CHARACTERIZATION OF GAS PHASE ORGANIC COMPOUNDS DURING A WINTER-TIME AIR POLLUTION EVENT

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Introduction

Background

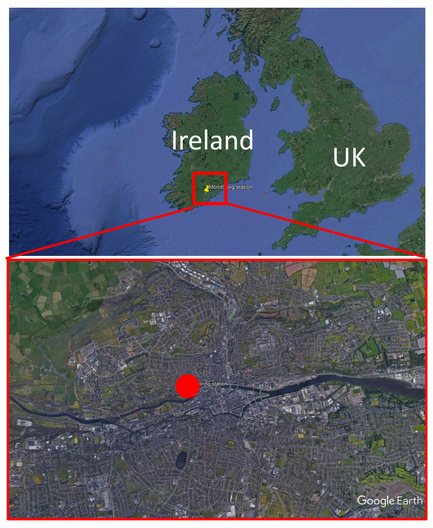
- ✓ Air pollution is known to cause adverse health effects and premature deaths
- ✓ Characterization of pollution sources is essential to reduce their emissions
- ✓ Secondary organic aerosols (SOA) from the oxidation of anthropogenic volatile organic compounds (VOCs) is an important contributor air pollution in urban areas

Aim of the study

- ✓ Characterize the chemical composition of gaseous and particulate phases during a winter-time pollution event
- ✓ The contribution of primary and secondary sources of air pollution is discussed based on gas phase analysis

Experimental set up

Field site



- ✓ Monitoring station in Cork City, Ireland
- ✓ Field campaign conducted from 26 January to 8 February 2019
- ✓ $PM_{2.5}$, NO_x, ozone and meteorological conditions were monitored
- ✓ Air mass backward trajectories were computed using the HYSPLIT model

FIGAERO-ToF-CIMS

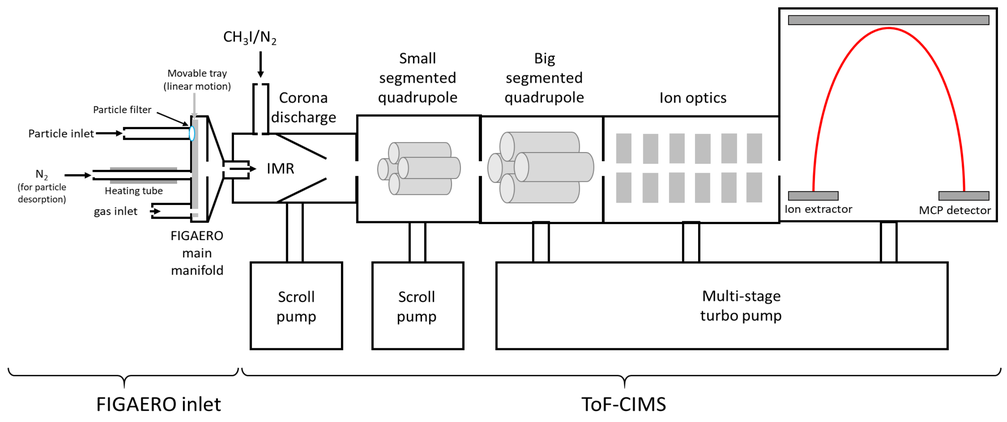


***Figure 1**: Schematic representation of the ToF-CIMS coupled to the FIGAERO inlet*

- ✓ FIGAERO-ToF-CIMS operated using I^- as reagent ion
- ✓ I^- ions were produced by flushing N_2 over a CH_3I permeation tube, then passing into a corona discharge (Fig. 1)
- ✓ Iodide mainly forms adducts with oxygenated species
- ✓ Gas phase was measured for 30 min while particles are simultaneously sampled on a filter
- ✓ Particles are then desorbed and analyzed by the ToF-CIMS over 30 min

Results and discussion

General conditions

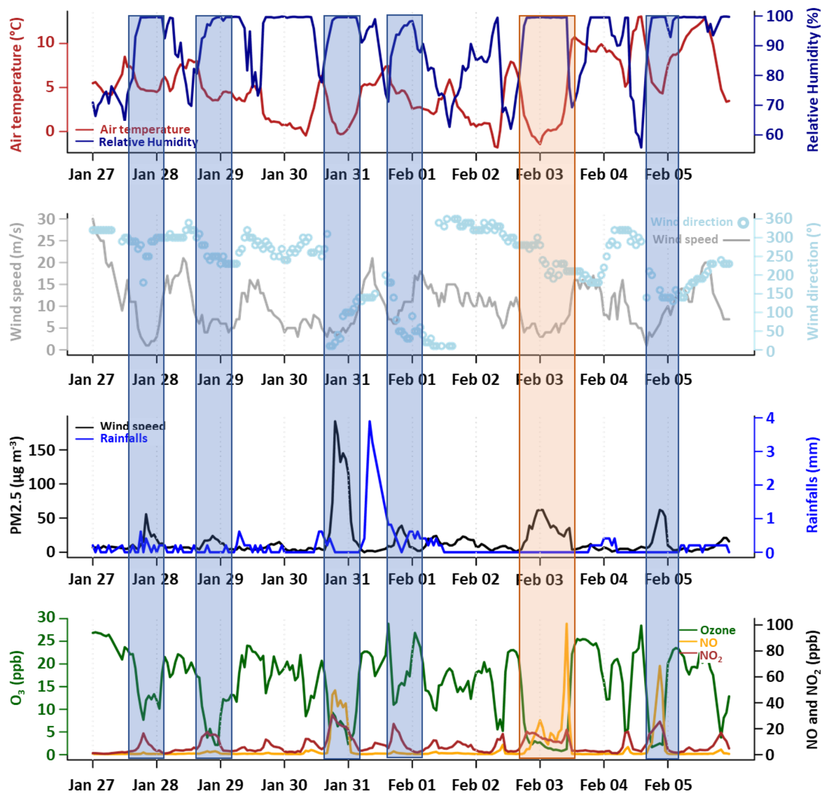


***Figure 2**: Time series of temperature, relative humidity, wind speed and direction, rainfall, $PM_{2.5}$, ozone, NO and NO_2. Blue areas denote night-time $PM_{2.5}$ pollutions events, whereas orange area represents a different type of event.*

- ✓ Frequent $PM_{2.5}$ pollution observed at night-time, reaching values up to 180 µg m^{-3} (blue areas, Fig.2)
- ✓ A more sustained specific event was observed from 2 to 3 February with high $PM_{2.5}$ and concentrations (orange area, Fig.2)
- ✓ NO_x seems to be emitted together with $PM_{2.5}$ (Fig. 2 and 3)
- ✓ Anticorrelation between $PM_{2.5}$ and T suggests that solid fuel burning may highly contribute to pollution events (Fig. 3)
- ✓ Pollution rose plot suggests main source of $PM_{2.5}$ is a nearby residential area (Fig. 3)

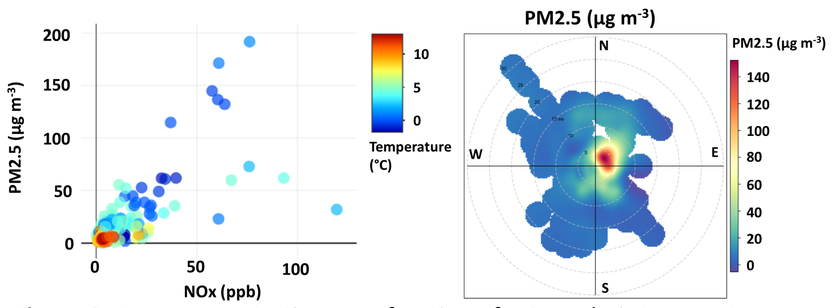


***Figure 3**: $PM_{2.5}$ concentration as a function of NO_x and air temperature (left panel) and $PM_{2.5}$ pollution rose (right panel)*

Chemical composition of the gas phase

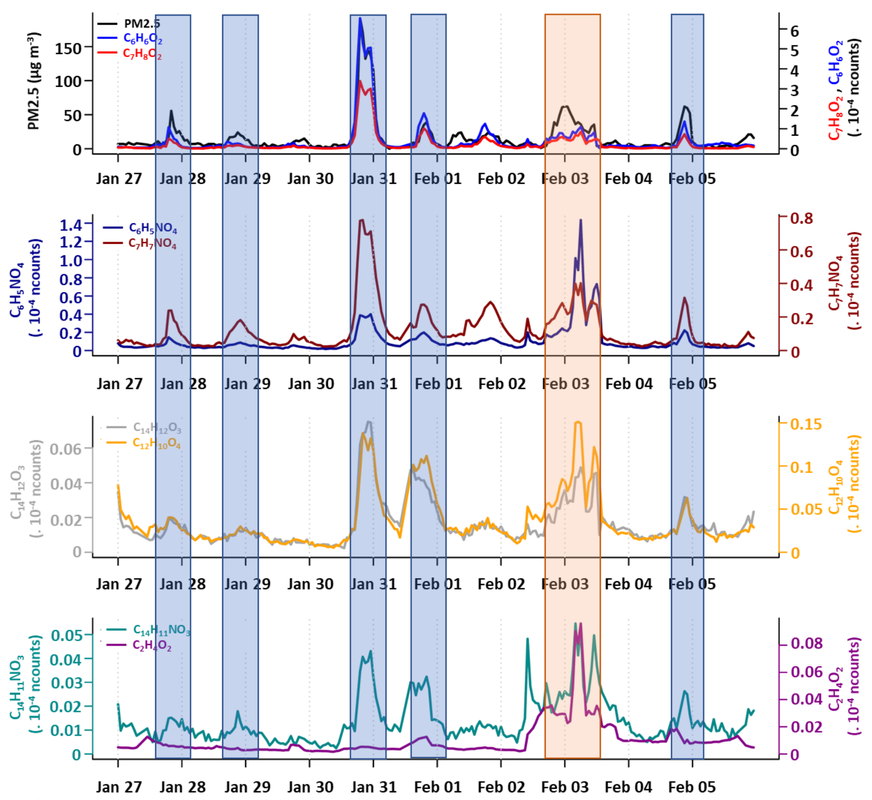


***Figure 3**: Time series of $PM_{2.5}$, $C_6H_6O_2$ (dihydroxybenzene), $C_7H_8O_2$ (methoxyphenol), $C_6H_5NO_4$ (dihydroxy-nitrobenzene), $C_7H_7NO_4$ (methoxy-nitrophenol), $C_{14}H_{12}O_{13}$ (O-PAH), $C_{12}H_{10}O_4$ (O-PAH), $C_{14}H_{10}NO_3$ (N-PAH), $C_2H_4O_2$ (oxalic acid). Blue areas denote night-time PM pollution events, whereas orange area represents a specific event.*

- ✓ Dihydroxybenzene ($C_6H_6O_2$) and methoxyphenol ($C_7H_8O_2$), well known biomass burning tracers, are highly correlated with $PM_{2.5}$
- ✓ It confirms that residential solid fuel burning is the main source of $PM_{2.5}$ during night-time pollution events
- ✓ Dihydroxy-nitrobenzene ($C_6H_5NO_4$) and methoxy-nitrophenol ($C_7H_7NO_4$ show the same overall trend as their supposed precursors: this suggests primary emission and/or very fast formation in the combustion plume
- ✓ O-PAHs, N-PAHs and oxalic acid are higher during the specific event, traducing more processed emissions

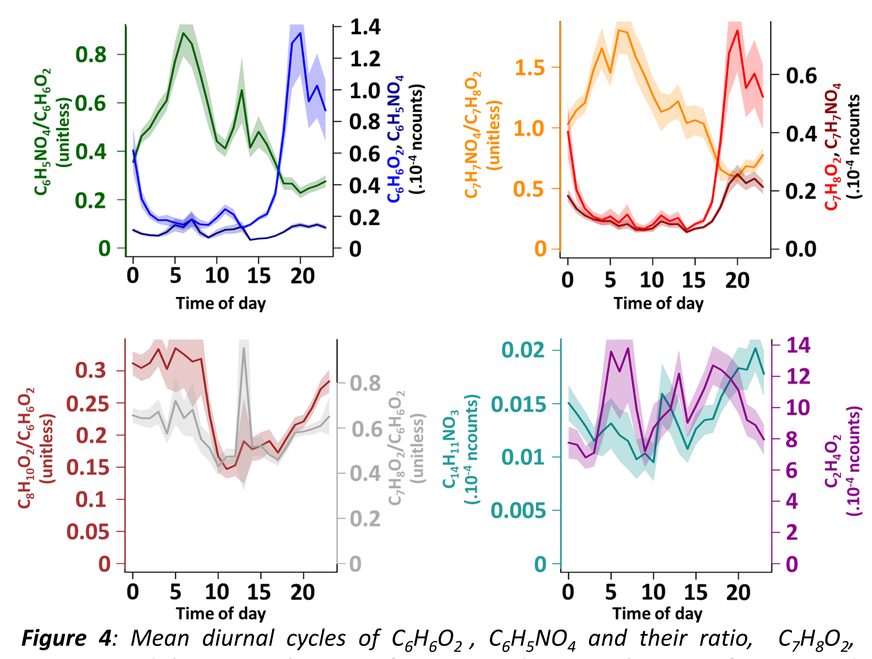


***Figure 4**: Mean diurnal cycles of $C_6H_6O_2$, $C_6H_5NO_4$ and their ratio, $C_7H_8O_2$, $C_7H_7NO_4$ and their ratio, the ratio of $C_8H_{10}O_2$ and $C_6H_6O_2$, the ratio of $C_7H_8O_2$ and $C_6H_6O_2$, $C_{14}H_{10}NO_3$ and $C_2H_4O_2$.*

- ✓ Ratios of nitro-oxygenated products to their precursors increase during the night, indicating secondary formation of nitro-oxygenated species, probably due to reactions with NO_3 radicals
- ✓ Dimethoxybenzene ($C_8H_{10}O_2$) and methoxyphenol ($C_7H_8O_2$) have a lower reaction rate coefficient with NO_3 compared to dihydroxybenzene ($C_6H_6O_2$), explaining why their ratios against dihydroxybenzene increase at night
- ✓ Oxalic acid ($C_2H_4O_2$) does not present a clear diurnal cycle due to its major increase during the specific event
- ✓ Diurnal cycle of N-PAHs is clearly a combination of both night-time increase and the specific event on 2-3 February

Conclusion and outlooks

- ✓ Strong $PM_{2.5}$ pollution events frequently occurred at night-time during winter in Cork, Ireland
- ✓ $PM_{2.5}$ pollution event is attributed mainly to solid fuel burning in residential areas
- ✓ A second type of pollution event is observed (2-3 February), pointing to a different air mass origin
- ✓ Secondary formation of nitro-oxygenated compounds at night, possibly by precursor reaction with NO_3 radicals
- ✓ The origin of the specific pollution event seems to be related to more processed emissions
- ✓ Analysis of the chemical composition of the particle phase is still on going

Acknowledgements

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