THE OZONE TRIANGLE – HOW COMBUSTION AND NON-COMBUSTION SOURCES MAY INFLUENCE OZONE GENERATION AND REDUCTION

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THE OZONE TRIANGLE

- Title I of the Clean Air Act Amendments of 1990 establishes Attainment and Non-Attainment areas of pollutants based on the National Ambient Air Quality Standards (NAAQS) which are based on average background concentrations of ozone and other criteria pollutants.
- Any area that is designated as Non-Attainment must provide regulations to ensure reduction of the generation of the criteria pollutant.
- Most emissions come from combustion sources.

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- True or False: Ozone comes directly from emission sources.

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- **FALSE** - Most ozone that is generated is from a photochemical reaction of other pollutants including oxides of nitrogen (NOx) and Volatile Organic Compounds (VOC).
- The interdependence of this is why we have what is known as “The Ozone Triangle.”
- The Ozone Triangle is derived from the Fire Triangle in which there are three factors the cause the formation of ground level ozone.

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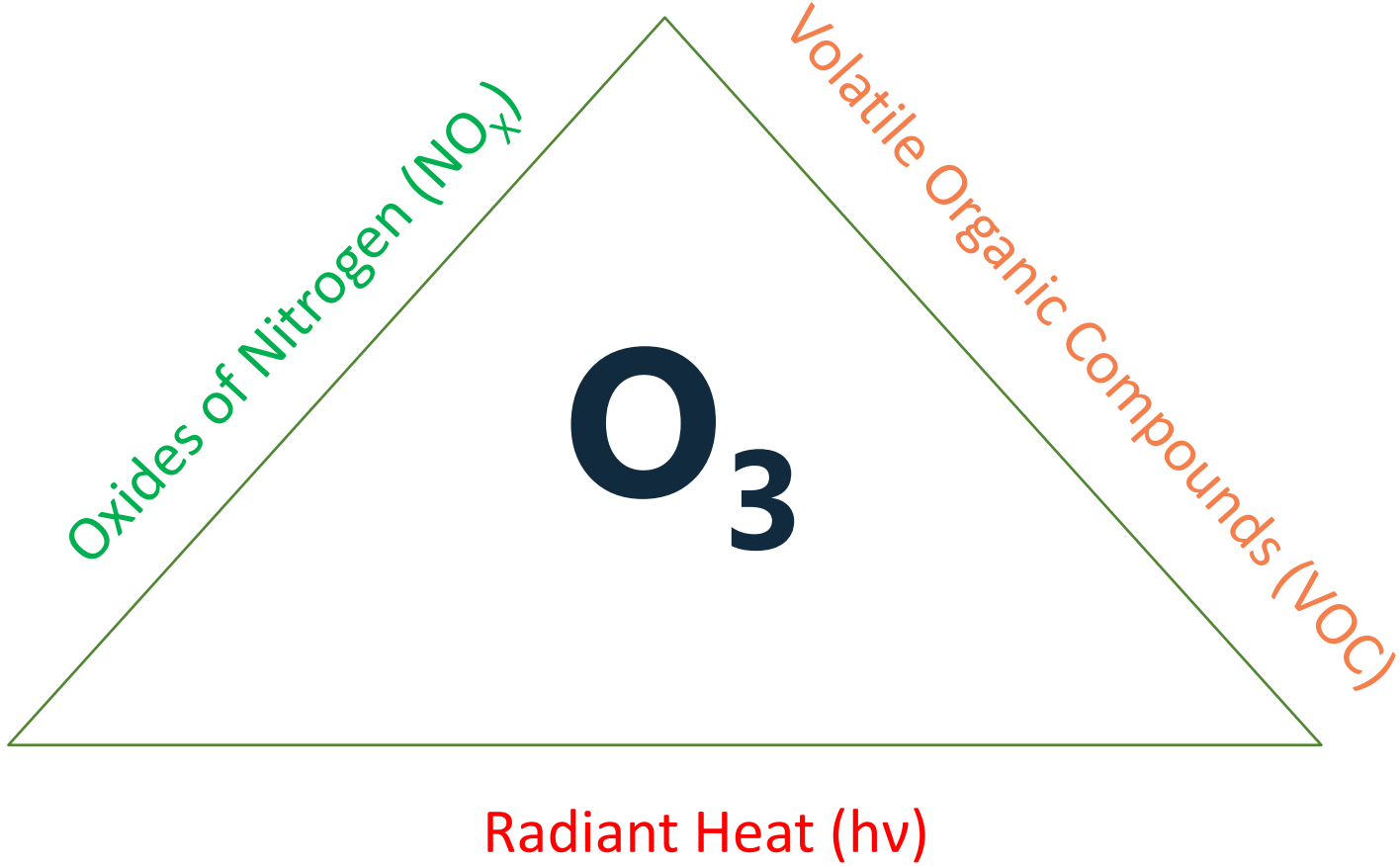

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CLEAN AIR ACT AMENDMENTS OF 1990

- Title I: National Ambient Air Quality Standards (NAAQS), Attainment vs. Non-Attainment
- Title II: Mobile Sources
- Title III: Hazardous Air Pollutants (Air Toxics)
- Title IV: Acid Deposition Gases (SO2 and NOx)
- Title V: Facility Wide Permitting Program
- Title VI: Stratospheric Ozone (Ozone Layer)

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- Title I of the Clean Air Act Amendments establishes areas in the US determining attainment or non-attainment based on the following air contaminants:
  - *Carbon Monoxide (CO)*
  - *Oxides of Nitrogen (NOx)*
  - *Sulfur Dioxide (SO_2)*
  - *Particulate Matter (PM)*
  - *Ozone (O_3)*
  - *Lead*
- These pollutants are derived from products of combustion and have established National Ambient Air Quality Standards (NAAQS).
- Attainment areas are areas in which the concentration of any of the listed air contaminants is below a set concentration based on monitoring stations. If the concentration for any pollutant exceeds the established NAAQS level during a certain time frame (8 hours) then the region is considered "non-attainment."

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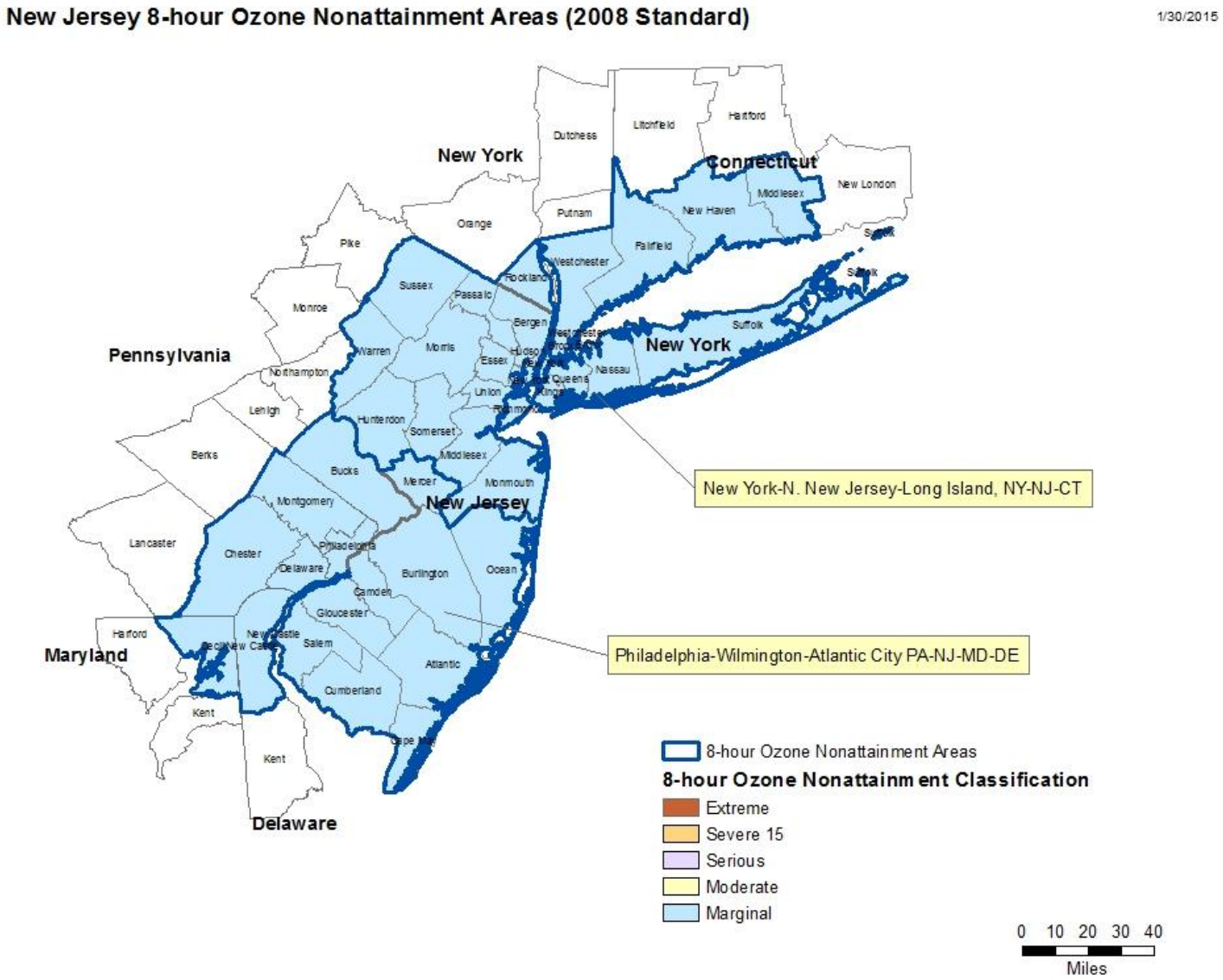

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- Ozone (O_3) is a molecule with three oxygen atoms and can be used as a very strong oxidizer. However, unlike oxygen gas (O_2) it can cause health problems.
- The health effects of ozone include*:
  - *Breathing difficulties*
  - *Coughing and sore scratchy throat*
  - *Aggravation of breathing conditions like emphysema, asthma and chronic bronchitis*
  - *Makes lungs susceptible to infection*
  - *Cause inflammation and damage to airways*

*Source - EPA Website on Ozone Health Effects

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- Oxides of nitrogen (NOx) is a regulated air contaminant under Title I of the Clean Air Act Amendments.
- NOx is basically consists of two compounds:
  - *Nitric Oxide (NO)*
  - *Nitrogen Dioxide (NO_2)*
- NO and NO_2 can convert to nitrous (HNO_2) and nitric acids (HNO_3).
- **True or False – NOx generated is dependent on combustion of nitrogen containing fuels only.**

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- **FALSE** - Most nitrogen oxygen compounds are generated by reaction of a very small percentage of the nitrogen and oxygen in combustion air.
- The higher the temperature and more excess air is introduced, the more NOx is generated.

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- Volatile Organic Compounds (VOC) are not directly regulated by Title 1 of the Clean Air Act Amendments but are monitored as a precursor for Ozone generation.
- VOCs are usually measured as Non-Methane Hydrocarbons (Total Hydrocarbons minus Methane or NMHC) or Non-Methane and Non-Ethane Hydrocarbons (NMNEHC).

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- Volatile Organic Compounds
- Definition as of 40 CFR 51.100(s)
- An Organic Compound is any carbon compound that is not elemental carbon, carbon dioxide, carbon monoxide, carbonic acid, metallic carbides and carbonates and ammonium carbonate.
- Volatile Organic Compounds are Organic Compounds except for what is listed in 40 CFR 51.100(s) which are demonstrated not be Ozone precursors.
- The vast majority of the organic compounds listed as non-ozone precursors are refrigerants (chlorofluoro hydrocarbons). These include compounds regulated by Title VI of the Clean Air Act Amendments which can deplete Stratospheric Ozone.

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- Other compounds listed:
  - *Methane*
  - *Acetone*
  - *Methyl Formate*
  - *1,1,1 Trichloroethane (Methyl Chloroform)*
  - *2-Amino – 2- Methyl – 1- Propanol*
  - *T- Butyl Acetate*
  - *Ethane*
  - *Methyl Acetate*
  - *Methylene Chloride*
  - *Perchloroethylene (Tetrachloroethylene)*
  - *Propylene Carbonate*
  - *Dimethyl Carbonate*
  - *Cyclic, Branched or Completely Linear Methylated Siloxanes*
- Note that while they are not VOCs, some are hazardous air pollutants while methane is a greenhouse gas.
- **What is the difference between Tropospheric and Stratospheric Ozone?**

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- Tropospheric (Ground Level) Ozone (O_3) is generated when radiant heat (hν) causes Nitrogen Dioxide (NO_2) to break down to Nitric Oxide (NO) and an oxygen free radical (O) which in turn reacts with oxygen gas (O_2) to form ozone with the presence of particulates(M).
- However, NO can immediately react with ozone to form NO_2 and O_2 completing the nitrogen cycle.
- The Nitrogen Cycle
  - $NO_2 + h\nu = NO + O$
  - $O + O_2 + M = O_3 + M$
  - $O_3 + NO = NO_2 + O_2$
- **If NO can deplete ozone then how does it accumulate?**

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- Volatile Organic Compounds (VOC) and Oxygen with the aid of free radicals can deplete available NO which cannot react with O_3. Thus, O_3 accumulates.
- The VOC Oxidation Cycle
  - $OH + HCHO = H2O + HCO$
  - $HCO + O_2 = HO_2 + CO$
  - $HO_2 + NO = NO_2 + OH$
- Stratospheric Ozone is the Ozone Layer that protects earth from ultraviolet rays from coming to the earth's surface.
- Chlorofluorohydrocarbons (CFCs) or certain refrigerants can deplete stratospheric ozone and deplete the ozone layer.
- **Why can't tropospheric ozone rise in the atmosphere to be stratospheric?**

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- Ozone is more dense than air. Thus it cannot rise in the atmosphere. With that, Tropospheric Ozone cannot reinforce the Ozone layer and the efforts replacing ozone depleting compounds listed in Title VI of the Clean Air Act Amendments are necessary.

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- Combustion is based on the following formula:
  - $C_XH_XO_X + O_2 = CO_2 + H_2O$
- However, if the compound being combusted has a different substance in the compound, then a product of combustion will contain the substance.
- For example, if the compound burned has sulfur in it then then along with water and carbon dioxide, the product of combustion is SO_2 (sulfur dioxide).
- However, not all combustion reactions complete itself and there are Products of Incomplete Combustion (PIC)
- **What is the most common PIC?**

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Carbon Monoxide!

- Carbon Monoxide is a toxic gas generated from incomplete combustion of hydrocarbons.
- Also, the VOCs generated are either PICs or unburned fuel which contribute to the ozone formation.
- To reduce it as well as other products of incomplete combustion you need to increase the temperature and excess air. But here is problem.

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Air Hole Open

Air Hole Closed

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- The problem is that if you increase temperature and excess air you will increase NOx emissions and not just NO and NO_2 which are the ozone precursors, but nitrous oxide (N_2O) which is a greenhouse gas.
- For combustion you need to find the optimal temperature excess air content for lower NOx and CO and VOC emissions.

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- NOx and VOC emissions can form ozone only if:
  - *A. They both come from the same source*
  - *B. They can come from different sources but only within the same facility.*
  - *C. They can come from any source from any location*

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- The answer is “C.” **Air contaminants know no boundaries.**
- While the majority of NOx emits as products of combustion, VOCs can emit from evaporative sources like gasoline and other fuel storage to coating and painting processes.

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- What season does more ozone generate (summer or winter)?
- What season does more carbon monoxide generate (summer or winter)?

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- Ozone generates more during the summer due to higher temperatures and longer days (increased hν). Higher temperatures can also increase NOx generation from combustion sources.
- During the winter months colder weather can mean lower combustion temperatures and increased carbon monoxide and other products of incomplete combustion (increased VOCs). So while ozone generation may be lower, it is definitely not absent.

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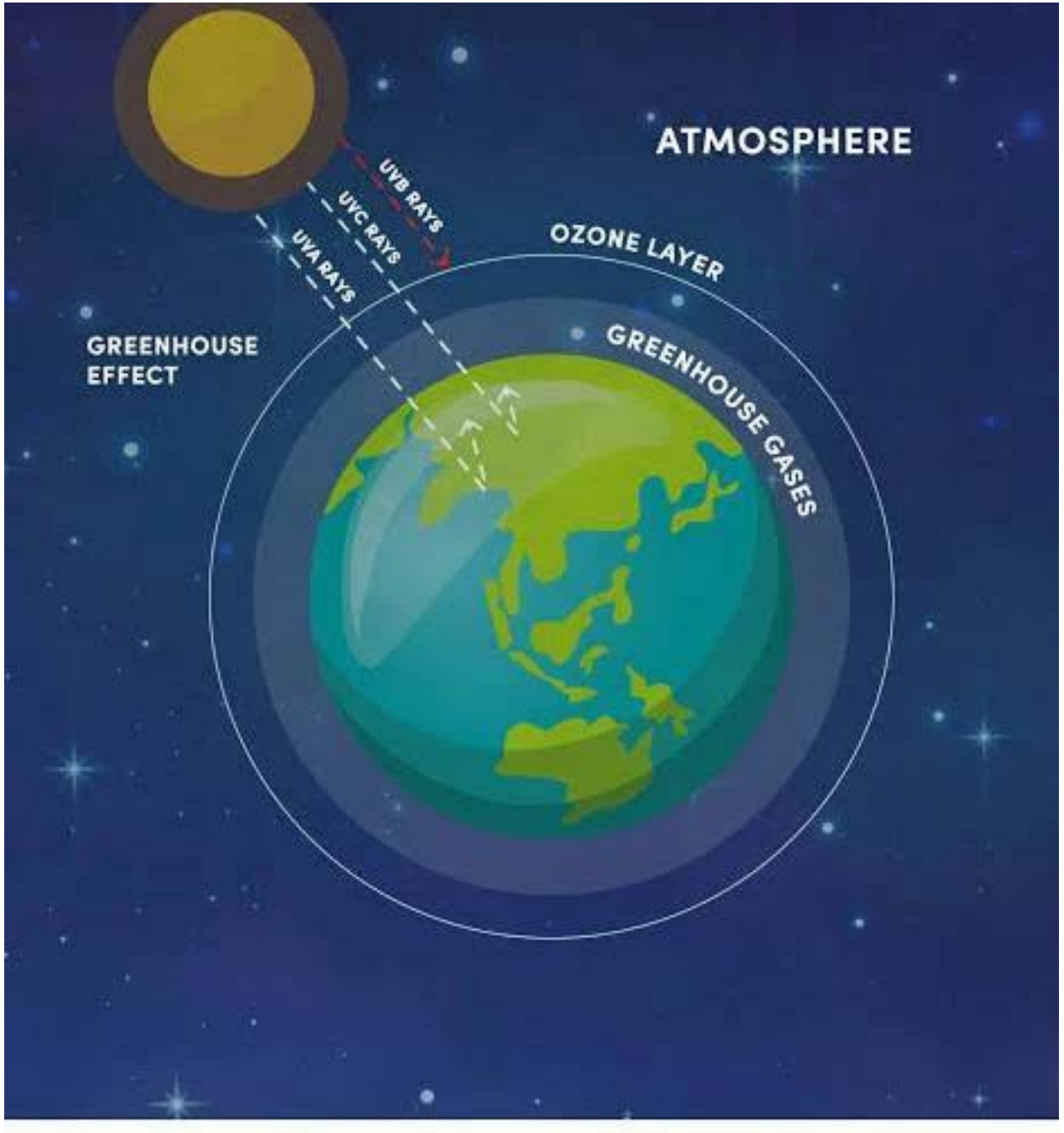
- While ozone generation can be caused by combustion emissions and other types of emissions (on the VOC) side, it can correlate with another type of pollution issue for the long term.
- Greenhouse Gases!


ATMOSPHERE
UVB RAYS
UVC RAYS
UVA RAYS
OZONE LAYER
GREENHOUSE GASES
GREENHOUSE EFFECT

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- The greenhouse effect is the natural process where greenhouse gases (such as carbon dioxide methane, and water vapor) in Earth's atmosphere trap heat radiated from the surface, preventing it from escaping into space and keeping the planet warm enough to sustain life. It functions like a blanket or greenhouse glass, absorbing infrared light and re-radiating it back toward the surface.

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- The most common greenhouse gas is…

  Carbon Dioxide

- Carbon Dioxide (CO_2) has the ability to retain infrared heat and naturally occurs in the atmosphere.
- Carbon Dioxide is the main product of combustion for all carbon materials that burn or react with oxygen.
- $C_XH_X + O_2 \Rightarrow CO_2 + H_2O$
- Note that Carbon Dioxide is a product of combustion and not just a combustion by product.
- **What is the main source of CO_2 depletion?**

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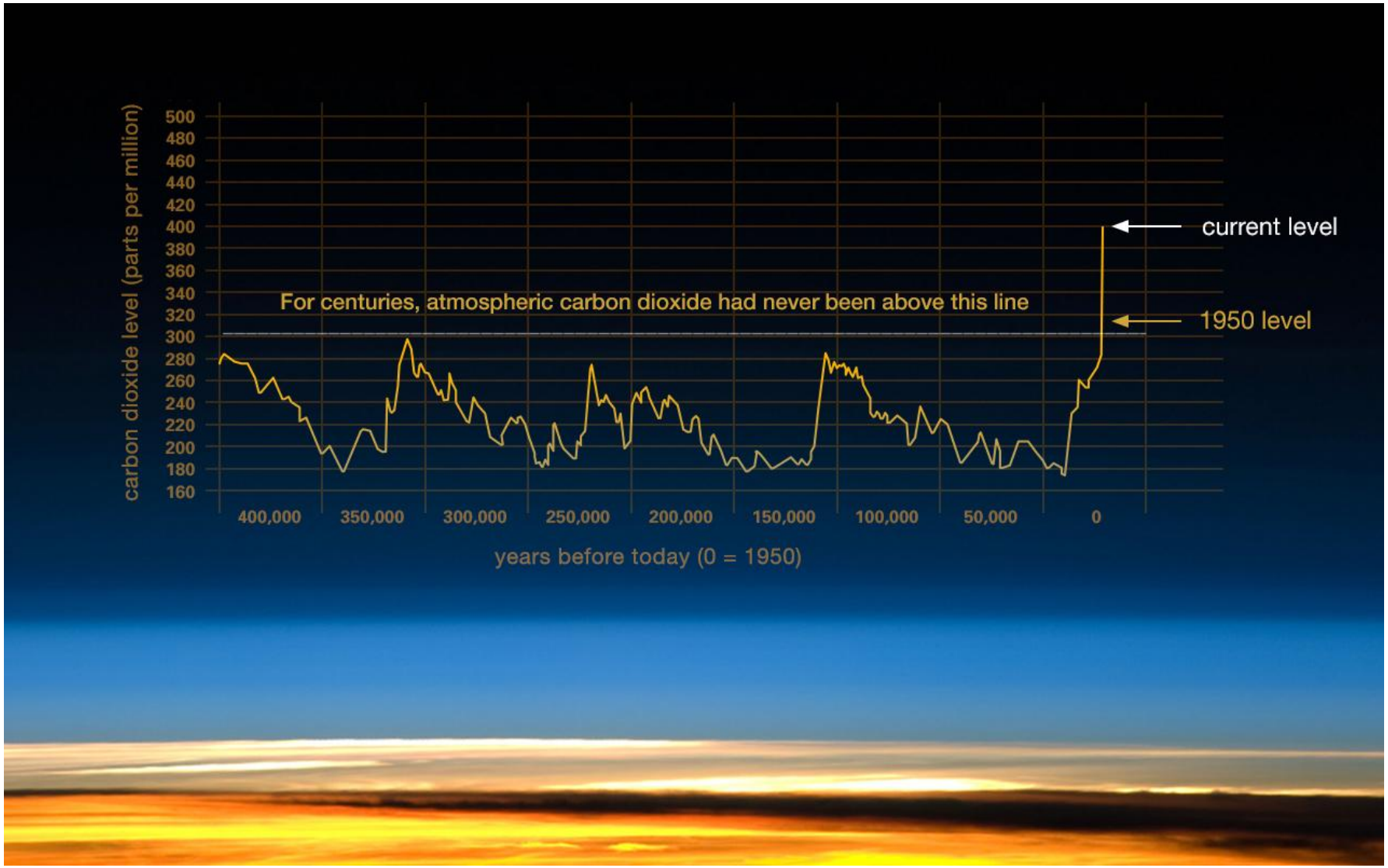
- Carbon Dioxide (CO_2) can be consumed by plants via photosynthesis. However, the CO_2 generation has outweighed the consumption especially in recent years.


carbon dioxide level (parts per million)
500
480
460
440
420
400
380
360
340
320
300
280
260
240
220
200
180
160
For centuries, atmospheric carbon dioxide had never been above this line
current level
1950 level
400,000
350,000
300,000
250,000
200,000
150,000
100,000
50,000
0
years before today (0 = 1950)

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- Carbon Dioxide concentrations recently reached a record high of 430 ppm.
- While Carbon Dioxide is the most common greenhouse gas, other gases have similar if not greater capability of holding infrared rays and thus contribute to global warming.
- The 100-year global warming effect is measured for each greenhouse gas compared to CO_2 or is classified as CO_2 equivalents (CO_2 (e)).

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Greenhouse Gas Reduction of Digester Gas

- Table A-1 Subpart A of Federal Regulations 40 CFR 98 global warming potentials for all greenhouse gases as follows

Carbon Dioxide	1
Methane	28
Nitrous Oxide	265

- CO_2 equivalent is the mass of greenhouse gases emitted multiplied by the global warming potentials and summed up.
- **What sources generate greenhouse gases as well as ozone contributors?**

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- Note that Table A-1 of 40 CFR 80 also has Global Warming Potentials for CFCs and HCFCs as well and can range from single digits to tens of thousands. Many have been banned based on Title VI of the Clean Air Act Amendments but can be influential to CO_2 equivalent emissions from a facility.
- For sewage treatment plants, while ozone generating compounds come from mostly combustion sources and some evaporative sources (including wastewater treatment processes), greenhouse gases can come from similar sources. But the most likely source is anaerobic digesters where methane gas is generated during this sludge treatment process.

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- Percent CO_2 equivalent reduction is based on 99 percent removal by weight of methane (converted to CO_2) and addition of N_2O post combustion multiplied by their respective global warming potential. Here are the reduction results based on methane content:

Percent Methane	Percent CO_2 Equivalent Reduction
67.5 percent	79.23 percent
60 percent	77.32 percent
55 percent	75.82 percent

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- Combustion of biogas is necessary due to safety reasons at a sewage treatment plant. However, instead of flares which is necessary, some facilities use it as fuel for boilers to generate heat at the facilities (digester processes and building heat) and generators (turbines or engines) for cogeneration.
- While there is net reduction of greenhouse gas based on biogas combustion, there is potential increased generation on ozone due to increased NOx as well as products of incomplete combustion.

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- For Summer, while there is potential increase in ozone as stated earlier, there is increased in CO_2 as a whole due to less products of incomplete combustion (i.e. Carbon Monoxide) and a greater proportion of N_2O with the increased NOx.
- For Winter, there is less CO_2 and more products of incomplete combustion but possible increase on unburned methane not just in biogas but natural gas combustion as well.
- If green house gases were incorporated in the ozone triangle it will be as follows:

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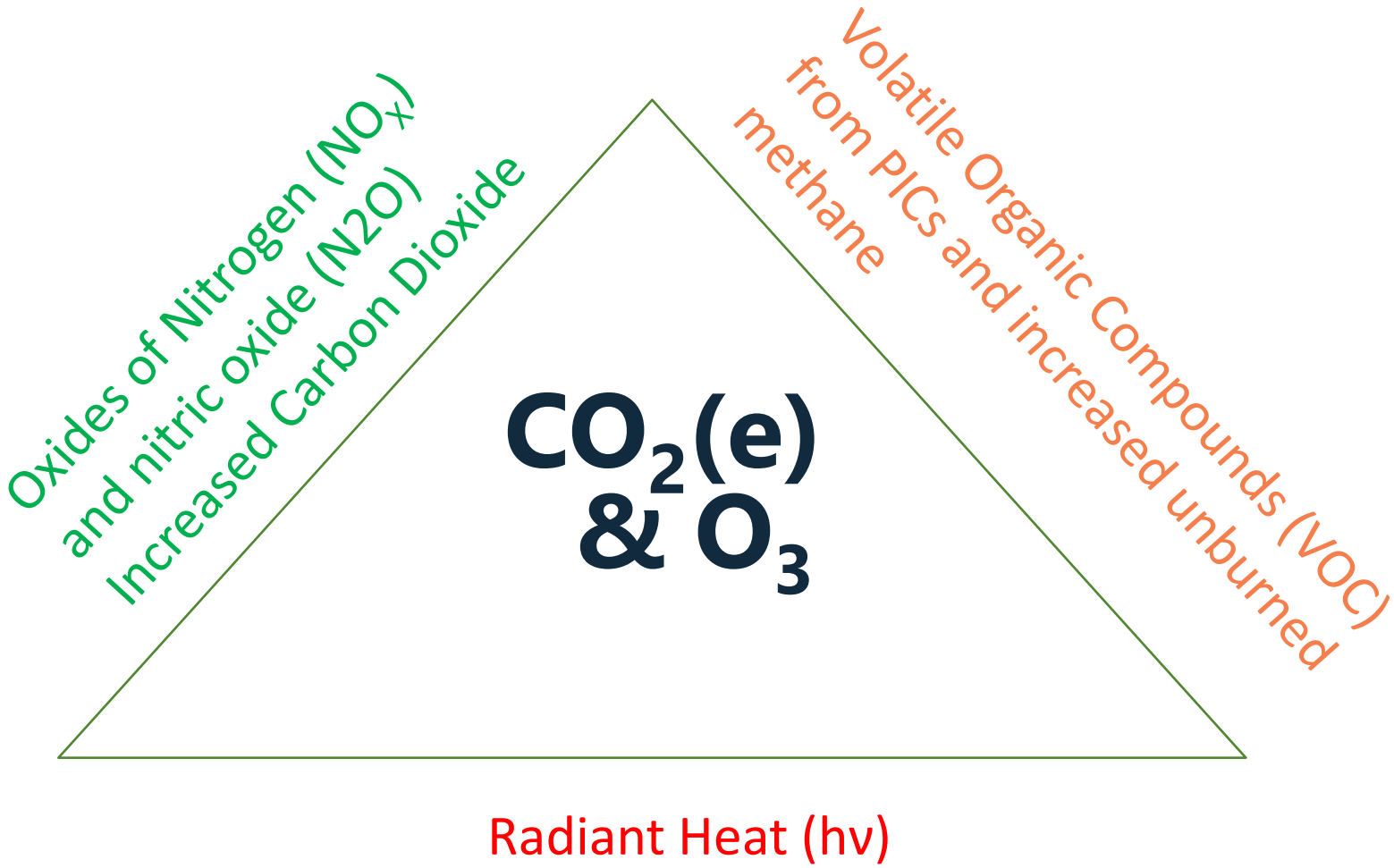

THANK YOU

Questions?

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