Atmospheric mysteries unraveling: New findings may be key to explaining mercury, much more

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The Differential Optical Absorption Spectroscopy instrument hangs under the wing of a research aircraft. Relying on measurements from the instrument, CIRES Fellow Rainer Volkhamer and international colleagues report that halogens, natural chemicals from the ocean, can contribute to much more vigorous atmospheric chemistry than previously understood. The discovery may help explain levels of mercury contamination in the air, on land and in the oceans, and some climate mysteries as well. Credit: David Oonk/CIRES

It's been difficult to explain patterns of toxic mercury in some parts of the world, such as why there's so much of the toxin deposited into ecosystems from the air in the southeastern United States, even upwind of usual sources.

A new analysis led by researchers at the University of Colorado Boulder shows that one key to understanding mercury's strange behavior may be the unexpected reactivity of naturally occurring halogen compounds from the ocean.

"Atmospheric chemistry involving bromine and iodine is turning out to be much more vigorous than we expected," said CU-Boulder atmospheric chemist Rainer Volkamer, the corresponding author of the new paper published in the *Proceedings of the National Academy of Sciences*. "These halogen reactions can turn mercury into a form that can rain out of the air onto the ground or into oceans" up to 3.5 times faster than previously estimated, he said.

The new chemistry that Volkamer and his colleagues have uncovered, with the help of an innovative instrument developed at CU-Boulder, may also help scientists better understand a longstanding limitation of global climate models. Those models have difficulty explaining why levels of ozone, a greenhouse gas, were so low before the Industrial Revolution.

"The models have been largely untested for halogen chemistry because we didn't have measurements in the tropical free troposphere before," Volkamer said. "The naturally occurring halogen chemistry can help explain that low ozone because more abundant halogens destroy ozone faster than had previously been realized."

Volkamer is a Fellow of CIRES, the Cooperative Institute for Research in Environmental Sciences, at CU-Boulder and is an associate professor in the Department of Chemistry and Biochemistry. For the new paper, he worked with scientists from the U.S., China, Denmark and England.

CIRES Fellow Rainer Volkhamer, shown here inside a research aircraft, is co-author of a new paper finding that halogens, natural chemicals from the ocean, can contribute to much more vigorous atmospheric chemistry than previously understood. The discovery may help explain levels of mercury contamination in the air, on land and in the oceans, and some climate mysteries as well. Credit: David Oonk/CIRES

The international team relied on a differential optical absorption spectroscopy instruments (DOAS) that Volkamer's research group built to measure tiny amounts of atmospheric chemicals including highly reactive bromine oxide and iodine oxide radicals. Those radicals are very short-lived in the air, and collecting air samples doesn't work well. DOAS uses solar light, measuring the scattering and absorption of sunlight by gases and particles to identify the chemicals' distinct spectroscopic fingerprints and to quantify extremely small amounts directly in the atmosphere.

Reactions involving those bromine and iodine radicals can turn airborne mercury—emitted by power plants and other sources—into a water-soluble form that can stay high in the atmosphere for a long time. High in the air, the mercury can sweep around the world. Towering thunderstorms can then pull some of that mercury back out of the atmosphere to the ground, lakes or oceans. There, the toxin can accumulate in fish, creating a public health concern.

Volkamer's team's measurements show that the first step in that process, the oxidation of mercury in the atmosphere by bromine, happens up to 3.5 times faster than previously estimated because of halogen sources in oceans. Their work may help explain a mystery: For many pollutants, thunderstorms can rain out the chemicals quickly, so by the end of the storm there's little left in the air. Not so for mercury. Volkamer said its concentration in rainwater remains constant throughout a storm.

"To some extent, because of these halogens, we have a larger pool of oxidized mercury up there," Volkamer said.

Naturally occurring bromine in air aloft illustrates the global interconnectedness between energy choices affecting mercury emissions in developing nations, and mercury deposition in the U.S.

Finally, the measurements will be helpful for climate modelers seeking to improve their understanding of halogen impacts on ozone and other greenhouse gases.

More information: Active and widespread halogen chemistry in the tropical and subtropical free troposphere, *PNAS*, www.pnas.org/cgi/doi/10.1073/pnas.1505142112

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