

# Developing a <sup>14</sup>CO<sub>2</sub> sampling system and strategy to verify fossil fuel emissions from Rotterdam area

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## 1. Introduction

Radiocarbon – <sup>14</sup>C, a rare isotope of carbon – is a valuable and accurate tracer for quantifying CO<sub>2</sub> emissions from fossil fuels (ffCO<sub>2</sub>)<sup>(1)</sup>. <sup>14</sup>C is produced mostly from cosmic rays and is exchanged with different carbon reservoirs. However, fossil fuels are isolated from these reservoirs for millions of years, while <sup>14</sup>C has a half-life of only about 5730 years. Thus, fossil fuels are deprived of <sup>14</sup>C, and when they are combusted, the resulting CO<sub>2</sub> emissions dilute the current atmospheric <sup>14</sup>C concentration (the Suess’s effect)<sup>(2)</sup>. By measuring the <sup>14</sup>C concentration of an airmass before and after it passes through an area with fossil fuel emissions, the CO<sub>2</sub> attributed to fossil fuels can be quantified using<sup>(3)</sup>:

$$CO_{2ff} = CO_{2obs} \frac{\Delta^{14}CO_{2bg} - \Delta^{14}CO_{2obs}}{\Delta^{14}CO_{2bg} + 1}$$

(Where CO<sub>2ff</sub> is the fossil fuel concentration in the sample; CO<sub>2obs</sub> is the total CO<sub>2</sub> concentration in the sample; Δ<sup>14</sup>CO<sub>2bg</sub> and Δ<sup>14</sup>CO<sub>2obs</sub> are the <sup>14</sup>C content values of the background and the sample, respectively.)

My research project is part of a multinational ICOS project named “RINGO” and aims to develop a sampling system and strategy to quantify the fossil fuel emissions from the Rotterdam area in the Netherlands using a station pair approach.

## 2. Objectives

The project is planned in several phases, each of which has specific goals to foster the main aim of the project:

- **Phase 1:** Establish a pair of stations “upwind” and “downwind” of Rotterdam in terms of wind direction. Then together with our RINGO partners, develop a suitable sampling strategy.
- **Phase 2:** Develop an automated flask sampling system and put one in each station. Then collect and analyse the flask samples for 1 year along with standard continuous monitoring.
- **Phase 3:** Collaborate with partners to interpret the results and evaluate the sampling strategy.

In this presentation, I discuss the results obtained from Phase 1 and Phase 2.

## 3. Station information

### Locations:

#### - Upwind station (MAS):

a building of the Rotterdam Port Authority, situated in the 2e Maasvlakte harbour area. The air inlet and equipment are installed on/inside the building (figures below).

#### - Downwind station (CBW):

Cabauw atmospheric station, which is already an ICOS station.

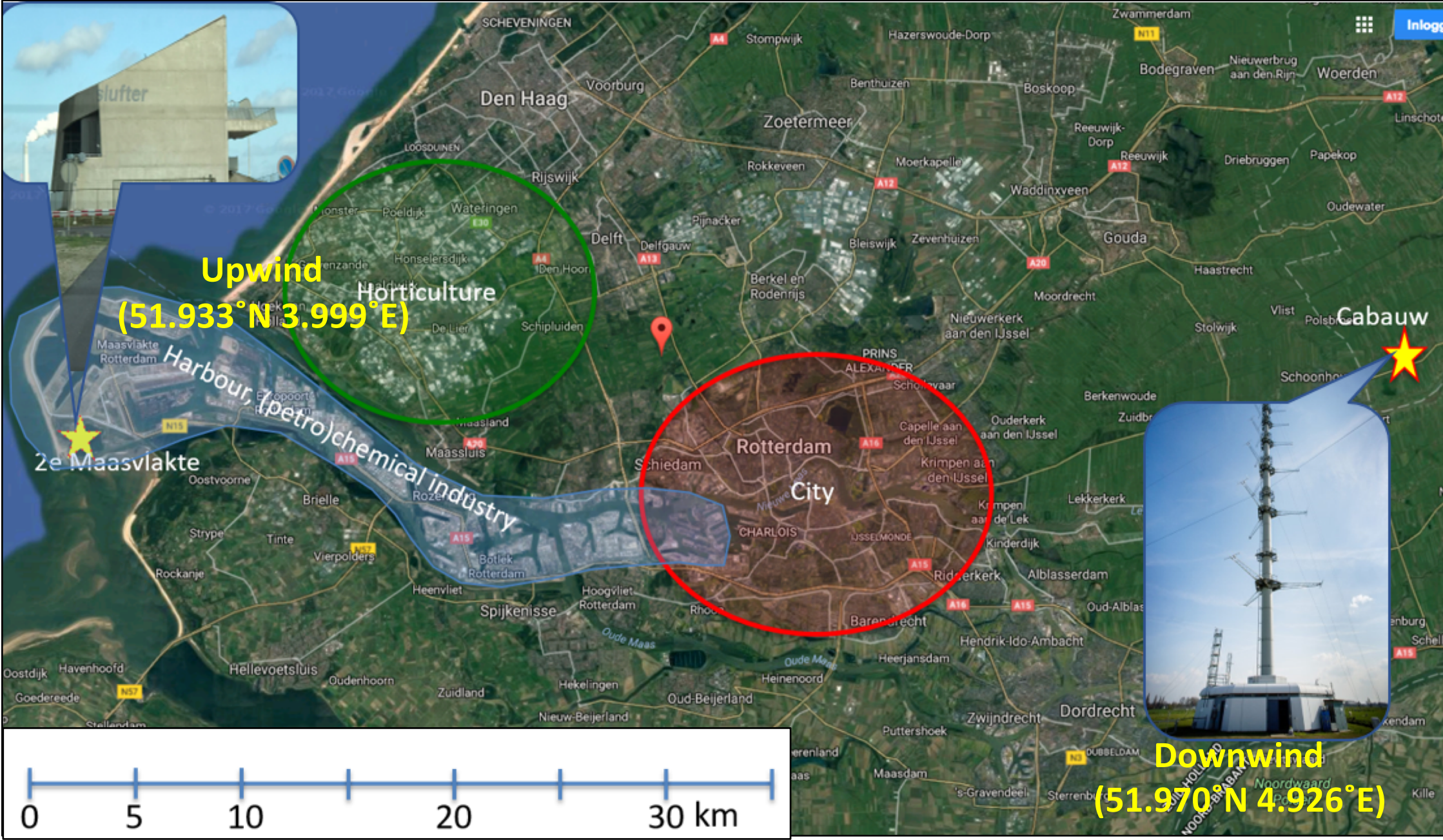


Figure 1: The Rotterdam area and the locations of the upwind and downwind station

### System setup:

- At each station, an automated flask sampling system (Autosampler) is placed to collect air samples.
- At MAS station, a Picarro G2301 analyser is also installed to provide continuous monitoring of the air around the station (a same analyser is already at CBW station as part of the research centre).

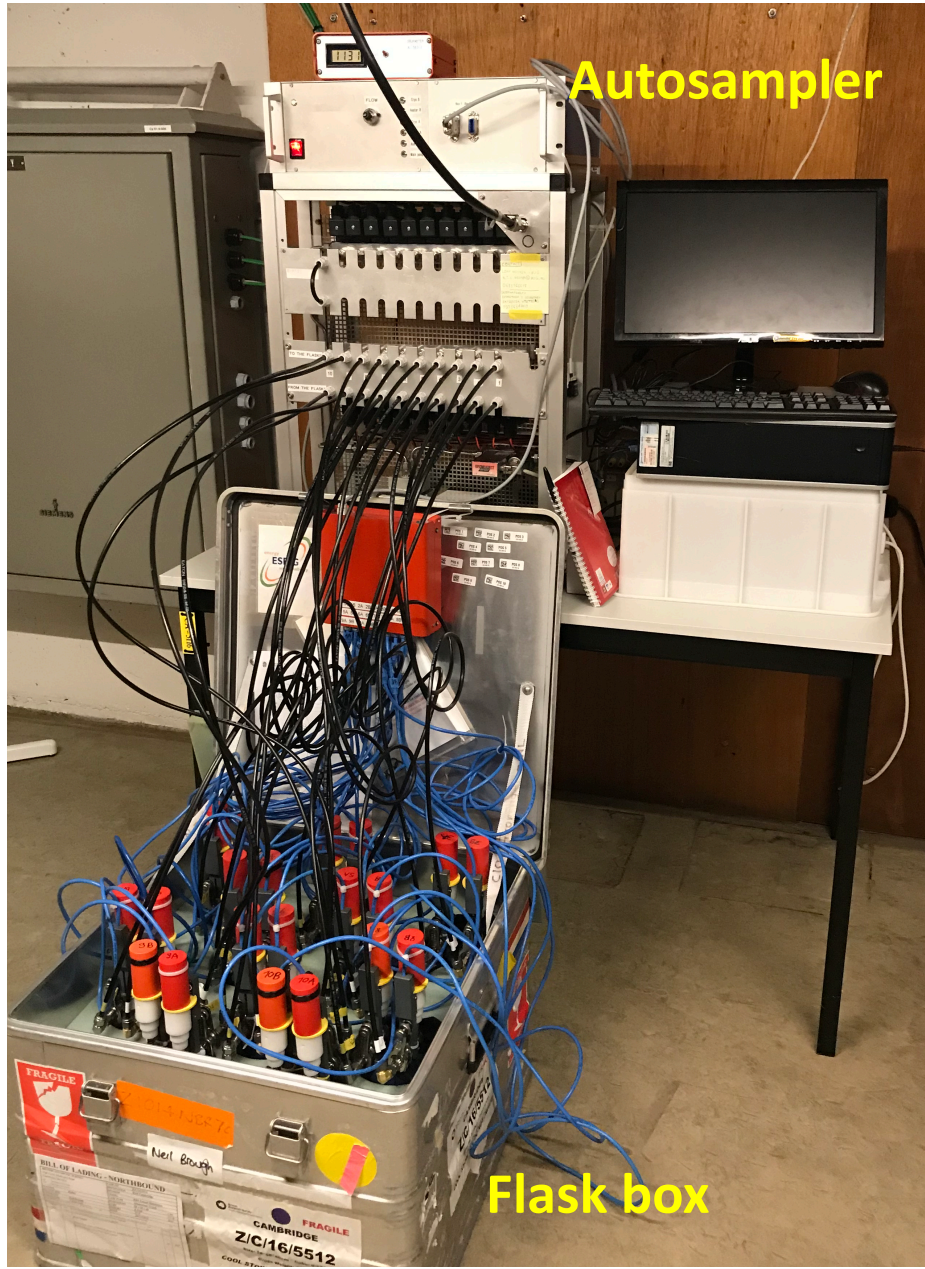


Figure 2: The Autosampler system setup

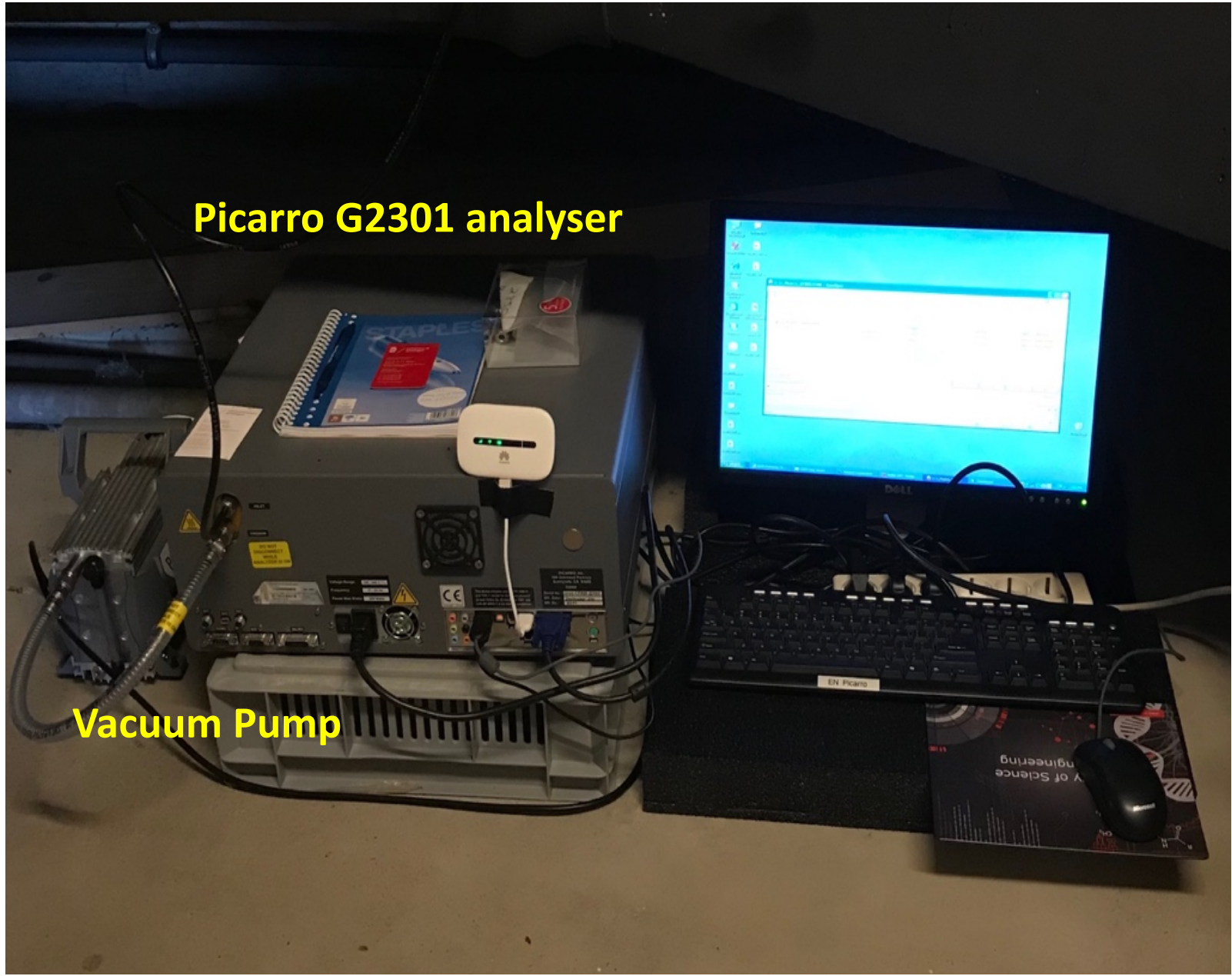


Figure 3: The Picarro analyser at MAS

### Procedure:

- The wind information is provided by the German and Dutch meteorological institutes (DWD and KNMI, respectively) with the help of our German partner (Heidelberg University, UHEI) and our KNMI contacts.
- Sampling criteria: during the afternoon (between 11am and 4pm) and wind is from the West, and preferably during the winter. These criteria are determined by the modelling groups from UHEI, University of Versailles Saint-Quentin-en-Yvelines (UVSQ, Paris), and Wageningen University (WUR).
- When sampling criteria are satisfied, the air samples are collected at both locations and later transported to Groningen for <sup>14</sup>C analysis using an “Accelerator Mass Spectrometer (AMS)”.

### Progress:

In January 2019, 6 flask samples were collected, 2 of which are official RINGO-class samples. CO<sub>2</sub> and <sup>14</sup>C analyses were performed on the samples to determine ffCO<sub>2</sub> signals from Rotterdam.

## 4. Preliminary Results

The preliminary data collected over the last year are present below.

All wind and pollution data from Jan 2018 to Feb 2019:

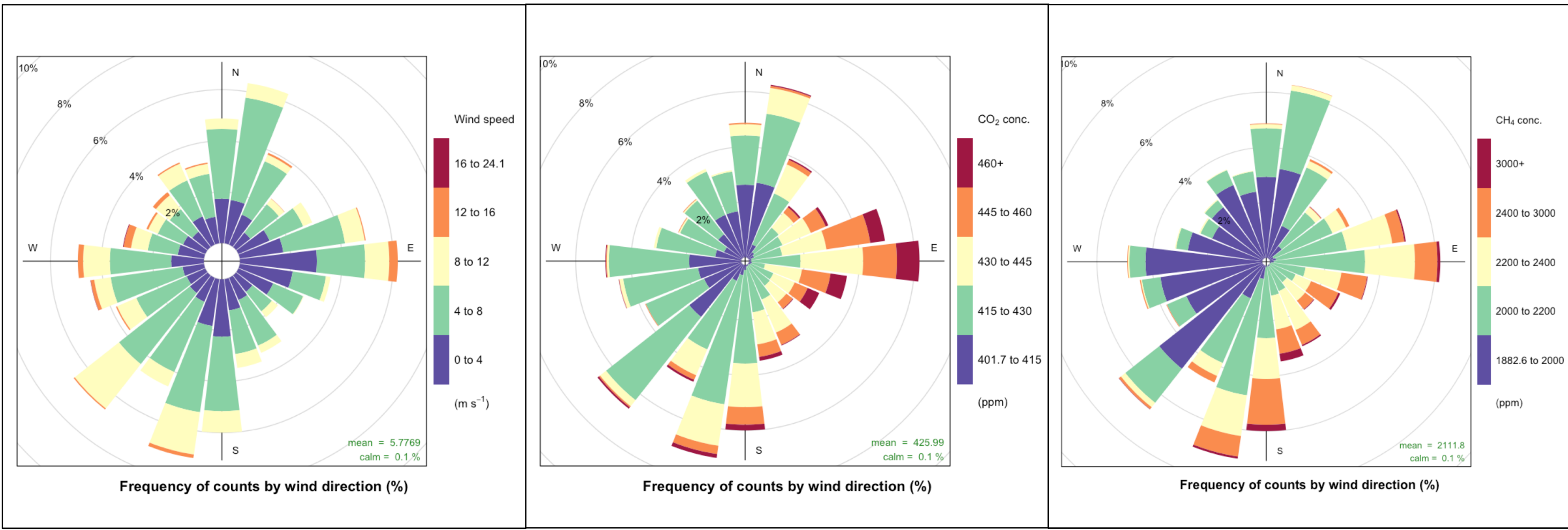


Figure 4: All data from Jan 2018 to Feb 2019. From left to right: wind speed frequencies plotted by wind directions; CO<sub>2</sub> and CH<sub>4</sub> concentrations plotted against wind direction. [All data are measurements made at MAS]

Wind and pollution data selected from only winter periods (Dec-Jan-Feb of 2018 and 2019):

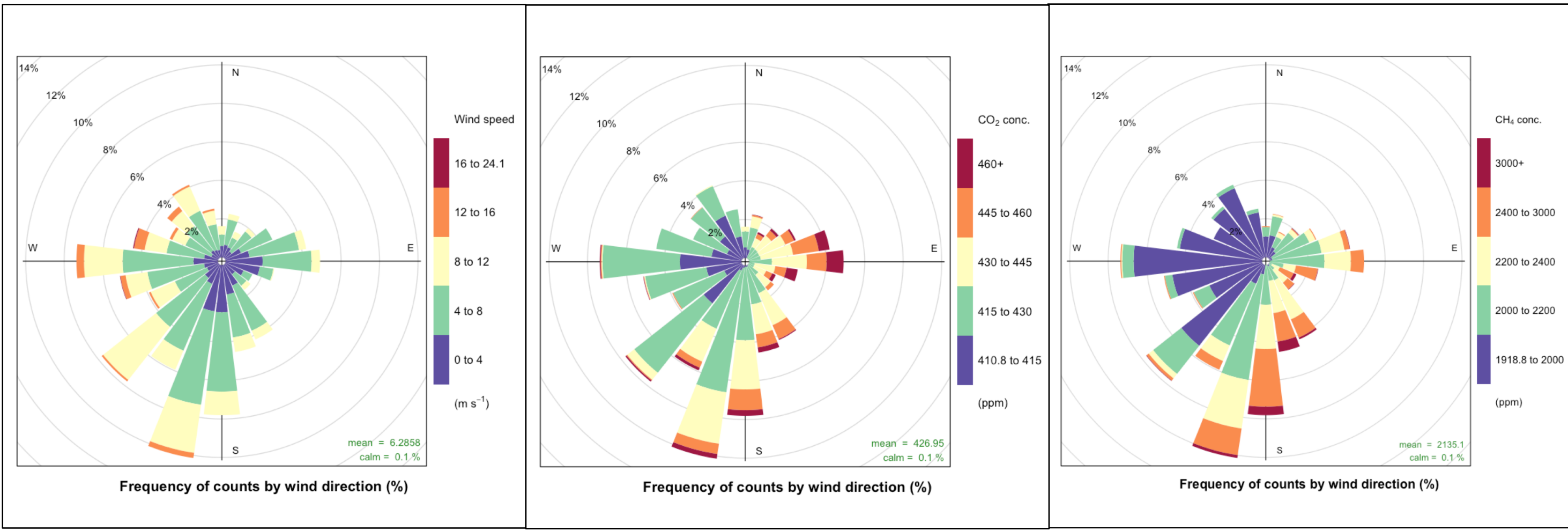


Figure 5: Data for winter periods of Dec-Jan-Feb 2018 and Jan-Feb 2019. From left to right: wind speed frequencies plotted by wind directions; CO<sub>2</sub> and CH<sub>4</sub> concentrations plotted against wind directions. [All data are measurements made at MAS]

Wind and pollution data for only Jan 2019 (when the flasks were collected):

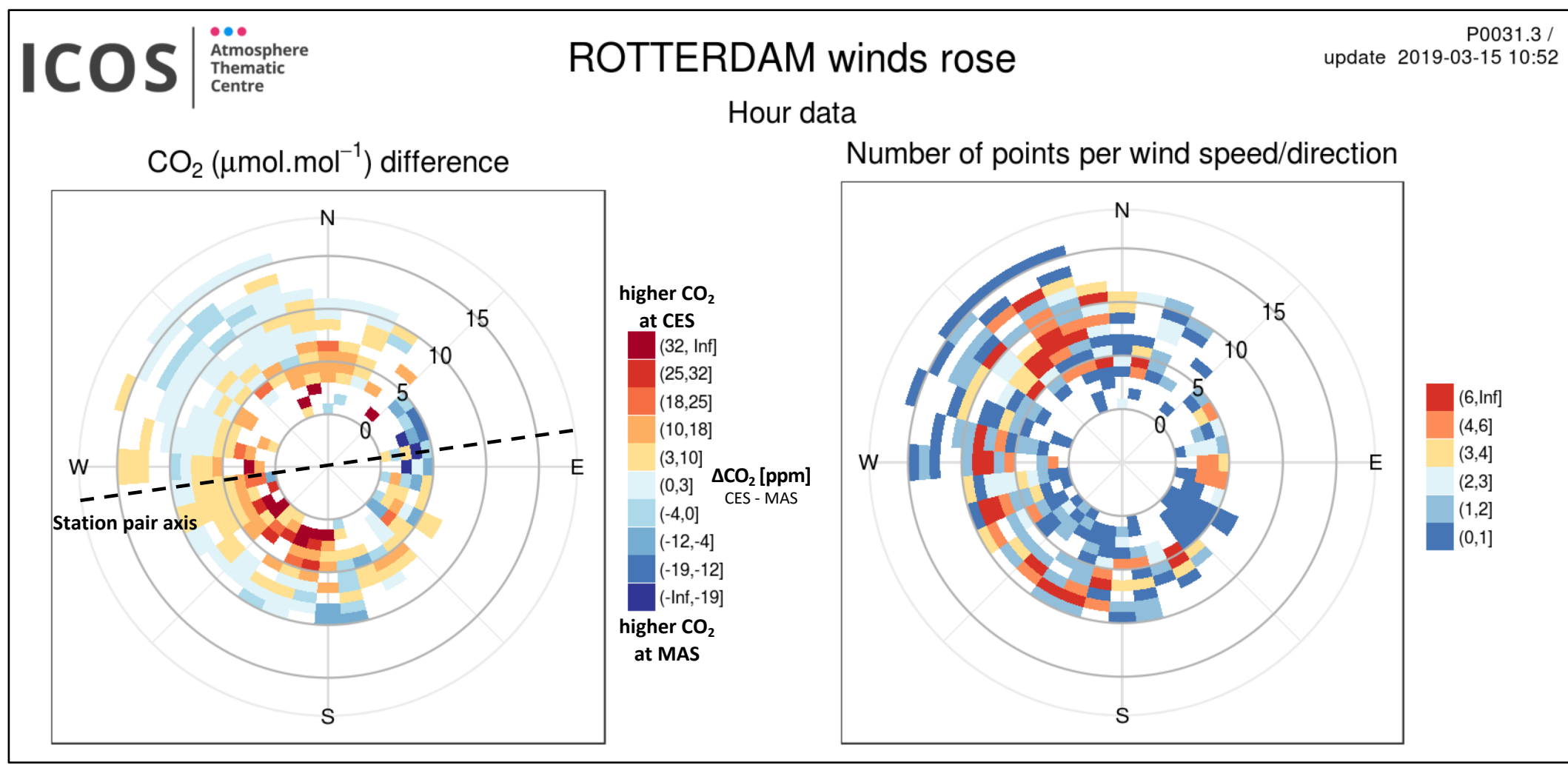


Figure 6: Data for Jan 2019. The left panel shows the CO<sub>2</sub> gradient between CES and MAS (CES minus MAS) according to wind directions. The right panel shows the frequencies of wind speed/direction. These plots were provided with the courtesy of our Paris partner: the Laboratory of Climate and Environmental Sciences (LCE) from UVSQ.

First <sup>14</sup>C data:

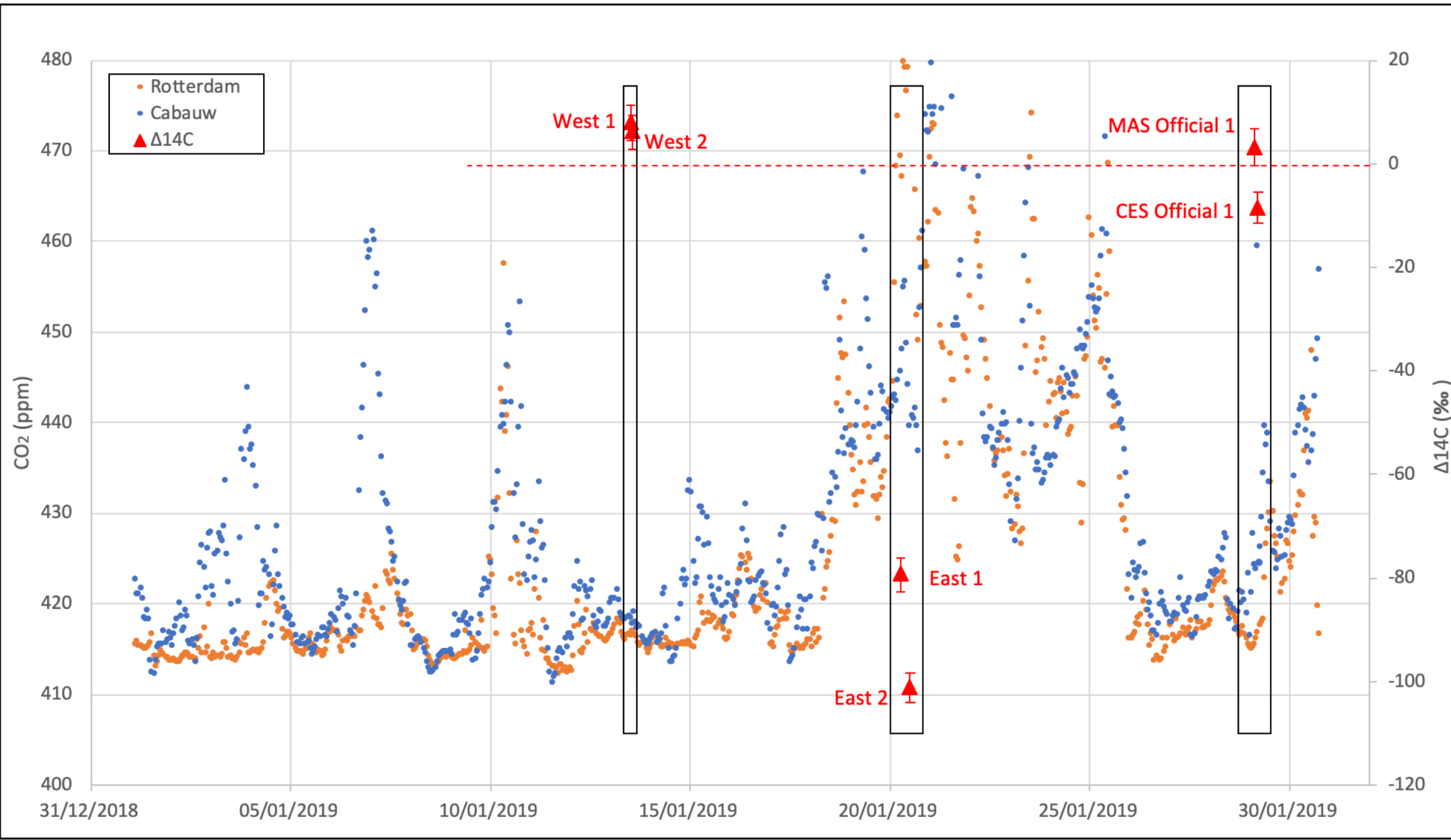


Figure 7: Time series of CO<sub>2</sub> concentrations measured at MAS and CBW in Jan 2019. 6 data points marked with triangles are the <sup>14</sup>C content of the 6 collected flasks.



Figure 8: Using HYSPLIT back trajectory model to confirm the travel path of the air mass.

Sample	Status	CO <sub>2</sub>	Δ <sup>14</sup> C (‰)	ffCO <sub>2</sub> [ppm]
MAS West 1	Upwind	415.45 ± 0.04	7.93 ± 3.49	N/A
MAS East 1	Downwind	470.10 ± 2.70	-79.38 ± 3.26	N/A
MAS West 2	Upwind	474.47 ± 9.81	6.12 ± 3.25	N/A
MAS East 2	Downwind	485.71 ± 0.01	-101.13 ± 2.84	N/A
MAS official 1	Upwind	419.19 ± 0.66	3.12 ± 3.59	5.34 ± 2.12
CES official 1	Downwind	459.51 ± 0.38	-8.55 ± 2.97	

Table 1: Results of the <sup>14</sup>C analysis and determination of ffCO<sub>2</sub> signal from Rotterdam

## 5. Conclusion and planning

The results obtained so far from support the initial speculations that the wind coming from the West is relatively clean and can be used as background air, and <sup>14</sup>C analysis confirms the contribution of ffCO<sub>2</sub> to the airmass. In the coming months, more measurements will be done, and later Rn<sup>222</sup> analysis will be used to translate concentrations of ffCO<sub>2</sub> into fluxes for interpretation<sup>(4)</sup>.

### Acknowledgements

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### References

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