Atmospheric Transformation of Diesel Emmissions

Barbara Zielinska
Desert Research Institute. Division of Atmospheric Sciences. Reno, NV. USA
Barbara.Zielinska@dri.edu

ABSTRACT

The overall hypothesis of this work was that atmospheric transformation of diesel exhaust would result in a change in composition and the resulting toxicity of the starting material. The specific aims were: (1) to characterize the gas- and particle- phase products of atmospheric transformations of diesel emissions under the influence of sunlight, ozone, hydroxyl radicals, and nitrate radicals; and (2) to explore the changes in biological activity of diesel exhaust before and after the atmospheric transformations take place. The project was executed with the aid of the EUPHORE simulation chamber in Valencia, Spain, which is currently one of the largest (~200 m^3) and the best equipped outdoor simulation chamber in the world, allowing investigation of atmospheric transformation processes under realistic ambient conditions (dilution in the range of 1:300). Diesel exhaust was generated on-site using a light-duty diesel engine and a dynamometer system, which is equipped with the Horiba continuous gas analyzer. A modern diesel engine (i.e. a common rail direct injection, turbocharged, intercooled engine) was obtained from Ford Motor Company for this study. The first series of experiments was carried out in January 2005 (winter campaign), the second in May 2005 and the third in May-June 2006 (summer campaigns). A diesel fuel that most closely matched what is currently used in most of the United States was employed (47 ppm sulfur and 15% aromatic content). The test matrix provided experiments that examine the effects of aging and NO_3 radical reactions in the dark and photooxidation and OH radical reactions in the sunlight on the composition of diesel exhaust, with or without addition of volatile organic compounds (VOC). In order to remove excess NOx, a NOx denuder was constructed and used for low-NOx experiments during both summer campaigns. A Scanning Mobility Particle Sizer (SMPS) was utilized to determine the particle size, number and volume concentrations. Ozone, NOx and NOy species were monitored using chemiluminescence and Fourier Transfer Infrared (FTIR) instruments. The semi-volatile and particle-associated organic compounds (SVOC) were collected from the chamber at the end of the exposures, using an XAD coated annular denuder followed by a filter and XAD cartridge. The samples for toxicity evaluation were collected using Teflon filters followed by two XAD cartridges. Chemical analyses included determination of carbon (organic/elemental and carbon fractions), inorganic ions (e.g., sulfate/nitrate), and speciated organics (PAH, nitro-PAH, polars, alkanes, hopanes/steranes). In vivo toxicology experiments were performed with extracts of particulate material combined with the semi-volatile organics. The biological activity of the atmosphere constituents was evaluated by instilling the extracted material into the trachea of rodents followed by evaluation pulmonary toxicity, inflammation and oxidative stress response. The results indicate that all light exposures and NO_3 radical dark exposures formed additional particles and SVOC mass due to reactions of VOC, SVOC, and inorganic gases. The greatest increase in mass occurred with the addition of VOC as co-reactants. The organic mass formed increased the proportions of pyrolized organic carbon fraction, which suggests formation of very polar and oligomeric compounds. Toxicity data are consistent with the hypothesis that the biological potency of samples collected from these atmospheres is affected by changes in composition. This change came about both by atmospheric aging conditions and by changes in exhaust composition presumably associated with the engine became older.