A STUDY OF ATMOSPHERIC DEPOSITION OF AIR TOXICS TO

THE WATERS OF PUGET SOUND

A Senior Scholars Thesis

by

DANIELLE AGUIRRE

Submitted to the Office of Undergraduate Research
Texas A&M University
in partial fulfillment of the requirements for the designation as

UNDERGRADUATE RESEARCH SCHOLAR

April 2009

Major: Marine Biology

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Approved by:

Research Advisor: Patrick Louchouarn
Associate Dean for Undergraduate Research: Robert C. Webb

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ABSTRACT

Study of Atmospheric Deposition of Air Toxics to the Waters of Puget Sound.
(April 2009)

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Department of Marine Biology
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Research Advisor: Dr. Patrick Louchouarn
Department of Marine Sciences - TAMUG
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Air pollutants can be deposited in many forms such as rain, snow, and gases. Urban centers are major sources of combustion-derived particulate matter, black carbon, and volatile organic carbon to the atmosphere. Expansion of urban centers in the 20th Century, especially in coastal areas, and their concomitant influence on land use, vehicular traffic, and industrial growth have been responsible for major outputs of combustion-derived hydrocarbon to the atmosphere and fallout of such carbon-rich particulate matter over the urban airsheds. This, in turn, has led to local health effects on human populations and a decrease in the quality of regional hydrological cycling. Due to continuous coastal development and increase in population in Puget Sound, Washington, it is vital to determine what the impacts of such growth have had on air and water quality and if greater needs in regulation are needed to curtail emissions. A bi-weekly deposition study of atmospheric particulate matter at seven sites around the Puget Sound (from urban to rural) have been performed for the purpose of developing appropriate regional

and temporal estimates of contaminant fluxes to the surface of Puget Sound. The present study focuses on anhydrosugars, molecular markers of biomass combustion, in atmospheric particles to characterize the sources of combustion-derived materials. These are then compared to combustion-derived condensed hydrocarbon (PAH) concentrations and their signature ratios. Sample series were extracted for anhydrosugars and analyzed via gas chromatography mass spectrometry. All stations showed temporal variability in fluxes of levoglucosan, a major biomass combustion anhydrosugar, over the four months studied (Aug-Nov, 2008), with values ranging close to two orders of magnitude (15-450 uGu/m^2.day). Replicate sampling at different stations during the study period showed a good reproducibility (<15% variability). Regional similarities were observed with major fluxes reported (230-450 µg/m^2.day) in September to mid-October. This peak follows the occurrence of major wildfire events reported in the Pacific Northwest during August-September. A second smaller peak in November suggests the start of winter and domestic heat-derived wood burning. Levoglucosan concentrations are not correlated to pyrogenic PAHs in all but one rural station suggesting a predominant biomass source of combustion at that site. A specific PAH ratio associated with biomass combustion (1,7 DMP/[1,7+2,6 DMP]) was positively correlated to levoglucosan at all stations confirming the usefulness of this ratio for tracing non fossil fuel sources of pyrogenic PAHs in natural environments.

DEDICATION

To my research advisor and friends who have helped make this tough semester so much

better and one to remember.

ACKNOWLEDGMENTS

NOMENCLATURE

Pb	Lead
Cu	Copper
As	Arsenic
CWA	Clean Water Act
PM	Particulate Matter
BC	Black Carbon
GC/MS	Gas Chromatography/Mass Spectrometry
PAHs	Polycyclic Aromatic Hydrocarbons
PB	Padilla Bay (Site 1)
SB	Sequim Bay (Site 2)
WP	West Point (Site 3)
PO	Port Orchard (Site 4)
HC	Hood Canal (Site 5)
TCB	Tacoma Bay (Site 6)
NR	Nisqually River (Site 7)
DMP	Di-Methyl Phenanthrene

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CHAPTER I

INTRODUCTION

Air pollutants can be deposited by rain, snow, gases, particles, and fog droplets. The analysis of the rates and patterns of atmospheric deposition then allows to evaluate ecosystem responses when subjected to various pollutants. Urban centers are major sources of combustion-derived particulate matter (PM), black carbon (BC), and volatile organic carbon to the atmosphere. Expansion of urban centers in the 20th Century, especially in coastal areas, and their concomitant influence on land use, vehicular traffic, and industrial growth have been responsible for major outputs of combustion-derived hydrocarbon to the atmosphere and fallout of such carbon-rich particulate matter over the urban airsheds. This, in turn, has led to environmental impacts, ranging from local health effects on human populations [1, 2], to a decrease in quality of regional hydrological cycling [3] and potential global influence on the earth's radiation budget [3, 4]. Evidence is mounting that atmospheric emissions from combustion sources remain major contributors to air pollution and storm water run-off of urban systems [5-8]. In particular, the continued exposure of humans to ultrafine PM and associated BC constituents (i.e. polycyclic aromatic hydrocarbons, PAH) in major cities leads to adverse health effects including heightened asthma and respiratory endpoints, and increased risks of cardiovascular disease [9, 10].

_____

This thesis follows the style of the journal of *Environmental Science & Technology*.

Due to the continuous coastal development and increase in population in Puget Sound, Washington, it is vital to determine what the impacts of such growth have had on air and water quality and if greater needs in regulation are needed [11].

In the middle of the twentieth century, point sources such as Pb, Cu, and As, were decreasing in quantity due to regulations put in place, such as the Clean Water Act (CWA). Regulations like the CWA, markedly decreased point source input as well as created a positive effect in water quality [11]. As the twentieth century continued into the twenty-first century, marked increases in nonpoint source discharge, such as atmospheric loading of combustion PAHs and metals, was observed and regulation and implementation, such as the CWA, have grown less effective, due to increased coastal development. For instance in Puget Sound's three coastal counties (King, Pierce, and Kitsap), which has grown linearly over the past 50 years [12], resulting from the urbanization of Puget Sound lowlands [11, 13], the recovery trend initially observed with the implementation of regulations will likely slow or even reverse [14, 15]. Nonpoint source input is not considered to be associated with a specific process or responsible party [11]. Only one comprehensive study of atmospheric deposition exists for that region[11], though the data are dated and incomplete, and as such probably not relevant to today's situation.

For example, Pb increases and decreases can be traced throughout history from cores taken in 1982, 1991, and 2005. In the Puget Sound area, signs of Pb anthropogenic accumulation showed around 1890 when metal smelting began [11]. Then anthropogenic

Pb concentrations continued to increase during the early 1900s, with the first peak occurring during World War I, significant industrialization began [11]. Pb concentrations then show a decrease during the Great Depression followed by an increase during WWII, then with a peak in the 1960s, and finally a decrease in trends due to the implementation of environmental regulations [11].

Previous research viewed core samples to show natural recovery rates of inorganic chemicals. Previous research determined that when regulations are put into effect and implemented that they are able to decrease point source inputs effectively. The three coring studies are analyzed via sediment mixing and diagenesis and surface sediment recovery rates can be estimated in a site-specific manner [11]. The PI's group has been charged by the Washington State's Dept. of Ecology to perform a bi-weekly deposition study of atmospheric PM over a year at seven sites around the Puget Sound (from urban to rural) for the purpose of developing effective environmental policies to manage air quality in the region.

Molecular markers of biomass combustion (anhydrosugars) in atmospheric particles were used to characterize the sources of combustion-derived materials and compared to those derived from a suite of combustion sources, including biomass as well as fossil fuels (PAH ratios). The molecular markers were extracted and quantified according to methods established in the advisor's lab [16-19]. The proposed work thus extracted sample series for anhydrosugars and analyzed them using gas chromatography mass

spectrometry (GC/MS)[17-19]. A specific solvent extraction was applied to the samples for the anhydrosugar extraction[17, 19]. This work was performed in collaboration and coordination with a PhD student who is finishing his research on inputs of combustion-derived by-products to urban coastal airsheds/watersheds over the last 100-150 years. Atmospheric deposition samples have been collected at a minimum of seven sites distributed along the shoreline of Puget Sound. In order to capture the dry season (May through October) and the wet season (November through April), sampling begun in the late summer of 2008 and will continue into the spring of 2009. Each site is anticipated to collect 12 integrated samples for a total count of 84 samples. After each collection, samples were shipped to TAMUG for extraction of PAHs, molecular fingerprinting compounds, as well as other organic contaminants.

Therefore, in order to better acknowledge the nonpoint source inputs, this study will try to identify what specific nonpoint sources, regionally, are in the atmosphere and surrounding area to try and assess the natural recovery of the environment and potentially to reduce targeted nonpoint sources. Furthermore, this study will try to determine if there are any seasonal trends observed with specific weather patterns. More specifically, the study will enable the quantification of molecular markers that are specific to biomass combustion to assess the seasonal influence of wildfires and domestic wood combustion on atmospheric quality in the greater Puget Sound area.

CHAPTER II

METHODS AND TECHNIQUES

Atmospheric particles were sampled sampled on glass fiber filters and solid phase extraction disks for periods of 10-15 days at each station (Figures 1 and 2). THe filters and SPE disks were combined and extracted using the method described in Kuo et al (2008)[16] with slight modifications. A Standard Reference Material (Urban Dust SRM 1649a) was purchased from the U.S. National Institute of Standards and Technology (Gaithersburg, MD, USA) used for quality control purposes and to test for analytical consistency during the course of the study.

In summary, samples are extracted via pressurized fluid extraction (PFE) with an accelerated solvent extractor (Dionex ASE 200) at 10.3 MPa and 100°C. Prior to extraction, all cells are spiked either with the surrogate standard d_7-levoglucosan (NIST SRM 2267). The samples were then extracted using a mixture of dichloromethane and methanol (DCM:MeOH: 9:1, v/v) as described in Kuo et al. (2008).

The extracts were evaporated to dryness using a LabConco™ solvent concentrator. Samples were redissolved in 700 μL pyridine. An aliquot (75 μL) was transferred to a glass vial to which 75 μL of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS; Supelco, PA, USA) was added. The sample was derivatized by heating at 80°C for 1 h in a heating block. After

derivatization, 50 µL of triisopropylbenzene (Aldrich, MO, USA; Simpson et al., 2004)

was added to serve as a GC-internal standard to all of the samples.
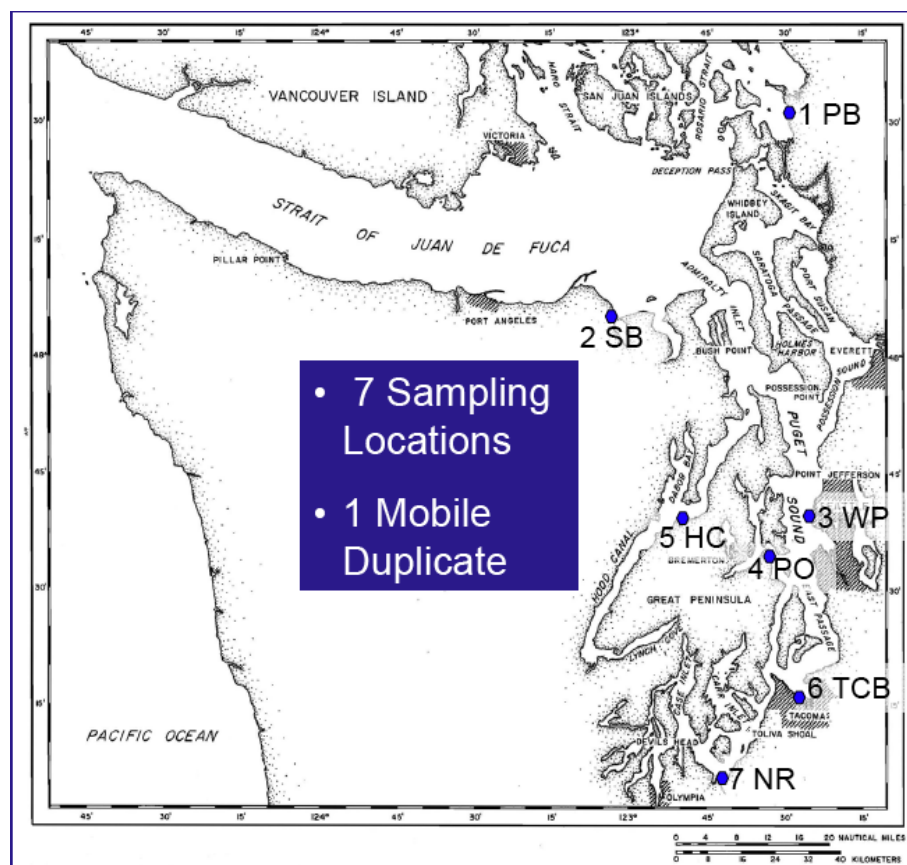
Figure 1. A map of the study area of Puget Sound, Washington with identification of sampling stations: PB (1), Padilla Bay; SB (2), Sequim Bay; WP (3), West Point Seattle; PO (4), Port Orchard; HC (5), Hood Canal; TCB (6), Tacoma Bay; NR (7), Nisqually River.

Figure 2. Sampling set up at a rural site (Padilla Bay) and an urban site (Tacoma).

All analyses are performed using gas chromatography-mass spectrometry (GC/MS) with

a Varian Ion Trap 3800/4000 system fitted with a fused silica column (VF 5MS, 30 m x

0.25 mm i.d.; Varian Inc.). Each sample is injected, under splitless mode, into a straight

glass liner inserted into the GC injection port; He was used as the carrier gas (~ 1.0

mL/min). The GC oven is programmed from 65°C (2 min) to 300°C (5 min) at 6°C/min.

The GC injector and GC/MS interface are both maintained at 270°C. The mass

spectrometer is operated in the electron ionization (EI, 70 eV) and full scan modes. Data

are acquired and processed with the Varian MS Workstation software (version 6.6).

Compound identification is performed using GC retention times and by comparing full

mass spectra with those of commercially available standards (levoglucosan, 99%,

Aldrich, St. Louis, MO, USA). Quantification is performed using relative response

factors obtained from a 5-points calibration curve ($r^2 = 0.999$) with levoglucosan

concentration ranging from 0.1 to 20 ng/uL.

During the extraction procedure the use of methanol reduces the recovery of the more

hydrophobic hydrocarbons, such as PAHs, we tested a sequential extraction procedure in

which we extracted first the hydrophobic hydrocarbons using only dichloromethane

followed by a second extraction, using the dichloromethane:methanol mixture, to extract

the anhydrosugars (levoglucosan). Recovery efficiency was tested in two ways. First,

solid phase extraction (SPE) disks were spiked with known amounts of levoglucosan as

well as surrogate and extracted using the sequential extraction protocol mentioned

above. Secondly, replicates of the NIST Urban Dust SRM were extracted using the same

sequential protocol. In all cases, the second extraction yielded 100% of the levoglucosan

spiked onto the SPE disks or known to be in the NIST Urban Dust SRM.

CHAPTER III

RESULTS

Methods

Solid Phase Extraction disks (SPE) (.15 m²) were spiked with known amounts of standards and extracted sequentially with 100% Dichloromethane for PAHs, followed by DCM:MeOH (9:1) for anhydrosugars. The average recovery for levoglucosan was $105\pm13\%$, which shows that the sequential extraction protocol is appropriate for quantitative recovery of anhydrosugars from SPE disks. Variability for levoglucosan concentration's field replicates were $\leq 20\%$ (with a 6-30% range). Variability for PAHs concentration's field replicates were $\leq 25\%$ (with a 5-36% range). These values indicate that there intra-site variabilities in depositional fluxes were sufficiently low to allow inter-site and inter-sampling event comparisons.

Flux totals for levoglucosan

Seven sites, located in Puget Sound, were sampled from early September to early November (Figure 1.). The anhydrosugar, levoglucosan, in particular was found to be prevalent at all seven sites. Levoglucosan is an unambiguous molecular biomarker for biomass combustion. Total levoglucosan fluxes, observed from early September-early November (Figure 2.) showed substantial fluxes for the second sampling event in September for sites WP, SB, HC, PB, and PO with the highest peak occurring at site WP. In the sampling event for early October and November there were substantial fluxes

at site NR and HC, respectively. The TCB site's levoglucosan flux taken on the second sampling event of September showed to be about average or below average in comparison to the other fluxes sampled on the other dates. In contrast, the TCB site showed a difference in distribution in levoglucosan flux values (Figure 3). The highest flux at this site was observed during the second sampling event of November. Detailed characterization of the yield of levoglucosan to one of its isomers (mannosan) in fuel source emissions can further permit to discriminate between specific inputs of biomass combustion (i.e. softwood *vs*. hardwood, recent biomass *vs*. brown coal) in atmospheric particulate matter (PM). The positive relationship between levoglucosan and mannosan (Figure 4) confirms that both anhydrosugars are indeed derived from the same source. The slope of the relationship (~4.0) further points to softwood as the primary source of biomass being combusted. The levoglucosan fluxes from Figure 3, also show to be independent of precipitation patterns (Figure 5). The highest total fluxes, arranged in order of sampling date, occurred in these sites as follows WP, WP, NR, PB, HC, and WP. The average total flux of the entire study area and sampling events was 123μg/m².d (22-418μg/m².d).

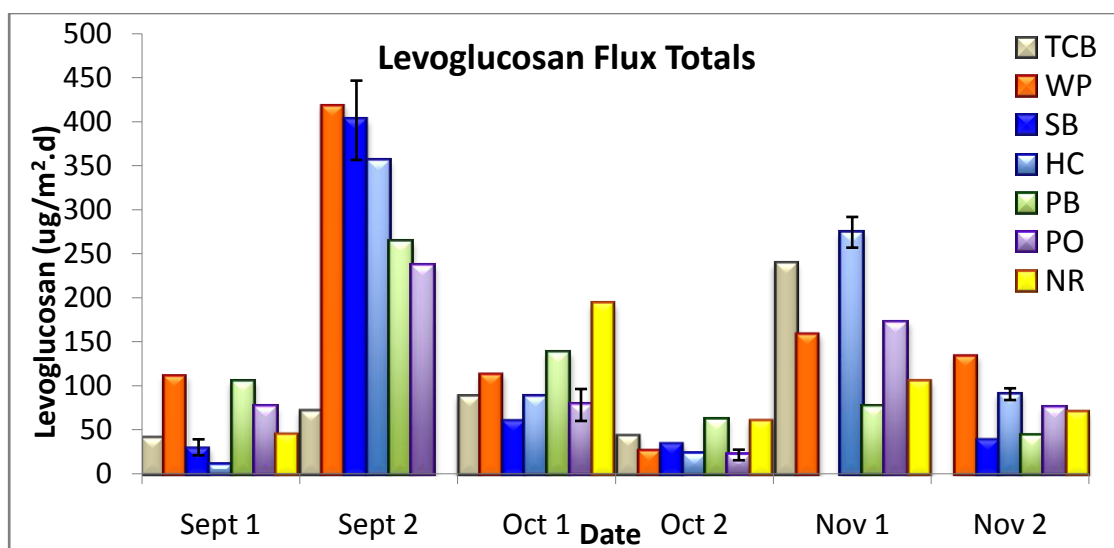**Figure 3.** Levoglucosan flux from the seven sample sites over a period of three months with the average at 123µg/m².d (22-418µg/m².d).
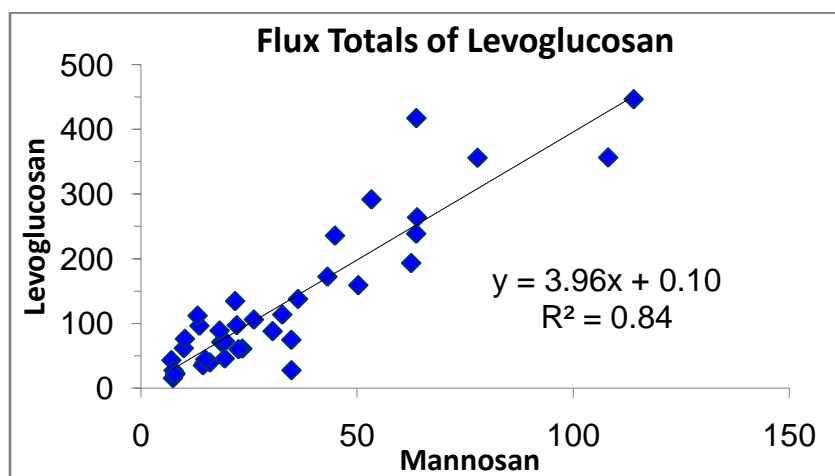
Figure 4. The levoglucosan/mannosan ratio discriminates sources of combustion. It indicates whether it is hardwood or softwood combustion. The relationship of the slope (4±1) indicates softwood combustion is the main source of biomass combustion.
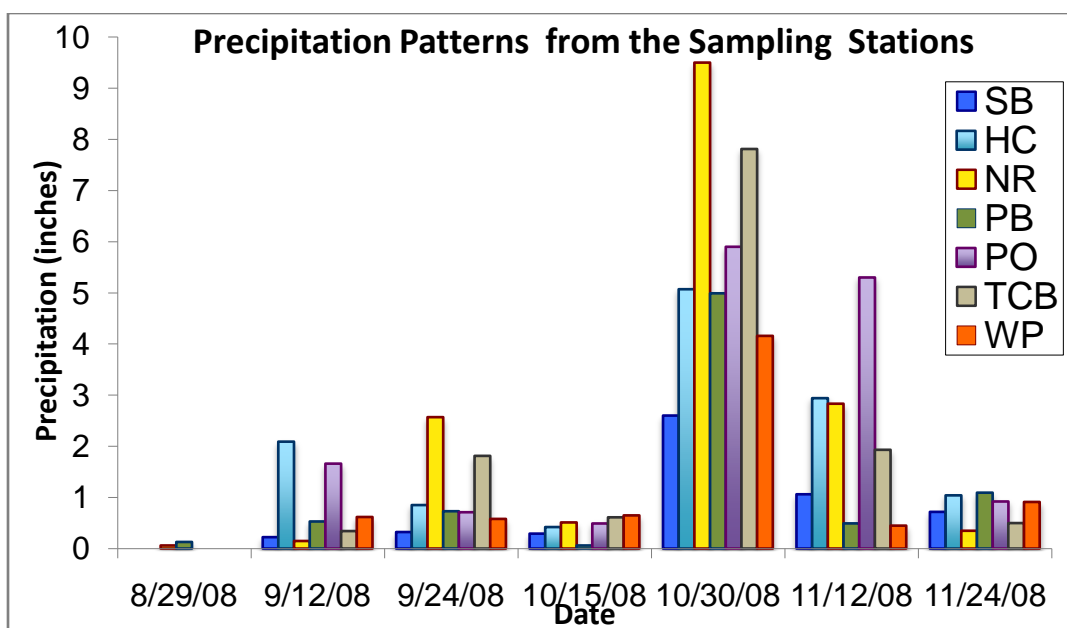
Figure 5. Temporal patterns show to be independent of precipitation patterns.

PAHs flux totals

Polycyclic aromatic hydrocarbons (PAHs) flux totals for the seven sampling stations were observed (Figure 6) from early September – mid November. Three substantial fluxes occurred during the sampling event of early October and November [at] WP and TCB (October) and TCB (November). The highest total fluxes, arranged in order of sampling date, occurred in these stations: TCB, SB, WP, TCB, TCB, and PO with an average flux of 250 ng/m².d (27-1767 ng/m².d). The temporal variation in PAHS fluxes indicated that it is independent of precipitation pattern (Figure 5). An extremely high level of PAHs (~ 40,000 ng/m².d) was observed during the second sampling event of

October at the station, WP (Seattle). Due to the orders magnitude difference in concentrations between this and other events and sites, it is believed this particular site was contaminated probably from a local source input (i.e. an idle diesel truck in close proximity). Hence, we treated this WP event as an outlier and removed it from average calculations. The average flux, 90 ng/m^2 .d (1-275 ng/m^2 .d), was calculated without the "contaminated" event from site WP (October 1st). Three substantial pyrogenic PAHs fluxes (Figure 7) were observed again in the sampling event of early October and November in sites WP and TCB (October) and TCB (November). The highest total fluxes, arranged in order of sampling date, occurred at these sites: TCB, TCB, WP, TCB, TCB, and PO. Figures 8 and 9 show the relative distribution of specific PAHs which help discriminate between input sources of these organic contaminants. Both figures demonstrate that the PAHs in all atmospheric particles are predominantly derived from combustion sources (pyrogenic) rather than oil sources (petrogenic). Additional discriminant ratios can also be used to further characterize the sources of combustion-derived atmospheric particulates. Figures 10-12 show that the source of pyr-PAHs is derived from a mixture of petroleum and biomass combustion sources. Figure 13 and 14, suggests that softwood is the predominant source of biomass fuel being combusted in the region.
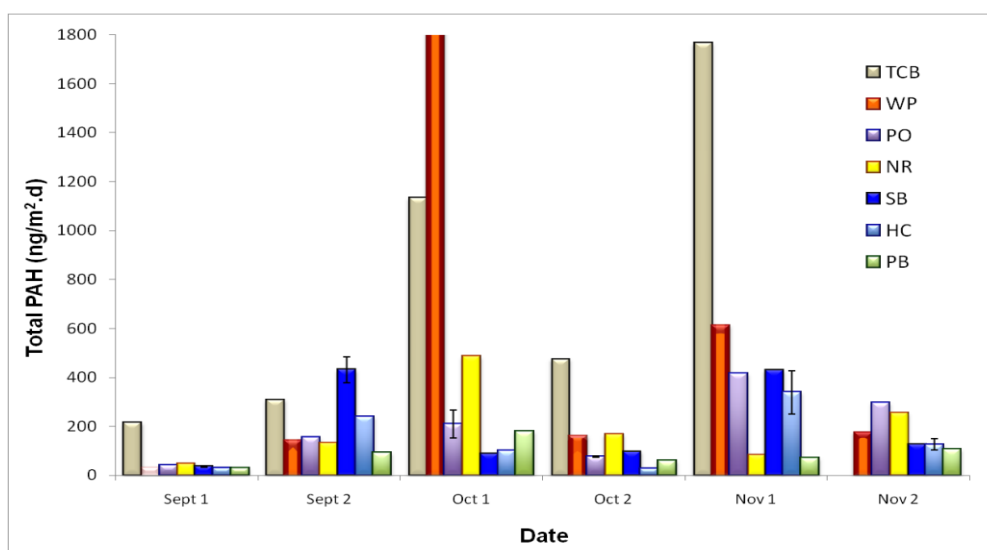
Figure 6. Total PAHs fluxes of the seven sites between September and November. Average total PAHs flux, 250 ng/m².d with a range of (27-1767 ng/m².d). Average fluxes were calculated without the "contaminated" event at WP (Oct 1 event). The error bars represent field replicates (two collectors).
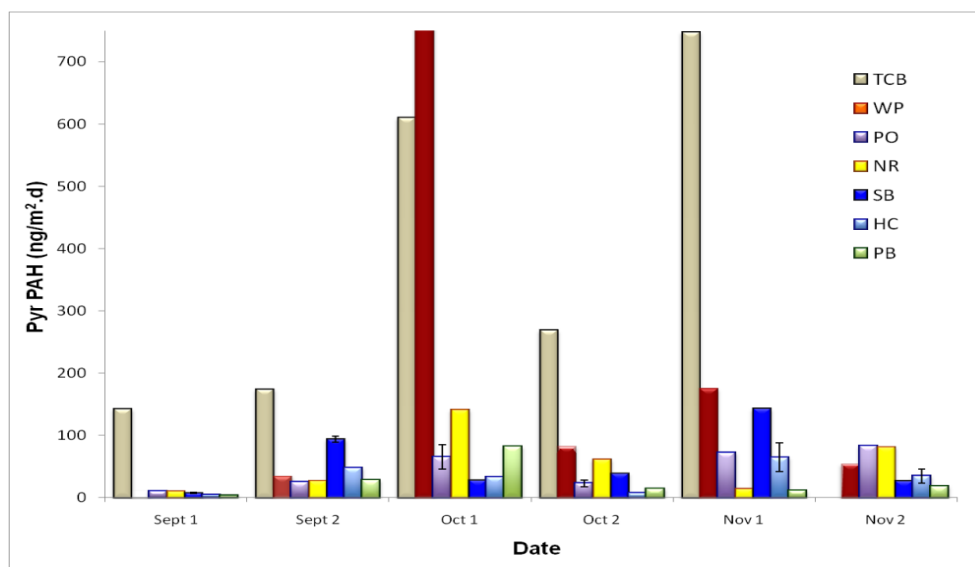
Figure 7. Pyrogenic PAHs fluxes of the seven sites reported for early-September-early November. The average pyrogenic PAHs flux at 90 ng/m².d (1-275 ng/m².d).
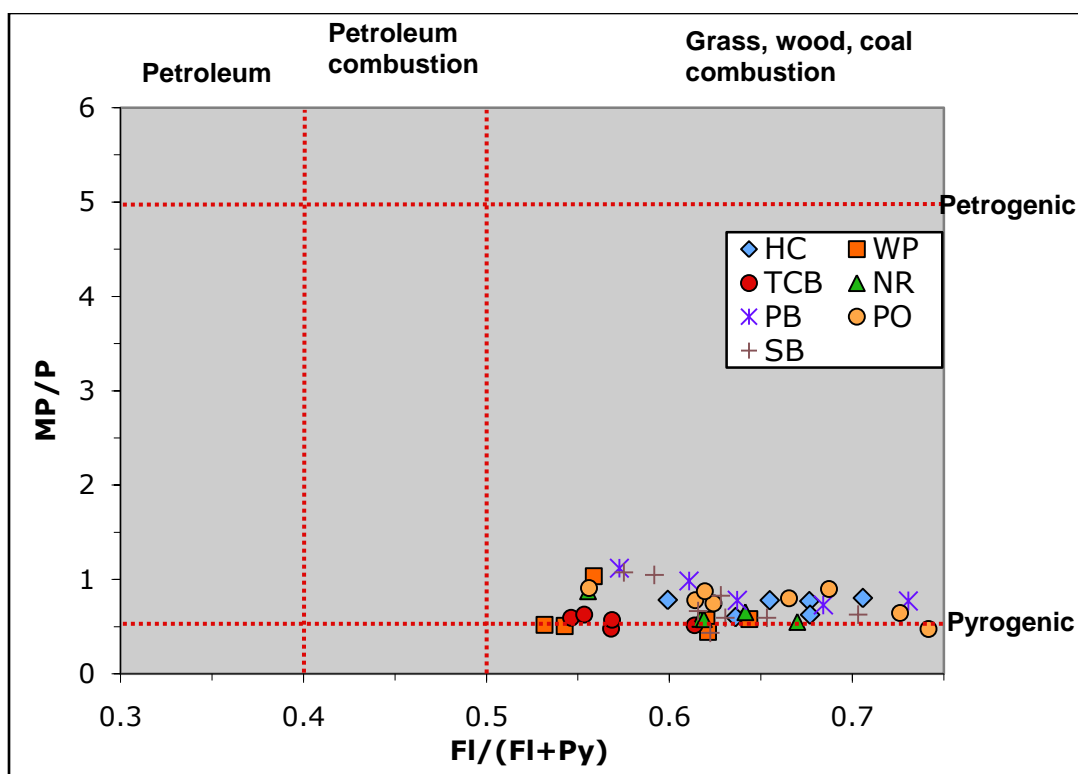
Figure 8. The ratio values of the seven stations discriminated between combustion sources (pyrogenic) and oil sources (petrogenic). All seven stations indicated a mixed source of combustion (pyrogenic) of grass, wood, and coal combustion.
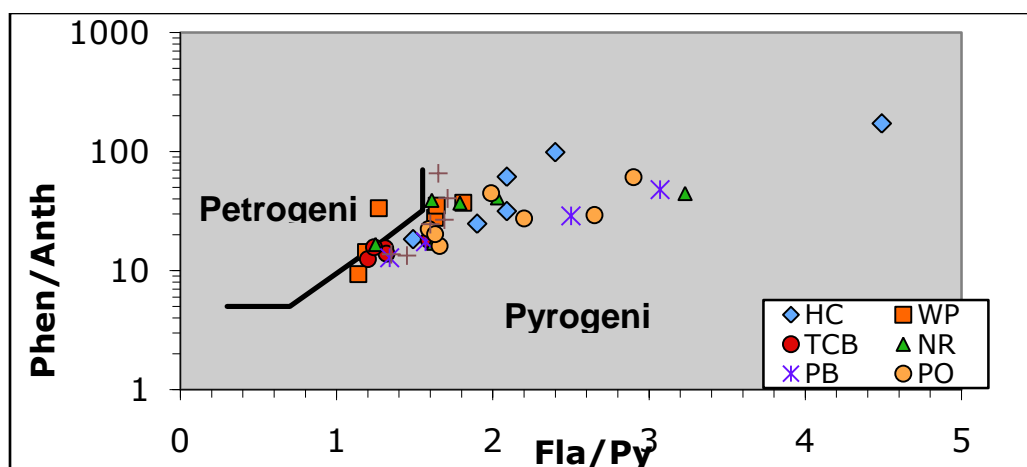
Figure 9. The ratio values show a strong movement towards pyrogenic PM, indicating combustion derived PAHs, especially in sites PO,WP, HC, and NR.
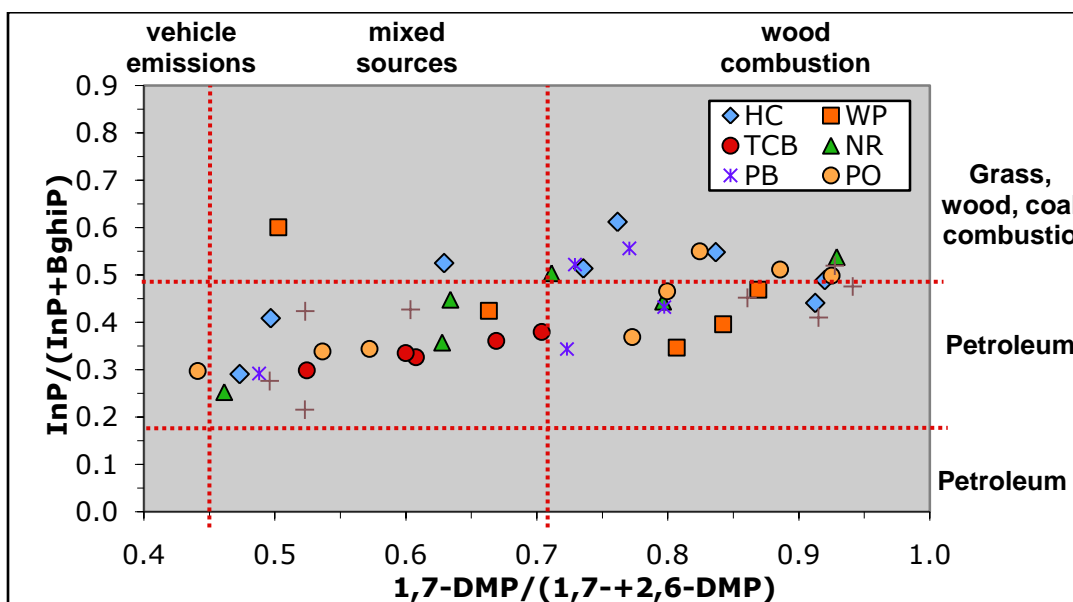
Figure 10. The ratio values indicate there is a mixed source of combustion derived PM. The PAHs are derived from petroleum, grass, wood, and coal combustion, with some sites, such as HC, showing stronger tendencies for grass, wood, and coal combustion.
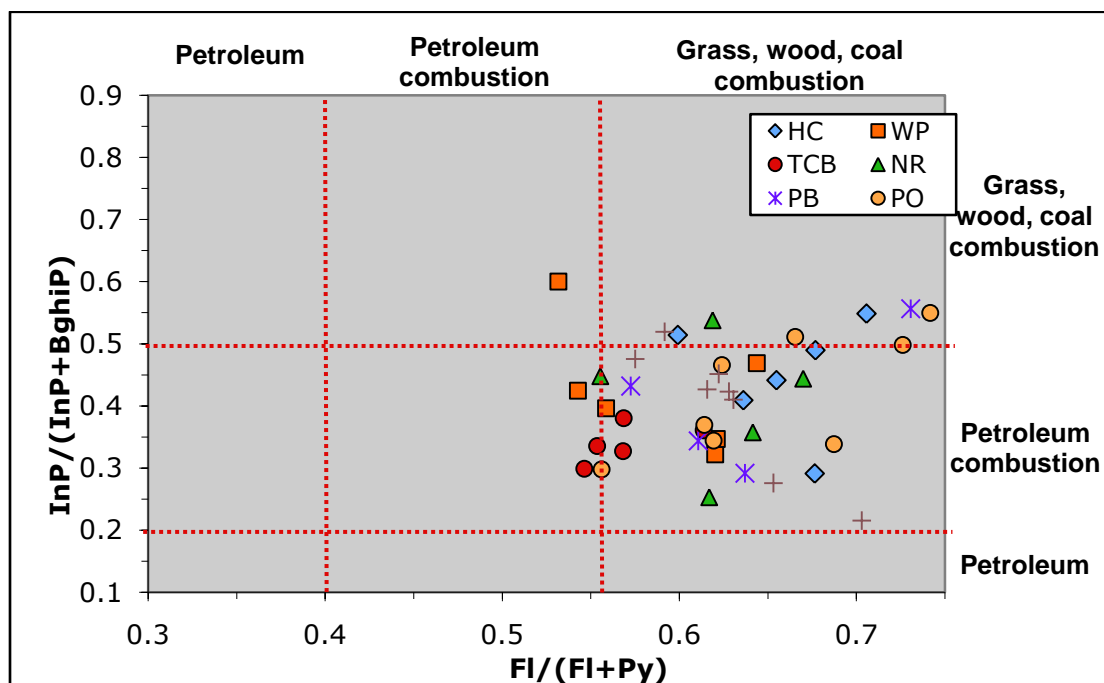
Figure 11. The ratio values indicate that there is a mixed source of combustion of PM for the entire study area composed of petroleum, grass, wood, and coal combustion. Some sites such as HC and PO show greater tendencies for the PM to be more derived from grass, wood, and coal combustion.

1
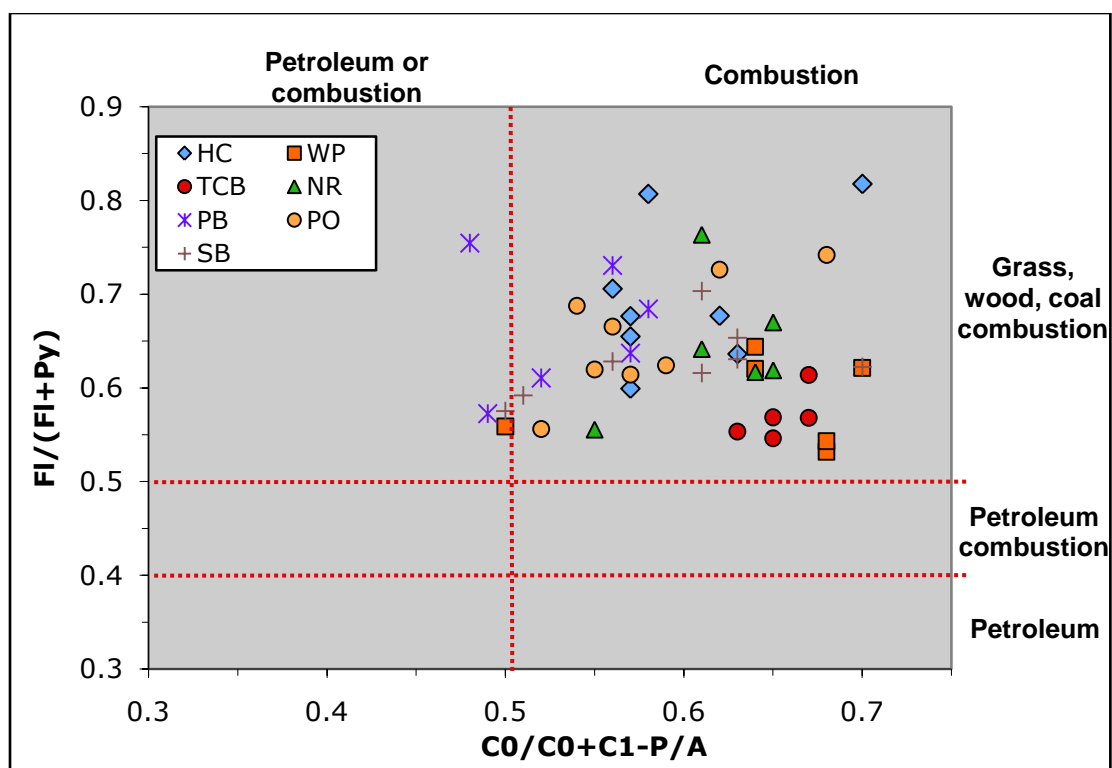
Figure 12. The ratio values indicate specifically that there is a mixture of PM sources, but the main source of combustion for PAHs are derived from grass, wood, and coal combustion.
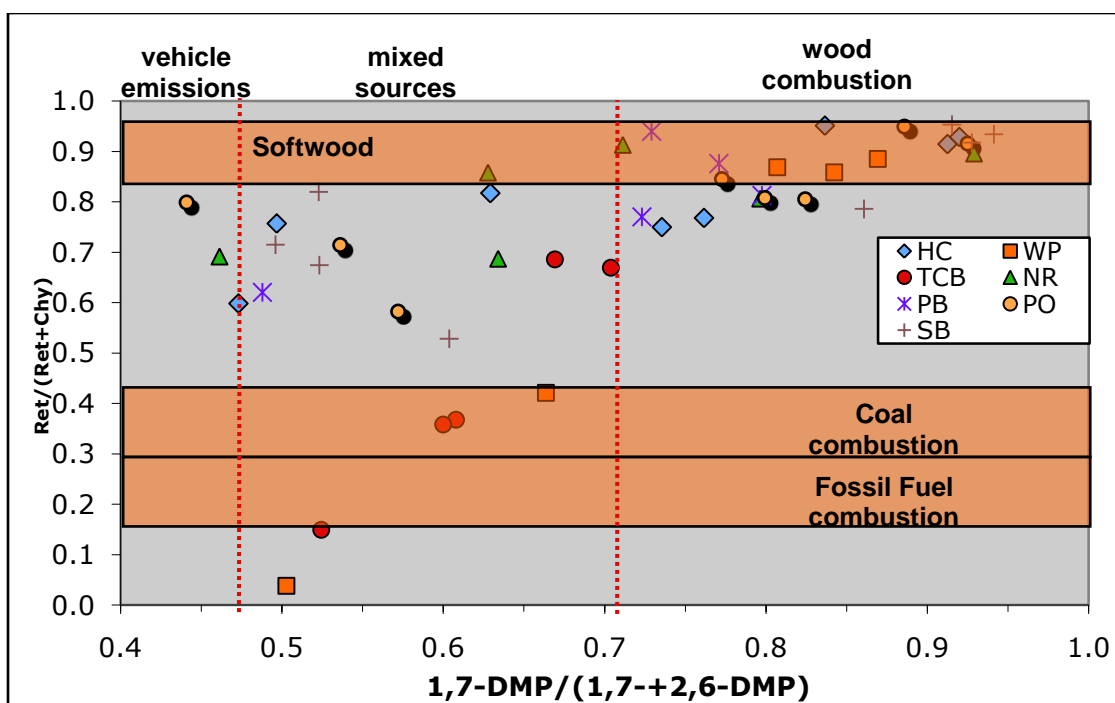
Figure 13. Retene-Chrysene ratio and 1,7-DMP/(1,7-+2,6 DMP) ratio show the
sources of the PM to be mainly derived from softwood combustion. The
exception being TCB, PO, and WP with a mixture of softwood, coal, and
petroleum combustion, but with the main component of the PM source still
softwood derived.
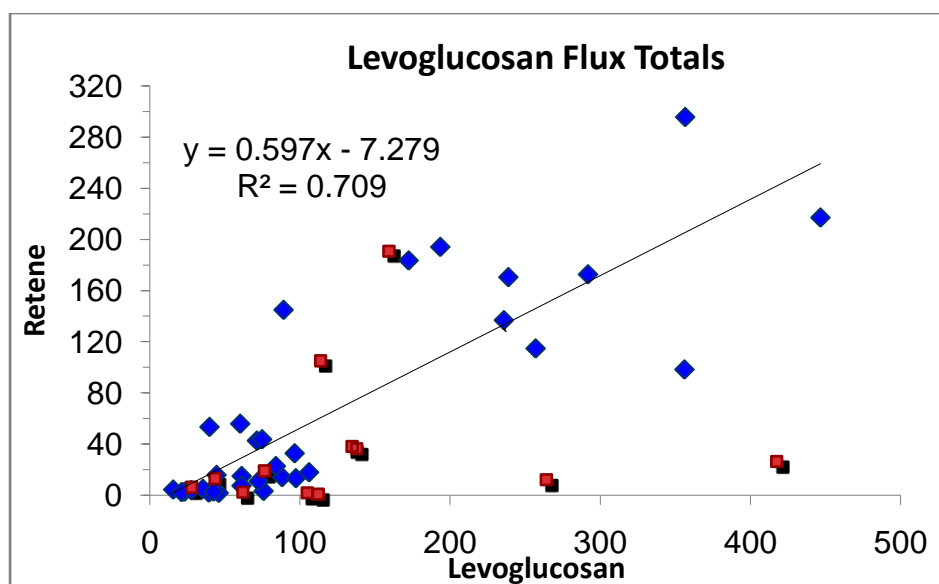
Figure 14. Linear relationship between levoglucosan and the PAH retene (derived from softwood combustion). Two stations, PB and WP, (in red) did not show a correlation between the two markers

Individual site fluxes

North Sound-Padilla Bay (Site 1)

Levoglucosan and PAHs fluxes for Padilla Bay (PB) were recorded from late August-early November (Figure 15, 16). Figure 15, indicates the flux for levoglucosan ranges from 43.3 – 264.1 µg/m².d, where as figure 16. shows the total flux for PAHs ranges from 28.98- 178.47 ng/m².d. The highest levoglucosan flux occurred in mid September, 264. 1 µg/m².d, while the highest PAHs flux occurred in late September, 178.47 ng/m^2.d. Subsequent lower fluxes of levoglucosan occurred before, late August, and after, late September- mid November. The fluxes are listed in order of sampling date, from highest to lowest, 9/12/08, 9/24/08, 8/24/08, 10/28/08, 10/14/08, and 11/12/08 (Figure 15.). The

remaining PAHS fluxes were much lower in comparison to the highest flux total

observed on 9/25/08. The fluxes are listed in order of sampling date, from highest to

lowest, 9/25/08, 11/13/08, 9/12/08, 10/29/08, 10/15/08, and 8/28/08.

<figure>

North Sound - Padilla Bay

Levoglucosan Flux (µg/m².d) vs Date

400
300
200
100
0

8/27/04   9/24/04   10/28/04

Date

</figure>
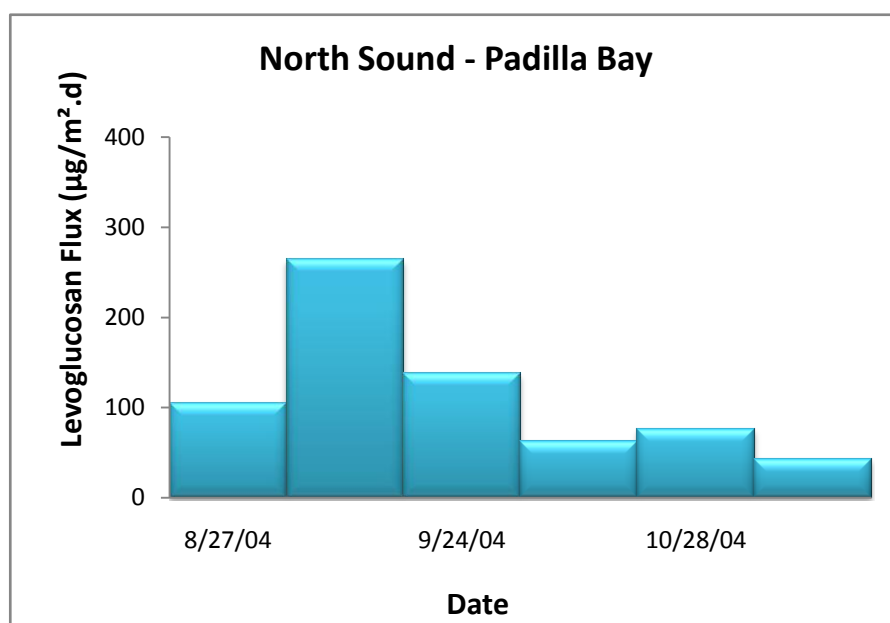
Figure 15. Levoglucosan flux at Padilla Bay, taken monthly, showed to be highest
during early-mid September.
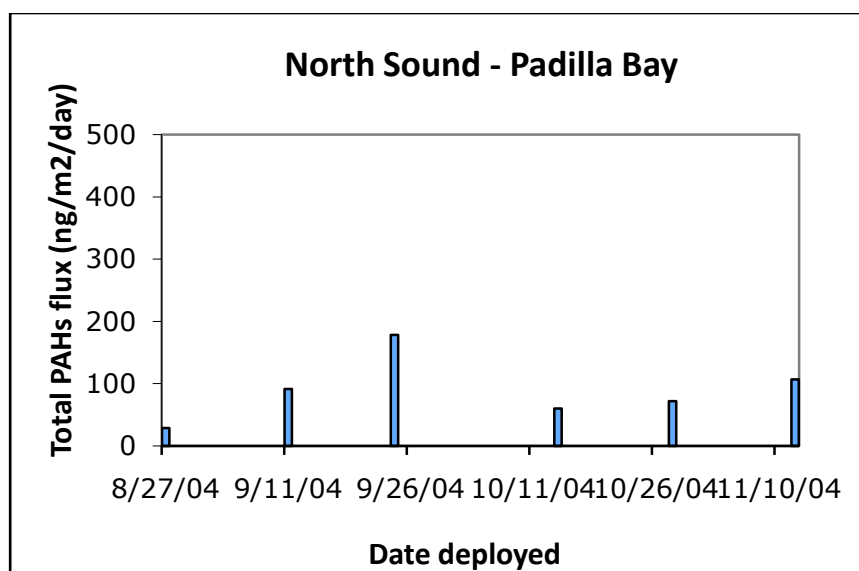
Figure 16. The flux totals of PAHs for Padilla Bay. Highest flux observed occurred on
September 25th, 2008. Not really sure how to make sentence better more
professional.

Sequim Bay (Site 2)

Levoglucosan and PAHs flux totals were recorded for Sequim Bay (SB) from early

September- mid November. The levoglucosan and PAHs flux were both observed to be

highest during mid September. The highest levoglucosan and PAHs flux totals were

401.7μg/m².d and 430.8 ng/m².d (Figure 17,18). The highest PAHs flux was replicated at

the field site. The replication showed a difference in amount of PAHs of $\leq 25\%$,

indicating the reproducibility and value amount at this site is correct. Both the

levoglucosan and PAHs fluxes showed to be highest during mid September, but another

significant PAHs flux occurred in late October, 428.86 ng/m^2.d, unlike the fluxes for

levoglucosan (Figure 18.). The levoglucosan fluxes are listed in order of sampling date, from highest to lowest: 9/18/08, 10/2/08, 11/10/08, 10/15/08, 9/2/08, with the fluxes ranging from 30.2-401.7 µg/m².d (Figure 17.). PAHs flux totals are listed in order of sampling date, from highest to lowest: 9/18/08, 10/30/08, 11/10/08, 10/15/08, 10/2/08, and 9/2/08 (Figure 17.). The PAHs flux totals range from 36.42-430.8 ng/m².d.
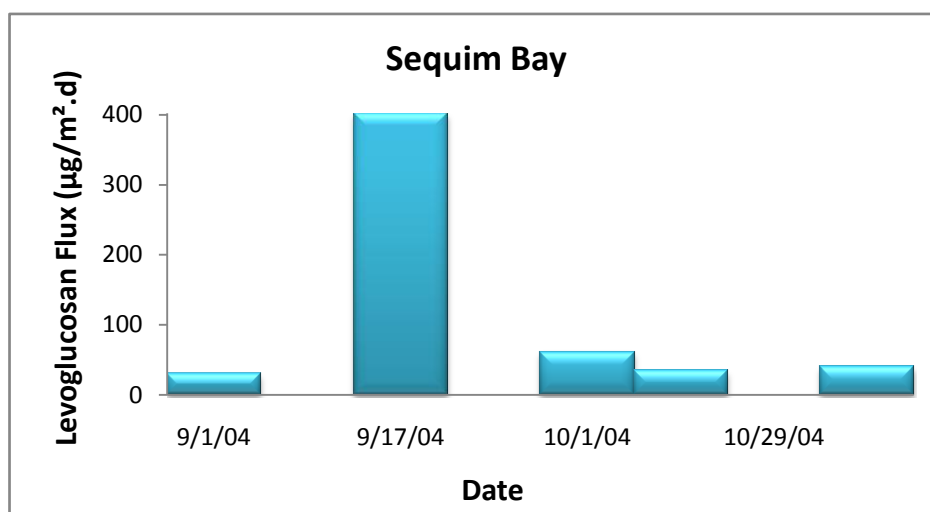
Figure 17. Levoglucosan flux for Sequim bay during September and October with the highest flux observed on the 18th of September, 400 µg/m².d.
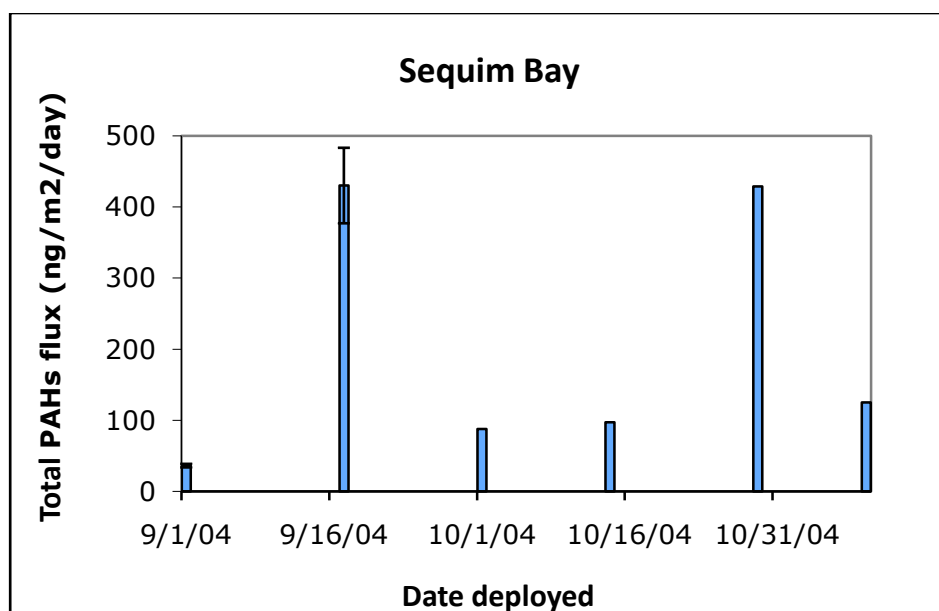
Figure 18. Total PAHs fluxes observed for Sequim Bay. The highest and equal fluxes observed in mid September and early November. A replication for the sampling period of mid September was performed to determine the variability.

Seattle- West Point (Site 3)

Levoglucosan and PAHs fluxes were recorded from late August-Mid November from West Point (WP) (Figure 19, 20). The fluxes for levoglucosan ranged from 27.8- 417.5 µg/m².d, whereas the flux totals for PAHs ranged from 32.25-39751.68 ng/m².d. The highest flux for levoglucosan and PAHs occurred in mid September, 417.5 µg/m².d, and late September, 39751.68 ng/m².d. Levoglucosan fluxes occur prominently in mid September, but then decrease in amount significantly and occur, second highest, again in late October. This trend is repeated in PAHs flux totals, except that the highest flux occurs in late September instead of mid September. Flux totals are listed in order of

sampling date, from highest to lowest for levoglucosan, 9/12/08, 10/29/08, 11/13/08,

9/25/08, 8/28/08, 10/14/08 and for PAHs, 9/25/08, 10/29/08, 11/13/08, 10/14/08,

9/12/08, 8/28/08 (Figures 19, 20).
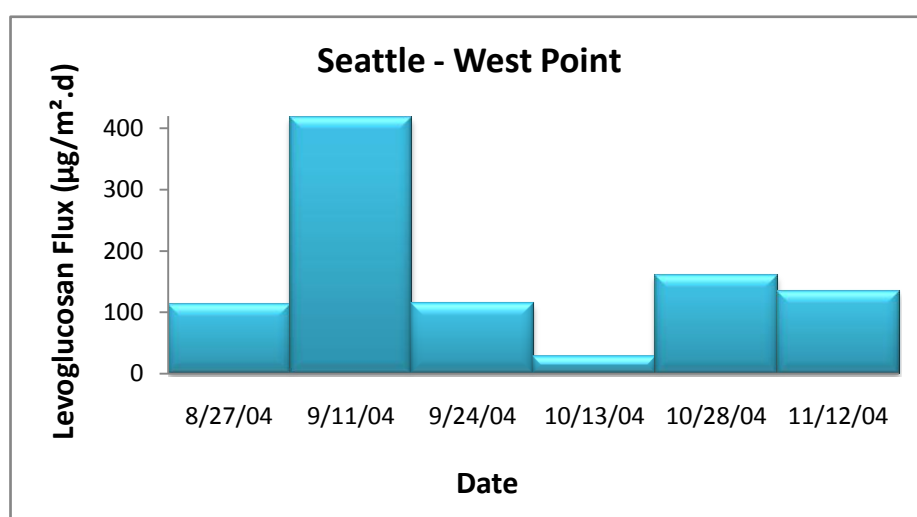
Figure 19. Levoglucosan flux, sampled in West Point, shows the sampling event for
mid- September to have the highest flux, 400 μg/m².d.
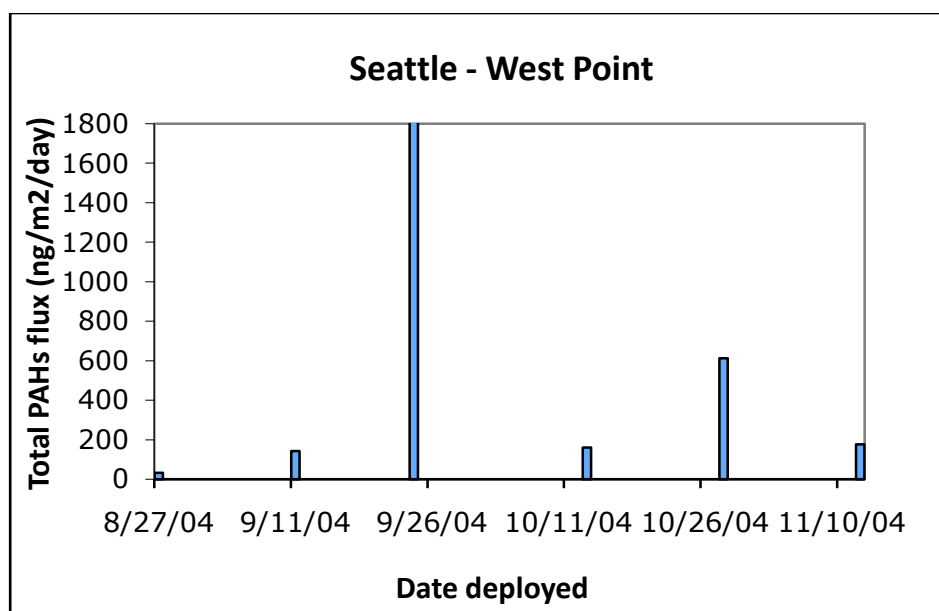
Figure 20. Flux totals of PAHs observed at West Point with the highest flux observed in late September.

Port Orchard-Central Sound (Site 4)

Levoglucosan and PAHs flux totals were recorded for Port Orchard (PO) in early

September-early November. The highest flux for levoglucosan was recorded in mid

September with the second highest flux recorded in late October. The PAHs flux totals

highest and second flux were recorded in late October and early November. The fluxes

range from 21.6-235.8 µg/m².d for levoglucosan and 42.25-416.70 ng/m².d for PAHs

(Figures 21, 22). A second replication recorded on 10/6/08 was performed and

determined that there was a variability $\leq 25\%$.The fluxes for levoglucosan are listed in

order of sampling date from highest to lowest: 9/17/08, 10/29/08, 10/6/08, 9/3/08,

11/7/08, 10/16/08 (Figure 21.). The flux PAHs totals are also listed in order of sampling

date from highest to lowest: 10/29/08, 11/7/08, 10/6/08, 9/17/08, 10/16/08, and 9/3/08

(Figure 22.).
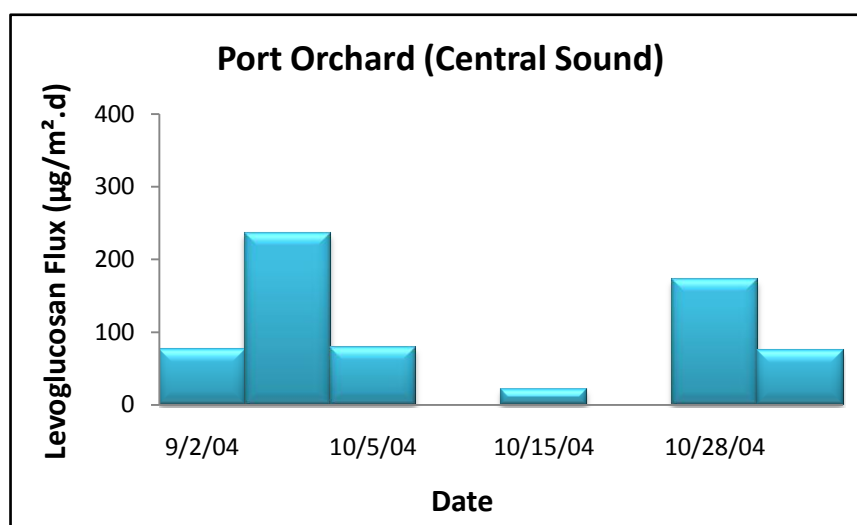
Figure 21. The Levoglucosan flux for Port Orchard showed to be highest during the
month of September with another peak during October, 235.8 µg/m².d and
172.4 µg/m².d.
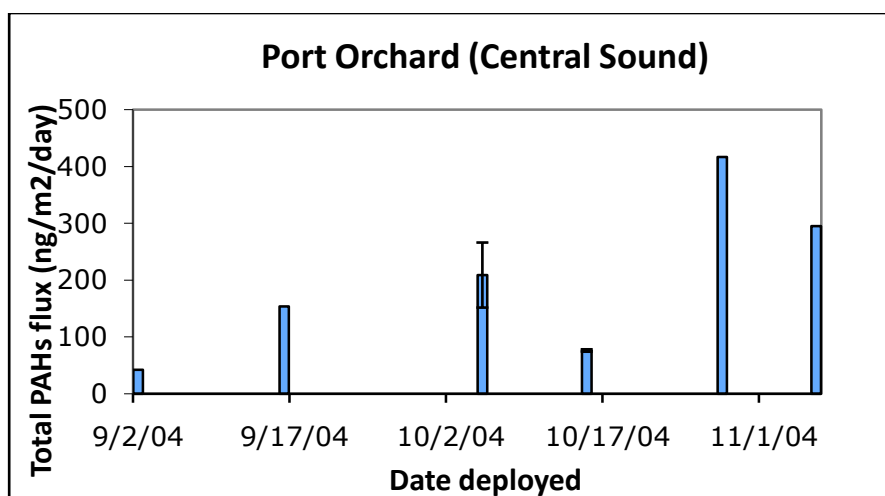
Figure 22. PAHs flux totals for Port Orchard with the highest flux observed in early November. There was a double deployment in early October with an average of less than 25% difference between the flux totals.

Hood Canal (Site 5)

Levoglucosan and PAHs fluxes were recorded for Hood Canal (HC) from late August-early November. The highest and second highest levoglucosan flux occurs in mid September and late October, whereas, PAHs highest and second highest flux occurs in late October and mid September, respectively. Two replications were performed and recorded for the sampling dates of 10/29/08 and 11/8/08. Both replications showed to have an average of ≤ 25% variability. The levoglucosan and PAHs fluxes ranged from 10.97-356.12 µg/m².d and 27.31-339.15 ng/m².d, respectively (Figures 23, 24). The fluxes for levoglucosan are listed in order of sampling date from highest to lowest: 9/17/08, 10/29/08, 11/8/08, 10/6/08, 10/16/08, and 9/3/08, as well as, the fluxes for

PAHs: 10/29/08, 9/17/08, 11/8/08, 10/6/08, 9/3/08, and 10/16/08. For this station, there

was a strong relationship observed between pyr-PAHs and levoglucosan, suggesting a

common biomass combustion source (Figure 25-27).
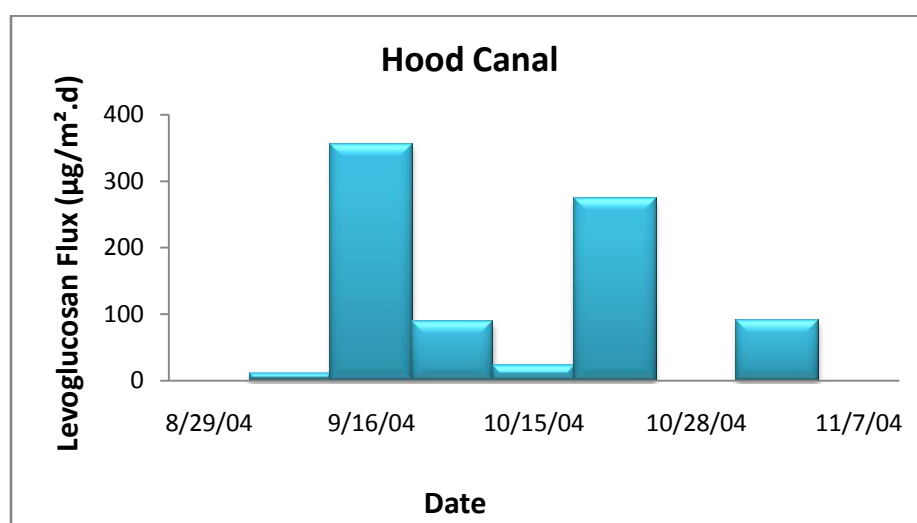
Figure 23. Levoglucosan Flux for Hood Canal showed to be highest during mid
September and with a lesser flux in mid October.
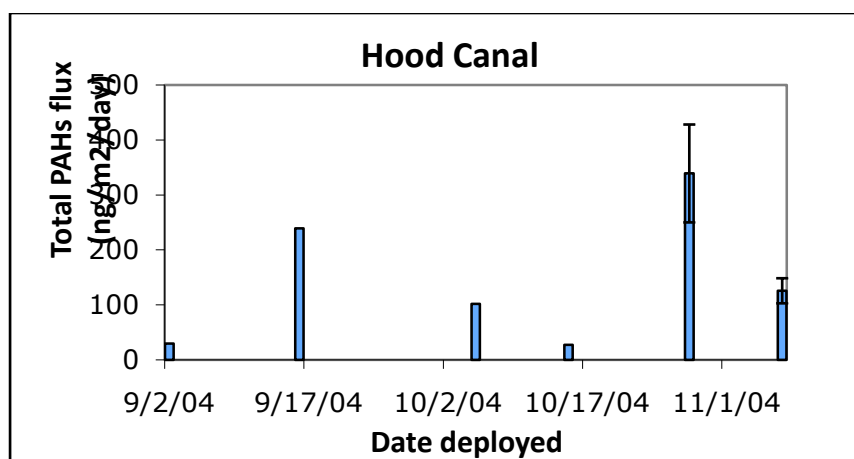
Figure 24. Flux totals for PAHs with the highest flux occurring in Hood Canal in late October–early November.
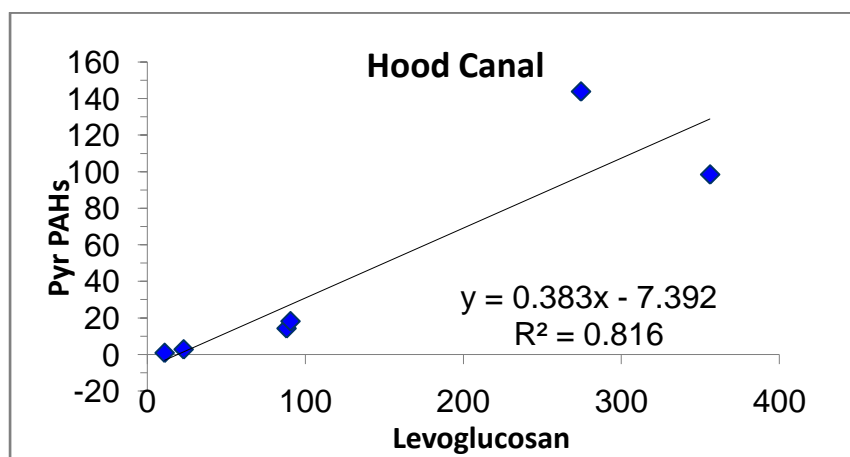
Figure 25. There is a strong correlation between the two as the fluxes of levoglucosan increases along with the pyrogenic PAHs.
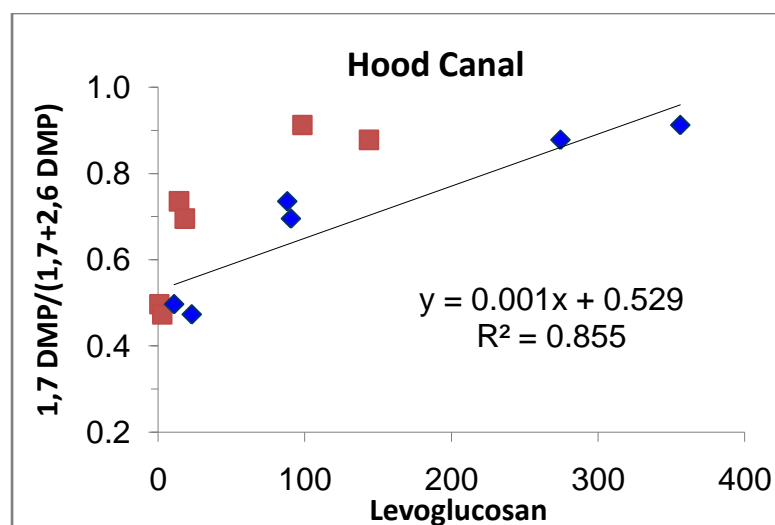
Figure 26. There is a linear increase between the levoglucosan flux and 1,7 DMP/(1,7+2,6 DMP) ratio. As the flux increases the DMP ratio's value increases.
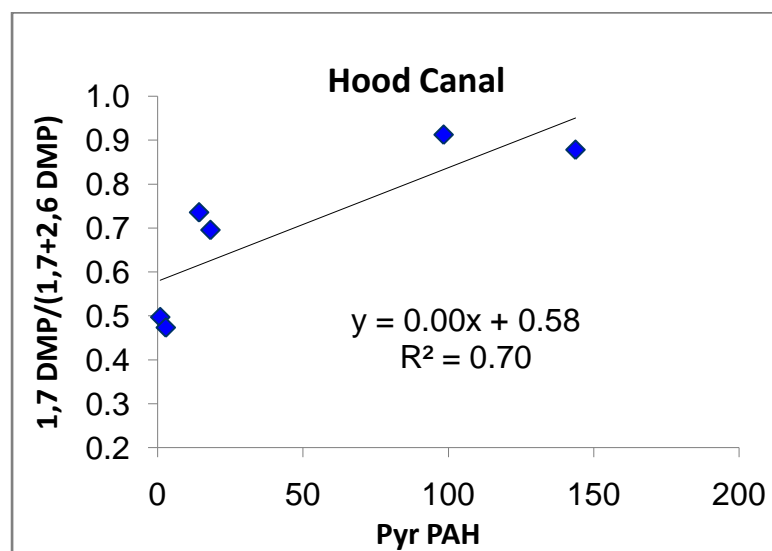
Figure 27. There is a positive linear relationship observed between pyrogenic PAHs and the 1,7 DMP/(1,7+2,6 DMP) ratio, the abundance of diverse di-methyl phenanthrenes permits the discrimination of biomass combustion.

Tacoma Central Bay (Site 6)

Levoglucosan and PAHs fluxes were recorded in Tacoma Central Bay (TCB) from late August-late October. Both of the highest fluxes of levoglucosan and PAHs occurred in the sampling period of late October, with the second highest fluxes occurring in mid September. The levoglucosan fluxes ranges from 42.4-238.8 µg/m².d, where as the PAHs fluxes range from 214.79-1767.06 ng/m².d. (Figures 28, 29). The increase and decreasing trends according to collecting periods for levoglucosan and PAHs are the exact same. For Figures 30-31, there is a correlation between the 1,7 dmp ratio and pyrogenic PAHs particulate matter. The abundance of 1,7-DMP permits the discrimination of biomass combustion. Similar to station (HC), a strong relationship between pyr-PAHs and levoglucosan was observed.
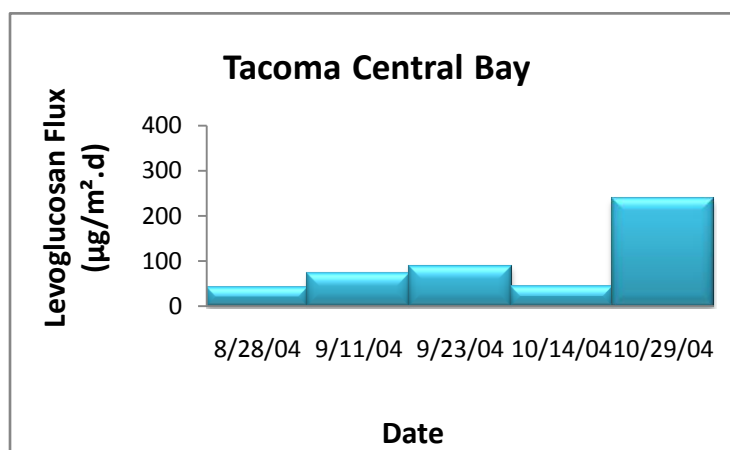
Figure 28. Levoglucosan flux showed to be highest during mid-late October with a smaller peak during the month of September, 250 µg/m².d and (90-100) µg/m².d, respectively.
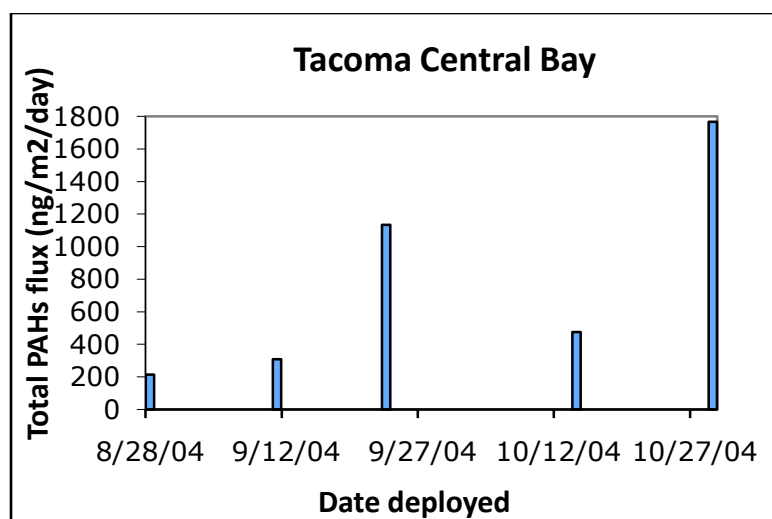
Figure 29. PAHs flux totals from (TCB) showed to have the highest and second highest flux occur in late October and late September, respectively.
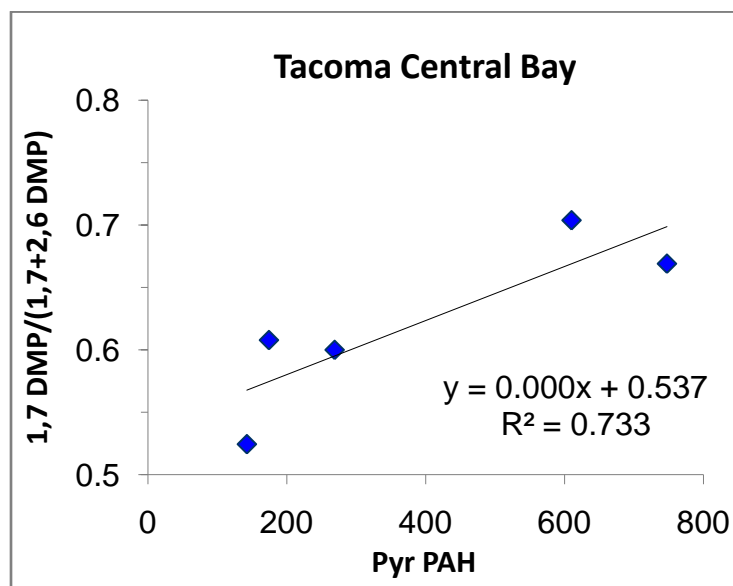
Figure 30. There is an increase in the 1,7 DMP/(1,7+2,6 DMP) ratio's value as the amount of pyrogenic PAHs flux increases.
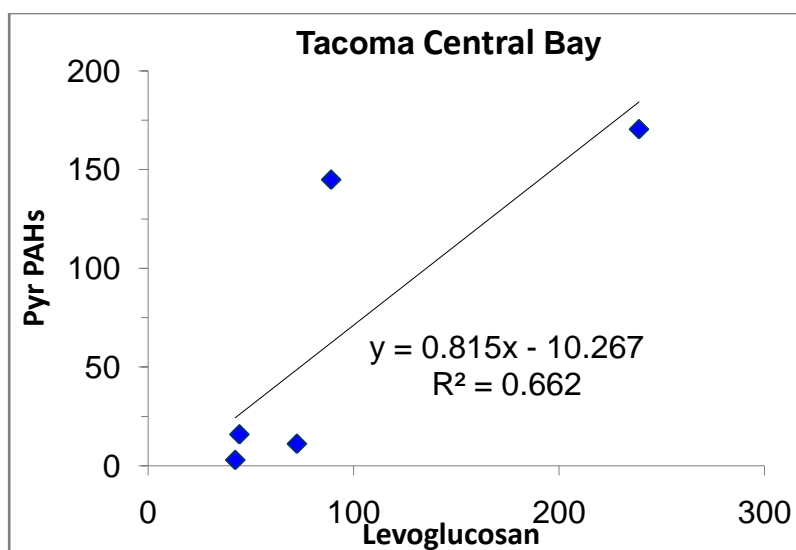
Figure 31. There is a strong correlation between the levoglucosan fluxes and pyrogenic
PAHs for TCB.

Nisqually River- South Sound (Site 7)

Levoglucosan and PAHs fluxes were recorded for Nisqually River for the sampling

period of late August-early November (Figures 32, 33). The highest fluxes for both

levoglucosan and PAHs were observed in mid September. The second highest fluxes for

levoglucosan were observed for the collecting period in late October, where as the

second highest flux for PAHs was early November. The levoglucosan fluxes range from

45.9-193.5 µg/m².d, whereas the PAHs flux range from 47.81-484.65 ng/m².d. The

fluxes for levoglucosan are listed in order according to the collecting period, from

highest to lowest: 9/23/08, 10/29/08, 11/11/08, 10/14/08, and 8/28/08 (Figure 32.). The

flux PAHs totals are listed in order according to the date sampled from highest to lowest:

9/23/08, 11/11/08, 10/14/08, 9/11/08, 10/29/08, and 8/28/08 (Figure 33.).
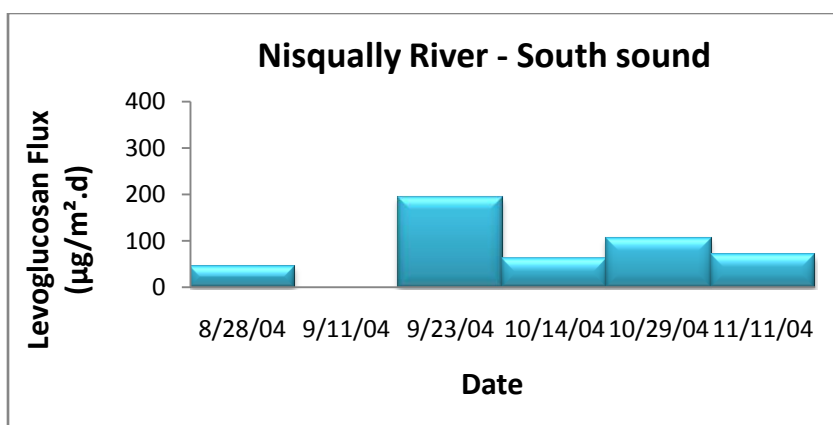
Figure 32. Levoglucosan flux showed to be highest during mid September with lesser
peaks during October and November.
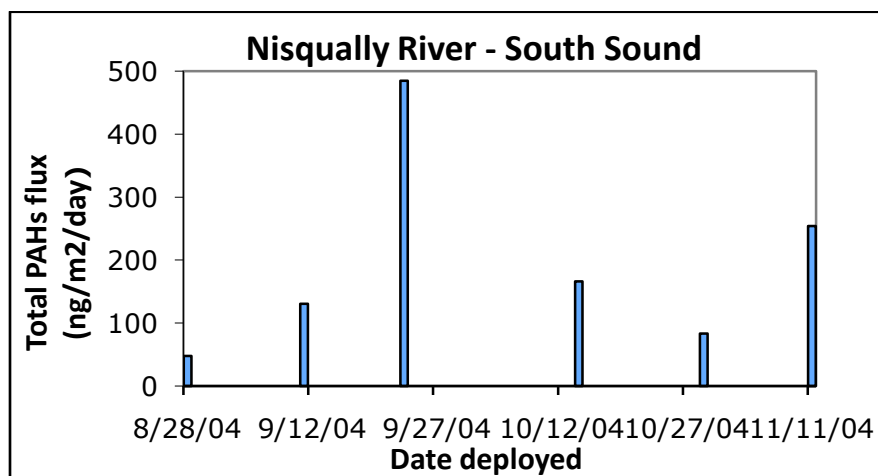
Figure 33. The highest flux total for PAHs observed at the Nisqually River were in late
September and the second highest occurred in mid November.

CHAPTER IV

DISCUSSION AND CONCLUSIONS

Levoglucosan, an anhydrosaccharide, results from the pyrolysis process of thermal degradation of cellulose and hemicelluloses, which usually occurs spontaneously and at temperatures below 300°C [20, 21]. Levoglucosan was determined to be an efficient, unambiguous molecular biomarker of biomass combustion (Figure 3.). Biomass combustion can be considered combustion of wood, grass, leaves (foliar combustion), or coal [21]. Events such as natural wildfires, prescribed fires, domestic wood stoves, agricultural burning, deforestation, and municipal burning of wood for fuel can all are types of biomass combustion and would produce levoglucosan upon combustion, or thermal degradation of cellulose, and producing soot [22]. Varying levels of levoglucosan would be present depending upon the temperature of combustion. The lower the temperature the greater the amount of levoglucosan emitted into the atmosphere. As the temperature increases the amount of levoglucosan present decreases and at temperatures greater than 300°C, levoglucosan emissions become negligible.

Each of the sampled stations showed measurable levels of levoglucosan. The amount of levoglucosan present was determined by the sampling stations characteristics (Figure 1.). For instance, Padilla bay (PB) is within a National Estuarine Research Reserve, but the site is considered to be urban due to surrounding air emissions from oil refineries. Sequim Bay (SB) is at the entrance of the bay and has the lowest rainfall of all of the

sites, indicating that the fluxes wouldn't be as affected by rain as the other sites might

be. West Point (Seattle) is near a waste water treatment plant, but is also influenced by

ships and trains and is considered to be an urban site. The Port Orchard site represents a

moderate density urban area and receives the second largest amount of total annual

rainfall. Hood Canal is located near rural forested land and receives the highest amount

of rainfall in comparison to other Puget Sound stations. Tacoma Central Bay (TCB)

located in downtown Tacoma in the Tacoma Campus of the University of Washington is

considered to be an urban/industrial site. The Nisqually River site is located in a Nature

Center, which is a relatively pristine area.

Total levoglucosan fluxes recorded from early September-mid November (Figures 3, 15-

24, 28-29) showed substantial fluxes occurring in early-mid September for all seven of

the stations, with the WP station showing the greatest amount in the fluxes for

levoglucosan (Figure 3). Other substantial fluxes occur in early October and early

November. The reasonable cause of this occurrence is possibly due to natural wildfires

that had occurred months previously in Oregon and generally in the western U.S.. Until

early September, droughts were occurring throughout the states of Oregon and

Washington. Fluxes, which are a measured total amount per unit time and area, can

drastically change, increasing or decreasing, with natural events such as rainfall.

Therefore, it is thought once the annual precipitation started in early to late fall,

alleviating drought conditions and washing out of suspended PM from the atmosphere,

fluxes of levoglucosan would occur in significant amounts. The cause of the substantial

fluxes early in the fall (September-October) are further thought to be derived from wildfires because the analyzed suspended particulate matter showed to have a strong biomass combustion signature, specifically from softwood, (L/M $\leq$ 5). Indeed, the levoglucosan to mannosan ratio confirms that the specific source of biomass combustion is derived from softwood. The average levoglucosan/mannosan (L/M) ratio from all of the sampling sites and events (4±1) is equivalent to the slope of the relationship between these two markers (Figure 4.) which is also concurrent with previous research in western States showing the predominance of softwood inputs to atmospheric PM during wildfire events [23].

The total PAH fluxes showed to have similar peaks during the same months as levoglucosan. The three peak fluxes occurred in early October and November at stations TCB, WP (October) and TCB (November) (Figure 6,7). In contrast to levoglucosan fluxes (Figure 3), the temporal variation in PAHS fluxes for figures 5 and 6 indicated that it is independent of precipitation pattern (Figure 5.). The pyrogenic PAHs fluxes confirmed that the PM analyzed was derived from a mixed source of petroleum and biomass combustion (Figure 7.) and that there were no indications of the PM being petrogenic (Figure 8,9). Three substantial pyrogenic PAHs fluxes were observed again in early October, stations TCB and WP, and early November, station TCB (Figure 7.). The TCB station, when recorded for all of the sampling period, was found to have the most substantial fluxes, if not the highest fluxes, for each of the sampling periods, with an exception of early September and November (Figure 6,7). Fluxes of pyrogenic PAHs

were found to be more prevalent in TCB, than would have been expected due to TCB's location in downtown Tacoma. The TCB station is also near the Port of Tacoma and is considered to be an urban/industrial site; more influences of vehicular traffic and domestic on goings would occur here. The average flux of pyrogenic PAHs is one order of magnitude (5-10 folds) higher than that of other stations, including WP, which is also an urban site (Figure 7.). Urban sites are observed to show the highest PAH fluxes (Figure 6).

As previously stated, the seven total sites show significant fluxes of levoglucosan occurring in early-mid September (Figures 15-24, 28-29). The levoglucosan present in all of the seven sites was determined to be derived from biomass combustion with varying levels, depending upon each of the sites characteristics. There are two stations, HC and TCB, which showed to have strong correlations between the fluxes of levoglucosan and pyrogenic PAHs (Figures 25, 31). For instance, HC (Hood Canal) in contrast to the station TCB (Tacoma Central Bay), showed to have a substantial flux of levoglucosan during the early-mid September sampling event (Figure. 23, 28). For HC, the PAH fluxes though still prominent were not substantial during the sampling event in early-mid September, like TCB. The peak flux of PAHs for HC was observed in early-mid November. The substantial peaks of fluxes observed in early-mid November of PAHs, for most of the stations, are believed to indicate the start of the winter season (Figures 24, 29). It is believed that during the sampling event of early-mid November, peak PAHs fluxes are observed due to the change in temperature. More wood stoves are

used for heating and depending on the temperature a switch from the wood stoves to central heating in the home would occur, indicating an increase in PAHs fluxes [21, 23]. HC, also like TCB, showed to have a strong correlation between levoglucosan and pyrogenic PAHs fluxes (Figure 25, 31). The TCB station, in contrast to the rest of the stations, did not show a strong flux in levoglucosan during the early-mid September sampling event (Figure 23, 28). Though, the flux of levoglucosan was not as strong as the other stations fluxes, there was still levoglucosan present, but in small amounts. These results were surprising since it was expected that at this station vehicular, gasoline, and petroleum PAH signatures to completely mask the signature of anhydrosugars, specifically levoglucosan, since it is a highly industrialized city with the Port of Tacoma and Interstate 5 in close proximity to the site. The pyrogenic PAH fluxes were found to be more prevalent in TCB during the time period of early-mid September, when the substantial fluxes for levoglucosan were observed at other stations. Since natural wildfires are not prominent in the area, huge fluxes in levoglucosan were not anticipated. In TCB, domestic wood stoves and industrial boilers using wood-derived "hog fuel" are probably the most important source of biomass combustion for this site. It is possible that levoglucosan is not as heavily observed at this site because of the higher efficiency in the combustion process in boilers combusting hog fuel. Efficiency will be higher during the combustion process due to extreme temperatures being used to combust the wood or product in such boilers being used in Tacoma. In contrast, in wildfires combustion may not be as efficient in combusting, which would produce more levoglucosan per mass of biomass combusted than would be seen in machines in TCB.

Therefore, at TCB we still expect levoglucosan to be present due to the combustion derived biomass products, but possibly not as importantly because of the efficiency of combusting at temperatures greater than 300 degrees Celsius observed in machines or boilers in factories.

TCB is an industrial site whereas WP is urban, thus confirming major sources of combustion-derived PM in urban/industrial sites. Other sites in the region also show continued inputs of combustion-derived PM. At these sites however, the major source of combustion seems to be from biomass burning. The relationship between the flux of levoglucosan at all sites, and the PAH ratio 1,7 DMP/ (1,7-DMP + 2,6-DMP) (Figure 34.) further strengthens that interpretation. Indeed, these two biomass indicators are independent of each other not only because they are derived from different organic compound class (anhydrosugars *vs*. condensed aromatic hydrocarbons), but because one is a flux (levoglucosan) and the other is a ratio (1,7 DMP ratio) thus independent of any process that controls fluxes (i.e. precipitation).
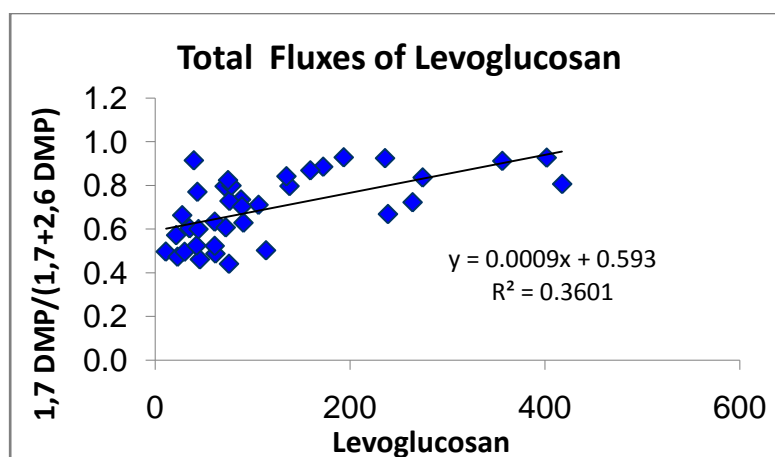
Figure 34. As the flux of Levoglucosan increases the DMP ratio value increases, showing a positive relationship.

The prevalent presence of biomass combustion PM at all sites and sampling events demonstrates a common message presented in many recent studies, namely the significant impact of biomass combustion (whether from anthropogenic processes or natural wildfires) on air quality [22, 24]. The high proportion of softwood combustion should prevail at relatively pristine or rural sites (i.e. HC). That this proportion should still be significant and correlated to major combustion markers (pyr-PAHs) at the most industrial site (TCB: Tacoma) is however, compelling. A possible explanation for the large amounts of biomass derived PM is the use in the area of hog fuel, which is derived from local wood, from pulp and paper factories, and is used in industrial activities as well as a source of fuel for their machines. Another potential explanation is the high proportion of domestic wood stoves in Tacoma proper, yielding high fluxes of biomass

combustion by-products [24]. Although these are potential sources, more research is needed to resolve what the source of biomass combustion in the urban/industrial area of Tacoma.

Conclusions

Levoglucosan is an efficient, unambiguous molecular biomarker of biomass combustion. It was concluded that the predominant source of PM came from softwood combustion. The derived product was observed due to heavy usage of softwoods for pulp and paper as well as a source of hog fuel. Future endeavors for this study would be to further the research by understanding the components of the sources of combustion in order to determine better policies for reducing emissions. As well as, go forward with the current study and determine if annual trends are observed in summer and winter months. Also, a health aspect of the study could occur. A potential for levoglucosan/mannosan ratio could be used as a discriminate to determine the sources of combustion in urine, whether from second hand smoke or biomass burning from wood stoves or natural fires.

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