

MYSTERY IN THE OZONE LAYER

High above Earth, more than 20 miles above sea level, a diaphanous layer of ozone surrounds our planet, absorbing energetic UV rays from the sun. It is, essentially, **sunscreen for planet Earth**. Without the ozone layer, we would be bathed in dangerous radiation on a daily basis, with side effects ranging from cataracts to cancer.

People were understandably alarmed, then, in the 1980s when scientists noticed that manmade chemicals in the atmosphere were destroying this layer. Governments quickly enacted an international treaty, called the

Montreal Protocol, to ban the manufacture and use of ozone-destroying gases such as CFC (chlorofluorocarbon). On September 16, 1987, the first 24 nations signed the treaty; 173 more have signed on in the years since. CFC is an organic compound that contains carbon, chlorine, and fluorine, produced as a volatile derivative of methane, ethane, and propane. They are also commonly known by the DuPont brand name Freon. The most common representative is dichlorodifluoromethane. CFCs used to be widely used as refrigerants, propellants (in aerosol applications), and solvents that have now been replaced with other products such as hydrocarbons and CO₂. However, such products are similar in effect as pollutants. Fast forward 27 years. Ozone-depleting chemicals have declined and the ozone hole appears to be on the mend. The United Nations has called **the Montreal Protocol "the most successful treaty in UN history."** Yet, **despite Montreal's success, something is not ... quite ... right.**

New investigations show a surprising abundance of carbon tetrachloride in the ozone layer. Where is it coming from?

A new study by NASA researchers shows that a key ozone-depleting compound named carbon tetrachloride (CCl₄) is surprisingly abundant in the ozone layer.

Between 2007 and 2012, countries around the world reported zero emissions of CCl₄, yet measurements by satellites, weather balloons, aircraft, and surface-based sensors tell a different story. The new study shows worldwide emissions of CCl₄ average **39 kilotons per year, approximately 30 percent of peak emissions prior to the international treaty going into effect.**

In the 1980s, chlorofluorocarbons became well-known to the general public. As the ozone hole widened, "CFC" became a household word. Fewer people, however, have heard of CCl₄, a colourless liquid with a "sweet" smell once used in applications such as dry cleaning and fire-extinguishers. It is the 3rd most important anthropogenic ozone-depleting compound behind CFC-11 and CFC-12. Levels of CCl₄ have been declining since the Montreal Protocol was signed, just not as rapidly as expected. With zero emissions, abundances should have dropped by 4% per year. Instead, the decline has been closer to 1% per year.

To investigate this discrepancy, the CCl₄ data gathered by NOAA and NASA was plugged it into a NASA computer program, the 3-D GEOS Chemistry Climate Model. This sophisticated program takes into account the way CCl₄ is broken apart by solar radiation in the stratosphere as well as how the compound can be absorbed and degraded by contact with soil and ocean waters. Model simulations pointed to an unidentified ongoing current source of CCl₄. **It is now apparent there are either unidentified industrial leakages, large emissions from contaminated sites, or unknown CCl₄ sources.** Another possibility is that the chemistry of CCl₄ might not be fully understood. Tellingly, the model showed that CCl₄ is lingering in the atmosphere 40% longer than previously thought. It could be there something about the physical CCl₄ loss process that we don't understand. It all adds up to a mystery in the ozone layer.



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