

Ozone depletion: Uncovering the hidden hazard of hairspray

A usual morning routine might include a spritz of hairspray, a spurt of shaving cream, or a spray of deodorant. We do these things almost automatically, not really even thinking about it. Aerosols are common, convenient, and harmless, right? It's hard to imagine that these everyday activities could be affecting the atmosphere ten miles above Earth's surface for the next hundred years, but in the 1970s, chemists Mario Molina and F. Sherwood Rowland (Fig. 1) discovered just that.

At the time, many normal household items contained CFCs—a class of chemicals that are made up of combinations of chlorine (C), fluorine (F), and carbon atoms (C). Developed in the 1930s under the trade name Freon, they were thought to be wonder chemicals. They are nontoxic, nonflammable, don't react with any common chemicals, and thus were assumed to be safe for the environment. When Molina and Rowland began their work, CFCs were used in all kinds of things—refrigerators, Styrofoam, and aerosols (like hairspray or cleaning supplies), to name a few (Fig. 2). Rather than assume, as others had, that CFCs had no effect on the environment, Rowland and Molina decided to scientifically examine the question of what happens to CFCs released into the atmosphere. What they found would not only alter the contents of hairspray, but would also earn them a Nobel Prize and change environmental policy the world over.

This case study highlights these aspects of the nature of science:

- Science is a community endeavor that benefits from a diverse and broad range of perspectives, practices, and technologies.
- Science helps us understand how our actions today are likely to affect future outcomes.
- Science affects our day-to-day lives.
- Data require analysis and interpretation. Different scientists can interpret the same data in different ways.
- Scientific ideas evolve with new evidence; however, well-supported scientific ideas are not tenuous.

The tip of the iceberg

The discovery of CFCs' environmental impact began in 1970, in the unlikely setting of a vacation home on the bucolic west coast of Ireland. James Lovelock (Fig. 3), a medical researcher turned self-employed scientist, wanted to know whether the haze obscuring the view from his home was natural or from human sources. He hypothesized that if pollution were causing the haze, then its source would be an urban area and it would contain large concentrations of synthetic chemicals. Since CFCs don't occur naturally, Lovelock thought that



Figure 1. At left, Mario Molina addresses the Mexican Senate in 2008. At right, F. Sherwood Rowland during a 2007 interview.



Figure 2. Examples of household items that used to contain CFCs.

Mario Molina photo courtesy of the Senado de la República de México; F. Sherwood Rowland photo by William J. Cooper, UC Irvine The following images are used under a Creative Commons Attribution-Share Alike 2.0 Generic license: spray can photo from Thomas Hawk's flickr photostream; refrigerator photo from SuziJane's flickr photostream; foam packing peanuts photo from ThrasherDave's flickr photostream

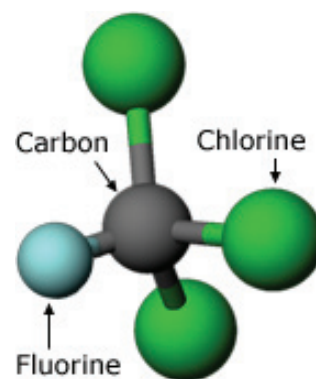
looking for these chemicals in the air would be a good test. Using an instrument he'd designed himself, he detected CFCs in the haze, confirming its human-made origins.

However, what really piqued his curiosity were the results on clear days. According to his hypothesis, on clear days, when the air was coming from over the Atlantic without having passed over an urban area for thousands of miles, CFCs should be close to undetectable. Surprisingly, he was easily able to detect CFCs even on pristine days. Wanting to know if CFCs were building up in the atmosphere everywhere, Lovelock brought his instrument on a sea voyage from England to Antarctica, taking measurements all along the journey. Wherever he traveled, he found CFCs.

Lovelock presented his findings in 1972 at a scientific meeting that aimed to bring together meteorologists and chemists—two sets of researchers which, up to this point, had mixed very little. There, his observations caught the attention of Sherwood Rowland, a chemist at the University of California, Irvine. Rowland was curious about what happened to these chemicals once they were released into the atmosphere. Even very stable chemicals can react under the right conditions; for example, even stainless steel will react when it's exposed to salty water and high temperatures. Rowland wanted to know what the right conditions were for CFCs to react and what effects this might have.

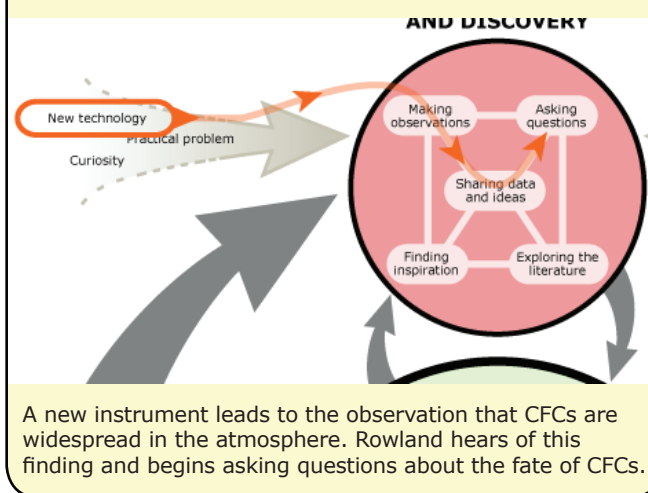


Figure 3. A 2005 photo of James Lovelock holding a key component of the device he built to detect airborne CFCs.



The molecular structure of trichlorofluoromethane (CCl_3F), a banned CFC once widely used as a refrigerant.

See how the ozone story corresponds to the science flowchart:



Putting the pieces together

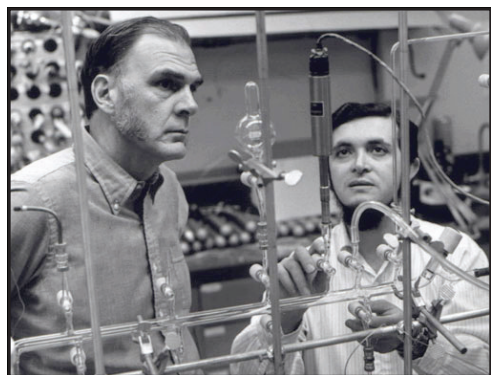


Figure 4. A 1970s photo of F. Sherwood Rowland (left) and Mario Molina in the lab.

Rowland was joined in his investigation by the newest member of his research group—Mario Molina (Fig. 4), a chemist fresh out of graduate school. Rowland had suggested a few different topics for a first project and Molina thought that investigating the fate of CFCs released into the environment was the most interesting of the bunch. Excited to learn about a new field—atmospheric chemistry—Molina plunged right in. As is expected of a scientist, he began with a thorough review of the scientific literature on the subject; perhaps someone else had investigated a chemical reaction that would affect CFCs. He found that many chemicals are broken down in the lower atmosphere near where they are released—but not CFCs. No known chemical processes seemed to be able to affect CFCs in the lower atmosphere.

James Lovelock photo by Bruno Comby, EFN (Environmentalists For Nuclear Energy); Rowland and Molina photo courtesy of the University of California Irvine

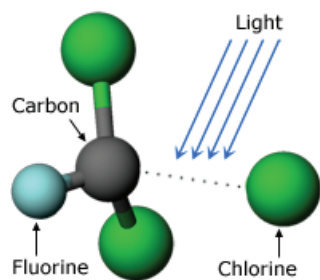


Figure 5. CFCs like trichlorofluoromethane (CCl_3F) break down when exposed to solar radiation in the upper atmosphere, freeing up chlorine atoms.

He wondered what might happen to CFCs as they drifted upwards. At low altitudes, much solar radiation has been filtered out by the atmosphere, but at high altitudes, solar radiation is much more intense. From his understanding of chemistry, Molina knew that once any molecule got high enough, strong solar radiation would break it apart (Fig. 5). Using atmospheric scientists' discoveries about air movement, Molina calculated that it would take somewhere between 40 and 150 years for a CFC molecule to randomly diffuse up to the height where it would be broken down by solar radiation, releasing a chlorine atom in the process.

To find out what would become of this chlorine atom, Molina searched through other scientists' publications to see what atmospheric molecules would be near this chlorine atom when it split off.

Among the many possibilities, one molecule stood out: ozone—three oxygen atoms linked together. Molina learned that chlorine would react catalytically with ozone—meaning that the chlorine atom could act like an axe, encouraging a reaction that chops up ozone without hurting the chlorine at all. In fact, a single chlorine atom could destroy around 100,000 ozone molecules (Fig. 6)! Molina wasn't sure how big a difference this would make in the atmosphere, so he compared effects of CFCs to natural ozone depletion mechanisms investigated by other researchers. He found that CFCs could lead to even more ozone destruction than the natural mechanisms did!

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Sounding the alarm

The ozone layer protects Earth from dangerous UV radiation (Fig. 7)—which can cause mutations. In humans, a depleted ozone layer would likely mean higher rates of skin cancer, cataracts, and immune system problems. Further, an increase in UV radiation could affect plants and marine ecosystems in unpredictable ways—which could, in turn, trigger other ecological changes. Because it seemed that CFCs could destroy our protective ozone shield, Molina and Rowland were alarmed! But they were also skeptical: if this ozone destruction were actually going on, why hadn't atmospheric scientists discovered it already? After checking their calculations, they decided to consult a colleague in atmospheric chemistry and learned that, only a few months earlier, researchers had found the same chlorine-ozone interaction in the exhaust from space shuttles—a very small cause of ozone destruction compared to CFCs. After being assured that their findings warranted serious concern, Molina and Rowland published their work.¹ Then, to increase the likelihood that action would be taken on these disturbing results, they took their findings to the news, media, and policymakers, calling for a ban on the production and use of CFCs. But they didn't stop there ...

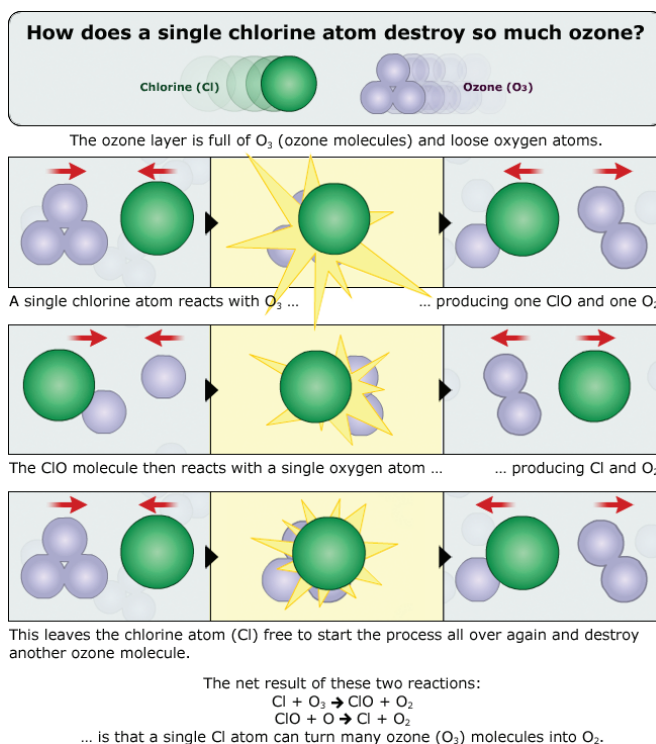


Figure 6.

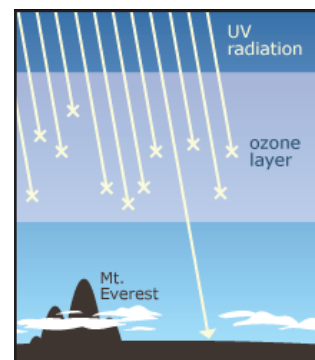
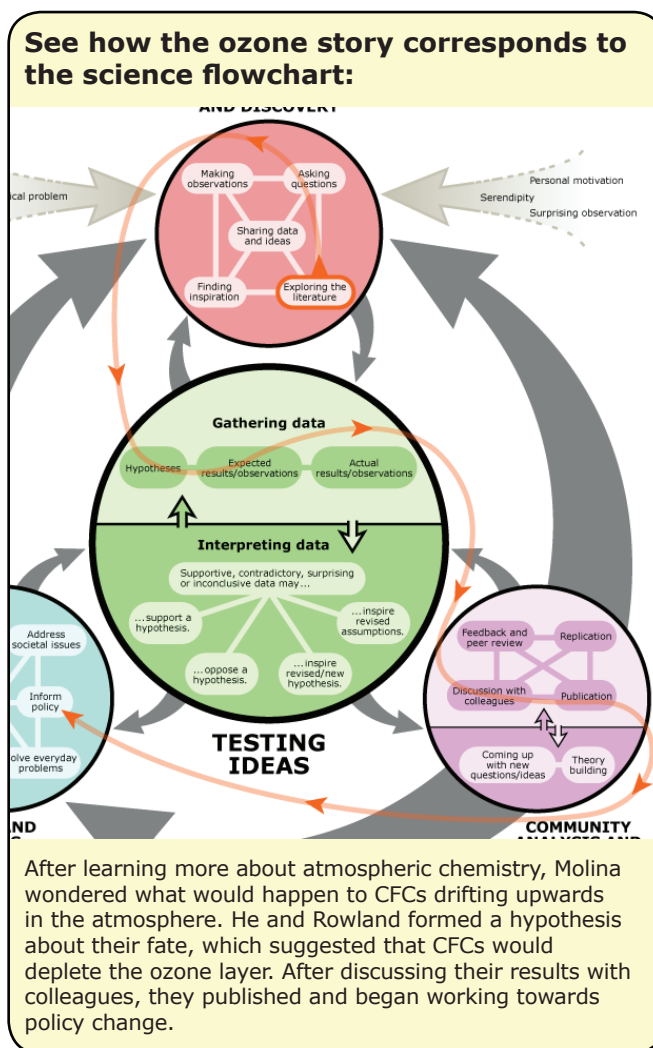


Figure 7. The ozone layer protects the Earth's surface from UV radiation.

¹Molina, M.J., and F.S. Rowland. 1974. Stratospheric sink for chlorofluoromethanes: chlorine atom-catalyzed destruction of ozone. *Nature* 249:810-812.



The devil in the details

Though the stereotype of scientific progress is that it's driven by critical new evidence, Molina's breakthrough, like many efforts in science, was a bit different. He didn't perform any experiments or gather any new data. Instead, he took on the tough job of pulling together a lot of existing facts and hypotheses about chemical reactions, atmospheric processes, and CFC levels, to show that if all the individual facts and hypotheses were accurate, the result would be a serious environmental threat. It was the sum of this scientific evidence that provided him with nearly all the information he and Rowland used to form their hypothesis about how CFCs could affect atmospheric ozone. All they had needed to do was to use known chemical theory to calculate an estimate for the long-term effects of CFCs on ozone.

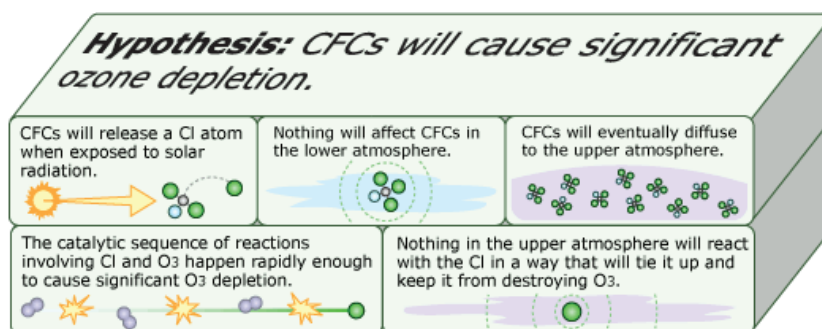


Figure 8.

Molina and Rowland's over-arching hypothesis (that releasing CFCs into the atmosphere would cause significant ozone depletion) was based on many supporting hypotheses (sometimes called auxiliary hypotheses or as-

sumptions) (Fig. 8). For example, one of the sub-hypotheses contained within the Molina-Rowland hypothesis was how fast chlorine reacts with ozone. These sub-hypotheses were backed up by their own lines of evidence, but also came with their own uncertainties. If a key sub-hypothesis turned out to be false, it could mean that Molina and Rowland's over-arching hypothesis about ozone depletion was also false. In fact, some scientists were skeptical of the importance of ozone depletion due to CFCs, not because they doubted Molina and Rowland's work, but because they were skeptical of some of the sub-hypotheses. For example, at the time the paper was published, there was not yet any experimental evidence to support the idea that CFCs would release a chlorine atom when exposed to solar radiation. It did not take long before this hypothesis was checked in a laboratory experiment and confirmed. However, some of the other hypotheses were not so easy to test, and a lot of hard work would be needed to persuade skeptics.

Making models

To overcome skepticism and convince other scientists and policymakers of the importance of the Molina-Rowland hypothesis, they needed to test their ideas with actual atmospheric evidence. However, figuring out just what evidence to look for was tricky (Fig. 9). Sometimes the expectations generated by a particular hypothesis are obvious (e.g., if you hypothesize that smoking causes lung cancer, you'd expect smokers to have

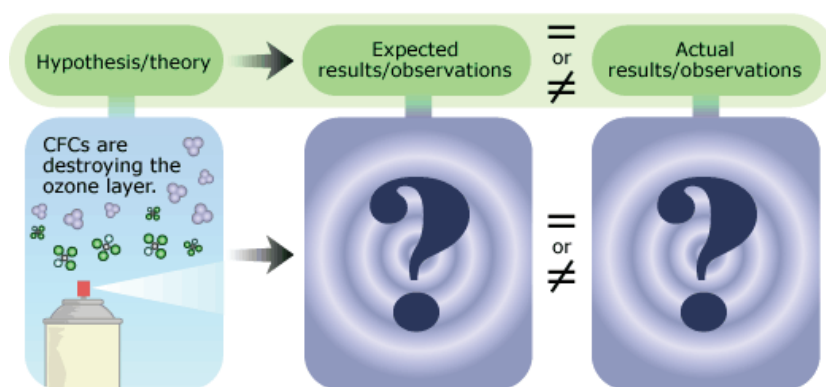


Figure 9.

higher rates of lung cancer than non-smokers)—but in this case, it was much more complicated. In fact, atmospheric interactions are so complex that the full implications of the hypothesis couldn't be worked out by hand. Instead, scientists relied on mathematical models of the atmosphere which could be studied using computers.

WHAT'S A MATHEMATICAL MODEL?

“Model” can mean several different things in science, but as a research method, modeling often means creating a mathematical model—a set of equations that represents a real system. That system could be any aspect of the natural world—from the movement of molecules in a balloon, to the connections among neurons in your brain, to the interactions among species in an ecosystem. For example, a simple mathematical model of a species interaction might describe how the number of rabbits is related to the birth rate of the rabbits and the number of wolves present (Fig. 10). A more complex model of the same system could include more information, such as the effects of hunting, how the number of rabbits affects the wolves' birthrate, and how rabbit grazing affects their food supply. Though scientists try to limit the factors represented in models to the ones essential for their purposes, these sets of equations are often so complex that they require a computer to solve.

To create a mathematical model, scientists must

Modeling the rabbit/wolf relationship:

$$x' = (b - py)x \quad y' = (rx - d)y$$

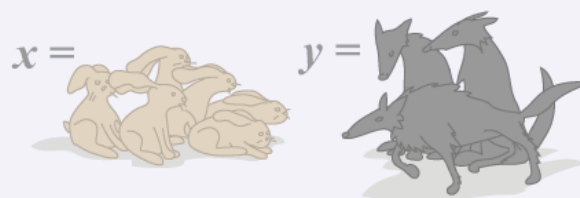


Figure 10.

first gather all the relevant information on the system. In the case of the ecosystem model, this might mean knowledge of how rabbits and wolves interact. Atmospheric models relating to CFCs, on the other hand, were based on information about how molecules move through the atmosphere, what chemical reactions occur there, the concentrations of the atmosphere's chemical constituents, etc. This information was combined with basic principles, like conservation of energy, to create a set of equations that represents the behavior of the real-world system—the atmosphere.

Models are based on sets of hypotheses about how a system works. The wolf-rabbit model is essentially a hypothesis about how the two species interact and how these interactions affect their numbers. The CFC-atmosphere models represent a set of hypotheses about how molecules interact with one another as they move through the atmosphere. Models, and the hypotheses within them, are supported when the model generates expectations that match the behavior of its real-world counterpart—e.g., if removing hunting from the model has a similar effect to that observed in the real world when wolves are protected from hunting (Fig. 11). If a model is supported and seems to be a good representation of the real world, we can use it to answer “what if” questions: What would happen to rabbit populations if we allowed wolf hunting in particular areas—or more pertinently for Molina and Rowland, what would happen in 50 years if we continued CFC production at 1974 rates?

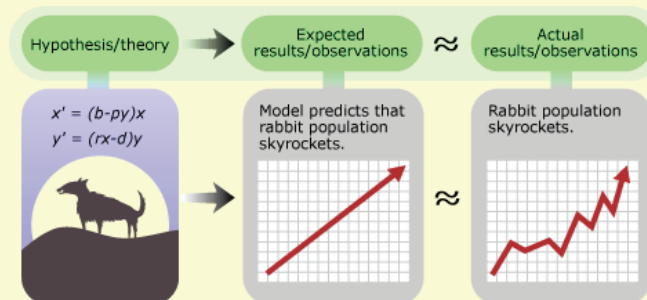


Figure 11.

Several groups of scientists added Molina and Rowland's proposed set of reactions to their models of the atmosphere, and used the models to generate expectations about what should be going on in the atmosphere if the model and reactions were correct. Now, they just needed to find out if observations matched the models' predictions ...

Evidence at last

One of the benefits of a large, diverse scientific community is that many scientists can simultaneously work on the same problem from different angles. Some scientists worked in labs refining the sub-hypotheses contained within the models and the Molina-Rowland hypothesis. Some worked on developing more sophisticated models that could more accurately determine the expected results. And others worked on getting atmospheric measurements to test the hypothesis.

Ozone levels fluctuate so widely that it is difficult to detect subtle trends over a short-term period, as shown by these ozone measurements for the atmosphere over Switzerland taken between 1926 and 1975.

The ultimate test of the Molina-Rowland hypothesis would be finding actual ozone depletion, but in 1975, that evidence was not easy to come by. First of all, according to the models, it would take a long time for CFCs to move high enough in the atmosphere to be broken down—and that means that we should expect a delay between when CFCs are released and when the ozone layer is damaged. Secondly,

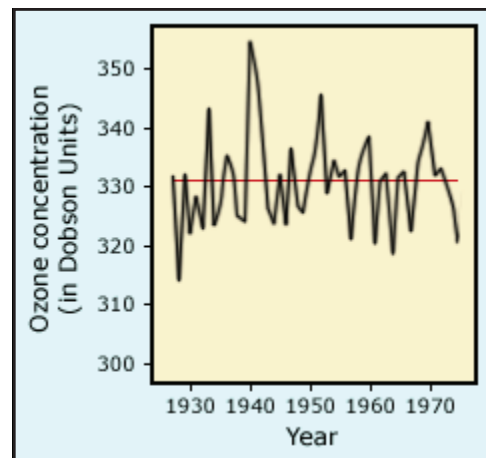


Figure 12. Ozone levels fluctuate so widely that it is difficult to detect subtle trends over a short-term period, as shown by these ozone measurements for the atmosphere over Switzerland taken between 1926 and 1975.

ozone levels fluctuate naturally (Fig. 12)—up to 10% given the season, time of day, and the sun’s energy output—and all this variation makes it more difficult to detect subtle changes in average ozone level. The Molina-Rowland hypothesis predicted that, even with the delayed reaction, some ozone depletion would have occurred by 1975, but it would have been impossible to separate from all the natural fluctuations in ozone levels.

Instead, scientists turned to a different expectation generated by the models: the levels of CFCs that ought to be found at different altitudes. According to the models, CFCs should be completely unaffected in the lower atmosphere but destroyed by solar radiation at higher altitudes. In 1975, using high-flying aircraft and balloon-borne instruments, two independent groups of scientists measured CFC concentrations at different altitudes. Their results confirmed that CFCs

reached the upper atmosphere in amounts consistent with the idea that CFCs are unscathed by their journey through the lower atmosphere. The results also showed that, as CFCs moved through the upper atmosphere, they were being destroyed at the rates predicted by the Molina-Rowland hypothesis (Fig. 13).

Despite this evidence, some weren’t convinced that a ban on CFCs was the right action. Given the large economic impact of a ban—it was estimated that industries relying on CFC production generated \$8 billion in business and employed 200,000 people in 1974—several scientists in the field advocated waiting a few years for science to make more progress on the issue before making any policy decisions. They didn’t doubt the scientific validity of the hypothesis, just the wisdom of a ban. CFC manufacturers, on the other hand, were trying to cast doubt on the Molina-Rowland hypothesis any way they could. Industry spokespeople repeatedly downplayed the idea as “just a hypothesis,” neglecting to mention the evidence supporting it. The industry also brought out their own “expert” to challenge Molina and Rowland’s ideas, sponsoring a month-long speaking tour for Richard Scorer—a professor well known for his research on pollution, a lower atmosphere phenomenon. Despite all the hype from the CFC industry, the facts that Scorer had not published a single scientific paper on the chemistry of the upper atmosphere or conducted any research within the field made him an untrustworthy source of information on the Molina-Rowland hypothesis.

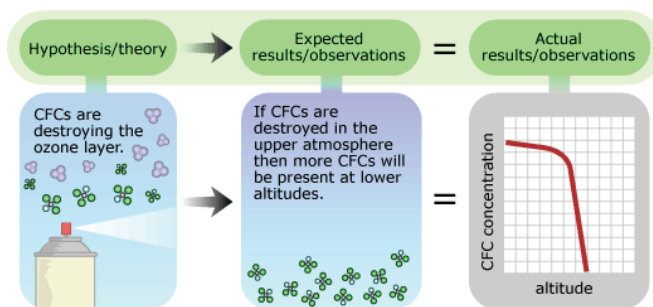
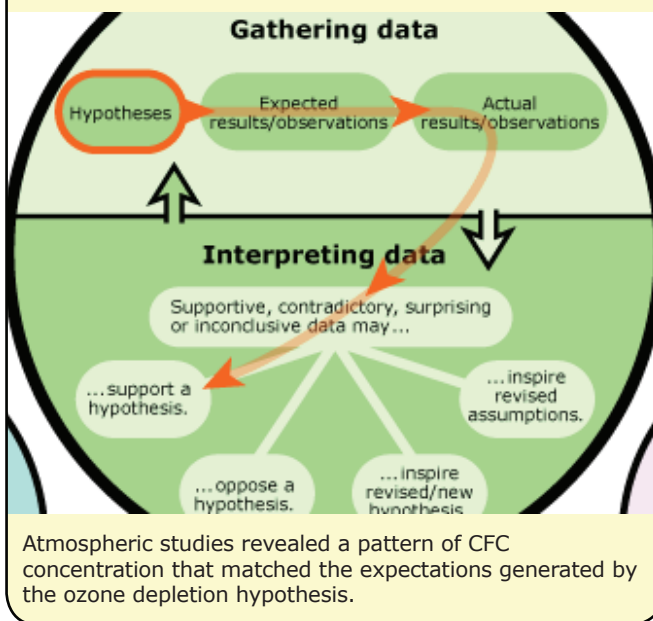


Figure 13.

See how the ozone story corresponds to the science flowchart:



A wrench in the gears

Things were looking good for Molina and Rowland’s hypothesis—but bad for the ozone layer. Their ideas now had supporting atmospheric evidence and were gaining acceptance within the scientific community. However, a hallmark of scientific thinking is skepticism—even towards your own hypotheses. Though it was supported

by many lines of evidence, Molina and Rowland didn't assume that their hypothesis was correct, but continued looking for processes in the atmosphere that might offset the effects of CFCs.

One possibility was nitrogen dioxide. Scientists knew that nitrogen dioxide could react with chlorine—the atom from CFCs that actually breaks down ozone—and potentially tie up the destructive atom in a harmless form: chlorine nitrate (Fig. 14). However, Molina and Rowland hadn't taken this reaction into account earlier because 1950s measurements had indicated that chlorine nitrate is short-lived—that is, shortly after it is formed, it will be broken down by sunlight, releasing the harmful chlorine back into the atmosphere. Now, Molina and Rowland decided to check those old measurements with more lab experiments. They found that chlorine nitrate stuck around much longer than previously thought and might be able to take chlorine atoms out of commission.

This reaction needed to be considered in the atmospheric models. Even though these findings cast doubt on their hypothesis, they quickly brought this information to the attention of the scientific community, reporting and publishing their results.

As researchers rushed to incorporate chlorine nitrate into their models (Fig. 15), they encountered some surprises. Several groups were involved in testing the Molina-Rowland hypothesis, and up to this point, all of them had agreed on what should be observed in the atmosphere if Molina and Rowland were right. But once the modelers added the chlorine nitrate reactions to their models, different groups got conflicting results. Some models even predicted a net increase in ozone!

What could be going on? The problem was traced to an approximation used as a means of simplifying some of the models. Scientists try to limit the factors represented in models to the ones essential for their purposes. Often this is because overly complex models can require calculations that would take a computer, even a supercomputer, years to complete. Scientists use their background knowledge to try to figure out what simplifications might be appropriate for a particular model and then try to check their validity. These simplifications form another set of sub-hypotheses. If a model is inaccurate, it might be because one of the central ideas in the model is wrong, or it might be because one of its approximations gives an oversimplified result.

In the case of the atmospheric models, scientists found that those models predicting a net increase in ozone had one thing in common: they all used the approximation that the sun shines at its average intensity all

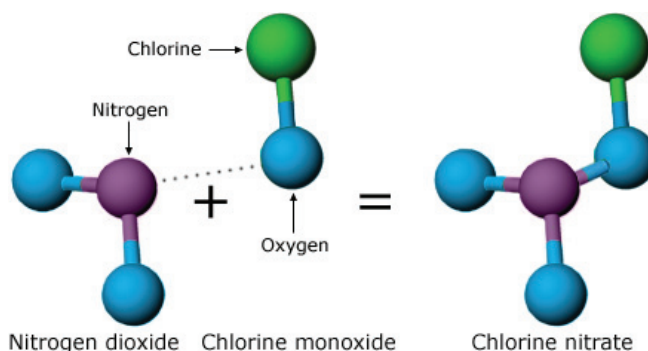


Figure 14. In the presence of another molecule to serve as a catalyst (not shown), nitrogen dioxide (NO_2) and chlorine monoxide (ClO), a byproduct of the breakup of ozone molecules by CFCs, react to form chlorine nitrate (ClONO_2). Sherwood and Molina found that chlorine nitrate did not break down in the atmosphere as quickly as they had thought—could the formation of this molecule actually decommission ozone-damaging chlorine atoms?

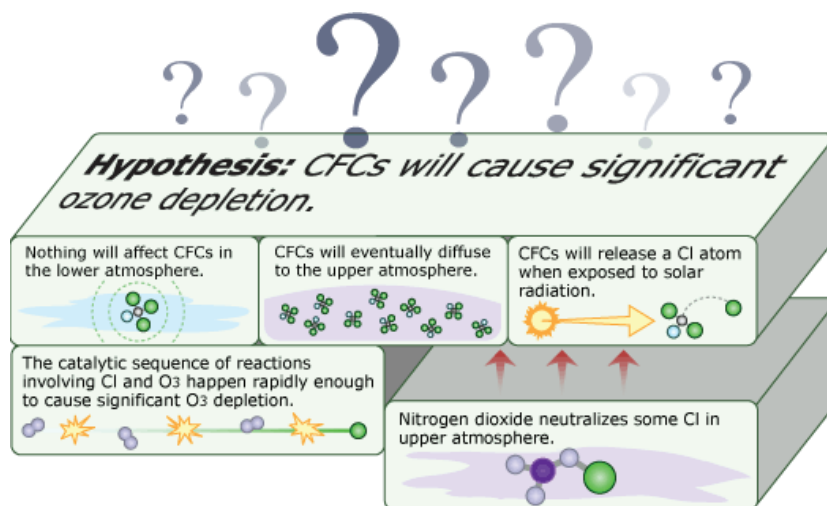
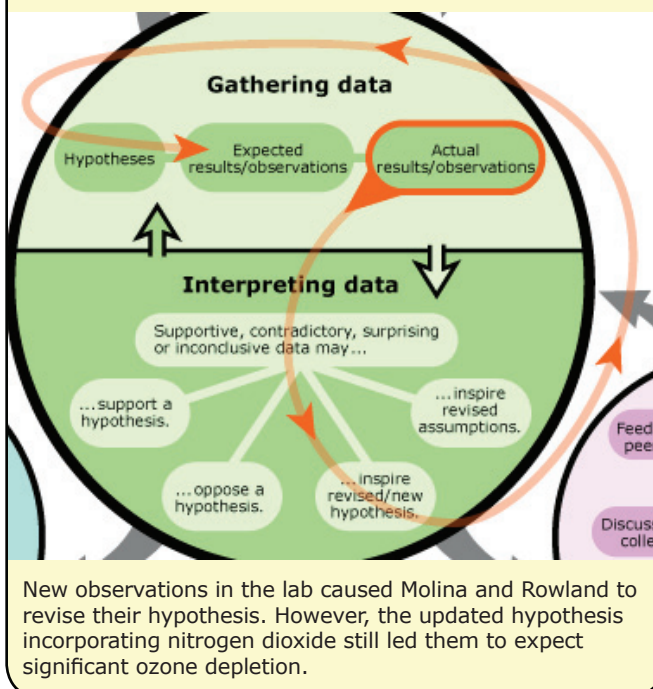


Figure 15. Researchers needed to incorporate nitrogen dioxide into the hypothesis—but they weren't sure how it would affect the expectations generated by the hypothesis. Would we still expect to see significant ozone depletion?

the time, instead of varying throughout the day. This turned out to be an oversimplification—an incorrect sub-hypothesis. Removing this approximation brought these models into agreement with the other models and the actual atmospheric measurements of chlorine nitrate. Even with the chlorine nitrate reactions incorporated into the models, the Molina-Rowland hypothesis predicted significant (though lower) levels of ozone depletion.

See how the ozone story corresponds to the science flowchart:



The evidence mounts

With one major hiccup resolved and a better understanding of the atmosphere, Molina and Rowland were ready for the next test of their hypothesis. The object of attention was chlorine monoxide (Fig.

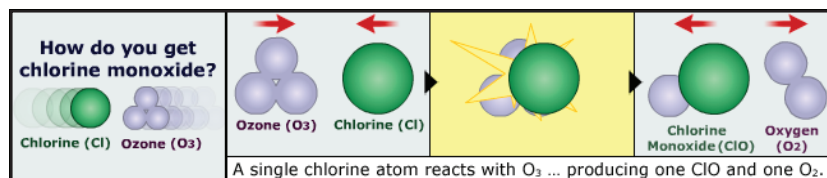


Figure 16.



Figure 18. High-altitude balloons carry sensitive measuring devices into the upper atmosphere to check on ozone levels.

16)—one of the products of ozone destruction. Since there is no other known source of chlorine monoxide, finding this chemical in the upper atmosphere would strongly support the idea that chlorine is destroying ozone (Fig. 17). However, the amount of chlorine monoxide scientists were looking for was miniscule—it would be like trying to detect a single drop of dye in an Olympic-sized swimming pool full of water.

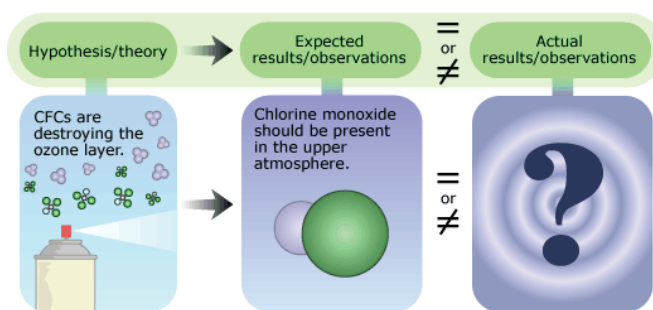


Figure 17.

The task was even more challenging because the sensitive instruments necessary to detect the molecules had to be ballooned up into the atmosphere, take measurements quickly, and survive the parachute ride back down to earth (Fig. 18). Despite these difficulties, atmospheric scientist James Anderson succeeded in getting

Ozonesonde photo from NASA/Goddard Space Flight Center's SHADOZ website

the critical evidence. Announced in late 1976, his results showed a ratio of chlorine to chlorine monoxide that was very close to the value expected if the Molina-Rowland hypothesis were accurate.

This evidence was summed up in a report on CFCs requested by the federal government—the dire outcome predicted by the Molina-Rowland hypothesis had attracted more than just scientific interest. Given the growing body of scientific evidence in support of the Molina-Rowland hypothesis, the government felt it was time to act. On May 11, 1977 the US government announced a timetable for phasing out CFCs in aerosols. Canada, Norway, and Sweden followed suit shortly after. With the aerosol phase-out in place and increased monitoring of the world's ozone level, things seemed to be moving in the right direction. But that momentum soon dissipated and failed to inspire further policy changes. In fact, the world production of CFCs dipped only slightly before beginning to grow rapidly again in the early 1980s (Fig. 19). Molina and Rowland advocated a total ban on CFC production from all sources (not just aerosols), but policymakers were not responding. Despite stalls in environmental action, the two continued their efforts to fully understand ozone depletion, motivated by both scientific interest and a desire to prevent a potential environmental disaster. In the meantime, a key piece of evidence was revealing itself in an unlikely place ...

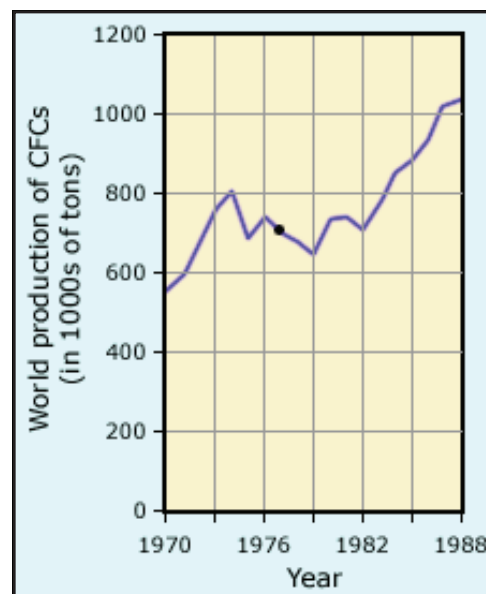
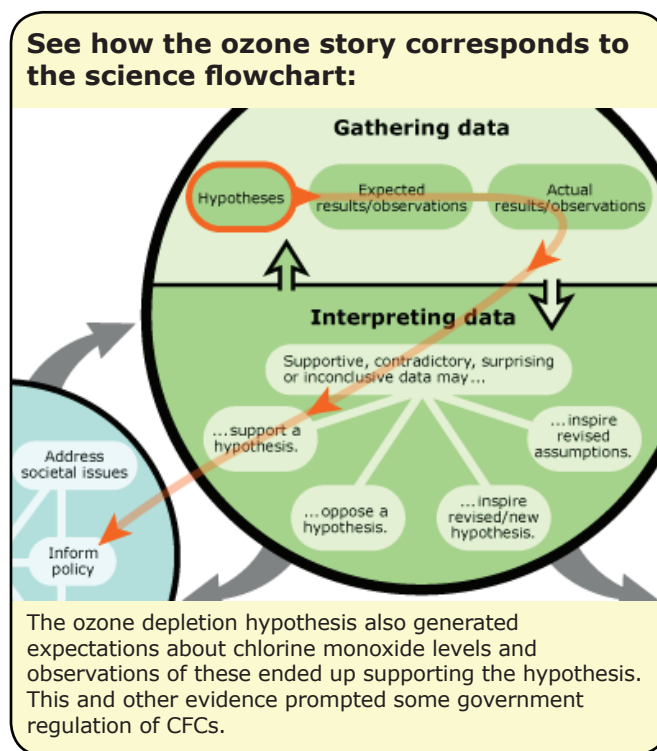


Figure 19. A graph showing world production of three major CFC types between 1970 and 1988. The dot marks the year (1977) that the US phaseout of CFCs was announced.



An undeniable problem in Antarctica

Researcher Joseph Farman (Fig. 20) had been collecting atmospheric data at Halley Bay, Antarctica since 1957. Every year he sent a team of research assistants to measure ozone levels and concentrations of trace gases like

CFC production graph adapted from the United Nations Environment Programme website—Global Environment Outlook

CFCs. In 1982, his ozone reading showed a dramatic dip—around 40%. Rather than being alarmed, he was skeptical of the data and thought it must be an instrument malfunction. The machine was notoriously difficult to keep working in the severe Antarctic cold, and this particular instrument was old. Besides, he reasoned, NASA scientists had satellites collecting atmospheric data from all over the world, and they hadn't reported any anomalies. Farman's instrument was ground-based and only had one data point—the part of the atmosphere directly above it. Surely NASA's thousands of data points would have revealed a drop in ozone if there had been one. Farman ordered a new instrument for next year's measurement.

But the following year, Farman still found a drastic decline. He dug up his old data and found that the decline had really started back in 1977 (Fig. 21). Now Farman suspected that something odd was happening strictly over Halley Bay, leaving other areas unaffected. So the next year, his team took measurements from a location 1,000 miles northwest of Halley Bay. Even there, a large decline in ozone occurred. The mounting evidence was undeniable. Farman decided it was time to publish his data.

Why hadn't NASA's satellite caught this plunge in ozone levels? Much to their chagrin, NASA scientists realized that they did have data indicating ozone loss but had overlooked it. Since their satellite recorded data 24 hours a day, it supplied scientists with information much faster than they could analyze it. To deal with this deluge, a data processing program had been set up to filter out all measurements below or above cut-off values that were considered to be impossible for actual ozone measurements. This program was based on the assumption that these "impossible" measurements were due to instrument malfunctions. The two groups of scientists (Farman's group and the NASA group) looked at the same data, but interpreted them differently because of their data analysis techniques. Farman's group concluded that the data reflected real changes in ozone, while the NASA group had concluded that the data reflected an instrument problem.

Farman's evidence showed NASA's group the problem with their data analysis procedure. When NASA scientists reanalyzed their Antarctic measurements, they discovered a gigantic hole in the ozone layer—a region of depleted ozone the size of the United States (Fig. 22)! Our protective shield from solar radiation had already been damaged even more than scientists had thought possible. The ozone depletion in Antarctica was real, but why was it so much larger than any of the models had predicted?

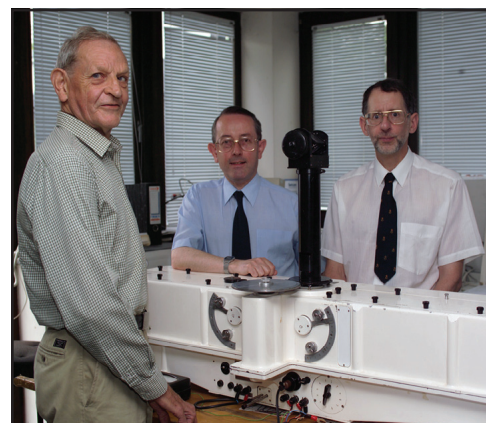


Figure 20. Joseph Farman (left) with his 1985 co-authors, Brian Gardiner and Jonathan Shanklin, and a spectrophotometer used to measure stratospheric ozone concentrations.

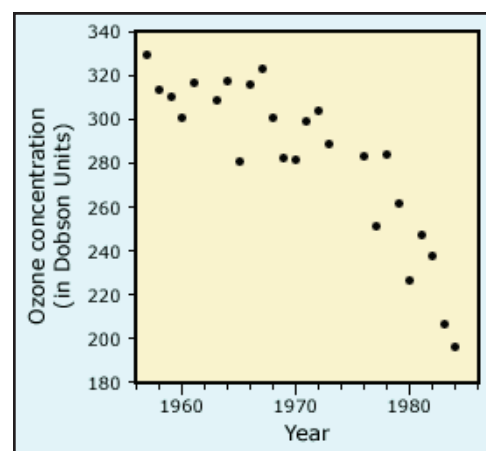


Figure 21. Average October ozone levels recorded by Farman's group at Halley Bay, Antarctica, from 1957 through 1984.

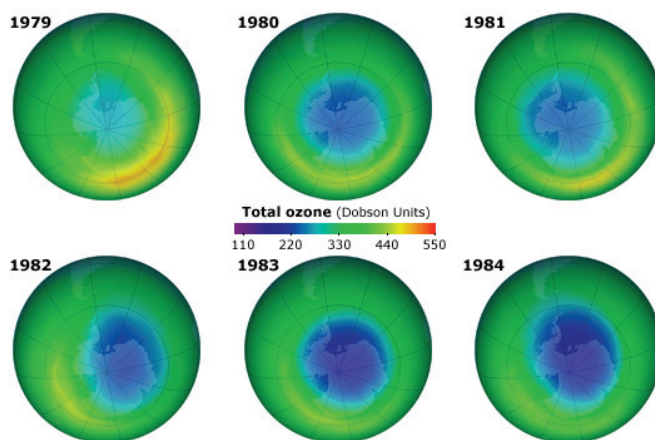


Figure 22. These maps, generated from NASA satellite data, show the growing hole in the ozone layer over Antarctica for each October from 1979 to 1984. These correspond well with Farman's measurements which show a significant decline in ozone for this period.

Photo of Farman, Gardiner, and Shanklin © British Antarctic Survey, used with permission; graph adapted from Figure 2a in Farman, J.C., B.G. Gardiner, and J.D. Shanklin. 1985. Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction. *Nature* 315:207-210; Antarctic ozone hole images courtesy of NASA

Dynamite in a fluffy package

The shocking Antarctic ozone losses had many scientists intrigued, including atmospheric chemist Susan Solomon (Fig. 23, left). Based on her expertise in modeling atmospheric chemistry and air movements, Solomon suspected that some unknown chemical processes involving CFCs or CFC products were causing these losses. Racking her brain for something that might be missing from the models, Solomon recalled an unusual phenomenon that occurs in Antarctica: high-altitude clouds of ice particles, called polar stratospheric clouds (Fig. 24), that form in the ozone layer. Curious, she and colleague Rolando Garcia (Fig. 23, right), a fellow atmospheric scientist, built an atmospheric model that included these polar clouds, with the ice particles providing a solid surface on which reactions could occur.

This seemingly small change in the hypothesis led to big changes in the results—the model was now predicting a large ozone loss. It looked like the presence of these tiny ice crystals made the destruction of ozone from CFCs much more efficient. With some preliminary results in hand, Solomon contacted Rowland. As it happened, Rowland was also wondering what would happen if solid surfaces were added into atmospheric models. Through laboratory experiments, he had already found that some key reactions (e.g., the release of destructive chlorine from ozone-friendly chlorine nitrate) occurred more readily on the surface of solids like glass and Teflon—and by extension, perhaps also ice from polar clouds.

Since Rowland was on a similar track to Solomon and Garcia, they decided to collaborate. With their proposed reactions, they explained how ice particles could not only free ozone-destroying chlorine, but also tie up the chemicals that could take chlorine out of commission, like nitrogen dioxide (Fig. 25). The model they created with these reactions was able to match the Antarctic ozone observations, but more evidence was needed to determine if the ice clouds were really to blame for the extent of ozone destruction in Antarctica.



Figure 23. Researchers Susan Solomon, at left, and Rolando Garcia, at right, examined how ice particles in polar stratospheric clouds might affect ozone depletion.

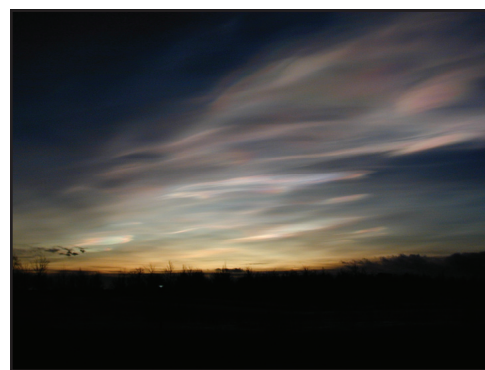


Figure 24. Polar stratospheric clouds over northern Sweden.

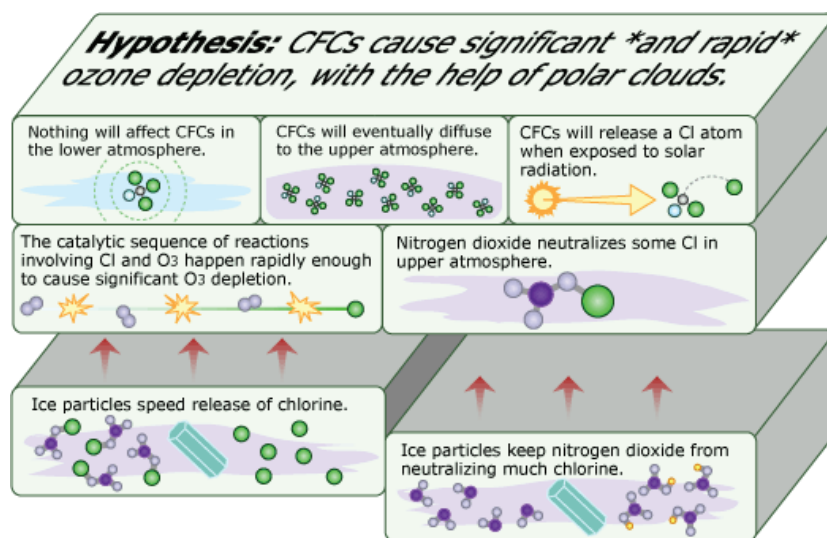
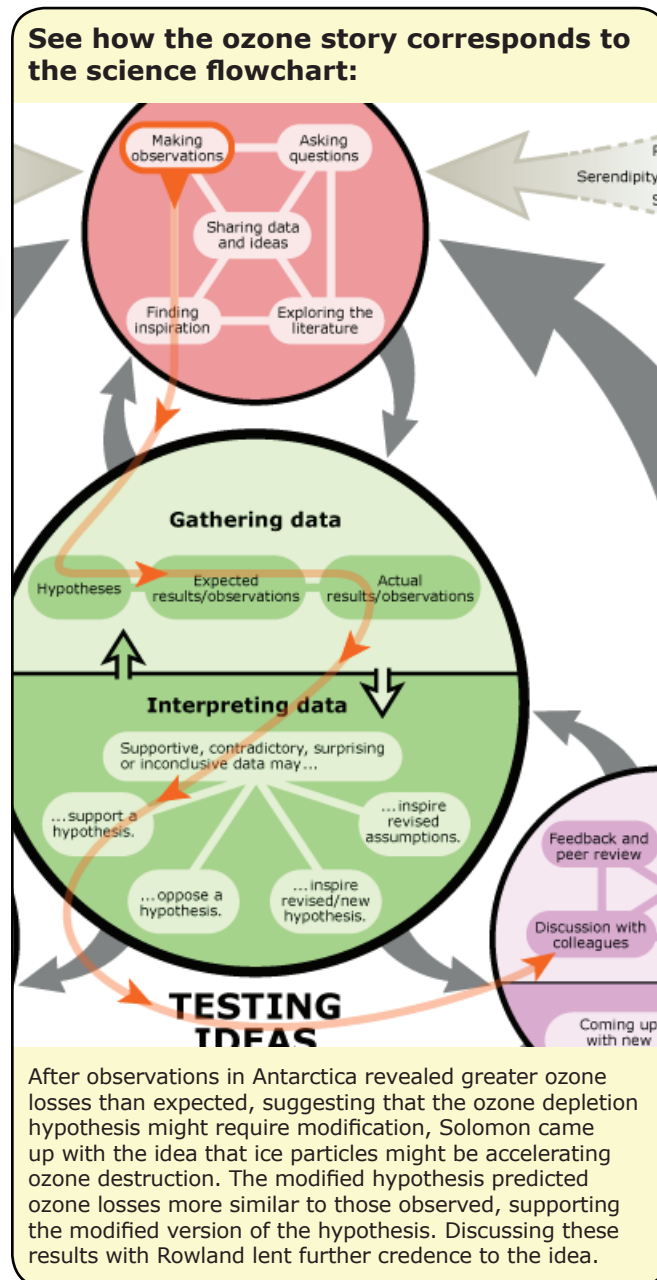


Figure 25. Rowland, Solomon, and Garcia's work suggested a modification to the original hypothesis: CFCs cause significant ozone depletion—and they do it much more rapidly with the help of polar clouds.

Susan Solomon photo courtesy of Dr. Solomon; Rolando Garcia photo courtesy of Dr. Garcia; polar stratospheric clouds photo by Lamont Poole, NASA Langley Research Center



Atmospheric evidence

The modified Molina-Rowland hypothesis (that CFC-related reactions, sped up by polar clouds, were leading to ozone losses) helped to inspire a flurry of experiments and atmospheric studies. These investigations produced several different lines of evidence, which turned out to support the updated hypothesis:

- **Evidence that the proposed reactions actually happen on ice:** Molina created a thin film of ice in a narrow glass tube and blew chlorine-containing chemicals into it. Sure enough, the proposed reactions ensued. Molina then went on to show that these reactions occur much more quickly than previously thought.
- **Evidence that reactions on ice particles actually take place in the atmosphere:** If the revised hypothesis were correct, scientists would expect that the abundances of chlorine monoxide and nitrogen dioxide (among other chemicals) would be affected by reactions on ice. Measurements of atmospheric chlorine

monoxide revealed values about 100 times too large to be accounted for unless ice particles played an important role. Measurements of nitrogen dioxide provided similar evidence in support of reactions on ice particles.

- **Evidence that increased ozone loss occurs whenever icy polar clouds are present:** These clouds also form in the Arctic. If reactions on ice particles in these clouds really are to blame, then we'd expect to see ozone depletion in the Arctic as well—although less severe than in Antarctica, since the clouds are less common around the North Pole. Observations revealed exactly what the updated hypothesis predicted they would: a lesser degree of ozone depletion in the Arctic (Fig. 26).
- **Evidence that chlorine is causing the ozone depletion:** According to the hypothesis, when CFCs break down they produce chlorine, which destroys ozone and generates chlorine monoxide. So scientists reasoned that if these reactions were occurring, ozone levels should be low where chlorine monoxide levels are high and vice versa. James Anderson was able to get this critical data by situating his measurement instrument on the wing of a plane (Fig. 27) flying through the Antarctic ozone hole. Just as predicted, ozone was low where chlorine monoxide was high, strengthening the link between chlorine and ozone depletion (Fig. 28).

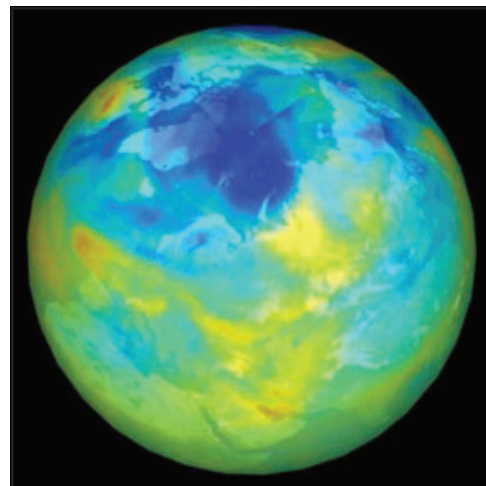


Figure 26. In this NASA image of the Arctic, blue regions represent the decrease in observed ozone levels between the early 1980s and the 1999-2000 winter.

The evidence gathered from these and other investigations, collected by many different people over the course of a decade, ultimately supported the hypotheses that chlorine, predominately from CFCs, was the primary cause of the Antarctic ozone loss, that reactions on the ice particles of polar clouds accelerated this process, and that the same kind of chemical reactions were taking place in the Arctic.



Figure 27. The specially equipped NASA research aircraft that gathered much of the data used in James Anderson's study of the Antarctic ozone hole. The wing pod in the center foreground contains the instrument for measuring chlorine monoxide concentrations in the upper atmosphere.

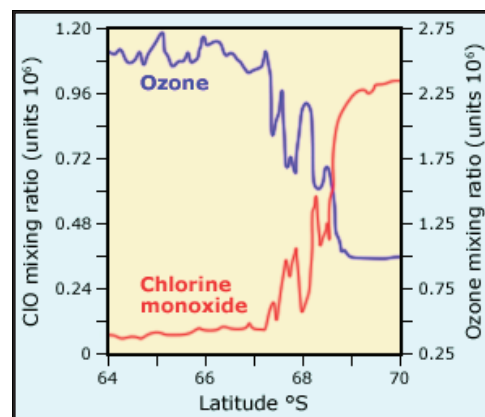
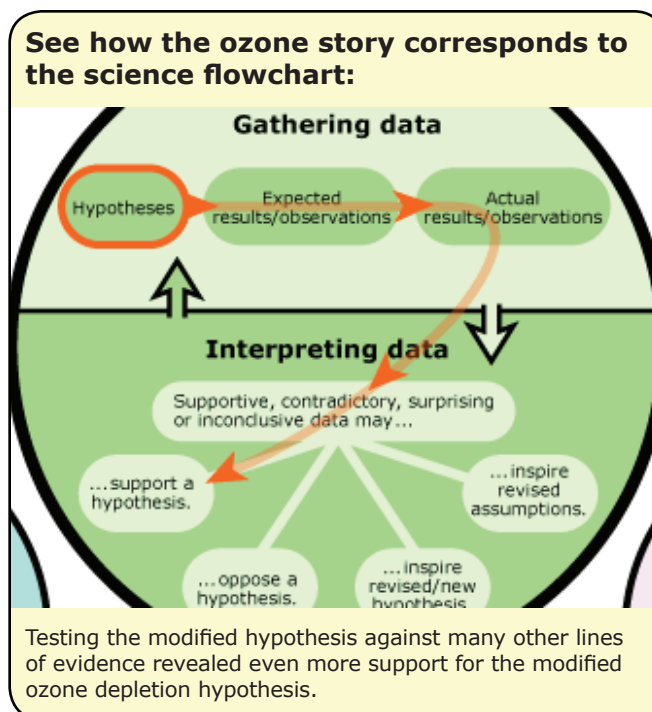


Figure 28. A plot of chlorine monoxide and ozone concentrations from data collected by the aircraft. Outside the hole (left side of graph), ozone levels are high and chlorine monoxide levels are low, while the reverse is true inside the hole (right side of graph)—just as the Molina-Rowland hypothesis would lead us to expect.

Arctic satellite data image courtesy of NASA SVS; Aircraft photo from NASA, photo by Dr. Mark Schoeberl; ClO-ozone graph adapted from Figure 19 in Anderson, J.G., W.H. Brune, and M.H. Proffitt. 1989. Ozone destruction by chlorine radicals within the Antarctic vortex: the spatial and temporal evolution of ClO-O₃ anticorrelation based on in situ ER-2 data. *Journal of Geophysical Research* 94:11465-11479



More than a Polar problem

Evidence for ozone depletion over the Poles was piling up—but what about over the rest of the planet? Here, scientists encountered an apparent paradox. In the 1950s, measurement stations at various locations around the world had begun to track local ozone levels. Prior to the discovery of the Antarctic hole, researchers had analyzed the data from these stations many times and found no evidence for ozone depletion (Fig. 29)—which didn't seem to square with recent evidence of Antarctic ozone depletion. Could these analyses of global ozone levels be trusted? To answer this question, NASA organized the Ozone Trends Panel in 1987. Composed of 150 scientists from around the world, the panel re-analyzed these ground-based ozone data sets using a new procedure and found an annual ozone loss of 1.7–3% in the Northern Hemisphere.

How could two interpretations of the same data have given different results—no ozone loss versus 1.7–3% ozone loss? As with the atmospheric models discussed earlier, the explanation is in the details—the assumptions the analysts used to combine the data. The original analysis (the analysis that detected no problem with the ozone layer) assumed that ozone depletion was the same year round, lumped all the ozone measurements together, and averaged annually. The new analysis took into account additional evidence that suggested that ozone loss varies seasonally, and so considered data from different latitudes separately (Fig. 30) and averaged data for each month separately. Because the new procedure incorporated much more of the



Figure 29. Data from ground-based instruments, like this Dobson spectrophotometer in Arosa, Switzerland, didn't seem to show any decrease in ozone levels. What was going on?

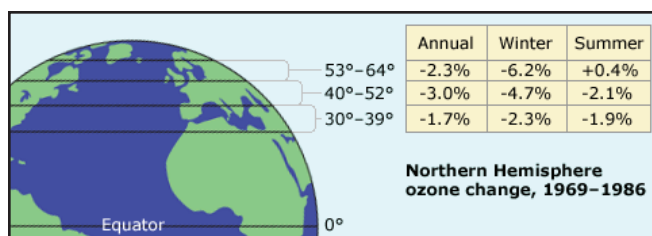
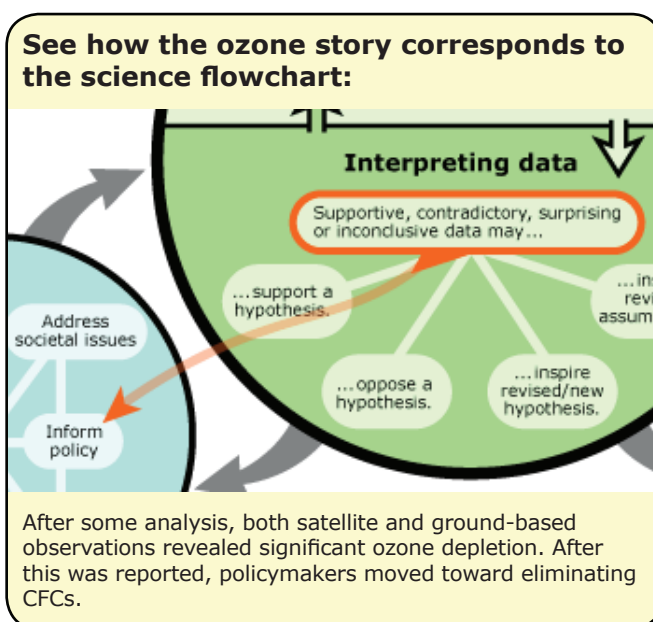


Figure 30. Change in the amount of ozone in the Northern Hemisphere over a 17-year period. Note the large decline in ozone during the winter months and how the winter decline is greatest at higher latitudes.

Spectrophotometer photo courtesy of the Federal Office of Meteorology and Climatology, MeteoSwiss, Switzerland; ozone change graphic adapted from Figure 6.3 in Parson, E.A. 2003. *Protecting the Ozone Layer: Science and Strategy*. Oxford University Press: New York.

CFC-induced variation in ozone levels, it was able to detect an ozone loss that the original procedure could not.

The Ozone Trends Panel report, released in 1988, was the nail in the coffin for CFCs. It verified that ozone depletion existed worldwide and that chlorine chemicals, mainly CFCs, seemed to be the cause. Finally, the international community felt compelled to legislate a ban on CFCs. In 1990, policy makers from 93 countries gathered in London to sign a treaty, agreeing to phase-out CFCs by 2000 (with poorer countries allowed additional time to come up with alternatives). Over the next two years, as more results from scientific studies indicated increasing ozone depletion, the elimination date was moved up to 1996.



Conclusions

Looking back over the scientific investigation of ozone depletion, we can see how the Molina-Rowland hypothesis evolved with new data. When chlorine nitrate, a chemical that ties up chlorine in an ozone-safe form, was added to the hypothesis, the expected amount of ozone loss decreased. Then, when polar clouds were considered, the expected ozone loss increased. Through all these minor revisions, the core of the hypothesis, the idea that CFCs lead to ozone depletion, never changed. Taken out of their scientific context, these fluctuations in expectations about ozone loss might have seemed to indicate that scientists were confused or disagreeing with each other, but on closer inspection, we saw that the fluctuations were a normal part of the scientific process as scientists came to a more complete understanding of an immensely complex system, the atmosphere.

Now the hairspray you see on drugstore shelves is CFC-free, as are the refrigerators in appliance stores, and the air conditioners in new cars and homes. Modifying regulatory policies to bring about these changes was a hard-won battle for politicians and citizens concerned about the environment—and for Molina, Rowland, and many other scientists. Not only did they collect scientific evidence; they also invested a considerable amount of time and energy in conveying their results and the implications to lawmakers and the public. Molina and Rowland had to persist in these efforts for more than a decade before the ban they had been calling for all along was finally achieved! With the CFC-ban in place, atmospheric levels of chlorine are beginning to decline and the ozone layer is, we hope, on its way to recovery (Fig. 31). If our current scientific understanding of the situation is correct, the ozone hole will start to shrink significantly by around 2018, with full recovery not expected until around 2070.

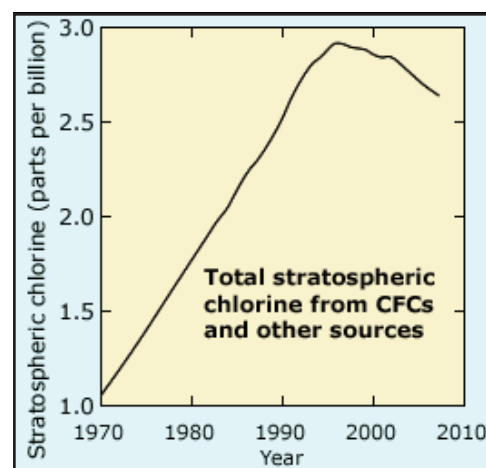


Figure 31.

While Molina and Rowland are given much of the credit—their work has earned them many awards and honors, including the most prestigious award in chemistry, the Nobel Prize—successfully averting an environmental disaster required more than just their efforts. It was the accumulated knowledge of the scientific community that allowed Molina and Rowland to meld a bunch of seemingly disjointed pieces of information into

Data for total stratospheric chlorine from CSIRO Atmospheric Research and Cape Grim Baseline Air Pollution Station, The Australian Antarctic Division and Australian Bureau of Meteorology

a new hypothesis about the effects of CFCs in the atmosphere. The dire results predicted by their ideas—the depletion of the ozone layer and prospect of increased health and environmental problems—led many scientists to become involved in testing and fine-tuning the hypothesis, with chemists, atmospheric scientists, and mathematical modelers all contributing pieces of the puzzle. These diverse perspectives played a crucial role in the scientific process, allowing science to build a much more complete understanding of the phenomenon than if Molina and Rowland had worked alone. As with many scientific triumphs, this success belongs to no one individual, but to the scientific community as a whole—and to the broader community, which took it upon itself to act on pressing scientific findings.

WANT TO LEARN MORE? CHECK OUT THESE REFERENCES

Popular and historical accounts:

Roan, S. 1989. *Ozone Crisis: The 15-year Evolution of a Sudden Global Emergency*. New York, NY: John Wiley & Sons, Inc.

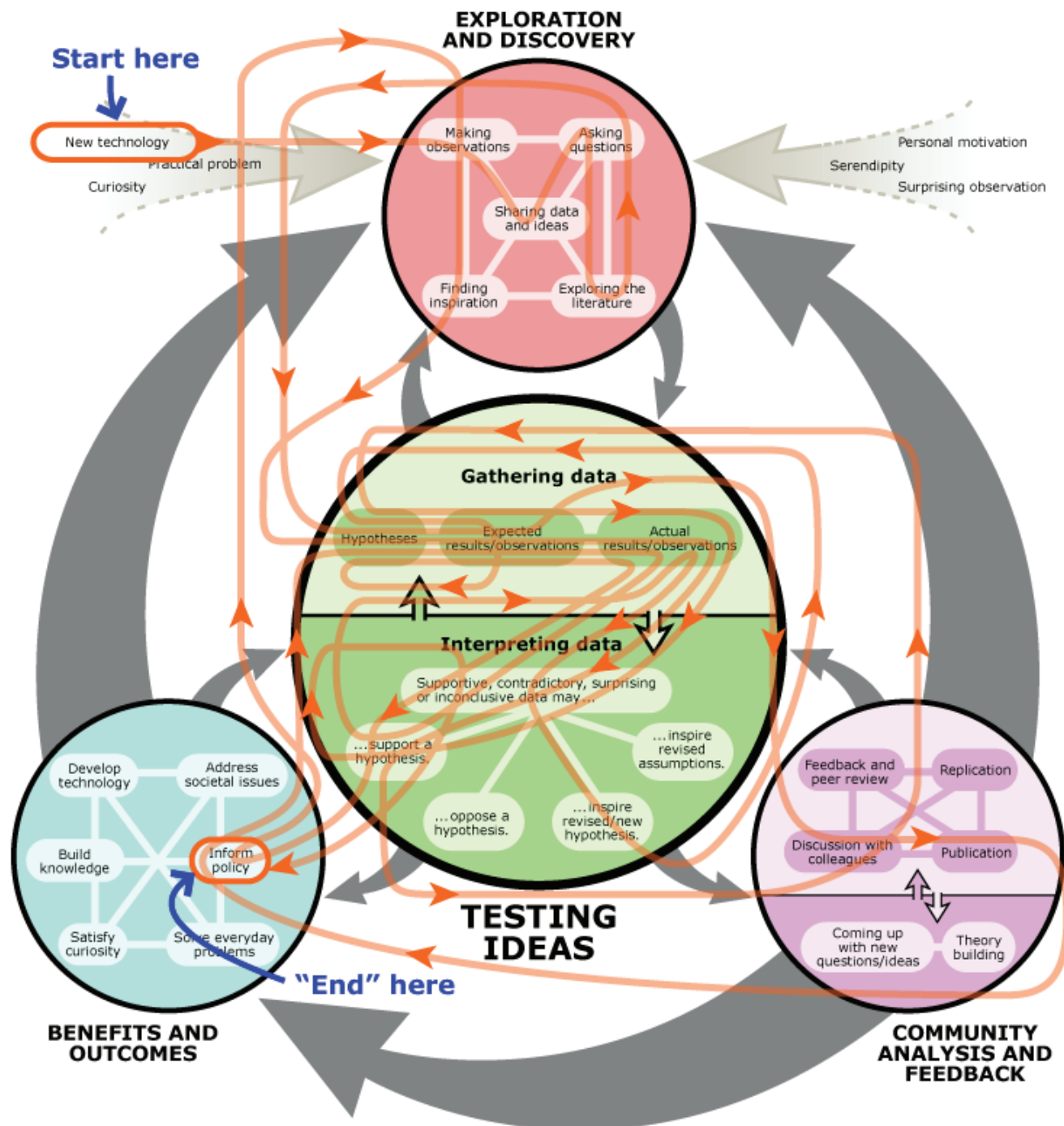
Dotto, L., and H. Schiff. 1978. *The Ozone War*. Garden City, NY: Doubleday & Company, Inc.

Some scientific papers:

Molina, M.J., and F.S. Rowland. 1974. Stratospheric sink for chlorofluoromethane: chlorine atom-catalyzed destruction of ozone. *Nature* 249:810-812.

Solomon, S. 1999. Stratospheric ozone depletion: review of concepts and history. *Review of Geophysics* 37:375-316.

Review how the ozone story corresponds to the science flowchart:



Key points:

- The process of science is non-linear, unpredictable, and ongoing.
- Scientific ideas evolve with new evidence.
- Many lines of evidence may be used to help test a single idea.
- Science affects our day-to-day lives.