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Discovering the Impact of Catalytic Converters on Vehicular Nitrogen Oxides by Using Stable Nitrogen Isotopes

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Finding the source of pollutants is important for developing a better understanding of how humans have affected the earth. Nitrogen oxides (NOx = NO + NO_2) are trace gases involved in atmospheric chemistry, air quality, and climate and are key to controlling ozone, hydroxyl radical, and nitrate aerosol concentrations in the troposphere. NOx can be particularly dangerous because it is oxidized into nitric acid in the atmosphere. This forms acid rain, which leads to dangers to the ecosystem such as drinking water degradation and soil acidification. It has been proposed that the nitrogen-15 stable isotope ratio of NOx can be used to trace regional NOx back to a particular source. The issue of partitioning NOx arises from a limited knowledge of nitrogen-15 isotope values of various NOx sources. Because of this we analyzed vehicle exhaust, which is the largest source of anthropogenic NOx. By modifying a U.S. EPA NOx collection method, we sampled 26 different vehicles and prepared them for analysis by isotope ratio mass spectrometry to obtain their isotope profiles. It has been established that approximately 60% to 80% of total emissions are from the first 200 seconds from cold ignition. This correlates with the large range in both stable nitrogen-15 isotope values of NOx (-19.1‰ to 9.8‰) and emitted NOx concentrations (8.5 to 286 ppm) we obtained in the samples. This occurs because the catalytic converters take a couple of minutes to reach operational temperatures. From this data we constructed a model to predict how NOx is thermally produced and its associated isotope fraction. Using this, we also estimated regional NOx emission profiles based on commute times across the country, proposing that areas such as cities will have a more negative isotope value due to longer vehicle run times. Our continued research includes sampling diesel vehicles, farming equipment, power plants, and airplanes, with future research goals of comparing cars equipped with a catalytic converter to cars without one to provide more insight into the chemistry involved with anthropogenic NOx.

Research advisor Greg Michalski writes, "Stanford's research on the isotopic composition of nitrogen oxide emitted by automobiles filled a critical gap in our scientific understanding of the sources and fate of atmospheric pollution. His research was published in 2015 in the peer-reviewed journal Environmental Science and Technology—a great accomplishment for an undergraduate researcher. He will begin attending graduate school at Texas A&M in the fall of 2015."

Commuting to and from campus could influence nitrogen-stable isotopes due to vehicle emissions.

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