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1. Chemical Families and Cycles (60 pts: 10, 10, 10, 10, 10, 10)

a) What is NO_x? How does NO_x differ from NO_y?

NO_x is the chemical family consisting of nitrogen oxides NO, NO_2 and NO_3. Mostly NO and NO_2 is okay too. NO_y includes precursors and products that can be easily converted to or from NO_x, such as PAN, HONO.

b) What is the most important type of anthropogenic source of NO_x?

Fossil fuel burning.

c) What is the Nitrogen cycle? Describe its components, interfaces, and processes.

The Nitrogen cycle is the pathways by which and reservoirs through which compounds of nitrogen are transferred among the atmosphere, the hydrosphere (including the oceans), the biosphere (including plants), the cryosphere, and the geosphere (including soil). The primary interfaces across which nitrogen is transferred are the ocean-atmosphere and the biosphere-atmosphere interfaces. The processes that control these transfers include combustion emissions (fossil fuel and biomass, anthropogenic and natural) and evaporation of NH_3, N_2, NO_x, and wet/dry deposition of HNO_3 and NO_x to the ocean and land surfaces, as well as denitrification and fixation.

d) Name the main atmospheric reservoirs of nitrogen. For each reservoir, name the chemical compound, write its chemical formula, and identify the oxidation state of nitrogen.

The four atmospheric reservoirs of nitrogen are nitrogen N_2 (0), nitric oxide NO (+2) plus nitrogen dioxide NO_2 (+4) plus nitrogen trioxide NO_3 (+6), nitrite NO_3^- (+5) plus ammonia NH_4^+ (-3), and nitrous oxide N_2O (+1).

e) Which reservoir is responsible for the removal of most of the reactive nitrogen? What is the process (or processes) responsible for this removal?

Most of the reactive nitrogen is removed by wet deposition or precipitation as HNO_3 or NO_3^-.

f) If the atmosphere contains 0.15 Tg(N) of NO_x and the total removal rate is 45 Tg(N) per year, what is the residence time of NO_x in the troposphere?

τ_{NOx}=M/F=0.15/45=0.0033 a or 29 hr.

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2. Smog (60 pts: 10, 10, 10, 10, 10, 10)

a) Define air pollution. Give an example of a pollutant and identify what makes it a pollutant in the atmosphere.

Air pollution is 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.

b) What is smog? Identify the similarities between smog and what happened in the demonstration in class with an orange peel.

Smog is a severe pollution episode. The name smog is derived from such events in London in the early to mid-20th century in which smoke from industries was mixed with fog. It is usually characterized by severe detrimental effects on visibility, health, and crops. The orange demonstration is very similar to photochemical smog, in which high O_3 results in VOC oxidation, the products of which condense and grow particles large enough to visibly scatter light.

c) Identify the key differences in pollutants, meteorology, and chemical reactions between smog in London (in 1952) and smog in Los Angeles (today)?

London fog results from SO_2 emitted by combustion of coal which is oxidized on particles to form sulfate. Los Angeles photochemical smog involves gas phase reactions with NO_x and VOCs to produce high O_3, and high amounts of organics and nitrates in particles.

d) Write the reaction(s) for photolysis of NO_x.

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

$O + O_2 \rightarrow O_3$

e) What beneficial and detrimental roles does OH play in the troposphere? Name four pollutants that are affected by OH, and illustrate using generalized reaction pathways how each pollutant is affected.

The beneficial role of OH is that it removes pollutants by acting as an "atmospheric detergent." The detrimental role is that it produces additional secondary pollutants. Both of these roles are accomplished by gas-phase oxidation by OH: e.g.

$SO_2 + OH \rightarrow \ldots \rightarrow H_2SO_4 + \ldots$

$NO_2 + OH \rightarrow \ldots \rightarrow HNO_3 + \ldots$

$CH_4 + OH \rightarrow \ldots \rightarrow CO + \ldots \rightarrow CO_2 + \ldots$

$NH_3 + OH \rightarrow \ldots \rightarrow NO + \ldots$

f) How is OH related to O_3? Write the most important reactions.

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ (or O^*)

$O(^1D) + H_2O \rightarrow 2OH$

$O(^3P) + O_2 \rightarrow O_3$

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3. Tropospheric Ozone (80 pts: 20, 10, 50)

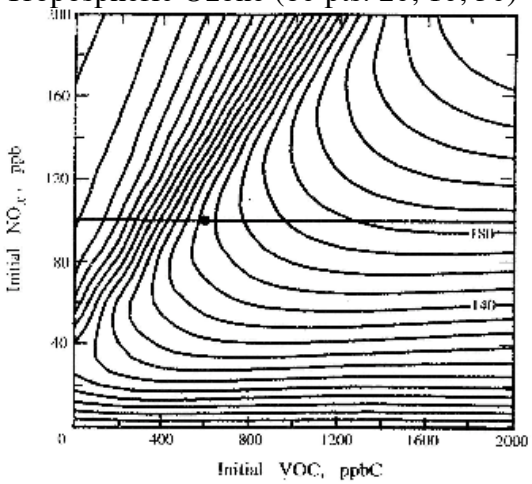

Figure Caption: Ozone isopleth plot based on simulations of chemistry along air trajectories in Atlanta (Jeffries and Crouse, 1990). Each isopleth is 10 ppb higher in ozone as one moves upward and to the right.

a) Use the figure above for ozone in Atlanta.
   i) What is an ozone isopleth?

An ozone isopleth is a line showing constant ozone concentration.

   ii) What is the ozone mixing ratio that corresponds to initial VOC of 620 ppbC and NO_x of 100 ppb?

140 ppb.

   iii) How will the ozone mixing ratio change if this initial VOC mixing ratio increases by 200 ppbC?

It will increase by 20 ppb to 160 ppb.

   iv) At the initial NO_x of 100 ppb, mark on the plot the VOC range for which ozone is insensitive to VOCs.

From VOC of 1400 ppbC to 2000 ppbC at NO_x of 100 ppb.

b) What is a VOC? Name the most abundant VOC in the troposphere. Name another VOC.

VOC refers to volatile organic compounds. The most abundant VOC is methane (CH_4). Another VOC is α-pinene.

c) CH_4 has a mixing ratio of about 2 ppm and is well mixed with a mean residence time of approximately 4 a (~10^8 s) in the atmosphere.
   i) Write the balanced chemical reaction for the initial and limiting oxidation step for CH_4 oxidation in the troposphere.

$CH_4+OH \rightarrow \alpha CH_3+H_2O$

   ii) If the rate coefficient for the chemical reaction in part (ii) above is ~0.02 ppm^{-1} s^{-1}, what is the concentration (in ppt) of oxidant?

For a bimolecular reaction $\tau = 1/(k*[OH])$. We know τ=4 a=~10^8 s and k~0.02 $ppm^{-1}s^{-1}$. Solve for $[OH]=1/\tau k=1/(10^8*0.02)=0.5$ ppt.

   iii) Name the product(s) of CH_4 oxidation in the troposphere. Write the net reaction for CH_4 oxidation in the majority of the troposphere.

CHOOH, HCHO, CO, CO_2 (also H_2O. HO_2, OH, O_3).

Low NO_x (70% of troposphere): $CH_4+O_2 \rightarrow CH_2O+H_2O$ or $CH_4+2O_3 \rightarrow CH_2O+H_2O+2O_2$ or $CH_4+3O_3 \rightarrow CO_2+H_2O+2HO_2+O_2$, also CH_2O+O_2 (or O_3) $\rightarrow CO+HO_2$ (and OH).

   iv) What pollutant changes the products of CH_4 oxidation in the troposphere and in the polluted boundary layer?

NO_x

   v) What happens to the products of CH_4 oxidation in the troposphere at high and very high concentrations of this pollutant?

At high NO_x, O_3 and HO_x are produced at a higher rate than at low NO_x. At very high NO_x, HNO_3 is produced and the rate of O_3 production begins to decrease.

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4. Particle Composition (50 pts: 10, 10, 20, 10)

a) What is an aerosol? Identify all required constituents and their physical states.

An aerosol is a colloidal suspension of liquid or solid particles in a gas.

b) How big is an aerosol particle? Give an example of aerosol particles that you can see with the unaided human eye, and state the approximate size of the particles in your example.

Aerosol particles may range in size from about 1 nm to more than 1 mm, but most typically occur in atmospheric conditions between 10 nm and 100 μm.

c) What are the main chemical components of atmospheric aerosol particles? For each component, specify their primary source(s) and approximate size.

The main chemical components of atmospheric aerosol particles are sulfates (combustion, 0.1 to 1 μm), nitrates (combustion, 0.1 to 1 μm), ammonium (0.1 to 1 μm), organic carbon (combustion, 0.01 to 1 μm), elemental carbon (combustion, 0.1 to 1 μm), sea salts (ocean wave-breaking, 1 to 10 μm), minerals (urban and desert dust, 2 to 20 μm).

d) Name three consequences or characteristics of atmospheric particles that have significant differences because of their size.

Size-dependent consequences include: visibility, health effects, climate effects.
Size-dependent characteristics include: lifetime, mass, composition, number.