Thermal Inversions and Photochemical Smog

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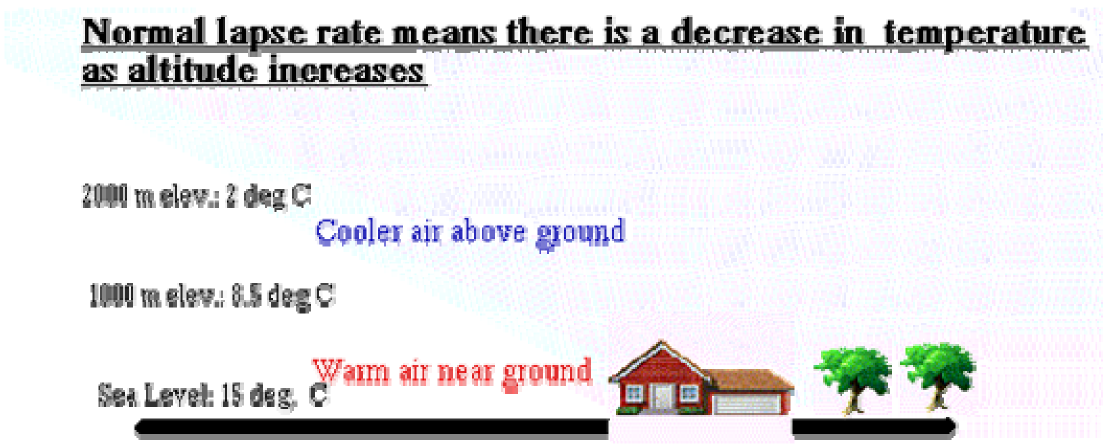
Thermal Inversions

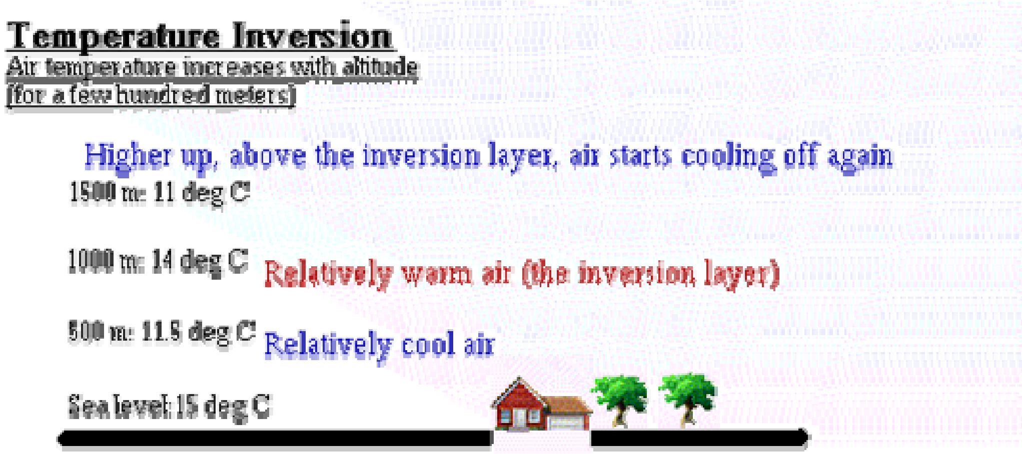
In the normal situation, the temperature decreases as you go up in altitude in the troposphere. The rate of decrease varies, but an accepted average value is 6.5 degrees Celsius per 1000 meters (this is called the normal lapse rate). That is, if you start at sea level and go up (say, in a balloon) 1000 meters in the atmosphere, you can expect that the temperature of the surrounding air will drop an average of 6.5 degrees Celsius. Go up another 1000 meters (one kilometer), and the temperature will drop another 6.5 degrees (that is, it will be 13 degrees colder than it was when you started at sea level). If you are measuring in feet and Fahrenheit degrees, this translates to a drop of about 3.6 degrees F per 1000 feet.



This normal decrease in temperature with altitude has lots of implications for weather. In the context of air pollution, it means that the decrease in temperature helps to mix the air, and disperse pollutants. If a parcel of air is warmer than the surrounding air, it is less dense, more bouyant, and it has a tendency to rise up until it finds air that is about the same temperature and density as it is. This helps disperse pollutants at the surface. On the other hand, air which is cold and dense is likely to be stable, and stay put.

A very stable situation would occur when cold air is near the ground, and there is a

layer of warmer air above it. This is a departure from the normal situation, and is called a temperature inversion, or thermal inversion. This cold air is denser than the warm air above it. It resists rising, and is described as stable air. Above the inversion layer, the air will again cool off with increasing altitude.

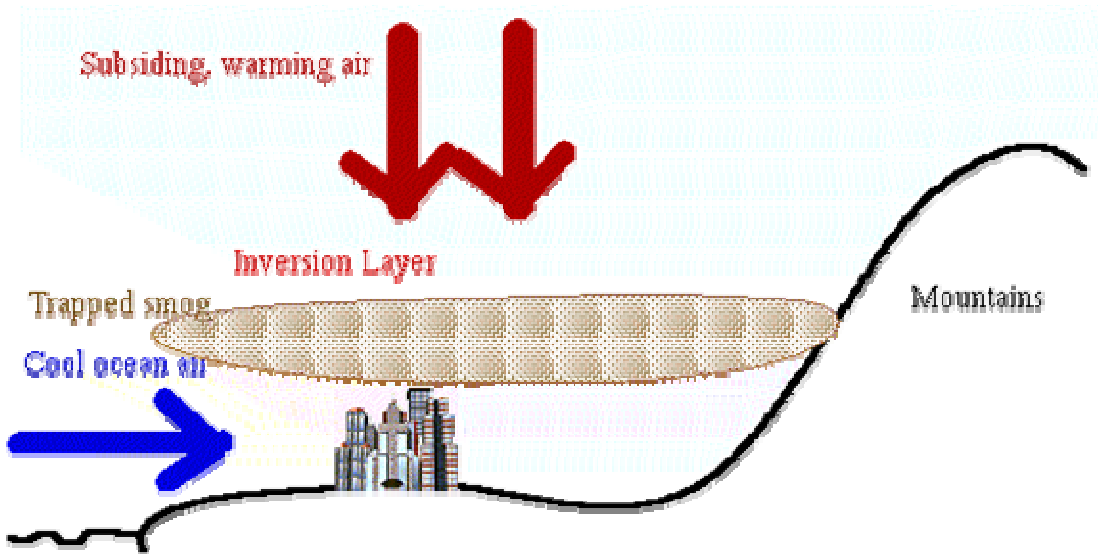


There are several reasons why an inversion might develop. One situation in which a low level, or surface inversion, might take place is on a clear night, when the earth's surface radiates heat away rapidly. If the air is clear, the ground, and the air directly above it, can be cooler than the air at higher altitudes. This type of situation may occur on winter nights in California, and can be a problem for citrus growers, because if enough heat radiates away, the temperature at the ground surface can drop below the freezing level.

Another type of inversion, called an advectional inversion, involves a horizontal inflow of cold air. This might be air blowing in from cold water to a coastal area. Along the California coast, winds frequently blow onshore, passing over the cold ocean waters before reaching land. When this occurs, the air at ground level may be colder than the air above it, and the air is stable.

A third type of surface inversion takes place at night in valleys, when cold, dense air flows downslope under the influence of gravity, draining off the slopes and uplands, and into the valleys. The air in the valley bottoms is colder than the air above. Other types of inversions may also develop under various conditions.

In California, upper air inversions develop because much of California is on the eastern edge of the subtropical high pressure cell in the Pacific Ocean. This high pressure cell develops in response to global patterns of atmospheric pressure and circulation, rather than local conditions. The presence of high pressure means that the air in the region is subsiding from high altitudes in the atmosphere. Subsiding air is compressed by the increasing pressure of the surrounding air as it descends, so the air warms up as it subsides. So not only is there cool air at ground level (from onshore flow of cool air), there is also a general subsidence of warm air aloft. The inversion layer acts as a lid to prevent air at ground level from rising and dispersing. If there are mountains inland, the mountains can also help trap the air. This means that any pollutants emitted accumulate in the trapped air.



The bottom line is that conditions in California frequently favor the development of temperature inversions. The pollutants will continue to become more concentrated until a change in the weather leads to the breakup of the inversion layer.

For more information on the web about thermal inversions, try the following links:

- **A good discussion of Regional Inversions in Los Angeles, apparently done as a class project.**
- **Why downward motion creates inversions, from USA Today Weather.**
- **Subsidence Inversions (as applied to lighter-than-air flight).**

For a more complete discussion, any good physical geography or meteorology textbook should cover this subject in more detail. Some good books are:

Aguado, Edward, and J. E. Burt. 1999. Understanding Weather and Climate. Prentice Hall.

Gabler, R.E., R.J. Sager, D.L. Wise, and J.F. Petersen. 1999. Essentials of Physical Geography. Saunders College Publishing.

Lutgens, Frederick K., and E.J. Tarbuck.1995. The Atmosphere. Prentice Hall.

McKnight, Tom. 1999. Physical Geography. Prentice Hall.

Moran, Joseph M., and M.D. Morgan. 1994. Meteorology. Macmillan College Publishing Co.

Strahler, A.H., and A.N. Strahler. 1992. Modern Physical Geography. John Wiley and Sons, Inc.

Photochemical Smog

What follows is a brief description of photochemical smog formation, from a non-chemist. For those who want to pursue this topic, there are also some links to follow for more information.

Photochemical smog is brown smog, the gray-brown haze that fills the air in many cities. It is especially a problem in warm, sunny regions where there are lots of cars burning gasoline. Researchers in the 1940's and 1950's in Los Angeles noticed that the kinds of pollutants in the air varied over the course of the day. Some pollutants increased in the morning, as people started driving their cars. Other pollutants, including the visible, brown smoggy haze, were most common in the middle of the day. The mix of pollutants changed again in the late afternoon and evening. It became apparent that the chemical reactions among the various pollutants were related to sunlight. Smog is worse in Los Angeles--and everywhere--in the summer, because the light energy from the sun moves some of the reactions along.

To form photochemical smog, three main ingredients are needed: nitrogen oxides (NO_x), hydrocarbons, and energy from the sun in the form of ultraviolet light (UV).

The first thing that starts the chain of events is that people start driving in the morning. As gasoline is burned, nitrogen (N_2) in the atmosphere is also burned, or oxidized, forming nitric oxide (NO)

$$N_2 + O_2 = 2NO$$

Hydrocarbons and carbon monoxide (CO) will also be emitted by cars. Hydrocarbons are volatile organic compounds that may include acetaldehyde, formaldehyde, ethylene, and many other compounds.

In the air, nitric oxide combines with molecular oxygen to form nitrogen dioxide within a few hours.

$$2NO + O_2 \text{--------->} 2NO_2$$

Nitrogen dioxide absorbs light energy and splits to form nitric oxide and atomic oxygen:

$$NO_2 \text{-->} NO + O$$

Then, in sunlight, the atomic oxygen combines with oxygen gas to form ozone (O_3):

$$O + O_2 \text{--->} O_3$$

If no other factors are involved, ozone and nitric oxide then react to form nitrogen dioxide and oxygen gas.

$$O_3 + NO \text{<------>} NO_2 + O_2$$

This last reaction can go in <u>either</u> direction, depending on temperature and the amount of sunlight. If there is a lot of sunlight, the equation moves to the left, and more ozone is produced. If nothing else gets in the way, an equilibrium is reached, and the ozone level stabilizes.

However, there is something else involved. Remember that the cars are also emitting hydrocarbons as well as oxides of nitrogen. Hydrocarbons are the other main ingredient in photochemical smog. When hydrocarbons are present, nitric oxide reacts with them instead of the ozone. This reaction produces a variety of toxic products, such as a volatile compound known as PAN (peroxyacetyl nitrate).

NO + hydrocarbons---------------->PAN and various other compounds. Also,

NO_2 +hydrocarbons----------------->PAN and various other compounds

So, there are two results (at least) from the reaction of nitrogen oxides with hydrocarbons. One is that a lot of volatile, reactive organic compounds are generated directly. The other is that when the nitric oxide (NO) is busy reacting with hydrocarbons, it is not reacting with ozone to break it back down to molecular oxygen. So the amount of ozone in the air increases. With nitric oxide reacting with hydrocarbons, ozone may accumulate to damaging levels. (Ozone may also be released into the air naturally by forest fires. But in a natural situation, ozone would react with nitric oxide and be broken down to oxygen, as noted above).

The result, then, is an accumulation of ozone and volatile organic compounds such as PAN. These are referred to as secondary pollutants, because they are formed by the reaction of primary pollutants, nitrogen oxides and hydrocarbons, emitted by burning fossil fuels. The energy from the sun moves the reactions along. This forms photochemical smog, the brown gunk we see in the sky, especially on hot sunny days.

Photochemical smog can cause eye irritation and poor visibility. Strong oxidants such as ozone can damage the lungs. The oxidants irritate the linings of lungs. Damage to the lungs may stress the heart. Health damage is worse for people with existing lung and heart conditions. Other health implications may include loss of immune system function, increased susceptibility to infections, and fatigue. The damage can be caused by exposure to large amounts of the pollutant over a short time span, and also by chronic exposure to small amounts over long periods of time. Oxidants can kill plant cells, causing leaves to develop brown spots or drop off the plant, reduce plant growth, and make plants more susceptible to damage from other causes. Oxidants such as ozone can also corrode and destroy many materials such as rubber, nylon, fabric, and paint.

The above is a simplified discussion of photochemical smog formation. There are more reactions involved, and a number of loops and subloops in the sequence of reactions. Some of the links below can provide more detail about the reactions involved, or give a different point of view of the process.

Links to websites about photochemical smog:

- **A brief description of Photochemical Smog formation from the Hong Kong Institute of Education.**
- **A clear general discussion of Smog, including development, chemistry, and a few meteorological factors.**
- **For a technical discussion of Smog Formation, see this review from the National Alternative Fuels Consortium.**
- **A discussion of the chemistry of photochemical smog may be found in Reaction Mechanisms: Photochemical Smog., from a web site on Computational Atmospheric Science.**
- **Also try Photochemical Oxidant Formation (Smog)**

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Comments, Questions, or Suggestions? Email: J.R. Thorngren

(but I can't do calculations for you...or do your homework)

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The grizzly bear is the state animal of California, and is the bear on the California flag. There are no grizzly bears in the wild in California today. The last one in the state was killed in 1922, or possibly in 1924.