HEALTH EFFECTS INSTITUTE

Atmospheric Transformation of Diesel Emissions

BACKGROUND

Diesel exhaust (DE) is an important contributor to air pollution and consists of a complex mixture of hundreds of compounds in either gas or particle form. After emission, DE undergoes chemical and physical transformations, or "aging," in the atmosphere as well as dispersion and transport. The aging process depends on the environment into which the DE is emitted; the atmosphere contains many compounds, including oxidizing and nitrating radicals, as well as organic and inorganic compounds from sources other than diesel engines. These compounds can influence the chemical composition and toxicity of DE as well as how long its various components remain in the atmosphere. Because of substantial changes in diesel engine technology and after-treatment over the past decade, there is a need to evaluate the newer technologies, including their emissions, the atmospheric processing of their emissions, and the corresponding health effects.

In response to Request for Preliminary Applications 98-6, "Health Effects of Air Pollution," Dr. Barbara Zielinska of the Desert Research Institute in Reno, Nevada, and her colleagues submitted an application to study the effects of photochemical transformations on DE constituents and whether such changes in chemical and physical form would be reflected in changes in toxicity. The investigators' atmospheric aging experiments would be conducted at the European Photoreactor (EUPHORE) outdoor simulation chamber in Valencia, Spain. Samples would then be shipped to Dr. Zielinska's laboratory in the United States for detailed chemical analyses and to her collaborator Dr. JeanClare Seagrave at the Lovelace Respiratory Research Institute in Albuquerque, New Mexico, for toxicologic experiments in rodents. The HEI Health Research Committee thought that Dr. Zielinska's approach to studying the photochemical transformations of DE and their potential effects on its toxicity was novel and likely to produce interesting results. The Committee recommended the proposed study for funding, with a strong recommendation that the investigators use a modern diesel engine.

APPROACH

DE was generated at EUPHORE using a 2003-model-year Ford light-duty diesel engine that was run on a dynamometer at about 50% load. EUPHORE has two outdoor simulation chambers with a volume of about 200 m^3 and a retractable cover that allows atmospheric reactions to take place in daylight (allowing photochemical reactions to occur) or in the dark, simulating nighttime conditions. In addition to DE, several compounds (precursors to hydroxyl [OH] or nitrate [NO_3] radicals, toluene, or a mixture of volatile organic compounds [VOCs]) were added to the atmospheric mixture to create various aging conditions. The mixture was then allowed to react for 3 to 5 hours; after completion of the reactions, the chamber cover was closed (if open), and integrated air samples were collected overnight using Teflon filters to collect particles and XAD adsorbent-resin cartridges to collect gaseous species. Parallel samples were collected for detailed chemical analyses and in vivo toxicologic experiments.

Zielinska and colleagues conducted three sampling campaigns, in January 2005, May 2005, and May and June 2006. During the first campaign, the investigators found that high concentrations of

nitrogen oxides (NO_x) were interfering with the experiments and therefore decided to develop a NO_x denuder to remove the majority of NO_x from the engine exhaust before its injection into the chamber. A particular challenge was to find an efficient method of removing NO_x without substantially altering the concentrations and properties of the particulate matter (PM) in the exhaust. In the end, cobalt oxide was selected for use as the absorption material to capture the NO_x from the exhaust stream. After the second sampling campaign, the design of the NO_x denuder was improved further to allow even more efficient removal of NO_x for use in the third, final campaign.

The investigators measured a large number of compounds known to be present in DE, including alkanes, polycyclic aromatic hydrocarbons (PAHs), nitro-PAHs, and polar compounds, as well as hopanes and steranes that are known to be present in lubricating oil. They also measured elemental carbon (EC) and organic carbon (OC), NO_3, and sulfate.

Two series of toxicologic experiments were conducted. The investigators used rats initially but, after the third sampling campaign, switched to mice because the sample masses were insufficient for intratracheal instillation in rats (mice require less sample mass because of their much lower body weight compared with that of rats). The animals were killed 24 hours after intratracheal instillation for evaluation of markers of inflammation in blood and lung lavage fluid as well as signs of inflammation, cytotoxicity, and parenchymal changes in lung tissue. The mice, in addition, were evaluated for markers of oxidative stress and macrophage phagocytosis in lung tissue and lavage fluid cells, respectively.

RESULTS AND INTERPRETATION

The investigators reported that most of the exposures in daylight as well as the exposures in the dark with added NO_3-radical precursors led to particle formation and increased concentrations of semivolatile organic compounds. These results were evident in the increased fraction of OC in the samples and the increased ratios of OC to EC compared with atmospheres containing only DE. The addition of toluene or VOC in daylight led to the highest increases in organic compounds, including the formation of pyrolized OC, which is indicative of the presence of highly polar or oligomeric organic compounds. The investigators reported increased concentrations of many organic compounds, such as 9-fluorenone and other oxy-PAHs; nitro-naphthalene and other nitro-PAHs; certain nitropyrenes and nitrofluoranthenes; and polar compounds, such as heptanoic acid and oxalic acid. In addition, exposures in daylight led to the formation of ozone (O_3) and formic acid. On the other hand, concentrations of primary pollutants such as alkanes were reduced, indicating that these compounds had reacted to form secondary organics.

The investigators examined toxicologic outcomes using samples collected in the second and third campaigns. Some general patterns appeared that were consistent in both rats and mice. For example, the investigators observed increased cytotoxicity after the addition of toluene to DE in daylight, increased histopathologic indications of inflammation after the addition of OH radicals or toluene to DE in daylight, and increased concentrations of polymorphonuclear neutrophils in lavage fluid (also an indicator of inflammation) after the addition of OH radicals to DE in daylight. Other results were less consistent. Concentrations of protein in lavage fluid, for example, increased in rats but to a lesser extent in mice exposed to DE aged in daylight. Markers of oxidative stress in mice yielded mixed results: significant changes were observed under some exposure conditions but not others, and in some cases the changes were the opposite of those that would have been expected. The investigators concluded that the addition of toluene and, to a lesser extent, OH-radical precursors to DE in daylight increased the toxic potential of the samples compared with DE aged in daylight without any additional compounds.

In its independent review of the study, the HEI Health Review Committee stated that Dr. Zielinska and colleagues had successfully conducted a complex study to characterize the atmospheric transformations of DE under the influence of sunlight, O_3, radicals, and organic compounds. The report presented novel results on the atmospheric aging of DE derived from a 2003-model-year light-duty engine under a variety of conditions. Strengths of the study design included the use of state-of-the-art atmospheric chamber facilities, the use of a realistic set of atmospheric aging conditions, and the analysis of a large number of organic compounds. The Committee noted that a minor criticism might be that the use of a light-duty engine could be considered less relevant to the United States, which has a much lower percentage of light-duty diesel engines than Europe does.

The Committee commended the investigators' efforts to develop an efficient NO_x denuder but concluded that the additional work had led to a reduced number of experiments and a set of somewhat disparate results that remain predominantly descriptive and qualitative in nature. The results of the first sampling campaign, conducted without a NO_x denuder, were not representative of reactions that might take place in ambient air. In addition, results from the second and third sampling campaigns are difficult to compare because of the use of two different denuders and rodent species.

The Committee agreed with the investigators' conclusion that exposing DE to daylight (with or without additional VOCs), as well as adding NO_3-radical precursors to DE in the dark, resulted in increased particle mass concentrations and the formation of secondary organic compounds, such as oxy-PAHs and nitro-PAHs. The Committee thought that the list of compounds analyzed was extensive but agreed with the investigators that future studies could further characterize the formation of secondary products by, for example, analyzing additional organic compounds in PM and measuring additional carbonyls, such as glyoxal and acetaldehyde. One of the limiting factors of the study was the variable number of replicate experiments. Some atmospheric aging conditions were tested only once; others were tested up to four times. It thus remains difficult to assess the extent of variability in the formation of certain compounds within and among the experimental conditions. Although the investigators were appropriately cautious in their interpretations, further research will be needed to obtain a more complete, systematic, and quantitative set of results.

The assessment of the toxicity of aged DE samples was considered well designed. Samples to be tested were collected using filters and XAD cartridges to capture both particles and gaseous components, an important improvement over many older studies of DE that assessed the effects of diesel particles only. The investigators observed increased inflammation under some conditions; changes in biochemical measures correlated fairly well with changes in histopathologic findings. The Committee noted that several endpoints were used as indicators of oxidative stress and that some of these have been shown to be more reliable than others. This variation could account for certain discrepancies in the results, such as changes in heme oxygenase-1 and oxidized glutathione but not in thiobarbituric-acid–reacting substances. It remains difficult to draw firm conclusions other than that atmospheric aging of DE generally seemed to increase the toxicity of the samples. Further research will be needed to evaluate which of the atmospheric reaction products might be contributing to the increased toxicity.

In summary, this study has generated a large, complex data set on the detailed chemical composition of samples collected under a variety of experimental conditions intended to simulate real-world atmospheric aging of DE. The investigators observed that atmospheric aging under certain conditions, such as in daylight (which facilitates photochemical reactions) or with the addition of radical precursors (which facilitates chemical reactions), led to the formation of particles and secondary organic compounds. Atmospheric-aging conditions generally also increased the toxicity of samples, as indicated by increased concentrations of markers of inflammation and oxidative stress in exposed rodents. However, it remains difficult to relate specific chemical-reaction products to increases in toxicity. Further systematic research on the composition and toxicity of DE and other pollution mixtures after atmospheric transformation is needed to provide more quantitative answers. Importantly, such research should cover the most recent diesel engine technologies that comply with the 2007 and 2010 PM and NO_x standards in the United States and that have much lower emissions compared with those of older technologies, including the 2003 engine used in this study.

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