CHM135 Virtual Laboratory 1
The Chemistry of Air Quality Introductory Video
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The chemistry of air quality. What makes for a poor air quality day, and how do scientists use atmospheric measurements to understand the chemistry taking place and then use that information improve the air we breathe?

Slide 2
Vehicles are a major contributor to air quality issues in an urban setting, so let's take a closer look at what comes out of the tailpipe. The reaction of hydrocarbons in gasoline with molecular oxygen in the air is the explosive reaction that makes vehicles run. The products of this reaction are carbon dioxide and water.

$$\mathbf{C_XH_Y + photon \rightarrow CO_2 + H_2O} \qquad [1]$$

Carbon dioxide is a major concern when it comes to climate change, because of its ability to absorb infrared radiation, but this reaction is actually quite clean and does not contribute to issues around air quality.

A side reaction that can occur in the high temperatures and pressures inside a combustion engine is that between molecular nitrogen and molecular oxygen, two gases that are typically inert to one another. This reaction produces nitric oxide, which is a very important player in urban air quality.

$$\mathbf{N_2 + O_2 \rightarrow 2NO} \qquad [2]$$

Volatile organic compounds or VOCs are another important player. One source of VOCs is the emission of unreacted gasoline from a combustion engine, however there are also many natural sources.

The catalytic converter is one-way auto engineers have worked to curb the emission of these troublesome chemicals. The catalytic converter uses a solid catalyst to reaction nitric oxide with VOCs transforming them into nitrogen gas, carbon dioxide and water. The catalytic converter has significantly reduced the emission of nitric oxide and VOCs but not eliminated them entirely.

$$\mathbf{VOC + NO \rightarrow\rightarrow N_2 + CO_2 + H_2O} \qquad [3]$$

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VOCs and nitric oxide emitted directly out of the tailpipe of the vehicle are called primary pollutants. Once in the atmosphere VOCs are oxidized in a multistep process that eventually produces a peroxy radical.

$$\mathbf{VOC + O_2 \rightarrow\rightarrow VOC - O_2} \qquad [4]$$

Nitric oxide plays one role in the atmosphere and that is to steal an oxygen atom from chemicals that have too many, like this peroxy radical. This reaction produces nitrogen dioxide, which is a secondary pollutant and a very important one.

$$\mathbf{VOC - O_2 + NO \rightarrow VOC - O + NO_2} \qquad [5]$$

Nitrogen dioxide is a coloured gas with a reddish hue which is responsible for the brownish look that smog events often have. Because it is coloured we know that it interacts with visible light and it turns out that some of these interactions result in the breaking of one of its nitrogen-oxygen bonds regenerating nitric oxide and an oxygen atom.

$$\mathbf{NO_2 + photon \rightarrow NO + O} \qquad [9]$$

As you can imagine this oxygen atom is very reactive and does not last long in the atmosphere. Its major fate is reaction with molecular oxygen to produce ozone.

$$\mathbf{O + O_2 \rightarrow O_3} \qquad [10]$$

Ozone is another important secondary pollutant. Ozone is our friend 30 Km above sea level where the stratospheric ozone layer protects us from harmful solar radiation. However, at ground level, in the troposphere where we live, ozone is toxic and is one of the major metrics on which poor air quality days are determined, together with concentrations of fine particles. High concentrations of ozone can damage crops and cause difficulty breathing particularly in those with underlying health issues.

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To better understand how these two chemicals, ozone and nitrogen dioxide, are related to one another let's look at some air quality data collected in downtown Toronto starting at 6 AM on May 21, 2019 to the next morning, 6 AM on May 22, 2019.

First let's focus on the morning between 6-9 AM. This is an important time because the morning rush hour means that vehicle emissions are increasing and also the sun is rising, and we know light plays a role in the chemistry taking place. As you might expect we see an increase in nitrogen dioxide but then it starts decreasing as it is photolyzed by the increasing light intensity. Ozone on the other hand starts low and increases through the morning.

This trend of high ozone and low nitrogen dioxide continues throughout the day where nitrogen dioxide, in the presence of light and molecular oxygen produces ozone.

Now let's look around 9 PM when the sun is setting and nighttime chemistry takes over. Here we see a decrease in ozone with a subsequent increase in nitrogen dioxide. What's happening? Well it turns out the reactions we have discussed so far are only half of the equation so to speak. I mentioned before that nitric oxide likes to steal an oxygen atom from molecules with too many, and, just like the peroxy radical we discussed before, ozone has too many oxygen atoms so it reacts with nitric oxide to regenerate nitrogen dioxide and molecular oxygen.

$$\mathbf{O_3 + NO \rightarrow O_2 + NO_2} \qquad [11]$$

This reaction completes the cyclic relationship between nitrogen dioxide and ozone.

$$\mathbf{NO_2 + photon \rightarrow NO + O} \qquad [9]$$
$$\mathbf{O + O_2 \rightarrow O_3} \qquad [10]$$
$$\mathbf{O_3 + NO \rightarrow O_2 + NO_2} \qquad [11]$$

During the day when light is abundant nitrogen dioxide is lost and ozone generated. Overnight, in the absence of light, the loss mechanism for nitrogen dioxide is gone and it accumulates as ozone is lost by reaction with nitric oxide.

Because of the intimate relationship between nitrogen dioxide and ozone, atmospheric chemists have defined the term “odd oxygen” or Ox which refers to the sum of the concentration of nitrogen dioxide and ozone.

$$[\mathbf{O}_x] = [\mathbf{NO_2}] + [\mathbf{O_3}] \qquad \textbf{[12]}$$

The odd oxygen concentration is plotted here in the grey dotted line and you can see how consistent it is as compared to the concentrations of ozone or nitrogen dioxide alone.

When we consider one day alone the situation can seem quite simple, but when we open up this window…

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…to include 6 days we can see there is more variability in the data in the longer term, but the oscillating relationship between ozone and nitrogen dioxide remains, as does the ability of the total odd oxygen concentration to give a representation of the cumulative contamination present at a given moment.

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Thank you for watching this video and I wish you nothing but blue skies ahead.