Air Quality

Recommended books & references:

(1) *Introduction to Environmental Engineering and Science*, G.M. Masters & W.P. Ela, 2008, Pearson International.

(2) *Air Pollution Control Engineering*, Noel de Nevers, McGraw Hill, 2000 (2nd ed).

(3) *Atmospheric Pollution: History, Science and Regulation*, Mark Z. Jacobson, Cambridge, 2002.

Air Pollutants & Air Quality: Part 1

- Overview & unit conversion
- Air pollutant & air quality system
- Local air quality issues
- Characteristics of SOx, NOx & particulates

Air Pollution: Definition

Any atmospheric condition in which “substances” are present at concentrations high enough above their normal ambient levels to produce a measurable effect on man, animals, vegetation, or materials.

- from Seinfeld, J.H. (1986) Atmospheric Chemistry and Physics of Air Pollution, John Wiley, New York

Concentration of Trace Compounds

Species	Clean Troposphere (ppb)	Polluted Urban Air
SO_2	1–10	20–200
CO	120	1000–10,000
NO	0.01–0.05	50–750
NO_2	0.1–0.5	50–250
O_3	20–80	100–500
HNO_3	0.02–0.3	3–50
NH_3	1	10–25
HCHO	0.4	20–50
HCOOH	BD	1–10
HNO_2	0.001	1–8
$CH_3C(O)O_2NO_2$	BD	5–35
NMHC	BD	500–1200

BD: Below detection limit
Source: *Air Pollution* by J.H. Seinfeld, John Wiley & Sons, 1986

Units of Measurements: Air Quality

Parameter	Unit (e.g.)	Description
Mass concentration	mg/m^3, $\mu g/m^3$	Pollutant mass per m^3 air
Volume concentration (mixing ratio)	cm^3/m^3, ppmv	Pollutant volume per air volume
Pollutant concentration in rain water	mg/l	Pollutant mass per liter of rain water
Pollutant deposition (e.g., deposited particulate matter, wet precipitation and gases)	$\mu g/m^2/day$	Deposited pollutant mass per surface area and time
Pollutant dose	$(mg/m^3)h$	Concentration x time
Dose of effect	µg/kg	Received (effective) pollutant mass per acceptor mass.

Units of Measurements: Emissions

Parameter	Unit (e.g.)	Description
Mass concentration	mg/m^3 at 0^oC, 1013 mbar	Pollutant mass per cubic meter in normal condition, usually dry
Volume concentration	cm^3/m^3, ppmv	Pollutant volume per exhaust gas volume
Emission mass flow	kg/h	Emitted pollutant mass per unit of time

Units of Measurements

Commonly used unit systems:

International System of Units (SI)

U.S. Customary System (USCS)

Atmospheric Concentration/Mixing Ratio of gases:

- Traditional concentration:
  - Amount (mass) of a substance in a given volume/volume, e.g., mg/m^3
  - According to ideal gas law, $PV = nRT$

    - Depending on pressure and temperature

Units of Measurements: Gases

Atmospheric concentration/mixing ratio of gases:

- Atmospheric Concentration: Mixing Ratio

amount of the substance in a given volume **($C_i = n_i/V = P_i/RT$)**

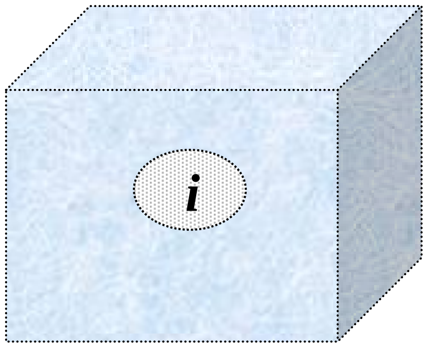
to

total amount of all constituents in that volume, **($C_{total} = n/V = P/RT$)**

That is, fraction of the total amount contributed by the one of interest

$\xi_i = C_i / C_{total} = n_i/n = V_i/V = P_i/P$

- independent from pressure and temperature
- excluding particulate matter and condensed water
- presence of water vapor (varying with humidity)
- based on dry air



Units of Measurements: Gaseous Pollutants

Concentration/mixing ratio:

• (volume of substance)/(volume of air mixture)

(1) parts per million – **ppm/ppmv** **μmol mol^{-1}**

(volume of gaseous pollutant)/(10^6 volumes of air mixture)

(2) parts per billion – **ppb/ppbv** **nmol mol^{-1}**

(volume of gaseous pollutant)/(10^9 volumes of air mixture)

(3) parts per trillion – **ppt/pptv** **pmol mol^{-1}**

(volume of gaseous pollutant)/(10^{12} volumes of air mixture)

Units of Measurements: Gases

Employing ideal gas law to convert

ppmv $\leftrightarrow$ **mass of pollutant / unit volume of air**

mg of airborne pollutants / m^3 air (mg/m^3)

Ideal Gas Law: $PV = nRT$

P = absolute pressure (atm)

V = volume (m^3); n = mass (mol)

R = ideal gas constant

= 0.082056 L atm K^{-1} mol^{-1}

T = absolute temperature (K); K= ^oC + 273.15

Units of Measurements: Gases

- Employing ideal gas law to convert

ppmv to **mass of pollutant / unit volume of air**

x mg CO / m^3 air $\leftrightarrow$ y ppm CO

Try: y ppmv CO $\rightarrow$ x µg CO / m^3

Units of Measurements: Gases (Example)

The Air Quality Standard for carbon monoxide (based on an 8-hour measurement) is 9.0 ppm. Express this standard as a percent by volume as well as in mg/m^3 at 1 atm and 25^oC.

AQ: Monitoring, Assessment & Communication

- How do we determine that airborne materials are pollutants?

  Concentration standards

- What are effective ways to inform the public about air quality?

  Consistent systems with straightforward description

Air Pollutants: Criteria Pollutants

- Based on US Environmental Protection Agency (EPA) :
  - Ground level ozone (O_3),
  - Carbon monoxide (CO),
  - Sulfur dioxide (SO_2),
  - Small particulates (e.g., PM_{10}, $PM_{2.5}$),
  - Nitrogen dioxide (NO_2), and
  - Lead (Pb)

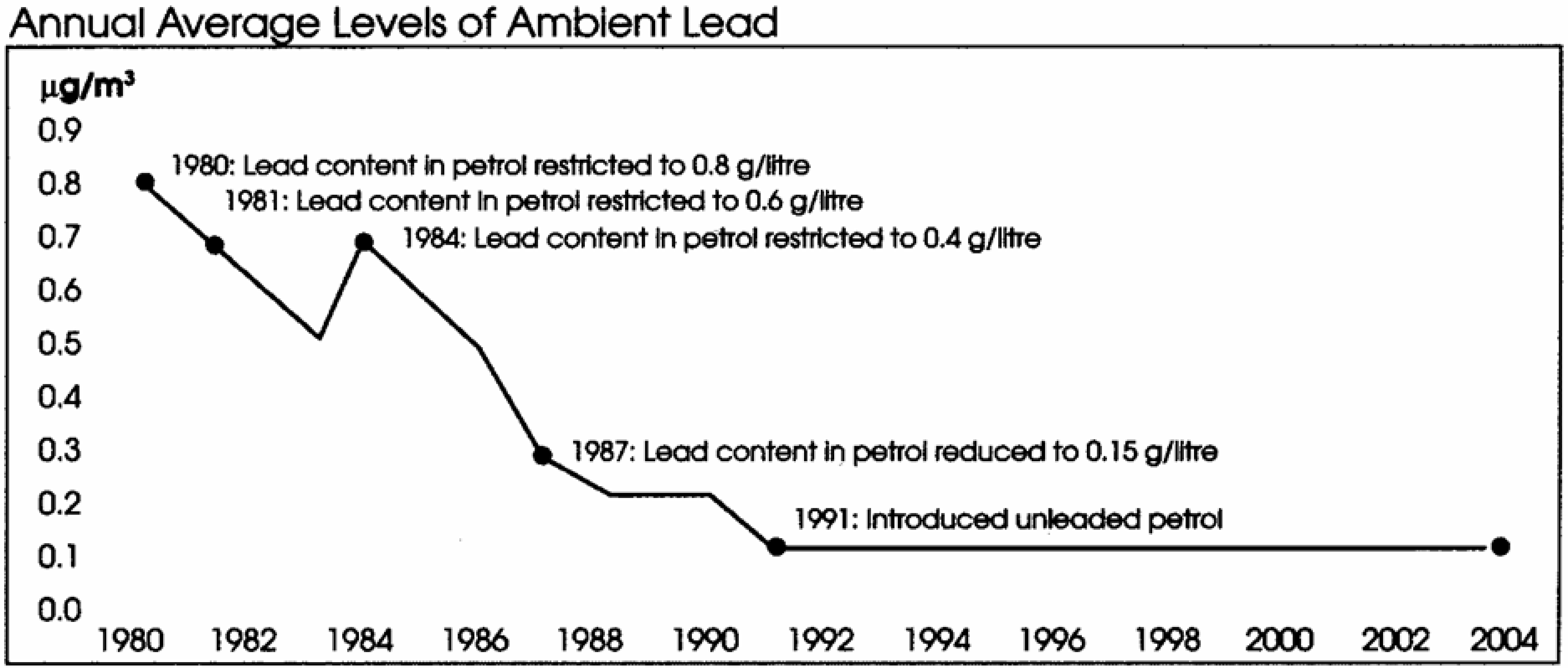
Update of Air Quality Index (AQI), USEPA

Example: Standard-Regulation Implementation

- **Donora episode in 1948 & Clean Air Act**
- **Review periodically:**
  - Example: USEPA strengthen air quality standards for particle pollution in 2006. Designations will take effect in 2009
  - Review periodically: 1997 (PSI) → 2006 → 2012 → …
  - A time period is given prior to implementation
  - Local governments have three years to develop implementation plans to attain and maintain the standards
  - Example: USEPA expects designations based on 2007-2009 air quality data will take effect in 2010
  - Continual review & update

Source: USEPA (http://www.epa.gov/airquality/particlepollution/designations/index.htm)

Singapore Air Quality: Lead Level



Ambient lead level – No more a concern since 1992 !

Source: Towards Environmental Sustainability -- State of the Environment 2005 Report, Ministry of the Environment and Water Resources, Singapore, 2005.

Pollutant Standards Index (PSI) pre-1997

PSI	Designation	1hr O_3 (ppm)	8 hr CO (ppm)	24 hr PM_{10} ($\mu g/m^3$)	24 hr SO_2 (ppm)	1 hr NO_2 (ppm)
0	-	0	0	0	0	--[a]
50	-	0.06	4.5	50	0.03	--[a]
100	NAAQS	0.12[b]	9	150	0.14	--[a]
200	Alert	0.20	15	350	0.30	0.6
300	Warning	0.40	30	420	0.60	1.2
400	Emergency	0.50	40	500	0.80	1.6
500	Significant harm	0.60	50	600	1.00	2.0

[a]No index values reported at concentrations below the Alert level.
[b]Does not yet reflect 1997 change in standard
from U.S. EPA, 1994, *National Air Quality and Emissions Trends Report*, 1993, EPA-454/R-94-026, Environmental Protection Agency, Washington, DC.

Pollutant Standards Index (PSI) pre-1997

PSI	Descriptor	General health effects
0-50	Good	None for the general public
51-100	Moderate	Few or none for the general public
101-199	Unhealthful	Mild aggravation of symptoms among susceptible people, with irritation symptoms in the healthy population
200-299	Very unhealthful	Significant aggravation and decreased exercise tolerance in persons with heart or lung disease; widespread symptoms in the healthy population
>=300	Hazardous	Significant aggravation of symptoms in healthy persons; early onset of certain disease; above 400, premature death of ill and elderly

Air Quality Index (AQI) by USEPA 2010-

PSI	Designation	1-hr O_3 (8-hr O_3) (ppm)	8-hr CO (ppm)	24-hr PM_{10} (24-hr $PM_{2.5}$) ($\mu g/m^3$)	1-hr SO_2 (24-hr SO_2) (ppm)	1-hr NO_2 (ppm)
0-50	Good	-- (0-0.059)	0-4.4	0-54 (0-15.4)	0-0.035 --	0-0.053
51-100	Moderate	-- (0.060-0.075)	4.5-9.4	55-154 (15.5-35.4)	0.036-0.075 --	0.054-0.1
101-150	Unhealthy (sensitive groups)	0.125-0.164 (0.076-0.095)	9.5-12.4	155-254 (35.5-65.4)	0.076-0.0185 --	0.101-0.36
151-200	Unhealthy	0.165-0.204 (0.096-0.115)	12.5-15.4	255-354 (65.5-150.4)	0.0186-0.304 --	0.361-0.64
201-300	Very unhealthy	0.205-0.404 (0.116-0.374)	15.5-30.4	355-424 (150.5-250.4)	-- (0.305-0.604)	0.65-1.24
301-400	Hazardous	0.405-0.504 (=1-hr std.)	30.5-40.4	425-504 (250.5-350.4)	-- (0.605-0.804)	1.25-1.64
401-500		0.505-0.604 (=1-hr std.)	40.5-50.4	505-604 (350.5-500.4)	-- (0.805-1.004)	1.65-2.04

Source: U.S., Environmental Protection Agency (EPA), Washington, DC.
(http://airnow.gov/index.cfm?action=topics.about_airnow; http://airnow.gov/index.cfm?action=resources.aqi_conc_calc)

Air Quality Index (AQI) by USEPA

PSI	Descriptor	General health effects
0-50	Good	No health impacts
51-100	Moderate	Unusually sensitive people: consider reducing prolonged/heavy exertion.
101-150	Unhealthy	For sensitive groups: active children & adults, people with lung diseases (e.g., asthma), should reduce prolonged/heavy exertion outdoors. The general public is unlikely to be affected.
151-200	Unhealthy	Everyone (sensitive groups) may begin to experience (more serious) health effects.
201-300	Very unhealthy	Health alert: Everyone may experience more serious health effects.
301-500	Hazardous	Health warnings of emergency conditions: Entire population is likely to be affected.

Obtaining Pollutant Standards Index (PSI)

Two Factors: (1) Linear correlation for each range

(2) Highest PSI value

Example:

PSI	Designation	1hr O_3 (ppm)	8 hr CO (ppm)	24 hr PM_{10} ($\mu g/m^3$)	24 hr SO_2 (ppm)	1 hr NO_2 (ppm)
0	-	0	0	0	0	--
50	-	0.06	4.5	50	0.03	--
100	NAAQS	0.12	9	150	0.14	--
200	Alert	0.20	15	350	0.30	0.6
300	Warning	0.40	30	420	0.60	1.2
400	Emergency	0.50	40	500	0.80	1.6
500	Significant harm	0.60	50	600	1.00	2.0

Pollutant Standards Index (PSI): Example

On a certain day, the following concentrations are measured:

1 hr O_3	8 hr CO	24 hr PM_{10}	24 hr SO_2	1 hr NO_2
0.18 ppm	9 ppm	130 $\mu g/m^3$	0.20 ppm	0.3 ppm

Find the AQI/PSI and the corresponding descriptor representing the day’s air quality.

Pollutant Standards Index (PSI)

- In the AQI/PSI chart, what does the duration specified for each individual criteria pollutants imply?
- What are the air quality issues not addressed by AQI or PSI?

Air Quality in Singapore

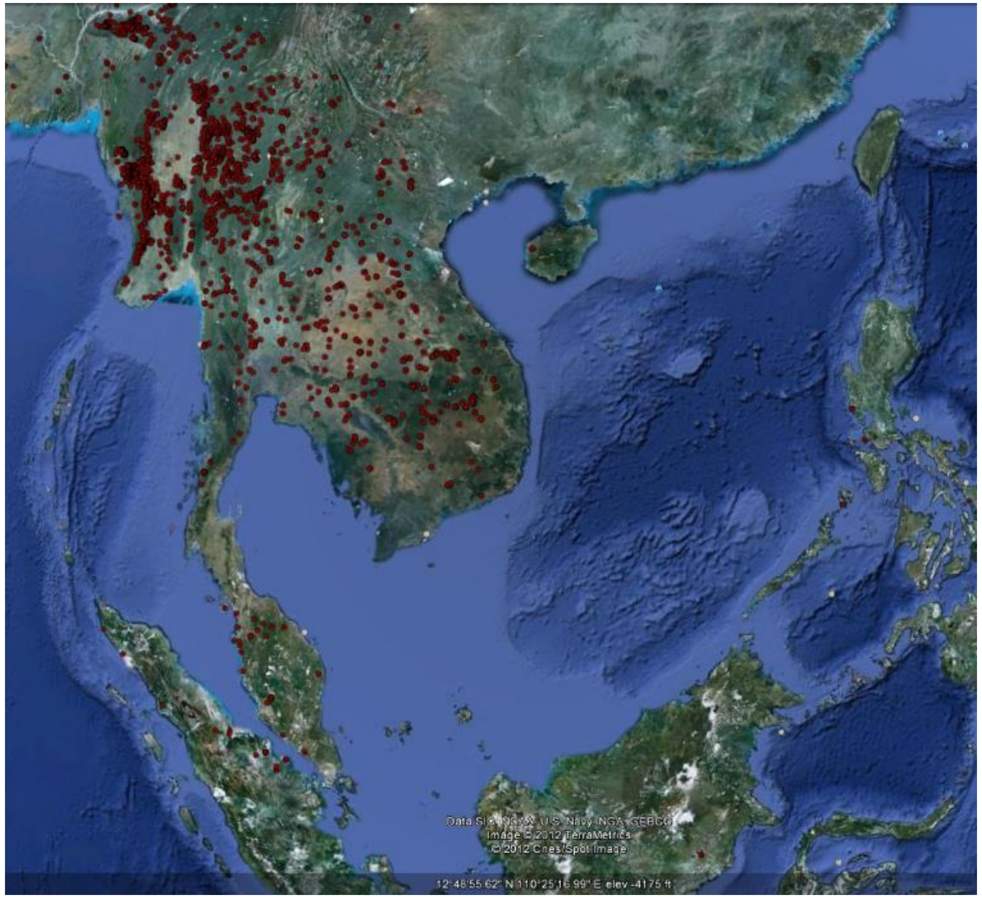
What is the general air quality in Singapore?

What are the major emission sources in Singapore?

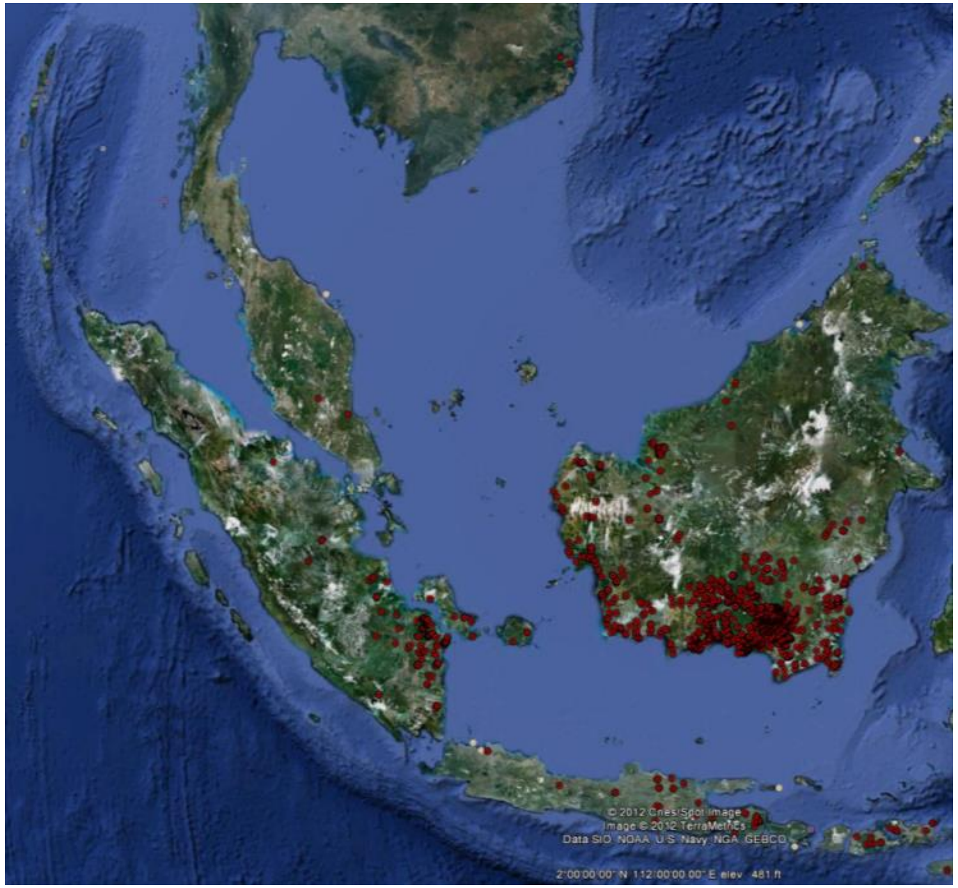
What are factors important to evaluate air quality in Singapore?

Transboundary Smoke of Biomass Burning

- Recurrent, all year round
- Variable timing, duration, impacts, etc.



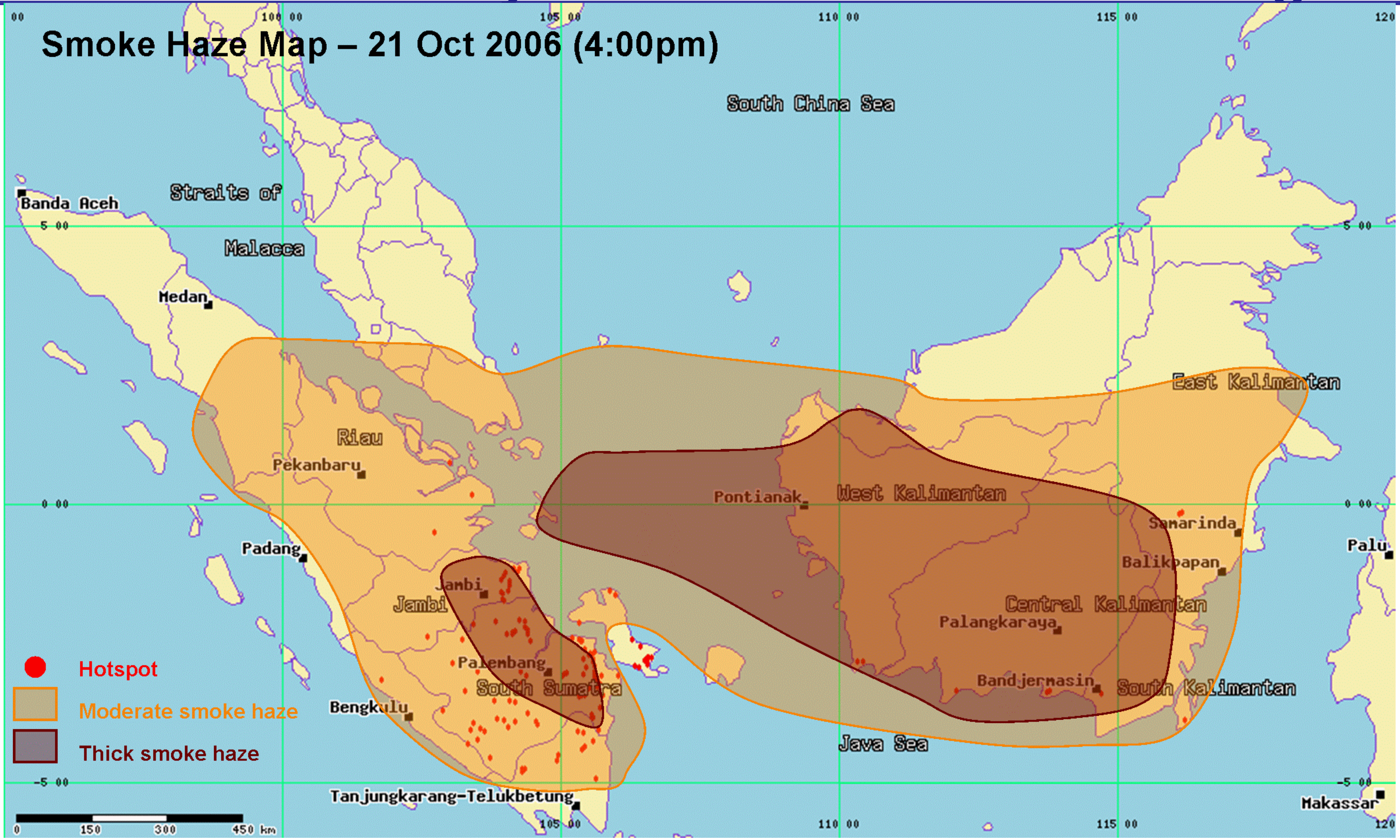
Northern Transboundary Smoke
06 March (JD 65) 2011



Southern Transboundary Smoke
25 September (JD 268) 2009

Source: 7SEAS FLAMBE (http://www.nrlmry.navy.mil/flambe/7seas/7seas.htm)

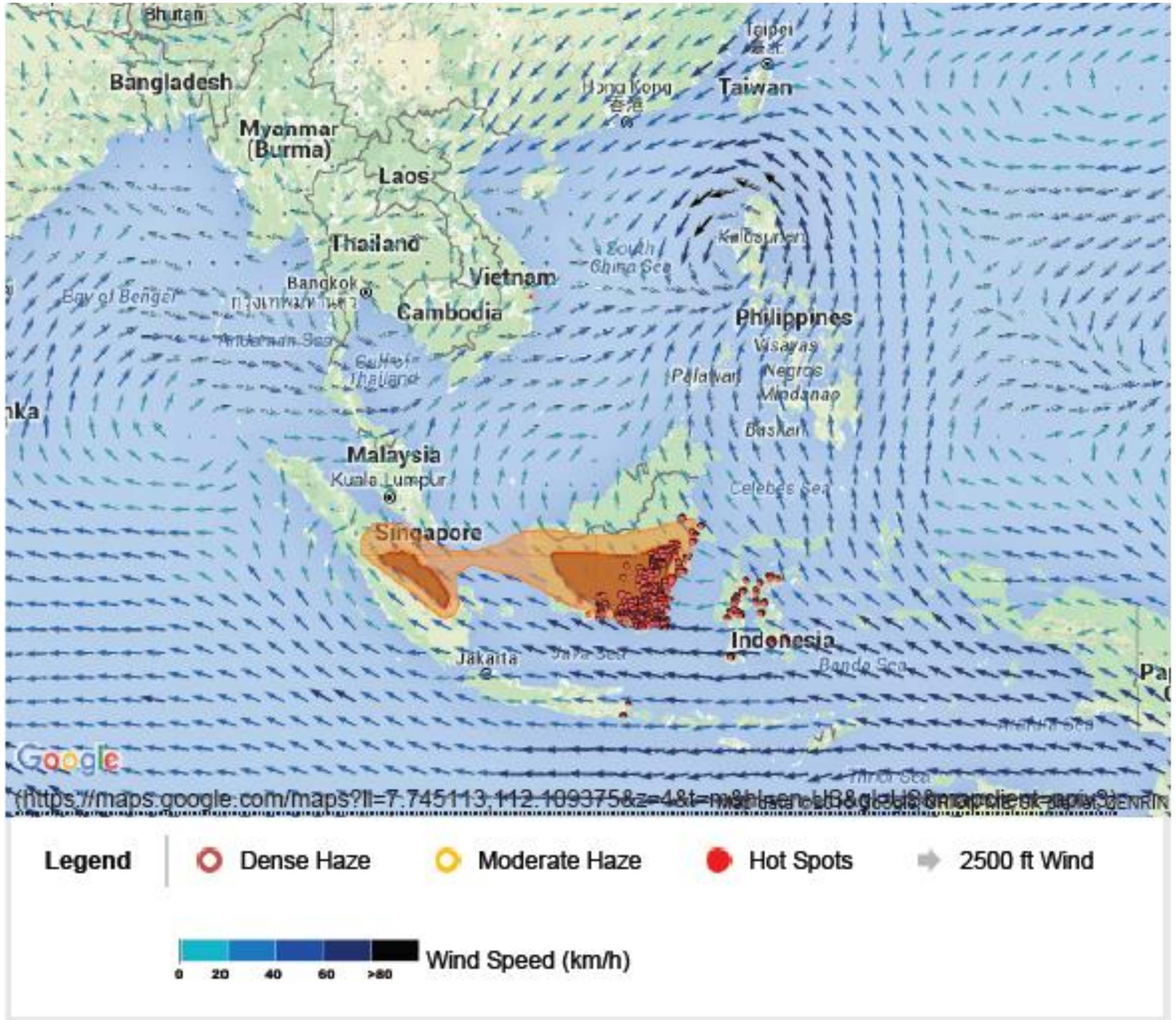
Transboundary Smoke of Biomass Burning



From NEA web site, Singapore

Regional Transport & Peat-Forest Burning Smoke

From NEA web site, Singapore

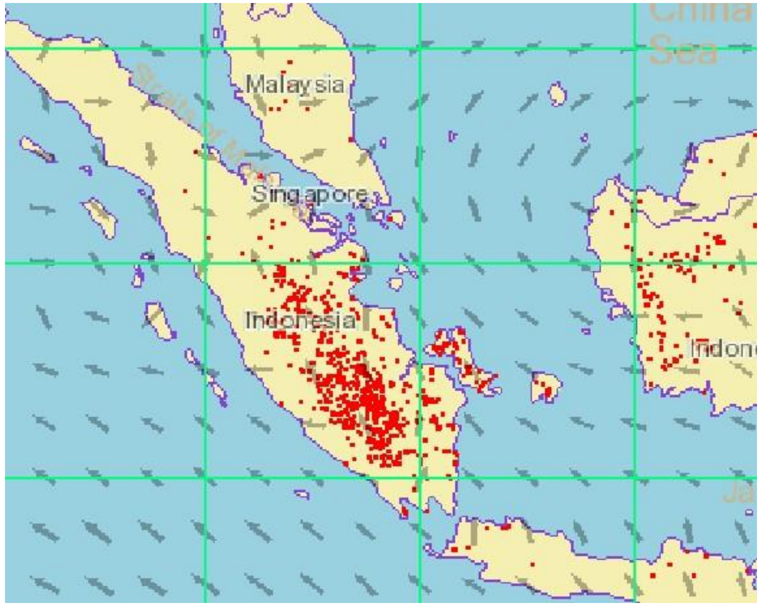


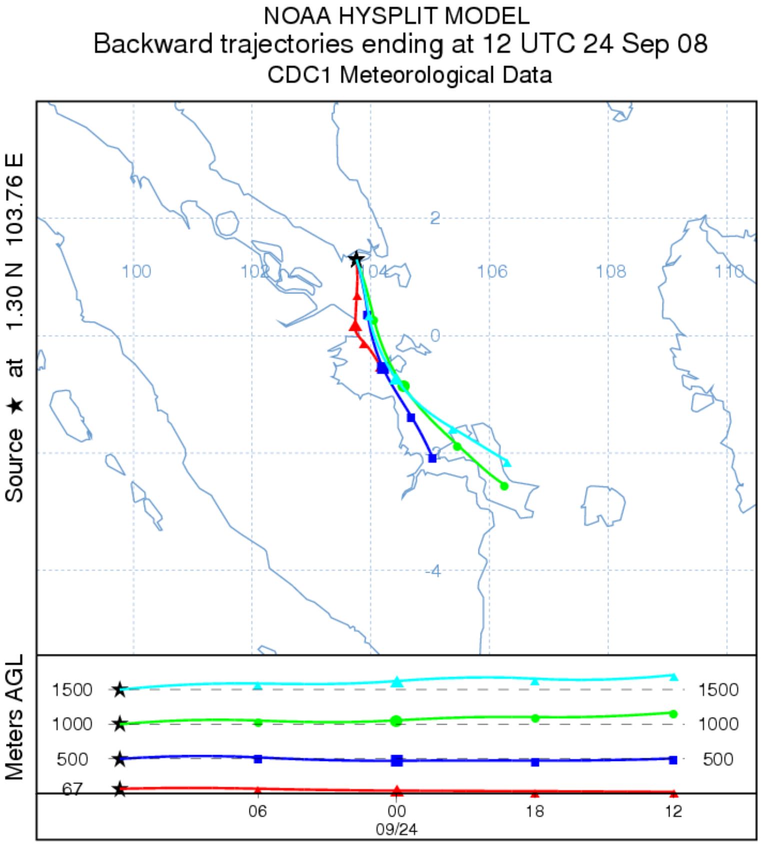
Regional Haze Update

Due to partial pass and cloud cover, the hotspot activities in Sumatra could not be fully determined. Nonetheless, moderate to dense haze remained visible over central and southern Sumatra. Elevated hotspot activities continued to be detected in Kalimantan with many parts of the Borneo island shrouded in moderate to dense haze. Some haze has also spread to the sea areas between Kalimantan and Sumatra.

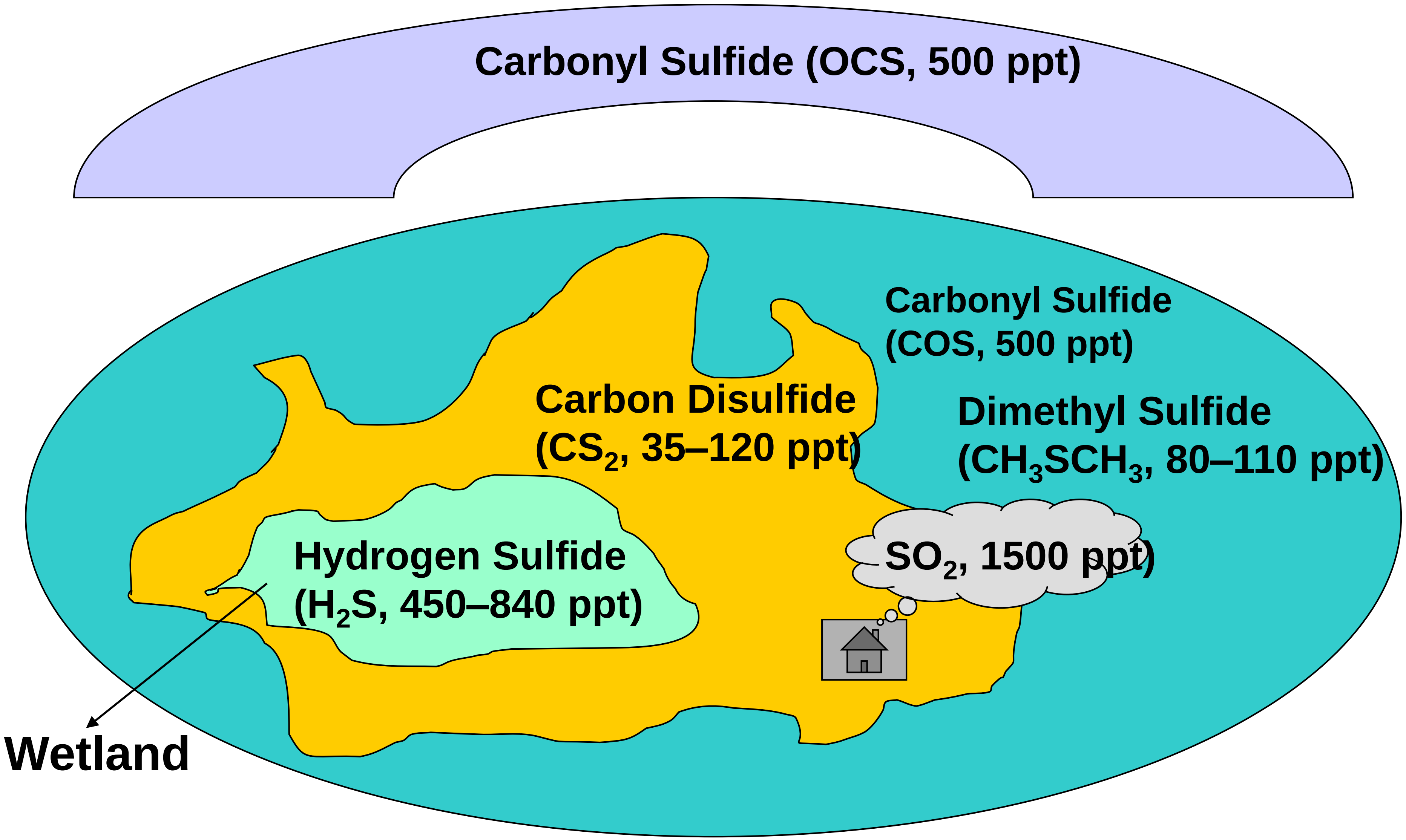
Updated 6:48 pm 2 Oct.

Regional Transport & Peat-Forest Burning Smoke





Sulfur Containing Pollutants



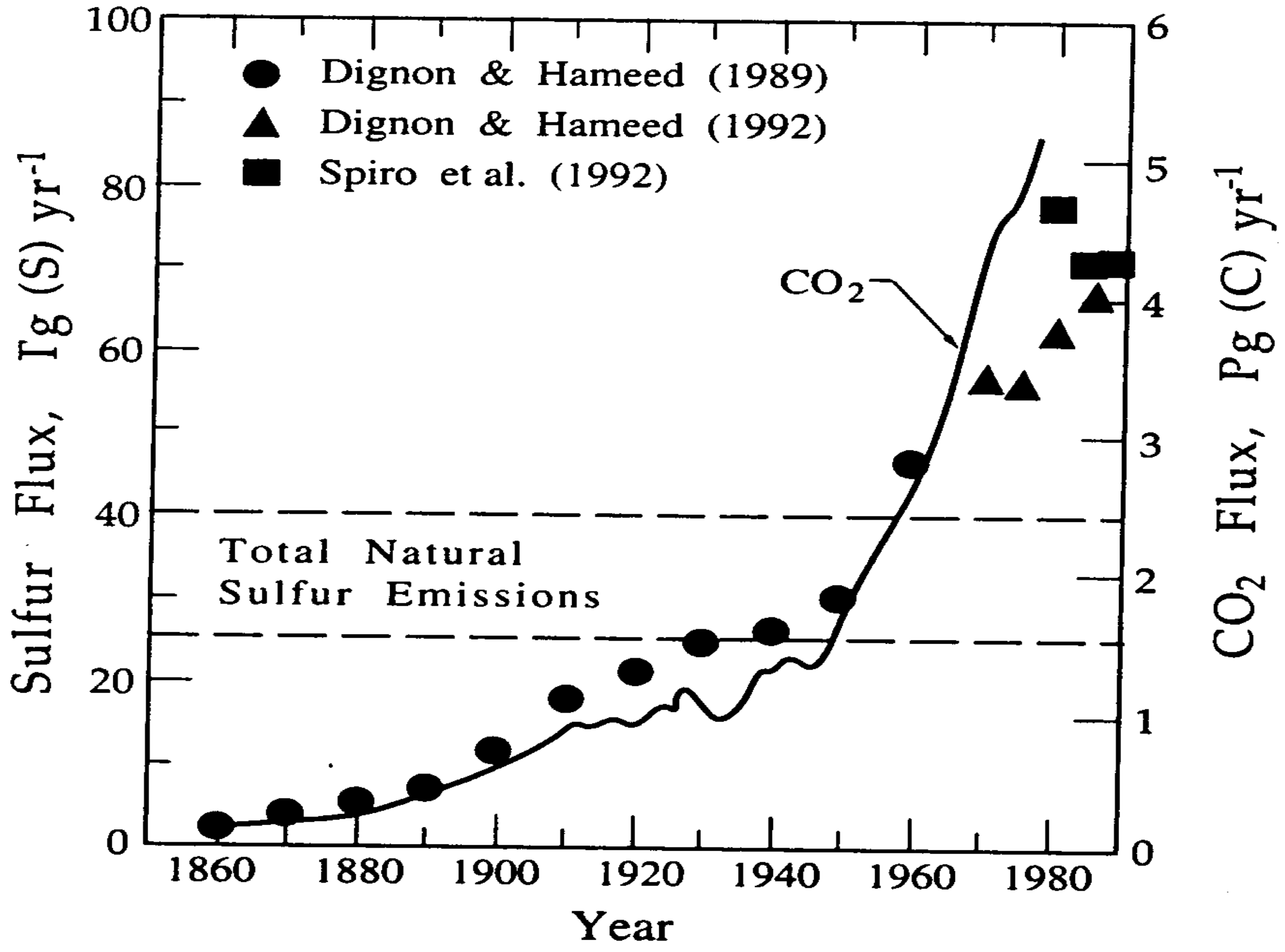
Global Sulfur Flux

Source	SO_2	SO_4^{2-}	Hemisphere		Total Sulfur ($Tg(S)\ yr^{-1}$)*
			N	**S**	
Fossil-fuel burning & industry	70	2.2			71–77
Biomass burning	2.8	0.1	1.4	1.1	2.2–3.0
Oceans (DMS)	--	40–320	8.4[a]	11.6[a]	15–25[a]
Wetlands (H_2S, DMS & CS_2)	--	--	0.8	0.2	0.01–2
Plants + soils	--	2–4	0.3[b]	0.2[b]	0.25–0.78[b]
Volcanoes	7–8	2–4	7.6	3.0	9.3–11.8
Anthropogenic (Total)					73–80
Natural					25–40
Total					**98–120**

***(w/o sea salt[a] or soil dust[b])**

Source: Berresheim et al., 1995

Anthropogenic Sulfur Emissions



Source: Dignon and Hameed (1989), Hameed and Dignon (1992), and Spiro et al. (1992)

Oxides of Sulfur (SOx)

- ~ 90% of the anthropogenic related SOx emitting from fossil fuel combustion

- Transformation of $SO_{2(g)}$ to sulfuric acid (H_2SO_4):

  - Reaction with hydroxyl radicals:

$$SO_2 + OH^{\bullet} \longrightarrow HOSO_2^{\bullet}$$

$$HOSO_2^{\bullet} + O_2 \longrightarrow SO_3 + HO_2^{\bullet}$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Oxides of Sulfur (SOx)

- Transformation of $SO_{2(g)}$ to sulfuric acid (H_2SO_4) (ctd.):

  - Reaction with O_2 (needs large activation energy):

$$2SO_{2(g)} + O_2 \longrightarrow 2SO_{3(g)}$$

$$SO_{3(g)} + H_2O_{(pte)} \longrightarrow H_2SO_{4(pte)}$$

  - Soluble in water:

$$SO_{2(g)} + H_2O_{(pte)} \longrightarrow H_2SO_{4(pte)}$$ …. (not balanced)

- Neutralization reactions of $SO_{2(g)}$ & H_2SO_4 to $(NH_4)_2SO_4$:

$$H_2SO_{4(pte)} + 2NH_{3(g)} \longrightarrow (NH_4)_2SO_{4(pte)}$$

SOx Effects

- Precursor of sulfate particles
- Most sulfate particles in urban air: 0.2–0.9 μm
  - ↓ visibility
  - easily penetrating deep in human lungs
  - synergistic effects
- Highly water soluble: erosion of building materials

Nitrogen & Sulfur Compounds: Comparison

Elementary oxidation & reduction

Reduction	Elemental	Oxidation		Reaction with	
		1st step	2nd step	H_2O	NH_4^+ / other cations
NH_3	N_2	NO	NO_2	HNO_3	Nitrate particles
H_2S	S	SO_2	SO_3	H_2SO_4	Sulfate particles
High pressure, high temp. catalytic reactions		Reaction with O_2 @ high and low temperature	Atmosphere; Catalytic reactions	Depends on moisture content	Depends on [cation]

Unit of anthropogenic emission:

- % or mass of SO_2 / NOx emitted per heat energy delivered
- Example: mg/m^3, lb/10^6 Btu, g/GJ, μg/kcal

Nitrogen Containing Pollutants

N_2O, NO_x, HNO_3, and NH_3

- N_2O
  - Colorless
  - Almost completely from natural sources
  - Long residence time $\approx$ 120 years
  - Important green-house gas
- NH_3
  - Emitted from natural & anthropogenic sources

NO_2 and Ozone

- **NO_2**

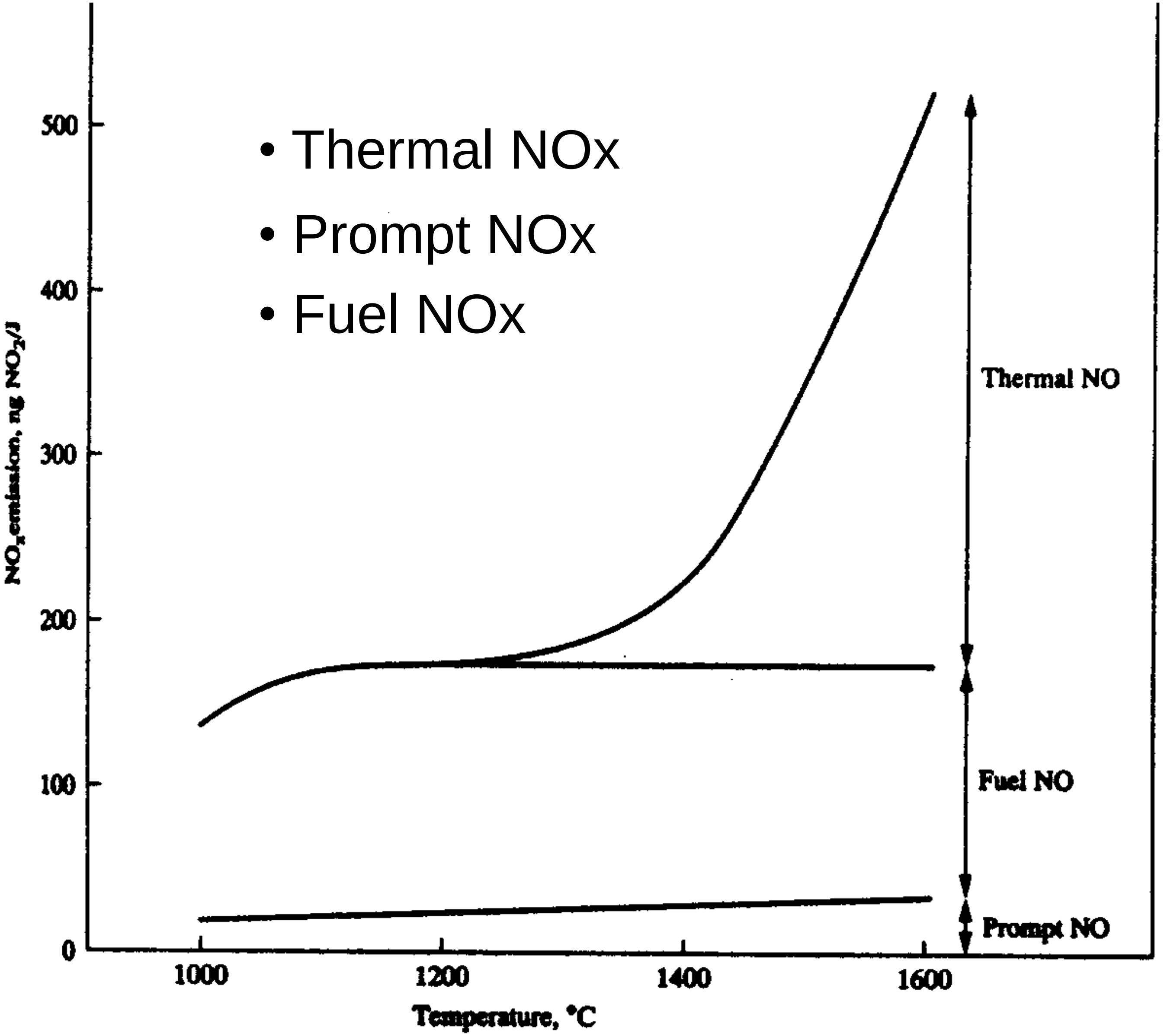
  irritating the lungs, causing bronchitis and pneumonia, and lower resistance to respiratory infections

$$NO_x + OH\bullet \longrightarrow HNO_3$$

$$NO_x + \text{volatile organic compounds} \xrightarrow{h\nu} \text{photochemical pollutants}$$

Formation of NOx

- Thermal NOx
- Prompt NOx
- Fuel NOx



(Source: Air Pollution Control Engineering by Noel De Nevers, McGraw Hill,'95)

Prompt NOx

- During the 1st part of combustion
- Mainly converted from original form in fuel
- Carbon bearing radicals

$$CH\cdot + N_2 \rightleftharpoons HCN + N\cdot$$

$$N\cdot + O_2 \rightleftharpoons NO + O$$

$$HCN + O_2 \rightleftharpoons NO$$

$$HCN + NO \rightleftharpoons N_2$$

Control NOx: Fuel NOx

- Most of the fuel nitrogen is converted in the flame to HCN, subsequently converted to NH or NH_2.

$$NH + O_2 \longrightarrow NO + H_2O, \text{ or } NH + NO \longrightarrow N_2 + H_2O$$
$$NH_2 + O_2 \longrightarrow NO + H_2O, \text{ or } NH_2 + NO \longrightarrow N_2 + H_2O$$

- [NOx] from fuel depends on [NO]/[O_2] ratio in the flame zone
- At high-temp. zone of flame, if $[O_2]\downarrow \Rightarrow [NO]\downarrow$
- Usually, 20-50% of fuel nitrogen is converted to NOx, depending on (1) furnace conditions, and (2) chemical nature of nitrogen in fuels.

Regulating NOx in Exhausts

- Preventing artificial dilution of exhausts before release:
  - depending on dilution of excess air
  - standard limit/regulation based on O_2% in the exhaust (Max. 6-7% of O_2, by volume)

Photochemical Reactions: Ground Level O_3

- Most abundant photochemical oxidants, in addition to formaldehyde (HCHO), peroxybenzoyl nitrate (PBzN), peroxyacetyl nitrate (PAN), and acrolein (CH_2CHCOH)

Health effects of photochemical pollutants

- O_3: chest constriction & irritation of mucous membranes
- Others (PAN, HCHO, acrolein, etc.): irritation of eyes and respiratory systems (coughing), …

Photochemical Reactions: Ground Level O_3

NO-NO_2-O_3 photochemical reaction sequence

$$N_2 + O_2 \longrightarrow 2NO$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$NO_2 + h\nu \longrightarrow NO + O$$

$$O + O_2 + M \longrightarrow O_3 + M$$

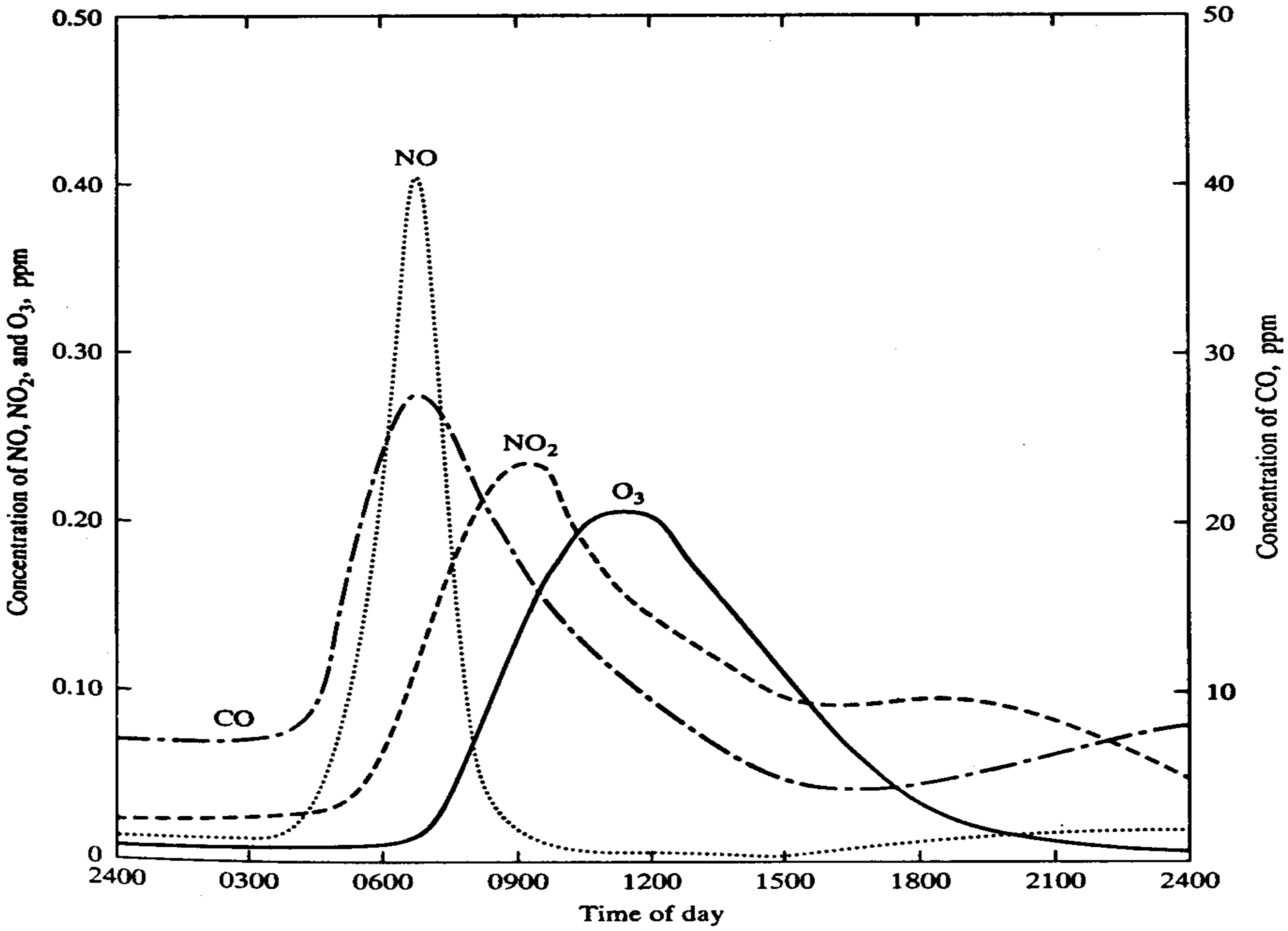
$$O_3 + NO \longrightarrow NO_2 + O_2$$

When $RCOO\cdot + NO \rightarrow RCO\cdot + NO_2$

($RCOO\cdot$ & $RCO\cdot$: VOC radicals)

Air Pollutants and Ground Level O_3

Concentrations measured in Los Angeles, CA, USA, Jul/19/1965



Source: U.S. HEW, 1970, *Air Quality Criteria for Carbon Monoxide*, AP-62, National Air Pollution Control Administration, Washington, DC

Particulate Matter: Terminology

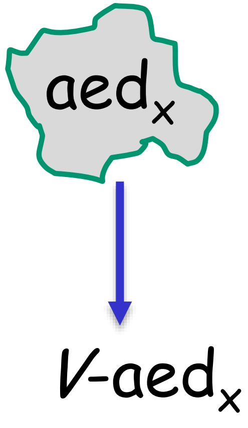
- Aerosol: any tiny particles, liquid, and solid, dispersed in the atmosphere
- Dusts: solid particles caused by grinding or crushing operations
- Fumes: particles formed through vapor condensation
- Mist/fog: liquid particles
- Smoke/soot: mainly comprising carbon emitting from incomplete burning
- Smog: air pollution in general

- **Primary particles:** Present airborne form = Form at emission point
- **Secondary particles:** Formed in the atmosphere

Particulate Matter

- Aerodynamic Equivalent Diameter (aed)

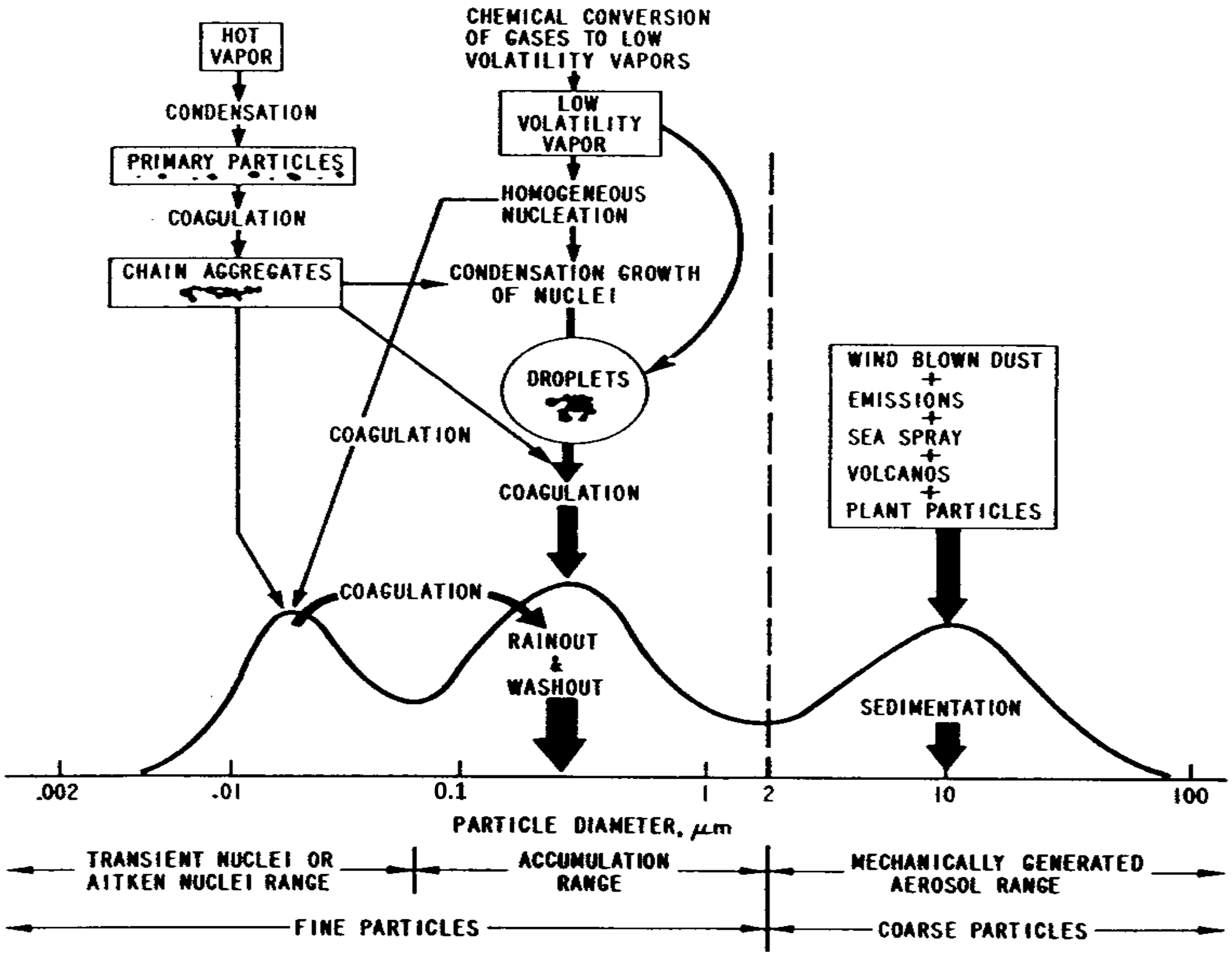
When V-aed$_x$ = V-D_y, aed$_x$ = D_y



V-aed$_x$: Terminal velocity of particle-aed$_x$

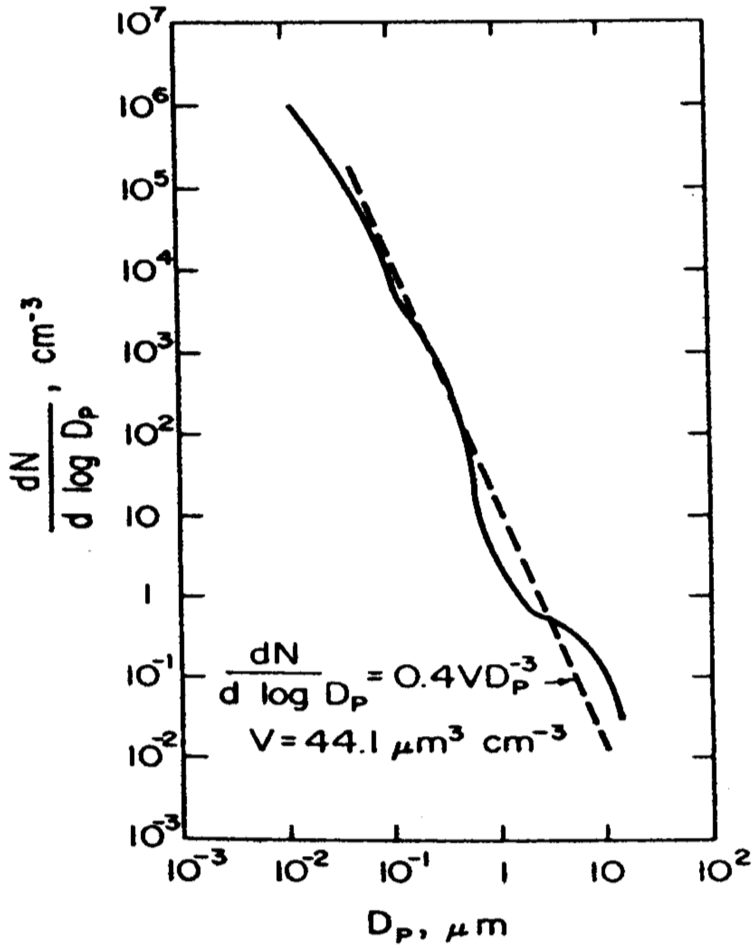
V-D_y: Terminal velocity of particle-D_y

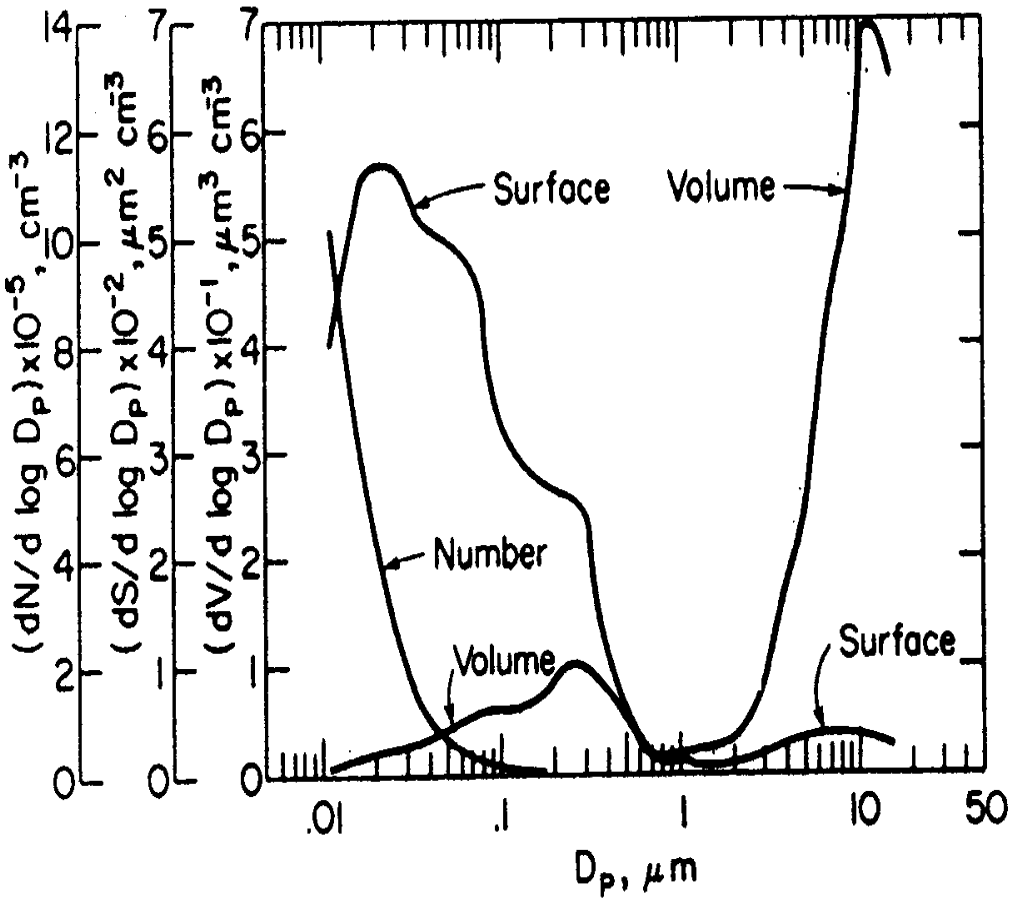
Particulate Matter: Size Distribution



Source: *Atmospheric Chemistry and Physics of Air Pollution* by J.H. Seinfeld, J. Wiley & Sons, 1986

Particulate Matter: Size Distribution





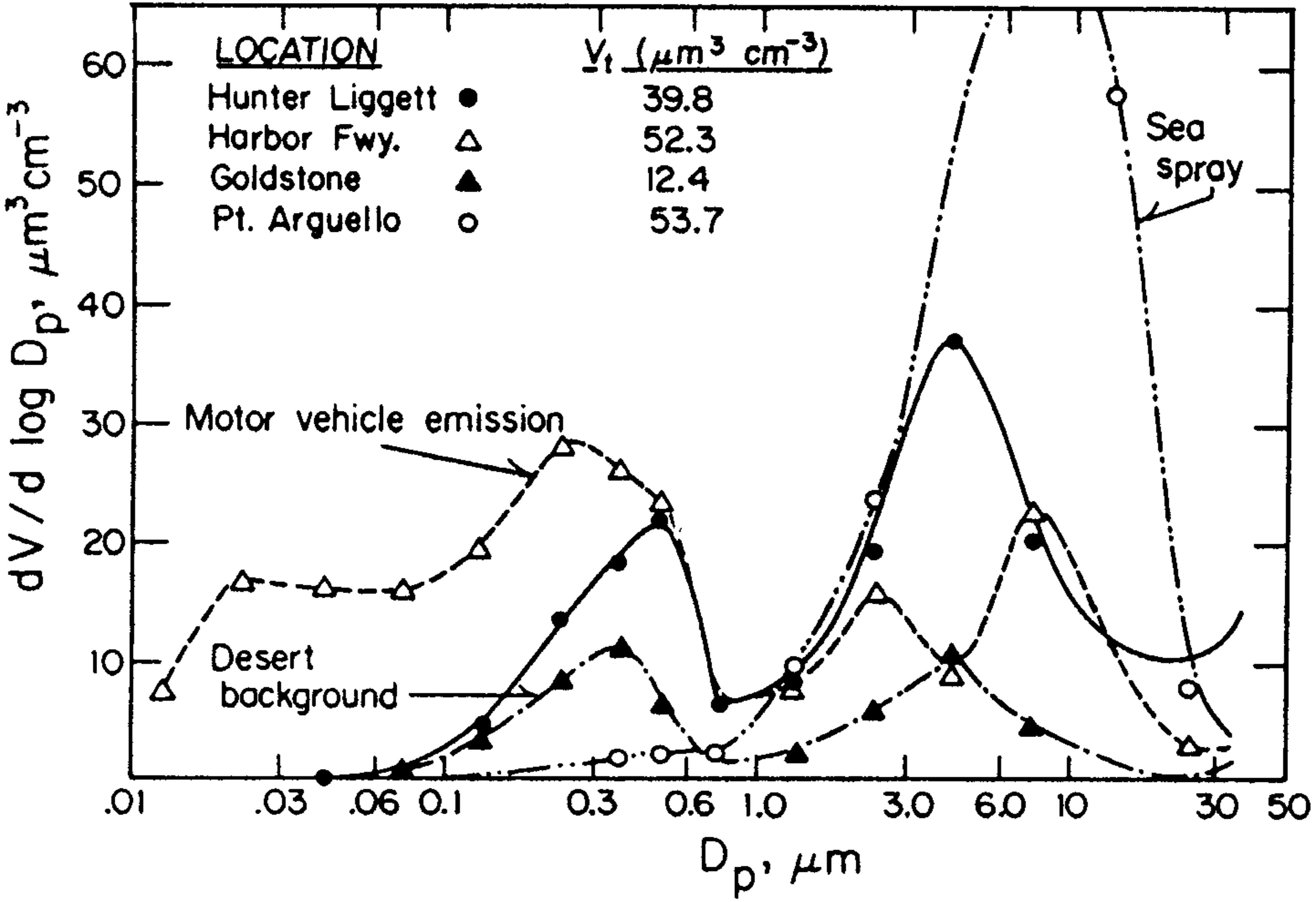
Source: *Atmospheric Chemistry and Physics of Air Pollution* by J.H. Seinfeld, J. Wiley & Sons, 1986

Particulate Matter: Size Distribution

Why does the mass-based $PM_{2.5}$ concentration insufficiently regulate smaller particles?

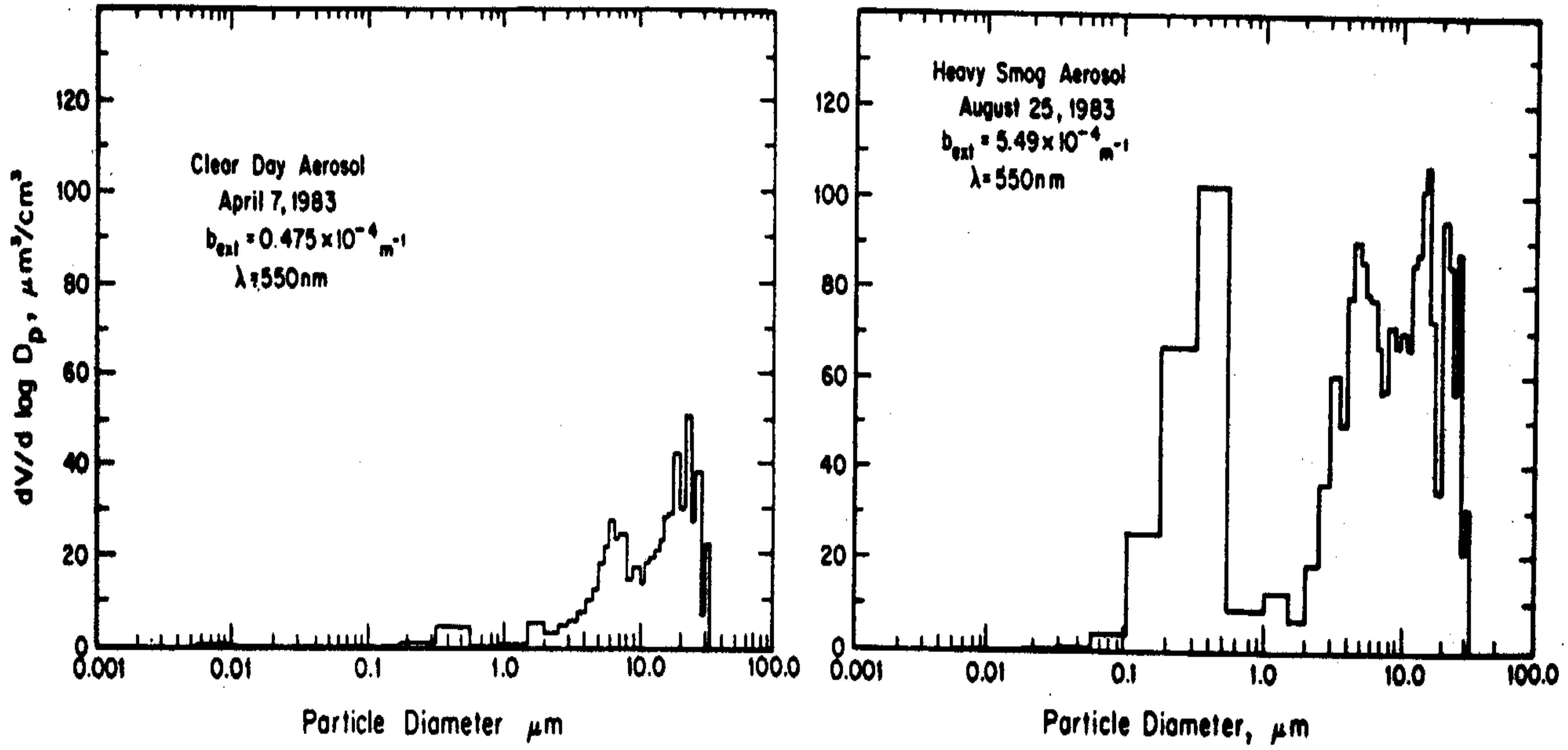
How many 10-nm particles are needed to weigh the same as one 1-μm particle?

Particulate Matter: Size Distribution



Source: *Atmospheric Chemistry and Physics of Air Pollution* by J.H. Seinfeld, J. Wiley & Sons, 1986

Particulate Matter: Size Distribution



Source: *Atmospheric Chemistry and Physics of Air Pollution* by J.H. Seinfeld, J. Wiley & Sons, 1986