12.335/12.835 EXPERIMENTAL ATMOSPHERIC CHEMISTRY, FALL 2014

TOPIC 1
ATMOSPHERIC PHOTOCHEMISTRY and AIR POLLUTION

MODELING GASES AND AEROSOLS

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GASEOUS CHEMICAL RATE EXPRESSIONS IN MODELS

Consider the simplified ozone layer chemical reactions:

$$O_2 + h\nu \xrightarrow{J_1} O + O$$

$$O + O_2 + M \xrightarrow{l} O_3 + M$$

$$O_3 + h\nu \xrightarrow{J_1} O_2 + O$$

$$O + O_3 \xrightarrow{k} O_2 + O_2 \quad \text{(catalysed!)}$$

The relevant chemical reaction rates are expressed using <u>first</u> (J_i), <u>second</u> (k) and <u>third</u> (l) <u>order rate constants</u>:

$$\frac{d[i]}{dt}\left(\frac{\text{molecule}}{\text{cm}^3\,\text{sec}}\right) = \begin{cases} -J_i[i] & \left(\text{sec}^{-1}\cdot\text{molecule}\cdot\text{cm}^{-3}\right) \\ -k_{ij}[i][j] & \left(\text{sec}^{-1}\cdot\text{cm}^3\cdot\text{molecule}^{-1}\cdot\left(\text{molecule}\cdot\text{cm}^{-3}\right)^2\right) \\ -l_{ijM}[i][j][M] & \left(\text{sec}^{-1}\cdot\text{cm}^6\cdot\text{molecule}^{-2}\cdot\left(\text{molecule}\cdot\text{cm}^{-3}\right)^3\right) \end{cases}$$

The <u>chemical rate constants</u> (k,l) are measured in the laboratory.

Some typical expressions for their dependence on temperature (T) and density $([M])$ are:

$$k = A\exp\left(-\frac{B}{T}\right) \qquad \text{(measure A and B)}$$

$$l = l\left(T_{ref},[M]\right)\left(\frac{T}{T_{ref}}\right)^{-\alpha} \qquad \left(\text{measure } l\left(T_{ref},[M]\right) \text{ and } \alpha\right)$$

The <u>rate constant for photodissociation</u> is calculated in a non-scattering atmosphere using:

$$J_i = \int_{\lambda_1}^{\lambda_2} \sigma_i(\lambda)\phi_i(\lambda)I(\infty)\exp\left[-\sum_{j=1}^{N}\sigma_j(\lambda)\frac{M_j(z)}{\cos\theta}\right]d\lambda$$

where

$\sigma_i(\lambda) =$ absorption cross-section at wavelength λ $\left(\text{cm}^2 \cdot \text{molecule}^{-1}\right)$

$\phi_i(\lambda) =$ photodissociation yeild (dimensionless)

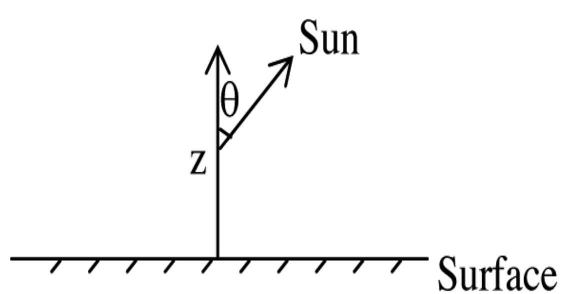
$\lambda_2 - \lambda_1 =$ width of electronic absorption band

$I(\infty) =$ solar photon flux at altitude $z = \infty$ $\left(\text{photon} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}\right)$

$N =$ number of gases (j) absorbing at wavelength λ

$M_j(z) =$ molecules of j per unit area above z $\left(\text{molecule} \cdot \text{cm}^{-2}\right)$

$\theta =$ solar zenith angle



Summary of gaseous chemical rate expressions for production and loss of species i including surface sources and sinks:

(1) $J_i[i]$ where J_i can be derived from UV measurements

(1) $k_{ij}[i][j]$ where k_{ij} is given

(1) $l_{ijm}[i][j][m]$ where l_{ijm} is given

(2) $\Phi_{i\ sink}^{surface} = w_{dep}[i]$ where w_{dep} is given

(1) $\Phi_{i\ emissions}^{surface}$ either given or estimated from model-measurement comparison

AEROSOL PHYSICAL RATE EXPRESSIONS IN MODELS

$\frac{dN_k}{dt}$ = Rate of change of aerosol number density

(with size between k and $k + dk$)

= Emission (surface and in situ)

+ Condensation of precursor gases

+ Complete evaporation of water from cloud droplets

+ Coagulation of smaller aerosols

+ Fragmentation of larger aerosols

± Sedimentation (net into & out of layer)

- Coagulation with any other aerosols

- Coalescence (into water droplets)

- Fragmentation by collisions with other aerosols

- Deposition (all surfaces)

- Rainout (to surface)

- "Activation" to form cloud droplets

$$\frac{dN_{coag}}{dt} = -k_{coag} N^* N$$

$$\frac{dN_{coal}}{dt} = -k_{coal} N^{**} N$$

$$\frac{dN_{dep}}{dt} = -v_{dep} N$$

$$\frac{dN_{rain}}{dt} = -\frac{N}{\tau_{rain}}$$

etc.

DIAGNOSTIC EQUATIONS ASSUME A PHOTOCHEMICAL STEADY STATE (PSSA)

Recall PSSA equations ignore influence of meteorology so valid only when wind speed u ~ 0

In PSSA: rate of loss (L_i) = rate of production (P_i)
e. g. for the ozone chemical reaction set including NOx and HOx chemistry:

(1) $NO + O_3 \rightarrow NO_2 + O_2$
(2) $NO_2 + h\nu \rightarrow NO + O$
(3) $O + O_2 + M \rightarrow O_3 + M$
(4) $O_3 + h\nu \rightarrow O_2 + O$
(5) $NO_2 + OH + M \rightarrow HNO_3 + M$
(6) $OH + CO \rightarrow H + CO_2$
(7) $H + O_2 + M \rightarrow HO_2 + M$
(8) $HO_2 + NO \rightarrow OH + NO_2$

We have for NO, HO_2, H and O concentrations:

$k_1[O_3][NO] + k_8[HO_2][NO] = J_2[NO_2]$
i.e. $[NO_2]/[NO] = (k_1[O_3] + k_8[HO_2])/J_2$

$k_8[HO_2][NO] = l_7[H][O_2][M]$
i.e. $[HO_2]/[H] = l_7[O_2][M]/(k_8[NO])$

$l_7[H][O_2][M] = k_6[CO][OH]$
i.e. $[H]/[OH] = k_6[CO]/(l_7[O_2][M])$

$l_3[O][O_2][M] = J_2[NO_2] + J_4[O_3]$
i.e. $[O]/[O_3] = (J_2[NO_2]/[O_3] + J_4)/(l_3[O_2][M])$

Recall the PSSA analytical solution when we consider NOx but not HOx chemistry:

$$[O_3]^2 + \left([NO]_0 - [O_3]_0 + \frac{k_1}{k_3}\right)[O_3] - \frac{k_1}{k_3}\left([O_3]_0 + [NO_2]_0\right) = 0$$

$$[O_3] = -\frac{1}{2}\left([NO]_0 - [O_3]_0 + \frac{k_1}{k_3}\right) + \frac{1}{2}\left[\left([NO]_0 - [O_3]_0 + \frac{k_1}{k_3}\right)^2 + 4\frac{k_1}{k_3}\left([O_3]_0 + [NO_2]_0\right)\right]^{\frac{1}{2}}$$

$$[O_3] = \frac{k_1[NO_2]}{k_3[NO]}$$

$$[NO_2] = [NO_2]_0 + [O_3]_0 - [O_3]$$

PROGNOSTIC (CONTINUITY) EQUATIONS TAKE ACCOUNT OF PROGNOSTIC CHEMISTRY AND TRANSPORT BY WINDS

$$\frac{\partial[i]}{\partial t} = \left[\frac{d[i]}{dt}\right]_{chem} - \frac{\partial}{\partial x}(u[i]) - \frac{\partial}{\partial y}(v[i]) - \frac{\partial}{\partial z}(w[i])$$

The local change (rate of accumulation) of i in the box

Actual production or destruction of i within the box

Change in [i] due to loss to downstream boxes or arrival from an upstream box (called advection or convection)

HYBRID CHEMICAL KINETIC EQUATIONS

(1) Use prognostic equations, ($d[i]/dt)_{chemistry} = P_i - L_i$) for long lived species like [O_x] (=[O] + [O_3]) and [NO_x](=[NO + [NO_2])

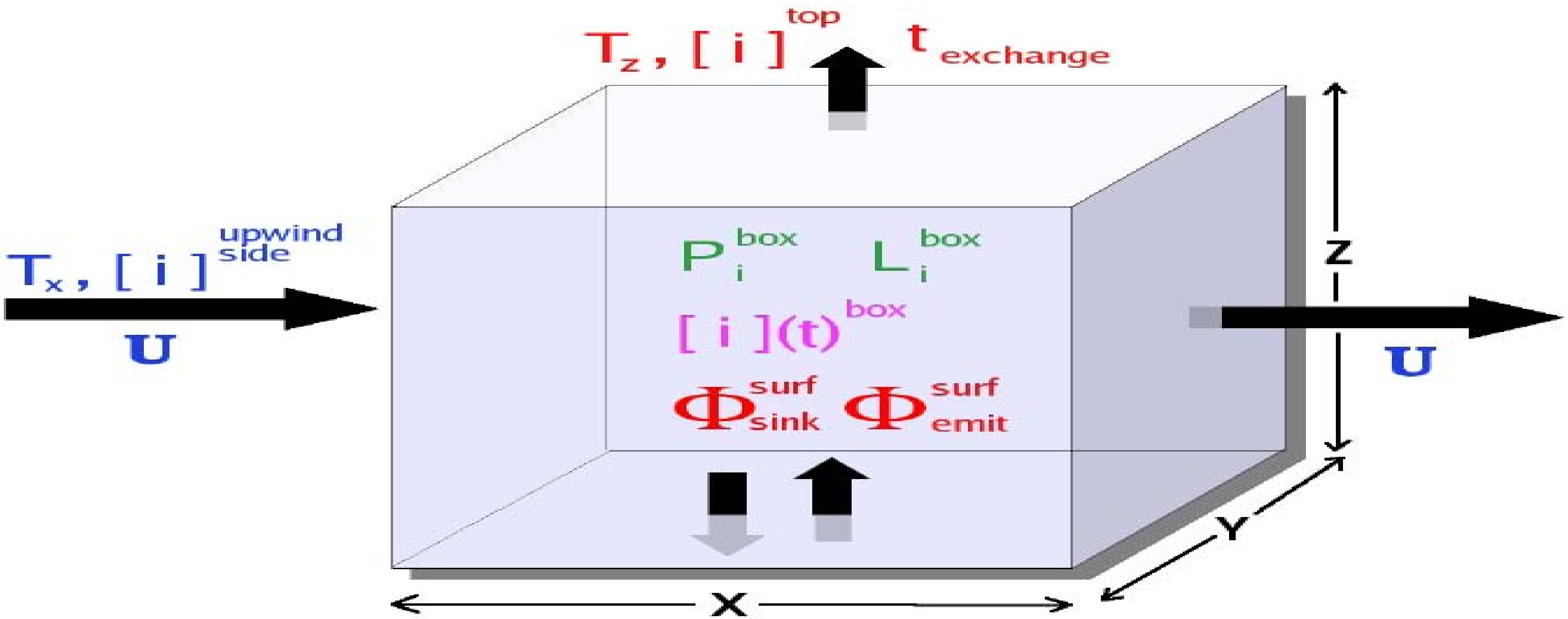
(2) Use diagnostic (steady state) equations, $P_i = L_i$ for short lived species like O, NO, H and HO_2 to provide the ratios [O]/[O_3], [NO_2]/[NO], [HO_2]/[H] and [H]/[OH]

(3) Assume [HO_x] = [H] + [OH] + [HO_2] ~ [HO_2] is given

(4) Use observed values for [CO]

(5) Use lowest observed [NO_x] and [O_3] as boundary conditions for NO_x and O_x

A SIMPLE PHOTOCHEMICAL BOX MODEL to simulate time-varying concentrations of trace gases and aerosols using the PROGNOSTIC CONTINUITY EQUATION



$$\frac{d[i]^{box}}{dt} = P_i - L_i + \frac{u}{X}\left([i]^{upwind} - [i]^{box}\right) + ([i]^{top} - [i]^{box})/\tau_{exchange} + (\Phi^{surface}_{i,emissions} - \Phi^{surface}_{i,\sin k})/Z$$

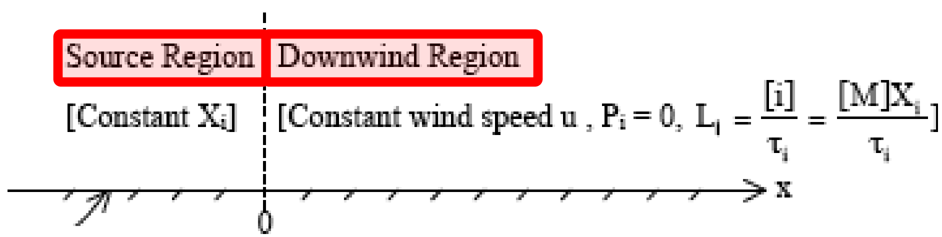
EXAMPLE: ANALYTICAL SOLUTION TO THE CONTINUITY EQUATION RELATING MOLE FRACTION (X_i) OF i=NO (as a function of distance (x) from a source region) ASSUMING A CONSTANT HORIZONTAL WIND SPEED (u), A PHOTOCHEMICAL STEADY-STATE, A ONE DIMENSIONAL (x AXIS) MODEL and LOSS DUE TO NO + O_3 → NO_2 + O_2 WITH $[O_3]$ >> [NO]

$\boxed{STEADY\text{-}STATE:}$

$$\frac{d[i]^{downwind}}{dt} = 0 = P_i - L_i - u\frac{d[i]}{dx} = P_i - L_i - [M]u\frac{dX_i}{dx}$$

$$(X_i = [i]/[M] = mole\_fraction)$$

Define τ(NO) = 1/(k[O_3]) where k is rate constant for reaction of NO (e.g. from engine exhausts) with ozone



$$P_i - L_i = 0 - [M]\frac{X_i}{\tau_i}$$

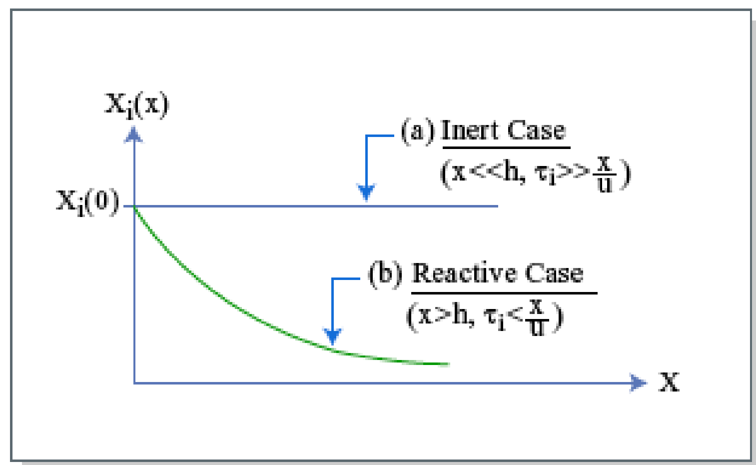
$$= [M]u\frac{dX_i}{dx}$$

$$\text{i.e.}\quad \frac{d\ln X_i}{dx} = -\frac{1}{u\tau_i}$$

$$\boxed{\text{i.e. } X_i(x) = X_i(0)\exp\left(-\frac{x}{u\tau_i}\right)}$$

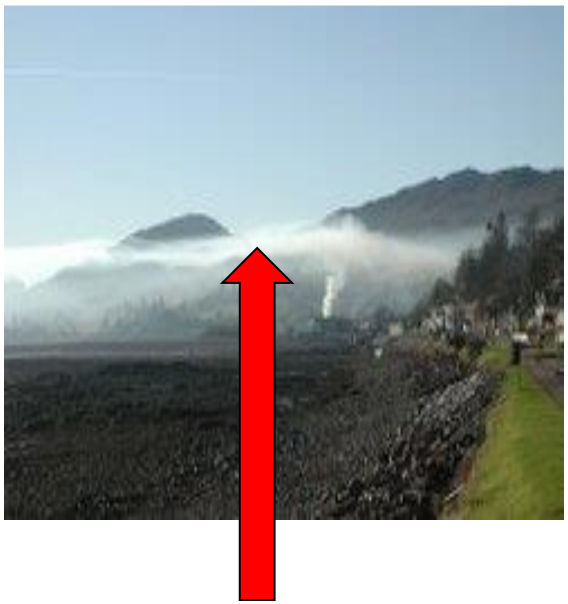
[chemical (e-folding) distance, $h = u\tau_i$]

[advection time = x/u]



INCORPORATING METEOROLOGY IN THE BOX MODEL

1. USE THE u MEASUREMENTS TO ALIGN THE MODEL x AXIS AND USE IN THE BOX MODEL ADVECTION TERMS.
2. USE THE T & u MEASUREMENTS TO CALCULATE A RICHARDSON NUMBER TO HELP CHOOSE SUITABLE $t_{exchange}$ VALUES.



T OP OF BOUNDARY LAYER

POTENTIAL TEMPERATURE (θ)

$$\theta = T\left(\frac{P_0}{P}\right)^{R/C_p}$$ where T = absolute temperature, P = pressure,

R = gas constant, and

C_p = heat capacity at constant pressure P

RICHARDSON NUMBER (Ri)

$$Ri = g\frac{\partial \ln\theta}{\partial z}\left[\left(\frac{\partial u}{\partial z}\right)^2 + \left(\frac{\partial v}{\partial z}\right)^2\right]^{-1}$$

$Ri > 0 \rightarrow$ stable (if $Ri > \frac{1}{4}$ get laminar flow)

$Ri < 0 \rightarrow$ unstable (if $|Ri| \leq 1$ then forced convection

and if $|Ri| > 1$ then free convection)

$Ri = 0 \rightarrow$ neutral

MOIST POTENTIAL TEMPERATURE (θ_E)

$$\theta_E = \theta \exp\left(\frac{Lw_s}{C_p T}\right)$$ where w_s = water vapor density,

and L = latent heat of vaporization

$$\frac{\partial \theta_E}{\partial z} \leq 0 \rightarrow \text{moist convective instability}$$

3. USE TEMPERATURE SOUNDINGS OR HAZE LAYER HEIGHT TO ESTIMATE Z

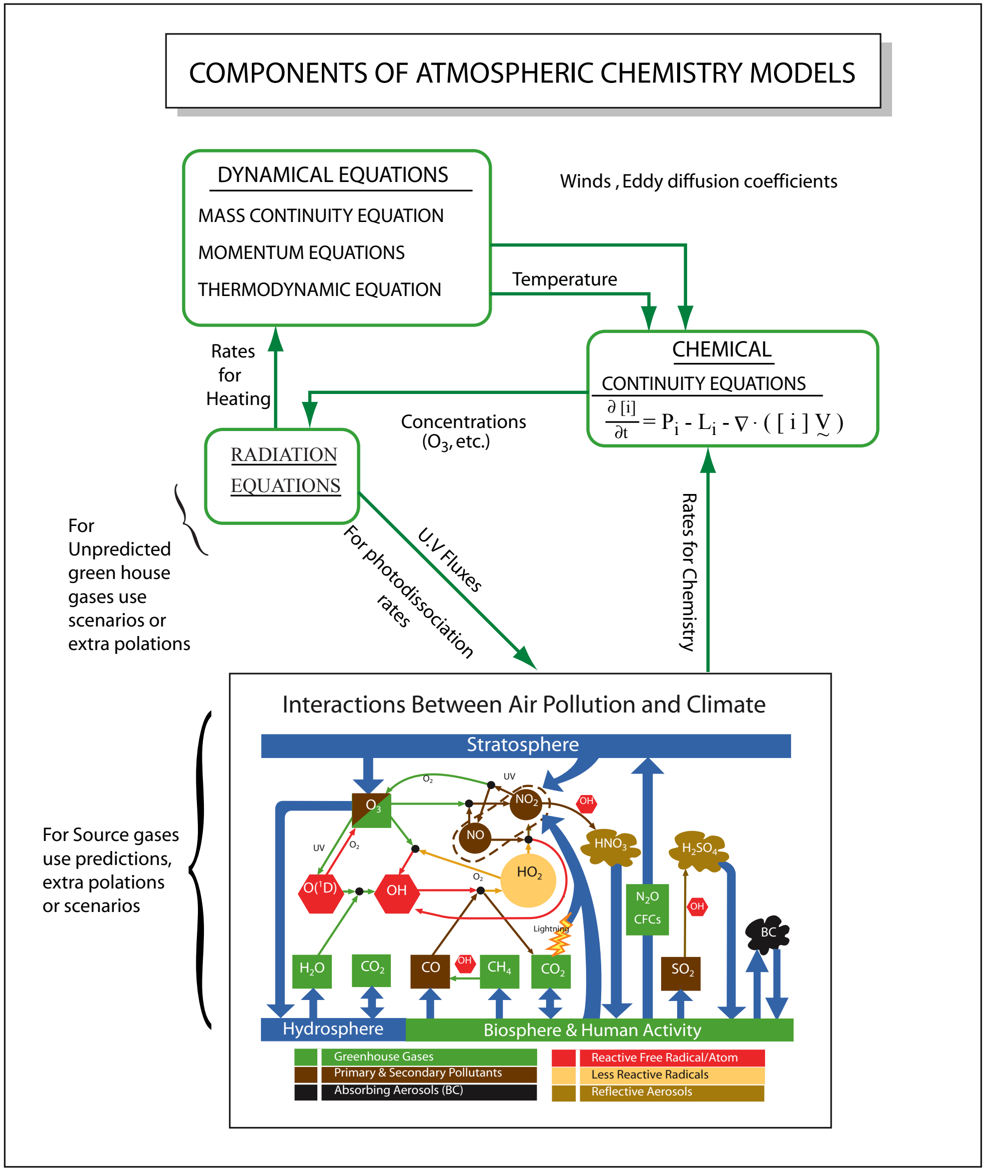


Figure by MIT OpenCourseWare.

TRANSPORT, CHEMISTRY AND RADIATION COMPONENTS IN COMPLEX 3D MODELS

UV fluxes for photodissociation rates

For all species involving OH in their chemistry need to include:

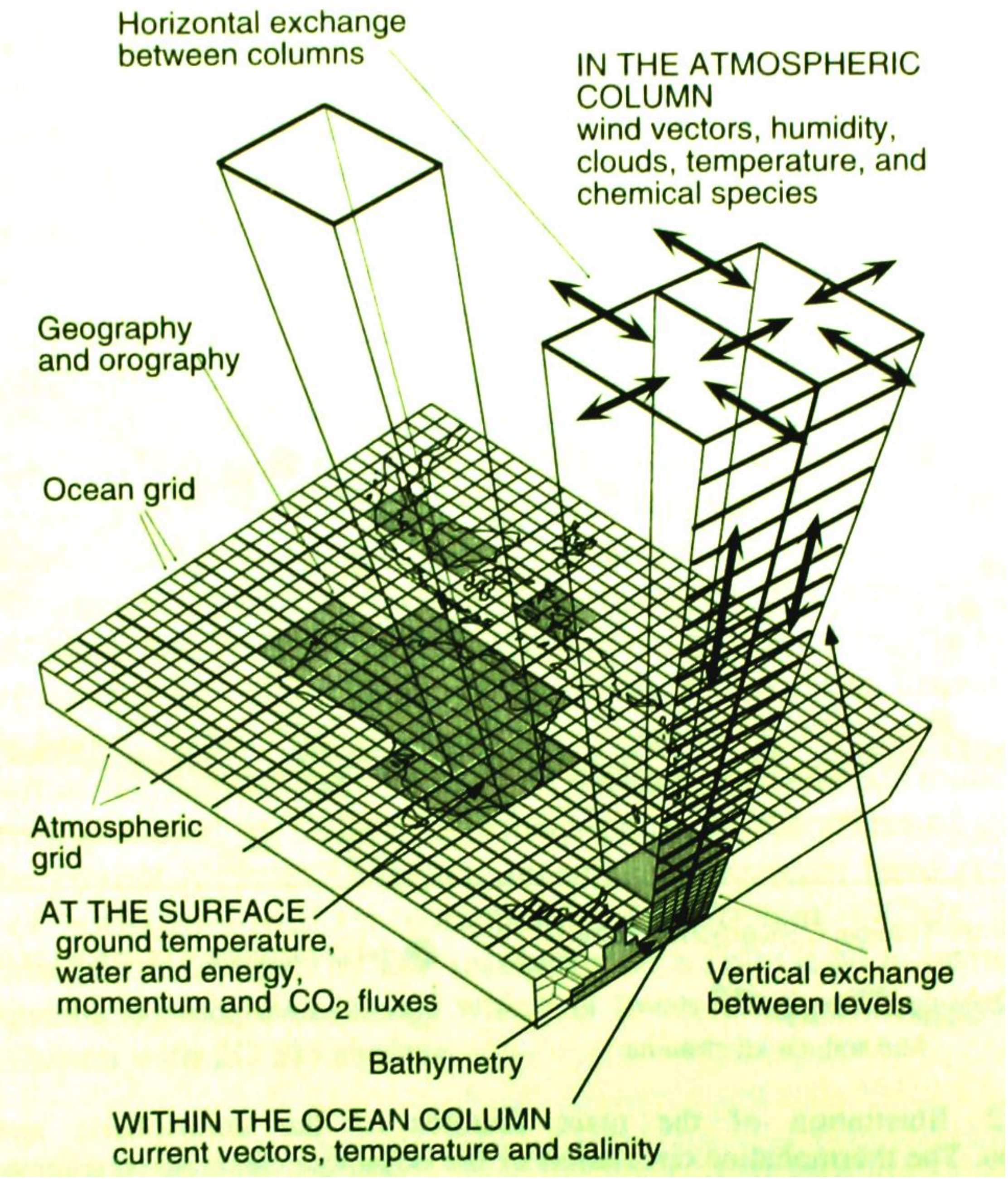
1. $O_3, O_2, O(^1D)$
2. H, OH, HO_2, H_2O_2, with latter 3 in gas and aqueous phase
3. $NO, NO_2, NO_3, N_2O_5, HNO_3$ with latter 2 in gas and aqueous phase
4. $CH_4, CH_3, CH_3O_2, CH_3O, CH_3O_2H, CH_2O, CHO, CO$ (also selected heavier hydrocarbons such as isoprene and terpenes in forested areas and anthropogenic hydrocarbons in urban areas)

The spatial grid

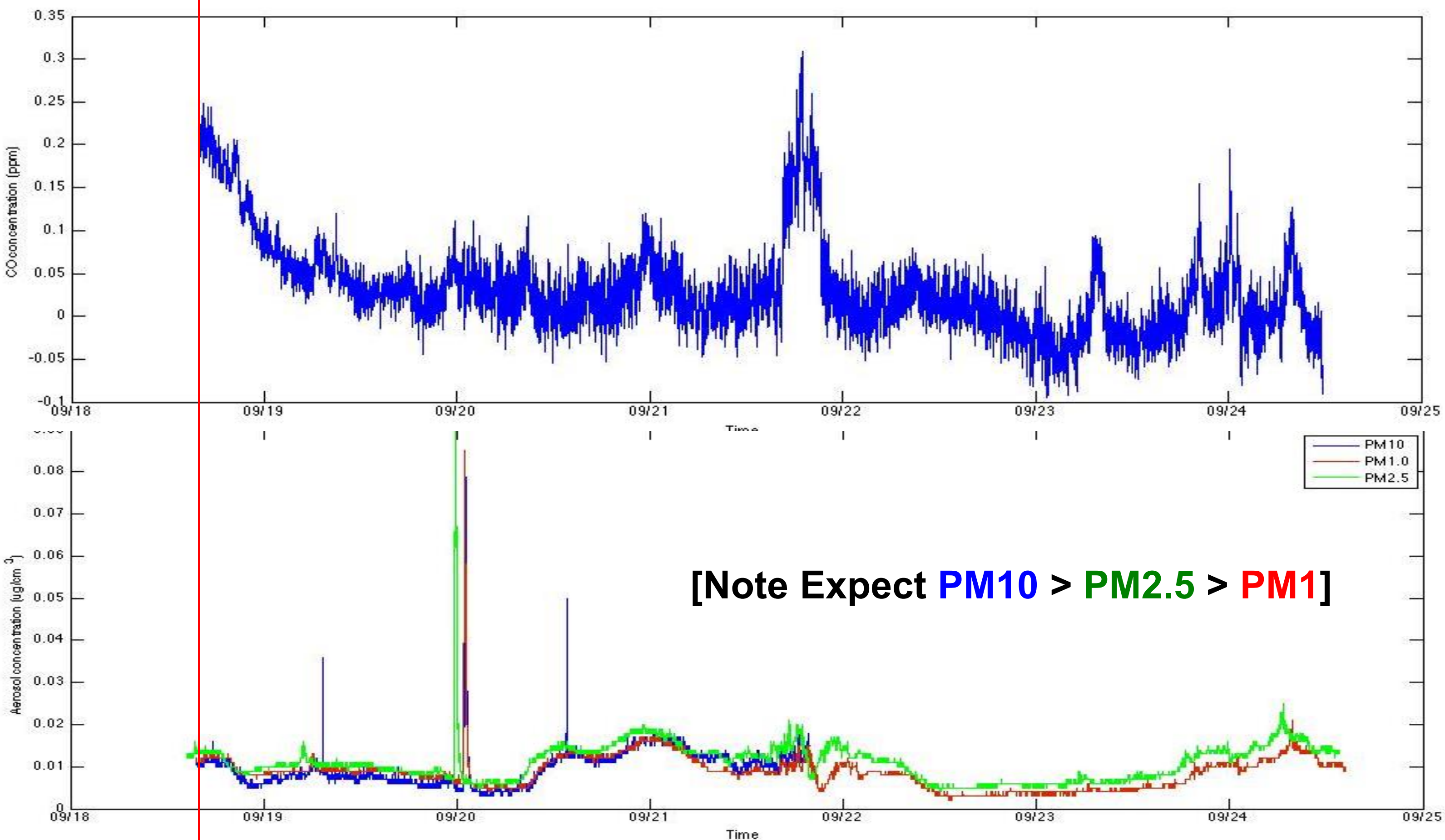
We divide the earth's atmosphere into a finite number of boxes (grid cells).

Assume that each variable has the same value throughout the box.

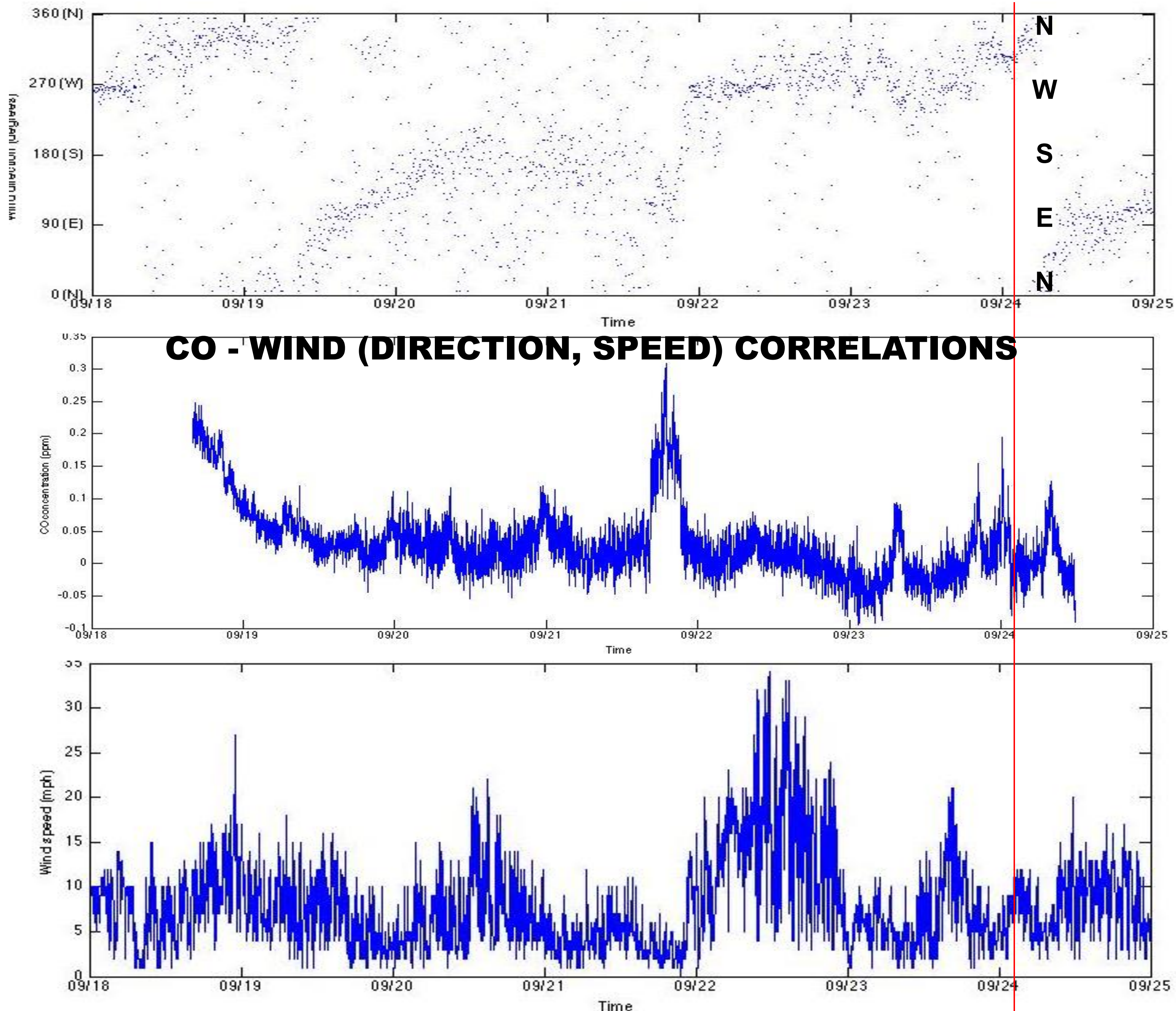
Write a budget for each each box, defining the changes within the box, and the flows between the boxes.



INTERSPECIES (CO-PM) CORRELATIONS

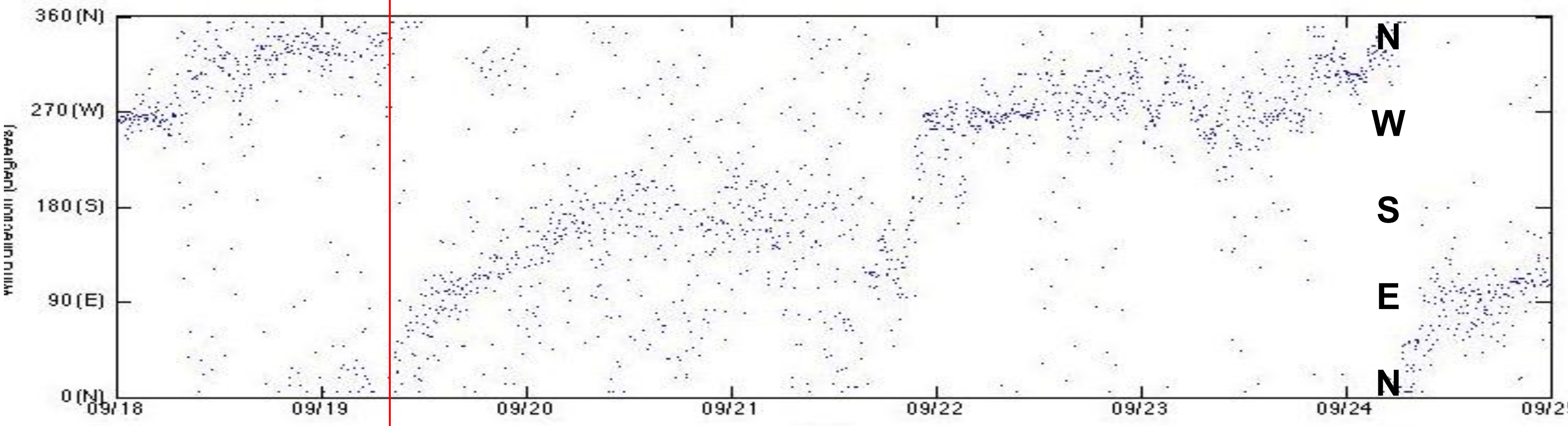


CO - WIND (DIRECTION, SPEED) CORRELATIONS

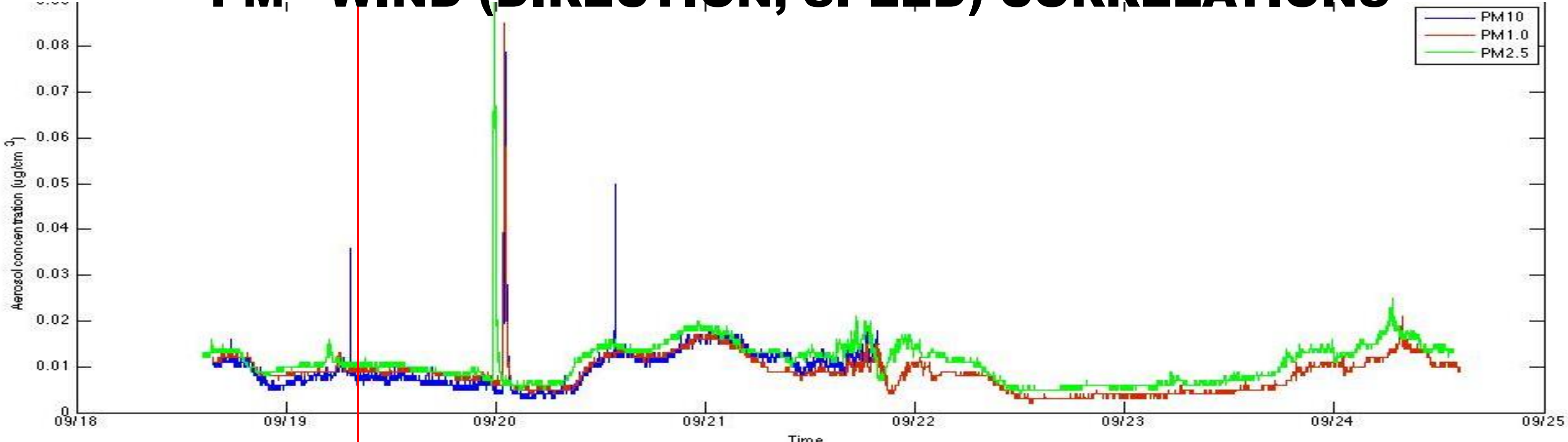


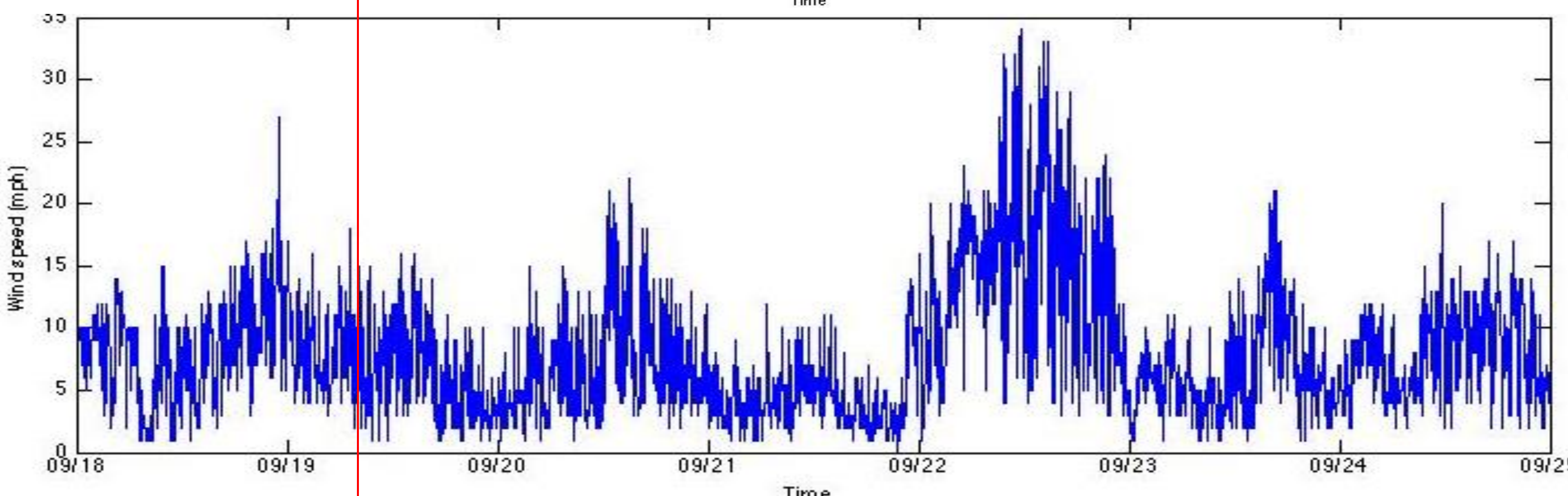
USE i-PHONE COMPASS TO INTEPRET RE BLDG 54

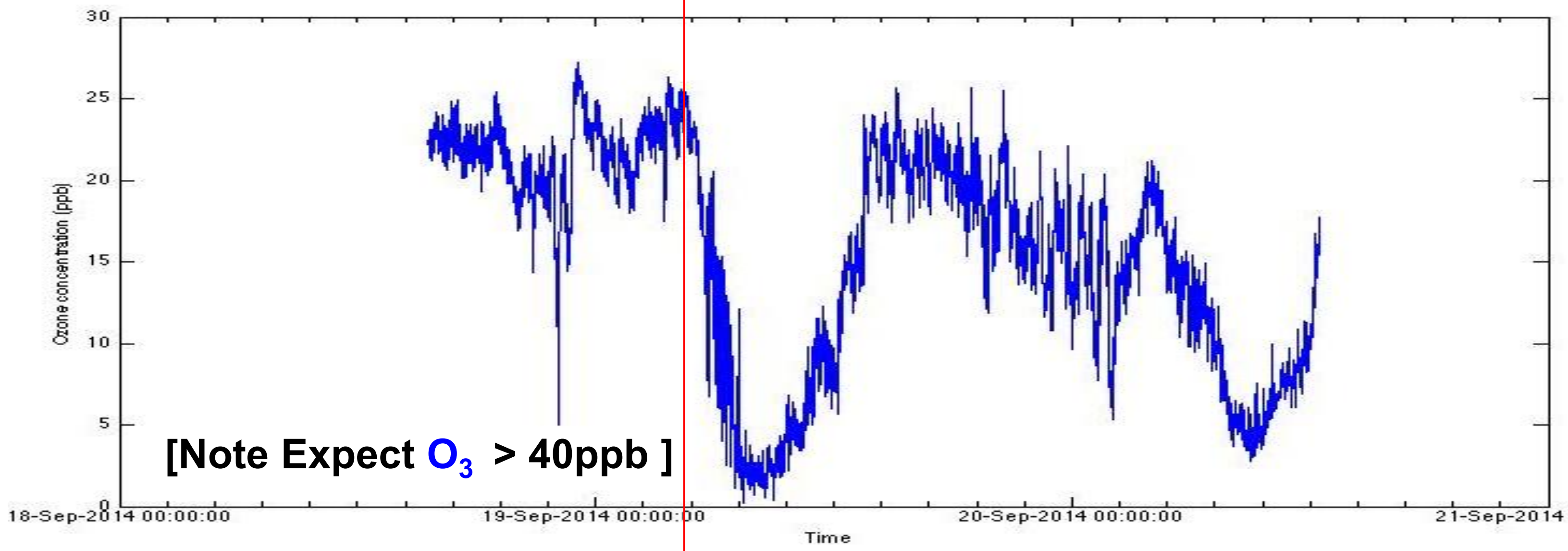
PM - WIND (DIRECTION, SPEED) CORRELATIONS



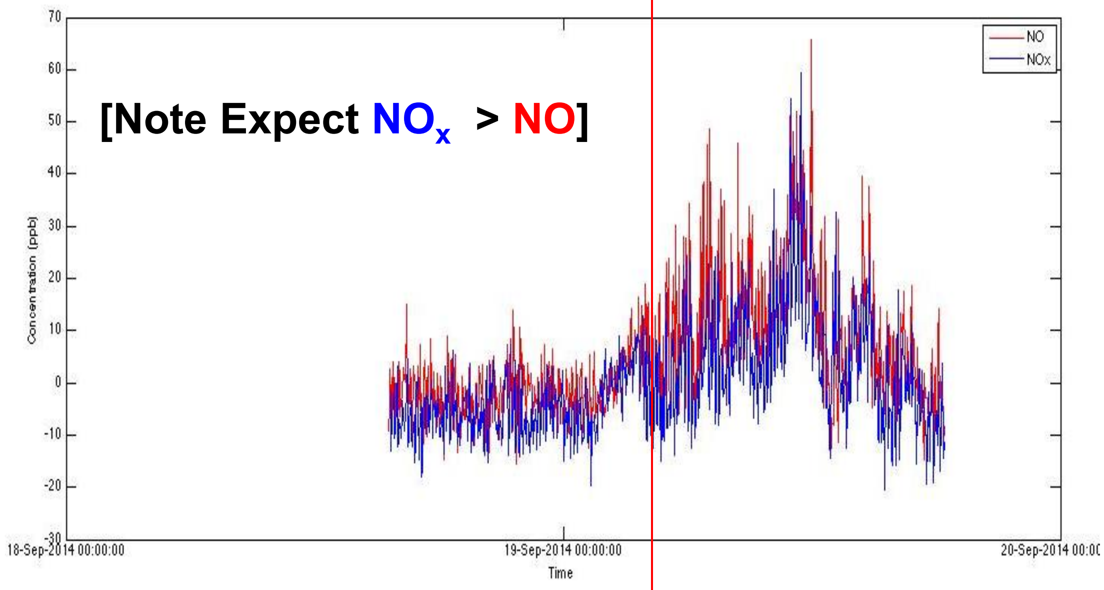
USE i-PHONE COMPASS TO INTEPRETE BLDG 54



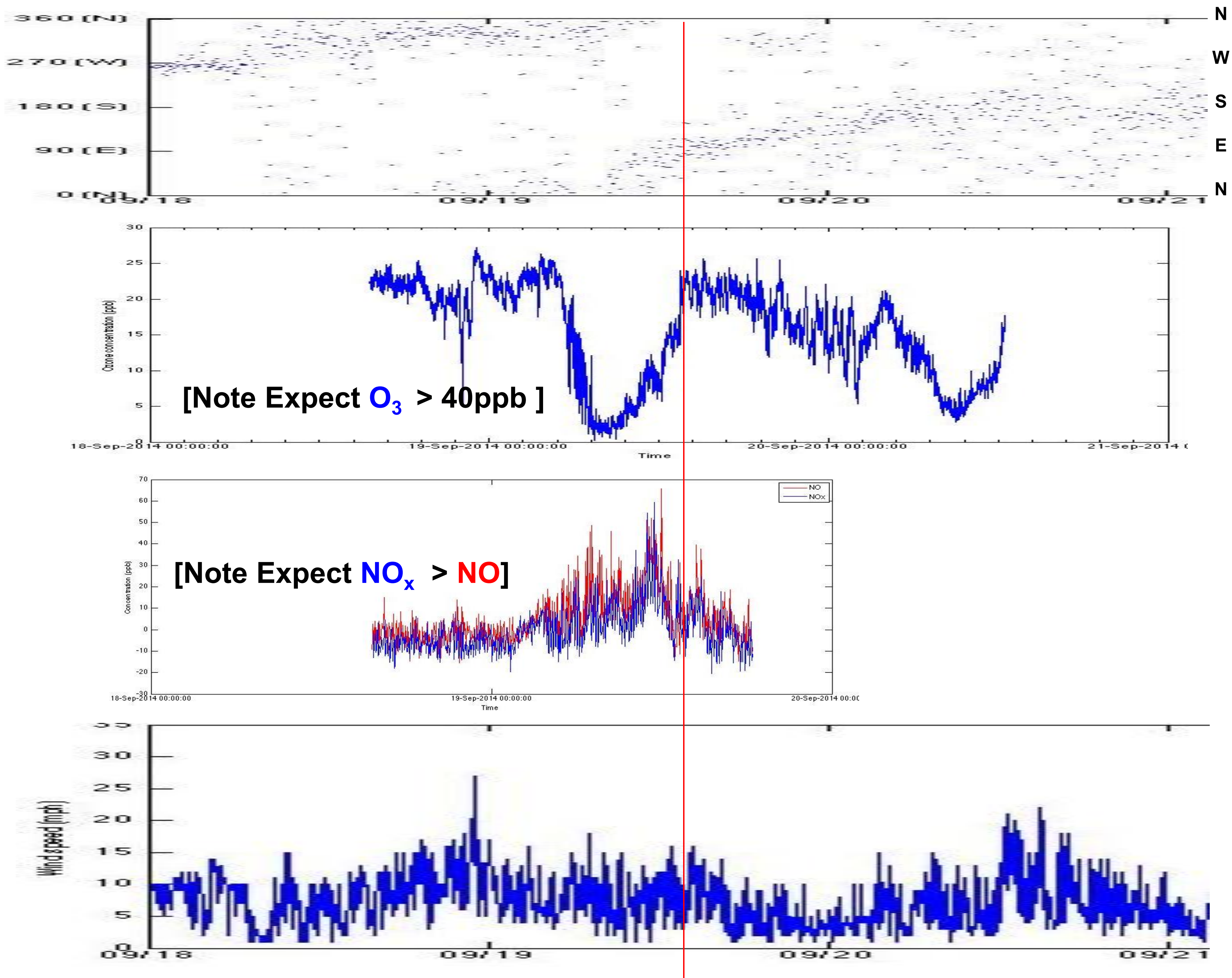




30
25
20
15
10
5
0
Ozone concentration (ppb)
18-Sep-2014 00:00:00
19-Sep-2014 00:00:00
20-Sep-2014 00:00:00
Time
[Note Expect O_3 > 40ppb]



70
60
50
40
30
20
10
0
-10
-20
-30
Concentration (ppb)
18-Sep-2014 00:00:00
19-Sep-2014 00:00:00
Time
NO
NOx
[Note Expect NO_x > NO]


360 (N)
270 (W)
180 (S)
90 (E)
0 (N)
N
W
S
E
N
09/18
09/19
09/20
09/21
Ozone concentration (ppb)
18-Sep-2014 00:00:00
19-Sep-2014 00:00:00
20-Sep-2014 00:00:00
Time
[Note Expect O_3 > 40ppb]
NO
NOx
Concentration (ppb)
[Note Expect NO_x > NO]
Wind speed (mph)

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