



Analysis of Aerosol Nitrogen by Thermal Evolution-Chemiluminescence Based Method

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Introduction

Airborne nitrogen-containing pollutants are important sources of exogenous nitrogen (N) in terrestrial and aquatic ecosystems. They are ubiquitous in the atmosphere and play important roles in global N nutrient budget, air quality, and human health. A wide variety of nitrogenous species have been identified to exist in ambient aerosols. However, most previous studies mainly focused on inorganic nitrogen (IN) species such as NH_4^+ , NO_3^- and NO_2^- .

Organic nitrogen (ON) includes a broad range of compounds (e.g. urea, amines, amino acids, nitroaromatics, peroxyacetyl nitrates, etc.), which originate from both anthropogenic and natural source. Compared with IN, ON is much less studied, which is due to a lack of simple analytical methods. ON is usually determined as the difference between total nitrogen (TN) and IN. As such, TN measurement techniques can provide indirect solutions for ON determination.

We are developing an aerosol nitrogen analyser for analysis of nitrogenous species in aerosol samples collected on a filter substrate. This system is built on a combustion-based aerosol carbon analyser (Sunset Laboratory, Forest Grove, OR, USA) and a chemiluminescent NOx analyzer (Model 200E, T-API, San Diego, CA, USA).

Methodology

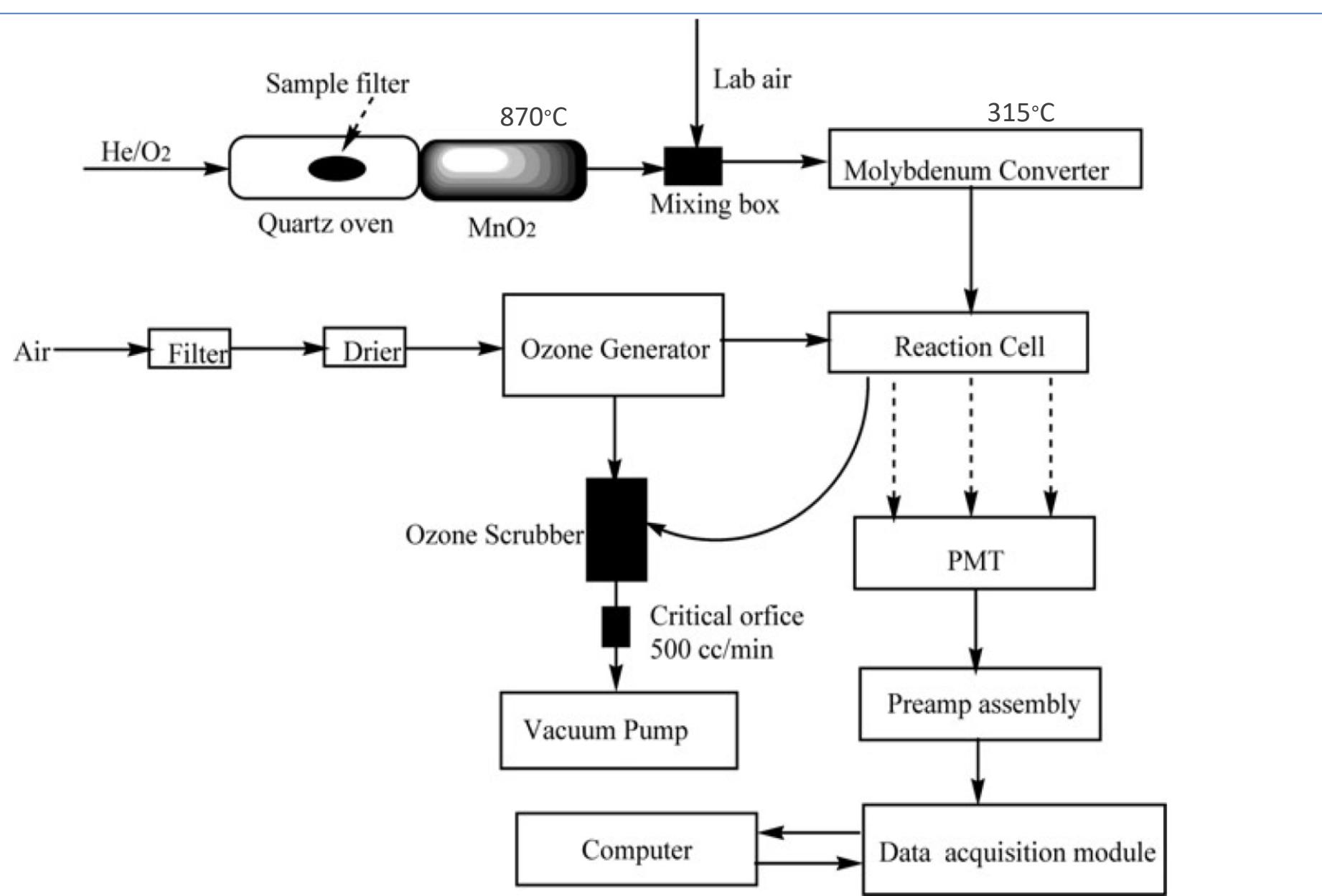


Fig 1. Block diagram of aerosol nitrogen analyser

This aerosol nitrogen analyzer is designed for determination of microgram levels of aerosol nitrogen. The quartz oven (Fig 1.) is divided into two zones, the front oven zone and the back oven zone. During analysis, the temperature of the front oven is programmed (Table 1.) to allow stepwise thermal evolution of aerosol materials into the carrier gas (2.5% O₂/ 97.5% He) stream. The MnO₂ in back oven oxidizes all nitrogen-containing gas products into nitrogen oxides (e.g., NO, NO₂).

Mode	Time (sec)	Temp (°C)	Power constant %
O ₂	360	150	0.010
O ₂	360	300	0.025
O ₂	240	400	0.06
O ₂	180	500	0.08
O ₂	180	800	0.12

Table 1. Temperature program of front oven

The molybdenum converter is heated to 315°C to reduce various forms of nitrogen oxides (e.g., NO₂, N₂O₅) to nitric oxide (NO) when the sample stream is routed through the converter:



The detector module consists of a reaction cell, a photo multiplier tube (PMT), and a preamplifier assembly. In the reaction cell, ozone mixes with the NO gas to produce electronically excited NO₂* molecules:



The excited NO₂ molecules emit chemiluminescent light when they drop to a lower energy level. The chemiluminescent light intensity is directly proportional to the NO concentration:



Results and Discussion

Temperature program and typical sample plots

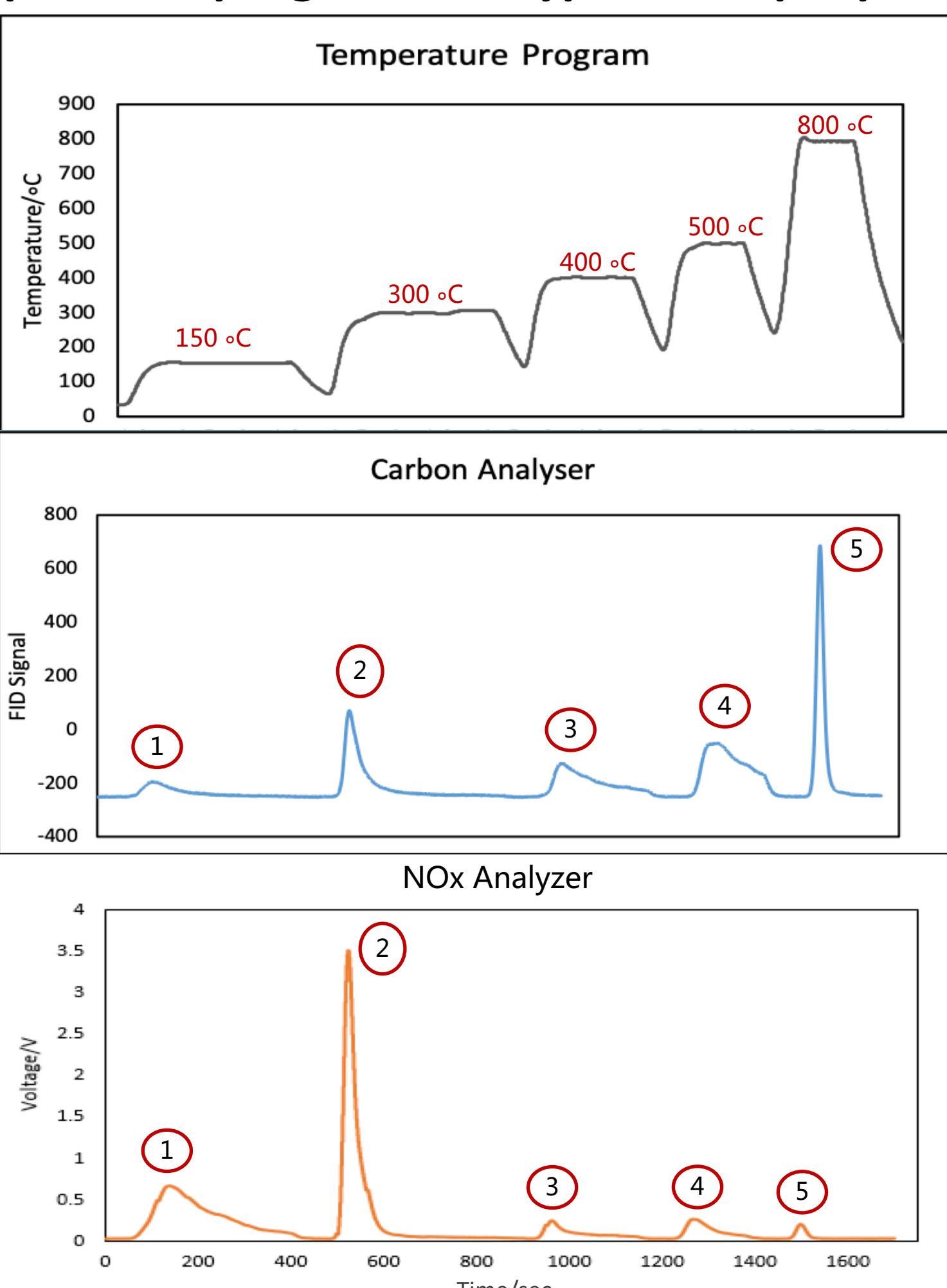


Fig 2. Typical plots of temperature, C and N signal.
Sample: 4th Dec 2016 Tsuen Wan

The temperature program is divided into 5 steps. Under each step, there are corresponding C peaks and N peaks. Different N and C peaks represent different kinds of species:

$$TN = \sum_{i=1}^5 N_i \quad TC = \sum_{i=1}^5 C_i$$

N_i, C_i: the N or C content in ith peak

Characteristic of Different Kinds of N and C Peaks

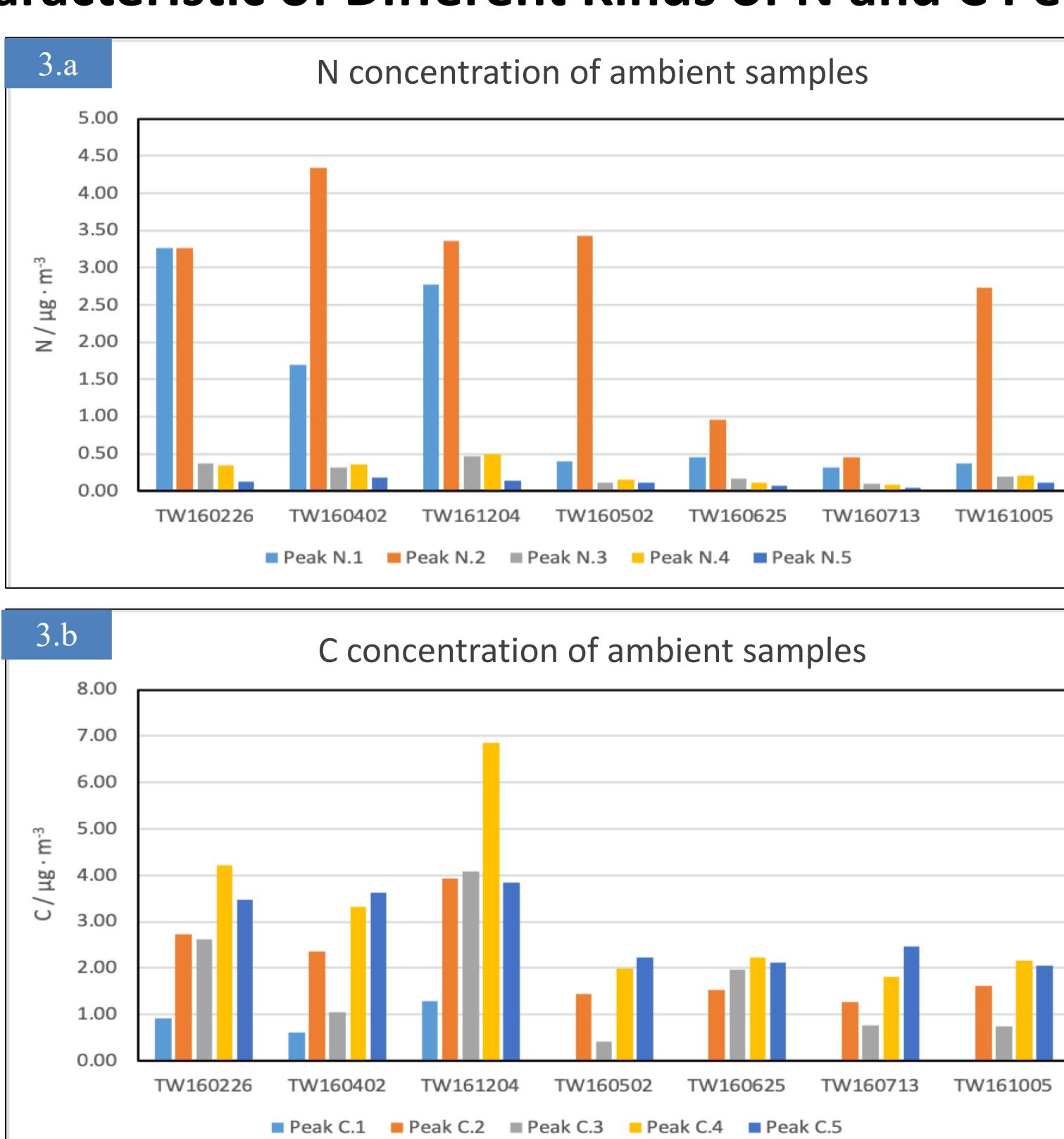


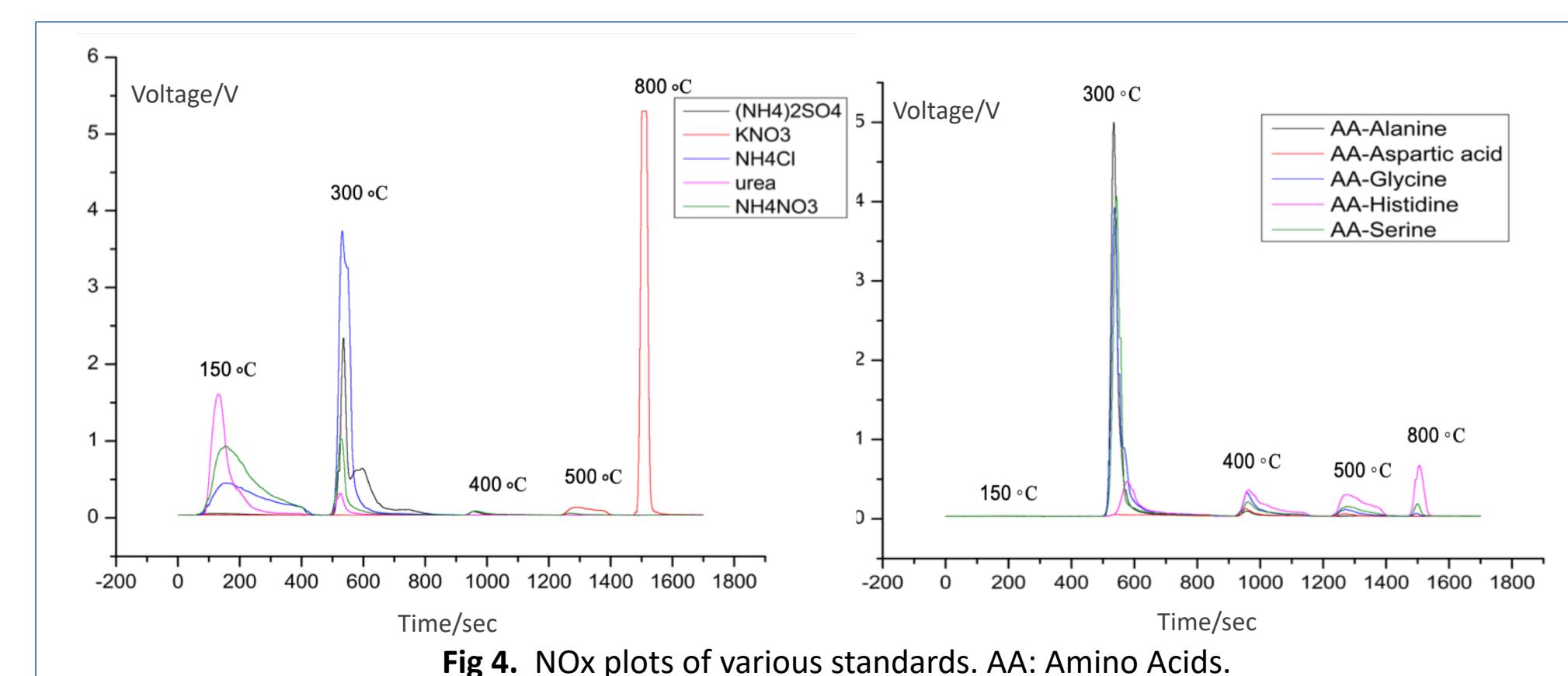
Fig 3.a, 3.b N and C concentrations of ambient samples, Tsuen Wan 2016

Fig 3. shows results of N and C concentrations of ambient samples in different peaks. Among the 5 peaks, 1st and 2nd peaks have pretty high N concentrations, but relatively low C concentrations (some samples even don't have 1st carbon peak). As a result, we deduce that the first 2 peaks mainly contain IN species. As for the last 3 peaks which evolve out at higher temperature, they all have low N content, but pretty high C content, so they are most likely related to ON species.

Averaged molar N/C	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5
TW161204	2.46				
TW160226					
TW160402					
TW160502					
TW160625					
TW160713					
TW161005					
n.a.					

Table 2. Averaged molar N/C ratios of individual peaks

Table 2 indicates the first 2 peaks have highest N/C ratio. In comparison, the 3rd, 4th, and 5th peaks have N/C ratios as low as ~ 0.24. Such low values are close to some reported N/C ratios of organic matter in other places, which suggests a relation between the last 3 peaks and atmospheric organic matter.



The results from standards test (Fig 4.) can also corroborate such deduction. Almost all inorganic salts (except for KNO₃) finished thermal decomposition in first 2 steps.

TN, ON, and IN Concentrations of Ambient Aerosol Samples

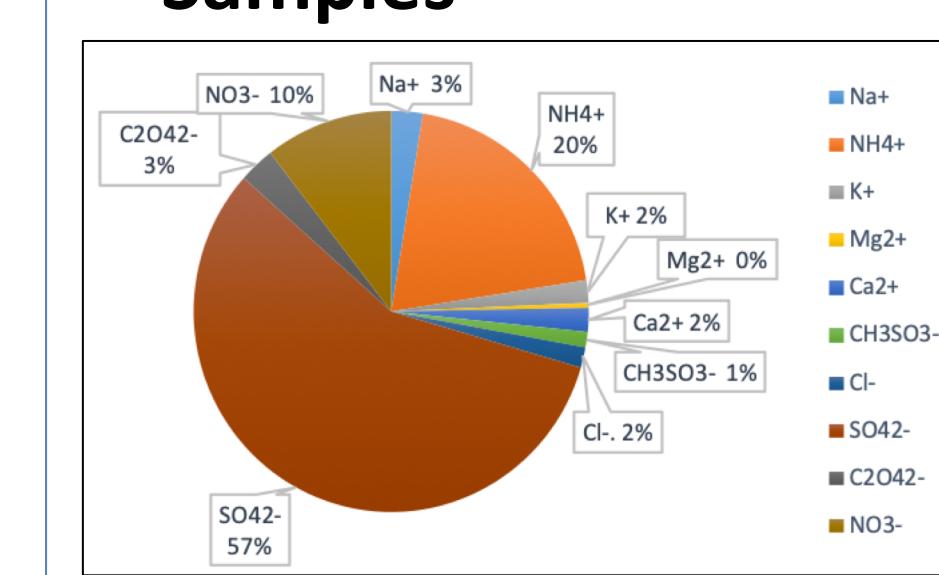


Fig 5. Ion Composition of PM_{2.5}
Tsuen Wan 2016

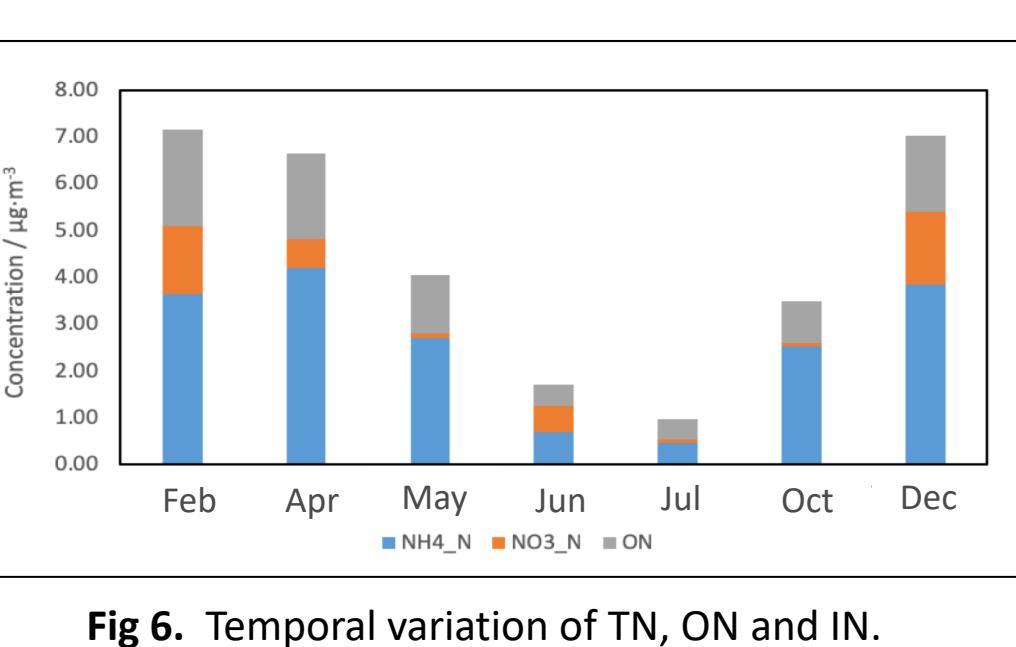


Fig 6. Temporal variation of TN, ON and IN.
Tsuen Wan 2016.

The water-soluble ions are determined by Ion Chromatography. Fig 5. indicates that SO₄²⁻, NH₄⁺, NO₃⁻ are three most abundant inorganic components in PM_{2.5}, which suggests that SO₂ and NO_x are still major precursors to ambient PM_{2.5}. As NO₂⁻ is below detection limit in all samples, the IN concentration is the sum of N from NO₃⁻ and NH₄⁺, ranging from 0.55 to 5.62 μg N/m³ in 2016.

The TN is determined by the aerosol nitrogen analyzer and its concentration in air is in 0.99~7.36 μgN/m³ range.

$$ON = TN - IN$$

The ON content is in 0.44~2.05 μgN/m³ range, while the ON/TN ratio ranges from 22.3% to 44.2% with an annual average ON/TN ratio of 28.84%. Fig 6. shows that IN, ON and TN concentrations are highest in winter and lowest in summer, while the ON/TN ratio shows a reverse trend.

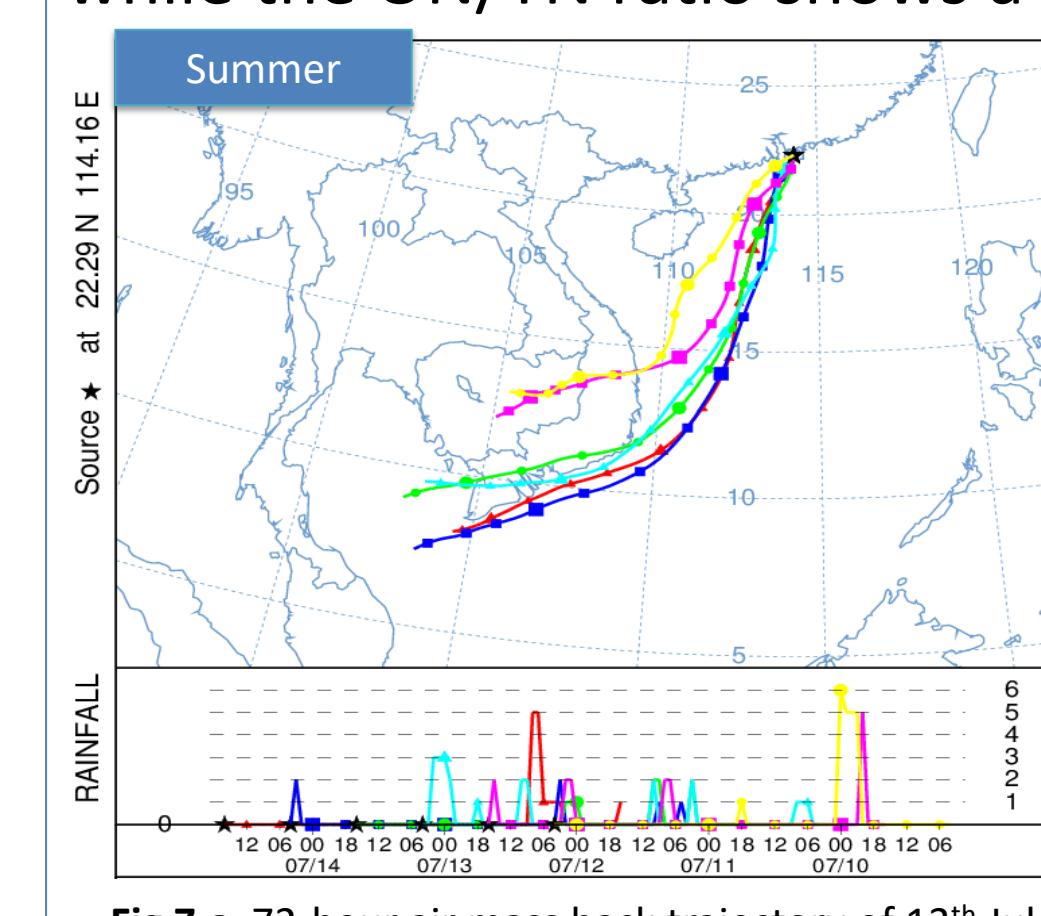


Fig 7.a 72-hour air mass back trajectory of 13th Jul

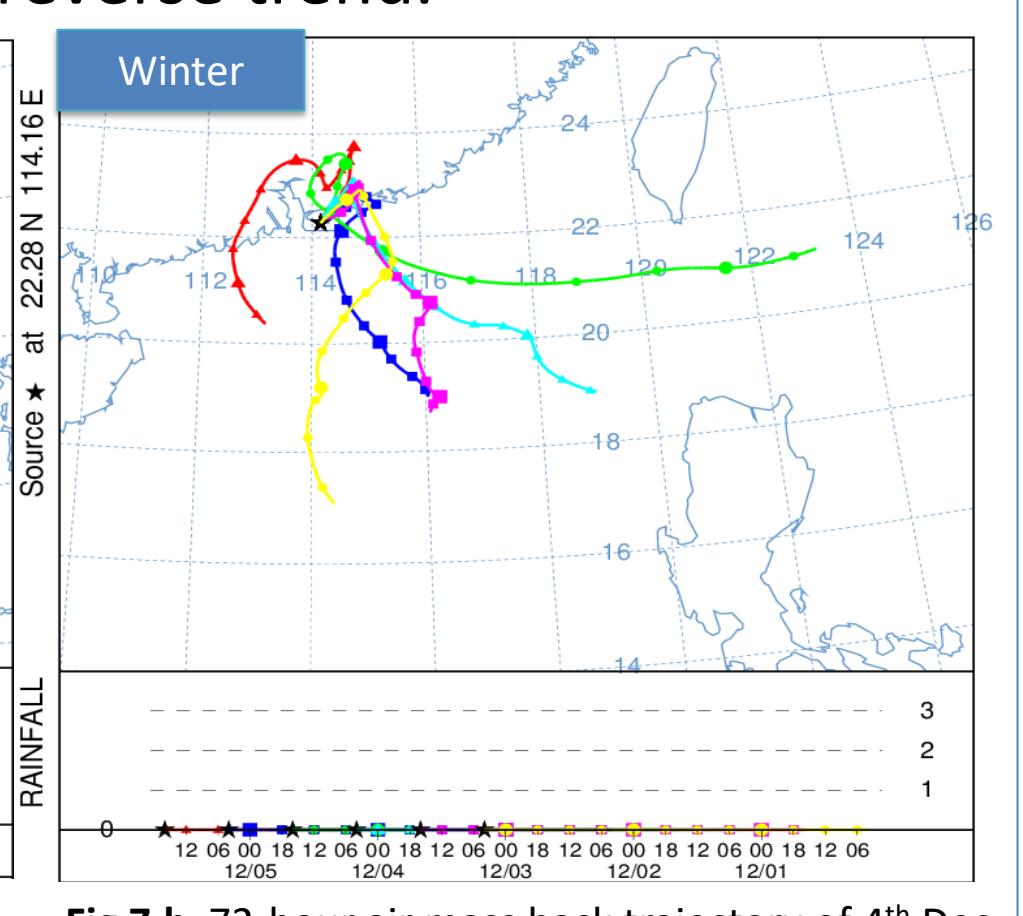


Fig 7.b 72-hour air mass back trajectory of 4th Dec

Above seasonal variation can be explained by the air mass back trajectory. Fig 7.a is the back trajectory of a summer sample, which has the lowest value of TN, ON and IN. This plot shows that these air masses have undergone a long-distance traveling over the sea, which is a much cleaner environment. Many airborne particles are removed out of the atmosphere by wet/dry deposition during transport. Moreover, the marine air masses bring HK plenty of precipitation, which are favorable conditions for the atmosphere to metabolize air pollutants.

The back trajectory of a winter sample (Fig 7.b) which has the highest TN and ON indicates a different story. Although the air masses have a marine origin, they circle around many urban areas in Guangdong Province, consistently picking up air pollutants from anthropogenic activities. Consequently, they have brought severe air pollution to HK at that time.

Future Work

There is an inherit problem with the approach of taking a small difference (i.e., ON) between two large numbers (i.e., TN and IN). Large ON measurement uncertainties are observed in Tsuen Wan samples (e.g., when TN and IN are of similar magnitudes, the ON is calculated to be negative).

We are now testing different mixtures of N-containing standards with the aim of figuring out the contribution of IN and ON in individual peaks. The future work is to re-analyze the TW samples to determine ON using the resolved thermogram peaks.