AP 3050 Air Pollution

Air Pollution and Global Warming: History, Science, and Solutions

Chapter 3: Urban Air Pollution

Lecturers: Neng-Huei Lin

Spring 2024

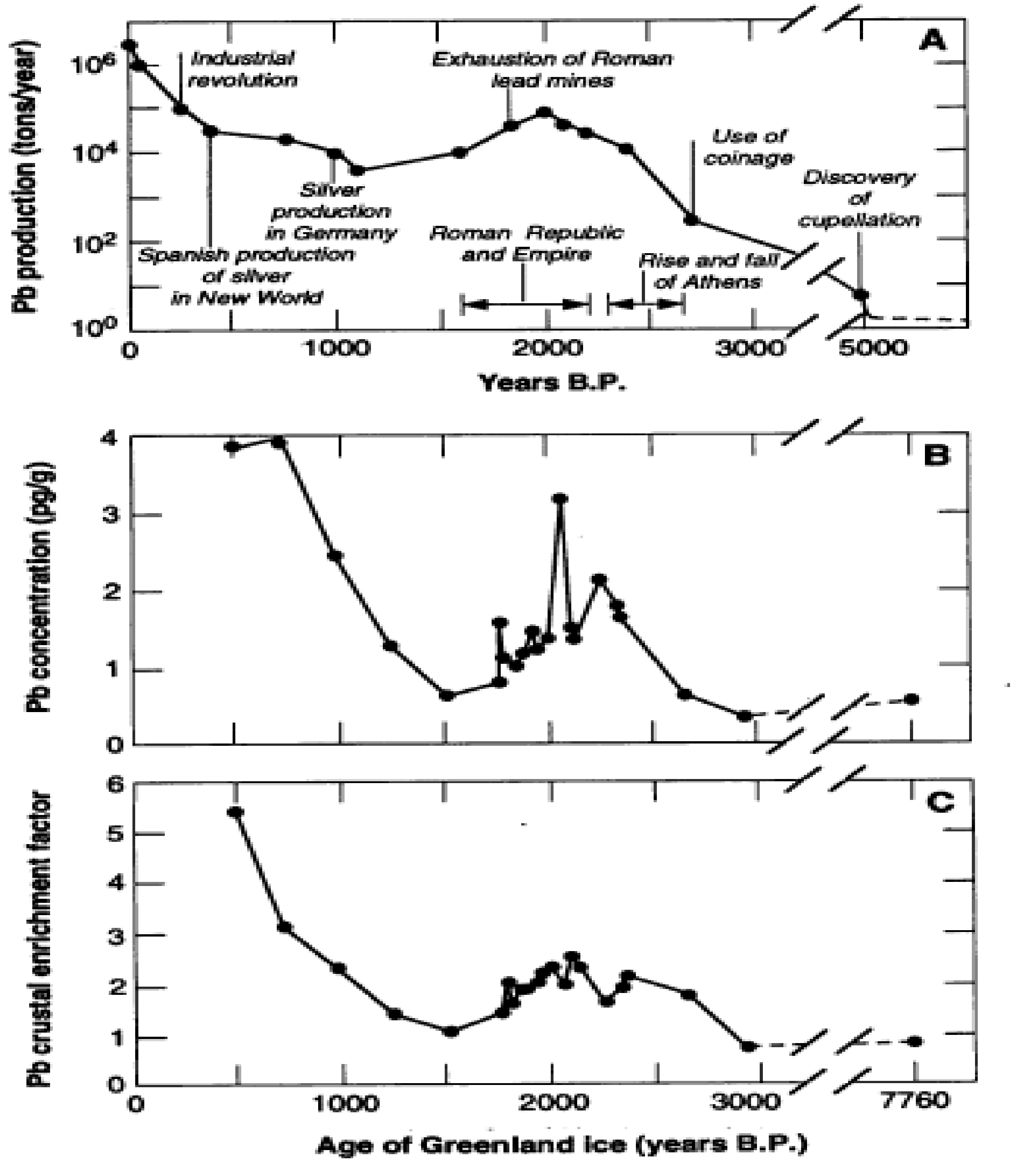
By Mark Z. Jacobson
Cambridge University Press (2012)

Urban-scale air pollution types

- London type smog
- Photochemical smog

Smog = Smoke + Fog


Athens
Pollution due to
metal production
wood burning
Pb/Ag mining
www.worst-city.com



SCIENCE • VOL. 265 • 23 SEPTEMBER 1994

Hong et al. 1994

Rome

Heavy heavens

Metal smelting wood burning

I238.photobucket.com

Horace, Wiki

Sea Coal, KE I, Lime Kiln, Slaked Lime

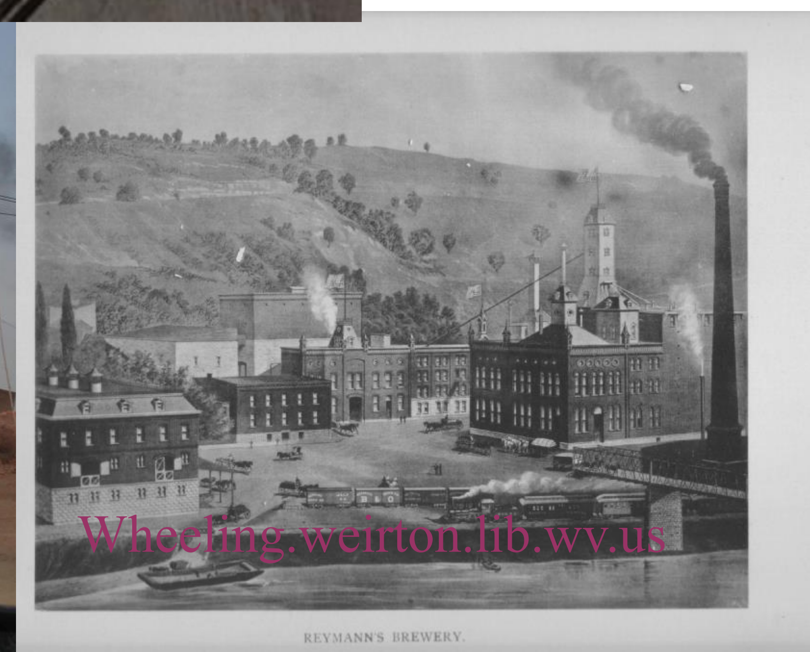
$CaCO_3$ + heat
→ CaO

$CaO + H_2O$
→ $Ca(OH)_2$

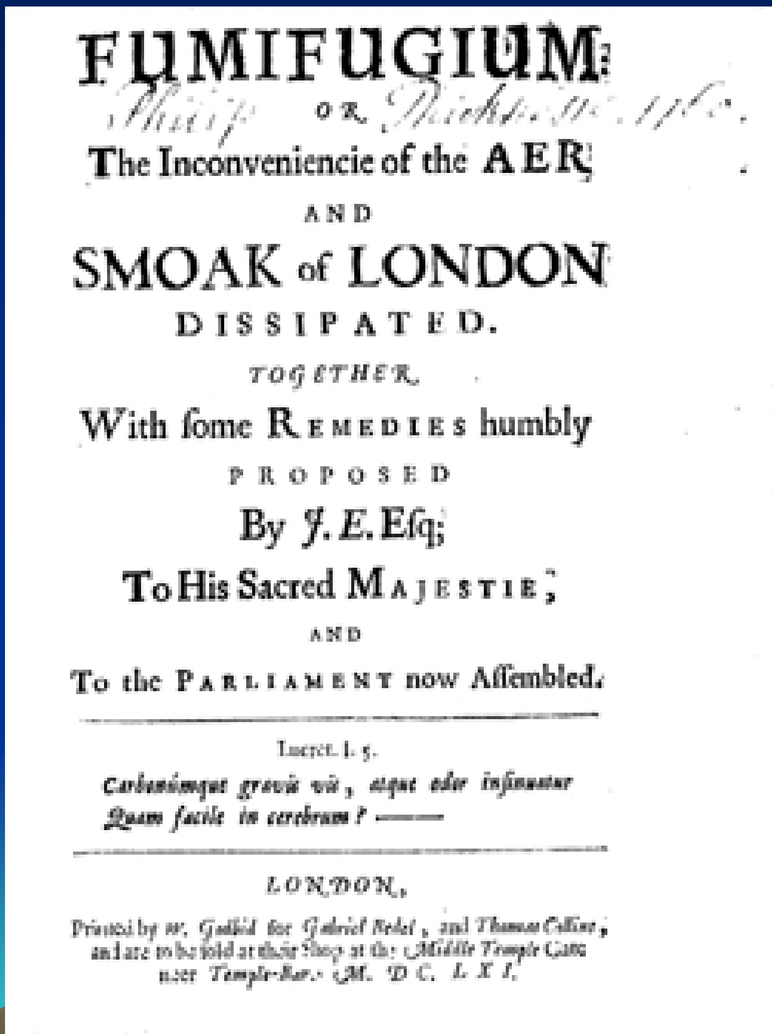
https://www.youtube.com/watch?v=02AzWORkMBM

Forge, Glass & Brick Furnaces, Brewery

1300-1800 AD



John Evelyn (1620-1706)



FUMIFUGIUM:

OR,

The Inconveniencie of the AER

AND

SMOAK of LONDON

DISSIPATED.

TOGETHER,

With some REMEDIES humbly

PROPOSED

By J. E. Esq;

To His Sacred MAJESTIE;

AND

To the PARLIAMENT now Assembled.

Lucret. l. 5.

Carbonúmque gravis vis, atque odor insinuatur
Quam facile in cerebrum! ———

LONDON,

Printed by *W. Godbid* for *Gabriel Bedel*, and *Thomas Collins*; and are to be sold at their Shop at the *Middle Temple Gate* neer *Temple-Bar*. *M. DC. LXI.*

"London by reason of the excessive coldness of the air, hindering the ascent of the smoke, was so filled with the fuliginous (sooty) steam of sea-coal, that hardly could one see across the street, and this filling the lungs with its gross particles exceedingly obstructed the breast, so as one would scarce breathe." (Diary, 1684)

Papin Pressure Cooker (1679)

Denis Papin
1647-1712

Savery Steam Engine (1698)

Thomas Savery
1650-1715

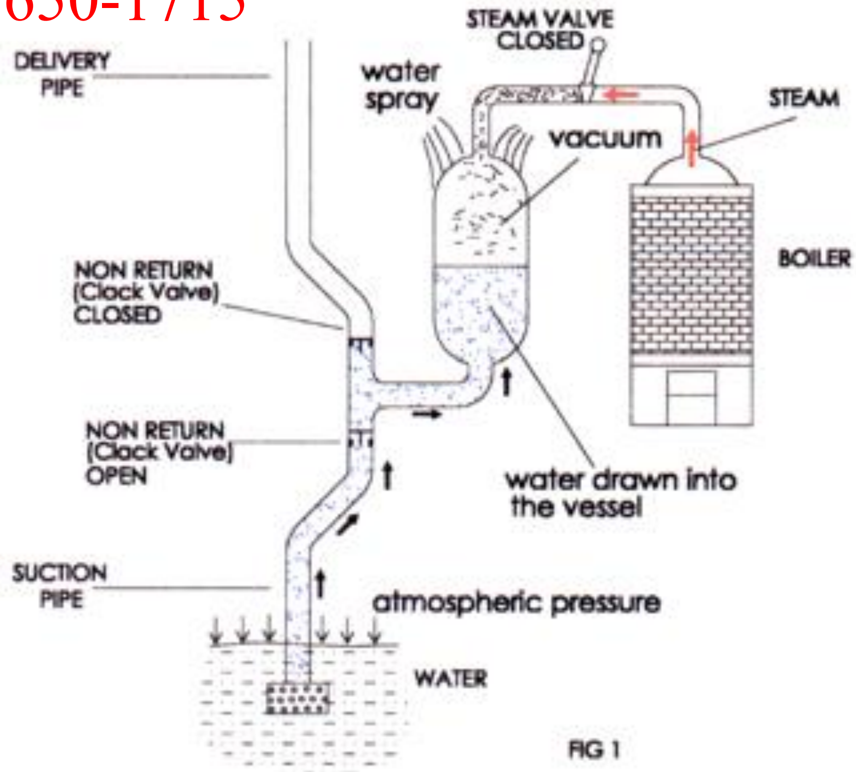


FIG 1

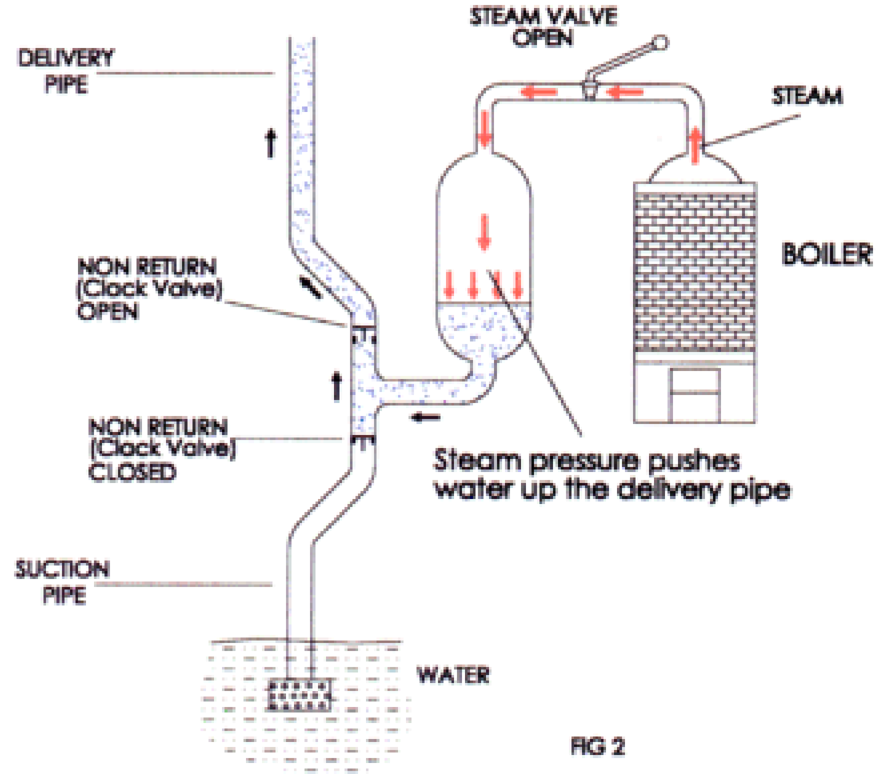


FIG 2

Step 1: Evaporate water in boiler, then spray liquid to recondense vapor in vessel, creating vacuum to draw water from well into vessel.

Step 2: Evaporate water in boiler to force water in vessel up delivery pipe.

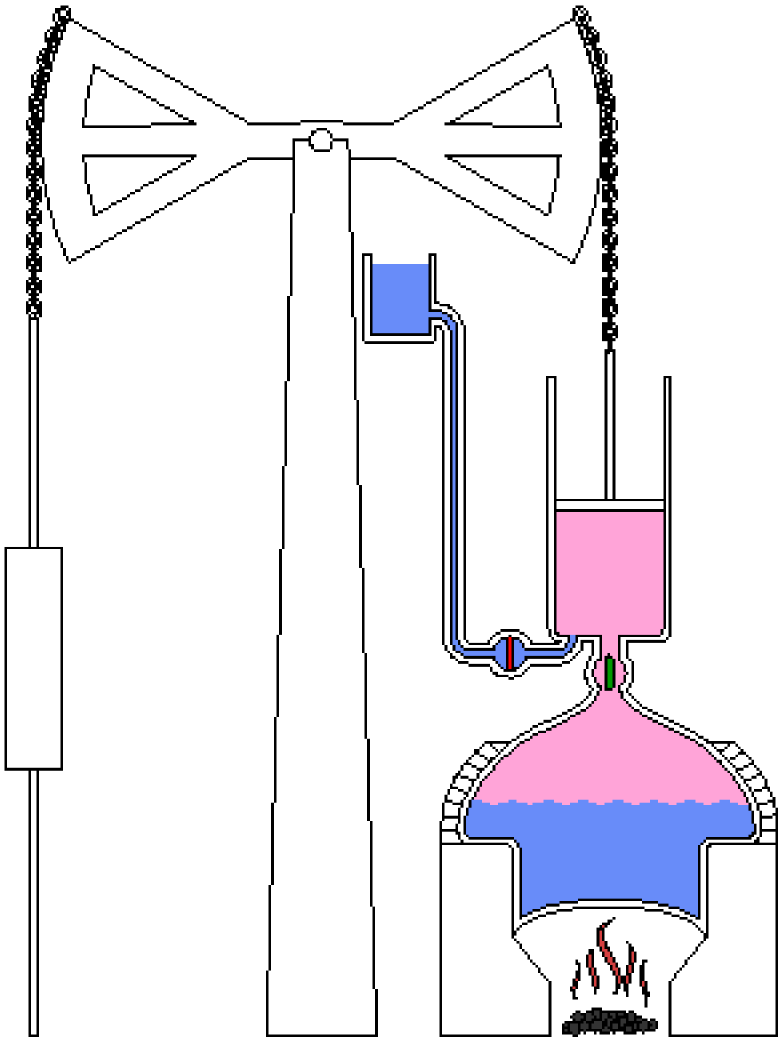
www.mgsteam.btinternet.co.uk/savery2

Newcomen Steam Engine (1712)

Thomas Newcomen
1663-1729

Step 1: Boil water to create steam to push piston up.

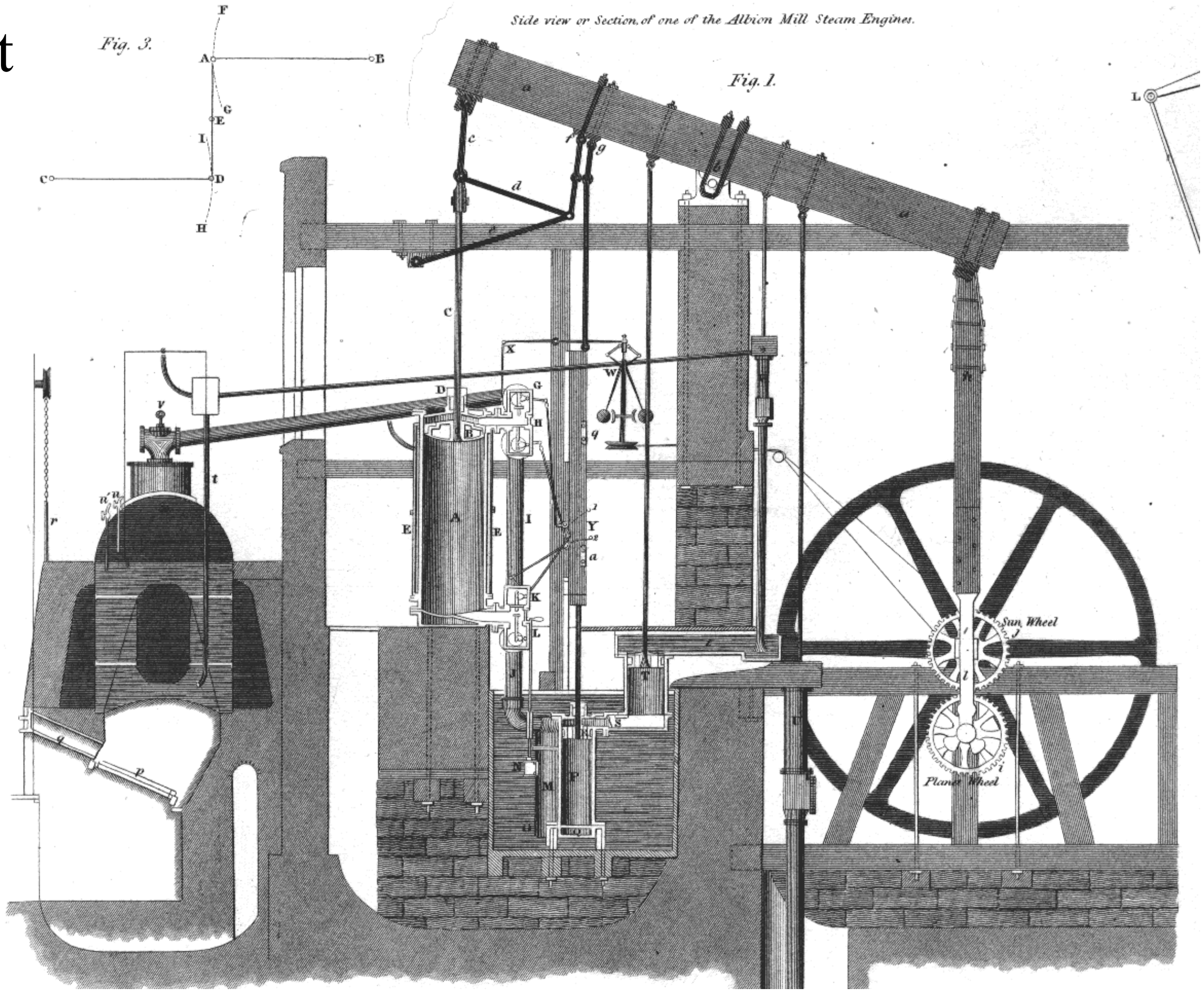
Step 2: squirt liquid water into steam chamber to recondense vapor to create vacuum that pulls piston down.



www.csa.com

Watt Steam Engine (1769 ff.)

James Watt
1736-1819



Separate chamber for condensing steam
Motion circular rather than up and down

Brewster (1832)

Early U.K. Regulations

Railway Clauses Act (1845)
"Every locomotive steam engine to be used on a railway shall, if it use coal or other similar fuel emitting smoke, be constructed on the principle of consuming, and so as to consume its own smoke."

Smoke Nuisance Abatement (Metropolis) Act (1853)
Inspector to reduce nuisance from the smoke of furnaces in London and steam vessels below London Bridge.

Alkali Act (1863)

Monet’s House of Parliament (1899-1901)

Early U.S. Regulations

Pittsburgh (1869) Outlawed burning soft coal in locomotives in city

Cincinnati (1881) Required smoke reductions, appointed inspector

Chicago (1881) Smoke reduction law, supported by judiciary

St. Louis (1893) Outlawed "dense black or thick gray smoke"

Massachusetts (1910) Boston smoke ordinance – first state regulation

Dept of Interior Bureau of Mines (1910) Office of air pollution – first federal involvement

London-Type Smog

Smog

Harold Antoine Des Voeux of London's Coal Smoke Abatement Society, introduced word in 1905 to describe combination of smoke and fog visible in several cities in Great Britain.

London-type smog:

Arises from coal- and chemical-combustion smoke in presence of fog or low-lying temperature inversion.

Reading, Pennsylvania (c. 1909)

Library of Congress Prints and Photographs Division, Washington, D. C.

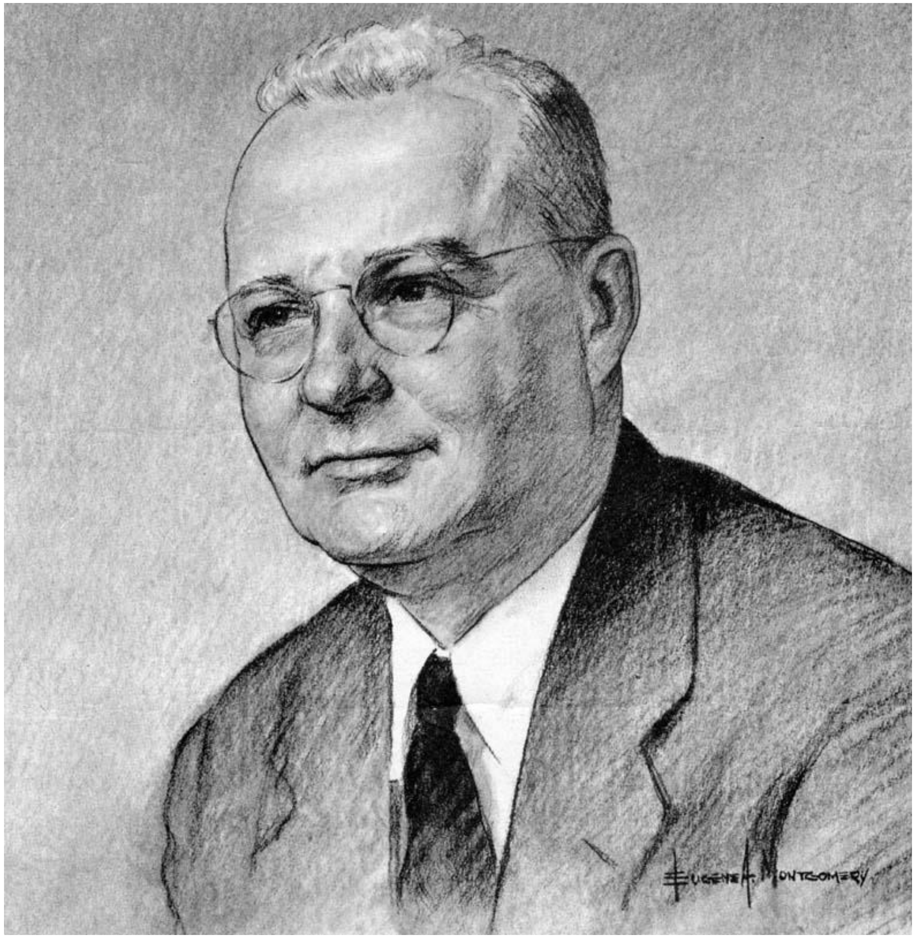
Youngstown, Ohio (c. 1910)

Library of Congress Prints and Photographs Division, Washington, D. C.

Gary, Indiana (c. 1912)

Library of Congress Prints and Photographs Division, Washington, D. C.

Thomas Midgley (1889-1944)



Edgar Fahs Smith Collection, U. Penn. Library

Leaded Gasoline

1921: Invented leaded gasoline and named it Ethyl.

1923: Midgley suffered lead poisoning, but defended lead:

"The exhaust does not contain enough lead to worry about, but no one knows what legislation might come into existence fostered by competition and fanatical health cranks.”

Leaded Gasoline

1923-5: 17 workers died, 149 injured due to lead poisoning

1925: Despite working on ethanol/benzene blends, iron carbonyl alternatives, Midgley countered,

"...tetraethyl lead is the only material available which can bring about these (antiknock) results, which are of vital importance to the continued economic use by the general public of all automotive equipment, and unless a grave and inescapable hazard exists in the manufacture of tetraethyl lead, its abandonment cannot be justified"

1925: U.S. Surgeon General organized committee to investigate lead. Observed drivers/garage workers did not experience poisoning

--> "no grounds for prohibiting the use of Ethyl gasoline."

Leaded Gasoline

1930s: 90 percent of vehicles leaded

1936: Federal Trade Commission outlawed commercial criticism of lead:

"...entirely safe to the health of (motorists) and to the public in general when used as a motor fuel, and is not a narcotic in its effect, a poisonous dope, or dangerous to the life or health of a customer, purchaser, user or the general public."

1959: U.S. Public Health Service

"...regrettable that the investigations recommended by the Surgeon General's Committee in 1926 were not carried out by the Public Health Service."

1975: Catalytic converter invented; lead deactivates catalyst

1977: Lead regulated as criteria air pollutant in the U.S.

Donora, Pa (1948)

www.eoerth.org

Noon, Donora, Pa. Oct. 29, 1948

Pittsburgh Post-Gazette

London Smog (1952) 4000 deaths

Also events in 1873, 1880, 1892, 1948, 1956, 1957, 1962

Los Angeles, California
(December 3, 1909)

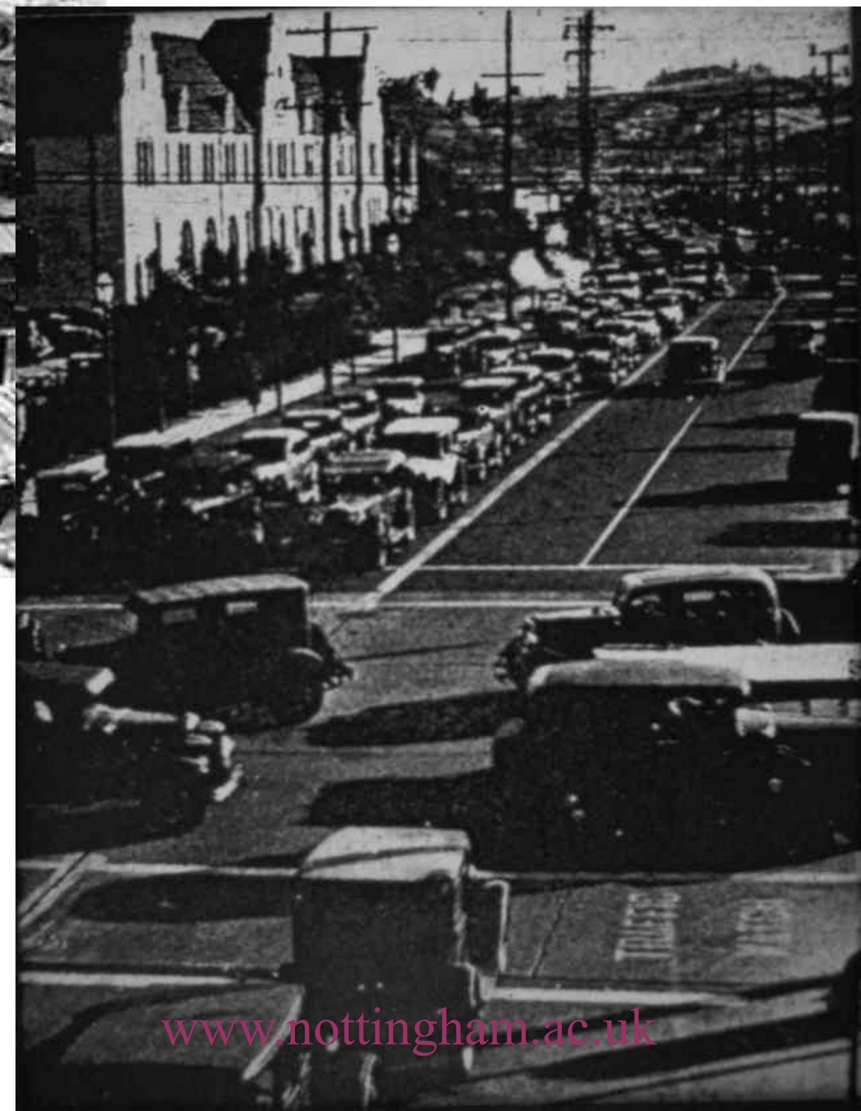
Library of Congress Prints and Photographs Division, Washington, D. C.

Los Angeles (1920s)

Los Angeles (1930s)

Images.encarta.msn.com

Uplaod.wikimedia.org



www.nottingham.ac.uk

Los Angeles 1940s

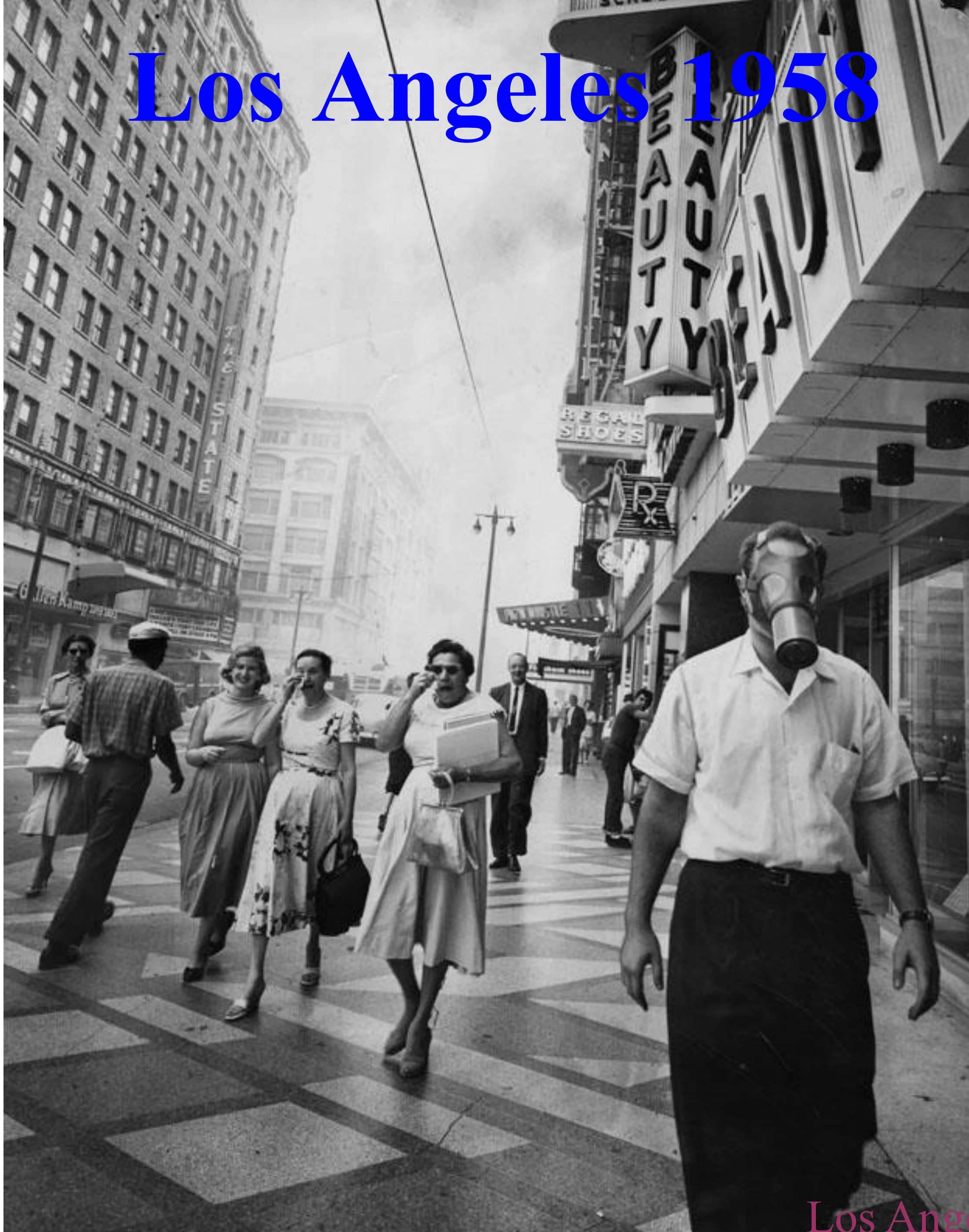
Open Waste Incineration LA (1945)

Los Angeles Public Library

Los Angeles 1950s

Time, Inc.

Los Angeles 1958



Los Angeles 1964

Daytime in Pittsburgh (1945) and NY City (1953)

U.S. Library of Congress

LA Effects of Air Pollution

Smog damage to sugar beets

LA nonsmoker's lungs

www.aqmd.gov

Arie Haagen-Smit (1900-1977)

The Archives, California Institute of Technology

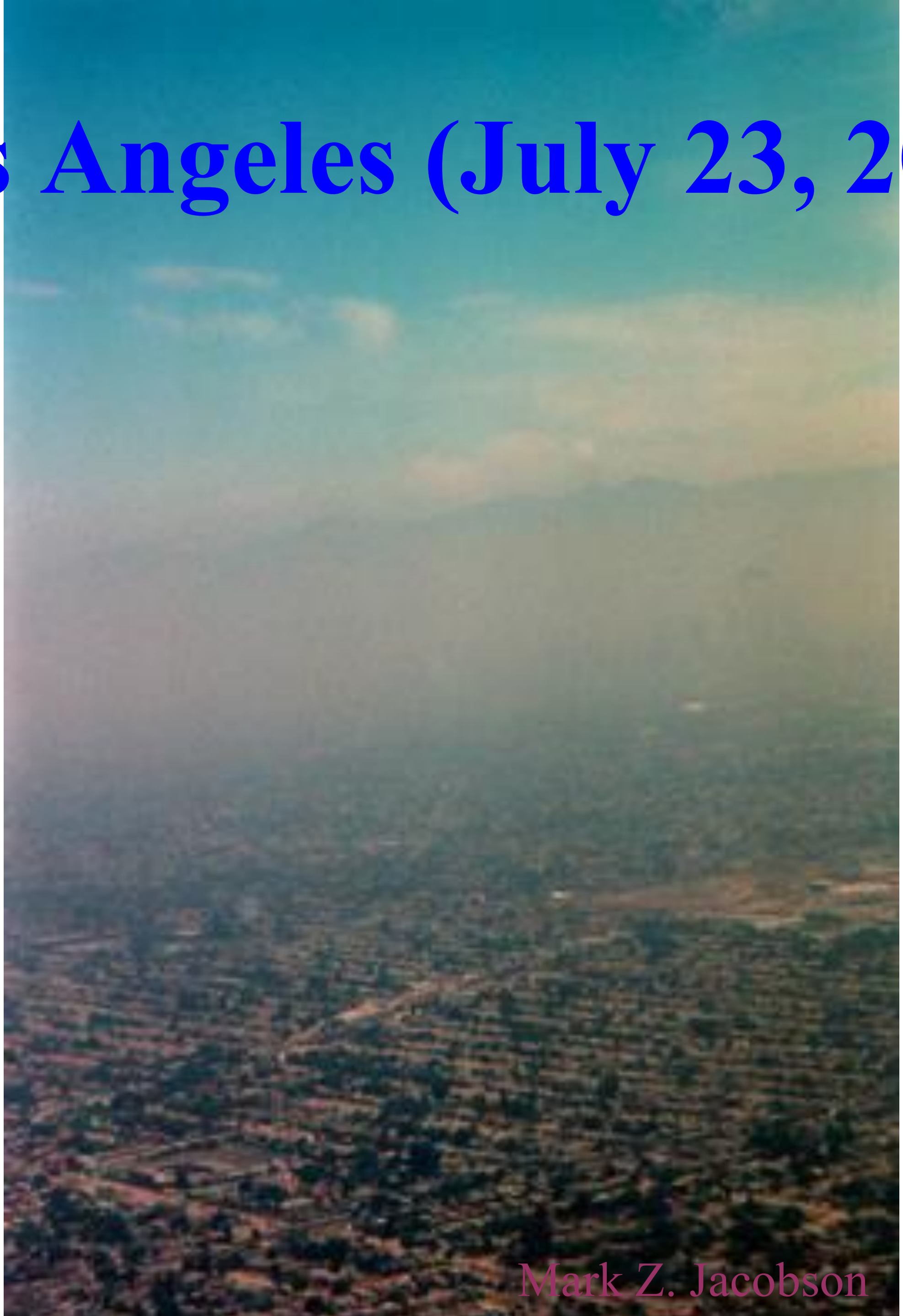
Backyard Incinerator Ban (1957)

Herald-Examiner Photo Collection, Los Angeles Public Library

Warning of Backyard Incinerator Ban (1960)

Los Angeles Public Library

Los Angeles (July 23, 2000)



Chemistry of Background Troposphere and Polluted Air

Background troposphere

- Inorganic gases
- Long-lived, light organic gases
- Naturally-emitted short-lived heavy organic gases

Polluted air

- Inorganic gases
- Short-lived light and heavy organic gases

Photostationary State Ozone

$$\dot{N}O(g) + O_3(g) \longrightarrow \dot{N}O_2(g) + O_2(g)$$

Nitric oxide | Ozone | Nitrogen dioxide | Molecular oxygen

$$\dot{N}O_2(g) + hn \longrightarrow \dot{N}O(g) + \cdot\dot{O}(g) \qquad l < 420\ nm$$

Nitrogen dioxide | Nitric oxide | Atomic oxygen

$$\cdot\dot{O}(g) + O_2(g) \xrightarrow{M} O_3(g)$$

Ground-state atomic oxygen | Molecular oxygen | Ozone

(4.1) - (4.3)

Photostationary State Ozone

$$\chi_{O_3} = (J/N_d k_1)(\chi_{NO_2(g)}/\chi_{NO(g)}) \qquad (4.4)$$

J = photolysis rate coefficient of $NO_2(g)+h\nu \rightarrow NO(g)+O(g)$

k_1 = rate coefficient of $NO(g)+O_3(g) \rightarrow NO_2(g)+O_2(g)$

Example 4.1:

Estimate ozone mixing ratio when

p_d = 1013 mb; T = 298 K

$\chi_{NO(g)}$ = 5 pptv; $\chi_{NO_2(g)}$ = 10 pptv

k_1 = 1.8×10^{-14} cm^3 molec.$^{-1}$ s^{-1}; J = 0.01 s^{-1}

----> N_d = 2.46×10^{19} molec. cm^{-3}

----> $\chi_{O_3(g)}$ = 45.2 ppbv

Daytime Nitrogen Oxide Removal

$$\dot{N}O_2(g) + \dot{O}H(g) \xrightarrow{M} HNO_3(g)$$

Nitrogen dioxide + Hydroxyl radical → Nitric acid

(4.5)

Hydroxyl Radical Production

$$O_3(g) + h\nu \longrightarrow O_2(g) + \cdot\dot{O}(^1D)(g) \qquad \lambda < 310\ \text{nm}$$

Ozone		Molecular oxygen	Excited atomic oxygen

$$\cdot\dot{O}(^1D)(g) + H_2O(g) \longrightarrow 2\dot{O}H(g)$$

Excited atomic oxygen	Water vapor	Hydroxyl radical

(4.6) - (4.7)

Nighttime Nitrogen Chemistry

$$\dot{N}O_2\,(g) + O_3\,(g) \longrightarrow \dot{N}O_3\,(g) + O_2(g)$$

Nitrogen dioxide · Ozone · Nitrate radical · Molecular oxygen

$$\dot{N}O_2\,(g) + \dot{N}O_3\,(g) \overset{M}{\rightleftharpoons} N_2O_5\,(g)$$

Nitrogen dioxide · Nitrate radical · Dinitrogen pentoxide

$$N_2O_5\,(g) + H_2O(aq) \longrightarrow 2HNO_3\,(aq)$$

Dinitrogen pentoxide · Liquid water · Dissolved nitric acid

(4.8) - (4.10)

Ozone From Carbon Monoxide

$$CO(g) + \dot{O}H(g) \longrightarrow CO_2(g) + \dot{H}(g)$$

Carbon monoxide | Hydroxyl radical | Carbon dioxide | Atomic hydrogen

$$\dot{H}(g) + O_2(g) \xrightarrow{M} H\dot{O}_2(g)$$

Atomic hydrogen | Molecular oxygen | Hydroperoxy radical

$$\dot{N}O(g) + H\dot{O}_2(g) \longrightarrow \dot{N}O_2(g) + \dot{O}H(g)$$

Nitric oxide | Hydroperoxy radical | Nitrogen dioxide | Hydroxyl radical

$$\dot{N}O_2(g) + hn \longrightarrow \dot{N}O(g) + \cdot\dot{O}(g) \qquad l < 420\ nm$$

Nitrogen dioxide | Nitric oxide | Atomic oxygen

$$\cdot\dot{O}(g) + O_2(g) \xrightarrow{M} O_3(g)$$

Ground-state atomic oxygen | Molecular oxygen | Ozone

(4.11) - (4.15)

Ozone From Methane

$CH_4(g)$	+ $\dot{O}H(g)$	→	$\dot{C}H_3(g)$	+ $H_2O(g$
Methane	Hydroxyl radical		Methyl radical	Water vapor

$\dot{C}H_3(g)$	+ $O_2(g)$	$\xrightarrow{M}$	$CH_3\dot{O}_2$ (g)
Methyl radical	Molecular oxygen		Methylperoxy radical

$\dot{N}O(g)$	+ $CH_3\dot{O}_2(g)$	→	$\dot{N}O_2(g)$	+ $CH_3\dot{O}(g)$
Nitric oxide	Methylperoxy radical		Nitrogen dioxide	Methoxy radical

$\dot{N}O_2$ (g)	+ hn	→	$\dot{N}O(g)$	+ •$\dot{O}(g)$	l < 420 nm
Nitrogen dioxide			Nitric oxide	Atomic oxygen	

•$\dot{O}(g)$	+ $O_2(g)$	$\xrightarrow{M}$	$O_3(g)$
Ground-state atomic oxygen	Molecular oxygen		Ozone

(4.16) - (4.20)

Ozone From Ethane

$$C_2H_6(g) + \dot{O}H(g) \longrightarrow \dot{C}_2H_5(g) + H_2O(g)$$

Ethane | Hydroxyl radical | Ethyl radical | Water vapor

$$\dot{C}_2H_5(g) + O_2(g) \xrightarrow{M} C_2H_5\dot{O}_2(g)$$

Ethyl radical | Molecular oxygen | Ethylperoxy radical

$$\dot{N}O(g) + C_2H_5\dot{O}_2(g) \longrightarrow \dot{N}O_2(g) + C_2H_5\dot{O}(g)$$

Nitric oxide | Ethylperoxy radical | Nitrogen dioxide | Ethoxy radical

$$\dot{N}O_2(g) + hn \longrightarrow \dot{N}O(g) + \cdot\dot{O}(g) \qquad l < 420\ nm$$

Nitrogen dioxide | Nitric oxide | Atomic oxygen

$$\cdot\dot{O}(g) + O_2(g) \xrightarrow{M} O_3(g)$$

Ground-state atomic oxygen | Molecular oxygen | Ozone

(4.26) - (4.30)

Formaldehyde and Acetaldehyde Formation

Formaldehyde

$$CH_3\dot{O}(g) + O_2(g) \longrightarrow HCHO(g) + H\dot{O}_2(g)$$

Methoxy radical | Molecular oxygen | Formal- dehyde | Hydroperoxy radical

Acetaldehyde

$$C_2H_5\dot{O}(g) + O_2(g) \longrightarrow CH_3CH(=O) + H\dot{O}_2(g)$$

Ethoxy radical | Molecular oxygen | Acetaldehyde | Hydroperoxy radical

(4.21), (4.31)

Ozone From Formaldehyde

$$HCHO(g) + hn \rightarrow \begin{cases} H\dot{C}O(g) + \dot{H}(g) & l < 334\ nm \\ CO(g) + H_2(g) & l < 370\ nm \end{cases}$$

Formal-dehyde → Formyl radical + Atomic hydrogen (l < 334 nm)

Formal-dehyde → Carbon monoxide + Molecular hydrogen (l < 370 nm)

$$HCHO(g) + \dot{O}H(g) \rightarrow H\dot{C}O(g) + H_2O(g)$$

Formal-dehyde + Hydroxyl radical → Formyl radical + Water vapor

$$H\dot{C}O(g) + O_2(g) \rightarrow CO(g) + H\dot{O}_2(g)$$

Formyl radical + Molecular oxygen → Carbon monoxide + Hydroperoxy radical

$$\dot{H}(g) + O_2(g) \xrightarrow{M} H\dot{O}_2(g)$$

Atomic hydrogen + Molecular oxygen → Hydroperoxy radical

--> Form O_3 from both CO and HO_2

(4.22) - (4.25)

PAN From Acetaldehyde

$$CH_3CH(=O)(g) + \dot{O}H(g) \longrightarrow CH_3\dot{C}(=O)(g) + H_2O(g)$$

Acetaldehyde | Hydroxyl radical | Acetyl radical | Water vapor

$$CH_3\dot{C}(=O)(g) + O_2(g) \xrightarrow{M} CH_3C(=O)\dot{O}_2(g$$

Acetyl radical | Molecular oxygen | Peroxyacetyl radical

$$CH_3C(=O)\dot{O}_2(g) + \dot{N}O_2(g) \overset{M}{\rightleftharpoons} CH_3C(=O)O_2NO_2(g)$$

Peroxyacetyl radical | Nitrogen dioxide | Peroxyacetyl nitrate (PAN)

(4.32) - (4.34)

Photochemical Smog Formation

$$\dot{N}O(g) + R\dot{O}_2(g) \longrightarrow \dot{N}O_2(g) + R\dot{O}(g)$$

Nitric oxide	Organic peroxy radical	Nitrogen dioxide	Organic oxy radical

$$\dot{N}O(g) + O_3(g) \longrightarrow \dot{N}O_2(g) + O_2(g)$$

Nitric oxide	Ozone	Nitrogen dioxide	Molecular oxygen

$$\dot{N}O_2(g) + hn \longrightarrow \dot{N}O(g) + \cdot\dot{O}(g) \qquad l < 420\ nm$$

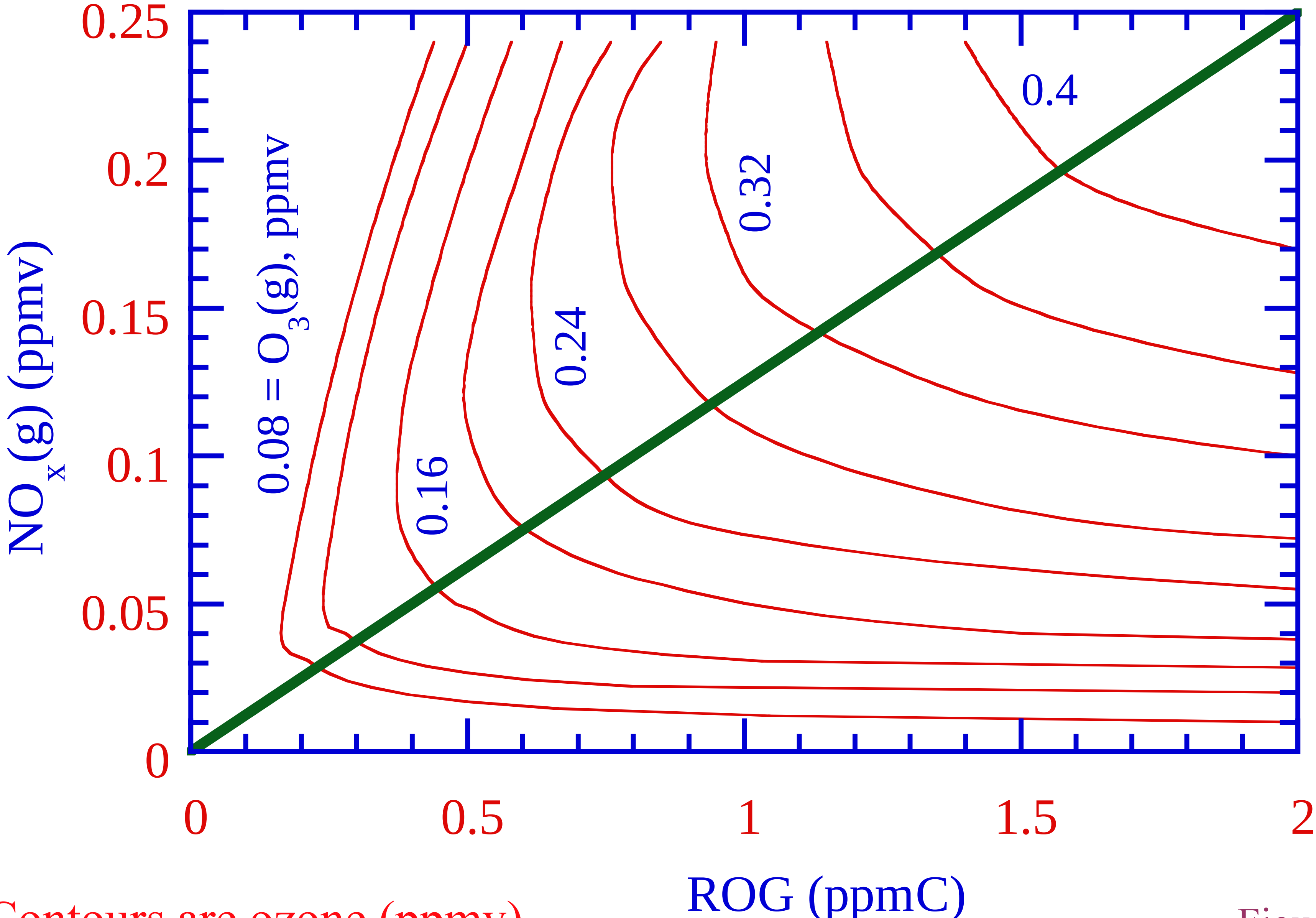
Nitrogen dioxide	Nitric oxide	Atomic oxygen

$$\cdot\dot{O}(g) + O_2(g) \xrightarrow{M} O_3(g)$$

Ground-state atomic oxygen	Molecular oxygen	Ozone

(4.37) - (4.40)

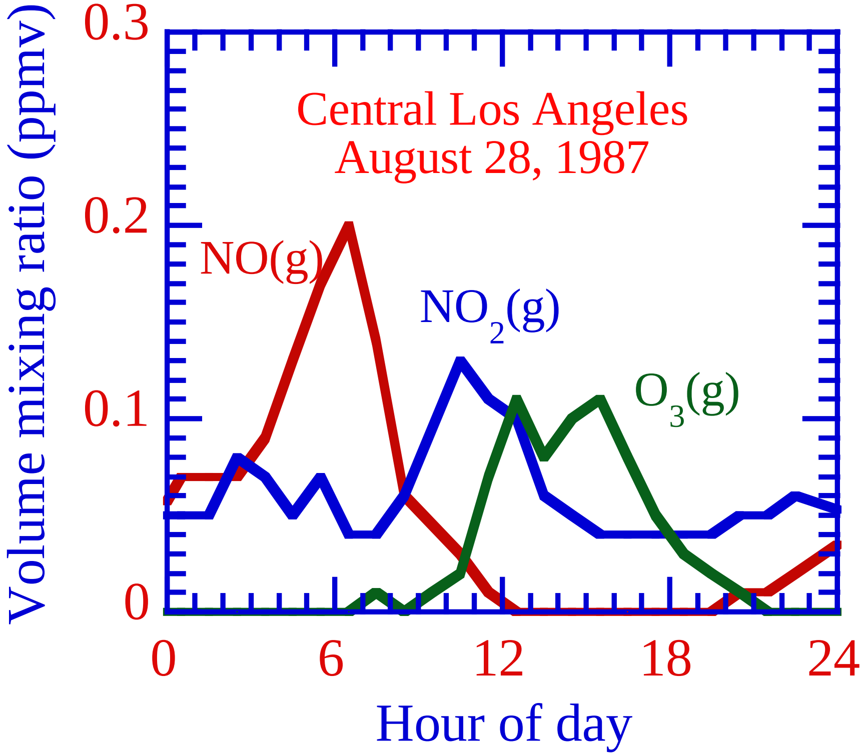
Ozone Isopleth

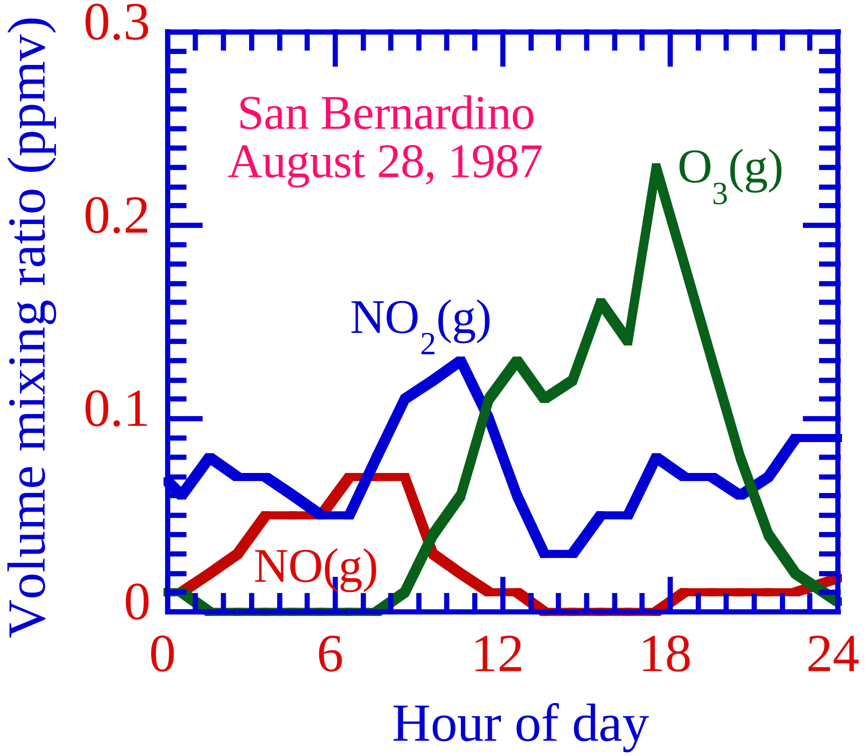


Contours are ozone (ppmv)

Figure 4.12

Source/Receptor Regions in Los Angeles





https://www.google.com.tw/maps/@34.0838772,-117.7079554,10z?hl=zh-TW

Figure 4.13

Lifetimes of ROGs Against Chemical Loss in Urban Air

ROG Species	Phot.	OH	HO_2	O	NO_3	O_3
n-Butane	---	22 h	---	---	29 d	---
trans-2-butene	---	52 m	---	6.3 d	4 m	17 m
Acetylene	---	3 d	---	---	---	---
Formaldehyde	7 h	6 h	1.8 h	---	2 d	---
Acetone	23 d	9.6 d	---	---	---	---
Ethanol	---	19 h	---	---	---	---
Toluene	---	9 h	---	---	33 d	---
Isoprene	---	34 m	---	4 d	5 m	4.6 h

Table 4.3

Most Important Gases in Smog in Terms of Ozone Reactivity and Abundance

1. *m*- and *p*-Xylene
2. Ethene
3. Acetaldehyde
4. Toluene
5. Formaldehyde
6. *i*-Pentane
7. Propene
8. *o*-Xylene
9. Butane
10. Methylcyclopentane

Table 4.4

Early Morning OH Source in Polluted Air

$$HONO(g) + hn \longrightarrow \dot{O}H(g) + \dot{N}O(g) \qquad l < 400\ nm$$

Nitrous acid — Hydroxyl radical — Nitric oxide

(4.42)

Mid-Morning OH Source in Polluted Air

$$HCHO(g) + hn \longrightarrow H\dot{C}O(g) + \dot{H}(g) \qquad l < 334\ nm$$

Formal-dehyde → Formyl radical + Atomic hydrogen

$$\dot{H}(g) + O_2(g) \xrightarrow{M} H\dot{O}_2(g)$$

Atomic hydrogen + Molecular oxygen → Hydroperoxy radical

$$H\dot{C}O(g) + O_2(g) \longrightarrow CO(g) + H\dot{O}_2(g)$$

Formyl radical + Molecular oxygen → Carbon monoxide + Hydroperoxy radical

$$\dot{N}O(g) + H\dot{O}_2(g) \longrightarrow \dot{N}O_2(g) + \dot{O}H(g)$$

Nitric oxide + Hydroperoxy radical → Nitrogen dioxide + Hydroxyl radical

(4.43) - (4.46)

Afternoon OH Source in Polluted Air

$$O_3(g) + hn \longrightarrow O_2(g) + \cdot\dot{O}(^1D)(g) \qquad l < 310\ \text{nm}$$

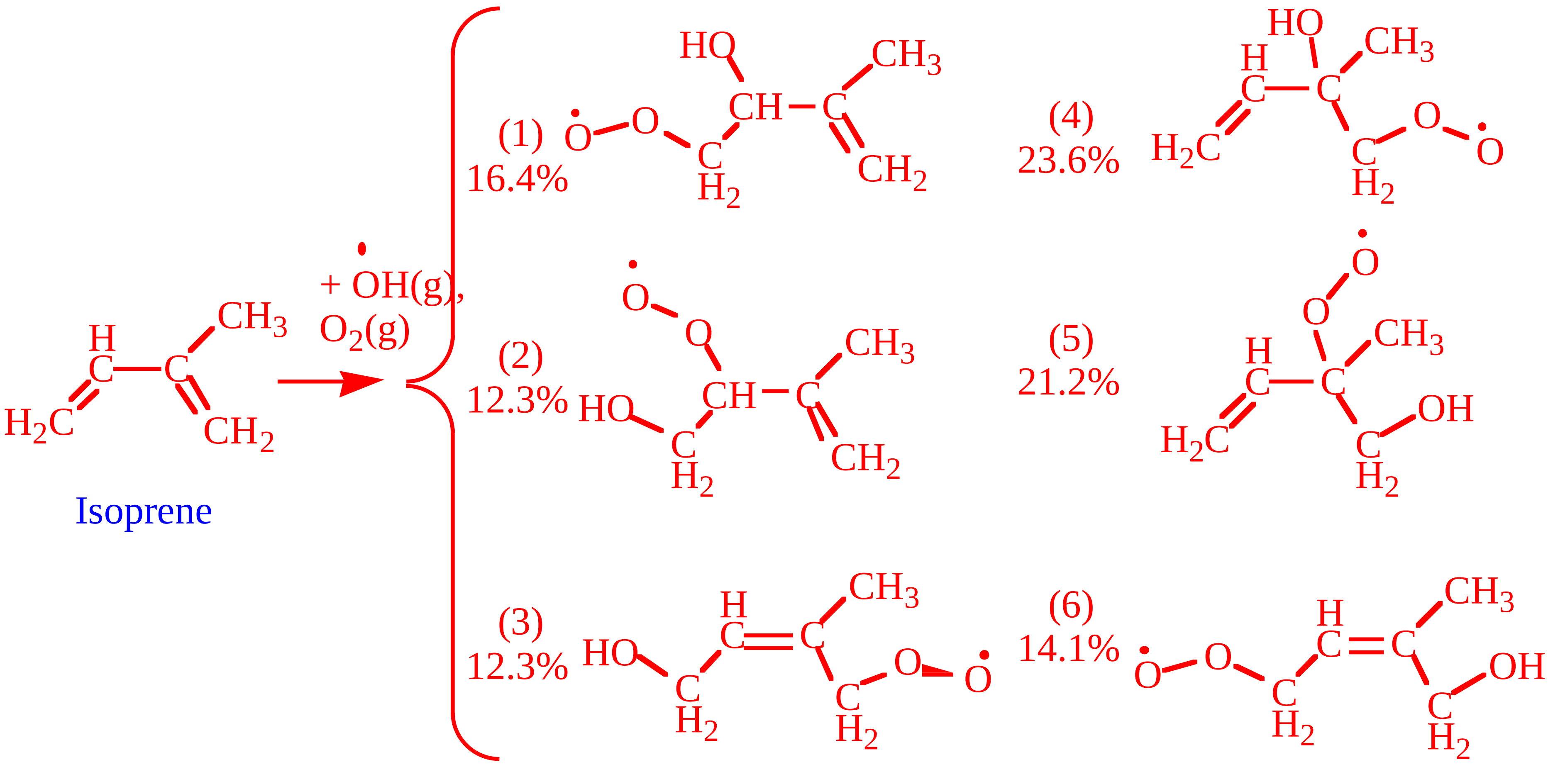
Ozone | Molecular oxygen | Excited atomic oxygen

$$\cdot\dot{O}(^1D)(g) + H_2O(g) \longrightarrow 2\dot{O}H(g)$$

Excited atomic oxygen | Water vapor | Hydroxyl radical

(4.47) - (4.48)

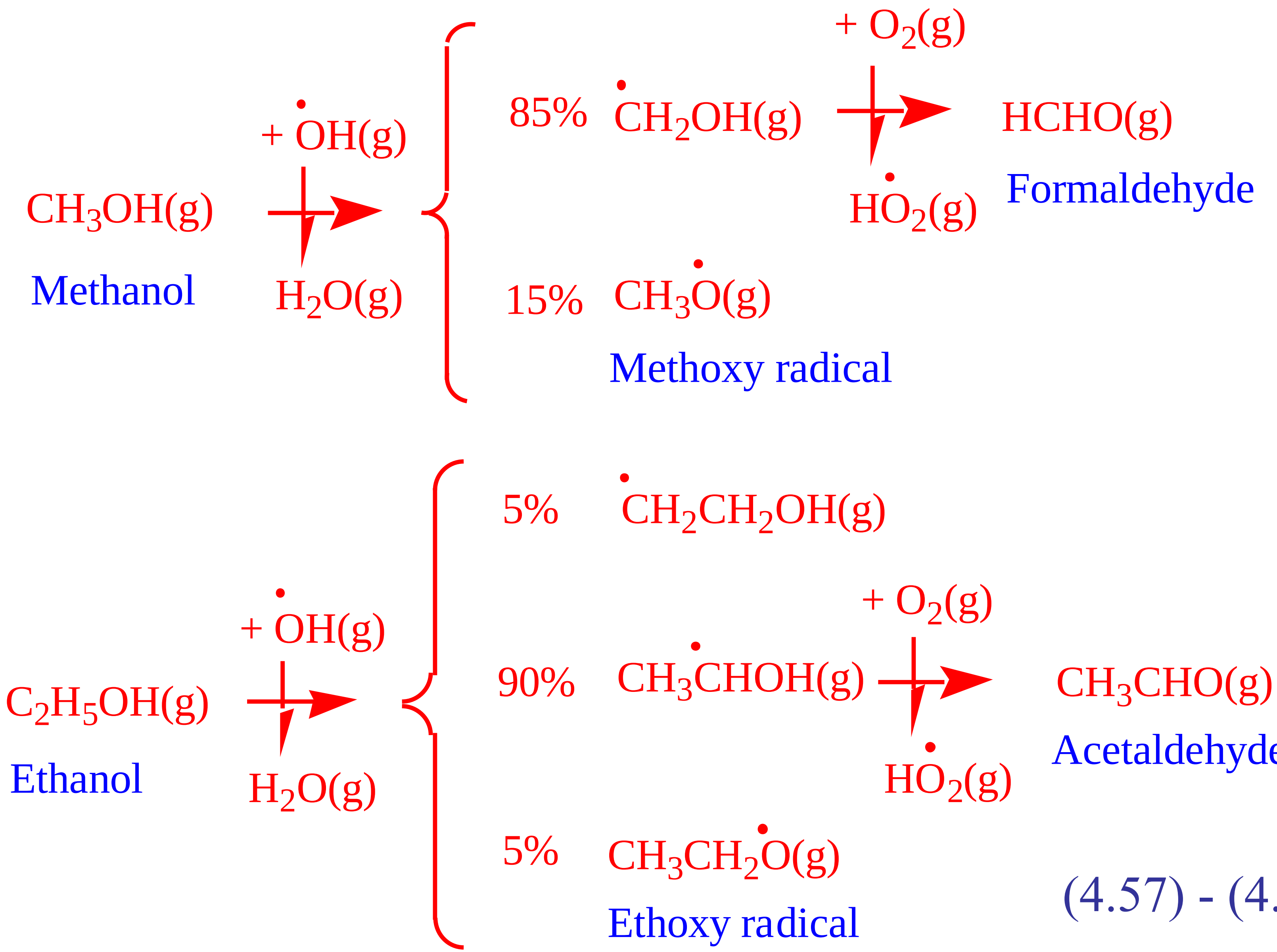
Isoprene Reaction with OH



Isoprene peroxy radicals

(4.54)

Alcohol Reactions with OH



(4.57) - (4.58)

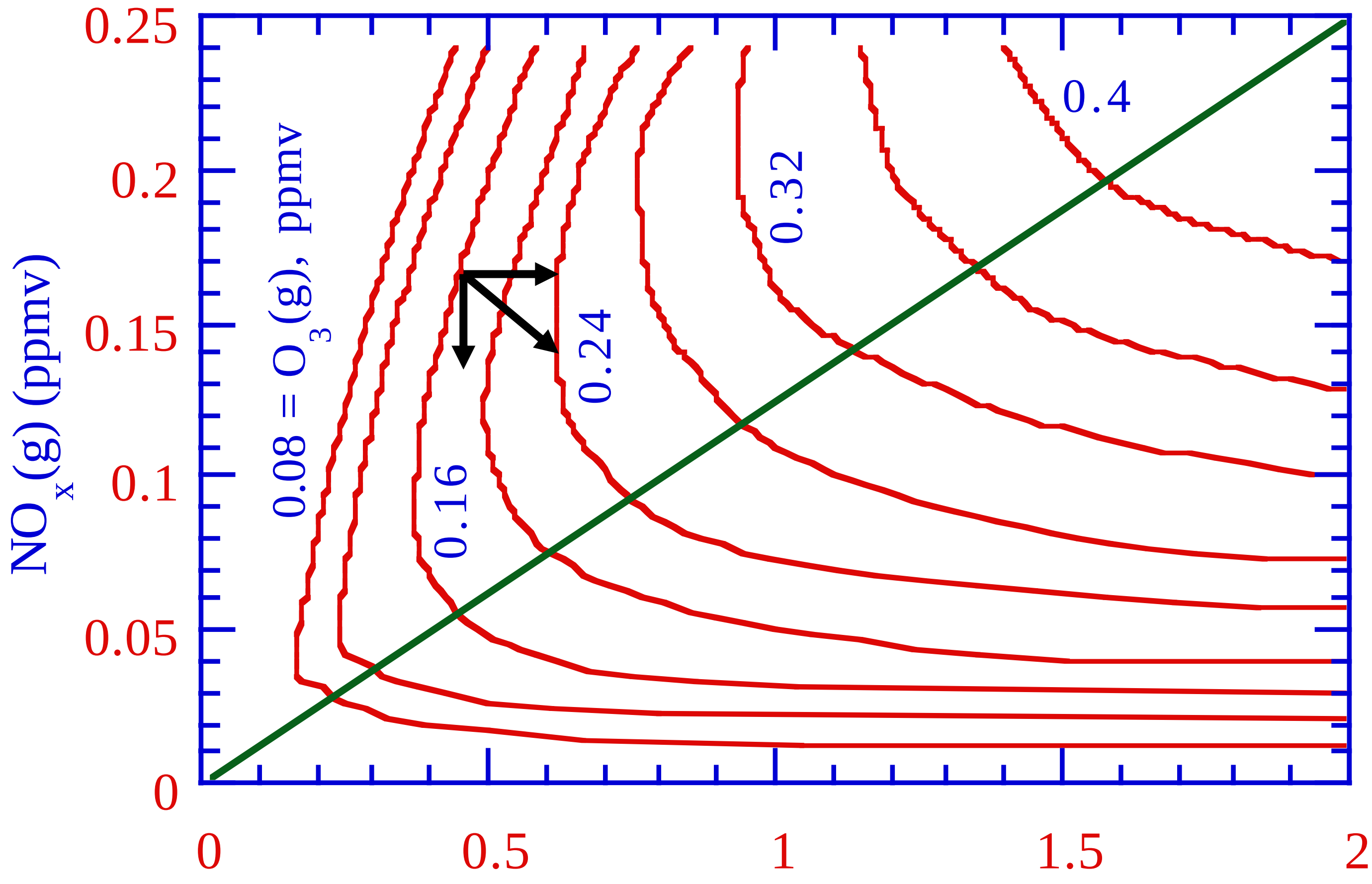
Percent Changes E85 Minus Gas From Data

NMOG	+ 45%
NO_x	- 30%
Benzene	- 64%
1,3-butadiene	- 66%
Acetaldehyde	+ 4500%
Formaldehyde	+ 200%

E85 = 81% ethanol
19% gasoline

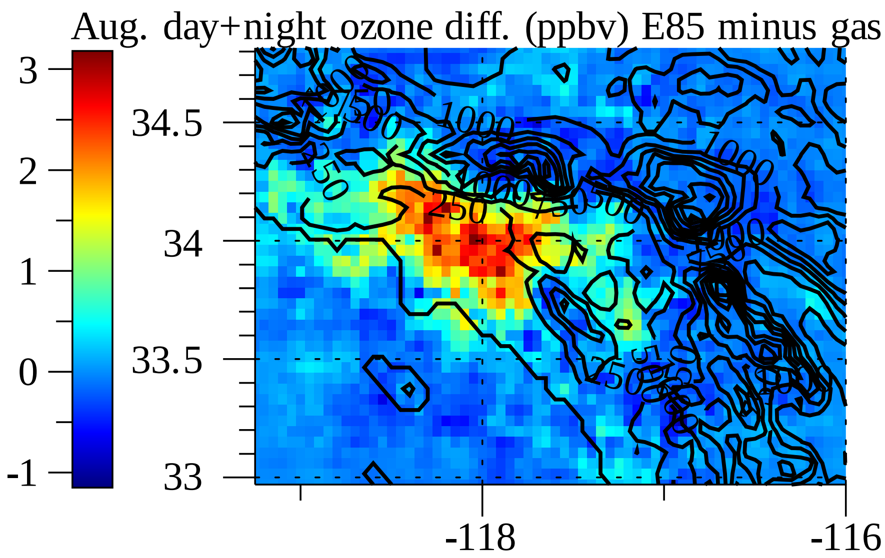
Whitney (2007)

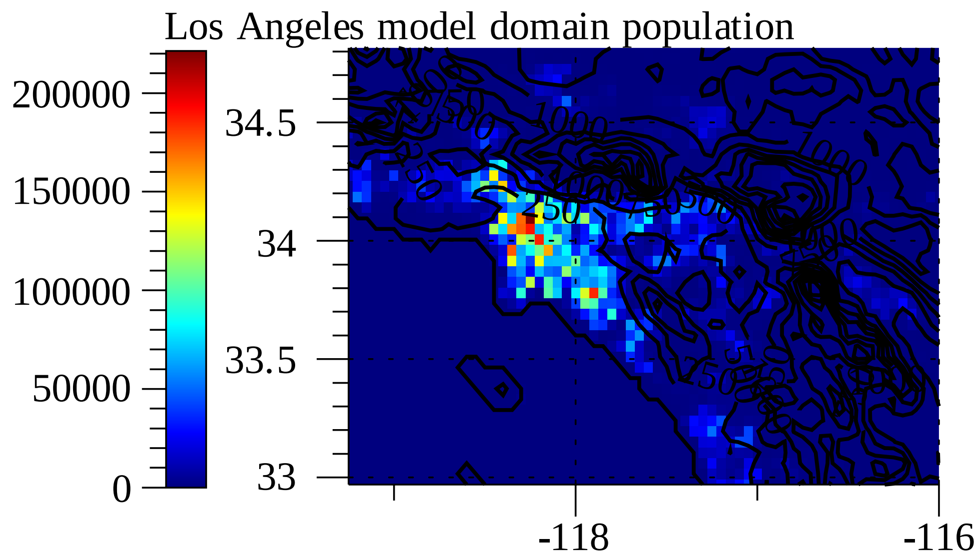
Ozone isopleth



Contours are ozone (ppmv)

Effect in 2020 of E85 vs. Gasoline on Ozone and Health in Los Angeles

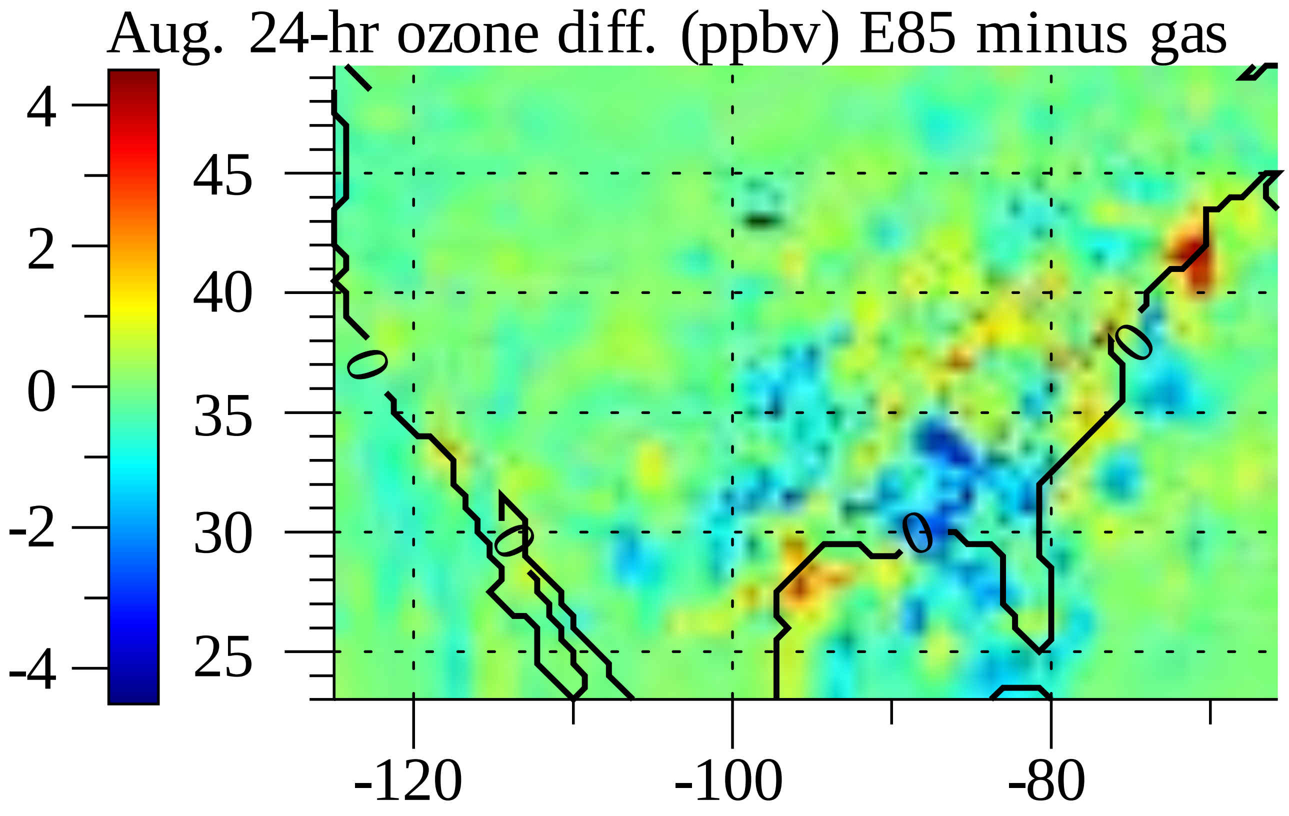




Change in ozone deaths/yr due to E85: +120 (+9%) (47-140)

Changes in cancer/yr due to E85: -3.5 to +0.3

2020 U.S. Effects of E85 vs. Gasoline



Additional ozone deaths/yr: +185 (72-213)

E85, regardless of source, causes as much or more U.S. air pollution mortality from the tailpipe as gasoline

Air Pollution AP3050
Assignment #6
Due 1:00 pm, 13 April 2022

請就以下VOCs (NMHC)之物化特性、工業製程、相關產業產品與應用、污染(或有害)性質，以及台灣有那些主要生產公司等面向，做一統合報告。

（a）烷類
（b）烯類
（c）苯類
（d）醇類