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About three decades ago, it was reported that a correlation existed between wet winters in San Francisco and episodes of air pollution the following summer. Wet winters, it was hypothesized, led to greater plant growth, with an associated rise in natural, or biogenic, emissions. These biogenic emissions, it was held, caused the increase in air pollution.

This hypothesis generated many headlines and cartoons along the lines of "Forests unsafe to walk in!" and "Trees are the source of air pollution." The idea that natural emissions were at fault for air pollution flew in the face of abundant evidence that human activities, particularly fossil-fuel combustion, are the source of air pollution.

The combustion of fossil fuels generates nitrogen oxides (NO_x) – which include nitric oxide (NO) and nitrogen dioxide (NO_2) – as well as particles, organic compounds, and sulfur dioxide (SO_2). Amounts produced vary, depending on the nature of the particular fuel and the combustion conditions. While these initial emissions, or primary pollutants, are harmful, the greater threat comes from the chemical transformations that the primary pollutants undergo in air. These reactions form pollutants that are often more toxic than are primary pollutants, and certainly more wide-ranging in their impacts. These 'secondary pollutants' include ozone (O_3), acids such as nitric and sulfuric acids, and new aerosol particles.

Ozone damages agricultural products, weakens ecosystems, and causes materials such as those made of rubber to deteriorate. In fact, in the past, one way of measuring ozone was to count the number and depth of cracks formed per hour in a stretched rubber band suspended in air. The damage ozone inflicts on health has been particularly well documented. As a result, air quality standards (AQS) for ozone, set to protect public health, have become more stringent, as evidence of the harmful effects of ozone at lower atmospheric levels has accumulated. While ozone produced in natural cycles in the upper atmosphere acts as a shield against ultraviolet light from the sun, ozone in the lower atmosphere, where people live, is a highly toxic pollutant. The current U.S. federal AQS for ozone is 80 parts per billion (ppb) over eight hours.

Particulate matter, especially those particles with a diameter of 2.5 microns

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and smaller (PM2.5), is of particular concern because it penetrates deep into the respiratory system. Epidemiological studies show PM2.5 increases mortality, despite the extremely small size of the particles, whose diameters are less than about 1 percent of the diameter of a human hair. Moreover, a recent study showed that PM2.5 had negative effects on lung development in children living in Southern California.

Nitric and sulfuric acids are also major secondary pollutants, and nitric acid has a negative correlation with lung development in children as well. These acids, furthermore, are responsible for acid rain and can be taken up into fogs and clouds. Indeed, the fog in Southern California some years ago was found to have an acid concentration about ten thousand times higher than unpolluted rainwater or fog.

How do these secondary pollutants originate? Nitrogen oxides and volatile organic compounds (VOC) drive the formation of a whole host of secondary pollutants – including ozone, acids, and PM2.5 – through a complex set of chemical reactions in air that require sunlight. In the course of this chemistry, reactive intermediates are generated that also convert sulfur dioxide to sulfuric acid and sulfate particles. These are sufficiently long-lived to be distributed over a large geographical area, thus having not only local and regional impacts, but global ones as well.

The VOC category encompasses literally thousands of compounds. These include anthropogenic emissions – such as those from incomplete fossil-fuel combustion, solvent use, etc. – and biogenic emissions from plants. The rate with which each compound participates in the chemical cycles with nitrogen oxides in air depends on its particular chemical structure, and can vary many orders of magnitude from one compound to another. As it happens, many of the biogenic species are not only volatile but also highly reactive. For example, pinene, which gives pine forests their wonderful odor, reacts quickly in sunlit air when nitrogen oxides are present (and they usually are) to generate ozone and associated air pollutants. Many of the biogenics then react further with the ozone itself to generate additional gaseous and particulate air pollutants. It is this chemistry that led to the hypothesis of a connection between wet winters and summer air pollution many years ago.

So, are plants responsible for smog? Absolutely not. The critical ingredient is nitrogen oxides, which is formed when air is heated during fuel combustion. At these high temperatures, nitrogen, which makes up the majority of molecules in air, reacts with oxygen to form nitric oxide and smaller amounts of nitrogen dioxide. Once emitted into the environment, nitric oxide is converted to form more nitrogen dioxide (this is where the VOCs come in), which then absorbs sunlight and reacts further with oxygen to generate ozone. Without the nitrogen oxides, then, there is no significant anthropogenic source of ozone, and VOC chemistry slows down dramatically. This connection between biogenic and anthropogenic emissions is intriguing – and, as it turns out, not at all uncommon.

Measurements of ozone in the lower atmosphere, taken in a number of locations around the world, dramatically illustrate the nitrogen dioxide-ozone connection. Around about 1850, when measurements began to be taken, ozone levels were typically 10 to 15 ppb. Today, ozone levels, even in the remotest regions of the Earth, are 30 to 40 ppb, a factor of three to four higher. This dramatic change has been attributed to the increase in nitrogen oxide emissions resulting from ever-increasing fossil-fuel combustion.

Ozone also contributes significantly to climate change. While the focus of the public debate on climate warming has been on carbon dioxide (CO_2), the most recent Intergovernmental Panel on Climate Change report estimates that ozone's contribution to climate change is about 20 percent of carbon dioxide's. Particles are another major player in climate change. They have a direct effect in scattering incoming sunlight, and an indirect effect in changing cloud properties such as the frequency of cloud formation and their lifetimes, both of which affect the amount of sunlight reflected from clouds. Their net effect is cooling, counteracting in part the warming by carbon dioxide and the other greenhouse gases.

Ironically, this cooling may have partially masked global warming over the past decades. Updated observations of the Earth's climate suggest warming is taking place faster than expected based on models and previous measurements. One hypothesis is that the increase in combustion of high-sulfur fossil fuels after World War II led to a global increase in sulfate particles in air, which through their light-scattering properties and impact on cloud formation led to the cooling of the Earth's surface. At the same time, this combustion increased carbon dioxide and other greenhouse gases such as ozone, which led to warming. Without the partial counterbalancing of sulfate particles, global warming over the past century would have been significantly larger than observed. And the fact that climate change now seems to be happening more rapidly than expected may be due to the diminishing counterbalancing effect of particles. Of course, this is not an argument for increased sulfur dioxide emissions, since controls that have been instituted have significantly reduced the impact of air pollution on health and the environment.

Another contributor to particle formation in air is the reaction of some highly reactive biogenic emissions with ozone. These reactions produce less volatile compounds, which either coalesce to form new particles or end up as deposits on existing particles to make them larger. The particles formed by oxidation of such organic gaseous precursors are known as secondary organic aerosols (SOA). It has been said that the Smoky Mountains were so named because of a persistent haze that may have been due to light scattering by SOA from ozone-biogenics reactions.

The formation of particles in urban and regional pollution episodes is clearly associated with areas of high fossil-fuel combustion and anthropogenic emissions. However, measurements of the carbon isotopes in SOA typically reveal that about 75 percent of the carbon is not derived from fossil fuels. In addition, the amounts of SOA measured in a number of studies are as much as an order of magnitude larger than predicted based on measurements of the known gas-phase precursors to particle formation. It seems likely that biogenic VOC must be involved in resolving discrepancies. This again illustrates the close interactions between anthropogenic and natural emissions. The involvement of VOC in ozone and particulate air pollution has led to significant controls on anthropogenic VOC. However, nitrogen oxides are the only anthropogenic source of ozone and ultimately keep the air pollution cycle moving, which suggests that even stricter control of nitrogen oxide emissions will be required to meet air quality standards for ozone and PM2.5.

A third example of the intertwining of natural and anthropogenic emissions is the role of sea salt in the air quality of coastal marine areas. Sea salt is mainly sodium chloride (NaCl), with smaller amounts of other species such as sodium bromide (NaBr). Wave action generates small (typically micron-sized) droplets of seawater that become airborne and are carried inland. While most of them are sufficiently large that they settle by gravity not too far from the source, many sea salt particles remain suspended for prolonged times and have been measured as far as five hundred kilometers inland. Salt particles are also generated from salt lakes such as the Dead Sea in Israel and the Great Salt Lake in Utah.

It is well known from the Nobel Prize–winning work of F. Sherwood Rowland and Mario Molina that chlorine atoms from chlorofluorocarbons destroy ozone in the upper atmosphere, thus diminishing the shield against ultraviolet radiation. In the lower atmosphere, however, chlorine atoms actually increase ozone levels undermost conditions by interacting with the VOC-nitrogen oxide chemistry. Briefly, nitrogen oxides and nitric acid react with sea salt particles to generate gases containing chlorine, which then react in the presence of sunlight to produce highly reactive chlorine atoms. These initiate the VOC oxidation that leads to the nitric oxide to nitrogen dioxide to ozone conversion, and does so much faster than in the absence of chlorine atoms. Models suggest that sea salt could be responsible for as much as an additional 12 ppb in the peak ozone concentrations in coastal urban areas. Given that the preindustrial global concentrations of ozone were about 10 to 15 ppb, and current levels in remote areas are about 30 to 40 ppb, this is a significant contribution.

So, does sea salt cause smog, as some newspaper headlines trumpet when reporting on this research? Anthropogenically produced nitrogen oxides are again the critical ingredient. However, as is the case for the interaction of biogenic VOC with anthropogenic emissions, many of the details of this interaction between sea salt and fossil-fuel combustion remain obscure, and is the subject of current laboratory and field studies as well as computer kinetics modeling.

Air pollution and climate change are intimately intertwined and must be treated comprehensively. As part of such assessments, both the anthropogenic and natural contributions and their interactions must be measured and taken into account. It is certainly clear, however, that one cannot attribute air pollution and climate change to natural sources as an excuse to forgo controls on emissions from human activities. Indeed, once the close interrelationships between human activities and natural cycles are well understood, the result may well be that even greater control of anthropogenic emissions will be required to minimize the significant harmful effects of air pollution as well as global climate change.