

Chapter Two – Ozone Basics and Atmospheric Conditions, 2011-2012

The Basics

Tropospheric ozone is a principal component of smog, a word derived from the words “smoke” and “fog.” Such ozone is located in an atmospheric layer located next to Earth’s surface, the troposphere (See Figure 2.1). This ozone is not to be confused with stratospheric ozone, located in a layer of the upper atmosphere, the stratosphere. Both layers contain the same chemical (O_3) but the ozone in the stratosphere is beneficial as a filter of ultraviolet (UV) rays while the tropospheric ozone is harmful to living tissues.

What Is Ozone?

Ozone gas is a molecule of three atoms of oxygen. The oxygen we breathe is a molecule

of two oxygen atoms. Ozone, O_3 , naturally occurs in the upper atmosphere (the stratosphere) approximately 10 to 30 miles above the Earth’s surface. Ultraviolet light breaks normal oxygen molecules, O_2 , apart. The free oxygens, O_1 , joins with O_2 molecules to form O_3 . This ozone protects Earth from the sun’s harmful ultraviolet rays. In the lower atmosphere, the troposphere, ozone is harmful to people, animals, crops and other living things. We call ozone “Good Up High. Bad Near By.”

In the troposphere, ozone is created by the interactions of natural and anthropogenic (human-made) emissions of volatile organic compounds (VOCs) and nitrogen oxides. The nitrogens include nitrogen oxide (NO),

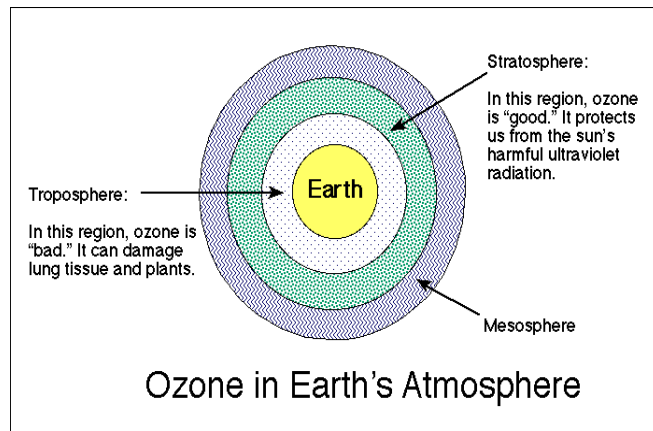


Figure 2.1: Ozone occurs in both the troposphere and the stratosphere. The Earth’s entire atmosphere is about 80 km thick. The troposphere is 10 to 15 km from the surface of the Earth. The next atmospheric layer is the stratosphere, 15 to 30 km thick. Beyond the stratosphere, are the mesosphere and a thin outer layer called the exosphere. Note that the depths of each layer are not to scale. (Figure taken from http://spsso.gsfc.nasa.gov/NASA_FACTS/ozone/fig1.gif).

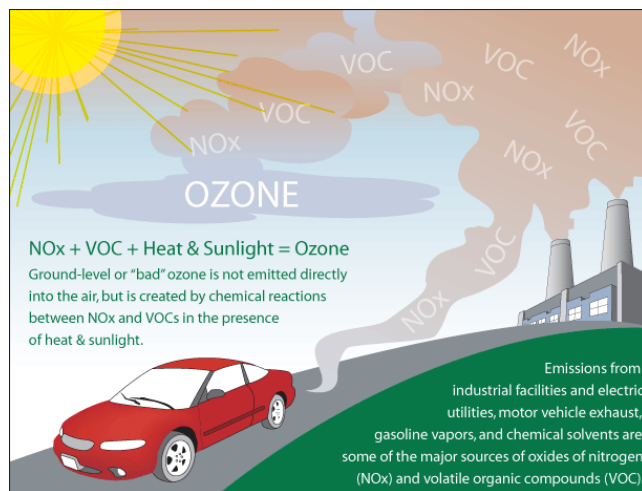


Figure 2.2: Tropospheric ozone is formed when high temperatures and bright sunlight allow NOx and VOCs to react. Image adapted from EPA 2010.



nitrogen dioxide NO_2), and many other molecules based on nitrogen, so numerous we call them NO_x . VOCs and NO_x combine photolytically, in light and heat. Historically, the highest ozone levels in the troposphere occur when the temperature reaches 90°F or more, when there is bright sun, and when both VOCs and NO_x are readily available.

Volatile organics include natural gases produced by plants. White pines and other conifers emit isoprene, a delicious forest scent. Isoprene evaporates readily in the air on a hot summer day. It is volatile and organic. As mentioned above, human beings produce many other VOCs -- cleansers, preservatives, inks, fragrances, fabric softeners, hair dyes, fingernail polish, paint, glue, engine maintenance fluids—all of which evaporate quickly into the atmosphere. Human-made VOCs are made from fossil fuels, carbon compounds; thus they are called “organic” even though they are not made from living leaves or wood.

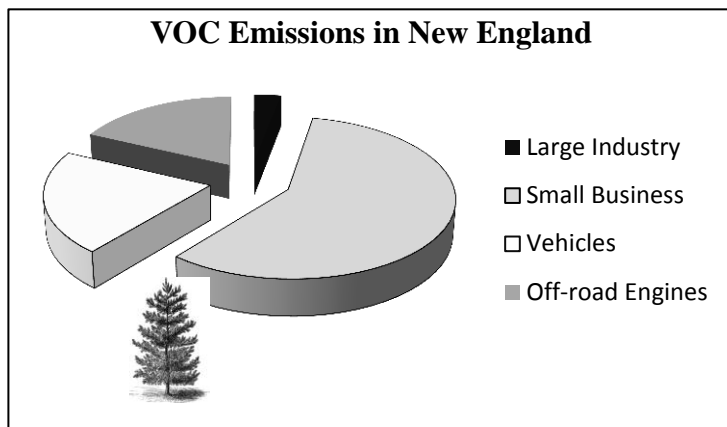


Figure 2.3: VOCs in New England come primarily from small business. Large amounts are produced by chemical plants in the mid-west. Homes also release VOCs. The New England forest also releases substantial amounts of VOCs. Graph built using EPA Region 1 data, <http://www.epa.gov/region1/airquality/piechart.html>.

As Figure 2.3 shows, the largest producer of man-made VOCs is small business—print shops, auto repair shops, hair salons, dry cleaners, and cabinet shops. If you use fabric softener, paint thinner or hair spray at your home, your home emits VOCs too.

Nitrogen oxides, NO_x , are produced by the interaction of atmospheric nitrogen and oxygen in high heat. NO_x is created when lightning strikes. It is released in forest fires. And it forms on the surfaces of hot engines. The largest sources of anthropogenic NO_x are generating plants, primarily coal-burning electric plants many of which are located in the Ohio Valley industrial belt. NO_x are soluble in water vapor and pass right through scrubbers which capture and contain other air pollutants produced in such plants.

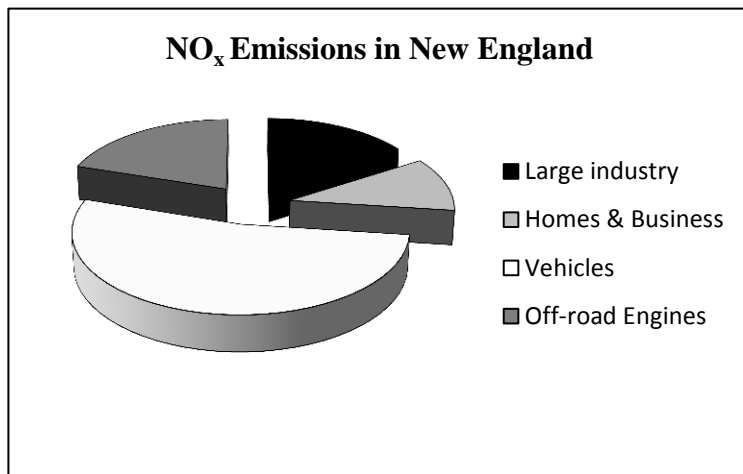


Figure 2.4: NO_x in New England is created primarily on the hot surface of automotive engines—cars and trucks in the densely populated urban corridor. Graph built using EPA Region 1 data, <http://www.epa.gov/region1/airquality/piechart.html>.

As Figure 2.4 shows, in New England, the major producers of NO_x are automobiles and trucks.

In Nature, plants and animals have been dealing with VOCs, NO_x and ground-level ozone for millions of years. In fact, these reactive gases cleanse the atmosphere, removing particulates and other pollutants from the atmosphere. Nature quickly deactivates and absorbs these gases, thus maintaining a balance in the chemistry of the atmosphere. For example, ozone which forms on a hot summer day is transformed to ordinary oxygen and water each night when the sun goes down and temperatures cool. Or it is transported high into the stratosphere where it becomes a helpful shield around the Earth.

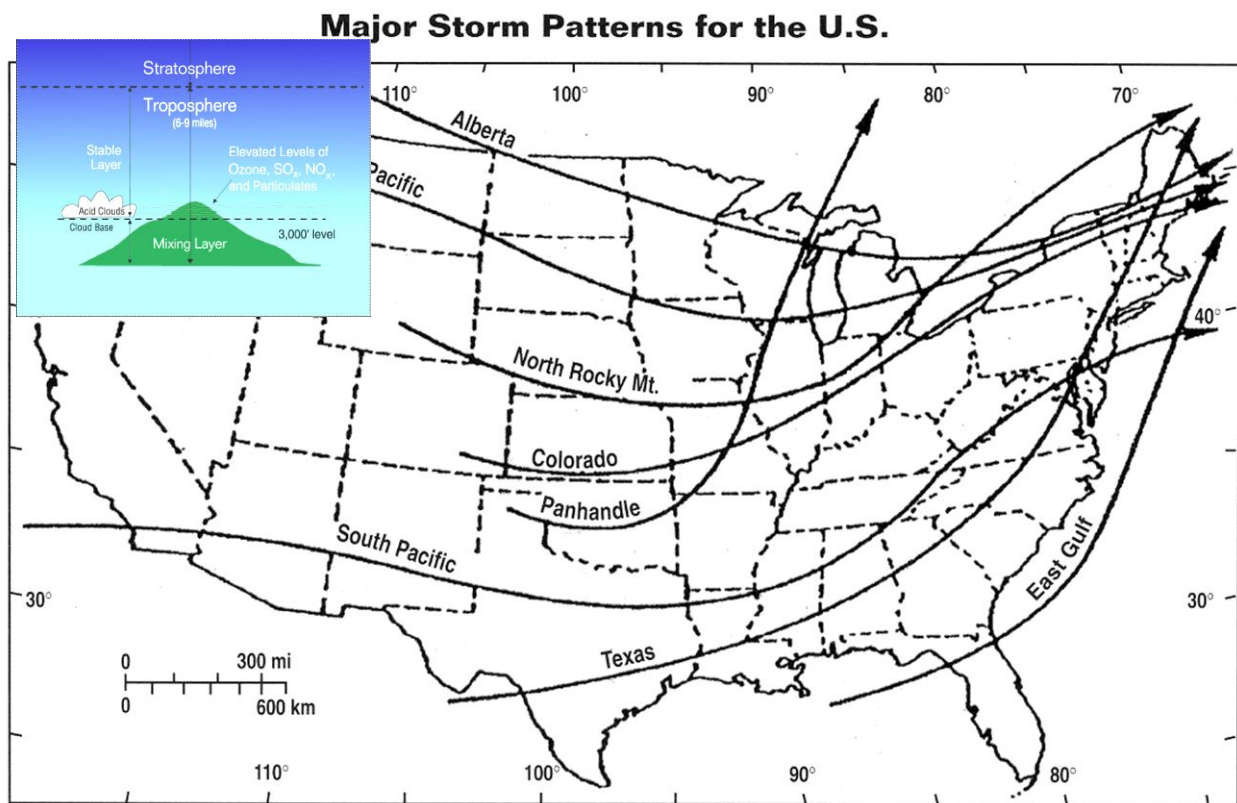


Figure 2.5: Westerly and southwesterly winds bring air pollutants from every part of the nation to New England. Pollutants are most heavily concentrated at about 3000 feet elevation. (NERA 2001).

Anthropogenic additions to the chemistry of our atmosphere have changed the natural balance. Air pollution has increased. Unfortunately New England experiences some of the worst air pollution in the United States. Wind patterns bring this region pollutants from the Gulf of Mexico, the far West, the Ohio industrial belt and the East coast's metropolitan corridor. Dr. Rock calls New England "the tail pipe of the nation," where all of the exhaust of all of our activities comes together. Wind patterns and cloud formations intensify the air pollutants most at about 3,000 feet. Ozone, dust and carbon particulates and sulphur and nitrogen gases which form oxidants and acids are most concentrated just below the peaks in our White Mountains. That is a sad piece of information for hikers and skiers.

How Does Ozone Cause Damage?

Ozone is a strong oxidant. Three atoms of oxygen in one molecule are unstable, a molecule looking for two extra electrons. Whatever a molecule of ozone encounters—delicate tissues around your eye, a mountain hiker’s lung tissue, or a loosely bound molecule of lipid in a plant cellular membrane—ozone will steal electrons. Instantly the affected molecule will steal electrons from any nearby molecule, starting a chain reaction. Eyes sting. Lungs feel irritated. Plant cells begin to leak. Chloroplasts are de-activated.

In white pines, ozone enters the needle through the stomate which is open to draw in carbon dioxide and to transpire water and release oxygen. Inside the needle, in the intercellular space, the ozone encounters the delicate membranes of mesophyll cells. When the membranes are oxidized, water leaks out. The chain reaction may damage internal membranes of chloroplasts.

Forest Watch students recognize such damage in the yellow spots and smears of chlorotic mottling. When cells of the needle tips die, needles may exhibit brown tip necrosis. Figure 2.6 shows yellow spots and smears on either side of stomata, chlorotic mottle. Tip necrosis is visible as a brown and dry section at the outer or distal tips of needles. These cells are necrotic or dead. These particular types of damage are unique to ozone.

Forest Watch students measure the length of each damage on 30 different needles. Then they calculate the percent of each type of damage for the group of needles and the percent of needle lengths with both types of damage.

Living things, plants as well as animals, react quickly to oxidants. Cells call on anti-oxidant chemicals to stop and contain the chain reaction. Enzymes and phenolic compounds are produced to seal off the wounds. As Forest Watch students know, mildly damaged needles continue to make sugar and may stay on a branch for months or years.

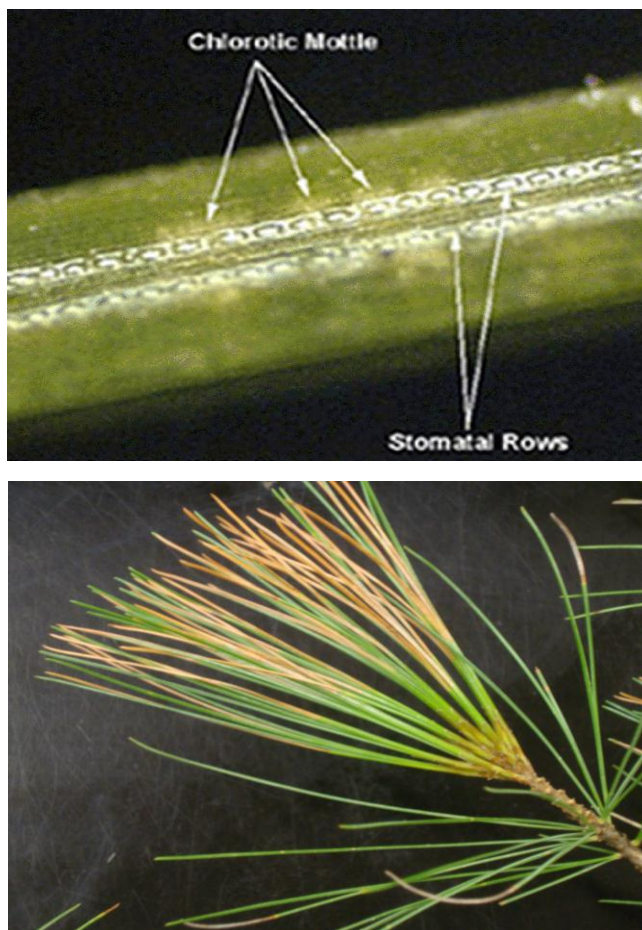


Figure 2.6: Chlorotic mottle at top and tip necrosis below are key indicators of ozone damage. Students measure both.

Chronic ozone exposure may cause enough damage to impair a plant's overall capacity to produce and store sugar and starch. Needles may drop prematurely and forest canopies become less dense. A tree may produce less wood and grow in diameter more slowly. And plants may have reduced capacity to cope with other stressors such as harsh weather, other air pollutants, to compete for light and water, and to protect themselves from insects, fungi and infections. Over time, populations of trees in heavily polluted forests will be eliminated. The ecosystem will lose biodiversity and resilience.

Monitoring Ozone Events

The Environmental Protection Agency began wide scale monitoring of ozone and the gases which form it in 1990 when the Clean Air Act was amended. The EPA rated ozone levels with the chart below, Figure 2.7. Today health officials and many weather stations make regular announcements of high ozone levels to help guide citizens who may have asthma or other health conditions that can be influenced by ozone. As the chart in

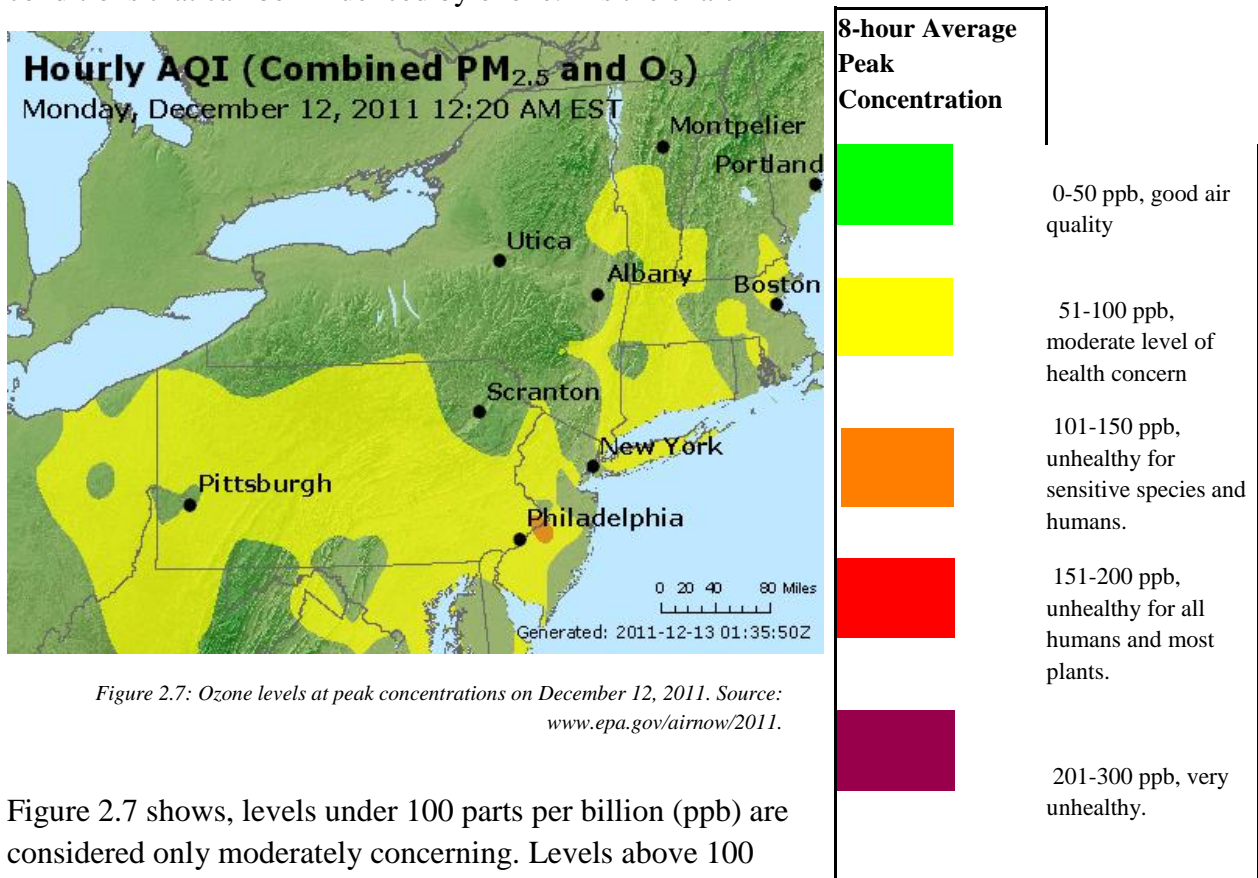


Figure 2.7: Ozone levels at peak concentrations on December 12, 2011. Source: www.epa.gov/airnow/2011.

Figure 2.7 shows, levels under 100 parts per billion (ppb) are considered only moderately concerning. Levels above 100 ppb are considered to be unhealthy. During the early 1990s, levels in the low 100-150 ppb area were measured frequently on hot summer days. In 1990, the EPA set 85 ppb as the maximum allowed level. This was a goal which the EPA and

environmental advocates hoped would drive auto designers and industry to reduce production of NO_x and VOCs. Slowly, ozone levels have fallen.

The EPA also has wrestled with how to define an ozone event which exceeds its standard. Ozone usually forms on a warm summer day. Levels begin to climb as the sun reaches peak heat, at about noon or 2 p.m. Levels may spike and then fall as the sun goes down. Or levels may remain high for several hours. Should a two-hour exceedance be recorded? Or is damage only done when plants and animals are exposed to high levels for numerous hours? The EPA settled on an 8-hour time frame. High levels of ozone are not counted as an exceedance unless levels over the limit last for 8 hours or more.

As research examined ozone more closely, scientists learned that lower levels of ozone could be harmful. We know from our research at UNH that gradual increases of ozone at relatively low levels are very significant. Plants and people are especially sensitive to tropospheric ozone between 60 and 85 ppb. In higher levels, plants can sense the pollutant and close their stomata, protecting delicate mesophyll cell membranes and chloroplasts. At high levels, human beings can also sense the feeling that they are having trouble breathing and wisely choose to stay inside. It is the mid-levels, around 75 ppb, when pines cannot close their stomata against ozone. Human beings may not realize they are having breathing problems when ozone is at these mid-levels.

It is also possible that repeated short peaks of ozone may be as irritating to living organisms as a single 8-hour exceedance. More research is needed. Responding to such questions, the EPA lowered its maximum from 85 to 75 ppb in 2006.

Across the country, ozone average “exceedances,” hours or days when ozone levels exceeded federal standards, continue to decline. The annual average of exceedances measured at 507 ozone monitoring sites indicates a 17% decline in ground-level ozone since 1990 (EPA Airtrends ozone, 2011). The average has dropped from 86 ppb to 72 ppb. We are making progress in a highly sensitive zone of measurement. As Forest Watch students and teachers know, our white pine measures follow this trend clearly in increasing health of the trees.

Changing Ozone Conditions in 2011-2012

The U.S. Environmental Protection Agency reported in its 2011 Report on Air Quality in New England that a wetter, cooler summer in 2011 produced fewer high ozone days than we saw in 2010. In 2011, there were only 16 exceedances of the 8-hour ozone standard (0.075 ppm) compared with 29 exceedance days in 2010. The highest ozone event was measured in Madison, CT. The entire state of Connecticut failed to meet the ozone standard as did Dukes County in Massachusetts. Other states showed fewer exceedance days as shown in Table 2.1. When the New England exceedances are graphed, we see in Figure 2.8 a continuing decline in ozone events.

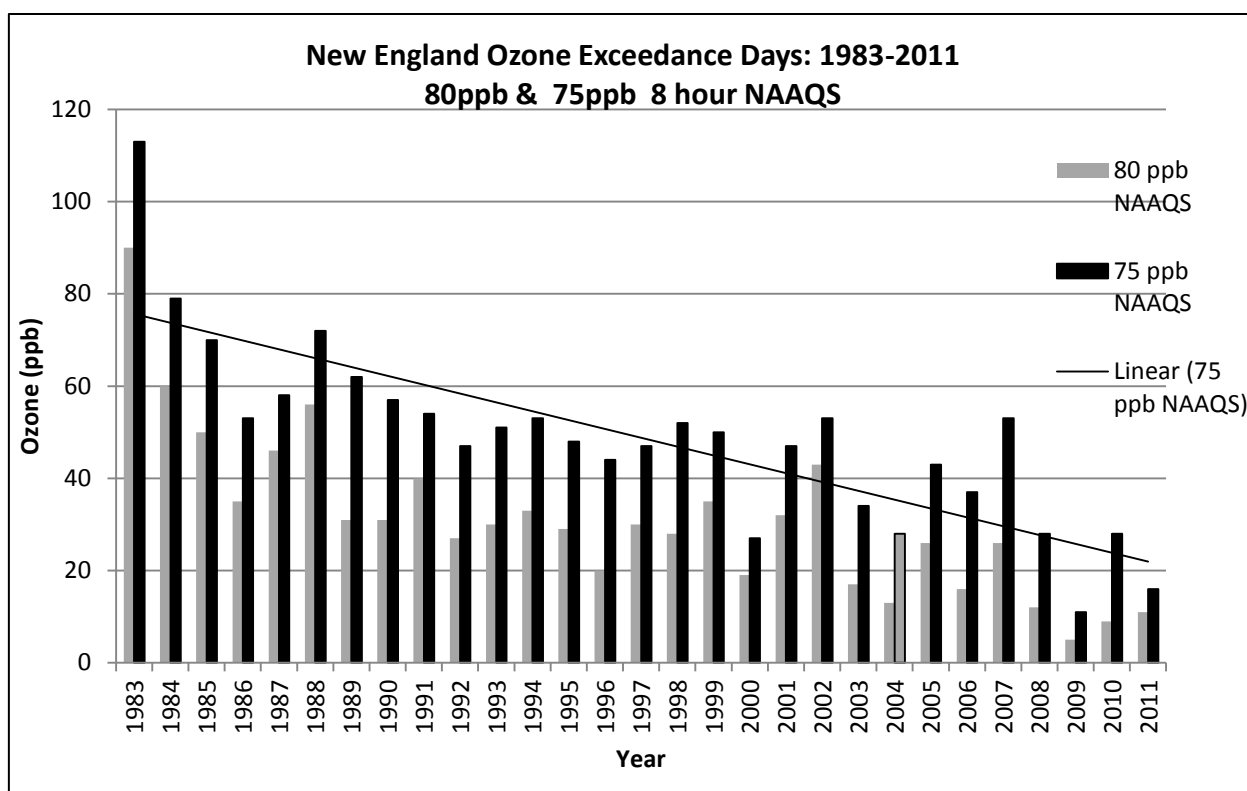


Figure 2.8: Exceedances continue a trend of fewer and fewer occurrences at lower and lower levels (EPA, Region 1, airquality) To allow for comparison of new national ambient air quality standards (NAAQS) against old standards, the EPA adjusts historic measures to fit new standards.

Table 2.1: Exceedance days 2000-2011 by New England State (EPA, 2011). The * indicates recent measurements which are still being confirmed. Historical Exceedance Days in New England, [epa.gov/ http://www.epa.gov/region1/airquality/standard.html](http://www.epa.gov/region1/airquality/standard.html)

Exceedance Days Per Area																
Year	<u>New England</u>				<u>CT</u>		<u>ME</u>		<u>MA</u>		<u>NH</u>		<u>RI</u>		<u>VT</u>	
	# days >		# days >		# days >		# days >		# days >		# days >		# days >		# days >	
	0.084	0.075	0.084	0.075	0.084	0.075	0.084	0.075	0.084	0.075	0.084	0.075	0.084	0.075	0.084	0.075
1983	90	113	84	103	21	36	62	84	10	18	24	34	4	7		
1984	60	79	54	63	25	34	44	65	10	20	28	42	4	10		
1985	50	70	41	58	21	35	38	53	8	16	16	27	6	9		
1986	35	53	28	41	9	17	24	32	9	16	12	22	1	6		
1987	46	58	37	44	10	20	23	35	13	28	18	27	3	11		
1988	56	72	50	62	35	40	43	63	27	37	19	29	14	26		
1989	31	62	26	41	16	21	21	43	11	16	9	14	2	5		
1990	31	57	24	44	15	21	22	37	9	20	13	18	5	8		
1991	40	54	34	46	17	26	26	45	13	22	20	28	10	16		
1992	27	47	19	29	12	22	20	36	8	18	5	12	6	11		
1993	30	51	27	39	14	20	23	40	8	17	7	11	4	9		
1994	33	53	28	39	10	22	20	39	9	19	8	21	2	13		
1995	29	48	24	35	14	20	20	39	9	19	11	18	3	13		
1996	20	44	16	33	5	20	15	28	6	14	4	12	3	4		
1997	30	47	27	34	11	16	24	38	10	16	11	19	2	11		
1998	28	52	25	44	11	16	12	36	7	14	5	11	0	5		
1999	35	50	33	43	10	21	22	36	10	19	13	16	3	11		
2000	19	27	13	23	3	5	5	16	1	5	8	14	1	2		
2001	32	47	26	39	15	22	27	37	11	22	15	26	2	9		
2002	43	53	36	49	17	28	30	43	13	23	17	33	5	13		
2003	17	34	14	26	5	15	11	27	1	10	10	13	0	4		
2004	13	28	6	20	1	11	8	16	5	10	4	5	2	4		
2005	26	43	20	30	5	15	17	31	4	17	8	17	0	4		
2006	16	37	13	29	2	10	12	26	2	10	3	13	0	0		
2007	26	53	17	42	8	14	20	38	8	22	8	18	1	5		
2008	13	30	8	22	0	4	9	18	2	10	4	6	0	3		
2009	4	11	1	6	2	3	1	8	0	2	0	1	0	0		
2010	9	29	5	24	2	8	4	14	0	8	1	6	0	0		
2011	11	16	10	14	2	3	5	10	1	2	0	6	0	1		
2012*	14	29	13	27	0	4	6	17	1	4	3	12	0	0		

This is good news for Forest Watch researchers. Again this year, our chart of ozone in New Hampshire and spectral measurements of white pines shows a striking inverse relationship between the two: As ozone events have declined in number and intensity, the health of white pines, as measured from needle reflectance of light, indicates abundant chlorophyll, Figure 2.9

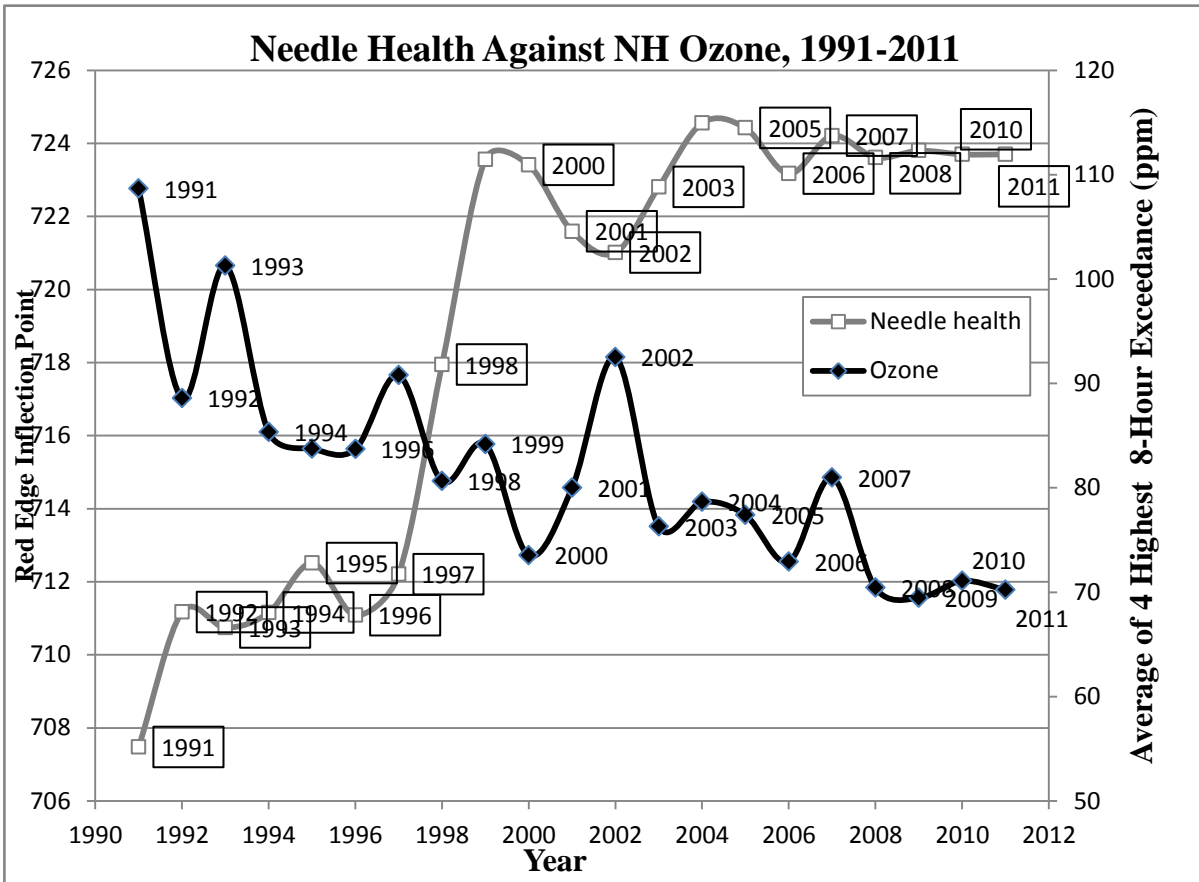


Figure 2.9: The inverse relationship between ozone levels and white pine health, continues to show strong improvement in air quality and tree health. White pine health is rated by the red edge inflection point, an index of light reflectance, to be explained in Chapter 4. These levels of ozone are an average of the four highest ozone events in seven monitoring stations in New Hampshire. This year, since measurements were no longer made in Manchester and Claremont, we used Lebanon and Laconia measurements to build our average. Other long-term monitoring stations include Concord, Keene, Nashua, where highest levels in New Hampshire were recorded, Portsmouth and Rye. The source for these data is the EPA, Region 1, Air Quality, NH_over, (http://www.epa.gov/region1/airquality/nh_over.html).

Forest Watch teachers know that ozone levels have fallen since the Clean Air Act was improved in 1996. Further emission controls were imposed on large utility plants in 2005. The satellite images interpreted in Figure 2.10 show dramatic evidence that it is working. The images were produced by Bryan Duncan, a researcher with the Air Quality Applied Science Team, ACAST, a recent offshoot developed by NASA’s Applied Sciences Program. ACAST brings scientists from many disciplines together with data sets and tools from every satellite and monitoring station in the nation to provide rapid interpretation, response to and publication of air quality

information. This study finds that annual mean observations of tropospheric nitrogen dioxide, the chief ingredient in ozone, has declined markedly since 2005.

(http://acmg.seas.harvard.edu/aqast/docs/Bryan_Duncan_Lenticular_Sep2012.pdf).

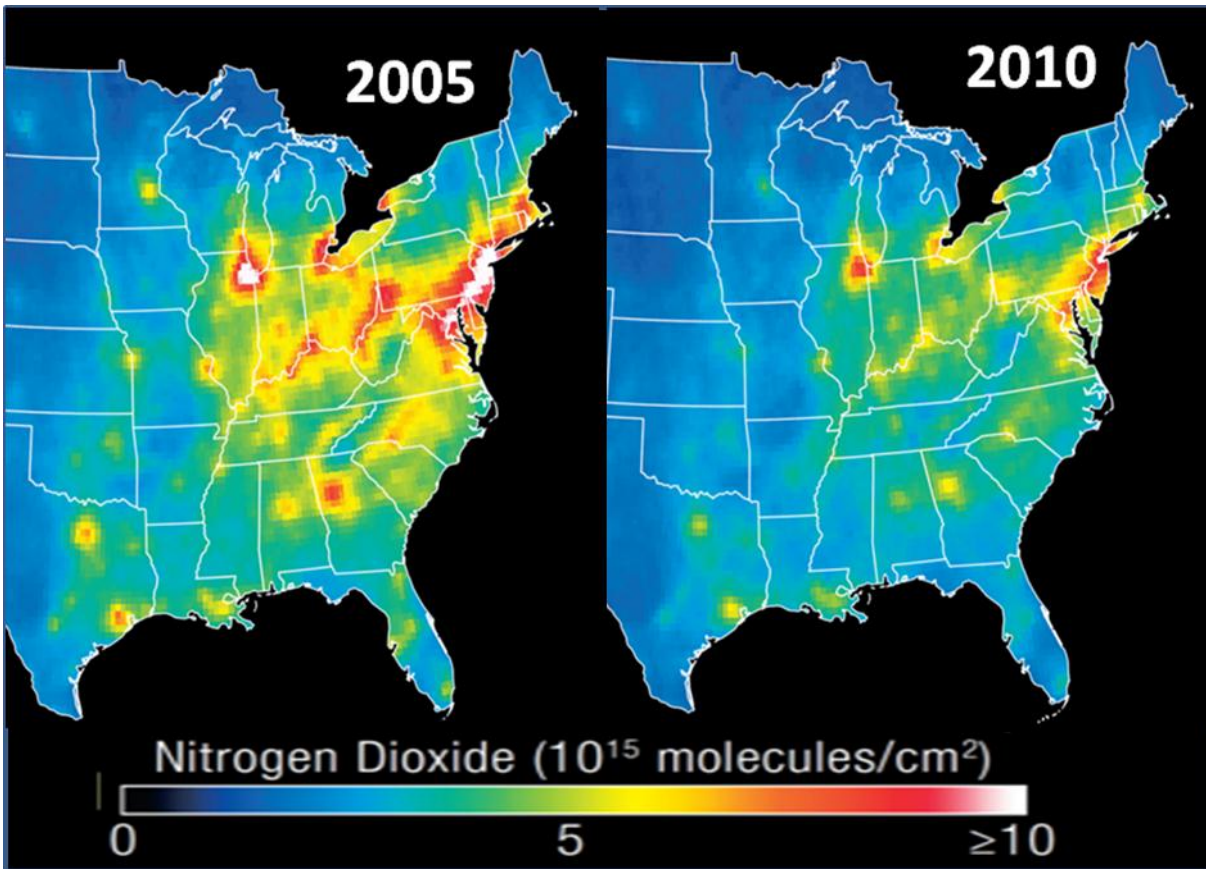


Figure 2.10: Nitrogen dioxide in the troposphere has declined between 2005 and 2010, as measured by interpretations of remote sensing imagery, NASA AQAST.

Duncan's study is not only good news for Forest Watch. It led us to AQAST and the remarkable information this new program is producing and publishing free of charge, with open access to all, on their web sites. Reported by The Smog Blog, which we'll meet in Chapter Four, sulfur dioxide has also been reduced, at least the SO₂ released from and measured near coal-fired power plants. AQAST scientists attribute the reduction to the Clean Air Interstate Rule which the EPA issued in 2005. This observation used the Ozone Monitoring Instrument (OMI) aboard NASA's Aura satellite. Vitali Fioletov of Environment Canada, produced the maps of sulfur dioxide in Figure 2.11.

The EPA continues to strength air quality standards for these two pollutants. More monitors will be placed throughout New England. The agency reported that one monitor in Pembroke, NH,

recorded SO₂ at 263 ppb for one hour in 2011, far exceeding air quality standards. Sulfur dioxide, the EPA reports, can cause wheezing, shortness of breath and chest tightness and is especially harmful to older adults and children who suffer from asthma. SO₂ is also harmful to plants. As Dr. Rock's research found in Vermont, New Hampshire and the Czech Republic, SO₂ can cause extreme damage and needle cast to conifers.

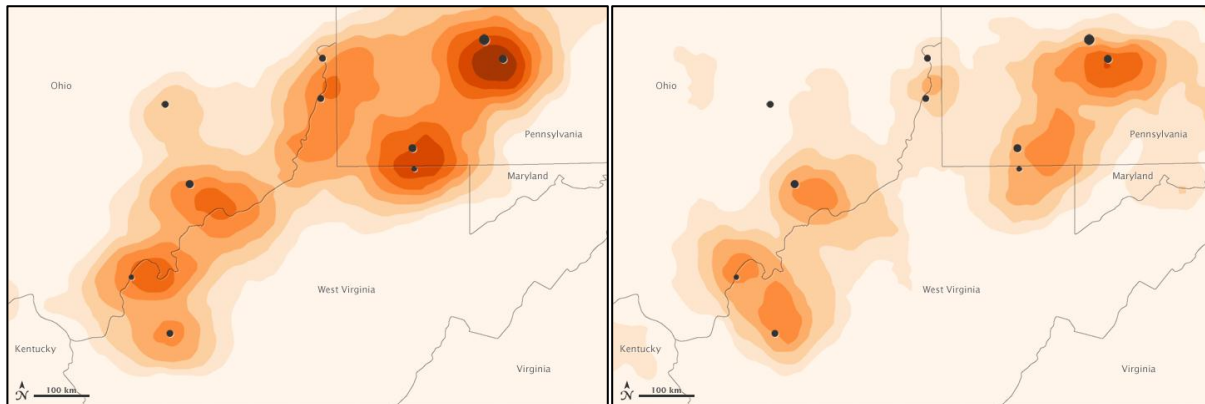


Figure 2.12. Sulfur dioxide levels from point sources, utility plants in Ohio, West Virginia and Pennsylvania, have fallen nearly half since the map at left, 2005-2007, compared to the map at right, 2008 to 2010 (The Smog Blog, Dec. 1, 2011).

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