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# Detection of Polybrominated Diphenyl Ethers in Ambient Air at a Wastewater Treatment Facility in Tampa, Florida

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Detection of Polybrominated Diphenyl Ethers in Ambient Air at a Wastewater Treatment  
Facility in Tampa, Florida

by

Brenda L. White

A thesis submitted in partial fulfillment  
of the requirements for the degree of  
Master of Science  
Department of Environmental and Occupational Health  
College of Public Health  
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## Table of Contents

List of Tables .....	ii
List of Figures .....	iii
Abstract .....	iv
Background and Literature .....	1
Objectives .....	6
Howard Curren Wastewater Treatment Facility .....	7
Preparation of Sampling Materials .....	9
Tisch Sample Cartridge Preparation .....	10
Sampler Siting and Calibration .....	11
Sampling and Transport .....	11
Soxhlet Extraction .....	12
Volume Reduction and Sample Blow Down .....	12
Silica/Alumina Column Clean Up .....	12
GC/MS Analysis .....	13
QA/QC .....	13
Results .....	15
Discussion .....	23
Conclusions .....	26
Limitations .....	27
List of References .....	28
Appendices .....	31
Appendix 1: Samper Calibrations .....	32
Appendix 2: Flow Rate Logs .....	34
Appendix 3: Wind Trajectory Models .....	35

## List of Tables

Table 1 Concentrations in ng/m <sup>3</sup> of PBDEs Above the Limit of Detection .....	16
Table 2 P Values from Nonparametric Analysis of Filter Media by Location.....	17
Table 3 P Values from Nonparametric Analysis of PUF Media by Location .....	17
Table 4 P Values from Nonparametric Analysis of XAD Media by Location.....	18

## List of Figures

Figure 1 Sampling Locations at Howard Curren.....	8
Figure 2 Mean Concentration in ng/m <sup>3</sup> by Location for Filter Media .....	19
Figure 3 Mean Concentration in ng/m <sup>3</sup> by Location for PUF Media.....	20
Figure 4 Mean Concentration in ng/m <sup>3</sup> by Location for XAD Media .....	21
Figure 5 Mean of the Sum of the PBDEs Concentration in ng/m <sup>3</sup> by Location for All Media .....	22
Figure 6-A Calibration for EPA Sampler .....	32
Figure 7-A Calibration for Hillsborough Sampler.....	33
Figure 8-A EPA Sampler Logsheet and Flow Calculation.....	34
Figure 9-A Hillsborough Sampler Logsheet and Flow Calculation .....	34
Figure 10-A Wind Trajectory for Sampling Period 1 .....	35
Figure 11-A Wind Trajectory for Sampling Period 2.....	36
Figure 12-A Wind Trajectory for Sampling Period 3.....	37
Figure 13-A Wind Trajectory for Sampling Period 4.....	38
Figure 14-A Wind Trajectory for Sampling Period 5.....	39
Figure 15-A Wind Trajectory for Sampling Period 6.....	40
Figure 16-A Wind Trajectory for Sampling Period 7.....	41
Figure 17-A Wind Trajectory for Sampling Period 8.....	42
Figure 18-A Wind Trajectory for Sampling Period 9.....	43
Figure 19-A Wind Trajectory for Sampling Period 10.....	44

## Abstract

The goal of this study was to quantify the ambient air concentrations of polybrominated diphenyl ethers (PBDEs) from three locations within the Howard Curren Wastewater Treatment Facility located in Tampa, Florida. PBDEs have been linked to endocrine disruption, cancer, developmental concerns in children, as well as other toxic effects; however their precise roles concerning these deleterious effects remains to be determined. The present study was motivated by these potential health concerns posed by inhalational exposure to PBDEs. Ambient air was monitored with a Tisch Environmental PUF high volume sampler for 48 hours with collection on three types of media-quartz filter, PUF (polyurethane foam) and XAD-2 resin. The samples were then analyzed with GC/MS (gas chromatography/mass spectrometry) for eight PBDEs that are routinely detected.

The results showed elevated levels of PBDEs at the 2<sup>nd</sup> and 3<sup>rd</sup> sampling locations indicating a possible increased presence in the ambient air at the facility. Levels of PBDE 47 ranked highest amongst the detected congeners. PBDE 209 was not detected at any site.

The present results indicate that PBDEs may lead to an inhalational exposure, thus future experimentation is needed to fully evaluate the health complications associated with inhalational exposure route to PBDEs.

## Background and Literature

Polybrominated diphenyl ethers (PBDEs) are man-made chemicals utilized for their flame-retardant properties. In the event of a fire, the PBDE preparations exploit vapor phase chemical reactions that restrict the combustion process, consequently delaying ignition and inhibiting the extent of a fire. These features have promoted the extensive use of PBDEs in textiles, upholstery stuffing, electronic and electrical components, and plastics used in the casings of electronic equipment (U. S. EPA, 2010). The PBDEs are mixed into materials to provide the flame-retardant properties, however because they are not bonded they are easily removed from the mixture and leach into the environment (ATSDR, 2011).

PBDEs are a family of chemicals that are differentiated by the number of bromine molecules contained within their structures; anywhere from 1 to 10 bromine atoms attached. There are 209 possible PBDE compounds; each are termed *congener* and are assigned an individual brominated diphenyl ether (BDE) number (U. S. EPA, 2010). PBDEs are manufactured under three commercial names/mixes. The three mixtures of PBDEs are penta-BDE (used in furniture), octa-BDE (used in computers and appliances), and deca-BDE (used in fabrics, wiring, electronics, etc.). The European Union banned the use of certain PBDEs in a preventative gesture in 2003 and 2006, adding it to the list of Priority Pollutants in the Annex X of the Water Framework Directive. The Government of Canada states that use and/or release to the environment of these PBDEs be stringently controlled; namely, the manufacture of the PBDEs has been prohibited in Canada and the



consumption and importation of certain PBDEs is banned (Canada, 2009). In the United States, the manufacture of penta-PBDE and octa-PBDE ceased in 2004, and the production of deca-PBDE is scheduled to end in 2013; despite this, they will persist in homes and consumer goods for decades (U. S. EPA, 2010; Song, Chu, Letcher, & Seth, 2006). In this study, eight PBDEs (PBDE 28, 47, 99, 100, 153, 154 183, and 209) that are routinely detected in environmental samples will be analyzed.

The potential negative health concerns associated with PBDEs include liver toxicity, thyroid toxicity, developmental and reproductive toxicity, and developmental neurotoxicity (ATSDR, 2011). These findings are of particular concern when the potential risks relate to children. The carcinogenic potential of some PBDEs have been investigated (ATSDR, 2011). The toxicological studies for EPA's Integrated Risk Information System, found animal data for decabromodiphenyl ether (BDE 209) supports a finding of "suggestive evidence of carcinogenic potential". The congeners 99, 153, and 47 are reported as "inadequate information to assess carcinogenic potential"(EPA, 2008). These warnings and risks are associated with oral ingestion; currently, there are currently no inhalational reference doses on the EPA IRIS site (EPA, 2008); however ATSDR has issued a MRL (Minimal Risk Level) for the lower brominated PBDEs of  $6.0 \text{ ng/m}^3$  for an intermediate-inhalational dose. Intermediate-inhalational doses are exposures for >14 to 364 days.(ATSDR, 2011) Despite the fact that both the penta and octa formulations were withdrawn from the U.S. market, previous contamination and possible debromination of higher-brominated congeners to form lower-brominated congeners may be responsible for the presence of lower-brominated congeners in humans and the environment to date (U. S. EPA, 2010; Song, et al., 2006). The fate of PBDEs in the environment has been

modeled in a study by Schenker et al, which shows that even though the production of penta-PBDEs and octa-PBDEs are no longer being released from production, they continue to be generated from the degradation of deca-PBDE (Schenker, Soltermann, Scheringer, & Hungerbuhler, 2008). The argument regarding whether or not to continue the use of these chemicals involves whether the benefit of their flame retarding properties outweighs the threat of health concerns or environmental damage (Betts, 2002).

After being released into the air, PBDEs separate between the vapor (i.e. gas) and particle phases in the atmosphere depending upon their respective vapor pressures. Lower-brominated PBDEs usually exist in the vapor phase, while higher-brominated congeners are most often adsorbed to particles present in the air. Photolysis (chemical break down due to sunlight) in air is a key removal process for lower brominated congeners, including PBDE 47 and PBDE 99. PBDE 209 is more commonly removed via atmospheric wet and dry surface deposition because it predominantly exists bound to particles (U. S. EPA, 2010). Bezares-Cruz et al, performed a study showing that PBDE 209 degrades with a regular path of intermediates to form PBDE 47 under the influence of ultraviolet radiation (Bezares-Cruz, Jafvert, & Hua, 2004). Additionally, BDE 209 can produce a different form of breakdown product referred to as dibenzofurans which are considered to be an additional health risk (Eriksson, Green, Marsh, & Bergman, 2004). This degradation of PBDE 209 by UV radiation has been shown to occur on several particle surfaces as well as in liquid medium at a fast rate, sometimes with a half-life around 15 minutes (Soderstrom, Sellstrom, De Wit, & Tysklind, 2004).

Humans are exposed through food intake, breast milk, the air and in some circumstances working in occupations where PBDEs are part of a manufacturing process

(ATSDR, 2011). Foods are especially important sources when they are fertilized with land-applied waste water effluent (Munoz et al., 2009). Domingo et al. have established a link between bioaccumulation in marine species and the consumption of these species by humans (Domingo, Bocio, Falco, & Llobet, 2006). Munoz et al. performed experiments to determine levels of a multitude of chemicals emerging from wastewater plants in the effluent waters that were cleared for agricultural irrigation. These chemicals are adsorbed or absorbed onto the food we eat and lead to a route of exposure (Munoz, et al., 2009). An exposure assessment of Mexican children by Perez-Maldonado and colleagues, showed that levels of PBDEs in children (who should be free from occupational exposures) were still much higher in urban settings in the developing world than in rural ones (Perez-Maldonado et al., 2009).

PBDE levels in breast milk could be evidence of the bioaccumulation and body burden in humans. Americans seem to be doubling the PBDE breast milk levels every two to five years, which tallies up to levels 40 times higher than women in other countries (Betts, 2002). Data has shown that PBDEs are present in umbilical cord serum and the placenta in addition to breast milk which demonstrates that exposure occurs in the fetus even before birth and during early childhood indirectly through the mother's exposure (Gomara et al., 2007).

It is important to know the levels of PBDEs in wastewater to understand the potential release to the environment; these chemicals are relatively unchanged by the process of wastewater treatment, therefor retaining their potential to cause health effects (Clarke et al., 2008). Gomes' work on the detection of these chemicals in the wastewater matrix also expresses a concern for the possibility that byproducts of these chemicals

may behave as more potent endocrine disruptors than the parent compounds; however, experimental data addressing this concern is minimal (Gomes, Scrimshaw, & Lester, 2003). There have been several studies following the deposition of PBDEs into California waterways and rivers in China from releases due to wastewater, as well as, the effects on the marine biota, sediment and water (North, 2004; Oros, Hoover, Rodigari, Crane, & Sericano, 2004; Peng et al., 2009; Petreas & Oros, 2009). Song et al. conducted a study showing the fate of PBDEs through a wastewater treatment facility; however there was no air monitoring or explanation of PBDEs unaccounted for in the effluent or Waste Activated Sludge (Song, et al., 2006). The culmination of this data provides evidence that the levels of unaccounted for PBDEs exist either in the wastewater itself, end up in the sludge, waterways or land-applied pellets. The majority of the PBDEs do exit the wastewater through the sludge stream; however that value is not the complete picture. This study provides additional data regarding the levels of PBDEs that are present in the ambient air at a wastewater treatment facility in Tampa.

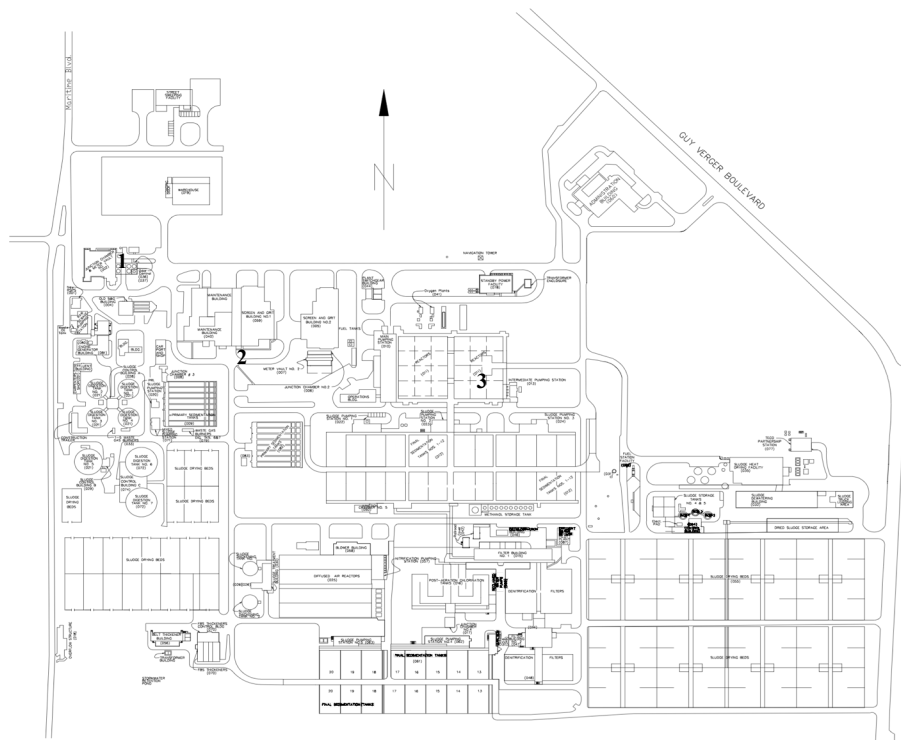
## Objectives

- To quantify the ambient air concentrations of polybrominated diphenyl ethers (PBDEs) from three locations within the Howard Curren Wastewater Treatment Facility located in Tampa, Florida.
- To investigate whether concentrations were similar or unique at each of the locations.
- To evaluate which PBDEs were detected in the greatest and least concentrations.

## **Materials and Methods**

### **Howard Curren Wastewater Treatment Facility**

At the Howard F. Curren wastewater treatment plant, the influent wastewater flows into the odor control station first, proceeds to the screen and grit building, then to the primary sedimentation tanks. At that point the primary sludge is removed and the liquid portion moves to the carbonaceous reactors. Then the piqued material sits in the carbonaceous sedimentation process where additional sludge is removed. The remaining liquid is sent to the nitrification reactors and sedimentation where the last sludge is removed. The resulting liquids then are filtered for de-nitrification and chlorinated after aeration. Reclaimed water is siphoned out at this point and processed by a de-chlorination step using sulfur dioxide. The water then flows into the Hillsborough Bay.



**Figure 1 Sampling Locations at Howard Curren**

Figure 1 illustrates the locations of the three sampling sites used during this experiment: the odor control building, the screen and grit building, and the rooftop of the carbonaceous tanks. Tim Ware, Plant Operations Manager, provided this site map. These sites were selected to coordinate with possible sludge and effluent water sampling. Assumptions were made before sampling that the wastewater plant would be in a steady state at the time of sampling and that the majority of PBDEs would sorb onto the solids in the wastewater. The first location (odor control building) is a relatively sealed system where sampling occurred outside in a space near the piping. This site was selected under the assumption that it would provide a baseline for any PBDEs being released into the air because this is the first point that the wastewater is exposed, and it is the location where there is the highest concentration in the wastewater. The second location (screen and grit

building) is a warehouse style building where sampling occurred near the tanks with slow moving stirrers. This location was selected for its exposed nature. This is the second location where the wastewater is being manipulated and should have a lower concentration of PBDEs than Location 1. The third location (rooftop of the carbonaceous tank) is open to the elements location directly above the tanks where pure oxygen is pumped into the sludge. This location was selected due to the high level of mixing occurring at the site. The PBDEs that are attached to the solids should be almost completely removed by this point with the sludge.

### **Preparation of Sampling Materials**

All methods are adapted from the EPA TO-13A method, Tisch operating manual, and EPA Technical Assistance Document for NATTSP (EPA, 1999, 2009; Tisch Environmental, 2008). These methods were selected based upon the use of the Tisch sampler and their ability to detect PBDEs. The materials below were selected based on the requirements of the above protocols.

#### *Tisch glass cartridge*

The Tisch glass sample cartridges were triple rinse with hexane. Once they were dry the cartridges were placed in aluminum foil until ready to use.

#### *Filter*

The quartz filters were wrapped in aluminum and baked in a glassware furnace at 400°C for 5 hours. Once they were cool the filters were stored in a zip top bag inside of aluminum foil for transport to the testing sites.

#### *PUF plug*



The PUF plugs were cleaned using a Soxhlet apparatus and extracted using 250ml of DCM (dichloromethane) for 16 hours at approximately 4 cycles per hour. Boiling chips were used in the flat/round bottom flasks to prevent explosion. Once the PUF plugs were removed from the Soxhlet apparatus they were moved to a vacuum evaporator and dried at room temperature for approximately 2-4 hours (or until no solvent odor could be detected). The cleaned PUF plugs were stored in amber jars until ready to use in the glass cartridge.

#### *XAD-2 resin*

XAD-2 was transferred into a baked thimble in the amount of 30-40 grams, then inserted inside a Soxhlet apparatus and extracted with DCM for 16 hours at approximately 4 cycles per hour. After 16 hours, the used DCM is discarded and replaced with fresh DCM and the XAD-2 is again extracted for another 16 hours at approximately 4 cycles per hour. Once the extraction was completed the XAD-2 resin (within the thimble) was removed from the Soxhlet apparatus and placed within a vacuum evaporator to dry at room temperature for approximately 2-4 hours (or until no solvent odor could be detected). The cleaned XAD-2 resin was then stored in cleaned/baked amber jar, sealed with hexane-rinsed aluminum foil under cap, in refrigerator (<4° C) until ready to use in the glass cartridge.

#### **Tisch Sample Cartridge Preparation**

The PUF was cut in half using solvent rinsed scissors. One half of the PUF is pushed inside the cleaned glass Tisch sampling cartridge using cleaned forceps until it is correctly seated flush and flat against the screen at the bottom. Roughly 15 g of cleaned XAD-2 resin is dispensed on top of the PUF inside the cartridge. The second half of the

cleaned PUF plug is then placed on top of the XAD-2 resin and pressed down to ensure good compaction (The pressure of sampling will further compress the materials). The entire loaded cartridge was then wrapped in hexane-rinsed aluminum foil. Each wrapped cartridge was stored inside the cleaned shipping containers. The entire shipping container was also wrapped with hexane rinsed aluminum foil. The containers were refrigerated (<4° C) until ready to use.

One sample cartridge was made for each field sample, lab blank (only exposed in the lab during preparation) and each field blank (only exposed during transport to the sampling site and while samples were being installed onto the sampling units). This experiment had 18 field samples, 3 lab blanks, and 3 field blanks.

### **Sampler Siting and Calibration**

Before sampling began, the Tisch High volume sampler was properly sited in a location with minimal airflow restrictions, where the exhaust hose could extend all the way away from the sampler, where it was secured from tipping over, and with appropriate power connections.

The Tisch sampler was also calibrated according to the operator's manual before use after being transported to the site. The calibration sheets are located in Figure 7-A and Figure 8-A in the Appendix 1.

### **Sampling and Transport**

The samples were transported in a cooler with enough ice packs to maintain a temperature of approx. 10° C. This was monitored with a thermometer in the cooler. The

samples were installed according to the EPA methods, using clean nitrile gloves for each sample. The timers for this experiment were set for 48 hours from midnight to the second consecutive midnight. The samples were collected before 0700 the morning the run was completed. Sampling temperatures and barometric pressures were recorded utilizing data from NOAA. Flow rates were assessed and recorded at the beginning and end of each run as well as the reading from the elapsed time monitor. The log sheets for each sampler are located in the Appendix 2 as Figure 9-A and Figure 10-A. Each sample was labeled with the sample number and the Tisch unit it ran on. Once returned to the lab the samples were frozen at -20° C until extraction.

### **Soxhlet Extraction**

Each piece of media is extracted separately- the filter, the XAD-2 resin, and the PUF. The extraction was performed using the Soxhlet extraction unit once they have been triple solvent rinsed using DCM as solvent and spiked with a standard to assess the performance of the process. The extraction was run for 18hrs. The cooled samples were sealed with stoppers and refrigerated until the volume was reduced.

### **Volume Reduction and Sample Blow Down**

The volume of sample was reduced using the rotary evaporator to approximately 2 mL. The sample was then quantitatively transferred to 10mL amber vials using hexane and loosely covered with foil. The vials were placed on the nitrogen blow down apparatus with the needle piercing the foil. The sample was monitored for volume reduction to approximately 1 mL.

### **Silica/Alumina Column Clean Up**

Ambient air samples that are transparent do not require clean up; however for this project all samples were treated the same and cleaned. A silica alumina column was used to collect 25 ml and the nitrogen blow down process was repeated.

### GC/MS Analysis

Sample material was added to the GC-vial with three small hexane washes. The standards were added as well as dodecane to prevent drying. The instrument was calibrated and quality controlled according to the operation instructions. The standard curve was developed by external standards. The analysis for these samples was blinded and conducted by a third party lab. Prior to analysis, mirex was added to the extracts as an internal standard. The analysis was performed by capillary gas chromatography - mass spectrometry (Agilent 6890 GC – 5973 MSD) in electron capture negative ion mode (ECNI). Analysis was done on a DB-5MS column (15 m × 0.25 mm i.d., 0.25 μm film thickness, Agilent Technologies), with helium as the carrier gas and methane as reagent gas at 1.2 mL min<sup>-1</sup>. The GC oven temperature program was: 60 °C held for 1 min, ramped to 150°C at 10°C min<sup>-1</sup>, to 300°C at 5°C min<sup>-1</sup> and held for 5 min. Inlet temperature was 250°C. Sample volumes of 1 μL were injected splitless. Ion source and quadrupole temperatures were 150°C and 106 °C respectively. Transfer line was set at 250°C. The monitored ions for the PBDEs are 79 and 81.

### QA/QC

A peak was positively identified if it was within ±0.05 min of the retention time in the calibration standard and quantified only if the S/N ≥ 3, and the ratio of the target ion to its qualifier ion was within ±20% of the standard value. The PBDEs present in the appropriate blanks were subtracted from those in the sample extracts. The method

detection limits (MDLs) were calculated as the mean blank + 3×SD. Average recoveries (%) for surrogates spiked in samples were between 70 (± 10 SD) for BDE 35 and 84 (± 5 SD) for BDE 181.

## **Results**

The GCMS data was reviewed by initially identifying the blanks (field and lab blanks) for each type of media (filters, PUFs, and XAD) and finding the mean concentration for the groups of media. The detection limits for the lab and field blanks ranged from 0.05-0.1ng m<sup>3</sup>. The PBDEs (28, 47, 99, 100, 153,154, 183, and 209) concentrations were calculated as ng/m<sup>3</sup> by dividing by the air volume passing through the media during the sampling process. The limit of detection corrected concentration data is shown below in Table 1.

**Table 1 Concentrations in ng/m3 of PBDEs Above the Limit of Detection**

	LOCATION 1						LOCATION 2						LOCATION 3															
	FILTER MEDIA																											
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18										
PBDE 28													0.11	0.26	0.10	0.10		0.40										
PBDE 47													0.81	0.78	0.69	0.96	3.49	1.07	1.26	1.18	5.26							
PBDE 99													0.11	0.11	0.11	0.10	0.27	0.13	0.17	0.13	0.40							
PBDE 100													0.25	0.26	0.22	0.76	0.51	0.48	0.42	1.32								
PBDE 153													0.06							0.10	0.07	0.08	0.05	0.14				
PBDE 154													0.07	0.09	0.07	0.08	0.07	0.15	0.11	0.13	0.06	0.20						
PBDE 183																									0.30	0.11		0.11
PBDE 209																												
PUF MEDIA																												
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18											
PBDE 28							0.41	0.41	0.30			0.30	0.39	0.38	0.30													
PBDE 47													3.06			1.13	1.39	3.64	3.73	4.79	4.33							
PBDE 99													0.16	0.19				0.43	0.51	0.52	0.48							
PBDE 100													0.57			0.43	1.34	1.29	1.75	2.11								
PBDE 153																			0.18	0.20	0.14	0.16						
PBDE 154																			0.20	0.23	0.17	0.22						
PBDE 183																			0.09		0.14							
PBDE 209																												
XAD MEDIA																												
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18											
PBDE 28																												
PBDE 47																									0.27			
PBDE 99																									3.78			
PBDE 100																									0.28	0.41	0.22	
PBDE 153																									1.09			
PBDE 154																									0.09	0.10		
PBDE 183																									0.09		0.12	
PBDE 209																												

The data was then analyzed using a nonparametric regression model to establish if the concentrations in each location were significant. Table 2 gives the associated P values for the filter concentrations. Table 3 gives the associated p values for the PUF media concentrations. Finally, Table 4 shows the p values for the XAD media.

**Table 2 P Values from Nonparametric Analysis of Filter Media by Location**

Filter Media	
Congener	p value
PBDE 28	0.0172
PBDE 47	0.0031
PBDE 99	0.0062
PBDE 100	0.0055
PBDE 153	0.0071
PBDE 154	0.0138
PBDE 183	0.0484
PBDE 209	Not significant

**Table 3 P Values from Nonparametric Analysis of PUF Media by Location**

PUF Media	
Congener	p value
PBDE 28	0.0114
PBDE 47	Not significant
PBDE 99	0.0488
PBDE 100	0.0362
PBDE 153	0.0393
PBDE 154	0.0393
PBDE 183	0.0493
PBDE 209	Not significant

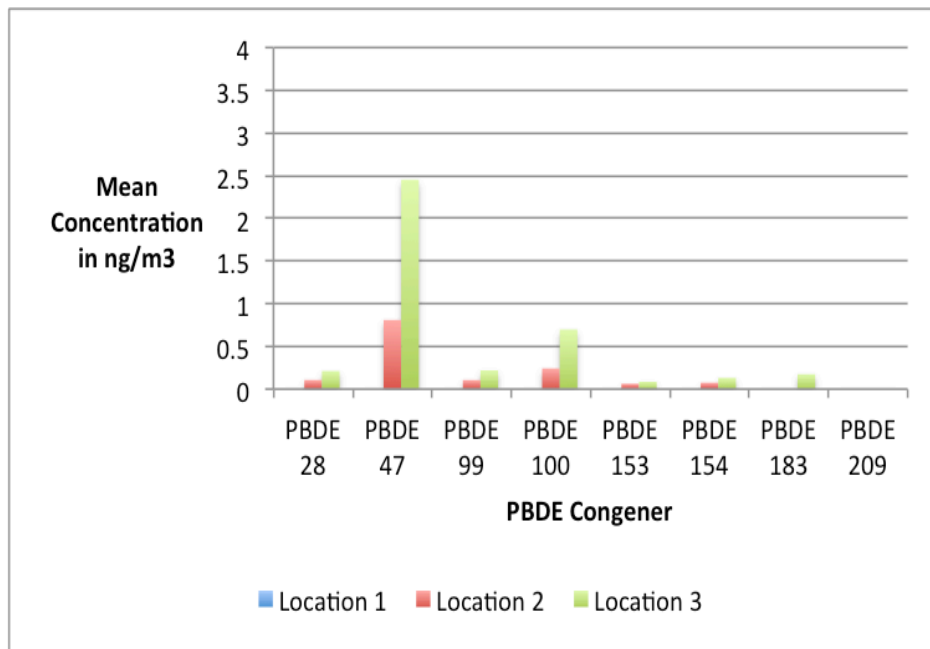


**Table 4 P Values from Nonparametric Analysis of XAD Media by Location**

XAD Media	
Congener	p value
PBDE 28	Not significant
PBDE 47	Not significant
PBDE 99	0.0015
PBDE 100	Not significant
PBDE 153	0.0062
PBDE 154	0.0062
PBDE 183	0.0371
PBDE 209	Not significant

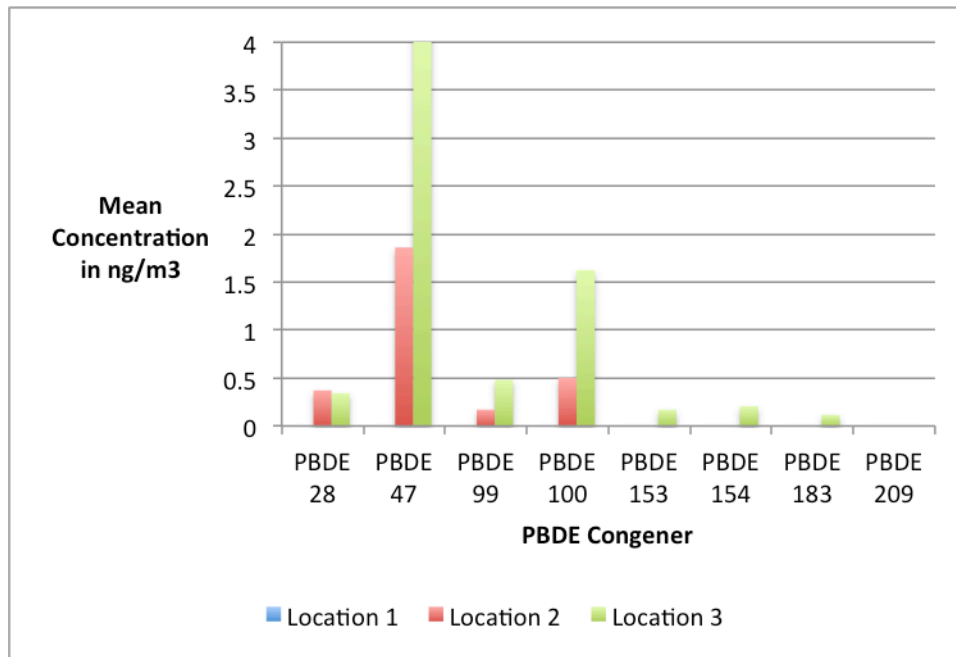
The alpha value used to evaluate the data for this study was 0.05 with a 95% confidence level. Table 2 demonstrates that for all the congeners tested for the concentrations for the filters were significantly different across the three locations tested. Table 3 demonstrates that the concentrations for PBDEs 47 and 209 were not significant, however the concentrations of all other congeners were significantly different in the three locations for the PUF media. Table 4 demonstrates that the concentrations for the XAD media across the three locations were significantly different for PBDEs 99, 153, 154, and 183 only.

Figure 2 shows the mean PBDEs concentrations for the filter media by location. The congener with the highest concentration was PBDE 47 for both Location 2 and 3, but not detected at Location 1. Congener 209 was not detected at any location.



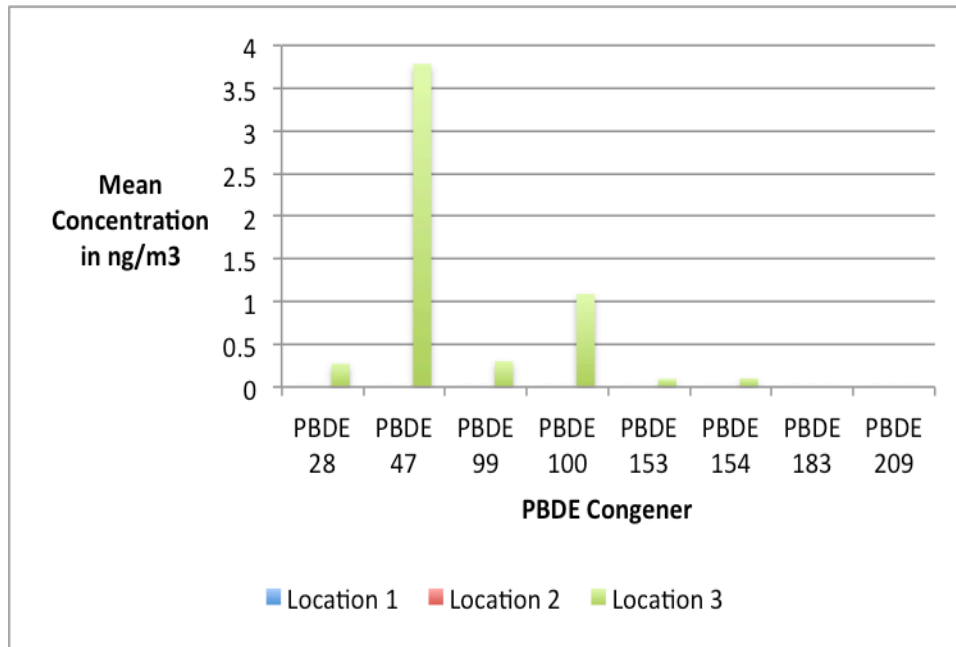
**Figure 2 Mean Concentration in ng/m<sup>3</sup> by Location for Filter Media**

Figure 3 shows the mean concentrations of PBDEs for the PUF media by location. The congener with the highest concentration was PBDE 47 for both Location 2 and 3, but was not detected at Location 1. Congener 209 was not detected at any location.



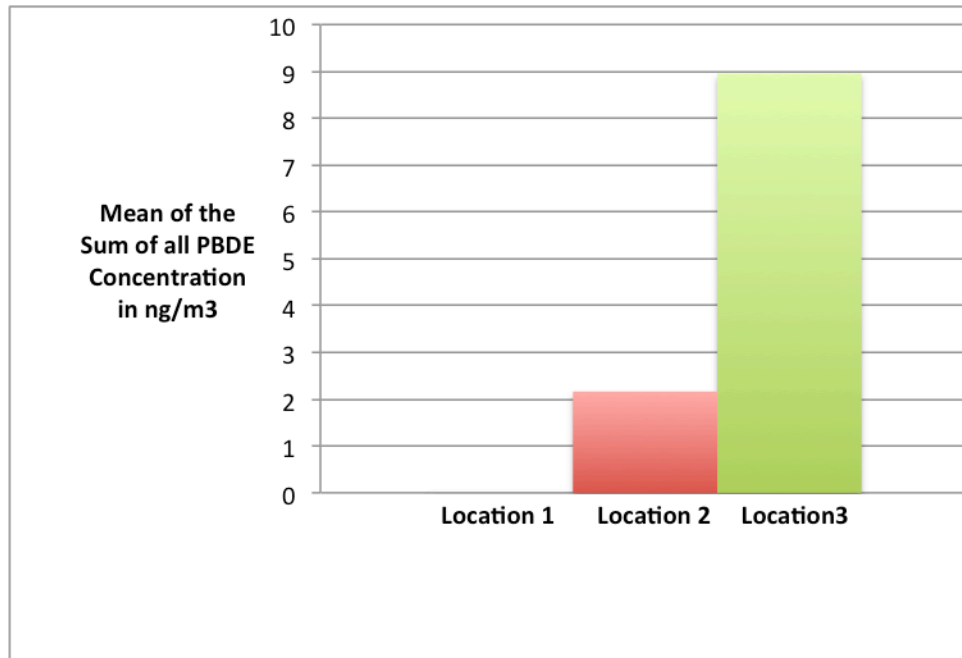
**Figure 3 Mean Concentration in ng/m<sup>3</sup> by Location for PUF Media**

Figure 4 shows the mean concentration of PBDEs for the XAD media by location. The congener with the highest concentration was PBDE 47 at Location 3, but it was not detected at Location 1 or 2 with XAD media. Again, congener 209 was not detected at any location.



**Figure 4 Mean Concentration in ng/m<sup>3</sup> by Location for XAD Media**

Figure 5 is an overall concentration for all PBDEs on all media types (filter, PUF and XAD combined) for each location. Location 1 had no concentrations, Location 2 had a mean concentration of all PBDEs of slightly more than 2 ng/m<sup>3</sup>, and Location 3 demonstrated a mean of concentration slightly below 9 ng/m<sup>3</sup>. The trend seen was an increase in concentration through the progression of wastewater treatment.



**Figure 5 Mean of the Sum of the PBDEs Concentration in ng/m3 by Location for All Media**

## Discussion

The ambient air concentrations of polybrominated diphenyl ethers (PBDEs) from three locations within the Howard Curren Wastewater Treatment Facility located in Tampa, Florida were quantified. Upon the undertaking of this study it was hypothesized that there would not be high enough concentrations to detect the PBDEs, which is why the sampling times were increased to 48-hour increments; however as the results show this was incorrect. The lack of detection of any PBDEs at Location 1 is not unexpected. This location is next to a sealed, closed system so it is unlikely that any aerosolized or volatilized materials would escape from the closed piping even though the concentrations within the wastewater are at the highest level. Surprisingly, the combined mean concentration value for all PBDEs at Location 3 were roughly 4.5 times greater even though Location 2 was juxtaposed to the open stirring vat. Consequently this suggests that the activity in Location 3 is aiding in the aerosolization or volatilization of the PBDEs.

When the overall pattern of detected congeners was examined by location it was interesting to see that Locations 2 and 3 were similar. The relative concentrations of each congener remained consistent even though the overall amount detected at Location 3 was greater than Location 2.

Additionally, the data was evaluated to see which PBDEs were detected in the greatest and least concentrations. The absence of PBDE 209 is not unexpected. This is likely due to the large molecular weight and very high partitioning coefficient preventing

volatilization as well as the likelihood that it has been degraded by UV radiation present at a high index in the summer months in Florida. The degradation product found in the highest abundance from PBDE 209 is PBDE 47 (Bezares-Cruz, et al., 2004), which is the congener found in the highest concentration in this study. The detected values over the LOD (Limit of Detection) did not exceed the ATSDR MRL of 6.0 ng/m<sup>3</sup> during this testing for the lower brominated PBDEs; however air sampling was only conducted for 48-hour periods for three days at each location. There are no MRL's for the higher brominated PBDEs that were also detected.

The filter media is utilized mainly to detect particulate matter and chemicals that have adhered to particles. PUF media is more useful for detecting gaseous phase chemicals. XAD-2 is used as a breakthrough barrier for the PUF media to prevent loss of the gaseous chemicals during sampling. It is interesting that we see a much higher general trend in the concentration of the gaseous phase materials (PUF and XAD) than in the particulate phase. During the sampling, there was a substantial construction process occurring to replace major underground piping at Howard Curren, which may have had an influence on the particulate concentrations.

The presence of PBDEs in ambient air is an indication that they are in the respirable air column and could pose an inhalational exposure. Additional testing may be warranted to discern if the aerosolization and volatilization is affected by seasonal changes such as cooler temperatures, changes in barometric pressure, or precipitation. This experiment was conducted from June 7, 2011 to July 12, 2011. During this time frame the temperatures, barometric pressures and precipitation events were stable. The wind trajectories for the sampling periods are located in Appendix 3. The wind,

according to National Weather Service data and National Oceanic and Atmospheric modeling rarely exceeded 5 knots throughout the sampling period and originated from locations varying from the Gulf of Mexico traveling to the East, from the Caribbean traveling North, and from the Atlantic crossing the state to the West. These different wind patterns do not appear to have changed the detected limits; however longer studies with wind monitors at the site may be more informative.



## Conclusions

It can be concluded from the concentrations measured at the wastewater treatment facility in Tampa, that there is a possibility for exposure via the inhalational route to PBDE 28, 47, 99, 100, 153, 154, and 183 at Locations 2 and 3; however, at the time of this study Location 1 did not demonstrate an increased opportunity for inhalational exposure. From this data PBDE 209 does not appear to be an inhalational exposure at any of the locations at the time of this study. Additionally, the PBDEs that were aerosolized or volatilized by the processes at a given location at the wastewater treatment facility do not appear to migrate to other locations; indicating the exposure would likely be closest to the sampling locations. The elevated levels of PBDE47 are likely due to the degradation of heavier PBDEs, such as PBDE 209. Future studies to evaluate inhalational risks could benefit the wastewater treatment facility, as well as, the surrounding population, by preventing adverse health outcomes from exposure to elevated PBDEs in the respirable ambient air.

## **Limitations**

It is important to state that since this was a pilot study there are several limitations. First, the sample size was small and sampling was confined to only the summer months. Increasing the sample number and including additional samples will give a more representative data set for the entire year. Second, the data for ambient temperatures, rainfall, barometric pressure, and wind were referenced from the NOAA and NWS. Taking measurements from the sampling sites may provide more accurate data. Finally, sampling was limited to specific sites at Howard Curren for logistical reasons and safety.

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## Appendices

## Appendix 1: Samper Calibrations

Howard Curren Odor Control Calibration EPA Sampler PUF Sampler Calibration							
SITE							
Location:	Howard Curren Wastewater			Date:	17-Jun-11		
Sampler:	Te-1000 EPA			Tech:	B. White		
CONDITIONS							
Sampler Elevation (feet):	9			Pressure (mm Hg):	756		
Sea Level Pressure (mm Hg):	756.22			Temperature (deg K):	305		
Temperature (deg F):	89			Seasonal (mm Hg):	762		
Seasonal SL Press. (mm Hg):	761.70			Seasonal Temp. (deg K):	301		
Seasonal Temp. (deg F):	82						
CALIBRATION ORIFICE							
Make:	Tisch			Qstd Slope:	5.79890		
Model:	TE-5040A			Qstd Intercept:	0.19110		
Serial#:	1f3			Date Certified:	3/29/11		
CALIBRATION							
Plate or Test #	H2O (in)	Qstd (m3/min)	FLOW (magn)	FLOW (corrected)	LINEAR REGRESSION		
1	9.10	0.480	100.0	9.87	Slope =	19.2270	
2	8.00	0.448	80.0	8.82	Intercept =	0.3245	
3	5.30	0.359	50.0	6.98	Corr. coeff.=	0.9935	
4	4.20	0.316	40.0	6.24			
5	1.90	0.202	20.0	4.41	# of Observations	5	

### Calculations

$$Qstd = 1/m[\text{Sqrt}(H2O(Pa/Pstd)(Tstd/Ta))-b]$$

$$\text{Flow (corrected)} = \text{Sqrt}((\text{magn})(Pa/Pstd)(Tstd/Ta))$$

Qstd = standard flow rate  
 Flow (magn)= reading off of magnehelic gauge  
 Flow (corrected)= corrected flow rate  
 m = calibrator Qstd slope  
 b = calibrator Qstd intercept  
 Ta = actual temperature during calibration (deg K)  
 Pa = actual pressure during calibration (mm Hg)  
 Tstd = 298 deg K  
 Pstd = 760 mm Hg  
 For subsequent calculation of sampler flow:  
 $1/m[(\text{Sqrt}(\text{magn})(Pav/760)(298/Tav)]-b$

m = sampler slope  
 b = sampler intercept  
 (magn)= magnehelic reading  
 Tav = daily average temperature  
 Pav = daily average pressure

**Figure 6-A Calibration for EPA Sampler**

**Howard Curren Odor Control Calibration Hills Sampler  
PUF Sampler Calibration**

SITE		
Location:	Howard Curren Wastewater	Date: 17-Jun-11
Sampler:	TE-1000 hills	Tech: B. White

CONDITIONS			
Sampler Elevation (feet):	9	Corrected Pressure (mm Hg):	756
Sea Level Pressure (mm Hg):	756.22	Temperature (deg K):	305
Temperature (deg F):	89	Corrected Seasonal (mm Hg):	762
Seasonal SL Press. (mm Hg):	761.70	Seasonal Temp. (deg K):	301
Seasonal Temp. (deg F):	82		

CALIBRATION ORIFICE			
Make:	Tisch	Qstd Slope:	5.79890
Model:	TE-5040A	Qstd Intercept:	0.19110
Serial#:	1f3	Date Certified:	3/29/11

CALIBRATION							
Plate or Test #	H2O (in)	Qstd (m3/min)	FLOW (magn)	FLOW (corrected)	LINEAR REGRESSION		
1	9.50	0.491	90.0	9.36	Slope =	19.3566	
2	7.40	0.430	70.0	8.25	Intercept =	-0.1451	
3	5.70	0.373	50.0	6.98	Corr. coeff.=	0.9996	
4	3.50	0.285	30.0	5.40			
5	1.40	0.168	10.0	3.12	# of Observations	5	

Calculations

$$Qstd = 1/m[\text{Sqrt}(H2O(Pa/Pstd)(Tstd/Ta))-b]$$

$$\text{Flow (corrected)} = \text{Sqrt}((\text{magn})(Pa/Pstd)(Tstd/Ta))$$

Qstd = standard flow rate  
 Flow (magn)= reading off of magnehelic gauge  
 Flow (corrected)= corrected flow rate  
 m = calibrator Qstd slope  
 b = calibrator Qstd intercept  
 Ta = actual temperature during calibration (deg K)  
 Pa = actual pressure during calibration (mm Hg)  
 Tstd = 298 deg K  
 Pstd = 760 mm Hg  
 For subsequent calculation of sampler flow:  
 $1/m([\text{Sqrt}(\text{magn})(Pav/760)(298/Tav)]-b)$

m = sampler slope  
 b = sampler intercept  
 (magn)= magnehelic reading  
 Tav = daily average temperature  
 Pav = daily average pressure

**Figure 7-A Calibration for Hillsborough Sampler**



## Appendix 2: Flow Rate Logs

Howard Curren EPA Air Monitor

### Puff Sampler Information 2011

$1/19.2270(\text{sqrt}(\text{mag})(\text{pa}/760)(298/\text{ta}))-0.3245$

$(1/19.2270)(\text{sqrt}-0.3245)^{(.001)}$

Date on	Date off	Time Start	Time End	Time Total	Time Minutes	F deg Temp F	C deg Temp C	K deg Temp	mmHg Baro	Magnehelic Start	End	Aver mag	calculation	std./m3/min Flowrate	Total Liters of air
6/7/11	6/10/11	2980.14	3005.26	25.1	1507.2	89	31.67	304.82	762.0	50	52	51	7.070370631	0.351	529,027
6/10/11	6/13/11	3005.27	3052.70	47.4	2845.8	89	31.67	304.82	760.0	52	54	53	7.198207098	0.358	1,018,796
6/13/11	6/16/11	3052.70	3100.13	47.4	2845.8	89	31.67	304.82	760.0	52	52	52	7.129978107	0.354	1,007,413
6/17/11	6/20/11	3100.25	3148.68	48.4	2905.8	89	31.67	304.82	763.0	34	34	34	5.776720218	0.284	825,247
6/20/11	6/23/11	3148.72	3196.10	47.4	2842.8	89	31.67	304.82	762.0	38	42	40	6.261625477	0.309	878,425
6/23/11	6/26/11	3196.13	3244.19	48.1	2883.6	89	31.67	304.82	761.0	38	38	38	6.09907162	0.300	865,080
6/30/11	7/3/11	3244.27	3292.29	48.0	2881.2	89	31.67	304.82	762.0	46	42	44	6.567248204	0.325	936,390
7/3/11	7/6/2011*	3292.42	3292.44	0.0	1.2	89	31.67	304.82	762.0	44	44	44	6.567248204	0.325	390
7/6/11	7/9/11	3292.44	3340.24	47.8	2868	89	31.67	304.82	760.0	57	55	56	7.399125884	0.368	1,055,424
7/9/11	7/12/11	3340.25	3388.07	47.8	2869.2	90	32.22	305.37	763.0	55	55	55	7.340603477	0.365	1,047,258

Comments: \* lost power and sample did not run

Figure 8-A EPA Sampler Logsheet and Flow Calculation

Howard Curren Hillsborough Air Monitor

### Puff Sampler Information 2011

$1/19.35659(\text{sqrt}(\text{mag})(\text{pa}/760)(298/\text{ta}))+0.14507$

$(1/19.35659)(\text{sqrt}+0.14507)^{(.001)}$

Date on	Date off	Time Start	Time End	Time Total	Time Minutes	F deg Temp F	C deg Temp C	K deg Temp	mmHg Baro	Magnehelic Start	End	Aver mag	calculation	std./m3/min Flowrate	Total m3 of air
6/7/11	6/10/11	0.36	25.09	24.7	1483.8	89	31.67	304.82	762.0	42	46	44	6.567248204	0.347	520,814
6/10/11	6/13/11	25.19	72.78	47.6	2855.4	89	31.67	304.82	760.0	28	24	26	5.041654455	0.268	1,022,233
6/13/11	6/16/11	72.79	117.78	45.0	2699.4	89	31.67	304.82	760.0	47	45	46	6.706027322	0.354	955,588
6/17/11	6/20/11	117.89	165.53	47.6	2858.4	89	31.67	304.82	763.0	40	38	39	6.186915421	0.327	811,786
6/20/11	6/23/11	165.54	214.09	48.6	2913	89	31.67	304.82	762.0	48	46	47	6.787440276	0.358	900,117
6/23/11	6/26/11	214.11	262.54	48.4	2905.8	89	31.67	304.82	761.0	44	40	42	6.412045273	0.339	871,740
6/30/11	7/3/11	262.60	311.70	49.1	2946	89	31.67	304.82	762.0	45	43	44	6.567248204	0.347	957,450
7/3/11	7/6/11	311.71	358.92	47.2	2832.6	89	31.67	304.82	762.0	42	40	41	6.339412627	0.335	920,595
7/6/11	7/9/2011*	358.98	407.13	48.2	2889	89	31.67	304.82	760.0	56	56	56	7.399125884	0.390	1,063,152
7/9/11	7/12/11	407.15	454.75	47.6	2856	90	32.22	305.37	763.0	54	52	53	7.205902061	0.380	1,042,440

Comments: \* sample motor did not run

Figure 9-A Hillsborough Sampler Logsheet and Flow Calculation

### Appendix 3: Wind Trajectory Models

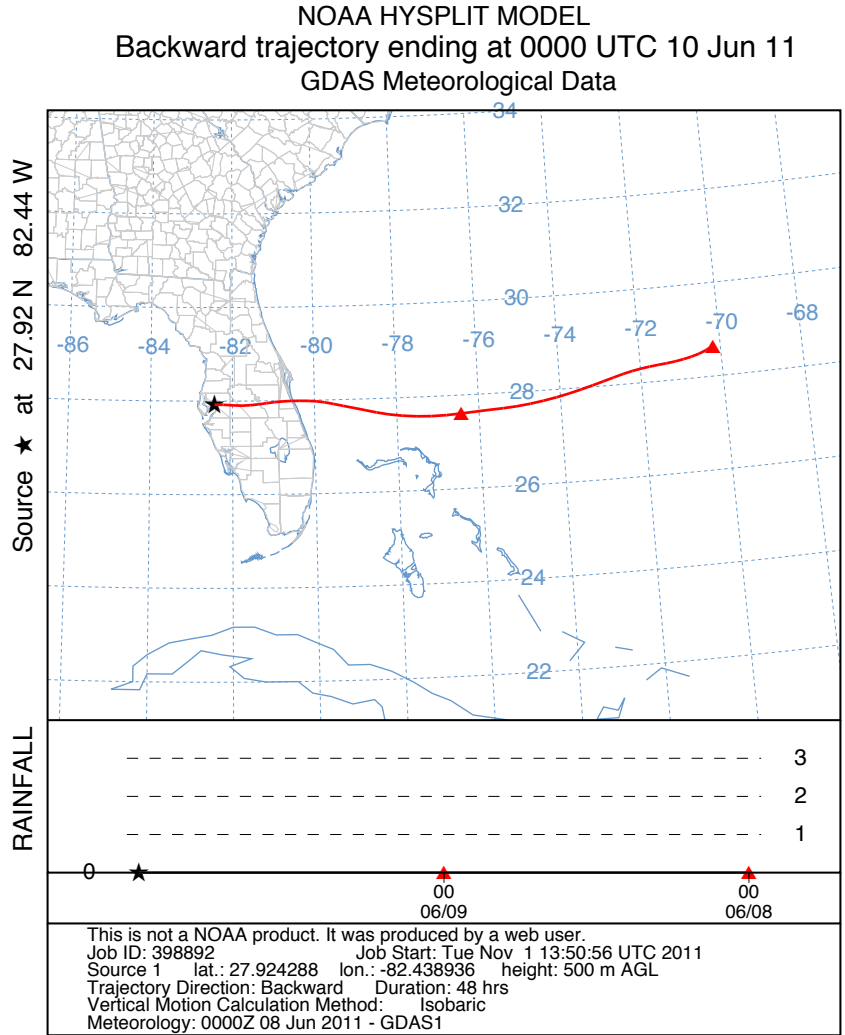


Figure 10-A Wind Trajectory for Sampling Period 1

NOAA HYSPLIT MODEL  
 Backward trajectory ending at 0000 UTC 13 Jun 11  
 GDAS Meteorological Data

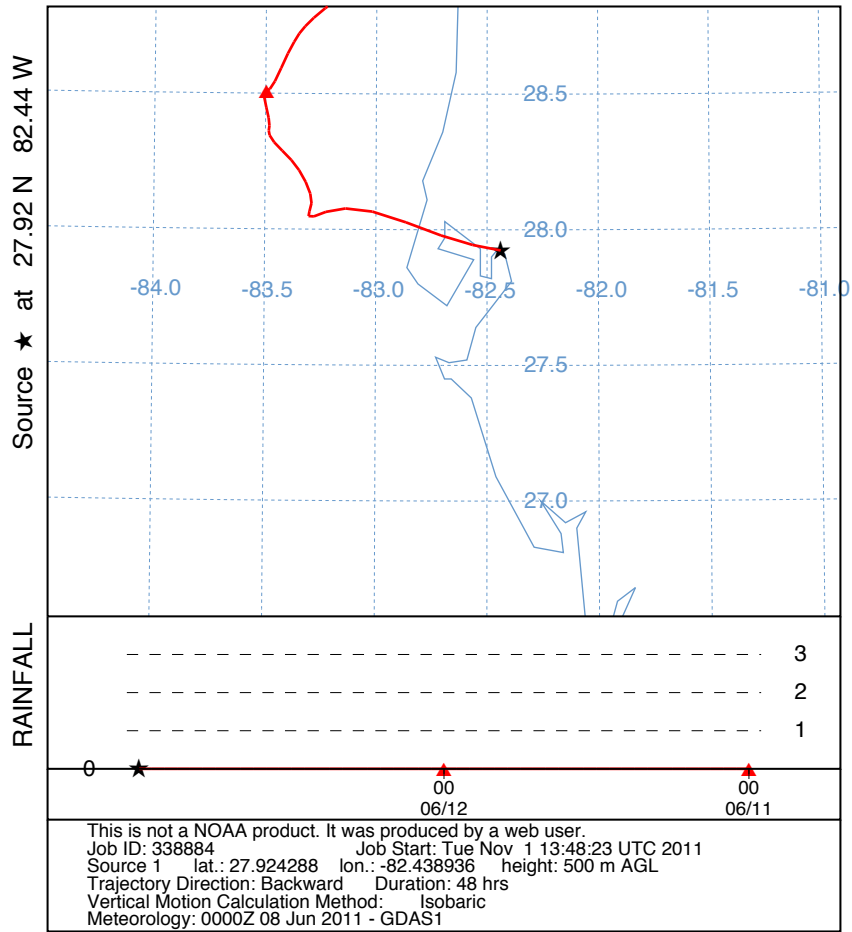


Figure 11-A Wind Trajectory for Sampling Period 2

NOAA HYSPLIT MODEL  
 Backward trajectory ending at 0000 UTC 16 Jun 11  
 GDAS Meteorological Data

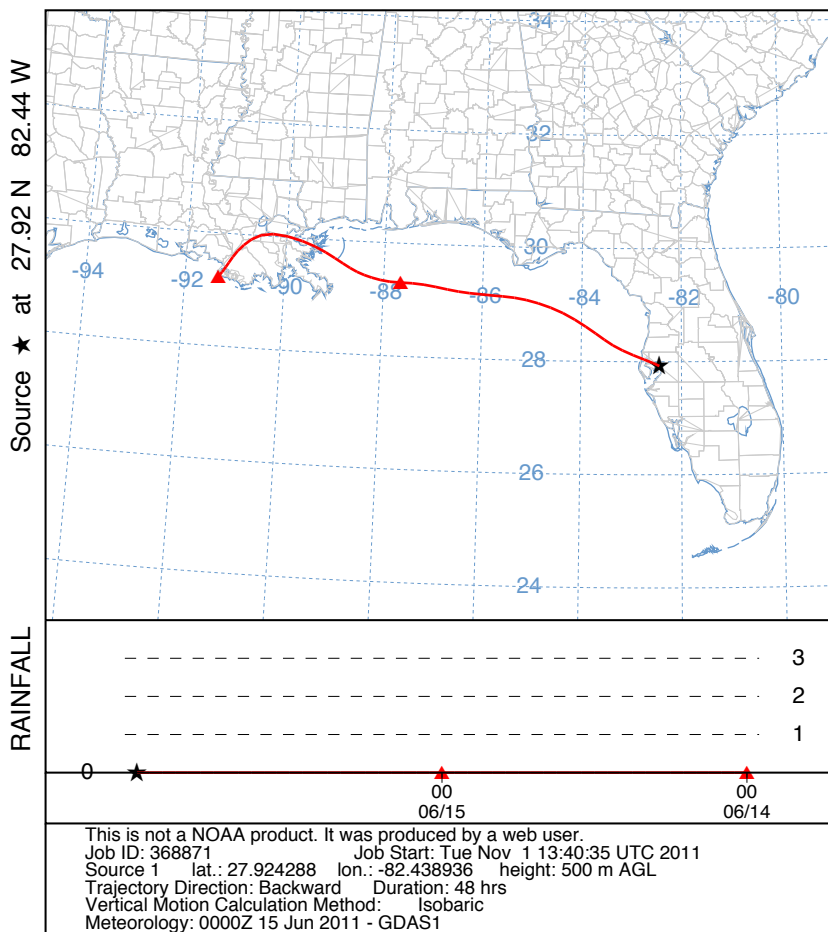


Figure 12-A Wind Trajectory for Sampling Period 3

NOAA HYSPLIT MODEL  
 Backward trajectory ending at 0000 UTC 20 Jun 11  
 GDAS Meteorological Data

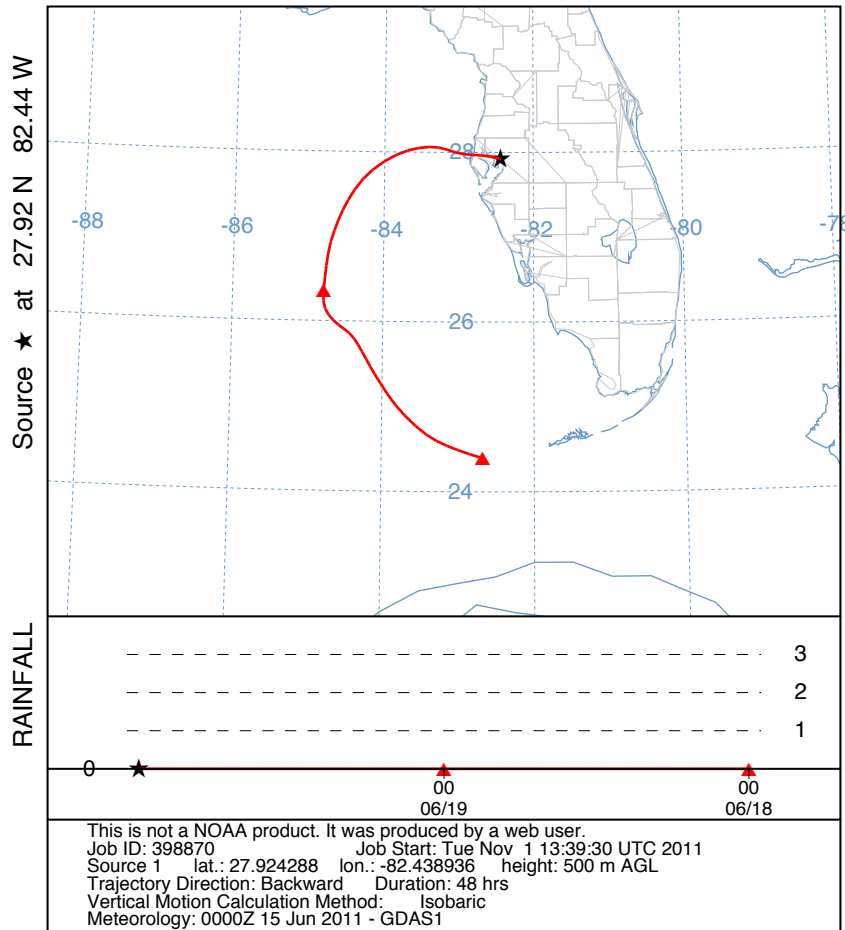


Figure 13-A Wind Trajectory for Sampling Period 4

NOAA HYSPLIT MODEL  
 Backward trajectory ending at 0000 UTC 23 Jun 11  
 GDAS Meteorological Data

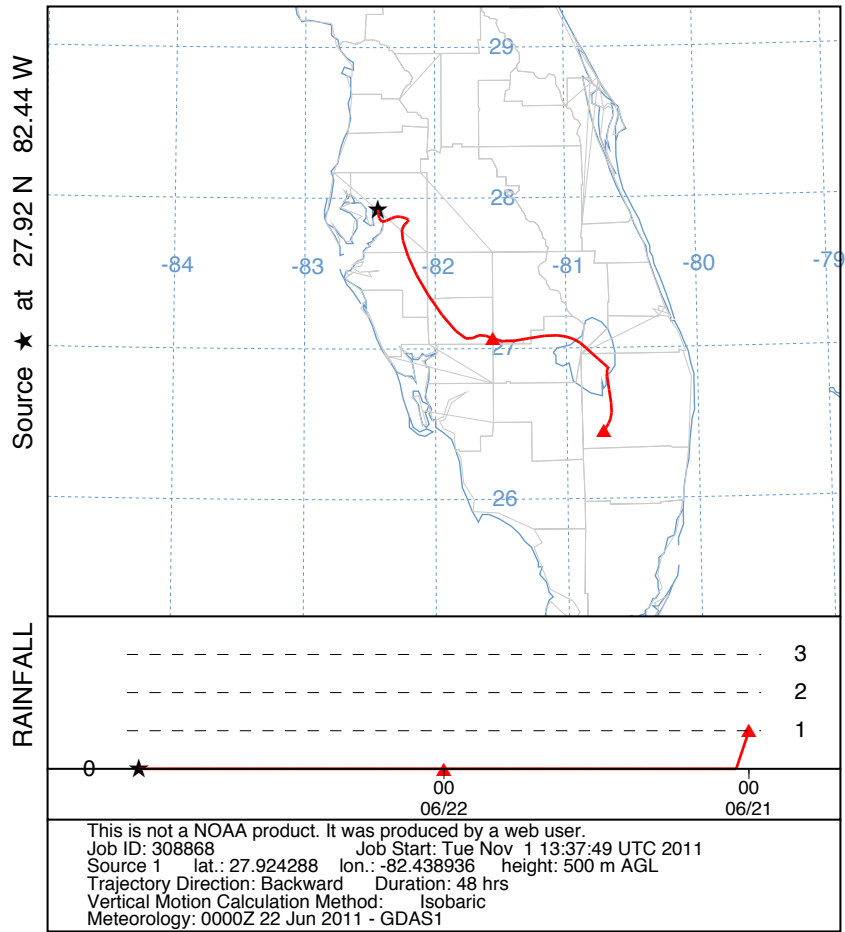


Figure 14-A Wind Trajectory for Sampling Period 5

NOAA HYSPLIT MODEL  
 Backward trajectory ending at 0000 UTC 26 Jun 11  
 GDAS Meteorological Data

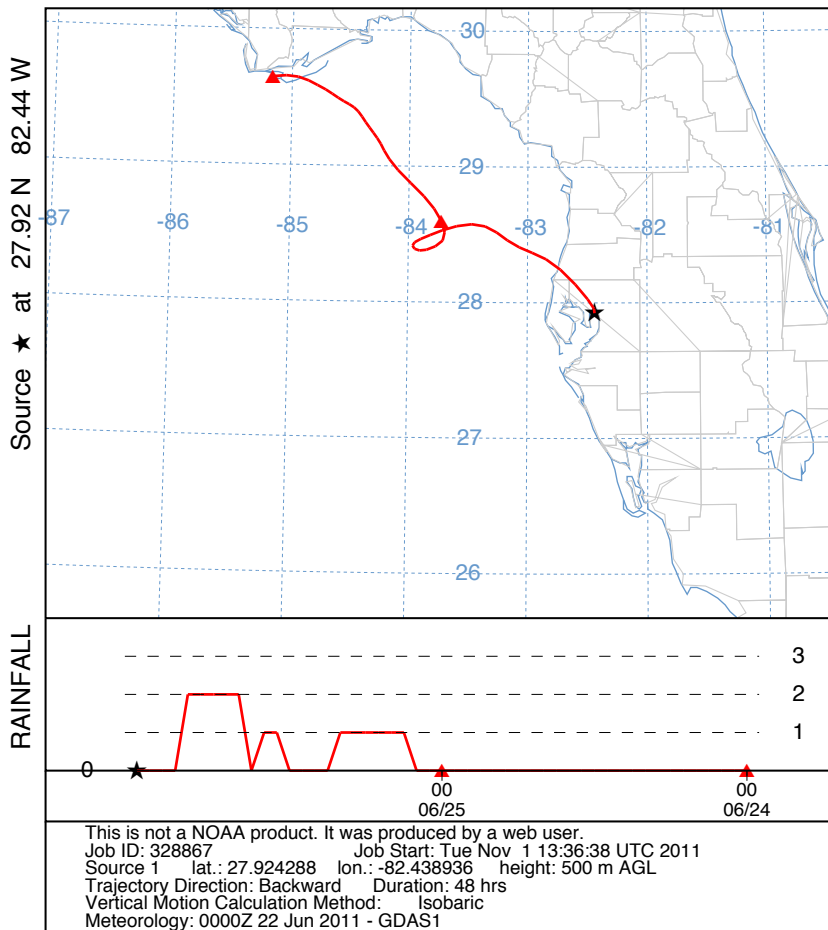


Figure 15-A Wind Trajectory for Sampling Period 6

NOAA HYSPLIT MODEL  
 Backward trajectory ending at 0000 UTC 03 Jul 11  
 GDAS Meteorological Data

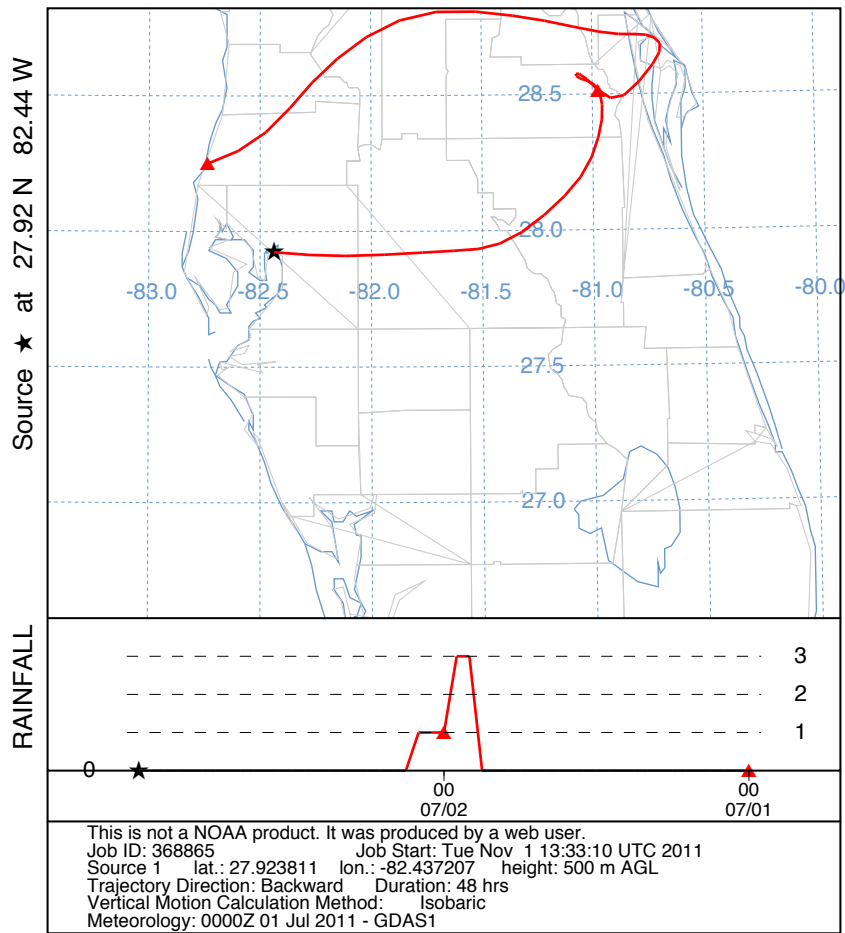


Figure 16-A Wind Trajectory for Sampling Period 7



NOAA HYSPLIT MODEL  
 Backward trajectory ending at 0000 UTC 06 Jul 11  
 GDAS Meteorological Data

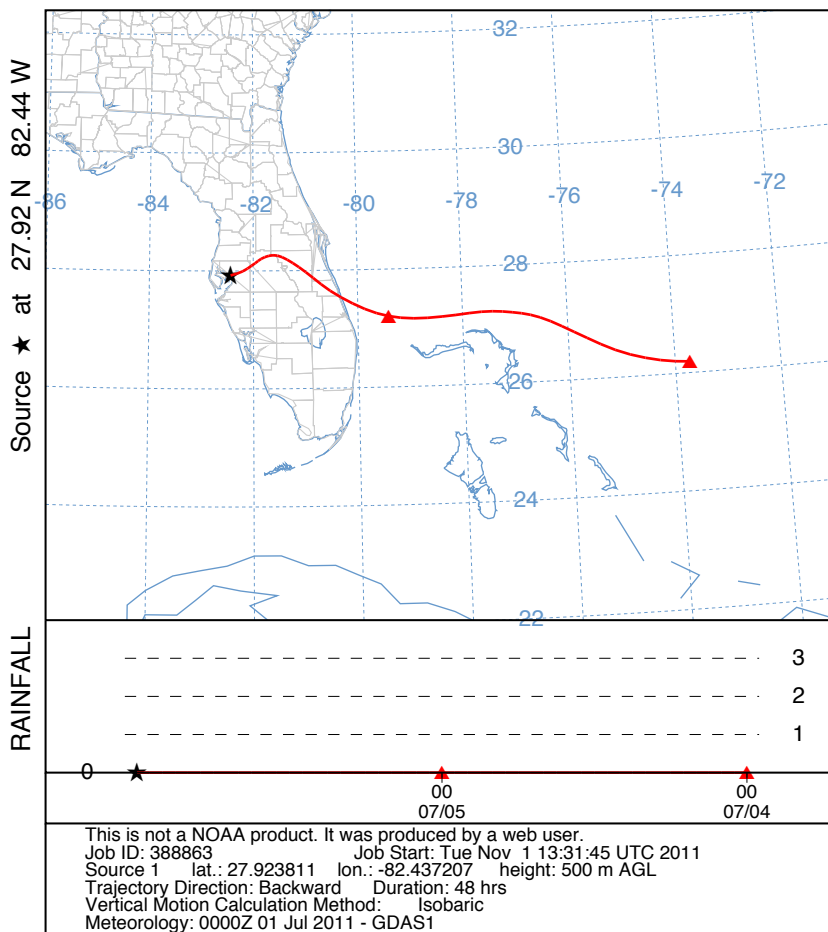


Figure 17-A Wind Trajectory for Sampling Period 8

NOAA HYSPLIT MODEL  
 Backward trajectory ending at 0000 UTC 09 Jul 11  
 GDAS Meteorological Data

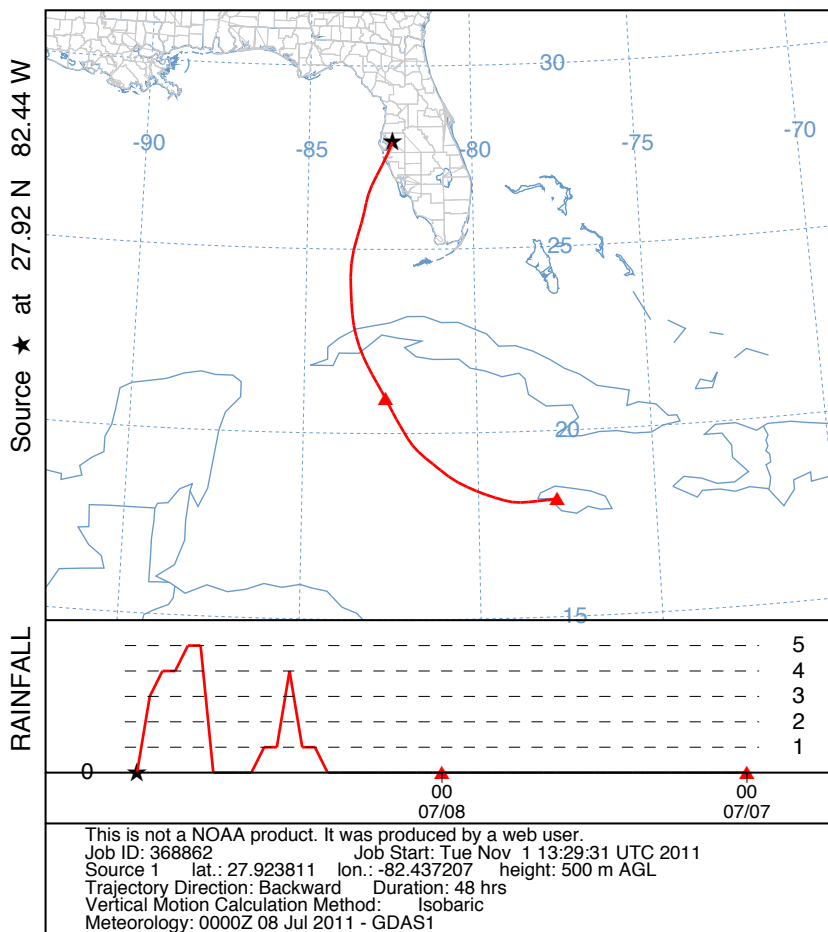


Figure 18-A Wind Trajectory for Sampling Period 9

NOAA HYSPLIT MODEL  
 Backward trajectory ending at 0000 UTC 12 Jul 11  
 GDAS Meteorological Data

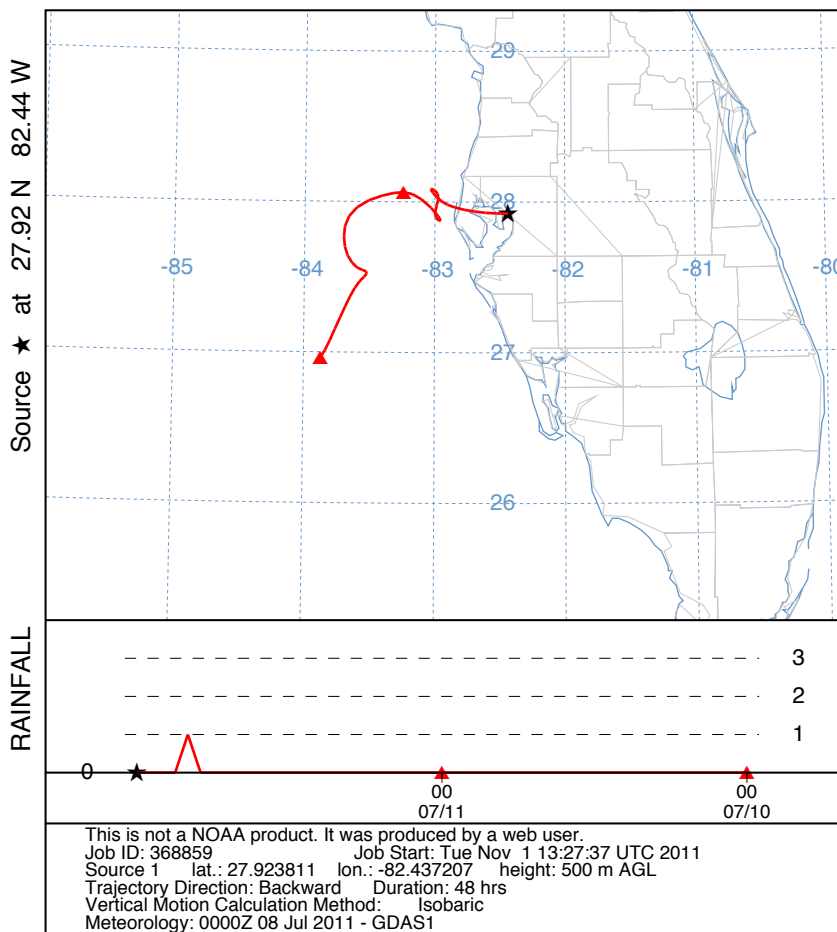


Figure 19-A Wind Trajectory for Sampling Period 10