Australian Government
Department of Defence
Defence Science and Technology Group

Polycyclic Aromatic Hydrocarbon (PAH) emissions from diesel exhausts: A review

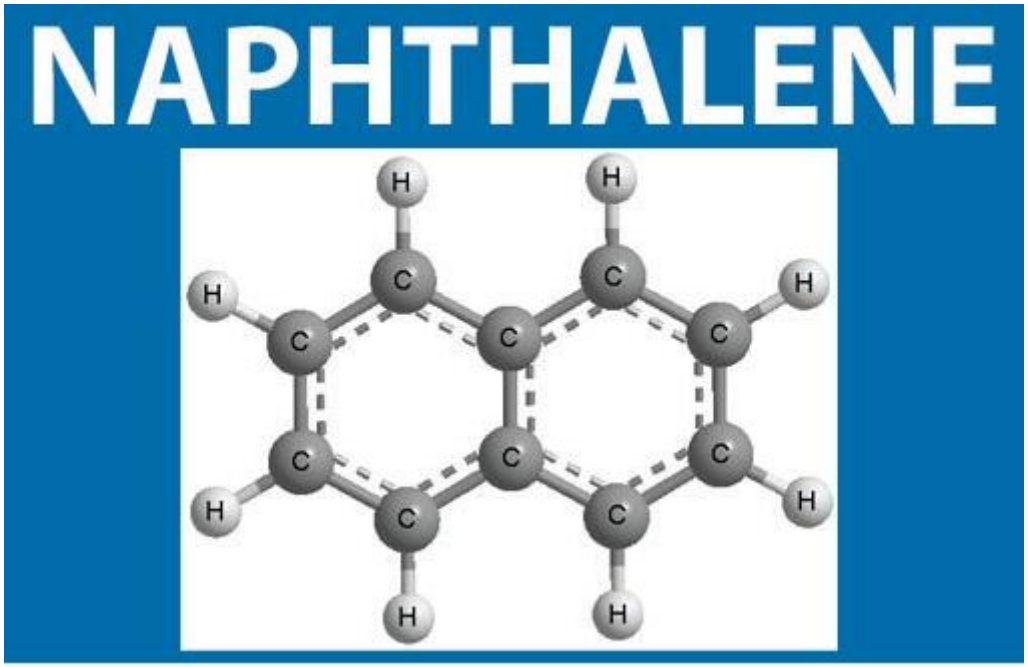
Michael Leist

Why are we interested in PAHs? Why the review?

- Polycyclic Aromatic Hydrocarbons
  - Air pollutant
  - Potential for exposure on both the surface and sub surface fleet of the RAN
- Review assists with identifying;
  - Increasing knowledge of PAHs
    - Likelihood of exposure
    - Techniques/procedures that may assist with reducing PAH exposure
    - Analysis techniques

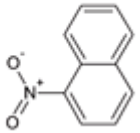
Polycyclic Aromatic Hydrocarbons (PAHs)

- PAHs all have a similar structure – Aromatic rings consisting of carbon and hydrogen

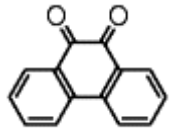


Polycyclic Aromatic Hydrocarbons (PAHs)

- There are over 100 different PAHs, as well as..
  - Nitro PAHs
    - Nitrated PAHs
    - Reaction of PAHs with atmospheric oxidants
    - Potential mutagens and carcinogens
    - Up to 45 have been identified in diesel exhaust
    - Emissions of nitro PAHs are typically at least an order of magnitude lower than PAHs



  - Oxy PAHs
    - Oxygenated PAHs
    - Semi-volatile
    - Many directly toxic and mutagenic



Polycyclic Aromatic Hydrocarbons (PAHs)

- Why are we interested in PAHs
  - Health Effects
    - Irritation to the eyes, throat and bronchial tubes
    - PAHs have been classified as carcinogens;
      - Group 1 carcinogens (known human carcinogen)
      - Group 2A (probably human carcinogen)
      - Group 2B (possible human carcinogen)
      - Group 3 (not classifiable due to insufficient information)

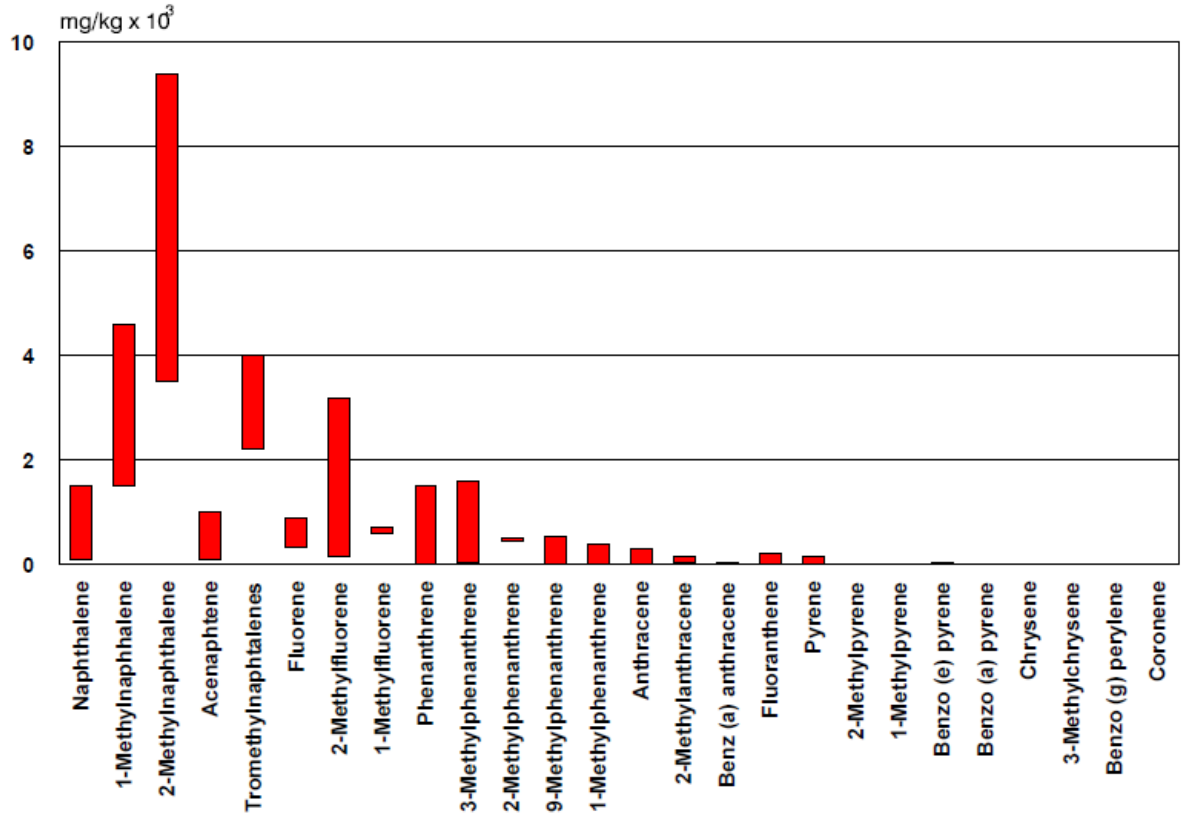
Polycyclic Aromatic Hydrocarbons (PAHs)

- PAHs are most commonly produced during the incomplete burning of organic substances.
  - Burning of wood and biomass
  - Waste incineration
  - Tobacco smoke
  - Coal tar products
  - Engine emissions

PAHs – Diesel exhaust emissions

- Why are PAHs present in diesel exhaust emissions?
- PAHs produced from the combustion of diesel fuel
  - Creation of PAHs
    - Non PAH, aromatic, non-aromatic fuel components
  - Contributions from lubricating oil
  - Entrainment from the exhaust system
    - Exhaust may act as a source or sink for PAHs
- PAHs can be present in Diesel fuel
  - Survive the combustion process
    - Vary for each PAH
    - Influenced by engine design

PAHs present in diesel fuel



Source: Hall et al

Polycyclic Aromatic Hydrocarbons (PAHs)

- The emission profiles of PAHs vary between sources
  - Source fingerprint (chemical signature)

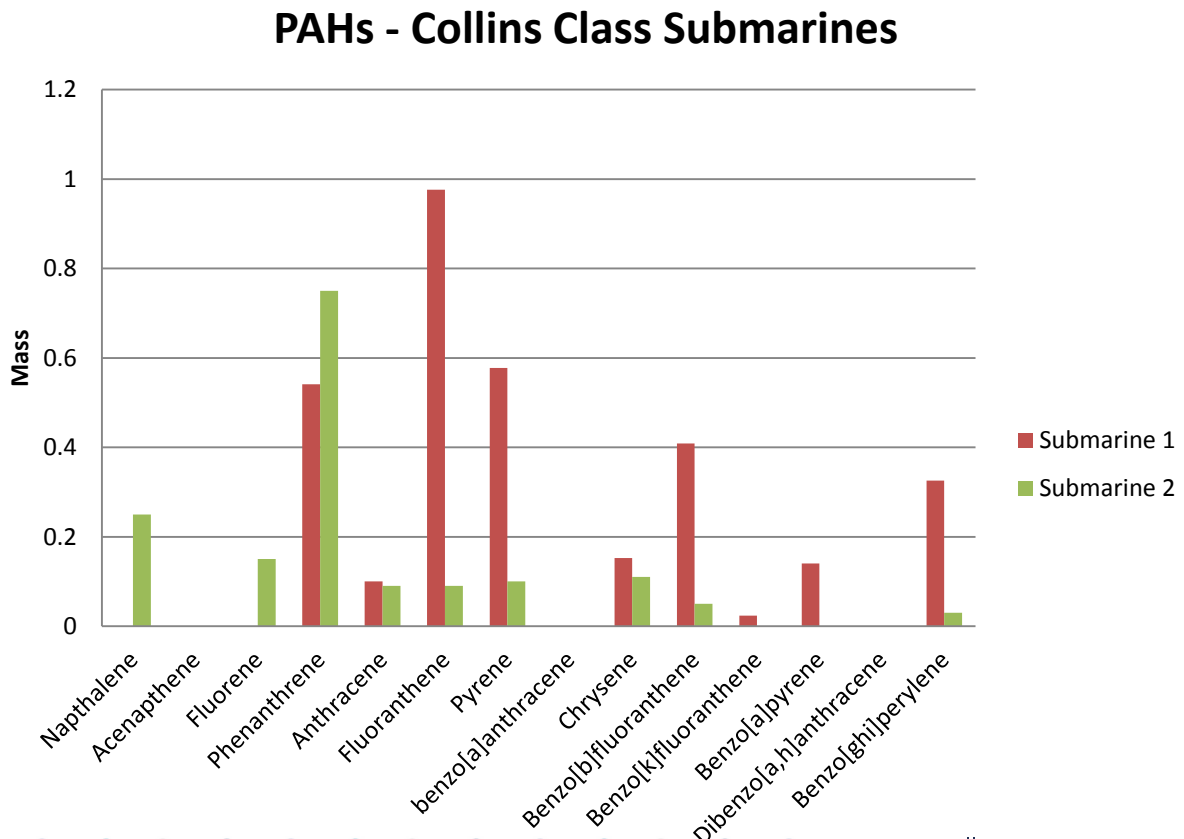
- Diesel emissions contain elevated concentrations of methylated naphthalene's and methylated phenanthrene isomers
  - Enrichment of benzo[a]anthracene and benzo[a]pyrene

PAHs – Maritime Diesel Engine Emissions

- Maritime Emissions
  - Naphthalene
  - 2-Methyl-naphthalene
  - 1-Methyl-naphthalene
  - 2,6-Dimethyl-napthalene
  - 2,3,5-Trimethyl-napthalene
  - Phenanthrene
  - 1-Methyl-phenanthrene

Polycyclic Aromatic Hydrocarbons (PAHs)

- Collins Class Submarines
- Swab samples by Hanhela et al identified dimethylnaphthalene isomers
  - 1-Methylnaphthalene, 2-Methylnapthalene



Complications in characterising PAHs present in diesel exhaust emissions

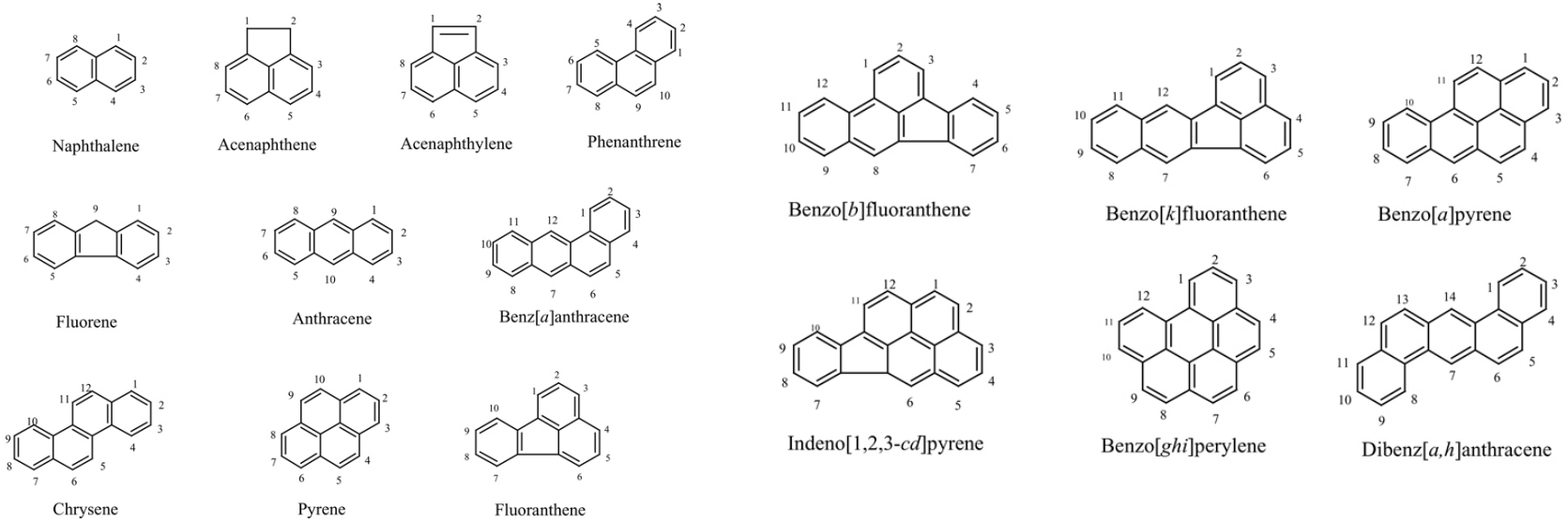
- Many parameters can influence diesel PAH exhaust emissions
  - Engine size
  - Operating conditions
  - Maintenance
  - Engine technology
  - Fuel composition
    - Reduction in
      - aromatic content
      - sulphur content

Complications in characterising PAHs present in diesel exhaust emissions

- The number and types of PAHs investigated often differs
- No workplace exposure limits for many PAHs
  - little regulatory guidance as to what PAHs to monitor
    - Naphthalene only PAH with an exposure limit air (Aust.)
    - Benzo[a]pyrene only PAH with an aqueous exposure limit (Aust.)
  - Biomarkers used to determine PAH exposure
    - Metabolite of Pyrene, 1-hydroxypyrene (1-HP)

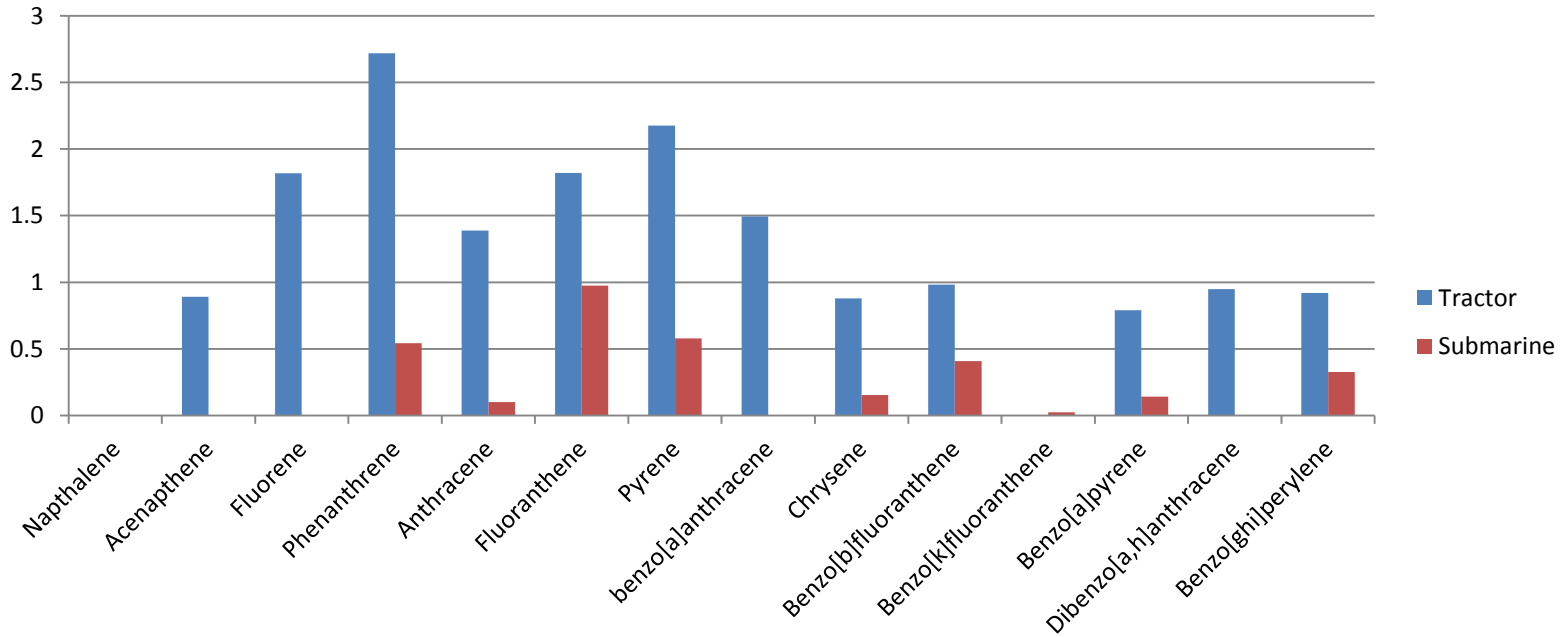
Complications in characterising PAHs present in diesel exhaust emissions

- United States Environmental Protection Agency (EPA)
  - Classified 16 PAHs as priority pollutants
    - Toxicity
    - Human exposure

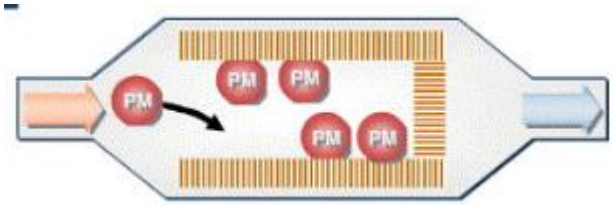


Complications in characterising PAHs present in diesel exhaust emissions

- Lack of maritime specific research



Engine and exhaust after treatment systems



- Diesel Particulate Filters (DPFs)
  - Not designed for a reduction in PAH emissions
    - Nitrogen Oxides
    - Particulate Matter
  - Comprised of a large number of parallel channels
  - Channels are alternatively open and closed
  - The exhaust gas is forced to flow through the porous walls of the honeycomb structure

Diesel Particulate Filters (DPFs)

- Can assist in reducing PAH emissions by a factor of 3 to 4
- Some evidence that DPFs can act as a reaction chamber for nitration of PAHs
  - Nitration of pyrene and benzo(a)pyrene

Biodiesel

- RAN has not set any biodiesel targets
- US Navy aims to generate 50% of its energy from alternative sources, including biofuels by 2020

Biofuels are included in latest U.S. Navy fuel procurement

Source: U.S. Navy, used with permission
Note: Above, clockwise from left: Fleet replenishment oiler USNS Henry J. Kaiser (T-AO 187), aircraft carrier USS Nimitz (CVN 68), destroyer USS Chung-Hoon (DDG 93), and cruiser USS Princeton (CG 59). Great Green Fleet demonstration, July 2012.

Biodiesel

- Biodiesel feedstocks can include
  - Canola oil
  - Palm oil
  - Coconut oil
  - Animal fats
- Biofuels can be added (blended) with conventional diesel fuel at varying percentages
- Biofuel can have significant changes to viscosity and the cetane number

Biodiesel

- Biodiesel can produce a reduction in PAH emissions
  - >80% achievable
  - Nitro PAHs can also be reduced
- Highly dependant upon the type of biofuel feedstock used and the percentage at which it is added to conventional diesel
  - Reduced reduction in all PAHs
  - Enhancement of some PAHs (Phenanthrene, Anthracene)
  - Oxy PAHs increase

Summary

- Maritime emissions dominated by lower molecular weight PAHs
- Engine after treatment technologies typically reduce, however not eliminate PAHs
- Biodiesels, can result in mixed results
  - Biodiesel feedstock
  - Blending percentage with conventional fuel


That's all Folks!