

Researchers looking at light-induced toxins in air and water

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Is the air we breathe on a daily basis slowly killing us? It may not be that severe, but the air we breathe and water we drink may be more harmful than we realize.

Toxic nitro-aromatic pollutants (or nitro-polycyclic aromatic hydrocarbons), both manmade and naturally occurring, continue to be emitted into the air and are present in food, water systems, soils and sediments, says Carlos Crespo, the Case Western Reserve University chemistry assistant professor whose research team is studying how ultraviolet-visible light interacts with and transforms these compounds under controlled laboratory settings.

The goal of his group is to assess the physical and chemical consequences of sunlight absorption by these pollutants in the environment. In particular, the Crespo research group wants to know the relaxation pathways used by these pollutants to redistribute the excess electronic energy gained when they absorb light and how this energy is used to transform these compounds into other harmful compounds or products. Their work is being funded by a \$100,000 grant from the American Chemical Society Petroleum Research Fund.

"Degradation by sunlight is thought to be the main route of natural removal of nitro-aromatic compounds from the environment. Consequently, understanding how the absorption of light transforms these compounds holds the key for predicting their environmental fate and for designing effective pollution control strategies," says Crespo.



He added, "These relatively small compounds are formed primarily through incomplete combustion processes, like municipal incinerators, motor vehicles and power plants."

While these compounds do occur naturally in the environment, through actions like volcanic eruptions or forest fires, the use of fossil fuels increases the amount emitted into the atmosphere, increasing exposure to their harmful effects.

"Epidemiological studies show that exposure to diesel exhaust and urban air pollution is associated with an increased risk of lung cancer," Crespo says, noting that laboratory mammals and in vitro tests have found the compounds to be toxic, mutagenic and even carcinogenic.

Previous research works have shown that light-induced degradation of a number of nitro-aromatic compounds leads to products that are more toxic than their parent compounds. Further evidence suggests that these pollutants contribute as much as 10% of the total mutagenicity of inhalable, suspended particles in polluted areas. However, the specific pathways through which these compounds are transformed into products by sunlight are not well understood.

The Crespo group expects that by using sophisticated laser techniques with less than a trillionth of a second time resolution, in combination with computations based on quantum mechanical theories, a better understanding of the fundamental processes controlling the light-induced transformation of these pollutants can be obtained.

"Once we understand the physico-chemical factors that control the degradation of these compounds by light absorption at the molecular level, we might be able to use this knowledge to reduce some of these chemical transformations."



It is known that these compounds can release a nitric oxide (NO) radical when exposed to light. Crespo says one of the long-term goals of this research is to harness the power of these radical compounds for biological applications.

"Once we understand the factors that control the release of NO radicals, we could envision the use nitro-aromatic compounds as light-triggered, time- and site-controlled NO radical donors for therapeutic applications," he says. "But we are currently a long way from that."

Their 2008 paper, "Environmental Photochemistry of Nitro-PAHs: Direct Observation of Ultrafast Intersystem Crossing in 1-Nitropyrene," was one of the first scholarly works using femtosecond laser techniques (1 femtosecond = 10^{-15} seconds) to investigate the electronic energy relaxation pathways of these environmental pollutants. However it is an area that is gaining more interest.

"There have been several additional articles since, including one our group submitted this past December," Crespo says. "Research in this subject is getting competitive, but positive competition is great for science. "

His group is also focused in studying the light-induced ultrafast relaxation pathways in other relevant bio-organic compounds.

Source: Case Western Reserve University

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