Sources and Health Effects of Oxygenated PAHs

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Introduction:

Like PAHs, oxygenated PAHs (Oxy-PAHs), i.e. ketone and quinone – substituted PAHs, can be produced from combustion processes, but they may also form post emission via photo-oxidation, chemical oxidation, etc. Increasing usage of biodiesel could lead to a rise in the level of oxygenated PAHs in the air. EPA emission testing has observed decreases in emissions of elemental carbon, PAHs, nitrated PAHs, and increases in CO_2 emissions from the combustion of biodiesel, suggesting a more complete combustion process with the addition of biodiesel to conventional diesel fuel; however, there is evidence that emission of Oxy-PAHs will increase substantially. Previous data demonstrated that the increase of oxygen levels in coal tar resulted in a substantial increase in Oxy-PAH emissions during pyrolysis and combustion processes.

Method:

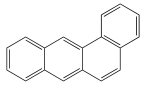
◆Glass fiber and PUF filters were soxhlet extracted with 6% ethyl ether in hexane.

◆Sediment samples were oven dried at 35ºC. Following extraction by an ASE 200 (Dionex) with a mixture of methanol and dichloromethane, alumina column cleanup was done to remove more polar compounds.

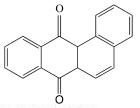
◆Biota samples were first homogenized in methanol then extracted with the ASE 200. To remove biological matrix interference, gel permeation chromatography (Biobeads S-X3) was used to separate macromolecules, such as proteins, from lower molecular weight compounds.

◆Silica gel chromatography was used to isolate aromatic groups (PAHs, Oxy-PAHs) from the saturated hydrocarbon fraction (e.g., alkanes) in the sediment and biota extracts.

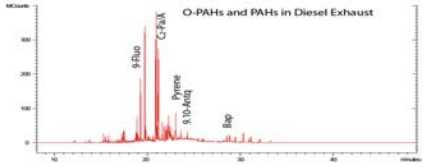
◆ All PAH and Oxy-PAH analyses were performed by GC/MS (Varian; Agilent). Chemical ionization (CI) was used to detect Oxy-PAHs and electron ionization (EI) was used to detect PAHs.

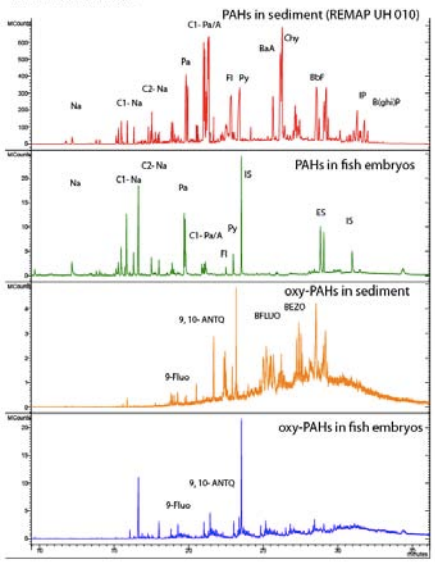


Benz[a]anthracene



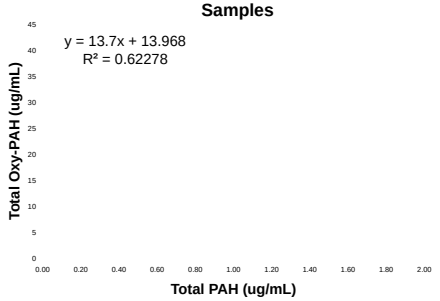
7,12-Benz[a]anthracenequinone



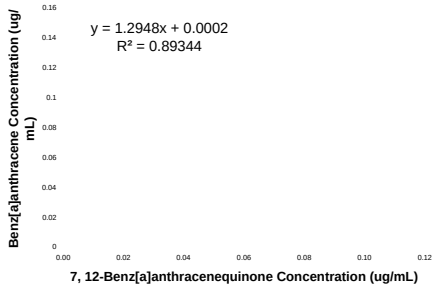


Acknowledgements: This research is supported by American Chemistry Council (SACC # 5093) and NIEHS Center Program (ES009089).

Total Oxy-PAH vs Total PAH in Filter Samples



7,12-BaAQ vs BaA in Filter Samples



Results and Discussion:

◆A reliable and sensitive method of detecting certain Oxy-PAH compounds using GC/MS has been developed in our lab at LDEO.

◆Oxy-PAHs have been detected in diesel exhaust particles, PM2.5, sediments, and biota samples.

◆Analyses show positive correlation between Oxy-PAHs and parental PAHs. This is likely due to the similarity in their sources; however, the scatter in the regression shows that they are not completely dependent variables, justifying a closer look at Oxy-PAHs in the environment.

◆The children who were exposed to the highest indoor levels of Oxy-PAHs and PAHs developed asthma in Year 5.

◆Oxy-PAHs may play a, largely unexamined, role in sediment toxicity.

◆In conjunction with the Mailman School of Public Health, the effects of Oxy-PAH exposure on development of asthma will be fully explored.

◆Further method development will be done using a novel APLI ionization method for improved sensitivity on a wider range of aromatics in an American Chemistry Council-funded study.