Air pollution overview with relevance to Durban: Review of studies - SO_2

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November 2007: Storage tank fire at Engen refinery. Fire burned for five days

7 000 000 litres of petrol exploded after the storage tank was struck by lightning

1. Air pollution overview
- Emission sources: Anthropogenic / Natural sources
- Ambient air pollution / Indoor air pollution
- Primary and secondary pollutants
- Factors affecting air quality

2. Selected pollutants with relevance to Durban:
- CO, NO_2, SO_2, O_3, Particulate matter (PM10 / PM2.5), VOC (Volatile organic compounds)
- Emission sources and health impacts of individual species

3. Air quality in Durban
- The Durban South Industrial Basin (DSIB)
- Ethekwini air quality monitoring network

4. Review of air pollution studies in Durban:
- SO_2 (three studies)

5. Conclusion

1. Air pollution overview

1.1 What is Air pollution?

- Gases
- Liquid droplets
- Solid particulates

that are emitted / discharged into the atmosphere and adversely affect the health of humans, animals, ecosystems or the usefulness of natural resources.

1.2 Air pollution emission sources:

- Air pollution may be categorized according to its emission source and may be classified:
- Anthropogenic (ie. arising from human activity)
- Natural

- **Anthropogenic emission sources:**
- **Stationary source:** A single identifiable source eg. emissions from a combustion furnace flue stack.

- **Mobile sources**: Exhaust emissions from cars / aeroplanes etc
- **Area source:** Two-dimensional source of diffuse air pollution emissions eg. Methane emissions from livestock grazing over a large area.

- **Evaporative sources**: Volatile liquids that, when not completely enclosed in a container / tank, release volatile vapours over time. Examples of these liquids include: paint / solvent / pesticide etc.....

Benzene storage tanks

- **Controlled burns:** Controlled burning is a useful technique practiced in forestry management / agriculture. Such controlled burns result in the formation / release of smoke, ash, dust, CO_2, NO_2 and other pollutants

- **<u>Natural emission sources:</u>**
- **<u>Volcanoes:</u>** **Volcanic activity produces smoke, ash, CO_2, SO_2**
- **<u>Geysers:</u>** **Air pollutants emitted by geysers include SO_2, H_2S (hydrogen sulphide), Arsenic and other heavy metals**


- **<u>Digestive gases:</u>** **Methane and other gases generated by the digestion of food and emitted by animals**
- **<u>Dust:</u>** **Windblown dust from areas with little or no vegetation eg. Deserts / arid environments**
- **<u>Sea salt:</u>** **Wind-blown sea water which evaporates in the atmosphere and releases NaCl and other particulates into the atmosphere**
- **<u>Forest fires:</u>** **Forest fires initiated by lightening or other natural causes result in the formation and release of smoke, ash, dust, CO_2, NO_X and other pollutants**

1.3 Anthropogenic emission can be classified:

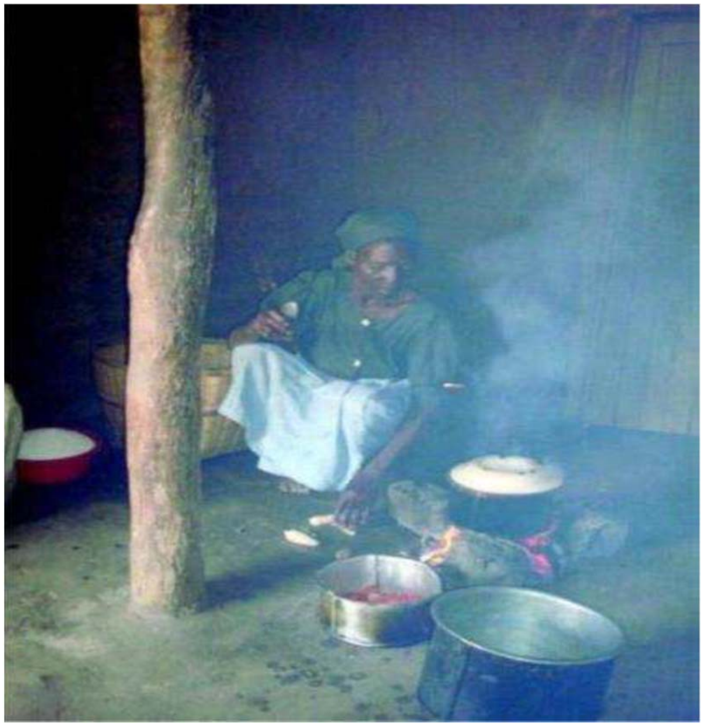
- **Ambient air pollution**
- **Indoor air pollution**

- Ambient air pollution: **Emission or release of pollutants into the atmosphere**

Eg. Sapref: flaring (combustion of flammable waste products)

South African refineries produce approximately 82 tons of sulphur dioxide gas daily. [Mail & Guardian, April 28, 2000]

Indoor air pollution: Indoor pollution sources that result in poor indoor air quality.



- **Sources:** Primarily domestic fuel eg: coal, wood, paraffin. It has been reported that average daily PM10 concentrations in households that use biomass fuels often exceed WHO (World Health Organisation) daily exposure guidelines

- **Incomplete combustion of biofuels** also results in a release of high concentrations of other air pollutants associated with combustion into the immediate living environment eg. Benzene, toluene, eythlbenzene, xylene (BTEX compounds)

- **Poor ventilation** can increase indoor pollutants levels due to weak dilution of emissions creating conditions that are not conducive to pollutant dispersal.

1.4 Primary and secondary air pollutants

- There are two types of ambient air pollutants: Primary and secondary pollutants

- Primary pollutants: Emitted directly into the air directly from source.
- They can have both direct environmental effects as well as act as precursors for secondary air pollutants.
- Important examples: CO, $SO_{2,}$ NO_X, VOC (volatile organic compounds).

- Secondary pollutants: Chemical species formed in the atmosphere as a result of photochemical reactions eg O_3, VOC

- Some groups of compounds may act as both primary and secondary pollutants (eg. VOC)

1.5 Factors affecting air quality

- **Nature of emission source:** Air quality depends on the amount of pollutants released into the atmosphere by anthropogenic activities eg. Vehicles, industrial emissions etc.

- **Rate at which pollutants disperse.**
- Dispersion is dependant on both wind direction and strength.
- Strong winds result in rapid dispersal of air pollution to other areas whereas little or no winds results in the accumulation, and in some cases, high concentration of air pollution.
- Local factors such as

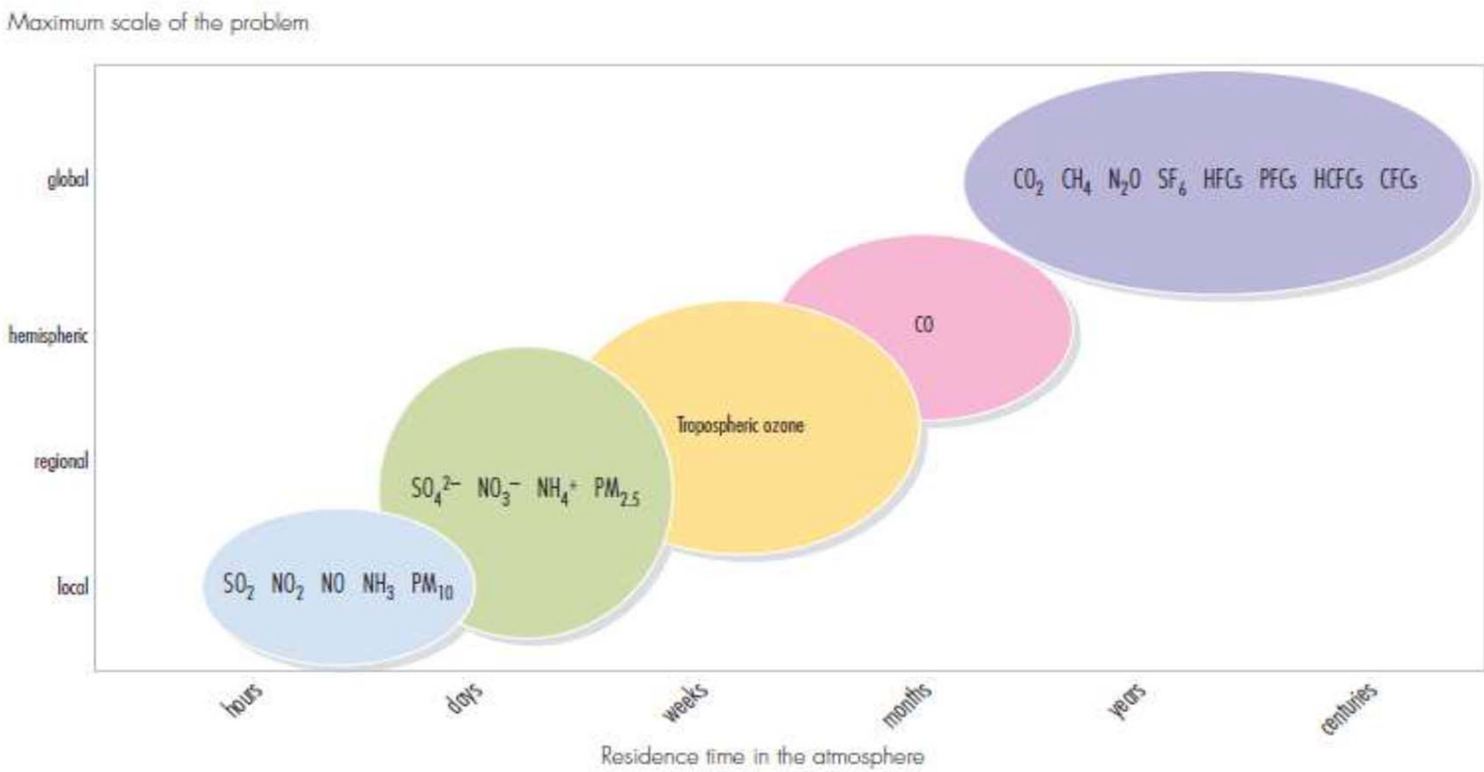
    topography (hills / mountains etc.) / proximity to coast

    building height

    time of year

  can all affect local wind conditions and can play a role in increasing air pollution levels.

- **Residence times of air pollutants in the atmosphere. Air pollutants have varying residence times in the atmosphere – directly related to chemical reactivity of species**
- **Air pollutants with very short residence times affect indoor and outdoor air quality locally (short-range effects) eg SO_2, NO_X**
- **Air pollutants with very long residence times result in continental and global effects. They can be transported long distanced without undergoing chemical processing eg CFCs**



2. Selected pollutants: CO, NO_2, SO_2, O_3, PM10 / PM2.5, VOC - Emission sources and health impacts:

2.1 Carbon monoxide (CO):

CO is a colourless, odourless, non-irritating but poisonous gas.

Two emission sources:

- **It is formed as a by-product of incomplete combustion processes involving carbon based energy sources** (eg. petrol, coal or wood). During combustion, under conditions of insufficient oxygen, CO is produced as by-product. The biggest source of CO comes from vehicles / transportation.
- Generated by photo-chemical breakdown of methane / non-methane hydrocarbons

Health impact:

- Acute exposure to CO includes headache, dizziness, vomiting, and nausea. At high levels loss of conscious or death can result (CO binds irreversibly with haemoglobin).
- Chronic exposure to moderate / high levels of CO has been linked with increased risk of heart disease.

2.2 Nitrogen dioxide (NO_2):

- **Nitrogen dioxide is a reddish, brown gas that has an unpleasant smell and is poisonous at high concentrations.**
- **NO_2 is one of the components responsible for producing brown haze which inhibits visibility in areas of high pollution**

Typical NO_2-rich photochemical haze over large cities

Multiple emission sources:

- Natural emission sources: Biomass burning, lightning, microbial activity in soils
- Anthropogenic emission sources: Motor vehicles / transportation and combustion sources that burn fossil fuels / biomass burning

- Studies indicate that Nitric oxide (NO) is the main oxide of nitrogen produced in combustion processes
- Between 85% and 97% of NO_X is emitted as NO. This is oxidised by O_3 in the atmosphere to produce NO_2:

$$\mathbf{NO + O_3 \rightarrow NO_2 + O_2}$$

Health impact:

- Acute exposure to NO_2 can lead to shallow respiratory rate, rapid heart rate and wheezing.
- Continued exposure to NO_2 can cause chronic respiratory irritation and lead to long term pulmonary changes.
- NO_2 is also known to negatively affect the immune system

2.3 Sulphur Dioxide (SO_2):

- **SO_2 is a toxic gas with a pungent, irritating smell.**

Multiple emission sources:

- SO_2 is emitted naturally: Volcanoes, grassland and forest fires
- **SO_2 is emitted from anthropogenic sources involving fossil fuels.** Coal and petroleum often contain sulphur compounds and their combustion generates sulphur dioxide.
- It is also produced as a by-product of metal smelting (of sulphur containing ores).
- Approx. 90% of sulphur present in fossil fuels enters the gas phase in the form of SO_2 during combustion (unless it is deliberately removed from flue gas)
- **About 99% of SO_2 in ambient air comes from anthropogenic sources**

Typical SO_2 – rich emissions from an oil refinery

Health impact:

- The target organ of SO_2 exposure is **the respiratory system.**
- Acute exposure to SO_2 (5 minutes - 24 hours) is associated with an array of adverse respiratory effects including broncho-constriction, wheezing and increased asthma symptoms.
- It has been linked to aggravation of pre-existing cardiovascular disease
- It has also been found that SO_2 is toxic to plants. It has been implicated in tissue damage and destruction of chlorophyll.

Leaf damage due to SO_2 exposure

2.4 Ozone (O_3):

- **Ozone is a toxic, irritant, pale blue gas with a distinctively pungent smell**
- **Ozone is a reactive oxidant gas playing a key role in the photo-chemistry of air pollution and atmospheric oxidation processes**

Sources:

- **Ozone is a secondary pollutant and a major component of photochemical smog**
- it is not emitted directly by any natural source but is formed through a set of photochemical reactions involving primary precursors **NO_x and VOC's under conditions of high solar radiation flux.**
- The chemical interdependence between O_3, NO_X and VOC's is complex and non-linear.
- As a result of these formation processes tropospheric ozone concentrations have been found to be highly variable over space and time.

Health impact:

- **Ozone can cause irritation to the eyes and respiratory tract and cause tightness, coughing and wheezing.**
- It can worsen bronchitis, emphysema and asthma symptoms and reduce lung function. Chronic exposure may permanently scar lung tissue.
- It is particularly harmful to the section of population suffering from heart disease.
- Elevated levels of O_3 are also a concern because of their effect on vegetation.

Ozone damage to leaves

2.5 Particulate matter (PM10, PM2.5):

- **Particulate matter (PM) is a broad term used to describe fine particles found in the atmosphere including soil, dust, dirt, soot, smoke, pollen, ash, aerosols and liquid droplets**.
- **Particulate matter is classified as:**

  PM 2.5 (Particles less than or equal to 2.5 µm in diameter) or PM 10 (Particles less than or equal to 10 µm in diameter).
- Apart from particle size **chemical composition is important**. These particles may often consist of hundreds of different chemical species eg. C, S, N, metals
- Once airborne, particles can **change size and composition** by

  condensation of vapour species onto particle surface

  coagulating with other particles

  chemical reactions on surface

Sources:

- **Anthropogenic aerosols primarily derive from fuel combustion**
- **Regional biomass burning** in Southern Africa occurs from June – October. The impact of **biomass burning** on particulate levels in South Africa is significant.

- **In South Africa** low-income households utilize energy sources such as **coal, wood and paraffin for heating / cooking**
- Suboptimal burning conditions in domestic settings often result in large emissions of particulates and particulate precursors leading to high concentrations of PM indoors
- South Africa is an arid country with high levels of naturally-occurring dust compounded by industrial and vehicular emissions. Both sources contribute to PM levels

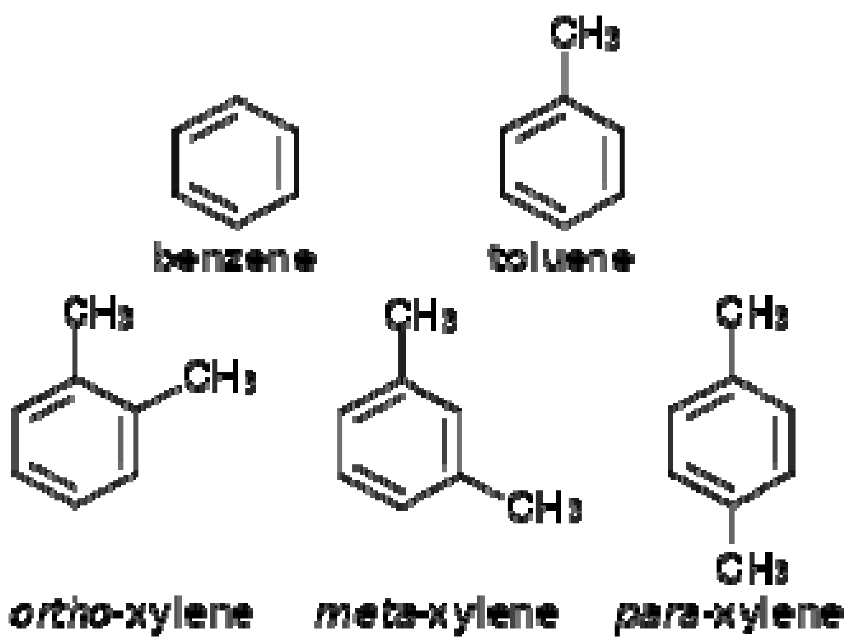
Health Impact:

- **Residence times:** PM2.5 Days / weeks. (PM10) minutes / hours

  Smaller particles remain suspended longer, ability to travel further is increased with corresponding increase in exposure risk.
- **Size:** Particles larger than 10 microns are filtered out of the body via nose and throat.
- Particles smaller than 10 microns are inhaled into the deepest part of the lungs. Fine particles smaller than 2.5 microns are small enough to pass from lungs into the blood supply
- **Adverse effects include:** Exacerbating existing respiratory diseases (eg asthma), cardiovascular diseases and possible link to lung cancer.

2.6 VOC (Volatile organic compounds):

- **Volatile organic compounds (VOCs) are organic compounds that easily become vapours or gases (ie. low boiling points). Contain C, H, O, F, Cl, S, N etc.**
- VOCs are a well-known ambient and indoor air pollutants. They are categorized as either methane-VOC (CH_4) or non-methane-VOC (NMVOCs).
- **BTEX compounds**: Benzene, toluene, ethylbenzene, xylene – routinely included in air quality monitoring programs in urban environments worldwide



Emission sources:

- BTEX compounds are highly reactive in the troposphere and play a key role in atmospheric chemistry as important **photochemical pre-cursors for tropospheric ozone**
- In urban environments BTEX are principally emitted by **vehicle exhaust gases** because of their presence in fuels and lubricating agents and heating oil.
- Other sources are gasoline evaporation, use of solvents and paint, biomass burning, leakage from natural gas storage facilities.

Health Impact:

- **Benzene exposure:** Acute inhalation causes neurological effects such as drowsiness, rapid heartbeat, tremors, headaches, confusion and loss of consciousness at high concentrations.
- **Toluene, Xylene exposure:** Depression of the central nervous system occurs together with numbness and nausea.
- **BTEX are carcinogenic**

3. Air quality in Durban

- The problem of air pollution in Durban has a long history, particularly in relation to the Durban South Industrial Basin (DSIB).
- Poor historical land-use planning has resulted in juxtaposition of residential and industrial areas - a long term conflict between local communities and industry,
- The DSIB is an approx 4 km wide extending south from the Durban (CBD) for 24 km to Umbogintwini. This area includes the CBD and Port of Durban

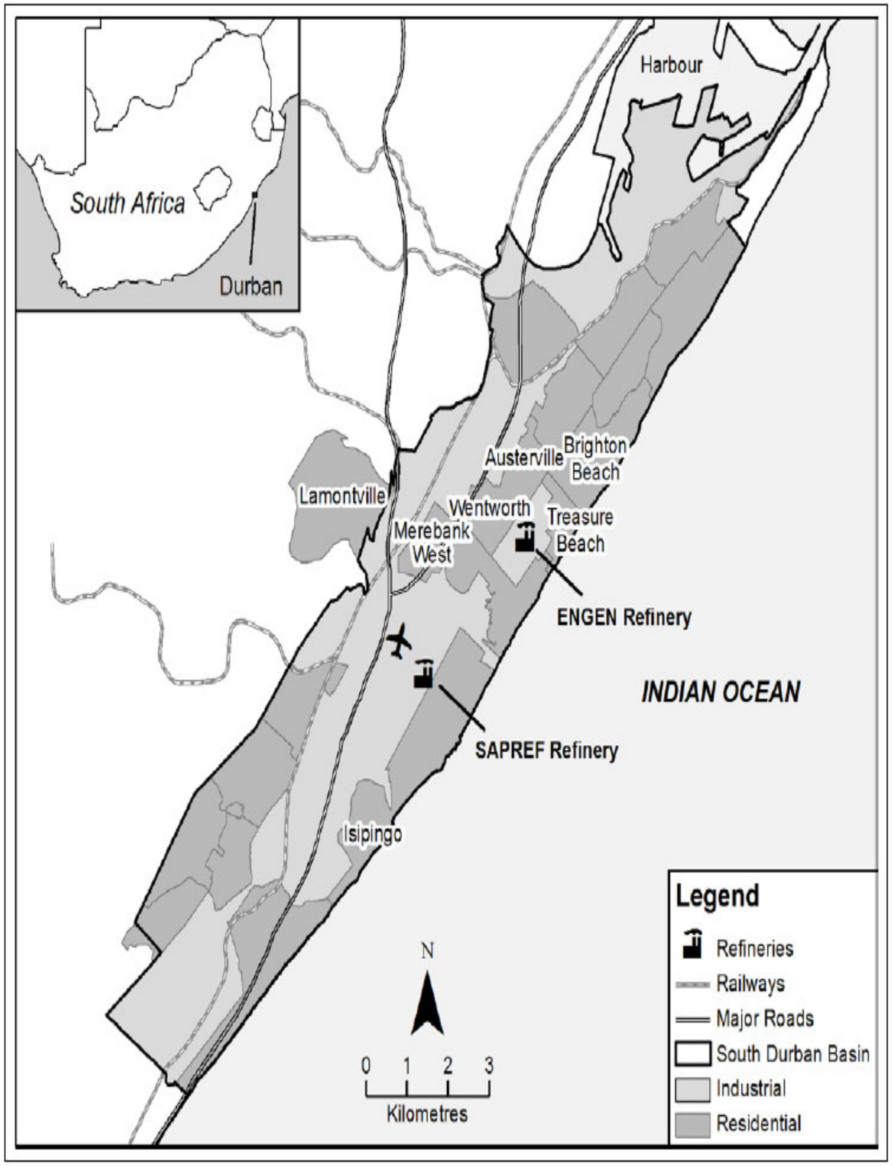


FIGURE 1
Details of the areas where interviewed residents of the South Durban Industrial Basin reside

- **At present, approx 600 industries are reportedly located in South Durban.**
- **Emission sources include:**

  Refineries: Sapref, Engen

  Paper manafacturing plant: Mondi

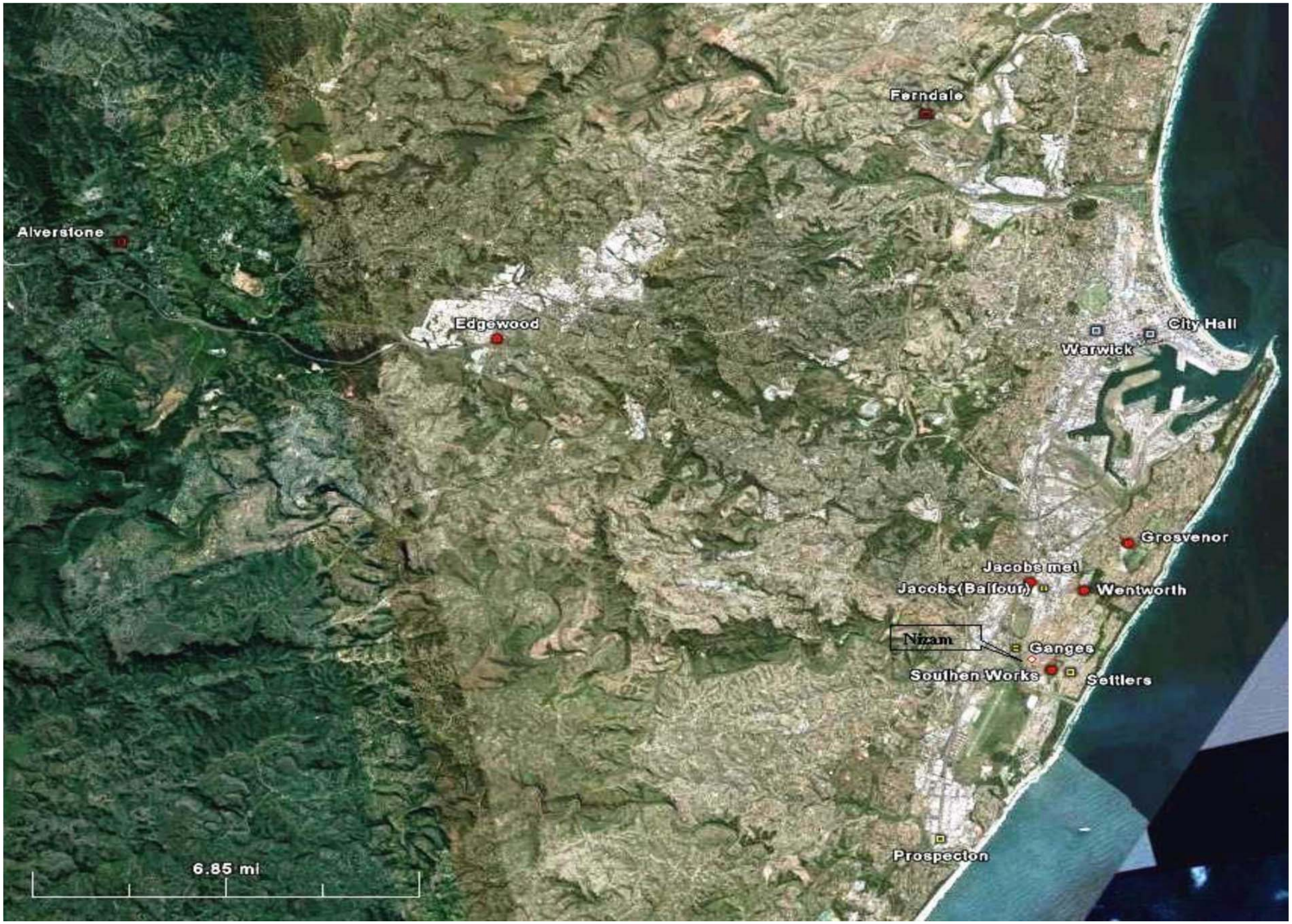
  Sugar refinery

  Sewage treatment works

  A cluster of chemicals industries, major petrochemical and chemical storage facilities, textile manufacturing, metal smelting etc.
- **80% of the SO_2 pollution load: oil refineries, paper producer and sugar refinery (eThekwini Health report 2007).**
- **The DSIB is the focal point of many of the city's major transport routes. This adds a large contribution to emissions from vehicular traffic and shipping**
- **South Durban has a basin-like topography that is conducive to the accumulation of pollution.**

The Ethekwini air quality monitoring network:

- **Ethekwini Municipality commissioned the continuous air quality monitoring network in December 2003, as one of the major elements of its Air Quality Management System.**
- **The network is composed of instrumentation owned and operated by the Ethekwini municipality.**
- **The main objectives of the work are to monitor air quality in Durban as well as measure compliance with air quality standards**
- **The network consists of 13 monitoring stations,**
- **Monitoring stations are situated at a range of sites representing heavy industry, urban, residential and rural locations.**
- **The network instruments continuously measure priority pollutants – these are: NO_x, SO_2, PM10 as well as other species (eg. CO, O_3, PM2.5, VOC, TRS – total reduced sulphates) at selected sites.**



Location of Ethekwini air quality monitoring stations

Table 1: Ethekwini air quality monitoring sites grouped according to location: rural / north / central / south with corresponding species monitored at each site

Site	CO (ppm)	NO (ppb)	NO_2 (ppb)	NO_X (ppb)	O_3 (ppb)	SO_2 (ppb)	Total reduced sulphates (ppb)	Benzene (ppb)	p-Xylene (ppb)	Toluene (ppb)	PM10 μgm^{-3}	PM2.5 μgm^{-3}
Cato-ridge		*	*	*	*	*						
Alverstone					*						*	
New-Germany		*	*	*	*	*						
Ferndale		*	*	*		*					*	
City Hall		*	*	*							*	
Warwick-Avenue	*	*	*	*			*					
Grosvenor						*						
Jacobs (air)		*	*	*		*						
Went-Worth reservoir		*	*	*		*					*	
Ganges		*	*	*		*					*	
Settlers School						*	*	*	*	*		
Southern Works		*	*	*		*	*				*	*
Prospecton						*						

4. Air pollution studies in Durban:

- **Detailed pollution studies in the South African context are not well represented in the literature with even fewer investigations for the greater Durban area.**
- Review of studies of SO_2 (three studies)

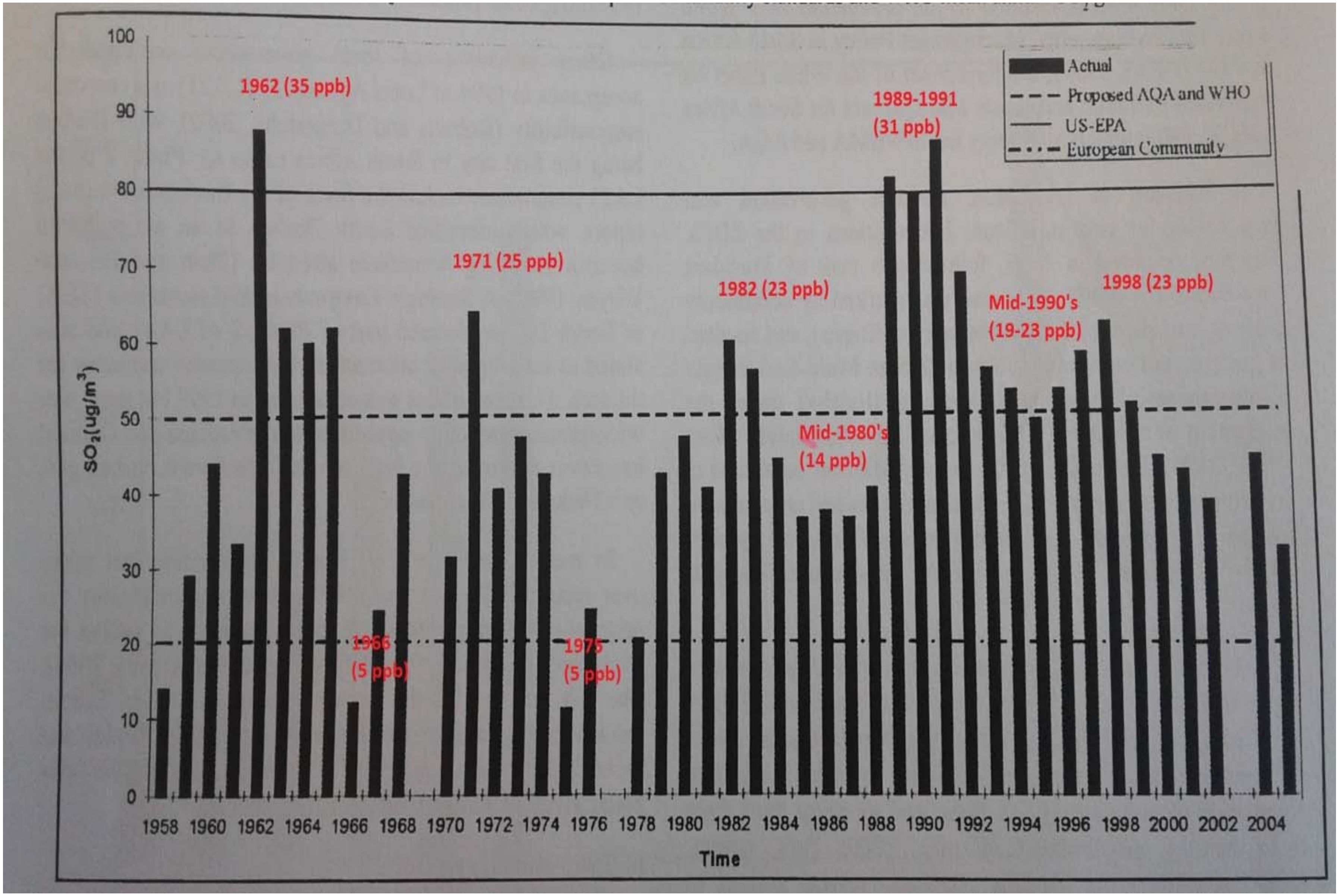
4.1 Sulphur Dioxide (SO_2):

South African National SO_2 exposure guidelines (2004):

Pollutant	Averaging period	Concentration (ppb)
Sulphur dioxide	10 min	191
	1 hr	134
	24 hr	48
	1 year	19

- **Diab et. al. 2007**
- **SO_2 is used as an indicator pollutant as it is one of the main pollutants emitted by industrial combustion processes.**
- It is also the pollutant with the longest record (data has been collected since 1958 at Wentworth in south Durban.
- Mean monthly SO_2 data (µg m^{-3}) over the period October 1958 to December 2005 were derived from SO_2 bubbler records based on the hydrogen peroxide method of collection*.
- Data were averaged over a 2-3 day period and are sufficiently accurate to indicate medium / long term trends.
- **Significant changes in ambient air quality have occurred** over the more than 50 years of recorded measurements
- **Extended periods of increasing trends in air pollution are interspersed with generally shorted periods that are characterised by decreasing trends.**

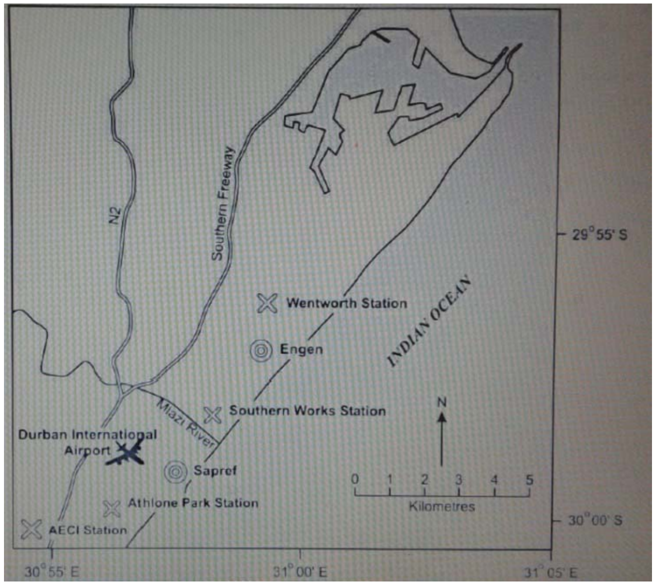
* Sulphur dioxide is absorbed by aspirating a measured volume of air through a solution of dilute hydrogen peroxide. SO_2 is oxidized to sulphuric acid (fast reaction). Sulphate collected in absorber is then determined by various analytical methods



Mean annual SO_2 concentrations (µg m^{-3}) based on data from bubbler stations at Wentworth for the period 1958 – 2005 together with the proposed AQA mean annual SO_2 standard, EPA and European Community standards and WHO mean SO_2 guidelines. Dashed line is equivalent to South African air quality guidelines for SO_2 exposure. (To convert from ppb to µ g m^{-3} multiply by 0.382 – SA guideline = 19 ppb yearly average)

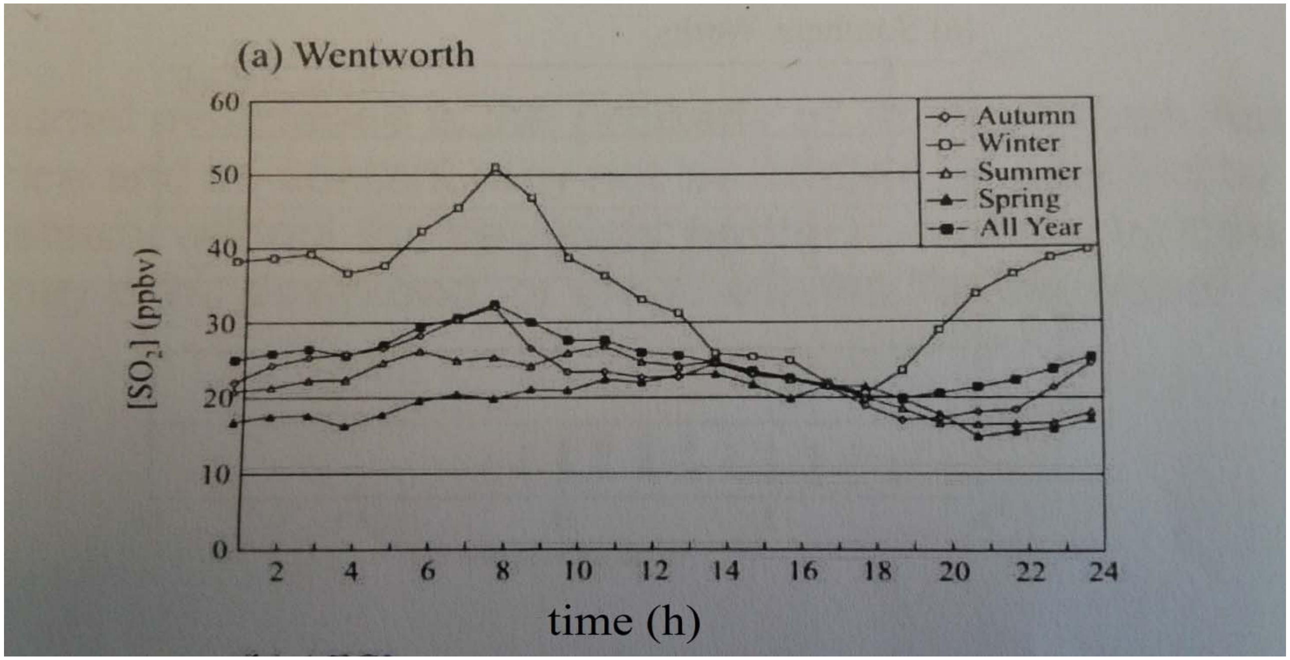
- **1958 – early 1960's**: Steady increase to a peak annual concentration of 88 μg m^{-3} in **1962 (35 ppb)**. Maximum level for study period.
- **1963 - 1965:** SO_2 levels stabilize at approx 60 μg m^{-3} (23 ppb) and then drop sharply to 12 μg m^{-3} **(5 ppb) in 1966.**
- **Late 1960's – early 1970's**: Rise in SO_2 levels to maximum **1971 of 65 μg m^{-3} (25 ppb)** then decline.
- **Late 1970's – early 1980's:** Increasing trend, maximum in **1982 of approx 60 μg m^{-3} (23 ppb)**
- **Mid 1980's:** Levels stabilize at approx **35 μg m^{-3} (14 ppb)**
- **Late 1980's and early 1990's**: Increasing trend with levels exceeding **80 μg m^{-3} (31 ppb) in 1989 and 1991** – a threshold that had not been reached in the past 30 years.
- **After 1991**: Concentrations decline and levels stabilize between **50 – 60 μg m^{-3} (19 – 23 ppb)** over the following few years.
- **Since 1998:** An approximate downward trend to 2005. Values recorded in **2005 correspond to approx 30 μg m^{-3} (12 ppb)**

- **<u>Diab et. al. (2002): Measurements of SO_2 1997 - 1999</u>**
- **This study investigated variations of SO_2 in the DSIB (1997 – 1999)**
- Network of monitoring stations were set up at four sites: AECI, Athlone, Wentworth, Southern Works. Data was collected hourly using UV fluorescence method to quantify SO_2 *
- **No obvious <u>seasonal trend</u> in data for period 1997 - 1999**
- **Spectral analysis of data shows that the dominant feature of the data is the <u>diurnal cycle</u>** – this is very well developed in winter at the two stations closest to an industrial source. These were Southern Works and Wentworth in close proximity to Engen refinery.



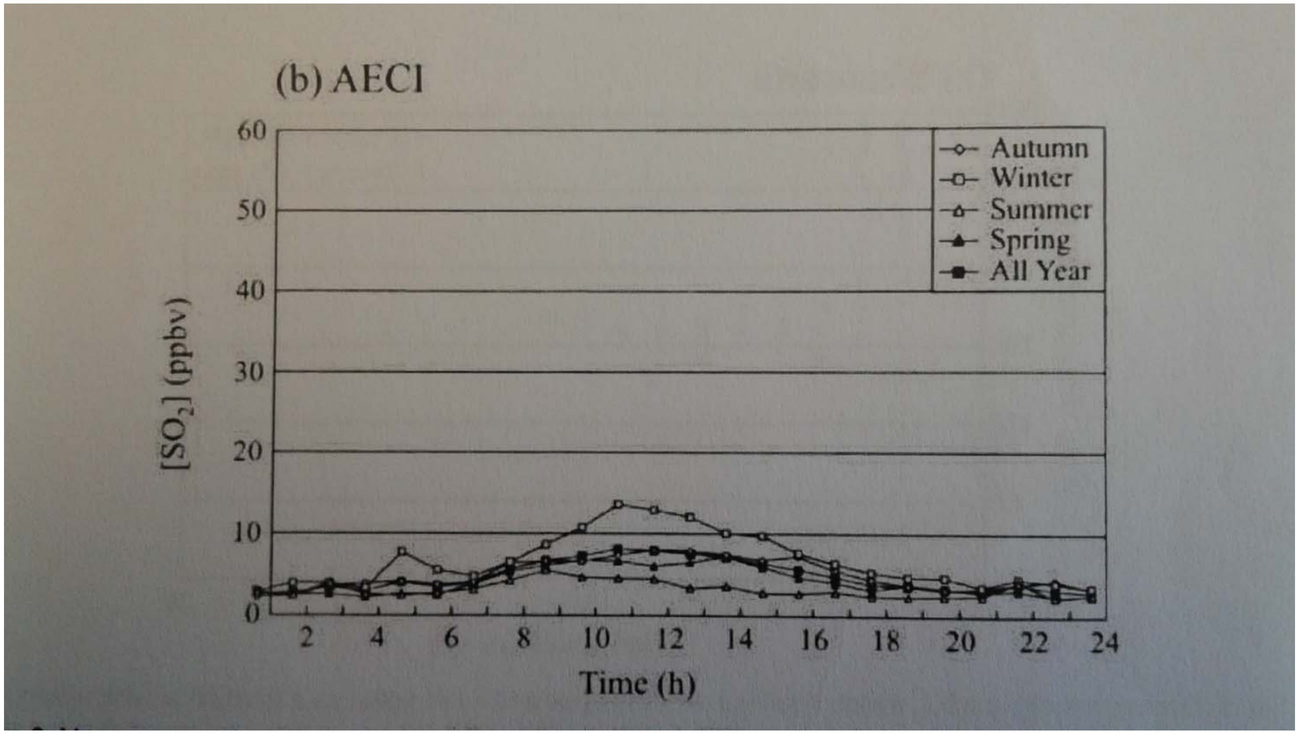
- Plots of hourly averages by season and mean annual conditions – shown for AECI and Wentworth.

*UV radiation passed through sample and fluorescence due to SO_2 measured



Mean seasonal and mean annual diurnal variations in SO_2 concentration (ppb) at Wentworth.

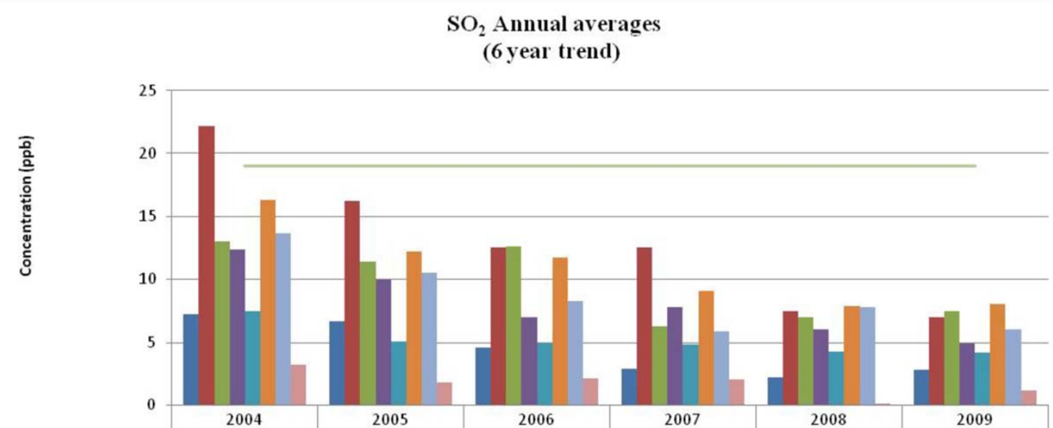
- **Wentworth:** Diurnal curves had an amplitude of approx 10 ppb in winter (or less – other seasons). Values recorded in winter markedly higher than other seasons. Distinctive peak at 8:00: Authors not sure of explanation but could be related to a traffic peak or industrial cycle. Minimum values occurred in mid-late afternoons.
- **In winter:** SO_2 levels remained elevated throughout the night relative to other seasons. Concentrations increase from 20:00 and reach a maximum at midnight. Authors suggest that Wentworth is exposed to a nocturnal source of pollution in evening hours not seen at other stations.



Mean seasonal and mean annual diurnal variations in SO_2 concentration (ppb) at AECI monitoring station.

- **AECI:** Less diurnal variation relative to Wentworth site
- Winter levels are slightly higher than values recorded in other seasons. Variation between 5 – 15 ppb
- SO_2 at approx 5 ppb level (Spring / Summer / Autumn).
- During the day maximum levels recorded at 11 am
- No second peak in concentration in evening hours as seen at Wentworth

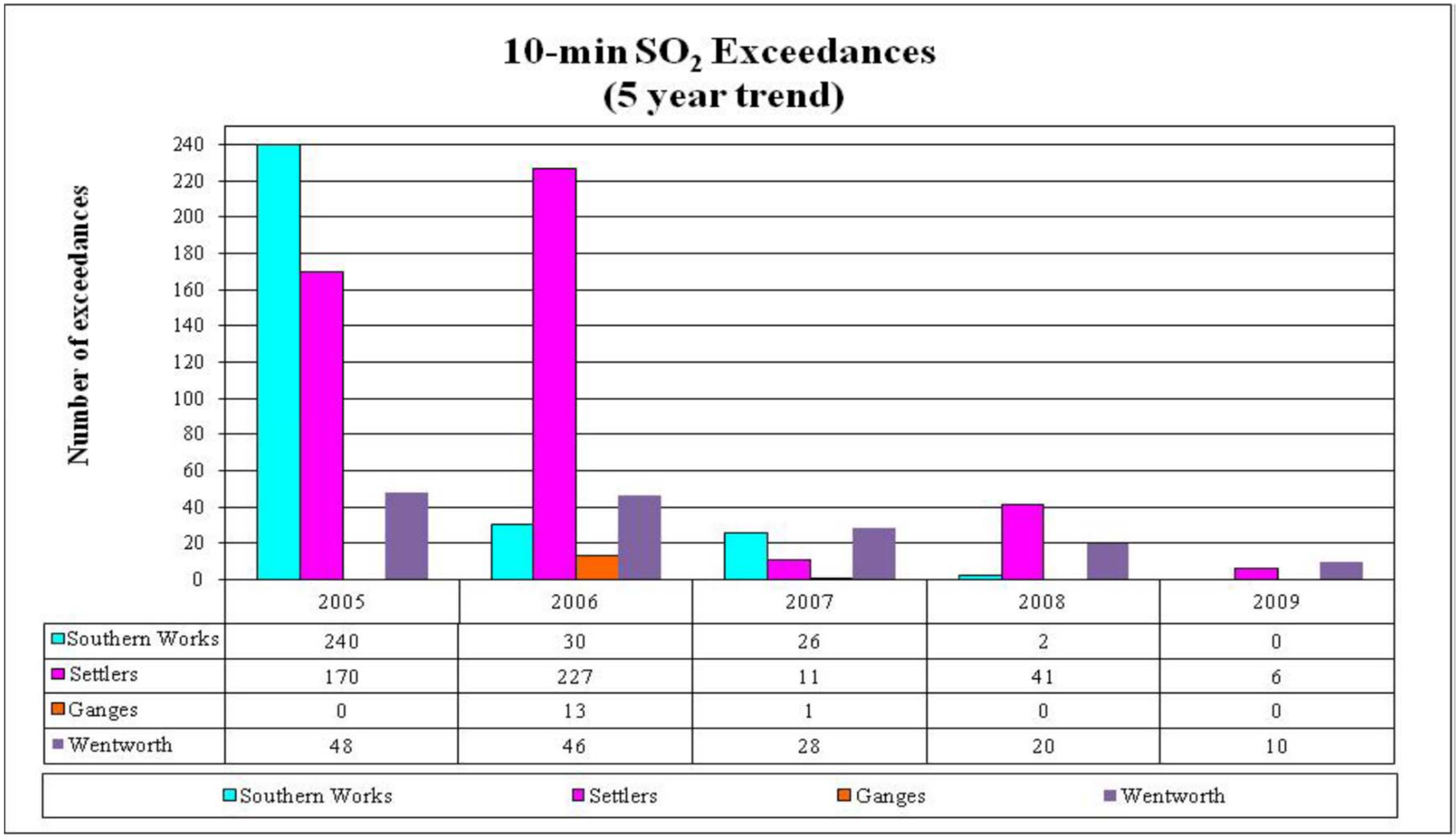
Ethekwini municipality Air quality report (2009):



	2004	2005	2006	2007	2008	2009
Prospecton	7.2	6.7	4.6	2.9	2.2	2.8
Southern Works	22.2	16.2	12.5	12.5	7.5	7
Settlers	13	11.4	12.6	6.3	7.0	7.5
Ganges	12.4	10	7	7.8	6.0	4.9
Grosvenor	7.5	5.1	5	4.8	4.3	4.2
Wentworth	16.3	12.2	11.7	9.1	7.9	8
Jacobs (Balfour)	13.7	10.5	8.3	5.9	7.8	6
Ferndale	3.2	1.8	2.1	2	0.1	1.1
GLV	19	19	19	19	19	19

Prospecton, Southern Works, Settlers, Ganges, Grosvenor, Wentworth, Jacobs (Balfour), Ferndale, GLV

- **SO_2 annual averages: 2004 – 2009 for 8 monitoring stations**
- **Southern sites: Ganges, Southern works, Settlers school, Grosvenor, Wentworth, Jacobs**
- **Northern sites: Ferndale**
- **There is an approx downward trend over the period 2004 – 2009 at all stations**
- **National guideline for annual SO_2 exposure is 19 ppb – all stations record below this limit except Southern Works in 2004**
- **Levels at southern sites higher than levels at northern sites – proximity to emission sources**



	2005	2006	2007	2008	2009
Southern Works	240	30	26	2	0
Settlers	170	227	11	41	6
Ganges	0	13	1	0	0
Wentworth	48	46	28	20	10

- **10-min SO_2 exceedances for Southern monitoring stations**
- **10-min exceedance corresponds to 191 ppb**
- **Trend indicates significant decrease in number of exceedances over the period 2004 – 2009 for four stations**
- **Maximum number of exceedances recorded at Southern Works in 2004 – corresponding to 240 10-min exceedances**
- **All four sites in close proximity to ENGEN refinery, SAPREF and MONDI paper mill.**

5. Conclusion / plan for future work:

- There is an approximate decreasing trend in SO_2 levels from 1998 to present (Wentworth) – this is used as a broad indicator of air quality in Durban.
- **To date no comprehensive, long term study of major atmospheric pollutants in the greater Durban area has been undertaken.**
- Pollutants need to be monitored more extensively and for longer periods in order to clarify the complex relationships that exist between species / photo-chemistry and meteorological factors.
- A long term study of target pollutants using data from Ethekwini monitoring stations for the period 2003 - present is proposed

6. Acknowledgements:

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