

**A 300 YEARS RECORD OF POLYCYCLIC AROMATIC
HYDROCARBONS IN LAKE BOTANISK, COPENHAGEN: A
HISTORICAL RECONSTRUCTION OF COMBUSTION PROCESSES IN
A SCANDINAVIAN URBAN LAKE**

An Undergraduate Research Scholars Thesis

by

KENDRA NICOLE DEAN KOPP

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Research Advisor:

Dr. Patrick Louchouart

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ABSTRACT

A 300 Years Record of Polycyclic Aromatic Hydrocarbons in Lake Botanisk, Copenhagen:
Historical Reconstruction of Combustion Processes in a Scandinavian Urban Lake. (May 2013)

Kendra Nicole Dean Kopp
Department of Marine Biology
Texas A&M University at Galveston

Research Advisor: Dr. Patrick Louchouart
Department of Marine Sciences

Lake Botanisk, a small isolated body of water in Copenhagen, Denmark, has remained relatively undisturbed for four centuries, making its sediments an excellent historical archive of past deposition rates of atmospheric contaminants. The concentrations and composition of polycyclic aromatic hydrocarbons (PAHs) measured in a sediment core of Lake Botanisk assisted in reconstructing the historical combustion activities for that region. Source diagnostic ratios indicate that PAHs were primarily derived from pyrogenic rather than petrogenic sources throughout the entire core. Marked increases in PAH concentrations during the pre-industrial era (<1860) trace major geopolitical events of the period (e.g. bombing of Copenhagen by British Navy in late 1700s). A significant rise in combustion-derived PAHs was observed with the start of the industrial revolution, which corresponds to the start of coal imports in Denmark (1860s). The ratio of Retene/(Retene+Chrysene) demonstrates that until ~1860, Copenhagen's combustion sources were dominated by wood burning. The shift to coal consumption starting in 1860 leads to simultaneous increases in pyrogenic PAHs and isomer ratios

(Benzo[b]fluoranthene/Benzo[k]fluoranthene) typical of coal usage. Variations in PAH concentrations and ratios during the 20th Century track the shifts in energy sources (coal to oil, oil to natural gas), major political events such as the oil embargo of 1970s (oil back to coal), as well the implementation of air quality standards and improvements in combustion technologies in recent decades (>1980s). In spite of significant decreases in PAH concentrations since the early-20th century peak, levels still remain 10-fold above preindustrial values in recent decades suggesting an impact from the growth in urban development.

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NOMENCLATURE

Anth	Anthracene
ASE	Accelerated solvent extractor
BaA	Benzo[a]anthracene
BbF	Benzo[b]fluoranthene
BkF	Benzo[k]fluoranthene
BaP	Benzo[a]pyrene
BeP	Benzo[e]pyrene
BghiP	Benzo[g,h,i]perylene
BC	Black carbon
Chrys	Chrysene
DA	Dibenz[a,h]anthracene
Fl	Fluoranthene
GC-MS	Gas chromatography- mass spectrometry
HCl	Hydrochloric acid
IP	Indeno[1,2,3-c,d]pyrene
MePhe	Methylphenanthrene
NIST	National Institute of Standards
PAH	Polycyclic aromatic hydrocarbon
Phe	Phenanthrene
Pyr	Pyrene
Ret	Retene

SIM	Selective ion monitoring
SRM	Standard Reference Material
1,7-DMP	1,7-dimethylphenanthrene
2,6-DMP	2,6-dimethylphenanthrene

CHAPTER I

INTRODUCTION

Black carbon (BC) and polycyclic aromatic hydrocarbons (PAHs) are molecular carcinogenic contaminants that are emitted from the incomplete combustion of organic matter. BC is a general term applied to a spectrum of pyrogenic combustion products ranging from slightly charred biomass, which primarily remains in the solid phase, to soot particles, which are derived via the condensation of volatile organic carbon from the gaseous phase (Figure 1; Masiello, 2004). Unlike BC, PAHs are derived from both petrogenic as well as pyrogenic sources. Petrogenic PAHs are formed via long-term maturation of organic matter, often under pressure, as is seen in petroleum and diagenesis of organic matter in anoxic sediments (Killops and Killops, 2005; Stout and Emsbo-Mattingly, 2008). These PAHs are comprised predominantly of low-molecular weight units (2-4 aromatic rings) and enriched in alkyl groups (Wang et al., 1999; Yunker et al., 2003). In contrast, pyrogenic PAHs contain a much higher proportion of high-molecular weight constituents (4-6 aromatic rings) and are almost completely devoid of alkyl functional groups (Wang et al., 1999; Yunker et al., 2003).

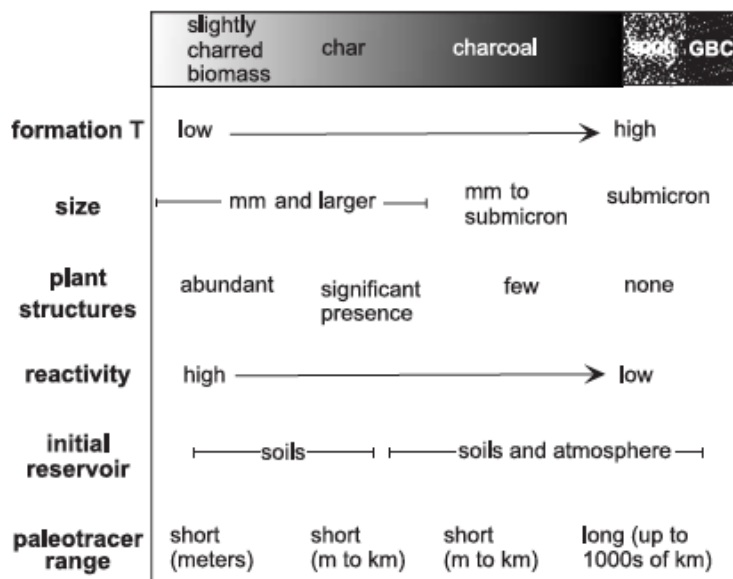


Figure 1. Black carbon combustion continuum as proposed by Masiello, 2004.

Significant increases in concentrations of BC and PAHs in the environment and atmosphere in the last 100-150 years have been primarily associated with the rise of industrial activities and extensive urban development since the onset of the Industrial Revolution (Gustafsson et al., 1997; Lima et al., 2005; Elmquist et al., 2007). Many PAHs have been shown to have both mutagenic as well as carcinogenic effects and are therefore of concern as environmental contaminants (Bostrom et al., 2002). Several studies have monitored the concentrations of PAHs in atmospheric particles as a measure of air quality (Menichini, 1992; Jiang et al., 2005). However, these approaches are limited in time and provide little information on air quality beyond the sampling period. In particular, historical reconstructions in periods prior to regular monitoring need to rely on appropriate environmental archives, in which chronology is well constrained.

In 1978, Laflamme and Hites proposed measuring PAHs in sediment cores to study the historical fluxes of combustion by-products to urban centers vs. rural areas (Lima et al., 2005). Since then, sediment cores have been used to analyze PAH and BC fluxes because they provide relatively undisturbed historical records of atmospheric and/or water quality in specific areas (Lima et al., 2005; Louchouart et al., 2007; Elmquist et al., 2007; Kuo et al., 2011). In light of this, lakes that have existed in urban centers for a hundred years or more provide the opportunity to conduct a time-trend-analysis of the effects of, and changes in, anthropogenic combustion products due to large-scale changes from urbanization and industrialization (Louchouart et al., 2007).

Similar studies have been conducted in areas such as the Hood Canal in Washington (Kuo et al., 2011; Louchouart et al., 2012), Aspöreten, Sweden (Elmquist et al., 2007), as well as Central Lake in New York City (Louchouart et al., 2007). The results from these studies demonstrate that sediment cores are useful for the investigation of anthropogenic inputs of BC and PAHs, and help illustrate regional differences in the environmental impacts of urbanization/industrialization.

The goal of this study is to quantify the presence of PAHs in a sediment core from Lake Botanisk in Copenhagen, Denmark. This lake was originally part of a moat which was constructed in 1647 AD. During the years 1872 - 1874, portions of the moat were filled in; several parts of the moat were left as isolated lakes, including Lake Botanisk (Figure 2). This lake has no entering or exiting streams, therefore any PAHs detected in its sediments can be assumed to be from atmospheric deposition.

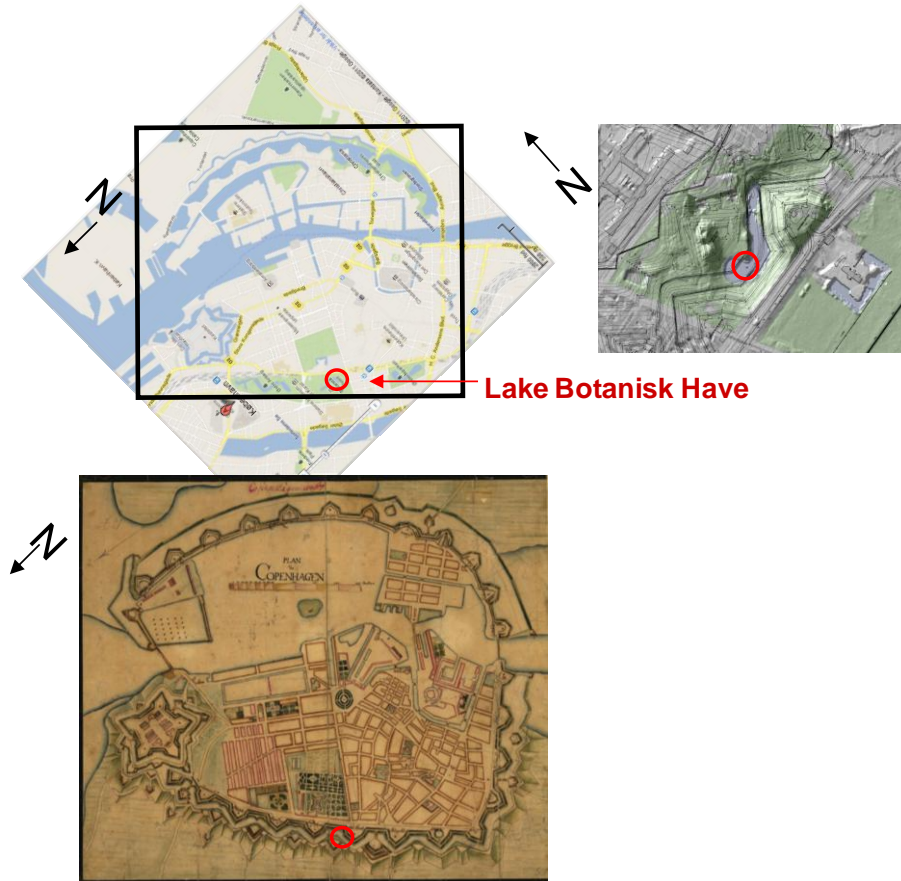


Figure 2. (Bottom left) Lake Botanisk as part of the moat surrounding Copenhagen during the 17th century. (Top) Lake Botanisk as seen today.

It is hypothesized that the ratios of specific PAHs present in sediment layers can be used to trace the source(s) and quantity of combustion changes, respectively, over time. The data collected will then be compared with historical combustion data and other contaminants (e.g. heavy metals), in order to corroborate the accuracy of utilizing PAHs to characterize combustion sources. Furthermore, it is hypothesized that the combustion sources identified by PAH signatures will correspond with historical shifts in combustion technology and fuel sources (e.g. wood vs. coal vs. petroleum).

CHAPTER II

METHODS

Site information and sample collection

Sediment cores were sampled from Lake Botanisk in Copenhagen's Botanical Garden in the winter of 2011. The cores (150 cm long) were collected through the ice and were subsectioned every cm depth in the lab after retrieval. Sediment intervals were then freeze-dried and sent to the lab at Texas A&M University at Galveston. Each sediment sub-sample was then homogenized using a ball mill prior to any analysis. The sediments were dated by the National History Museum of Denmark and the Geological Survey of Denmark and Greenland using ^{210}Pb and ^{137}Cs dating methods.

PAH analysis

Samples were analyzed using the procedure outlined by Kuo et al (2011). Approximately 1 g of homogenized sediment was spiked with PAH surrogate standards (d10-phenanthrene and d12-chrysene) and extracted using a pressurized fluid extraction in an accelerated solvent extractor (Dionex ASE 200) with dichloromethane (DCM) as a solvent. The extraction was carried out at a pressure of 10.3 MPa and a temperature of 100°C. The resulting extracts were treated overnight with pre-cleaned and activated granular Cu to remove the elemental sulfur. Using a RapidVap solvent exchanger (Labconco), the extracts were then concentrated and solvent-exchanged into approximately 2 mL of hexane. Following purification using alumina column chromatography and approximately 35 mL of petroleum ether as an eluent, the extracts were again concentrated and solvent exchanged into 1 mL hexane before being transferred into glass vials for storage.

GC-internal standards (d10-fluorene and d12-benzo[a]pyrene) were then added to the final concentrated extracts prior to gas chromatography mass spectrometry (GC-MS) analysis. One sample of a standard reference material (NIST, SRM 1944) and a blank were also included in each run to test for accuracy of the method.

Separation and quantification of PAHs were 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., 0.25 μ m film thickness; Varian Inc.). Each sample was injected under splitless mode, into a deactivated glass liner inserted into the GC injection port and using Helium as the carrier gas (\sim 1.0 mL min⁻¹). The GC oven was programmed from 60 °C (with a 2 min initial delay) to 150°C using a temperature ramp rate of 15°C/min. This was followed by an increase to 220°C at a rate of 5°C/min and a third increase to 300°C at a rate of 10°C/min. (held 10 min). The GC injector and GC/MS interface were maintained at 300 °C and 280 °C, respectively. The mass spectrometer was operated in the electron ionization mode (EI, 70 eV) using selective ionization mode (SIM). Compound identification was performed using GC retention times and by comparing mass spectra with those of commercially available standards. The following compounds were included in the pyrogenic PAHs: pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluroanthene (BbF), benzo[k]fluorathene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (IP), dibenz[a,h]anthracene (DA), and benzo[g,h,i]perylene (Bghi). All blanks yielded non-detectable levels for the PAHs of interest. The PAHs from the SRMs fell within the \pm 20% variability of the certified values.

CHAPTER III

RESULTS AND DISCUSSION

Several diagnostic ratios distinguishing between pyrogenic PAH and petrogenic or combustion-based inputs have been summarized by various groups (Table 1). The ratio of benzo[a]anthracene to the sum of benzo[a]anthracene and chrysene ($BaA/(BaA+Chry)$) was described by Yunker et al. (2002) as being indicative of pyrogenic sources if it ranges from 0.3 - 0.6 and petrogenic if they are < 0.2 . Ratios of $BaA/(BaA+Chry)$ throughout the core fall consistently within the pyrogenic source ratio.

In addition, the methylphenanthrenes to phenanthrene ratio ($MePhe/Phe$) differentiates combustion-derived PAHs (0.4 - 0.7) from petrogenic sources (> 5) (Elmquist et al., 2007). The low values for this ratio in the Botanisk core (0.8 ± 0.5) confirm combustion as the predominant source of PAHs, with the exception of a slight shift towards petrogenic signatures (1.5 ± 0.2) in the early 1600's to approximately 1780. This may be due in part to diagenetic PAHs accumulating on particulate matter or to a small fraction of alkylated PAHs derived from petrogenic sources (e.g. tar) during that period. Furthermore, the ratio of Fluoranthene to the sum of Fluoranthene and Pyrene ($Flu/(Flu+Pyr)$) holds fairly constant at approximately 0.59 ± 0.02 throughout the depth of the core. A diagnostic ratio of this value indicates that PAH concentrations in the core are dominated primarily by combustion of coal and/or wood (De La Torre-Roche et al., 2009). The combination of these ratios thus provides independent confirmation that combustion inputs have been a major source of PAHs to these sediments over

the last 400 years of history (Figure 3). Specific ratios (see discussion below) suggest that shifts in fuels, combustion activities, and technology have led to different levels of input to the system.

Table 1. Diagnostic ratios and reported values for various processes.

Ratio	Value Range	Source	Reference
Σ LMW / Σ HMW	< 1	Pyrogenic	Zhang et al., 2008
	> 1	Petrogenic	
BaA / (BaA+Chry)	0.3 - 0.6	Pyrogenic	Yunker et al., 2002
	0.0 - 0.2	Petrogenic	
MePhe / Phen	0.0 - 1.0	Pyrogenic	Elmquist et al., 2007
	5.0 - 6.0	Petrogenic	
BbF / BkF		Coal combustion	Louchouart et al., (2012)
Flu / (Flu+Pyr)	< 0.4	Petrogenic	De La Torre-Roche et al., 2009
	0.4 - 0.5	Oil Combustion	
	> 0.5	Coal and Wood combustion	
Ret / (Ret+Chry)	~ 1	Wood Burning	Yan et al., 2005
1,7-DMP / (1,7-DMP / 2,6-DMP)	0.7 - 0.9	Wood Burning	Yunker et al., 2002
	~0.45 - 0.7	Coal/ Lignite	
	<0.45	Vehicle Emissions	

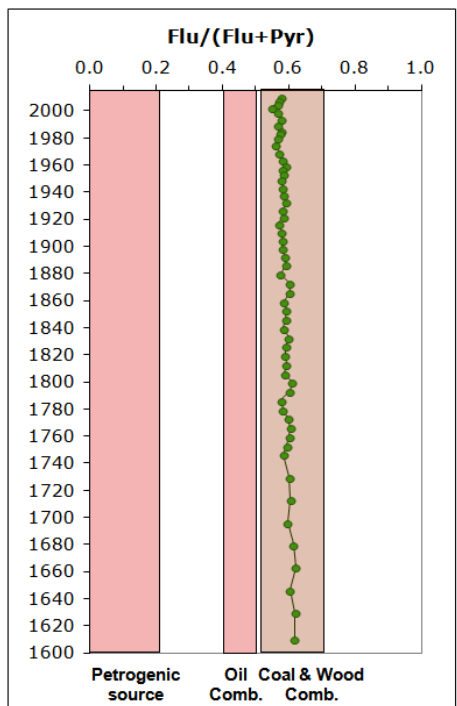
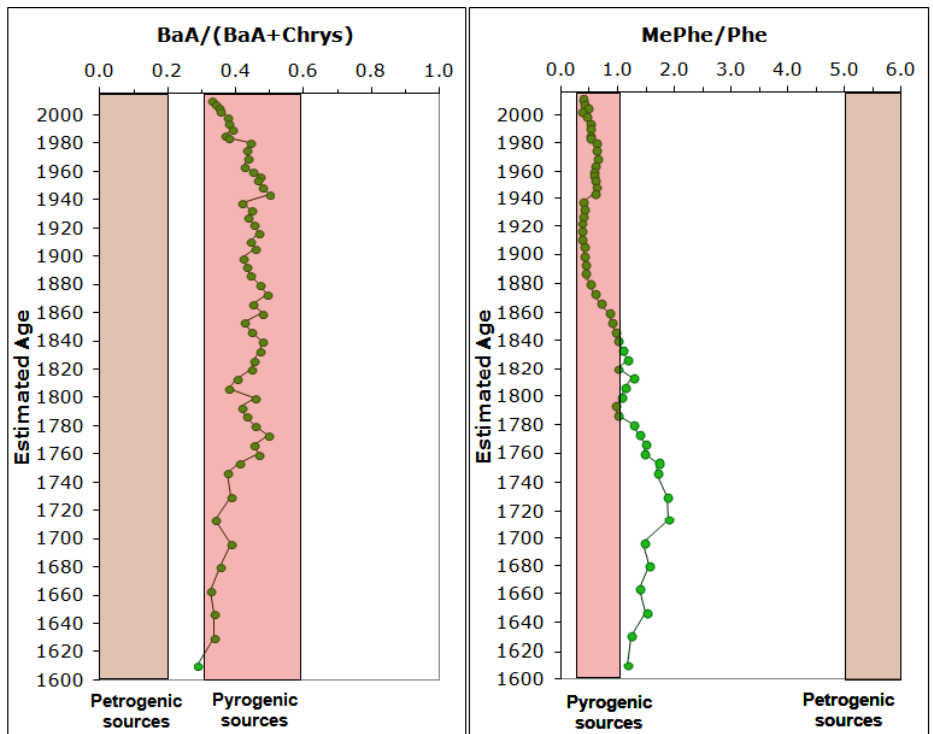


Figure 3. Diagnostic ratios for BaA/(BaA+Chrys), MePhe/(MePhe+Phe), and Flu/(Flu+Pyr) with sources for each.

1600 - 1860: Wood and war

Two diagnostic ratios were used for the discrimination of softwood combustion inputs from other pyrogenic sources throughout the Botanisk core. Because retene is found as a product in the smoke from wood combustion (Ramdahl, 1983) and is formed during biogenic processes (Boonyatumanond et al., 2006), Yan et al proposed (2005) that the ratio of retene to the sum of retene and chrysene ($\text{Ret}/(\text{Ret}+\text{Chry})$) is indicative of wood combustion if it has a value of ranging from 0.9 - 1.0. This is contrasted to ratios ranging from 0.17 - 0.45, which indicate oil or coal combustion. Similarly the ratio of 1,7-dimethylphenanthrene to the sum of 1,7-dimethylphenanthrene and 2,6-dimethylphenanthrene ($\text{1,7-DMP}/(\text{1,7-DMP}+\text{2,6-DMP})$) were described by Yunker et al. (2002) as a means to delineate PAHs derived from wood combustion (ranging ~0.8 - 1.0) from coal/lignite combustion (ranging ~0.45 - 0.7), and vehicular emissions (<0.45; Table 1). The combination of these ratios shows that from 1600 to the middle of the 19th century, Copenhagen was largely dominated by softwood combustion (Figure 4). The ratio of $\text{1,7-DMP}/(\text{1,7-DMP}+\text{2,6-DMP})$ falls within the range 0.7-1.0 throughout the bottom half of the core and remains there until approximately 1860, where it rapidly drops towards the range of coal combustion. This is paralleled quite closely by the $\text{Ret}/(\text{Ret}+\text{Chry})$ ratio despite its greater variability. The marked dip in this latter ratio around the end of the 18th Century is synchronous with a significant increase in PAH concentrations (Figure 4) and points to a shift in combustion inputs during this period (see discussion below).

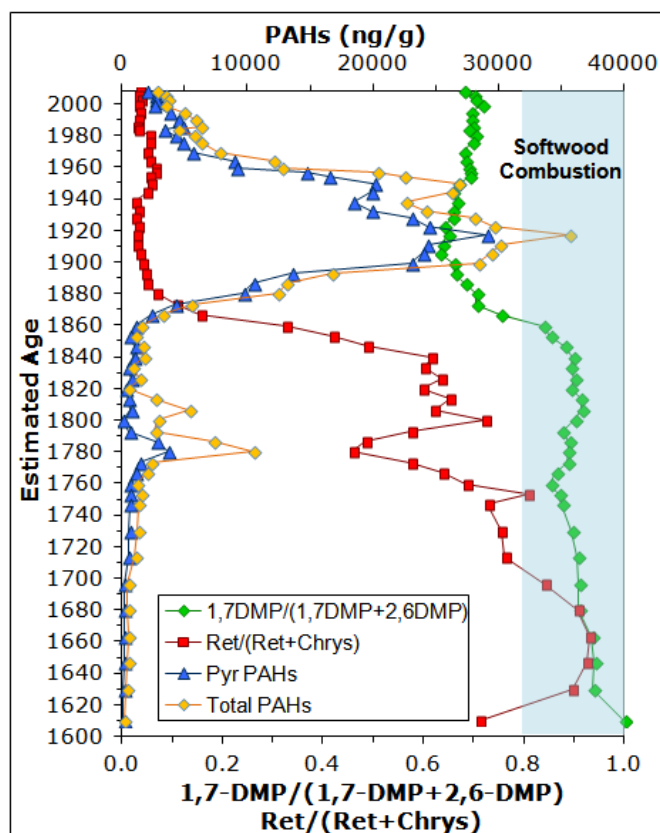


Figure 4. Comparison of softwood diagnostic ratios 1,7-DMP/(1,7-DMP+2,6-DMP) to Ret/(Ret+Chrys).

From 1600 to the mid 1750's, the average total PAH and pyrogenic PAH concentrations remain close to background (~660 and ~280 ng/g, respectively). Two peaks occur during the 1760-1820 period. The largest of these peaks (~1780 - 1790: 10400 and 3700 ng/g for total and pyrogenic PAHs, respectively) corresponds to a decrease in the Ret/(Ret+Chry) ratio (Figure 4). It is possible that this marked change in both concentrations and signatures was largely due to a fire that occurred in Copenhagen in the year 1795 when warehouses used for the storage of coal and wood barrels caught fire at the navy's old base in Gammelholm. The fire spread and consumed 941 houses, destroying much of the medieval portion of the city (Dansk turisforening

1898). In light of these events, the combustion of the navy's coal stores is a probable source for the observed increase in pyrogenic PAHs in the core at that particular depth. The discrepancy in dates is most likely due to a propagation of errors in the chronology calculated using the surface 60 cm of the core (^{210}Pb and ^{137}Cs dating) down through the deeper sediment intervals.

The second peak in total PAH concentrations occurs at approximately 1810. This peak coincides with the Napoleonic Wars, during which Denmark experienced two major battles. The first of the battles was in 1801 and primarily involved the British destruction of several Danish ships. The second battle occurred in 1807 and involved a three day long bombardment of the city which destroyed approximately 30% of its buildings. The total PAH concentrations (~5400 ng/g) for this period are approximately half those of the 1780 peak. Interestingly, the pyrogenic PAHs (680 ng/g) only increase to approximately a quarter of those observed in the preceding years. It is possible that this is due, in part, to lack of coal combustion that was seen in the 1795 fire or to higher inputs of petrogenic residue PAHs (lower molecular weights and higher alkyl content; Wang et al., 1999) resulting from the bombardment of the city. The slight increase in the MePhe/Phe ratio during that time (Figure 3) supports the latter hypothesis.

1860 - Mid 1900's: Industrial Revolution and the World Wars

In the mid 1800's, Denmark experienced the onset of its Industrial Revolution, during which the import of coal began to increase (Figure 5) and wood burning became less common. This is evidenced by the rapid increase in PAH concentrations starting in ~1860. The ratios of both Ret/(Ret+Chry) and 1,7-DMP/(1,7-DMP+2,6-DMP) drop significantly from pre-Industrial levels (Fig 4). By 1890, Ret/(Ret+Chry) fell to a ratio of approximately 0.05, demonstrating a marked

decrease in the use of wood as a major fuel source. Congruently, the ratio of 1,7-DMP/(1,7-DMP+2,6-DMP) drops to approximately 0.5 - 0.65, placing it within the diagnostic range of coal and lignite combustion.

Simultaneous to the decrease in softwood diagnostic ratios, the total PAH and pyrogenic PAH concentrations begin to increase steadily till they reach a peak (35600 and 29100 ng/g for total and pyrogenic PAHs, respectively) slightly before 1920. These values are two orders of magnitude higher than background values measures in pre-1700 sediments. The increase of pyrogenic PAHs corresponds with importation and consumption of coal throughout this time (Figure 5). Due to the relatively inefficient methods of coal combustion during these years, pyrogenic PAH emissions were high with large particulate matter (PM) emissions per ton of coal consumed. A decrease in coal consumption is observed over the course of both the first and second world wars (1914 - 1918 and 1939 - 1945, respectively). Simultaneous decreases in pyrogenic PAH emissions are observed during these years as well. Following WWI, Denmark began to shift its fuel sources to incorporate a higher proportion of petroleum. The import of oil began in ~1920 and continued to increase until WWII, where nearly all importation ceased (Figure 5) till after the war.

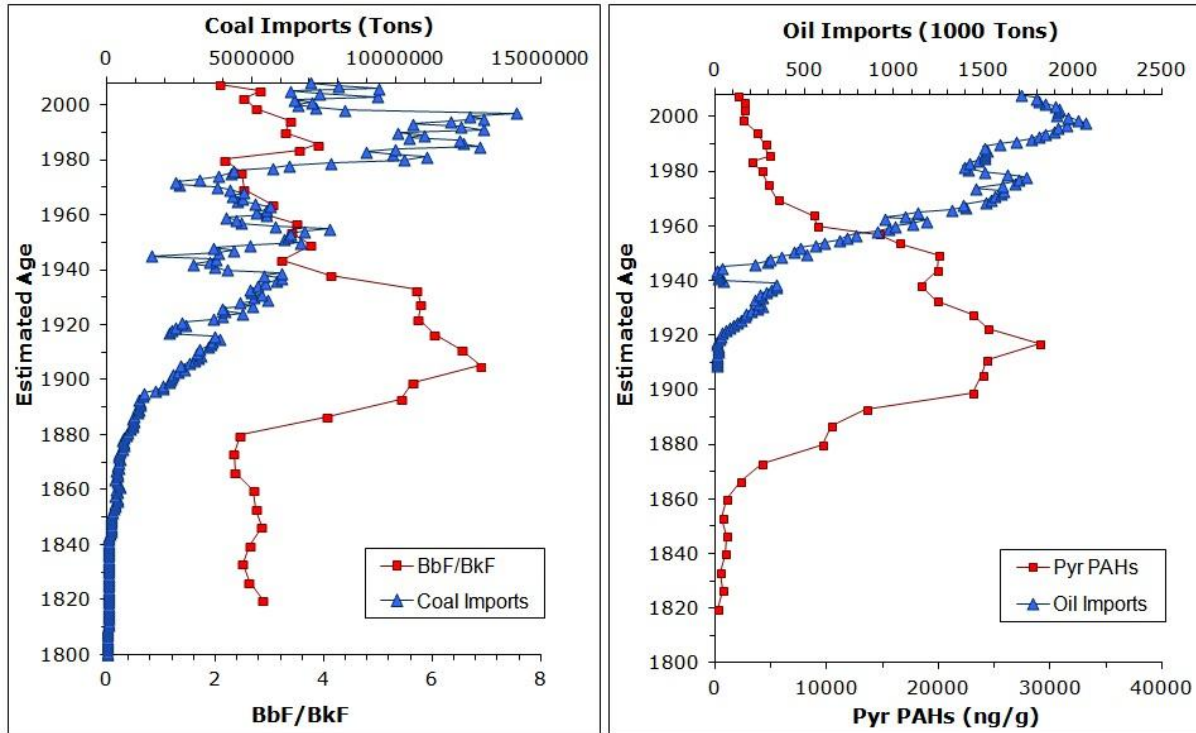


Figure 5. Left panel: Importation of coal into Denmark and BbF/BkF. Right panel: Oil importation in Denmark and pyrogenic PAHs.

1950's - 1970's: Post war technology and the EPA

Following 1945, importation of petroleum resumed and increased while that of coal, after a small resurgence post WWII, started to decline. Furthermore, advances in combustion technology enabled more efficient burning of both coal and petroleum, thus leading to the reduction of overall particulate matter emissions (Figure 6). The rapidly declining PAH concentrations during these two decades show the influence of shifts in fuel consumption and improvement in combustion technology. These trends continued until the early 1970's when a total oil embargo was placed on Denmark as a result of its aid to the USA and Israel during the OPEC oil crisis.

Because of this embargo, Denmark's petroleum imports were significantly reduced and it was forced to increase its importation and utilization of coal once more (Figure 5). This shift in fuel source is reflected in a small increase in PAH concentrations and a significant increase in the ratio of Benzo[b]fluoranthene (BbF) to Benzo[k]fluoranthene (BkF). This ratio is particularly useful for the characterization of PAH emissions from coal combustion (Louchouart et al., 2012). In the Botanisk core, the BbF/BkF ratio shows a strong relationship with pyrogenic PAH concentrations since the onset of the Industrial Revolution (1860's; Figure 7). It is important to note that while this ratio increases in tandem with the spike in coal imports during the 1980 - 1990's, the total and pyrogenic PAH levels remain significantly lower and experience much less of an increase. This is most likely due to the Environmental Protection Act in 1974 which enabled Denmark to begin enforcing air quality regulations. Further legislation followed this act by imposing limits to pollutants and PM emissions from a broadening sector of factories and combustion plants. High levels of coal importation continued from 1980 - 1997 until the oil embargo was lifted and petroleum importation into Denmark could recover. However, the oil crisis of 1973 had caused Denmark to reevaluate its fuel sources and make a push towards more renewable energy (Fenger 2003).

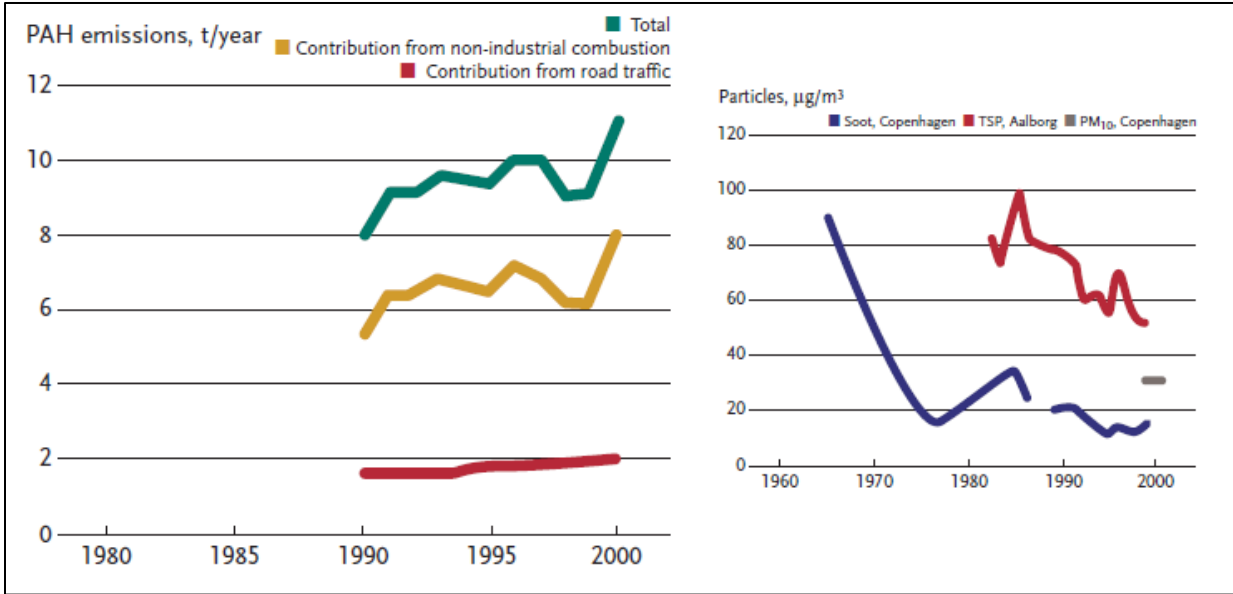


Figure 6. The first graph demonstrates the increases in four PAHs (BaP, BbF, BkF, and IP) while the second graph represents the lowered PM emissions measured in a busy street in Copenhagen. Both studies were conducted by the National Environmental Research Institute and reported by Fenger (2003).

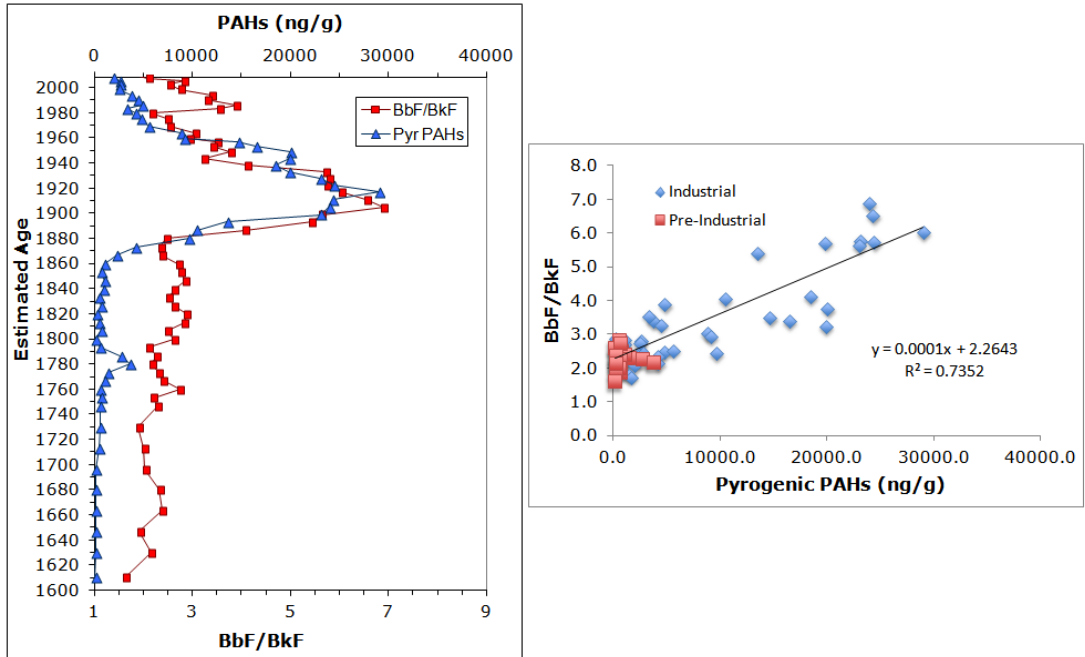


Figure 7. Pyrogenic PAHs plotted against the ratio of BbF/BkF as well as the correlation between increasing concentrations of BbF/BkF and pyrogenic PAH emissions.

Late 1980's - Present: New millennium

In the late mid to late 1880's, Denmark began to move towards achieving a more stable economy based upon mixed fuel sources and lowered emissions. A shift to less energy consuming activities was underway and wind was adopted as a renewable energy source (Walsh/Samso 2009). In addition, natural gas became a significant contributor to the gross energy consumption of the nation (Figure 8). These changes resulted in decreases in the total and pyrogenic PAH emissions in Copenhagen as well the in ratio of BbF/BkF, which drops down below preindustrial levels (Figures 7, 8).

It is interesting to note that while a decrease in PM has been observed due to cleaner forms of combustion, a recent study (Fenger 2003) found that emissions of BaP, BbF, BkF, and indeno(1,2,3-cd)pyrene (IP), have actually increased from 1990 - 2000 (Figure 6). These increases are credited primarily to nonindustrial emissions, such as domestic fireplaces. When compared to the results of this study, it is seen that the ratio of BbF/BkF does indeed show a slight increase in the upper core (Figures 7, 8). However, this increase is seen slightly after the year 2000, a discrepancy which could be credited to the slight mixing of sediments in the lake. The ratio of 1,7-DMP/(1,7-DMP+2,6-DMP) provides the strongest support of the recent use of domestic wood burning, as it is seen to move slightly back into the softwood combustion range of > 0.7 (Figure 5). Despite the recent decreases in overall emissions in Copenhagen, PAH concentrations are still tenfold higher than preindustrial levels.

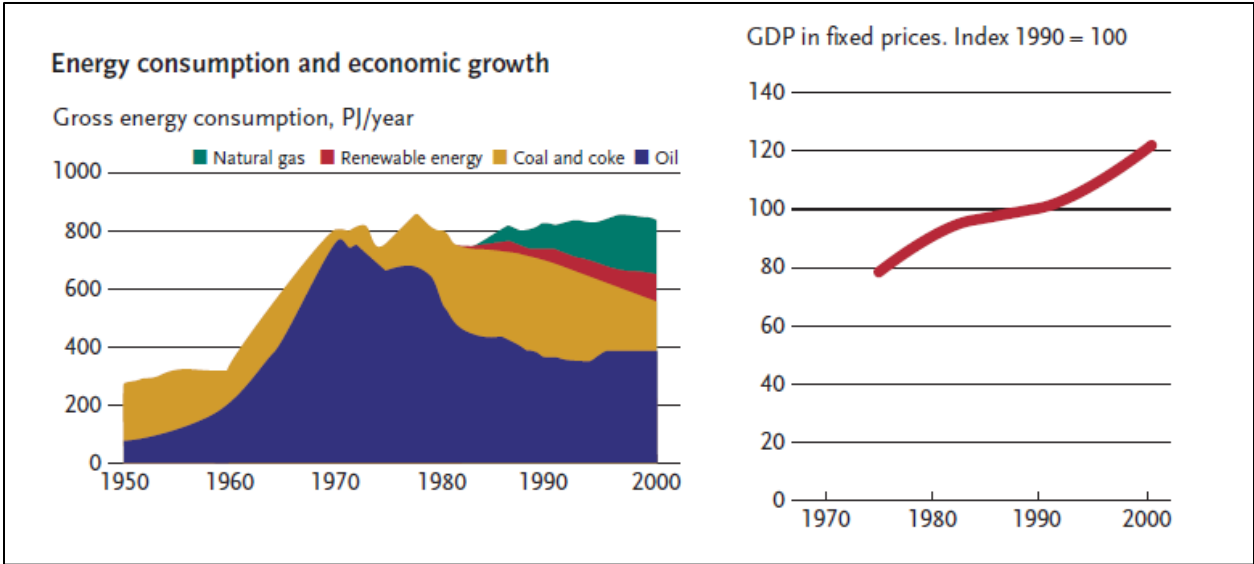


Figure 8. Denmark's gross energy consumption according to fuel sources as well as the increase in GDP as a result of lowered energy usage (Fenger, 2003).

CHAPTER IV

CONCLUSIONS

This study demonstrates the usefulness of PAH concentrations and source diagnostic ratios in the reconstruction of historical combustion records. Lake Botanisk provides a unique opportunity for monitoring PAH trends over time due to its relative proximity to a major urban city and its long undisturbed record (~400 years). Furthermore, its isolation from other bodies of water suggests that hydrocarbon concentrations within the sediments are predominantly derived from atmospheric deposition within the lakes watershed. Very few urban lakes exist with such an extensive history and which allow for a detailed reconstruction of past combustion trends resulting from the urban and industrial development of a single city.

Combustion trends as delineated by PAH source diagnostic ratios parallel fuel shifts and technological advancements throughout Denmark's history. From 1600 - 1850 wood was the primary fuel source, resulting in the production of high levels of alkylated PAHs (Fig. 9). During the industrial revolution, Denmark shifted from the use of wood towards coal. The relatively inefficient combustion methods of from 1860 to ~1950 led to high levels of PM and high molecular weight (HMW) PAHs. Following WWII, Denmark again shifted its fuel source to favor the use of petroleum. However due to advancements in combustion technology, lower levels of HMW PAHs are produced during this time. The OPEC oil crisis forced the nation to revert back to the use of coal in 1973. Very low PAH emissions are seen at this time due to the enforcement of air quality acts as well as the improved efficiency of combustion and emission abatement approaches. Finally, from ~1980 on, Denmark has moved towards the use of a

combination of petroleum, coal, and natural gas. All of these fuels sources are currently producing very low emissions due to the large advances in emission control technologies.

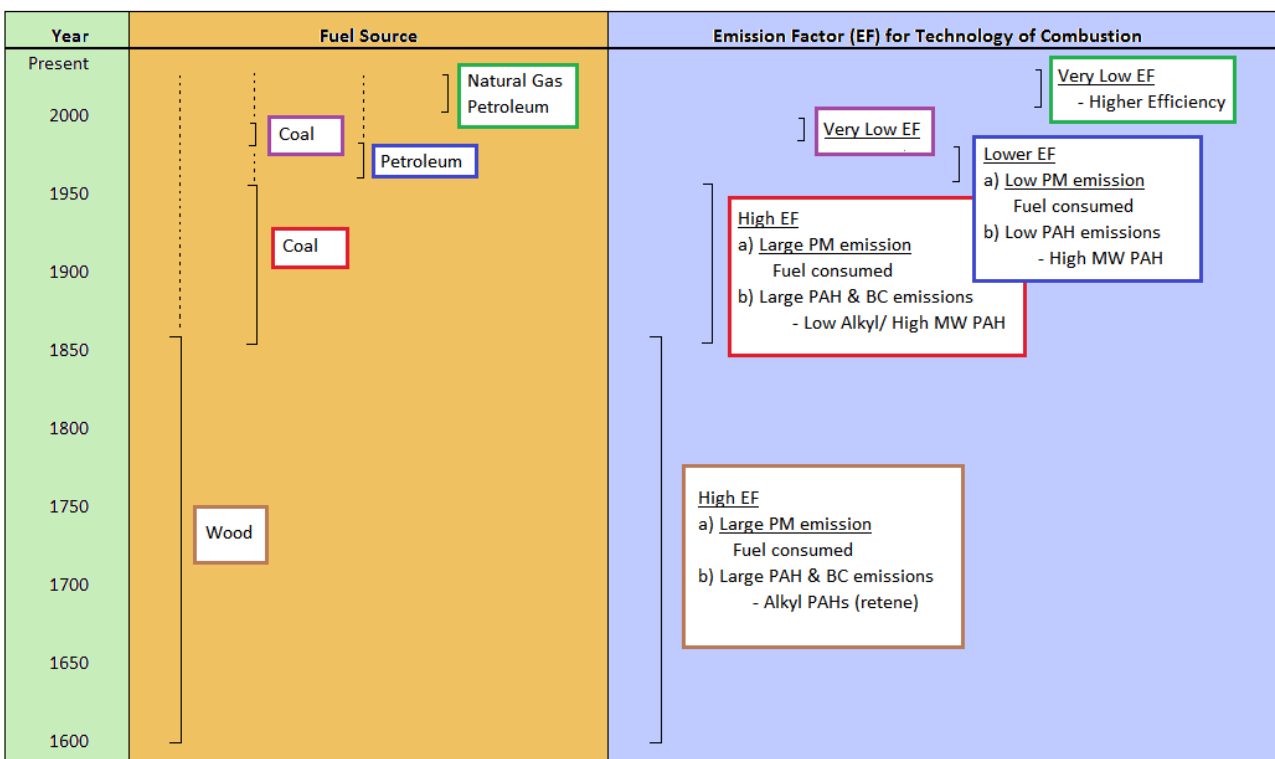


Figure 9. Progression of fuel sources utilized in Denmark through time with corresponding emission factors and PAH characteristics.

Because the results of this study can be compared to a known historical record they may be used to support the accuracy of certain source diagnostic ratios to determine the source of PAHs in sediment cores. In addition, they provide a background against which current PAH concentrations can be compared to determine whether emissions have returned to preindustrial levels. Further research should include black carbon analysis and refinement of PAH trends throughout the lower core.

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