12.335/12.835 EXPERIMENTAL ATMOSPHERIC CHEMISTRY, FALL 2014

TOPIC 1
ATMOSPHERIC PHOTOCHEMISTRY and AIR POLLUTION

AIR POLLUTION: HUMAN HEALTH, REGULATION, MONITORING & COSTS

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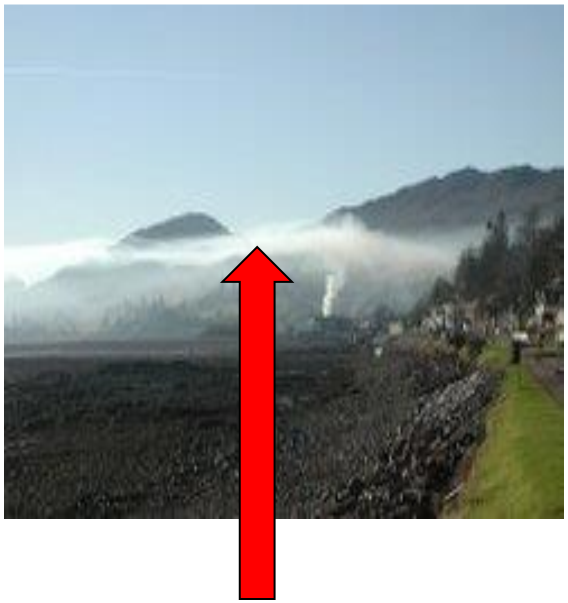
INCORPORATING METEOROLOGY IN THE BOX MODEL

1. USE THE u MEASUREMENTS TO ALIGN THE MODEL x AXIS AND USE IN THE BOX MODEL ADVECTION TERMS.
2. USE THE T & u MEASUREMENTS TO CALCULATE A RICHARDSON NUMBER TO HELP CHOOSE SUITABLE $t_{exchange}$ VALUES (e.g. unstable~1 hour, neutral~6 hours, stable~12 hours).



POTENTIAL TEMPERATURE (θ)

$$\theta = T\left(\frac{P_0}{P}\right)^{R/C_p} \text{ where } T = \text{absolute temperature}, P = \text{pressure},$$

R = gas constant, and

C_p = heat capacity at constant pressure P

RICHARDSON NUMBER (Ri)

$$Ri = g\frac{\partial \ln\theta}{\partial z}\left[\left(\frac{\partial u}{\partial z}\right)^2 + \left(\frac{\partial v}{\partial z}\right)^2\right]^{-1}$$

$Ri > 0 \rightarrow$ stable (if $Ri > \frac{1}{4}$ get laminar flow)

$Ri < 0 \rightarrow$ unstable (if $|Ri| \leq 1$ then forced convection

and if $|Ri| > 1$ then free convection)

$Ri = 0 \rightarrow$ neutral

MOIST POTENTIAL TEMPERATURE (θ_E)

$$\theta_E = \theta \exp\left(\frac{Lw_s}{C_p T}\right) \text{ where } w_s = \text{ water vapor density},$$

and L = latent heat of vaporization

$$\frac{\partial \theta_E}{\partial z} \leq 0 \rightarrow \text{moist convective instability}$$

3. USE TEMPERATURE SOUNDINGS OR HAZE LAYER HEIGHT TO ESTIMATE Z

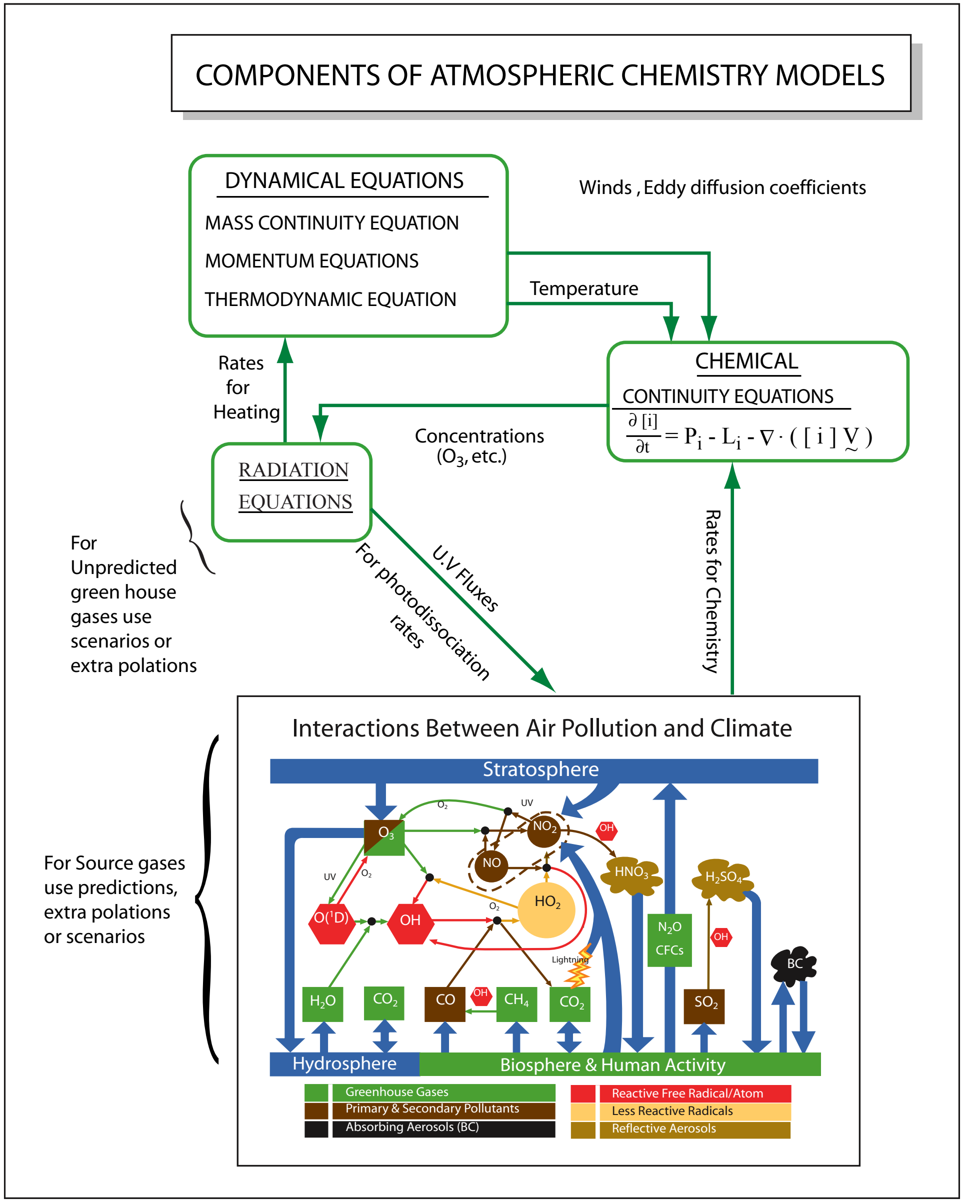


Figure by MIT OpenCourseWare.

TRANSPORT, CHEMISTRY AND RADIATION COMPONENTS IN COMPLEX 3D MODELS

UV fluxes for photodissociation rates

For all species involving OH in their chemistry need to include:

1. $O_3, O_2, O(^1D)$
2. H, OH, HO_2, H_2O_2, with latter 3 in gas and aqueous phase
3. $NO, NO_2, NO_3, N_2O_5, HNO_3$ with latter 2 in gas and aqueous phase
4. $CH_4, CH_3, CH_3O_2, CH_3O, CH_3O_2H, CH_2O, CHO, CO$ (also selected heavier hydrocarbons such as isoprene and terpenes in forested areas and anthropogenic hydrocarbons in urban areas)

The spatial grid

We divide the earth's atmosphere into a finite number of boxes (grid cells).

Assume that each variable has the same value throughout the box.

Write a budget for each each box, defining the changes within the box, and the flows between the boxes.

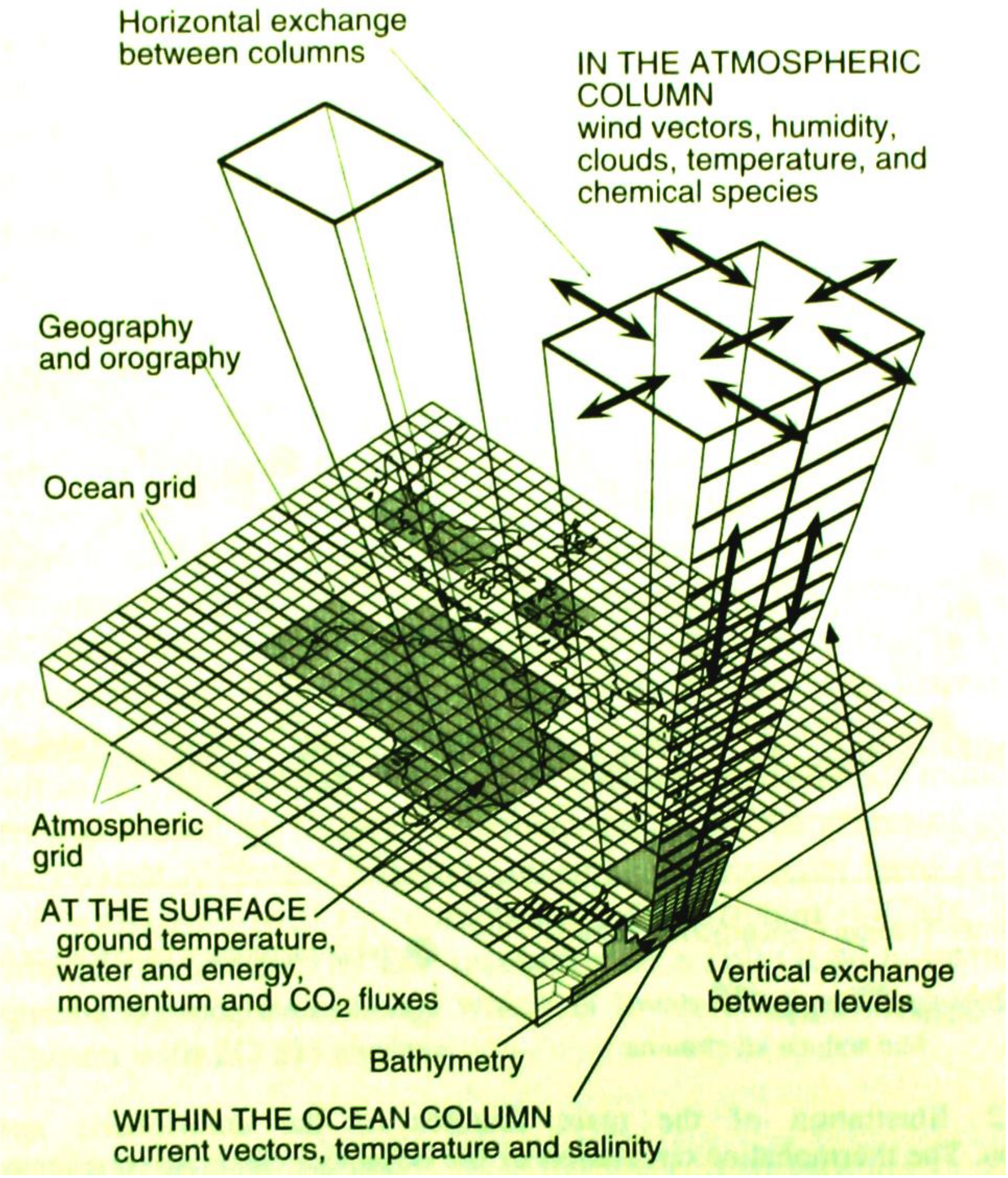


Figure © Henderson-Sellers: A Climate Modeling Primer.

Air Pollution and Human Health

(Reference: Adapted from http://www.air-quality.org.uk/18.php)

Introduction Pollution-related health problems result from primary pollutants such as sulfur dioxide, nitrogen dioxide, and some particulates, and secondary pollutants like ozone and particulates produced from primary gas-phase pollutants.

Particulates The extent to which particulates are considered harmful depends largely on their composition. Sea salt, for example, is believed to have a positive effect on health. Man-made sources of particulates, however, are rarely harmless. In towns and cities, these are extensively from diesel vehicle exhausts. The effects of man-made particulate emissions are considered detrimental due to their composition, containing mainly **unburned fuel oil and polycyclic aromatic hydrocarbons (PAHs) that are known to be carcinogenic** among laboratory animals. Particulates may originate from many other sources including cement manufacturing processes, incineration and power generation, so localized particulate pollution is common. The sizes of particles are important when assessing their effects on health. $PM_{2.5}$ and PM_{10} as well as total suspended particulates are routinely monitored. This is due to the fact that **particles of less than 2.5-10 micro-meters (mm) in diameter can penetrate deep into the lung and cause more damage,** as opposed to larger particles that may be filtered out through the airways' natural mechanisms.

Ozone Ozone is created by the action of sunlight on CO, volatile organic compounds (VOCs) and nitrogen oxides over 1-3 day time periods. This results in ozone being widely dispersed as a pollutant, and can form in greater concentrations in rural areas. As ozone concentrations are particularly dependant on sunlight, episodes are always likely to develop following sustained periods of warmth and calm weather. **Ozone is a toxic gas that can bring irreversible damage to the respiratory tract and lung tissue if delivered in high quantities. Levels during air pollution episodes range up to 100-250 ppb (0.1-0.25 ppm). At these concentrations ozone impairs lung function and causes irritation to the respiratory tract.** Asthmatics are especially affected.

Oxides of Nitrogen The oxides of most concern are **nitric oxide (NO) and nitrogen dioxide (NO_2). The latter is more damaging to health, due to the toxic nature of this gas.** NO is emitted to the atmosphere as a primary pollutant, from traffic and power stations, and is oxidized to nitrogen dioxide following dispersal. Health effects of exposure to NO_2 include shortness of breath and chest pains. The effects of NO include changes to lung function at high concentrations.

Carbon Monoxide Carbon monoxide **combines with hemoglobin, the oxygen carrying component of the blood stream, to form carboxy-hemoglobin (COHb)** which can be life-threatening in high doses. The effects of CO pollution are more damaging to pregnant women and their fetus. Research into smoking during pregnancy shows that concentrations within the blood stream of unborn infants is as high as 12%, causing retardation of the unborn child's growth and mental development.

Lead Lead is still a serious air pollutant especially to those living near to areas of dense traffic in cities where leaded fuel is still used or to coal-fired power plants. **Damage to the central nervous system, kidneys and brain can result when levels in the blood reach concentrations of 800 mg/liter.** Much of the concern regarding pollution from lead centers around its effects on child health. Children exhibit vulnerability to the toxic effects of lead at much lower concentrations than for adults. There is a strong link between high lead exposures and impaired intelligence.

Sulfur dioxide The health effects of sulfur dioxide include **heart disease and bronchitis.** SO_2 emissions have been significantly reduced through legislative measures in developed countries. Asthmatics are especially sensitive for whom concentrations above 125 ppb may result in a fall in lung function. Tightness in the chest and coughing may also result at levels approaching 400 ppb. **At levels above 400 ppb the lung function of asthmatics may be impaired to the extent that medical help is required.** Sulfur dioxide pollution is more harmful when particulate and other pollution concentrations are also high **(the synergistic effect).**

Volatile Organic Compounds (VOCs)

Some VOCs are directly harmful, including: ***Benzene*** which may increase susceptibility to leukemia, if exposure is maintained over a period of time; ***Polycyclic Aromatic Hydrocarbons (PAH)*** some of which can cause cancer (there are several hundred different forms of PAH, and sources can be both natural and man-made); ***Dioxins,*** whose sources include manufacturing of organic compounds as well as the incineration of wastes and various other combustion processes involving chlorinated compounds, and which has health effects due to inhalation and ingestion (e.g. dioxins entering the food chain from soils); ***1,3 Butadiene,*** for which there is an apparent correlation between exposure and a higher risk of cancer, and which is produced from manufacturing of synthetic rubbers, gasoline-driven vehicles and cigarette smoke.

General Air Quality Problems

Air quality indoors Many different compounds are contained in tobacco smoke, including carbon monoxide, ammonia, dioxins and PAH; the latter two are thought to be carcinogenic. Other sources of indoor pollution include particulates from mineral fibers as well as household dust. Dust in buildings is known to cause problems including fatigue and nausea. One of the most pressing concerns with indoor air pollution is with carbon monoxide built up from gas, oil or wood fired appliances. Open gas flames and fire places also produce BC.

Asthma and air pollution There has been a steady rise in the number of reported asthma cases since the 1970s, and air pollution problems are believed to be a significant (but not sole) contributor to the rise. High concentrations of nitrogen dioxide, sulfur dioxide, ozone and particulates (especially PM_{10}) can all trigger breathing difficulties in asthmatics.

NATIONAL AMBIENT AIR QUALITY STANDARDS (NAAQS)

The Clean Air Act, which was last amended in 1990, requires EPA to set **National Ambient Air Quality Standards** (40 CFR part 50) for pollutants considered harmful to public health and the environment. The Clean Air Act established two types of national air quality standards. ***Primary standards*** set limits to protect public health, including the health of "sensitive" populations such as asthmatics, children, and the elderly. ***Secondary standards*** set limits to protect public welfare, including protection against decreased visibility, damage to animals, crops, vegetation, and buildings.

The EPA Office of Air Quality Planning and Standards (OAQPS) has set National Ambient Air Quality Standards for six principal pollutants, which are called "criteria" pollutants. They are listed below. Units of measure for the standards are parts per million (ppm) by volume, milligrams per cubic meter of air (mg/m^3), and micrograms per cubic meter of air ($\mu g/m^3$).

National Ambient Air Quality Standards

	Primary Standards		Secondary Standards	
Pollutant	**Level**	**Averaging Time**	**Level**	**Averaging Time**
Carbon Monoxide	9 ppm ($10\ mg/m^3$)	8-hour (1)	None	
	35 ppm ($40\ mg/m^3$)	1-hour (1)		
Lead	$0.15\ \mu g/m^3$ (2)	Rolling 3-Month Average	Same as Primary	
	$1.5\ \mu g/m^3$	Quarterly Average	Same as Primary	
Nitrogen Dioxide	0.053 ppm ($100\ \mu g/m^3$)	Annual (Arithmetic Mean)	Same as Primary	
Particulate Matter (PM_{10})	$150\ \mu g/m^3$	24-hour (3)	Same as Primary	
Particulate Matter ($PM_{2.5}$)	$15.0\ \mu g/m^3$	Annual (4) (Arithmetic Mean)	Same as Primary	
	$35\ \mu g/m^3$	24-hour (5)	Same as Primary	
Ozone	0.075 ppm (2008 std)	8-hour (6)	Same as Primary	
	0.08 ppm (1997 std)	8-hour (7)	Same as Primary	
	0.12 ppm	1-hour (8) (Applies only in limited areas)	Same as Primary	
Sulfur Dioxide	0.03 ppm	Annual (Arithmetic Mean)	0.5 ppm ($1300\ \mu g/m^3$)	3-hour (1)
	0.14 ppm	24-hour (1)		

(1) Not to be exceeded more than once per year.

(2) Final rule signed October 15, 2008.

(3) Not to be exceeded more than once per year on average over 3 years.

(4) To attain this standard, the 3-year average of the weighted annual mean PM2.5 concentrations from single or multiple community-oriented monitors must not exceed 15.0 µg/m3.

(5) To attain this standard, the 3-year average of the 98th percentile of 24-hour concentrations at each population-oriented monitor within an area must not exceed 35 µg/m3 (effective December 17, 2006).

(6) To attain this standard, the 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area over each year must not exceed 0.075 ppm. (effective May 27, 2008)

(7) (a) To attain this standard, the 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area over each year must not exceed 0.08 ppm.
(b) The 1997 standard—and the implementation rules for that standard—will remain in place for implementation purposes as EPA undertakes rulemaking to address the transition from the 1997 ozone standard to the 2008 ozone standard.

(8) (a) The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is ≤ 1.
(b) As of June 15, 2005 EPA revoked the 1-hour ozone standard in all areas except the 8-hour ozone nonattainment Early Action Compact (EAC) Areas.

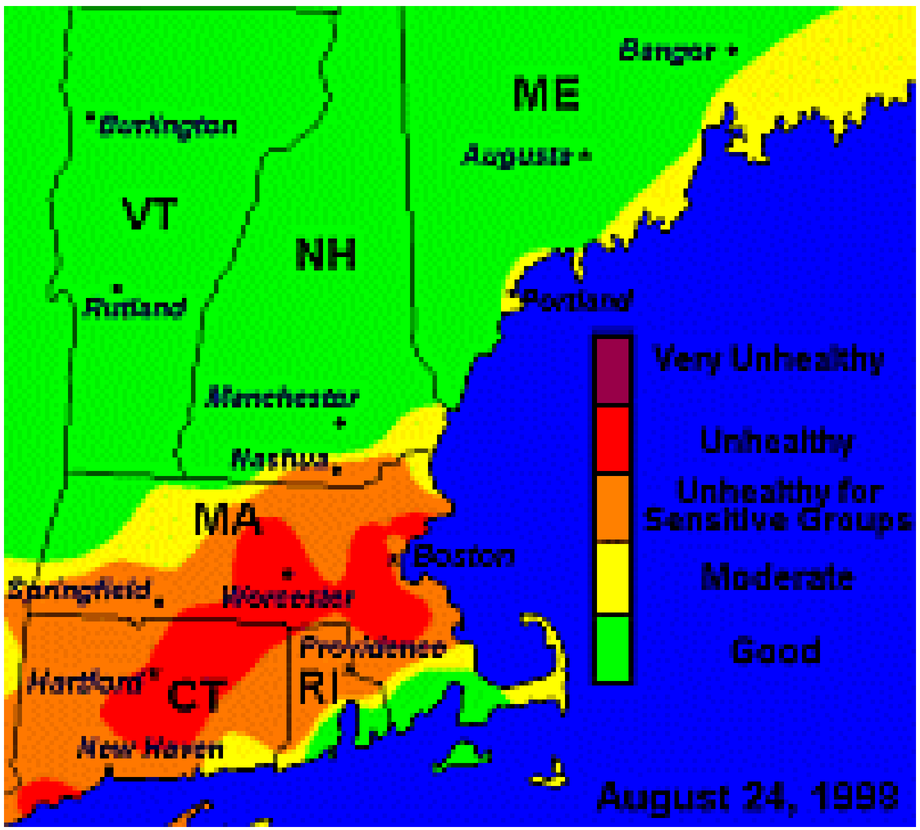
OZONE MONITORING NETWORK IN NEW ENGLAND

High concentrations of ozone near ground level can be harmful to people, animals, crops, and other materials. Ozone can irritate your respiratory system, causing you to start coughing, feel an irritation in your throat and/or experience an uncomfortable sensation in your chest. Ozone can aggravate asthma, and can inflame and damage cells that line your lungs. Ozone may also aggravate chronic lung diseases such as emphysema and bronchitis and reduce the immune system's ability to fight off bacterial infections in the respiratory system. Lastly, ozone may cause permanent lung damage. These effects can be worse in children and exercising adults

Image courtesy of EPA.

O_3 at BOSTON - LONG ISLAND STATION (Operating 1999 to Present)										
Year	**Total Days > 0.084**	**1st High (ppm)**	**Date**	**2nd High (ppm)**	**Date**	**3rd High (ppm)**	**Date**	**4th High (ppm)**	**Date**	**MAP**
2007	0	0.082	Sept 25	0.080	April 23	0.076	Sept 26	0.073	Aug 3	
2006	0	0.083	June 22	0.083	July 2	0.083	July 18	0.079	July 1	
2005	5	0.095	June 25	0.091	June 26	0.089	Aug 11	0.086	June 24	
2004	1	0.094	June 8	0.081	July 22	0.080	July 23	0.079	July 30	
2003	1	0.102	June 27	0.083	June 25	0.078	June 26	0.078	July 4	
2002	10	0.126	Aug 13	0.117	Aug 14	0.102	July 3	0.102	Sept 9	*
2001	9	0.111	June 20	0.107	June 19	0.100	Aug 2	0.094	July 24	
2000	0	0.084	June 10	0.073	June 1	0.072	Aug 9	0.070	June 2	
1999	4	0.102	July 16	0.100	June 24	0.089	June 1	0.087	May 31	*

REGIONAL OZONE HEALTH ALERTS IN NEW ENGLAND BASED ON THE MONITORING NETWORK. Human health is affected by exposure to ozone expressed as a function of the AOT40 Index (AOT40 = hourly ozone exposure above 40 ppb in units of ppb.hr/mo; see earlier lecture for USA AOT40 map)



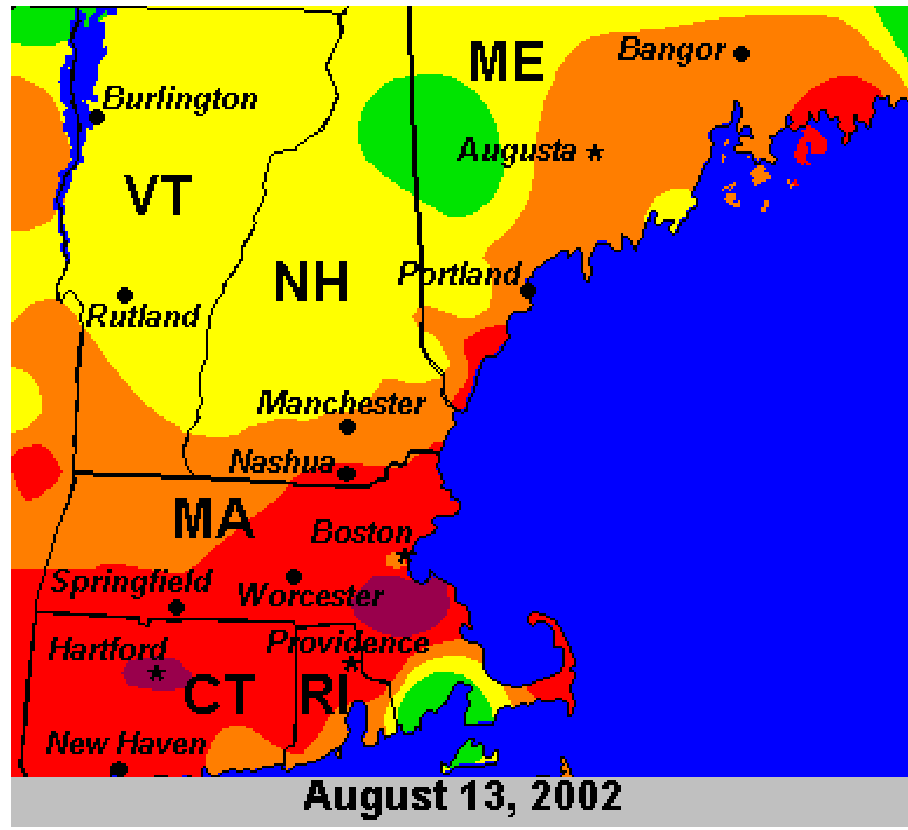


Image courtesy of EPA.

Air Pollution Economic Effects

(Yang et al, Report 113, MIT Joint Program on the Science & Policy of Global Change: http://globalchange.mit.edu)

- **Approach**
  - **Extensive data set on epidemiological effects of air pollution exposure**
  - **Resultant illness, death, demand for medical services**
  - **Lost labor, leisure, diversion of resources to medical and health services introduced into MIT economic model**
- **Results based on historical pollution levels**
  - **evaluated US benefit of air pollution regulation, and remaining burden of air pollution (1975-2000)**

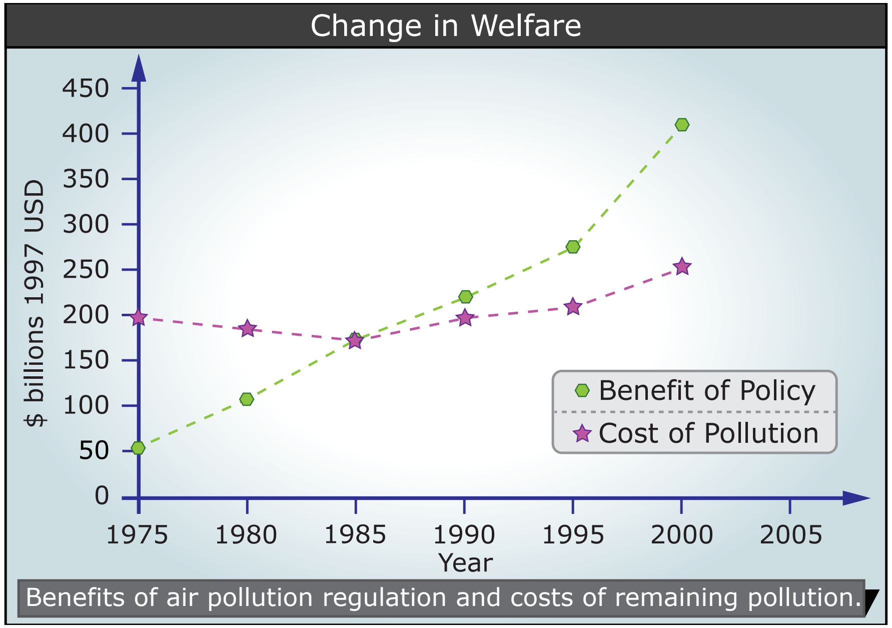


Figure by MIT OpenCourseWare.

***Benefit of Policy* is avoided health costs due to the policy.**

Remaining *Cost of Pollution* decreases due to lower pollution levels, but is offset by increases due to rising income and population.

***Welfare* is a measure of total consumption of goods and services.**

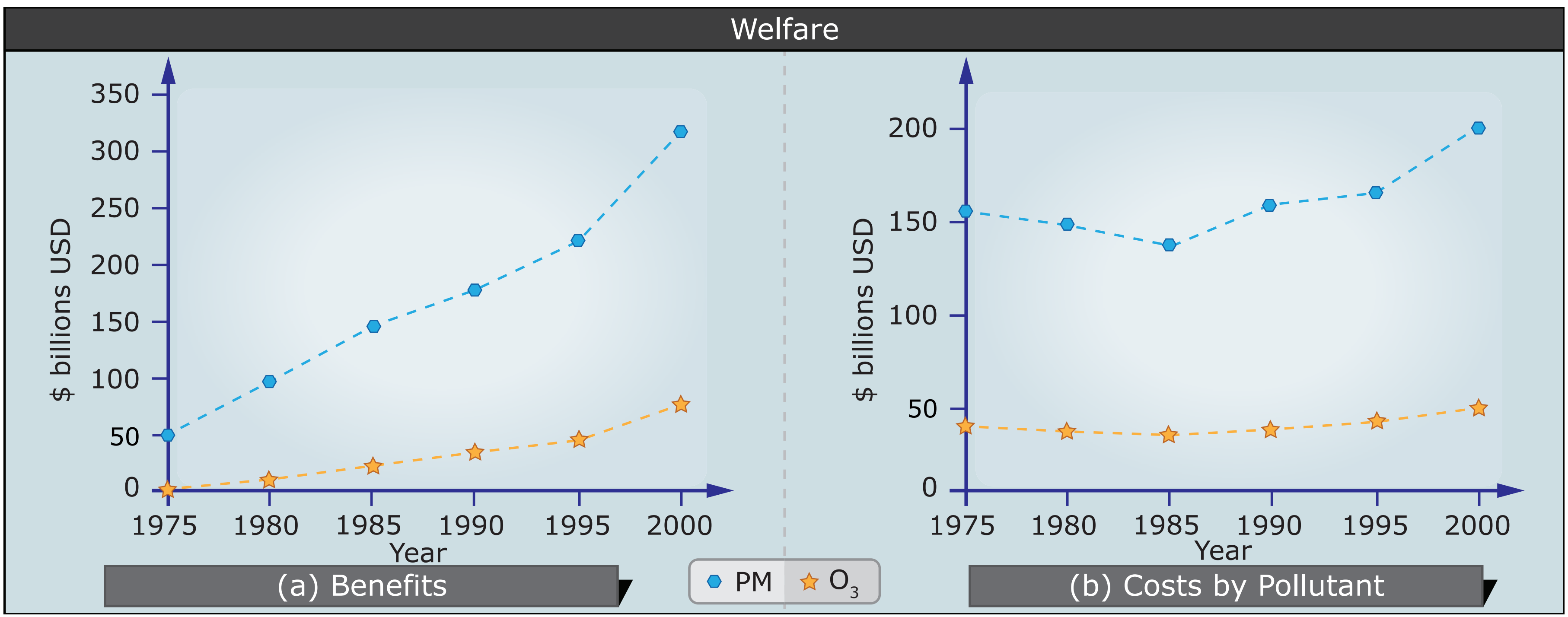


Figure by MIT OpenCourseWare.

12.335 / 12.835 Experimental Atmospheric Chemistry
Fall 2014