TROPOSPHERIC OZONE PRODUCTION AS INFLUENCED BY SOLAR IRRADIANCE

GCEP END OF SUMMER WORKSHOP
PNNL
19 AUGUST 2001

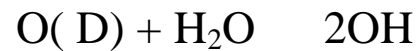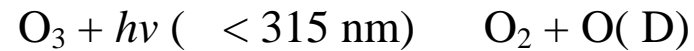SHELBY WINIECKI
UNIVERSITY OF CHICAGO

OUTLINE

1. INTRODUCTION

2. DATA

3. QUESTIONS

4. PRELIMINARY RESULTS

5. FUTURE WORK

AN INTRODUCTION

IN THE PAST: DOWNWARD TRANSPORT OF OZONE FROM THE STRATOSPHERE

PRESENT DAY: INDUSTRIAL PROCESSES PRODUCE HIGH LEVELS OF OZONE

PHOTODISSOCIATION:

$$O_3 + hv\ (\ < 315\ nm) \quad O_2 + O(\ D)$$

$$O(\ D) + H_2O \quad 2OH$$

$$\cdot$$
$$\cdot$$
$$\cdot$$

$$O + O_2 + M \quad O_3 + M$$

THE HARMFUL EFFECTS OF TROPOSPHERIC OZONE

ON HUMANS:
- MAY CAUSE PERMANENT DAMAGE TO LUNGS
- INHALING IT TRIGGERS CHEST PAINS, COUGHING, NAUSEA, THROAT IRRITATION, AND CONGESTION

ON PLANT LIFE:
- INTERFERES WITH THE ABILITY OF PLANTS TO PRODUCE AND STORE FOOD, MAKING THEM MORE SUSCEPTIBLE TO DISEASE, INSECTS, OTHER POLLUTANTS, AND HARSH WEATHER
- RESPONSIBLE FOR $500 MILLION IN REDUCED CROP PRODUCTION IN THE U.S. EACH YEAR!

www.ems.org/air_pollution/ozone_leaf.html

www.plpa.agri.umn.edu/~robertb/labphotos/Lab_air_pollution.htm

HGIC, U of MD

Each spot on this leaf indicates the location of a stoma that has been adversely affected by ozone

BREWER SPECTROPHOTOMETER

- A SINGLE GRATING SCIENTIFIC MEASURING INSTRUMENT FOR OZONE AND UV RESEARCH

- MEASURES THE GLOBAL UV IRRADIANCE FROM 286.5 NM TO 363 NM THROUGH A HORIZONTALLY POSITION DIFFUSER.

- SCANS ARE MADE AT FIXED 5° INTERVALS IN THE SZA

- THE BREWER IS PART OF A NETWORK OF 21 SITES MANAGED BY THE EPA.
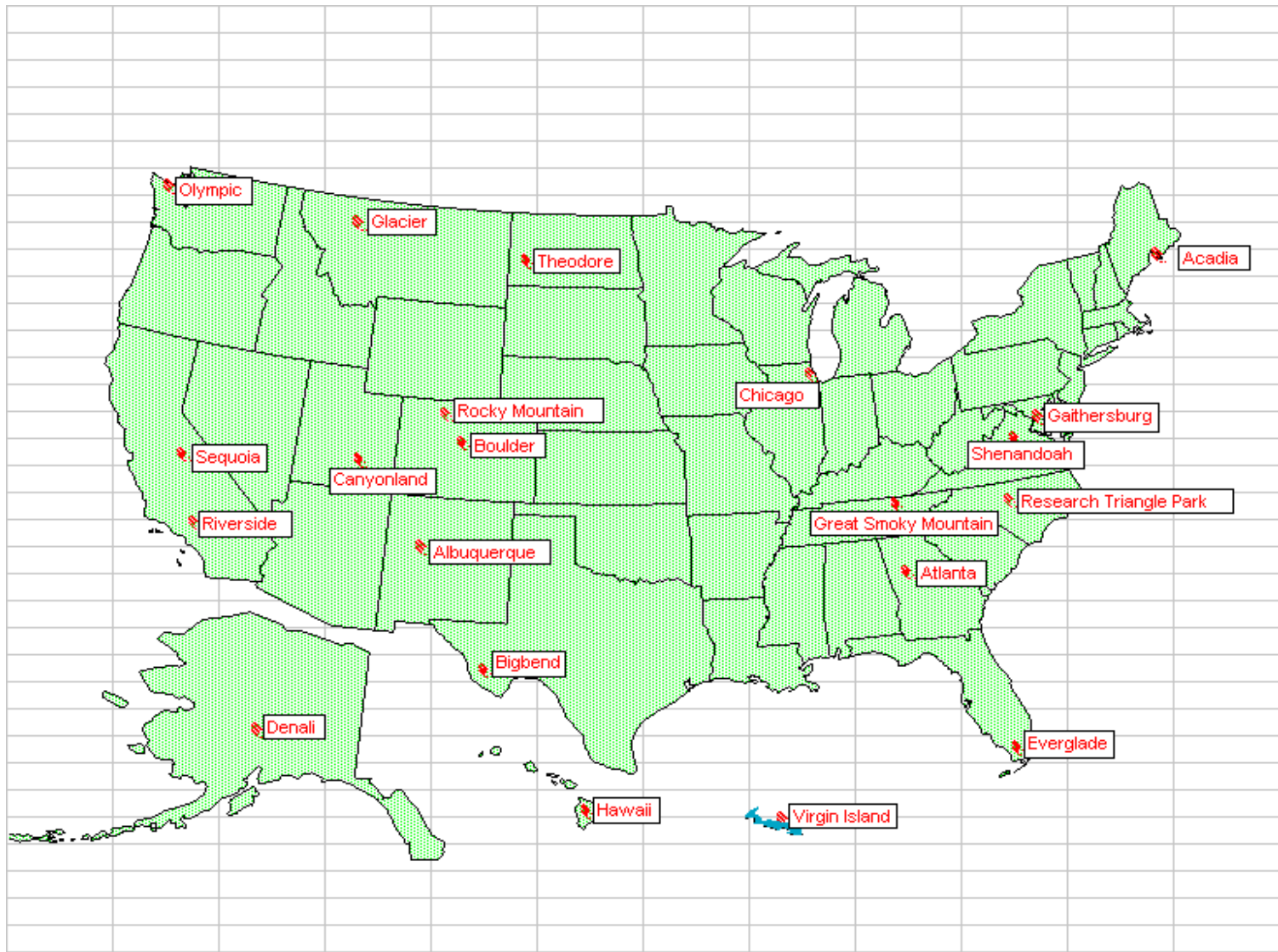
MORE DATA

- METEOROLOGICAL CONDITIONS IN THE CHICAGO AREA ARE RECORDED HOURLY AT MIDWAY AIRPORT, APPROXIMATELY 15 MILES FROM THE UNIVERSITY OF CHICAGO

    o THESE INCLUDE TEMPERATURE, WIND SPEED, WIND DIRECTION, AND RELATIVE HUMIDITY

- OZONE IS ALSO RECORDED ON AN HOURLY BASIS BY THE AIR QUALITY MONITORING SITE LOCATED AT THE UNIVERSITY OF CHICAGO

A SHORT TERM CAMPAIGN

WE ARE ALSO CONDUCTING A FOCUSED CAMPAIGN TO OBSERVE VISIBLE IRRADIANCE, AEROSOLS, AND TRACE GASES IN CHICAGO
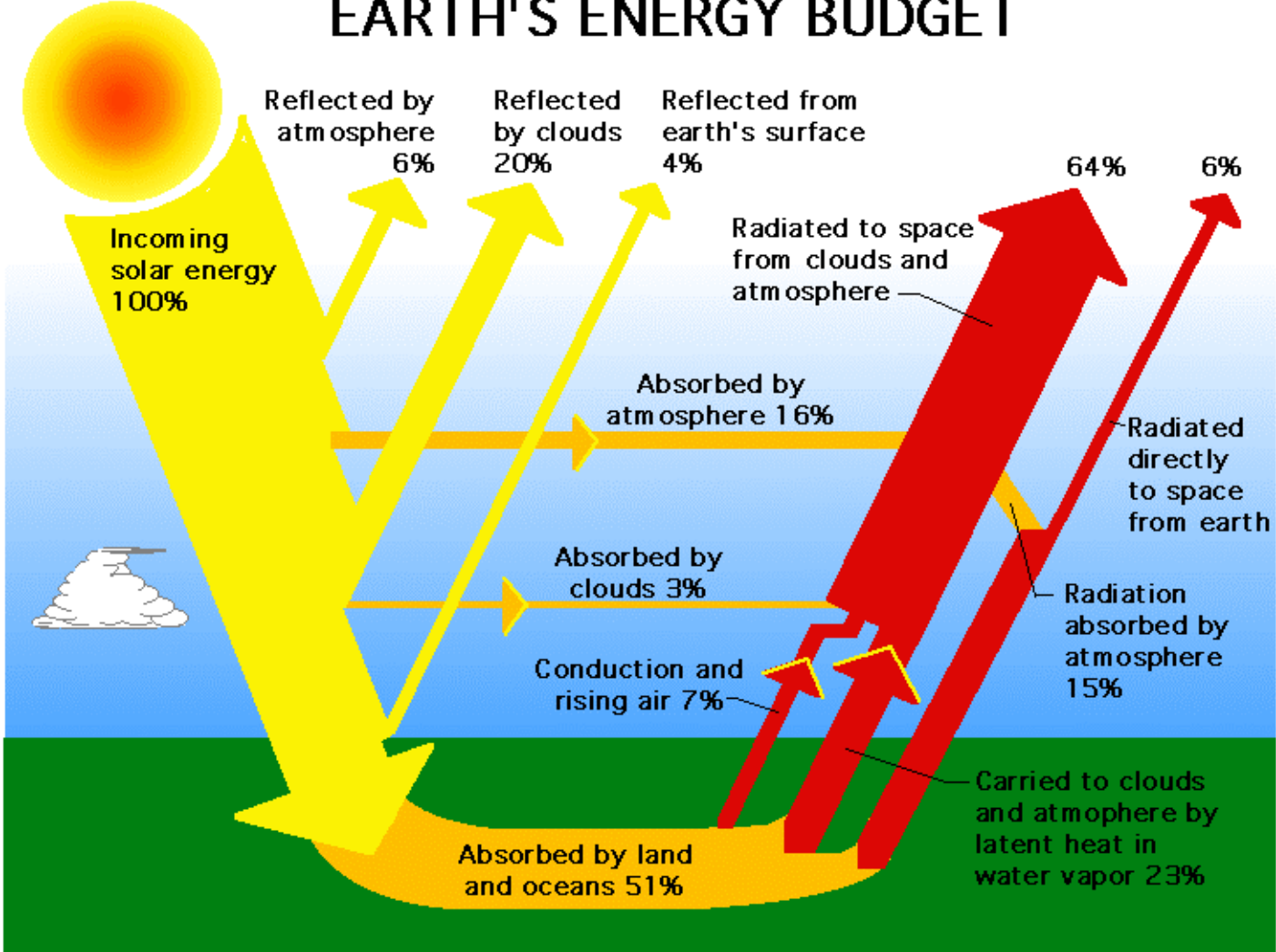
MFRSR

- USES INDEPENDENT INTERFERENCE-FILTER-PHOTODIODE DETECTORS AND THE AUTOMATED ROTATING SHADOWBAND TECHNIQUE TO MAKE SPECTRALLY RESOLVED MEASUREMENTS

- 416.6, 497.1, 613.1, 672.0, 869.3, AND 937.1 NM

- THE MFRSR MEASURES DIRECTLY THE GLOBAL AND DIFFUSE IRRADIANCE AND CALCULATES THE DIRECT COMPONENT

- FROM SUCH MEASUREMENTS, ONE MAY INFER THE ATMOSPHERES OPTICAL DEPTH AT THE WAVELENGTHS MENTIONED ABOVE.

- IN TURN, THESE OPTICAL DEPTHS MAY BE USED TO DERIVE INFORMATION ABOUT THE COLUMN ABUNDANCES OF O_3 AND WATER VAPOR, AS WELL AS AEROSOL AND OTHER ATMOSPHERIC CONSTITUENTS

KEEPING IN MIND THE FOCUS: *TO DEVELOP AN UNDERSTANDING OF THE ROLE OF SOLAR RADIATION AS A DRIVER OF URBAN AIR CHEMISTRY, THERE ARE SOME QUESTIONS THAT NEED ADDRESSING!*

1. HOW MUCH SUN IS ACTUALLY REACHING THE GROUND?

2. WHAT, IF ANYTHING, IS PREVENTING THE PHOTONS FROM REACHING GROUND?

3. WHICH CHEMICAL REACTIONS ARE OCCURRING TO PRODUCE INCREASED LEVELS OF TROPOSPHERIC OZONE?

4. WHAT MECHANISMS OR CHEMICAL REACTIONS ARE CONTROLLING THE SPEED AT WHICH O_3 INCREASES (DECREASES) AT SUNRISE (SUNSET)?

EARTH'S ENERGY BUDGET

Reflected by atmosphere 6%

Reflected by clouds 20%

Reflected from earth's surface 4%

64%

6%

Incoming solar energy 100%

Radiated to space from clouds and atmosphere

Absorbed by atmosphere 16%

Radiated directly to space from earth

Absorbed by clouds 3%

Radiation absorbed by atmosphere 15%

Conduction and rising air 7%

Carried to clouds and atmophere by latent heat in water vapor 23%

Absorbed by land and oceans 51%

Source: http://asd-www.larc.nasa.gov/erbe/components2.gif

OPTICAL DEPTH

OPTICAL DEPTH MEASURES THE ABSORBING AND SCATTERING POWER OF THE ATMOSPHERE.

$$* = \text{Rayleigh} + \text{ozone} + \text{aerosol \& clouds} + \text{water vapor} + \text{NO}$$

TO DETERMINE THE TOTAL OPTICAL DEPTH, WE USE THE LANGLEY METHOD

BEER'S LAW STATES:

$$F_{measured} = F_o \, e^{-\, */\mu o}$$

OR,

$$\ln F_{measured} = *(-1/\mu_o) + \ln F_o$$

NOW THAT WE'VE CALCULATED THE TOD FOR EACH WAVELENGTH, WE CAN BEGIN TO BREAK IT DOWN!

OUR EXAMPLE AGAIN: 416.6 nm

$$_{aerosol} \; = \quad * \; - \quad _{Rayleigh}$$

THE RAYLEIGH OPTICAL DEPTH IS A WELL KNOWN FUNCTION OF WAVELENGTH THAT WE CAN APPLY TO THE ABOVE EQUATION.

$$_{Rayleigh} \; = \; 0.008569 \;^{-4}(1 + 0.0113 \;^{-2} + 0.00013 \;^{-4})$$
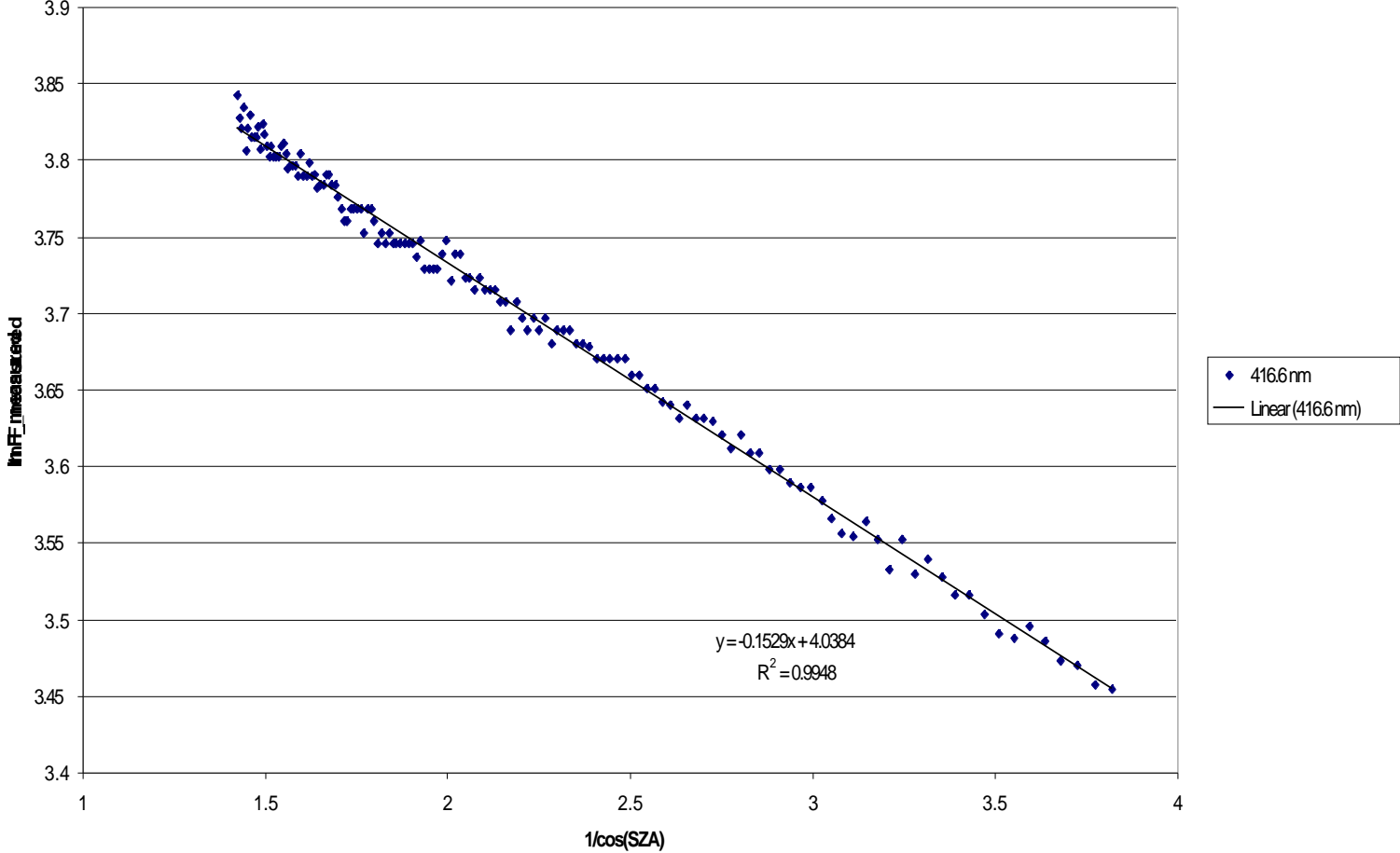
$$_{aerosol} = 0.1529 \; - \; 0.008569(416.6)^{-4}(1 + 0.0113(416.6)^{-2} + 0.00013(416.6)^{-4})$$

$$_{aerosol} \; = \; 0.1529 - 2.8448\text{e-}13$$

$$_{aerosol} \; = \; 0.1529$$
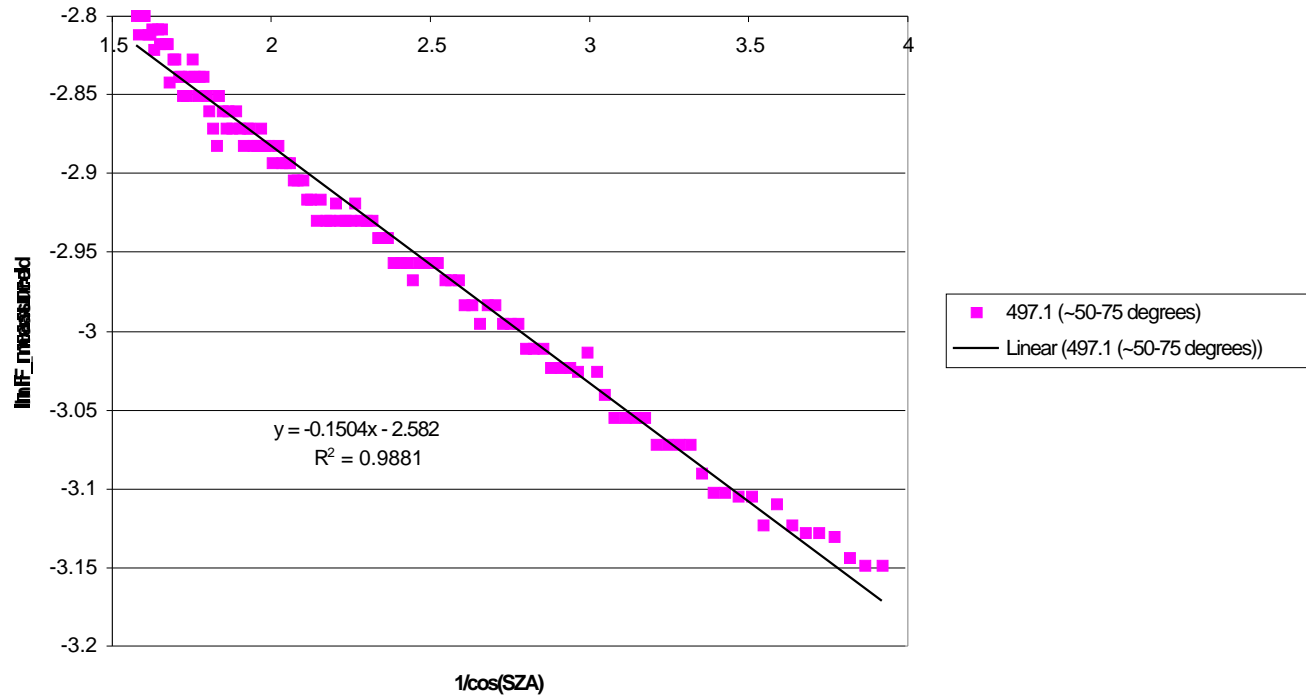
416.6 Direct (~45-75 degrees) 06/15

Chart showing ln FF_measured versus 1/cos(SZA) for 416.6 nm with linear fit:

y = -0.1529x + 4.0384

$R^2 = 0.9948$

Legend:
- 416.6 nm
- Linear (416.6 nm)

X-axis: 1/cos(SZA)

Y-axis: ln FF_measured

497.1 nm 06/15

$y = -0.1504x - 2.582$
$R^2 = 0.9881$

- ■ 497.1 (~50-75 degrees)
- — Linear (497.1 (~50-75 degrees))

x-axis: 1/cos(SZA)

y-axis: lnF_measured

$\text{aerosol} = * - (_{\text{Rayleigh}} + _{\text{ozone}})$

$\text{aerosol} = 0.1504 - (1.403\text{e-}13 + _{\text{ozone}})$

PHOTODISSOCIATION

$$O_3 + h\nu \ (\lambda < 315 \text{ nm}) \rightarrow O_2 + O(^1D) \qquad 1$$

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

OH IS A KEY PRODUCT OF THE PHOTODISSOCIATION OF OZONE FOR ITS HIGH REACTIVITY WITH PRIMARY POLLUTANTS SUCH AS RH & NO

HYDROCARBONS

$$RH = C_NH_{2N+2} \qquad AND\ldots \qquad R = C_NH_{2N+1}$$

SOURCES:

NATURAL: DECIDUOUS TREES

ANTHROPOGENIC: COMBUSTION ENGINES

NITRIC OXIDES

NO

ANTHROPOGENIC SOURCES: COMBUSTION ENGINES

$$OH + RH \quad R + H_2O \qquad\qquad 3$$

WE KNOW THAT WATER VAPOR WILL REACT WITH O(D) TO PRODUCE 2 OHs, BUT WHAT ABOUT THE HYDROCARBON…

$$R + O_2 + M \quad RO_2 + M \qquad\qquad 4$$

$$NO + RO_2 \quad NO_2 + RO \qquad\qquad 5$$

$$NO_2 + hv(\quad < 420 \text{ nm}) \quad NO + O \qquad\qquad 6$$
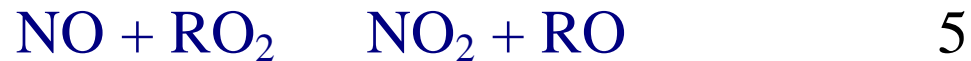
THE EXTRA OXYGEN ATOM FINDS ONE OF THE MANY O_2 ALREADY IN THE ATMOSPHERE AND PRODUCES ANOTHER OZONE MOLECULE

$$O + O_2 + M \rightarrow O_3 + M \qquad 7$$

LEFT OVER FROM EQUATION 5….

$$RO + O_2 \rightarrow R\ O + HO_2 \qquad 8$$

AND THE NO FROM THE PHOTODISSOCIATION OF NO_2…

$$NO + HO_2 \rightarrow NO_2 + OH \qquad 9$$

AGAIN THE PHOTODISSOCIATION OF NO_2…

$$NO_2 + h\nu(\ < 420 \text{ nm}) \rightarrow NO + O \qquad 6$$

PRODUCES MORE OZONE!!!

$$O + O_2 + M \rightarrow O_3 + M \qquad 7$$

ACKNOWLEDGEMENTS