Scientists find chlorine may contribute to ozone formation

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Standard methods of predicting air pollution don't take atmospheric chlorine into account, but the chemical could be responsible for 10 percent or more of daily ozone production in local air, research at UC Irvine has found.

Air measurements taken nearly nonstop in the Irvine area over a two-month period showed that daytime chlorine gas levels typically measured five parts per trillion or less, but occasionally reached as high as 15 parts per trillion. Observation of daytime chlorine is surprising because chlorine molecules break apart just minutes after entering the atmosphere and being exposed to sunlight.

With these measurements, scientists estimate that chlorine photochemistry creates five to eight parts per billion of the maximum daily ozone level, which in California typically ranges between 40 and 80 parts per billion.

"Chlorine chemistry can have a direct impact on surface ozone even at parts per trillion levels," said Eric Saltzman, professor of Earth system science in the School of Physical Sciences at UCI. "Because of the strong link between ozone and human health, we need to fully understand the role chlorine may play in ozone chemistry in coastal urban environments."

Saltzman and Brandon Finley, a graduate student researcher in the Department of Earth System Science, published their findings in the current issue of *Geophysical Research Letters*.

Chlorine salts are naturally present in coastal air in sea salt aerosols, which are swept from the ocean into the air by the wind. Chlorine gas also is used to treat water in swimming pools, cooling towers and municipal water supplies. Chlorine atoms react rapidly with hydrocarbons and nitrogen oxides from automobile and power plant emissions, contributing to the complex chain of reactions that leads to ozone formation. The primary cause of urban ozone is the reaction of hydroxyl radical (OH) with hydrocarbons and nitrogen oxides. OH is a highly reactive molecule made of oxygen and hydrogen that forms photochemically in air.

“For the last 30 years, we’ve known that the hydroxyl radical is the primary cause of ozone,” Saltzman said. “Chlorine plays a similar role. It doesn’t take much chlorine to affect ozone chemistry.”

This study is the first to extensively measure atmospheric chlorine in Southern California air over several consecutive weeks. Researchers made extremely sensitive chlorine measurements, detecting the chemical at levels as low as three parts per trillion.

Results showed that chlorine is present in the atmosphere both day and night, and that its levels fluctuate with little regularity. Saltzman and Finley couldn’t pinpoint the cause of these changes, finding no obvious link between chlorine levels and meteorological conditions such as wind, temperature or relative humidity or existing pollution levels. They also don’t know for sure what created the chlorine they detected.

“We found more chlorine in the daytime than expected. It must be rapidly produced, because sunlight destroys it so quickly,” Saltzman said. “Most likely the process involves airborne marine particles, but research is needed to understand how it occurs.”

Inland ozone levels typically are higher than on the coast, mainly because of meteorological conditions that restrict air circulation and trap pollutants. Ozone is a highly reactive and unstable gas that damages living cells. Even low levels of ozone can harm the upper respiratory tract and the lungs, causing a cough, throat irritation and reduced lung function, and aggravating the effects of asthma, bronchitis and emphysema.

Said Saltzman, “Understanding the chemistry of chlorine is important to understanding its role in ozone chemistry, especially in California where air quality is such an important issue.”

Source: University of California, Irvine

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