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Baseline Studies of Selected Polybrominated Diphenyl Ethers in the Air

of the Nandamojo Watershed, Costa Rica

by

Mary Sophia Geesey

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science
Department of Environmental and Occupational Health
with a concentration in Environmental Health
College of Public Health
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Persistent Organic Pollutants, Spatial Distribution

Dedication

To my husband, Robert Beltron Geesey, for being my personal motivator; and my mother and first teacher, Judith Ann Martin, for always believing in me.

Acknowledgments

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Abstract

Polybrominated diphenyl ethers (PBDEs) have been used as flame retardants in a number of common household and commercial products around the world. PBDEs enter the environment in a variety of ways, such as through emissions, leaching from end-of-life electronics in landfills, and incineration. While many countries have phased out the manufacturing of penta-, octa-, and deca-PBDEs or have banned the manufacture and use of these congeners altogether, these persistent organic pollutants (POPs) continue to be detected in humans and the environment.

This study investigates spatial and temporal variations of selected PBDEs in the air of the Nandamojo watershed area in Costa Rica by comparing air concentrations of PBDEs in the dry winter vs. wet summer seasons and rural vs. urban areas and also investigates the impact of anthropogenic activities on air concentration of PBDEs. This study is significant to the field, because there are no baseline studies nor are there currently any monitoring programs to assess the environmental levels of PBDEs or other POPs for this region of the Guanacaste province. Baseline information is needed to track spatial

and temporal trends as well as evaluate the effectiveness of control measures employed nationally and internationally.

Samples obtained from passive air sampling devices were analyzed via GC/MS for a number of congeners. PBDE-47 and -99 were found to be the congeners present in greatest concentration in air samples from the Nandamojo watershed area. Air concentrations were estimated assuming an average sampler uptake rate of 3.5 m^3/day and ranged as follows: $\Sigma PBDE_5$ 35.20-1549.25 pg/m^3 over the entire study. The presence of PBDEs in remote and pristine environments indicates that PBDEs are now a global concern.

This study suggests that the spatial and temporal distribution patterns observed are strongly related to anthropogenic activities and presence of a population similar to that observed in other studies. The presence of PBDEs has become a global issue and, as such, these results provide background information on air concentrations of PBDEs for use in a global-scale multimedia model. In order to monitor PBDEs globally, it is imperative to implement and/or expand surveillance programs internationally.

Chapter 1:

Introduction

1.1 Polybrominated Diphenyl Ethers

1.1.1 Background

Polybrominated diphenyl ethers (PBDEs) are organobromine compounds belonging to a broader class of brominated chemical compounds. PBDEs historically have been heavily used as flame retardants in a number of common household and commercial products around the world (Frouin et al., 2013). PBDEs consist of two halogenated aromatic rings and are classified by the number and position of the bromine atoms on the rings (EPA, 2013).   There are 209 possible configurations of $C_{12}H_{10-x}Br_xO$:

Where x = 1, 2, …, 10 = m + n
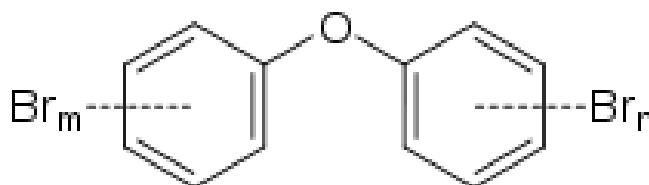
Figure 1: Chemical structure of PBDEs

The various configurations are called congeners. The three primary

formulations of PBDEs, penta-, octa-, and deca-BDE (representing the

dominant homolog groups), are part of a class of chemicals that are

added to a variety of plastics, especially thermoplastic materials

(Goosey, 2006); polyurethane foam; textiles; printed circuit board

laminates and other electronics; and building materials too numerous

to list. PBDEs are present in common household electrical appliances,

electronics, and soft goods, including televisions, computers, furniture,

carpets, and draperies. These compounds are also found in motor

vehicles and airplanes. Additionally, PBDEs have even been used in

children's sleepwear (Goosey, 2006) and bedding materials

(Richardson, 2008).

The penta-BDE technical mixture is used primarily in foams and

soft goods, while the octa- and deca-BDE technical mixtures are

primarily used in the hard plastics of molded casings, building

materials, and small components (Vonderheide et al., 2008). At the

molecular level, PBDEs are problematic in that they are an *additive*,

which is incorporated into polymers and resins (Stapleton, 2006)

during the manufacturing phase of plastics, foams, and textiles and

are, therefore, not covalently bonded (Gevao et al., 2006; Goosey,

2006; Losada, Parera, Abalos, Santos, & Galceran, 2010; Palm et al.,

2002).

The sole purpose of PBDEs is to delay ignition of household goods or electronics and, in the event of a fire, to melt and form a blanket, thereby reducing the rate of the fire's growth (EPA, 2013). As a result, any delay or slowing of the growth rate of a fire increases valuable escape time, which, in turn, saves lives.

1.1.2 Movement into Environment

PBDEs have migrated into the environment through emissions; incineration; leaching from end-of-life electronics, building materials, and foams in landfills; and sewage and effluents from wastewater treatment plants as well as intentional or unintentional industrial discharge into waterways (Goosey, 2006; Jones-Otazo et al., 2005). Factors that influence emissions from objects containing PBDEs include direct physical contact with an object (Gevao et al., 2006), the physical use of the object (a.k.a., wear and tear) (Goosey, 2006; Jones-Otazo et al., 2005), environmental conditions, such as temperature and humidity during use (Mandalakis, Stephanou, Horii, & Kannan, 2008), and their location within the object (Goosey, 2006). Emissions can occur without use (Klösener, Swenson, Robertson, & Luthe, 2008), at room temperature (Kajiwara, Nomo & Takigami, 2011), increase during the physical use of the object (Goosey, 2006), subsequently moving into the surrounding air. Automobile interiors

are an excellent case in point. Air samples from automobile interiors,

used to analyze emissions from foams and plastics which contain

penta- and octa-BDE technical formulations, are up to 30-fold higher

when compared to those from residences (Fromme et al., 2009).

These emissions then readily migrate from the automobile interior to

the outdoor environment.

1.1.3 Environmental Fate and Transport

PBDEs have not only demonstrated regional transport (Jones-

Otazo et al., 2005) but also long-range atmospheric transport

capabilities (LRAT) (Ali, Harrad, Goosey, Neels, & Covaci, 2011;

Vonderheide et al., 2008). Their movement through the environment

occurs via a number of complex mechanisms, such as fractionation

(Goosey, 2006; Shen et al., 2006) or hopping (Goosey, 2006; Gouin,

Mackay, Jones, Harner, & Meijer, 2004; Wania & Westgate, 2008),

which are greatly influenced by wind and temperature patterns.

Fractionation involves the separation or division of ΣPBDEs into

congeners with varying vapor pressures and is similar to the process of

distillation of oil (Goosey, 2006). Hopping is a form of LRAT whereby

temperature-sensitive PBDEs move to a higher latitude or altitude with

the warmth of the day and are deposited as the air temperature begins

to cool after sunset, then they are re-volatilized with the warmth of

the next day and the process is repeated until they are trapped in regions with low temperatures or high elevations (Goosey, 2006).

PBDEs have been found to exist as far away as the Arctic and Antarctica (Li et al., 2012) in the air and snow as well as on high mountain tops in other parts of the world (Meire, Lee, Targino, Torres, & Harner, 2012; Pozo et al., 2012; Wania & Westgate, 2008) and in wildlife inhabiting these regions, such as polar bears and other animals with diets rich in fat.

Additionally, PBDEs bioaccumulate in humans, fish, birds, and other mammals (Frouin et al., 2013) as well as accumulate in entire ecosystems (Goosey, 2006). The highest concentrations are, however, found in regions having an extensive industrial presence (Goosey, 2006; Jones-Otazo et al., 2005), though areas with electronic equipment recycling facilities (Richardson, 2008), areas with end-of-life disposal sites (Watanabe & Sakai, 2003), and municipal waste disposal sites, especially in developing countries or countries that receive bulk end-of-life electronic wastes (Athanasiadou, Cuadra, Marsh, Bergman, & Jakobsson, 2008), and particularly waste combustion sites (Wyrzykowska-Ceradini, Gullett, Tabor, & Touati, 2011) have also shown high air concentrations of PBDEs.

1.1.4 Adverse Health Effects

While the United States and the European Union, as well as many other countries, have phased out the manufacture of penta-, octa-, and deca-PBDEs or have banned the manufacture and use of these congeners altogether, these persistent organic pollutants (POPs) continue to be detected in humans (Chevrier et al., 2010) and the environment as well as in areas where no manufacturing has ever occurred (EPA, 2013). PBDEs have characteristics of other POPs, such as polychlorinated biphenyls (PCBs), dioxins, and furans (see Figure 2) and similarly are persistent and ubiquitous in the environment (Palm et al., 2002). A September (2004) public health statement from the Agency for Toxic Substances and Disease Registry (ATSDR) states that while the Centers for Disease Control and Prevention (CDC) do not know if PBDEs cause cancer in humans, based upon numerous animal and cellular studies, PBDEs are a likely human carcinogen.
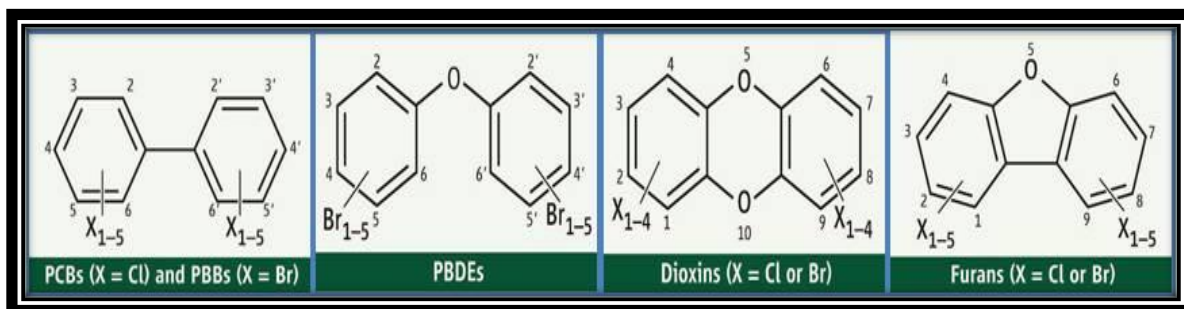
Figure 2: Chemical structure of PCBs, PBDEs, Dioxins, & Furans

The National Institute of Health (NIH) research website on PBDEs (2013) attributes the persistence of PBDEs in the environment to the chemicals' lipophilic nature, relative stability, and resistance to chemical or physical degradation. These characteristics result in half-lives as long as twelve years (Chevrier et al., 2010). For these reasons, PBDEs bioaccumulate in wildlife, humans, and ecosystems; and have been identified as a class of chemicals that pose a risk to the health of humans.

Animal research and cellular studies have uncovered a potential for liver and thyroid toxicity (EPA, 2013; Martin, Lam, & Richardson, 2004) and interference with the development of the central nervous system (Fromme et al., 2009) as well as carcinogenicity (Palm et al., 2002; Vonderheide et al., 2008). Further animal studies have indicated that, in addition to these effects, low levels of PBDEs have a negative effect on fetal development (Fromme et al., 2009). Qualitative studies have been performed to determine the potency of many PBDE congener mixtures (Palm et al., 2002). The studies reviewed focused predominantly on assessing the level of effect on the endocrine system from exposures to PBDEs (Palm et al., 2002; Vonderheide et al., 2008).

Endocrine disruptors are chemicals that interfere with, or mimic, the effects of the body's endocrine system. These disruptors can produce adverse developmental, reproductive, neurological, immunological effects, and overall homeostasis in both humans and wildlife (Vonderheide et al., 2008). In a research study supported by the National Institute of Health, Chevrier et al. (2010) showed that decreased levels of thyroid stimulating hormone around the beginning of the third trimester of pregnancy were associated with exposure to flame retardant compounds. In another paper based on the same study, high levels of PBDEs correlated with infertility (Harley et al., 2010). Women with elevated exposures took longer to conceive, in essence, they were sub-fertile. The probability of a woman becoming pregnant decreased by 30% for every ten-fold increase of ΣPBDE level in her blood (Harley et al., 2010). Additionally, PBDEs have been implicated in thyroid cancer (Zhang et al., 2008) and non-Hodgkin's lymphoma (Kalantzi & Siskos, 2011).

The body burden of PBDEs in humans and wildlife as well as the environmental levels detected in ecosystems double every few years (Chevrier et al., 2010; Jones-Otazo et al., 2005; Richardson, 2008) in the United States, reflecting not only the historical mass production of these chemicals in the United States, but the elevated desire of the American consumer for PBDE-laden goods, many of which are

imported. Primary routes of exposure differ, however, for infants,
children, teenagers, and adults. The exact amount of PBDEs absorbed
by an individual during an exposure event is not fully known or
understood at this time (Fromme et al., 2009) and, therefore, requires
additional research.

Under the Stockholm Convention, the European Union, Japan,
and China have banned the use of penta- and octa-PBDEs since 2004
(Miglioranza et al., 2013). Additionally, the European Union has
banned deca-PBDE since 2008 (Ali et al., 2011). Despite the phase-
out of deca-PBDEs and the ban under the Stockholm Convention of
penta- and octa-PBDEs, these persistent organic pollutants continue to
make their way into remote and pristine ecosystems in a variety of
ways, such as through products currently in use or through end-of-life
disposal activities. Costa Rica, for example, is a region that contains a
number of remote and pristine ecosystems. While this country has
never manufactured PBDEs directly, it does manufacture goods that
likely include components containing PBDEs, such as printed circuit
board laminates and other electronics.

1.2 Study Site

Located in Central America, Costa Rica is situated between the
Pacific Ocean and the Caribbean Sea, with Nicaragua to the north and

Panama to the southeast. Costa Rica's least populated province,

Guanacaste, is home to almost 350,000 inhabitants.

Figure 3: Nandamojo Watershed within Guanacaste Province, Costa Rica

Of major importance is the Nandamojo watershed, which, according to the non-profit organization Restoring Our Watershed, covers approximately 115 km^2 of the approximate 10,145 km^2 of the Guanacaste province (Guanacaste Costa Rica, 2013). This area, primarily a dry-tropical forest, has a wet summer season from May 1st to October 31st and a dry winter season from November 1st to April 30th.

The Nandamojo watershed lies on the Pacific side of the isthmus-dwelling nation in the northwestern province, Guanacaste, and is an important source of fresh water to the region. Primary agricultural activity in this region includes cattle-raising and subsistence farming of corn and rice as well as the cultivating of cash crops such as coffee and bananas (Restore Our Watershed, 2013). It is important to note that Costa Rica is a major consumer of pesticides (Galt, 2008; Gouin, Wania, Ruepert, & Castillo, 2008), such as carbofuran, chlorpyrifos, and phorate. In addition to atmospheric deposition, the Nandamojo watershed is subject to contamination from agricultural run-off as well as urban run-off stemming from anthropogenic activities.

The province's chief economic activity is tourism due to its balmy climate, beaches, and warm waters. Guanacaste province is well known as a surfing destination. Other popular tourist activities include fishing, diving, zip-lining, swimming, and ecotourism. The urban

population centers are located primarily near the coast. Moving farther inland and up the low plains of the region, human populations generally decrease, and the region becomes more rural and remote, thereby, demonstrating an urban-rural-remote population gradient. The burning of all household refuse, a common practice in developing countries (Vonderheide et al., 2008), takes place in small piles outside of homes or at larger dump sites.

1.3 Goals

The main purpose of this study is to provide baseline data for future studies of PBDEs in the Nandamojo watershed region while addressing a number of issues, including:

1. Do air concentrations of PBDEs decrease during the rainy season in this region?

2. Are air concentrations of PBDEs lower in rural areas than in urban areas of this region?

3. Are air concentrations influenced by anthropogenic activities in this region?

This study investigates temporal and spatial distribution of selected PBDEs in the air of the Nandamojo watershed area of

Guanacaste province in Costa Rica. In addition, this study compares air concentrations of PBDEs through the dry season into the wet season; urban, rural, and remote areas; and investigates the impact of regional and local anthropogenic activities on air concentrations.

This study is significant to the field, because there are no baseline studies nor are there currently any monitoring programs to assess the environmental levels of PBDEs or other POPs for this region of the Guanacaste province of Costa Rica. Information on concentration levels for PBDEs in air is needed, first to establish a baseline, then to track temporal and spatial trends as well as evaluate the effectiveness of control measures employed nationally and internationally.

Chapter 2:

Materials and Methods

2.1 Introduction

2.1.1 Background

The purpose of collecting air samples in the Nandamojo watershed region is to obtain baseline data for future studies by determining the presence and distribution of PBDEs in the air of this region. Physiochemical properties, such as vapor pressure and water solubility, affect the behavior of the specific congener in the air (Watanabe & Sakai, 2003). Many of the heavier PBDE congeners, specifically BDE-209, have low vapor pressures and low water solubilities (Martin et al., 2004; Vonderheide et al., 2008; Watanabe & Sakai, 2003), which suggests that the higher brominated congeners have an affinity for binding to particulate matter (Watanabe & Sakai, 2003); whereas the lesser brominated congeners, which are more bioaccumulative, have higher vapor pressures as well as higher water solubilities and tend to stay in the vapor phase (Watanabe & Sakai, 2003). It is important to note that researchers, such as La Guardia, Hale, and Harvey (2006) and Watanabe and Sakai (2003), hypothesize

that the bioaccumulative lower-brominated congeners, with enhanced toxicity, may be the result of the debromination of PBDE-209, a product still manufactured and widely used today in the hard plastics of electronics. These researchers and others have called for additional studies, as this congener may serve as a significant source of lower brominated congeners in the environment (Vonderheide et al., 2008).

2.1.2 Passive Air Sampling

Passive air sampling is a low-cost and simple method, which is readily deployed in rural, urban, and/or remote locations. The collection medium utilized in these devices is an inexpensive polyurethane foam (PUF) disk. The uptake rate of 3.5 m^3 per day is used to estimate air concentrations (Jaward et al., 2005).

For this study, passive air sampling units with PUF disks were deployed in four periods (covering one year); however, only three periods (Period I, II, and III) have been retrieved to date. This type of monitoring device has been shown to be successful at sequestering PBDEs in tropical settings (Gouin et al., 2008). The sequestered amount of PBDEs in each sampling device in each period was then extracted, analyzed, and compared. PBDEs are readily extracted from PUF disks by means of an organic solvent, such as DCM via soxhlet apparatus.

2.2 Sample System Deployment and Collection

2.2.1 Materials

The PUF disks were purchased from Tisch Environmental, Inc. (USA). Prior to deployment, the PUF disks were pre-cleaned with DCM, dried, and stored in baked amber glass jars. The sampler assemblies were purchased from Environment Canada and are designed for easy on-site construction and deployment. Each unit consists of a mounting bracket, a 2-piece stainless steel housing, a 40.6 cm threaded rod, 4 wing nuts, 4 flat washers, and a 5.5 x 0.5in. circular PUF disk (see Figure 4).
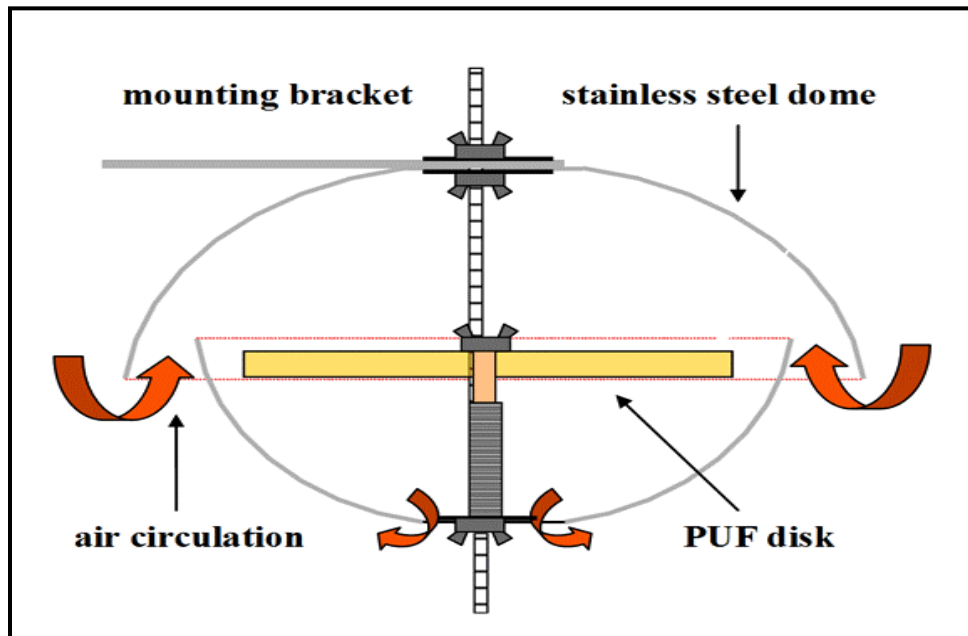
Figure 4: Diagram of PUF Disk Air Sampling Unit

Other materials needed for collection include the following:

Pliers, wrench, pocket knife, fishing line, Sharpie® marker, latex

gloves, aluminum foil, and sandwich-sized (BPA-free) ZipLoc® bags.

2.2.2 Deployment and Collection

Twenty sites were selected (see Table 1 and Figures 5 & 6) for

deployment based upon three general factors: Personal convenience,

such as closeness to a road; proximity to a body of water, such as a

river, stream, or estuary; and ease of placement/deployment, such as

the location provides an adequate attachment point for a sampling

unit. Additionally, sample Sites cover urban, rural, and remote areas.

Air samples were obtained via passive air sampling units described in

section 2.2.1, which were tagged with the study's point of contact

information. There was no direct communication (verbal or written)

with property owners regarding placement of sampling units.

In the Figure 6 satellite view of the Nandamojo watershed study

site, the watershed boundary is indicated by the purple line. The blue

circles with numbers beside them indicate Period I deployment Sites,

which correspond to the grey numbered circles in Figure 5 with Site

descriptions listed in Table 1.
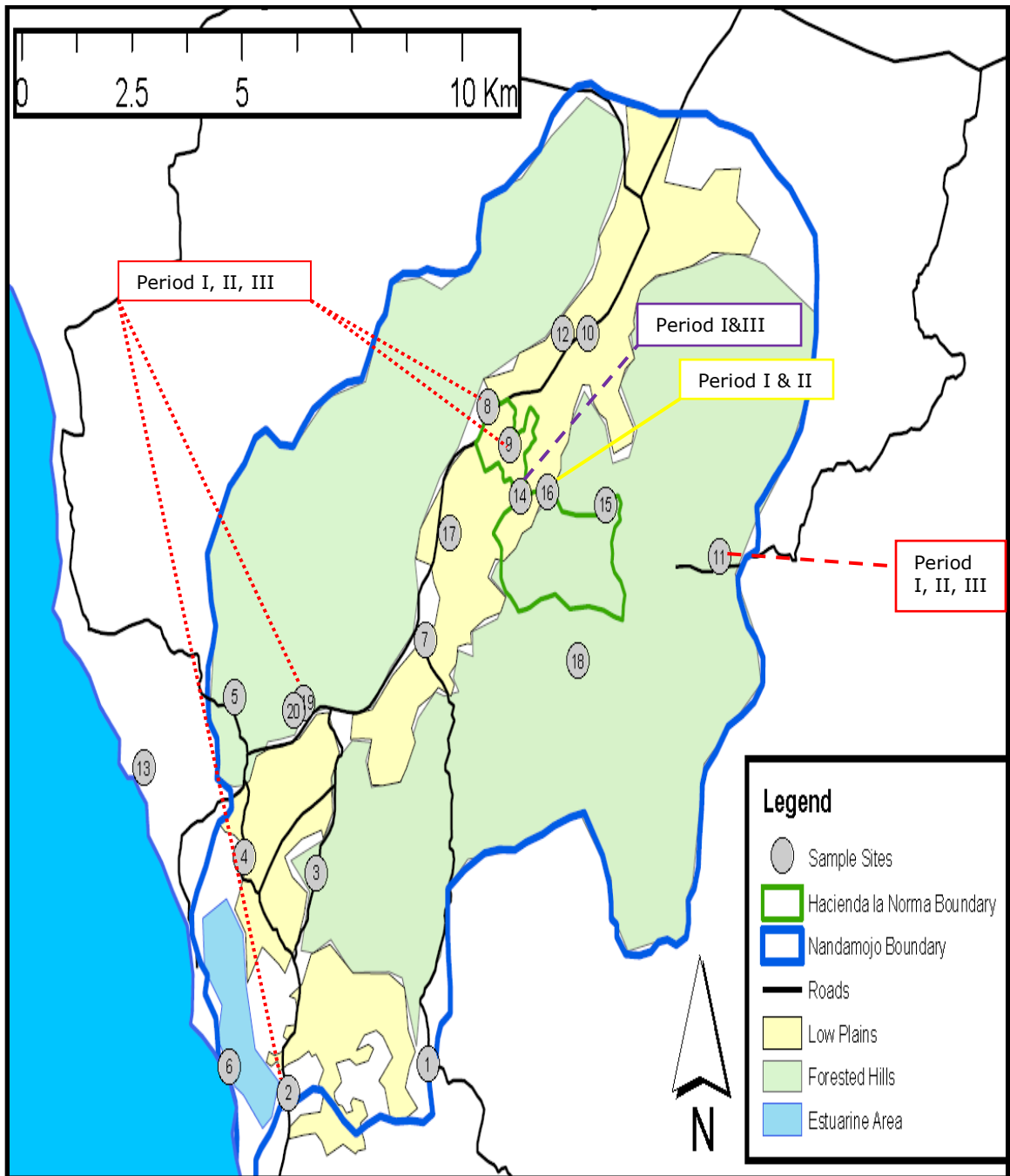
Figure 5: Nandamojo watershed study site plan view
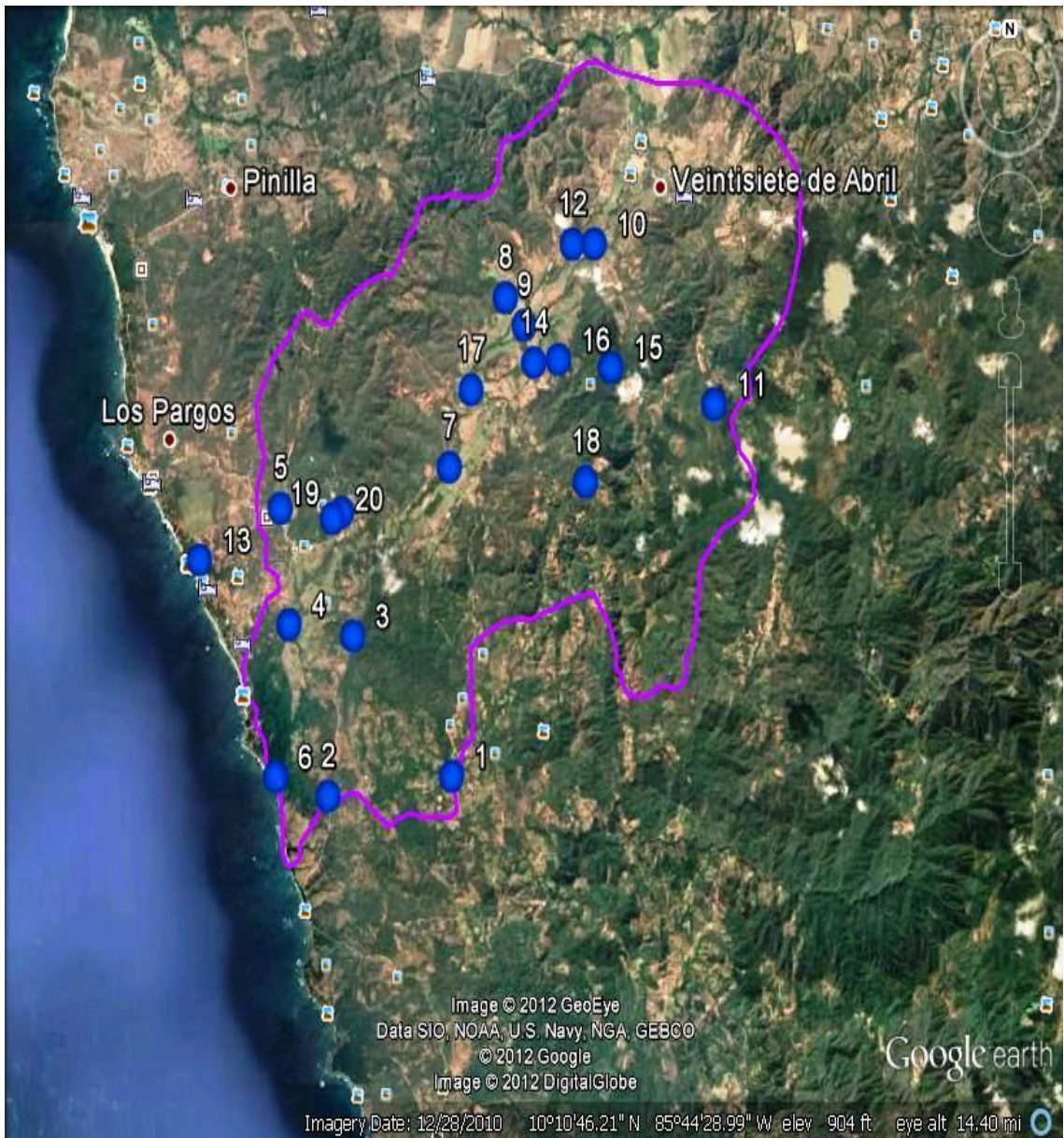
Figure 6: Nandamojo watershed study site satellite view

Table 1: Deployment sites by number and description

Sample Site	Description of Location
1	La Florida Bridge (Rio Pilas)
2	Venado Bridge
3	Vulture Creek
4	Tortuga Creek (close to street)
5	Paraiso North Creek
6	The Estuary
7	Rio Seco Bridge
8	Ranch (Behind Lodge)
9	Near Creek - stream 1 (Behind Field)
10	Latrine Creek (Very close to road)
11	San Jose De La Montagna
12	Chicago Title Creek
13	Playa Negra Creek (very little air flow)
14	Far Creek second stream (Behind field)
15	Horse trail (start of zip line)
16	End of Zip Line
17	Rio Seco Creek
18	Plunge pools (Water Falls)
19	Tom's Upper Cabin
20	Matt's cul-de-sac

The location of each deployment site for the passive air sampler is described in Table 1 with the corresponding number located on both the plan view (Figure 5) and satellite (Figure 6) maps. In Figure 5, roads are indicated by black lines, while the low plains and forested hills are denoted by beige and green shaded areas, respectively. Trees as well as other plants have been shown to act as filters for air contaminants (Gouin et al., 2008; Jaward et al., 2005) and can

influence air concentrations of PBDEs.   For this study, however, forest vegetation composition and mass were not included.

Sample sites 2, 8, 9, 11, and 19, highlighted in red in Table 1 and indicated in the Study Site plan view map (Figure 5), were sampling units recovered in Periods I, II, and III. The sampling unit from sample Site 14, highlighted in purple (see plan view map, Figure 5), was recovered in Periods I and III; while the sampling unit from sample Site 16 (see plan view map, Figure 5), highlighted in yellow, was recovered in Periods I and II.

Procedures were followed during deployment to avoid contamination and/or cross-contamination of the PUF disks. Additionally, while securing the sampling units, relevant data and observations were recorded (see Chapter 3). At each site, prior to collection and deployment, materials from section 2.2.1 were laid out. Each sampling unit was handled with clean latex gloves to minimize contamination. PUFs containing samples were gently wrapped in aluminum foil and enclosed tightly. Foil-wrapped PUFs were then secured in ZipLoc® bags. The description of location, sample site number, and date and time of collection were recorded on the outside of the bag with the Sharpie® marker. A second pair of clean latex gloves was then used for resetting the sampling unit for deployment to minimize cross-contamination. A clean PUF was carefully removed

from its packaging, inserted into the sampling unit, reassembled, and remounted on its location. Successful deployment and collection of passive air sampling units are listed by location within each Period in Table 2.

Table 2: Deployment and collection sites by period

Period I	Period II	Period III
2	2	2
3	n/a	n/a
8	8	8
9	9	9
10	n/a	n/a
11	11	11
14	14	n/a
16	n/a	16
19	19	19

Deployment at twenty original locations (see Table 1) resulted in the collection of nine units in Period I (see Table 2). Collection of deployed units decreased each successive period due to tampering and/or destruction of units or from loss due to unknown reasons.

2.3 Sample Extraction and Preparation

2.3.1 Materials

Dichloromethane (DCM) was obtained from Fisher Scientific (Pittsburg, PA). The activated silica (Silica gel 60 with ASTM mesh

rating of 70-230) and the sodium sulfate were obtained from Merck

and baked four (4) hours at 450° C. Other chemicals, solutions, and

glassware as well as the glass wool were from available laboratory

stock. All glassware, including the rotary evaporator, flasks, amber

wide-mouthed vials, glass syringes and Pasteur pipettes, glass rods,

specialty columns with reservoirs, gas chromatograph/mass

spectrogram (GC/MS) vials and caps, and spatulas, were either baked

at the appropriate temperature and time or rinsed with acetone,

hexane (HEX), and DCM prior to use to ensure sterility. The PBDE

standards mixture used for the Standard at selected concentrations for

the GC/MS included BDE-28, -47, -99, -100, -153, -154, -183, and

-209 and was purchased from AccuStandard (New Haven, CT). Mirex

and the individual standards used to prepare the spike were from

laboratory stock (purchased from AccuStandard).

2.3.2 Extraction

Soxhlet extraction apparatuses with flasks at the base were used

to extract contaminants from the PUF disks. Each flask was clearly

labeled, then filled with 250 ml of DCM and a few anti-bumping

granules, and subsequently placed into the extraction apparatus. The

DCM contained in the apparatus with attached flask was then allowed

to work overnight for approximately 20 hours. Corresponding samples

were collected into the appropriate flasks. The next morning, the flasks with the samples inside were removed from the apparatus, stoppered, and wrapped with paraffin film. Each labeled flask, in turn, was then placed on the rotary evaporator to remove excess solvent by evaporation. The rotary evaporator was washed three (3) times each with acetone, HEX, and DCM before attaching a flask. Each flask ran 25 to 30 minutes with the contents reduced to approximately one (1) ml. Each reduced sample was then transferred via baked Pasteur pipette to a correspondingly labeled amber wide-mouthed vial, capped with a foil-lined lid, and sealed with paraffin film to prevent evaporation and contamination. The samples were then placed in the refrigerator to await cleanup.

2.3.3. Sample Cleanup

Specialty columns were washed with acetone, HEX, and DCM and then placed on ring stands secured with clamps. In each column, a small square of glass wool was inserted, using an acetone rinsed glass rod to push it all the way down to the reservoir. Using a modified AccuStandard EPA method 1614, the layers of the silica gel column were constructed as follows: A small square of glass wool (packed in reservoir), 1 g silica, 4 g basic silica (33% w/w NaOH), 1 g silica, 8 g acidic silica (40% w/w H_2SO_4), 2 g silica, and 4 g sodium sulfate. All

were slurry-packed with 1 HEX: 1 DCM, with the exception of the sodium sulfate, which was dry-packed. Each column was rinsed between layers and each layer was allowed to settle before adding the next layer. After constructing the column, the solvent was drained until the level remaining in the column was approximately one (1) cm above the reagents.

Next, the samples were added to the columns. After adding a sample to each corresponding column, each vial was rinsed three (3) times with 1 HEX: 1 DCM to ensure that the entire sample was removed from the vial. This was followed by the addition of 100 ml of 1 HEX: 1 DCM in 50 ml increments. Each sample was collected into a correspondingly labeled flask, stoppered, sealed with paraffin wrap, and returned to the refrigerator until needed for further processing.

Cleaned samples from the refrigerator were allowed to come to room temperature each time they were removed for processing. Each labeled flask was then placed on the rotary evaporator to remove excess solvent by evaporation. The rotary evaporator was washed three (3) times each with acetone, HEX, and DCM before attaching a flask. Each flask ran 25 to 30 minutes and was reduced to approximately one (1) ml.   Each cleaned and evaporated sample was then transferred via baked Pasteur pipette to an appropriately labeled amber wide-mouthed vial and then transferred to the Nitrogen turbo-

evaporator for blow-down. Each vial was checked after seven (7) minutes, then after an additional 15 minutes, and after a final 15 minutes. Samples were then transferred to labeled amber GC vials via baked Pasteur pipette, fixed with 50 µl of dodecane, and returned to the Nitrogen turbo-evaporator to be reduced to 50 µl. Five (5) µl of Mirex (100 pg/µl), an internal standard, were added to each labeled GC vial containing the samples and all were re-capped and placed in the GC/MS for analysis.

2.4 GC/MS Analysis

A brief literature review indicates that GC/MS is the gold standard for analysis of PBDEs in air (Palm et al., 2002; Stapleton, 2006; Wise, Barceló, Garrigues, & Turle, 2006). Samples, field blanks, calibration blanks, and standards were analyzed on an Agilent 7890A using methane as the reagent gas and the splitless injection technique. Splitless injection is the most common technique used (Stapleton, 2006) for analyzing PBDEs. The Agilent 7890A splitless injection utilizes a 1 µl injection volume at 300˚C. The oven's program begins at 80˚C, at which the temperature is held for 2 minutes, then it begins to ramp up at a rate of 25˚C per minute until 210˚C is reached. This temperature is held for 2 minutes, whereby the temperature then ramps up again at a rate of 5˚C per minute until

the temperature ultimately reaches 315°C. The oven temperature is then held at 315°C for 10 minutes. For optimal resolution of the specific congeners of interest in this study, the 20 m chromatographic column with 0.25 mm i.d. and a film thickness of 0.25 µm was used.

A known mixture and concentration of calibration standards were used to identify and quantify compounds of interest from the samples. The congeners included in the mixture were: BDE-28, -47, -99, -100, -153, -154, -183, and -209 at total concentrations of 5pg/µl, 10pg/µl, 25pg/µl, 50pg/µl, and 100pg/µl.

2.5 Quality Control and Quality Assurance

The measurement of polybrominated diphenyl ethers presents a number of analytical challenges as applied to environmental analysis (Wise et al., 2006), such as developing methods to detect BDE-209, injection techniques, GC column selection, chromatographic interferences, and calibration standards. Other challenges, such as cost, analysis time required, and GC/MS resolution and sensitivity (Stapleton, 2006) are important to consider as well.

Strict quality control and quality assurance measures were used for all analytical procedures. Every effort was made to ensure that each sample was treated in exactly the same manner, using the exact same procedures. Field blanks were obtained during each deployment

of passive sampling units; each PUF disk, including the field blanks, was spiked prior to the extraction process; and system calibration blanks were used every six samples in the GC/MS. Wide-mouth amber vials and amber GC/MS vials were used to minimize photodegradation. Foil-lined caps and paraffin film were used to minimize loss via evaporation. Method detection limits (MDLs) were obtained from laboratory blanks, which were quantified at 3 times the standard deviation of the concentration of the mean. Only peaks with signal to noise ratios ≥3 were integrated. Reported values were not recovery corrected.

Chapter 3:

Results

3.1 Introductory Remarks

PBDE congeners -28, -47, -99, -154, and -153 were detected analytically in air samples at each Site during each Period of this study. Two congeners, BDE-47 and BDE-99, dominate the concentration of $\Sigma PBDE_5$ found in the air samples of this study. These results are consistent with findings from other studies in which the congeners making up the penta- formulation dominate the $\Sigma PBDE$ in air samples (La Guardia et al., 2006; Vonderheide et al., 2008). In this study, a sampling rate of 3.5 m^3 of air per day was used to calculate estimated PBDE volumetric concentrations (Jaward et al., 2005). All table results are listed in concentrations in pg/m^3. In addition, concentrations reported are blank and limit of detection (LOD) corrected.

Table 3 shows the summary of study results with $\Sigma PBDE_5$ ranging from 35.20 to 1549.25 pg/m^3 over the course of the entire study. The first sampling device from Period I was deployed on

October 12, 2012, and the last device collected from Period III was
July 3, 2013.

Table 3: Summary of Study Results in pg/m^3

Summary of Study Results					
Compound	Mean	Min.	Max.	SD	GM
PBDE 28	1.15	0.28	2.51	0.6997	0.949974
PBDE 47	89.46	8.89	1205.91	256.58	34.03078
PBDE 99	155.44	1.63	562.19	181.5	58.95858
PBDE 154	0.61	0.24	1.04	0.2829	0.549799
PBDE 153	11.15	0.00	33.48	10.19	8.46906
ΣPBDE$_5$	257.81	35.20	1549.25	342.71	150.456

The concentration of specific congeners by individual Period and
Site are available in Appendix A. Sampling Periods I and II were
conducted during the dry winter season while sampling Period III was
conducted during the end of the dry winter season and the onset of
the wet summer season. In general, a larger range and higher total
concentration of ΣPBDEs were measured in Period I for all Sites.

3.2 Summary of Results by Period

3.2.1 Period I Results

In Period I, the sampling devices were deployed for an average of 66.27 days at 20 Sites. This period extended from mid-October, 2012, to mid-December, 2012. The $\Sigma PBDE_5$ concentrations detected from each Site in Period I ranged from 54.81 to 1549.25 pg/m^3 (see Table 4).

Table 4: Period I results in pg/m^3

Summary of Results – Period I

Congener	Mean	Min.	Max.	SD	GM
PBDE 28	0.79	0.36	1.29	0.3195	0.7275
PBDE 47	155.15	13.79	1205.91	394.08	35.697
PBDE 99	271.41	36.08	562.19	202.31	177.45
PBDE 154	0.61	0.24	1.03	0.3189	0.5424
PBDE 153	13.91	3.36	33.48	12.122	10.177
ΣPBDE	440.32	54.81	1549.25	459.91	276.75

Of the 20 Sites where the sampling devices were deployed, only 9 Sites were recovered (see Table 2). According to the National Oceanic and Atmospheric Administration (NOAA) (2014) station in Liberia,

Costa Rica, the mean temperature reported for this Period was 26.6˚C. Temperatures were warm and consistent during this Period; therefore, a correction for equilibrium conditions was not required (Jaward et al., 2005). Precipitation for this Period was < 2.62 in., with 1.78 in. observed for the month of October.

3.2.2 Period II Results

The sampling time span of deployment for Period II averaged 81.90 days, which commenced mid-December, 2012, and ended in early March, 2013.

Table 5: Period II results in pg/m^3

Summary of Results - Period II					
Congener	Mean	Min.	Max.	SD	GM
PBDE 28	1.36	0.62	2.51	0.8017	1.1652
PBDE 47	35.11	16.24	59.08	17.52	31.403
PBDE 99	78.00	7.69	338.01	128.77	30.795
PBDE 154	0.57	0.34	0.92	0.2466	0.5314
PBDE 153	9.00	3.58	17.61	5.4431	7.6729
ΣPBDE	124.05	35.20	418.12	144.94	86.07

Nine (9) sampling devices were deployed, but only 6 were collected (see Table 2). The $\Sigma PBDE_5$ concentrations detected from each Site in Period II ranged from 35.20 to 418.12 pg/m^3 (see Table 5). Temperatures were warm and consistent during this Period with a mean reported temperature of 27.6˚C (NOAA, 2014); therefore, like Period I, a correction for equilibrium conditions was not needed (Jaward et al., 2005). Precipitation for Period II was < 0.01 in.

3.2.3 Period III Results

Period III's sampling time span averaged 111.38 days of deployment, the longest of the Periods, and returned 6 sampling devices (see Table 2). This Period's deployment began with the day of collection of Period II; therefore, it began early March, 2013, and ended with the collection of the sampling media at around July 1, 2013. Period III $\Sigma PBDE_5$ concentrations ranged from 71.88 to 266.86 pg/m^3 (see Table 6). The NOAA (2014) weather station located at Liberia, Costa Rica, reported the mean temperature for this Period as 28.4˚C. Like Periods I and II, a correction for equilibrium conditions was not required (Jaward et al., 2005). Precipitation for Period III was = 24.68 in. with no observable precipitation from January to April and, 19.00 in. observed in May alone.

Table 6: Period III results in pg/m^3

Summary of Results - Period III					
Congener	**Mean**	**Min.**	**Max.**	**SD**	**GM**
PBDE 28	1.48	0.28	2.23	0.8555	1.1557
PBDE 47	45.29	8.89	82.08	29.935	34.328
PBDE 99	58.94	1.63	225.29	84.417	21.617
PBDE 154	0.64	0.37	1.04	0.3066	0.5805
PBDE 153	11.48	2.62	26.72	11.715	7.3166
ΣPBDE	117.82	71.88	266.86	73.527	105.42

3.2.4 Back-Trajectories

Air mass back-trajectories were determined using the NOAA
HYSPLIT model with the Nandamojo watershed coordinates and
sampling dates to demonstrate the origin of air masses that pass
through the region during each sampling Period. Back-trajectory
analysis can help to determine whether PBDEs detected were likely to
have been influenced by meteorological events and origin of air mass.
In general, air masses that originate over the Pacific are denoted as
clean air, which means lower background concentrations of pollutants
(Jaward, Barber, et al., 2004). On the other hand, air masses

traveling long distances over land and heavily populated areas have the potential to carry POPs, including PBDEs. This can significantly influence environmental levels of PBDEs (Bustamante, Monge-Nájera, & Lutz, 2011).

Back-trajectories were obtained for all weeks of Period I. Weeks ending October 15, 2012, October 22, 2012, and October 29, 2012, represent the tail-end of the wet summer season (final three weeks), with weeks ending October 15 and 22 having back-trajectories different from the remainder of Period 1.
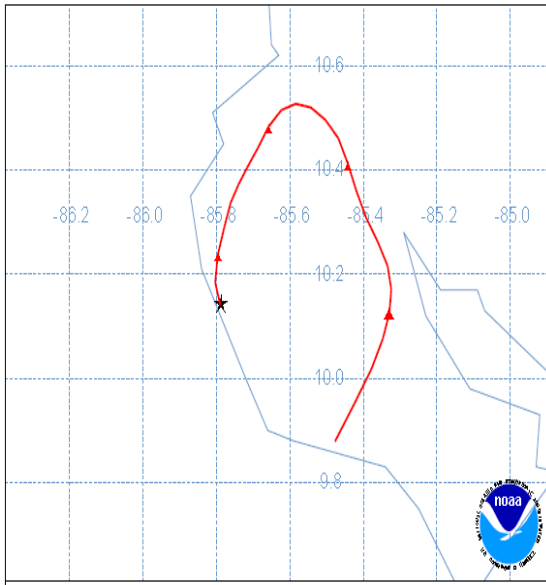

Figure 7: October 15, 2012
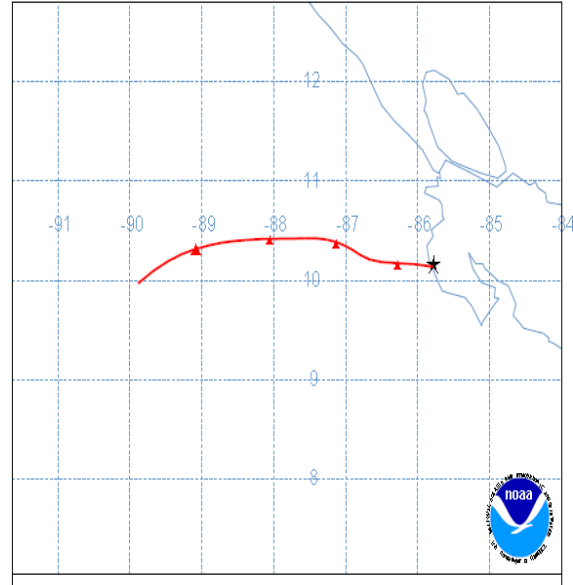Back-Trajectory (Period I, Week 1)

Figure 8: October 22, 2012
Back-Trajectory (Period I, Week 2)

Weeks ending October 29, 2012, through December 22, 2012 (dry winter season), have a consistent pattern throughout the Period, with air masses originating north and east over Nicaragua and/or the Caribbean Sea, traveling over land, and down the low plains to the Pacific Coast. The dry season is windier than the wet summer season (Gouin et al., 2008). The remaining back-trajectory figures for Period I can be found in Appendix C.
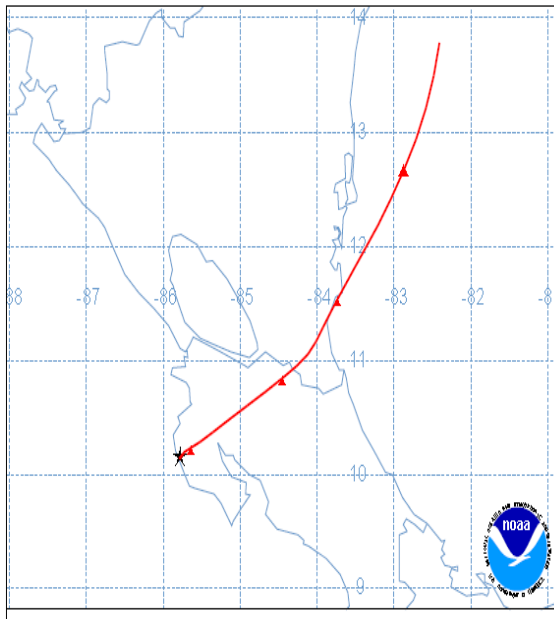

Figure 9: October 29, 2012
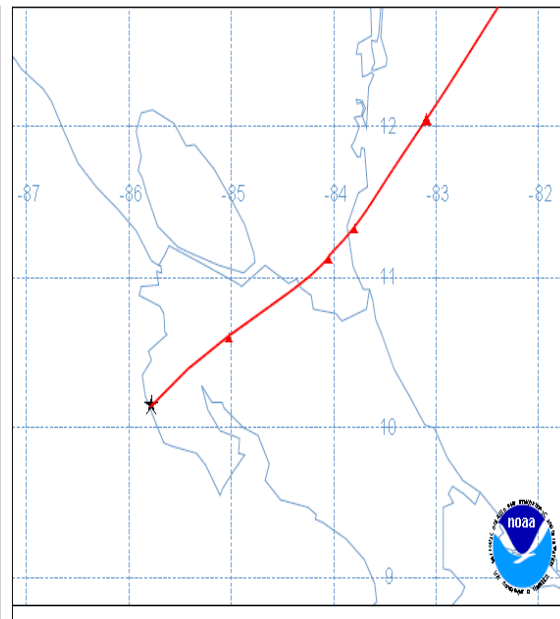Back-Trajectory (Period I, Week 3)

Figure 10: December 22, 2012
Back-Trajectory
(Period I, Week 9/Period II, Week 1)

Period II's back-trajectories generally show that air masses originate over the Caribbean Sea and travel over northern Costa Rica before arriving at the top of the Nandamojo watershed and down the low plains to the Pacific Ocean.
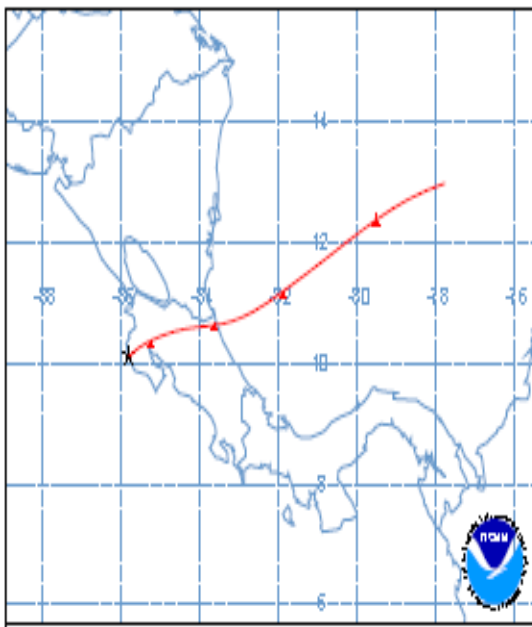

Figure 11: December 29, 2012
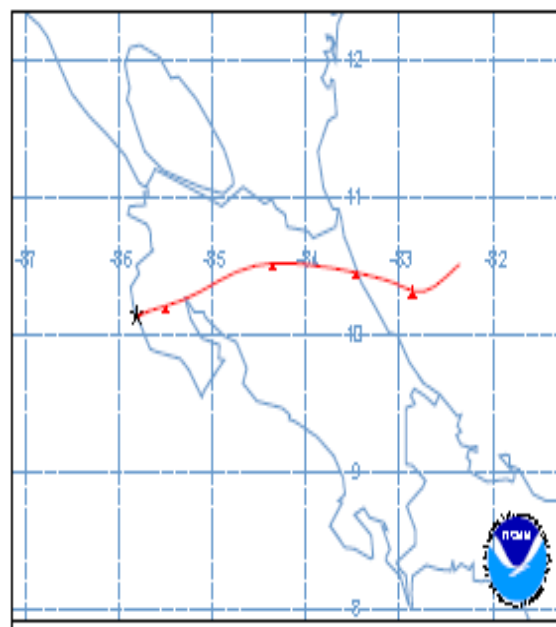Back-Trajectory (Period II, Week 2)

Figure 12: January 29, 2013
Back-Trajectory (Period II, Week 7)

The general pattern seen in the back-trajectories (see Figures 11 & 12) continues through Period II, Week 11 when the origin of the air mass shifts back over Nicaragua as seen in Period II, Week 12 (see Figure 14). The remaining back-trajectory figures for Period II can be found in Appendix C.
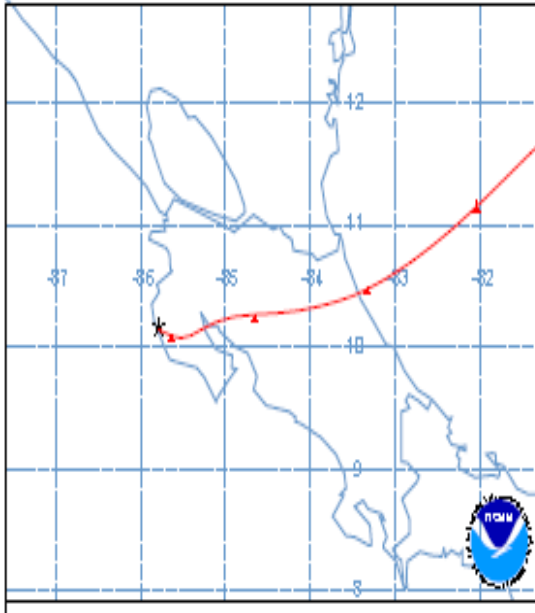
Figure 13: February 22, 2013
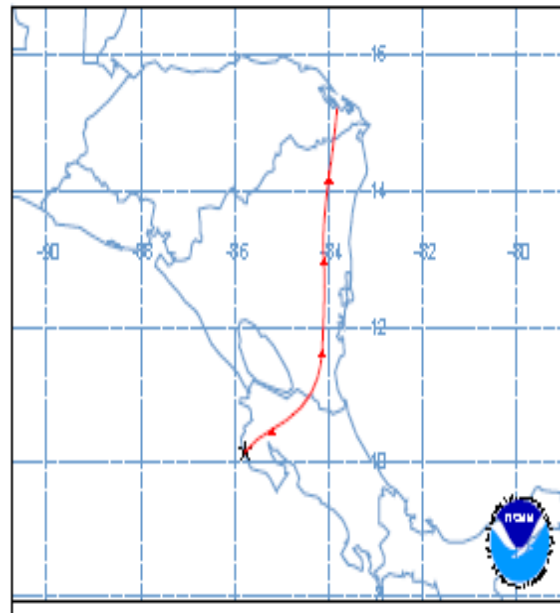Back-Trajectory (Period II, Week 10)

Figure 14: March 8, 2013
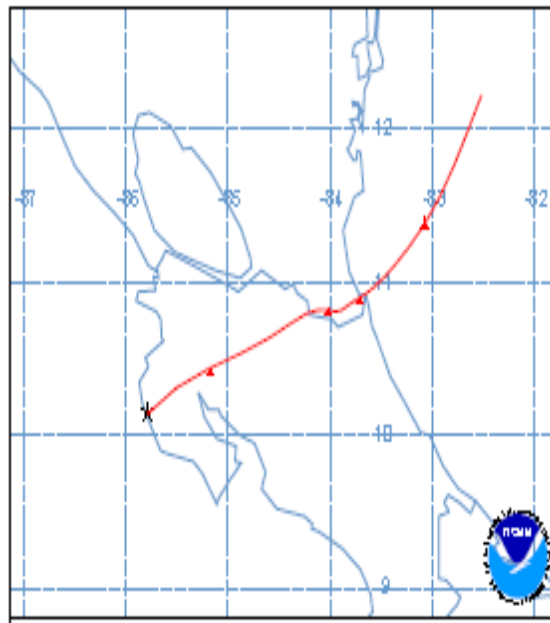Back Trajectory (Period II, Week 12)

Figure 15: March 15, 2013
Back-Trajectory
(Period II, Week 12/Period III, Week 1)

The longest sampling campaign, Period III, begins at the end of the dry winter season, which is reflected in the back-trajectories of Figures 15 and 16. The wet summer season begins May 1st. The back-trajectory models in Figures 17 to 23 show the shifting origins of Nandamojo watershed air masses. The remaining back-trajectory figures for Period III can be found in Appendix C.
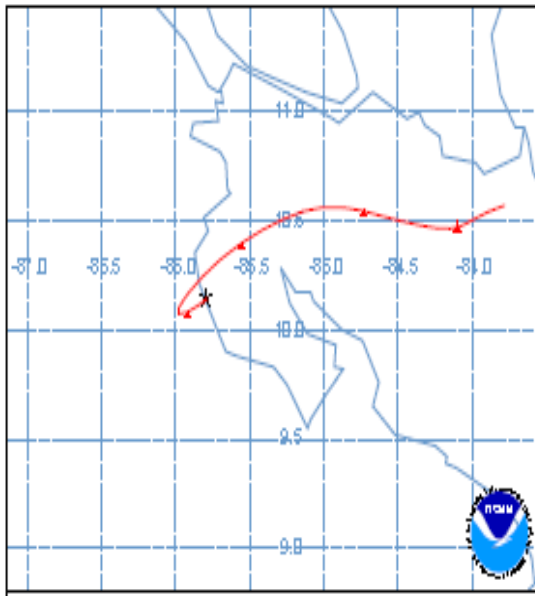

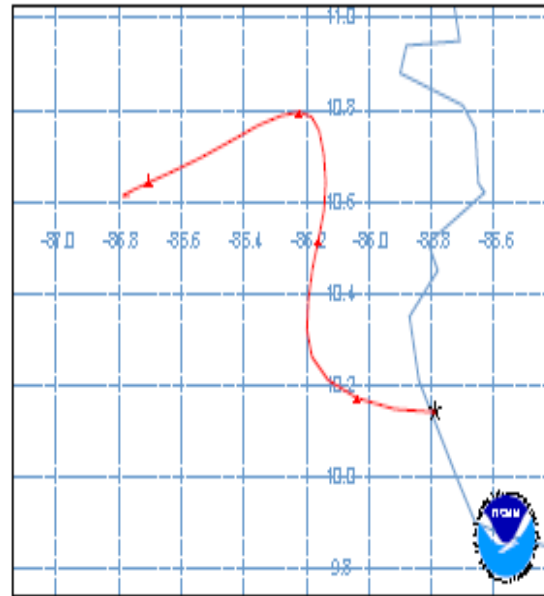Figure 16: April 29, 2013
Back-Trajectory (Period III, Week 7)

Figure 17: May 1, 2013
Back-Trajectory (Period III, Week 8)
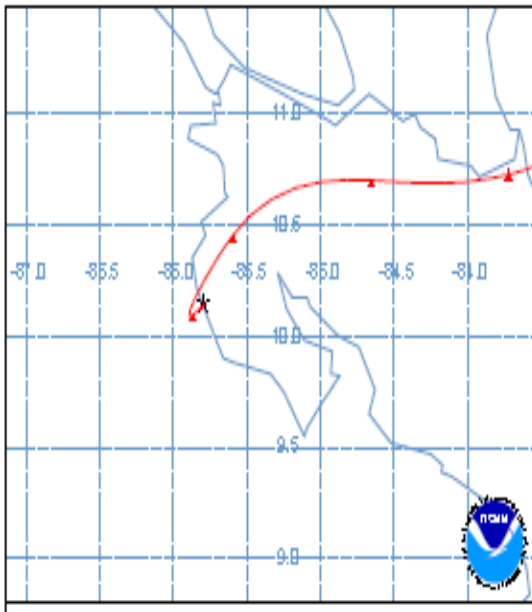
Figure 18: May 8, 2013
Back-Trajectory (Period III, Week 9)
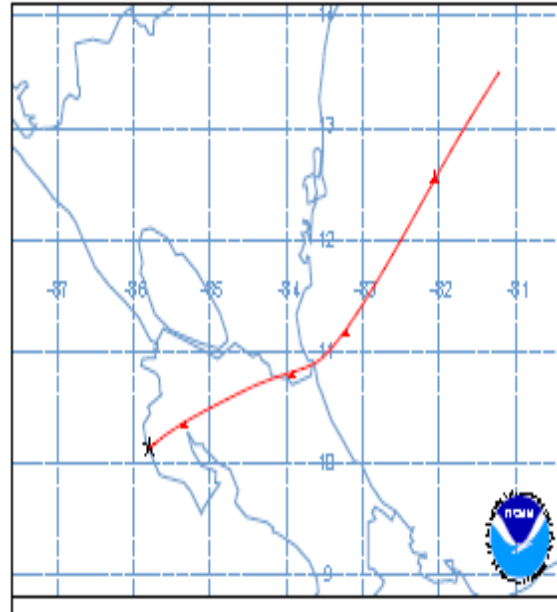
Figure 19: May 15, 2013
Back-Trajectory (Period III, Week 10)
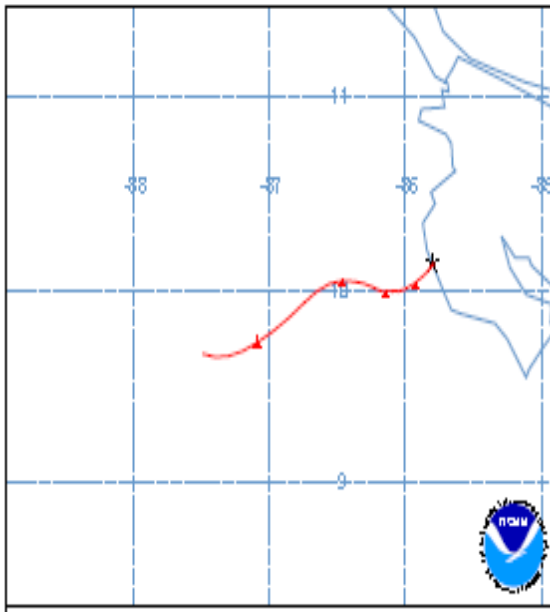
Figure 20: May 22, 2013
Back-Trajectory (Period III, Week 11)
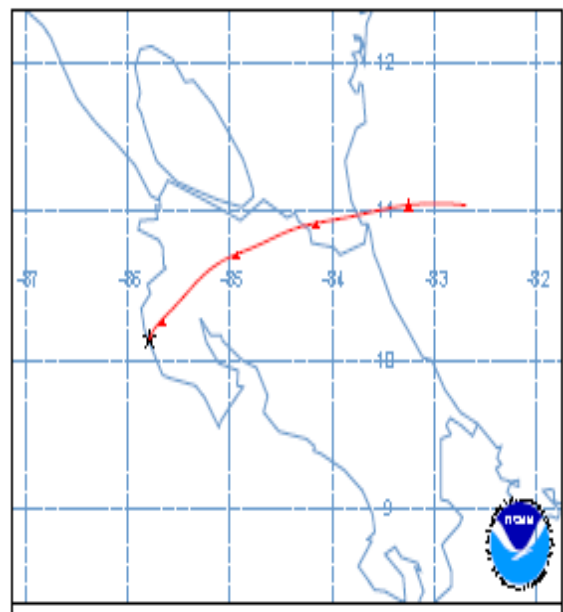
Figure 21: June 8, 2013
Back-Trajectory (Period III, Week 13)
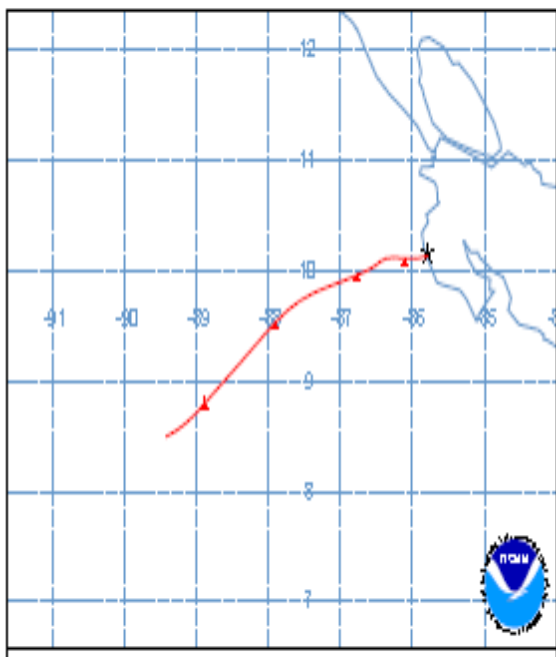
Figure 22: June 29, 2013
Back-Trajectory (Period III, Week 15)
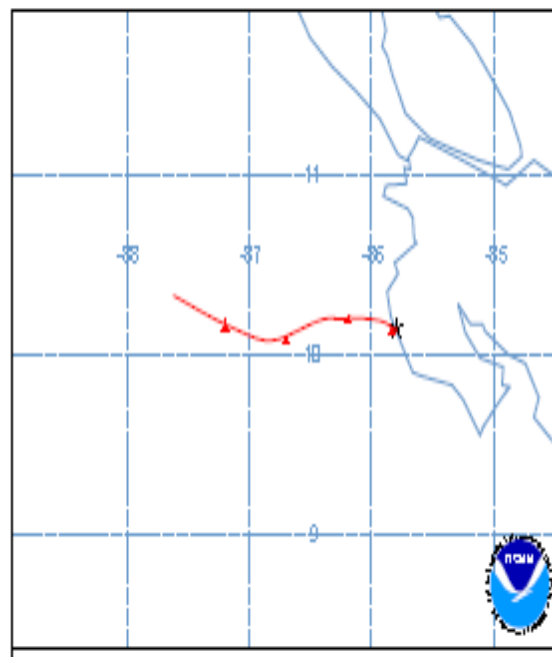
Figure 23: July 1, 2013
Back-Trajectory (Period III, Week 16)

Seasonal, temporal, and spatial distribution can be influenced by changes in meteorology (wet vs. dry seasons), the origin of the air mass (Jaward, Meijer, Steinnes, Thomas, & Jones, 2004), and passage over urban and industrialized regions (Jaward et al., 2005). Additionally, precipitation scavenges PBDEs from the air, depositing them to bodies of water and to the soil (Tourbier & Pierson, 1976).

3.3 Seasonal Variation

Passive air sampling devices provide a measurement over a period of time; therefore, they do not have the ability to distinguish between moments of extreme highs or lows (Gevao, Jaward, Macleod, & Jones, 2010). They are, however, useful for providing an average over a short time span, such as a season. Statistical analysis of the data was performed to test for significant differences between seasonal air concentrations within the study's time frame. Three comparisons were used to elucidate the dry winter-wet summer seasonal variation as follows:

1. Periods I and II (dry winter) to Period III (wet summer).

2. Period I (dry winter) to Period III (wet summer).

3. Period II (dry winter) to Period III (wet summer).

Seasonal variation, with dry winter > wet summer, was apparent for most congeners at most of the Sites. This is reinforced by the findings of the High/Low concentration ratio and simple linear regression analysis discussed as follows. The High to Low (H/L) concentration ratio of Periods I + II vs. Period III = 4.0, while an r^2 =

42

0.754 and a non-significant (n.s.) value of p = 0.246 was obtained

using simple linear regression. In Period I vs. Period III, the H/L

concentration ratio = 6.3, while the simple linear regression analysis

returned an r^2 = 0.999 and a p-value of 0.117 (n.s.). For the last

comparison, Period II vs. Period III, the H/L concentration ratio is not

as pronounced (H/L = 1.6) and the r^2 = 0.878. The p-value for this

comparison was p = 0.927 (n.s.). The standard deviation of the mean

concentration of each period was higher than the mean except in

Period III (see Tables 4, 5, & 6).

It appears that seasonal variations in total air concentrations of

PBDEs in the Nandamojo watershed were significantly influenced by a

burning event, a known point source of PBDEs (Vonderheide et al.,

2008), at the dump area near Site 2 during Period I. Results, such as

these, are consistent with the findings of other studies involving

combustion events (Wyrzykowska-Ceradini et al., 2011). Additionally,

a true seasonal comparison may be difficult to ascertain without

further studies. This may in part be attributed to the Period III

sampling campaign beginning six weeks before the wet summer

season officially began on May 1st.
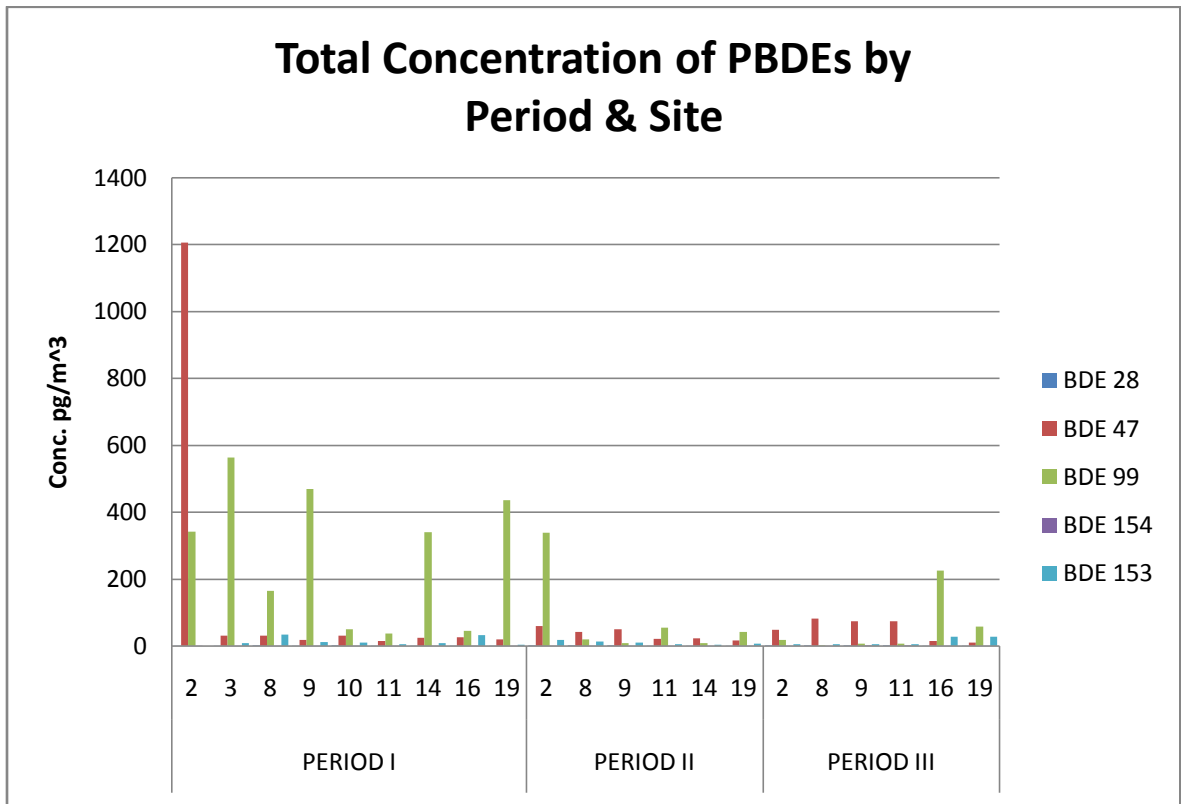
Figure 24: Total Concentration of PBDEs by Period & Site

Air concentration spike events are often associated with anthropogenic activities (Gevao et al., 2010). Additionally, the proximity to human population centers has been shown to have a greater effect on the concentration of PBDEs in the air (Shen et al., 2006). Elevated concentration of congener BDE-99 at Site 16 in Period III may be influenced by the proximity to the road (Choi et al., 2009) or some other spike event (Farrar et al., 2004; Martin et al., 2004). While the heavier congeners were not analytically detected in

the air samples of this study, such as those consistent with the octa-or deca-BDE technical mixtures, other PBDE congeners were detected at each site during each Period. As previously discussed in Section 3.1, regardless of location or Period, lower brominated congeners BDE-47 and BDE-99 were found to make up the dominant percentage of the $\Sigma PBDE_5$, which ranged from 67.5% to 99.9% (see Figure 25). This is consistent with the penta-PBDE technical flame-retardant mixture (La Guardia et al., 2006; Vonderheide et al., 2008) and is also consistent with findings from other studies (La Guardia et al., 2006).

Figure 25: PBDE congener distribution
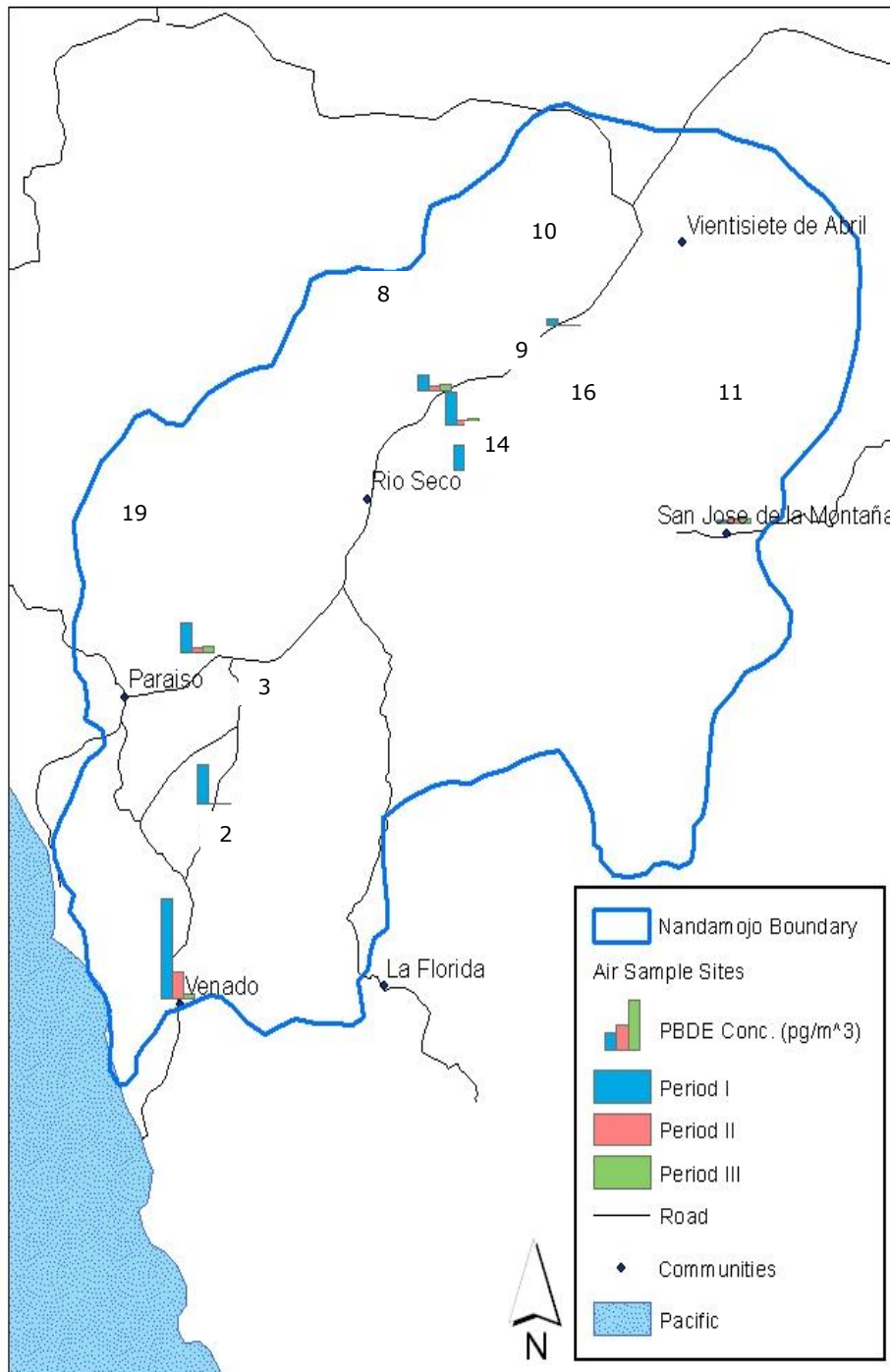
Figure 26: Spatial & Temporal distribution of $\Sigma PBDE_5$ in air (pg/m^3). Note: The largest bar is located at Site 2 during Period I = $\Sigma PBDE_5$ 1549.25 pg/m^3
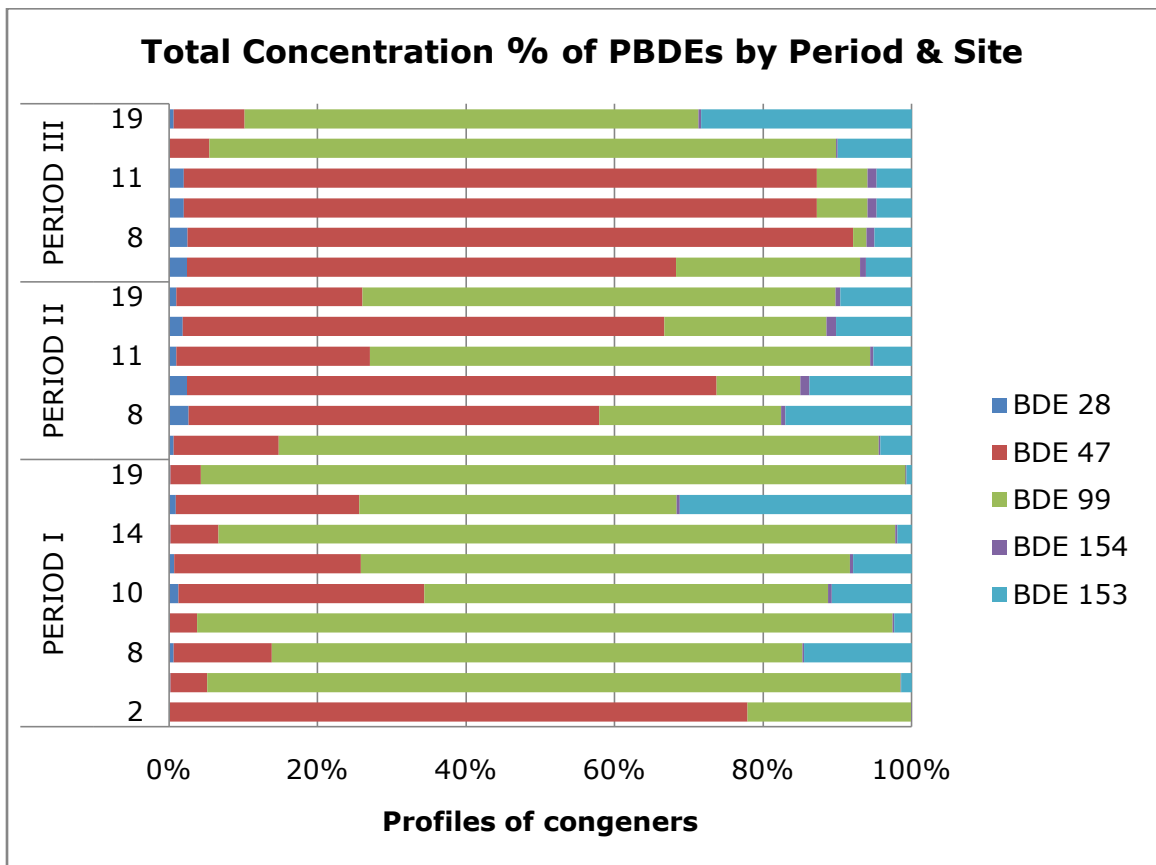
3.4 Temporal Distribution

As previously discussed, passive air sampling devices are useful for providing information for an average concentration over a span of time. Like seasonal variation, it appears that temporal distribution was also influenced by weather patterns in addition to anthropogenic activities, such as a significant waste combustion event at a dump area located near Site 2 during the deployment of Period I. Period-by-Period H/L concentration ratios were calculated to demonstrate the change in concentration over time.

It is clear from Figure 24 that the Periods differ substantially in $\Sigma PBDE_5$ concentrations. Total $\Sigma PBDE_5$ concentrations for Period I, the sampling Period with a significant combustion event at the dump area near Site 2, were higher than the other Periods. Each successive Period showed a decrease in $\Sigma PBDE_5$ concentrations. A complete summary of results by Period is contained in Tables 4, 5, and 6, and Figure 24.

3.5 Spatial Distribution

3.5.1 Introductory Remarks

The highest concentrations of PBDEs were measured in Sites closest to urban areas, while the lowest concentrations were from the rural and remote Sites. The pattern of all $\Sigma PBDE_5$ reflected the

localized hotspot of Site 2. As you move inland from the coastal area and Site 2 (see Figures 5, 6, & 26) and follow the urban-rural-remote population gradient, concentrations generally decrease up the low plains area and into the forested hills. Variations in this pattern can be explained, in part, by a large presence of trees and other vegetation, which have been shown to filter PBDEs from the air (Jaward et al., 2005). Site 11 is located in the forested hills and is considered the most remote location with consistent observed low total concentrations (see Figure 26).

Statistical analysis of the data was performed to test for significant differences between each Site's air concentrations within the study's time frame. The mean, standard deviation, geometric mean, and Site-by-Site H/L concentration ratios were calculated.

Closest to Site 2 is Site 3, known as Vulture Creek. This site is located near the road in the forested hills of the Nandamojo watershed (see Figures 5, 6, & 26). Site 10, known as Latrine Creek, is located very close to the road in the low plains area of the watershed (see Figures 5, 6, & 26) and is the Site farthest away from the coast. Sampling data for Sites 3 and 10, situated at opposing ends of the low plains, are available only for Period I as a result of the loss or destruction of sampling units. Individual and total concentrations for these two Sites are located in Appendix A.

3.5.2 Site 2 Description and Results

As previously mentioned, Site 2 is located nearest to the Pacific coast (see Figures 5, 6, & 26). Furthermore, the sampling unit at this Site is located near a road on the southern border of the Nandamojo watershed, which studies have found influence total air concentrations (Choi et al, 2009).
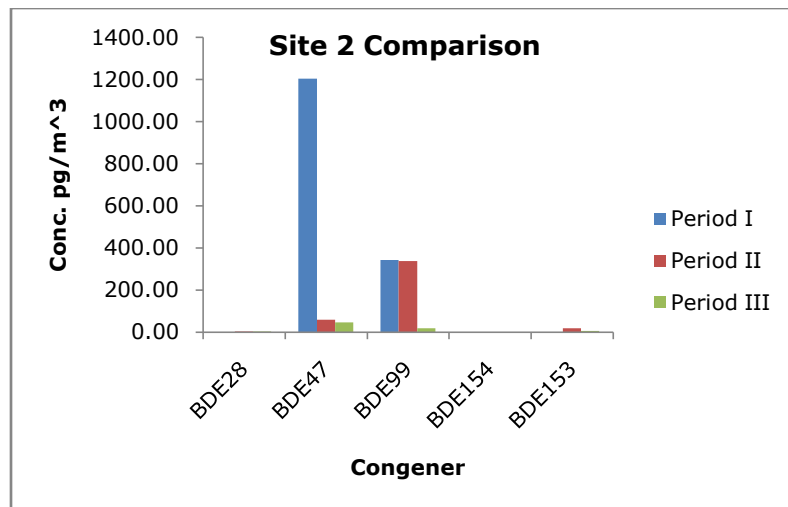

Figure 27: Site 2 Comparison Conc. (pg/m^3) by congener

This Site, known as Venado Bridge, is also nearest to the estuarine area and is located closest to a garbage dump area. Of special importance, this is also the location where a significant burning

event occurs during Period I. Figure 27 shows the comparison of select congeners by Period at Site 2. Very high levels of BDE-47 and BDE-99 were observed in all Periods, comprising 90.3% to 99.9% of total congeners measured (see Figure 25). These levels are consistent with other studies analyzing air samples from waste combustion sites (Wyrzykowska-Ceradini et al., 2011) and may be a result of burning electronic wastes at low temperatures (Martin et al., 2004). The mean, standard deviation, and geometric mean for $\Sigma PBDE_5$ at Site 2 are 679.78, 772.64, and 359.79, respectively. The H/L concentration ratio is 21.6 for Site 2.

3.5.3 Site 19 Description and Results

The next site moving inland is Site 19, which is located in the forested hills near the road bordering the low plains. This location is known as Tom's upper cabin. The congener of prominence for this Site is BDE-99, which was significantly elevated during Period I (see Figure 28). These findings are consistent with other studies analyzing air samples of major anthropogenic combustion events (Farrar et al., 2004; Martin et al., 2004).

Figure 28: Site 19 Comparison Conc. (pg/m^3) by congener

The mean, standard deviation, and geometric mean for $\Sigma PBDE_5$ at Site 19 are 205.54, 219.54, and 140.50, respectively. The H/L concentration ratio is 3.09 for Site 19.

3.5.4 Sites 14 & 16 Descriptions and Results

Site 14 lies within the boundary of Hacienda la Norma in the low plains area near Far Creek, noted as Stream #2 (see Figures 5 & 6). The concentration levels of PBDEs measured in air samples from this location fit the spatial trend observed. Site 16, known as End of the Zip Line, is located near the Hacienda la Norma boundary and borders both the low plains and forested hills. This is an area of high human activity related to tourism.

3.5.5 Site 9 Description and Results

Following Sites 14 and 16 inland is Site 9, which is located within the boundary of Hacienda la Norma in the low plains area. The sampling unit for this Site is located near a creek, noted as stream #1, and situated behind a large field.
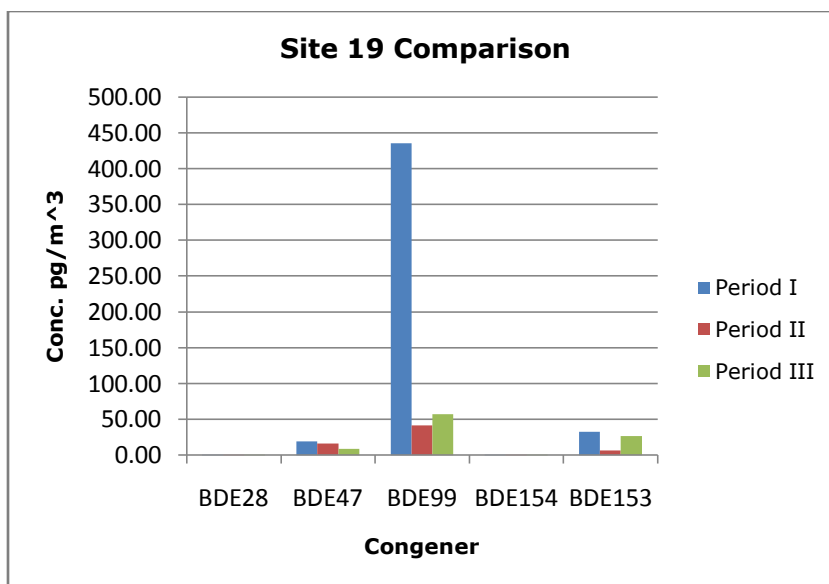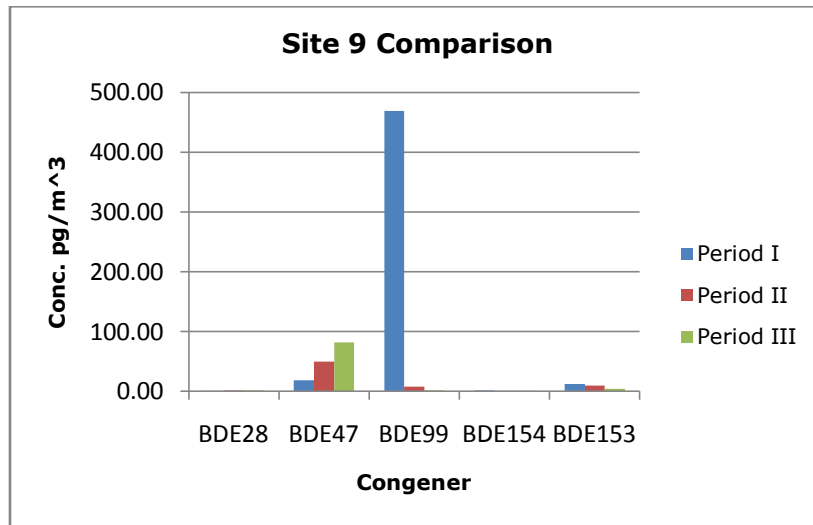

Figure 29: Site 9 Comparison Conc. (pg/m^3) by congener

The mean, standard deviation, and geometric mean for $\Sigma PBDE_5$ at Site 9 are 220.59, 242.39, and 147.47 respectively. The H/L concentration ratio is 7.14 for Site 9.

3.5.6 Site 8 Description and Results

Site 8 is located near a road behind the lodge at the Ranch (see Figures 5, 6, & 26). This Site is the next to the farthest away from the coast inland. The Ranch is situated near the northern border of Hacienda la Norma in the low plains area. Figure 30 shows the comparison of select congeners by Period.

Figure 30: Site 8 Comparison Conc. (pg/m^3) by congener

The mean, standard deviation, and geometric mean for $\Sigma PBDE_5$ at Site 8 are 134.04, 84.42, and 118.57 respectively. The H/L concentration ratio is 3.09 for Site 8.

3.5.7 Site 11 Description and Results

Site 11 (see Figures 5, 6, & 26) is located the farthest inland from the coast and is situated in the forested hills. The sampling unit for this location is stationed very near a road. This location is known as San Jose De La Montagna and is the location farthest from the low plains. It is by far the most remote location with reported observations in this study. Total concentration levels are consistently low for this Site (see Figure 31). The concentrations for BDE-47 and BDE-99 measured for this Site are the dominant constituents in the total concentration of PBDEs observed and ranged from 91.0% to 93.4% per Period (see Figures 25 & 31).
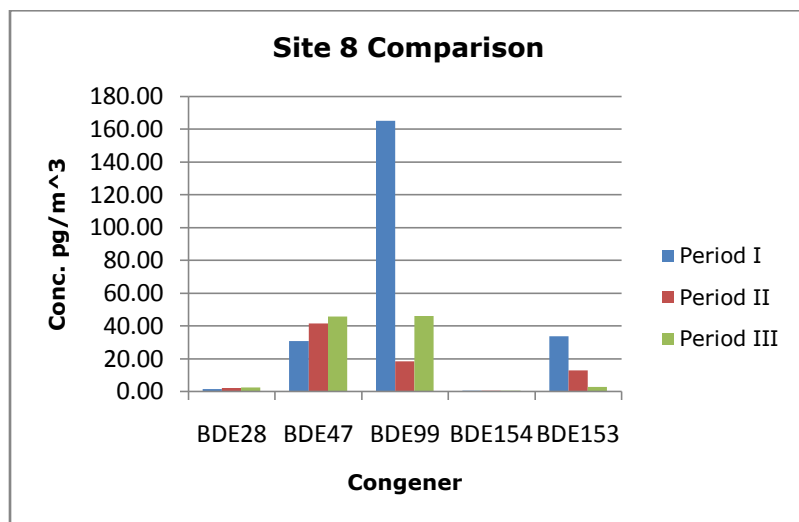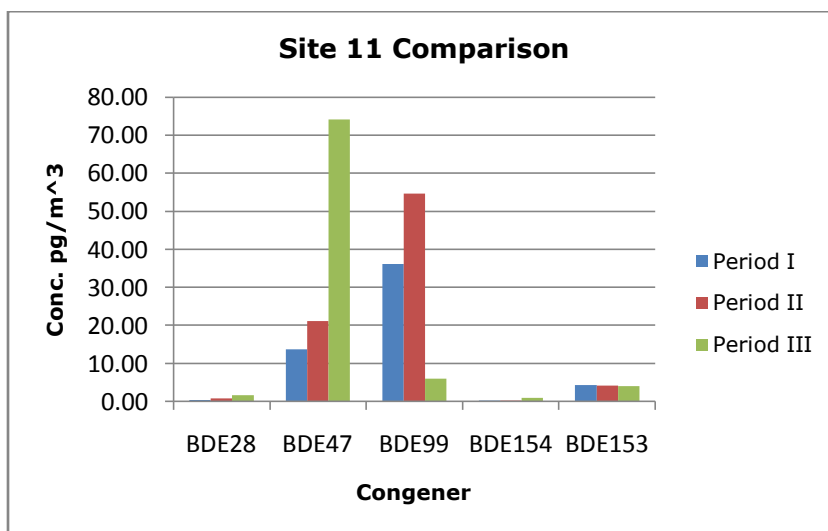
Figure 31: Site 11 Comparison Conc. (pg/m^3) by congener

The mean, standard deviation, and geometric mean for $\Sigma PBDE_5$ at Site 11 are 74.28, 17.10, and 72.84 respectively. The H/L concentration ratio is 1.58 for Site 11.

Chapter 4:

Discussion

This study suggests that the spatial distribution pattern observed is strongly related to the proximity to human populations and anthropogenic activities, which is similar to patterns observed in other parts of the world (Shen et al., 2006). This is particularly evident during Period I when a spike event occurred near Site 2.

PBDEs have long been classified as new and emerging contaminants of concern (Richardson, 2008). Environmental concentrations of PBDEs have steadily increased since their discovery in the 1970s (Watanabe & Sakai, 2003) and, along with this, is of growing concern for risks to human health as well as to wildlife and entire ecosystems. The presence of PBDEs is increasingly observed in greater concentrations in remote and pristine environments, which indicates that PBDEs have become a global concern and is not just a problem for large industrialized nations.

PBDEs, depending upon degree of bromination, behave differently in the air. The heavier congeners tend to move to other environmental compartments and, as such, congener BDE-209 is not

readily detected in the air. This study did not analytically detect BDE-209, which is consistent with the findings of other studies (Palm et al., 2012; Pozo et al., 2012). Congener BDE-209 is, however, hypothesized to be a source of environmental levels of lower-brominated congeners observed (La Guardia et al., 2006; Vonderheide et al., 2008). This is a concern as this congener is still actively in use today and, while not manufactured in Costa Rica, PBDE-laden goods may be imported into the region, especially in urbanized areas.

Congeners BDE-47 and BDE-99 contain 4 to 6 bromines, which primarily make up the penta- technical mixture. Due to their physiochemical properties, these congeners are the most susceptible to long-range atmospheric transport (LRAT), bioaccumulation, and biomagnifications (Harley et al., 2010). The high presence of these congeners in the air suggests LRAT (Goosey, 2006; Palm et al., 2012), regional use of penta-BDE treated goods (Miglioranza et al., 2013), and combustion events (Farrar et al., 2004; Wyrzykowska-Ceradini et al., 2011) are likely taking place in this region. The octa- mixture consists primarily of congeners containing 6 to 10 bromines, including BDE-153, while the deca- mixture is almost exclusively BDE-209 (Harley et al., 2010). In general, total concentrations of PBDEs are higher than expected.

Chapter 5:

Summary and Conclusion

5.1 Summary

This study represents the first effort to obtain baseline data on the seasonal, temporal, and spatial distribution of PBDEs in the air of the Nandamojo watershed region of Guanacaste province, Costa Rica. PBDE congeners -28, -47, -99, -154, and -153 were analytically detected in air samples at each Site during each Period of this study. Two congeners, BDE-47 and BDE-99, dominate the concentration of $\Sigma PBDE_5$ found in the air samples of this study.

Seasonal, temporal, and spatial variations were demonstrated. In general, a greater range and higher total concentration of $\Sigma PBDEs$ were measured in Period I for all Sites. Temperatures were warm and consistent throughout the study. In addition, precipitation was consistent with historical measurements. While Period I deployment began during the last three weeks of the wet summer season, it appears that rainfall during these three weeks did not have an effect on the $\Sigma PBDE_5$ measured. Back-trajectory analysis demonstrated

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consistent seasonal trends of the origins of air masses. In general, total concentrations of PBDEs are higher than expected.

5.2 Conclusion

This study measured levels of PBDEs in the air of the Nandamojo watershed region of the Guanacaste province, Costa Rica. In short, while concentrations of $\Sigma PBDE_5$ measured were at low levels, they were higher than those of other comparable global background studies. The dominant congeners BDE-47 and BDE-99 found in air samples from all Sites during all Periods were consistent with findings from other studies (Vonderheide et al., 2008).

The main purpose of this study was to provide baseline data for future studies of PBDEs in the Nandamojo watershed region while addressing a number of issues, including:

1. Do air concentrations of PBDEs decrease during the rainy season? Seasonal variations were elucidated, with the greatest H/L concentration ratio of 6.3, which compared Period I to Period III. A general trend for temporal distribution was demonstrated by a decrease in concentrations from each successive Period.

2. Are air concentrations of PBDEs lower in rural areas than in urban areas? It appears that spatial distribution was shown to follow the urban-rural-remote population gradient, whereby concentrations decreased when moving from the populated coastal area to inland and the more rural areas up the low plains, and finally into the most remote area of the forested hills. While local point sources, such as the presence of PBDE-laden goods and combustion events are suspected to contribute to the air concentrations of ΣPBDEs measured, long-range atmospheric transport was also suspected due to the high percentage of congeners BDE-47 and BDE-99 detected.

3. Are air concentrations influenced by regional and local anthropogenic activities? It appears that the combustion event at the dump area near Site 2 during Period I (dry winter season), served as a significant point source of ΣPBDE concentrations in air of the watershed region.

The consistency of the results suggests that this analytical method was successful for evaluating the quantity of the selected PBDE congeners in the air samples.

5.2.1 Limitations

Limitations of this study include available resources and the time allotted to complete this portion of the project.

5.2.2 Future Research Needed

Environmentally safe disposal and containment methods are needed, since traditional and sanitary landfills as well as waste facilities allow for migration of PBDEs into the environment. Further studies are, therefore, necessary to achieve to this end. Additionally, further studies are necessary to evaluate how PBDEs react with other chemical pollutants in the atmosphere and with particulate matter as well as with ultraviolet radiation. Mechanisms that break down PBDEs into compounds less likely to bioaccumulate in humans and wildlife should also be explored. It is imperative to determine how to degrade PBDEs into substances that are non-toxic.

5.2.3 Recommendations

In the interest of public health and safety, it is time to eliminate the use of PBDEs in the manufacture of consumer goods and building materials in order to minimize further impact on human health and the environment. Studies have shown that PBDEs pose a health risk to the population. Health risks due to exposure to PBDEs have become a

global issue, so the results from this study provide background information on air concentrations of PBDEs for use in a global-scale multimedia model. The implementation and/or expansion of surveillance programs would contribute to global monitoring programs, which can help to predict distribution and movement of PBDEs.

This study is a part of a larger, ongoing study of the College of Public Health Interdisciplinary Studies.

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Appendices

Appendix A: Total Concentrations per Period and Site

These tables show congener concentrations obtained by extraction from sampling media. These tables also contain individual as well as total concentrations per Period and Site for congeners BDE-28, -47, -99, -154, and -153.

Table A1: Period I Congener conc. (pg/m^3)

Period I

Site #	2	3	8	9	10	11	14	16	19
BDE 28	0.66	1.07	1.29	0.48	1.14	0.36	0.66	0.87	0.56
BDE 47	1205.91	29.64	30.45	18.06	30.01	13.79	23.99	25.77	18.73
BDE 99	341.65	562.19	165.02	468.76	49.41	36.08	339.54	44.56	435.46
BDE 154	1.03	0.52	0.45	1.02	0.41	0.24	1.03	0.40	0.41
BDE 153	Bdl	8.67	33.48	11.88	9.81	4.33	7.18	32.58	3.36
Total	1549.25	602.08	230.69	500.19	90.78	54.81	372.38	104.17	458.52

Note: bdl = below detection limit

Table A2: Period II Congener conc. (pg/m^3)

Period II

Site #	2	8	9	11	14	19
BDE 28	2.51	1.96	1.68	0.77	0.63	0.62
BDE 47	59.08	41.30	50.00	21.20	22.82	16.24
BDE 99	338.01	18.34	7.90	54.70	7.69	41.38
BDE 154	0.92	0.44	0.85	0.34	0.47	0.41
BDE 153	17.61	12.71	9.66	4.22	3.58	6.25
Total	418.12	74.75	70.10	81.24	35.20	64.90

Table A3: Period III Congener conc. (pg/m^3)

Period III

Site #	2	8	9	11	16	19
BDE 28	1.95	2.23	2.20	1.66	0.28	0.54
BDE 47	47.18	45.44	82.08	74.05	14.12	8.89
BDE 99	17.76	46.02	1.63	5.96	225.29	56.97
BDE 154	0.58	0.37	1.00	1.04	0.45	0.38
BDE 153	4.41	2.62	4.57	4.11	26.72	26.43
Total	71.88	96.67	91.49	86.82	266.86	93.21

Appendix B: Summary of Results

Table B1: Summary of Results

Summary of Results – Periods I, II, & III			
Congener	**Mean**	**Min.**	**Max.**
PBDE 28	1.15	0.28	2.51
PBDE 47	89.46	8.89	1205.91
PBDE 99	155.44	1.63	562.19
PBDE 154	0.61	0.24	1.04
PBDE 153	11.71	2.62	33.48
ΣPBDE	257.81	35.20	1549.25

Appendix C: Back-Trajectories for Periods I, II, & III

Period I:
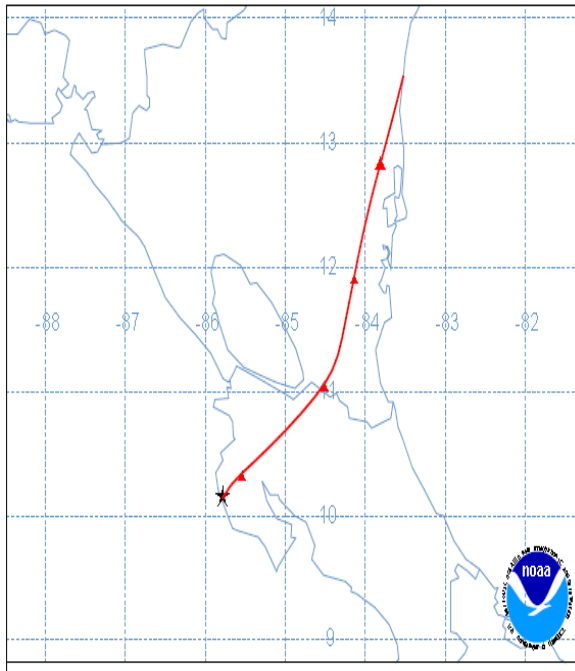
Figure C1: November 1, 2012
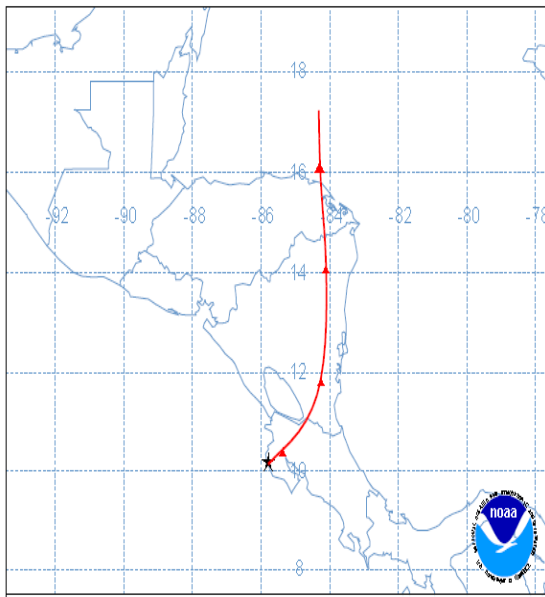
Figure C2: November 8, 2012
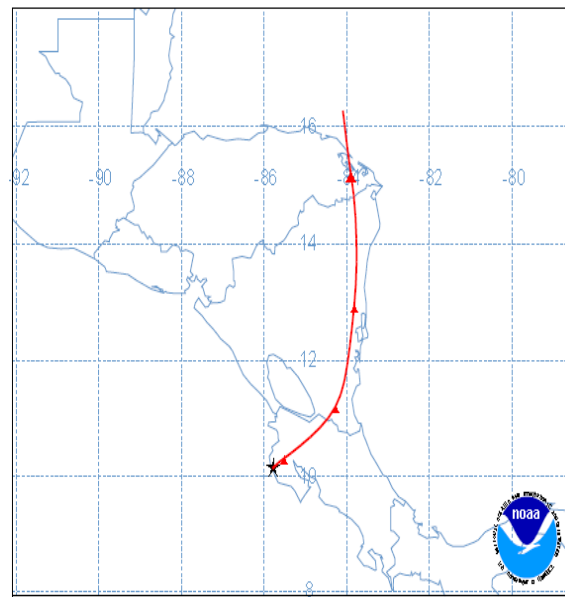
Figure C3: November 15, 2012
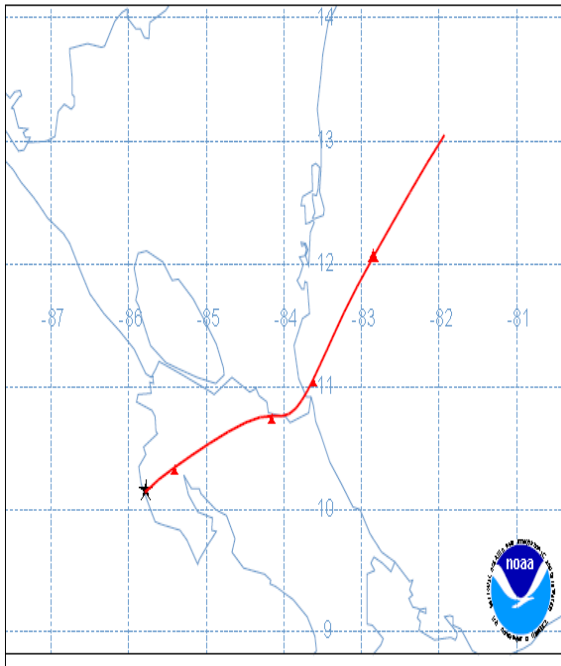
Figure C4: November 29, 2012
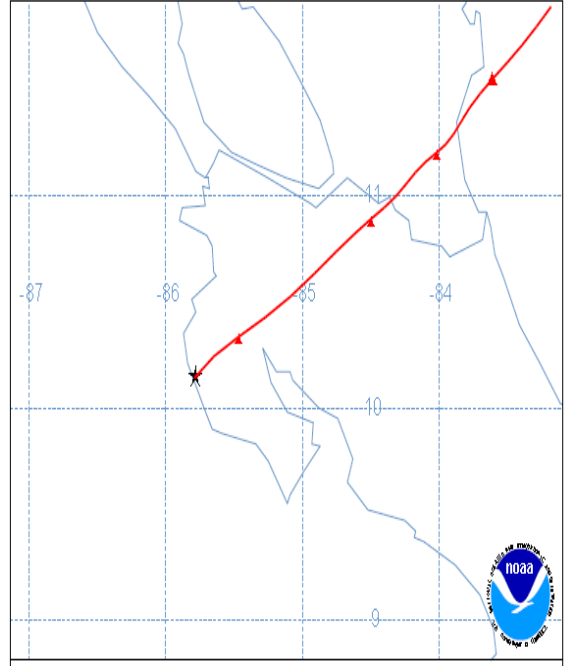
Figure C5: December 1, 2012
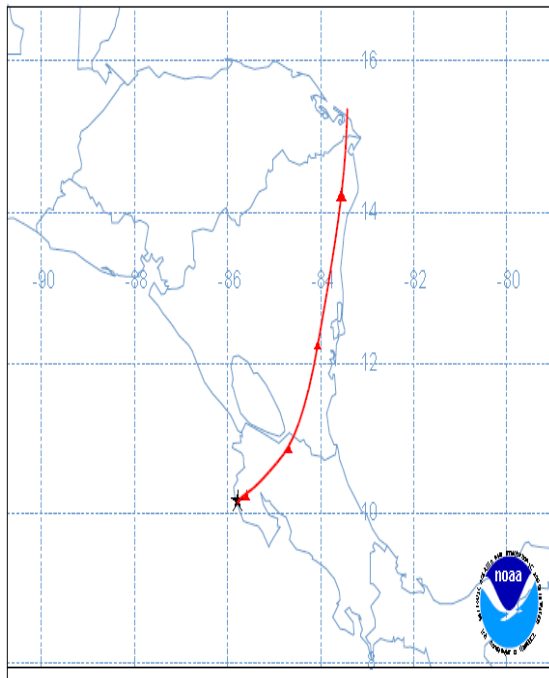
Figure C6: December 8, 2012
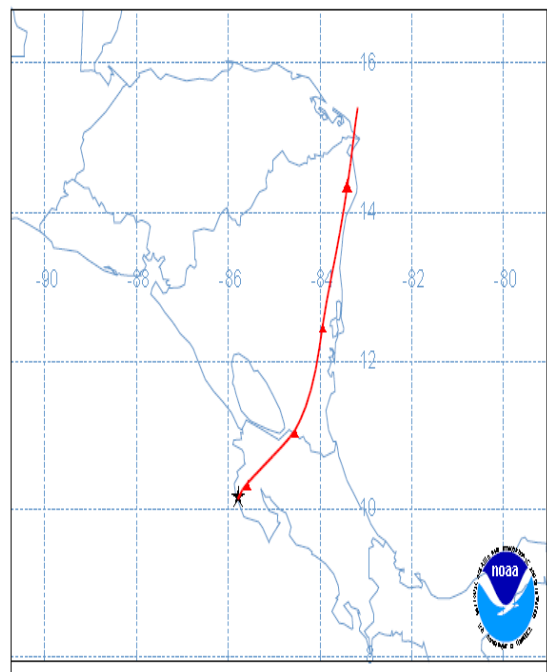
Figure C7: December 15, 2012

Period II:
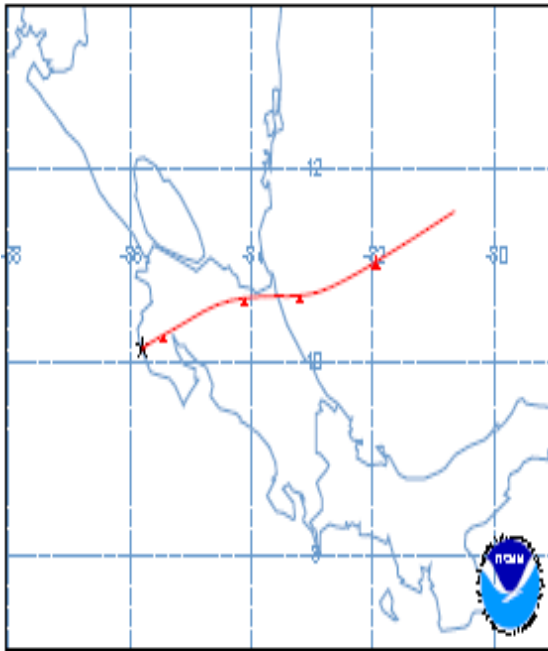
Figure C8: January 1, 2013
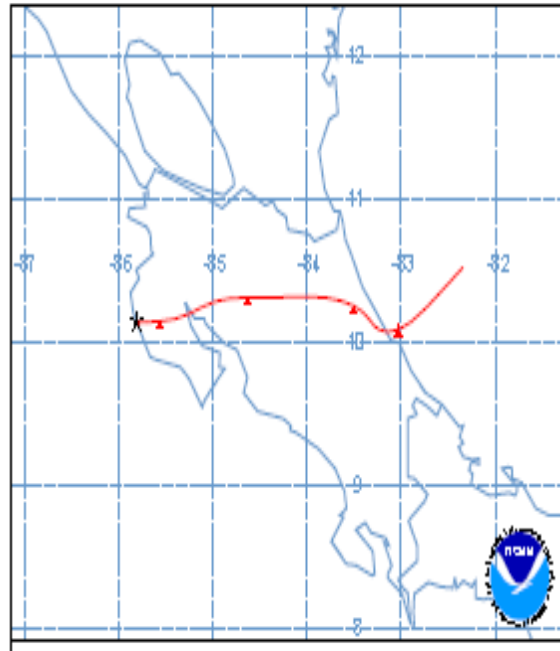
Figure C9: January 8, 2013
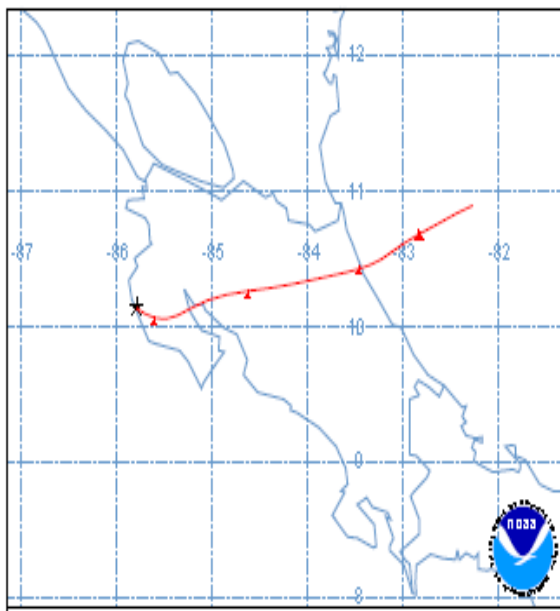
Figure C10: January 15, 2013
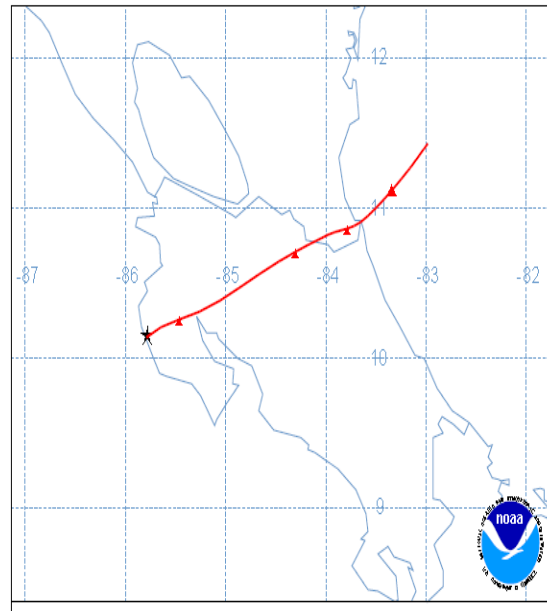
Figure C11: January 22, 2013

Period III:
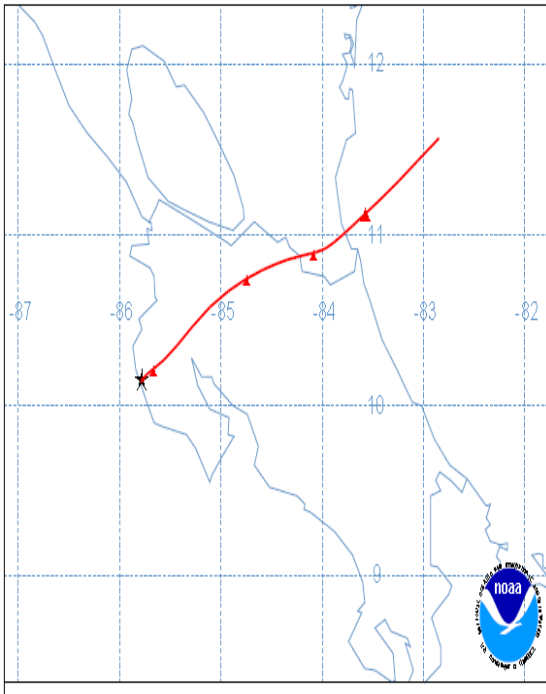
Figure C12: April 1, 2013
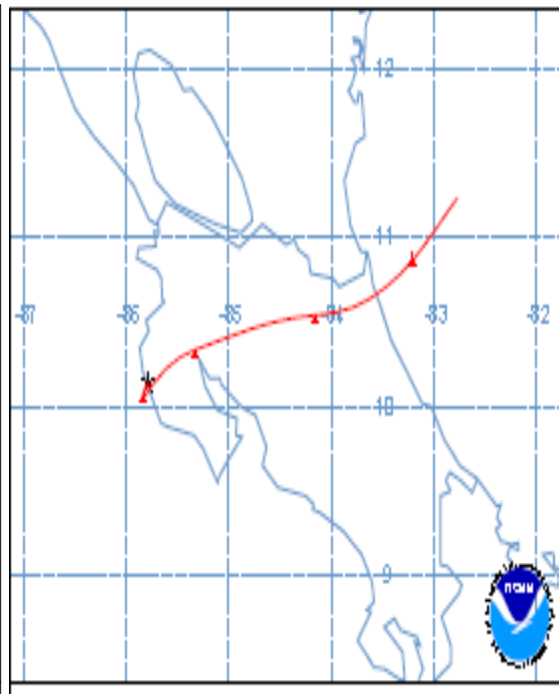
Figure C13: April 8, 2013
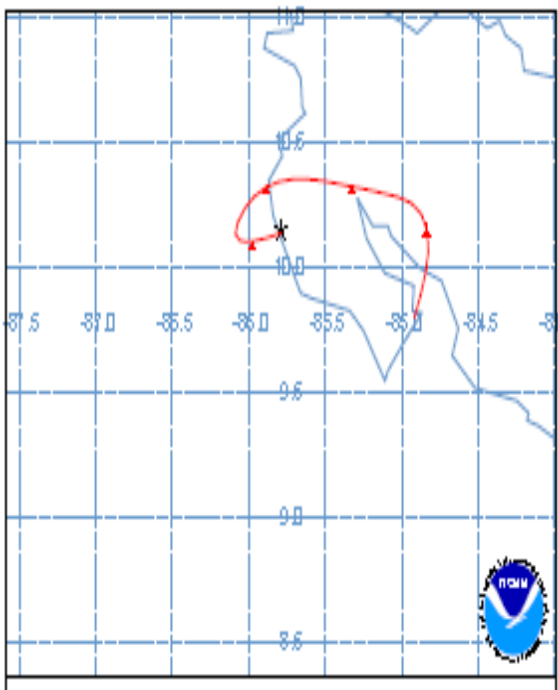
Figure C14: April 15, 2013
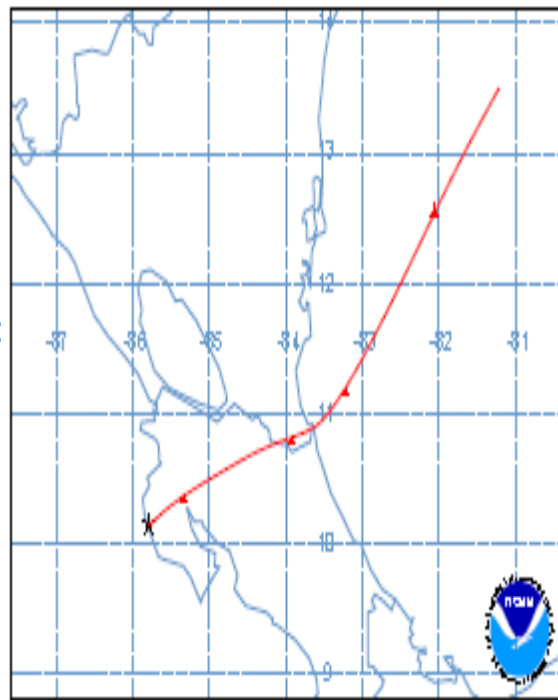
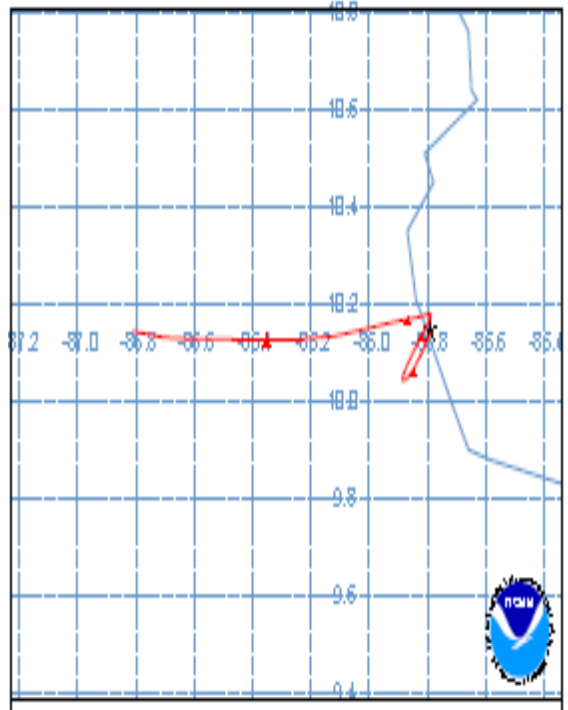Figure C15: April 22, 2013

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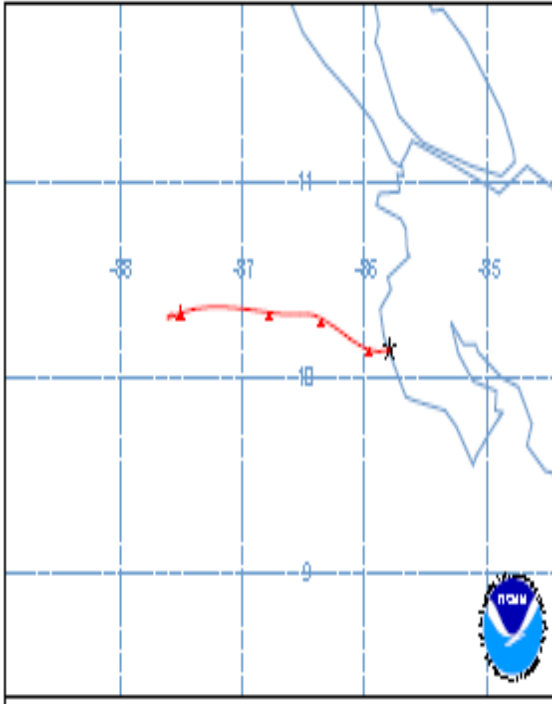
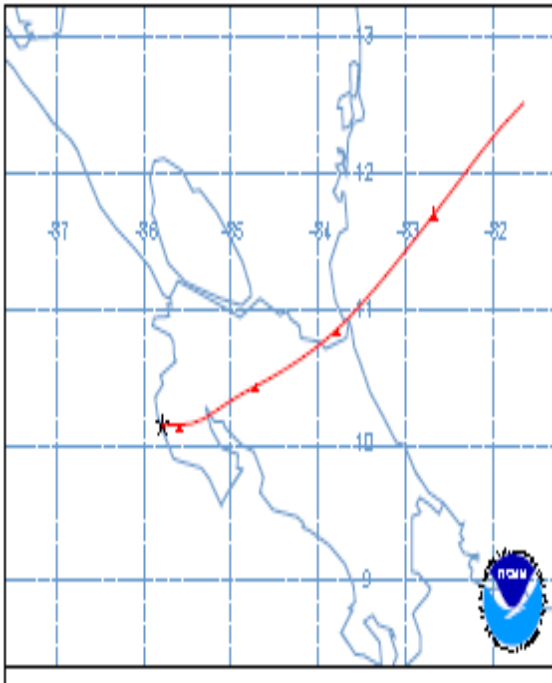Figure C16: May 29, 2013

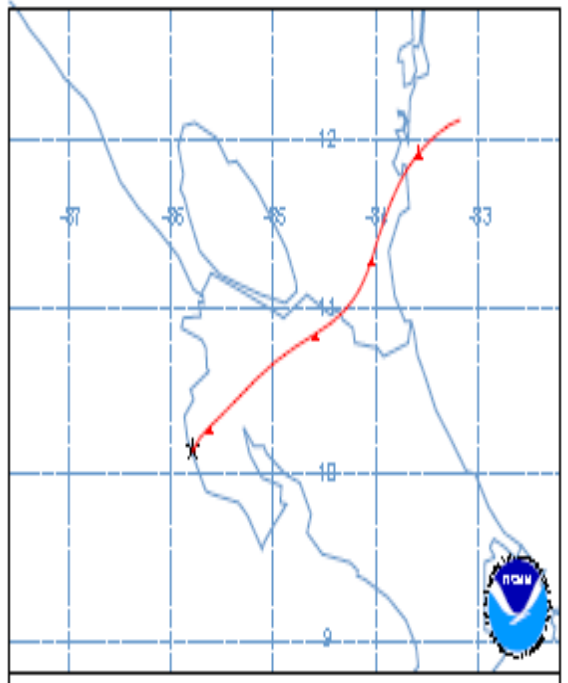Figure C17: June 1, 2013

Figure C18: June 15, 2013

Figure C19: June 22, 2013

About the Author

Mary S. Geesey received her Bachelor of Arts degree in History from the University of South Florida. Her areas of research interest include organic pollutants in air and water, mosquito control, and sustainability of natural resources. Mary's love of the outdoors began as a child, growing up in a small college town in central Washington near the foothills of the Cascades where she enjoyed freedoms not readily available to children today. Much of her time was spent in parks, riding bikes and horses, and climbing trees. She has a deep desire to improve the environment and, in turn, improve the health of people.