Smog: Clearing the Air

By Bill Pisciella

INTRODUCTION

The goal of this unit is to enhance abstract modeling skills through the design of a computer model of ground level ozone, the leading component in Houston's smog. The unit will increase student understanding of the factors that lead to the formation of this ozone.

In modeling, the first step is to ask questions. As answers are sought, more questions are developed. The questioning never ends. Neither does learning. The process of questioning leads students in directions of their choice. Only when the student is satisfied or time runs out does the questioning stop. I believe that the following quote from Teaching as a Subversive Activity explains it best:

> "*Once you have learned how to ask questions-relevant and appropriate and substantial questions-you have learned how to learn and no one can keep you from learning whatever you want or need to know.*"
>
> *Source: Postman and Weingartner, Teaching as a Subversive Activity. Delacorte Press, NY 1969. P23.*

Hopefully the most important outcome of this unit will be that students will learn how to apply the modeling process. The goal will be to produce the simplest model that predicts this ozone formation with reasonable accuracy. The processes that the student will go through are essential to the development of higher level problem-solving skills.

THE UNIT FORMAT

There the four major sections of the unit: Solar Radiation, Chemistry of Ozone, Meteorological Factors, and the Computer Model. The sections can be considered as individual stand-alone units. The first unit is fairly complete with activities and suggested research projects. For the other units, suggested activities and research projects are given in the annotated bibliography.

The " Big Picture" for this unit is that it models ozone formation. The major steps in the formation of ozone are as follows:

- Ground level ozone is formed when nitrogen dioxide, NO_2, reacts with Oxygen, O_2

- Nitrous Oxide, NO, forms in combustion and makes up 95% of the nitrogen oxides that are formed by combustion.
- Nitrogen Dioxide is formed by the reaction of NO and VOCs at a temperaure of 29^0 C (84^0 F) or higher.
- The Nitrogen Dioxide formation occurs through a series of intermediate reactions.
- Meteorological factors affect both the ozone production and its transport.

One source helps in the model is the database of readings made at Texas Natural Resource Conservation Commission (TNRCC) Continuous Air Monitoring Stations (CAMS). These TNRCC CAMS sites record hourly meteorological values the following: solar radiation, temperature, horizontal wind speed and direction, and barometric pressure. They also measure nitrogen oxide, nitrogen dioxide and ozone.

Volatile Organic Compound (VOC) data is not available hourly from the TNRCC. This is probably due to the sheer number of such compounds. There is very useful data on VOCs available from a study performed in the early 1990s. (see Revisons in the State Implementation Plan in the bibliography.)

Data used in this unit will be from the TNRCC for October, 1999. This data was selected because the worst ozone day occurred on October 7, 1999 and there were sharp contrasts in ozone level during the month.

When using this data in graph form. Several points must be noted:

- All data is in 24 Hour Format
- All data is Central Standard Time.
- The data is the average of readings for the preceding one-hour period.
- The values are in the middle of the vertical grid lines.
- The graphs were smoothed. This slightly distorts the graphs.
- Values between hourly points are interpolated and do not represent actual data.

SECTION 1: SOLAR RADIATION

Solar radiation is the primary source of energy on Earth. It is also a required entity in ground level ozone development. The area of concern for this radiation is the lowest level of the atmosphere, the troposphere. Both the amount and type of energy are important parameters in the creation of ground level ozone.

Our sun, called Sol, is a gaseous sphere that has a diameter of 1.39 million kilometers (about 109 Earth diameters). Its mass is 1.99×10^{30} kilograms (about 333,000 times the mass of the Earth). Almost all of the mass of the sun is in its core where its density is approximately 160 times the density of water (1 g/ cm^3) and about 10 times the density of lead or gold. Its average density, however, is only 1.41 g/cm^3 which is only about one fourth of the average density of the Earth. The sun emits an average of 3.83×10^{23} Kilowatts or about 6.29×10^4 KW/m^2.

The sun consists of concentric layers. These are the core, radiative zone, interface layer, convection zone, and the photosphere. A description of these regions and their relationship to solar energy is described below.

The "atmosphere" of the sun consists of the chromosphere, the transition region and the corona. This solar atmosphere is beyond the scope of this unit. Sources in the annotated bibliography are available for future research.

The core is at the center of the sun. It has a radius of about 175,000 kilometers (about one fourth of the sun's radius. Its density (160 g/cm^3) and its temperature (15 million degrees Kelvin) are very high at its center. The core consists mainly of hydrogen and helium ions.

Nuclear fusion reactions occur in the core. These reactions are the source of the sun's energy. Nuclear fusion requires four hydrogen ions and two electrons to from one helium ion. This fusion results in a loss of $.05 \times 10^{-27}$ Kilograms. This tiny loss of mass becomes nuclear energy. Einstein stated that the lost mass times the square of the speed if light is the amount of energy released: $E = mc^2$. For this one reaction, the energy released is 4.5×10^{-12} joules. Since the sun is radiating 3.83×10^{26} Watts (or joules per second), there must be at least 8.5×10^{27} nuclear reactions per second.

The radiative zone surrounds the core. The outside of this zone is about 485,000 kilometers from the center (70% of the sun's radius). In this zone, photons created in the core radiate outward. The region is so dense near the core (about the density of gold) that the photons make may collisions. The average photon takes approximately one million years to escape the radiative layer. This density has dropped to about .2 g/cm^3 at the outside edge. The temperature at the edge has dropped to about two million degrees Kelvin.

The next layer is the interface layer. It is a thin layer that is believed to cause the sun's magnetic field. The radiative zone has very little flow while the layer outside the interface layer, the convection zone is very turbulent. The shear flows that result in this layer are thought to be the reason that there is a solar magnetic field.

The convection zone reaches nearly to the sun's surface. The energy from its interior flows toward the surface by convection rather than radiation. This is because the region is "cool enough" to allow for heavier elements to hold some of their electrons. As these heavier ions rise they lose energy, the temperature decreases from about two million degrees to near the temperature of the photosphere (about 6000^0 K).

The outermost layer is called the photosphere. This is the surface that is visible from the Earth. Its thickness is only about 100 kilometers. This layer produces the radiation that reaches the Earth. The spectrum of this energy is dependent on the temperature of the photosphere, which is approximately $6{,}000^0$ K. The spectrum of radiation is an important concept that is explained below. (MSFC Solar Physics)

Radiation theory involves concept developed in quantum mechanics. This theory is an attempt to relate the wave and particle properties of light. The particle property is called a photon. Light is considered as a flow of photons. A photon has energy that is proportional to the frequency and inversely proportional to the wavelength of the light. The derivation is shown below.

$$c = f\lambda$$

$$f = \frac{c}{\lambda}$$

$$E = hf = \frac{hc}{\lambda}$$

Where:
c is the speed of light (3×10^{14} µm/s)
f is the frequency in Hertz
λ is the wavelength in micrometers
h is Planck's Constant (6.625×10^{-34} joule sec.)
E is energy in joules

The photon is created when an electron lowers its orbital level. In classic physics the orbital levels are continuous. In quantum theory, there are only certain stable orbitals. A photon is emitted when an electron goes from a higher energy orbital to a lower level orbital. For a particular atom, there are only specific wavelengths that can be emitted.

Conversely a photon is absorbed when it moves an electron from a lower level orbital to a higher level orbital. The photon must be only specific wavelengths to be absorbed. Above this energy, the electron will completely leave the atom. This is called the ionization potential. Quantum behavior is an important factor in the response of the atmosphere to solar energy.

There are four laws that are used to determine the behavior of electromagnetic waves. The sun is approximated as a perfect blackbody radiator. These laws that are described below are based on this approximation.

The first of these sets of laws are Kirchhoff's Laws. These laws concern the emission and absorption of gases. The laws are:

- **A hot opaque body, such as a hot, dense gas produces a continuous spectrum.** The sun is a hot, dense, opaque object. Therefor the sun emits a continuous spectrum.
- **A hot, transparent gas produces an emission line spectrum.** This could represent gases in the atmosphere that have absorbed photons.
- **A cool, transparent gas in front of a source of continuous emission produces an absorption line spectrum.** The atmosphere represents relatively cool, transparent gases.

Wien's Displacement Law states that the wavelength of maximum energy, $\lambda_{MA\Xi,}$ is inversely proportional to the temperature in degrees Kelvin. This law in formula form is:

$$\lambda_{MAX} = \frac{3x10^3}{T}$$ Where the wavelength is measured in micrometers.

The Stefan-Boltzman Law determines the power density, E, from a blackbody at a certain temperature. The equation is:

$$E = \sigma T^4$$ Where σ is 5.67×10^{-11} KW/m^2 (Stefan-Boltzman constant)

All of these laws flow from the Planck Radiation Law. This law states that the amount of power density at any wavelength can be found from the following equation:

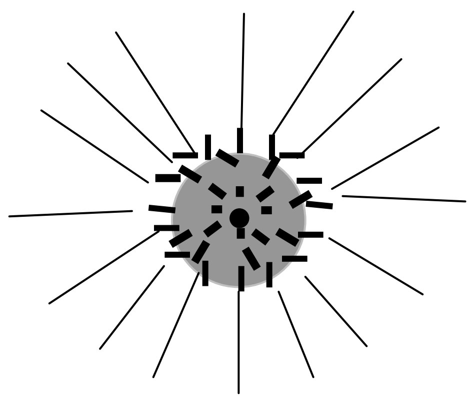
$$E = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1}$$ where $k = 1.38 \times 10^{-23}$ (Boltzmann Constant)

The equations above can give quantitative approximations for the power density of the energy leaving the sun. The next step is to find how much of that energy reaches the top of the Earth's atmosphere.

The amount of solar radiation that reaches the Earth's upper atmosphere can be considered constant as a first approximation. The amount of radiation actually varies on a yearly basis due to the elliptical nature of the Earth's orbit. It also varies with the sun's rotation about its axis (about 30 day cycle) and its emissivity on an approximately eleven-year cycle. There are also some variations that occur over much longer time periods. These variations make interesting topics for further research. (See suggested research projects below.) For purposes of this unit, the energy can be considered constant. (A New Sun, 37)

The physical model for radiation is to consider it to be solar flux. Flux density can be thought of as lines of flux. The number of flux lines is proportional to the energy (In this case solar energy). Two models can simplify the concept of flux lines. The first is a magnet with iron filings. The iron filings line up in lines from one pole to the other. These lines can be thought of as representing flux.

A better model for a spherical distribution is the Koosh™ Ball. The plastic spokes can be thought of as solar flux. Imagine if the plastic spokes were very long. The further out that they reached, the further apart they would become. The closer the lines of flux are, the greater the density. (See the drawing below)



The lines all come out of the center of the sphere. If we pretend that there is a imaginary sphere with a radius of R, then the density of the flux would be the flux divided by the surface area of the sphere. The flux represents the total power The surface area of a sphere is $4\pi R^2$. The equation of the flux density, I, would be:

$$E = \frac{F}{4\pi R^2}$$ Where, F is in KW and E is in KW/m^2

If R is the radius of the sun, the flux density would be the total flux of the sun (about 3.83×10^{23} KW). The flux density for the surface of the sun ($R = .7 \times 10^9$ m) would be about 6.2×10^4 KW/m^2. This is within the round-off error of the value supplied by NASA.

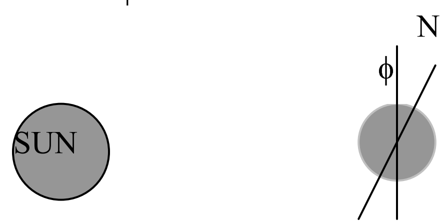
The generally accepted value for the flux density reaching the Earth is 1.372 KW/m^2. If we use the mean radius of the Earth's orbit (about 1.5×10^{11} m), The flux density reaching the Earth would be 1.35 KW/m^2, again within round-off error.

The maximum amount of solar radiation that can strike the Earth's surface is mostly determined by the tilt of the Earth in its rotation around the sun; it's rotation about its axis; and the composition and nature of the Earth's atmosphere. The Earth's tilt and daily rotation will be explored first followed by the nature and composition of the Earth's atmosphere.

The Earth's axis is tilted at 23.45^0 from the perpendicular to the plane of the Earth's orbit around the sun. The tilt remains constant. However, the tilt of the North Pole in relationship to the sun changes affecting both the radiation that any point on the surface can receive and the length of the day. The derivation demonstrates these phenomena:

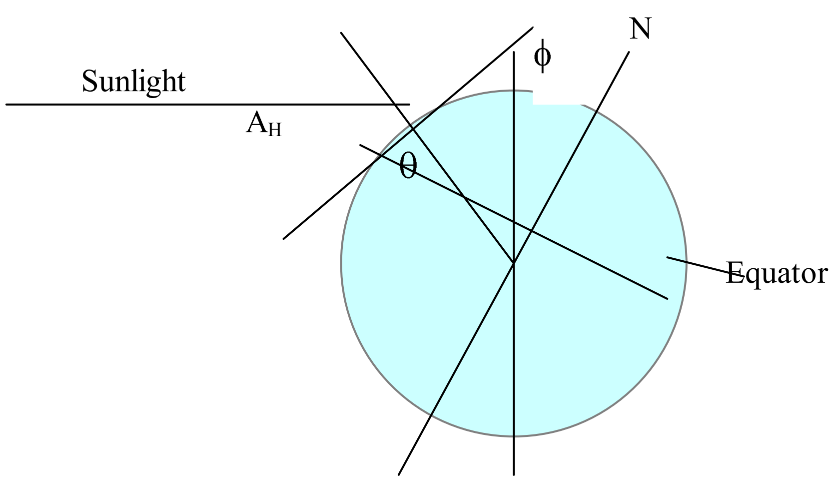
Let ϕ be the angle that the North Pole makes with a perpendicular to the sun. This angle will be assumed positive when the North Pole is tilted toward the sun. Also let "D" be the day of the year (1 to 365 or 366 for leapyear. and "S" be the first day of spring. The first day of spring is 80 if it falls on March 21. Then ϕ is:

$$\phi = 23.45\sin\left[\frac{360}{365.25}(D - S)\right]$$



The angle, ϕ, will vary from -23.45^0 on the first day of winter in the northern hemisphere (winter solstice) to 23.45^0 the first day of summer in the northern hemisphere (summer solstice). The angle will be 0^0 both the first day of spring (vernal equinox) and the first day of fall (autumnal equinox).

Let θ represent the latitude. The latitude is assumed to vary between 90^0 at the North Pole to -90^0 at the South Pole. The equator is at 0^0. The angle that the sun makes above the horizon, A_H is then:

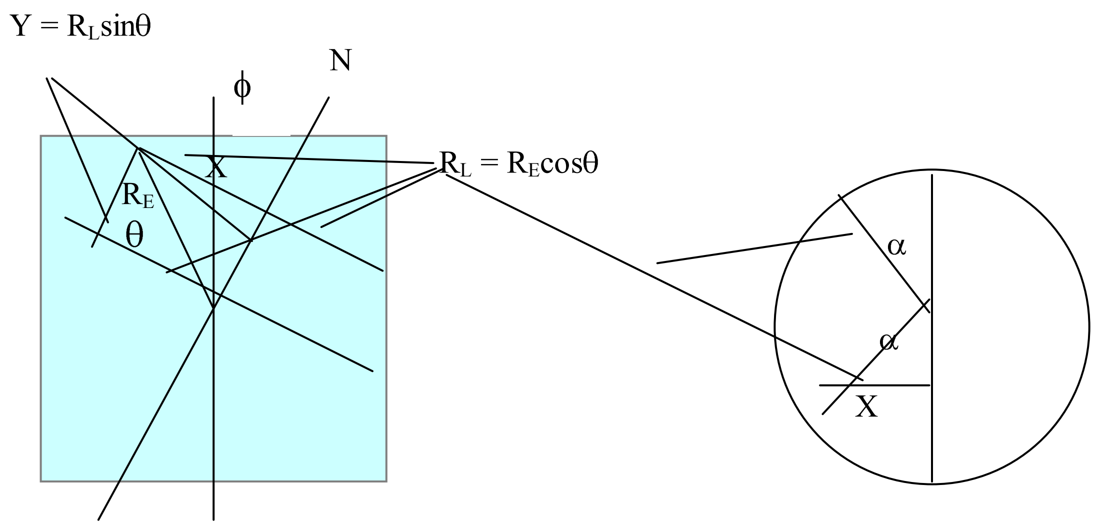


$A_H = 90 + \phi - \theta$ for the Northern Hemisphere.

The next step is to find the total hours of sunlight. The derivation may be beyond the level of many students.

Let:
H_S represent the hours of sunlight.
R_E represent the radius of the Earth.
R_L represent the radius at a particular latitude
α represent the angle of sunlight that is more or less than 180^0
X represent the distance from the North Pole to the Vertical Line

Two drawings are needed. One is looking at the Earth from its side. The other is looking at the Earth downward from the North Pole at the circle that represents latitude.



$R_L = R_E\cos\theta$
$Y = R_E\sin\theta$
$X = Y\tan\phi = R_E\sin\theta\tan\phi$

$$\sin\alpha = \frac{X}{R_E\cos\theta} = \frac{R_E\sin\theta\tan\phi}{R_E\cos\theta} = \tan\theta\tan\phi$$

$$\alpha = \sin^{-1}\tan\theta\tan\phi$$

Angle of sunlight is $180 + 2\alpha$

The Earth rotates 15^0 each hour. To find the hours of sunlight, divide the angle of sunlight by 15:

$$H_S = \frac{180 + 2\sin^{-1}(\mathrm{Tan}\theta\,\mathrm{Tan}\phi)}{15}$$

The time that the sun rises highest in the sky, T_Z, is given by:

$$T_Z = 12 + \frac{\text{Longitude} - 15N}{15}$$

Where 15N is the closest multiple of 15 to the longitude.

The times that the sun rises, T_R, and sets, T_S, are given by:

$$T_R = T_Z - \frac{H_S}{2}$$

$$T_S = T_Z + \frac{H_S}{2}$$

These are the calculated times. There are at least four major effects that affect actual times for sun rise and sun set. These are:

- Because of the refraction of the sun through the atmosphere, the sun appears to rise 3 minutes earlier and set 3 minutes later than it actually does.
- Since the Earth s orbiting the sun, the Earth takes about 4 minutes longer than one rotation for the sun to appear at the same point in the sky.
- Because the Earth's orbit is slightly elliptical, the speed that it travels around the sun varies slightly.
- The Earth is not a perfect sphere, but is closer to an oblate spheroid. This shape distortion will slightly affect sun rise and sun set at different latitiudes.

The angle that the sun makes with the horizon, A_T, is given by:

$$A_T = \frac{T_D - T_R}{H_S}(180^0)$$ Where T_D is the time of day

The amount of solar radiation, S_R, is given by:

$$S_R = 1372\sin(A_H)\sin(A_T)$$

Thus we can approximate the amount of solar energy that would reach any point on the Earth's surface at any time if the Earth were a vacuum. This radiation is for all practical purposes, is in the ultraviolet, visible light, and infrared regions of the electromagnetic spectrum. The wavelengths vary from about .2 (ultraviolet to 2.5(infrared) μmeters. The shorter the wavelength, the more the energy.

The highest energy radiation is ultraviolet radiation. Ultraviolet radiation makes up about 9% of solar radiation. The ultraviolet radiation is divided into three types: UVC with wavelengths of .2 to .29 μm, UVB with wavelengths of .29 to .32 μm, and UVA with wavelengths of .32 to .39 μm.

Visible light makes up about 45% of the radiation emitted by the sun. The wavelengths are between .39μm (violet) to .76 μm (red). The visible light spectrum in terms of increasing energy is: Red, Orange, Yellow, Green, Blue and Violet.

Infrared radiation makes up 46% of the sun's radiation. The wavelengths of infrared radiation emitted by the sun vary between .76 μm and 2.5 μm. Most of the radiation (75%) is between .76 μm and 1.5 μm (called near infrared). Only about 25% is from 1.5 μm and 2.5 μm.

The radiation that reaches the top of the Earth's atmosphere will be transmitted, reflected, refracted, absorbed or scattered. All of these parameters are wavelength dependent. To approximate the amount of radiation that reaches the surface of the Earth, we need to know what the transmission, reflection, refraction, absorption and scattering rates are for the various wavelengths by the atmosphere. The absorption rate will also vary with meteorological conditions.

Oxygen and ozone are very effective absorbers of ultraviolet radiation. The ozone layer in the stratosphere absorbs UVC radiation. Some of the UVB and UVA are absorbed by the ozone layer. However, a decrease in the ozone layer results in an increase in UVB and UVA radiation reaching the Earth's surface. For a1% decrease in the ozone layer, there is a 2% increase in UVB and UVA. A 2.5% decrease results in a 10% increase in UVB and UVA. UVB in particular is a major cause of skin cancer.

Very little visible light is absorbed. Therefor, most of the visible light is transmitted to the Earth' surface on clear days. Clouds will scatter visible light, lowering the amount transmitted to the Earth's surface. Infrared energy transmitted by the sun is absorbed very effectively by water. This is especially true for higher wavelengths of solar radiation.

The table below indicates the absorption wavelengths for various molecules that exist in the atmosphere. They are ranked from 0 to 100%.

Molecule	Wavelengths and Absorptivity
Methane CH_4	Peaks of about 90% at 3 and 10 micrometers (infrared) with small absorption between 2.5 and 10 micrometers
Nitrous Oxide N_2O	Major peaks of about 90% at 5 and 8.5 micrometers (infrared) with small absorption between 2.5 and 10 micrometers
Oxygen and Ozone O_2 and O_3	Nearly 100% absorption below .3 micrometers (ultraviolet). A small peak (about 50%) at .7 micrometers and small absorption between.3 and .8 micrometers.(visible light). Also major absorption of nearly 100% at about 10 micrometers (infrared)
Carbon Dioxide CO_2	Very strong absorption in the infrared region. Nearly 100 % at 2.5,4.5 and above 10 micrometers. About 30% at 2.5 micrometers
Water Vapor H_2O	Very strong absorption in the infrared region. Nearly 100 % at 1.8, between 2.5 and 3.5 and 4 to 7 micrometers.. Significant absorption at 1.1 and 1.3 micrometers (about 80%). Some absorption between .8 and 1 micrometer.
Net Effect of Atmosphere	Very high absorption in all of the ultraviolet wavelengths. Almost no absorption in the visible light wavelengths. In the infrared region: sporadic absorption up to about 2.5 micrometers; very high absorption with small gaps from 2.5 to 15 micrometers; and very high absorption above 15 micrometers.

From the table above, it can be seen that most of the visible light reaches the surface of the Earth. Very little ultraviolet and infrared radiation reaches the surface. Since the solar radiation that is emitted peaks in the visible light region, the major portion of the sun's energy reaches the Earth.

The Earth, however, emits mostly in the infrared region. Much of this energy is absorbed and re-radiated as heat energy. This is called the "Greenhouse Effect."

The ability to reflect radiation is called albedo. Albedo is expressed as a number between 0 and 1. The energy that is absorbed will be retransmitted at a different wavelength. An albedo of 0 means that the object absorbs all of the radiation that strikes it.

A body that has an albedo of 1 reflects all of the radiation that strikes it. Such a body would be a perfect reflector, an impossibility. All real objects therefor have an albedo between 0 and 1.

On average, the Earth's surface and atmosphere absorb about 69% of the solar radiation that strikes it. It therefor has an albedo of approximately .31. The atmosphere absorbs 23% of the radiation and the Earth on average about 46%.

SOLAR ENERGY ACTIVITIES

1. Find the following for the sun and the Earth:
    - Volumes of Earth and sun
    - Densities of Earth and sun
    - g at the surface of the sun
    - g caused by the sun at the Earth

    The Earth and the sun are approximated as spheres. The following information should help:

$$\text{Volume} = \frac{4}{3}\pi R^3$$

R is the Radius of the Planet. For the Earth, r = 6.378 x 10^6 meters. For the sun, R = 6.955×10^5 km

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

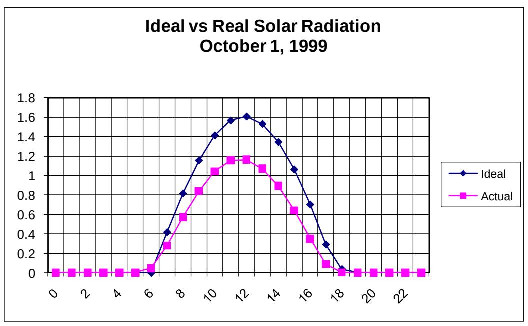
$$g = \frac{Gm}{R^2}$$

G = 6.67 x 10^{-11} (for meters and kilograms) R is distance from the center of the cause of the gravity (R for the Earth is its orbital distance of 1.5 x 10^{11} meters) The mass,m, is the mass of the cause of the gravity, in this case the sun.

1. Describe each of the sun's layers and their importance in the production of solar energy.
2. Using the energy radiated by the fusion of hydrogen into helium, find:
    A mole has 6.023 x 10^{23} molecules. Four hydrogen atoms are needed to produce one helium atom.
    - Energy produced by a mole of hydrogen
    - Length of time that a mole of hydrogen can provide the total power emitted by the sun.
    - The wavelength and frequency of photons radiated by the fusion reaction.
1. Describe how the magnetic field of the sun could be produced.
    The shearing causes ions to rotate in loops. These chrged particles in motion create a field perpendicular to the loop by the right hand rule.
2. Using the appropriate radiation law, find the following for the sun and the Earth:
    - Frequency and wavelength for the maximum power density.
    - The total power density

- The power density at each end of the spectrum for ultraviolet, visible light, and infrared

3. Find the power density that strikes Mars (R = 2.2 x 10^{11} meters).
4. Find the aperture angles for the solar radiation that strikes the Earth.
5. or the Earth, find the following for October 1, 1999:
   - sunrise and sunset
   - solar altitude
   - ideal power density for each hour of daylight in Langleys/minute
6. Compare predicted and real data for October 1, 1999 from the graph below.
   - Describe the differences.
   - Find the percentage loss at maximum power.



1. Describe the processes for photon interaction with molecules:
   - Emission
   - Absorption
   - Reflection
   - Scattering
   - Refraction
2. Using the absorption spectrum data for molecules in the atmosphere, determine:
   - Power density absorbed
   - Power density reflected, refracted and scattered

Possible research projects:

1. Find the sunrise and sunset for any day. Compare it to actual numbers from the newspaper. There will be differences. Some possible explanations are:
   - Refraction makes sunrise come earlier than it should geometrically.
   - The Earth rotates precisely once in 24 hours. But in those 24 hours it has moved. Try to find the effect of that movement.
   - The Earth's orbit is not perfectly circular. Try to find the effects of the orbit.
   - The Earth is an oblate spheroid, not a sphere. The southern hemisphere also bulges. These differences are only slight. Try to find the effect of these differences on the time.
2. The sun has various cycles that effect its radiation. Try to find these cycles and the effect on the radiation that reaches the Earth.

SECTION 2: THE CHEMISTRY OF OZONE

There are two primary ingredients in the making of ground level ozone (sometimes called photochemical smog). These are Nitrogen Dioxide, NO_2, and Volatile Organic Compounds (VOCs). The presence of sufficient quantities of these two ingredients at a high enough temperature and with enough solar radiation can cause the proper reactions to take place.

Different compounds of nitrogen oxides are produced as a by-product of combustion. Nearly 95% of these compounds are nitrous oxide. Nitrogen dioxide, NO_2, does not exist naturally. Nitrous oxide must be formed by a chemical reaction. The reaction that causes NO_2 to be formed from NO requires the existence of VOCs.

VOCs are hydrocarbons that can exist in vapor form in the atmosphere. They generally enter the atmosphere through evaporation. There are many such hydrocarbons that exist. Among these are methane, ethane propane, butane, ethene, propene, trans-2-butene, benzene, toluene, 2,3-dimethyl-butane, m-xylene, formaldehyde, and acetaldehyde.

One source of VOCs is anthropogenic or human-produced. Anthropogenic sources are categorized by type. The types with examples are listed below:

- **Point Sources**: Smoke tanks, storage tanks, fugitives (leaking pipes), large coating operations, evaporation from engines, boilers, and other large-scale industrial operations.
- **On Road Mobile Sources:** automobiles & other vehicles travelling on roadways, start-up of engines, hot soak (evaporation of fuels after engine shut –off, diurnal fuel evaporation caused by heating and cooling of fuel tanks, and fuel pumps at service stations.

- **Area Sources (small sources):** solvents and coatings, lawn mowers, generators, forklifts, tractors, construction equipment, aircraft, boats, and railroad engines.

There are also many biogenic or natural sources. The primary biogenic sources are the hydrocarbons released through the leaves of trees and plants. These hydrocarbons are often released as a defense mechanism against predators. Live oak trees and pine trees dominate the biogenic VOC production in the Gulf Coast region. Cattle, however, also release large amounts of methane.

The Texas Natural Resource Conservation Commission studied the sources for the Gulf Coast Region in 1992 and 1993. Up to 10,000 tons per day of VOCs were produced from biogenic sources. This compares to a maximum of about 2,500 tons/day for anthropogenic sources. If Harris County were isolated, the maximum biogenic sources (350 tons/day) were only about half of the anthropogenic sources (700 tons/day). These studies indicate that a regional attempt to reduce VOCs would not be valuable, but within Harris County results could be significant.

For nitrogen oxides, the production in Harris County was roughly equivalent to the VOC production in Harris County. These sources were overwhelmingly anthropogenic in nature (980 tons/day versus 4). The other significant result was that mobile sources (automobiles and trucks) were the largest source of nitrogen oxides making up almost 40% of the total.

The only known anthropogenic reaction that produces ozone is the reaction of NO_2 with oxygen in the presence of solar radiation that is below .42 μm (UV). This reaction is a two step process as shown below:

$$NO_2 + h\nu(\lambda < .42\mu m) \rightarrow NO + O$$
$$O + O_2 \rightarrow O_3$$

Where hν represents solar radiation

(Finlayson-Pitts, 1045-50).

A series of reactions produce ozone from NO and a VOC. The following example assumes that ozone is the VOC.

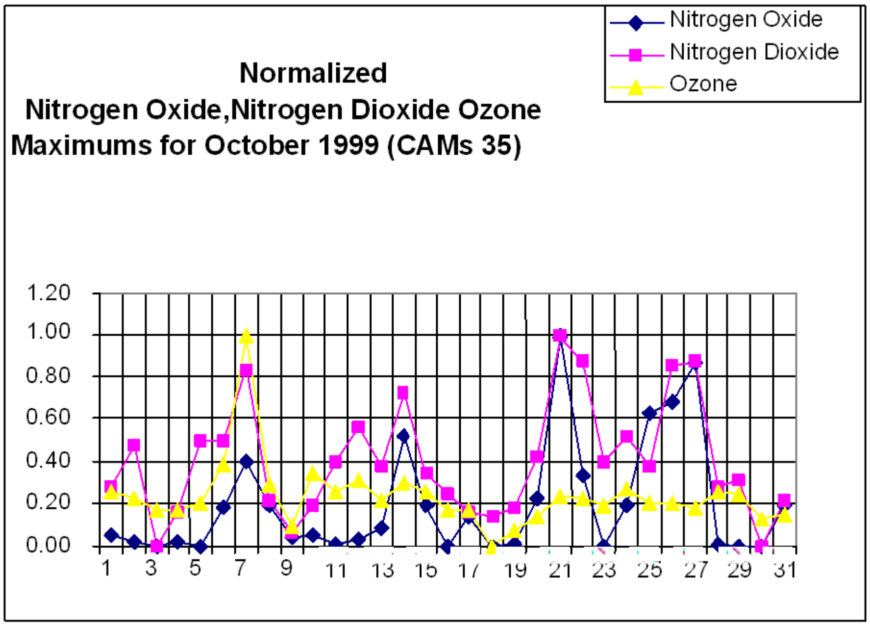
$$CH_4 + OH \rightarrow CH_3 + H_2O$$
$$CH_3 + O_2 \rightarrow CH_3O_2$$
$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$
$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$2NO_2 \xrightarrow{2h\nu} 2NO + 2O$$
$$2O + 2O_2 \rightarrow 2O_3$$

(Chemistry of Ozone)

In the series of reactions above, the net effect is that two NO molecules react with one methane, CH_4 to form two ozone molecules. After this reaction, two new NO molecules exist. As long as there are enough VOCs, this reaction can occur again. This multiplying effect can mean that the amount of ozone produced can be much larger than original concentration of the NO.

The other item of note is the necessity of having a hydroxyl ion, OH, present. Therefor, humid air is much more effective in producing ozone.

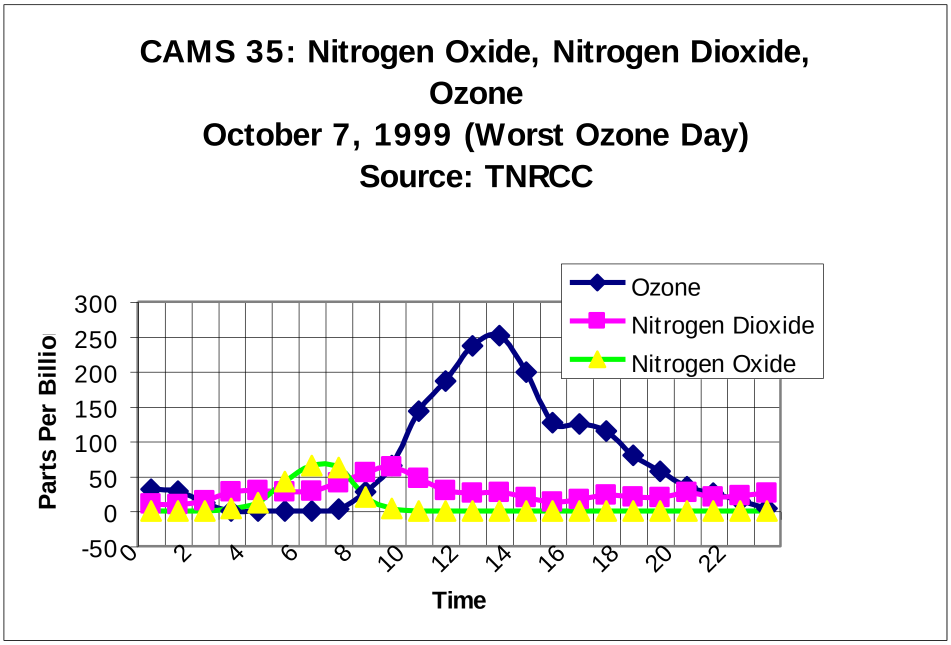
There is data available that can help. The graph below compares normalized ozone to normalized nitrogen oxide and nitrogen dioxide for the month of October 1999 at the site for the worst ozone level for 1999, CAMS 35 in Houston.



The days are in the center of the grid lines. For the only major peak in ozone there was a corresponding peak in nitrogen dioxide and a smaller peak in nitrogen oxide. Minimums in ozone corresponded to minimums in nitrogen oxide and nitrogen dioxide. However, several peaks in nitrogen oxide and nitrogen dioxide did not cause corresponding peaks in ozone.

This seems to indicate that high concentrations of nitrogen oxide and nitrogen dioxide are necessary but not sufficient to produce ozone.

One more analysis of data is helpful. The relative amounts of nitrogen oxide, nitrogen dioxide and ozone will indicate the relationship between them. the graph below is for the worst ozone day in 1999.



This graph shows that a relatively small amount of nitrogen oxide and nitrogen dioxide can cause a very high ozone level. The factor here is about four to one.

The other important factor is the question of cause and effect. The first to rise is nitrogen oxide. It dissipates as the nitrogen dioxide rises. This rise is followed by a rapid rise in ozone as the sun rises. This seems to indicate the relationship between ozone and solar radiation.

SECTION 3: METEOROLOGICAL FACTORS

In most areas of the North and Northeast US, meteorological factors can be a major pr.edictor for ozone production. In Houston-Galveston (H/G) and the Beaumont Port Arthur (B/PA) areas the relationship between meteorological factors and ozone production are not as strong. Quoting from a Texas Natural Conservation Commission report:

"The persistent high temperatures (both maximum and minimum) and high humidity during summers distinguishes the H/G and B/PA nonattainment areas from many other nonattainment areas in other parts of the country. In most areas of the north and northeast, meteorological variables (especially high temperatures and humidity) are strongly correlated with ozone formation. Ozone potential calculations for the Houston and Beaumont areas based on meteorological factors alone have correlation factors of

only .62 and .48 respectively. Therefore, meteorological variables alone cannot serve as predictors for high ozone events in the H/G and B/PA areas."

(Revisions to the State Implementation Plan for the Control of Ozone Air Pollution: Appendix A, Episode Selection and Meteorology, Volume 1)

Correlation factors in the above quote refer to the coefficient of correlation. When the absolute value of this coefficient is close to 1, there is a strong relationship between events. When this coefficient is close to 0, there is little or no relationship. The coefficients .62 and .48 indicate that there is a relationship but it is not strong.

The quote above can be looked at in an interesting way. Because the Houston area is almost always prime for ozone production the effects of sunlight intensity and meteorological factors are more clearly evident.

The wind is clearly a factor. The effect of the wind is complex, however. The very long quote below describes the complexity very clearly. Again quoting from the same TNRCC report on the next page:

"Weather patterns over the region may either improve or degrade air quality. Sustained winds serve to improve air quality by dispersing precursor pollutants and carrying them downwind. In contrast, low wind speed sallow precursors to accumulate in an area, further enhancing ozone formation. In other, cases, moderate winds may bring together ozone precursors from the mobile sources and the Houston Ship Channel and carry them to other locations, creating urban ozone concentrations well away from the original pollutant sources. On other days, strong winds may carry NO_X *out to rural areas with high biogenic emissions and form ozone well outside the consolidated metropolitan statistical area in regions that have few anthropogenic sources.*

Coastal meteorology is a complex mix of large scale and small- scale factors during the summer months when ozone frequently forms. Typically, a large-scale high atmospheric pressure area patterns exist over land and spread into the Gulf of Mexico, frequently lasting for days and sometimes lingering for weeks with little variation. The effect of the persistent high pressure is to stagnate air under its core and to generate a clockwise flow at its periphery, which results in a tendency toward coastal breezes throughout the area.

However, the local effects of solar heating on land and sea cause large temperature changes over land and smaller temperature changes over the sea. The differential daytime heating frequently enhances the local sea breeze. Although stagnant conditions under a persistent high tend to trap pollutants under a temperature inversion and elevate ozone levels, the counterclockwise flow of a high over the gulf can also strengthen the sea breeze, ventilate the metropolitan area, and reduce ozone levels instead.

When high-pressure areas weaken, local winds and a land/sea breeze develop. Recent studies (GMAQS/1995) have suggested that many of the Houston episodes are associated with a land/sea breeze particularly when the flow is oriented up and down the

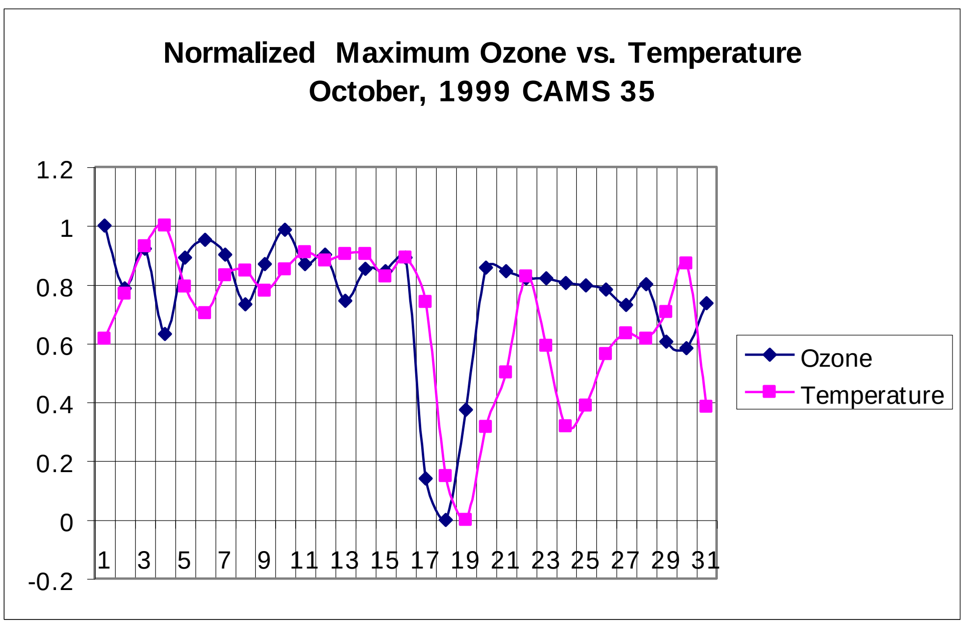
Houston ship channel. Typically, the nighttime land breeze carries air parcels of NO_X and VOC sources and carries the ozone precursors offshore during the early morning, and then exposes them to sunlight. Later, the sea breeze carries the air parcels back over land to the metropolitan area in the afternoon. If the land/sea breeze crosses over the same sources on its return, the parcels receive a double shot of pollutants and are likely to generate significant ozone."

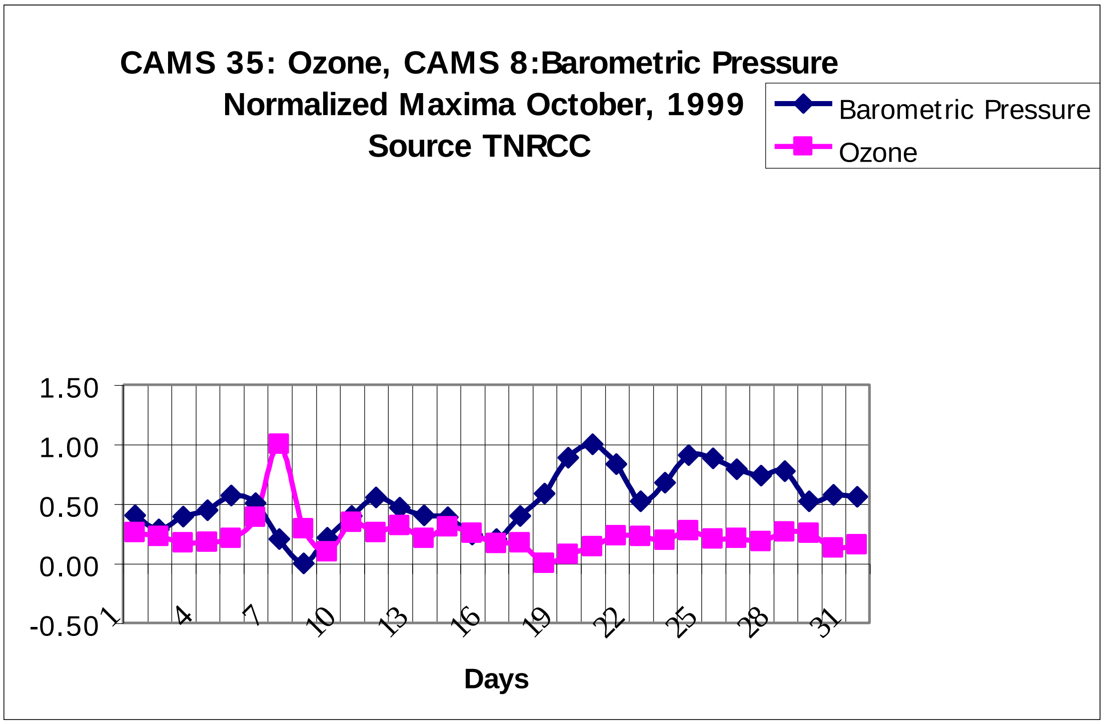
The above quote is fairly complex. However, from this quote and the other sections it can be deduced that the major meteorological factors are:

- Solar Radiation
- Temperature
- Wind Speed
- Wind Direction

Data for all of the above exists on the Internet at the TNRCC site. Also data exists for NO_X, NO, NO_2, ozone, and solar radiation. In selected sites, data exists for barometric pressure. These parameters therefor are the best candidates for developing a model.

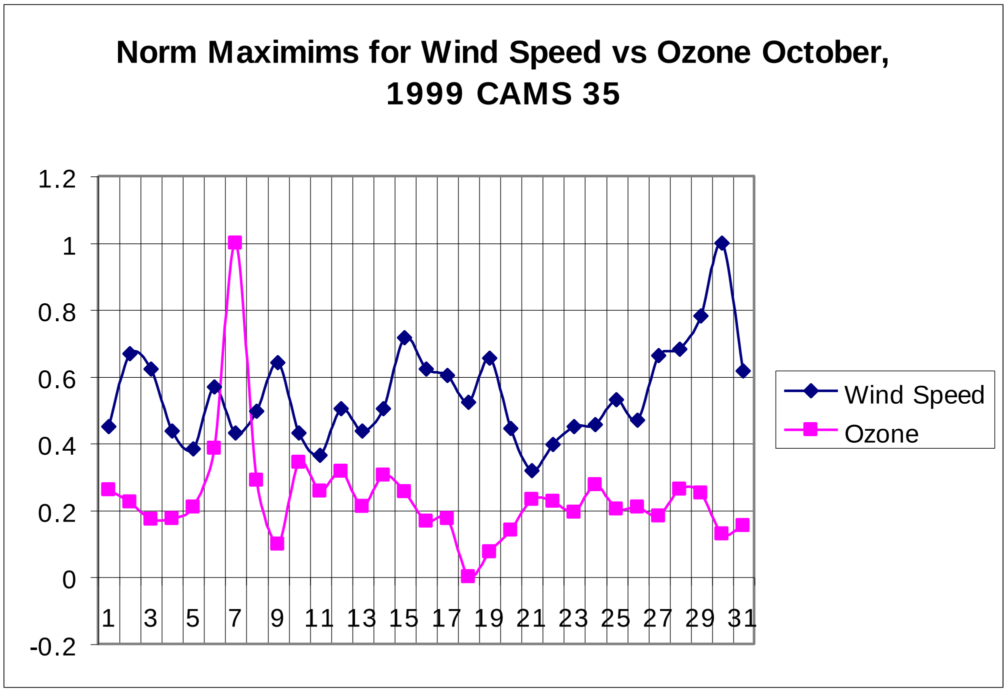
The graphs below are for solar radiation, temperature and barometric pressure vs. ozone. They are normalized maximums for October, 1999.





The graph for ozone vs. temperature illustrates a strong relationship between the two. High temperatures seem to mean high ozone levels and low temperatures mean low ozone levels. The variations, however, indicate that other factors influence the amount of ground level ozone.

The barometric pressure was very high during October 1999. The data shows that the barometric pressure variations almost seemed to have an inverse relationship to the ozone level. Most studies indicate that high pressure is a factor in high ozone levels. More research in this area could prove to be interesting.



There seems to be an inverse relationship between wind speed and ozone levels. High wind speeds mean low ozone levels and low wind speeds and low wind speeds mean high ozone levels. While not perfect, this relationship seems very strong.

SECTION 4: THE COMPUTER MODEL

The "real world" is too complex for total understanding. Scientists and engineers approximate behaviors by the use of abstract models. The goal is to describe the behaviors in as much detail as necessary to understand and predict. With students, the distinction between the real world and models must be made very clear. This is probably the area in science education that is most short-changed.

Much of secondary science education is built around "inviolate" laws and gross simplifications. Students are led to believe that these laws and facts are reality. Later they are told that what they learned was wrong. Students then become confused and disillusioned.

It would be much better if the student were to learn that science consists of models that are used when appropriate. When a model does not adequately describe behavior, a more complex model is developed.

Modeling is also called systems thinking. The reason that this approach is becoming increasingly important is described in <u>An Introduction to Systems Thinking</u>, a manual supplied by High Performance Systems Inc. with Stella™ software. Here are some selected abstracts their rationale:

"*The issues and problems today's students will face as they take their places are ever daunting! In the social arena, in the sphere of technology, in the biological and ethical realms, everywhere the tradeoffs are becoming more acute, the decisions more profound, the risks more serious-and all the while the pace of change is accelerating…"*

"Unfortunately, although the nature of the challenges is growing more daunting, the response of the education system has been to serve up more of the same… The learning objective continues to be knowledge accumulation. Students take in content, store it for awhile, then spit it back on content –recall tests to demonstrate what they know.

At the same time, very little attention has been focused on building the capacity to think, develop understanding, and generate insight-especially as these capacities apply to systems of interdependent relationships. Yet these capacities last a lifetime and can be enormously useful in addressing the ever daunting set of challenges we face."

Source: An Introduction to Systems Thinking. Stella Software, 1997. Pages 1-1,1-2

Before developing the computer model, data needs to be analyzed. Using the data supplied by TNRCC at its Internet site, a large number of sequential days should be selected that are diverse. This data can be easily placed in a spreadsheet if the data is downloaded in comma-delimited form. For each of the parameters, a maximum and minimum should be found. Using the following formula, the data for each parameter should be normalized:

$$\text{NORM\_DATA} = \frac{\text{DATA} - \text{MINIMUM}}{\text{MAXIMUM} - \text{MINIMUM}}$$

The data should be normalized over the many days to study how parameters vary with conditions. The data from each day should be normalized to study the relationship between the parameters. Graphs comparing parameters should be created over all of the days and for each day using the appropriate normalized data.

The graphs over the sequential days can be used to see which parameters are related. Similar shape or inverse shape will indicate a relationship. The most similar shapes are candidates for the computer models.

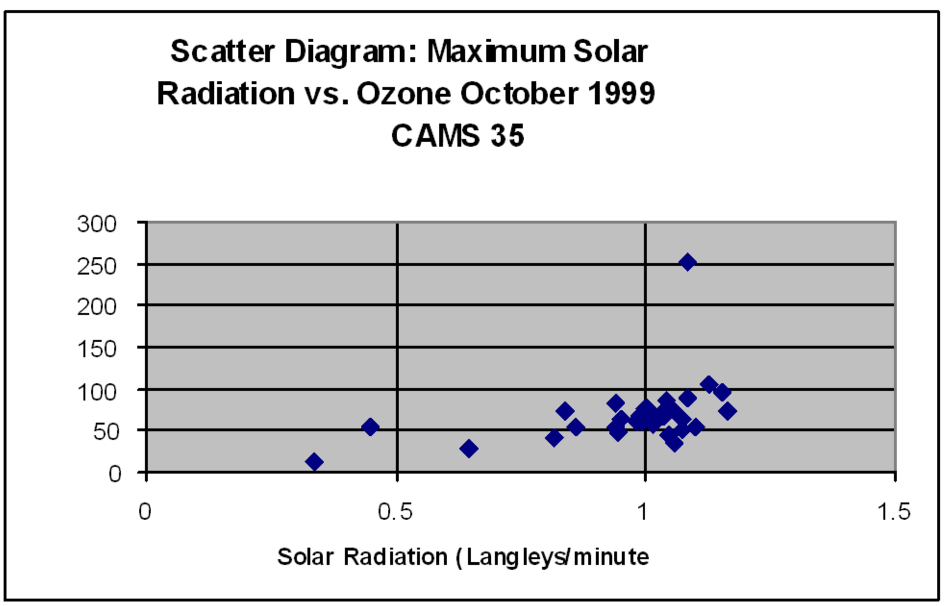
Graphs for single days can demonstrate cause and effect. This is an obvious but sometimes overlooked phenomenon. Causes must happen before effects. Also, single day graphs can be used as the reference node described in the beginning discussion of modeling.

Often the relationship between data sets can be determined by the use of scatter diagrams. Values for the corresponding data sets are plotted on the "x" and "y" axes respectively. If there is a correlation, the points tend to line up in a straight line. An equation can be deduced from the line. This is called linear regression. At other times the points arrange themselves along a recognizable curve. Again an equation can be developed.

If scatter diagrams for any of various parameters vs. ozone were to line up either along a line or a recognizable curve, the task of predicting ozone would be easy. there would be a simple equation. Unfortunately, this is not the case.

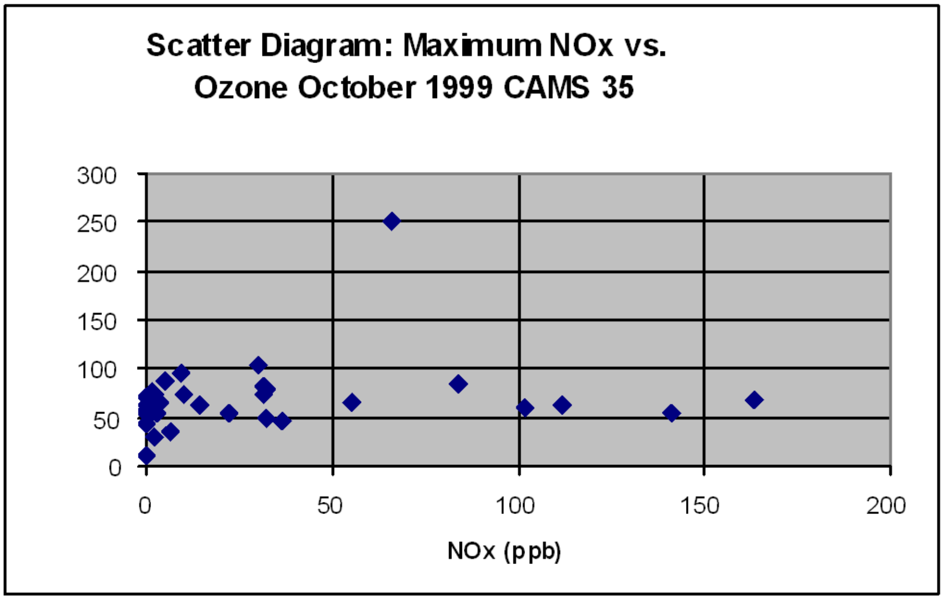
Much can be hypothesized from the scatter diagrams nonetheless. The scatter diagrams for various parameters vs. ozone levels are given below for October 1999. Under each graph possible hypotheses are stated in italics for teacher use. The hypotheses that students come up with should be very interesting. This is definitely a team activity.

The task is for the students to hypothesize as much as they can from each scatter diagram. To make the task easier, the students should compare values that have ozone levels near or above 100 parts per billion.

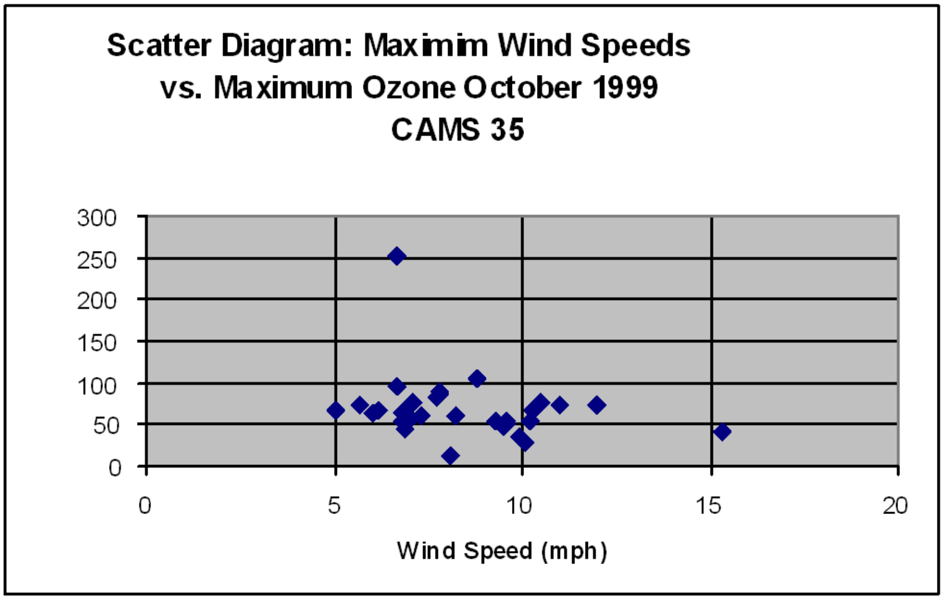


In the scatter diagram for solar radiation vs. ozone, note that about half of the days had a maximum of 1 langley/minute. Only on one of those days did the ozone level approach 100 parts per billion. Above 1 langley/ minute, there were five days close to or above 100 parts per billion of ozone.

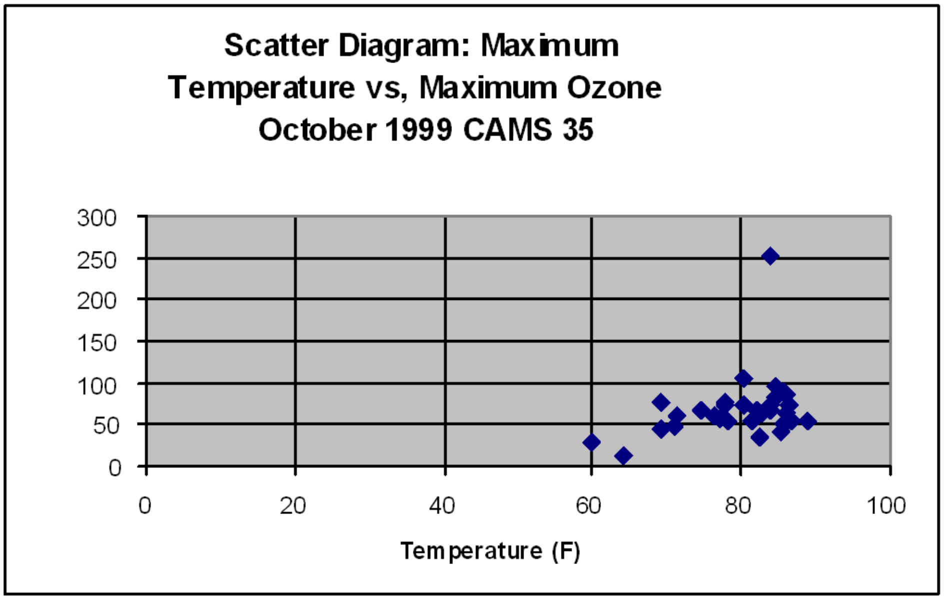
An excellent hypothesis would be: "If the solar radiation level exceeds 1, there is a one-third probability of the of the ozone reaching 100. If solar radiation is at or below 1, the probability of the ozone reaching 100 is close to 0."



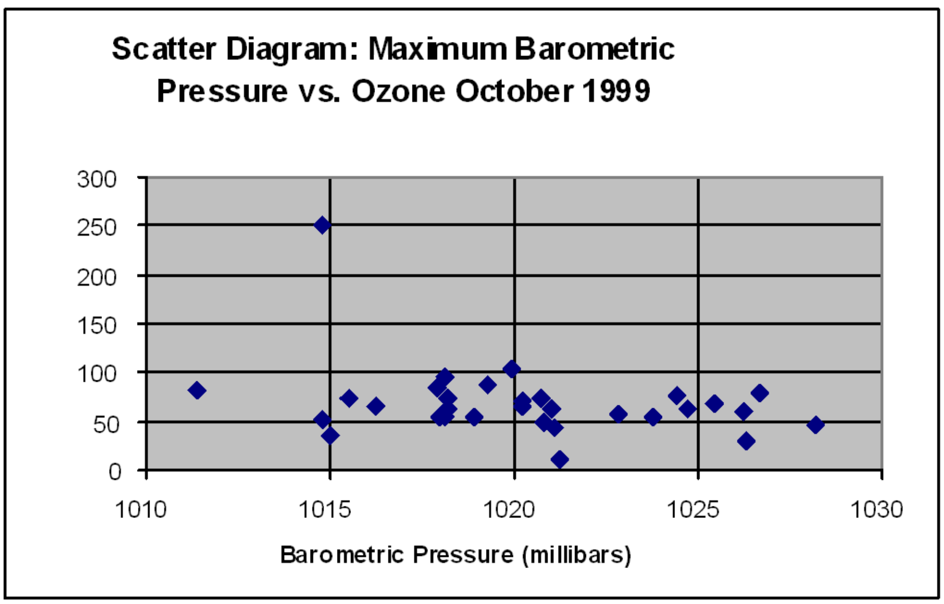
Most nitrogen oxide levels are below 50 parts per billion. The one very high ozone level is not enough to form any hypothesis. More data sets are needed.



Maximum wind speeds of about 6 to 8 miles per hour had the highest ozone levels. Hypothesizing that wind speeds in this range would be most conducive to ozone is a good guess.



It looks like maximum temperatures at 80 degrees F or above are more conduce to high ozone levels.



Maximum barometric pressure vs. ozone levels is very interesting. It looks like the highest ozone levels occur in a range of about 1015 to 1020 millibars.

MODELING ACTIVITIES.

One more way of looking at the data is to compare various parameters on high ozone days to parameters on low ozone days. High ozone days will be considered above 100 parts per billion. Low ozone days will be considered under 60 parts per billion. All of the readings are maximums for the day. Each parameter will be tested as a possible necessary condition for ozone production. The hypoethesis value for each parameter is in parentheses. The parameters measured for comparison and their abbreviations are:

- Ozone: measured in parts per billion. The ozone level is the dependent variable.
- Pressure: This is ground level barometric pressure measured in millibars. A reading of 1013 is considered average. (at or below 1020)
- NO: This is nitrogen oxide. Nitrogen oxide readings are in parts per billion. (at or above 25 parts per billion)
- Temp: This is temperature in degrees Fahrenheit. (at or above 80^0 F)
- SolRad: This is solar radiation in Langleys/ minute. (at or above 1 Langley/min)
- Wind Speed: Wind Speed is measured in miles per hour. (below 10 mph)

The month used to develop the hypothesis was October, 1999. The monitoring site was CAM 35. There were two days that had high ozone and eleven days that had low ozone. Three of the days with low ozone had missing data. Therefor, only fourteen days were used for low ozone.

High Ozone (above 100 parts per billion)

Day	Ozone	Pressure	NO	Temp	SolRad	Wind Speed
6	104.47	1019.9	29.9	80.3	1.125	9.2
7	236.89	1014.8	65.7	84	1.082	6.9
Averages	170.68	1017.35	47.8	82.15	1.1035	8.05

Both of these days met the criteria for all parameters.

Low Ozone (below 60 parts per billion)

Day	Ozone	Pressure	NO	Temp	SolRad	Wind Speed
3	53.49	1018	0	86.9	1.099	9.8
4	53.93	1018.9	3.1	88.9	0.858	7.9
16	52.2	1014.8	0.7	85.8	1.074	9.9
17	53.86	1018.1	22.5	81.4	0.451	9.8
18	11.95	1021.2	0.2	64.3	0.334	8.4
19	29.98	1026.3	2.4	60	0.645	10.8
20	45.84	1028.2	36.7	69.1	1.045	7.9
23	58.42	1022.8	0	77.1	1.016	7.6
27	55.53	1023.8	141.3	78.3	0.94	10.6
30	42.95	1021.1	0	85.2	0.818	16.2
31	48.76	1020.8	32.3	71.1	0.946	10
Averages	46.08	1021.27	21.75	77.10	0.84	9.90

The parameters that failed to meet the criteria are shaded. Only October 3rd and October 16th had one parameter that failed to meet the criteria.

To test the hypothesis, another month and site were chosen. This site was CAMS 8 and the month was August 1999. There were many more high ozone days (9) and fewer low ozone days (6).

The high ozone days and their parameters are in the table below:

Day	Ozone	Pressure	NO	SolRad	Temp	Wind Speed
1	109.78	1016	15.7	1.301	94.2	6.9
6	121.75	1014.5	35.5	1.035	95.1	7
7	122.71	1015.5	7.2	1.269	94.5	8.3
16	101.19	1019.7	21.8	1.339	93.3	7.7
18	123.32	1017.6	39	1.361	95.7	4.9
20	118.73	1015.3	28.2	1.251	101.6	8.7
21	144.88	1014.6	25.3	1.16	93.5	10.6
28	106.62	1015.8	25.1	1.245	94.6	6.5
31	115.85	1013.8	57.8	1.131	92.8	8.6
Averages	118.31	1015.87	28.40	1.23	95.03	7.69

In the table for high ozone days above, the parameters that failed to meet the criteria are highlighted. There were three days that failed to meet one criterion: August 1st, August 16th and August 21st.

In the table for low ozone levels below, there are six low ozone days (below 60 ppb).

Day	Ozone	Pressure	NO	SolRad	Temp	Wind Speed
10	56.25	1014.1	7.4	1.277	96.1	10.1
11	50.05	1015.9	12.8	1.28	95.3	9.1
12	41.28	1016.1	5.6	1.308	95.6	10.1
13	58.06	1015.9	7.3	1.241	97.1	9.9
22	36.67	1013.4	9.5	1.101	91.3	10.5
23	31.13	1013	30.7	0.77	88.5	6.5
Averages	45.57	1014.73	12.22	1.16	93.98	9.37

In the table above, all days had at least one parameter not meet the criterion. The hypothesis therefor has some merit. The conclusion is that there seems to be some relationship between the parameters and the amount of ozone.

There may be other factors. One of these could be the stability of the atmosphere. When the atmosphere is highly stable, air parcels at ground level cannot rise. This would result in a better chance that the various chemical components can mix. Another factor may be that the source may be in another location. Thus the ozone present may be transported ozone. These factors would make very valuable research projects for students.

ANNOTATED BIBLIOGRAPHY

Solar Radiation
Glossary of Solar Radiation Resource Terms www.rredc.nrel.gov/glossary
The terminology of solar radiation can be daunting. Have this glossary available when doing research. The explanations are clear at this Internet site. It should be the first site that is downloaded.

Observing Solar Cycles
www.hpcc-k12.nasa.gov/gesep987/science-briefs/ed-sticlkler/ed-solarcycles.html
This Internet site is an excellent resource for understanding the sun and solar radiation. It provides material that can be downloaded and reproduced for students. It should be the second site that is downloaded.

Astronomy162: Stars, Galaxies and Cosmology
www.csep10.phys.utk.edu/astr162/tect/index.html
This is the primary source for light, the electromagnetic spectrum, quantum mechanics and its equations. This is the third Internet site that should be downloaded.

Eddy, John A. A New Sun: The Solar Results from Skylab. National Aeronautics and Space Administration. Washington D.C., 1979
Although a bit dated, this NASA publication provides an excellent overview of the sun and solar radiation. Research projects on solar radiation should definitely include this text. It is available through the US Governemnt Printing Office

The Astronomical Almanac. U.S. Government Printing Office. Washington D.C., 1993
There are versions printed each year through the US Government Printing Office. The data is from an Earth-centered perspective (astronomical). This publication has equations that are very accurate in finding solar radiation at any time and any point on the Earth. It is an excellent source for advanced research projects on solar radiation as a function of time, day and location.

Radiation. www.eas.slu.edu/People/Atokay/chapter2.html
This Internet site provides a basic overview on solar radiation. It is somewhat lacking in detail, but it is an excellent first source.
Radiation www.rossby.ou.edu/~metr1014/27aug987/sld051.htm
This material is in slide form. it provides a general overview of solar energy.

Shining On www.asd.nrel.gov/solar/pubs/shining
This Internet site is focused on solar energy as a renewable source. It also provides an overview of solar radiation in easily understandable terms. Its major value for this unit is its links to other sources.

Necessary Conditions for Nuclear Fusion
www.zebu.uoregon.edu/~imamura/208/jan27/cond.html
This is a starting source for understanding nuclear fusion.

Radiation and the Diurnal Cycle www.met.tamu.edu/class/Metr151/tut/rad/radmain.html
This is an excellent interactive tutorial on the relationship of solar radiation and temperature as a function of a 24 hour day.

Chemistry of Ozone
Atmospheric Chemistry Glossary www.shsu.edu/~chemistry/glossary/glos.html
This glossary will prove to be invaluable when reading other sources. there are some misspelled words and grammatical errors in the glossary. It is, however, worth using.

Living Landscapes
www.royal.onakagan.bc.ca/mpidwirn/atmosphereandclimate/smog.html
This is the best of several Internet sources. It provides a basic understanding of the chemistry of ozone production. It does have enough detail to provide a fairly good understanding.

Tropospheric Chemistry Overview www.uow.edu.au/~swilson/327intro99
This particular web site is actually a slide show. Although only in outline form, the material does provide a bridge from the basic to a deeper conceptual understanding.

Revisions to the State Implementation Plan for the Control of Ozone Air Pollution
Texas National Resource Conservation Commission, P.O. Box 13087 Austin, TX 770387
These documents are fairly technical. There are some sections, however, that are very readable. The appendices are the most valuable. Both the plan and the appendices are available from TNRCC.

Select a Monitoring Site in Region 12 (Houston)
www.tnrcc.tx.us/cgi-bin/monops/select-month?region12.html
This is the best source of actual data. All of the graps in the entire unit are based on this source. By downloading data in comma delimited form, data can be used in spreadsheets. This allows for graphical analysisand and mathematical manipulation.

The articles below from Science magazine are excellent sources for research. They are very technical abd should not be read until students have a fairly sophisticated understanding of the principle of ground level ozone formation.

Finlayson-Pitts, Barbara J. & Pitts, James N. Jr. "Tropospheric Air Pollution: Ozone, Airborne Toxics, Polycyclic Aromatic Hydrocarbons, and Particles." Science, Vol. 276, 16 May 1997, 1045-50.

Ravishankara, A.R. "Heterogeneous and Multiphase Chemistry in the Troposphere." Science, Vol. 276, 16 May 1997, 1058-65.

Roscoe, Howard K. & Clemitshaw, Kevin C. "Measurement Techniques in Gas-Phase Tropospheric Chemistry: A Selective View of Past, Present and Future." Science, Vol. 276, 16 May 1997, 1065-72.

Brunner, Dominick, et al. "Large-Scale Nitrogen Oxide in the Tropopause Region and Implications for Ozone." Science, Vol. 282, 13 November 1998, 1305-1309.

Dickerson, R.R. et al. "The Impact of Aerosols on Solar Ultraviolet Radiation and Photochemical Smog." Science, Vol. 278, 13 October 1997, 827-30.

Odum, Jr., et al. "The Atmospheric Aerosol-Forming Potential of Whole Gasoline Vapor." Science, Vol. 276, 4 April 1997, 96-99.

Meteorology and Atmosphere
Williams, Jack. The Weather Book 2nd Edition. Vintage Books, 1997

Revisions to the State Implementation Plan for the Control of Ozone Air Pollution: Appendix A, Episode Selection and Meteorology, Volume 1. Texas Natural resource Conservation Commission, February 28,1998.

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Ford, Andrew. Modeling the Environment. Island Press, 1999

An Introduction to Systems Thinking. Stella Software, 1997.

Postman and Weingartner, Teaching as a Subversive Activity. Delacorte Press, NY 1969. P23.