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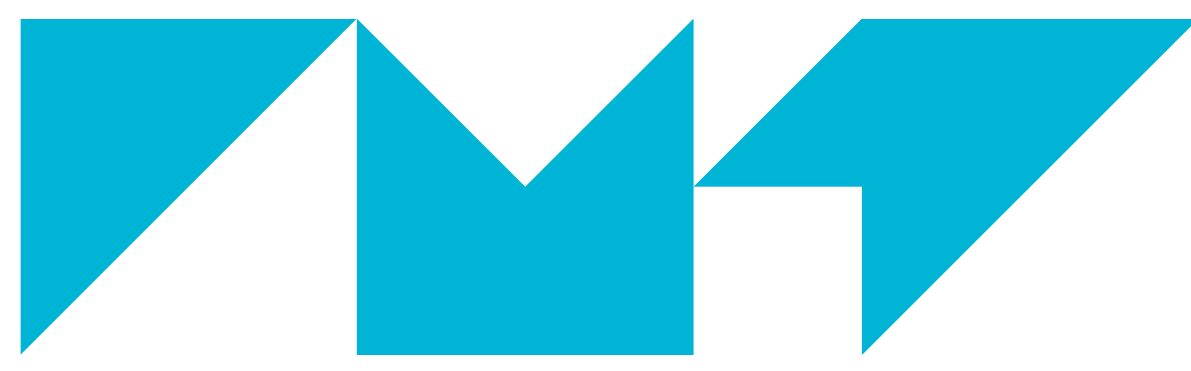
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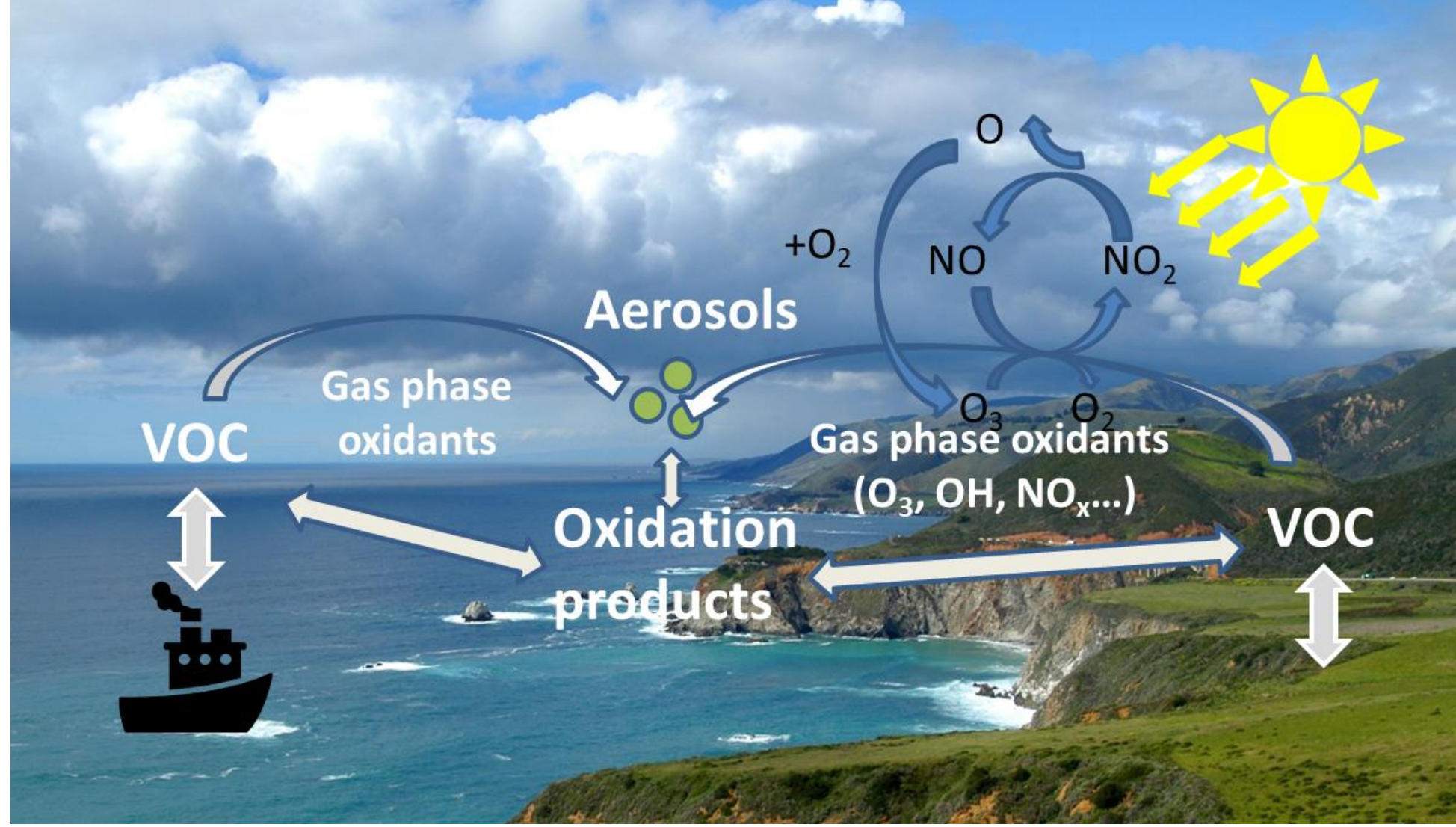


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# Shipping-related emissions of volatile organic compounds (VOCs)

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## Why are we interested in VOCs emitted by ships?



Although much progress has been made in the regulations on shipping emissions, notably for SO<sub>2</sub> and NO<sub>x</sub>, several hurdles still need to be overcome in order to **accurately estimate and mitigate the impact of shipping emissions on air quality**. This requires (1) a better understanding of **emissions at berth and in port**, since these have the largest impact on urban air quality and (2) **field measurements** in specific ports to better understand **regional differences**.

Indeed, changing practices (e.g. the use of fuel with lower SFC, alternative fuels, use of scrubbers) may increase the relative importance of other pollutants, such as Particulate Matter (PM) and Volatile Organic Compounds (VOCs). Therefore, it seems critically important to **monitor changes in unregulated pollutants**, and particularly VOCs as precursors for PM (mainly Secondary Organic Aerosol). However, few studies have addressed the emission of these pollutants from ships so far.

*This work focusses on the emission of VOC by ships in two harbours in France through field measurements on land using ea. on-line VOC measurements. This allowed for the determination of speciated Emission Factors (EF) of a suite of pollutants and VOCs that will be used in regional air quality models. The results are compared for the two different harbors, one on the North sea channel and one on the Mediterranean Sea that have different emission regulations for SO<sub>2</sub> (Marseille 0.5% S (m:m) and Dunkirk 0.1% S (m:m))*

## How did we work?



Two intensive field campaigns:

- ▶ Juin 2021: Marseille
- ▶ Septembre 2022: Dunkirk

Land-based measurement sites

← Map of the port of Marseille with the measurement stations (green circle) and ship traffic density (Marine traffic, 2022) [2]

Picture of the Dunkirk harbour →



Determining EFs using the carbon ratio method [3]

$$EF_x = \frac{\int_s^e X - X_{BG}}{\int_s^e CO_2 - CO_{2,BG}} \times \frac{M_C}{M_{CO_2}} \times w_c$$

Where  $w_c$  represents the carbon mass fraction in fuel,  $M_C/M_{CO_2}$  is the mass fraction of carbon. Background concentrations ( $X_{BG}$ ,  $CO_{2,BG}$ ) were taken as the median on a 30 mins window either side.

Category	Target Species	Instrument
Gases	inorganic (NO <sub>x</sub> , O <sub>3</sub> , SO <sub>2</sub> , NH <sub>3</sub> )	standard analyzers
	VOCs/BTEX/IVOC ; CO, CO <sub>2</sub> , (CH <sub>4</sub> )	PTR-ToF-MS, GC-FID; CRDS
Particles	number concentration and size distribution	SMPS, CPCs, OPC
	elemental carbon, PM <sub>2.5</sub> , PM <sub>10</sub>	aethalometer, TEOM-FDMS
	chemical composition	HR-ToF-AMS
	Metals/particle morphology	Filters (ICP-MS) and X-Act online analysis (EDXRF)

## What do ships emit in French harbours?

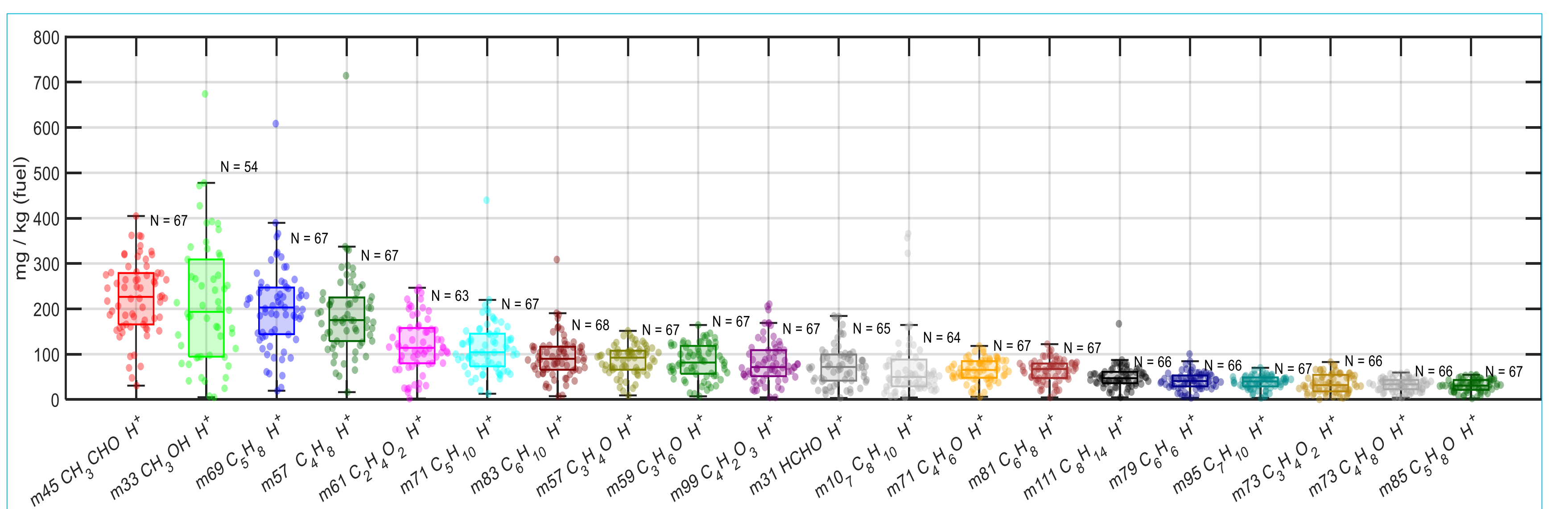
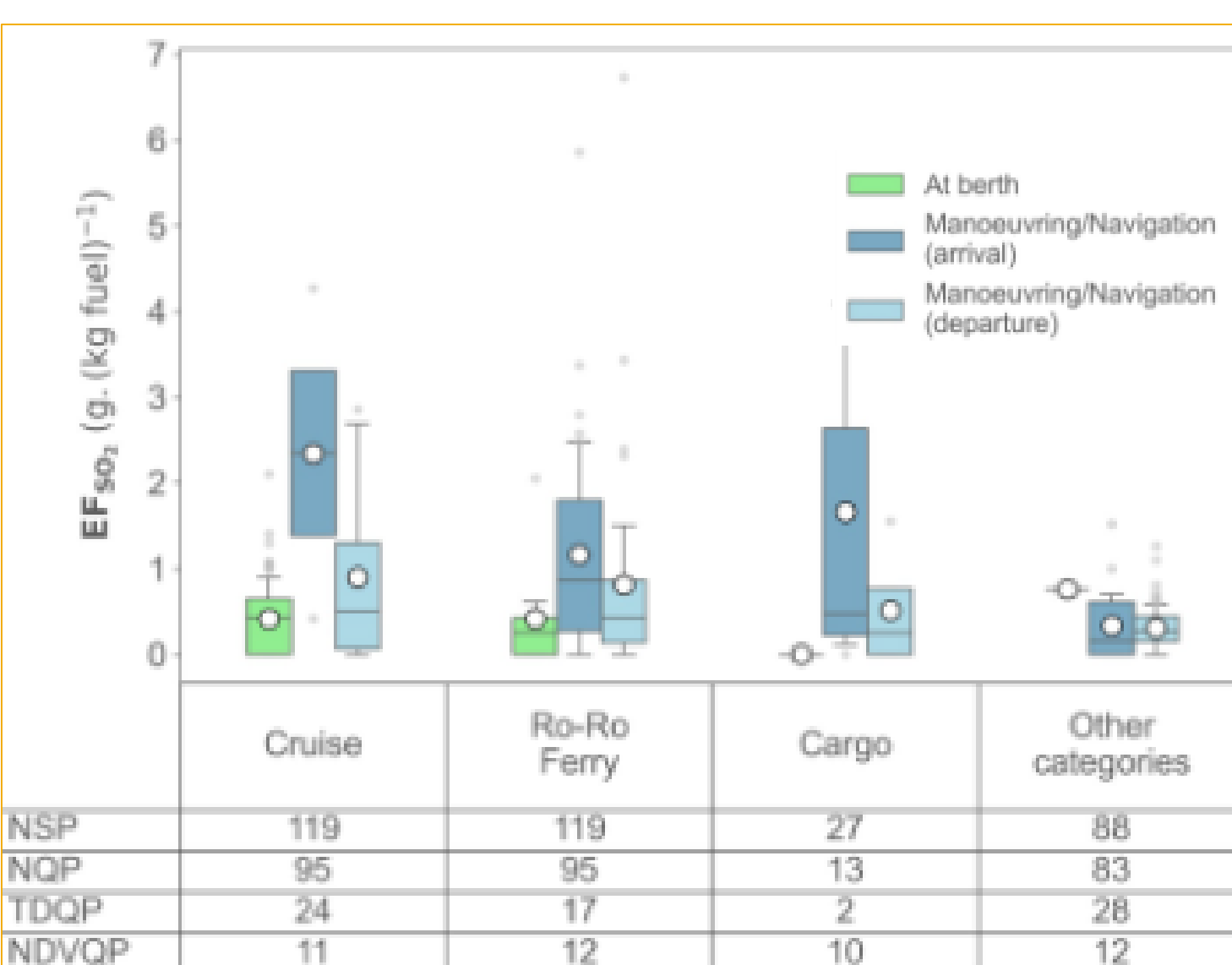
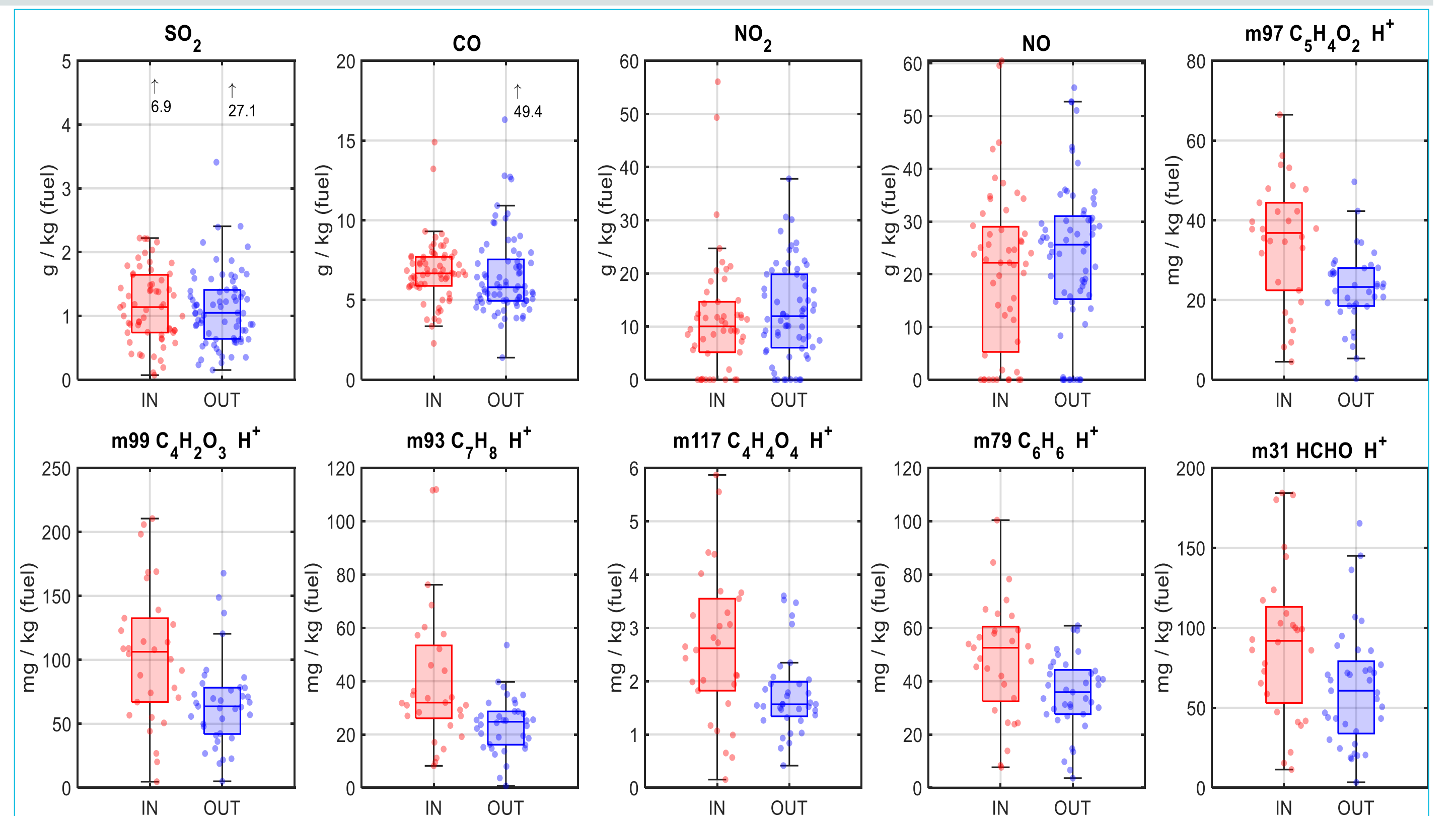
### Dunkirk shipping emissions:

- ▶ 149 shipping peaks measured, lasting for 3 – 12 mins
- ▶ Sulphur regulations are generally met, mean EF=1.36 g/kg<sub>fuel</sub>
- ▶ Highest emission factors for NO<sub>x</sub> (med. EF = 24 g/kg<sub>fuel</sub>)
- ▶ The **most emitted VOCs** are formaldehyde, acetaldehyde, methanol, cyclopentane and BTEX aromatics. VOCs account for 2.3 g/kg<sub>fuel</sub> which is 4.3% of the (measured) mass emitted

- ▶ Very similar emissions for three rotating sister ferries
- ▶ Significant **differences between in- and outgoing ferries** for certain pollutants : PN, BC, and VOCs

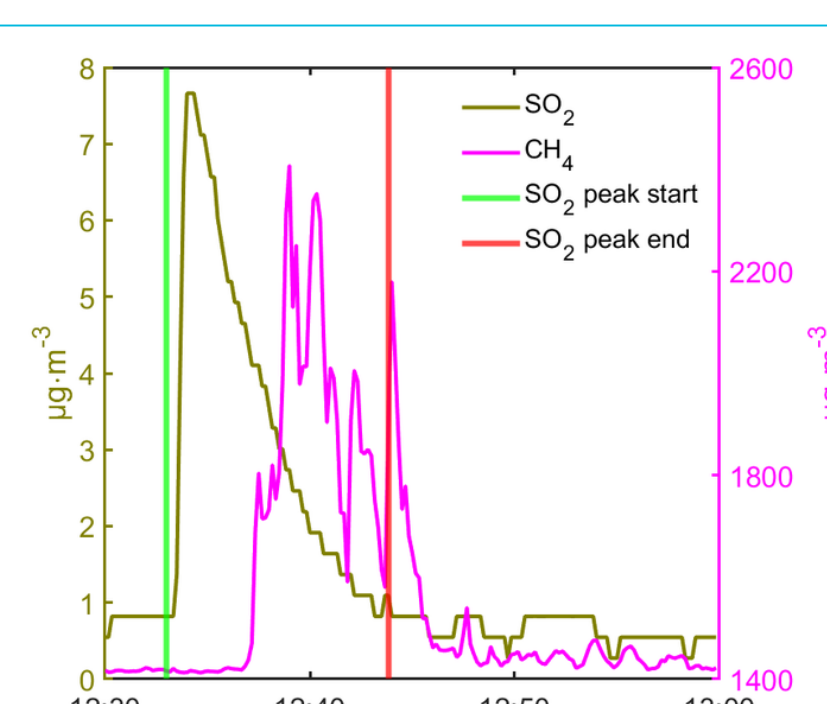
### Marseille shipping emissions:

- ▶ 353 shipping peaks detected, lasting for 2-14 mins, from many different ship types
- ▶ **VOCs make up less than 0.1% of the gaseous phase** on average, but up to 10% in certain cases. EFs for VOCs are very low (0.03 ppb), below the LoD for most species. Identified VOCs with the **highest EFs** are methanol, acetaldehyde, acetic acid, **C8 aromatics**, toluene (+ C<sub>5</sub>H<sub>9</sub><sup>+</sup> and C<sub>4</sub>H<sub>9</sub><sup>+</sup>)
- ▶ Significant differences between different operational phases for certain pollutants; differences in- and outgoing vessel only for SO<sub>2</sub> (engine use?)



### The methane case

- ▶ Methane is the highest organic compound emitted in Dunkirk (med EF = 0.9 g/kg<sub>fuel</sub>) and Marseille (med EF = 0.4 g/kg<sub>fuel</sub>)
- ▶ ... however, its emission peaks don't coincide with those of other combustion products ⇒ could CH<sub>4</sub> be outgassing from seawater?



## Conclusion:

- ▶ Measuring shipping EF requires measurements at a minute resolution
- ▶ Sulphur regulation generally respected, NO<sub>x</sub> is the dominant pollutant emitted in SECA zones in France
- ▶ VOCs represent a small fraction but include some high intensity peaks and toxic species (BTEX)

## Authors

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