# When less is more: Study tracks down lingering source of carbon tetrachloride emissions

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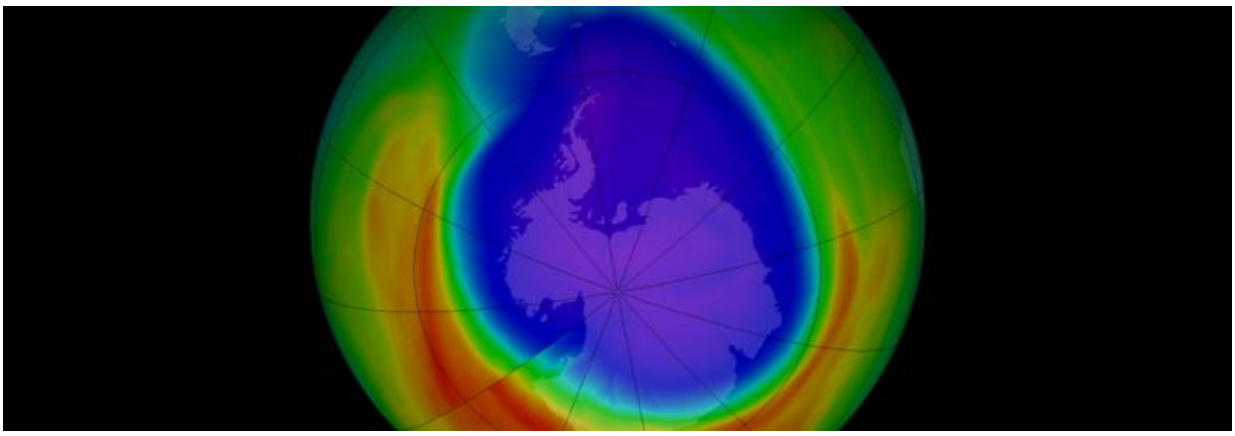
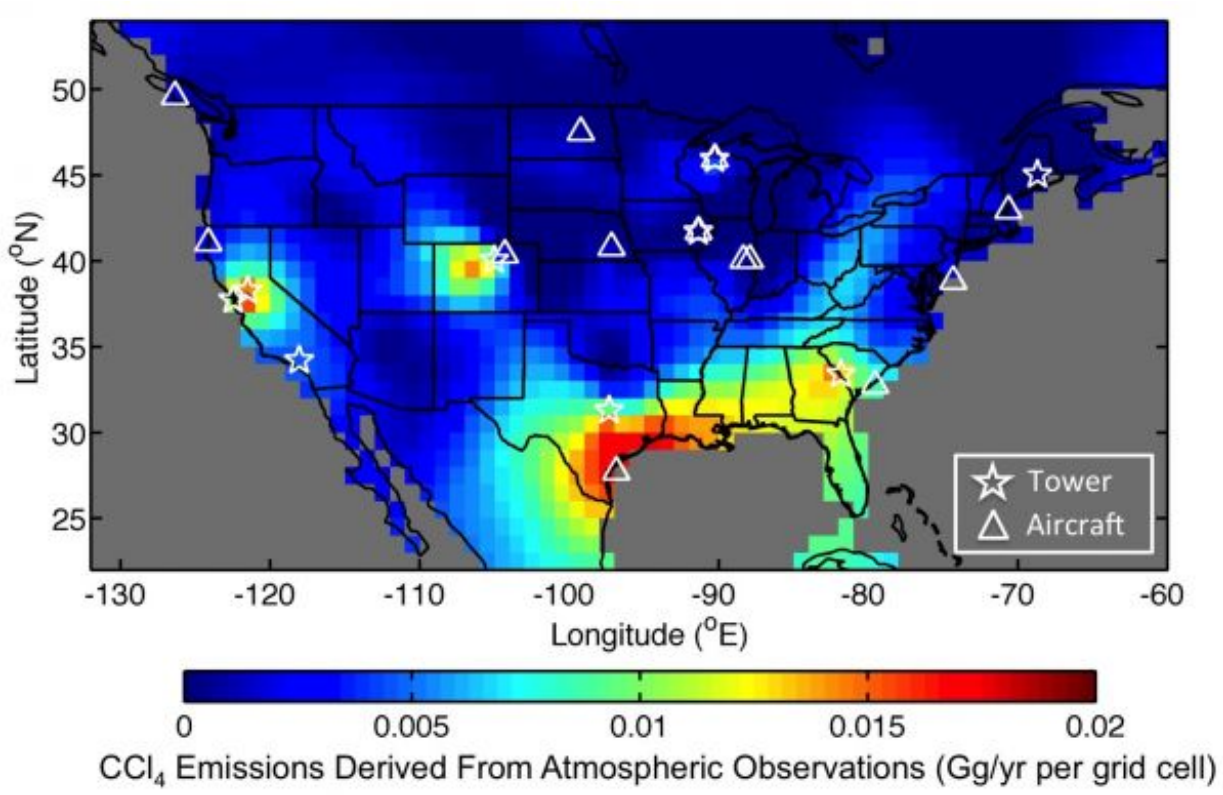


A graphic of the Earth's ozone layer. Credit: NASA

Carbon tetrachloride ($CCl_4$) was once commonly used as a cleaning agent and remains an important compound in chemical industry. $CCl_4$ is responsible for that sickly sweet smell associated with dry cleaning solvents from decades ago. It's a known air toxin and it eats away at the ozone layer—the gas accounts for about 10-15 percent of the ozone-depleting chemicals in the atmosphere today. As a result, production across the globe has been banned for many years for uses that result in $CCl_4$ escaping to the atmosphere.

Given these stringent limits, the chemical is being released into the air at small rates here in the United States, but a new study reports those rates are still 30 to 100 times higher than amounts reported to emission inventories.That study, led by CIRES scientist Lei Hu and NOAA scientist Stephen Montzka, also suggests that the source of the unexpected emissions in the U.S. appears associated with the production of chlorinated chemicals (such as those ultimately used to create things like Teflon and PVC). The new analysis is published today in the *Proceedings of the National Academy of Sciences*.

In the 1980s, when scientists discovered that CCl4 was contributing to the destruction of the ozone layer, the synthetic compound was included on a list of substances to be phased out of production. That list, part of the Montreal Protocol on Substances that Deplete the Ozone Layer, required that production for dispersive use (uses that would result in escape to the atmosphere) of CCl4 be discontinued in developed countries by 1996, and in developing countries by 2010.




Based on measurements made at sites indicated by the symbols, researchers derived US emissions of the ozone-depleting chemical carbon tetrachloride (CCl4). Emission rates were highest in three regions: The Gulf Coast, Denver, and San Francisco areas. Credit: CIRES/NOAA

Despite that phase out, the decline of CCl4 in the atmosphere has been unexpectedly slow. That left many scientists puzzled, including Montzka, who works in NOAA's Earth System Research Laboratory (ESRL) and is also a CIRES Fellow. "We've been scratching our heads, trying to understand why," he said. "When we look at the amounts produced and destroyed, which industry throughout the world has reported to the Ozone Secretariat, we would expect the chemical's global concentration to be decreasing at a rate of nearly 4 percent per year. But it's only decreasing at 1 percent per year. So what's happening?"

To investigate the U.S. contribution, Montzka, Hu and colleagues from NOAA, CIRES, and other scientific institutions studied observations made from NOAA's North American air sampling network. Since the late 2000s, they tracked the composition of the atmosphere from this network of nine tall towers and many more regular aircraft-sampling sites across North America. "We wanted to identify where these emissions were coming from, as well as their magnitude," Hu said.

She and her colleagues considered landfills, where residual amounts of $CCl_4$ might still be leaking from old fire extinguishers or solvent cans, given that $CCl_4$ was used for these purposes in the early to mid-1900s. The team looked at high-density population areas to determine if the use of bleach or chemicals in laundry or swimming pools might be responsible for the emissions they detected. They also checked into industrial sources—and here they had some help. The Environmental Protection Agency requires industries to report $CCl_4$ emissions. Hu and Montzka were able to compare that information against what they derived from their precise atmospheric measurements of $CCl_4$ concentrations across the country. The analysis of all those data suggests that the $CCl_4$ emissions arise from the same geographic areas as those industries reporting to the EPA. Not a huge surprise, but the amount found was 30 to 100 times higher than what was being reported. The most significant hot spot was the Gulf Coast region, with smaller emissions in Colorado and California.

"We can't tell exactly what the sources of emissions are," said Montzka. "It could be underreporting from known sources, it could be an unknown source, it could be both. It could be some other activity that's geographically tied to the production of chlorinated chemicals and products that hasn't been recognized previously as a significant source."

Hu and Montzka said they hope their work inspires more research, both here in the United States and internationally, to better pin down the

precise reasons for excess emissions. The researchers reported in the new paper that the United States has been responsible for about 8 percent of the overall global CCl4 emissions in recent years. If the processes that emit CCl4 in the U.S. also happen in other places, it would go a long way towards explaining the slow rate of decline of CCl4 in the global atmosphere.

"Before this work," said Montzka, "There'd been very little progress on understanding the mystery of continuing global emissions of CCl4. Now we have a better picture, at least in the United States, of where some of those emissions are coming from. That's the first step towards minimizing emissions in the future and speeding up the recovery of the ozone layer."

**More information:** *Proceedings of the National Academy of Sciences* (2016).DOI: 10.1073/pnas.1522284113

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