The missing greenhouse gas

Growth of the electronics industry will boost emissions of a 'hidden' — but extremely potent — greenhouse gas. **Hannah Hoag** reports.

Our insatiable appetite for gadgets — mobile phones, MP3 players and flat-screen TVs — may be adding a hidden greenhouse gas to the Earth's atmosphere. Countries that ratified the Kyoto Protocol committed to reducing their emissions of carbon dioxide and five other heat-trapping gases: methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons and sulfur hexafluoride. But these aren't the only climate-altering chemicals being produced by human activity. In the 13 years since the Protocol was first drawn up, scientists have discovered that other gases, such as nitrogen trifluoride (NF_3), could become an increasing part of the climate problem.

The dominant use of NF_3 is in the manufacturing of semiconductors — an industry worth more than US$250 billion annually — where the gas was first introduced as an alternative to the perfluorocarbon C_2F_6, which has an atmospheric lifetime of 10,000 years and is nearly 9,000 times more powerful a greenhouse gas than carbon dioxide. Although it is primarily employed in equipment cleaning, NF_3 is also marketed as a plasma etchant for thin-film liquid crystal displays (LCDs) and thin-film photovoltaics, which convert the sun's energy into electricity.

Increasing demand for plasma products saw worldwide production of the gas surge in 2007. Air Products and Chemicals, Inc., a global supplier of industrial gases based in Hometown, Pennsylvania, bumped up its production of NF_3 from 2,000 tonnes to 3,000 tonnes. This increase looks likely to become a trend, as the company's planned expansion in the United States and Korea will see a further boost to 3,200 tonnes by 2009. Other companies, including Kanto Denka, DuPont, Formosa Plastics and Mitsui Chemicals, are following suit, each producing or planning to produce about 2,000 tonnes of the gas annually.

POTENTIAL HEAT

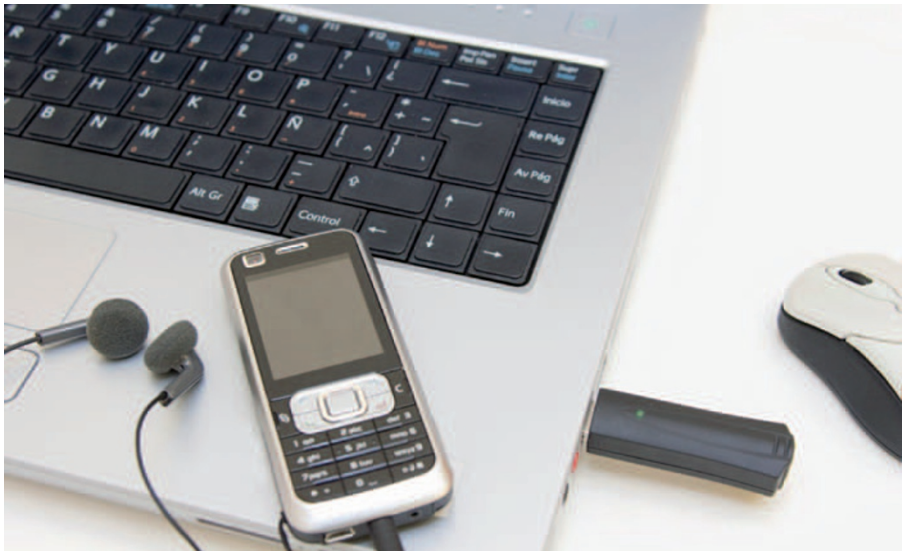
Though the gas goes unmonitored, a new study in the 27 June issue of *Geophysical Research Letters* shows that NF_3 is a 'missing greenhouse gas' with a high potential for global warming[1], and one that author Michael Prather says we should be keeping an eye on.

Prather, an atmospheric scientist at the University of California, Irvine, became curious about the potential of NF_3 to contribute to global warming during the drafting of the 2001 Intergovernmental Panel on Climate Change report[2]. "We said we'd look into it since we knew almost nothing," he says. "We need to try to figure out what is going on with the production of the gas and see if it is in the atmosphere."

Using a state-of-the-art model that follows the flow of the gas through the atmosphere in three dimensions, Prather and Juno Hsu calculate a new NF_3 lifetime of 550 years, about 25 per cent shorter than previous calculations, but "still beyond any societal time frames," they write. "The lifetime is shorter, which is good, but it is still long," says Prather.

Using the new lifetime, the 100-year global warming potential (GWP) of NF_3 also adjusts slightly, dropping from 17,200 to 16,800. The GWP is an index used to estimate the potential future impacts of a gas on the climate system. It represents how much a given mass of greenhouse gas is estimated to contribute to global warming, compared to an equal amount of carbon dioxide, which carries a GWP of 1. By this comparison, NF_3 is quite potent. "Fluorinated gases can absorb a lot of the Earth's outgoing radiation," says Keith Shine, an atmospheric scientist at the University of Reading and lead author of the 1995 IPCC report on climate change. "It has all the warning signs: large production, large lifetime and large global warming potential," says Prather.

If all the NF_3 produced this year were to be released into the atmosphere, it would be on par to adding 67 million tonnes of carbon dioxide to the air. In 2005, carbon dioxide emissions exceeded 15 billion tonnes globally. However, most of the NF_3 produced is destroyed and never reaches the atmosphere. Two earlier studies found that only two to three per cent of the gas escapes destruction after its use[3,4].



ANDRES BALCAZAR/ISTOCKPHOTO

A powerful but unmonitored greenhouse gas, nitrogen trifluoride, is used in the manufacture of LCD screens for many electronic gadgets.

John Langan, director of electronics technology at Air Products, says their experience with NF_3 indicates that the gas is destroyed with high efficiency. "The 97 percent destruction efficiency is at the lower end. We've measured 98 percent or 99 percent. To put it in perspective, the other chamber cleaning gases have destruction efficiencies from 30 to 70 percent," he says.

KEEPING WATCH

But Prather is sceptical about these numbers. He says the industry has a poor track record for self-reporting — a 1982 study found that atmospheric levels of the ozone-depleting gas CFC-12 didn't match estimates of the Chemical Manufacturers Association[5] — and that atmospheric levels of NF_3 should be measured and monitored. Although it is difficult to measure the gas, he aims to do just that.

Even if emissions are low, Prather believes caution is warranted because, like the ozone-destroying chemical CFC-12, NF_3 is long-lived and will take centuries to be removed. "Compared to all global CO_2, [the amount being produced] is small. But it is not small compared to the CO_2 emitted by things that we think are big," he says. For comparison, the 3,600-megawatt Scherer coal-fired power plant in Georgia, among the largest in the United States, generates 25 million tonnes of carbon dioxide annually. "All the little pieces add up. That's why we're looking at the pieces."

> Nitrogen trifluoride "has all the warning signs: large production, large lifetime and large global warming potential."
> Michael Prather

However, Shine says the study is overstated and uses extreme numbers. "It considers a scenario where all of it is emitted into the atmosphere. That is unlikely to happen," he says. But he does agree that NF_3 should be watched closely. "If there continues to be a massive growth in production, even if emissions are only 1 to 3 percent … it could become important. It could become a big part of national emissions," he says.

There are a whole host of gases in the atmosphere, from known and unknown sources, that have the potential to contribute to global warming, but only a handful were included in the Kyoto Protocol when it was first drafted in 1995. "It's rather strange that it has stuck to those gases and that we don't have a mechanism for bringing in new gases," says Shine.

"I don't think it should be included in Kyoto yet, to be honest — there is no point in adding gases to a treaty that we are still trying to get enforced," says Prather.

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