Implications of regional surface ozone increases on visibility degradation in south east China

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Abstract

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Implications of regional surface ozone increases on visibility degradation in southeast China

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Data Sources:

- **Visibility Data (1968–2010)** from Hong Kong Observatory (HKO).
- **Air Pollutants (1984–2010)** including O_3, SO_2, NO_x, NO_2, and PM_{10} from HKEPD.

Objective of the Study:

- To investigate the **long-term visibility degradation** in Southeast China, particularly Hong Kong, and determine the role of **surface ozone (O_3) increases** and **atmospheric oxidation** in this phenomenon.
- To identify the **chemical and meteorological mechanisms** influencing visibility through a multi-decadal analysis.

Methodology:

- **Trend analysis** using linear regression to quantify changes in visibility and pollutant concentrations.
- **Multiple linear regression** and **partial correlation analysis** to link pollutants with reduced visibility (RV).
- **Seasonal and annual comparisons** to highlight evolving pollutant influences.

What is Reduced Visibility?

- The visibility is the measure of the distance at which an object or light can be clearly discerned. In meteorology, it depends on the transparency of the surrounding air and as such, it is unchanging no matter the ambient light level or time of day.

- It is defined as the percentage of hours per month with visibility below 8 km in absence of rain, fog, mist or relative humidity.

Introduction

In China, particularly in industrial areas like Pearl River Delta, Yangtze River Delta and Beijing in Eastern China, the visibility was observed to reduce significantly due to increase in air pollution due to fossil fuel combustion and industrial development.

- Increase in RV was prominent after 1990.
- South East China is strongly influenced by regional O_3 formation and accumulation due to continental outflow of pollution.
- We will understand the relationship between visibility degradation and air quality deterioration, and the underlying physical and chemical mechanisms.

Introduction

- Hong Kong is strongly impacted by air pollutants transported from upwind source regions along the east Asian coast, particularly under the influence of the winter monsoon.

- The paper analyses visibility over 43 years and air quality data sets over 27 years from Hong Kong.

- We study in detail the possible effects on visibility degradation due to the increased oxidizing power in the atmosphere in south east China.

Data and Methods

- Atmospheric visibility data covering the period from January 1968 to December 2010 were provided by the HKO.
- Because the precipitation frequency in the Hong Kong region does not show any significant trend over the time period, we believe it does not exert any significant impact on the derived long-term RV trends.
- Ambient SO_2, PM_{10}, NOx, NO_2 and O_3 data were obtained from an automatic air quality monitoring station operated by HKEPD
- The gaseous pollutant data used in this study covered the period from January 1984 to December 2010. However, PM_{10} measurement at this station began in 1993 and thus the PM_{10} data only cover the period from January 1993 to December 2010.

Results and Discussion

Long-term trends of visibility from 1968 to 2010

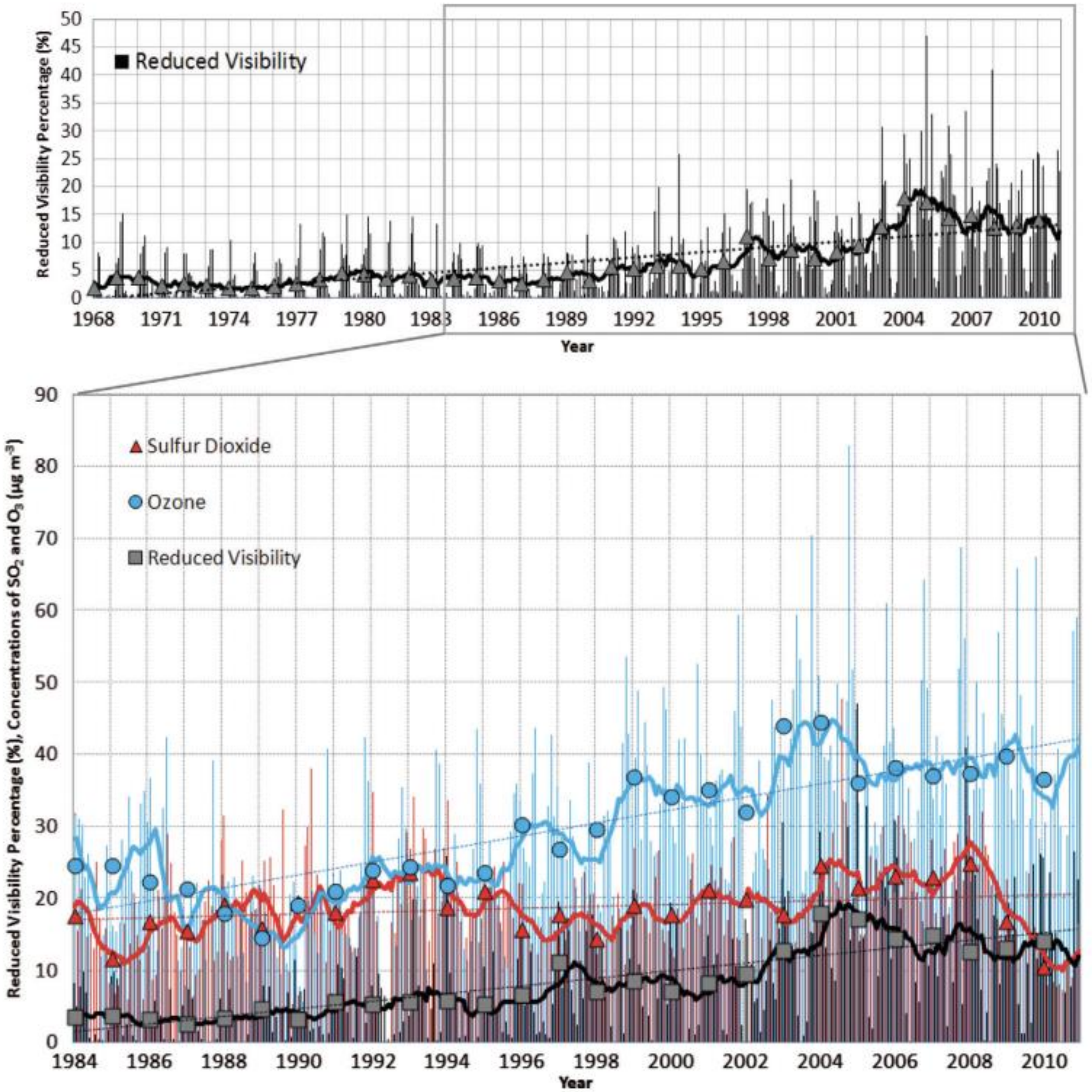
- visibility and hence air quality degradation were more pronounced after 1990
- Clear seasonal pattern- **lowest visibility** in **winter (heating period)** and **maximum** in **summer**.
- **Lowest visibility** occurring in winter (the heating period) in northern China due to the **high coal usage** and **associated aerosol emissions**

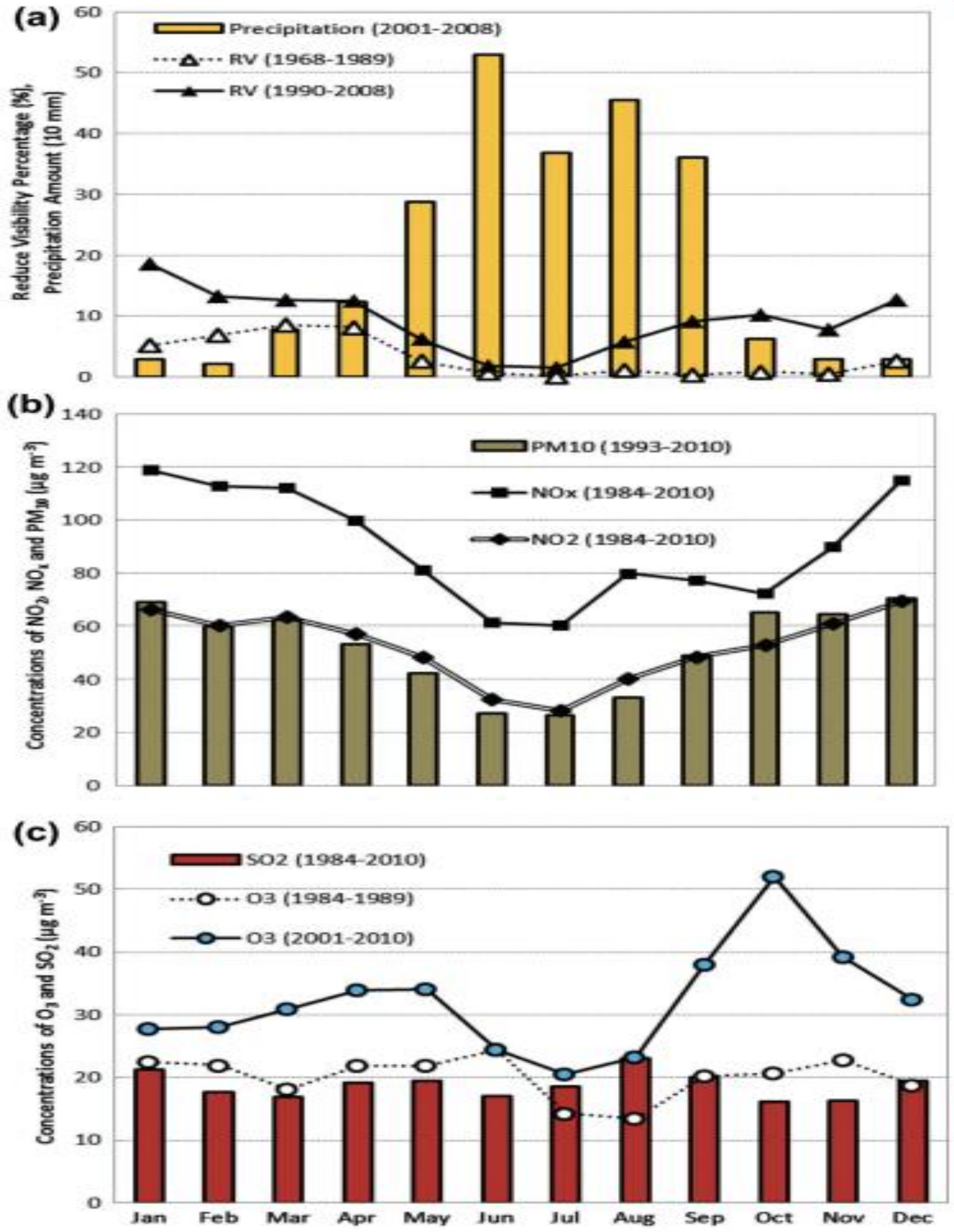
Table 1. Overall and seasonal annual trends of RV, SO_2, NO_2, NO_x, O_3, and PM_{10} (winter: December, January, and February; spring: March, April, and May; summer: June, July, and August; autumn: September, October, and November)

	Period	Overall	Winter	Spring	Summer	Autumn
Reduced visibility (% per yr)	1968–2008	0.31% ($p < 0.001$)	0.48% ($p < 0.001$)	0.22% ($p < 0.001$)	0.11% ($p < 0.001$)	0.43% ($p < 0.001$)
	1990–2008	0.61% ($p < 0.001$)	0.80% ($p < 0.001$)	0.58% ($p < 0.001$)	No trend[a]	0.90% ($p < 0.001$)
O_3 ($\mu g\ m^{-3}$ per yr)	1984–2008	0.90 ($p < 0.001$)	0.75 ($p < 0.001$)	0.98 ($p < 0.001$)	0.63 ($p < 0.001$)	1.47 ($p < 0.001$)
	1990–2008	1.06 ($p < 0.001$)	1.06 ($p < 0.001$)	1.20 ($p < 0.001$)	0.76 ($p < 0.001$)	1.32 ($p < 0.001$)
SO_2 ($\mu g\ m^{-3}$ per yr)	1984–2008	No trend	No trend	No trend	No trend	0.20 ($p < 0.01$)
NO_2 ($\mu g\ m^{-3}$ per yr)	1984–2008	No trend	No trend	No trend	No trend	0.45 ($p < 0.10$)
NO_x ($\mu g\ m^{-3}$ per yr)	1984–2008	No trend	No trend	No trend	No trend	No trend
PM_{10} ($\mu g\ m^{-3}$ per yr)	1993–2008	No trend	No trend	No trend	No trend	No trend

[a]'No Trend' indicates that the trend is statistically insignificant at the significance level of 0.10.

Long-term trends of visibility from 1968 to 2010





Seasonal Patterns of (a) precipitation and RV, (b) concentrations of PM_{10}, NO_2, NO_x, (c) SO_2, and O_3.

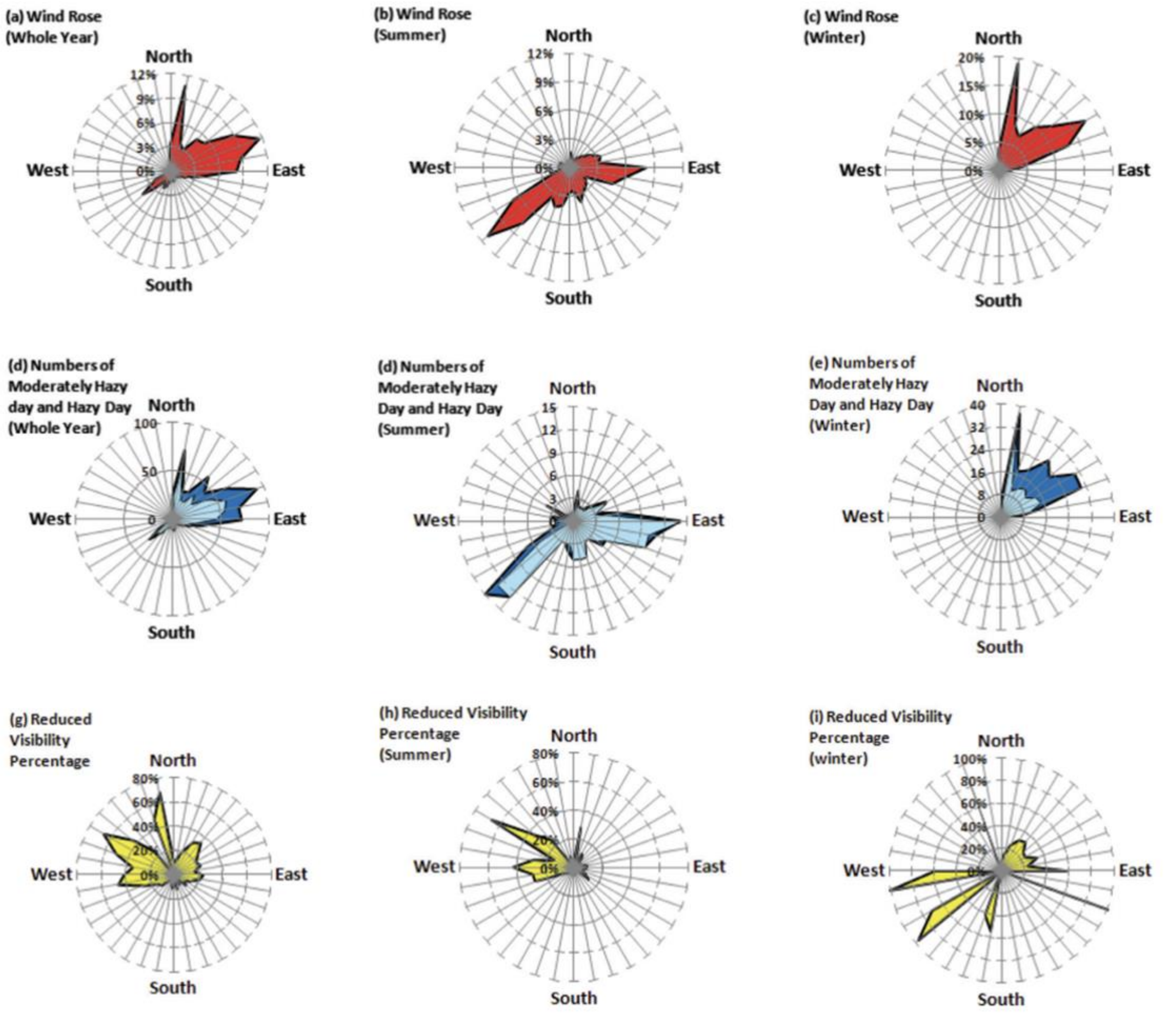


Fig. 4. (a, b, c) Wind roses, (d, e, f) number of moderately hazy days (light blue) and hazy days (blue) and (g, h, i) RV vs. wind direction sectors during 2001–2004.

- Other **contributing factors** to **seasonal pattern** may be the **higher summer rainfall abundance**, leading to **pollutant washout** and **higher mixing layer height** (i.e., better dispersion capacity of the atmosphere) during summer due to solar thermal heating
- The **north easterly winds** in the dry season plays an important role in transporting pollutants from east Asia to south China.
- **High summer rainfall abundance** which results in **pollutant washout** and better dispersion capacity during summer due to **solar thermal heating**.

Changes of surface ozone levels and related species during 1984-2010

- **O_3 concentration** were **maximum** during **autumn** and **second maximum** during **spring**.
- Such seasonal patterns are driven primarily by continental monsoon in winter and maritime monsoon in summer.
- There was **no significant seasonal cycle** followed by SO_2 concentrations.
- **Increases in the emissions of O_3 precursors** in upwind source regions **lead to annual increase in O_3.**
- SO_2 concentrations reached a peak in 1993 and then they decreased gradually till 1999. Ship emissions and bunker fuel usage were major contributors to SO_2 concentrations.
- Due to increasing O_3 levels enhanced the NO to NO_2 conversion through the following reaction:

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

Changes in CO, VOCs may also contribute to this trend through NO peroxy radical reactions.

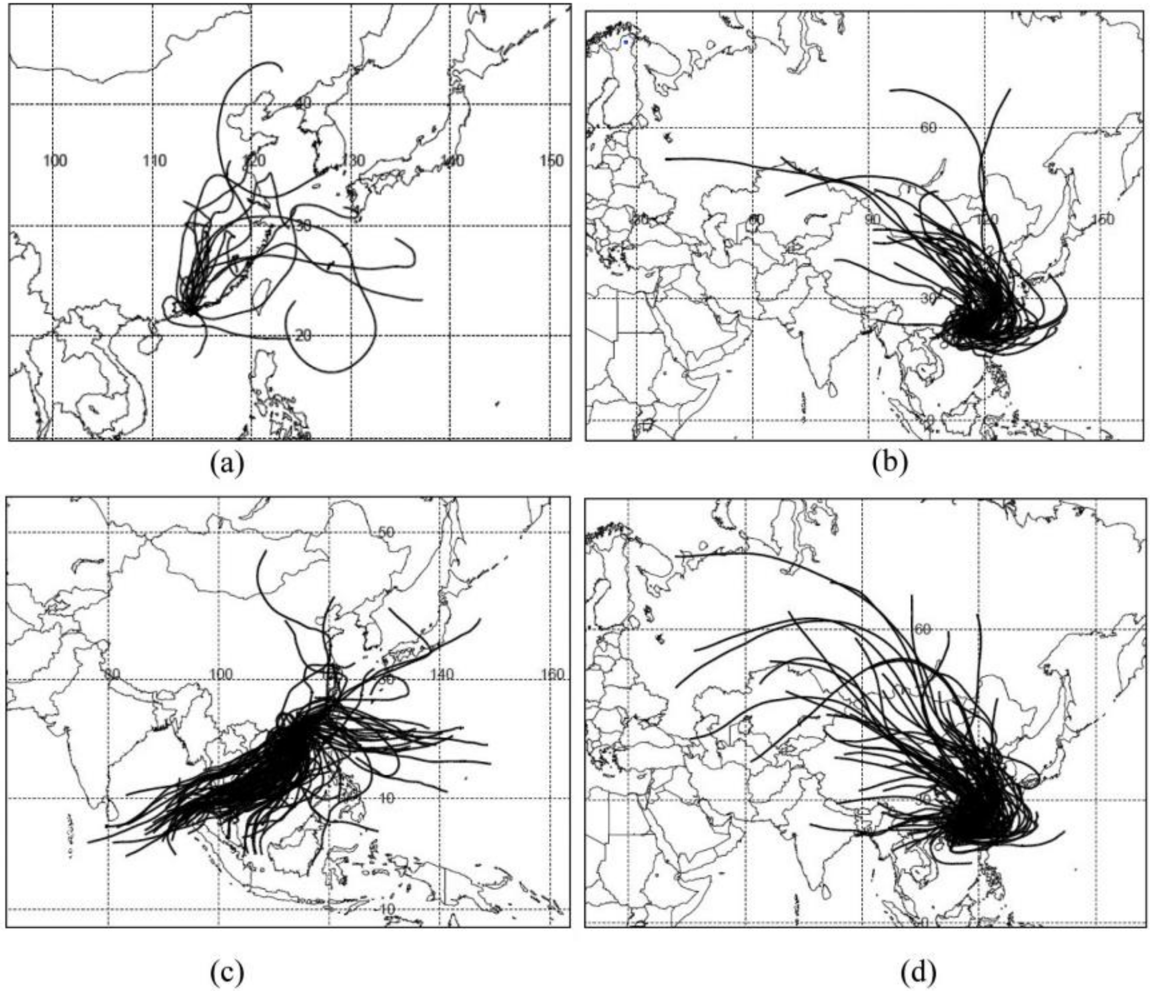


Fig. 5. 120-h backward air trajectories on hazy days (a: summer; b: winter) and moderately hazy days (c: summer; d: winter) at Hong Kong during 2001–2004.

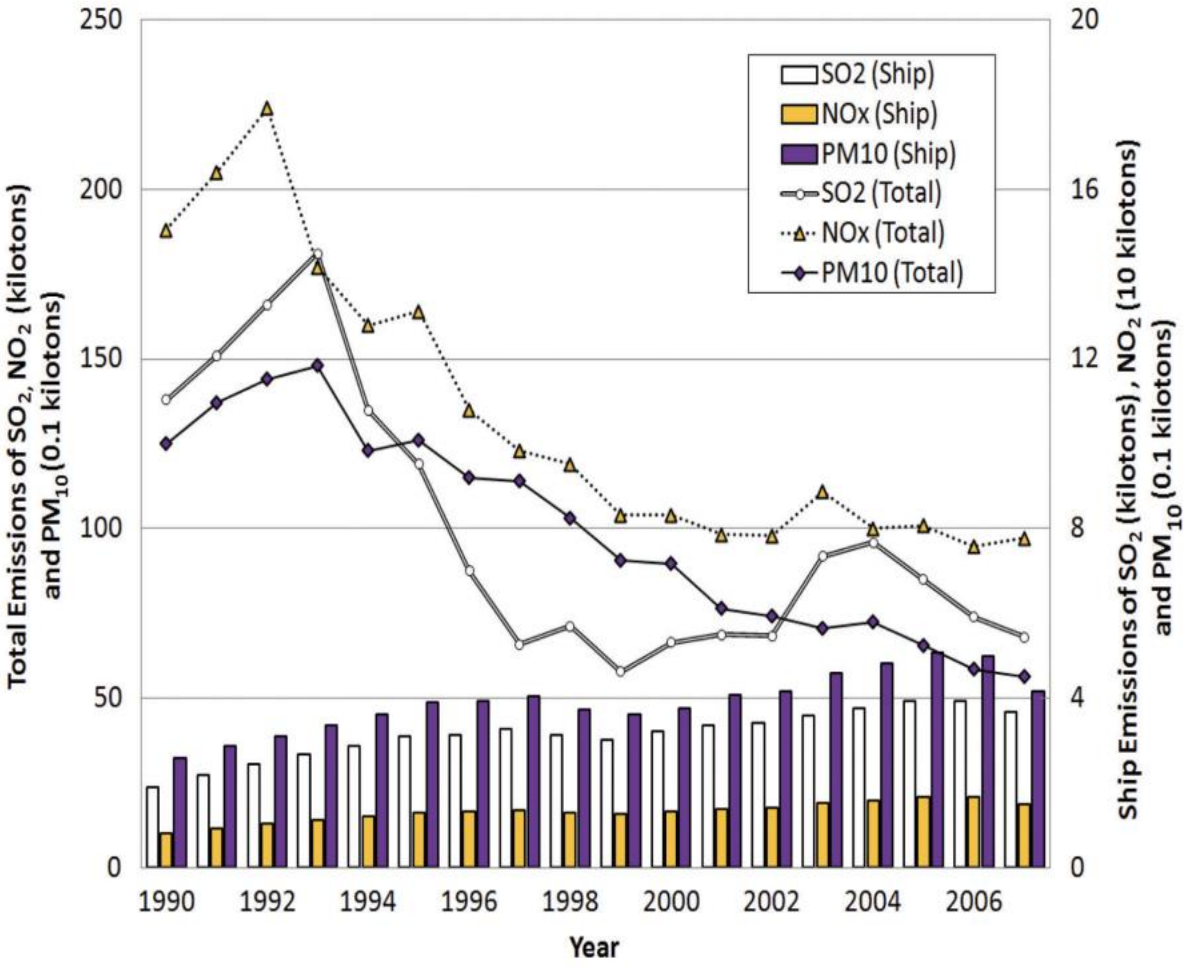


Fig. 6. Annual total emissions and ship emissions of SO_2, NO_x and PM_{10} (Data source: http://www.epd.gov.hk/epd/english/environmentinhk/air/data/emission_inve.html).

Statistical Models: Understanding Pollutant Contributions

- Multiple linear regression used to isolate pollutant impacts on Reduced Visibility (RV)

Multiple Linear Regression Models

- Model 1 (1993–2008): O_3, SO_2, NO_x, NO_2, PM_{10}
- Model 2 (1984–2008): O_3, SO_2, NO_x, NO_2
- Model 3 (1993–2008): O_3, SO_2, NO_x, NO_2 (excludes PM_{10})
- Model 4 (1984–1992): O_3, SO_2, NO_x, NO_2

Key Findings:

- Before 1993 → NO_2 and NO_x were dominant RV influencers
- After 1993 → O_3, SO_2, and NO_2 became significant
- PM_{10} had no significant influence on RV

Relationship between visibility and air pollutants

- On performing multiple linear regressions, a relationship between reduced visibility and air pollutants was found.

Table 2a. Summary of equations calculated by multiple linear regression method

Regression model	Period	Independent variables	Equation[a]
Model 1	1993–2008	O_3, SO_2, NO_x, NO_2, PM_{10}	$[RV] = 0.17\,[SO_2] + 0.31\,[NO_2] + 0.17\,[O_3] - 15.89$
Model 2	1984–2008	O_3, SO_2, NO_x, NO_2	$[RV] = 0.20\,[SO_2] + 0.11\,[NO_2] + 0.27\,[O_3] - 12.63$
Model 3	1993–2008	O_3, SO_2, NO_x, NO_2	$[RV] = 0.18\,[SO_2] + 0.32\,[NO_2] + 0.18\,[O_3] - 16.34$
Model 4	1984–1992	O_3, SO_2, NO_x, NO_2	$[RV] = 0.11\,[NO_x] - 0.09\,[NO_2] - 1.12$

[a]Units of RV are % and those of all air pollutants are $\mu g\ m^{-3}$.

Trends in Ozone and Reduced Visibility

Trends (from regression analysis):

Period	O_3 Trend (µg/m³/yr)	RV trend (%/yr)
1984–2008	+0.90	+0.31
1990–2008	**+1.06**	**+0.61**

- Steepest increase in autumn: **+1.47 µg/m³/yr (O_3)**
- Clear **post-1990 rise in both pollutants and reduced visibility.**

Inferences of the regressions

- In **model 2**, the **partial correlation coefficients** between **RV** and the **air pollutants** passed the student t-test meaning the **RV was primarily influenced by those air pollutants.**
- In **model 1 and 3**, **coefficient of partial correlation** for the air pollutants, regardless of whether PM_{10} was included or not, **all passed the student t-test.**
- In **model 4**, **coefficient of partial correlation** for **NO_2 and NO_x passed the test.**
- This implies that the RV was influenced majorly by NO_2 and NO_x before 1993 and by O_3, SO_2 and NO_2 afterwards.

Implications of visibility degradation and air quality changes

- ***Formation of secondary sulphate in an O_3 enhanced atmosphere.***
- Oxidants such as **OH, HO_2 and H_2O_2** play an important role in formation of secondary particle formation and rate of production of such oxidants is proportional to concentration of O_3 in the atmosphere.
- In sufficient solar radiation and atmospheric oxidation, SO_2 can be oxidized to secondary sulphate rapidly thus increasing the ratios of sulphate concentration to concentrations of sulphate plus SO_2, $[SO_4^{2-}]/[SO_4^{2-}] + [SO_2]$.
- Data indicates that **secondary sulphate** is the predominant factor responsible for the visibility degradation.
- The major mechanisms for oxidation of **S(IV) to S(VI)** are:

1) **Gas phase oxidation of SO2 by OH radical.**

2) **Aqueous oxidation of dissolved SO2 with dissolved H2O2 or O3**

- Lifetime of SO_2 with respect to oxidation by OH is approximately 13 d. Hence increase in O_3 will increase condensed phase SO_4^{2-}.
- Gas phase oxidation is important in summer/autumn due to strong solar radiation and high levels of O_3 which will enhance OH production.
- The pathway of H_2O_2 oxidation would be important as **increasing HO_x** levels will **enhance the peroxide production.**

Why Autumn Matters?

- **Autumn: Peak Season for Photochemical Formation**
- **Strong solar radiation** and stagnant air → **high photochemistry**
- **Continental outflow** from East China coast → **pollution transport**
- O_3 peaks in autumn, enhancing oxidant formation
- **Conclusion:**
- **Autumn** is the **most critical season** for **controlling secondary aerosol** and **RV**

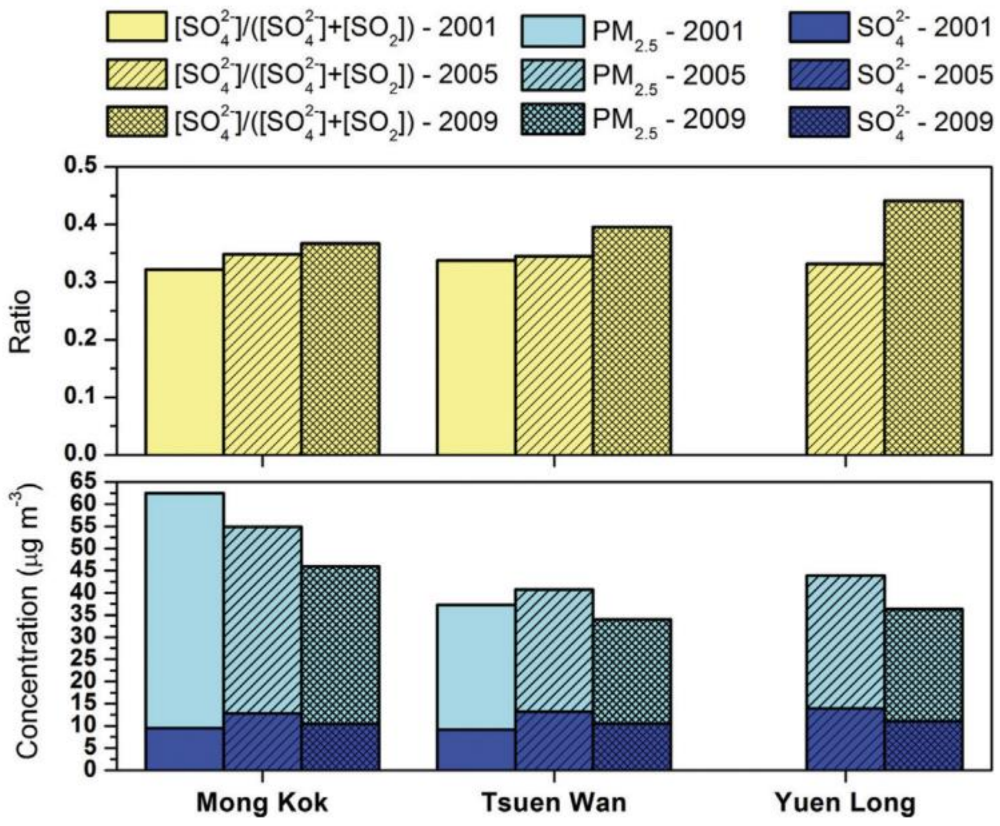


Fig. 7. Ratios of sulphate concentrations in $PM_{2.5}$ to the concentrations of sulphate plus SO_2 (upper panel). $PM_{2.5}$ and sulphate concentration data (lower panel) were adopted from Chow et al. (2010).

Current day SO_2 concentrations were similar during 1993 but RV occurrences was lower than present day which makes us conclude that **O_3 has an important role in conversion of S(IV) to S(VI)** and in **enhancing photochemical formation of secondary pollutants** such as sulphate which **contribute significantly to RV.**

Chemical coupling of O_3, NO_2 and other species

- **NO_2** strongly absorbs in the **blue region of the spectrum** and contributes directly to the **visibility degradation.**
- Under high oxidant O_3/OH conditions, if VOCs or CO are present in sufficient amounts, the photo-stationary state of the NO-NO_2-O_3 will be modified as NO_2 can be regenerated through the reaction between NO and HO_2 resulting in the formation of O_3.
- Hence, **accumulation of O_3** in the atmosphere would **amplify the production of several oxidants** and therefore **increase in ambient NO_2 concentrations** also indicates the **impact of other secondary pollutants (O_3).**
- Also, NO_2 reacts with the oxidants to form nitric acid HNO_3 and peroxyl nitrate (PAN). In the presence of NH_3, subsequent formation of particulate ammonium nitrate (NH_4NO_3) also plays important role in visibility degradation.
- Formation of dicarboxylic acids via photo-oxidation plays and important role in affecting visibility and global radiative balance. Particulate organic matter has been found to be a major light scattering component and contained a significant amount of secondary organic carbon.

Not All PM Is Equal

PM_{10} vs $PM_{2.5}$ and Composition

- PM_{10} showed **no significant correlation** with RV
- 50% of PM_{10} mass is $PM_{2.5}$ → stronger light scatterers
- Rise in **fine particles + secondary species (e.g. sulphates, organics)** drives RV.
- RV linked to **aerosol composition**, not just mass concentration

Other possible causes of visibility degradation

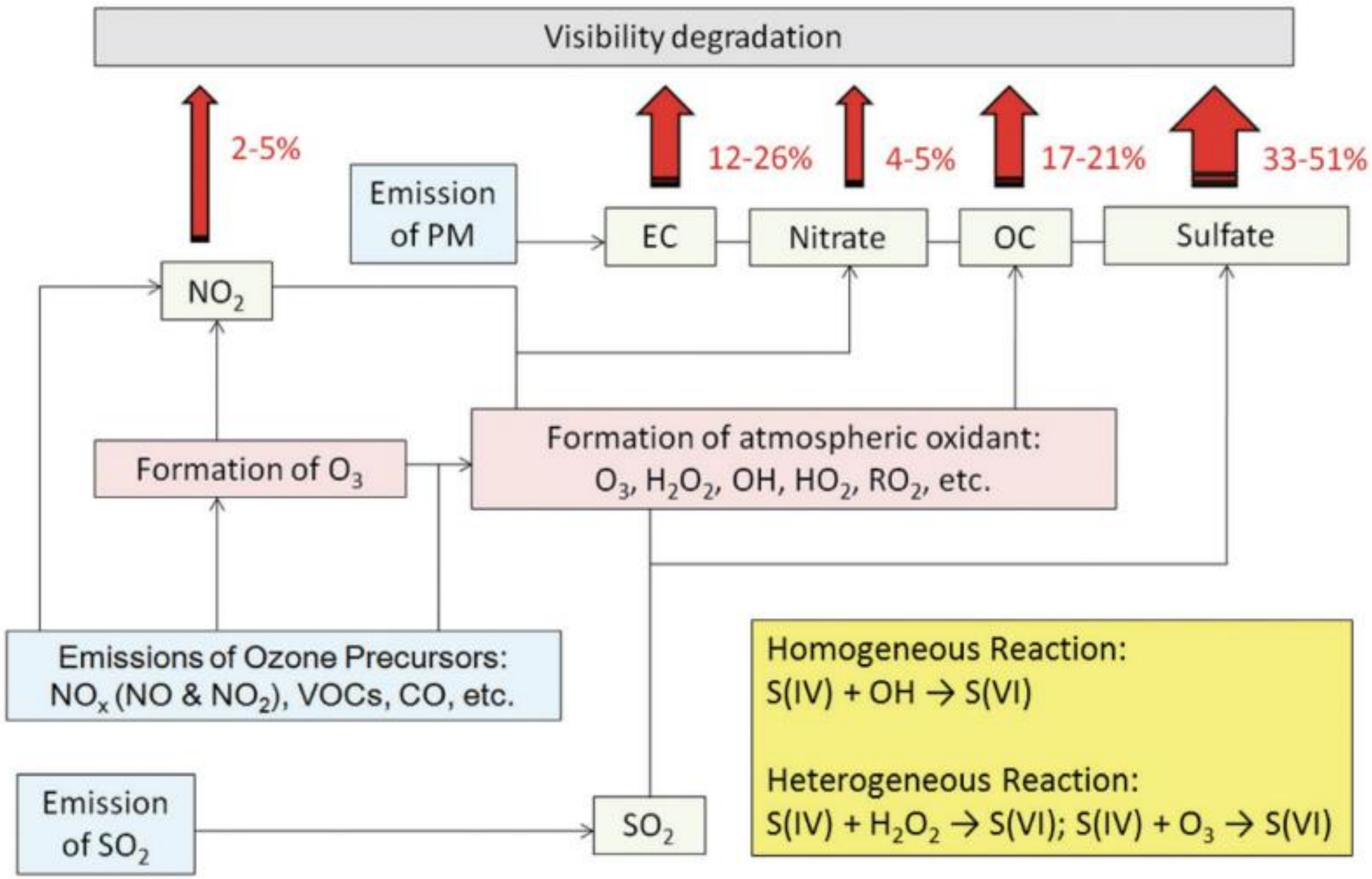


Fig. 8. Chemical coupling among trace gases leading to impacts on visibility degradation in the Hong Kong region – see text for details. Percentage values indicate the light extinction contributions of various species given by Wang (2003).

Continued….

- More than half of PM_{10} consists of $PM_{2.5}$.
- Fine particles scatter light more effectively than coarse particles. Increase in RV occurrences suggests that there was a steady increase in fine particles.
- However, relatively constant PM_{10} concentrations suggest that there might have been decrease in coarse particles.
- Pollutants such as **Elemental Carbon (EC)** is an **effective light absorber** and is one of the **major pollutants causing RV**.
- Water soluble K^+, through light scattering, and primary sulphate emissions from ship also cause RV.

Summer RV Events: A Puzzle

- Unexplained Summer RV Events
- Unexpected RV during summer with southerly winds
- **Likely causes:**
  - Biomass burning aerosols from SE Asia (e.g., Philippines)
  - Marine air mass transport with pollutants
- **Future Work:**
- Requires further research using isotopic and trajectory analysis

Summary

- Most pronounced increases in the occurrence of RV, and in O_3, SO_2 and NO_2 concentrations, were all observed in autumn which can be attributed to the influence of rapid development and associated emissions in the highly populated cities in eastern China.
- **Autumn** is the season most favourable for the regional formation and accumulation of surface O_3 in the region.
- Several possible causes of visibility degradation are proposed; in particular the **enhanced oxidation capacity** may play a dominant role in **increasing the formation of secondary particulates, especially secondary sulphate.**
- The enhancement of secondary particulate formation may modify both loadings and composition of tropospheric aerosol, and thus have vital impacts on regional climate via **aerosol radiative forcing**, in addition to the immediately apparent environmental impact of reduced visibility.
- PM_{10} mass concentrations are not necessarily proportional to visibility.

Key Implications

Surface O_3 is a major contributor to visibility degradation via enhanced formation of **secondary sulphate aerosols**.

Chemical coupling of O_3, NO_2, SO_2, and secondary organics intensifies aerosol loading and light extinction.

PM_{10} mass alone is not a reliable indicator of visibility loss; composition (esp. $PM_{2.5}$, secondary species) matters more.

Policy & Environmental Relevance:

- Highlights the **need to regulate ozone precursors** (NO_x, VOCs) and **track secondary aerosol trends**, not just primary PM.
- Underlines the **climate co-benefits** of improved air quality—secondary aerosols affect radiative forcing.

Scope for future work

Future Scope:

- **Detailed aerosol chemical speciation** to assess long-term $PM_{2.5}$ contributions.
- **Isotopic studies** to identify sulphate origins and formation pathways.
- **Integrated satellite + model studies** for regional transport analysis.
- Explore links between **visibility, health impacts, and climate effects** more deeply.

THANK YOU