CE666A Air Pollution and Its Control

References:

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Origin of the atmosphere

- The original atmosphere
 - Probably made up of hydrogen and helium.
 - These are fairly common in the universe.
- Original atmosphere stripped away by the solar wind
 - H and He are very light
 - Hydrogen and helium have the smallest atoms by mass.
 - The early earth was not protected by a magnetic field.
 - Thus the current atmosphere is secondary

The secondary atmosphere

- Formed from degassing of volcanoes
- Gasses emitted probably similar to the gasses emitted by volcanoes today.
 - H₂O (water), 50-60%
 - CO₂ (carbon dioxide), 24%
 - SO₂ (sulfur dioxide), 13%
 - CO (carbon monoxide),
 - S₂ (sulfur),
 - Cl₂ (chlorine),
 - N_2^- (nitrogen),
 - H₂ (hydrogen),
 - NH₃ (ammonia) and
 - CH₄ (methane)



Modern atmosphere

Nitrogen (N_2) -78%, Oxygen (O_2) -21%, Carbon Dioxide (CO_2) 0.03 %,

Where did all the oxygen come from?



Volcanic outgassing	Modern Atmosphere
H ₂ O – 50-60%	N ₂ – 78%
CO ₂ -24%	O ₂ – 21%
SO ₂ – 13%	CO ₂ - 0.03%

- 1. Where did all the O_2 come from?
- 2. Where did all the CO_2 go?

Formation of the oceans

- The earth is cool enough that H₂O condenses to form the oceans.
 - Estimates of the amount of H₂O outgassed is not enough to fill the oceans
 - It seems likely that a large volume of water was added by the impact of icy meteors on the atmosphere.
- CO₂ dissolves into the oceans.



In the oceans life evolves

- Ingredients necessary for life
 - NH₃ ammonia
 - CH₄ Methane
 - H₂O Water
- These can produce amino acids, the building blocks of life
- Nucleotides consists nucleobase, 5-carbon sugar and phosphate





- Life may have originated
 - under the primitive atmosphere
 - or at hydrothermal vents deep in the oceans
 - or deep in the earth's crust



Life changes the atmosphere

 With the evolution of life the first cellular organisms (cyanobacteria) began to use the gasses in the early atmosphere (NH₃ – ammonia, CH₄ – methane, H₂O – water) for energy.

Photosynthetic organisms evolve.

These organisms use CO₂ and produce oxygen (O2) as a waste product.



- Where did the O₂ come from?
 Produced by photosynthetic life.
- Where did the CO₂ go?
 - Dissolves in water in the oceans
 - Used by life by photosynthesis and buried when plants and micro-organisms die.
 - The source of coal and oil

Early history of life and the atmosphere

- The Earth is about 4.5 billion years old.
- Life first appeared in the oceans at least 3.5 billion years ago.
- 0.9 billion years ago there is enough oxygen in the atmosphere to produce the ozone layer and life can finally move onto land.
 - The ozone layer protects the earth from harmful ultra violet radiation from the sun.

The other planets

- Venus
 - Closer to the sun
 - Very hot at the surface so water vapor in the atmosphere does not condense.
 - Runaway greenhouse effect (482°C, 900°F).
 - No oceans or rainfall so CO_2 does not dissolve.
 - Has a very dense atmosphere.



The other planets

- Mars
 - Further from the sun
 - Smaller than Earth
 - So small that most of the atmosphere escaped into space.
 - No oceans or rainfall so CO₂ stays in atmosphere.
 - 98% of atmosphere is CO_2 .



• Jupiter

- Huge (318x earth's mass)

- Kept all its original atmosphere
- 80% Hydrogen
- 20% Helium



Summary

1 st atmosphere	H and He from solar nebula	Lost to solar wind
2 nd atmosphere	H_20 , CO_2 and SO_2 from volcanic degassing	Transformed by photosynthesis
Current atmosphere	N2, O2, from photosynthesis and constant N2 production	

Thickness of the atmosphere

- Relative to size of the earth, the atmosphere is extremely thin
- 90% of mass below 16 km
- Given that the earth's diameter is 12,756 km, the atmosphere is about the thickness of the skin on an apple

Vertical structure of the atmosphere

- Gravity holds the atmosphere to the earth
- Consequently, the pressure for any area can be defined by the weight (force) of a vertical column of air over the area



Pressure decrease: I

• PART I

 $P = \rho g h$

- $P = pressure (Pa = N m^{-2} = kg m^{-1} s^{-2})$
- ρ = density (kg m⁻³)
- g = gravitational acceleration (9.81 m s⁻²)
- h = height of air column (m)

Pressure decrease: II

- PART II
- Expressed in a differential form:
- dP = ρ g dz (negative indicates decrease with height) This is the hydrostatic law
- Or, change in pressure is equal to density times acceleration times change in height
- A parcel of air is balanced by the upward and downward forces acting upon it

Pressure decrease: III

- The ideal gas law
- $P = \rho RT$
- R is the gas constant. For air R is 287.07 J kg⁻¹ K⁻¹
- T is temperature in Kelvin
- Rearrange to $\rho = P/RT$ and substitute into the hydrostatic law to obtain:



Pressure decrease: IV

• Integration of the previous equation gives:

$$\frac{P_2}{P_1} = e^{-\frac{g}{RT}(z_2 - z_1)}$$

Vertical atmospheric structure: Pressure



Vertical atmospheric structure: Temperature



Reasons for vertical temperature profile

- Troposphere: temperature declines due to decreases in pressure causing decreases in the average kinetic energy
- Conceptually the molecules of air are moving around more slowly, causing temperature to decline
- This can be predicted mathematically

Temperature profiles

- Increasing temperature in the stratosphere
 Caused by ozone absorption of UV radiation
- Decreasing temperature in the mesosphere
 - Caused by decreasing ozone
- In the thermosphere
 - Warming caused by absorption of UV radiation by O_2
 - since the air is so thin within the thermosphere, such temperature values are not comparable to those of the troposphere or stratosphere. Although the measured temperature is very hot, the thermosphere would actually feel very cold to us because the total energy of only a few air molecules residing there would not be enough to transfer any appreciable heat to our skin

Refresh:

$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ $\frac{P_2V_2}{T_2}$

Troposphere and Stratosphere

- •0 to 15 km altitude
- •The lowest region of the atmosphere, where life & weather exist.
- •Temperature decreases with altitude.
- •Long-wave radiation emitted from Earth is absorbed by the atmosphere, the atmosphere becomes less dense with increasing altitude, less air to absorb
- •Top of the troposphere is known as the tropopause

- •15 to 50 km altitude
- •Temperature increases with altitude.
- •Heating occurs because ozone (O_3) absorbs ultraviolet radiation from the Sun.
- •Top of the stratosphere is known as the stratopause

Mesosphere and Thermosphere

•50 to 90 km altitude

•Temperature decreases with altitude

•The lowest temperatures in the entire atmosphere are found at the mesopause during summer at high latitudes, 130 K (-226°F) can occur

•Top of the mesosphere is known as the mesopause

•90 to 500 km altitude

•Temperature increases with altitude above 90 km, and is constant above 200 km.

•This heating is due to absorption of solar radiation (wavelengths less than 0.2 microns) by molecular oxygen (O_2).

•The highest temperatures in the atmosphere can be found in the thermosphere, 2000 K can occur

Atmosphere – Major Sink for Air Pollutants



Air Pollution

" presence of any substances, solid, liquid or gas in atmosphere in such a concentration that may or may tend to be injurious to the humans, animals, plants, property or the atmosphere itself, is referred to as air pollution and the substance and the substance air as air pollutant"

Key - words :"such a concentration"What is that Concentration ?

Clean Atmosphere





Reduction of pollutant(s) emission to a point such that no noticeable adverse effects associated with pollutant(s) exist.

To determine extent of reduction –

Understand / Established Linkages between sources and receptors using meteorology; and

Understand / Establish safe air quality levels for receptors

Air Quality Standards ~ to protect receptors

Primary Health Standards Secondary Standards for vegetation/crops Sensitive area standards

Challenges of Managing Air Pollution System

- Problem 3-Dimensional
- Transport Medium beyond Control/regulation
- Impacts Instant and Chronic
- Receptors Remediation almost Impossible
- Solution cannot be delayed
- **Types of Remediation**
 - (i) Medium Remediation
 - (ii) Source Remediation
 - (iii) Receptor Remediation

Criteria Pollutants PM, SO₂, NO_x, and CO

Non- criteria Pollutants Pb, Asbestos, Vinyl chloride, Mercury, Arsenic TOC (Trace Organic Carbon) and others How much external addition ?

Develop the basis ~ Criteria

Dose-Response/Cause – Effect Knowledge (receptor specific)

Dose-Response Curve



National Consensus, background levels, financial resources Ambient Air Quality Standards, Goals, Guidelines





BBC: London Smog 1952



$$RfD = \frac{NOAEL}{\left(\prod_{i=1}^{n} UF_i \times MF\right)}$$

$$RfD = \frac{LOAEL}{\left(\prod_{i=1}^{n} UF_i \times MF\right)}$$

 $UF = 10H \times 10A \times 10S$



No Threshold

Slope factor, Cancer Potency factor or Unit Risk factor Slope factor = risk/(mg/kg-day) Unit Risk Factor = risk/(µg/m³)

Example

Acceptable Air Concentration = Target Risk /(Unit risk factor)

Target risk = 1x 10⁻⁵; URF = 1 x10⁻³ (μ g/m³)⁻¹

Concentration = $1 \times 10^{-5} / 1 \times 10^{-3} (\mu g/m^3)^{-1} = 0.01 \ \mu g/m^3$



Area	Average PM10 (μg/m ³)	Mean AM/hpf	% individual with high (>10/hpf) AM count
North	140.1	11.8	17
North East	160.5	13.2	24
North West	158.2	12.8	22
Central	186.9	16.7	32
East	132.1	11.9	14
West	181.4	16.8	30
South	140.5	11.9	16
South East	104.2	7.2	10
South West	101	6.8	9



Exercise ~ Vol/min has significant bearing

FEV₁ decrements as a function of O₃ concentration following a 2 h exposure with incremental exercise (15 min intervals) or rest. Points are experimental data (mean ± SE) and lines are model predictions for each activity level. Minute ventilation (\dot{V}_E) represent average across intervals of rest and exercise.

Source: McDonnell et al. (1997).



The forced expiratory volume in 1 s (FEV₁) is shown in relation to exposur duration (hours) under three exposure conditions. Subjects exercised (minute ventilation ≈ 40 L/min) for 30 min during each hour; FEV₁ was measured at the end of the intervening rest period. Standard error of the mean for these FEV₁ averages (not shown) ranged from 120 to 150 mL.



Proposed Standard (8-hr) = [(1/10)x.04]x2+0.030 (background), ppm = 110 ppb.

Why Factor 2? Personal Exposure = 1/2 of ambient Concentration



Proposed Standard (1-hr) = [(1/10)x.5]x2+0.030 (background), ppm = 130 ppb Why Factor 2? Personal Exposure = 1/2 of Ambient Concentration

This also prevents ill effects during exercise and it is conservative enough as it will be 1-hr standard.

Criteria Pollutants:

 These are commonly found, show threshold in D_R curve having short term effects

 Emitted from many large diverse sources, including mobile and stationary sources

 Omnipresent and, therefore, pose the greatest overall threat to human health

✓ Assumption: the adverse health effects are not cancerous, and their dose-response relationship exhibits a threshold
 ✓ PM, SO₂, NO_x, CO, Pb, O₃

Non- criteria Pollutants

Asbestos, Vinyl chloride, Mercury, Arsenic, TOC (Trace Organic Carbon) and others

Criteria:

Complete knowledge about dose-response relationship for the pollutant.

Standards:

Legally binding concentration in a country arrived from criteria, factor of safety and other concentrations. The following points should be considered at the time of deciding the standards

- Averaging time (short term or long term)
- Allowable exceedance (98% of time standards must be met)
- Method of measurement must be specified (along with Accuracy and Precision)
- Local air quality levels (including background pollution levels)
- Economics of the local areas
- Precursor levels responsible for the secondary pollutant formation

Guidelines/Goal:

Desirable concentration without legal binding

Hazardous Air Pollutants (HAPs):

- Sources may be limited and industry specific
- More toxic and even carcinogenic
- -~188 chemicals
- For example, benzene, formaldehyde, cadmium, vinyl chloride
- Separate strategies exist for regulating criteria and hazardous pollutants
- HAPs are more toxic than criteria pollutants; they "... may reasonably be expected to result in serious irreversible ... disease, including cancer"
- For examples: Heavy metals (chromium, mercury), Organics (benzene, perchloroethylene), VOCs (volatile organic compounds)

Accuracy:

It describes the relationship between the average of several repeated determinations and the goals.

Precision:

The degree to which further <u>measurements</u> or calculations will show the same or similar <u>results</u> or it can be repeatedly determined with little variability.

Country variations NO₂ Romania Air quality standards Netherland for 1-hour NO₂ [µg/m3] Czech Republic Korea New Zealand Brazil Indonesia Taiwan Poland Saudi Arabia Argentina Israel EC and WHO 700 100 200 300 400 500 600 800 900 1000 0



NATIONALAMBIENTAIR QUALITY STANDARDS CENTRAL POLLUTION CONTROL BOARD NOTIFICATION

New Delhi, the 18th November, 2009

No. B-29016/20/90/PCI-L-In exercise of the powers conferred by Sub-section (2) (h) of section 16 of the Air (Prevention and Control of Pollution) Act, 1981 (Act No.14 of 1981), and in supersession of the Notification No(s). S.O. 384(E), dated 11th April, 1994 and S.O. 935(E), dated 14th October, 1998, the Central Pollution Control Board hereby notify the National Ambient Air Quality Standards with immediate effect, namely:-

S. Pollutant Time Weighted			Concentrat	Concentration in Ambient Air		
No.		Average	Industrial, Residential, Rural and Other Area	Ecologically Sensitive Area (notified by Central Government)	Methods of Measurement	
(1)	(2)	(3)	(4)	(5)	(6)	
1	Sulphur Dioxide (SO ₂), µg/m ³	Annual*	50 80	20	- Improved West and Gaeke	
		•				
2	Nitrogen Dioxide (NO ₂), µg/m ³	Annual*	40	30	- Modified Jacob & Hochheiser (Na-	
		24 hours**	80	80	Arsenite) - Chemiluminescence	
3	Particulate Matter (size less than	Annual*	60	60	- Gravimetric - TOEM	
	10μm) or PM ₁₀ μg/m ³	24 hours**	100	100	- Beta attenuation	
4	Particulate Matter (size less than	Annual*	40	40	- Gravimetric - TOEM	
	2.5μm) or PM _{2.5} μg/m ³	24 hours**	60	60	- Beta attenuation	
5	Ozone (O ₃) µg/m ³	8 hours**	100	100	- UV photometric - Chemilminescence	
		I hour**	180	180	- Chemical Method	
6	Lead (Pb) ug/m ³	Annual*	0.50	0.50	 AAS /ICP method after sampling on EPM 2000 	
	-	24 hours**	1.0	1.0	or equivalent filter paper - ED-XRF using Teflon filter	
?	Carbon Monoxide (CO)	8 hours**	02	02	- Non Dispersive Infra Red (NDIR)	
0	Ammonia (MU)	1 nour**	100	100	Chemiluminessence	
•	µg/m ³	24 hours**	400	400	-Indophenol blue method	

NATIONAL AMBIENT AIR QUALITY STANDARDS

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THE GAZETTE OF INDIA : EXTRAORDINARY

[PART III-SEC. 4]

(1)	(2)	(3)	(4)	(5)	(6)	
9	Benzene (C ₆ H ₆) µg/m ³	enzene (C ₆ H ₆) Annual* 05		05	 Gas chromatography based continuous analyzer Adsorption and Desorption followed by GC analysis 	
10	Benzo(a)Pyrene (BaP) - particulate phase only, ng/m ³	Annual*	01	01	 Solvent extraction followed by HPLC/GC analysis 	
11	Arsenic (As), ng/m ³	Annual*	06	06	- AAS /ICP method after sampling on EPM 2000 or equivalent filter paper	
12	Nickel (Ni), ng/m ³	Annual*	20	20	- AAS /ICP method after sampling on EPM 2000 or equivalent filter paper	

 Annual arithmetic mean of minimum 104 measurements in a year at a particular site taken twice a week 24 hourly at uniform intervals.

** 24 hourly or 08 hourly or 01 hourly monitored values, as applicable, shall be complied with 98% of the time in a year. 2% of the time, they may exceed the limits but not on two consecutive days of monitoring.

Note. — Whenever and wherever monitoring results on two consecutive days of monitoring exceed the limits specified above for the respective category, it shall be considered adequate reason to institute regular or continuous monitoring and further investigation.

Forms of Air Pollutants:

• Solid:

(It also includes liquid, e.g. acid mist) example- dust, particulate matter, soot etc.

- Gases:
- example: SO_2 , NO_x etc.
- Partitioned between solid and gas
 example: semivolatile hydrocarbons like PAH (Polycyclic Aromatic
 - Hydrocarbon)

Formation of Secondary Pollutants from Primary Pollutants

Type of Reaction	Primary Pollutants	Secondary Pollutants	Unpolluted Atmosphere
Simple reaction			
	Acid gases		
	Alkaline Particles	Salt particles	

Formation of Secondary Pollutants from Primary Pollutants





Agriculture Crop Residues (Biomass) Burning



Image of biomass burning induced smoke captured by **Moderate Resolution Imaging Spectroradiometer** (MODIS) on NASA's **Aqua satellite**, November 5, 2012

- The fire active (agricultural-waste burning) area: IGP including Punjab, Haryana and western part of Uttar Pradesh) ~ 48,400 sq. km (Justice et al., 2002)
- CRB is active for four months in a year: rice-residue burning during October–November and wheat-residue burning during April–May.

Photochemical Brown Smog





Assignment Questions

<u>Q 1</u> The area of Kanpur city is (20 x 30) km². The height of heavily polluted air layer is assumed to be 1 Km. One solution to Kanpur problems would be to pump the contaminated air away through a pipe. Suppose it is decided to pump out the Kanpur air once in 24 hours towards the city of Lucknow,80 km away from Kanpur. Other information:

a) velocity of air in pipe is 5 m/sec. find the diameter of pipe?

b) Find the pressure drop between two ends of the pipe;

Considering i) frictional losses

ii) Entrance loss

iii) Exit loss

Assume K_{exit} = 1.5

 $K_{entrance} = 0.7$

take friction constant 0.0015 and velocity through pipe 12 m/s

c) Estimate the power requirement of the pump?

d) If power requirement of Kanpur people is 0.5 KW/person; what population equivalent of power will be taken by pump?

e) Is the idea workable – Justify?

<u>Q 2</u> Develop the relationship between ppm and μ g/m³ by using gas law, PV=nRT?

Apply Bernoullis Equation

$$\Delta P = \frac{\rho V^2}{2} \left(\frac{4 fL}{D} + K_{entrance} + K_{exit} \right)$$

Use Moody's Chart to find 'f'

And Power, P? Q x delp P



Moody Diagram

Background Information

Particulate matter (PM)						
			Aerody	<u>namic</u>	: Diameter	
	SPM	-	≤ 100 µı	n		
	TSPM	-	$\leq 40 \ \mu m$			
	PM ₁₀	-	$\leq 10 \ \mu m$			
\bigcirc	PM _{2.5} (Fine pa	articles)	-		$\leq 2.5 \ \mu m$	
\circ	PM _{0.1} (Ultrafin	ne partic	les) -		$\leq 0.1 \ \mu m$	

USEPA (1996)