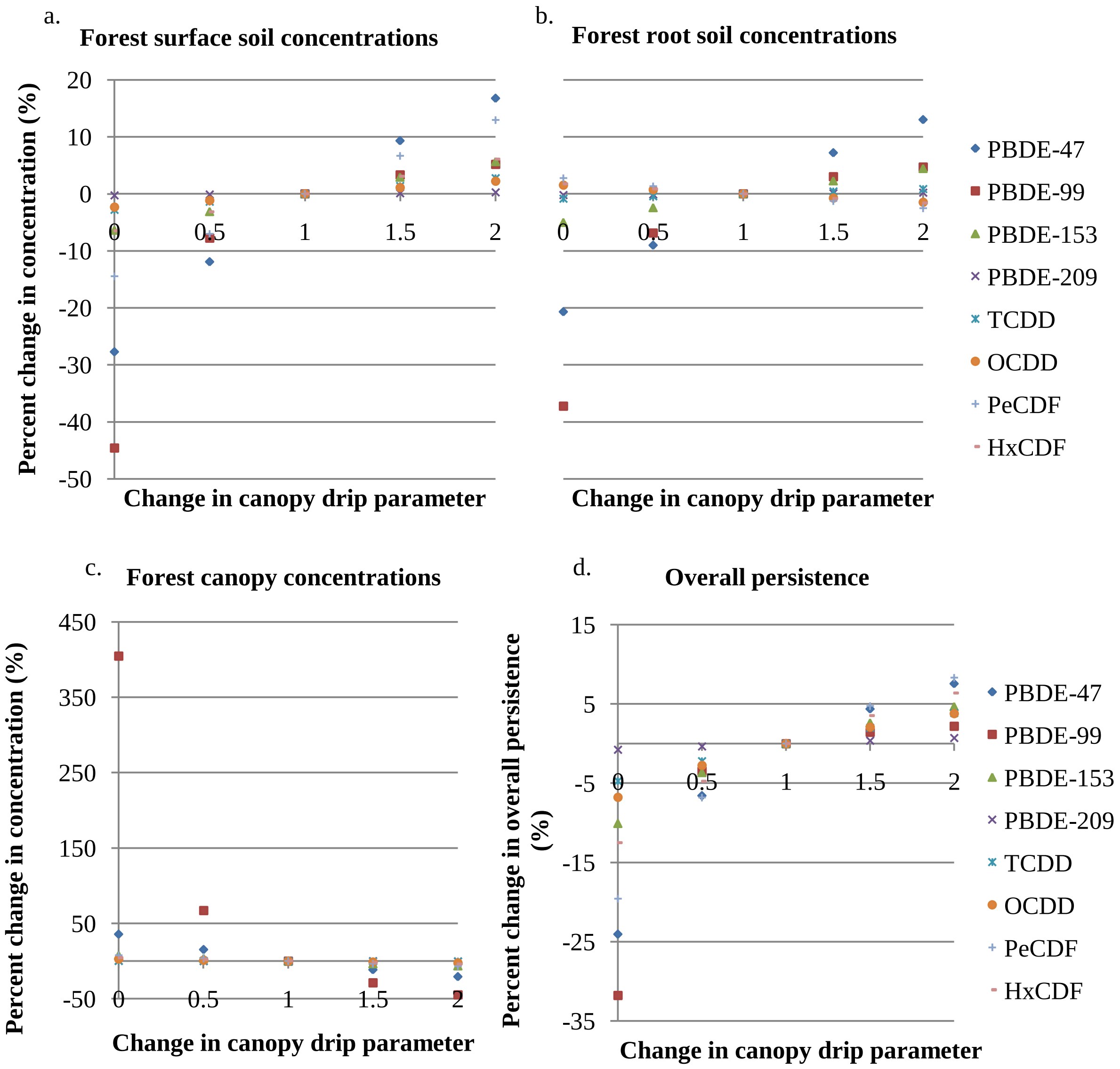


Figure 4.13: Percent change in select outputs given changes in canopy drip parameter – persistent pollutants

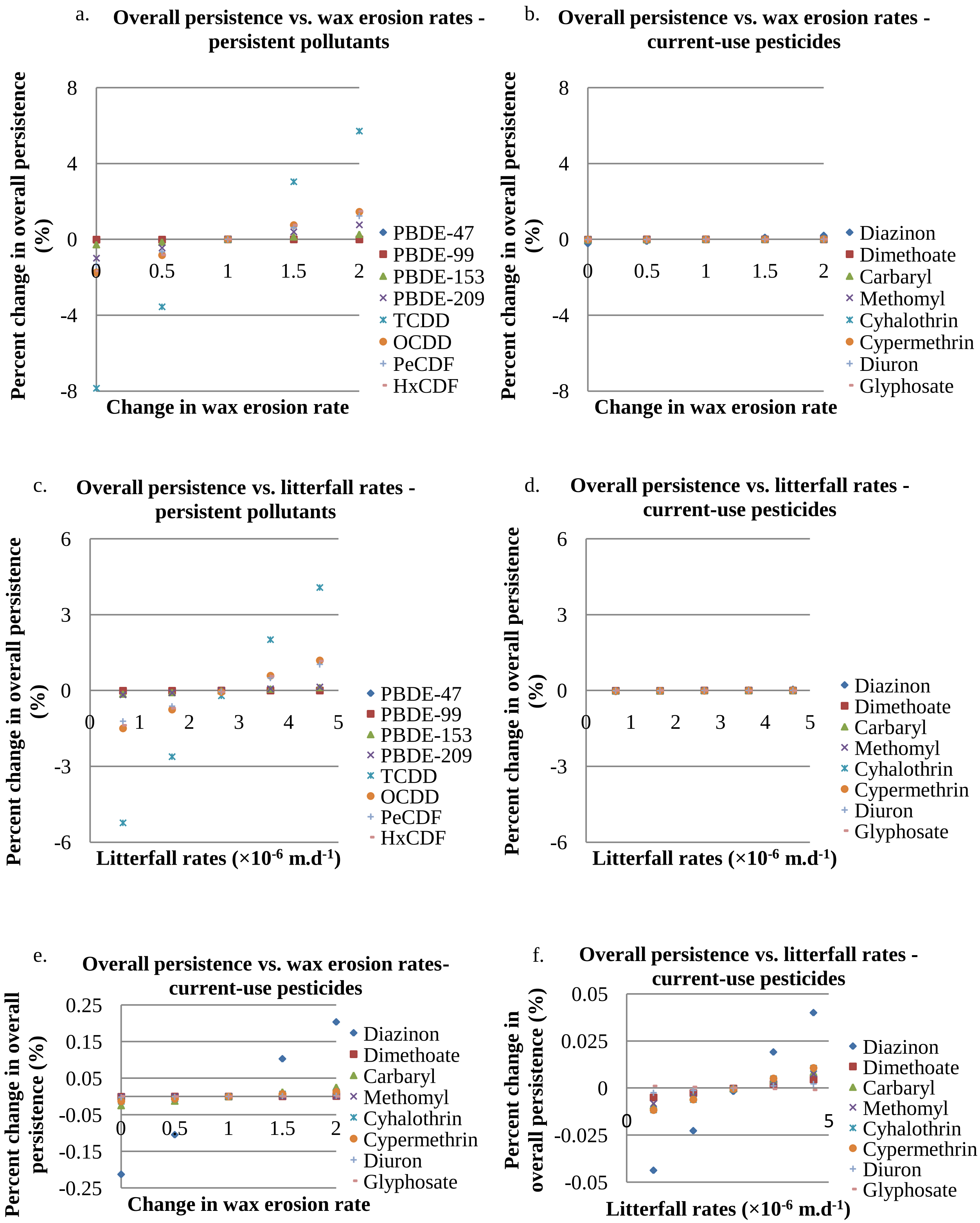


Figure 4.14: Changes in overall persistence for the organic contaminants given varying forest parameters

Canopy drip is one mechanism by which vegetation, such as forests, transfer organic contaminants from the leaf surface to the surface soils. The results were similar for the persistent pollutants and the current-use pesticide. Figure 4.12 illustrates the changes in select relevant compartments, as well as the overall persistences of the persistent organics as canopy drip was altered. As the canopy drip parameter was increased, the concentrations in forest surface and root-zone soils also increased, whereas the concentrations in the forest vegetation decreased.

Overall persistence also increased as the canopy drip parameter increased. As seen in Figure 4.13, there were notable similar positive correlations between the canopy drip parameter and the arithmetic means of the overall persistences of the current-use pesticides, as well as the persistent pollutants, with respective coefficients of determination (R-squared values of 0.82 and 0.86, respectively). However, it appears that the overall persistence of the persistent pollutants were slightly more responsive to changes in the canopy drip parameter than of the current-use pesticides.

Wax erosion and litterfall serve similar purposes, to canopy drip, in enhancing the delivery of contaminants from the leaves to soils. Therefore, as expected, the overall persistences of all evaluated chemicals increased as litterfall and wax erosion rates increased. This is illustrated in Figure 4.14. Given the increased delivery to soils as the canopy drip parameter, wax erosion rates or litterfall rates increased, the associated increases in overall persistence were expected. Soils are typically sinks or reservoirs for organic contaminants, which often exhibit longer degradation half-lives in these compartments thereby leading to amplified residence times and, consequently, overall persistence.

The canopy drip parameter was simultaneously altered for the agricultural and urban vegetation. The expected respective increases and decreases in the annual average concentrations in the surface soils and vegetation of these land uses were observed. However, concentrations in the root- and vadose- zone soils decreased as the canopy drip parameter increased. It was expected that since surface soil concentrations increased with increased canopy drip parameter, so should root- and vadose- zone soil concentrations, due to diffusion from upper to lower soils. An explanation is that leaves also transfer to root soils via phloem flow. Therefore, with decreased canopy concentrations due to increased canopy drip, transfers via phloem flow are retarded. This is associated with lower concentrations in the root and, consequently, vadose soils. It therefore appears that for some organics, such as octachlorodibenzodioxin (OCDD), in select land uses, phloem flow may be a more important transfer path to root soils than diffusion from surface soils.

4.4 Conclusions

An evaluative multimedia environmental model has been developed for the watershed scale. The required inputs are simple and obtainable or estimable. Computing and resource requirements are relatively insignificant. Additionally, both steady-state and dynamic outputs are speedily generated. This model may be useful for local and regional fate and health assessments, while remaining efficient and transparent.

The sensitivity analysis demonstrated that long range transport potential via surface waters was primarily dependent on properties such as water outflow current and water depth. However, atmospheric long range transport potential was influenced not only by the properties of the atmosphere, including wind speed and area, but also by select chemical properties such as octanol-air partition coefficient. On the other hand, overall persistence was highly dependent on the compartmental half-lives, as well as the octanol-air partition coefficient of the chemical.

Temperature, precipitation and the emission receiving compartment were the main determinants of compartmental concentrations. However, of the climate variables, precipitation appears to take the lead role in influencing contaminants' fates.

Tropical forests influence the environmental fates and, potentially, the health impacts of select organic contaminants. It has been shown that tropical forests reduce the atmospheric concentrations, and hence the atmospheric long range transport potential, of the assessed contaminants at the expense of forest soils. Also, these forests reduce not only the atmospheric concentrations and long range transport potential, but also the overall persistences, possibly through enhanced uptake and ensuing increased vegetative degradation.

Tropical evergreen forests were seen to be more efficient at reducing atmospheric long range transport potential than tropical deciduous or semi-evergreen forests, especially for the more polar organic chemicals. The tropical forests appear more effective at reducing overall persistence than the grasslands of similar acreages. This was enhanced if the forest was evergreen. It also appears that tropical forests and croplands act similarly in influencing the fates of current-use pesticides. The canopy drip parameter, wax erosion rate and the leaf area index are forest parameters that exhibit notable positive influences on the surface soil concentrations, as well as overall persistences of the organic compounds.

Foley (2003) highlighted that grasslands often display lower precipitation rates and higher surface temperatures than forests. In this first-step evaluation, this phenomenon was not considered. It is quite possible that the observed effects of the tropical forests would have been enhanced, had it been incorporated.

Temperature has been shown to influence the fates of organic compounds in the watershed. Many parameters, such as the partition coefficients and the compartmental half-lives, are temperature dependent. In this application, the temperature dependences of the variables were not considered. Future assessments should incorporate temperature dependence for a more realistic outcome.

Also, many of the input parameters in this study were estimated as best as possible where actual values were unavailable. For more accurate assessments, future work should use actual data or improved estimation methods, as they become available. Needless to say, this first requires more research geared towards measuring region-specific landscape properties as well as experimental determination of the chemical properties under varying conditions, such as temperature and pressure. Also, many estimation methods require data that are not always available. Therefore, estimation methods that require more of the currently available data, without sacrificing accuracy, are necessary.

In conceptualizing RioShed, accounting for the spatial heterogeneity of landscapes was considered important. Although the model is considered representative, it is recommended that more research be directed at modestly increasing the resolution of the landscape representation, without adding resource burden, such that more land uses can be simultaneously modeled at the watershed scale. Although the results, obtained in applying RioShed to the Rio Cobre watershed, may be applicable to other similar tropical developing regions, region-specific assessments are recommended when possible.

Chapter 5

The climate change and land-use impacts on the environmental fates of organic contaminants in a tropical watershed

5.1 Introduction

A number of organic compounds have raised global concern, due to their propensity for human and environmental toxicity, as well as their ubiquitous nature. Among these are pesticides, poly-brominated diphenyl ethers (PBDEs), dioxins and furan. Many of these organic compounds are produced for their essential services. For example, pesticides are manufactured and used globally to control the proliferation of pests, such as weeds, rodents, fungi, among others (Moore, 2007), whereas PBDEs are used as flame retardants (Sjödin, Patterson, & Bergman, 2003). However, some, such as dioxins and furans, are the unintentional by-products of combustion processes, including those processes involved in the manufacture of beneficial/essential organic compounds. These organic contaminants are all released in and distribute among environmental media, with the ensuing potential to cause harm. As a result, understanding the fate processes and governing factors, involved in the environmental distributions and fates, as well as the associated health impacts of these chemicals, is crucial for the development and implementation of appropriate control measures.

Among the environmental factors known to influence the fates of organic contaminants is vegetative cover. Recently, focus has been directed towards assessing the role of specific vegetative covers such as forests in the environmental movement of these chemicals. To date, it has been demonstrated that temperate and boreal forests transfer select semi-volatile organic compounds, those with octanol-air (K_{oa}) and air-water (K_{aw}) partition coefficients such that $7 < \log K_{oa} < 11$ and $\log K_{aw} > -6$, from the atmosphere to forest soils via a process termed 'the filter effect' (McLachlan & Horstmann, 1998). A global assessment has also shown that there is a filter effect, for some organics, for all forests combined worldwide (Su & Wania, 2005). Additionally, in Chapter 4 of this dissertation, it has been demonstrated that, at the watershed scale, tropical forests are also influential in the environmental fates of select organic compounds. It was found that both the overall persistences and atmospheric long range transport potentials, of select persistent pollutants and current-use pesticides, were reduced when forests were present in the tropical watershed. Such reductions were enhanced when the tropical forest contained evergreen trees. However, whereas temperate and boreal forests appear to transfer the organics to the soils, thereby increasing overall persistences, tropical forests may be reducing overall persistences by enhanced degradation in the canopy. Nevertheless, the general conclusion from all these studies is that forests govern the fates and distribution of many organic pollutants.

In the studies examining the influence of forests on the fates of the organic contaminants, it was also shown that climate drivers, especially temperature, were determinants of the forests' influences. Nizzetto et al. (2007) demonstrated that the atmospheric uptake ability of forests for organic contaminants was reduced at elevated temperatures. The forest filter effect appeared restricted when temperatures increased (McLachlan & Horstmann, 1998; Wania & McLachlan, 2000). Also, boreal and temperate forests led to increased atmospheric levels of organics with $8 \leq \lg Koa \leq 10.7$, during periods of elevated temperatures, due to re-volatilization (Nizzetto & Perlinger, 2012). Therefore the ability of forests to impact the environmental distribution of organic contaminants may be climate dependent. These are important considerations, especially as the climate changes.

Regional assessments of the effects of forests on the fates of organic contaminants, under varying climatic conditions, as well as how climate change may directly affect the fates of the contaminants, are highly informative. Studies evaluating the potential effects of climate change on the environmental fates of organic compounds are increasing (Bloomfield et al., 2006b; Ma et al., 2011; Paul et al., 2012; Steffens, Larsbo, Moeys, Jarvis, & Lewan, 2013; Steffens, Larsbo, Moeys, Jarvis, Kjellström, et al., 2013; Wöhrnschimmel et al., 2013). The general observation is that the direct impacts of climate change depend on the specific climate change scenarios/conditions. Climate variables impact pollutant fates differently. For instance, increased precipitation and temperature are associated with respective decreases and increases in atmospheric concentrations of organic contaminants. Therefore, the effects of climate on environmental fates depend on the specific combination of climatic variables. The possible combinations of climate variables are numerous, thereby making it difficult to predict impacts. A solution is to make predictions for as many combinations of climate variables as possible at varying scales – regional to global. This is a current undertaking (Dalla Valle, Codato, & Marcomini, 2007; Lamon et al., 2009; Ma et al., 2011; Wöhrnschimmel et al., 2013). However, to date, the focus has been on temperate and arctic regions and, otherwise, at the global scale. Research focusing specifically on environmental fates in varying climatic conditions for tropical developing countries is limited.

Long term fate metrics such as long range transport potential and persistence are key hazard indicators, often computed to evaluate environmental fates. However, these metrics require the use of multimedia models, since they are not measureable (Fenner et al., 2005). Other long term fate metrics, including annual average cocentrations, are also often computed using multi-media models, since field/monitoring data are often lacking or impractical. While many predictive multimedia models exist, many often include only one vegetative compartment. Regional-scaled assessments are inadequately accomplished with such models (Cousins & Mackay, 2001), especially in tropical watersheds, which often have many co-existing vegetative covers. To assist in such evaluations, a regional dynamic predictive multimedia model, RioShed, incorporating three (3) co-existing vegetative compartments, has been developed. This model has been described in Chapter 4. Outputs include the aforementioned long-term fate metrics.

This study sought to examine the effects of climate change on the long term environmental fates of select organic contaminants, released at the watershed scale, in a tropical developing country, using RioShed. The evaluated chemicals included some poly-brominated diphenyl ethers (PBDEs), dioxins, furans and some current-use pesticides. Further to this, an evaluation of how climate change influences the effects of tropical forests on the fates, as well as the ensuing health impacts, of these chemicals was conducted. To do so, a climate change perspective for the Caribbean, as predicted by the Intergovernmental Panel on Climate Change (IPCC), was applied to various forested landscapes/layouts for the Rio Cobre watershed, in the tropical country, Jamaica. The long-term environmental fate metrics of the organic compounds were computed and compared.

5.2 Methods

5.2.1 Study site

The Rio Cobre watershed is the third largest watershed in the Caribbean country, Jamaica. Given an area of 1249 km^2, it drains the 52.5 km Rio Cobre River, which exhibits average daily stream flows of 9.8 m^3/s. For the purpose of this dissertation, the watershed was re-classified as being occupied primarily by agricultural lands (25.19%), forests (60.15%), and urban zones (14.48%) (Forestry Department of Jamaica, 2015), as explained in Chapter 4.

The climate of the Caribbean is influenced by incident solar radiation, winds, precipitation and temperature. Precipitation is the most critical determinant of climate for the Caribbean (Granger, 1985). The Caribbean (and consequently the Rio Cobre watershed) displays a bi-modal precipitation pattern, with an early wet season in May-July and a late wet season in August-November (Taylor et al., 2002).

For the Rio Cobre watershed, annual average precipitation and ambient temperature for the 1986-2005 period were 1953 mm and 302.79 K, respectively (Meteorology Service of Jamaica, 2015). Since there are no climate change estimates specific to this watershed, climate change predictions for the Caribbean were instead applied.

5.2.2 Dynamic comparison of fates in two climate periods

In this assessment, two landscapes were considered for the Rio Cobre watershed. The first landscape employed was the current land-use distribution, in which agriculture, forest and urban regions occupied 25%, 60% and 15% of the land surface, respectively. This land-use distribution was labeled land-use distribution scenario I. In the second landscape, the forested portion was replaced by grassland, thereby generating an un-forested version of the Rio Cobre watershed. Therefore, this distribution, labeled land-use distribution scenario II, was such that agriculture, grassland and urban regions, respectively, occupied 25%, 60% and 15% of the land surface.

Table 5.1: Averaged monthly climate values for the 1986-2005 and 2005-2014 periods

Month number	**Month**	**1986-2005**		**2005-2014**	
		Temperature (K)	**Precipitation rate (× 10^{-3} $m.d^{-1}$)**	**Temperature (K)**	**Precipitation rate (× 10^{-3} $m.d^{-1}$)**
1	January	300.82	2.74	300.88	1.65
2	February	301.26	2.32	301.47	1.18
3	March	302.19	2.32	302.32	1.90
4	April	302.82	4.35	303.14	3.74
5	May	303.16	8.72	303.52	7.10
6	June	303.91	5.03	303.80	5.61
7	July	304.23	5.91	304.30	5.67
8	August	304.30	6.20	304.44	10.50
9	September	304.18	9.87	304.21	8.66
10	October	303.34	7.63	303.28	9.92
11	November	302.20	5.84	302.18	3.63
12	December	301.23	3.14	301.45	2.06

Data was obtained from the Meteorological Office of Jamaica, 2015.

Although emission data for Jamaica for the chemicals evaluated in this dissertation were not found, it was found that 32.2 metric tons of deca-PBDE (the only formulation manufactured and used in the US as at 2010) was released in the US in 2007, which gives a flux emission of 8.96 $ng.m^{-2}.d^{-1}$. Given that the Rio Cobre watershed has an area of 1249 km^2 (FDJ, 2015), applying the aforementioned flux rate gave an emission rate of 11.2 $g.d^{-1}$. Therefore, an emission rate of 10 $g.d^{-1}$ (3.65 $kg.y^{-1}$) was employed as the hypothetical emission rate for each chemical assessed in this dissertation.

Applying this hypothetical emission rate of 3.65 $kg.y^{-1}$, the daily compartmental concentrations of only dimethoate and PBDE-47 were computed over a one-year period, using monthly averaged precipitation rates and ambient temperatures for both the 1986-2005 and 2005-2014 periods.

First, total rainfall (in mm) for each calendar month from 1980 to 2014 was obtained, from the Meteorological Service of Jamaica (2015), for a major monitoring station (Tulloch Estates) in the watershed. The rainfall amounts for each calendar month were averaged over the periods 1986-2005 and 2005-2014, and divided by the number of days in the given calendar month, to generate monthly averaged daily rainfall rates, in $m.d^{-1}$. Also, the monthly rainfall amounts were summed for each calendar year. The annual rainfall amounts were averaged for each of the 1986-2005 and 2005-2014 periods, and divided by the number of calendar days in a year (365 days), to generate annually averaged rainfall rates for each period, in $m.d^{-1}$. Similarly, mean maximum temperatures for each calendar month were obtained from 1970 to 2014, from the Meteorological Service of Jamaica (2015), for a major temperature monitoring station (in Worthy Park, Jamaica) in the Rio Cobre watershed. The monthly average temperatures as well as annual average temperatures for the 1986-2005, as well as 2005-2014 periods were then calculated. The monthly average precipitation rates and temperatures for each period are presented in Table 5.1. The annual average precipitation rate and temperature were 5.35e-3 $m.d^{-1}$ and 302.79 K, respectively, for the 1986-2005 period, and 5.15e-3 $m.d^{-1}$ and 302.92 K, respectively, for the 2005-2014 period.

Using RioShed, steady state concentrations, pre-determined assuming an initially pristine environment receiving atmospheric inputs of 10.0 $g.d^{-1}$ of PBDE-47 and having the annual average precipitation rate and temperature of the 1986-2005 period, were inputted as initial compartmental concentrations at the beginning of the model run for land-use distribution scenario II (an un-forested landscape wherein the current forested portion of the Rio Cobre watershed was replaced with grassland). With the same atmospheric input of 10 $g.d^{-1}$ assumed, the model was run for the 31 days assumed for January, using the monthly averaged temperature and precipitation rate for January for the 1986-2005 period. The end-of month compartment inventories (inventories obtained on the last day of the month) were used as inputs for the following month and the model run for the number of calendar days associated with that following month using the monthly averaged temperature and precipitation rate calculated for the given month, for the same 1986-2005 period. This procedure was repeated for the remaining months of the calendar year. The entire process was repeated for land-use distribution scenario I (a forested landscape representing the current land-use distribution of the Rio Cobre watershed). All of the above was performed for dimethoate. The end-of-month compartmental concentrations were the outputs. The entire process was repeated for the 2005-2014 climate period. This allowed for the examination of the dynamic environmental fates of the two organics, in two different climate periods.

The compartmental concentrations of both chemicals in the un-forested versus forested landscapes, for both climate periods, were compared to evaluate the impacts of forests given changing climate variables.

5.2.3 Climate change evaluation

This section aimed to: 1) examine the effects of climate change on the long-term environmental fates of the 16 organic chemicals – the persistent pollutants and the current-use pesticides and 2) evaluate the effects of forests under potential climate change conditions. The 1986-2005 climatic conditions, as well as climate change scenarios, were employed in the calculation of long-term fate metrics, using RioShed. Not only were climatic conditions altered, but so were land-use distributions. The methods to generate the climate change and landscape scenarios, as well as the formulation of the fate metrics are explained below.

5.2.3.1 Climate change scenarios

The Caribbean is expected to display specific changes to its climate. In their fifth climate change assessment report in 2013, the Intergovernmental Panel on Climate Change (IPCC) evaluated and synthesized the results of climate models for four emission and concentration scenarios. The four (4) IPCC greenhouse gas concentration projections are referred to as Representative Concentration Pathways (RCP) (Rogelj, 2013). In the RCP2.6 scenario, small and constant net reduced emission of greenhouse gases (GHGs) and aerosols were assumed after 2070, with associated declines in the concentrations. However, in the RCP8.5 scenario, high emissions of greenhouse gases and aerosols were initially assumed from 2100 to 2150, with a steady linear decrease from 2150 to 2250, while concentrations were assumed to be stabilized by 2250. Both RCP6.0 and RCP4.5 were intermediate scenarios, which assumed that concentrations of greenhouse gases and aerosols stabilized by 2150 (Rogelj, 2013).

Given the results of the climate models for the two extreme scenarios, RCP2.6 and RCP8.5, it was forecasted that, for the periods 2016-2035 and 2046-2065, compared to the 1986-2005 period, the Caribbean should observe minimum and maximum temperature increases of 0.4 K and 2.5 K, respectively (Christensen, Kanikicharla, Marshall, & Turner, 2013). Also, during the same periods relative to the same 1986-2005 period, Caribbean precipitation is expected to decrease by a minimum of 19% or increase by a maximum of 10% (Christensen, Kanikicharla, Marshall, & Turner, 2013).

The minima and maxima of the estimates predicted by the IPCC for the Caribbean for the 2016-2065 period were combined to create four (4) climate change conditions:

A) a temperature increase of 0.4 K with a precipitation decrease by 19% (T1P1);

B) a temperature increase of 0.4 K with a precipitation increase of 11% (T1P2);

C) a temperature increase of 2.5 K with a precipitation decrease by 19% (T2P1);

D) a temperature increase of 2.5 K with a precipitation increase of 11% (T2P2).

To generate the climate change scenarios, these climate change conditions were applied to the annual average climate for the Rio Cobre watershed for the 1986-2005 period. Precipitation data for each month from 1980 to 2014, as well as temperature data for each month, from 1970 to 2014, were obtained for monitoring stations in the Rio Cobre watershed from the Meteorological Service of Jamaica (2015), as previously explained in section 5.2.2. The computed annual average maximum temperature and precipitation rate for the 1986-2006 period were 302.79 K and 5.35e-3 m.d^{-1}, respectively.

In this study, climatic conditions were applied to varying forest coverage and composition for the Rio Cobre watershed. Two land-use scenarios were employed as controls for comparisons. For control scenario I (also labeled land-use distribution scenario I), the current land-use distribution is assumed (25% for agriculture, 60% for forest, and 15% for urban). In control scenario II, also labeled land-use distribution scenario II, the forested portion of the Rio Cobre watershed was replaced by grassland. Additional land-use distribution scenarios for assessment/comparison were generated by applying the following changes to the current land-use distribution (25% for agriculture, 60% for forest, 15% for urban) for the Rio Cobre watershed: a) 30% decrease in coverage, assuming equal distribution of the difference to the urban and agricultural compartments; b) 30% decrease in coverage, due to urban expansion;

c) 30% decrease in coverage, due to agricultural expansion; d) 30% increase in coverage, via afforestation of agricultural lands. These scenarios were labeled land-use distribution scenarios III to VI and are presented in Table 5.2. The 1986-2005 climate and the four climate change scenarios were applied to all land-use distribution scenarios. Therefore, a total of 30 scenarios, including the controls, formed this assessment. The forest composition used throughout is the current estimated type for the watershed, with a 55%:45% deciduous:evergreen ratio. The schematic process employed is illustrated in Figure 5.1.

Table 5.2: Land-use distribution scenarios

Scenarios	**Land-use percentage distribution (%)**		
	Agriculture	**Forest/Grassland vegetation**	**Urban**
I	25	60 (forest)	15
II	25	60 (grassland)	15
II	34	42 (forest)	24
IV	25	42 (forest)	33
V	43	42 (forest)	15
VI	7	78 (forest)	15

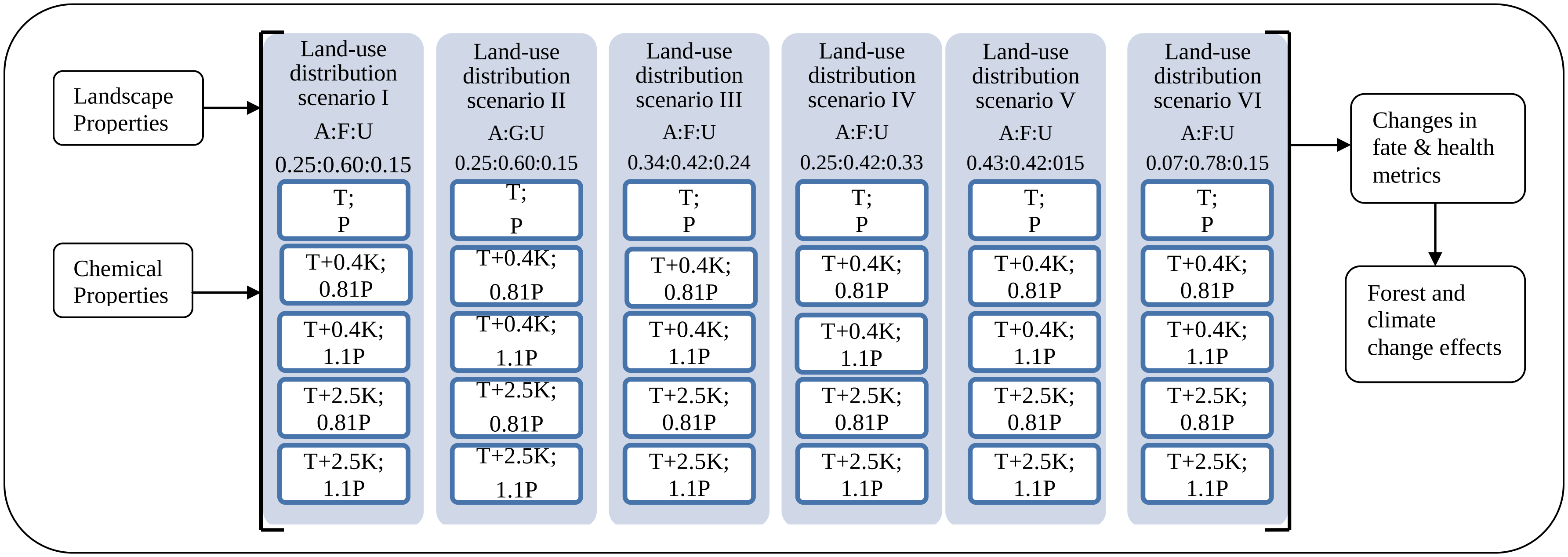


Figure 5.1: Schematics of the assessment process.

T is the current ambient temperature (302.79 K), K; P is the current precipitation rate (5.35e-3 m.d^{-1}), m.d^{-1}; A is agricultural vegetation; G is grassland vegetation; F is forest vegetation; U is urban area; the ratios are the fractions of land occupied by agriculture, forest/grassland vegetation and urban sites, respectively.

5.2.3.2 Quantification of long-term fate metrics

The following metrics for the 16 organic compounds were quantified, as explained in section 4.2.4.5: overall persistence (P_{ov}), atmospheric long range transport potentials ($LRTP_A$) and annual average concentrations in each medium. Further to this, percent changes to each metric were calculated for each chemical, in any given scenario with respect to the control scenarios.

5.2.3.3 Summary of assessments conducted

A number of assessments were conducted to establish the effects of climate, climate change and land-use distribution on the long-term environmental fates of the selected organics.

First, a dynamic analysis was conducted by calculating the end-of-month compartmental concentrations of dimethoate and PBDE-47, over a one-year period, using monthly averaged temperatures and precipitation rates for the 1986-2005 and 2005-2014 periods. The method employed is described in section 5.2.2. The environmental fates of these two (2) organics in the forested and un-forested landscapes were compared for the two (2) given climate periods.

Secondly, employing land-use distribution scenario I (the current landscape of the Rio Cobre watershed), daily compartmental concentration outputs were generated over a 365 day period, using the previously described climate change scenario A, for all 16 organic contaminants. The assumption of an initially pristine environment (free of the specific contaminant) was applied, with an atmospheric input of 10 $g.d^{-1}$. These compartmental concentrations were averaged over the 365-day model run. As before, overall persistence and atmospheric long range transport potential were also generated. This was repeated for all assessment chemicals, under the remaining three climate change scenarios. The comparison of the outputs of these climate change scenarios with the outputs for the climate of the 1986-2005 period allowed for the examination of the effects of climate change.

A comparison of the effects of forests and climate change was performed. The annual average and steady state concentrations, as well as overall persistences and atmospheric long range transport potentials for the 16 organics were generated as before for land-use scenario II (grassland/un-forested landscape landscape), using the climatic conditions of the 1986-2005 period. Such metrics were also generated for the organics when the climate change scenarios were applied to this land-use distribution scenario II (grassland/un-forested landscape). The changes to the outputs when the forests replaced the grassland (i.e., changes when the outputs of land-use distribution scenario I were compared with those from land-use distribution scenario II) were evaluated against those when the climate of land-use distribution scenario II changed (obtained when the outputs of each climate change scenario, applied to the grassland/un-forested landscape, were compared with those given the climate of the 1986-2005 period). In fact, the arithmetic means of the changes for each category consisting of the eight (8) persistent pollutants and the eight (8) current-use pesticides were compared in this analysis.

In yet another assessment, the four climate change scenarios were applied to the 1986-2005 average annual climate statistics, and used in both land-use distributions I and II, to compute the aforementioned output metrics for the 16 contaminants. The arithmetic mean outputs for each category of pollutant, for each climate change scenario, in land-use distribution scenario I (forested landscape), were evaluated against the outputs for the contaminant category in the corresponding climate change scenario, applied to land-use distribution II (grassland/un-forested landscape). This allowed for a general analysis of the effects of forests during climate change.

The effects of varying the proportion of forests in the landscape, as well as the proportion of co-existing land-uses, on the long-term fates of the organics were also evaluated. Herein, the long-term environmental fate metrics were computed for the 16 organics, using the 1986-2005 climatic conditions, in land-use-distribution scenario I, and compared to those calculated for land-use distribution scenarios III to VI. Also, the four (4) climate change scenarios were applied to land-use distribution I and compared to the corresponding climate change applied to land-use distributions III to VI, to examine the effects of climate change under various land-use allocations.

5.3 Results & Discussion

5.3.1 Environmental fates under varying monthly climatic conditions

The environmental fate metrics for PBDE-47 and dimethoate were examined, using the monthly varying climatic conditions for both the 1986-2005 and 2005-2014 periods. Figure 5.2 displays the monthly trends in ambient temperature and precipitation rate for both climate periods.

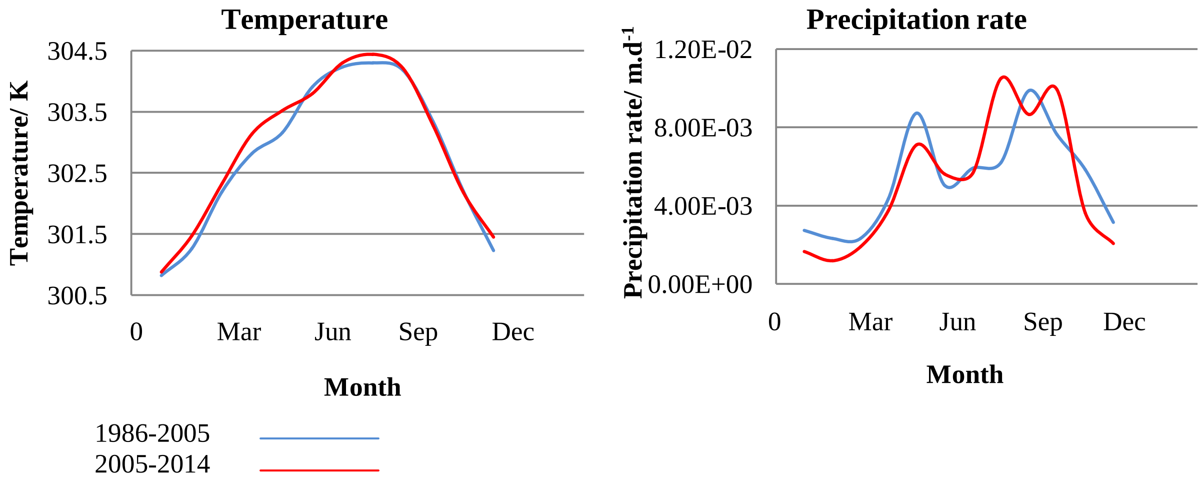


Figure 5.2: Average monthly variations in climate variable in two climate periods

Figure 5.3 displays the atmospheric and surface water concentrations of PBDE-47 and dimethoate in the forested and un-forested landscapes of the Rio Cobre watershed, given monthly varying climatic conditions for the 1986-2005 and 2005-2014 periods, having assumed initial steady state concentrations. Throughout the year, the concentrations predicted using varying monthly climatic conditions were either over- or under-estimates of the initial steady-state concentrations.

Under the dynamic weather assessment, atmospheric concentrations of PBDE-47 and dimethoate, in both the forested and un-forested landscapes, were highest in the months February and March, during which both temperature and rainfall rates were low, as seen when figures 5.2 and 5.3 are compared. The lowest recordings of atmospheric concentrations were obtained in the months May and September, in which precipitation rates were high. The atmospheric concentrations of these chemicals were always higher under grassland conditions, than in the forested landscape. On the other hand, surface water concentrations for both chemicals were highest in May and September, months in which precipitation rates observed the highest recordings.

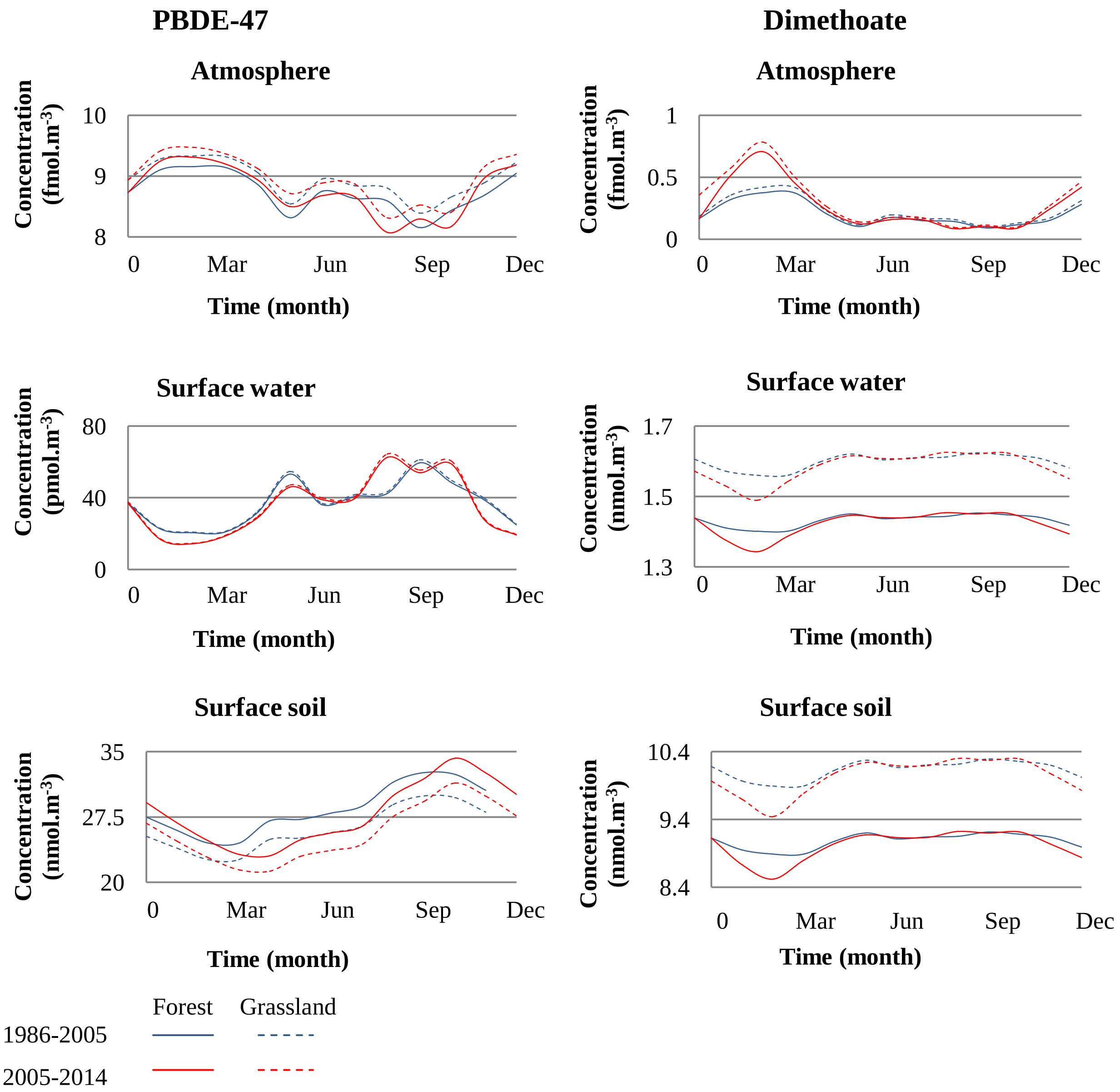


Figure 5.3: Monthly varying concentrations of PBDE-47 and dimethoate in select compartments in two climate periods

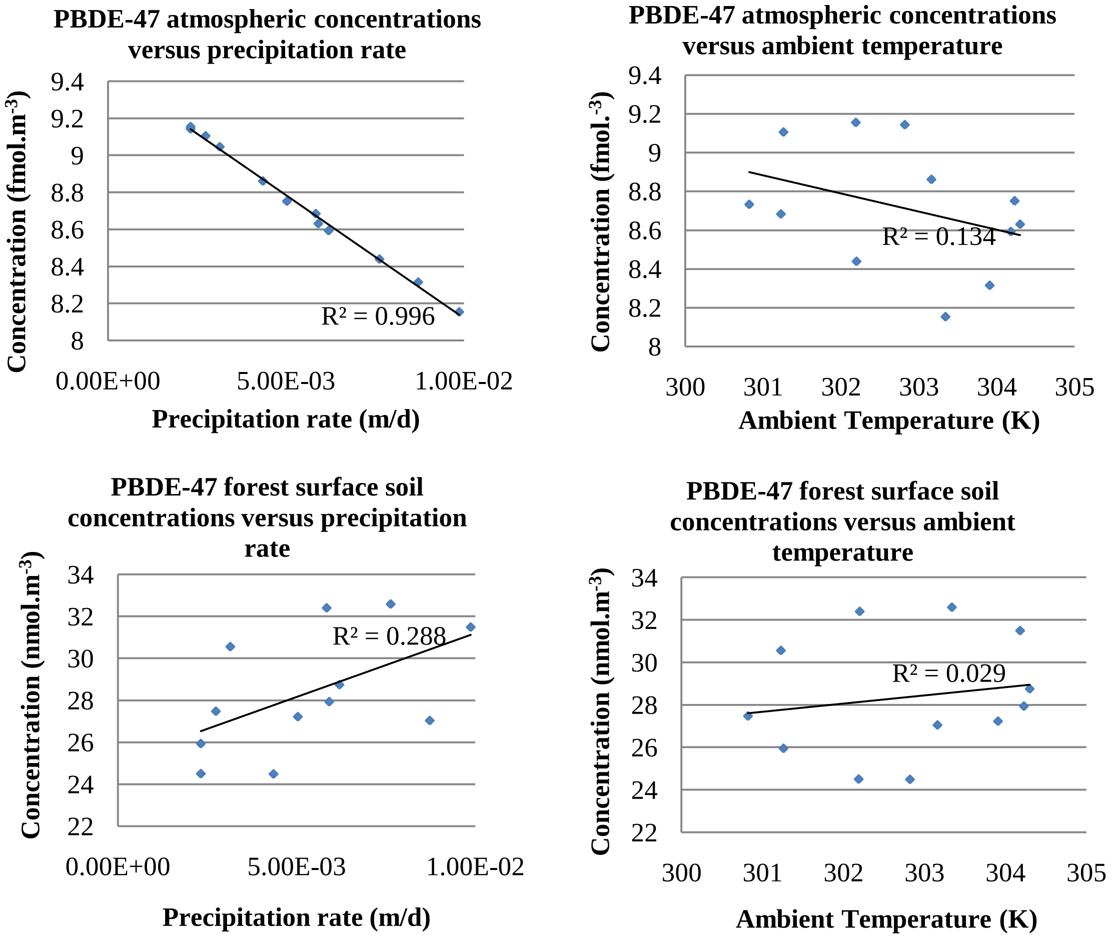


Figure 5.4: Compartmental concentrations of PBDE-47 with respect to given climate variables in the forested landscape (1986-2005)

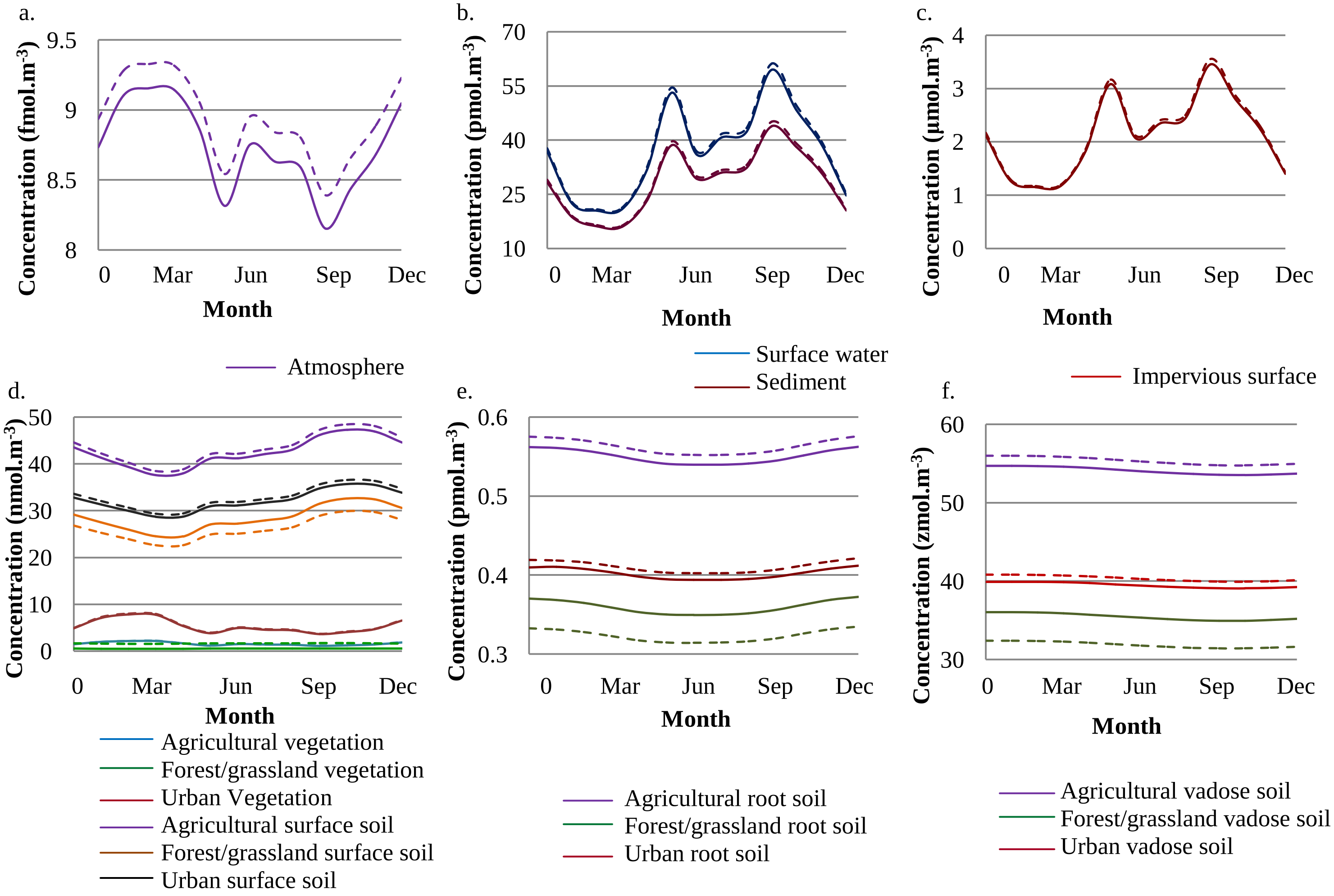
Table 5.3: Coefficients of determination for compartmental concentrations of PBDE-47 and dimethoate with respect to precipitation and temperature

Compartment	**Coefficient of determination/R-squared value (R^2)**							
	Precipitation				***Temperature***			
	PBDE-47		**Dimethoate**		**PBDE-47**		**Dimethoate**	
	Forested landscape	*Un-forested landscape*	*Forested landscape*	*Un-forested landscape*	*Forested landscape*	*Un-forested landscape*	*Forested landscape*	*Un-forested landscape*
Atmosphere	-0.996	-0.996	-0.859	-0.860	-0.588	-0.587	-0.619	-0.619
Surface water	0.996	0.996	0.868	0.868	0.584	0.583	0.618	0.618
Sediment	0.980	0.980	0.844	0.843	0.573	0.572	0.642	0.637
Impervious Surface	0.996	0.996	0.859	0.860	0.585	0.583	0.619	0.619
Agricultural vegetation	-0.910	-0.909	0.801	0.809	-0.610	-0.610	0.607	0.609
Forest/grassland vegetation	0.764	0.781	0.847	0.845	0.497	0.529	0.615	0.616
Urban vegetation	-0.875	-0.875	0.736	0.754	-0.634	-0.634	0.592	0.597
Agricultural surface soil	0.339	0.338	0.892	0.890	0.049	0.049	0.619	0.620
Forest/grassland surface soil	0.228	0.289	0.869	0.868	0.029	0.030	0.619	0.619
Urban surface soil	0.299	0.299	0.890	0.888	0.034	0.034	0.598	0.619
Agricultural root soil	-0.330	-0.323	0.835	0.837	-0.817	-0.809	0.602	0.599
Forest/grassland root soil	-0.210	-0.211	0.853	0.852	-0.678	-0.679	0.602	0.598
Urban root soil	-0.326	-0.292	0.822	0.826	-0.811	-0.770	0.595	0.596
Agricultural vadose soil	-0.441	-0.444	0.784	0.786	-0.334	-0.339	0.530	0.531
Forest/grassland vadose soil	-0.492	-0.491	0.796	0.788	-0.418	-0.417	0.528	0.521
Urban vadose soil	-0.454	-0.464	0.768	0.772	-0.347	-0.367	0.523	0.525

For PBDE-47, surface water concentrations were similar in the forested and un-forested landscape, with such concentrations in the un-forested landscape slightly higher than those in the forested landscape –irrespective of whether the climate varied monthly or if steady-state was assumed throughout the year. However, for dimethoate, surface water concentrations in the un-forested landscape were always distinctly higher than in the forested landscape, as seen in Figure 5.3.

Therefore, it appears that tropical forests more effectively reduce the atmospheric compared to surface water concentrations, for a chemical such as PBDE-47. Also, the reduction in atmospheric concentrations was more distinct for PBDE-47 than dimethoate. However, dimethoate, which has the lower air-water partition coefficient, observed notable reductions in surface water concentrations compared to PBDE-47, when the forest was present than when it was not.

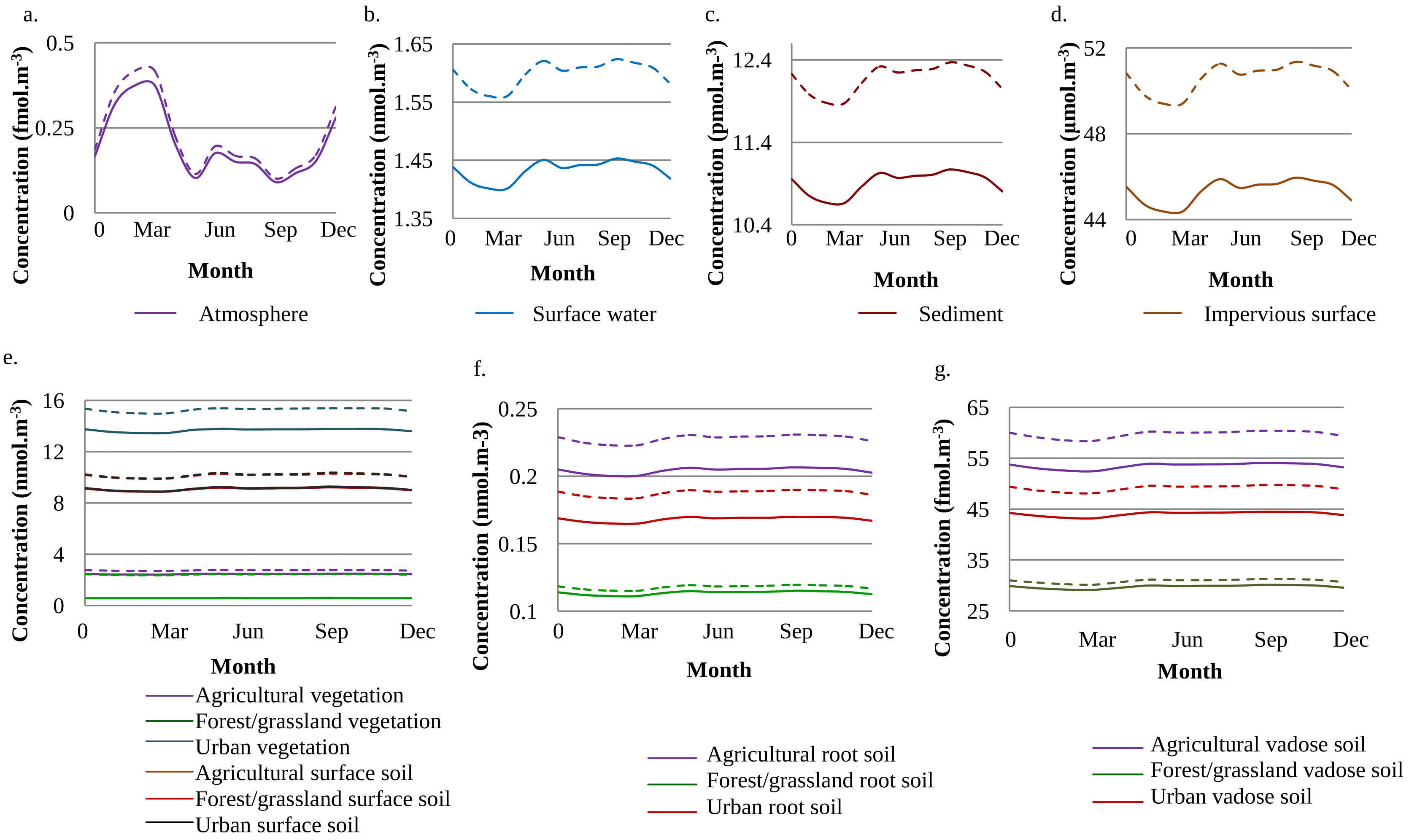
Interesting patterns were unveiled when the atmospheric and surface water concentrations of both organics were compared for the forested and un-forested landscapes, given average monthly and annual climatic inputs. Both chemicals displayed similar atmospheric concentration patterns throughout the year of assessment, which were inverses of the bi-modal climate pattern for the region. On the other hand, surface water concentrations displayed a bi-modal pattern, consistent with the bi-modal climate pattern of the region. In fact, using PBDE-47 as the example, Figure 5.4 shows that atmospheric concentrations of this chemical in the forested landscape displayed a strong negative correlation with precipitation rate. However, a high correlation could not be established, in the forested landscape, between the atmospheric concentration of the contaminant and ambient temperature, or between the climate variables and concentrations in other compartments such as forest surface soil, as seen in Table 5.3.



Solid line – forested scenario
Dashed line – un-forested scenario

To calculate concentrations, the average monthly temperature and precipitation for the 1986-2005 period were used with initial concentrations set at steady-state concentrations in all compartments and source input thereafter to the atmosphere

Figure 5.5: Monthly varying PBDE-47 concentrations (1986-2005)



Solid line – forested scenario
Dashed line – un-forested scenario

To calculate concentrations, the average monthly temperature and precipitation for the 1986-2005 period were used with initial concentrations set at steady-state concentrations in all compartments and source input thereafter to the atmosphere only.

Figure 5.6: Monthly varying dimethoate concentrations (1986-2005)

Although the end-of-year atmospheric concentrations (end of day 365) for both organics were higher, end-of-year surface water concentrations were lower, given monthly averaged climate inputs versus the annually averaged inputs. This can be seen in Figure 5.3. Therefore, for environmental or health impact assessments of effects in any given compartment, the use of known dynamic inputs is recommended, when available, as this should yield more realistic results. However, as before, the similarities in the outputs for the forested versus un-forested watershed, despite the nature of the inputs (dynamic or averaged) indicate that steady state conditions are relatively representative in comparative assessments.

Figure 5.5 shows that PBDE-47 concentrations, in the sediment and impervious surface, displayed similar relationships with the precipitation pattern as did surface water. Concentrations in the vegetation displayed a negative correlation with the precipitation pattern, with a delay of 1-2 months in the effect. Surface soil concentrations appeared to vary positively with the precipitation pattern with a 1-2 month delay in the response. However, no obvious relationship was apparent for this chemical in the root and vadose soils of the forested and un-forested landscapes.

Figure 5.6 displays the concentrations of dimethoate given the varying monthly climatic inputs. It can be seen that for this polar chemical, concentrations in the sediment, impervious surface, vegetation, surface soils, root soils as well as vadose soils were similarly correlated with the precipitation pattern, as was surface water concentration. Precipitation was therefore a determinant of the environmental fates of both PBDE-47 and dimethoate.

5.3.2 Comparing environmental fates in two climate periods

It can be seen in Figure 5.3 that in any given climate period, assuming initial steady state conditions, atmospheric concentrations of PBDE-47 observed the same distribution patterns in both the forested and un-forested landscapes. However, as expected, atmospheric concentrations were always higher in the grassland scenarios.

In the 1986-2005 period, PBDE-47 atmospheric and surface water concentrations fluctuated throughout the year in tandem with monthly precipitation rates. During the 1986-2005 period, the lowest recordings of atmospheric concentrations coincided with the highest recordings of surface water concentrations, occurring in the months of May and September when precipitation rates were highest. Similarly, for the 2005-2014 period, precipitation rates were highest in August to October, coinciding with respective lowest and highest atmospheric and surface water concentrations of PBDE-47.

As also seen in Figure 5.3, the 1986-2005 atmospheric concentrations of PBDE-47 exceeded those during the 2005-2014 period only in the months of June, August and October. On the other hand, the surface water concentrations of PBDE-47 in the 2005-2014 period exceeded those in the 1986-2005 period only in the aforementioned months – June, August and October. These were the only months that precipitation rates in 2005-2014 exceeded rates in corresponding months in the 1986-2005 period, as seen in Figure 5.2. In general, for this chemical, the atmospheric and surface water concentration patterns throughout the year copied the precipitation pattern, with negligible influence by temperature.

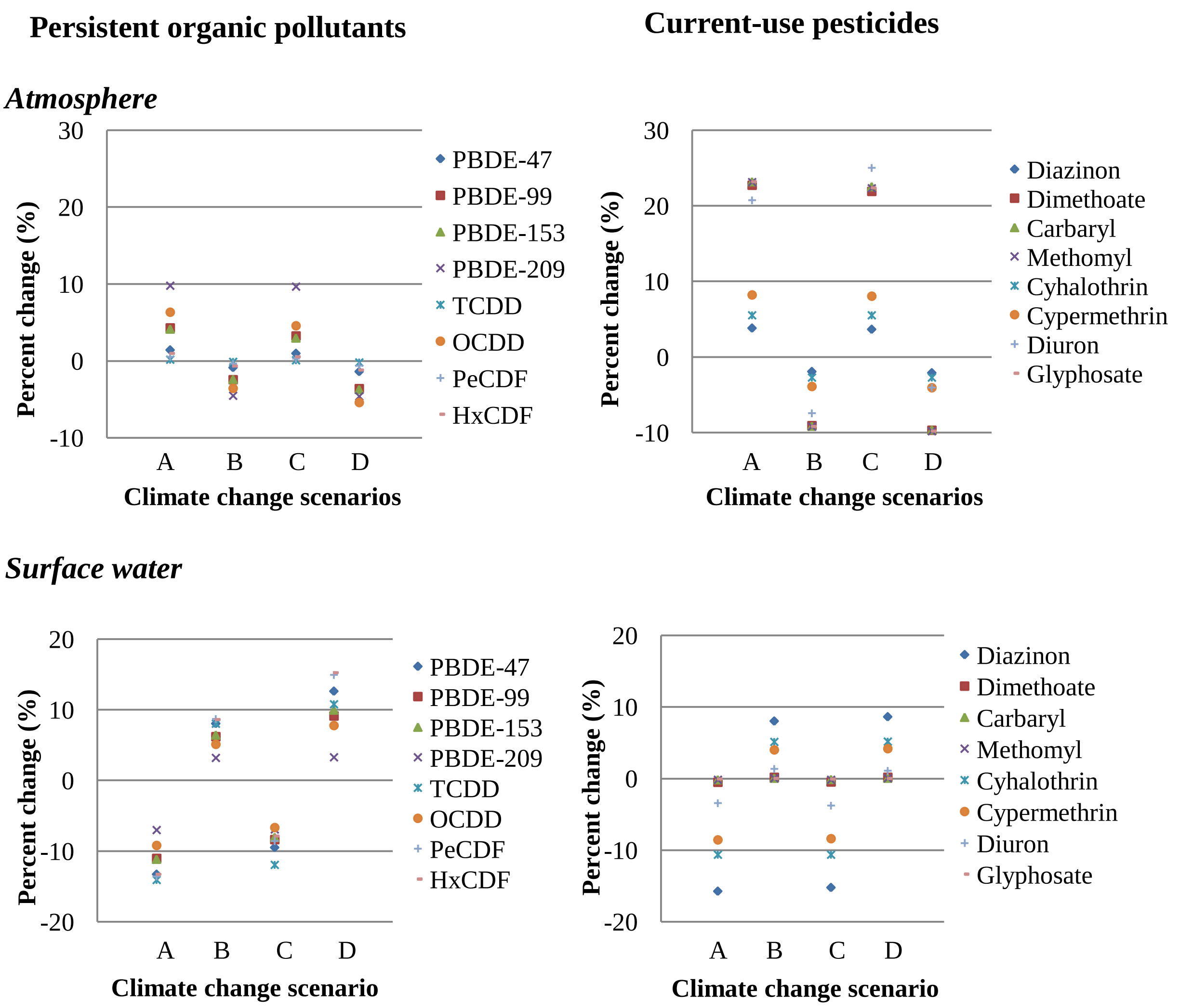
A relationship between the surface soil concentration pattern of PBDE-47 and the climate variables was not immediately apparent. However, a comparison between the patterns generated for the surface soil concentrations of this chemical in the 1986-2005 period and those for the

2005-2014, in Figure 5.3, revealed that the concentrations in 2005-2014 were higher only in the months of August and October. These were two (2) of the three (3) months during which precipitation rates in the 2005-2014 period exceeded those in the same months in the 1986-2005 period. Also, for both climate periods, forest surface soil concentrations always exceeded grassland surface soil concentrations, except in the months January to March (see Table H.1 and Table H.2 in Appendix H, as well as Table I.1 and Table I.2 in Appendix I for the monthly compartmental concentrations of PBDE-47 in both climate periods). During these months, average precipitation rates were the lowest recorded.

Dimethoate displayed similar climate-associated trends in the assessed compartments. However, as seen in Figure 5.3, the presence of forests appeared to be a notable determinant of concentrations with marked differences in concentration patterns in the forested versus un-forested landscapes. In both climate periods, atmospheric, surface water and surface soil concentrations in the forested landscape were always lower than in the un-forested landscape (see Table H.3 and Table H.4 in Appendix H, as well as Table I.3 and Table I.4 in Appendix I for the monthly compartmental concentrations of dimethoate in both climate periods).

5.3.3 Climate change effects

In this section of the assessment, land-use distribution scenario I was employed as the control, whereby approximately 60.15% of the land was considered occupied by forests, with a deciduous:evergreen distribution of 55%:45%. The remaining land was considered occupied by agricultural vegetation/crops (25.19%), urban centers (14.48%) and surface waters (0.18%). The ambient temperature (302.79 K) and precipitation rate (5.35e-3 $m.d^{-1}$) in this control scenario were altered according to climate change scenarios, as described in the Methods section, and the outputs compared to those generated for the aforementioned control scenario.



Climate Change Scenarios
A: Temperature – 303.19K; Precipitation rate – 4.33e-3 m/d
B: Temperature – 303.19K; Precipitation rate – 5.89e-3 m/d
C: Temperature – 305.29K; Precipitation rate – 4.33e-3 m/d
D: Temperature – 305.29K; Precipitation rate – 5.89e-3 m/d

Figure 5.7: Atmospheric and surface water concentration changes

In terms of atmospheric long range transport potential, the 16 assessed contaminants were found to be class III chemicals, having displayed characteristic travel distances less than 700 km under all climatic conditions in the watershed. They therefore displayed only regional-scaled atmospheric long range transport potential in this tropical watershed. For all 16 contaminants, annual average atmospheric concentrations were reduced, by up to 10% for the current-use pesticides and 6% for the persistent pollutants, whenever the precipitation was increased by the predicted 11% whereas concentrations increased, by as much as 25%, whenever precipitation was reduced by the estimated 19% - Figure 5.7 illustrates this. On the other hand, surface water concentrations increased and decreased with the respective increases and decreases in precipitation, as demonstrated in the same Figure 5.7. The effects of temperature were less noticeable for most of the 16 evaluated chemicals. However, annual average atmospheric concentrations of PBDE-99 and OCDD were notably lower during the increase in temperature of 2.5 K than the increase of 0.4 K. Of the current-use pesticides, the annual atmospheric concentration of diuron was higher when the temperature increased by 2.5 K than when it increased by 0.4 K.

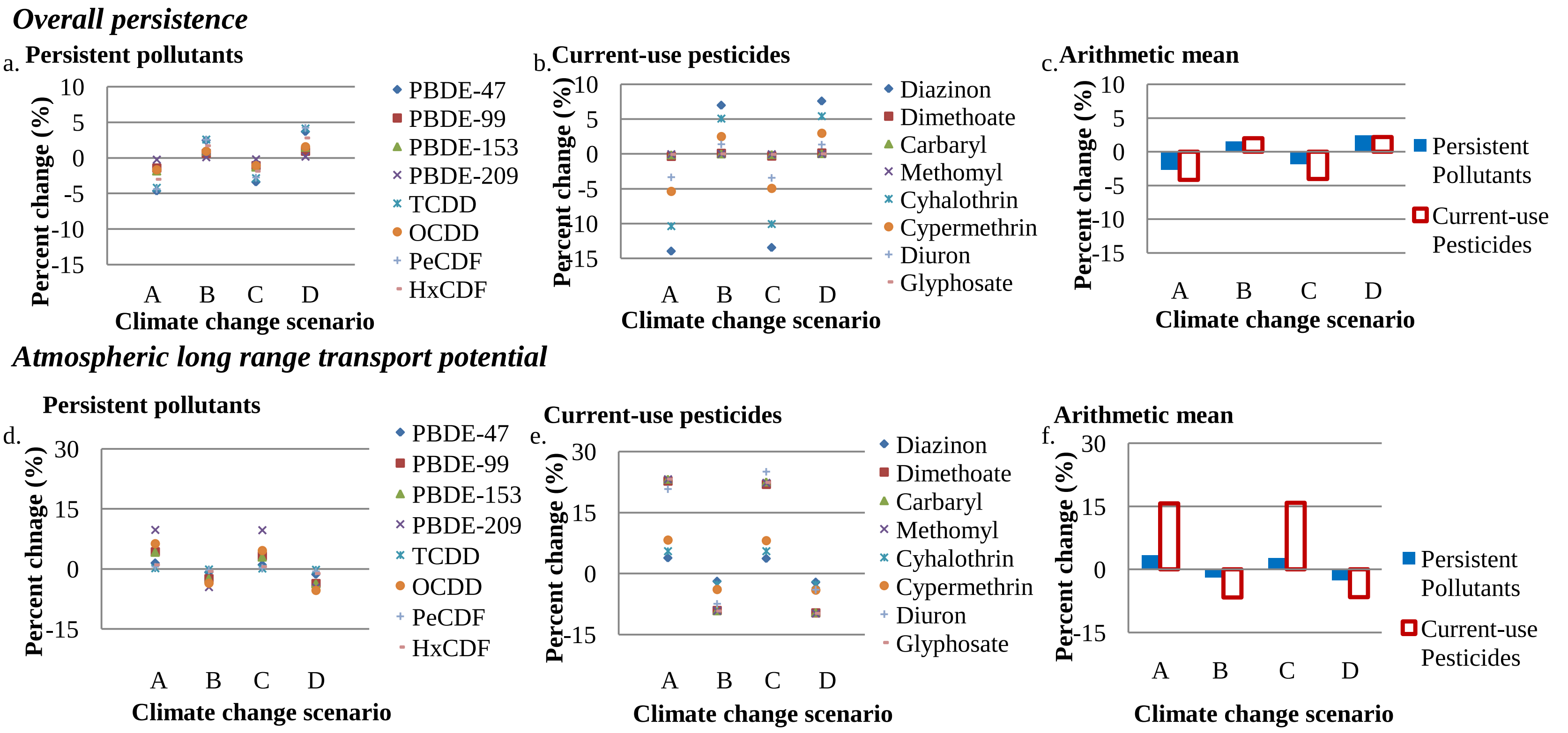
The effects of the climate change scenarios were different for the persistent pollutants compared to the more polar pollutants. Figure 5.7 shows that the degree of the effect on surface water and atmospheric concentrations was generally more varied for the current-use pesticides, demonstrated by the wider spread in the percentage changes. The mean atmospheric concentrations of the current-use pesticides and persistent pollutants observed general decreases and increases given respective increases and decreases in precipitation. For the current-use pesticides, a respective minimum and maximum increase in annual average atmospheric concentration of approximately 4% and 25% (denoted by an arithmetic mean increase of approximately 16%) were noted during decreased precipitation rates. However, the annual average atmospheric concentration decreased during increased precipitation, ranging from 0.1% to 10%, (with an arithmetic mean of 7%).

When the precipitation rate was increased, the larger temperature rise of 2.5 K (an ambient temperature of 305.29 K) led to larger reductions in the average annual atmospheric concentrations of the persistent chemicals than the smaller 0.4 K temperature rise (an ambient temperature of 303.19 K). This suggests that for these contaminants, increases in atmospheric concentrations due to temperature increases may potentially be tempered by co-occurring increases in precipitation. Further examination showed that for these persistent organics, the increases in average annual atmospheric concentrations during reduced precipitation was enhanced by the larger 2.5 K temperature increase. It is probable that, for these organics, temperature-dependent fate processes such as re-volatilization play greater roles as the temperature increases.

For the persistent pollutants, in scenarios with decreased precipitation (to a precipitation rate of 4.33e-3 m.d^{-1}), surface water concentrations were lower than under the 1986-2005 precipitation condition, as much as 16% (with an arithmetic means of 11.6%) when the temperature increased by 0.4 K, and up to 12% (with an arithmetic mean of 8.5%) when the change was 2.5 K. However, when precipitation increased to a precipitation rate of 5.89e-3 m.d^{-1}, arithmetic averages of the surface water concentrations consequently increased by 6.8% and 10.4% for the respective temperature increases of 0.4 K and 2.5 K. When the surface water concentrations of the current-use pesticides were assessed, it was found that the effects of temperature change on these chemicals in this medium were not as notable as for the persistent chemicals. In fact, irrespective of the temperature, the arithmetic averages observed increases of approximately 2.3% and decreases of approximately 5.2% in surface water concentrations of the current-use pesticides, given the respective increases and decreases in precipitation rates.

In comparing Figure 5.7 and Figure 5.8, whereas the overall persistences of the current-use pesticides changed by amounts similar to the surface water concentrations, the persistent pollutants observed changes that were similar in trend, but dissimilar in degree/value to the surface water concentration changes. As seen in Figure 5.8, when the temperature increased by 0.4 K and 2.5 K (to temperatures of 303.19 K and 305.29 K, respectively) during reduced precipitation (to 4.33e-3 m/d), the overall persistences of the persistent pollutants, decreased with ranges of 0.22%-4.64% and 0.17%-3.38%, respectively (with respective average decreases of 2.7% and 1.8%). However, during increased precipitation (a rate of 5.89e-3 m.d^{-1}), and given temperature increases of 0.4 K and 2.5 K, overall persistence increased with respective ranges of 0.12%-2.54% and 0.19%-4.23% (with respective mean increases of 1.5% and 2.4%).

The current-use pesticides experienced similar decreases in overall persistence in the ranges of 0.02-13.94% and 0.02-13.44% for the respective increases of 0.4 K and 2.5 K when the precipitation rate was decreased to 4.33e-3 m.d^{-1}. However, when the precipitation rate was increased to 5.89e-3 m.d^{-1}, increasing the temperature by 0.4 K and 2.5 K resulted in respective increases in the overall persistences of the current-use pesticides in respective, and similar, ranges of 0.01%-7.00% and 0.01%-7.60% (with respective averages of 2.02% and 2.20%). Temperature changes appear to more greatly affect the overall persistence of the persistent pollutants than the more polar current-use pesticides.



Climate Change Scenarios

A: Temperature – 303.19K; Precipitation rate – 4.33e-3 m/d
B: Temperature – 303.19K; Precipitation rate – 5.89e-3 m/d
C: Temperature – 305.29K; Precipitation rate – 4.33e-3 m/d
D: Temperature – 305.29K; Precipitation rate – 5.89e-3 m/d

Figure 5.8: Percent changes in long-term fate metrics under given climate change scenarios compared to current climate conditions

Figure 5.8 illustrates the changes to atmospheric long range transport potential, which can be seen to reflect the changes to atmospheric concentrations previously described. During reduced precipitation (4.33e-3 m.d^{-1}), the persistent contaminants observed mean increases in atmospheric long range transport potential of 3.47% and 2.81% (with respective ranges of 0.18%-9.78% and 0.11%-9.68%), when the temperature increased, respectively, by 0.4 K and 2.5 K. However, when the precipitation rate was increased to 5.89 e-3 m.d^{-1}, and temperature also increased by 0.4 K and later by 2.5 K, the atmospheric long range transport potential decreased, respectively, by mean values of 1.87% and 2.60% (the respective ranges for the decreases were 0.12%-4.51% and 0.20%-5.39%). For the current-use pesticides, the respective ranges for the decrease in atmospheric long range transport potential, when the precipitation rate increased and the temperatures increased by 0.4 K and 2.5 K, were 1.95%-9.18% and 2.11%-9.80% (with respective averages of 6.6% and 6.5%). When the precipitation rate decreased by 11% to 4.33e-3 m.d^{-1}, the atmospheric long range transport potentials of the current-use pesticides increased in ranges of 3.84%-23.20% (with an average of 16.3%) and 3.71%-25.00% (with an average of 16.4%), given respective increases in temperature of 0.4 K and 2.5 K. Temperature is marginally influential in the atmospheric long range transport potentials of the contaminants, more so for the current-use pesticides.

Climate change is therefore expected to affect the long-term environmental fates of the organic contaminants. Precipitation changes are expected to be particularly influential in the atmospheric concentrations and long range transport potential for the more polar current-use pesticides. This is so because precipitation is key in ‘washing out’ atmospheric organic contaminants, especially the more polar chemicals. For the persistent organic pollutants, temperature changes are expected to have notable effects on their surface water concentrations and overall persistence.

The observed smaller net effect of temperature on atmospheric fates is expected for the persistent pollutants, due to co-occurring temperature-regulated processes, such as re-volatilization. The current-use pesticides appear to be less subject to these types of processes, with more notable effects on atmospheric fates given temperature changes. However, ambient temperature changes appear to have greater effects on the overall persistences of the persistent pollutants than the more polar current-use pesticides. Although it has been shown that temperature is a major determinant of atmospheric (Lamon et al., 2009; Paul et al., 2012), and hence, environmental fates, in this tropical region, precipitation appears to be the major climate determinant of the environmental fates of the evaluated contaminants.

5.3.4 Forest versus climate change

The effects of replacing grasslands with forests and the potential effects of climate change were compared. In this evaluation, land-use distribution scenario II was employed as the control. Land-use distribution scenario I was used as the representative forested landscape.

The percent changes to the fate metrics, given the various scenarios for the 16 chemicals, are given in Table 5.4 and Table 5.5, whereas Table 5.6 highlights the arithmetic means of the changes (with given ranges in brackets). It can be seen that for the persistent pollutants, decreasing precipitation led to increased atmospheric long range transport potential by 0.1% - 9.2%. On the other hand, increased precipitation led to decreased atmospheric long range transport potential by a maximum of 5.1%.

Table 5.4: Changes in given fate metrics when climate change scenarios are applied to an un-forested landscape versus replacing the un-forested landscape with a forested landscape given the 1986-2005 climate – Persistent pollutants

		Percent change (%)							
Fate metric	Scenario	PBDE-47	PBDE-99	PBDE-153	PBDE-209	TCDD	OCDD	PeCDF	HxCDF
Overall persistence	A	-4.34	-1.14	-1.75	-0.43	-5.21	-1.65	-4.16	-2.45
	B	2.28	0.54	0.91	0.21	3.17	0.90	2.40	1.35
	C	-3.13	-0.85	-1.29	-0.37	-3.66	-1.09	-2.54	-1.54
	D	3.43	0.77	1.37	0.28	4.94	1.45	4.03	2.23
	Forest	-6.16	-1.49	-7.58	-6.29	13.79	-5.14	-4.39	-9.50
Atmospheric long range transport potential	A	1.30	3.99	3.82	9.19	0.17	5.90	0.48	0.91
	B	-0.80	-2.28	-2.24	-4.27	-0.11	-3.34	-0.32	-0.60
	C	0.89	3.01	2.71	9.09	0.12	4.23	0.27	0.50
	D	-1.28	-3.38	-3.49	-4.37	-0.17	-5.09	-0.58	-1.10
	Forest	-2.27	-3.46	-3.39	-5.42	-1.72	-4.26	-1.92	-2.11

Table 5.5: Changes in given fate metrics when climate change scenarios are applied to an un-forested landscape versus replacing the un-forested landscape with a forested landscape given the 1986-2005 climate – Current-use pesticides

		Percent change (%)							
Fate metric	Scenario	Diazinon	Dimethoate	Carbaryl	Methomyl	Cyhalothrin	Cypermethrin	Diuron	Glyphosate
Overall persistence	A	-14.48	-0.34	-0.09	-0.02	-10.42	-5.43	-3.20	-0.06
	B	7.32	0.14	0.05	0.01	5.11	2.54	1.26	0.03
	C	-13.96	-0.33	-0.08	-0.01	-10.16	-5.06	-3.45	-0.06
	D	7.94	0.15	0.06	0.01	5.41	2.92	1.08	0.03
	Forest	1.15	-5.12	-6.99	-9.65	0.10	-3.04	-2.07	0.28
Atmospheric long range transport potential	A	3.52	22.67	23.17	23.15	5.08	7.67	20.40	23.19
	B	-1.79	-9.03	-9.14	-9.17	-2.48	-3.66	-7.32	-9.18
	C	3.40	21.85	22.54	22.33	5.08	7.51	24.56	22.35
	D	-1.94	-9.64	-9.60	-9.77	-2.49	-3.81	-3.97	-9.80
	Forest	-1.56	-10.43	-10.58	-10.59	-3.18	-4.66	-9.35	-10.60

Table 5.6: Mean percent changes to fate metrics (with ranges in brackets) for various scenarios in the Rio Cobre watershed using grassland given the 1986-2005 climate as the control

Scenario	**Mean (range) percent change in select fate metrics for the persistent pollutants (%)**		**Mean (range) percent change in select fate metrics for the current-use pesticides (%)**	
	Overall persistence	Atmospheric long range transport potential	Overall persistence	Atmospheric long range transport potential
A	-2.6 (-5.21: -0.43)	3.2 (0.12: 9.19)	-4.3 (-14.48: -0.01)	16.1 (3.52: 23.19)
B	1.5 (0.21: 3.17)	-1.7 (-4.27: -0.11)	2.1 (0.01: 7.32)	-6.5 (-9.18: -1.79)
C	-1.8 (-3.67: -0.37)	2.6 (0.12: 9.09)	-4.1 (-13.96: -0.01)	16.2 (3.40: 24.56)
D	2.3 (0.28: 4.94)	-2.4 (-5.09: -0.17)	2.2 (0.01: 7.94)	-6.4 (-9.80: -1.94)
Forest	-3.8 (-9.50: 13.79)	-3.1 (-5.42: -1.72)	-3.3 (-9.65: 1.15)	-7.9 (-10.60: -2.58)

A: Temperature – 303.19K; Precipitation rate – 4.33e-3 m/d
B: Temperature – 303.19K; Precipitation rate – 5.89e-3 m/d
C: Temperature – 305.29K; Precipitation rate – 4.33e-3 m/d
D: Temperature – 305.29K; Precipitation rate – 5.89e-3 m/d

Replacing the grasslands with forests led to decreases in atmospheric long range transport potentials in the range of 1.7% - 5.4%. This suggests that for these pollutants, in this tropical region, replacing grasslands with forests may negate or even obliterate the negative effects of reduced precipitation on their atmospheric concentrations and, consequently, atmospheric long range transport potentials.

The atmospheric long range transport potential for the current-use pesticides in this tropical grassland scenario escalated, with mean increases of 16% (with ranges of 3.4% to 24.6%) when precipitation was reduced. However, replacing the grassland with forests saw a decrease in this metric for these contaminants by almost 8% (with decreases ranging from 2.6% to 10.6%).

Generally, overall persistence in the grassland increased during higher precipitation. However, this metric decreased when the vegetative cover was tropical forest. Therefore, it is possible that having forests, during conditions of increased precipitation, could reduce/obliterate the associated increases in overall persistence. Also, decreased precipitation was associated with increased atmospheric long range transport potential, a negative impact that can then be tempered/mitigated by replacing grasslands with forests, which has now been shown to reduce this metric in the tropical landscape.

Given the ability of forests to reduce overall persistence and atmospheric long range transport potential, it appears that forests could temper or obliterate the negative impacts of climate change. On the other hand, it can be expected that health risks would be enhanced in a deforestation project and could be exacerbated if deforestation is performed during select climate change conditions.

5.3.5 Forest effects given climate change

This section of the assessment involved computing fate metrics when the climate change scenarios were applied to land-use distribution scenarios I (forested landscape) and II (un-forested landscape). These were then compared to those obtained in an un-forested landscape under the 1986-2005 climate conditions.

The changes to overall persistence, atmospheric long range transport potential and annual average concentrations for both the forested and un-forested landscapes in equivalent climate change scenarios over the control climate (temperature - 302.79 K; precipitation - 5.35e-3 m.d^{-1}) were comparable to each other, with average differences typically less than 1%. For example, when the ambient temperature and precipitation were respectively increased by 0.4 K (to 303.19 K) and 11% (5.89e-3 m.d^{-1}), the mean atmospheric long range transport of the persistent pollutants in the grassland watershed (control) reduced by 1.77%. Also, applying the same climate change scenario to the current forested land resulted in a reduction of 1.89% in the atmospheric long range transport potential.

When the same climate change scenario was applied for the current-use pesticides in the grassland, the atmospheric long range transport potential was reduced by 6.57%. However, in the forested watershed, the pesticides displayed a reduction in the same metric of 6.65%, given the same climate change scenario. This trend was generally observed for all the assessed chemicals, whereby the long-term fate metrics were similarly altered by climate change in both the grassland and forest, with marginally larger effects in the forest. It can be concluded that fate metrics are similarly affected by climate change in both forests and grasslands over control climatic conditions, despite the observance of a slightly larger effect for forests.

Table 5.7: Percent changes in fate metrics for the tropical forest over the grassland for given climate change conditions

Climate Change Scenario	**Percent change in fate metrics for persistent pollutants (%)**		**Percent change in fate metrics for current-use pesticides (%)**	
	Overall persistence	***Atmospheric long range transport potential***	***Overall persistence***	***Atmospheric long range transport potential***
Current	-3.77	-3.08	-3.30	-7.86
A	-3.77	-2.82	-3.07	-7.42
B	-3.76	-3.23	-3.39	-8.05
C	-3.74	-2.87	-3.05	-7.42
D	-3.73	-3.28	-3.36	-8.05

Current: Temperature – 302.79 K; Precipitation rate – 5.35e-3 m/d
A: Temperature – 303.19K; Precipitation rate – 4.33e-3 m/d
B: Temperature – 303.19K; Precipitation rate – 5.89e-3 m/d
C: Temperature – 305.29K; Precipitation rate – 4.33e-3 m/d
D: Temperature – 305.29K; Precipitation rate – 5.89e-3 m/d

Another evaluation involved computing the fate metrics for land-use distribution scenario II (grassland/un-forested landscape), given the 1986-2005 climate conditions, as well as using climate change scenarios. The metrics were also computed for land-use distribution I (forested landscape), given the 1986-2005 climate conditions for the Rio Cobre watershed, as well as having applied climate change scenarios. The metrics computed for equivalent climate conditions in land-use distribution I and II were compared. The results in Table 5.7, which include the arithmetic means of the changes observed, reveal that for the persistent pollutants, the forest was able to reduce atmospheric transport potential compared to grasslands, by up to 3.3% during increased precipitation (a rate of 5.89e-3 $m.d^{-1}$), compared to 3.1% under current (control) conditions. However, the ability of the tropical forest to reduce this fate metric over grassland was retarded during decreased precipitation (a rate of 4.33e-3 $m.d^{-1}$): -2.82% and -2.87%, for the respective temperature increase of 0.4 K and 2.5 K (ambient temperatures of 303.19 K and 305.29 K, respectively), compared to -3.08% under control climate conditions. For these persistent chemicals, the forest was more effective at reducing the atmospheric long range transport potentials when precipitation increased, especially when the higher 2.5 K temperature rise was applied. The tropical forest was less effective at reducing these metrics during reduced precipitation, especially at the lower temperature rise of 0.4 K. On the other hand, the forest reduced the overall persistence of the persistent pollutants over grasslands similarly, between 3.73% and 3.77%, under all climatic conditions.

For the pesticides, having a forest in the landscape resulted in a reduction in the atmospheric long range transport potential, in the region of 8.1%, during increased precipitation compared to 7.9% with a forest under the current climate. The overall persistence of the pesticides were lowered by the forest compared to grassland, under all climatic conditions.

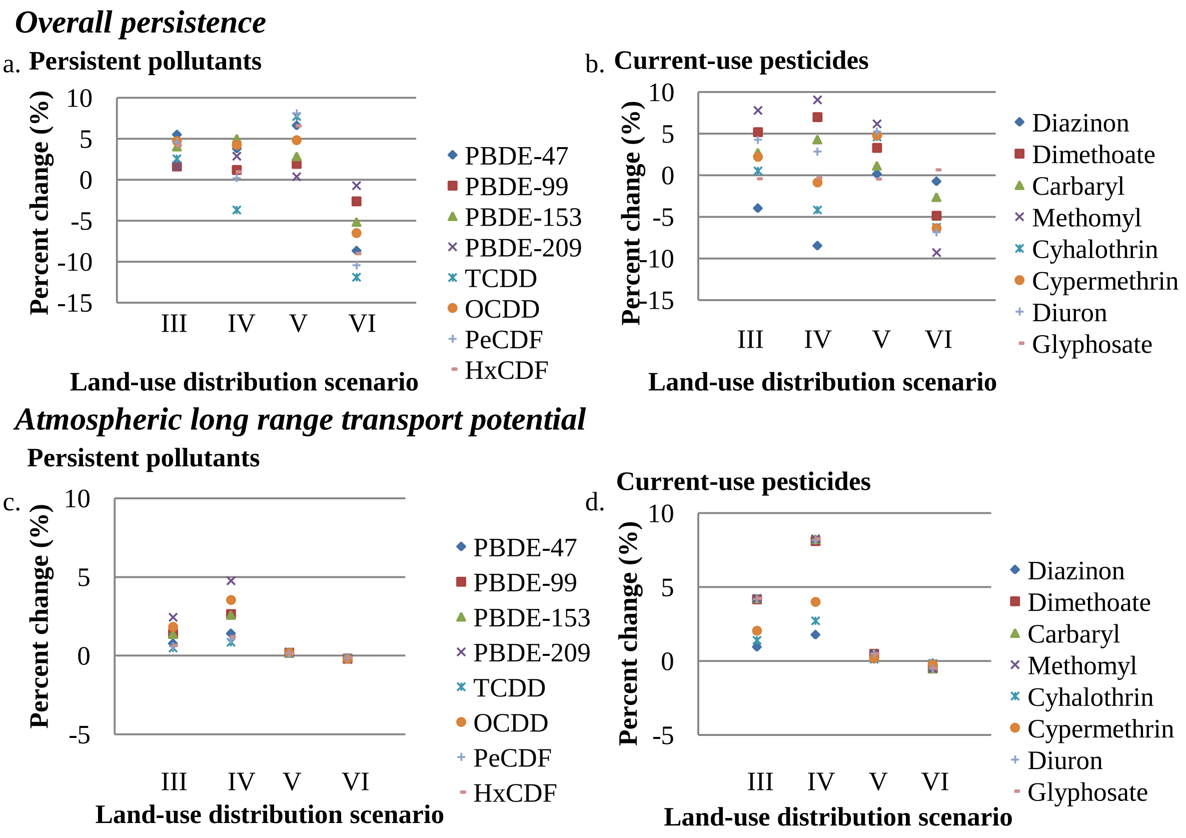
However, the reductions in the overall persistence of these chemicals were enhanced during increased precipitation, but reduced when precipitation rates decreased. The enhanced reductions in the overall persistence, due to increased precipitation rates, were lower when the temperature increase was the greater value – 2.5 K. The effect of temperature on the atmospheric long range transport potentials for these pesticides was negligible.

These all suggest that even as the climate changes, tropical forests may be more effective than grasslands at reducing the overall persistences of the organics through enhanced uptake and the ensuing vegetative degradation, especially the persistent pollutants. However, for the evaluated current-use pesticides, it appears that the tropical forests may be less effective in reducing overall persistence during lowered precipitation, but more effective during increased precipitation.

It appears then that tropical forests are better able to temper or counteract some of the negative effects of climate change than tropical grasslands. For instance, the tropical forest was notably better at reducing atmospheric long range transport potentials, during increased precipitation, than grassland. Also, the tropical forest was better at decreasing the atmospheric long range transport potential of the persistent pollutants during higher temperature rises, for any given precipitation rate. However, the tropical forest was slightly more effective at lowering the mean overall persistences of both the persistent contaminants and current-use pesticides during the lower temperature rise – they were marginally less capable at the higher temperature rise. The reductions in atmospheric long range potential due to the presence of the tropical forest were collectively greater for the current-use pesticides (given arithmetic means of 7.4% to 8.0%) compared to the collective reductions in this metric for the persistent pollutants (with arithmetic means of 2.8% to 3.3%), irrespective of climatic conditions. However, the presence of the forest in the landscape led to marginally larger reductions in the collective overall persistence of the persistent pollutants (with arithmetic means ranging from 3.7%-3.8%) than for the current-use pesticides (displaying arithmetic means of 3.1% to 3.4%). Therefore, tropical forests may become more important in regulating the environmental fates and health impacts of organic contaminants, especially the more polar ones, as the climate changes. The outgoing conclusion though is that climatic conditions dictate the effect of tropical forests on the fates, and ensuing health impacts, of organic contaminants, with the change also dependent on the properties of the chemical.

5.3.6 Land-use effects

The overall persistence and atmospheric long range transport potential for all 16 organic compounds were calculated for land-use distribution scenarios III to VI and compared to those calculated for land-use distribution scenario I, assuming the 1986-2005 climatic conditions. The changes to the computed fate metrics for land-use distribution scenarios III to VI over land-use distribution scenario I are illustrated in Figure 5.9. There is a general increase in the overall persistence of the persistent pollutants when the forest portion is reduced by 30%. The greater the allocation of this reduced forested portion for agricultural expansion, the greater the increase in overall persistence. In fact, for the persistent contaminants, reducing the forested portion, by 30% solely for agricultural expansion, was associated with increases in overall persistence, by up to 5%, whereas increasing the forested portion, by 30% through afforestation of agricultural land, led to decreased overall persistence, by as much as 12%.



Land-use distribution scenarios

III : Agriculture/Forest/Urban – 34%/42%/24%
IV: Agriculture/Forest/Urban – 25%/42%/33%
V: Agriculture/Forest/Urban – 43%/42%/15%
VI: Agriculture/Forest/Urban – 7%/78%/15%

Figure 5.9: Percent change in long-term fate metrics in given land-use distribution scenarios compared to the current land-use distribution

Most of the current-use pesticides experienced increased overall persistence when the forested portion of the landscape decreased by 30%. Typically, for these contaminants, the increases in overall persistence were higher as the portion of the forest allotted to urban sites increased. For a select few, such as diazinon and cypermethrin, the increases in the overall persistence during deforestation correlated with the amount turned into agricultural land. The overall persistence of the current-use pesticides generally decreased, by at most 9%, when afforestation of agricultural lands was employed.

The atmospheric long range transport potential of the 16 evaluated organics increased when deforestation was employed. The increases were more notable for the current-use pesticides. For example, when the forests were reduced by 30% solely for urban expansion, the increase in the atmospheric long range transport potentials of the pesticides ranged from 1.8% to 8.3%, whereas those for the persistent pollutants ranged from 0.8% to 4.8%. When the landscape was deforested for both urban and agricultural expansion, the atmospheric long range transport potentials of the persistent organics and the current-use pesticides increased with similar and respective ranges of 0.14%-0.20% and 0.14%-0.50%. Also, similar decreases in the atmospheric long range transport potentials of all 16 assessed chemicals were observed when the forested portion of the landscape was enhanced at the expense of agricultural land.

In this evaluation, the weighted leaf area index used for the forest in the Rio Cobre watershed was 4.3, whereas the leaf area indices for agricultural and urban lands were 3.6 and 1.2, respectively. Therefore, the uptake of chemicals from the atmosphere by forest vegetation should be marginally larger than by agricultural vegetation. Consequently, the observed marginal increases and reductions in the atmospheric long range transport potentials of the organics, given the respective deforestation for agricultural expansion and afforestation of agricultural lands, are reasonable. On the other hand, agricultural lands may be more effectively transferring the uptaken chemicals to the soils than forests, thereby allowing for the observed enhanced overall persistence during agricultural expansion.

It can be seen that land-use allocation impacts the environmental fates, and consequently the health impacts, of select organic compounds. Also, the type of co-existing land-use appears to affect the ability of forests to regulate the environmental fates of the contaminants. As a result, environmental modeling assessments should, as best as possible, employ detailed representation of the landscape.

5.3.7 Climate change effects given varying forested proportions

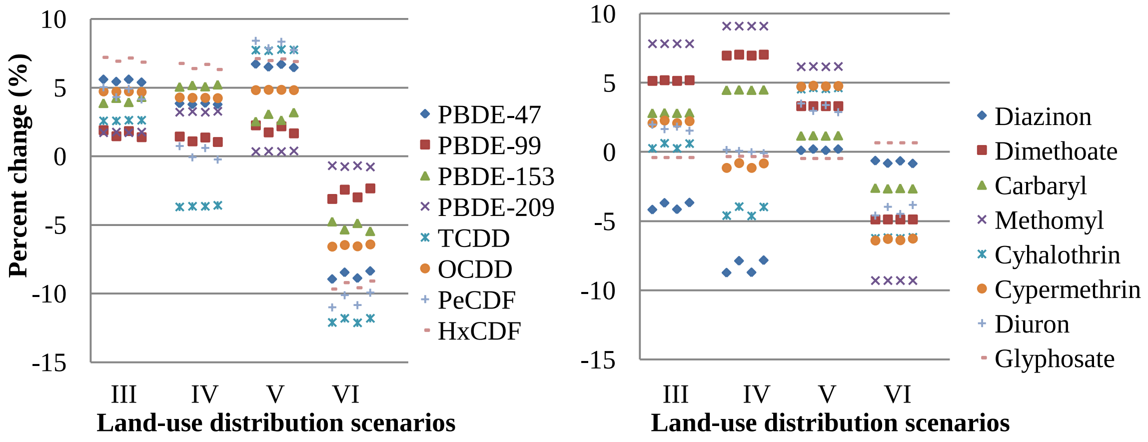
In the previous section, it was shown that land-use allocations impact the overall persistence and atmospheric long range transport potentials of select organics within the Rio Cobre watershed. In this section, the aim was to examine the combined effects of climate change and land-use allocations on the select fate metrics. Therefore, the fate metrics were computed when the four (4) climate change scenarios were applied to land-use distribution scenarios I and III to VI. The outputs of land-use distribution scenarios III to VI were compared to those in land-use distribution I with equivalent climatic conditions.

Figure 5.10 shows that for the persistent pollutants, differences in the effects of climate change, especially changes to the ambient temperature, on the fate metrics were almost imperceptible compared to those due to land-use allocations. In fact, compared to land-use allocation effects on environmental fates, changes to ambient temperature caused negligible effects. The effects of precipitation on environmental fates as land-use varied were more notable.

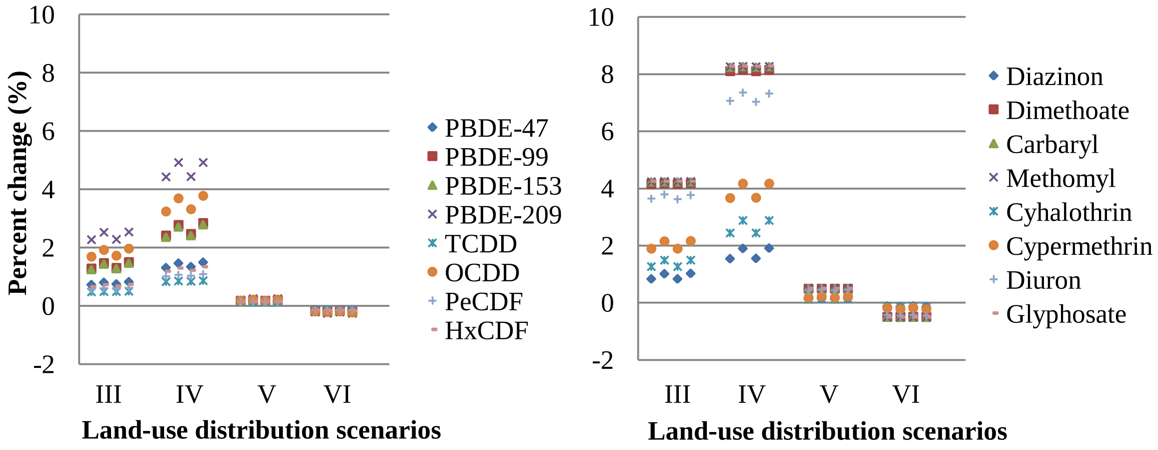
When agricultural lands were converted to forests, overall persistence was generally less efficiently reduced during increased precipitation. For example, for the persistent organics, when the forests were reduced solely for urban expansion, increased precipitation generated changes in overall persistences in the range of 0.38%-7.88%, whereas reduced precipitation generated changes with a range of 0.35%-7.79%.

Persistent pollutants **Current-use pesticides**

Overall Persistence



Atmospheric long range transport potential



Land-use distribution scenarios
III : Agriculture/Forest/Urban – 34%/42%/24%
IV: Agriculture/Forest/Urban – 25%/42%/33%
V: Agriculture/Forest/Urban – 43%/42%/15%
VI: Agriculture/Forest/Urban – 7%/78%/15%

For each land-use distribution set:
Column 1: Temperature – 303.19 K; Precipitation rate – 4.33e-3 m/d
Column 2: Temperature – 303.19 K; Precipitation rate – 5.89e-3 m/d
Column 3: Temperature – 305.29 K; Precipitation rate – 4.33e-3 m/d
Column 4: Temperature – 305.29 K; Precipitation rate – 5.89e-3 m/d

Figure 5.10: Land-use distribution effects during climate change

When some agricultural lands were converted to forests (during afforestation), the reductions in the overall persistence of some persistent organics, such as PBDE-153, were enhanced during increased precipitation, whereas for most of the remaining persistent organics, the reductions in overall persistence were tempered during increased precipitation (with reductions ranging from 0.75% to 11.79%). For some pollutants, such as PBDE-99, PBDE-153 and Hx-CDF, there were observed increases in their overall persistence during increased precipitation given deforestation, especially for urban expansion.

In general, the increases in the overall persistence of the current-use pesticides during deforestation were marginally enhanced during increased precipitation and maginally retarded during decreased precipitation, especially when deforestation occurred for some degree of urban expansion.

In all landscapes with reduced forest coverage, the atmospheric long range transport potentials of the organic chemicals were generally increased – enhanced whenever precipitation increased (given a range in this metric of 0.14%-8.28%) and tempered during decreased precipitation (given a range in this metric of 0.14%-8.27%). The increases were further enhanced during the higher temperature rise of 2.5 K. The effects of climate change, given deforestation for urban expansion and afforestation of agricultural lands, were not as notable.

Although land-use allocations have been shown to affect the environmental fates and consequent health impacts of select organics, the effects of these are also influenced by climate and climate change, and vice versa. Land use allocation therefore impacts the long-term fates of the organic pollutants and also the effects of climate change on the environmental fates. Additionally, climate change appears to impact the effects of land-use allocation on the environmental fates of the examined organics.

5.4 Conclusions

Climate change in tropical regions has the potential to substantially affect the long-term environmental fates of select organic pollutants. The dynamic assessment highlighted that the surface water, atmospheric, sediment and urban film concentrations of both PBDE-47 and dimethoate were regulated by the precipitation rate. Increased precipitation was associated with increased overall persistence but decreased atmospheric long range transport potential. Although precipitation appears to be the major determinant of the fates of the evaluated organics in the given tropical region, changes to ambient temperature also produce effects, which appear to be more important in the overall persistences of the persistent pollutants than the more polar organics.

The changes to the long term fate metrics were similar when climate change was applied to a tropical forested landscape and to the tropical un-forested landscape. However, when the absolute metrics in both biomes were compared, tropical forests were slightly more effective at combating the effects of climate change. However, the absolute effect depends not only on the properties of the pollutant, but also on the climate change scenario. Therefore, climatic conditions do influence the effects of tropical forests on the fates and, potentially, the health impacts of the evaluated organic compounds. There are indications that forests, in tropical regions, may temper any health risks associated with the evaluated contaminants under climate change conditions.

The influence of tropical forests on the environmental fates of the assessed contaminants during climate change appears to be dependent on the size of the forest as well as land-use allocations. Co-existing land-uses also appear to co-determine the long-term fates of the pollutants.

This study was considered among the first to attempt to quantify and evaluate the influence of forests, together with climate change and land-use distribution, on the environmental fates of select organic contaminants in a tropical region. The evaluation was associated with a number of limitations. Many input parameters had to be estimated and/or approximated when unavailable. Also, the temperature dependences of the variables were not considered for the climate change scenarios. At the same time, due to a lack actual data, a hypothetical emission scenario was applied. However, the evaluation was comparative, allowing for some compensation for the uncertainties in the parameters. It is recommended that future work be directed towards measuring/ascertaining currently unavailable parameters and, thereafter, re-evaluating the effects of climate, climate change and land-use distribution, together with forests on the environmental fates of the organics.

This analysis did not attempt to ascertain the role of specific mechanisms such as re-volatilization or uptake in the influence of tropical forests for various climatic conditions or according to climatic drivers. Such studies are recommended to elucidate the potential impacts of forests in different tropical climates.

Consideration must be given to the fact that this assessment employed grasslands as the control. Grasslands are a type of vegetative cover, as are forests, and therefore may be more similar to forests in their effects than other land covers/uses, such as bare rock or urban centers. Although differences between forests and grasslands, on the influence on the environmental fates, were notable, the effects of climate change on fates were comparable. It is expected that the comparisons between tropical forests and bare rock or even urban areas in varying climatic conditions will produce more considerable differences.

This evaluation showed that the long-term fates of the organic contaminants differed for various landscape architectures/layouts. When forest acreage was maintained, the fate metrics changed, depending on the proportions of the co-existing land uses or vegetation. This implies that landscape architecture (land-use allocation) influence the fates of organic contaminants in tropical watersheds. Also, the effects of forest versus the grassland on chemical fates varied, albeit slightly, depending on the land portions allocated to the co-existing vegetation or land-uses. This therefore demonstrated that the effect of tropical forests was influenced by land-use allocations or co-existing land uses. These are important considerations for regional land-use planning. Therefore, any assessment of contaminant fates and health impacts requires careful description and representation of the land.

For the purpose of land-use planning for sustainable development, the roles of other types of vegetative cover in governing the environmental fates of organic contaminants should be individually examined.

The results of this study are considered applicable to other regions displaying similar characteristics to the Rio Cobre watershed. However, site-specific evaluations are recommended, when possible.

Chapter 6

Summary

The overarching aim of this dissertation was to contribute to characterizing the role of tropical forests and climate change on the environmental fates of select organic compounds. A few organic compounds were chosen for this assessment with the criteria that they were of current global concern, ubiquitous and associated with adverse health and/or environmental effects. Among those chosen were some poly-brominated diphenyl ethers (PBDEs), current-use pesticides, dioxins and furans. To complete this assessment, a number of specific objectives were generated. The methods to achieve the objectives were then developed. The execution of the developed methods furnished information on the influence of tropical forests. These are summarized below.

The first objective was to ascertain, via field measurements, whether tropical forests filter organic pollutants. The Rio Cobre watershed in Jamaica was chosen as the study site. Within this area, samples of soil, bulk deposition, litterfall and air were collected from a forest and a nearby clearing. The concentrations of select polybrominated diphenyl ethers (PBDEs) in the samples were quantified and used to compute filter, accumulation and depletion factors. Filter and accumulation factors greater than one (> 1) and depletion factors less than one (< 1) signify a filter effect. It was found the tropical forests do filter the PBDEs by transferring them from the atmosphere to the forest soils. They therefore operate similarly to their temperate counterparts.

The goal of the second objective was to evaluate the effects of tropical forest parameters on the long-term fates of the select organic contaminants, using multimedia modeling. Multimedia modeling was the chosen method, since it allows for transparent assessment when monitoring data are unavailable or lacking. The challenges, encountered during the field measurements for the first objective, confirmed that field measurements are still encumbered for some developing countries, and that the practical alternative is the use of multimedia environmental models. In the absence of an appropriate spatially heterogeneous level IV evaluative environmental model, one was developed in this objective. To do so, components of the Multimedia Urban Model (MUM) were integrated into the domain of CalTOX 1.5 to create a 16-compartment dynamic multimedia model. The model, RioShed, was then applied to the Rio Cobre watershed using a hypothetical emission scenario. The outputs of various forested comparison scenarios were compared to those generated in select control scenarios, thereby also compensating for the uncertainties in the input parameters. The surface water long range transport potential was sensitive to parameters associated with the water, such as aquatic half-life, water depth, amongst others. The remaining long-term fate metrics were responsive to parameters not necessarily associated with specific compartments. The two forest parameters with substantial effects on the fates of the 16 evaluated organic chemicals were canopy drip and leaf area index.

The tropical forest generally decreased the overall persistence of the current-use pesticides and persistent pollutants, with evergreen forests being more effective in achieving the decrease. Additionally, the tropical forests, especially the evergreen, were more effective at reducing the atmospheric long range transport potential of all the contaminants, especially the current-use pesticides. The conclusion was that tropical forests do influence the long term fates of the select organic compounds, and that such influence depends on the properties of the chemicals, as well as the composition and other properties of the forest.

The final objective was to determine the effects of tropical climatic conditions, climate change and land use on the long-term environmental fates of the contaminants, as well as whether these phenomena also altered the effect of tropical forests on the aforementioned fates. Since field measurements were not possible, RioShed, developed in the second objective, was employed using a hypothetical emission scenario. The assessment scenarios were generated using the 2013 Intergovernmental Panel on Climate Change (IPCC) climate change predictions for the Caribbean. Under conditions of increased precipitation, overall persistence increased, whereas atmospheric long range transport potential decreased, with alternate outcomes given the alternate climate condition. In terms of overall persistence, the effect of forests was retarded under conditions of increased precipitation and decreased precipitation for the persistent pollutants and the current-use pesticides, respectively. Changes to precipitation rates were more important for the more polar current-use pesticides. However, although the changes to fate metrics were less perceptible given changes in temperature, this climatic variable appeared to more greatly affect the overall persistence of the persistent pollutants than the current-use pesticides. Even during climate change, co-existing land uses were found to influence the environmental fates of the chemicals. Nevertheless, it was established that tropical climate change will affect not only the long-term fates of organic contaminants, but that this phenomena will also impact the influence of tropical forests and landscape architecture on these fate and potential health impacts.

This study was associated with a number of limitations. The field measurements were impeded by inadequate resources, thereby restricting the scope of the assessment. In the modeling exercises, a number of the parameters were estimated, due to an unavailability of actual values. Emission data was absent for the study area and, as such, a reasonable but hypothetical emission scenario was applied in the modeling exercises. Also, this study was considered to be a first-step evaluation.

Future work should be directed towards measuring/ascertaining site-specific parameters, such as soil organic carbon content, porosity, leaf area index, among others. These were not available for the study area, and had to be estimated. Many of the properties, such as partition coefficients, are temperature-dependent. However, the values, which were typically available and therefore used, had been pre-determined at 25 °C. Values determined at the mean temperature of the study site (29 °C or 30 ° C) were generally unavailable. It is recommended that for improved accuracy, studies quantifying these variables at different temperatures should increase. Once more appropriate properties are available, this same study should be re-conducted using those ascertained parameters and properties.

This dissertation identified the presence of the select PBDEs only in the surface soils, atmosphere, litterfall and bulk deposition at two sites in the Rio Cobre watershed. Attempts were not made to quantify the presence in other media, such as surface water or root soils. Also, no attempt was made to identify the sources of the PBDEs in the given watershed. In order to elucidate the role of the forests, as well as assist decision-making regarding environmental contamination, these additional assessments are necessary and, as such, are recommended. It is also suggested that the scope be widened to include other forests and sites in the same watershed.

It is considered worthwhile to expand the nature of the current study to include assessments of the individual roles of other land uses or vegetative covers in the environmental fates and health impacts of the evaluated and/or other organic contaminants. Such assessments should also incorporate the influence of co-existing land uses on the fates and health impacts within the region. Regression analyses should be considered, which may require the inclusion of more scenarios.

Although the results of this dissertation are considered applicable to similar regions, region-specific evaluations are more informative, and are therefore recommended when possible. Also, making RioShed GIS compatible and integrating select GIS capabilities should produce more visual results, which are often helpful. With that said, improving the spatial heterogeneity of RioShed, without adding complexity and resource requirements, is also a worthwhile endeavor to undertake, thereby contributing to the ability of scientists and regulating agencies to quickly garner information about the environmental fates of organic contaminants in tropical developing countries.

In order to conduct some parts of the suggested research, such as field measurements, the challenges encountered in the current study would have to be alleviated. Some of the challenges were primarily associated with the developing status of the study area. For example, in order for this study to be relatively cost-effective, many of the sampling apparatus had to be transported from the US. Only one laboratory was found adequately equipped to perform the extraction and clean-up according to international standards. However, the cost to do so was exorbitant. Unfortunately also, shipping the soil, litterfall and deposition samples to the US was difficult. As a result, such samples were extracted and cleaned in Jamaica while the air samples were shipped to the US for extraction and clean-up. All samples were instrumentally analyzed in the US as the cost to do so in Jamaica was excessively high – above the available resources.These are common challenges in developing countries, such as Jamaica, where financial resources and analytical facilities are limited. Until they can be overcome, alternative tools such as multimedia environmental models should be employed to conduct the research/studies recommended above, so as to contribute knowledge of the role of tropical forests in the fates and health impacts of the evaluated organics, as well as other organic contaminants.

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Appendix A

Field monitoring data for the Rio Cobre watershed

Table A.1: PBDE masses in the atmosphere of a forest and adjacent clearing in Rio Cobre watershed sampled using poly-urethane foam (PUF) disks

	Contaminant mass (pg)									
Sampling area	***Forest***					***Clearing***				
PUF disk number	*1*	*2*	*3*	*4*	*5*	*1*	*2*	*3*	*4*	*5*
PBDE-28	3.14	2.64	2.59	2.54	2.55	2.85	5.40	2.45	2.49	4.33
PBDE-47	4.05	9.36	6.61	6.88	6.07	7.23	34.22	3.66	6.77	10.43
PBDE-100	3.32	3.54	3.28	2.50	2.97	2.63	6.80	2.61	3.03	3.19
PBDE-99	20.01	11.83	21.98	2.54	12.24	33.86	28.76	3.09	16.74	6.78
PBDE-154	2.71	2.96	3.13	-	2.69	3.12	4.17	3.13	2.80	12.26
PBDE-153	2.59	3.21	3.68	3.02	2.76	2.60	4.37	2.59	2.78	4.27
PBDE-183	2.71	3.13	6.02	-	2.63	3.01	3.66	2.59	2.84	2.68
PBDE-209	4.16	4.40	4.91	5.11	4.13	8.50	7.65	4.23	17.75	11.12
Total	42.69	41.08	52.19	-	36.04	63.81	95.04	24.34	55.20	55.06
Sampling rate ($m^3.d^{-1}$)	3	3	3	3	3	3	3	3	3	3
Sampling period (days)	105	105	105	105	105	105	105	105	105	105

Table A.2: PBDE masses in the depositions of a forest and adjacent clearing in the Rio Cobre watershed

Contaminant	**Contaminant mass (pg)**							
	Forest			***Clearing***				
PBDE-28	268.25	265.75	267.25	658.75	310.75	352.75	263.75	318.25
PBDE-47	475.62	285.12	327.12	283.12	447.62	303.62	316.12	254.62
PBDE-100	300.62	266.62	271.12	259.62	287.12	263.62	265.62	259.62
PBDE-99	466.06	290.06	307.06	275.56	412.06	265.56	282.06	267.56
PBDE-154	1624.68	262.68	260.18	260.68	272.68	262.68	260.68	262.18
PBDE-153	626.48	269.98	269.98	270.48	288.48	286.98	269.98	270.48
PBDE-183	1804.44	297.94	272.44	271.44	279.44	346.44	271.44	271.44
PBDE-209	7456.56	436.56	453.06	435.06	644.56	434.06	435.06	434.06
Sampling days	30	21	21	30	30	30	21	21
Sampling cross-sectional area (m^2)	5.67e-3	5.67e-3	5.67e-3	5.67e-3	5.67e-3	5.67e-3	5.67e-3	5.67e-3

Table A.3: PBDE mass concentrations in the litterfall of a forest and adjacent clearing in the Rio Cobre watershed

Contaminant	**Contaminant mass concentration (pg.g^{-1})**			
	Forest			***Clearing***
PBDE-28	43.24	65.86	65.73	399.25
PBDE-47	50.99	86.47	94.81	352.59
PBDE-100	36.69	68.93	72.54	271.40
PBDE-99	41.86	77.25	100.39	297.09
PBDE-154	34.11	64.72	64.72	284.34
PBDE-153	34.93	67.16	67.16	283.65
PBDE-183	35.31	67.52	67.65	326.67
PBDE-209	59.13	107.85	111.21	434.22

Table A.4: PBDE mass concentrations in soils of a forest and adjacent clearing in the Rio Cobre watershed

Contaminant	**Contaminant mass concentration (pg.g^{-1})**									
	Forest							***Clearing***		
PBDE-28	68.82	26.87	39.35	37.15	49.22	50.71	57.89	26.89	28.92	25.75
PBDE-47	35.01	42.89	56.35	35.64	78.58	48.65	82.91	37.77	32.10	25.63
PBDE-100	27.38	27.50	28.85	32.25	50.39	44.02	42.45	27.08	26.71	25.93
PBDE-99	34.50	42.83	30.79	40.67	78.48	55.53	45.31	27.02	26.40	26.33
PBDE-154	27.19	26.16	27.41	26.27	47.93	35.86	40.34	26.49	26.12	26.14
PBDE-153	43.67	142.83	162.07	102.04	261.68	139.30	238.47	27.56	27.14	26.92
PBDE-183	27.91	28.38	29.49	35.57	52.00	48.56	43.38	28.95	27.54	27.11
PBDE-209	44.17	45.18	47.36	46.11	82.77	62.95	69.69	44.28	43.37	43.28

Appendix B

Formulation details for RioShed

Table B.1: Compartment gains and losses for RioShed

Environmental Compartment	**Gains**	**Losses**
Atmosphere (A)	Diffusion from forest canopy Diffusion from surface water Diffusion from agricultural vegetation Diffusion from urban vegetation Diffusion from urban film Diffusion from forest surface soil Diffusion from agricultural surface soil Diffusion from urban surface soil Evapotranspiration from forest root soil Evapotranspiration from urban root soil Evapotranspiration from agricultural root soil Re-suspension of particles from forest surface soil Re-suspension of particles from agricultural surface soil Re-suspension of particles from urban surface soil Sources Inflow from external environment	Degradation/transformation Diffusion to forest canopy Diffusion to surface water Diffusion to agricultural vegetation Diffusion to urban vegetation Diffusion to urban film Diffusion to forest surface soil Diffusion to agricultural surface soil Diffusion to urban surface soil Deposition (wet, particle & gaseous) to forest canopy Deposition (wet, particle & gaseous) to agricultural vegetation Deposition (wet & particle) to urban vegetation Deposition (wet & particle) to urban film Deposition (wet & particle) to surface water Deposition (wet & particle) to forest surface soil Deposition (wet & particle) to agricultural surface soil Deposition (wet & particle) to urban surface soil Outflow to external environment
Forest Canopy (Cf)	Diffusion from atmosphere Deposition (wet & particle) from atmosphere Root uptake from forest root soil Sources	Degradation/transformation Diffusion to atmosphere Deposition (litterfall, wax erosion, canopy drip) to forest surface soil Phloem flow to forest root soil
Agricultural Vegetation (Ca)	Diffusion from atmosphere Deposition (wet & particle) from atmosphere Root uptake from agricultural root soil Sources	Degradation/transformation Diffusion to atmosphere Deposition (litterfall, wax erosion, canopy drip) to agricultural surface soil Phloem flow to agricultural root soil
Urban Vegetation (Cu)	Diffusion from atmosphere Diffusion from urban surface soil Deposition (wet & particle) from atmosphere	Degradation/transformation Diffusion to atmosphere Deposition (litterfall, wax erosion, canopy drip) to urban surface soil

	Root uptake from urban root soil Sources	Phloem flow to urban root soil
Urban Organic Film (Iu)	Diffusion from atmosphere Deposition (wet & particle) from atmosphere Sources	Diffusion to atmosphere Surface run-off to surface water
Surface Water (W)	Diffusion from atmosphere Diffusion from sediment Deposition (wet & particle) from atmosphere Surface run-off from urban film Run-off (surface and erosion) from agricultural surface soil Run-off (surface and erosion) from forest surface soil Run-off (surface and erosion) from urban surface soil Re-suspension from sediment Sources Inflow from external environment	Degradation/transformation Diffusion to atmosphere Diffusion to sediment Deposition to sediment Outflow to external environment
Forest Surface Soil (Sf)	Diffusion from atmosphere Diffusion from forest root soil Deposition (litterfall, wax erosion, canopy drip) from forest canopy Deposition (wet & particle) from atmosphere Sources	Degradation/transformation Diffusion to atmosphere Diffusion to forest root soil Leaching to forest root soil Re-suspension to atmosphere Run-off (surface and erosion) to surface water
Urban Surface Soil (Su)	Diffusion from atmosphere Diffusion from urban root soil Deposition (wet & particle) from atmosphere Deposition (litterfall, wax erosion, canopy drip) from urban vegetation Sources	Degradation/transformation Diffusion to atmosphere Diffusion to urban root soil Leaching to urban root soil Re-suspension to atmosphere Run-off (surface and erosion) to surface water
Agricultural Surface Soil (Sa)	Diffusion from atmosphere Diffusion from agricultural root soil Deposition (wet & particle) from atmosphere Deposition (litterfall, wax erosion, canopy drip) from agricultural vegetation Sources	Degradation/transformation Diffusion to atmosphere Diffusion to agricultural root soil Leaching to agricultural root soil Re-suspension to atmosphere Run-off (surface and erosion) to surface water
Forest Root Soil (Rf)	Phloem flow from forest canopy Diffusion from forest surface soil Leaching from forest surface soil Sources	Degradation/transformation Diffusion to forest surface soil Leaching to forest vadose soil Evapotranspiration to atmosphere Xylem sap flow to forest canopy
Urban Root Soil (Ru)	Diffusion from urban surface soil Leaching from urban surface soil Phloem flow from urban vegetation Sources	Degradation/transformation Evapotranspiration to atmosphere Xylem sap flow to urban vegetation Diffusion to urban surface soil Leaching to urban vadose soil

Agricultural Root Soil (Ra)	Diffusion from agricultural surface soil Phloem flow from agricultural vegetation Leaching from agricultural surface soil Sources	Degradation/transformation Evapotranspiration to atmosphere Diffusion to agricultural surface soil Leaching to agricultural vadose soil Xylem sap flow to agricultural vegetation
Forest Vadose Soil (Vf)	Leaching from forest root soil Sources	Degradation/transformation Leaching to groundwater
Urban Vadose Soil (Vu)	Leaching from urban root soil Sources	Degradation/transformation Leaching to groundwater
Agricultural Vadose Soil (Va)	Leaching from agricultural root soil Sources	Degradation/transformation Leaching to groundwater
Sediment (d)	Diffusion from surface water Deposition from surface water Sources	Degradation/transformation Diffusion to surface water Re-suspension to surface water

Advective transport from compartment i to j (T_{Aij}) includes non-particle deposition, evapotranspiration, root uptake, leaching, run-off, xylem sap flow and phloem flow; non-diffusive/advective physical transport (T_{Nij}) includes re-suspension and particle deposition; diffusive transport from compartment i to j (T_{Dij}) includes diffusion; losses from compartment i (L_i) includes degradation, burial and outflows to the external environment; source input into compartment i (S_i) includes sources and inflow from the external environment.

$$\begin{bmatrix} N_A \\ N_w \\ N_d \\ N_{iu} \\ N_{ca} \\ N_{cf} \\ N_{cu} \\ N_{sa} \\ N_{sf} \\ N_{su} \\ N_{ra} \\ N_{rf} \\ N_{ru} \\ N_{va} \\ N_{vf} \\ N_{vu} \end{bmatrix} = - \begin{bmatrix}
-L_A & T_{w,A} & 0 & T_{iu,A} & T_{ca,A} & T_{cf,A} & T_{cu,A} & T_{sa,A} & T_{sf,A} & T_{su,A} & 0 & 0 & 0 & 0 & 0 & 0 \\
T_{A,w} & -L_w & T_{d,w} & T_{iu,w} & 0 & 0 & 0 & T_{sa,w} & T_{sf,w} & T_{sf,w} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & T_{w,d} & -L_d & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
T_{A,iu} & 0 & 0 & -L_{iu} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
T_{A,ca} & 0 & 0 & 0 & -L_{ca} & 0 & 0 & 0 & 0 & 0 & T_{ra,ca} & 0 & 0 & 0 & 0 & 0 \\
T_{A,cf} & 0 & 0 & 0 & 0 & -L_{cf} & 0 & 0 & 0 & 0 & 0 & T_{rf,cf} & 0 & 0 & 0 & 0 \\
T_{A,cu} & 0 & 0 & 0 & 0 & 0 & -L_{cu} & 0 & 0 & 0 & 0 & 0 & T_{ru,cu} & 0 & 0 & 0 \\
T_{A,sa} & 0 & 0 & 0 & T_{ca,sa} & 0 & 0 & -L_{sa} & 0 & 0 & T_{ra,sa} & 0 & 0 & 0 & 0 & 0 \\
T_{A,sf} & 0 & 0 & 0 & 0 & T_{cf,sf} & 0 & 0 & -L_{sf} & 0 & 0 & T_{rf,sf} & 0 & 0 & 0 & 0 \\
T_{A,su} & 0 & 0 & 0 & 0 & 0 & T_{cu,su} & 0 & 0 & -L_{su} & 0 & 0 & T_{ru,su} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & T_{ca,ra} & 0 & 0 & T_{sa,ra} & 0 & 0 & -L_{ra} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & T_{cf,rf} & 0 & 0 & T_{sf,rf} & 0 & 0 & -L_{rf} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & T_{cu,ru} & 0 & 0 & T_{su,ru} & 0 & 0 & -L_{ru} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & T_{ra,va} & 0 & 0 & -L_{va} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & T_{rf,vf} & 0 & 0 & -L_{vf} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & T_{ru,vu} & 0 & 0 & -L_{vu}
\end{bmatrix}^{-1} \begin{bmatrix} S_{VA} \\ S_{Vw} \\ S_{Vd} \\ S_{Viu} \\ S_{Vca} \\ S_{Vcf} \\ S_{Vcu} \\ S_{Vsa} \\ S_{Vsf} \\ S_{Vsu} \\ S_{Vra} \\ S_{Vrf} \\ S_{Vru} \\ S_{Vva} \\ S_{Vvf} \\ S_{Vvu} \end{bmatrix}$$

Figure B.1: Matrix format for steady state solution of mass balance equations for RioShed.

L_i is the loss rate constant for compartment i (which includes reaction losses, as well as transport to other compartments and the external environment), d^{-1}; N_i is the i^{th} compartmental inventory, mol; $T_{i,j}$ is the transport rate constant from compartment i to j, d^{-1}; and S_i is the i^{th} compartmental input rate, mol.d^{-1}.

Table B.2: Equations for fugacity capacities (in mol.m^{-3}.Pa^{-1}) in respective media in RioShed

Medium	Fugacity Capacity Equation	Data Source
Pure water (water)	$Z_{water} = H^{-1}$	California Environmental Protection Agency (CEPA), 1993
Pure air (air)	$Z_{air} = (RT)^{-1}$	CEPA, 1993
Aerosol particles (ap)	$Z_{ap} = \frac{3\times10^6 Z_{air}}{VP}$	CEPA, 1993
Soil/sediment particles ((i = s, r, v, w or d)p)	$Z_{ip} = \rho_{ip} K_{oc} f_{ocip} Z_{water}$	CEPA, 1993
Aquatic biota (ab)	$Z_{ab} = BCF\ \rho_{water} Z_{water}$	Yang, 2007
Phloem (phl)	$Z_{phl} = f_{phlw} Z_{water}$	McKone et al., 1997
Leaf Cuticle (l)	$Z_l = f_{ocp} K_{OW} Z_{water}$	Diamond et al., 2001
Dissolved phase of urban film (h)	$Z_h = Z_{air} K_{OA} f_{och}$	Diamond et al., 2001
Bulk Surface Water (w)	$Z_w = f_{ww} Z_{water} + f_{wp} Z_{wp} + f_{wab} Z_{ab}$	Yang, 2007
Atmosphere (A)	$Z_A = f_{Aap} Z_{ap} + f_{Aair} Z_{air}$	Yang, 2007
Plant canopy (cm: m = a, f, u)	$Z_{cm} = K_{pa} \rho_{pm} Z_{air} + K_{pa}^{ap} Z_{ap} \rho_{pm} \beta_A \rho_{smp}^{-1}$ (for inorganic and dissociating organics, $Z_{air} = 0$)	Cousins and Mackay, 2000
Plant root (tm: m = a, f, u)	$Z_{tm} = K_{ps} \rho_p \rho_{rm}^{-1} f_{rmp}^{-1} (f_{rma} Z_{air} + f_{rmw} Z_{water} + f_{rmp} Z_{rmp})$	McKone et al., 1997
Root-zone soil (rm: m = a, f, u)	$Z_{rm} = f_{rma} Z_{air} + f_{rmw} Z_{water} + f_{rmt} Z_{tm} + f_{rmp} Z_{rmp}$	McKone et al., 1997
Surface-zone soil (sm: m = a, f, u)	$Z_{sm} = f_{sma} Z_{air} + f_{smw} Z_{water} + f_{smp} Z_{smp}$	CEPA, 1993
Vadose-zone soil (vm: m = a, f, u)	$Z_{vm} = f_{vma} Z_{air} + f_{vmw} Z_{water} + f_{vmp} Z_{vmp}$	CEPA, 1993
Sediment (d)	$Z_d = f_{dw} Z_{water} + f_{dd} Z_{dp}$	CEPA, 1993
Impervious surface (iu)	$Z_{iu} = f_{iuh} Z_h + f_{iuap} Z_{ap}$	Diamond et al., 2001

$$f_{rmt} = \frac{0.5 P_{dm} A_{cm}}{V_{rm} \rho_{pm} \theta_{df}} \qquad \text{(iii).}$$

Medium i is symbolized with s, r, v, w, and d, such that s, r, v, w, and d represent surface soil, root-zone soil, vadose-zone soil, surface water, and sediments respectively; vegetative cover m is symbolized with a, f, and u, such that a, f, u represent agricultural, forest and urban respectively; VP represents vapor pressure (Pa); H is the Henry's law constant (Pa.m^3.mol^{-1}); R is the Universal gas constant (J.K^{-1}.mol^{-1}); T is the temperature (K); ρ_{ip} represents the density of particles in ith medium (kg.m^{-3}); ρ_{water} is the density of water; K_{OA} and K_{OW} are the octanol/air and octanol/water partition coefficients, respectively; f_{phlmw} and f_{phlmnw} are the volume fractions of water and non-water (nutrients, etc.) in phloem, respectively (f_{phlmw} is assumed to be 0.99); f_{ocip} represents the fraction of organic carbon in soil/sediment particles in the ith medium where medium i is s, r, v, w, or d; f_{och} and f_{ocp} are the volume fractions of organic carbon in the dissolved phase of urban film and plant leaf, respectively; f_{ww}, f_{wp}, f_{wab} represent the fractions of water, particles and aquatic biota in surface water, respectively; f_{Aap} and f_{Aair} represent the fractions of aerosol particles and pure air in the atmosphere, respectively; ρ_{pm} is the density of the plant (kg.m^{-3}) in the mth vegetative cover; K_{pa}, K_{paap}, K_{ps} are the plant/air and plant/air particle and plant/soil partition coefficients, respectively ($m^3.kg^{-1}$); β_A is the atmospheric dust load ($kg.m^{-3}$)2; ρ_{smp} is the density of surface soil particles in the m^th^ vegetative cover ($kg.m^{-3}$); f_{rma}, f_{rmw}, f_{rmp}, f_{rmt} are the fractions of air, water, particle and plant root in the root-zone soils of the m^{th} vegetative cover; f_{sma}, f_{smw}, f_{smp} are the fractions of air, water and particle in the surface soils of the m^{th} vegetative cover; f_{vma}, f_{vmw}, f_{vmp} are the fractions of air, water and particle in the vadose-zone soils of the m^{th} vegetative cover; f_{dw} and f_{dd} are the fractions of water and particles in the sediment medium; f_{iuh} is the volume fraction of urban film that is dissolved phase; f_{iuap} is the volume fraction of urban film that is aerosol particles; 0.5 is the fraction of plant in the root-zone medium; P_{dm} is the vegetation dry mass inventory ($kg.m^{-2}$); A_{cm} is the canopy area of the m^{th} vegetative cover (m^2); V_{rm} is the volume of the root-zone soil compartment of the m^{th} vegetative cover (m^3); θ_{df} is the ratio of dry vegetation mass to fresh mass.

Table B.3: First-order transport rate constants estimation for RioShed

Medium i to j/d^{-1}	**Process**	**Transport Rate Equations**	**Data Source**
Air – Water ($T_{A,w}$)	Gaseous diffusion	$T_{DA,w} = A_{Aw}(\frac{\delta_{Aw}}{Z_A D_A} + \frac{\delta_{wA}}{Z_w D_w})^{-1} Z_A^{-1} V_A^{-1}$	Yang, 2007
	Wet deposition of gas	$T_{AA,w} = A_{Aw} Z_{water}\, u_{rain}\, Z_A^{-1} V_A^{-1}$	Yang, 2007
	Wet deposition of aerosol particles	$T_{wdA,w} = A_{aw} Z_{ap}\, u_{rain}\, f_{Aap}\, Q_r Z_A^{-1} V_A^{-1}$	Yang, 2007
	Dry deposition of aerosol particles	$T_{ddA,w} = A_{Aw} Z_{ap}\, u_{depo}\, f_{Aap}\, Z_A^{-1} V_A^{-1}$	Yang, 2007
	Total	$\boldsymbol{T_{A,w} = T_{DA,w} + T_{AA,w} + T_{NwdA,w} + T_{NddA,w}}$	
Air – mth Canopy ($T_{A,cm}$: m = a, f, u)	Gaseous diffusion	$T_{DA,cm} = LAI\ A_{Acm}(\frac{\delta_{Acm}}{Z_A D_A} + \frac{\delta_{scmA}}{Z_{sm} * D_{sm} *})^{-1} Z_A^{-1} V_A^{-1}$	McKone et al., 1997
	Wet deposition of gas	$T_{AA,cm} = A_{Acm} Z_{water}\, I_{wcm}\, u_{rain}\, Z_A^{-1} V_A^{-1}$	Diamond et al., 2001; Yang, 2007
	Wet deposition of aerosol particles	$T_{NwdA,cm} = A_{Acm} Z_{ap}\, u_{rain}\, I_{wcm}\, Q_r Z_A^{-1} V_A^{-1}$	Diamond et al., 2001 California Environmental Protection Agency (CEPA), 1993; McKone et al., 1997
	Dry deposition of aerosol particles	$T_{NddA,cm} = A_{Acm} Z_{ap}\, I_{dcm}\, u_{depo}\, f_{Aap}\, Z_A^{-1} V_A^{-1}$	Diamond et al., 2001; Yang, 2007
	Stomatal transfer	$T_{StA,cm} = (5.67e - 3)^{-1} A_{cm}\ LAI\ Z_{air} D_{air}\ Z_A^{-1} V_A^{-1}$	McKone et al., 1997
	Total	$\boldsymbol{T_{A,cm} = T_{DA,cm} + T_{AA,cm} + T_{NwdA,cm} + T_{NddA,cm}}$	
Air – mth Surface Soil ($T_{A,sm}$: m = a, f, u)	Gaseous diffusion	$T_{DA,sm} = A_{Asm}(\frac{\delta_{Asm}}{Z_A D_A} + \frac{\delta_{smA}}{Z_{sm} D_{sm}})^{-1} Z_A^{-1} V_A^{-1}$	Yang, 2007
	Wet deposition of gas	$T_{AA,sm} = A_{Asm} Z_{water}\, u_{rain}\, Z_A^{-1} V_A^{-1}$	Yang, 2007
	Wet deposition of aerosol particles	$T_{NwdA,sm} = A_{Asm} Z_{ap}\, u_{rain}\, f_{Aap}\, Q_r Z_A^{-1} V_A^{-1}$	Yang, 2007
	Dry deposition of aerosol particles	$T_{NddA,sm} = A_{Asm} Z_{ap}\, u_{depo}\, f_{Aap}\, Z_A^{-1} V_A^{-1}$	Yang, 2007
	Total	$\boldsymbol{T_{A,sm} = T_{DA,sm} + T_{AA,sm} + T_{NwdA,sm} + T_{NddA,sm}}$	
Air – Urban film ($T_{A,iu}$)	Gaseous diffusion	$T_{DA,iu} = [(\frac{\delta_{Aiu}}{Z_A D_A} + \frac{\delta_{iuA}}{Z_{iu} D_{iu}})^{-1}] A_{Aiu} Z_A^{-1} V_A^{-1}$	Diamond et al., 2001
	Wet deposition of gas	$T_{AA,iu} = A_{Aiu} Z_{water}\, u_{rain}\, Z_A^{-1} V_A^{-1}$	Diamond et al., 2001
	Wet deposition of aerosol particles	$T_{NwdA,iu} = A_{Aiu} Z_{ap}\, u_{rain}\, f_{Aap}\, Q_r Z_A^{-1} V_A^{-1}$	Diamond et al., 2001
	Dry deposition of aerosol particles	$T_{NddA,iu} = A_{Aiu} Z_{ap}\, u_{depo}\, f_{Aap}\, Z_A^{-1} V_A^{-1}$	Diamond et al., 2001
	Total	$\boldsymbol{T_{A,iu} = T_{DA,iu} + T_{AA,iu} + T_{NwdA,iu} + T_{NddA,iu}}$	
Urban film – Air($T_{iu,A}$)	**Gaseous diffusion**	$\boldsymbol{T_{Diu,A} = [(\frac{\delta_{Aiu}}{Z_A D_A} + \frac{\delta_{iuA}}{Z_{iu} D_{iu}})^{-1}] A_{Aiu} Z_{iu}^{-1} V_{iu}^{-1}}$	Diamond et al., 2001

Urban film – Water ($T_{iu,w}$)	**Surface run-off**	$\boldsymbol{T_{iu,w} = T_{Aiu,w} = A_{iu}Z_{iu}u_{iurunoff}Z_{iu}^{-1}V_{iu}^{-1}}$	Diamond et al., 2001
Water – Air ($T_{w,A}$)	**Vapor diffusion**	$\boldsymbol{T_{w,A} = T_{Dw,A} = A_{Aw}(\frac{\delta_{Aw}}{Z_A D_A} + \frac{\delta_{wA}}{Z_w D_w})^{-1}Z_w^{-1}V_w^{-1}}$	Yang, 2007
Water – Sediment ($T_{w,d}$)	Diffusion	$T_{Dw,d} = A_{wd}(\frac{\delta_{wd}}{Z_w D_w} + \frac{\delta_{dw}}{Z_d D_d})^{-1}Z_w^{-1}V_w^{-1}$	CEPA, 1993
	Sediment deposition	$T_{Nw,d} = A_{wd} Z_{wp} u_{sedi} f_{wwp} Z_w^{-1}V_w^{-1}$	Yang, 2007
	Total	$\boldsymbol{T_{w,d} = T_{Dw,d} + T_{Nw,d}}$	
Sediment – Water ($T_{d,w}$)	Diffusion	$T_{Dd,w} = A_{wd}(\frac{\delta_{wd}}{Z_w D_w} + \frac{\delta_{dw}}{Z_d D_d})^{-1}Z_d^{-1}V_d^{-1}$	CEPA, 1993
	Resuspension	$T_{Nd,w} = A_{wd} Z_{wp} u_{resus} f_{wp} Z_d^{-1}V_d^{-1}$	Yang, 2007
	Total	$\boldsymbol{T_{d,w} = T_{Dd,w} + T_{Nd,w}}$	
mth Surface Soil – Air ($T_{sm,A}$: m = a, f, u)	Diffusion	$T_{Dsm,A} = A_{Asm}(\frac{\delta_{Asm}}{Z_A D_A} + \frac{\delta_{smA}}{Z_{sm} D_{sm}})^{-1}Z_{sm}^{-1}V_{sm}^{-1}$	CEPA, 1993
	Wind resuspension	$T_{Nsm,A} = A_{Asm} Z_{smp} u_{winres} f_{smp} Z_{sm}^{-1}V_{sm}^{-1}$	Yang, 2007
	Total	$\boldsymbol{T_{sm,A} = T_{Dsm,A} + T_{Nsm,A}}$	
mth Surface Soil – Water ($T_{sm,w}$: m = a, f, u)	Soil run-off	$T_{Arsm,w} = A_{sm} Z_{water} u_{srunoff} Z_{sm}^{-1}V_{sm}^{-1}$	CEPA, 1993
	Erosion run-off	$T_{Aesm,w} = A_{sm} Z_{sp} f_{smp} u_{eros} Z_{sm}^{-1}V_{sm}^{-1}$	Yang, 2007
	Total	$\boldsymbol{T_{sm,w} = T_{Arsm,w} + T_{Aesm,w}}$	
mth Surface Soil – mth Root-zone Soil ($T_{sm,rm}$: m = a, f, u)	Diffusion	$T_{Dsm,rm} = A_{smrm}(\frac{\delta_{smrm}}{Z_{sm} D_{sm}} + \frac{\delta_{rmsm}}{Z_{rm} D_{rm}})^{-1}Z_{sm}^{-1}V_{sm}^{-1}$	McKone et al., 1997
	Leaching	$T_{Asm,rm} = A_{sm} Z_{water} u_{leach} Z_{sm}^{-1}V_{sm}^{-1}$	Yang, 2007
	Total	$\boldsymbol{T_{sm,rm} = T_{Dsm,rm} + T_{Asm,rm}}$	
mth Canopy - Air	Diffusion	$T_{Dcm,A} = LAI\ A_{Acm}(\frac{\delta_{Acm}}{Z_A D_A} + \frac{\delta_{cmA}}{Z_{cm} D_{cm}})^{-1}Z_{cm}^{-1}V_{cm}^{-1}$	McKone et al., 1997
	Wind re-suspension from leaves	$T_{Acm,A} = A_{cm} Z_{ap} f_{Aap} u_{winres} Z_{cm}^{-1}V_{cm}^{-1}$	Yang, 2007
	Total	$\boldsymbol{T_{A,cm} = T_{Dcm,A} + T_{Acm,A}}$	
mth Canopy – mth Surface Soil ($T_{cm,sm}$: m = a, f, u)	Litterfall	$T_{ALcm,sm} = A_{cm} Z_{cm} u_{litter} Z_{cm}^{-1}V_{cm}^{-1}$	Diamond et al., 2001
	Wax Erosion	$T_{AEcm,sm} = A_{cm} Z_l u_{waxer} Z_{cm}^{-1}V_{cm}^{-1}$	Diamond et al., 2001
	Canopy drip	$T_{ACcm,sm} = A_{cm} Z_{ap} C_d u_{rain}(I_{wcm} - I_{wcmevap})Z_{cm}^{-1}V_{cm}^{-1}$	Diamond et al., 2001
	Total	$\boldsymbol{T_{cm,sm} = T_{ALcm,sm} + T_{AEcm,sm} + T_{ACcm,sm}}$	
mth Canopy – mth Root-zone Soil ($T_{cm,rm}$: m = a, f, u)	**Phloem flow**	$\boldsymbol{T_{cm,rm} = T_{Apcm,rm} = A_{cm}Z_{phl}u_{phl}Z_{cm}^{-1}V_{cm}^{-1}}$	Yang, 2007
mth Root-zone Soil – mth Canopy ($T_{rm,cm}$: m = a, f, u)	**Plant uptake**	$\boldsymbol{T_{rm,cm} = T_{Aurm,cm} = A_{rm}Z_{water}u_{uptake}Z_{rm}^{-1}V_{rm}^{-1}}$	McKone et al., 1997

mth Root-zone Soil – mth Surface Soil ($T_{rm,sm}$: m = a, f, u)	**Diffusion**	$\boldsymbol{T_{rm,sm} = T_{Drm,sm} = A_{smrm}\left(\frac{\delta_{rmsm}}{Z_{rm}D_{rm}} + \frac{\delta_{smrm}}{Z_{sm}D_{sm}}\right)^{-1} Z_{rm}^{-1} V_{rm}^{-1}}$	CEPA, 1993
Mth Root-zone Soil – mth Vadose-zone Soil ($T_{rm,vm}$: m = a, f, u)	**Leaching**	$\boldsymbol{T_{rm,vm} = T_{Arm,vm} = A_{rm} Z_{water} u_{leach} Z_{rm}^{-1} V_{rm}^{-1}}$	Yang, 2007

*Assume soil layer on plant/leaf surface

δ_i and δ_j are the boundary layer depths for media i and j at the ij interface, respectively (m); D_i and D_j are chemical bulk diffusivities in media i and j, respectively($m^2.d^{-1}$); V_i is the volume of compartment i (m^3); A_{ij} is the interfacial area of the ith and jth compartments (m^2); A_i is the area of the ith compartment (m^2); u_{rain}, u_{depo}, u_{winres}, u_{resus}, $u_{iurunoff}$, u_{sedi}, $u_{srunoff}$, u_{litter}, u_{leach}, u_{waxer}, u_{eros}, u_{phl}, u_{uptake} are the rates of precipitation, dry deposition, wind resuspension, sediment resuspension, urban run-off, sedimentation, surface soil runoff, litterfall, leaching/infiltration, wax erosion, surface erosion, phloem flow and plant uptake, respectively ($m.d^{-1}$); f_{Aap}, f_{wp} and f_{smp} are the volume fractions of particles in the atmosphere, surface water and mth surface soil compartments, respectively; C_d is the canopy drip parameter; I_{wcm} and I_{dcm} are the respective fractions of wet and dry deposition intercepted by the mth canopy; $I_{wcmevap}$ is the fraction of the wet deposition intercepted by the mth canopy that evaporates; Q_r is the particle scavenging ratio for rain; LAI is the leaf area index.

Table B.4: Formulae to calculate required bulk diffusivity, compartmental boundary layer thickness and/or mass transfer coefficients

Variable	**Compartment**	**Interface**	**Formula or value used**	**Reference**
Diffusion coefficient in compartment i (D_i), $m^2.d^{-1}$	Air	N/A	$8.6\times10^{-3}T^{1.75}\dfrac{[\frac{29+M_x}{29M_x}]^{\frac{1}{2}}}{[2.7+(V_x)^{\frac{1}{3}}]^2}$	California Environmental Protection Agency (CEPA), 1993
	Surface water	N/A	$\dfrac{6.5\times10^{-7}(\varphi M_y)^{\frac{1}{2}}T}{\eta_y V_x^{0.6}}$	CEPA, 1993
	Surface-zone soil (s)	N/A	$\frac{Z_{air}}{Z_s}\frac{\alpha_s^{10/3}}{\phi_s^2}D_{air}+\frac{Z_{water}}{Z_s}\frac{\beta_s^{10/3}}{\phi_s^2}D_{water}$	CEPA, 1993
	Root-zone soil (r)	N/A	$\frac{Z_{air}}{Z_r}\frac{\alpha_r^{10/3}}{\phi_r^2}D_{air}+\frac{Z_{water}}{Z_r}\frac{\beta_r^{10/3}}{\phi_r^2}D_{water}$	CEPA, 1993
	Vadose-zone soil (v)	N/A	$\frac{Z_{air}}{Z_v}\frac{\alpha_v^{10/3}}{\phi_v^2}D_{air}+\frac{Z_{water}}{Z_v}\frac{\beta_v^{10/3}}{\phi_v^2}D_{water}$	CEPA, 1993
	Sediment (d)	N/A	$\frac{Z_{air}}{Z_d}\frac{\alpha_d^{10/3}}{\phi_d^2}D_{air}+\frac{Z_{water}}{Z_d}\frac{\beta_d^{10/3}}{\phi_d^2}D_{water}$	CEPA, 1993
Boundary layer depth in compartment i (δ_i), m	Surface-zone soil (s)	N/A	$0.108D_s^{0.229}$	CEPA, 1993
	Root-zone soil (r)	N/A	$318D_r^{0.683}$	CEPA, 1993
	Water (w)	Water-sediment	0.02	CEPA, 1993
	Sediment (d)	Water-sediment	$318D_d^{0.683}$	CEPA, 1993
	Air (a)	Air-urban film	$6(\frac{l_{iu}}{v_w})^{\frac{1}{2}}$	Diamond et al., 2001
	Air (a)	Air-surface soil	5E-3	CEPA, 1993
	Air (a)	Air-vegetation	5E-3	CEPA, 1993
	Vegetation (c)	Air-vegetation	5E-6	CEPA, 1993
Mass transfer coefficient in compartment i ($\frac{D_i}{\delta_i}$), $m.d^{-1}$	Water	Air-water	0.24 when $current_w < 0.04 \times v_w^{0.67}$; $5.64(\frac{current_w^{0.969}}{d_w^{0.673}})(\frac{32}{MW_x})^{\frac{1}{2}}$ when $v_w <$ 1.9 $m.s^{-1}$; $5.64(\frac{current_w^{0.969}}{d_w^{0.673}})(\frac{32}{MW_x})^{\frac{1}{2}}e^{0.526(v_w-1.9)}$ when $v_w >$ 1.9 $m.s^{-1}$	CEPA, 1993

	Air	Air-water	$273(v_w + current_w)(\frac{18}{MW_x})^{1/2}$ when v_w + current$_w$ > 0.5 m.s^{-1}; $140(\frac{18}{MW_x})^{1/2}$ when v_w + current$_w$ < 0.5 m.s^{-1}	CEPA, 1993
	Urban film (iu)	Air-urban film	$86400 \times 10^{(0.704 \times \log K_{ow} - 11.2)/K_{aw}}$	Diamond et al., 2001
	Vegetation (c)	Air-vegetation	$86400 \times 10^{(0.704 \times \log K_{ow} - 11.2)/K_{aw}}$	Diamond et al., 2001

D_{air}, D_{water}, D_s, D_r, D_d are the diffusivities in air, water, surface-zone soil, root-zone soil and sediment, respectively, m^2.d^{-1}; δ_i is the boundary layer depth in compartment i, m; T is the air temperature, K; MW_x is the molecular weight of compound x, g.mol^{-1} ; V_x is the molecular volume of compound x, cm^3.mol^{-1}; φ is the association factor for the solvent; M_y is the molecular weight of the solvent, g.mol^{-1}; ηy is the viscosity of the solvent y, cP; Z_{air}, Z_{water}, Z_s, Z_r, Z_v, Z_d are the fugacity capacities of air, water, surface-zone soil, root-zone soil, vadose-zone soil and sediment, respectively, mol.m^{-3}.Pa^{-1}; ϕ_s, ϕ_r, ϕ_v, ϕ_d are the void fractions in the surface-zone soil, root-zone soil, vadose-zone soil and sediment, respectively; α_s, α_r, α_v, α_d are the volume fractions of air in the surface-zone soil, root-zone soil, vadose-zone soil and sediment, respectively; β_s, β_r, β_v, β_d are the volume fractions of water in the surface-zone soil, root-zone soil, vadose-zone soil and sediment, respectively; l_{iu} is the mean length of the impervious surface in the direction of the wind, m; v_w is the wind speed, m.s^{-1}; d_w is the mean depth of the surface water compartment, m; current$_w$ is the surface water current, m.s^{-1}; K_{ow} is the octanol-water partition coefficient; K_{aw} is the air-water partition coefficient.

Summary of the fugacity approach

Fugacity describes the escaping potential of trace organic contaminant from a phase. In any given single phase, contaminants typically move from regions of high concentration to low concentration. However, such a phenomenon is not always observed at phase transfer interfaces (Mackay & Paterson, 1982). Instead, contaminants move across a fugacity gradient, moving from high fugacity to low fugacity. Hence, fugacity is used in lieu of concentration to describe the movement of trace organics across environmental media wherein phase changes commonly occur. Also, the fugacity approach is considered best for those nonionic organic compounds whose partitioning is highly associated with their physicochemical properties (Rong-Rong, Che-Sheng, Zhong-Peng &Xiao-Meng, 2012). At low concentrations, the fugacity-concentration relationship is:

$$C = fZ, \qquad \text{(i)}$$

where C is concentration, mol.m^{-3}; Z is the fugacity capacity of the medium, which acts as the constant of proportionality, mol.m^{-3}.Pa^{-1}; f is the fugacity, Pa (Mackay & Paterson, 1981). At equilibrium, the chemical's fugacity in corresponding phases, *i* and *j*, are equal such that

$$f_i = f_j = f. \qquad \text{(ii)}$$

This concept is applied to the different inter-media transport mechanisms – diffusive, advective and non-advective physical transport, such as rainfall or dust deposition – as well as for reaction losses.

As an example, in RioShed, diffusive transport, between any two well-mixed (homogenous) media, *i* and *j*, with differing phases (such as the atmosphere and surface water with the phases air and water), is calculated using the utilized two-film model. This two-film model is commonly employed and has been well described (Ramaswami, Milford, & Small, 2005). In this model, a chemical diffusing from one phase to the next is considered to have differing uniform concentrations in the bulks of both media, *i* and *j*, and to also display different concentration gradients in the stagnant films at either side of the interface between the two media. Fick's law,

$$J = -D\frac{\partial C}{\partial x}, \qquad \text{(iii)}$$

(where J is the molar mass flux rate of a chemical in a given phase in mol.m^{-2}.d^{-1}; $\frac{\partial C}{\partial x}$ is the concentration gradient in mol.m^{-4}; and D is the diffusion coefficient in m^{2}.d^{-1}), is employed to explain the diffusion of a chemical from the bulk portion of the medium across the film to the interface. For diffusion across the stagnant film in medium *i* to the interface, J_i, is such that

$$J_i = -D_i\frac{(C_i - C_n)}{\delta_1}, \qquad \text{(iv)}$$

where C_i and C_n are the concentrations in medium *i* and at the interface, respectively, in mol.m^{-3}; D_i is the diffusion coefficient in medium *i*, in m^{2}.d^{-1} and; δ_i is the film thickness in m. Applying the same concept to medium *j*, and at the same time employing the aforementioned fugacity-concentration relationship, as well as assuming that the diffusive flux rates are equal such that $J = J_i = J_j$, then

$$J = -\frac{D_i}{\delta_i}(Z_i f_i - Z_i f_n) = -\frac{D_j}{\delta_j}(Z_j f_n - Z_j f_j). \qquad \text{(v)}$$

Eliminating f_n and solving for J yields

$$J = (f_j - f_i)[\frac{\delta_i}{Z_i D_i} + \frac{\delta_j}{Z_j D_j}]^{-1}. \qquad \text{(vi)}$$

The diffusive flux rate in any medium *i* is the rate of change of inventory/molar amount $(\frac{\partial N_i}{\partial t})$ due to diffusion per unit area such that

$$J_i = \frac{\partial N_i}{\partial t} \cdot \frac{1}{A} \ . \qquad \text{(vii)}$$

A is the interfacial area in m^2. Therefore, given that the fugacity in any medium *i* is given by

$$f_i = N_i V_i^{-1} Z_i^{-1}, \qquad \text{(viii)}$$

where f_i, N_i, V_i and Z_i are the fugacity in Pa, molar inventory in mol, volume in m^3 and fugacity capacity in mol.m^{-3}.Pa^{-1} of medium *i*, respectively, then the rate of change of inventory in any medium *i* due to diffusion is

$$\frac{\partial N_m}{\partial t} = A[\frac{\delta_1}{Z_1 D_1} + \frac{\delta_2}{Z_2 D_2}]^{-1} V_2^{-1} Z_2^{-1} \ N_2 - A[\frac{\delta_1}{Z_1 D_1} + \frac{\delta_2}{Z_2 D_2}]^{-1} V_1^{-1} Z_1^{-1} \ N_1. \qquad \text{(ix)}$$

In RioShed, the transport rate constants for diffusion from medium *i* to *j*, $T_{i,j}$, in which media *i* and *j* both have different phases, are calculated using

$$T_{i,j} = A[\frac{\delta_i}{Z_i D_i} + \frac{\delta_j}{Z_j D_j}]^{-1} V_i^{-1} Z_i^{-1} . \qquad \text{(x)}$$

As employed for GIM3 by Luo et al. (2007), the general formats for the computation of the various terms, for transport from medium *i* to *j*, are as follows:

Advective transport, T_{Aij}, such that $T_{Aij} = A_{ij} Z_{ic} u_i Z_i^{-1} V_i^{-1}$; (xi)

Non-diffusive/advective physical transport, T_{Nij}, such that $T_{Nij} = A_{ij} Z_{ip} u_i f_{ip} Z_i^{-1} V_i^{-1}$; (xii)

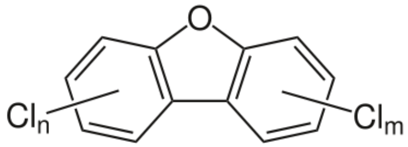
Diffusive transport, T_{Dij}, such that $T_{Dij} = A_{ij} (\frac{\delta_i}{Z_i D_i} + \frac{\delta_j}{Z_j D_j})^{-1} Z_i^{-1} V_i^{-1}$; (xiii) where δ_i and δ_j are the boundary layer depths for compartments *i* and *j* at the *ij* interface, respectively, m; D_i and D_j are chemical bulk diffusivities in compartments *i* and *j*, respectively, $m^2.d^{-1}$; V_i is the volume of compartment *i*, m^3; A_{ij} is the area of the interface between compartments *i* and *j*, m^2; u_i is the velocity of the carrying medium in the direction of interface transfer, $m.d^{-1}$; f_{ip} is the volume fraction of particles in compartment *i*; Z_i, Z_{ip} and Z_{ic} are the fugacity capacities of compartment *i*, particles in compartment *i*, and the carrying medium in compartment *i*, respectively.

Appendix C

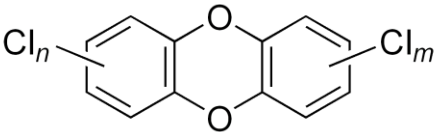
Physicochemical data for the select organics

Figure C.1: Chemical structures for the evaluated pollutants

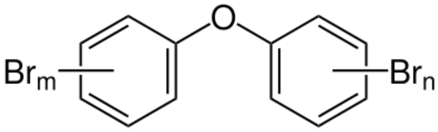
Furans



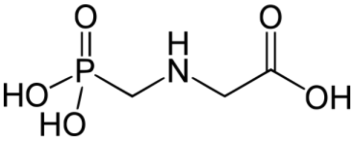
Dioxins



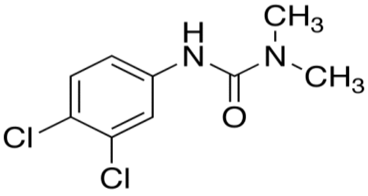
PBDEs



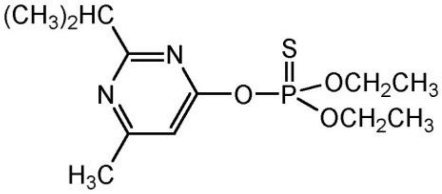
Glyphosate



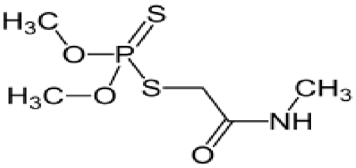
Diuron



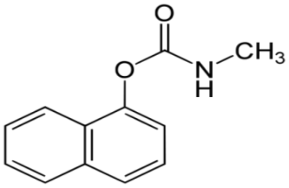
Diazinon



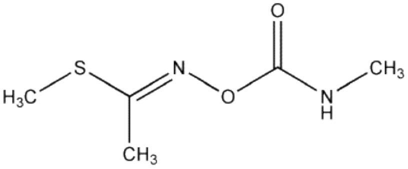
Dimethoate



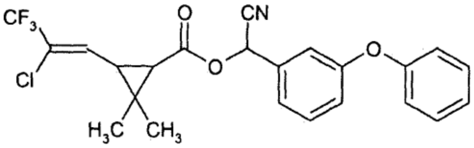
Carbaryl



Methomyl



Lambda-Cyhalothrin



Cypermethrin

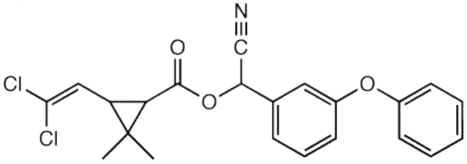


Table C.1: Physicochemical input properties for all considered poly-brominated diphenyl ethers (PBDEs)

	Poly-brominated diphenyl ethers (PBDEs)								
Parameter	**PBDE-28**	**PBDE-47**	**PBDE-99**	**PBDE-100**	**PBDE-153**	**PBDE-154**	**PBDE-183**	**PBDE-209**	**Data Source**
Henry's constant ($Pa.m^3/mol$)	1.924	1.107	0.53	0.384	0.342	0.24	7.40E-03	U	Mackay et al., 2006
Henry's constant ($Pa.m^3/mol$) - 30ºC	7.92	1.78	0.96	0.53	0.44	0.29	U	0.11	Cetin & Odabasi, 2005
Melting Point (K)	337.4	357.15	365.65	383.15	434.65	404.15-405.65	444.15-446.15	575.65	Mackay et al., 2006
Vapor Pressure (Pa)	1.57E-03	2.15E-04	3.63E-05	3.68E-05	8.87E-06	3.80E-06	4.68E-07	2.95E-09	as above
K_{oc}, Organic carbon partition coefficient (L/kg)		1.26E+06	2.36E+05		4.92E+06			3.83E+09	as above
K_{ow}, Octanol-water partition coefficient	6.31E+05	2.46E+06	5.75E+05	3.38E+05	1.20E+07	2.46E+07	1.38E+07	9.33E+09	as above
K_{aw}, Air-water partition coefficient	U	4.47E-04	U	U	U	U	U	U	as above
K_{oa}, Octanol-air partition coefficient	2.57E+09	2.75E+10	1.82E+11	1.05E+11	7.76E+11	6.05E+11	4.24E+12	U	as above
K_{paap}, Plant-air particle partition coefficient (m^3/kg)	3000	3.00E+03	3.00E+03	3.00E+03	3.00E+03	3.00E+03	3.00E+03	3.00E+03	McKone et al., 1997
K_{ps}, Plant root-soil partition coefficient (kg/kg)	5.38E-01	5.38E-01	5.38E-01	5.38E-01	5.38E-01	5.38E-01	5.38E-01	5.38E-01	CalTOX 2.3
Molecular Weight (g/mol)	406.895	4.86E+02	564.687	564.687	643.583	643.583	722.479	959.167	Mackay et al., 2006
Molecular Volume (cm^3/mol)	265.5	2.89E+02	312.1	312.1	335.4	335.4	358.7	428.6	as above
Bioconcentration factor fish/water (m^3/kg)	U	0.00E+00	U	U	U	U	U	U	as above
Atmospheric half-life (d)	5.33	1.07E+01	19.46	14.88	46.25	U	64.17	317.5	as above
Half-life in surface water (d)	60	1.50E+02	150	150	150	150	150	150	as above
Half-life in sediment (d)	240	6.00E+02	600	600	600	600	600	600	as above
Average half-life in vegetation (d)	U - 60	Half-life in surface soil/4	Half-life in surface soil/4	Half-life in surface soil/4	Half-life in surface soil/4	Half-life in surface soil/4	Half-life in surface soil/4	Half-life in surface soil/4	Juraske et al., 2008
Half-life in agricultural vegetation (d)	U - 60	3.75E+01	37.5	37.5	37.5	37.5	37.5	37.5	as above

Half-life in forest vegetation (d)	U - 60	3.75E+01	37.5	37.5	37.5	37.5	37.5	37.5	as above
Half-life in urban vegetation (d)	U - 60	3.75E+01	37.5	37.5	37.5	37.5	37.5	37.5	as above
Half-life in surface soil (d)	60	150	150	150	150	150	150	150	Mackay et al., 2006
Half-life in agricultural surface soil (d)	60	150	150	150	150	150	150	150	as above
Half-life in forest surface soil (d)	60	150	150	150	150	150	150	150	as above
Half-life in urban surface soil (d)	60	150	150	150	150	150	150	150	as above
Half-life in root-zone soil (d)	60	150	150	150	150	150	150	150	as above
Half-life in agricultural root-zone soil (d)	60	150	150	150	150	150	150	150	as above
Half-life in forest root-zone soil (d)	60	150	150	150	150	150	150	150	as above
Half-life in urban root-zone soil (d)	60	150	150	150	150	150	150	150	as above
Half-life in vadose-zone soil (d)	60	150	150	150	150	150	150	150	as above
Half-life in agricultural vadose-zone soil (d)	60	150	150	150	150	150	150	150	as above
Half-life in forest vadose-zone soil (d)	60	150	150	150	150	150	150	150	as above
Half-life in urban vadose-zone soil (d)	60	150	150	150	150	150	150	150	as above
Half-life in urban organic film (d)	60	150	150	150	150	150	150	150	as above
Half-life in biota (d)	36.5 - carp	30.1 - carp	5.6 - mussels	U	13.6 - carp	35 - carp	U	50 - carp	as above
Toxicity Equivalent Factor	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Reference Dose (mg/kg/d)	U	1.00E-04	1.00E-04	U	2.00E-04	U	U	7.00E-03	EPA, 2016
No observed effect level/ No observed adverse effect level	U	0.7	0.4	U	0.45	U	U	2.22	EPA, 2016
Oral cancer slope factor (mg/kg/d)$^{-1}$	U	U	U	U	U	U	U	7.00E-04	EPA, 2016

U – Unknown/unavailable

Table C.2: Physicochemical input properties for the remaining considered persistent pollutants

	Polychlorinated dibenzodioxins (PCDDs)		***Polychlorinated dibenzofurans (PCDFs)***		
Parameter	**2,3,7,8-TCDD**	**OCDD**	**2,3,4,7,8-PeDF**	**1,2,3,4,7,8-HxCDF**	**Data Source**
Henry's constant (Pa.m^3/mol) - 25°C	1.62	0.513	2.57	1.91	Mackay et al., 2006
Henry's constant (Pa.m^3/mol) - 30°C	U	U	U	U	N/A
Melting Point (K)	568.15	604.15	469.65	498.65-499.65	Mackay et al., 2006
Vapor Pressure (Pa)	5.75E-05	6.61E-08	5.50E-05	1.38E-05	as above
K_{oc}, Organic carbon partition coefficient (L/kg)	6.31E+06	3.17E+10	1.59E+08	6.31E+08	as above
K_{ow}, Octanol-water partition coefficient	1.15E+07	3.02E+08	1.29E+07	3.39E+07	as above
K_{aw}, Air-water partition coefficient	U	U	U	U	-
K_{oa}, Octanol-air partition coefficient	8.91E+09	6.31E+10	1.23E+10	4.37E+10	as above
K_{paap}, Plant-air particle partition coefficient (m^3/kg)	3.00E+03	3.00E+03	3.00E+03	3.00E+03	McKone et al., 1997
K_{ps}, Plant root-soil partition coefficient (kg/kg)	5.38E-01	5.38E-01	5.38E-01	5.38E-01	CalTOX 2.3
Molecular Weight (g/mol)	321.971	459.751	340.418	374.863	Mackay et al., 2006
Molecular Volume (cm^3/mol)	260.6	344.2	281.2	302.1	as above
Bioconcentration factor fish/water (m^3/kg)	1.12E+06	3.39E+07	6.17E+04	3.71E+04	as above
Atmospheric half-life (d)	3	9.6	15	5.9-22 or 58.3	as above
Half-life in surface water (d)	420	853.22	1.29E-01	1166.67 (7°C)	as above
Half-life in sediment (d)	7300-73000	7300-73000	7300-73000	7300-73000	as above
Average half-life in vegetation (d)	Half-life surface soil/4	Half-life surface soil/4	Half-life surface soil/4	Half-life surface soil/4	Juraske et al., 2008
Half-life in agricultural vegetation (d)	as above	as above	as above	as above	as above

Half-life in forest vegetation (d)	as above	as above	as above	as above	as above
Half-life in urban vegetation (d)	as above	as above	as above	as above	as above
Half-life in surface soil (d)	3650-36500	3650-36500	1825-18250	1825-18250	Mackay e al., 2006
Half-life in agricultural surface soil (d)	3650-36500	3650-36500	1825-18250	1825-18250	as above
Half-life in forest surface soil (d)	3650-36500	3650-36500	1825-18250	1825-18250	as above
Half-life in urban surface soil (d)	3650-36500	3650-36500	1825-18250	1825-18250	as above
Half-life in root-zone soil (d)	3650-36500	3650-36500	1825-18250	1825-18250	as above
Half-life in agricultural root-zone soil (d)	3650-36500	3650-36500	1825-18250	1825-18250	as above
Half-life in forest root-zone soil (d)	3650-36500	3650-36500	1825-18250	1825-18250	as above
Half-life in urban root-zone soil (d)	3650-36500	3650-36500	1825-18250	1825-18250	as above
Half-life in vadose-zone soil (d)	3650-36500	3650-36500	1825-18250	1825-18250	as above
Half-life in agricultural vadose-zone soil (d)	3650-36500	3650-36500	1825-18250	1825-18250	as above
Half-life in forest vadose-zone soil (d)	3650-36500	3650-36500	1825-18250	1825-18250	as above
Half-life in urban vadose-zone soil (d)	3650-36500	3650-36500	1825-18250	1825-18250	as above
Half-life in urban organic film (d)	3650-36500	3650-36500	1825-18250	1825-18250	as above
Half-life in biota (d)	8	15 - trout	6-69	24 - mussels	as above
Toxicity Equivalent Factor	1	3.00E-04	0.3	0.1	EPA, 2010
Reference Dose (mg/kg/d)	7.00E-10	U	U	U	EPA, 2016
No observed effect level/ No observed adverse effect level	2.00E-08	U	U	U	EPA, 2016
Oral cancer slope factor (mg/kg/d)$^{-1}$	1.50E+05	U	U	U	EPA, 2016

U – Unknown/unavailable

Table C.3: Physicochemical input properties for the current-use pesticides

	Current-Use Pesticides								
Parameter	**Organophosphates**		**Carbamates**		**Pyrethroids**		**Herbicides**		**Data Source**
	Diazinon	**Dimethoate**	**Carbaryl**	**Methomyl**	**λ-Cyhalothrin**	**Cypermethrin**	**Diuron**	**Glyphosate**	
Henry's constant (Pa.m^3/mol) - 25^{o}C	2.16E-02	1.15E-04	4.48E-05	6.48E-05	1.80E-02	1.95E-02	5.10E-05	1.41E-05	Mackay et al., 2006
Henry's constant (Pa.m^3/mol) - 30^{o}C	U	U	U	U	U	U	U	U	N/A
Melting Point (K)	U	325.15	418.15	351.15	322.35	343.15	431.15	503.15	Mackay et al., 2006
Vapor Pressure (Pa)	7.30E-03	3.63E-02	1.60E-04	6.67E-03	2.00E-07	3.23E-06	9.00E-06	1.00E-03	as above
K_{oc}, Organic carbon partition coefficient (L/kg)	2.29E+02	15.85	3.02E+02	72.44	2.47E5-3.3E5	3.47E+05	4.85E+02	2.63E+03	as above
K_{ow}, Octanol-water partition coefficient	6.46E+03	6.03	229.09	3.98	1.00E+07	4.17E+05	3.98E+02	8.71E+00	as above
K_{aw}, Air-water partition coefficient	8.58029E-06	4.56821E-08	1.77962E-08	2.57409E-08	7.15025E-06	7.7461E-06	2.0259E-08	5.60103E-09	as above
K_{oa}, Octanol-air partition coefficient	7.41E+08	11341388.14	3293680784	11728015.63	8.82428E+12	1.30946E+11	5932385514	149195607.4	as above
K_{paap}, Plant-air particle partition coefficient (m^3/kg)	3.00E+03	3.00E+03	3.00E+03	3.00E+03	3.00E+03	3.00E+03	3.00E+03	3.00E+03	McKone et al., 1997
K_{ps}, Plant root-soil partition coefficient (kg/kg)	5.38E-01	5.38E-01	5.38E-01	5.38E-01	5.38E-01	5.38E-01	5.38E-01	5.38E-01	CalTOX 2.3
Molecular Weight (g/mol)	304.345	229.258	201.221	162.21	449.85	416.297	233.093	169.074	Mackay et al., 2006
Molecular Volume (cm^3/mol)	320.2	205.6	218.7	179.9	Density=1.33 g/cm3	457.7	223.8	Density=1.74 g/cm3	as above
Bioconcentration factor fish/water (m^3/kg)	2.46E+02	100	3.02E+01	1.29	U	8.32E+02	3.02E+02	1.82E+02	as above
Atmospheric half-life (d)	1.71E-01	1.95E-01	5.25E-01	34.2	1.70E-01	0.75 (hydroyl radical)	0.12	0.125	as above
Half-life in surface water (d)	43	29	9	262	24.5 (photolysis)	5	10	70	as above
Half-life in sediment (d)	21.1	7	125	30	20	30	10	47	as above
Average half-life in vegetation (d)	10	2.95	Half-life in surface soil/4	2.5	Half-life in surface soil/4	Half-life in surface soil/4	50	60	Mackay et al., 2006; Juraske et al., 2008
Half-life in agricultural vegetation (d)	as above	as above	as above	as above	as above	as above	as above	as above	as above

Half-life in forest vegetation (d)	as above	as above	as above	as above	as above	as above	as above	as above	as above
Half-life in urban vegetation (d)	as above	as above	as above	as above	as above	as above	as above	as above	as above
Half-life in surface soil (d)	40	7	10	30	28	30	200	47	Mackay e al., 2006
Half-life in agricultural surface soil (d)	as above	as above	as above	as above	as above	as above	as above	as above	as above
Half-life in forest surface soil (d)	as above	as above	as above	as above	as above	as above	as above	as above	as above
Half-life in urban surface soil (d)	as above	as above	as above	as above	as above	as above	as above	as above	as above
Half-life in root-zone soil (d)	as above	as above	as above	as above	as above	as above	as above	as above	as above
Half-life in agricultural root-zone soil (d)	as above	as above	as above	as above	as above	as above	as above	as above	as above
Half-life in forest root-zone soil (d)	as above	as above	as above	as above	as above	as above	as above	as above	as above
Half-life in urban root-zone soil (d)	as above	as above	as above	as above	as above	as above	as above	as above	as above
Half-life in vadose-zone soil (d)	as above	as above	as above	as above	as above	as above	as above	as above	as above
Half-life in agricultural vadose-zone soil (d)	as above	as above	as above	as above	as above	as above	as above	as above	as above
Half-life in forest vadose-zone soil (d)	as above	as above	as above	as above	as above	as above	as above	as above	as above
Half-life in urban vadose-zone soil (d)	as above	as above	as above	as above	as above	as above	as above	as above	as above
Half-life in urban organic film (d)	as above	as above	as above	as above	as above	as above	as above	as above	as above
Half-life in biota (d)	32	2.95 - cabbage	22	2.5 - Bermuda grass	U	U	328	60	Mackay et al., 2006
Toxicity Equivalent Factor	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Reference Dose (mg/kg/d)	2.00E-04	2.00E-04	1.00E-02	2.50E-02	5.00E-03	1.00E-02	3.00E-03	1.00E-01	EPA, 2016; RRD, 2015
No observed effect level/ No observed adverse effect level	6.50E-02	0.05	9.6	2.5	0.5	1	0.625	10	EPA, 2016
Oral cancer slope factor (mg/kg/d)$^{-1}$	U	U	U	U	U	U	1.9E-2	U	RRD, 2015

U – Unknown/unavailable

Appendix D

Input Parameters for RioShed

Table D.1: Input parameters used in RioShed

Input Data	**Value or Estimation Equation**	**Data Source**
Universal gas constant (R), Pa.m^3/mol/K	R=8.314	
Density of water (rhow), kg/m3	rhow=1000	
Ambient air temperature (T), K	T=302.79	Meteorological Service of Jamaica (MOJ), 2015
Compartment Areas/m^2		
Area of atmosphere (AA), m^2	AA=1249e6	Forestry Department of Jamaica (FDJ), 2015
Area of surface water compartment (Aw), m^2	Aw=1.759e-3⁋×AA	FDJ, 2015
Area of agricultural compartment (Aca), m^2	Aca=2.519e-1⁋×AA	FDJ, 2015
Area of forest compartment (Acf), m^2	Acf=6.015e-1⁋×AA	FDJ, 2015
Area of urban canopy (Acu), m^2	Acu=0.3‡ × 1.448e-1⁋×AA;	Arnold & Gibbons, 1996; FDJ, 2015
Area of impervious surface (Aiu), m^2	Aiu=0.7‡ × 1.448e-1⁋×AA;	Arnold & Gibbons, 1996; FDJ, 2015
Area of sediment (Ad), m^2	Ad=Aw	-
Area of agricultural surface soil (Asa), m^2	Asa=Aca	-
Area of forest surface soil (Asf), m^2	Asf=Acf	-
Area of urban surface soil (Asu), m^2	Asu=Acu	-
Area of agricultural root soil (Ara), m^2	Ara=Aca	-
Area of forest root soil (Arf), m^2	Arf=Acf	-
Area of urban root soil (Aru), m^2	Aru=Acu	-
Area of agricultural vadose soil (Ava), m^2	Ava=Aca	-
Area of forest vadose soil (Avf), m^2	Avf=Acf	-
Area of urban vadose soil (Avu), m^2	Avu=Acu	-
Densities (kg/m^3)		
Atmospheric dust load (betaA), kg/m^3	betaA=4.96e-8†	National Environment and Planning Agency, 2013
Density of particles in soil (rhomp), kg/m^3	rhomp=2650	CalTOX 2.3
Density of particles in agricultural surface soil (rhosap), kg/m^3	rhosap=rhomp	CalTOX 2.3
Density of particles in forest surface soil (rhosfp), kg/m^3	rhosfp=rhomp	CalTOX 2.3
Density of particles in urban surface soil (rhosup), kg/m^3	rhosup=rhomp	CalTOX 2.3
Density of particles in agricultural root-zone soil (rhorap), kg/m^3	rhorap=rhomp	CalTOX 2.3
Density of particles in forest root-zone soil	rhorfp=rhomp	CalTOX 2.3

(rhorfp), kg/m^3		
Density of particles in urban root-zone soil (rhorup), kg/m^3	rhorup=rhomp	CalTOX 2.3
Density of particles in agri vadose-zone soil (rhovap), kg/m^3	rhovap=rhomp	CalTOX 2.3
Density of particles in forest vadose-zone soil (rhovfp), kg/m^3	rhovfp=rhomp	CalTOX 2.3
Density of particles in urban vadose-zone soil (rhovup), kg/m^3	rhovup=rhomp	CalTOX 2.3
Agricultural plant density (rhopa), kg/m^3	rhopa=830	CalTOX 2.3
Forest plant density (rhopf), kg/m^3	rhopf=rhopa	CalTOX 2.3
Urban plant density (rhopu), kg/m^3	rhopu=rhopa	CalTOX 2.3
Particle density in sediment (rhod), kg/m^3	rhod=2650	CalTOX 2.3
Lipid density in plants (rholp), kg/m^3	rholp=850	Diamond et al., 2001
Density of root-zone compartment (rhorm), kg/m^3	rhorm=1300	Diamond et al., 2001
Density of agricultural root-zone compartment (rhora), kg/m^3	rhora=rhorm	Diamond et al., 2001
Density of forest root-zone compartment (rhorf), kg/m^3	rhorf=rhorm	Diamond et al., 2001
Density of urban root-zone compartment (rhoru), kg/m^3	rhoru=rhorm	Diamond et al., 2001
Total suspended sediment in water (rhodw), kg/m^3	rhodw=0.088	CalTOX 2.3
Density of aquatic biota (rhoab), kg/m^3	rhoab=0	N/A – arbitrary selection
Fractions		
Deciduous fraction of forest (fdd)	ffd=0.55	FDJ, 2015
Evergreen fraction of forest (ffe)	ffe=0.45	as above
Plantation fraction of forest (ffp)	ffp=0	as above
Fraction of atmosphere occupied by aerosol particles (fAap)	fAap=betaA/rhomp	Mackay, 2001
Volume fraction of water in phloem (fphlmw)	fphlmw=0.99	McKone et al., 1997
Volume fraction of phloem that is not water (fphlmnw)	fphlmnw=0.01	McKone et al., 1997
Organic carbon fraction in pure film (foch)	foch=0.74	Diamond et al., 2001
Organic carbon fraction in plants (focpl)	focpl=0.02	Diamond et al., 2001
Organic carbon fraction in sediments (focdp)	focdp=0.02	CalTOX 2.3
Organic carbon fraction in agricultural surface soil (focsap)	focsap=0.036	Hennemann & Mantel, 1995
Organic carbon fraction in forest surface soil (focsfp)	focsfp=0.036	Hennemann & Mantel, 1995
Organic carbon fraction in urban surface soil (focsup)	focsup=0.036	Hennemann & Mantel, 1995
Organic carbon fraction in agricultural root soil (focrap)	focrap=focsap	Hennemann & Mantel, 1995
Organic carbon fraction in forest root soil (focrfp)	focrfp=focsfp	Hennemann & Mantel, 1995
Organic carbon fraction in urban root soil (focrup)	focrup=focsup	Hennemann & Mantel, 1995
Organic carbon fraction in agri vadose soil (focvap)	focvap=focsap	Hennemann & Mantel, 1995
Organic carbon fraction in forest vadose soil	focvfp=focsfp	Hennemann & Mantel,

(focvfp)		1995
Organic carbon fraction in urban vadose soil (focvup)	focvup=focsup	Hennemann & Mantel, 1995
Fraction of air in agricultural foliage (fcaa)	fcaa=0.18	Cousins and Mackay, 2000
Fraction of water in agricultural foliage (fcaw)	fcaw=0.80	Cousins and Mackay, 2000
Fraction of lipid in agricultural foliage (fcal)	fcal=0.02	Cousins and Mackay, 2000
Fraction of air in forest foliage (fcfa)	fcfa=0.18	Cousins and Mackay, 2000
Fraction of water in forest foliage (fcfw)	fcfw=0.80	Cousins and Mackay, 2000
Fraction of lipid in forest foliage (fcfl)	fcfl=0.02	Cousins and Mackay, 2000
Fraction of air in urban foliage (fcua)	fcua=0.18	Cousins and Mackay, 2000
Fraction of water in urban foliage (fcuw)	fcuw=0.80	Cousins and Mackay, 2000
Fraction of lipid in urban foliage (fcul)	fcul=0.02	Cousins and Mackay, 2000
Air content of agricultural surface soil (fsaa)	fsaa=0.068; (clay-loam)	Baver, 1963
Water content of agricultural surface soil (fsaw)	fsaw=0.339; (clay-loam)	Baver, 1963
Particle content of agricultural surface soil (fsap)	fsap=0.593; (clay-loam)	Baver, 1963
Air content of forest surface soil (fsfa)	fsfa=0.068; (clay-loam)	Baver, 1963
Water content of forest surface soil (fsfw)	fsfw=0.339; (clay-loam)	Baver, 1963
Particle content of forest surface soil (fsfp)	fsfp=0.593; (clay-loam)	Baver, 1963
Air content of urban surface soil (fsua)	fsua=0.068; (clay-loam)	Baver, 1963
Water content of urban surface soil (fsuw)	fsuw=0.339; (clay-loam)	Baver, 1963
Particle content of urban surface soil (fsup)	fsup=0.593; (clay-loam)	Baver, 1963
Air content of agricultural vadose-zone (fvaa)	fvaa=0.068; (clay-loam)	Baver, 1963
Water content of agricultural vadose-zone soil (fvaw)	fvaw=0.339; (clay-loam)	Baver, 1963
Particle content of agricultural vadose-zone soil (fvap)	fvap=0.593; (clay-loam)	Baver,1963
Air content of forest vadose-zone soil (fvfa)	fvfa=0.068; (clay-loam)	Baver,1963
Water content of forest vadose-zone soil (fvfw)	fvfw=0.339; (clay-loam)	Baver,1963
Particle content of forest vadose-zone soil (fvfp)	fvfp=0.593; (clay-loam)	Baver,1963
Air content of urban vadose-zone soil (fvua)	fvua=0.068; (clay-loam)	Baver,1963
Water content of urban vadose-zone soil (fvuw)	fvuw=0.339; (clay-loam)	Baver,1963
Particle content of urban vadose-zone soil (fvup)	fvup=0.593; (clay-loam)	Baver,1963
Fraction of particulate matter in urban film (fiuap)	fiuap=0.70	Diamond et al., 2001
Dissolved phase or pure film fraction in urban film (fiuh)	fiuh=0.30	Diamond et al., 2001
Fraction of surface water that is biota (fwab)	fwab=0	Arbitrary selection
Fraction of surface water that is particles (fwp)	fwp=rhodw/rhod	-
Water content of surface waters (fww)	fww=1-fwp-fwab	-
Water content of sediment compartment (fdw)	fdw=0.2	CalTOX 2.3
Particle fraction in sediment compartment (fdd)	fdd=0.8	CalTOX 2.3
Fraction of landscape that is surface water (fAAw)	fAAw=Aw/AA;	-
Fraction of rainfall that evaporates from agricultural canopy (Iwcaevap)	Iwcaevap=0.08	Dijk and Bruijnzeel , 2001

Fraction of rainfall that evaporates from forest canopy (Iwcfevap)	Iwcfevap=0.18	Dykes, 1997
Fraction of rainfall that evaporates from urban canopy (Iwcuevap)	Iwcuevap=0.08	Dykes, 1997
Areal densities (kg/m^2)		
Plant dry mass inventory for tropical broadleaf deciduous forest (Pdfd), kg/m^2	Pdfd=6.2	Vogt et al., 1995
Plant dry mass inventory for tropical broadleaf evergreen forest (Pdfe), kg/m^2	Pdfe=25.5	Vogt et al., 1995
Plant dry mass inventory tropical plantation forest (Pdfp), kg/m^2	Pdfp=25.5;	as above
Plant dry mass inventory for agricultural canopy (Pda), kg/m^2	Pda=2.8	CalTOX 2.3
Plant dry mass inventory for forest canopy (Pdf), kg/m^2	Pdf=ffe×Pdfe+ffd×Pdfd+ffp×Pdfp	-
Plant dry mass inventory for urban vegetation (Pdu), kg/m^2	Pdu=0.4	Diamond et al., 2001
Plant dry mass inventory for urban grassland vegetation (Pdg), kg/m^2	Pdg=0.8	Singh and Yadava, 1974
Dimensionless quantities/ratios		
Leaf area index for deciduous forest (LAIdf)	LAIdf=3.9	Asner et al., 2003
Leaf area index for evergreen forest (LAIef)	LAIef=4.8	Asner et al., 2003
Leaf area index for forested plantations (LAIpf)	LAIpf=8.7	Asner et al., 2003
Leaf area index for forest (LAIf)	LAIf=ffe×LAIef+ffd×LAIdf+ffp×LAIpf	-
Leaf area index for agricultural crops (LAIa)	LAIa=3.6	Asner et al., 2003
Leaf area index for urban vegetation (LAIu)	LAIu=1.2	Diamond et al., 2001
Rain particle scavenging ratio (Qr)	Qr=2e5	Mackay et al., 1997
Canopy drip parameter (Cd)	Cd=8.7e-4	Diamond et al., 2001
Ratio of vegetation dry to fresh mass for agricultural canopy (thetadfa)	thetadfa=0.22	CalTOX 2.3
Ratio of vegetation dry to fresh mass for forest canopy (thetadff)	thetadff= thetadfa	CalTOX 2.3
Ratio of vegetation dry to fresh mass for urban canopy (thetadfu)	thetadfu= thetadfa	CalTOX 2.3
Landscape mass fluxes (kg/m^2/d)		
Total litterfall production, dry deciduous forest (litdpr), kg/m^2/d	litdpr=1.452e-3	Sundarapandian & Swamy, 1999
Total litterfall production, dry evergreen forest (litepr), kg/m^2/d	litepr=3.255e-3	Sundarapandian & Swamy, 1999
Total litterfall production, dry plantation forest (litppr), kg/m^2/d	litppr=3.04e-3	Cuevas & Lugo, 1998
Landscape rates (m/d)		
Annual average windspeed (W), m/d	W=3.51e5	Amarakoon & Chen, 2001
Surface water current (wcur), m/d	wcur=3763.2	CalTOX 2.3
Surface water outflow rate (wout), m/d	wout=2.46e-3	Setegn et al., 2014
Groundwater recharge rate (gwrech), m/d	gwrech=1.09e-3	Setegn et al., 2014
Total litterfall rate, dry deciduous forest (ulitterfd), m/d	ulitterfd=litdpr/rhopf	-

Total litterfall rate, dry evergreen forest (ulitterfe), m/d	ulitterfe=litepr/rhopf	-
Total litterfall rate, dry plantation forest (ulitterfp), m/d	ulitterfp=litppr/rhopf	-
Total litterfall rate for forest (ulitterf), m/d	ulitterf=ffe*ulitterfe+ffd*ulitterfd+ffp *ulitterfp	-
Litterfall rate for agricultural canopy (ulittera), m/d	ulittera=1.51e-6	average of five tropical fields (Crespo et al., 2005; Cadisch et al., 1994; Christanty et al., 1996)
Litterfall rate for urban canopy (ulitteru), m/d	ulitteru=5.62e-7	Jo & McPherson, 1995
Precipitation rate (urain), m/d	urain=5.35e-3	MOJ, 2015
Dry deposition rate (udepo), m/d	udepo=259.2	Mackay et al., 1997
Wind resuspension rate (uwinres), m/d	uwinres=udepo	-
Sedimentation rate (usedi), m/d	usedi=3.962e-3	CalTOX 2.3
Sediment resuspension rate (uresus), m/d	uresus=usedi	-
Urban run-off rate (uiurunoff), m/d	uiurunoff=4.2e-7	Diamond et al., 2001
Surface soil run-off rate (usrunoff), m/d	usrunoff=2.82e-4	Setegn et al., 2014
Leaching rate (uleach), m/d	uleach=gwrech	Setegn et al., 2014
Wax erosion rate (uwaxer), m/d	uwaxer=1.932e-6	Diamond et al., 2001
Surface soil erosion rate (ueros), m/d	ueros=usrunoff/3e4	Yang, 2007
Agricultural transpiration rate (utranspa), m/d	utranspa=4.8e-3×LAIa	Yang, 2007
Forest transpiration rate (utranspf), m/d	utranspf=4.8e-3×LAIf	Yang, 2007
Urban vegetation transpiration rate (utranspu), m/d	utranspu=4.8e-3×LAIu	Yang, 2007
Sediment burial rate (usedibury), m/d	usedibury=1e-6	CalTOX 2.3
Compartment depths or lengths (m)		
Average atmospheric depth (dA), m	dA=700 (if area of the atmosphere, AA<6e8 m); dA=0.22×AA^0.4 (otherwise)	California Environmental Protection Agency (CEPA), 1993
Average depth of surface water (dw), m	dw=5	Arbitrary selection
Sediment layer depth (dd), m	dd=0.05	Santschi et al., 1990; Wang et al., 2003
Effective depth of agricultural canopy (dca), m	dca=0.5×Aca×Pda/(rhopa×thetadfa×AA)	CalTOX 2.3
Effective depth of forest canopy (dcf), m	dcf=0.5×Acf×(ffd×Pdfd+ffe×Pdfe+ffp×Pdfp)/(rhopf×thetadff×AA)	CalTOX 2.3
Effective depth of urban canopy (dcu), m	dcu=0.5×Acu×Pdu/(rhopu×thetadfu×AA)	CalTOX 2.3
Depth of agricultural surface soil (dsa), m	dsa=0.01	CEPA, 1993
Depth of forest surface soil (dsf), m	dsf=0.01	CEPA, 1993
Depth of urban surface soil (dsu), m	dsu=0.01	CEPA, 1993
Depth of agricultural root-zone soil (dra), m	dra=1	CalTOX 2.3
Depth of forest root-zone soil (drf), m	drf=1	CalTOX 2.3
Depth of urban root-zone soil (dru), m	dru=1	CalTOX 2.3
Depth of agricultural vadose-zone soil (dva), m	dva=34	CalTOX 2.3
Depth of forest vadose-zone soil (dvf), m	dvf=34	CalTOX 2.3
Depth of urban vadose soil (dvu), m	dvu=34	CalTOX 2.3
Depth of urban film (diu), m	diu=70e-9	Diamond et al., 2001
Length of impervious surface in wind direction (liu), m	liu=100	Diamond et al., 2001

Root-Zone Soil compartment fractions		
Air content of agricultural root-zone soil (fraa)	fraa=0.068; (clay-loam)	Baver, 1963
Water content of agricultural root-zone soil (fraw)	fraw=0.339; (clay-loam)	Baver, 1963

Plant root fraction in agricultural root-zone soil (frat)	frat=0;
	if required use:
	0.5×Pda/(thetadfa×dra×rhopa)
		CalTOX 2.3

Particle content of agricultural root-zone soil (frap)	frap=1-(fraa+fraw+frat)	-
Air content of forest root-zone soil (frfa)	frfa=0.068; (clay-loam)	Baver, 1963
Water content of forest root-zone soil (frfw)	frfw=0.339; (clay-loam)	Baver, 1963

Plant root fraction in forest root-zone soil (frft)	frft=0;
	if required use:
	0.5×Pdf/(thetadff×drf×rhopf)
		CalTOX 2.3

Particle content of forest root-zone soil (frfp)	frfp=1-(frfa+frfw+frft)	-
Air content of urban root-zone soil (frua)	frua=0.068; (clay-loam)	Baver, 1963
Water content of urban root-zone soil (fruw)	fruw=0.339; (clay-loam)	Baver, 1963

Plant root fraction in urban root-zone soil (frut)	frut=0;
	if required, use:
	0.5×Pdu/(thetadfu×dru×rhopu)
		CalTOX 2.3

Particle content of urban root-zone soil (frup)	frup=1-(frua+fruw+frut)	-

[⁋] The fraction of the landscape occupied by each surface compartment was provided by the Forestry Department of Jamaica (FDJ).

[⸸] Impervious surface fraction coverage for commercial land use in Olympia, Washington (Arnold & Gibbons, 1996) used in the absence of values for the Ro Cobre watershed.

[†] Mean total suspended particles in the atmosphere was obtained from measurements at six monitoring stations in the Rio Cobre watershed.

Appendix E

Matlab codes for RioShed

```
%*********************
%Run RioShed1.0
%*********************

%Instructions: 1) Complete the input file changing values as necessary
%              2) Save modified input file as user_a_input.m
%              3) Press the green button labeled 'run' under the editor
%              tab.

%U=input('Have you completed the input data, type Y for yes and N for no: ','s');
%while U=='N', fprintf('Please complete input file!\n');
%U=input('Have you completed the input data, type Y for yes and N for no: ','s');
%end;
%if 'Y', fprintf('Save file as user_a_input.m.\n'); end;
user_a_input;
b_vec_input;
c_calc_prop;
d_output;
%O=input('Do you want health impact assessment?, type Y for yes and N for no: ','s'); if O=='Y',
e_risk; end;
e_risk;


%******************************
%Input Data
%******************************

%***********************
% Standard Properties
%***********************
R=8.314; %universal gas constant (Pa.m3/mol/K)
rhow=1000; %density of water (kg/m3)

%***********************************
%Landscape Properties
%*************************************
T=302.79+2.5;                %Ambient air temperature (K)
```

```
%Compartment Areas/m2
AA=1249e6;             %area of atmosphere (m2) - Rio Cobre default
Aw=1.759e-3*AA;         %area of surface water compartment (m2) - Rio Cobre River default
Aca=2.519e-1*AA;        %area of agricultural compartment (m2)
Acf=0.5*6.015e-1*AA;        %area of forest compartment (m2)- Rio Cobre default
Acu=0.3*(0.5*6.015e-1+1.448e-1)*AA;    %area of urban canopy (m2)
Aiu=0.7*(0.5*6.015e-1+1.448e-1)*AA;    %area of impervious surface (m2)
Ad=Aw;                 %area of sediment (m2)
Asa=Aca;               %area of agri surface soil (m2)
Asf=Acf;               %area of forest surface soil (m2)
Asu=Acu;               %area of urban surface soil (m2)
Ara=Aca;               %area of agri root soil(m2)
Arf=Acf;               %area of forest root soil (m2)
Aru=Acu;               %area of urban root soil (m2)
Ava=Aca;               %area of agri vadose soil (m2)
Avf=Acf;               %area of forest vadose soil (m2)
Avu=Acu;               %area of urban vadose soil (m2)

%Densities (kg/m3)
betaA=4.96e-8;         %atmospheric dust load (kg/m3) - Jamaica default (Caltox - 6.15e-8)
rhomp=2650;            %density of particles in soil (kg/m3) - Caltox default
rhosap=rhomp;          %density of particles in agri surf soil (kg/m3)
rhosfp=rhomp;          %density of particles in forest surf soil (kg/m3)
rhosup=rhomp;          %density of particles in urban surf soil (kg/m3)
rhorap=rhomp;          %density of particles in agri root-zone soil (kg/m3)
rhorfp=rhomp;          %density of particles in forest root-zone soil (kg/m3)
rhorup=rhomp;          %density of particles in urban root-zone soil (kg/m3)
rhovap=rhomp;          %density of particles in agri vadose-zone soil (kg/m3)
rhovfp=rhomp;          %density of particles in forest vadose-zone soil (kg/m3)
rhovup=rhomp;          %density of particles in urban vadose-zone soil (kg/m3)
rhopa=830;             %agri plant density (kg/m3) - Caltox
rhopf=830;             %forest plant density (kg/m3) - Caltox
rhopu=830;             %urban plant density (kg/m3) - Caltox
rhod=2650;             %particle density in sediment (kg/m3) - Caltox default
rholp=850;             %lipid density in plants (kg/m3) - MUM
rhorm=1300;            %density of root-zone compartment (kg/m3)
rhora=rhorm;           %density of agricultural root-zone compartment (kg/m3)
rhorf=rhorm;           %density of forest root-zone compartment (kg/m3)
rhoru=rhorm;           %density of urban root-zone compartment (kg/m3)
rhodw=0.088;           %total suspended sediment in water (kg/m3)
rhoab=0;               %density of aquatic biota (kg/m3)

%Fractions (exempt root-zone soil)
ffd=0.55;              %deciduous fraction of forest
ffe=0.45;              %evergreen fraction of forest
```

```
ffp=0;                  %plantation fraction of forest
fAap=betaA/rhomp;        %calculated fraction of atmosphere occupied by aerosol particles
fphlmw=0.99;            %volume fraction of water in phloem
fphlmnw=0.01;           %volume fraction non-water (nutrients,etc.) in phloem
foch=0.74;              %organic carbon fraction in pure film - MUM
focpl=0.02;             %organic carbon fraction in plants - MUM
focdp=0.02;             %organic carbon fraction in sediments - Caltox
focsap=0.036;           %organic carbon fraction in agri surface soil - Jamaica, Worthy Park
focsfp=0.036;           %organic carbon fraction in forest surface soil - Jamaica, Worthy Park
focsup=0.036;           %organic carbon fraction in urban surface soil - Jamaica, Worthy Park
focrap=focsap;          %organic carbon fraction in agri root soil
focrfp=focsfp;          %organic carbon fraction in forest root soil
focrup=focsup;          %organic carbon fraction in urban root soil
focvap=focsap;          %organic carbon fraction in agri vadose soil
focvfp=focsfp;          %organic carbon fraction in forest vadose soil
focvup=focsup;          %organic carbon fraction in urban vadose soil
fcaa=0.18;              %fraction of air in agri canopy (foliage) - Cousins and Mackay, 2000
fcaw=0.80;              %fraction of water in agri canopy (foliage) - Cousins and Mackay 2000
fcal=0.02;              %fraction of lipid in agri canopy (foliage) - Cousins and Mackay 2000
fcaap=0;                %fraction of aerosol particles in agri canopy (foliage)
fcfa=0.18;              %fraction of air in forest canopy (foliage) - Cousins and Mackay, 2000
fcfw=0.80;              %fraction of water in forest canopy (foliage) - Cousins and Mackay 2000
fcfl=0.02;              %fraction of lipid in forest canopy (foliage) - Cousins and Mackay 2000
fcfap=0;                %fraction of aerosol particles in forest canopy (foliage)
fcua=0.18;              %fraction of air in urban canopy (foliage) - Cousins and Mackay, 2000
fcuw=0.80;              %fraction of water in urban canopy (foliage) - Cousins and Mackay 2000
fcul=0.02;              %fraction of lipid in urban canopy (foliage) - Cousins and MacKay 2000
fcuap=0;                %fraction of aerosol particles in urban canopy (foliage)
fsaa=0.068;             %air content of agricultural surface soil - clay-loam as default, Baver 1963
fsaw=0.339;             %water content of agricultural surface soil - clay-loam as default, Baver
1963
fsap=0.593;             %particle content of agricultural surface soil - 1-porosity of clay-loam as
default, Baver 1963
fsfa=0.068;             %air content of forest surface soil - clay-loam as default, Baver 1963
fsfw=0.339;             %water content of forest surface soil - clay-loam as default, Baver 1963
fsfp=0.593;             %particle content of forest surface soil - 1-porosity of clay-loam as default,
Baver 1963
fsua=0.068;             %air content of urban surface soil - clay-loam as default, Baver 1963
fsuw=0.339;             %water content of urban surface soil - clay-loam as default, Baver 1963
fsup=0.593;             %particle content of urban surface soil - 1-porosity of clay-loam as default,
Baver 1963
fvaa=0.068;             %air content of agricultural vadose-zone soil - clay-loam as default, Baver
1963
fvaw=0.339;             %water content of agricultural vadose-zone soil - clay-loam as default,
Baver 1963
```

```
fvap=0.593;            %particle content of agricultural vadose-zone soil - 1-porosity of clay-loam
as default, Baver 1963
fvfa=0.068;            %air content of forest vadose-zone soil - clay-loam as default, Baver 1963
fvfw=0.339;            %water content of forest vadose-zone soil - clay-loam as default, Baver
1963
fvfp=0.593;            %particle content of forest vadose-zone soil - 1-porosity of clay-loam as
default, Baver 1963
fvua=0.068;            %air content of urban vadose-zone soil - clay-loam as default, Baver 1963
fvuw=0.339;            %water content of urban vadose-zone soil - clay-loam as default, Baver
1963
fvup=0.593;            %particle content of urban vadose-zone soil - 1-porosity of clay-loam as
default, Baver 1963
fiuap=0.70;            %fraction of particulate matter in urban film - MUM
fiuh=0.30;             %dissolved phase or pure film fraction in urban film - MUM
fwab=0;                %fraction of surface water that is biota
fwp=3.32e-5;           %fraction of surface water that is particles
fww=1-fwp-fwab;        %water content of surface waters
fdw=0.2;               %water content of sediment compartment - Caltox
fdd=0.8;               %particle fraction in sediment compartment - Caltox
fAAw=Aw/AA;            %fraction of landscape that is surface water - Rio Cobre watershed
Iwcaevap=0.08;         %fraction of rainfall that evaporates from agri canopy (Dijk and Bruijnzeel
2001)
Iwcfevap=0.18;         %fraction of rainfall that evaporates from forest canopy (Dykes 1997)
Iwcuevap=0.08;         %fraction of rainfall that evaporates from urban canopy

%Areal densities (kg/m2)
Pdfd=6.2;                 %plant dry mass inventory for tropical broadleaf deciduous forest
(kg/m2) - Vogt et al. 1995
Pdfe=25.5;                %plant dry mass inventory for tropical broadleaf evergreen forest
(kg/m2) - Vogt et al. 1995
Pdfp=25.5;                %plant dry mass inventory tropical plantation forest (kg/m2) - default
for evergreen forest
Pda=2.8;                  %plant dry mass inventory for agricultural canopy (kg/m2) - default in
Caltox
Pdf=ffe*Pdfe+ffd*Pdfd+ffp*Pdfp; %plant dry mass inventory for forest canopy (kg/m2)
Pdu=0.4;                  %plant dry mass inventory for urban vegetation (kg/m2) - MUM

%Dimensionless quantities/ratios
LAIdf=3.9;                %Leaf area index for deciduous forest - Asner et al 2003
LAIef=4.8;                %Leaf area index for evergreen forest - Asner et al 2003
LAIpf=8.7;                %Leaf area index for forested plantations - Asner et al 2003
LAIf=ffe*LAIef+ffd*LAIdf+ffp*LAIpf; %Leaf area index for forest
LAIa=3.6;                 %Leaf area index for agricultural crops - Asner et al 2003
LAIu=1.2;                 %Leaf area index for urban vegetation - MUM
Qr=2e5;                   %Rain particle scavenging ratio - MacKay et al. 1997
Cd=8.7e-4;                %canopy drip parameter - MUM
```

```
thetadff=0.22;              %ratio of vegetation dry to fresh mass for forest canopy - Caltox
default
thetadfa=0.22;              %ratio of vegetation dry to fresh mass for agricultural canopy - Caltox
default
thetadfu=0.22;              %ratio of vegetation dry to fresh mass for urban canopy - Caltox
default

%Landscape mass fluxes (kg/m2/d)
litdpr=1.452e-3;       %total litterfall production, dry deciduous forest(kg/m2/d)
litepr=3.255e-3;       %total litterfall production, dry evergreen forest (kg/m2/d)
litppr=3.04e-3;        %total litterfall production, dry plantation forest (kg/m2/d)- Cuevas & Lugo
1998 (For. Ecol. & Managem.)

%Landscape rates (m/d)
W=3.51e5;              %Annual average windspeed (m/d)-Norman Manley Airport default
wcur=3763.2;           %surface water current (m/d) - Caltox default
wout=2.46e-3;          %surface water outflow rate (m/d) - Rio Cobre watershed, Setegn et al
2014
gwrech=1.09e-3;        %groundwater recharge rate (m/d) - Rio Cobre watershed, Setegn et al
2014
ulitterfd=litdpr/rhopf;  %total litterfall rate, dry deciduous forest (m/d)
ulitterfe=litepr/rhopf;  %total litterfall rate, dry evergreen forest (m/d)
ulitterfp=litppr/rhopf;  %total litterfall rate, dry plantation forest (m/d)
ulitterf=ffe*ulitterfe+ffd*ulitterfd+ffp*ulitterfp; %total litterfall rate for forest (m/d)
ulittera=1.51e-6;      %litterfall rate for agricultural canopy (m/d) - average of five tropical fields
ulitteru=5.62e-7;      %litterfall rate for urban canopy (m/d) - lower estimate urban grass, Jo &
McPherson 1995 - Chicago
urain=5.35e-3;         %precipitation rate (m/d)
udepo=259.2;           %dry deposition rate (m/d) - MacKay et al. 1997
uwinres=udepo;         %wind resuspension rate (m/d)
usedi=3.962e-3;        %sedimentation rate (m/d) - Caltox
uresus=usedi;          %sediment resuspension rate (m/d)
uiurunoff=4.2e-7;      %urban run-off rate (m/d) - MUM
usrunoff=2.82e-4;      %surface soil run-off rate (m/d) - Rio Cobre watershed, Setegn et al 2014
uleach=gwrech;         %leaching rate (m/d) - default aquifer recharge rate for Rio Cobre
watershed (Setegn et al 2014)
uwaxer=1.932e-6;       %wax erosion rate (m/d)- MUM
ueros=usrunoff/3e4;    %surface soil erosion rate (m/d) - GIM3
utranspa=4.8e-3*LAIa;  %transpiration rate (m/d) - GIM3
utranspf=4.8e-3*LAIf;  %transpiration rate (m/d) - GIM3
utranspu=4.8e-3*LAIu;  %transpiration rate (m/d) - GIM3
usedibury=1e-6;        %sediment burial rate (m/d) - Caltox

%Compartment depths or lengths (m)
dA=700; if AA<6e8, dA=0.22*AA^0.4; end; %average atmospheric depth (m)
dw=5;                  %average depth of surface water (m)
```

```
dd=0.05;            %sediment layer depth (m)
dca=0.5*Aca*Pda/(rhopa*thetadfa*AA);            %effective depth of agricultural canopy (m)
dcf=0.5*Acf*(ffd*Pdfd+ffe*Pdfe+ffp*Pdfp)/(rhopf*thetadff*AA);   %effective depth of forest canopy (m)
dcu=0.5*Acu*Pdu/(rhopu*thetadfu*AA);            %effective depth of urban canopy (m)
dsa=0.01;           %depth of agricultural surface soil (m)
dsf=0.01;           %depth of forest surface soil (m)
dsu=0.01;           %depth of urban surface soil (m)
dra=1;              %depth of agricultural root-zone soil (m)
drf=1;              %depth of forest root-zone soil (m)
dru=1;              %depth of urban root-zone soil (m)
dva=34;             %depth of agricultural vadose-zone soil (m) - Caltox default
dvf=34;             %depth of forest vadose-zone soil (m) - Caltox default
dvu=34;             %depth of urban vadose soil (m) - Caltox default
diu=70e-9;          %depth of urban film (m) - MUM
liu=100;            %length of impervious surface in wind direction (m)

%Root-Zone Soil compartment fraction data
fraa=0.068;                 %air content of agricultural root-zone soil - clay-loam as default, Baver 1963
fraw=0.339;                 %water content of agricultural root-zone soil - clay-loam as default, Baver 1963
frat=0;                     %plant root fraction in agricultural root-zone soil; if required use: 0.5*Pda/(thetadfa*dra*rhopa) - Caltox
frap=1-(fraa+fraw+frat);        %particle content of agricultural root-zone soil - 1-porosity of clay-loam as default, Baver 1963
frfa=0.068;                 %air content of forest root-zone soil - clay-loam as default, Baver 1963
frfw=0.339;                 %water content of forest root-zone soil - clay-loam as default, Baver 1963
frft=0;                     %plant root fraction in forest root-zone soil; if required use: 0.5*Pdf/(thetadff*drf*rhopf) - Caltox
frfp=1-(frfa+frfw+frft);        %particle content of forest root-zone soil - 1-porosity of clay-loam as default, Baver 1963
frua=0.068;                 %air content of urban root-zone soil - clay-loam as default, Baver 1963
fruw=0.339;                 %water content of urban root-zone soil - clay-loam as default, Baver 1963
frut=0;                     %plant root fraction in urban root-zone soil; if required, use: 0.5*Pdu/(thetadfu*dru*rhopu) - Caltox
frup=1-(frua+fruw+frut);        %particle content of urban root-zone soil - 1-porosity of clay-loam as default, Baver 1963
```

```
%**********************************
%Chemical Properties
%**********************************
Name_chem='Dimethoate';     %Chemical name
H=1.15e-4;               %Henry's constant (Pa.m3/mol)
MP=325.15;               %Melting Point (K)
VP=3.63e-2;              %Vapor Pressure (Pa)
Koc=15.85;               %Organic carbon partition coefficient (L/kg) - if unavailable use: Kd/foc or
0.41*Kow
Kow=6.03;                %Octanol-water partition coefficient
Kaw=H/(R*T);             %Air-water partition coefficient - if unavailable, use: H/(RT) or
10^(log10(Kow/Koa)-0.1+(0.3*log10(Kow)-1.20)) when Kow>1e4 and 10^(log10(Kow/Kaw)-
0.1 when Kow<1e4
Koa=10^(log10(Kow/Kaw)-0.1+(0.3*log10(Kow)-1.20));          %Octanol-air partition
coefficient - If unavailable, use: Kow*(RT)/H; or 10^(log10(Kow/Kaw)-0.1+(0.3*log10(Kow)-
1.20)) when Kow>1e4 and 10^(log10(Kow/Kaw)-0.1 when Kow<1e4 - MacKay 2006
Kpaap=3000;              %Plant-air particle partition coefficient (m3/kg) - Caltox
Kps=7.7*(Kow^(-0.578)); %Plant root-soil partition coefficient (kg/kg) - If unavailable, use:
7.7*(Kow^(-0.578)) - Caltox
MW=229.258;              %Molecular Weight (g/mol)
MV=205.6;                %Molecular Volume (cm3/mol)
BCF=0;                   %Bioconcentration factor fish/water (m3/kg) - if unavailable, use
BCF=0.048*Kow
HlA=1.95e-1;             %Atmospheric half-life (d)
Hlw=29;                  %Half-life in surface water (d)
Hld=7;                   %Half-life in sediment (d)
Hlc=2.95;                %Average half-life in vegetation (d); if unavailable, use HLs/4 - Juraske et al.
2008
Hlca=Hlc;                %Half-life in agricultural vegetation (d)
Hlcf=Hlc;                %Half-life in forest vegetation (d)
Hlcu=Hlc;                %Half-life in urban vegetation (d)
Hls=7;                   %Half-life in surface soil (d)
Hlsa=Hls;                %Half-life in agricultural surface soil (d)
Hlsf=Hls;                %Half-life in forest surface soil (d)
Hlsu=Hls;                %Half-life in urban surface soil (d)
Hlr=7;                   %Half-life in root-zone soil (d)
Hlra=Hlr;                %Half-life in agricultural root-zone soil (d)
Hlrf=Hlr;                %Half-life in forest root-zone soil (d)
Hlru=Hlr;                %Half-life in urban root-zone soil (d)
Hlv=7;                   %Half-life in vadose-zone soil (d)
Hlva=Hlv;                %Half-life in agricultural vadose-zone soil (d)
Hlvf=Hlv;                %Half-life in forest vadose-zone soil (d)
Hlvu=Hlv;                %Half-life in urban vadose-zone soil (d)
Hlh=7;                   %Half-life in urban organic film
```

```
%********************
%Source Terms (mol/d)
%********************

SA=10/MW;   %Source term to atmosphere (mol/d) - 3.65kg/y
Sw=0;   %Source term to surface water (mol/d)
Sd=0;   %Source term to sediment (mol/d)
Siu=0;  %Source term to urban impervious surface (mol/d)
Sca=0;  %Source term to agricultural canopy (mol/d)
Scf=0;  %Source term to forest canopy (mol/d)
Scu=0;  %Source term to urban canopy (mol/d)
Ssa=0;  %Source term to agricultural surface soil (mol/d)
Ssf=0;  %Source term to forest surface soil (mol/d)
Ssu=0;  %Source term to urban surface soil (mol/d)
Sra=0;  %Source term to agricultural root-zone soil (mol/d)
Srf=0;  %Source term to forest root-zone soil (mol/d)
Sru=0;  %Source term to urban root-zone soil (mol/d)
Sva=0;  %Source term to agricultural vadose-zone soil (mol/d)
Svf=0;  %Source term to forest vadose-zone soil (mol/d)
Svu=0;  %Source term to urban vadose-zone soil (mol/d)


%************************
%Initial conditions (mol)
%************************
NAin=0;     %Atmospheric inventory at time 0s (mol)
Nwin=0;     %Surface water inventory at time 0s (mol)
Ndin=0;     %Sediment inventory at time 0s (mol)
Niuin=0;    %Urban Film inventory at time 0s (mol)
Ncain=0;    %Agricultural canopy inventory at time 0s (mol)
Ncfin=0;    %Forest canopy inventory at time 0s (mol)
Ncuin=0;    %Urban canopy inventory at time 0s (mol)
Nsain=0;    %Agricultural surface soil inventory at time 0s (mol)
Nsfin=0;    %Forest surface soil inventory at time 0s (mol)
Nsuin=0;    %Urban surface soil inventory at time 0s (mol)
Nrain=0;    %Agricultural root-zone soil inventory at time 0s (mol)
Nrfin=0;    %Forest root-zone soil inventory at time 0s (mol)
Nruin=0;    %Urban root-zone soil inventory at time 0s (mol)
Nvain=0;    %Agricultural vadose-zone soil inventory at time 0s (mol)
Nvfin=0;    %Forest vadose-zone soil inventory at time 0s (mol)
Nvuin=0;    %Urban vadose-zone soil inventory at time 0s (mol)
```

```
%******************************
%Vectorize Input Data
%******************************

Vec_A=[AA,Aw,Ad,Aiu,Aca,Acf,Acu,Asa,Asf,Asu,Ara,Arf,Aru,Ava,Avf,Avu];
%1x16 compartmental areas (m2)
Vec_d=[dA,dw,dd,diu,dca,dcf,dcu,dsa,dsf,dsu,dra,drf,dru,dva,dvf,dvu];          %1x16
compartmental depths (m)
Vec_HL=[HlA,Hlw,Hld,Hlh,Hlca,Hlcf,Hlcu,Hlsa,Hlsf,Hlsu,Hlra,Hlrf,Hlru,Hlva,Hlvf,Hlvu];
%1x16 compartment half-lives (d)
Vec_fcm=[fcaa,fcfa,fcua,fcaw,fcfw,fcuw,fcal,fcfl,fcul,fcaap,fcfap,fcuap];          %1x12
canopy fractions
Vec_fma=[fsaa,fsfa,fsua,fraa,frfa,frua,fvaa,fvfa,fvua];                    %1x9 air content
of soil
Vec_fmw=[fsaw,fsfw,fsuw,fraw,frfw,fruw,fvaw,fvfw,fvuw];                         %1x9
water content of soil
Vec_fmp=[fsap,fsfp,fsup,frap,frfp,frup,fvap,fvfp,fvup];                    %1x9 particle
fraction of soil
Vec_fra=[fraa,frfa,frua];                                          %1x3 air content of root
soil
Vec_frw=[fraw,frfw,fruw];                                           %1x3 water content of
root soil
Vec_Pdc=[Pda,Pdf,Pdu];                                              %1x3 plant drymass
inventory (kg/m2)
Vec_rhop=[rhopa,rhopf,rhopu];                                         %1x3 densities of
plants in mth canopy (kg/m3)
Vec_frt=[frat,frft,frut];                                         %1x3 plant root fraction in
mth root-zone soil - Caltox
Vec_frp=[frap,frfp,frup];                                            %1x3 particle fraction of
root-zone soil - Caltox                                        %1x3 particle fraction in root
soil
Vec_ftm=[0,0,0,Vec_frt,0,0,0];                                        %1x9 fraction of plant
roots in mth soil
Vec_urates=[urain,udepo,uwinres,usedi,uresus,uiurunoff,usrunoff,ulittera,ulitterf,ulitteru,uleach,
uwaxer,ueros,utranspa,utranspf,utranspu,usedibury]; %1x17 landscape rates (m/d)
Vec_dfr=[thetadfa,thetadff,thetadfu];                                   %1x3 plant dry to
fresh mass ratio
Vec_focmp=[focsap,focsfp,focsup,focrap,focrfp,focrup,focvap,focvfp,focvup];
%1x9 OC fraction in soils
Vec_rhomp=[rhosap,rhosfp,rhosup,rhorap,rhorfp,rhorup,rhovap,rhovfp,rhovup];
%1x9 densities of particles in soil compartments (kg/m3)
Vec_rhosmp=Vec_rhomp(1:3);                                              %1x3 densities of
particles in surface soil (kg/m3)
Vec_rhorm=[rhora,rhorf,rhoru];                                        %1x3 densities of root-
zone soil compartments (kg/m3)
Vec_LAIc=[LAIa,LAIf,LAIu];                                              %1x3 LAI
```

```
Vec_Kij=[Koc,Kow,Koa,Kpaap,Kps,Kaw];                                    %1x5
partition coefficients
Vec_uphl=4.8e-4.*(Vec_LAIc);                                    %1x3 phloem flow
rates
Vec_Iwcevap=[Iwcaevap,Iwcfevap,Iwcuevap];                              %1x3 Fraction
of intercepted wet deposition that evaporates from canopy

%************************************
%Compute Landscape Properties
%************************************

%****************************
%Compartment Volumes (m3)
%****************************

Vec_V=Vec_A.*Vec_d.*[1,1,1,1,Vec_LAIc,1,1,1,1,1,1,1,1,1];   %Compartment volumes (m3)


%*********************************************
%Fugacity Capacities (FC) in mol/m3/Pa
%*********************************************

Zwater=1/H;                           %FC Pure water - Caltox
Zair=1/(R*T);                         %FC Pure air - Caltox
if T<MP, Zap=3e6*Zair*exp(6.81*(1-MP/T))/VP; else Zap=3e6*Zair/VP; end;    %FC Aerosol
particles - Caltox
Zdp=1e-3*Vec_Kij(1)*Zwater*rhod*focdp;            %FC Particles in sediment - Caltox
Vec_Zmp=(1e-3*Vec_Kij(1)*Zwater).*(Vec_rhomp.*Vec_focmp); %1x9 FC Particles in soil -
Caltox
Vec_Zrmp=Vec_Zmp(4:6);                          %1x3 FC Particles in root soil
Zab=1e-3*BCF*rhoab*Zwater;                        %FC Aquatic biota - GIM3
Zlc=focpl*Zwater*Vec_Kij(2);                    %FC leaf cuticle - MUM, Caltox
Zl=Kow*Zwater;                            %FC lipid
Zphl=0.9*Zwater;                          %FC Phloem - Caltox
Zh=Zair*Vec_Kij(3)*foch;                       %FC Urban film - MUM
Vec_Kpa=(0.5+(0.4+0.01*Vec_Kij(2))*Zwater/Zair)./Vec_rhop;

%Bulk Fugacity Capacities in mol/m3/Pa
Zw=fww*Zwater+fwp*Zdp+fwab*Zab;                                %FC Bulk surface water -
Caltox
ZA=fAap*Zap+(1-fAap)*Zair;                                %FC Atmosphere - Caltox
Vec_Zcm=Vec_fcm(1:3)*Zair+Vec_fcm(4:6)*Zwater+Vec_fcm(7:9)*Zl+Vec_fcm(10:12)*Zap;
%1x3 FC mth canopy - Caltox
Vec_Zt=((Vec_Kij(5).*Vec_rhop)./(Vec_rhomp(4:6).*Vec_frp)).*(Zair*Vec_fra+Zwater*Vec_f
rw+(Vec_Zrmp.*Vec_frp));  %1x3 FC mth plant roots
Vec_Ztm=[0,0,0,Vec_Zt(1:3),0,0,0];
```

```
Vec_Zmm=Zair.*Vec_fma+Zwater.*Vec_fmw+Vec_fmp.*Vec_Zmp+Vec_ftm.*Vec_Ztm;
%1x9 FC soils - Caltox
Zd=fdw*Zwater+fdd*Zdp;                                    %FC sediment - Caltox
Ziu=fiuh*Zh+fiuap*Zap;                                   %FC impervious surface - MUM


%*****************************************
%Calculate Diffusion Coefficients (m^2/d)
%*****************************************

Dair=0.001*T^1.75*sqrt((28.97+MW)/(28.97*MW))/((20.1^(1/3)+MV^(1/3))^2);   %calulated
diffusion coefficient in pure air (m2/d) - Caltox
Dwater=7.4e-8*sqrt(2.6*18)*T/(0.80*MV^(0.6));                    %calculated diffusion
coefficient in pure water at 30 deg cel (m2/d) - Caltox

ZaiD=Zair*Dair;
ZwaD=Zwater*Dwater;
Vec_fmpor=Vec_fma+Vec_fmw;

DA=ZaiD/ZA;            %Diffusion coefficient in atmosphere (m2/d) - GIM3
Dw=ZwaD/Zw;             %Diffusion coefficient in surface water (m2/d) - GIM3
Dd=ZwaD*fdw^(4/3)/Zd;   %Diffusion coefficient in sediment (m2/d) - Caltox
Vec_Dmm=(ZaiD.*(Vec_fma.^(10/3))+ZwaD.*(Vec_fmw.^(10/3)))./(Vec_Zmm.*(Vec_fmpor).
^2);    %1x9 Effective diffusion coefficient in soils (m2/d) - Caltox


%***************************
%Estimate Parameters
%***************************

%Compartment boundary layer depths (m)
Vec_deltasm=0.108*(Vec_Dmm(1:3).^(0.229));    %calculated surface soil boundary layer depth
(m) - Caltox
Vec_deltarm=318*(Vec_Dmm(4:6).^(0.683));      %calculated root soil boundary layer depth
(m) - Caltox
if (wcur/86400)/(W/86400)^0.673<0.04, Uaw_w=0.24; elseif W<=1.64e5,
Uaw_w=5.64*((wcur/86400)^0.969/dw^0.673)*sqrt(32/MW); else
Uaw_w=5.64*(wcur/86400)^0.969/dw^0.673*sqrt(32/MW)*exp(0.526*(W/86400-1.9)); end;
%water-side mass trans coeff (m/d))
if (wcur+W)<4.32e4, Uaw_a=140*sqrt(18/MW); else
Uaw_a=273*(wcur+W)/86400*sqrt(18/MW); end; %air-side mass trans coeff (m/d)
deltaaw=Dair/Uaw_a;                       %air-side atmos-wat boundary layer depth (m) - Caltox
deltawa=Dwater/Uaw_w;                       %water-side atmos-wat boundary layer depth (m) -
Caltox
deltadw=318*(Dd^(0.683));                   %calculated sediment-side wat-sed boundary layer
depth (m) - Caltox
```

```
deltaAiu=6*sqrt(liu*86400/W);            %calculated air-side air-film boundary layer depth (m)
- MUM
Uiu=86400*10^(0.704*log10(Kow)-11.2)/Kaw;     %film-side mass trans coeff (m/d)
Ulc=86400*10^(0.704*log10(Kow)-11.2)/Kaw;     %cuticle-side atm-canopy mass trans coeff
(m/d)
deltaAcm=0.005;          %airside atmos-canopy boundary layer depth (m) - Caltox
deltacmA=5e-6;           %canopy atmos-canopy boundary layer depth (m) - Caltox
deltaAsm=0.005;          %airside atmosphere-surface soil boundary layer depth (m) - Caltox
deltawd=0.02;            %waterside water-sediment boundary layer depth (m) - Caltox

%Diffusion mass transfer coefficients (MTC) (mol/m2/Pa/d)
Yaw_a=ZA*DA/deltaaw;       %air-side atmos-wat diff MTC - Caltox
Yaw_w=Zw*Dw/deltawa;       %water-side atmos-wat diff MTC - Caltox
Yaw=(1/Yaw_w+1/Yaw_a)^-1;   %atmos-wat diff MTC - Caltox
Ywd_w=Zw*Dwater/deltawd;    %water-side wat-sed diff MTC - Caltox
Ywd_d=Zd*Dd/deltadw;       %sediment-side wat-sed diff MTC - Caltox
Ywd=(1/Ywd_w+1/Ywd_d)^-1;   %wat-sed diff MTC - Caltox
YAiu_A=ZA*Dair/deltaAiu;    %air-side atm-film diff MTC - MUM
YAiu_iu=Zh*Uiu;            %film-side atm-film diff MTC - MUM
YAiu=(1/YAiu_A+1/YAiu_iu)^-1;   %atm-film diff MTC - MUM
YAcm_A=Zair*Dair/deltaAcm;      %air-side atm-can diff MTC
YAcm_cm=Zlc*Ulc;               %leaf-side atm-can diff MTC - MUM
YAcm=(1/YAcm_A+1/YAcm_cm)^-1;   %atm-can diff MTC - MUM
Vec_PzmmDmm=Vec_Zmm.*Vec_Dmm;   %1x9 vector
Vec_YAcm_cm=Vec_PzmmDmm(1:3)./deltacmA; %1x3 vector of canopy-side atm-can diff
MTC
Vec_YAcm=(1/YAcm_A+1./Vec_YAcm_cm).^-1; %1x3 vector of atm-can diff MTC - Caltox
YAsm_A=ZA*Dair/deltaAsm;                 %air-side atm-surf soil diff MTC - Caltox
Vec_YAsm_sm=Vec_PzmmDmm(1:3)./Vec_deltasm; %1x3 vector of surf soil-side atm-surf
soil diff MTC - Caltox
Vec_YAsm=(1/YAsm_A+1./Vec_YAsm_sm).^-1; %1x3 vector of atm-surf soil diff MTC -
Caltox
Vec_Ysmrm_sm=Vec_PzmmDmm(1:3)./Vec_deltasm; %1x3 vector of surf soil-side surf-root
soil diff MTC - Caltox
Vec_Ysmrm_rm=Vec_PzmmDmm(4:6)./Vec_deltarm; %1x3 vector of root soil-side surf-root
soil diff MTC - Caltox
Vec_Ysmrm=(1./Vec_Ysmrm_sm+1./Vec_Ysmrm_rm).^-1;    %1x3 vector of surf-root soil diff
MTC - Caltox

%Interception factors
Vec_Idc=1-exp(-2.8*Vec_Pdc);     %dry deposition interception factor for canopies
Vec_Iwc=1-exp(-0.5*Vec_LAIc);    %wet deposition interception fraction for canopies - assume
canopy is not saturated during rain event - Bulcock and Jewitt 2012 (Hydrol. Earth Syst. Sci.)
```

```
%**********************************
%Calculate Reaction rates (1/d)
%**********************************

Vec_adjR=ones(1,16);                              %1by16 array of ones
Vec_adjR(3)=Zwater*fdw/Zd;                        %change column 3
Vec_adjR(11:16)=(Zwater.*Vec_fmw(4:9))./Vec_Zmm(4:9);        %optional change columns
11:16
Vec_R=(0.693./Vec_HL).*Vec_adjR;                  %1by16 Compartment Reaction rates
vector (1/d)- Caltox


%************************************
%Calculate Transport Rates (mol/d)
%************************************

%****Precursors****
PzaDa=ZA*DA;
Pzava=ZA*Vec_V(1);
Pzwur=Zwater*Vec_urates(1);
Pzwusr=Zwater*Vec_urates(7);
Vec_Pzwut=Zwater.*Vec_urates(14:16);
Pzwul=Zwater*Vec_urates(11);
Vec_Pzpup=Zphl.*Vec_uphl;
PzufQ=Zap*Vec_urates(1)*fAap*Qr;
Pzudf=Zap*Vec_urates(2)*fAap;
Vec_Pzmmdmm=Vec_Zmm.*Vec_d(8:16);                 %1x9 vector
Vec_Pzcmdcm=Vec_Zcm.*Vec_d(5:7);                  %1x3 vector
Vec_PzCurI=Zap*Cd*Vec_urates(1).*(Vec_Iwc-Vec_Iwcevap); %1x3 vector
fuZ=fAap*Vec_urates(3)*Zap;
Vec_fuZs=Vec_urates(3)*fAap.*Vec_Zmm(1:3);
Pzluw=Zlc*Vec_urates(12);
PzwZQZf=Pzwur+PzufQ+Pzudf;

%**** Transport Rate Constants (mol/d)****
TAw=(Aw/Pzava)*(Yaw+PzwZQZf);          %Transport rate constant for atmosphere to water
TwA=Yaw/(Zw*dw);                       %Transport rate constant for water to atmosphere
Twd=(Ywd+Zdp*fwp*Vec_urates(4))/(dw*Zw);   %Transport rate constant for water to
sediment
Tdw=(Ywd+Zdp*fdd*Vec_urates(5))/(dd*Zd);   %Transport rate constant for sediment to water
Tiuw=Vec_urates(6)/diu;                %Transport rate constant for urban film to surface water
TAiu=(Aiu/Pzava)*(YAiu+PzwZQZf);       %Transport rate constant for atmosphere to urban
film
TiuA=YAiu/(diu*Ziu);                   %Transport rate constant for film to atmosphere
```

```
Vec_TAcm=(Vec_A(5:7)./Pzava).*((Vec_YAcm+ZaiD/5.67e-
3).*Vec_LAIc+(Pzwur+PzufQ).*Vec_Iwc+Pzudf.*Vec_Idc); %Transport rate constant for
atmos to mth canopy - Assume soil layer on plants
Vec_TAsm=(Vec_A(8:10)./Pzava).*(Vec_YAsm+PzwZQZf);      %1x3 Transport rate constant
for atmosphere to mth surface soil
Vec_TcmA=(Vec_LAIc.*Vec_YAcm+fuZ*Vec_Idc)./Vec_Pzcmdcm; %1x3 Transport rate
constant for canopy to atmos - GIM 3
Vec_TsmA=(Vec_YAsm+Vec_fuZs)./Vec_Pzmmdmm(1:3);        %1x3 Transport rate constant
for surface soil to atmos
Vec_Tcmsm=(Vec_urates(8:10)./Vec_d(5:7))+((Pzluw+Vec_PzCurI)./Vec_Pzcmdcm);     %1x3
Transport rate constant for mth canopy to same surface soil
Vec_Tcmrm=Vec_Pzpup./Vec_Pzcmdcm;                                    %1x3 Transport rate
constant for agri canopy to same root-zone soil
Vec_Tsmw=(Pzwusr+Vec_Zmp(1:3).*Vec_fmp(1:3).*Vec_urates(13))./Vec_Pzmmdmm(1:3);
%1x3 Transport rate constant for mth surface soil to water
Vec_Tsmrm=(Vec_Ysmrm+Pzwul)./Vec_Pzmmdmm(1:3);   %1x3 Transport rate constant for
mth surface soil to same root-zone soil
Vec_Trmsm=Vec_Ysmrm./Vec_Pzmmdmm(4:6);          %1x3 Transport rate constant for mth
root-zone soil to same surface soil
Vec_Trmcm=Vec_Pzwut./Vec_Pzmmdmm(4:6);          %1x3 Transport rate constant for forest
root-zone soil to same cano
Vec_Trmvm=Pzwul./Vec_Pzmmdmm(4:6);              %1x3 Transport rate constant for mth root
soil to same vadose soil


%***************************
%External Losses (1/d)
%***************************

XA=0.23*W/sqrt(AA);                         %Outflow rate constant from atmosphere to
external environment
Xw=wout*(Zwater+(Zdp*fwp))/(dw*Zw*fAAw);              %Outflow rate constant from
surface water to external environment
Xd=Vec_urates(17)*fdd*Zdp/(Zd*dd);                     %Sediment burial rate constant
Vec_Xvg=Zwater*gwrech./(Vec_d(14:16).*Vec_Zmm(7:9));    %Outflow rate constant from
vadose-zone soil to groundwater


%*************************
%Transport Loss Rate Constants (1/d)
%*************************

T_LA=TAw+sum(Vec_TAcm)+sum(Vec_TAsm)+TAiu+XA;   %Transport Loss rate constant
for atmosphere (1/d)
T_Lw=TwA+Twd+Xw;                              %Transport Loss rate constant for surface water
(1/d)
```

```
T_Ld=Tdw+Xd;                              %Transport Loss rate constant for sediment (1/d)
T_Liu=TiuA+Tiuw;                          %Transport Loss rate constant for urban impervious
surface (1/d)
T_Lca=Vec_TcmA(1)+Vec_Tcmsm(1)+Vec_Tcmrm(1);    %Transport Loss rate constant for
agri canopy (1/d)
T_Lcf=Vec_TcmA(2)+Vec_Tcmsm(2)+Vec_Tcmrm(2);    %Transport Loss rate constant for
forest canopy (1/d)
T_Lcu=Vec_TcmA(3)+Vec_Tcmsm(3)+Vec_Tcmrm(3);    %Transport Loss rate constant for
urban canopy (1/d)
T_Lsa=Vec_TsmA(1)+Vec_Tsmw(1)+Vec_Tsmrm(1);     %Transport Loss rate constant for
agricultural surface soil (1/d)
T_Lsf=Vec_TsmA(2)+Vec_Tsmw(2)+Vec_Tsmrm(2);     %Transport Loss rate constant for
forest surface soil (1/d)
T_Lsu=Vec_TsmA(3)+Vec_Tsmw(3)+Vec_Tsmrm(3);     %Transport Loss rate constant for
urban surface soil (1/d)
T_Lra=Vec_Trmcm(1)+Vec_Trmsm(1)+Vec_Trmvm(1);   %Transport Loss rate constant for
agri root-zone soil (1/d)
T_Lrf=Vec_Trmcm(2)+Vec_Trmsm(2)+Vec_Trmvm(2);   %Transport Loss rate constant for
forest root-zone soil (1/d)
T_Lru=Vec_Trmcm(3)+Vec_Trmsm(3)+Vec_Trmvm(3);   %Transport Loss rate constant for
urban root-zone soil (1/d)
T_Lva=Vec_Xvg(1);                         %Transport Loss rate constant for agri vadose-zone soil
(1/d)
T_Lvf=Vec_Xvg(2);                         %Transport Loss rate constant for forest vadose-zone
soil (1/d)
T_Lvu=Vec_Xvg(3);                         %Transport Loss rate constant for urban vadose-zone
soil (1/d)


%*************************
%Generate Outputs
%*************************

dt=1; %time step of 1 day
Vec_Nin=[NAin;Nwin;Ndin;Niuin;Ncain;Ncfin;Ncuin;Nsain;Nsfin;Nsuin;Nrain;Nrfin;Nruin;Nv
ain;Nvfin;Nvuin];    %Column array for compartment inventories at time 0 - initial conditions
Vec_X=[XA;Xw;Xd;zeros(10,1);(Vec_Xvg)'];    %16x1 vector of external loss rates (1/d)
Vec_Si=[SA;Sw;Sd;Siu;Sca;Scf;Scu;Ssa;Ssf;Ssu;Sra;Srf;Sru;Sva;Svf;Svu]; %Emissions/Sources
into compartments (mol/d)
Vec_S=dt.*Vec_Si;  %Column array for compartment sources by time increment
Vec_L=[T_LA;T_Lw;T_Ld;T_Liu;T_Lca;T_Lcf;T_Lcu;T_Lsa;T_Lsf;T_Lsu;T_Lra;T_Lrf;T_Lr
u;T_Lva;T_Lvf;T_Lvu]+(Vec_R)';   %Column array of loss rate constants (1/d)
Vec_L %#ok<NOPTS>
Mat_T=[0,TwA,0,TiuA,Vec_TcmA(1),Vec_TcmA(2),Vec_TcmA(3),Vec_TsmA(1),Vec_TsmA(
2),Vec_TsmA(3),0,0,0,0,0,0;
   TAw,0,Tdw,Tiuw,0,0,0,Vec_Tsmw(1),Vec_Tsmw(2),Vec_Tsmw(3),0,0,0,0,0,0;
```

```
   0,Twd,0,0,0,0,0,0,0,0,0,0,0,0,0,0;
   TAiu,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0;
   Vec_TAcm(1),0,0,0,0,0,0,0,0,0,Vec_Trmcm(1),0,0,0,0,0;
   Vec_TAcm(2),0,0,0,0,0,0,0,0,0,0,Vec_Trmcm(2),0,0,0,0;
   Vec_TAcm(3),0,0,0,0,0,0,0,0,0,0,0,Vec_Trmcm(3),0,0,0;
   Vec_TAsm(1),0,0,0,Vec_Tcmsm(1),0,0,0,0,0,Vec_Trmsm(1),0,0,0,0,0;
   Vec_TAsm(2),0,0,0,0,Vec_Tcmsm(2),0,0,0,0,0,Vec_Trmsm(2),0,0,0,0;
   Vec_TAsm(3),0,0,0,0,0,Vec_Tcmsm(3),0,0,0,0,0,Vec_Trmsm(3),0,0,0;
   0,0,0,0,Vec_Tcmrm(1),0,0,Vec_Tsmrm(1),0,0,0,0,0,0,0,0;
   0,0,0,0,0,Vec_Tcmrm(2),0,0,Vec_Tsmrm(2),0,0,0,0,0,0,0;
   0,0,0,0,0,0,Vec_Tcmrm(3),0,0,Vec_Tsmrm(3),0,0,0,0,0,0;
   0,0,0,0,0,0,0,0,0,0,Vec_Trmvm(1),0,0,0,0,0;
   0,0,0,0,0,0,0,0,0,0,0,Vec_Trmvm(2),0,0,0,0;
   0,0,0,0,0,0,0,0,0,0,0,0,Vec_Trmvm(3),0,0,0];
Mat_T %#ok<NOPTS>

%**************************************************
%Dynamic Solution - Compartment Inventories (mol)
%**************************************************

Mat_A=zeros(16,16);
for i=1:16;
   for j=1:16;
      if i==j, Mat_A(i,j)=1+dt*Vec_L(i);
      else Mat_A(i,j)=-dt*Mat_T(i,j);
      end;
   end;
end;
Mat_A %#ok<NOPTS>

%****************Method 1 of Mass budget check*****************************
%T_check=300; %Mass balance check time (d)
%To_check=T_check/dt;
%Mat_Ncheck=zeros(16,To_check);
%Mat_Ncheck(:,1)=(Mat_A)\(Vec_Nin+Vec_S);                 %Initial solution for time 0.01 d
 %     for n=2:To_check,
  %       Mat_Ncheck(:,n)=(Mat_A)\(Mat_Ncheck(:,n-1)+Vec_S); end; %Loop to calculate
inventory at check time t days (d)

%Mat_Ncheck(:,To_check)

%Mass balance for specific time steps - method 1
%perMBCdtp=100*(sum(-Mat_Ncheck(:,1)+(1+(Vec_R)'+Vec_X).*Mat_Ncheck(:,2)-
Vec_S))/sum(Mat_Ncheck(:,1)+Vec_S) %#ok<NOPTS>
%perMBCdtq=100*(sum(-Mat_Ncheck(:,4)+(1+(Vec_R)'+Vec_X).*Mat_Ncheck(:,5)-
Vec_S))/sum(Mat_Ncheck(:,4)+Vec_S) %#ok<NOPTS>
```

```
%perMBCdtr=100*(sum(-Mat_Ncheck(:,9)+(1+(Vec_R)'+Vec_X).*Mat_Ncheck(:,10)-
Vec_S))/sum(Mat_Ncheck(:,9)+Vec_S) %#ok<NOPTS>
%perMBCdts=100*(sum(-Mat_Ncheck(:,19)+(1+(Vec_R)'+Vec_X).*Mat_Ncheck(:,20)-
Vec_S))/sum(Mat_Ncheck(:,19)+Vec_S) %#ok<NOPTS>
%perMBCdtu=100*(sum(-Mat_Ncheck(:,39)+(1+(Vec_R)'+Vec_X).*Mat_Ncheck(:,40)-
Vec_S))/sum(Mat_Ncheck(:,39)+Vec_S) %#ok<NOPTS>


%***Inventories and required data at user-defined output
%time*******

To=3650; %input('output time (d): '); %Output time, d
Tou=To/dt;
Mat_N=zeros(16,Tou);
Mat_N(:,1)=(Mat_A)\(Vec_Nin+Vec_S);                  %Initial solution for time 0.01 d
    for n=2:Tou,
      Mat_N(:,n)=(Mat_A)\(Mat_N(:,n-1)+Vec_S);
    end; %Loop to calculate inventory at time t days (d)

Vec_Nt=Mat_N(:,Tou);            %Column array of inventories at time t (mol)
Vec_Nt %#ok<NOPTS>
Ntt=sum(Vec_Nt);            %Sum-total inventory at time t (mol)

%**********************
%Steady-State Solution
%**********************

Mat_Tss=Mat_T;
for i=1:16;
   for j=1:16;
      if (i==j), Mat_Tss(i,j)=-Vec_L(i);
      end;
   end;
end; %16by16 matrix for steady-state solution

Mat_Tss %#ok<NOPTS>
Vec_Sneg=-(Vec_Si); %Emission inventory into compartments (mol)
Vec_Nss=Mat_Tss\Vec_Sneg;     %Steady-state inventory column array (mol)
Vec_Nss %#ok<NOPTS>
Nsst=sum(Vec_Nss);          %Sum-total steady state inventory (mol)
```

```
%*************************
%Residence Times (d)
%*************************

Vec_Rt=1./Vec_L;           %Column array of compartment residence times/persistence (d) - Caltox

%*************************
%Persistence (d)
%*************************

Vec_Ksys=Vec_X+(Vec_R)';               %16x1 vector of system loss rates (1/d)
Pov_sys=Nsst/sum(Vec_Nss.*Vec_Ksys)    %#ok<NOPTS> %System overall persistence (d)

Vec_Kenv=(Vec_R)';                   %16x1 vector of degradation loss rates (1/d)
Vec_Kenv(3)=Vec_Kenv(3)+Xd;            %adjust sediment loss rate to include sediment burial (1/d)
Pov_env=Nsst/sum(Vec_Nss.*Vec_Kenv)    %#ok<NOPTS> %Environmental overall persistence (d)


%*************************************
%Long Range Transport Potential (m)
%*************************************
LRTPA=Vec_Rt(1)*W   %#ok<NOPTS> %Atmospheric LRTP (m)
LRTPw=Vec_Rt(2)*wcur    %#ok<NOPTS> %LRTP via surface water (m)


%************************************
%Concentrations (mol/m3)
%************************************

Vec_Ct=Vec_Nt./(Vec_V)';    %Column array of compartment concentrations at time t (mol/m3)
Ctt=sum(Vec_Ct);           %Sum-total concentration at time t (mol/m3)

Vec_Css=Vec_Nss./(Vec_V)';  %Column array of compartment steady state concentrations (mol/m3)
Csst=sum(Vec_Css);          %Sum-total steady state concentration (mol/m3)

Vec_Cavt=sum(Mat_N,2)./((Vec_V)'*Tou);    %Column array of average compartmental concentrations over time period To (mol/m3)
```

```
%**********************
%Outputs
%***********************

Com={'Atmosphere';'Water';'Sediment';'Impervious Surface';'Agriculture Vegetation';'Forest
Canopy';'Urban Vegetation';'Agricultural Surf Soil';'Forest Surf Soil';'Urban Surf Soil';
   'Agriculture Root Soil';'Forest Root Soil';'Urban Root Soil';'Agriculture Vadose Soil';'Forest
Vadose Soil';'Urban Vadose Soil'};   %Cell array of compartments

Outputs=struct('Compartments',Com,'Inventory_mol',num2cell(Vec_Nt),'SteadyState_Inventory
_mol',num2cell(Vec_Nss),'Concentration_mol_m3',num2cell(Vec_Ct),'SteadyState_Concentrati
on_mol_m3',num2cell(Vec_Css),'Residence_Time_d',num2cell(Vec_Rt));

fprintf('          Compartments              Inventory_mol   SteadyState_Inventory_mol
Concentration_mol_m3    SteadyState_Concentration_mol_m3    Residence_Time_d\n\n');
for n=1:length(Outputs), fprintf('\n%26s            %4.4e                %4.4e                   %4.4e
%4.4e                    %4.4e\n\n',...

Outputs(n).Compartments,Outputs(n).Inventory_mol,Outputs(n).SteadyState_Inventory_mol,Out
puts(n).Concentration_mol_m3,Outputs(n).SteadyState_Concentration_mol_m3,Outputs(n).Resi
dence_Time_d);
end;                          %Table of Outputs


%****************************************
%Calculate Health Impact
%****************************************

Age=25;         %Individual's age (y)
IRw=2e-3;       %Surface water intake rate (m3/d), check EPA Exposure Factors Handbook 2011
for specific values
IRa=15;         %Inhalation rate (m3/d), check EPA Exposure Factors Handbook 2011 for
specific values
EF=350;         %Frequency of exposure (d/y)
ED=30;          %Exposure durations (y)
Ca=Vec_Ct(1)*MW*1000; %Concentration of chemical in atmosphere (mg/m3)
Cw=Vec_Ct(2)*MW*1000; %Concentration of chemical in drinking water (mg/m3)
ATnc=10950;   %Averaging time (d) - default of 30 years for non-cancer risk
ATc=25550;   %Averaging time (d) - default of 70 years for cancer risk
BW=70;          %Average adult BW (kg), check EPA Exposure Factors Handbook 2011 for
specific values
RfDo=7e-10;      %Oral reference dose for the chemical (mg/kg/d)
RfDi=7e-10;   %Inhalation reference dose for the chemical (mg/kg/d)
NOEL=2e-8;     %No observed effect level or no observed adverse effect level for contaminant
TDI=4e-9;      %Tolerable daily intake (mgTEQ/kg/d)
TEF=1;      %Toxic equivalency factor for dioxin & dioxin-like compounds
```

```
Po= 516218;    %Population - St. Catherine parish default
K=0.5;            %volatilization factor
rhoa=1.225; %density of air (kg/m3)
SFo=1.5e5;     %oral slope factor (mg/kg/d)^-1
SFi=1.5e5;      %inhalation slope factor (mg/kg/d)^-1
ED_50nc=6.3e-9;       %Non-cancer effect dose-50 (kg/person/lifetime) - if no value in literature
for non-carcinogenic chemical, use ED_50nc=NOEL*9
ED_50c=5.3e-6;         %Cancer effect dose-50 (kg/person/lifetime) - if no value in literature, use
ED_50c=0.8/SF


%******************************************************
%Calculate Hazard Index - inhalation and surface water
%******************************************************
HQncw=((Cw*EF*ED)*(IRw/RfDo+IRa*K/RfDi))/(BW*ATnc); %Non-cancer hazard quotient
for surface water
HQnca=(Ca*IRa*EF*ED)/(RfDi*BW*ATnc); %Non-cancer hazard quotient for inhalation of air
Iwnc=((Cw*EF*ED)*(IRw+IRa*K))/(BW*ATnc); %Intake of contaminant in surface water
(mg/kg/d)
Ianc=(Ca*IRa*EF*ED)/(BW*ATnc); %Intake of contaminant in atmosphere (mg/kg/d)
if RfD==0, HQncw=Iwnc*TEF/TDI; end;    %Water Non-cancer hazard quotient for dioxins &
dioxin-like compounds
if RfD==0, HQnca=Ianc*TEF/TDI; end;    %Inhalation Non-cancer hazard quotient for dioxins
& dioxin-like compounds
HI=HQncw+HQnca; %Hazard index

%****************************************************
%Calculate Cancer Risk - inhalation and surface water
%****************************************************
CRw=((Cw*EF*ED)*(SFo*IRw+SFi*IRa*K))/(BW*ATc); %Surface water cancer risk
CRa=(Ca*IRa*EF*ED*SFi)/(BW*ATc); %Cancer risk for inhalation of air
CR=CRw+CRa; %Cancer risk

%*****************************************************************
%Calculate Human Toxicity Potential  (diseases per kg of emission)
%*****************************************************************
IRiw=3.9e-6; %Chemical intake rate from water, kg/d/person (Use IRiw=IRw*rhow/Po when
unavailable)
IRia=3.6e-5; %Chemical intake rate from air, kg/d/person (Use IRia=IRa*rhoa/Po when
unavailable)
HTPncw=(Vec_Rt(2)*IRiw*Po)/(rhow*Vec_V(2)*ED_50nc*2); %Non-cancer human toxicity
potential for surface water (cases/kg)
HTPnca=(Vec_Rt(1)*IRia*Po)/(rhoa*Vec_V(1)*ED_50nc*2); %Non-cancer human toxicity
potential for inhalation (cases/kg)
HTPcw=(Vec_Rt(2)*IRiw*Po)/(rhow*Vec_V(2)*ED_50c*2); %Cancer human toxicity
potential for surface water (cases/kg)
```

```
HTPca=(Vec_Rt(1)*IRia*Po)/(rhoa*Vec_V(1)*ED_50c*2); %Cancer human toxicity potential for inhalation (cases/kg)
HTP=HTPncw+HTPcw+HTPnca+HTPca; %human toxicity potential (cases/kg)

%**********
%Outputs
%***********
fprintf('The non-cancer hazard index for a %d year old is %.4f\n', Age, HI);
fprintf('The cancer risk for a %d year old is %.4f\n', Age, CR);
fprintf('The human toxicity potential is %d cases per kg', HTP);
```

Appendix F

Sensitivity Analysis Data

Table F.1a: Ratios of outputs in the control and comparison scenario (scenario given indicated adjustment) for sensitivity analysis

Parameter	Adjustment	Overall persistence	Atmospheric long range transport potential	Surface water long range transport potential	Annual average atmospheric concentration	Annual average surface water concentration	Annual average sediment concentration	Annual average urban film concentration	Annual average agricultural crop concentration	Annual average forest canopy concentration	Annual average urban vegetation concentration
Octanol-water partition coefficient	Halved	0.641806	1	1	0.996653	0.989301	0.989526	0.996653	313.4472	30.54277	681.5275
Air-water partition coefficient	Halved	1	1	1	1	1	1	1	1	1	1
Octanol-air partition coefficient	Halved	1	1	1	1	1.000034	1.000034	1.000042	1	1	1
Molecular weight (g.mol^{-1})	Halved	0.984322	1.001515	1.001199	0.500752	0.482905	0.482904	0.500749	0.483982	0.483651	0.4853
Half-life in atmosphere (d)	Halved	1.643897	1.087277	1	1.087197	1.087195	1.087192	1.087197	1.087134	1.087115	1.087193
Half-life in surface water (d)	Halved	1.000039	1	1.005814	1	1.005773	1.00577	1	1	1	1
Half-life in soil (d)	Halved	1.641545	1	1	1	1.000055	1.000051	1	1	1	1
Half-life in canopy (d)	Halved	1.317627	1	1	1.000007	1.00005	1.000046	1.000007	1.076789	1.088928	1.010779
Half-life in urban film (d)	Halved	1	1	1	1	1.000025	1.000025	1.000032	1	1	1
Half-life in sediment (d)	Halved	1	1	1	1	1	1	1	1	1	1
Atmospheric dust load (kg.m^{-3})	Halved	1.028404	0.998463	1	0.998468	1.128322	1.128328	1.163235	1.015823	1.013735	1.026884
Temperature (K)	Halved	1.102145	0.994887	1.00016	0.994904	1.161749	1.166468	1.200904	1.064945	1.094397	1.009837
Precipitation rate (m.d^{-1})	Halved	1.136214	0.99479	1	0.9948	1.61604	1.616072	1.884432	1.02102	1.046965	0.985556
Wind speed (m.d^{-1})	Halved	0.999999	1.136827	0.997887	0.568816	0.608556	0.60858	0.56884	0.569125	0.56922	0.568836
Dry deposition velocity (m.d^{-1})	Halved	1.005079	0.999672	1	0.999674	1.02285	1.02285	1.028292	1.00377	1.003185	1.007268
Surface water outflow rate (m.d^{-1})	Halved	1.000018	1	0.507208	0.999996	0.510774	0.510954	0.999996	0.999996	0.999996	0.999996

Area of urban film (m^2)	Halved	0.970535	1.000885	1	1.000879	1.665922	1.666057	1.000879	1.000879	1.000879	1.065374
Area of atmosphere (m^2)	Halved	1	1.357494	1	0.678581	0.678579	0.678571	0.678581	0.678453	0.678414	0.678573
Depth of atmosphere (m)	Halved	0.678876	1.049657	1	0.52475	0.52475	0.524751	0.52475	0.524744	0.52474	0.524751
Depth of urban film (m)	Doubled	0.999999	1	1	1	1.000394	1.000408	1.000489	1	1	1
Depth of surface water (m)	Doubled	1.000018	1	0.502907	1	1.015688	1.016048	1	1	1	1
Atmosphere emission rate ($mol.d^{-1}$)	Doubled	1	1	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Emission rate ($mol.d^{-1}$)	Agricultural surface soil only	0.217907	1	1	4497.006	4.395459	4.543442	4499.002	6134.554	6497.565	4673.905
Emission rate in agricultural surface soil ($mol.d^{-1}$)	Doubled	0.217907	1	1	2248.503	2.19773	2.271721	2249.501	3067.277	3248.783	2336.953
Emission rate ($mol.d^{-1}$)	Both atmosphere and agricultural surface soil	0.240592	1	1	0.999778	0.814659	0.819607	0.999778	0.999837	0.999846	0.999786
Particle fraction in surface water	Doubled	1	1	0.997328	1.000002	0.997248	0.960886	1.000002	1.000002	1.000002	1.000002
Film fraction in urban zone	Doubled	1	1	1	1	0.999999	0.999999	0.999999	1	1	1

Table F.1b: Ratios of outputs in the control and comparison scenario (scenario given indicated adjustment) for sensitivity analysis

Parameter	Adjustment	Annual average agricultural surface soil concentration	Annual average forest surface soil concentration	Annual average urban surface soil concentration	Annual average agricultural root soil concentration	Annual average forest root soil concentration	Annual average urban root soil concentration	Annual average agricultural vadose soil concentration	Annual average forest vadose soil concentration	Annual average urban vadose soil concentration
Octanol-water partition coefficient	Halved	0.382794	0.188874	0.967783	0.08016	0.012201	0.254806	0.062888	0.009397	0.2333
Air-water partition coefficient	Halved	1	1	1	1	1	1	1	1	1
Octanol-air partition coefficient	Halved	1	1	1	1	1	1	1	1	1
Molecular weight (g.mol^{-1})	Halved	0.490692	0.496496	0.490297	0.485262	0.489969	0.4867	0.48522	0.489989	0.486472
Half-life in atmosphere (d)	Halved	1.08707	1.087095	1.087102	1.087028	1.087016	1.087073	1.086938	1.086927	1.086986
Half-life in surface water (d)	Halved	1	1	1	1	1	1	1	1	1
Half-life in soil (d)	Halved	1.020496	1.022314	1.022532	1.020763	1.025827	1.02574	1.030842	1.034931	1.035752
Half-life in canopy (d)	Halved	1.030598	1.008624	1.006365	1.052247	1.035829	1.009086	1.043151	1.029111	1.00894
Half-life in urban film (d)	Halved	1	1	1	1	1	1	1	1	1
Half-life in sediment (d)	Halved	1	1	1	1	1	1	1	1	1
Atmospheric dust load (kg.m^{-3})	Halved	1.059635	1.099482	1.058679	1.024434	1.055636	1.036211	1.024219	1.055763	1.034731
Temperature (K)	Halved	1.198634	1.173678	1.136921	1.098657	1.14835	1.05614	1.099821	1.14729	1.051785
Precipitation rate (m.d^{-1})	Halved	1.328443	1.463655	1.233539	1.075289	1.222459	1.051866	1.076504	1.221874	1.044581
Wind speed (m.d^{-1})	Halved	0.569441	0.569318	0.569284	0.569649	0.56971	0.569427	0.570097	0.570148	0.569859
Dry deposition velocity (m.d^{-1})	Halved	1.011538	1.018138	1.012294	1.005348	1.010744	1.008776	1.005314	1.010768	1.008545
Surface water outflow rate (m.d^{-1})	Halved	0.999996	0.999996	0.999996	0.999996	0.999996	0.999996	0.999996	0.999996	0.999996
Area of urban film (m^2)		1.000879	1.000879	1.065561	1.000879	1.000879	1.103236	1.000879	1.000878	1.139493
Area of atmosphere (m^2)	Halved	0.678322	0.678374	0.678387	0.678237	0.678211	0.678328	0.678051	0.67803	0.67815
Depth of atmosphere (m)	Halved	0.524732	0.524736	0.524738	0.524724	0.524721	0.524732	0.524703	0.524701	0.524714
Depth of urban film (m)	Doubled	1	1	1	1	1	1	1	1	1
Depth of surface water (m)	Doubled	1	1	1	1	1	1	1	1	1
Atmospheric emission rate (mol.d^{-1})	Doubled	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Emission rate (mol.d^{-1})	Agricultural surface soil	0.004577	6868.203	6803.258	0.022524	8826.755	7406.835	0.023096	10968.43	9545.096
Emission rate in agricultural surface soil (mol.d^{-1})	Doubled	0.002289	3434.102	3401.629	0.011262	4413.378	3703.417	0.011548	5484.214	4772.548
Emission rate (mol.d^{-1})	Atmosphere and agricultural surface soil	0.004557	0.999854	0.999853	0.022028	0.999887	0.999865	0.022574	0.999909	0.999895
Particle fraction in surface water	Doubled	1.000002	1.000002	1.000002	1.000002	1.000002	1.000002	1.000002	1.000002	1.000002
Film fraction in urban zone	Doubled	1	1	1	1	1	1	1	1	1

APPENDIX G

Fate metrics data for the evaluated organics

Table G.1: Long-term fate metrics generated for the persistent pollutants in land-use distribution scenario II (un-forested scenario)

Fate Metrics	**PBDE-47**	**PBDE-99**	**PBDE-153**	**PBDE-209**	**TCDD**	**OCDD**	**PeCDF**	**HxCDF**
Overall Persistence	1.50E+02	2.03E+02	1.67E+02	1.56E+02	1.01E+03	4.39E+03	1.58E+03	2.05E+03
Atmospheric long range transport potential	1.33E+05	1.09E+05	1.11E+05	6.62E+04	1.35E+05	8.92E+04	1.42E+05	1.40E+05
Atmospheric concentration (mol.m^{-3})	8.93E-15	6.28E-15	5.63E-15	2.25E-15	1.36E-14	6.32E-15	1.36E-14	1.21E-14
Surface water concentration (mol.m^{-3})	3.72E-11	9.40E-11	8.08E-11	1.19E-10	7.99E-12	1.75E-10	1.08E-12	3.62E-11
Sediment concentration (mol.m^{-3})	2.76E-11	3.35E-11	7.56E-11	1.22E-10	7.72E-12	1.79E-10	1.12E-12	3.74E-11
Impervious surface concentration (mol.m^{-3})	2.16E-06	5.58E-06	4.69E-06	6.95E-06	3.77E-07	1.00E-05	1.17E-06	2.01E-06
Agricultural vegetation concentration (mol.m^{-3})	1.45E-09	2.69E-10	6.09E-09	1.50E-08	1.95E-08	5.61E-08	1.16E-08	1.68E-08
Forest canopy concentration (mol.m^{-3})	1.47E-09	6.62E-10	3.26E-09	4.86E-09	4.96E-09	2.49E-08	5.60E-09	7.12E-09
Urban vegetation concentration (mol.m^{-3})	2.48E-09	4.51E-10	1.78E-08	1.67E-07	5.38E-08	1.68E-07	1.99E-08	3.67E-08
Agricultural surface soil concentration (mol.m^{-3})	2.26E-08	5.17E-08	3.38E-08	3.57E-08	8.22E-09	1.03E-07	2.28E-08	2.79E-08
Forest surface soil concentration (mol.m^{-3})	1.34E-08	4.15E-08	2.39E-08	3.31E-08	4.18E-09	7.92E-08	1.11E-08	1.72E-08
Urban surface soil concentration (mol.m^{-3})	1.74E-08	4.03E-08	3.39E-08	4.66E-08	1.03E-08	1.13E-07	1.88E-08	2.72E-08
Agricultural root soil concentration (mol.m^{-3})	1.33E-13	1.05E-12	6.79E-14	2.94E-16	7.59E-14	7.34E-15	4.00E-14	2.08E-14
Forest root soil concentration (mol.m^{-3})	7.16E-14	8.33E-13	3.93E-14	2.34E-16	1.10E-14	7.95E-16	4.91E-15	2.40E-15
Urban root soil concentration (mol.m^{-3})	9.61E-14	8.11E-13	6.38E-14	4.47E-16	6.99E-14	6.33E-15	1.92E-14	1.29E-14
Agricultural vadose soil concentration (mol.m^{-3})	4.66E-21	1.93E-19	6.12E-22	3.37E-27	6.39E-22	1.29E-26	1.46E-23	1.87E-24
Forest vadose soil concentration (mol.m^{-3})	2.45E-21	1.53E-19	3.46E-22	2.65E-27	9.00E-23	1.32E-27	1.62E-24	1.99E-25
Urban vadose soil concentration (mol.m^{-3})	3.35E-21	1.49E-19	5.80E-22	5.30E-27	6.94E-22	1.34E-26	7.86E-24	1.34E-24

Table G.2: Long-term fate metrics generated for the persistent pollutants in land-use distribution scenario I (forested scenario)

Fate Metrics	**PBDE-47**	**PBDE-99**	**PBDE-153**	**PBDE-209**	**TCDD**	**OCDD**	**PeCDF**	**HxCDF**
Overall Persistence	1.41E+02	2.00E+02	1.54E+02	1.46E+02	1.15E+03	4.17E+03	1.52E+03	1.86E+03
Atmospheric long range transport potential	1.30E+05	1.05E+05	1.08E+05	6.26E+04	1.33E+05	8.54E+04	1.39E+05	1.37E+05
Atmospheric concentration (mol.m^{-3})	8.72E-15	6.07E-15	5.44E-15	2.12E-15	1.34E-14	6.05E-15	1.33E-14	1.19E-14
Surface water concentration (mol.m^{-3})	3.64E-11	9.08E-11	7.81E-11	1.13E-10	7.85E-12	1.68E-10	1.06E-12	3.54E-11
Sediment concentration (mol.m^{-3})	2.70E-11	3.23E-11	7.30E-11	1.15E-10	7.59E-12	1.71E-10	1.10E-12	3.66E-11
Impervious surface concentration (mol.m^{-3})	2.11E-06	5.39E-06	4.53E-06	6.57E-06	3.70E-07	9.60E-06	1.15E-06	1.97E-06
Agricultural vegetation concentration (mol.m^{-3})	1.42E-09	2.60E-10	5.88E-09	1.42E-08	1.92E-08	5.37E-08	1.14E-08	1.65E-08
Forest canopy concentration (mol.m^{-3})	4.56E-10	2.04E-10	8.13E-10	1.08E-09	1.90E-09	5.84E-09	1.92E-09	2.19E-09
Urban vegetation concentration (mol.m^{-3})	2.42E-09	4.36E-10	1.72E-08	1.58E-07	5.29E-08	1.61E-07	1.95E-08	3.60E-08
Agricultural surface soil concentration (mol.m^{-3})	2.21E-08	4.99E-08	3.26E-08	3.38E-08	8.08E-09	9.84E-08	2.23E-08	2.73E-08
Forest surface soil concentration (mol.m^{-3})	1.43E-08	4.65E-08	2.33E-08	3.13E-08	4.37E-09	7.62E-08	1.17E-08	1.74E-08
Urban surface soil concentration (mol.m^{-3})	1.70E-08	3.89E-08	3.28E-08	4.40E-08	1.01E-08	1.09E-07	1.84E-08	2.66E-08
Agricultural root soil concentration (mol.m^{-3})	1.30E-13	1.01E-12	6.56E-14	2.78E-16	7.46E-14	7.03E-15	3.92E-14	2.04E-14
Forest root soil concentration (mol.m^{-3})	7.99E-14	9.39E-13	3.94E-14	2.23E-16	1.61E-14	1.11E-15	9.04E-15	3.98E-15
Urban root soil concentration (mol.m^{-3})	9.39E-14	7.83E-13	6.17E-14	4.22E-16	6.87E-14	6.06E-15	1.88E-14	1.26E-14
Agricultural vadose soil concentration (mol.m^{-3})	4.56E-21	1.86E-19	5.91E-22	3.19E-27	6.28E-22	1.24E-26	1.43E-23	1.83E-24
Forest vadose soil concentration (mol.m^{-3})	2.74E-21	1.71E-19	3.48E-22	2.53E-27	1.32E-22	1.83E-27	2.99E-24	3.31E-25
Urban vadose soil concentration (mol.m^{-3})	3.28E-21	1.44E-19	5.60E-22	5.01E-27	6.82E-22	1.28E-26	7.70E-24	1.31E-24

Table G.3: Long-term fate metrics generated for the current-use pesticides in land-use distribution scenario II (un-forested scenario)

Fate Metrics	**Diazinon**	**Dimethoate**	**Carbaryl**	**Methomyl**	**Cyhalothrin**	**Cypermethrin**	**Diuron**	**Glyphosate**
Overall Persistence	1.01E+01	8.95E+00	1.10E+01	3.38E+01	1.47E+01	2.82E+01	3.63E+01	6.84E+01
Atmospheric long range transport potential	4.50E+04	1.30E+03	5.30E+02	7.49E+02	3.72E+04	5.74E+04	5.58E+03	1.63E+02
Atmospheric concentration (mol.m^{-3})	4.83E-15	1.85E-16	8.58E-17	1.51E-16	2.69E-15	4.50E-15	7.81E-16	3.14E-17
Surface water concentration (mol.m^{-3})	1.90E-10	1.58E-09	9.54E-10	2.48E-09	1.34E-10	1.56E-10	9.59E-10	1.30E-09
Sediment concentration (mol.m^{-3})	5.11E-12	1.16E-11	3.30E-11	4.62E-11	4.86E-11	6.61E-11	3.55E-11	1.31E-10
Impervious surface concentration (mol.m^{-3})	7.15E-06	5.08E-05	5.91E-05	7.40E-05	8.47E-06	1.33E-05	4.51E-05	7.11E-05
Agricultural vegetation concentration (mol.m^{-3})	4.73E-09	2.73E-09	6.91E-09	3.69E-09	6.08E-10	9.62E-10	8.29E-10	4.30E-09
Forest canopy concentration (mol.m^{-3})	1.48E-09	2.40E-09	2.82E-09	3.03E-09	7.97E-10	1.30E-09	1.76E-09	1.12E-08
Urban vegetation concentration (mol.m^{-3})	4.22E-08	1.43E-08	4.79E-08	2.01E-08	1.22E-09	1.90E-09	1.61E-09	1.93E-08
Agricultural surface soil concentration (mol.m^{-3})	1.03E-08	1.01E-08	3.16E-08	5.33E-08	2.24E-08	3.77E-08	1.01E-07	1.55E-07
Forest surface soil concentration (mol.m^{-3})	9.53E-09	1.00E-08	3.11E-08	5.30E-08	1.59E-08	2.69E-08	7.98E-08	1.55E-07
Urban surface soil concentration (mol.m^{-3})	1.21E-08	1.01E-08	3.22E-08	5.33E-08	1.91E-08	3.20E-08	8.17E-08	1.55E-07
Agricultural root soil concentration (mol.m^{-3})	5.21E-11	2.21E-10	1.30E-10	1.24E-09	1.62E-13	2.23E-13	2.50E-10	1.45E-09
Forest root soil concentration (mol.m^{-3})	4.15E-11	1.14E-10	4.02E-11	6.48E-10	1.15E-13	1.49E-13	1.92E-10	8.82E-10
Urban root soil concentration (mol.m^{-3})	7.12E-11	1.82E-10	1.65E-10	1.04E-09	1.38E-13	1.80E-13	1.95E-10	8.41E-10
Agricultural vadose soil concentration (mol.m^{-3})	5.78E-15	5.63E-14	3.30E-15	3.34E-13	1.29E-20	1.34E-20	1.38E-14	1.64E-14
Forest vadose soil concentration (mol.m^{-3})	4.60E-15	2.90E-14	1.02E-15	1.74E-13	9.13E-21	8.92E-21	1.06E-14	9.88E-15
Urban vadose soil concentration (mol.m^{-3})	7.92E-15	4.64E-14	4.20E-15	2.82E-13	1.10E-20	1.08E-20	1.08E-14	9.49E-15

Table G.4: Long-term fate metrics generated for the current-use pesticides in land-use distribution scenario I (forested scenario)

Fate Metrics	**Diazinon**	**Dimethoate**	**Carbaryl**	**Methomyl**	**Cyhalothrin**	**Cypermethrin**	**Diuron**	**Glyphosate**
Overall Persistence	1.02E+01	8.49E+00	1.02E+01	3.05E+01	1.47E+01	2.73E+01	3.56E+01	6.85E+01
Atmospheric long range transport potential	4.38E+04	1.17E+03	4.74E+02	6.70E+02	3.60E+04	5.48E+04	5.06E+03	1.46E+02
Atmospheric concentration (mol.m^{-3})	4.70E-15	1.66E-16	7.67E-17	1.35E-16	2.61E-15	4.29E-15	7.08E-16	2.81E-17
Surface water concentration (mol.m^{-3})	1.85E-10	1.42E-09	8.53E-10	2.22E-09	1.30E-10	1.49E-10	8.91E-10	1.16E-09
Sediment concentration (mol.m^{-3})	4.98E-12	1.04E-11	2.95E-11	4.13E-11	4.70E-11	6.30E-11	3.30E-11	1.17E-10
Impervious surface concentration (mol.m^{-3})	6.97E-06	4.55E-05	5.29E-05	6.61E-05	8.20E-06	1.27E-05	4.08E-05	6.36E-05
Agricultural vegetation concentration (mol.m^{-3})	4.61E-09	2.44E-09	6.18E-09	3.29E-09	5.89E-10	9.17E-10	7.52E-10	3.85E-09
Forest canopy concentration (mol.m^{-3})	3.88E-10	5.62E-10	6.40E-10	7.10E-10	2.01E-10	3.26E-10	4.94E-10	2.45E-09
Urban vegetation concentration (mol.m^{-3})	4.12E-08	1.28E-08	4.28E-08	1.80E-08	1.18E-09	1.81E-09	1.46E-09	1.72E-08
Agricultural surface soil concentration (mol.m^{-3})	1.00E-08	9.04E-09	2.83E-08	4.77E-08	2.17E-08	3.59E-08	9.15E-08	1.38E-07
Forest surface soil concentration (mol.m^{-3})	9.30E-09	9.00E-09	2.78E-08	4.74E-08	1.59E-08	2.66E-08	8.08E-08	1.38E-07
Urban surface soil concentration (mol.m^{-3})	1.17E-08	9.03E-09	2.88E-08	4.76E-08	1.85E-08	3.05E-08	7.41E-08	1.38E-07
Agricultural root soil concentration (mol.m^{-3})	5.07E-11	1.98E-10	1.16E-10	1.11E-09	1.57E-13	2.13E-13	2.26E-10	1.30E-09
Forest root soil concentration (mol.m^{-3})	3.93E-11	1.10E-10	4.06E-11	6.12E-10	1.15E-13	1.52E-13	2.00E-10	1.18E-09
Urban root soil concentration (mol.m^{-3})	6.93E-11	1.63E-10	1.48E-10	9.34E-10	1.34E-13	1.71E-13	1.76E-10	7.52E-10
Agricultural vadose soil concentration (mol.m^{-3})	5.63E-15	5.04E-14	2.95E-15	2.99E-13	1.25E-20	1.28E-20	1.25E-14	1.47E-14
Forest vadose soil concentration (mol.m^{-3})	4.37E-15	2.80E-14	1.03E-15	1.65E-13	9.15E-21	1.03E-20	1.11E-14	1.32E-14
Urban vadose soil concentration (mol.m^{-3})	7.72E-15	4.16E-14	3.76E-15	2.52E-13	1.06E-20	9.11E-21	9.75E-15	8.49E-15

Appendix H

Steady state and monthly varying concentrations of PBDE-47 and dimethoate in the forested and un-forested landscapes in the 1986-2005 climate period

Table H.1: Steady state and monthly varying concentrations of PBDE-47 in land-use distribution scenario I (forested scenario) given the 1986-2005 climate conditions

	Concentration (mol.m^{-3})							
	Atmosphere	Surface Water	Sediment	Impervious Surface	Agriculture Vegetation	Forest Vegetation	Urban Vegetation	Agriculture Surface Soil
Steady state	8.73E-15	3.68E-11	2.83E-11	2.12E-06	1.45E-09	5.09E-10	4.82E-09	4.35E-08
January	9.10E-15	2.24E-11	1.87E-11	1.27E-06	1.93E-09	4.93E-10	7.09E-09	4.13E-08
February	9.16E-15	2.04E-11	1.61E-11	1.15E-06	2.10E-09	4.83E-10	7.82E-09	3.93E-08
March	9.14E-15	2.08E-11	1.60E-11	1.17E-06	2.12E-09	4.79E-10	7.77E-09	3.76E-08
April	8.86E-15	3.18E-11	2.32E-11	1.82E-06	1.62E-09	4.91E-10	5.37E-09	3.80E-08
May	8.31E-15	5.32E-11	3.86E-11	3.08E-06	1.17E-09	5.13E-10	3.82E-09	4.11E-08
June	8.75E-15	3.61E-11	2.93E-11	2.07E-06	1.47E-09	5.11E-10	4.93E-09	4.12E-08
July	8.63E-15	4.07E-11	3.10E-11	2.35E-06	1.38E-09	5.15E-10	4.54E-09	4.21E-08
August	8.59E-15	4.23E-11	3.23E-11	2.44E-06	1.35E-09	5.17E-10	4.43E-09	4.30E-08
September	8.15E-15	5.94E-11	4.38E-11	3.45E-06	1.10E-09	5.25E-10	3.59E-09	4.61E-08
October	8.44E-15	4.83E-11	3.81E-11	2.80E-06	1.24E-09	5.24E-10	4.05E-09	4.73E-08
November	8.68E-15	3.88E-11	3.10E-11	2.23E-06	1.40E-09	5.17E-10	4.63E-09	4.69E-08
December	9.05E-15	2.47E-11	2.05E-11	1.40E-06	1.82E-09	5.00E-10	6.52E-09	4.46E-08

Table H.1 continued

	Concentration (mol.m^{-3})							
	Forest Surface Soil	Urban Surface Soil	Agriculture Root Soil	Forest Root Soil	Urban Root Soil	Agriculture Vadose Soil	Forest Vadose Soil	Urban Vadose Soil
Steady state	2.91E-08	3.28E-08	5.62E-13	3.70E-13	4.10E-13	5.47E-20	3.60E-20	3.99E-20
January	2.75E-08	3.13E-08	5.61E-13	3.68E-13	4.10E-13	5.47E-20	3.60E-20	3.99E-20
February	2.59E-08	3.00E-08	5.58E-13	3.65E-13	4.08E-13	5.47E-20	3.60E-20	3.99E-20
March	2.45E-08	2.87E-08	5.52E-13	3.59E-13	4.03E-13	5.46E-20	3.59E-20	3.98E-20
April	2.45E-08	2.87E-08	5.45E-13	3.53E-13	3.98E-13	5.44E-20	3.57E-20	3.97E-20
May	2.70E-08	3.10E-08	5.41E-13	3.50E-13	3.95E-13	5.42E-20	3.55E-20	3.96E-20
June	2.72E-08	3.11E-08	5.40E-13	3.50E-13	3.94E-13	5.40E-20	3.53E-20	3.94E-20
July	2.79E-08	3.18E-08	5.40E-13	3.50E-13	3.94E-13	5.38E-20	3.52E-20	3.93E-20
August	2.87E-08	3.25E-08	5.41E-13	3.52E-13	3.95E-13	5.36E-20	3.50E-20	3.92E-20
September	3.15E-08	3.48E-08	5.45E-13	3.56E-13	3.98E-13	5.35E-20	3.49E-20	3.91E-20
October	3.26E-08	3.57E-08	5.52E-13	3.63E-13	4.03E-13	5.35E-20	3.49E-20	3.91E-20
November	3.24E-08	3.55E-08	5.58E-13	3.69E-13	4.08E-13	5.36E-20	3.50E-20	3.91E-20
December	3.06E-08	3.39E-08	5.63E-13	3.72E-13	4.12E-13	5.37E-20	3.52E-20	3.92E-20

Table H.2: Steady state and monthly varying concentrations of PBDE-47 in land-use distribution scenario II (un-forested scenario) given the 1986-2005 climate conditions

	Concentration (mol.m^{-3})							
	Atmosphere	Surface Water	Sediment	Impervious Surface	Agriculture Vegetation	Forest Vegetation	Urban Vegetation	Agriculture Surface Soil
Steady state	8.94E-15	3.77E-11	2.90E-11	2.17E-06	1.48E-09	1.62E-09	4.93E-09	4.45E-08
January	9.28E-15	2.29E-11	1.90E-11	1.29E-06	1.96E-09	1.56E-09	7.22E-09	4.22E-08
February	9.33E-15	2.08E-11	1.64E-11	1.17E-06	2.14E-09	1.52E-09	7.97E-09	4.02E-08
March	9.32E-15	2.12E-11	1.63E-11	1.20E-06	2.16E-09	1.51E-09	7.91E-09	3.84E-08
April	9.06E-15	3.25E-11	2.37E-11	1.86E-06	1.65E-09	1.56E-09	5.48E-09	3.88E-08
May	8.54E-15	5.46E-11	3.96E-11	3.17E-06	1.20E-09	1.64E-09	3.92E-09	4.21E-08
June	8.95E-15	3.69E-11	3.00E-11	2.12E-06	1.51E-09	1.63E-09	5.05E-09	4.21E-08
July	8.84E-15	4.17E-11	3.17E-11	2.41E-06	1.41E-09	1.64E-09	4.65E-09	4.31E-08
August	8.80E-15	4.33E-11	3.31E-11	2.50E-06	1.38E-09	1.65E-09	4.54E-09	4.40E-08
September	8.39E-15	6.12E-11	4.51E-11	3.55E-06	1.14E-09	1.68E-09	3.69E-09	4.73E-08
October	8.66E-15	4.96E-11	3.91E-11	2.87E-06	1.27E-09	1.67E-09	4.15E-09	4.84E-08
November	8.89E-15	3.97E-11	3.17E-11	2.29E-06	1.43E-09	1.65E-09	4.74E-09	4.81E-08
December	9.23E-15	2.52E-11	2.09E-11	1.43E-06	1.86E-09	1.58E-09	6.65E-09	4.57E-08

Table H.2 continued

	Concentration (mol.m^{-3})							
	Forest Surface Soil	Urban Surface Soil	Agriculture Root Soil	Forest Root Soil	Urban Root Soil	Agriculture Vadose Soil	Forest Vadose Soil	Urban Vadose Soil
Steady state	2.68E-08	3.36E-08	5.75E-13	3.33E-13	4.19E-13	5.60E-20	3.24E-20	4.08E-20
January	2.53E-08	3.20E-08	5.74E-13	3.31E-13	4.19E-13	5.60E-20	3.24E-20	4.08E-20
February	2.39E-08	3.06E-08	5.71E-13	3.28E-13	4.16E-13	5.59E-20	3.24E-20	4.08E-20
March	2.26E-08	2.93E-08	5.65E-13	3.23E-13	4.12E-13	5.58E-20	3.23E-20	4.07E-20
April	2.26E-08	2.94E-08	5.58E-13	3.17E-13	4.06E-13	5.57E-20	3.21E-20	4.06E-20
May	2.49E-08	3.17E-08	5.53E-13	3.15E-13	4.03E-13	5.55E-20	3.19E-20	4.04E-20
June	2.51E-08	3.18E-08	5.52E-13	3.14E-13	4.02E-13	5.53E-20	3.18E-20	4.03E-20
July	2.57E-08	3.25E-08	5.52E-13	3.15E-13	4.02E-13	5.50E-20	3.16E-20	4.01E-20
August	2.64E-08	3.32E-08	5.54E-13	3.16E-13	4.04E-13	5.49E-20	3.15E-20	4.00E-20
September	2.89E-08	3.56E-08	5.58E-13	3.20E-13	4.07E-13	5.48E-20	3.14E-20	3.99E-20
October	2.99E-08	3.65E-08	5.64E-13	3.26E-13	4.12E-13	5.48E-20	3.14E-20	3.99E-20
November	2.97E-08	3.64E-08	5.71E-13	3.32E-13	4.18E-13	5.48E-20	3.15E-20	4.00E-20
December	2.81E-08	3.47E-08	5.76E-13	3.35E-13	4.21E-13	5.50E-20	3.16E-20	4.01E-20

Table H.3: Steady state and monthly varying concentrations of dimethoate in land-use distribution scenario I (forested scenario) given the 1986-2005 climate conditions

	Concentration (mol.m^{-3})							
	Atmosphere	Surface Water	Sediment	Impervious Surface	Agriculture Vegetation	Forest Vegetation	Urban Vegetation	Agriculture Surface Soil
Steady state	1.66E-16	1.44E-09	1.10E-11	4.55E-05	2.46E-09	5.69E-10	1.37E-08	9.15E-09
January	3.20E-16	1.41E-09	1.08E-11	4.47E-05	2.42E-09	5.60E-10	1.35E-08	8.97E-09
February	3.75E-16	1.40E-09	1.07E-11	4.44E-05	2.41E-09	5.56E-10	1.35E-08	8.90E-09
March	3.74E-16	1.40E-09	1.07E-11	4.44E-05	2.41E-09	5.56E-10	1.35E-08	8.90E-09
April	2.03E-16	1.43E-09	1.09E-11	4.53E-05	2.45E-09	5.67E-10	1.37E-08	9.11E-09
May	1.03E-16	1.45E-09	1.10E-11	4.59E-05	2.47E-09	5.73E-10	1.38E-08	9.25E-09
June	1.76E-16	1.44E-09	1.10E-11	4.55E-05	2.46E-09	5.69E-10	1.37E-08	9.14E-09
July	1.50E-16	1.44E-09	1.10E-11	4.56E-05	2.47E-09	5.70E-10	1.37E-08	9.18E-09
August	1.43E-16	1.44E-09	1.10E-11	4.57E-05	2.47E-09	5.71E-10	1.38E-08	9.19E-09
September	9.05E-17	1.45E-09	1.11E-11	4.59E-05	2.47E-09	5.74E-10	1.38E-08	9.27E-09
October	1.17E-16	1.45E-09	1.10E-11	4.58E-05	2.47E-09	5.73E-10	1.38E-08	9.22E-09
November	1.53E-16	1.44E-09	1.10E-11	4.56E-05	2.47E-09	5.70E-10	1.38E-08	9.17E-09
December	2.81E-16	1.42E-09	1.08E-11	4.49E-05	2.43E-09	5.62E-10	1.36E-08	9.01E-09

Table H.3 continued

	Concentration (mol.m^{-3})							
	Forest Surface Soil	Urban Surface Soil	Agriculture Root Soil	Forest Root Soil	Urban Root Soil	Agriculture Vadose Soil	Forest Vadose Soil	Urban Vadose Soil
Steady state	9.12E-09	9.15E-09	2.05E-10	1.14E-10	1.69E-10	5.37E-14	2.99E-14	4.43E-14
January	8.95E-09	8.96E-09	2.02E-10	1.12E-10	1.66E-10	5.30E-14	2.95E-14	4.37E-14
February	8.89E-09	8.90E-09	2.00E-10	1.11E-10	1.65E-10	5.26E-14	2.92E-14	4.33E-14
March	8.89E-09	8.90E-09	2.00E-10	1.11E-10	1.65E-10	5.25E-14	2.92E-14	4.32E-14
April	9.08E-09	9.10E-09	2.04E-10	1.13E-10	1.68E-10	5.32E-14	2.96E-14	4.38E-14
May	9.20E-09	9.24E-09	2.06E-10	1.15E-10	1.70E-10	5.39E-14	3.00E-14	4.44E-14
June	9.11E-09	9.14E-09	2.05E-10	1.14E-10	1.69E-10	5.38E-14	2.99E-14	4.43E-14
July	9.14E-09	9.17E-09	2.05E-10	1.14E-10	1.69E-10	5.38E-14	2.99E-14	4.43E-14
August	9.15E-09	9.18E-09	2.06E-10	1.14E-10	1.69E-10	5.39E-14	3.00E-14	4.43E-14
September	9.21E-09	9.26E-09	2.07E-10	1.15E-10	1.70E-10	5.41E-14	3.01E-14	4.45E-14
October	9.18E-09	9.22E-09	2.06E-10	1.15E-10	1.70E-10	5.40E-14	3.01E-14	4.45E-14
November	9.14E-09	9.17E-09	2.05E-10	1.14E-10	1.69E-10	5.39E-14	3.00E-14	4.44E-14
December	8.99E-09	9.01E-09	2.03E-10	1.13E-10	1.67E-10	5.32E-14	2.96E-14	4.39E-14

Table H.4: Steady state and monthly varying concentrations of dimethoate in land-use distribution scenario II (un-forested scenario) given the 1986-2005 climate conditions

	Concentration (mol.m^{-3})							
	Atmosphere	Surface Water	Sediment	Impervious Surface	Agriculture Vegetation	Forest Vegetation	Urban Vegetation	Agriculture Surface Soil
Steady state	1.85E-16	1.61E-09	1.22E-11	5.08E-05	2.75E-09	2.43E-09	1.53E-08	1.02E-08
January	3.57E-16	1.57E-09	1.20E-11	4.98E-05	2.70E-09	2.38E-09	1.51E-08	9.99E-09
February	4.18E-16	1.56E-09	1.19E-11	4.94E-05	2.68E-09	2.36E-09	1.50E-08	9.91E-09
March	4.17E-16	1.56E-09	1.19E-11	4.94E-05	2.68E-09	2.36E-09	1.50E-08	9.91E-09
April	2.27E-16	1.60E-09	1.21E-11	5.06E-05	2.74E-09	2.42E-09	1.53E-08	1.02E-08
May	1.15E-16	1.62E-09	1.23E-11	5.13E-05	2.76E-09	2.45E-09	1.54E-08	1.03E-08
June	1.96E-16	1.60E-09	1.22E-11	5.08E-05	2.75E-09	2.42E-09	1.53E-08	1.02E-08
July	1.68E-16	1.61E-09	1.23E-11	5.09E-05	2.75E-09	2.43E-09	1.54E-08	1.02E-08
August	1.60E-16	1.61E-09	1.23E-11	5.10E-05	2.76E-09	2.43E-09	1.54E-08	1.03E-08
September	1.01E-16	1.62E-09	1.24E-11	5.14E-05	2.77E-09	2.45E-09	1.54E-08	1.04E-08
October	1.31E-16	1.62E-09	1.23E-11	5.12E-05	2.76E-09	2.44E-09	1.54E-08	1.03E-08
November	1.71E-16	1.61E-09	1.23E-11	5.09E-05	2.75E-09	2.43E-09	1.54E-08	1.02E-08
December	3.13E-16	1.58E-09	1.20E-11	5.00E-05	2.71E-09	2.39E-09	1.52E-08	1.00E-08

Table H.4 continued

	Concentration (mol.m^{-3})							
	Forest Surface Soil	Urban Surface Soil	Agriculture Root Soil	Forest Root Soil	Urban Root Soil	Agriculture Vadose Soil	Forest Vadose Soil	Urban Vadose Soil
Steady state	1.02E-08	1.02E-08	2.29E-10	1.18E-10	1.89E-10	6.00E-14	3.10E-14	4.94E-14
January	9.97E-09	9.99E-09	2.25E-10	1.16E-10	1.85E-10	5.91E-14	3.06E-14	4.87E-14
February	9.89E-09	9.91E-09	2.23E-10	1.15E-10	1.84E-10	5.85E-14	3.03E-14	4.82E-14
March	9.89E-09	9.91E-09	2.23E-10	1.15E-10	1.84E-10	5.84E-14	3.02E-14	4.81E-14
April	1.01E-08	1.02E-08	2.28E-10	1.18E-10	1.87E-10	5.94E-14	3.07E-14	4.89E-14
May	1.03E-08	1.03E-08	2.30E-10	1.19E-10	1.90E-10	6.02E-14	3.12E-14	4.96E-14
June	1.02E-08	1.02E-08	2.29E-10	1.18E-10	1.88E-10	6.00E-14	3.11E-14	4.94E-14
July	1.02E-08	1.02E-08	2.29E-10	1.19E-10	1.89E-10	6.01E-14	3.11E-14	4.95E-14
August	1.02E-08	1.03E-08	2.30E-10	1.19E-10	1.89E-10	6.01E-14	3.11E-14	4.95E-14
September	1.03E-08	1.04E-08	2.31E-10	1.20E-10	1.90E-10	6.04E-14	3.13E-14	4.97E-14
October	1.03E-08	1.03E-08	2.30E-10	1.19E-10	1.90E-10	6.04E-14	3.13E-14	4.97E-14
November	1.02E-08	1.02E-08	2.29E-10	1.19E-10	1.89E-10	6.02E-14	3.11E-14	4.95E-14
December	1.00E-08	1.00E-08	2.26E-10	1.17E-10	1.86E-10	5.94E-14	3.07E-14	4.89E-14

Appendix I

Steady state and monthly varying concentrations of PBDE-47 and dimethoate in the forested and un-forested landscapes in the 2005-2014 climate period

Table I.1: Steady state and monthly varying concentrations of PBDE-47 in land-use distribution scenario I (forested scenario) given the 2005-2014 climate conditions

	Concentration (mol.m^{-3})							
	Atmosphere	Surface Water	Sediment	Impervious Surface	Agriculture Vegetation	Forest Vegetation	Urban Vegetation	Agriculture Surface Soil
Steady state	8.73E-15	3.68E-11	2.83E-11	2.12E-06	1.45E-09	5.09E-10	4.82E-09	3.53E-08
January	9.25E-15	1.67E-11	1.49E-11	9.31E-07	2.27E-09	4.86E-10	9.75E-09	4.03E-08
February	9.31E-15	1.44E-11	1.16E-11	7.92E-07	2.66E-09	4.72E-10	1.21E-08	3.74E-08
March	9.20E-15	1.86E-11	1.39E-11	1.04E-06	2.38E-09	4.70E-10	8.80E-09	3.57E-08
April	8.94E-15	2.88E-11	2.1E-11	1.65E-06	1.74E-09	4.84E-10	5.81E-09	3.60E-08
May	8.50E-15	4.59E-11	3.35E-11	2.66E-06	1.28E-09	5.06E-10	4.18E-09	3.85E-08
June	8.68E-15	3.89E-11	3.05E-11	2.24E-06	1.41E-09	5.10E-10	4.67E-09	3.94E-08
July	8.66E-15	3.96E-11	3.04E-11	2.28E-06	1.40E-09	5.13E-10	4.63E-09	4.03E-08
August	8.07E-15	6.25E-11	4.58E-11	3.64E-06	1.07E-09	5.25E-10	3.49E-09	4.43E-08
September	8.29E-15	5.40E-11	4.22E-11	3.13E-06	1.16E-09	5.27E-10	3.80E-09	4.64E-08
October	8.17E-15	5.87E-11	4.47E-11	3.41E-06	1.11E-09	5.28E-10	3.60E-09	4.89E-08
November	8.97E-15	2.78E-11	2.46E-11	1.58E-06	1.69E-09	5.09E-10	5.95E-09	4.67E-08
December	9.19E-15	1.92E-11	1.59E-11	1.07E-06	2.16E-09	4.90E-10	8.41E-09	4.35E-08

Table I.1 continued

	Concentration (mol.m^{-3})							
	Forest Surface Soil	Urban Surface Soil	Agriculture Root Soil	Forest Root Soil	Urban Root Soil	Agriculture Vadose Soil	Forest Vadose Soil	Urban Vadose Soil
Steady state	2.91E-08	3.28E-08	5.62E-13	3.70E-13	4.10E-13	5.47E-20	3.60E-20	3.99E-20
January	2.68E-08	3.07E-08	5.61E-13	3.68E-13	4.11E-13	5.47E-20	3.60E-20	3.99E-20
February	2.48E-08	2.88E-08	5.57E-13	3.63E-13	4.08E-13	5.47E-20	3.60E-20	3.99E-20
March	2.32E-08	2.75E-08	5.49E-13	3.55E-13	4.02E-13	5.46E-20	3.58E-20	3.98E-20
April	2.30E-08	2.74E-08	5.41E-13	3.48E-13	3.95E-13	5.44E-20	3.56E-20	3.97E-20
May	2.49E-08	2.91E-08	5.34E-13	3.42E-13	3.9E-13	5.41E-20	3.53E-20	3.95E-20
June	2.57E-08	2.98E-08	5.30E-13	3.40E-13	3.87E-13	5.38E-20	3.51E-20	3.93E-20
July	2.64E-08	3.05E-08	5.28E-13	3.39E-13	3.86E-13	5.35E-20	3.48E-20	3.91E-20
August	3.00E-08	3.34E-08	5.30E-13	3.42E-13	3.88E-13	5.32E-20	3.46E-20	3.89E-20
September	3.19E-08	3.50E-08	5.37E-13	3.49E-13	3.93E-13	5.30E-20	3.45E-20	3.88E-20
October	3.42E-08	3.70E-08	5.46E-13	3.58E-13	4.00E-13	5.30E-20	3.45E-20	3.87E-20
November	3.26E-08	3.55E-08	5.54E-13	3.67E-13	4.07E-13	5.31E-20	3.46E-20	3.88E-20
December	3.01E-08	3.33E-08	5.59E-13	3.70E-13	4.11E-13	5.32E-20	3.47E-20	3.89E-20

Table I.2: Steadystate and monthly varying concentrations of PBDE-47 in land-use distribution scenario II (un-forested scenario) given the 2005-2014 climate conditions

	Concentration (mol.m^{-3})							
	Atmosphere	Surface Water	Sediment	Impervious Surface	Agriculture Vegetation	Forest Vegetation	Urban Vegetation	Agriculture Surface Soil
Steady state	8.94E-15	3.77E-11	2.90E-11	2.17E-06	1.48E-09	1.62E-09	4.93E-09	4.45E-08
January	9.42E-15	1.7E-11	1.52E-11	9.47E-07	2.31E-09	1.53E-09	9.93E-09	4.12E-08
February	9.47E-15	1.46E-11	1.18E-11	8.06E-07	2.71E-09	1.48E-09	1.23E-08	3.83E-08
March	9.37E-15	1.89E-11	1.42E-11	1.06E-06	2.42E-09	1.47E-09	8.97E-09	3.65E-08
April	9.13E-15	2.94E-11	2.14E-11	1.68E-06	1.78E-09	1.53E-09	5.94E-09	3.68E-08
May	8.72E-15	4.71E-11	3.43E-11	2.73E-06	1.31E-09	1.62E-09	4.29E-09	3.94E-08
June	8.88E-15	3.98E-11	3.12E-11	2.29E-06	1.44E-09	1.63E-09	4.78E-09	4.03E-08
July	8.87E-15	4.05E-11	3.11E-11	2.34E-06	1.43E-09	1.64E-09	4.74E-09	4.12E-08
August	8.32E-15	6.44E-11	4.71E-11	3.74E-06	1.10E-09	1.68E-09	3.59E-09	4.54E-08
September	8.52E-15	5.55E-11	4.34E-11	3.22E-06	1.20E-09	1.69E-09	3.90E-09	4.75E-08
October	8.41E-15	6.04E-11	4.60E-11	3.51E-06	1.14E-09	1.69E-09	3.71E-09	5.02E-08
November	9.15E-15	2.83E-11	2.52E-11	1.61E-06	1.73E-09	1.62E-09	6.08E-09	4.79E-08
December	9.36E-15	1.95E-11	1.62E-11	1.09E-06	2.20E-09	1.54E-09	8.57E-09	4.46E-08

Table I.2 continued

	Concentration (mol.m^{-3})							
	Forest Surface Soil	Urban Surface Soil	Agriculture Root Soil	Forest Root Soil	Urban Root Soil	Agriculture Vadose Soil	Forest Vadose Soil	Urban Vadose Soil
Steady state	2.68E-08	3.36E-08	5.75E-13	3.33E-13	4.19E-13	5.60E-20	3.24E-20	4.08E-20
January	2.47E-08	3.14E-08	5.74E-13	3.31E-13	4.19E-13	5.60E-20	3.24E-20	4.08E-20
February	2.28E-08	2.95E-08	5.70E-13	3.26E-13	4.17E-13	5.59E-20	3.23E-20	4.08E-20
March	2.14E-08	2.81E-08	5.62E-13	3.19E-13	4.11E-13	5.58E-20	3.22E-20	4.07E-20
April	2.13E-08	2.80E-08	5.53E-13	3.13E-13	4.04E-13	5.56E-20	3.20E-20	4.06E-20
May	2.30E-08	2.97E-08	5.46E-13	3.08E-13	3.98E-13	5.53E-20	3.18E-20	4.04E-20
June	2.37E-08	3.05E-08	5.42E-13	3.06E-13	3.95E-13	5.50E-20	3.15E-20	4.01E-20
July	2.44E-08	3.12E-08	5.40E-13	3.05E-13	3.94E-13	5.47E-20	3.13E-20	3.99E-20
August	2.75E-08	3.42E-08	5.42E-13	3.08E-13	3.96E-13	5.44E-20	3.11E-20	3.97E-20
September	2.93E-08	3.59E-08	5.49E-13	3.14E-13	4.01E-13	5.43E-20	3.10E-20	3.96E-20
October	3.14E-08	3.79E-08	5.59E-13	3.22E-13	4.09E-13	5.42E-20	3.10E-20	3.96E-20
November	2.99E-08	3.64E-08	5.68E-13	3.29E-13	4.16E-13	5.43E-20	3.11E-20	3.97E-20
December	2.76E-08	3.41E-08	5.73E-13	3.33E-13	4.20E-13	5.45E-20	3.12E-20	3.98E-20

Table I.3: Steady state and monthly varying concentrations of dimethoate in land-use distribution scenario I (forested scenario) given the 2005-2014 climate conditions

	Concentration (mol.m^{-3})							
	Atmosphere	Surface Water	Sediment	Impervious Surface	Agriculture Vegetation	Forest Vegetation	Urban Vegetation	Agriculture Surface Soil
Steady state	1.66E-16	1.44E-09	1.10E-11	4.55E-05	2.46E-09	5.69E-10	1.37E-08	9.15E-09
January	5.19E-16	1.38E-09	1.05E-11	4.36E-05	2.37E-09	5.47E-10	1.32E-08	8.74E-09
February	7.07E-16	1.34E-09	1.03E-11	4.25E-05	2.31E-09	5.34E-10	1.29E-08	8.53E-09
March	4.52E-16	1.39E-09	1.05E-11	4.39E-05	2.39E-09	5.51E-10	1.33E-08	8.81E-09
April	2.35E-16	1.43E-09	1.08E-11	4.51E-05	2.44E-09	5.65E-10	1.37E-08	9.07E-09
May	1.26E-16	1.45E-09	1.10E-11	4.58E-05	2.47E-09	5.72E-10	1.38E-08	9.21E-09
June	1.58E-16	1.44E-09	1.10E-11	4.56E-05	2.46E-09	5.70E-10	1.37E-08	9.17E-09
July	1.56E-16	1.44E-09	1.10E-11	4.56E-05	2.46E-09	5.70E-10	1.37E-08	9.17E-09
August	8.5E-17	1.45E-09	1.11E-11	4.60E-05	2.47E-09	5.74E-10	1.38E-08	9.28E-09
September	1.03E-16	1.45E-09	1.11E-11	4.59E-05	2.47E-09	5.73E-10	1.38E-08	9.25E-09
October	9.03E-17	1.45E-09	1.11E-11	4.60E-05	2.48E-09	5.74E-10	1.38E-08	9.27E-09
November	2.43E-16	1.42E-09	1.09E-11	4.51E-05	2.44E-09	5.65E-10	1.36E-08	9.06E-09
December	4.2E-16	1.39E-09	1.06E-11	4.41E-05	2.4E-09	5.53E-10	1.34E-08	8.85E-09

Table I.3 continued

	Concentration (mol.m^{-3})							
	Forest Surface Soil	Urban Surface Soil	Agriculture Root Soil	Forest Root Soil	Urban Root Soil	Agriculture Vadose Soil	Forest Vadose Soil	Urban Vadose Soil
Steady state	9.12E-09	9.15E-09	2.05E-10	1.14E-10	1.69E-10	5.37E-14	2.99E-14	4.43E-14
January	8.73E-09	8.74E-09	1.97E-10	1.10E-10	1.63E-10	5.21E-14	2.90E-14	4.29E-14
February	8.52E-09	8.53E-09	1.93E-10	1.07E-10	1.59E-10	5.08E-14	2.82E-14	4.18E-14
March	8.80E-09	8.81E-09	1.98E-10	1.10E-10	1.63E-10	5.16E-14	2.87E-14	4.25E-14
April	9.04E-09	9.06E-09	2.03E-10	1.13E-10	1.67E-10	5.29E-14	2.94E-14	4.36E-14
May	9.17E-09	9.21E-09	2.06E-10	1.15E-10	1.69E-10	5.38E-14	2.99E-14	4.43E-14
June	9.13E-09	9.16E-09	2.05E-10	1.14E-10	1.69E-10	5.38E-14	2.99E-14	4.43E-14
July	9.13E-09	9.16E-09	2.05E-10	1.14E-10	1.69E-10	5.38E-14	2.99E-14	4.43E-14
August	9.22E-09	9.27E-09	2.07E-10	1.15E-10	1.70E-10	5.41E-14	3.01E-14	4.45E-14
September	9.20E-09	9.24E-09	2.06E-10	1.15E-10	1.70E-10	5.41E-14	3.01E-14	4.45E-14
October	9.21E-09	9.26E-09	2.07E-10	1.15E-10	1.70E-10	5.41E-14	3.02E-14	4.46E-14
November	9.03E-09	9.05E-09	2.04E-10	1.13E-10	1.68E-10	5.35E-14	2.98E-14	4.41E-14
December	8.84E-09	8.85E-09	1.99E-10	1.11E-10	1.64E-10	5.24E-14	2.92E-14	4.32E-14

Table I.4: Steady state and monthly varying concentrations of dimethoate in land-use distribution scenario II (un-forested scenario) given the 2005-2014 climate conditions

	Concentration (mol.m^{-3})							
	Atmosphere	Surface Water	Sediment	Impervious Surface	Agriculture Vegetation	Forest Vegetation	Urban Vegetation	Agriculture Surface Soil
Steady state	3.57E-16	1.57E-09	1.2E-11	4.98E-05	2.7E-09	2.38E-09	1.51E-08	9.99E-09
January	5.77E-16	1.53E-09	1.17E-11	4.84E-05	2.63E-09	2.32E-09	1.47E-08	9.71E-09
February	7.83E-16	1.49E-09	1.14E-11	4.71E-05	2.57E-09	2.26E-09	1.43E-08	9.46E-09
March	5.03E-16	1.54E-09	1.17E-11	4.89E-05	2.65E-09	2.34E-09	1.48E-08	9.80E-09
April	2.63E-16	1.59E-09	1.21E-11	5.04E-05	2.73E-09	2.41E-09	1.52E-08	1.01E-08
May	1.4E-16	1.62E-09	1.23E-11	5.11E-05	2.76E-09	2.44E-09	1.54E-08	1.03E-08
June	1.77E-16	1.61E-09	1.23E-11	5.09E-05	2.75E-09	2.43E-09	1.53E-08	1.02E-08
July	1.74E-16	1.61E-09	1.23E-11	5.09E-05	2.75E-09	2.43E-09	1.53E-08	1.02E-08
August	9.5E-17	1.63E-09	1.24E-11	5.14E-05	2.77E-09	2.45E-09	1.54E-08	1.04E-08
September	1.15E-16	1.62E-09	1.24E-11	5.13E-05	2.76E-09	2.45E-09	1.54E-08	1.03E-08
October	1.01E-16	1.62E-09	1.24E-11	5.14E-05	2.77E-09	2.45E-09	1.54E-08	1.04E-08
November	2.71E-16	1.59E-09	1.21E-11	5.03E-05	2.73E-09	2.4E-09	1.52E-08	1.01E-08
December	4.67E-16	1.55E-09	1.18E-11	4.91E-05	2.67E-09	2.35E-09	1.49E-08	9.85E-09

Table I.4 continued

	Concentration (mol.m^{-3})							
	Forest Surface Soil	Urban Surface Soil	Agriculture Root Soil	Forest Root Soil	Urban Root Soil	Agriculture Vadose Soil	Forest Vadose Soil	Urban Vadose Soil
Steady state	9.97E-09	9.99E-09	2.25E-10	1.16E-10	1.85E-10	5.91E-14	3.06E-14	4.87E-14
January	9.70E-09	9.71E-09	2.19E-10	1.13E-10	1.81E-10	5.79E-14	3.00E-14	4.77E-14
February	9.44E-09	9.45E-09	2.14E-10	1.10E-10	1.76E-10	5.63E-14	2.91E-14	4.64E-14
March	9.78E-09	9.80E-09	2.20E-10	1.14E-10	1.81E-10	5.74E-14	2.96E-14	4.72E-14
April	1.01E-08	1.01E-08	2.26E-10	1.17E-10	1.87E-10	5.90E-14	3.05E-14	4.86E-14
May	1.02E-08	1.03E-08	2.30E-10	1.19E-10	1.89E-10	6.00E-14	3.11E-14	4.94E-14
June	1.02E-08	1.02E-08	2.29E-10	1.19E-10	1.89E-10	6.01E-14	3.11E-14	4.95E-14
July	1.02E-08	1.02E-08	2.29E-10	1.19E-10	1.89E-10	6.01E-14	3.11E-14	4.95E-14
August	1.03E-08	1.04E-08	2.31E-10	1.20E-10	1.90E-10	6.04E-14	3.13E-14	4.97E-14
September	1.03E-08	1.03E-08	2.31E-10	1.20E-10	1.90E-10	6.05E-14	3.13E-14	4.98E-14
October	1.03E-08	1.04E-08	2.31E-10	1.20E-10	1.90E-10	6.05E-14	3.13E-14	4.98E-14
November	1.01E-08	1.01E-08	2.27E-10	1.17E-10	1.87E-10	5.97E-14	3.09E-14	4.92E-14
December	9.83E-09	9.85E-09	2.22E-10	1.15E-10	1.83E-10	5.84E-14	3.02E-14	4.81E-14