



# Optical Remote Measurements of Particles in Emission Gas Plumes

Thesis Presentation

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# Acknowledgement

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# Outline

Problem Statement

Related Background

Methodology

Data Analysis

Results and Discussion

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# Project Mission

- We aim to explore the aerosol traces in specific areas of Tianjing city, China.
  - Profound influences:
    - The Earth's radiation balance (scattering/absorbing, cloud condensation nucleus);
    - Human health (respiratory and cardiovascular disease).
  - Sources:
    - Urban and industrial aerosol;
    - Biomass burning aerosol;
    - Desert dust aerosol;
    - Sea salts, Volcanic ash, Re-suspended soil particles etc.

# Project Objectives

- Analyze the measured air pollutant concentrations and express in temporal-spatial domain.
  - Concentrations sampled through the DOAS and SOF methods.
  - Temporal-spatial expression via the Google Maps.
- Explore the correlation between the measured air pollutants and the aerosol traces.
  - The aerosol traces were measured from the 'Flame' spectrometer.
  - Optical depth (OD) instead of the aerosol optical depth (AOD).
  - Indirect solar light instead of direct solar light.

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# Aerosol Measurement Overview

- AOD characterizes the aerosol column concentration.
  - The integral of the attenuation coefficient of aerosol over a column of unit cross section in zenith direction.
  - The degree to which the aerosol block the transmission of the solar light ( $0.01 \sim$  a clean sky,  $0.4 \sim$  very hazy).
- Spaceborne.
  - Radiometers
  - Laser-based sensors
- Ground-based.
  - Networks of ground stations, eg AERONET
- Others.
  - Airborne measurements
  - Vehicle-based

# Related Atmospheric Phenomena

- Optical remote sensing covers spectrum ranges from the lower part of the Ultraviolet (UV), to the whole Visible light (VIS) until the Near-infrared (NIR).

Working wavelength range of the 'Flame' spectrometer is  
~ btw. 280 nm and 1100 nm.

Table: Electromagnetic spectrum of the optical remote sensing

Name	Wavelength (nm)	Frequency (THz)
soft UV	280 - 380	789 - 1071
VIS	380 - 750	400 - 789
NIR	750 - 1400	214 - 400

# Three Key Processes

- Energy received from the Sun will be filtered by the atmosphere. The interaction between radiation and matter (cloud, gases and aerosol) can all be included in:
  - Emission produces photos;
  - Absorption of an incoming radiation by the atmospheric matter, which leads to a decrease of the radiative energy in the incoming direction;
  - Scattering of an incident radiation by the atmospheric matter, which redistributes the radiative energy in all directions.

# Scattering

- Only changes the direction of a photon, not destroy or create any new photons.
- Rayleigh scattering, or molecular scattering, refers to the case when the size of scattering particles are much smaller than the light wavelength.
  - Intensity of the Rayleigh scattering is proportional to  $\lambda^{-4}$ .
- Mie scattering, or non-molecular or aerosol particle scattering, is the case when the size of scattering particles are comparable to the light wavelength.
  - It applies to most of the atmospheric aerosols (smoke, dust, etc) and water vapors (clouds).
  - Intensity of the Mie scattering is proportional to  $\lambda^{-1.3}$ .

# Beer-Lambert Law

- The relationship between the incoming and outgoing radiation through a medium can be expressed by the Beer-Lambert's law (**B-L** law).

$$I(\lambda) = I_0(\lambda) \cdot e^{(-\sigma(\lambda) \cdot c \cdot l)}, \quad (1)$$

- $I_0(\lambda)$  and  $I(\lambda)$  refers to intensity of the initial incident light and the transmitted light, respectively.  
([ $W m^2 sr^{-1} Hz^{-1}$ ]).
- $\sigma(\lambda)$  denotes the absorption cross section of a specific particle in the medium. ([ $m^2$ ]).
- $c$  refers to the uniformly distributed concentration of the medium. ([ $m^{-3}$ ]).
- $l$  ([ $m$ ]) is the path length that the light passes through the medium.
- The dimensionless quantity  $l \cdot \sigma \cdot c$  is sometimes called the **optical depth (OD)**,  $\tau$ .

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# Differential Optical Absorption Spectroscopy (DOAS) 1

- Analyze broadband spectra between the UV and the NIR regions.
- Active DOAS use man-made light source, whereas the passive utilize the natural light source.

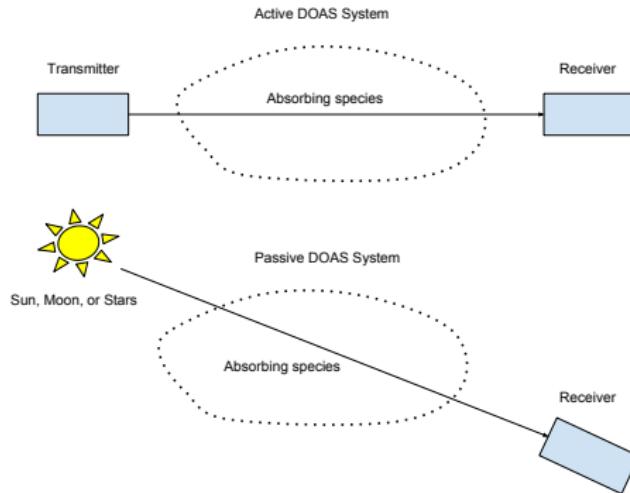


Figure: Active and passive DOAS systems configuration.

- In real applications, there are not only attenuation due to absorption by other specific trace gas species, but also influences from many other air molecules and aerosols.

$$I(\lambda) = I_0(\lambda) \cdot e^{-l(\sum_i(\sigma_i(\lambda) \cdot c_i) + \epsilon_R(\lambda) + \epsilon_M(\lambda))} \cdot A(\lambda), \quad (2)$$

- $\epsilon_R(\lambda)$  and  $\epsilon_M(\lambda)$  represent the Rayleigh and Mie scattering extinction coefficient, respectively.
- $A(\lambda)$  describes attenuation from the optic instruments and the turbulence effect of the atmosphere.

# Differential Optical Absorption Spectroscopy (DOAS) 3

- Aerosol extinction process, the instrument and the turbulence, and absorptions of many trace gases have slow variations with respect to wavelength while certain trace gases show very fast varying features.
- The absorption cross section for a certain gas species,  $\sigma(\lambda)$ , can be written as a summation of, one slowly varying with respect to wavelength,  $\sigma_s$ , and the other fast varying term,  $\sigma_f$ . The rapid varying cross section term is also called 'differential' cross section.

$$\sigma(\lambda) = \sigma_s(\lambda) + \sigma_f(\lambda). \quad (3)$$

- The first term in Equation (3) may describe a general 'slope' that might be caused by the Rayleigh and the Mie scattering, while the second term describes the difference between the slope and the cross section  $\sigma(\lambda)$ , might indicate an absorption band.

# Differential Optical Absorption Spectroscopy (DOAS) 4

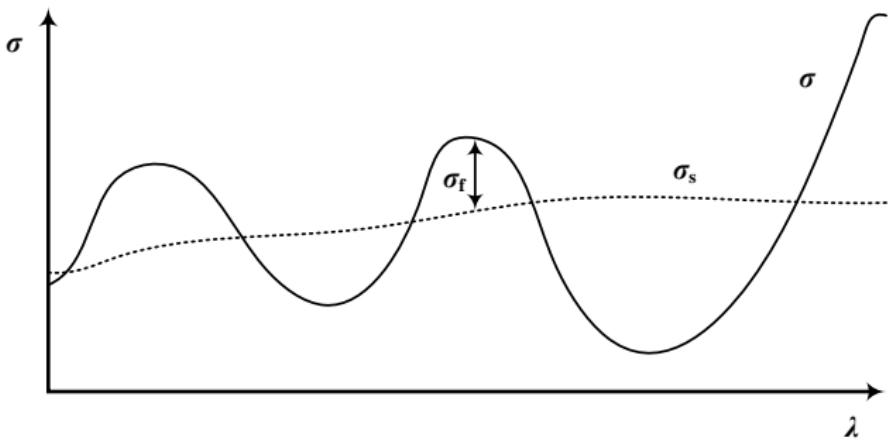


Figure: The 'differential' cross section,  $\sigma_f$ , is the difference between the total cross section,  $\sigma$ , and the slowly varying cross section,  $\sigma_s$ .

# Differential Optical Absorption Spectroscopy (DOAS) 5

- The B-L law can be rewritten with the fast and the slow variation part as

$$I(\lambda) = I_0(\lambda) \cdot \left( e^{-l \cdot (\sum_i (\sigma_{is}(\lambda) \cdot c_i) + \epsilon_R(\lambda) + \epsilon_M(\lambda))} \cdot A(\lambda) \right) \cdot e^{-l \cdot (\sum_j \sigma_{jf}(\lambda) \cdot c_j)}, \quad (4)$$

We can define a quantity  $I_s$  as the intensity in the absence of 'differential' absorption:

$$I_s(\lambda) = I_0(\lambda) \cdot \left( e^{-l \cdot (\sum_i (\sigma_{is}(\lambda) \cdot c_i) + \epsilon_R(\lambda) + \epsilon_M(\lambda))} \cdot A(\lambda) \right), \quad (5)$$

This can then be used together with the measured intensity  $I(\lambda)$  in order to define the following,

$$D_f(\lambda) = \ln \left( \frac{I(\lambda)}{I_s(\lambda)} \right) = -l \cdot \sum_j (\sigma_{jf}(\lambda) \cdot c_j), \quad (6)$$

which refers to the **differential optical density**.

- To find the concentrations of the different gas species one can use standard absorption cross sections from the reference database,

$$c = \frac{-\ln \left( \frac{I(\lambda)}{I_s(\lambda)} \right)}{\sigma_{ref}(\lambda) \cdot l}. \quad (7)$$

In order for this technique to work one has to measure intensities over a **wide** wavelength ranges otherwise it would not be possible to remove the slowly varying parts of the spectra in a correct way.

- Developed by the optical remote sensing group in Chalmers.
- Mature and widely used approach to estimate the emissions either from point sources (power plants, volcanoes, etc) or area sources (industrial park or urban areas, etc).
- Collect the scattered UV or VIS sunlight coming from the zenith direction.
- The spectra can be measured while the platform was traversing under the gas plume in a plane  $\sim$  perpendicular to movement direction of the plume.
- For each traverse, a 'dark' spectrum was collected when the telescope was pointing towards the ambient sky by blocking the telescope entrance. This dark spectrum was subtracted later from the ambient sky spectra for correctness purpose.

# Mobile Mini-DOAS 2

- The gas plume flux can be determined by integrating the total number of molecules in the vertical cross section of the plume, multiplying with the wind speed.

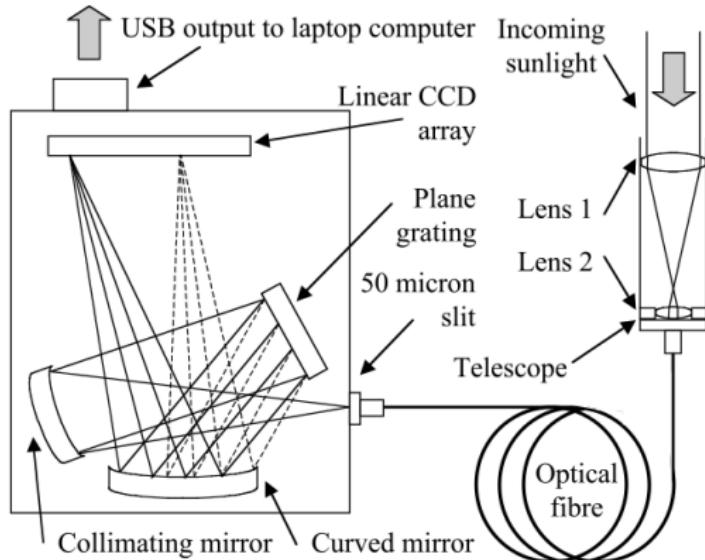


Figure: The configuration of a mini-DOAS system.

# Solar Occultation Flux (SOF) 1

- Developed by the optical remote sensing group in Chalmers.
- Retrieve the path-integrated concentration or column concentrations (molecules per  $cm^2$  ) of one or several type of trace gas species between the sun and the spectrometer.
- Record the IR intensity spectra from the sunlight.
- A solar-tracker is used to track the Sun and reflect the sunlight into the spectrometer.
- To estimate the flux (kg/s) from an emission source, the vehicle is driven in a direction so that the detected solar light cuts through the actual emission gas plume.
- The total mass can then be calculated as an integration of the retrieved path-integrated concentrations, multiplied by the wind speed and angle correction for the plume direction.

# Solar Occultation Flux (SOF) 2

- The largest error source comes from the wind speed estimation.

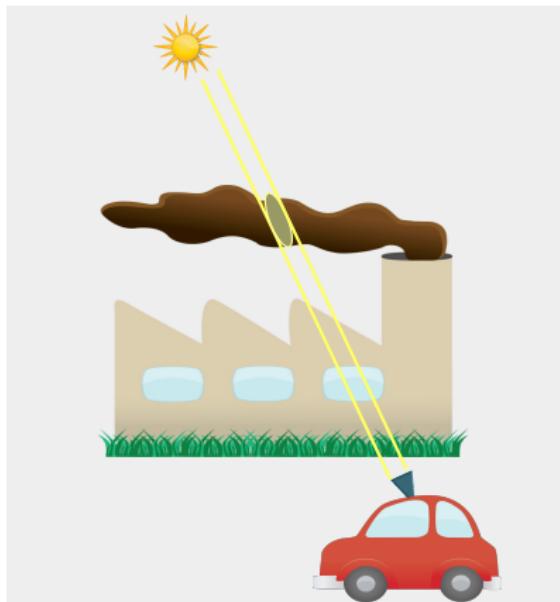


Figure: An illustration of vehicle-borne SOF and solar tracker configuration.

# 'Flame' Spectrometer

- Record the optical spectra from the UV to NIR between wavelength of about 280 nm and 1100 nm.

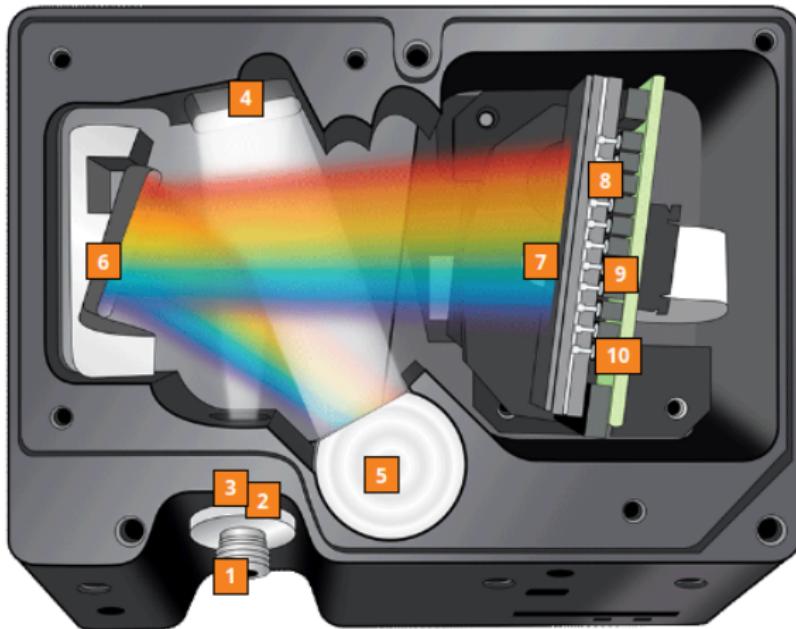


Figure: The inside illustration of a 'Flame' spectrometer.

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# Data Sets

- DOAS data
  - Conc. of SO<sub>2</sub>, NO<sub>2</sub> and HCHO, RMS error of the total concentrations, the measurement time.
- SOF data
  - Conc. of NH<sub>3</sub>, alkane (with Butane, Propane and Octane) and alkene (with Ethylene, Propene and Butadiene), RMS error of the total concentrations, the measurement time.
- 'Flame' data
  - light intensities (averaged over 1000 scans), the integration time (about 2 seconds), the specific measurement date.
- GPS log files
  - latitude and longitude positionings and the time instant.
- Wind meter data
  - wind velocity, wind direction, estimated error and the time.

# Wavelength Calibration 1

- Before recording the solar light spectra the spectrometer needs to be wavelength calibrated so as to establish the channel-to-wavelength mapping (**C-W** mapping) and the instrument lineshape function (**ILF**).
- The calibration is performed by measuring spectrum of light from a mercury pencil-type discharge lamp (**Hg** lamp).
- The observed ILF is a convolution of the intrinsic line shape measured in the lab with the instrument transfer function.
- The spectrum of the Hg lamp includes a few of very thin lines at precisely-measured wavelengths.
  - Lines so thin to be treated as the Dirac delta function. Thus, the measured Hg lines using the spectrometer can be assumed to evaluate the ILF.

# Wavelength Calibration 2

- Referring to one paper, recommended wavelengths and relative intensities of all mercury spectral lines emitted by the Hg lamp can be read out.

Table: Recommended wavelengths for selected Hg spectral lines emitted by pencil-type lamps.

Intensity	Wavelength	Intensity	Wavelength
300,000	253.6521	160	289.3601
2600	296.7283	280	302.1504
2800	312.5674	1900	313.1555
2800	313.1844	160	334.1484
5300	365.0158	970	365.4842
110	366.2887	650	366.3284
4400	404.6565	270	407.7837
34	434.7506	10,000	435.8335
10,000	546.0750	1100	576.9610

# Wavelength Calibration 3

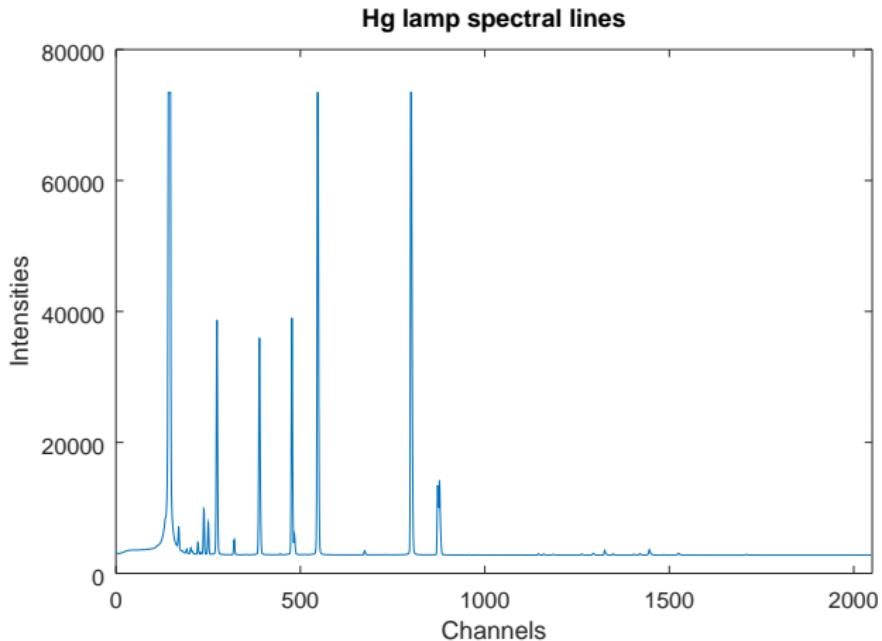


Figure: The spectrum measured by the standard Hg lamp. Here the integration time is also 2 s.

# Wavelength Calibration 4

- The numeric representation of the ILF can be acquired through the polynomial fitting.

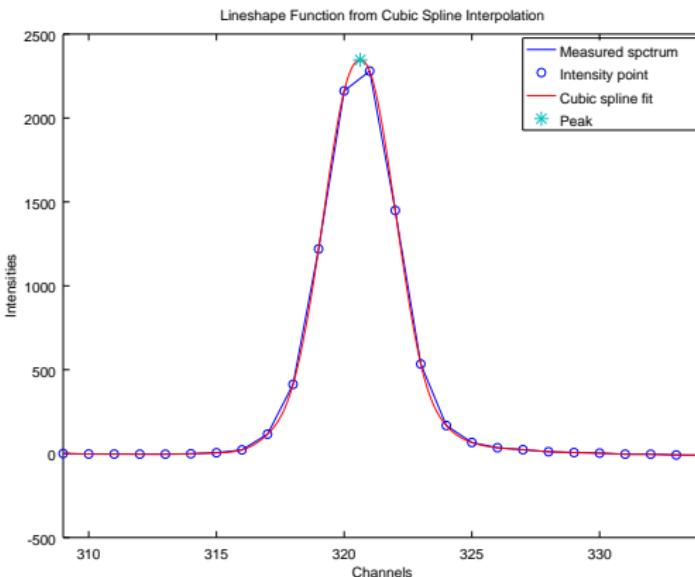


Figure: One calibrated ILF. The channel center, estimated from a m-code, lies at 320.63.

# Wavelength Calibration 5

- Channel: 273.87, 320.63, 388.83, 476.88, 546.50, 799.50  
Wavelength: 313.1844, 334.1484, 365.0158, 404.6565,  
435.8335, 546.0750

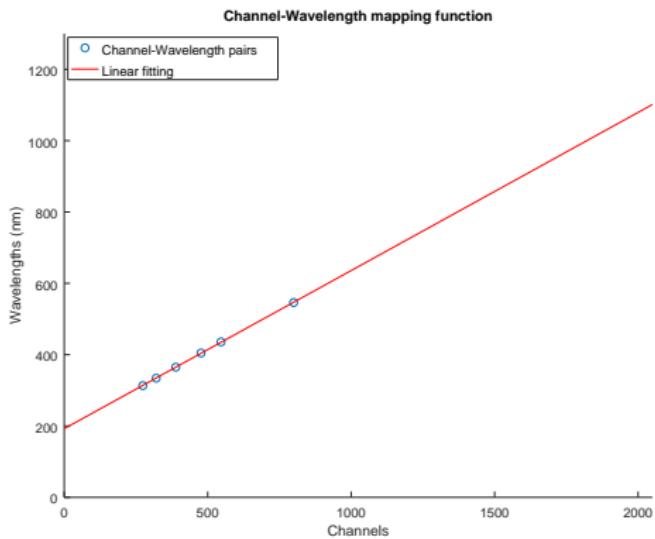


Figure: Linear interpolation was performed for C-W mapping function.

# General Flow Chart

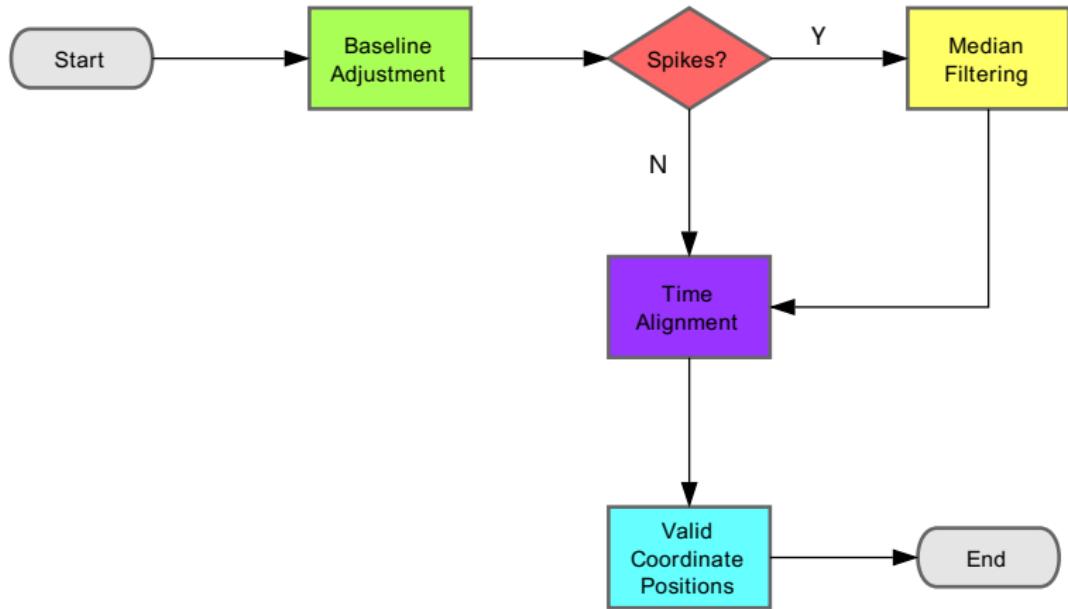


Figure: General flow chart of data processing.

# Spectrum Baseline Adjustment 1

- Spectrum offset generally be the same for all channels.
- Idea: Raw spectrum - 'dark' spectrum - further estimated term
  - 'dark' spectrum
    - To remove the baseline offset and fixed pattern noise.
    - Measured within the same integration time.
    - Avg. to suppress the electronic noise.
  - further estimated spectrum term
    - Spectrum before  $\sim 200^{th}$  channel are generally flat.
    - Mean value of a channel interval between the  $50^{th}$  channel and the  $100^{th}$  channel.
  - 'darkspctrl.m', 'caliSpectrl.m',

# Spectrum Baseline Adjustment 2

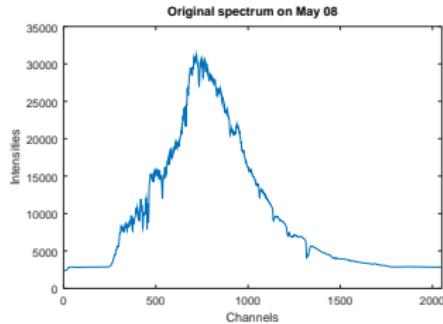


Figure: Original spectrum.

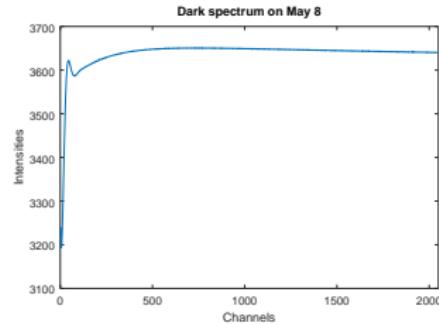


Figure: Dark spectrum.

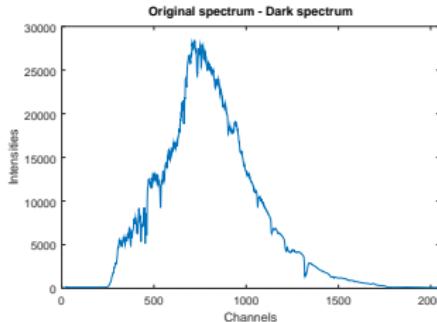


Figure: Temporary spectrum.

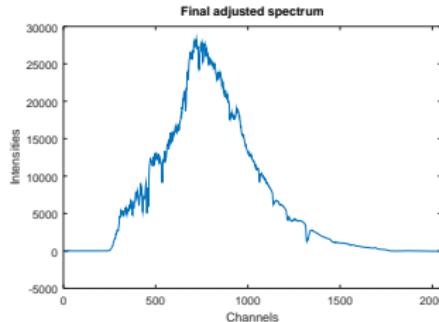


Figure: Final spectrum.

# Spikes Removing Procedure 1

- Can ruin the data.
- Spotted by first plot out the data, conc. for instance, in time series and observe whether sudden transients appear or not.
- Median filtering
  - A sliding window is applied, and for each step the median value in the window is returned.
  - Can use the “RMS” variable for the DOAS and SOF measurement.
    - Sliding window width of 3 or 5 is quite good.
    - The spikes of conc. of certain gas species can be confirmed from the indices of the corresponding RMS.
    - From rule of thumb, if the difference of the RMS value between two successive time instants excesses **5%**.
    - ‘SpikeFilter.R’, ‘spikesfromRMS.R’, ‘spikesfromRMS2.R’ and ‘spikesReplaced.R’.

# Spikes Removing Procedure 2

- Median filtering can use the “RMS” variable for the DOAS and SOF.

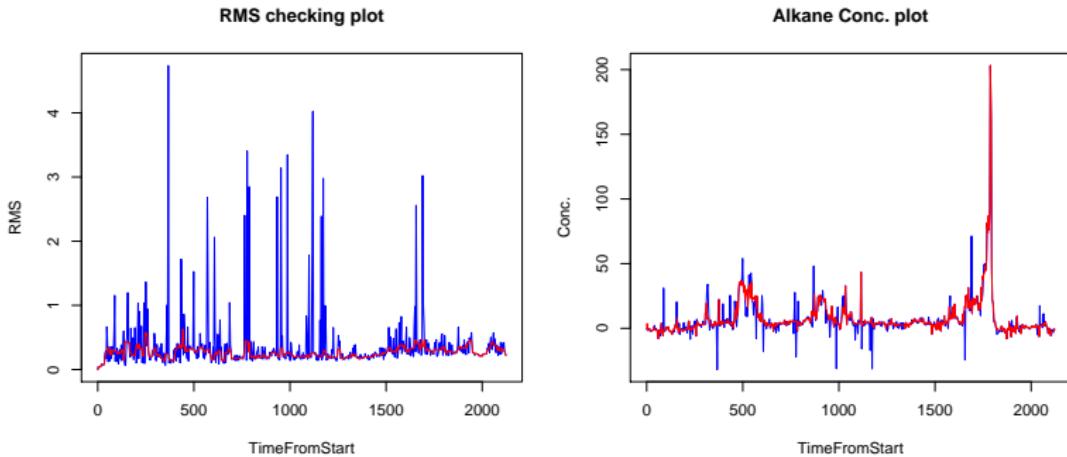


Figure: Bf (blue) and af (red) the spikes removed for the RMS.

Figure: Bf (blue) and af (red) the spikes removed for alkane conc.

# Spikes Removing Procedure 3

- For 'Flame' spectra, no RMS values can be referenced.  
Median filtering still works.

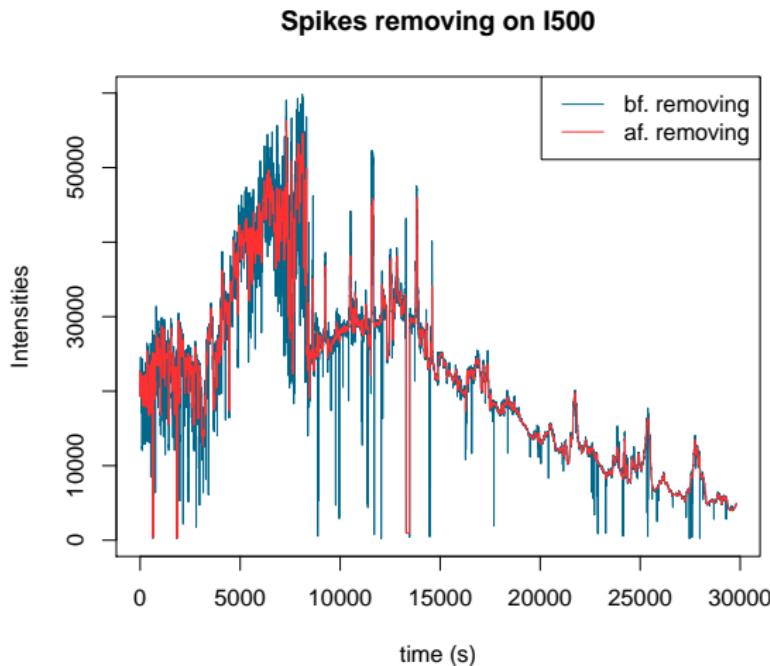


Figure: I500 before and after spikes removing on May 8.

# Spikes Removing Procedure 4

- Further filtering by setting a min and a max non-spike value. Then linear interpolating across any regions in which the IRs are out of the scope defined by the min and the max values.

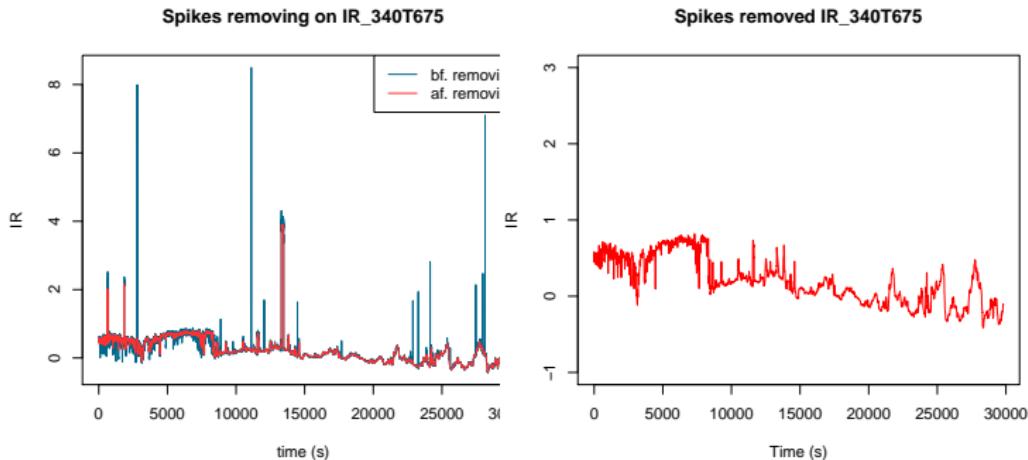


Figure: IR of 340 nm to 675 nm before and after spikes removing on May 8.

Figure: IR of 340 nm to 675 nm are further filtered to remove the car-parking effect.

## Two Problems

- 'ggplot2' and 'ggmap' package in R.
- Valid coordinate positions problem.
  - Remove coordinate outliers.
  - Locate the map center by knowing *a priori* geographic coordinates of Tianjing city and setting a small coordinate offset to limit the coordinate ranges.
- Time alignment problem.
  - Different devices have their own time variables.
  - time steps between the successive time instant records
  - the specific time instants at which the measurement was starting and ending.

# Time Series Plot 1

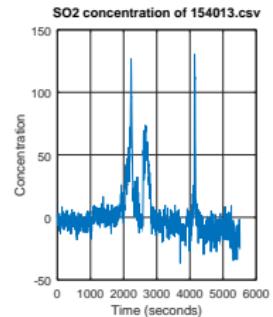
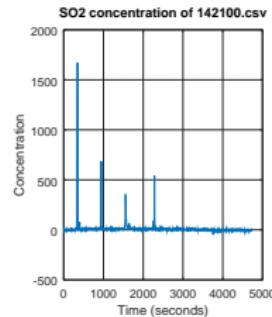
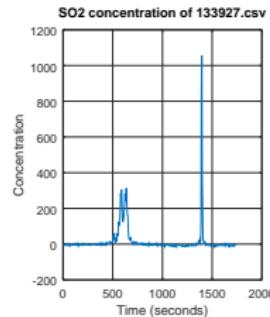
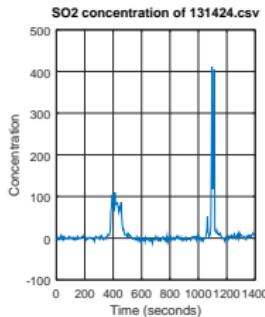
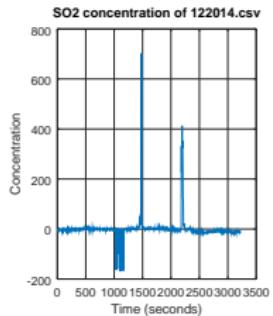
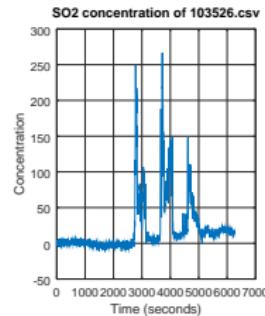
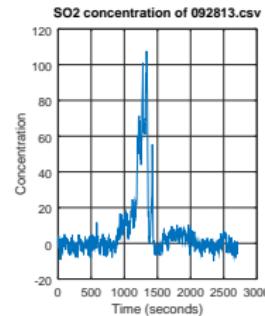
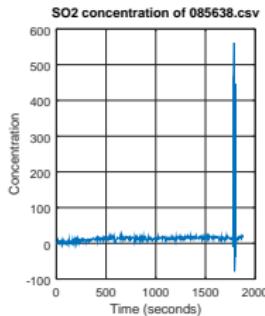


Figure: Segment plots of SO<sub>2</sub> concentration on May 8.

## Time Series Plot 2

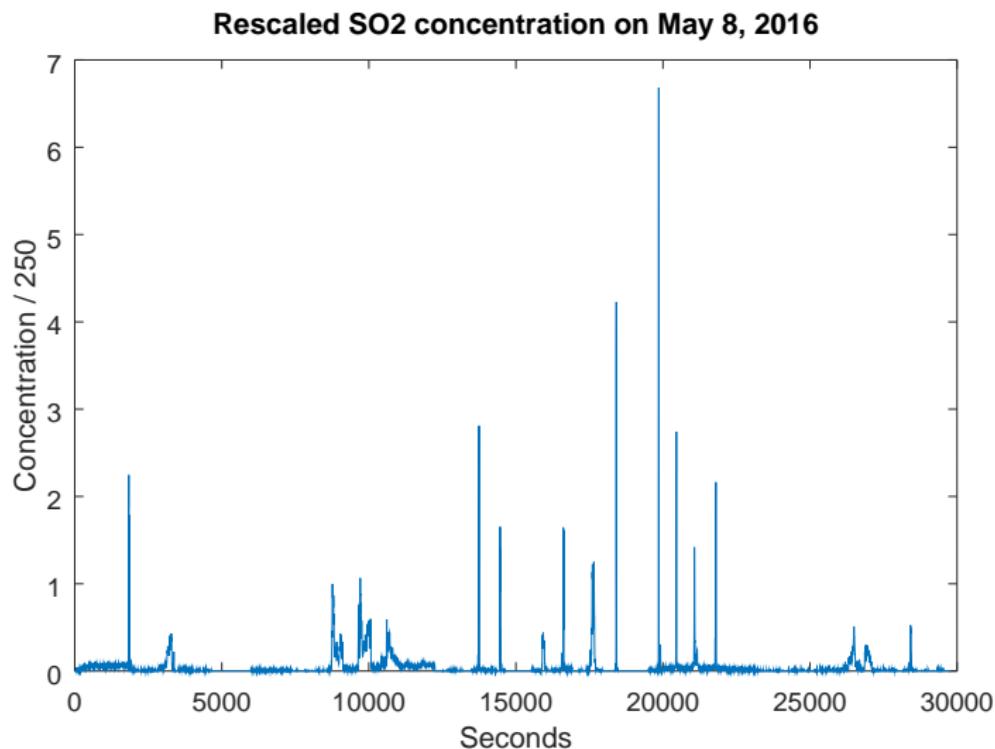


Figure: Re-scaled SO<sub>2</sub> concentration plot in time series on May 8.

# Time Series Plot 3

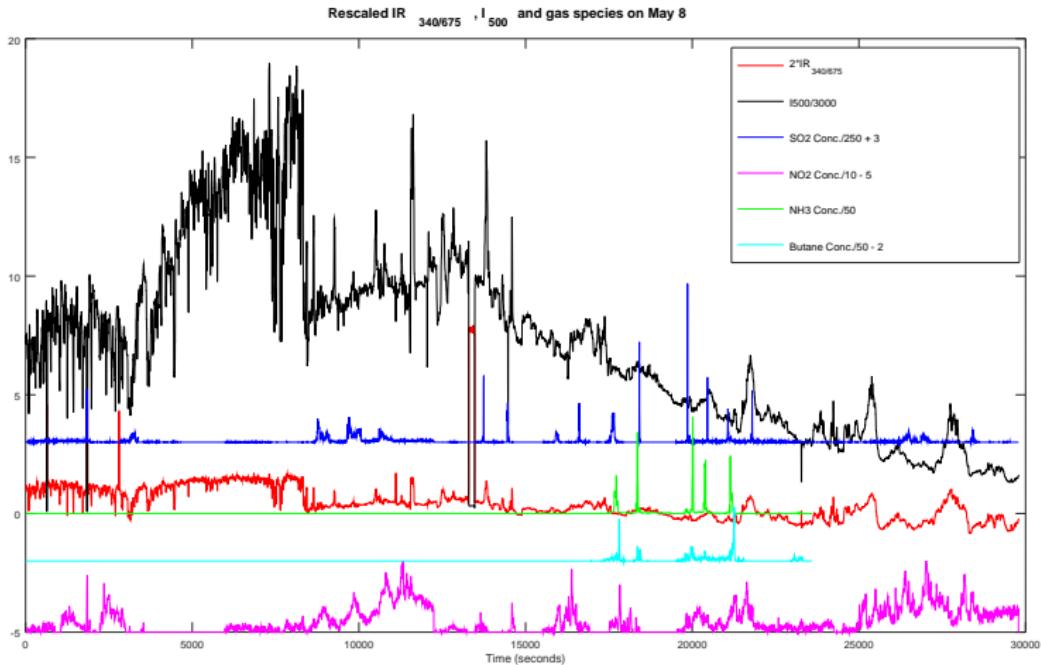


Figure: Time alignment issue was correctly solved for IR of 340 to 675, I<sub>500</sub> and several gas species characterized by several time variables on May 8.

# Temporal-Spatial Map Plot

- Although the time series plot can grant an overview of the variation of the solar light intensity and the alteration of the measured gas species concentration in time, it can not provide information regarding where the intensity or concentration has the most notable changes along the driving route.

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# Results of May 8

- IR of 340 nm to 675 nm and selected gas species.

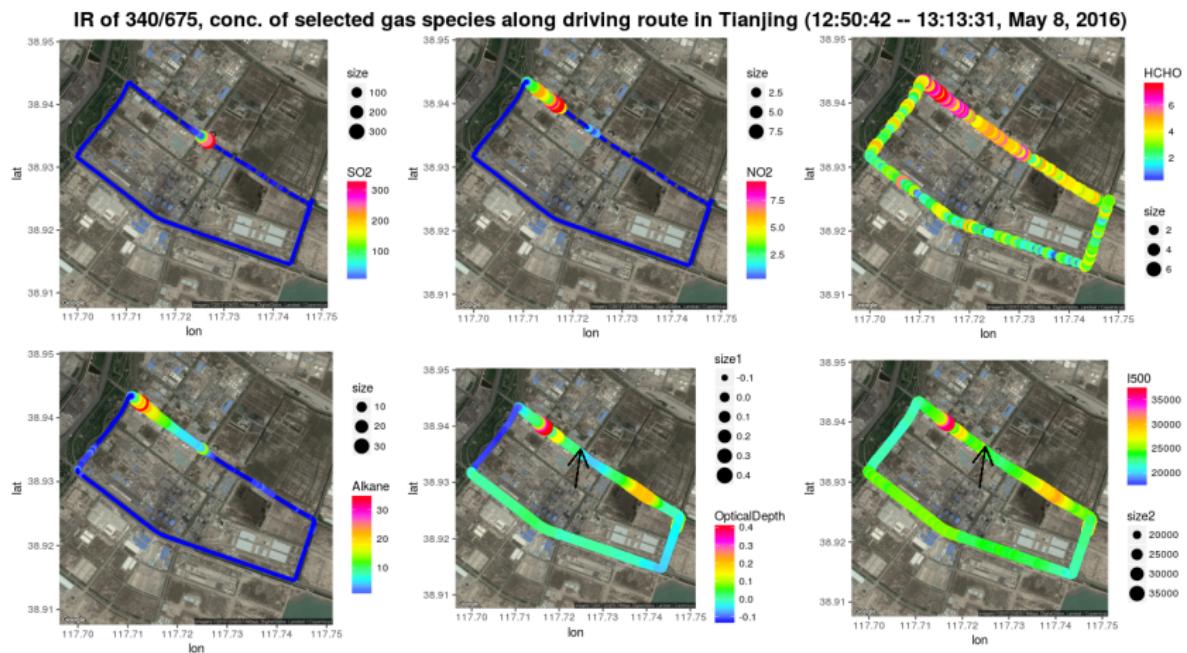


Figure: Concentrations of SO<sub>2</sub>, NO<sub>2</sub>, formaldehyde, alkane and OD, I500 at the Tianjing harbor between 12:50 and 13:13 are compared.

# Results of May 8

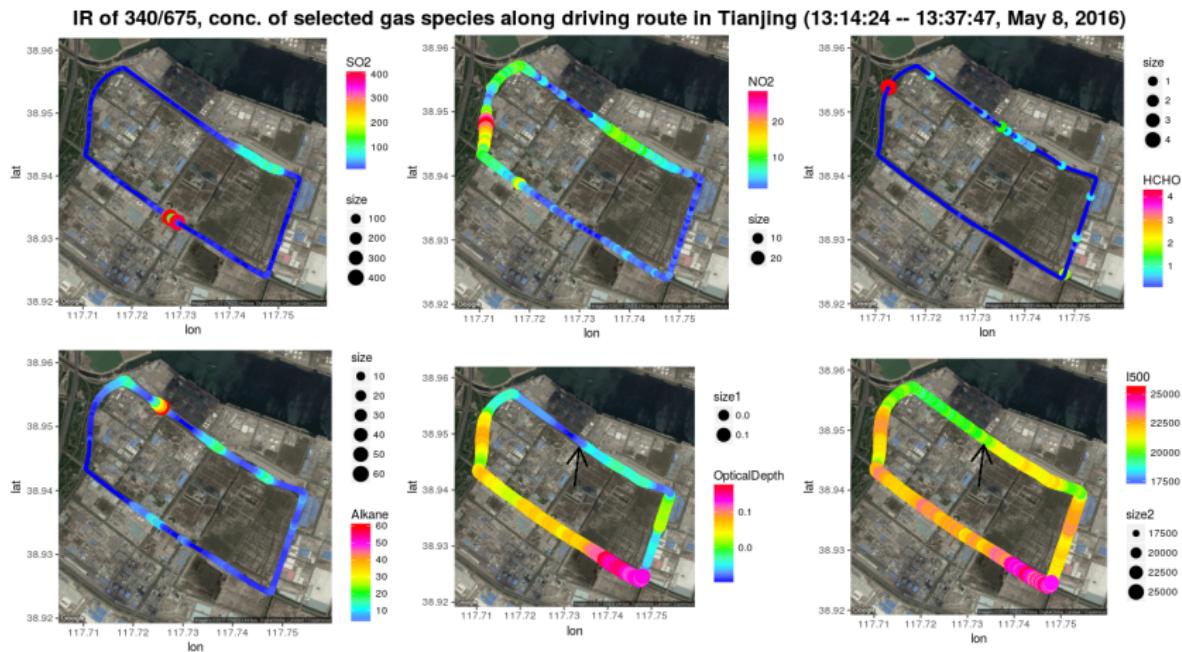


Figure: Concentrations of SO<sub>2</sub>, NO<sub>2</sub>, formaldehyde, alkane and OD, I500 at the Tianjing harbor between 13:14 and 13:37 are compared.

# Results of May 8

IR of 340/675, conc. of selected gas species along driving route in Tianjing (13:39:26 -- 14:08:33, May 8, 2016)

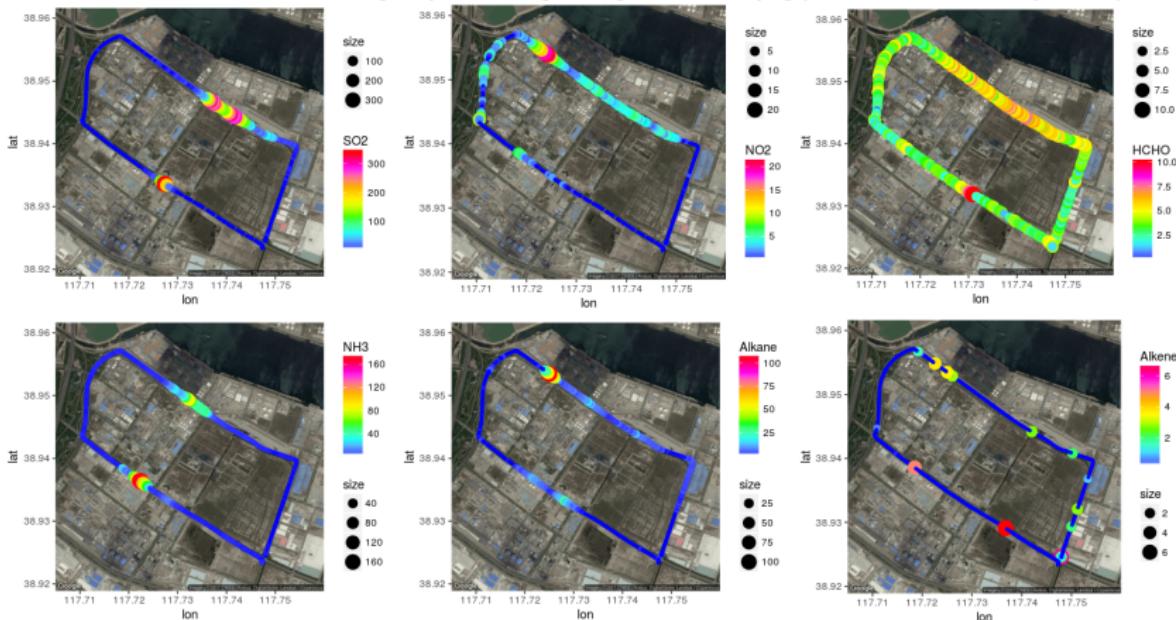


Figure: Concentrations of SO<sub>2</sub>, NO<sub>2</sub>, formaldehyde, NH<sub>3</sub>, alkane and alkene at the Tianjing harbor between 13:39 and 14:08 are compared.

# Results of May 8

IR of 340/675, conc. of selected gas species along driving route in Tianjing (13:39:26 -- 14:08:33, May 8, 2016)

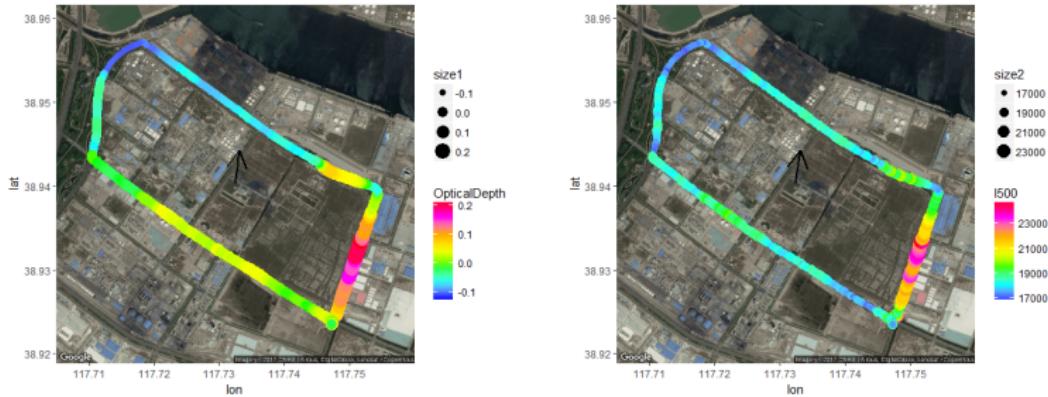


Figure: Comparison of I500 and OD at the Tianjing harbor between 13:39 and 14:08.

# Results of May 8

IR of 340/675, conc. of selected gas species along driving route in Tianjing (14:21:01 -- 14:56:32, May 8, 2016)

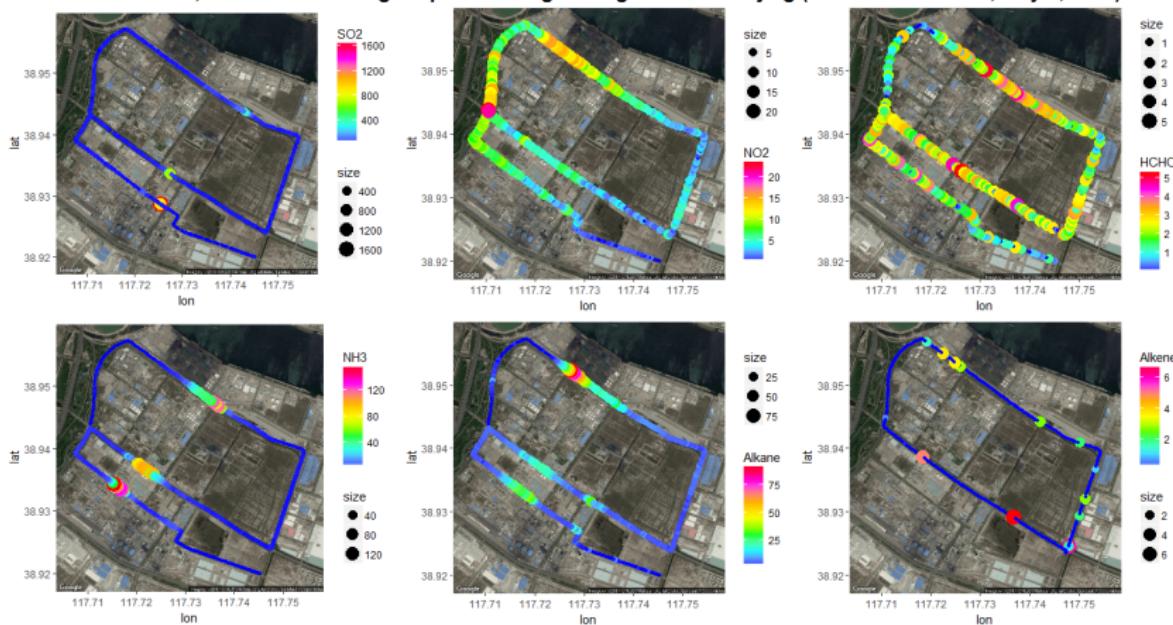


Figure: Concentrations of SO<sub>2</sub>, NO<sub>2</sub>, formaldehyde, NH<sub>3</sub>, alkane and alkene at the Tianjing harbor between 14:21 and 14:56 are compared.

# Results of May 8

IR of 340/675, conc. of selected gas species along driving route in Tianjing (14:21:01 -- 14:56:32, May 8, 2016)

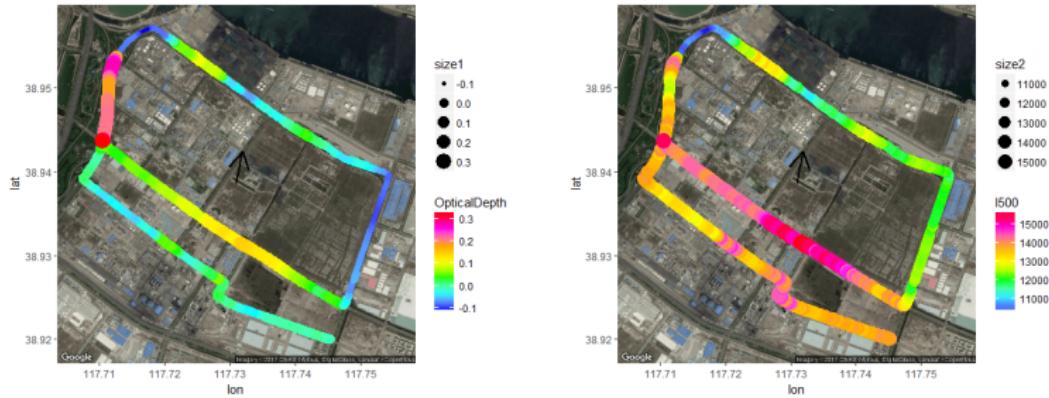


Figure: Comparison of I500 and OD at the Tianjing harbor between 14:21 and 14:56.

# Results of May 8

IR of 340/675, conc. of selected gas species along driving route in Tianjing (15:40:11 -- 16:20:02, May 8, 2016)

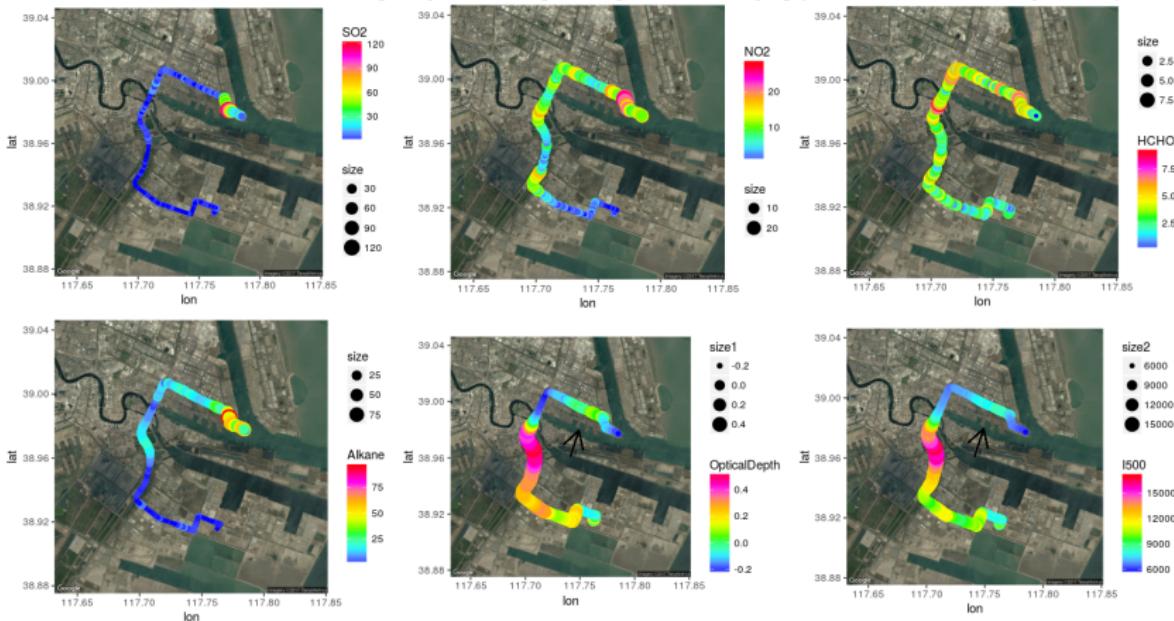


Figure: Concentrations of SO<sub>2</sub>, NO<sub>2</sub>, formaldehyde and alkane as well as I500 and OD at the Tianjing harbor between 15:40 and 16:20 are compared.

# Results of May 8

IR of 340/675, conc. of selected gas species along driving route in Tianjing (16:22:16 -- 17:12:34, May 8, 2016)

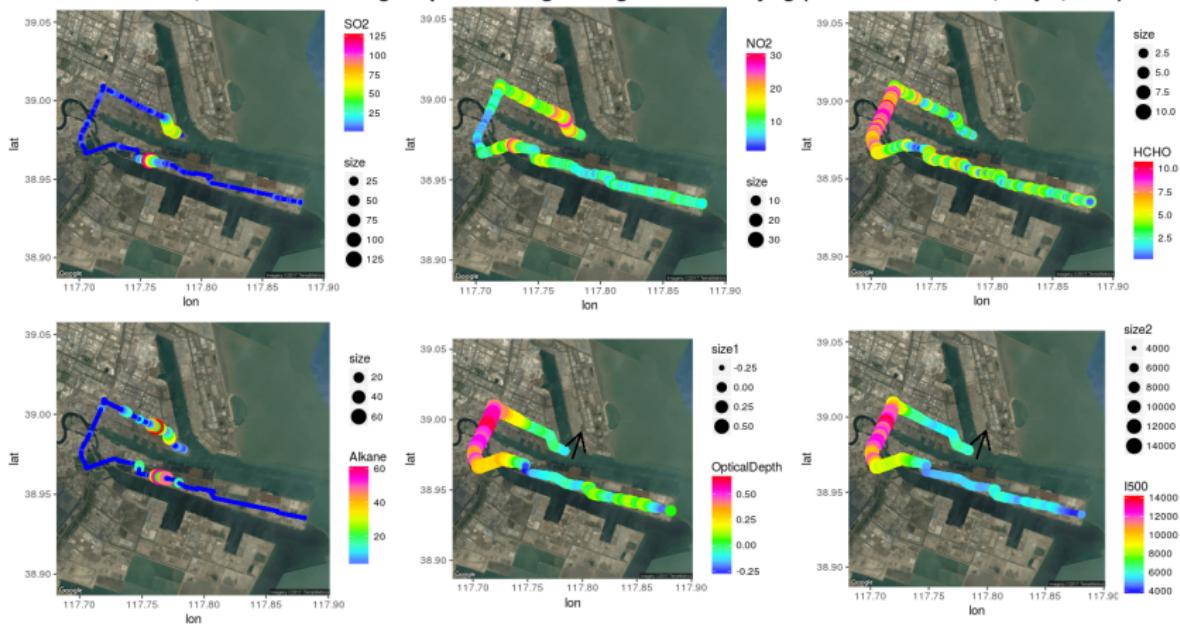


Figure: I500, OD and concentrations of SO<sub>2</sub>, NO<sub>2</sub>, formaldehyde and alkane at the Tianjing harbor between 16:22 and 17:12 are compared.

# Results of May 10

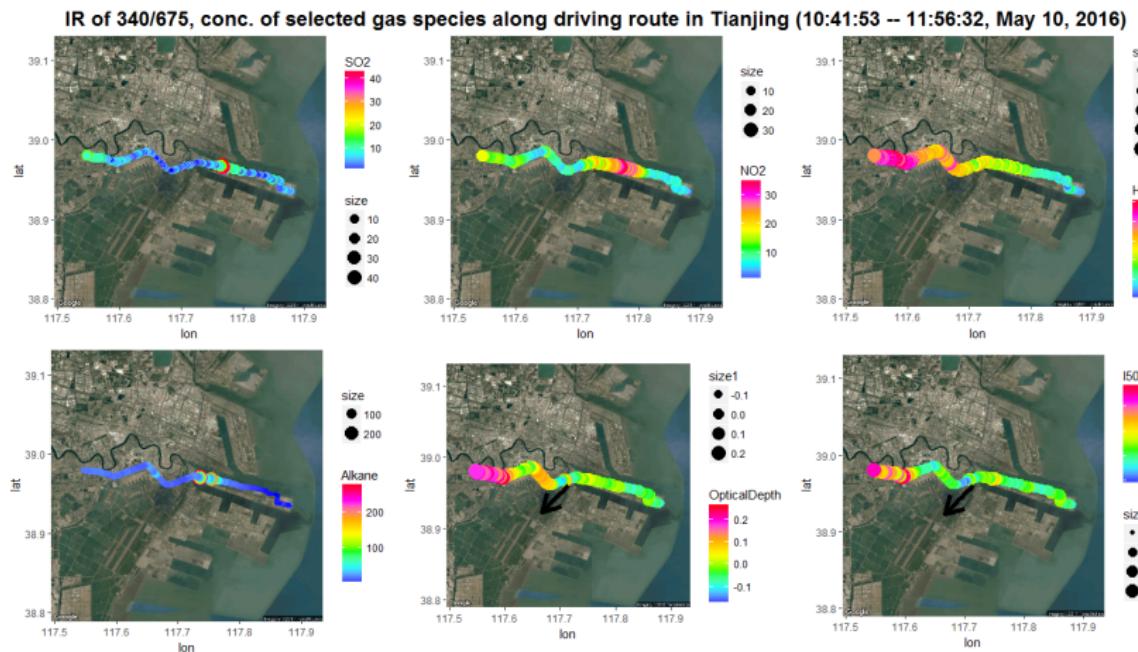


Figure: Local IR of 340 to 675 and concentrations of selected gas species between 10:41 and 11:56 on May 10 in Tianjing city.

# Results of May 10

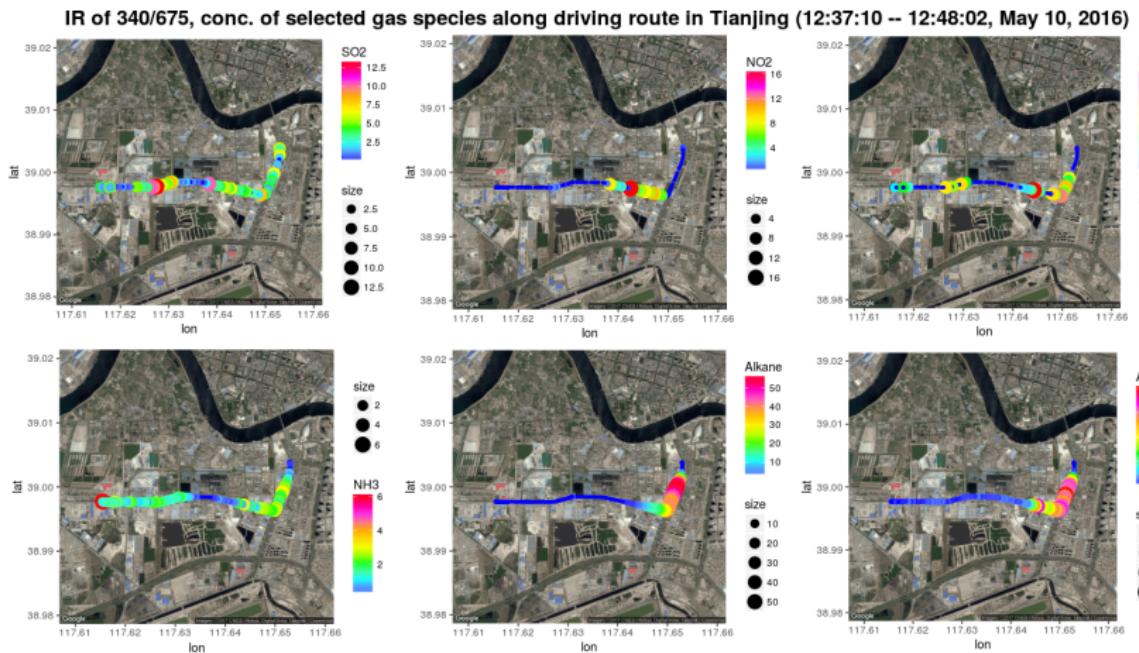


Figure: Concentrations of SO<sub>2</sub>, NO<sub>2</sub>, formaldehyde, NH<sub>3</sub>, alkane and alkene between 12:37 and 12:48 are compared.

# Results of May 10

IR of 340/675, conc. of selected gas species along driving route in Tianjin (12:37:10 -- 12:48:02, May 10, 2016)

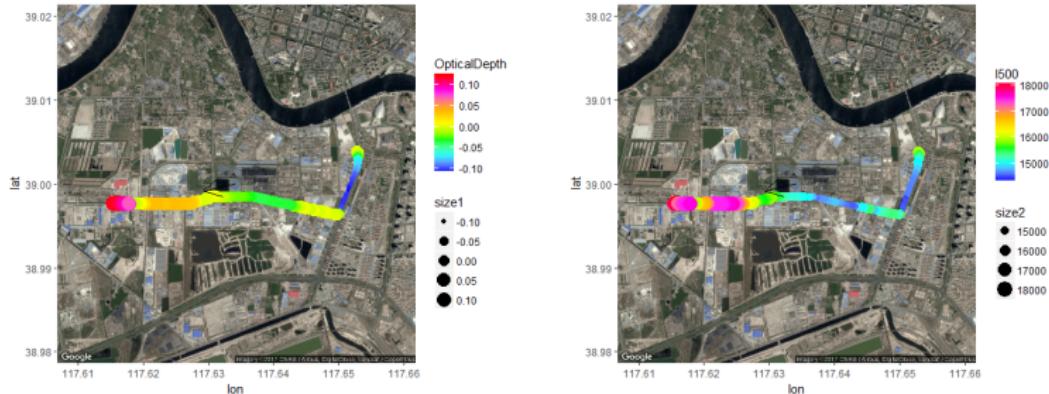


Figure: OD and I500 between 12:37 and 12:48 are compared.

# Results of May 10

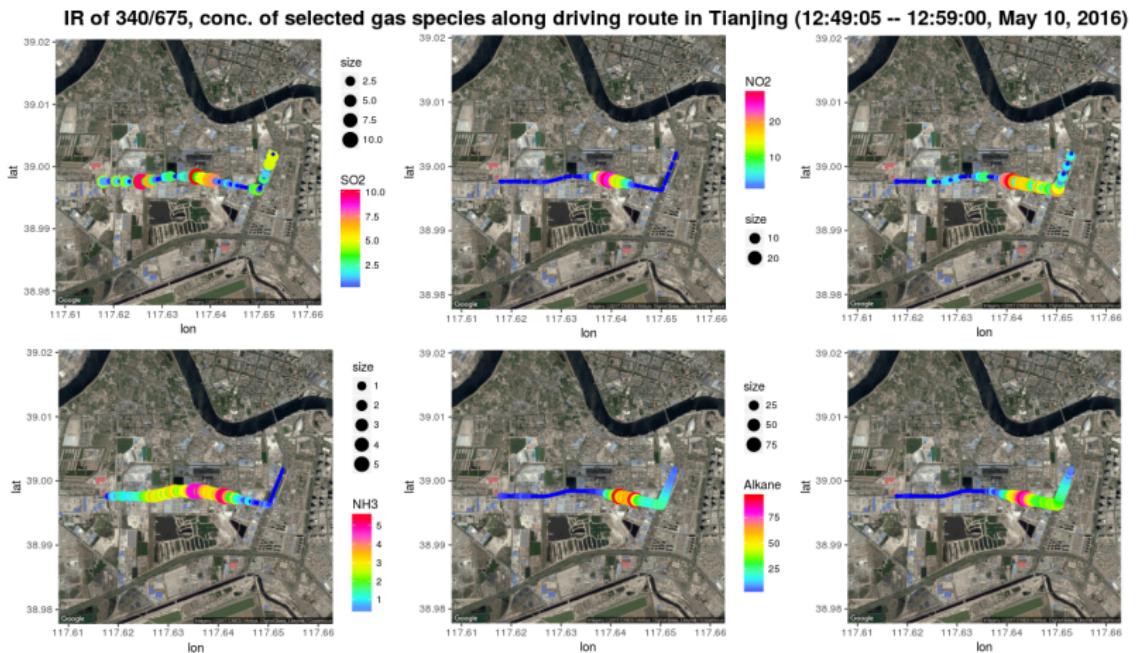


Figure: Concentrations of SO<sub>2</sub>, NO<sub>2</sub>, formaldehyde, NH<sub>3</sub>, alkane and alkene between 12:49 and 12:59 are compared.

# Results of May 10

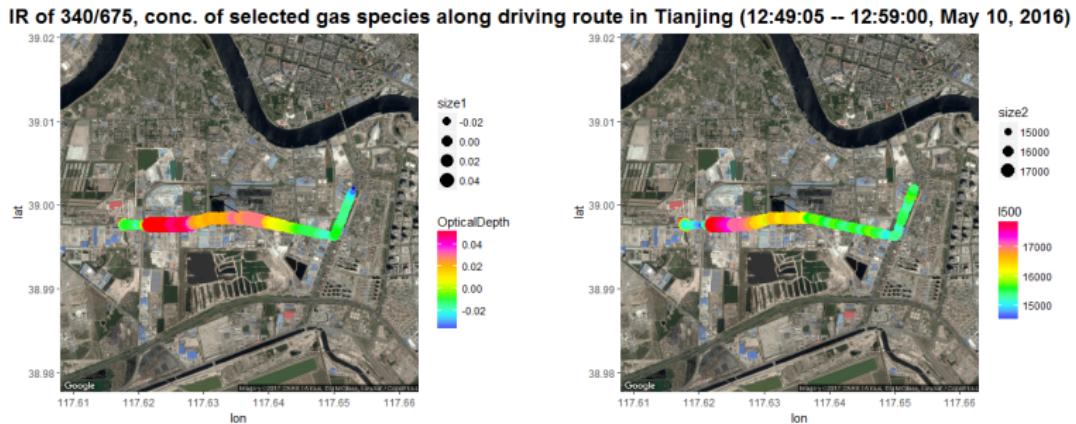


Figure: OD and I500 between 12:49 and 12:59 are compared.

# Results of May 10

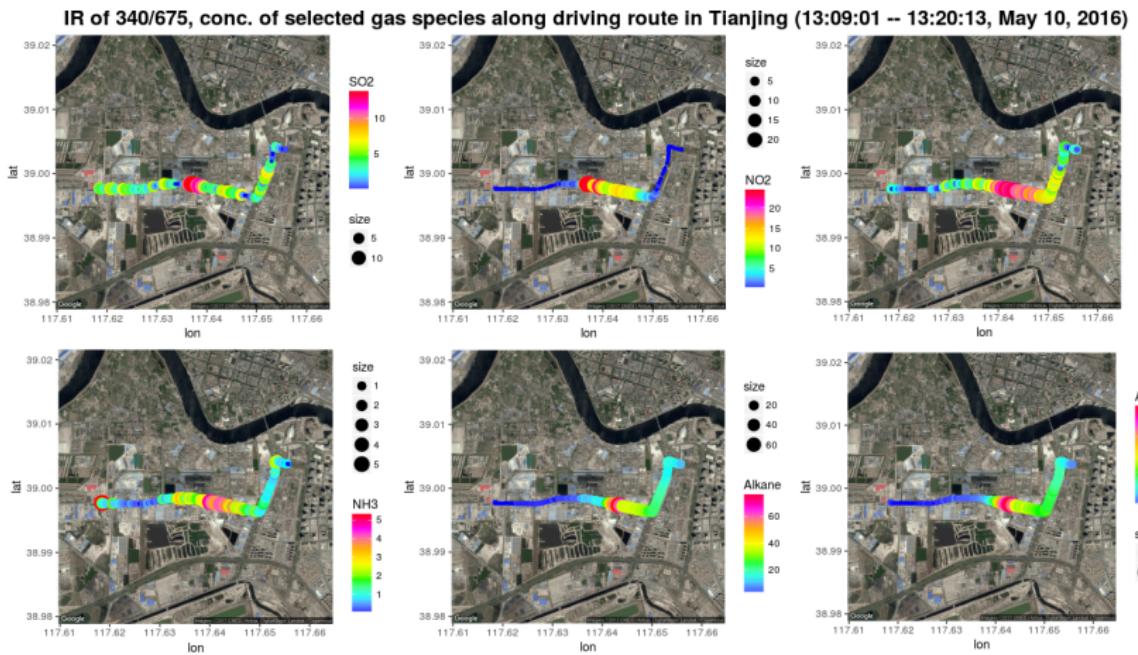


Figure: Concentrations of SO<sub>2</sub>, NO<sub>2</sub>, formaldehyde, NH<sub>3</sub>, alkane and alkene between 13:09 and 13:20 are compared.

# Results of May 10

IR of 340/675, conc. of selected gas species along driving route in Tianjing (13:09:01 -- 13:20:13, May 10, 2016)

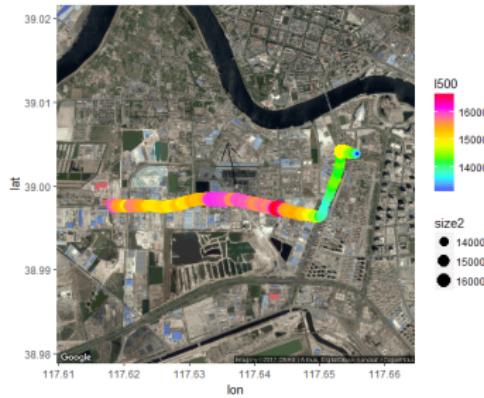
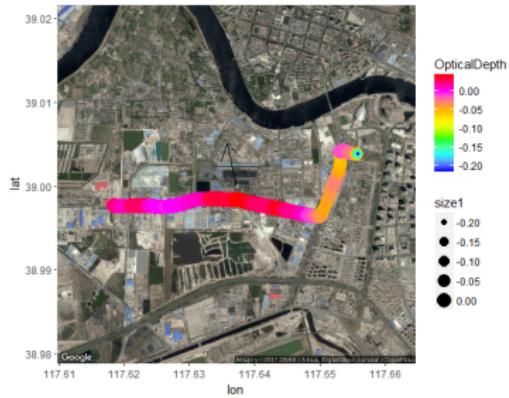


Figure: OD and I500 13:09 and 13:20 are compared. The high OD values may infer the biomass burning aerosols from the south.

# Results of May 10

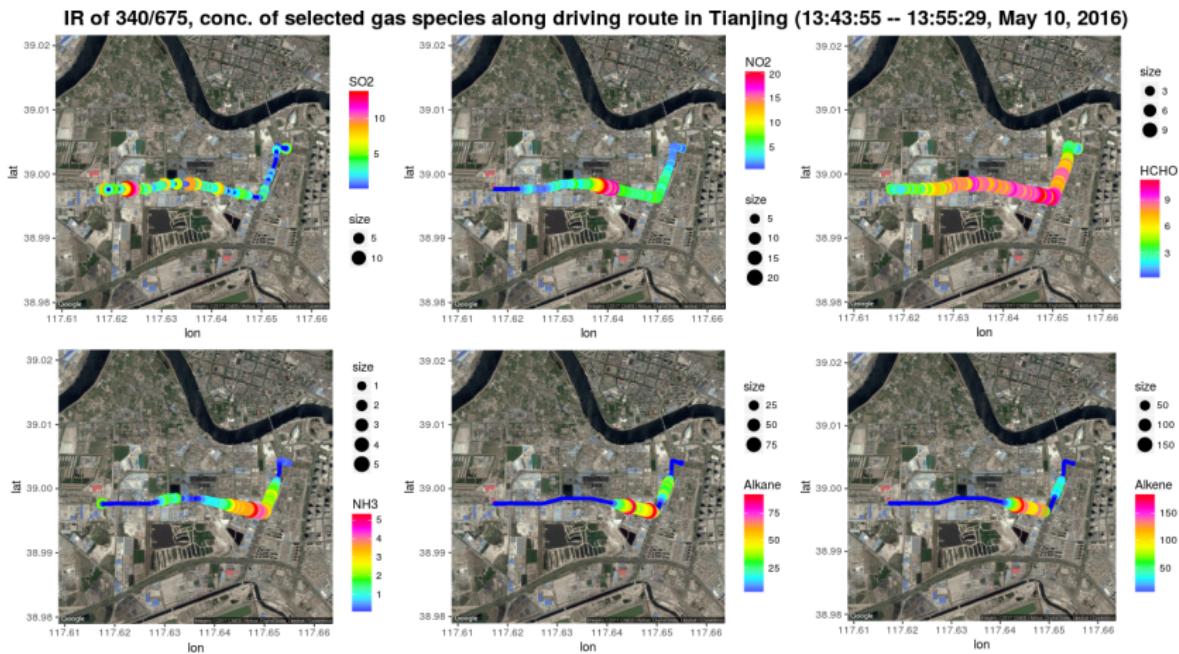


Figure: Concentrations of SO<sub>2</sub>, NO<sub>2</sub>, formaldehyde, NH<sub>3</sub>, alkane and alkene between 13:43 and 13:55 are compared.

# Results of May 10

IR of 340/675, conc. of selected gas species along driving route in Tianjing (13:43:55 -- 13:55:29, May 10, 2016)

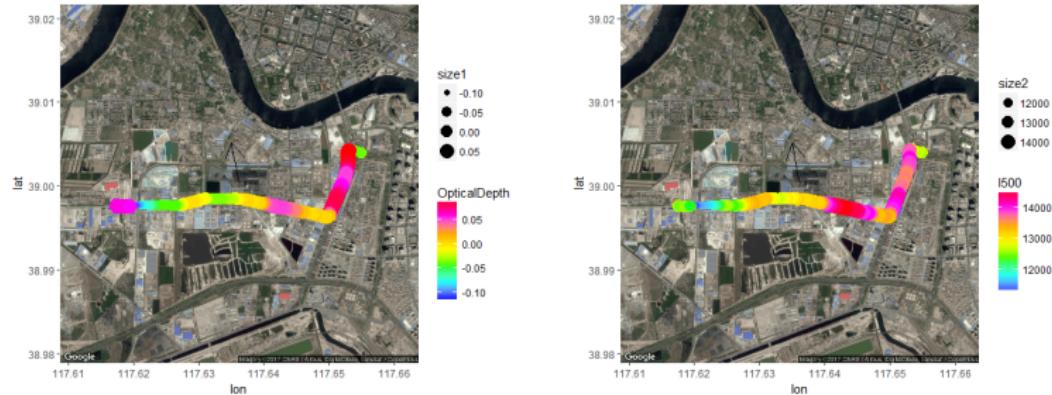


Figure: OD and I500 13:43 and 13:55 are compared.

# Results of May 10

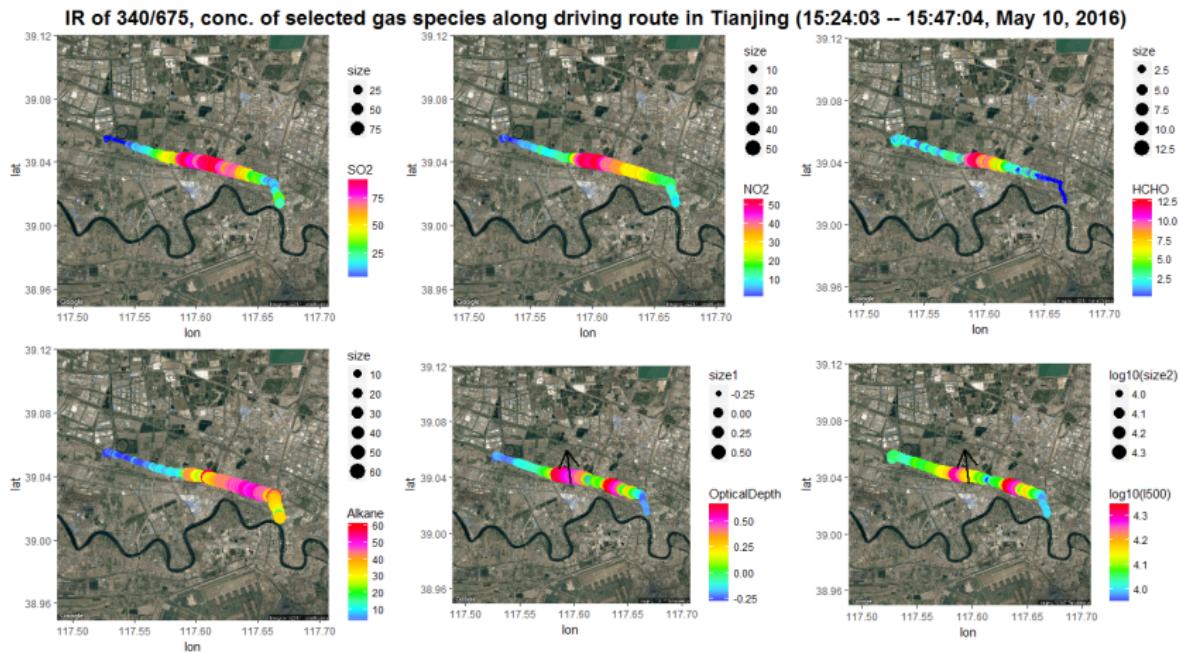


Figure: Concentrations of SO<sub>2</sub>, NO<sub>2</sub>, formaldehyde, NH<sub>3</sub>, alkane and alkene between 15:24 and 15:47 are compared.

# Results of May 10

IR of 340/675, conc. of selected gas species along driving route in Tianjing (15:47:06 -- 16:16:21, May 10, 2016)

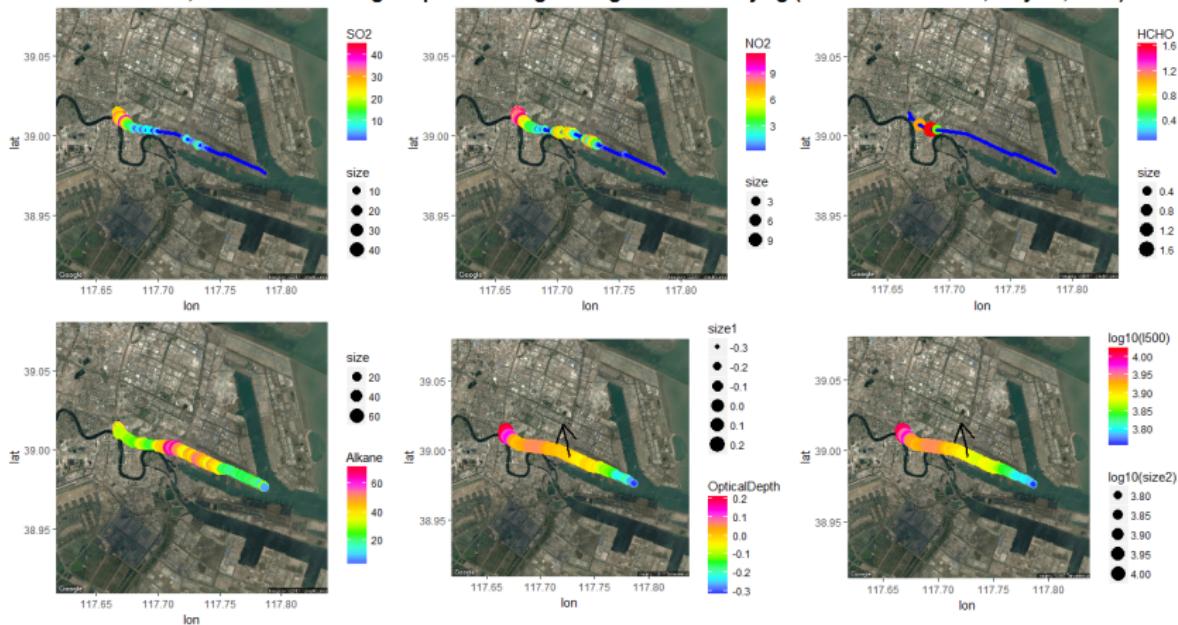


Figure: Concentrations of SO<sub>2</sub>, NO<sub>2</sub>, formaldehyde, NH<sub>3</sub>, alkane and alkene between 15:47 and 16:16 are compared.

## Results of May 13, 15

- Still took the same area where petrochemical plants reside.
- Repeated measurements were performed back and forth along the driving route.
- All the figures are attached in Appendix A and only brief summary is shown.
- The high OD outcomes generally jump from place to place and have good correlation with the high values of I500 (except one figure of A.31).
- None of the measured gas species has a stable correlation with the high OD.
- We suspect that the NO<sub>2</sub>, HCHO and alkane only make limit contribution to the aerosol traces, as can be compared btw those high conc. parts and the high OD parts in figures.

# Summary

- An aerosol traces detection method was proposed from comparison between the high OD and high conc. of gas species.
- Conc. of the selected gas species were measured by the DOAS and the SOF.
- The proposed aerosol traces sensing method does not yield stable result. Only one or two gas species, for example NO<sub>2</sub> and/or alkane, might partially contribute to the aerosol.
- The NO<sub>2</sub>-induced-aerosol mainly comes from the transport exhaust while the alkane-induced-aerosol stems from the petrochemical plants.
- The light intensity at 500 nm, generally presents good correlation with the OD.
- The temporal-spatial plots can reveal potential emission sources which enable to detect air pollution at fine spatial resolution.

## Future Work

- Apply a **direct** solar measurement with solar tracker following the Sun. Also, try to select the **sunny** day to perform the measurement.
- Apply a cloud detecting and removing filter so as to reduce the cloud effects as much as possible.
- Improve the spikes detecting and removing filter, for example, further develop the filter to automatically choose the filtering width based on the spikes interval.
- Perform further more field measurements with respect to biomass burning, traffic and industrial activities separately in different period of the year. To see if seasonal aerosol variation tendency and correlation can be found.
- Run the Radiative Transfer program in ‘Sciatran’ to further calculate spectra for different atmospheric conditions.