Atmospheric Pollution

Lecture 8

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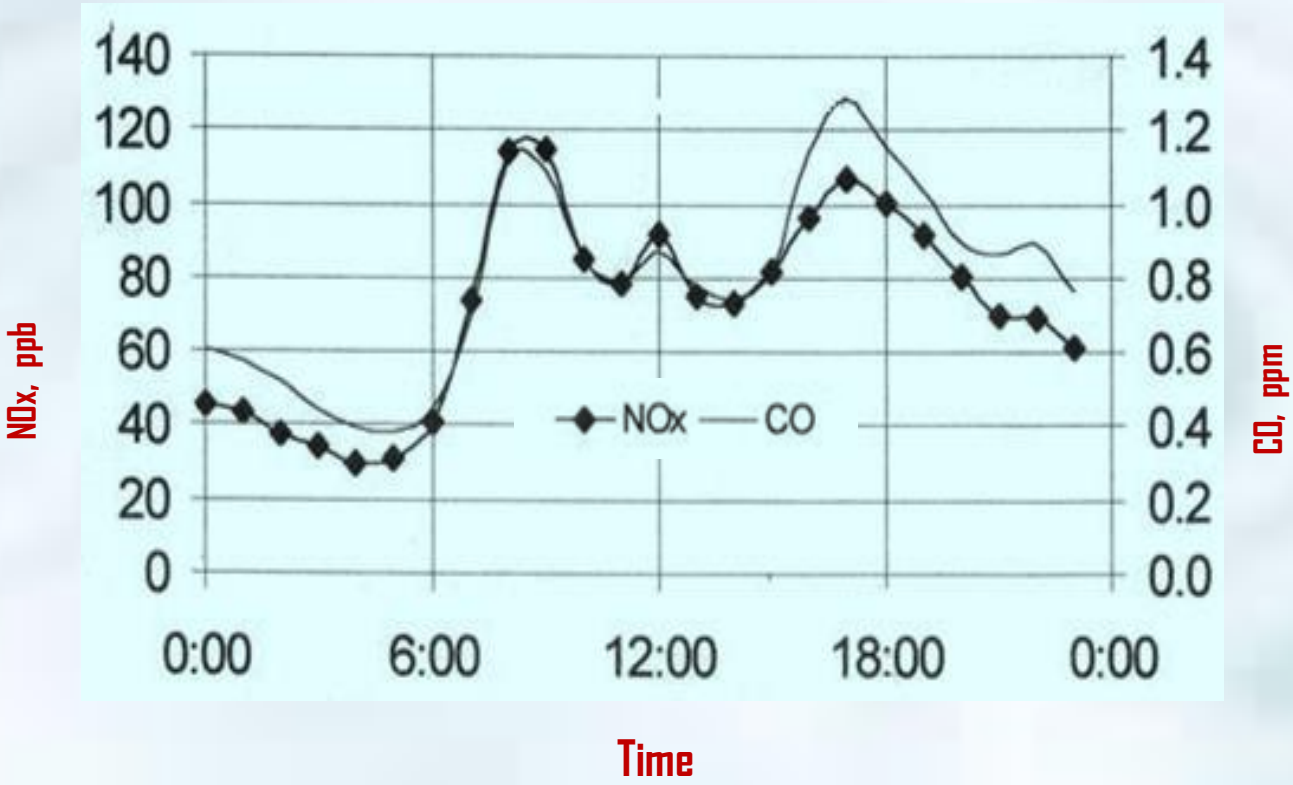
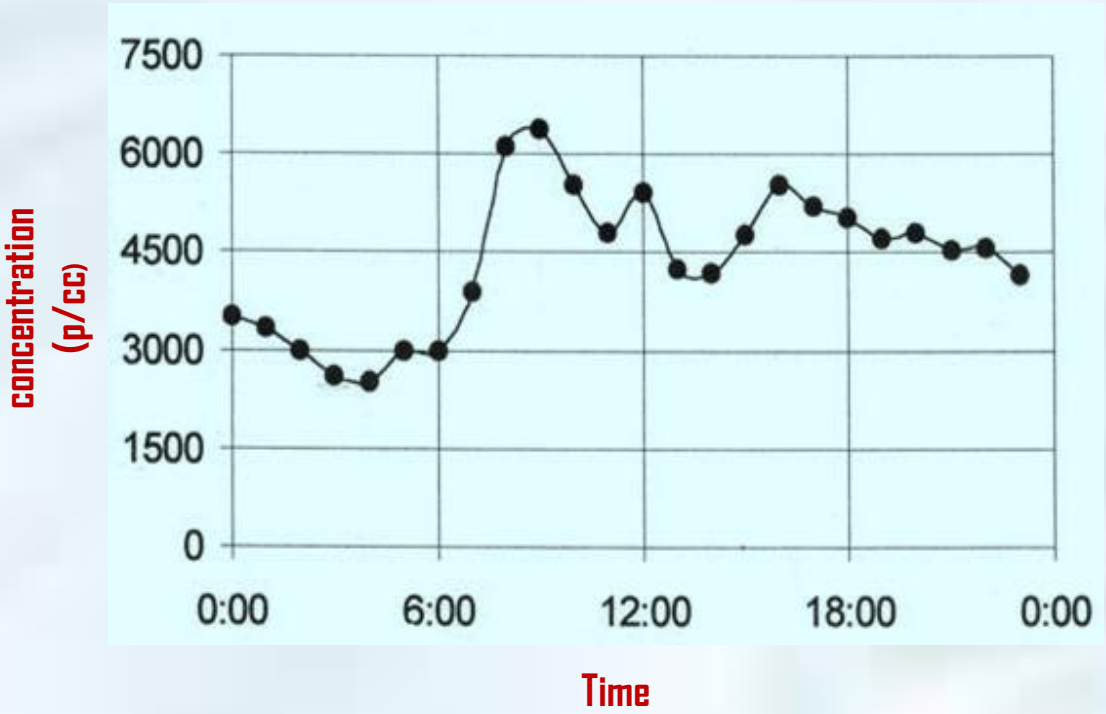
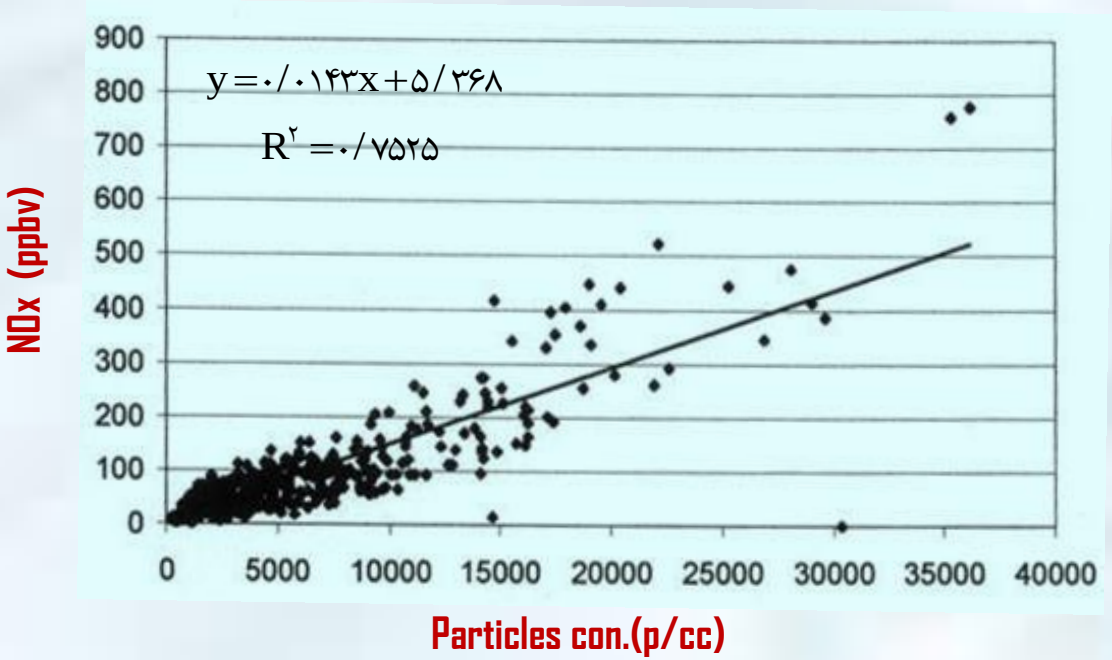
Hourly averaged NOx and CO concentrations from Manchester City Centre



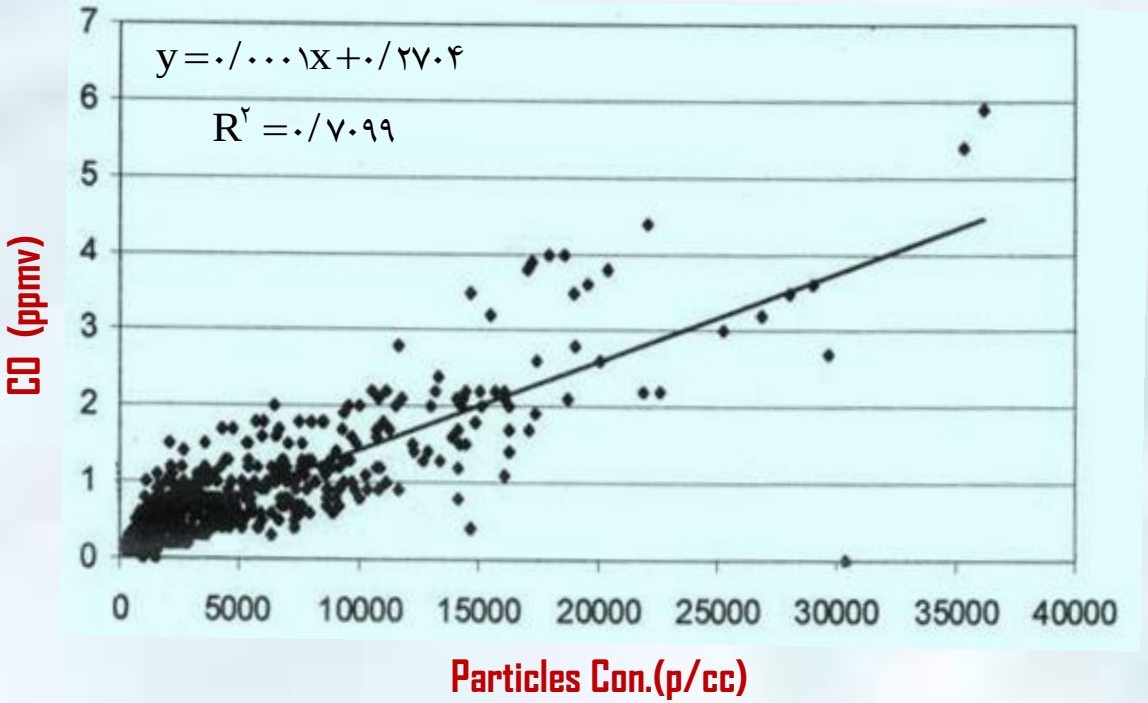
Accumulation Mode (100 - 500 nm)



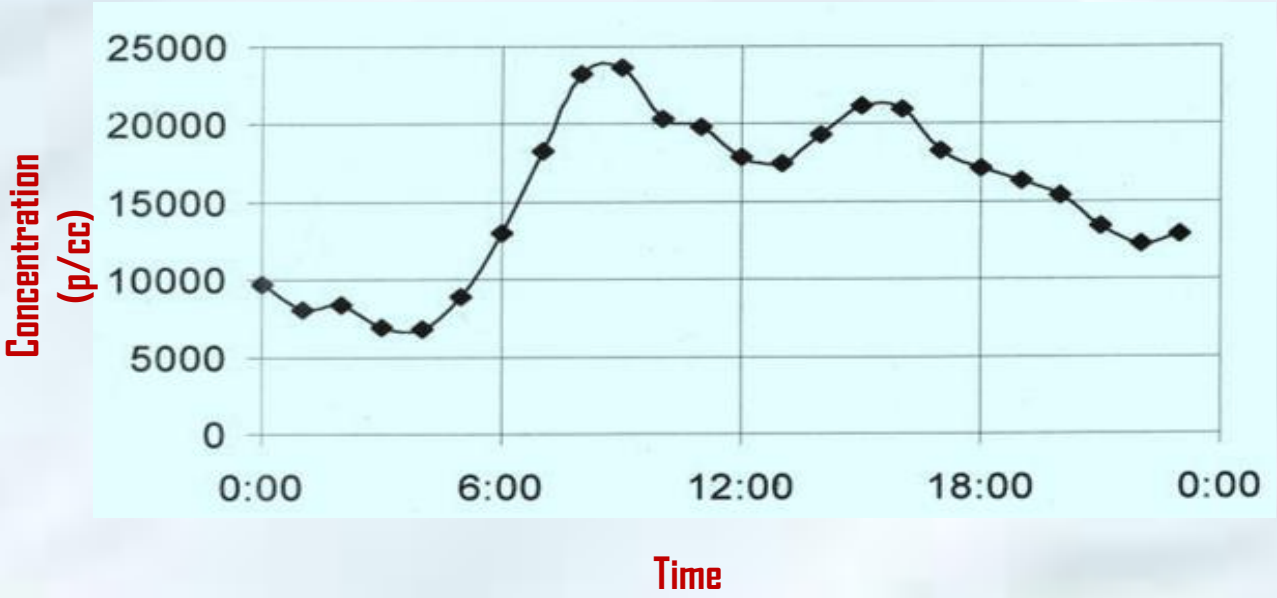
Accumulation Mode (100 - 470 nm)



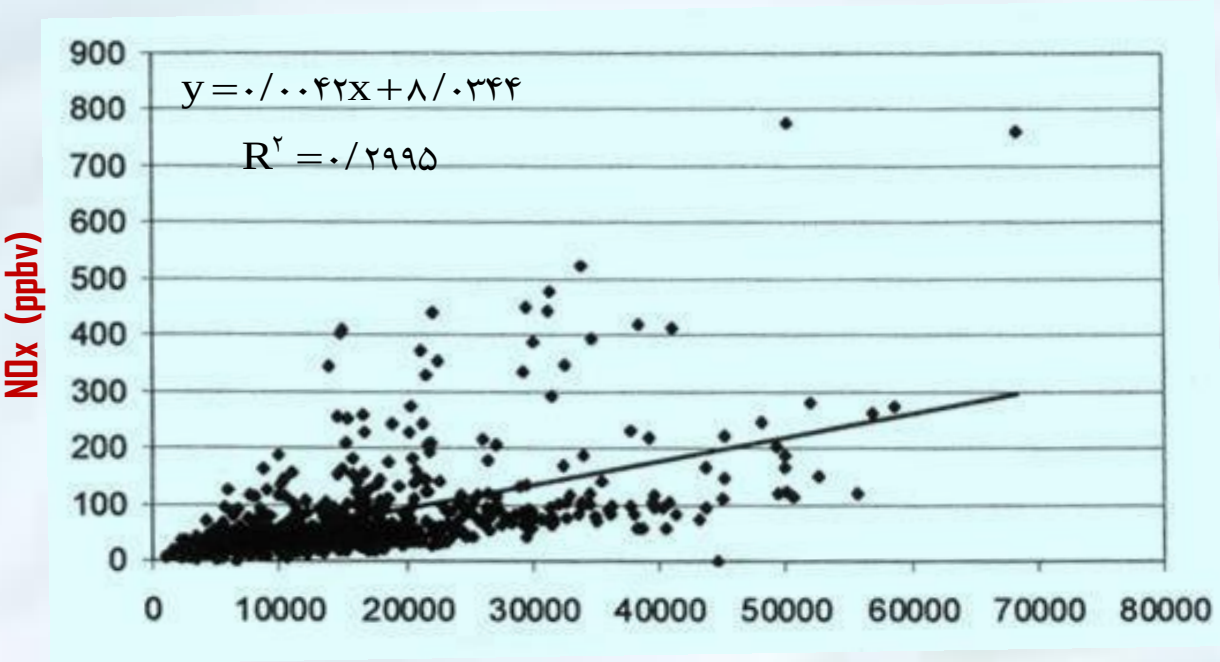
Accumulation Mode (100 - 470 nm)



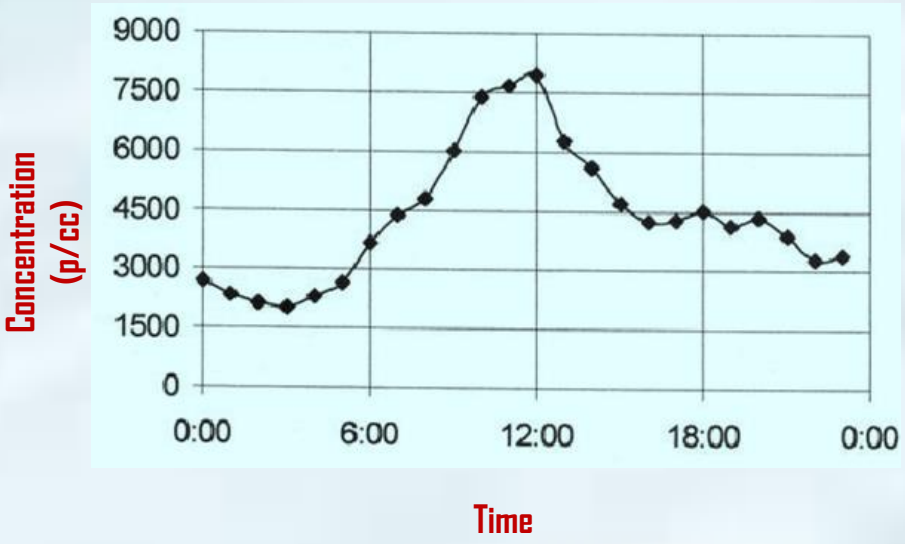
Aitken mode (13 - 30 nm)

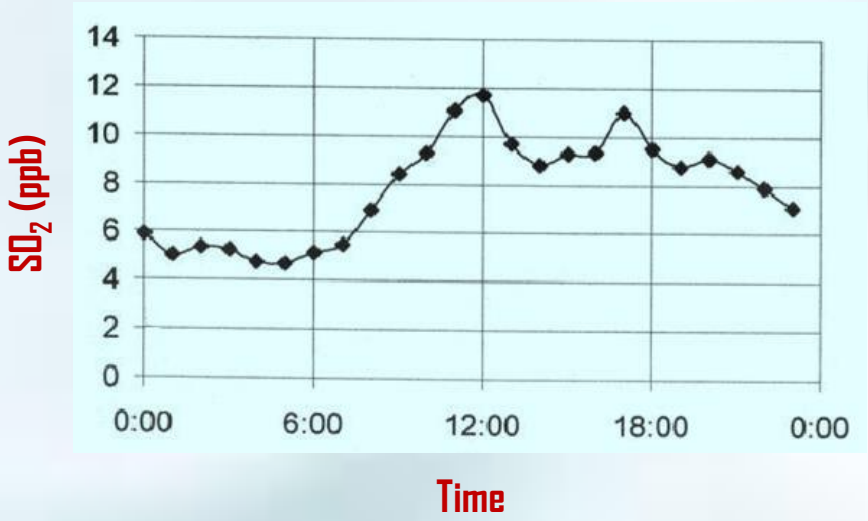


Aitken mode (13 - 30 nm)

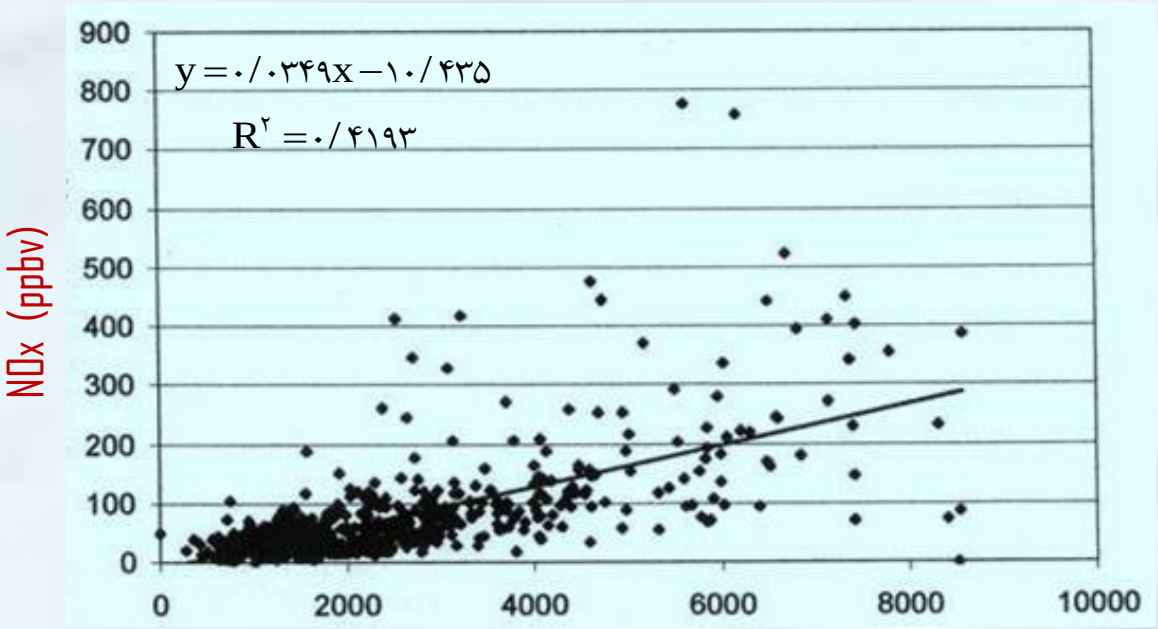


Ultrafine Mode (3 - 8 nm)





Mode (100 - 3000 nm)



The main pathway for nitric acid formation in daylight is from the reaction of NO_2 with the hydroxyl radical.

$$NO_2(g) + OH(g) \xrightarrow{M} HNO_3(g)$$

Nitrogen dioxide (radical) + Hydroxyl (radical) → Nitric acid

Hydroxyl Radical

$$O_3 + h\nu \rightarrow O_2 + O \qquad (\lambda < 1121\text{nm})$$

$$O_3 + h\nu \rightarrow O_2 + O^* \qquad (\lambda < 319\text{nm})$$

$$O^* + H_2O \rightarrow 2OH$$

or

$$O^* + CH_4 \rightarrow CH_3 + OH$$

Where O* is excited atomic oxygen and most O* is collisionally deactivated to the ground state O.

OH is rapidly consumed by SO_2, NO_2, CO and CH_4, so the gas phase production of sulphuric and nitric acid drops considerably during the night.

However, the OH radical is still the major gas phase source of both acids (Bradbury; 1998).

At night time, due to much reduce concentration of hydroxyl

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$

Subsequent conversion of the nitrate radical to nitric acid can occur by a number of chemical mechanisms.

Probably the most important involves further reaction with NO_2 to form dinitrogen pentoxide, which is converted to nitric acid, by reaction with water, generally in a process enhanced by the presence of liquid water:

$$NO_3 + NO_2 \Leftrightarrow N_2O_5$$

$$N_2O_5 + H_2O \Leftrightarrow 2HNO_3$$

Secondary Pollutants

NO_X reacts with other chemicals in sunlight to produce ozone →
Ozone is called smog (brownish haze) in the lower atmosphere

Smog and PM reduce visibility and lead to health problems (asthma, bronchitis, emphysema)

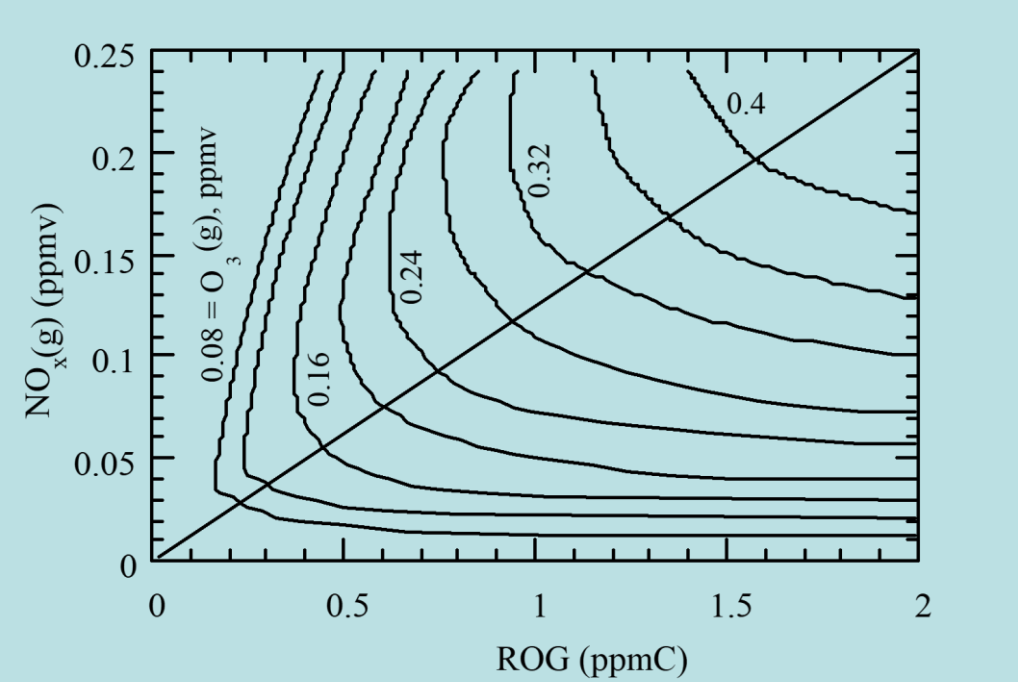
SMOG = SMOKE + FOG

Photochemical Smog Chemistry

NOx + ROGs + Sun Light = Ozone

$$\frac{NO_2\,(g)}{NO\,(g)} > 3 \qquad \frac{NO_2\,(g)}{NO\,(g)} < 0.3$$

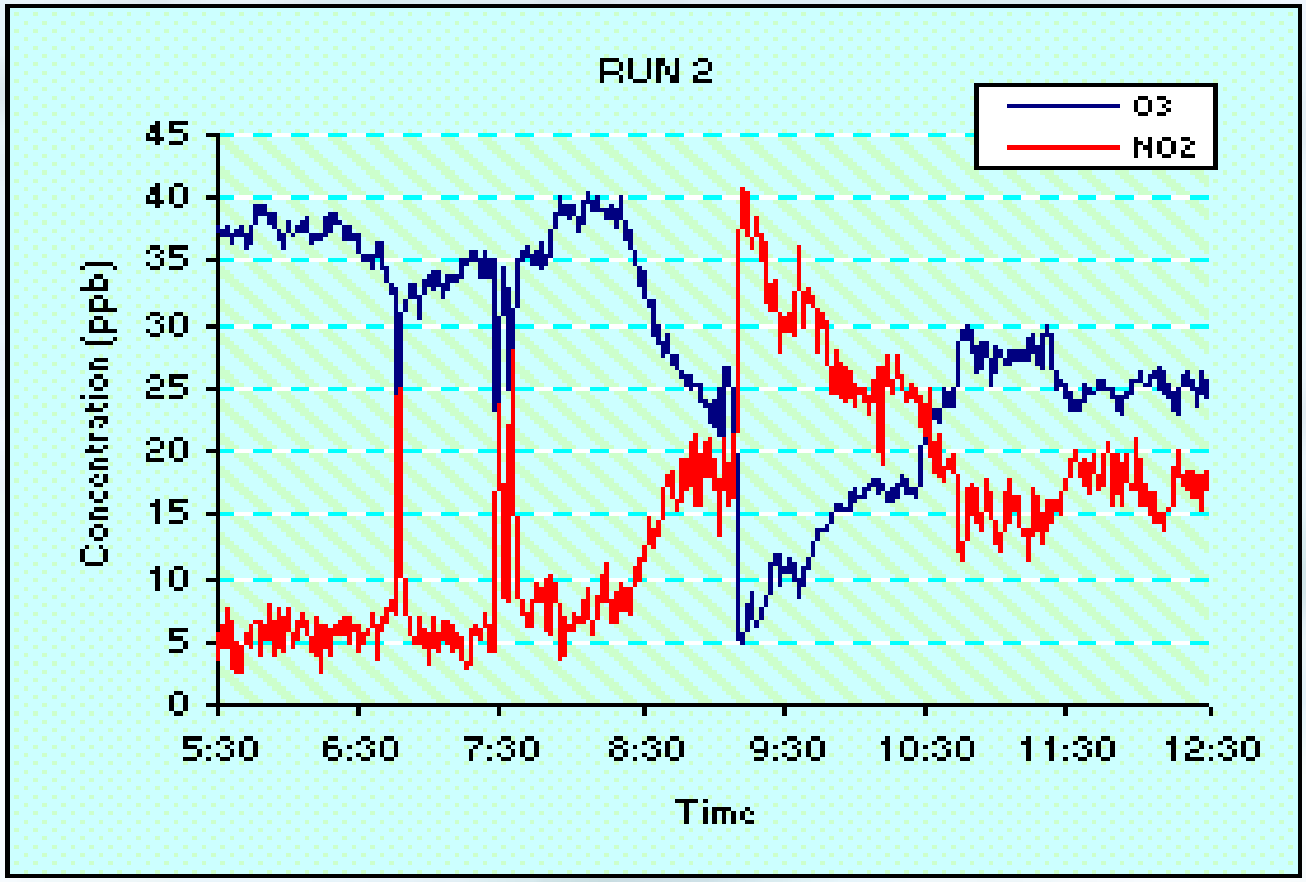
Ozone Isopleth

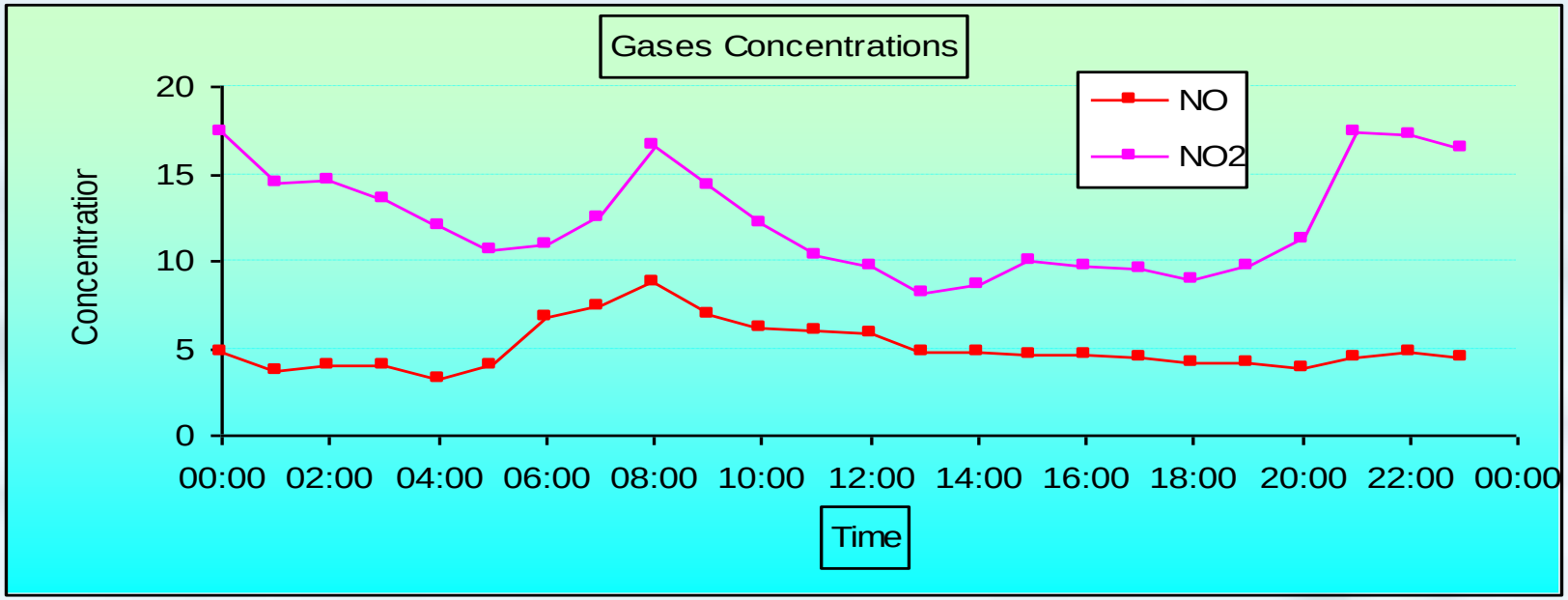


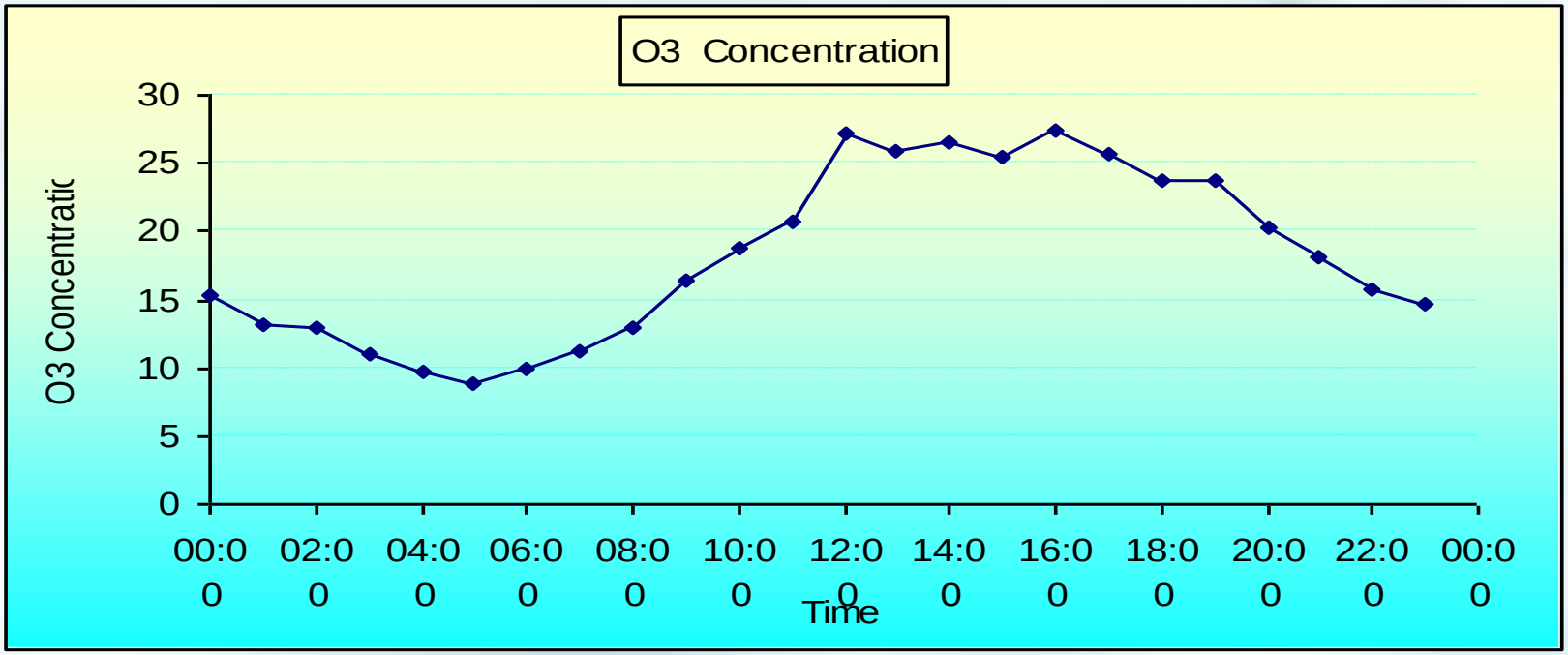
Contours are ozone (ppmv)

Near the surface of the Earth, there is anti correlation between O_3 and NO_2 by reaction:

$$O_3 + NO \rightarrow NO_2 + O_2$$




Gases Concentrations
NO
NO2
Concentration
20
15
10
5
0
00:00
02:00
04:00
06:00
08:00
10:00
12:00
14:00
16:00
18:00
20:00
22:00
00:00
Time


O3 Concentration
O3 Concentration
30
25
20
15
10
5
0
00:00
02:00
04:00
06:00
08:00
10:00
12:00
14:00
16:00
18:00
20:00
22:00
00:00
Time

formation of aerosol particles by gas-to-particle conversion

The formation of aerosol particles by gas-to-particle conversion take place through the following mechanisms (Hameri et al., 1996).

Reaction of gases to form low vapour pressure products

Nucleation of these low vapour pressure products

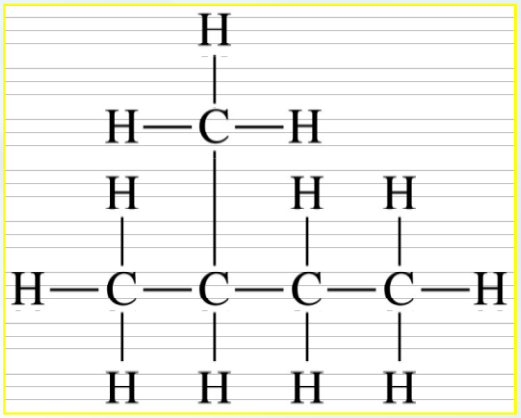
The condensation of vapours to the surface of particle

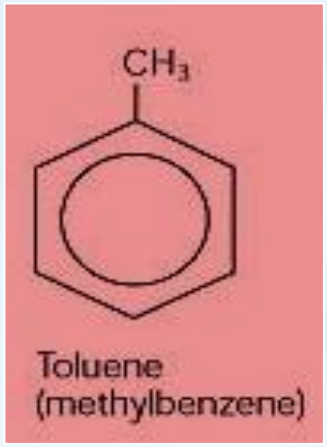
Reaction of gases with the surfaces of existing particle

Chemical reaction within particle.

Hydrocarbons

Major Atmospheric Pollutants.





Alkanes: C_nH_{2n+2} (saturated)

$CH_3 - CH_3$ ethane

Alkenes: C_nH_{2n} (unsaturated)

$CH_2 = CH_2$ ethene (ethylene)

Alkynes: C_nH_{2n-2} (unsaturated)

$CH \equiv CH$ ethyne (acetylene)