CH3041 Tutorial 8 Answers Air Pollution

1. Explain the physical basis for the "enhanced greenhouse effect".

The Earth's lower atmosphere traps and re-radiates to the surface much of the energy that has been emitted from the Earth's surface. The energy emitted from the surface is blackbody radiation resulting from the warming of the surface by solar radiation, this is emitted in the IR region of the electromagnetic spectrum. This natural greenhouse effect results in the Earth's surface having a mean temperature of +15^{o}C rather than -18^{o}C.
The natural greenhouse gases which trap IR energy are H_2O, CO_2, CH_4 and N_2O. Water is a non-permanent gas and so increases in H_2O vapour concentrations are hard to estimate and they are likely to be influenced indirectly by warming or cooling of the surface effecting evaporation and evapotranspiration.
The enhanced greenhouse effect comes about as a result of enhancement of the trapping mechanism in the atmosphere and this is then due to increased levels of the greenhouse gases CO_2, CH_4 and N_2O and to the addition of anthropogenic gases such as the Chlorofluorocarbons.
The greenhouse gases each have a characteristic window of absorption in the IR region. For CO_2 the absorption of radiation in the IR wavelengths (13 - 15μm) is quite significant with the current concentration of this gas in the troposphere (360 ppm) as it is a minor gas in the atmosphere. A doubling of the current CO_2 concentration will result in a significant increase in the amount of radiation absorbed, a positive radiative forcing will produce a warming effect at the Earth's surface - Greenhouse Warming. CO_2 is produced in enormous quantities, natural emissions are augmented by production from fossil fuel combustion, cement manufacture, land-use changes, and the concentration now is +25% compared with pre-industrial values.
The other gases CH_4 and N_2O are trace gases and they have shown substantial increases in concentration (+100%, +9%, resp.) since industrialisation. They absorb radiation in a window (8 - 12 μm) that shows very little absorption and so increases in the concentrations of these gases result in significant warming. The CFCs (and HCFCs) have been produced in large quantities by man, have long half lives in the atmosphere and absorb in the same region as CH_4 and N_2O. O_3 is another greenhouse gas. They result in tropospheric warming but stratospheric cooling.
The Global Warming Potentials of greenhouse gases express the relative ability of a greenhouse gas to increase the mean Earth surface temperature and this includes the IR characteristics of the gas (λ, ε), the lifetime of the gas in the atmosphere and any indirect effects it produces. CO_2 has a reference value of 1, CH_4 11, CFCs 1000's. A relative warming potential takes the GWP for a gas and includes the emission data to estimate the relative effect of a gas in influencing the global climate. Due to the extremely large emissions of CO_2 it will contribute to 50% of the RWP over the next 200 years.

2. Global Circulation Models are used in predicting global climate change. How does a GCM model work and what are the limitations of using this type of model to predict climate change?

Global Circulation Models are 3D coupled ocean-atmosphere computer models. These models calculate numerically the structure and processes of the troposphere versus time. They simulate the meteorology and air chemistry along with the global circulation of the Earths oceans to predict the climate either for a large region such as Australia or for the globe. The physics in the models is concerned with fluid flow and heat transfer and the relevant equations are solved for both the atmosphere and ocean to generate the major patterns of oceanic and tropospheric circulation.
A GCM uses a grid of the Earth's surface at low resolution 200 km(horizontal) x 1km(vertical) and calculates values for the various required parameters (such as T) at these points. The model covers the entire Earth's surface and extends up to the lower stratosphere. For use in Global Warming studies the computer model will typically simulate a period of less than 100 years to determine trends in the global climate. Models must accurately represent past data and reproduce major climate events such as El Nino (from the Enso cycle).

A large number of **approximations** are used to make the model computationally tractable and these include:
1) approximations to radiation effects (parameterise) eg. reflection vs absorption in forests, mountains
2) approx. to air chemistry (parameterise)

Complex chemistry: eg. involving the $OH^{\cdot}$ radical which cleans up the pollutant gases gives an '**indirect effect'**. Some molecules break down to give a greenhouse gas.
Feedback O_3 in the stratosphere warms the stratosphere & ∴ cools the troposphere.
aerosols, clouds, sea circulation.

3) approx. for cloud effects (parameterise) eg. cannot include single clouds
4) approx. air-sea energy & gas exchange
5) approx. for plant CO_2 & methane fluxes

The data input to the model includes detailed GIS geographic information, solar radiation,
+
Emissions data: CO_2, CH_4 & N_2O (rice),O_3, HCFC
Physical data : GWP (IR, t½ data)

The approximations lead to inaccuracies in the models and the major areas of concern at the moment are: Clouds, aerosols and sea circulation. The input data also includes many poorly constrained estimates of fluxes eg. CO_2 The growth of the human population is a very difficult variable as the energy use regime of the growing population has a major effect on emissions.
The limitations include the approximations above of which the human population may have the largest uncertainty and the cloud effects, aerosol effects and ocean circulation effects.
The grid size of the model limits the accuracy and resolution of the model and the performance of the computer dictates the grid size and the length of the time the simulation is run for. The accuracy of the current models is around $0.3 \pm 0.3\ ^{o}C$ for the current degree of global warming.

3. Provide details of the basic chemistry occurring in a photochemical smog, include the key compounds and the physical conditions required for a smog to form?
What measurements are carried out to declare a photochemical smog event?

The chemistry in photochemical smog is **oxidative** chemistry and this is a form of secondary pollution.
A photochemical smog event needs :
1) plenty of sunlight 2) plenty of VOCs 3) plenty of NOx (NO, NO_2) 4) still air (a temperature inversion is helpful) 5) $T > 18^{o}C$

The main reaction that initiates a smog event is the increase in VOC and NO concentrations in the morning air. When the NO reacts with ozone to form NO_2 the smog event starts.

$NO + O_3 \rightarrow NO_2 + O_2$ $NO_2 + h\nu (<420\ nm) \rightarrow O + NO$

$O + O_2 + M \rightarrow O_3 + M$ (M = a third body unreactive but able to moderate the energy of rxn)

Enhanced ozone concentrations are a characteristic feature of smog and are used to monitor the event. When the ozone concentration rises above the regulated maximum permissible level (Qld. 0.1ppm) a smog event is declared. Ozone measurements are usually carried out with a chemiluminescence instrument.

The hydroxyl radical is the normal oxidant in the troposphere and is also formed by photochemical processes. $O^* + H_2O \rightarrow 2OH^{\cdot}$
A high OH concentration when combined with high VOC concentrations and high NOx concentrations it reacts to form toxic aldehydes and peroxyacetylnitrate type compounds (PAN) $CH_3COO_2NO_2$. These are strong eye irritants and are another characteristic feature of photochemical smog.

$CH_4 + OH + 2O_2 + 2NO \rightarrow HCHO + 2NO_2 + H_2O + OH$

$CH_3CHO + OH + O_2 + NO_2 \rightarrow CH_3COO_2NO_2 + H_2O$

The progress of smog formation follows the inputs of pollutants (primarily from mobile sources (cars)) and the increase in solar radiation. In the early morning cars add NO, VOCs and CO. By mid-morning the early warmth has converted the NO to NO_2 which starts the chain reactions of NOx with the VOCs in the presence of high OH. and sunlight. These form the aldehydes, PANs and ozone (as well as CO_2 and H_2O). In the afternoon the rush hour CO and NO helps remove the products as there is now insufficient solar radiation.

4. Acid rain has a pH of less than 4.9 and typically contains the mineral acids H_2SO_4 and HNO_3. How is the **buffer capacity of a soil** important in determining if forests growing in regions affected by acid rain will be affected by acid rainfall?

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Acid rain has a pH less than 4.9. Acidic rain may be formed naturally in regions which have high sulphur emissions (eg. burning oil shales, geothermal activity) or it may formed anthropogenically. The anthropogenic emissions produce rain that has mineral acidity due to both H_2SO_4 and HNO_3 (around 7 : 3).
The H_2SO_4 if formed by subsequent reaction of the SO_2 which is released from fossil fuel combustion and the roasting of sulphidic minerals (emissions have increased 20 times since industrialisation).

($ZnS + O_2 \rightarrow Zn + SO_2$ $C_{100}H_{85}S_{2.1}N_{1.5}O_{9.5}$ forms SO_2 & NO_x)
(1) $2SO_2 + 2H_2O + O_2 \rightarrow 2H_2SO_4$ (aq., Mn cat.) - heterogenous catalyst, aqueous in raindrop
(2) $SO_2 + 1/2O_2 \rightarrow SO_3 + \mathbf{H_2O} \rightarrow 2H_2SO_4$ - homogenous gas phase

The HNO_3 is formed from NO_x which is produced from high T combustion primarily in cars and furnaces.

($N_2 + O_2 \rightarrow 2NO$ $NO + O_3 \rightarrow NO_2 + O_2$ $H_2O + O^* \rightarrow 2OH^\cdot$)
$OH^\cdot + NO_2 \rightarrow HNO_3$

The pH of the rain is determined by the amount of natural buffering in the raindrops (due to mainly to basic mineral dust and NH_3) and the additional natural acids (H_2SO_4, HNO_3, H_2CO_3, HCl, $MeSO_3H$). The formation of H_2SO_4 may occur in the gas phase, solution phase or as a heterogenously catalysed reaction. Which reaction dominates depends on the presence of sufficient moisture and the heterogenous catalysts such as Mn(II) being present in the raindrops. Both mineral acids are very water soluble and wet removal is rapid.
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The buffer capacity of a soil is determined largely by the cation exchange capacity (CEC) value and in particular that part of the CEC that is due to the base cations Na^+, K^+, Ca^{2+}, Mg^{2+}. The base cation saturation (BCS) determines how readily a soil may be acidified, a soil with a high BCS will be resistant to acidification a soil with a low BCS will be susceptible to acidification. The soils with high BCS values will be typically ones with significant clay mineral content, these clay minerals have exchangeable cations which can be replaced by H^+. High humic content and allophane content may also give significant CEC. The most important buffering materials in soils are carbonate minerals, after the buffering capacity due to this has been used up the CEC in clays, humic matter and allophane and next used up. Following from the weak buffering due to aluminosilicate dissolution is available. clay/organic-$M^+ + H^+ \rightarrow$ clay/organic-$H^+ + M^+$
The parent rocks from which the soil forms are important in determining the soil CEC:

I Low or no buffering : granite, quartz sandstones
II Medium to low buff. : shales, metamorphic
III High to medium buff.: basic volcanic
IV Infinite buffering : limestones, dolomites

Slow weathering rocks form thin soils and which few plants grow and so with little buffering capacity these soils are prone to acidification. At the start of acid rain input the additional S and N will make the forests grow well, the next stage the excess acid now starts to leach out the nutrients Ca^{2+} and Mg^{2+} and deficiency problems arise, in the final stage the soils become quite acidic (pH 4.2) which will mobilise toxic Al^{3+} and heavy metals such as Cd and Pb and the soil pore water will become toxic.