ARIE J HAAGEN-SMIT
AND THE HISTORY OF SMOG

TRANSFORMATION

The 20th century has been characterised by a transition from urban air dominated primary pollutants to one where secondary pollutants are very important.

LOS ANGELES
EARLY 1940s

Vanishing
streetcars

LOS ANGELES
EARLY 1940s

- Air pollution so bad baseball games not visible
- Japanese gas attacks

$1,000 Gold Bond certificate from the Southern California Gas Company (1931)

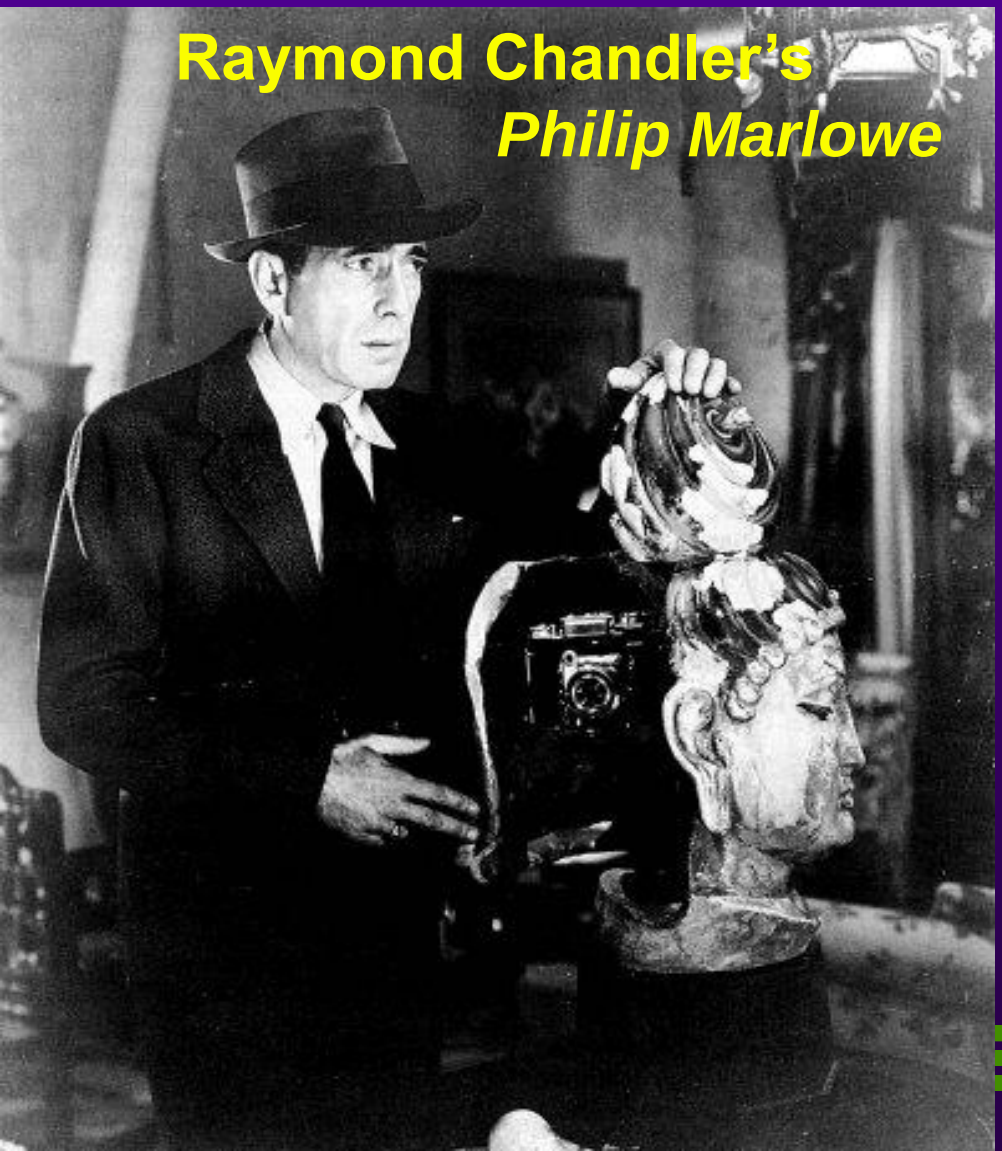
LOS ANGELES
EARLY 1940s

- However, smog even in the 1940s there was an awareness of its “peculiar nature”
- Subtlety did not emerge as LA set up a Bureau of Smoke Control in 1945, not recognising the irony in this nomenclature.

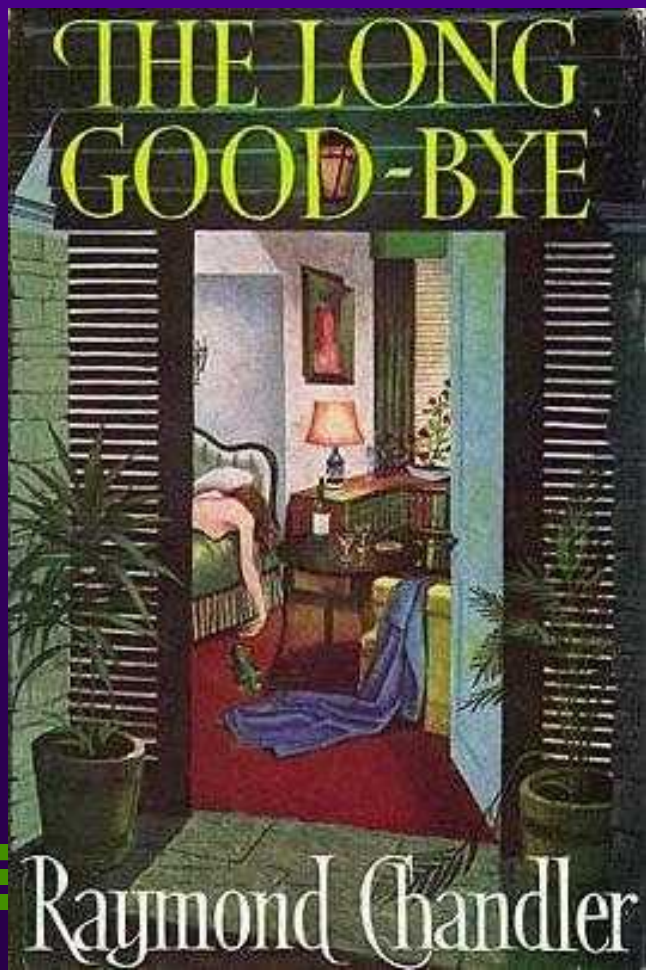
LOS ANGELES mid 1940s

- Post war: smog problem still serious
- LA administration suggests it will take a few months to solve
- Tucker invited from St Louis – he'd been successful in solving Pittsburgh's problems
- The automobile not really a problem – virtually no sulfur in the fuel
- 1947 Deutch recognised this easy attribution to a single source (butadiene plant) as an oversimplification

LOS ANGELES in FICTION



- Smog appears, but actually not in Chandler till 1953



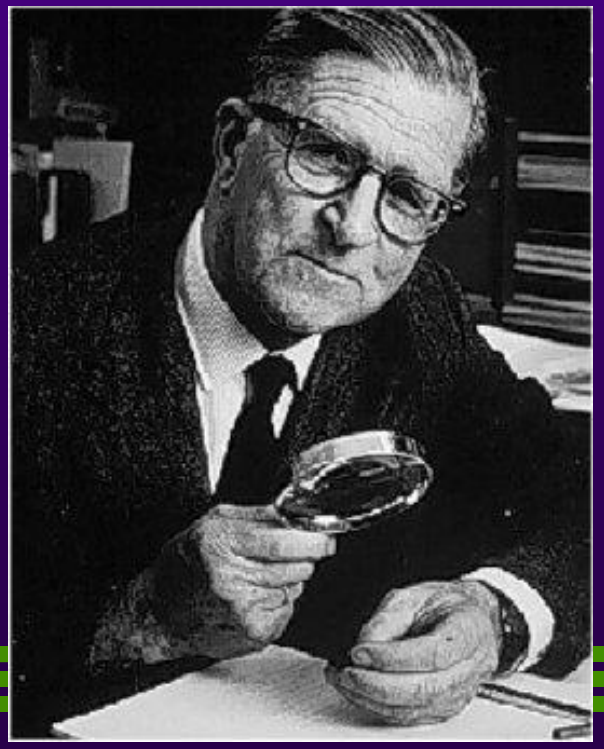
LONDON SMOG IN FICTION

- Fog and covering crime
- Fog and uncovering crime
- Jack the Ripper

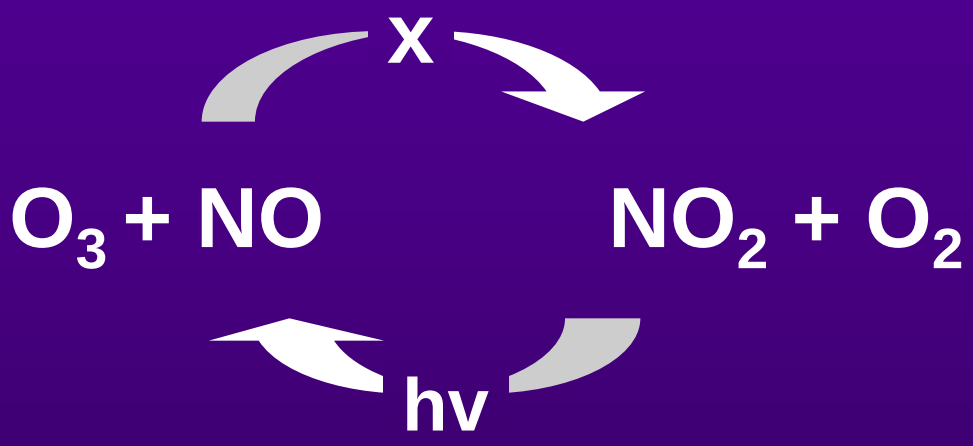

BLADE RUNNER
MICHAEL DOUGLAS
FALLING DOWN
A Joel Schumacher Film

A RADICAL IDEA

- Arie J Haagen-Smit – biochemist concerned with crop damage
- Smelling the air – like an organic chemistry lab
- “action of sunlight and automotive vapours”



NO_X PSUEDO-EQUILIBRIUM



…the nature of X forms a major part of what controls smog formation

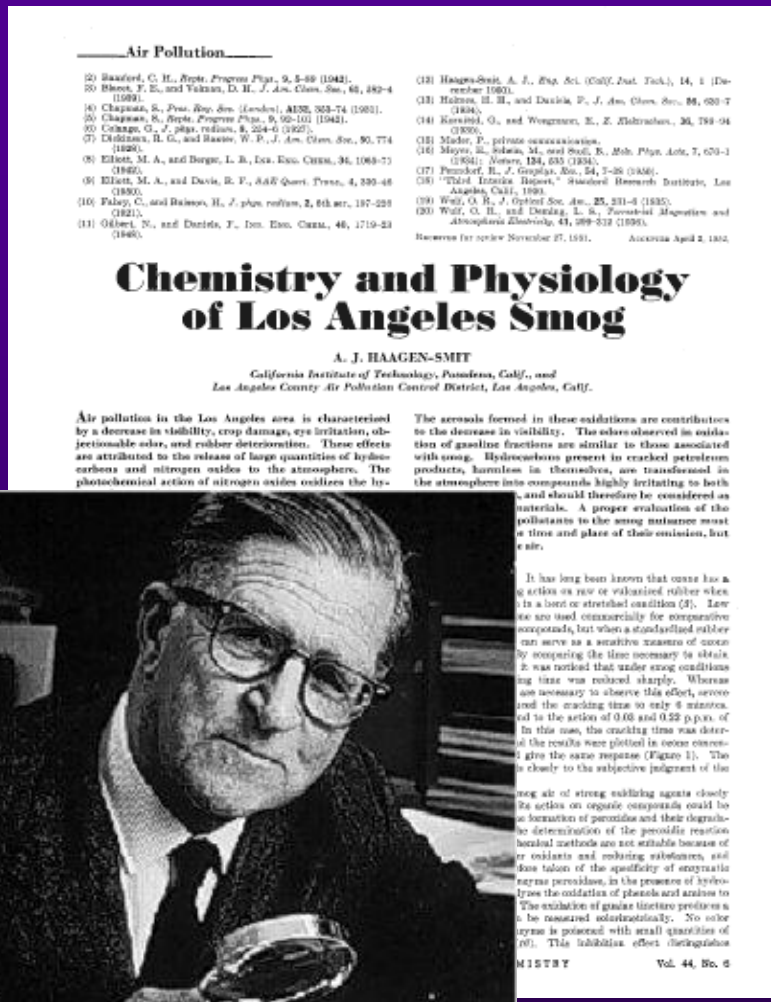
- ***"action of sunlight and automotive vapours"***

IMPACTS

- Cracking of rubber
  - **Conrad Vleck of the Los Angeles County Air Pollution Control District examines a rubber strip for the first signs of cracking due to ozone exposure.**
- Smoke from open waste burning
  - **Glendale city dump in October 1946**
- Eye irritation
  - **Marion E. Lent dabs at smog-induced tears on her way to work in downtown Los Angeles on Feb. 4, 1953.**

THE RADICAL IDEA

- In a submission to *Industrial and Engineering Chemistry*: Haagen-Smit refers to both ozone and peroxides
- “a proper evaluation of the contribution of air pollutants to the smog nuisance must include not only the time and place of their emissions, but also their fate in air”



Air Pollution

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Chemistry and Physiology of Los Angeles Smog

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Air pollution in the Los Angeles area is characterized by a decrease in visibility, crop damage, eye irritation, objectionable odor, and rubber deterioration. These effects are attributed to the release of large quantities of hydrocarbons and nitrogen oxides to the atmosphere. The photochemical action of nitrogen oxides oxidizes the hy-

The aerosols formed in these oxidations are contributors to the decrease in visibility. The odors observed in oxidation of gasoline fractions are similar to those associated with smog. Hydrocarbons present in cracked petroleum products, harmless in themselves, are transformed in the atmosphere into compounds highly irritating to both , and should therefore be considered as aterials. A proper evaluation of the pollutants to the smog nuisance must e time and place of their emission, but e air.

It has long been known that ozone has a g action on raw or vulcanized rubber when in a bent or stretched condition (3). Low ne are used commercially for comparative compounds, but when a standardized rubber can serve as a sensitive measure of ozone By comparing the time necessary to obtain It was noticed that under smog conditions ing time was reduced sharply. Whereas are necessary to observe this effect, severe ired the cracking time to only 6 minutes. ed to the action of 0.03 and 0.22 p.p.m. of In this case, the cracking time was deter- d the results were plotted in ozone concen- l give the same response (Figure 1). The is closely to the subjective judgment of the

nog air of strong oxidizing agents closely ke action on organic compounds could be e formation of peroxides and their degrada- he determination of the peroxidic reaction hemical methods are not suitable because of r oxidants and reducing substances, and done taken of the specificity of enzymatic zymes peroxidase, in the presence of hydro- lyzes the oxidation of phenols and amines to The oxidation of guaiac tincture proceeds n be measured colorimetrically. No color zyme is protected with small quantities of (9). This inhibition effect distinguishes

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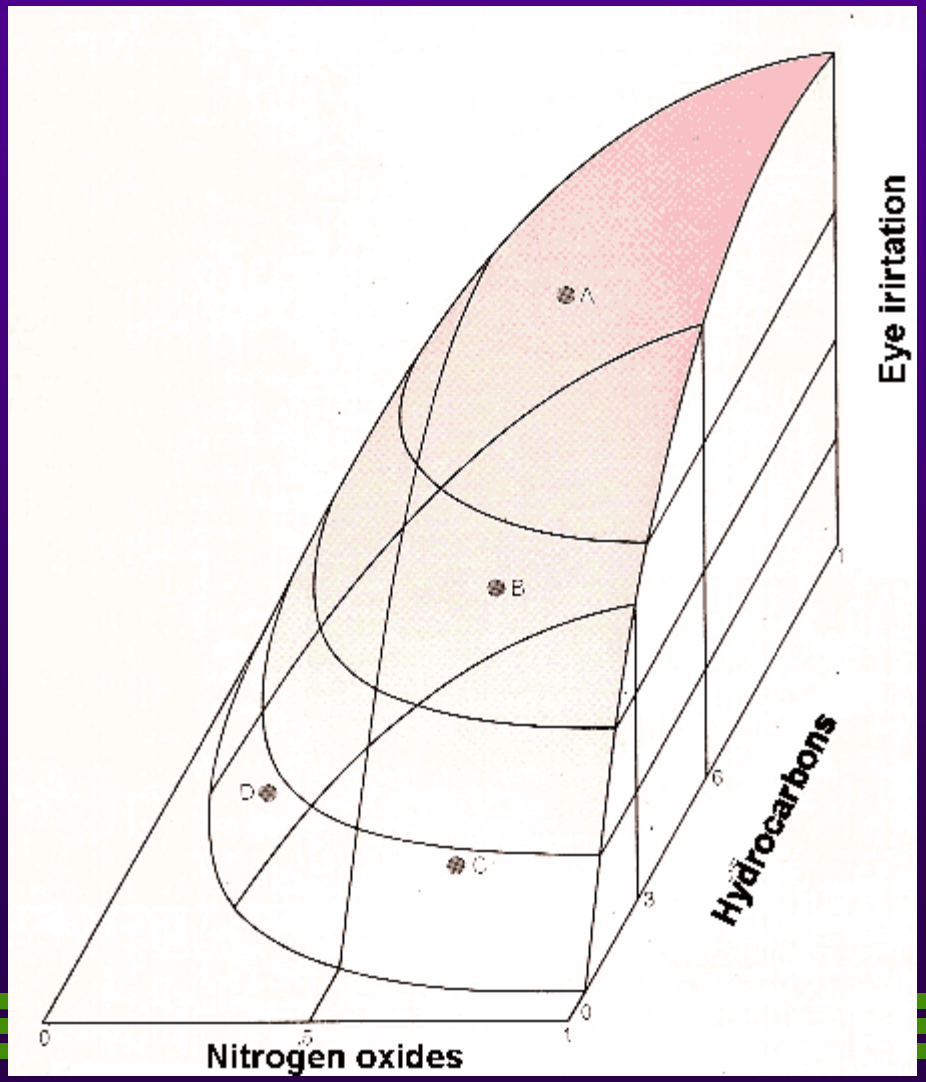
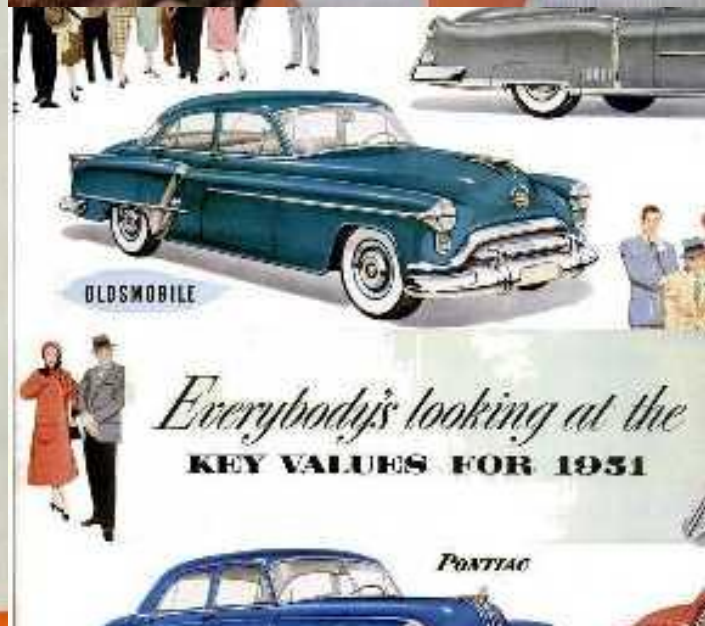
SCIENTIFIC AMERICAN ARTICLE

- “the Los Angeles atmosphere differs radically from that of most other heavily polluted communities”
- reduction of NO/HC by a half would give air quality
- linearity fails to sense the underlying the complexity




LIFE
February 12 1951
VEIL HATS
20 CENTS


Old Gold
We don't snow you under with medical claims...
For a TREAT instead of a TREATMENT
...smoke Old Golds


OLDSMOBILE
Everybody's looking at the
KEY VALUES FOR 1951
PONTIAC

LIFE article

"Now industrialisation has caught up with Los Angeles to the extent that it has its own special brand of smog – less grim, but more eye-burning chemicals…"

Good esrly video at:
http://www.arb.ca.gov/html/brochure/history.htm

DOMINANCE of the AUTOMOBILE

- Haagen-Smit opposed by auto manufacturers
- Initiated study at Stanford Research Institute
- The now classical understanding derives:

  P.A. Leighton, *Photochemistry of Air Pollution* (1961)

  and more fully Heicklen, Westberg and Cohen (1969/71)

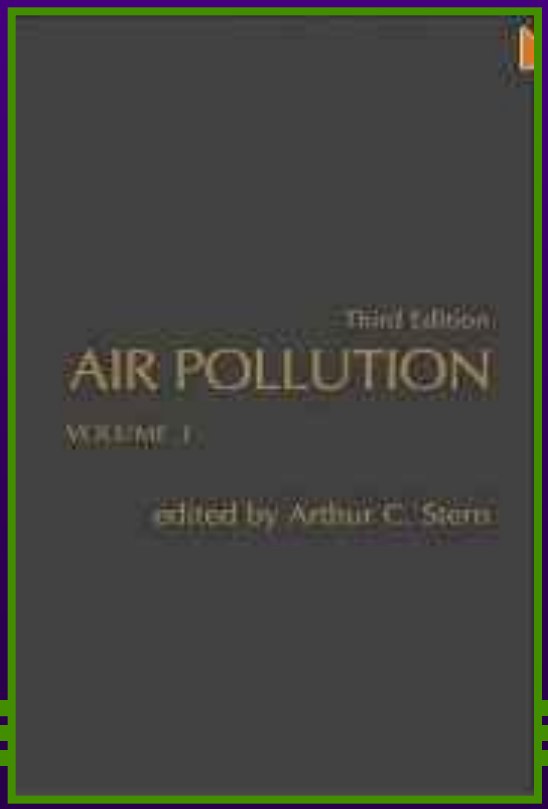
UCLA engineers Richard D. Kopa (left) and Hiroshi Kimura inspect a 1960 device that cut nitrogen oxide tailpipe emissions by 50%.

Philip Albert Leighton
Photochemistry of Air Pollution (1961)

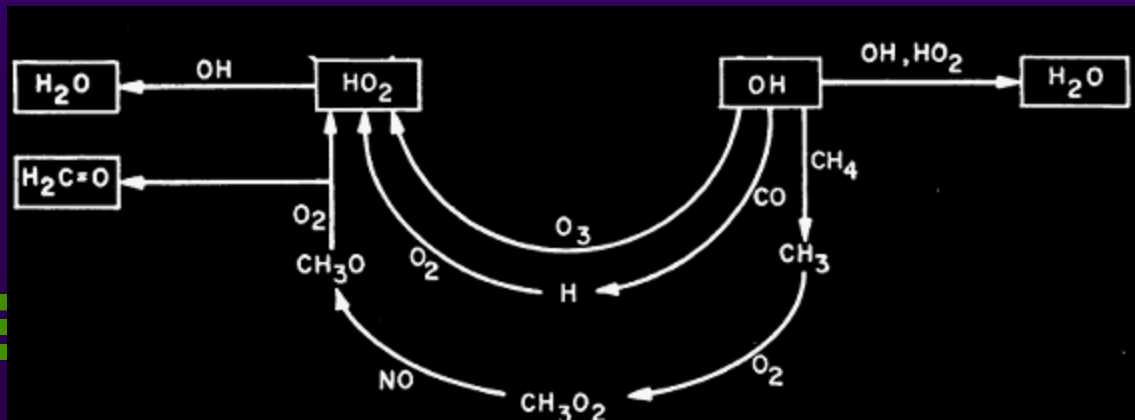
- Eyring reproduced Leighton's words " a major share of the photochemically originated organic particulates in photochemical smog are due to the nitrogen dioxide-olefin photolysis and the reactions which follow."
- Eyring not entirely convinced "many features will undoubtedly be modified and amplified with time.."
- Morris Katz realised the regulatory significance of the chemistry : "in order to control such harmful by products… know the facts concerning their formation and reactions"

HYDROXYL RADICAL

- Altshuller and Bufalini (1971) date understanding of smog to be in the last half of the 1960's., so failed to make Stern's *Air Pollution* of 1967
- Peroxides mentioned,
  but the hydroxyl radical
  does not emerge with a
  key role



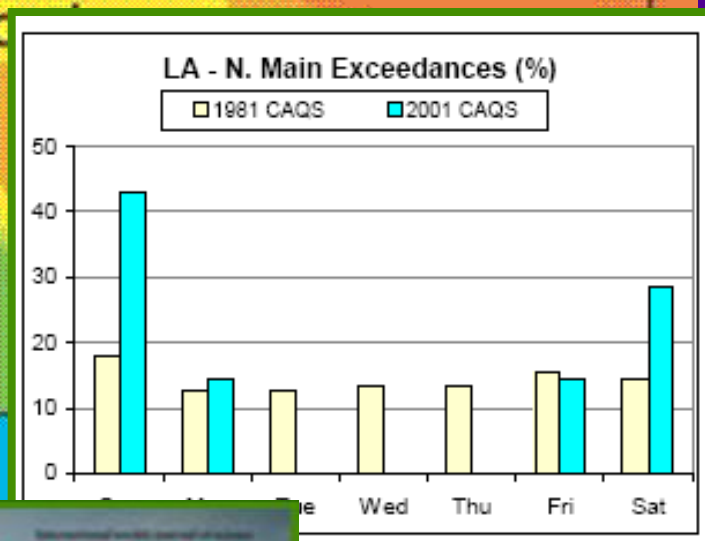
- Hiram Levy II (1971)- OH radical begins to be seen as a basic ingredient for the production of photochemical smog
- reactions of OH with CO seen as important once the reaction rate is seen as fast (Westberg et al., 1971)

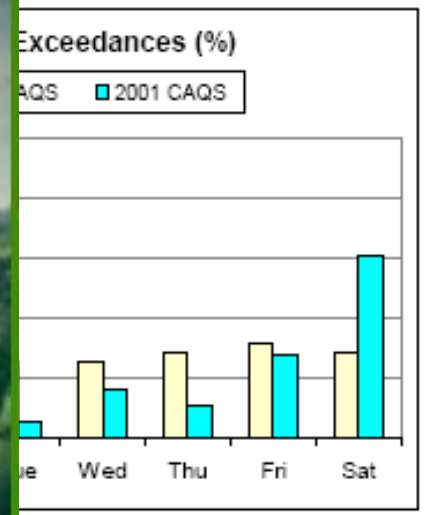


SOMETIMES OUTCOMES NOT OBVIOUS

- In some places the air has become worse
- in the weekends
- the parks

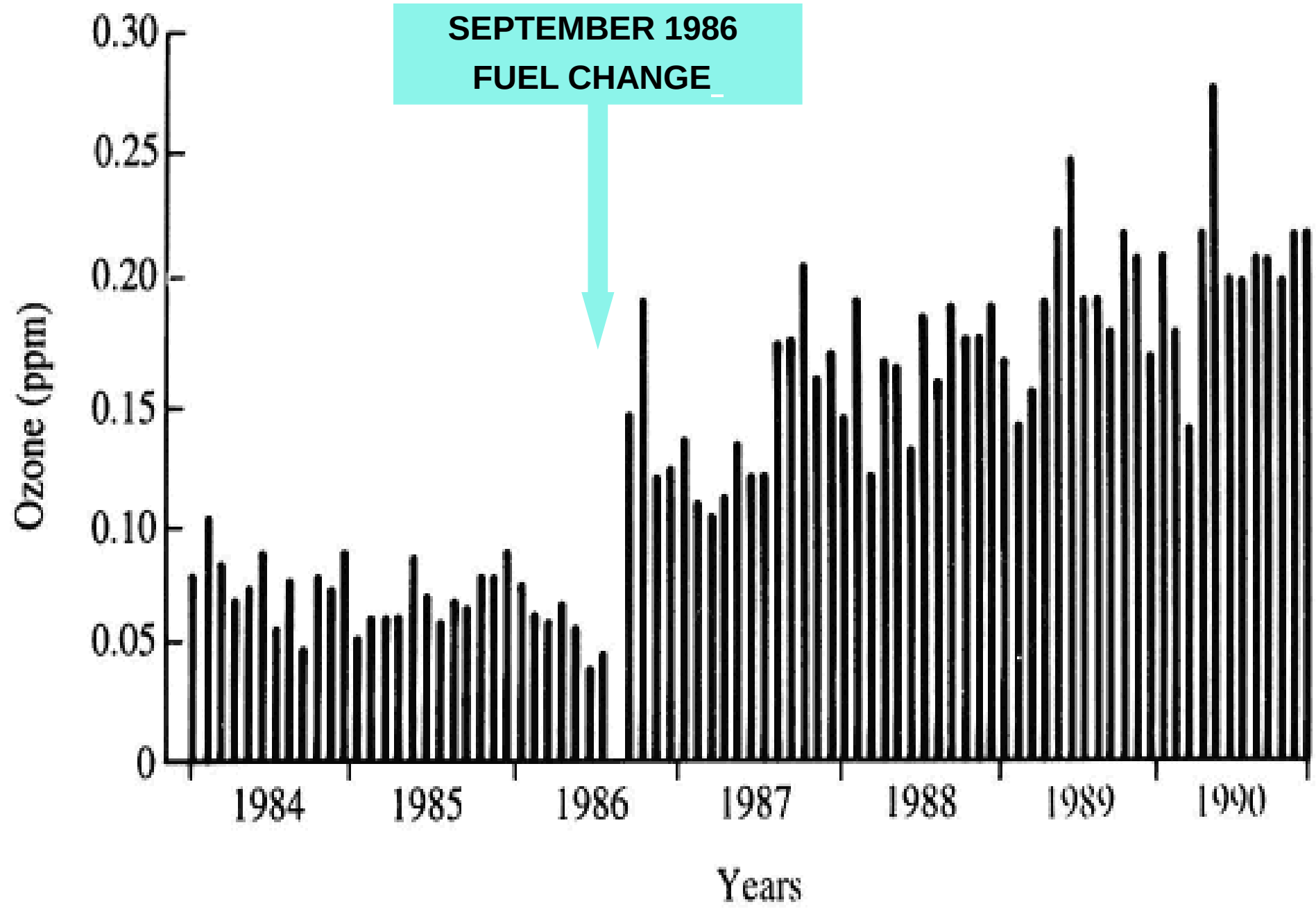
$$NO + O_3 \rightarrow NO_2 + O_2$$

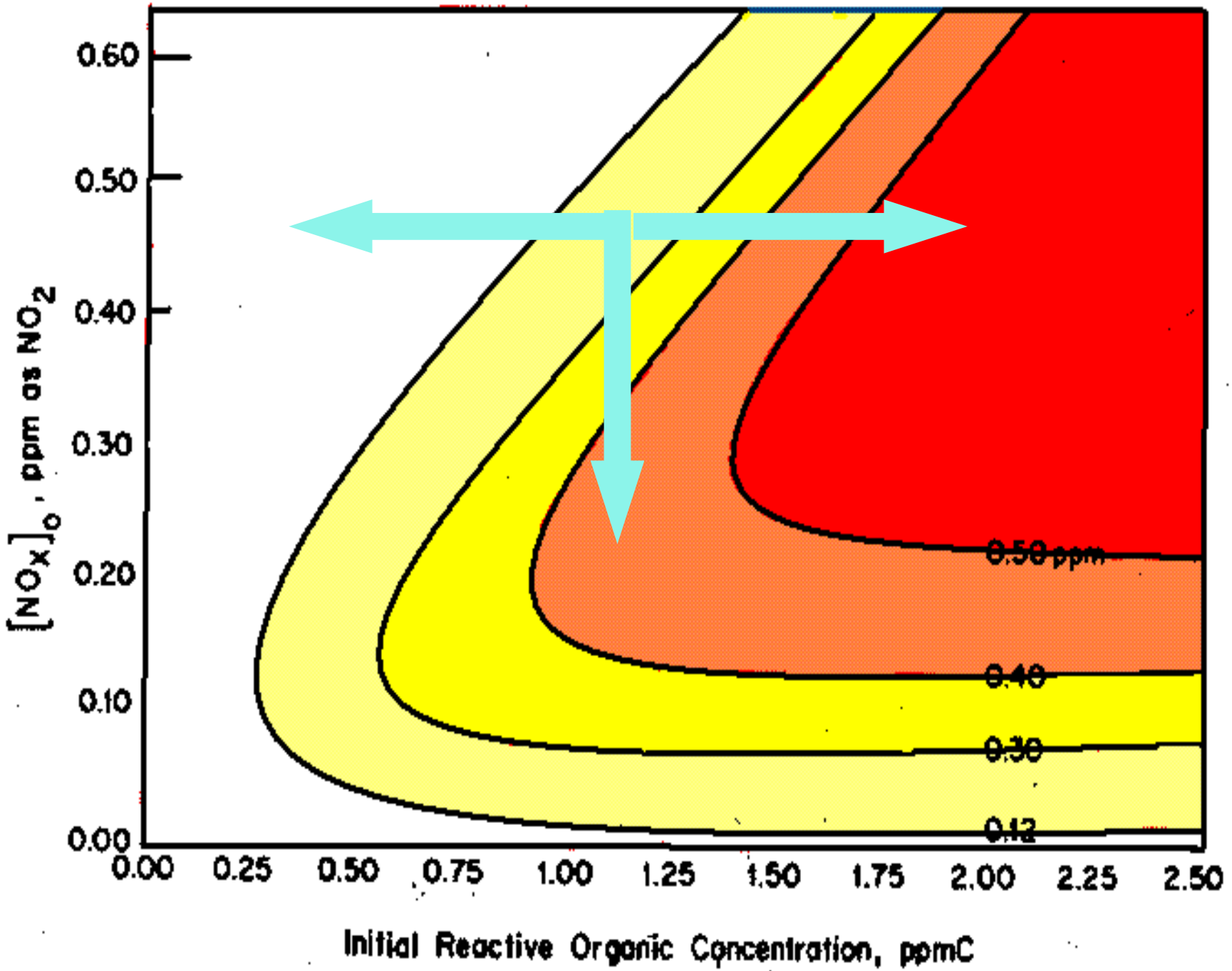




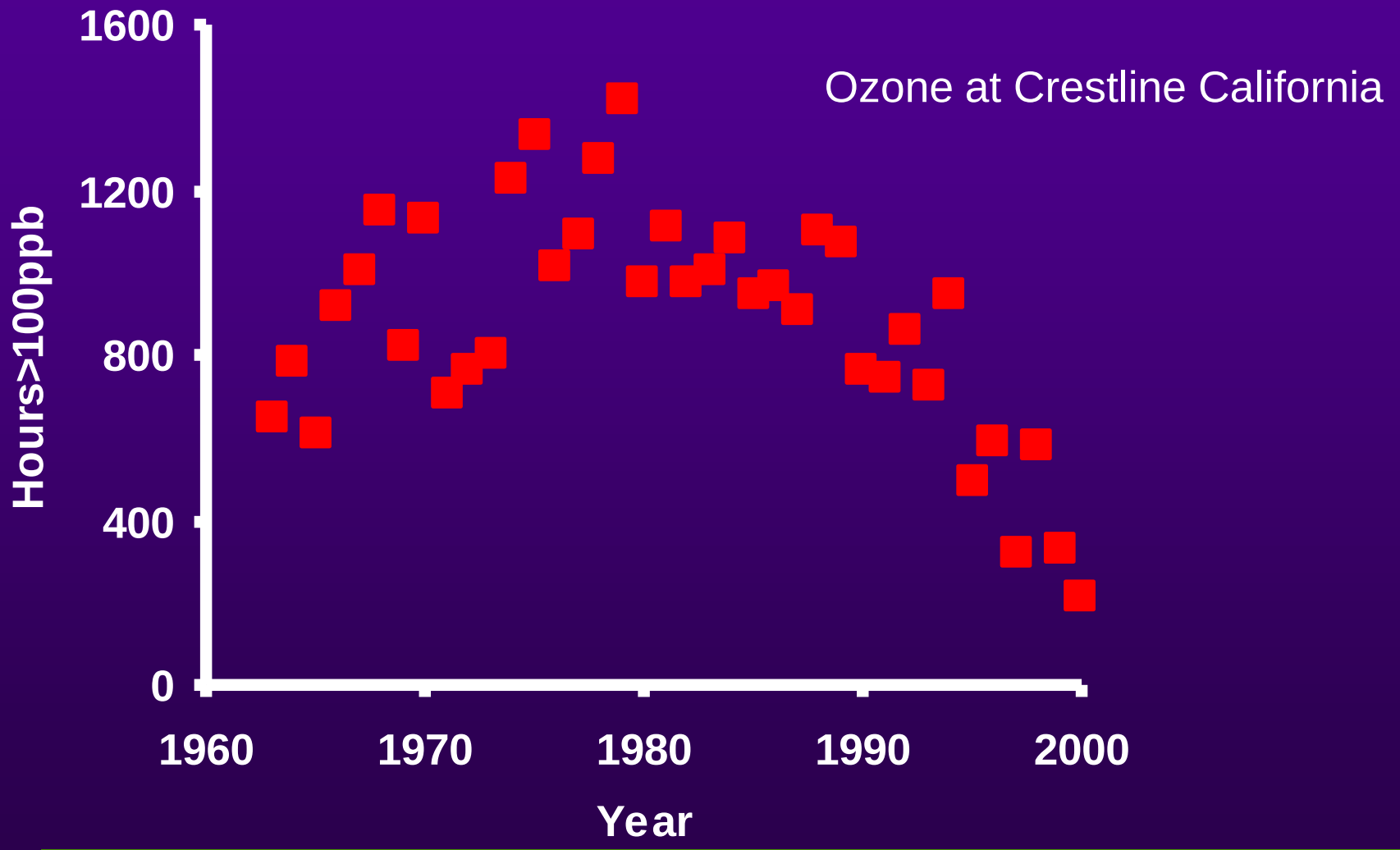
MEXICO CITY

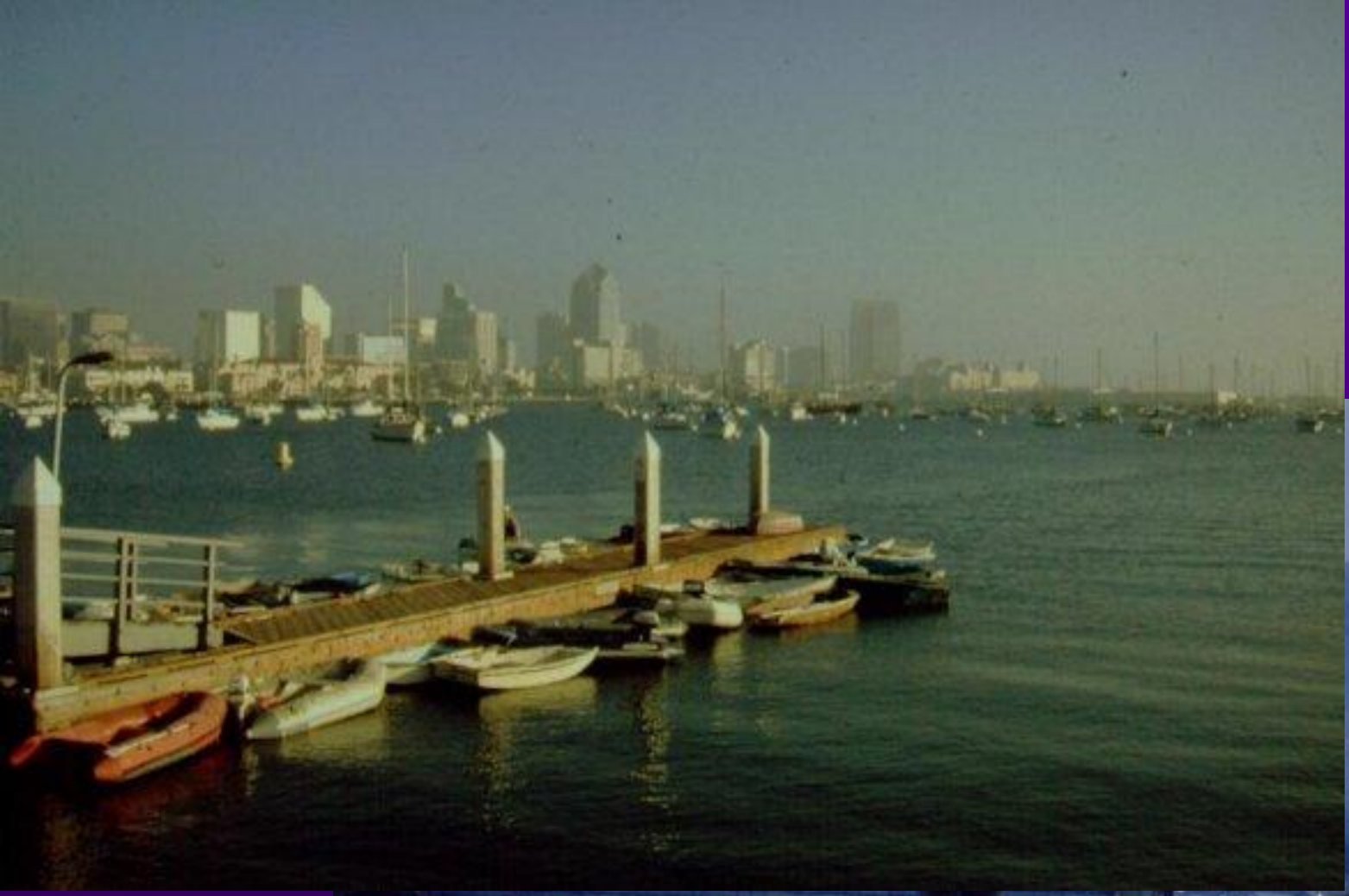
STUART FRANKLIN


SEPTEMBER 1986
FUEL CHANGE
0.30
0.25
0.20
0.15
0.10
0.05
0
Ozone (ppm)
1984
1985
1986
1987
1988
1989
1990
Years


0.60
0.50
0.40
0.30
0.20
0.10
0.00
$[NO_x]_o$, ppm as NO_2
0.50 ppm
0.40
0.30
0.12
0.00
0.25
0.50
0.75
1.00
1.25
1.50
1.75
2.00
2.25
2.50
Initial Reactive Organic Concentration, ppmC

A LONG AND DIFFICULT PROBLEM





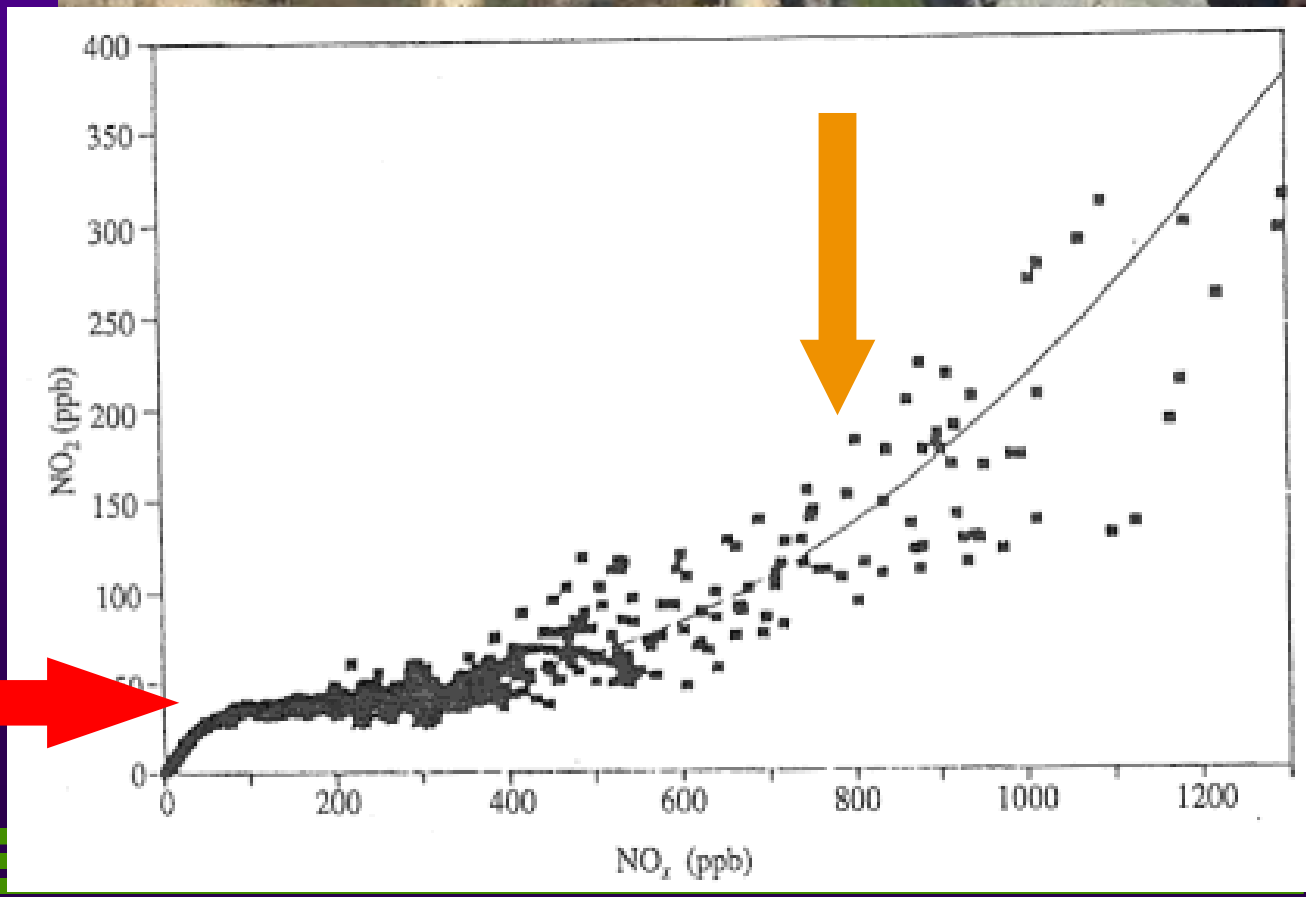
GOING BEYOND LA!

- Liquid fuels- Mobile sources- Multiple polluters
- POCP-MIR-SOA

WINTER NO_X SMOGS

Titration $NO+O_3$

Ter-molecular oxidation



TRANSFORMATION

The 20th century has been characterised by a transition from urban air dominated primary pollutants to one where secondary pollutants are very important.

Huge policy implications


THE END