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

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are molecular contaminants that are released in the environment through oil spills (petrogenic) or from the incomplete combustion of fossil fuel or organic matter (pyrogenic). Significant increases in concentrations of 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 (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. Several studies have monitored the concentrations of PAHs in atmospheric particles as a measure of air quality. 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.

Sediment cores have regularly 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; Louchouarn et al., 2007; Elmquist et al., 2007). 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 (Louchouarn et al., 2007).

The goal of this study was 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 1). This lake has no entering or exiting streams, therefore any PAHs detected in its sediments can be assumed to be from atmospheric deposition.

MATERIALS & METHODS

Site information and sample collection

- Sediment cores were sampled from Lake Botanisk in Copenhagen's Botanical Garden in the winter of 2011 (Figure 1).
- 150 cm long cores were subsectioned every cm in depth and freeze-dried.
- ^{210}Pb and ^{137}Cs sediment dating methods employed by National History Museum of Denmark and the Geological Survey of Denmark and Greenland.

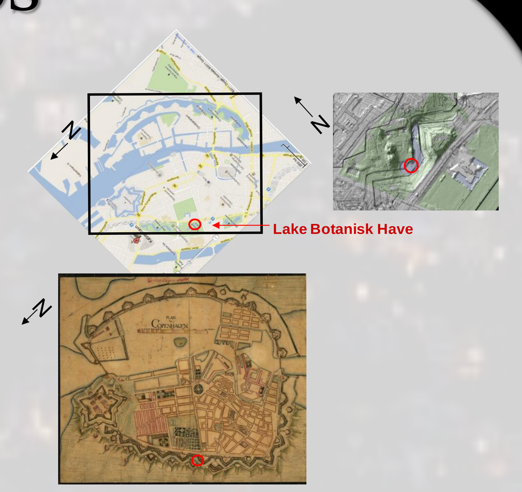
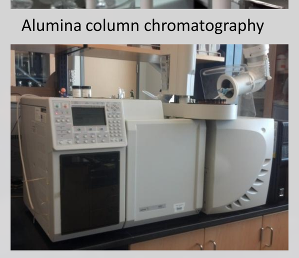


Figure 1. (Bottom left) Lake Botanisk as part of the moat surrounding Copenhagen during the 17th century. (Top) Lake Botanisk as seen today (Source: Natural History Museum - University of Copenhagen).

PAH analysis

Alumina column chromatography



Varian gas chromatography/mass spectrometer (GC/MS)

- Sediment samples were spiked with surrogate standards and extracted using pressurized fluid extraction in an accelerated solvent extractor (ASE).
- The extracted samples were purified using alumina column chromatography and petroleum ether as an eluent.
- Extracts were solvent exchanged into hexane following each step.
- Samples were analyzed with gas chromatography mass spectrometry in selective ionization mode. Blanks and standard reference materials were included with each run to test for accuracy.
- Compound identification was performed on a GC/MS in SIM mode, using retention times and by comparing mass spectra with those of commercially available standards. Specific compounds were included in source diagnostic ratios as determined by the literature (Table 1).

RESULTS

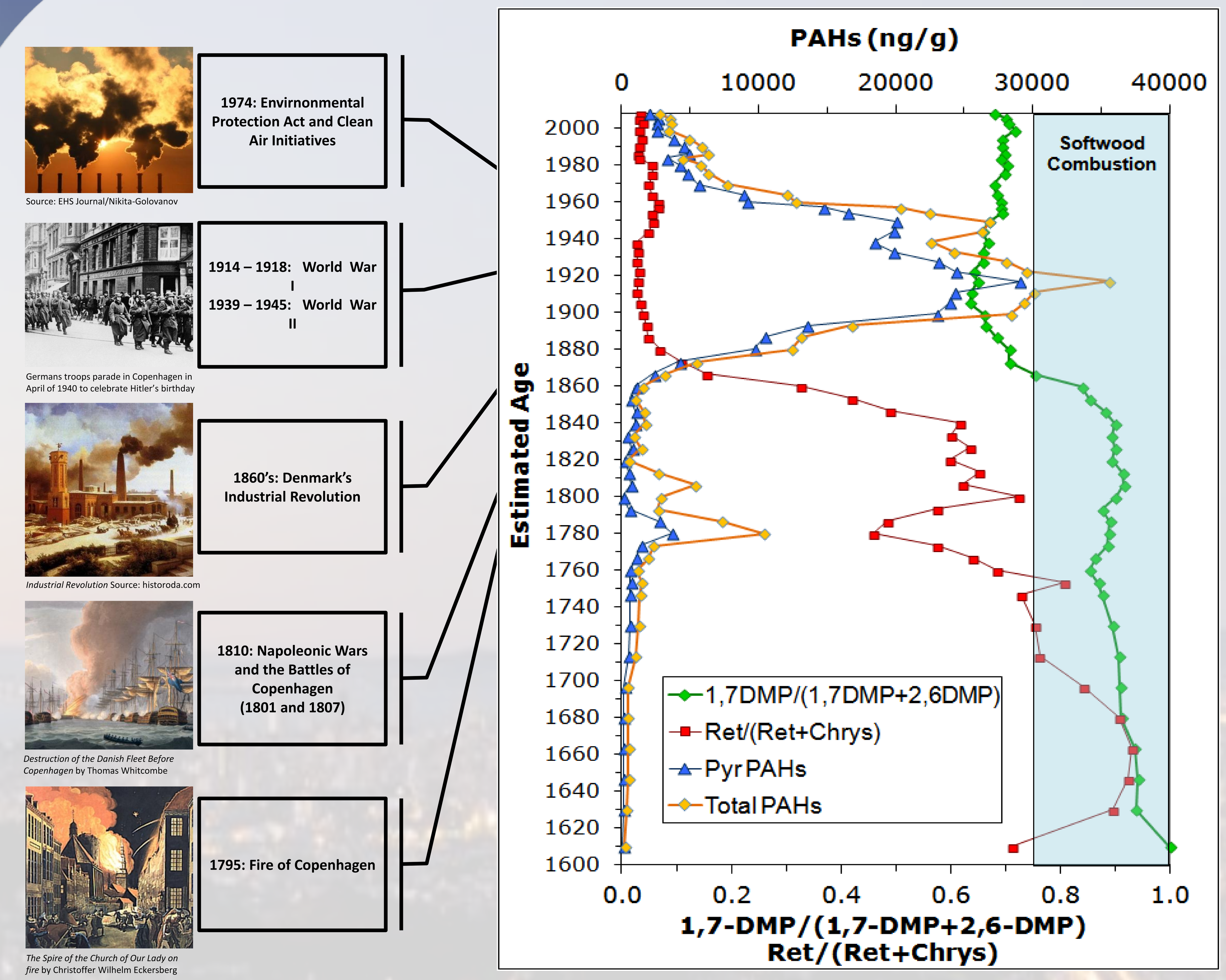


Figure 2. Comparison of softwood diagnostic ratios (1,7-DMP/ (1,7-DMP+ 2,6-DMP) and (Ret/(Ret+Chrys)) plotted against the total and pyrogenic PAHs (Tot PAHs and Pyr PAHs, respectively) measured throughout the core. The column on the left marks major historical events that correspond with shifts in the PAH composition throughout the core for specific dates.

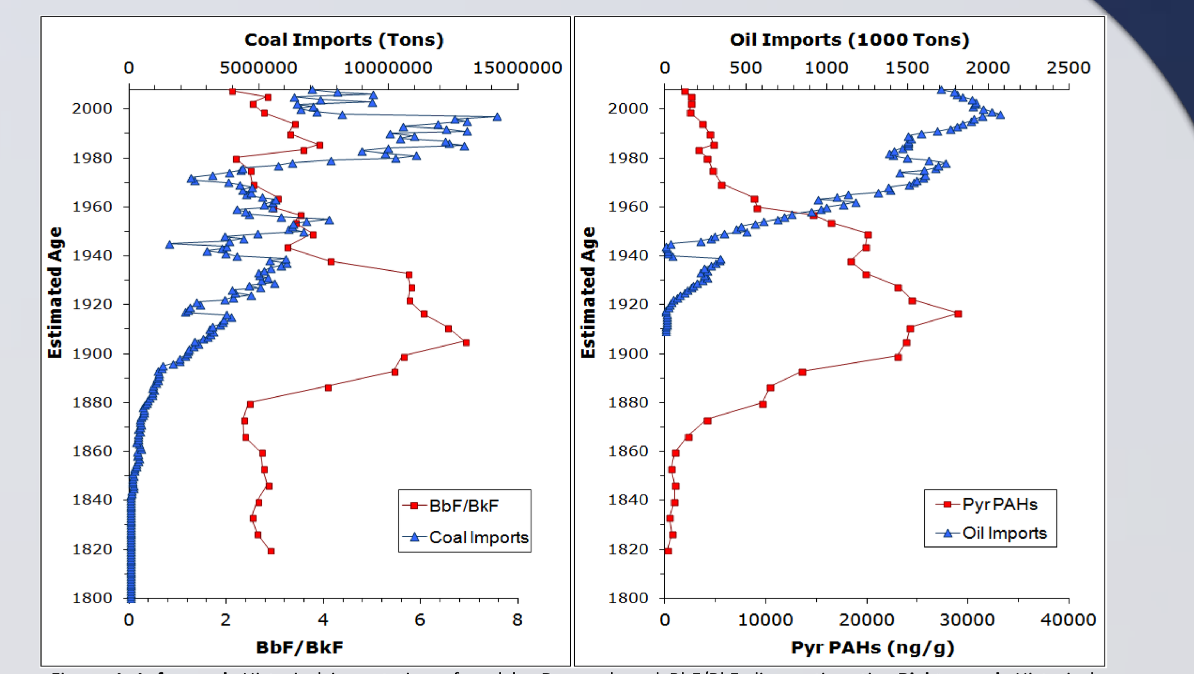


Figure 4. **Left panel**: Historical importation of coal by Denmark and BbF/BkF diagnostic ratio. **Right panel**: Historical importation of oil by Denmark and pyrogenic PAHs. Notice the reduction of oil importation and the spike in coal importation around 1970. This corresponds to the OPEC oil crisis and demonstrates Denmark's increased reliance on coal throughout this time. A small increase in Pyr PAHs and total PAHs appears around this time (see also Fig. 2). This small shift is marked by a much more significant in crease in the BbF/BkF ratio, which is diagnostic for coal combustion.

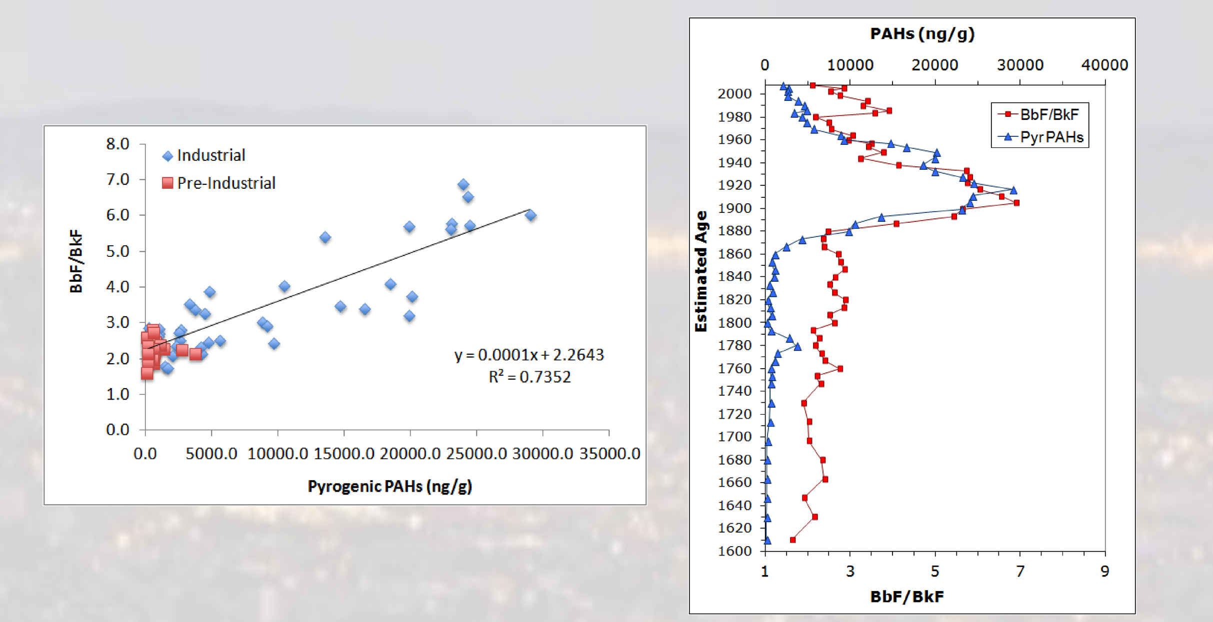


Figure 5. Left panel: Correlation between concentrations of pyrogenic PAHs and BbF/BkF signatures during pre- and Industrial periods. **Right panel**: Vertical profiles of pyrogenic PAHs and BbF/BkF ratios. The relationship between these two parameters, since the onset of the Industrial Revolution, confirms coal combustion as a predominant source of pyrogenic contaminants to the atmosphere of Copenhagen.

Table 1. Diagnostic ratios and reported values for various processes along with references.

Ratio	Value Range	Source	Reference
∑LMW / ∑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	Louchouarn 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	

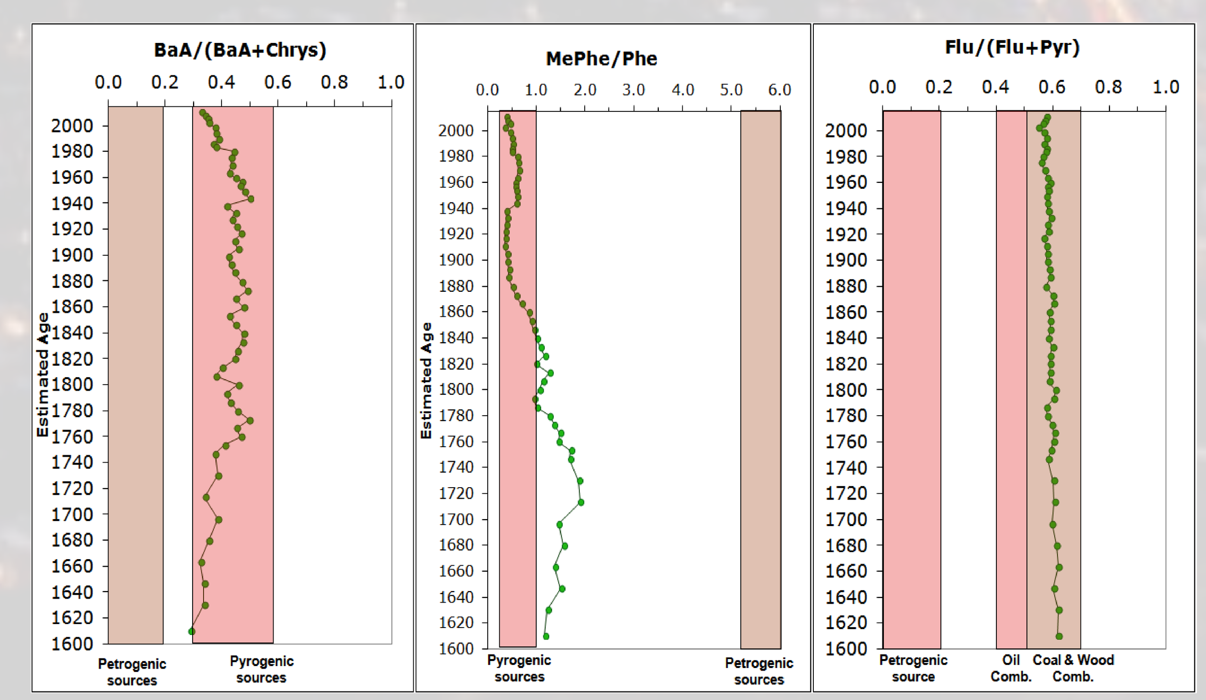


Figure 3. Diagnostic ratios (left to right) for Benzo[a]anthracene over the sum of Benzo[a]anthracene and Chrysene (BaA/(BaA+Chrys)), Methylphenanthrene over the sum of Methylphenanthrene and Phenanthrene (MePhe/(MePhe+Phe)), and Fluoranthene over the sum of Fluoranthene and Pyrene (Flu/(Flu+Pyr)) with sources for each.

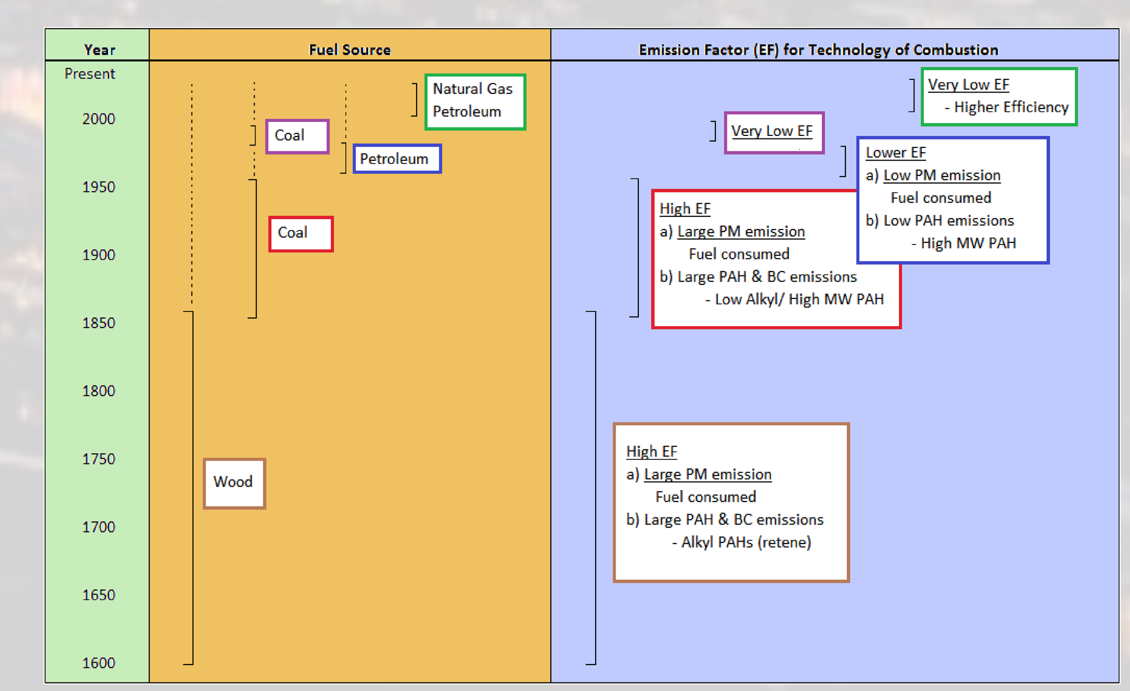


Figure 6. Progression of fuel sources utilized in Denmark through time with corresponding emission factors and PAH characteristics.

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CONCLUSIONS

- The urban location of Lake Botanisk provides a unique opportunity for monitoring historical trends in PAH emissions in Copenhagen due to its long undisturbed record (~400 years).
- Its isolation from other bodies of water suggests that hydrocarbon concentrations within the sediments are predominantly derived from atmospheric deposition within the lakes watershed.
- Combustion trends, as delineated by PAH source diagnostic ratios, parallel fuel shifts and technological advancements throughout Denmark's history (Figure 6).
  - From 1600 – 1850 wood was the primary fuel source, resulting in the production of high levels of alkylated PAHs (Figure 3).
  - 1860 – 1950 was marked by a shift towards coal combustion, producing high levels of particulate matter and high molecular weight PAHs (Figures 4-5).
  - Shifts in fuel sources and PAH emissions are seen in more recent years due to political events (e.g. OPEC oil crisis), and improvements in air quality regulation and combustion technology.
- Known historical records of fuel usage and political events can be used to support the accuracy of certain source diagnostic ratios to determine the source of PAHs in sediment cores.
- In addition, the results provide a background against which current PAH concentrations can be compared to determine whether emissions have returned to preindustrial levels.