

Chlorine chronicles

Barbara Finlayson-Pitts muses on how chlorine has come to play a role in many aspects of our lives — for better or for worse.

Chlorine is ubiquitous in both natural and man-made environments. Abundant in the Earth's crust and seawater, it is also present throughout the human body, for example as hydrochloric acid in gastric fluids, and is a major component in our cleaning products and pesticides.

The first documented observation of what would later be identified as molecular chlorine (Cl_2) appeared in 1774, when Scheele observed¹ a yellowish green gas from the reaction of “brunsten” (manganese dioxide) with “muriatic acid” (hydrochloric acid). The gas — at the time thought to be “oxymuriatic acid”, a compound of oxygen and muriatic acid — was observed to kill insects and have bleaching abilities. It was not until 1810 that Davy proposed² that it was in fact a separate chemical element, which he named chlorine the following year (from the Greek word *chloros* meaning yellowish green).

Gaseous Cl_2 , not practical for bleaching applications, was soon replaced by hypochlorite solutions that are still in use today for bleaching and disinfecting purposes, for example in the pulp and paper industry and in treatment of drinking and swimming pool water. Chlorine has also found its way into a wide range of products, from solvents and plastics (such as polyvinyl chloride) to pharmaceuticals.

Regrettably, deleterious effects of chlorinated compounds have also emerged: Cl_2 , phosgene (COCl_2) and mustard gas ($(\text{ClCH}_2\text{CH}_2)_2\text{S}$) have all been used as chemical weapons in a destructive and disturbing manner. Another example is DDT (dichloro-diphenyl-trichloroethane), whose impacts are chronicled in Rachel Carson's book *Silent Spring*³.

Element 17 is also linked to disastrous effects in the atmosphere, through the chlorofluorocarbons (CFCs) developed in the 1930s, and then widely used as refrigerants, aerosol propellants and blowing agents for foams. They are non-toxic and



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unreactive in the troposphere (the lower ~15 km part of the atmosphere), which initially seemed advantageous, but in 1974 Molina and Rowland discovered⁴ that it actually had significant global consequences — a finding that led to them being awarded the 1995 Nobel Prize in Chemistry, jointly with Crutzen.

Because the CFCs have no significant sinks in the lower atmosphere, they are transported to the upper atmosphere. There, irradiation at wavelengths below 240 nm induces their photodecomposition, which generates chlorine atoms that take part in a chain destruction of ozone (O_3). In the stratosphere (between ~15–50 km above the Earth's surface), ozone blocks ultraviolet light from solar radiation. Its concentration, normally well regulated, is lowered by the CFC-induced decomposition processes, causing enhanced ultraviolet light to reach the Earth's surface. The most dramatic manifestation of this chemistry is the development of the Antarctic ozone ‘hole’ in the polar spring, with essentially complete destruction of O_3 at some altitudes⁵. Furthermore, CFCs are also quite potent greenhouse gases⁵.

Another intriguing contribution of chlorine to tropospheric chemistry has come to light over the past few decades⁶. Wave action generates submicrometre airborne salt particles that consist primarily of NaCl from the sea. Dust from alkaline dry lakes also contains chlorine. Trace atmospheric

gases such as HNO_3 , NO_2 , N_2O_5 and the OH radical react with chloride ions in and at the surface of the particles, producing chlorinated products such as HCl, ClNO, ClNO₂, Cl_2 and HOCl (ref. 6).

Surprisingly, recent measurements show that this tropospheric chlorine chemistry seems to also occur quite broadly in mid-continental regions where ClNO₂ has been observed. The source is not clear, but may involve heterogeneous reactions of halogen compounds with surface-bound oxides of nitrogen (NO_x). Most of the chlorinated products are rapidly converted into chlorine atoms, highly reactive towards man-made and/or natural organic compounds. This commonly leads to increased formation of tropospheric ozone — a toxic air pollutant and a potent greenhouse gas⁵. This is a prime example of synergistic interactions of anthropogenic and natural emissions⁷, increasingly recognized as potentially important. Although these atmospheric processes are incredibly intricate and difficult to study, elucidating their chemistry is critical to quantitative predictions of processes, and in turn reducing or overcoming undesirable effects.

In any case, we cannot avoid chlorine in our daily lives, for better or for worse. The challenge is instead to maximize the former and minimize the latter. □

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References

1. *The Early History of Chlorine* (The Alembic Club, 1905).
2. Davy, H. *The Elementary Nature of Chlorine. Papers by Humphry Davy* Reprint 9 (The Alembic Club, 1902).
3. Carson, R. *Silent Spring* (Houghton Mifflin, 1962).
4. Molina, M. J. & Rowland, F. S. *Nature* **29**, 810–812 (1974).
5. Finlayson-Pitts, B. J. & Pitts, J. N. Jr *Chemistry of the Upper and Lower Atmosphere - Theory, Experiments, and Applications* (Academic Press, 2000).
6. Finlayson-Pitts, B. J. *Anal. Chem.* **82**, 770–776 (2010).
7. Finlayson-Pitts, B. J. *Daedalus* **137**, 135–138 (2008).

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