



Impact of Volatile Organic Compounds from shipping emissions on air quality in the Channel

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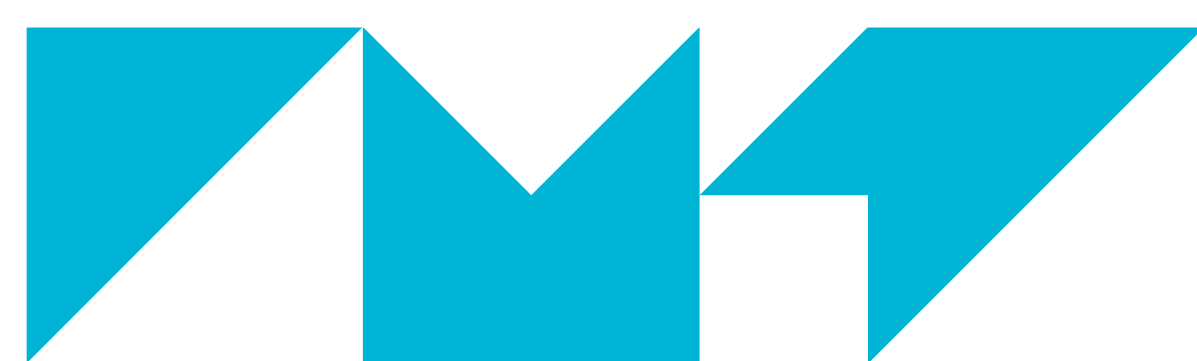
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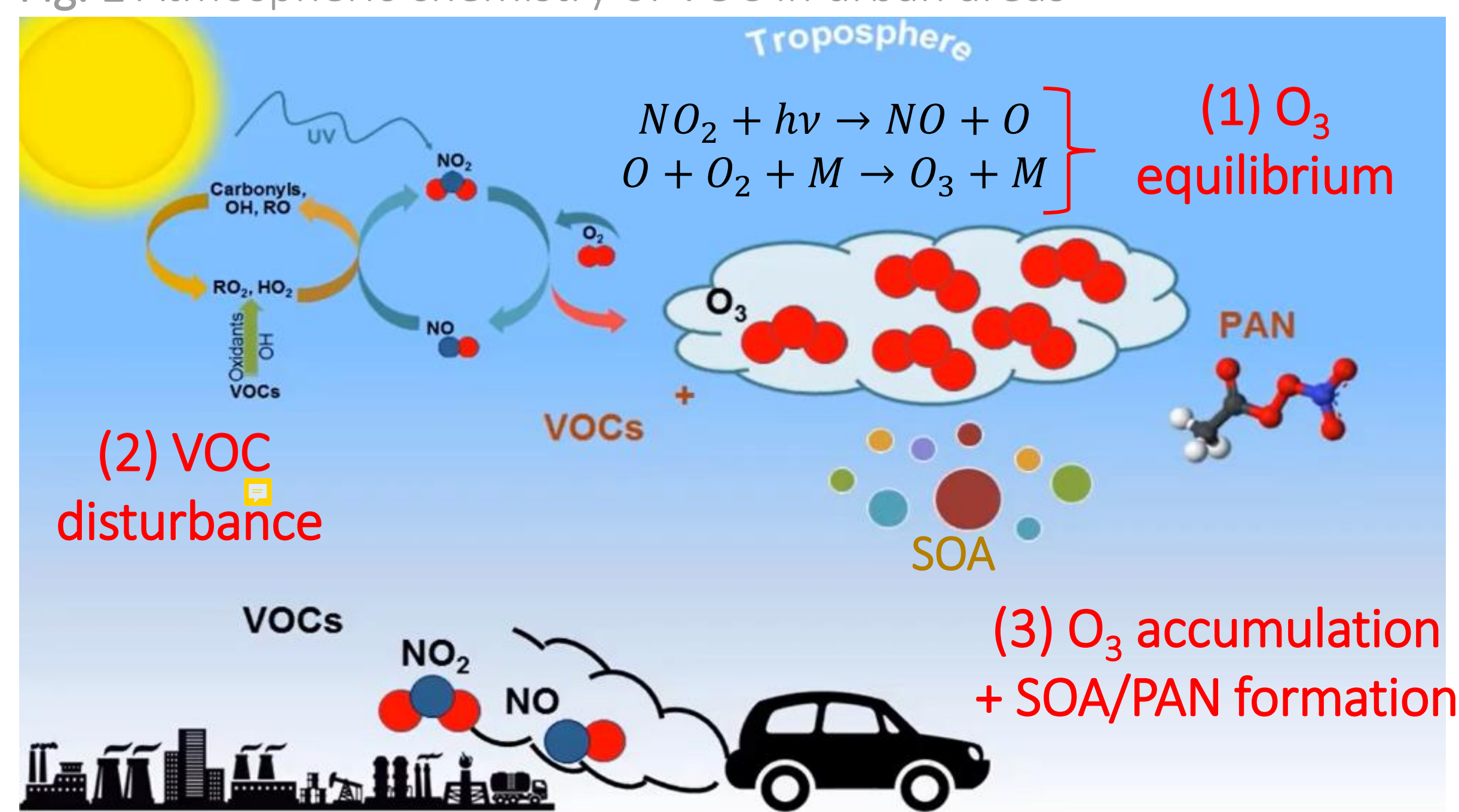
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Among the regulated sources of pollutants, shipping has a significant contribution to NO_x and SO_2 global emissions and causes an estimated mortality of 64 000 people each year around the globe^[1]. The regulations of maritime transport, Annex VI of MARPOL, was updated in 2020 lowering the sulfur content in marine fuel globally to maximum 0.5% in mass (from 3.5%). Specific Sulphur Emission Control Areas have been established where the emissions of sulphur are further restricted, such as the Channel between France and the U.K. However, other pollutants emitted by maritime transportation, such as VOCs or PM, are not regulated, although VOCs are of importance in the atmospheric chemistry processes, notably because of their role in harmful ozone and SOA formation in proximity of densely populated coastal zones. This raises the following questions: what are the VOCs emitted by ships under these new emission norms, what are their emission rates and their impact on air quality? Few studies considered the speciation of VOC, yet speciated data is crucial to provide reliable gas-phase atmospheric chemistry modelling. This study presents the analysis of a dataset obtained during a one-month intensive field campaign in the harbour of Dunkirk in the North of France, which is the third biggest French port. The site was located near ferry and cargo terminals and provides high time resolution measurements of VOCs, using a PTR-ToF-MS, and many other parameters (meteorology, particles, gases). Data analysis allowed the identification of 67 ship plumes on a two days period of favorable meteorological conditions, harbour office entries and tracers like SO_2 . The current goal is to present emission factors that represent the mass of pollutant emitted by the combustion of one kilogram of fuel in real condition with a diversity of ships, to better characterize shipping impact on pollutant levels in a harbour. Statistical methods show that we overestimate emission rates of VOCs compared to past measurements at the stack of a ferry, although our VOCs emission factors are inferior to those of SO_2 , CO and CH_4 which are consistent with the existing factors^[3,4].

Keywords : Volatile Organic Compounds, shipping, sources, emission factors

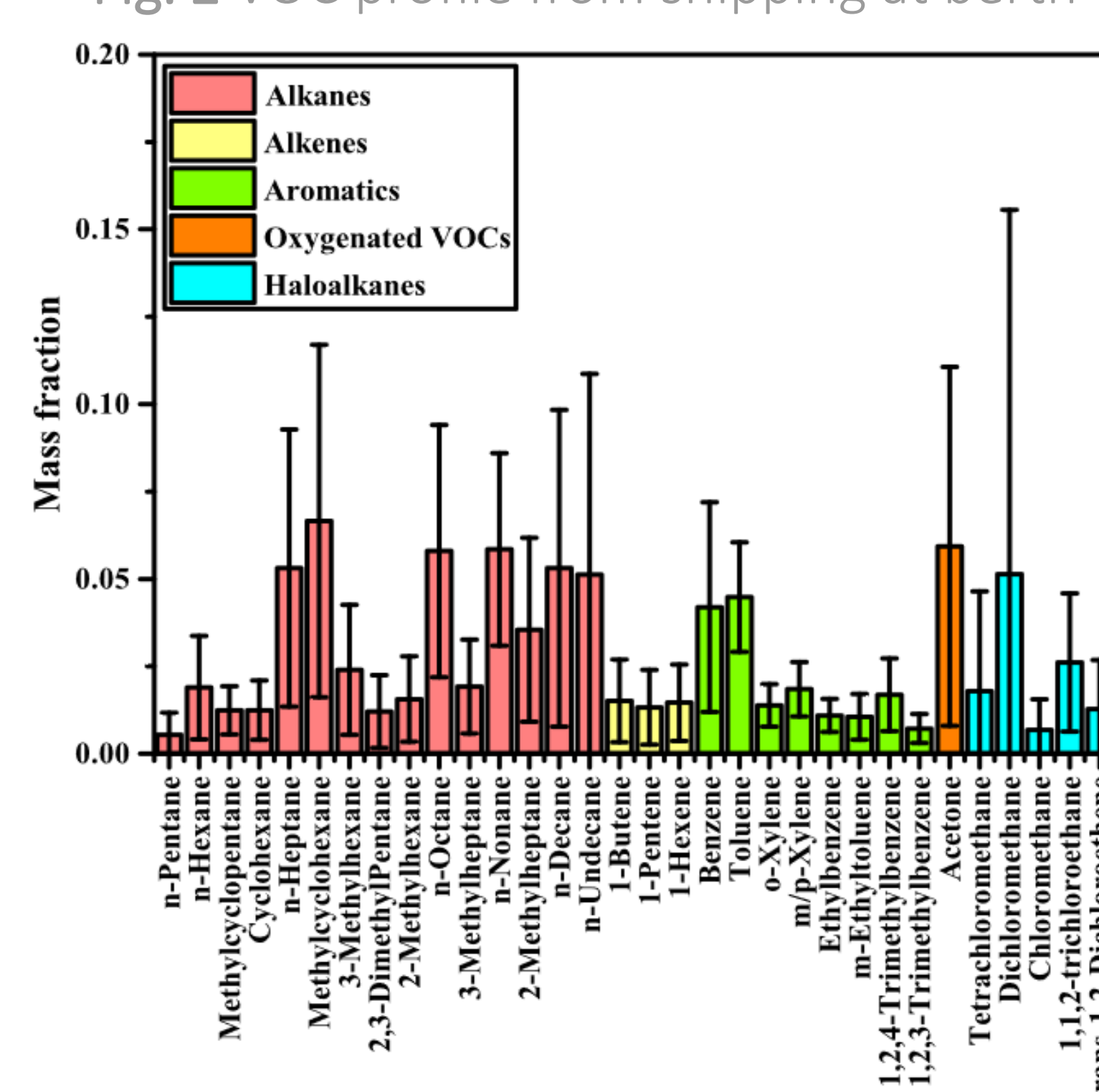
1. Scientific context

Fig. 1 Atmospheric chemistry of VOC in urban areas



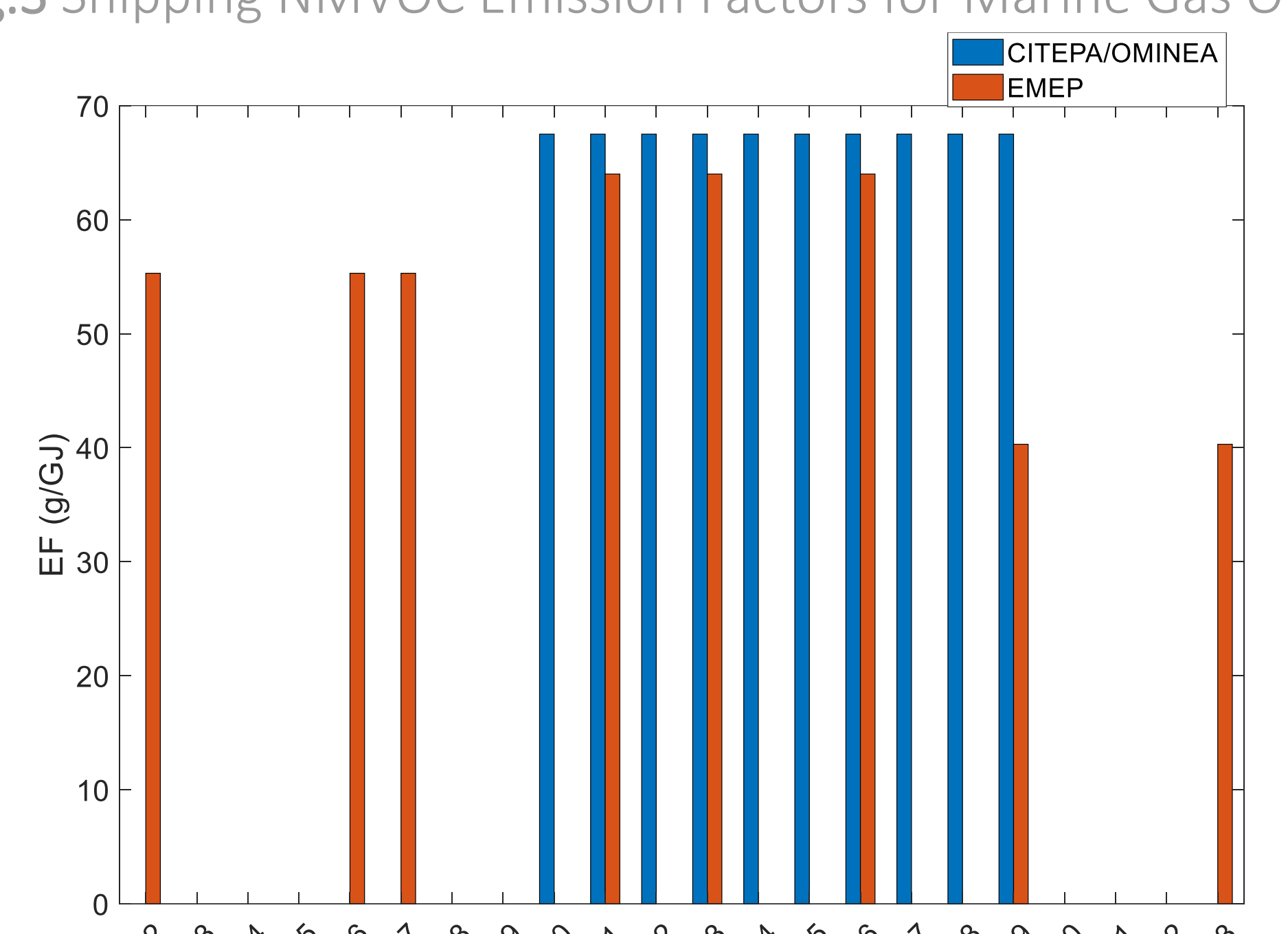
- VOC emission can lead to Photochemical Smog
- O_3 formation is dependant of VOC/ NO_x

Fig. 2 VOC profile from shipping at berth^[2]



- Various VOC emitted from the ships

Fig.3 Shipping NMVOC Emission Factors for Marine Gas Oil

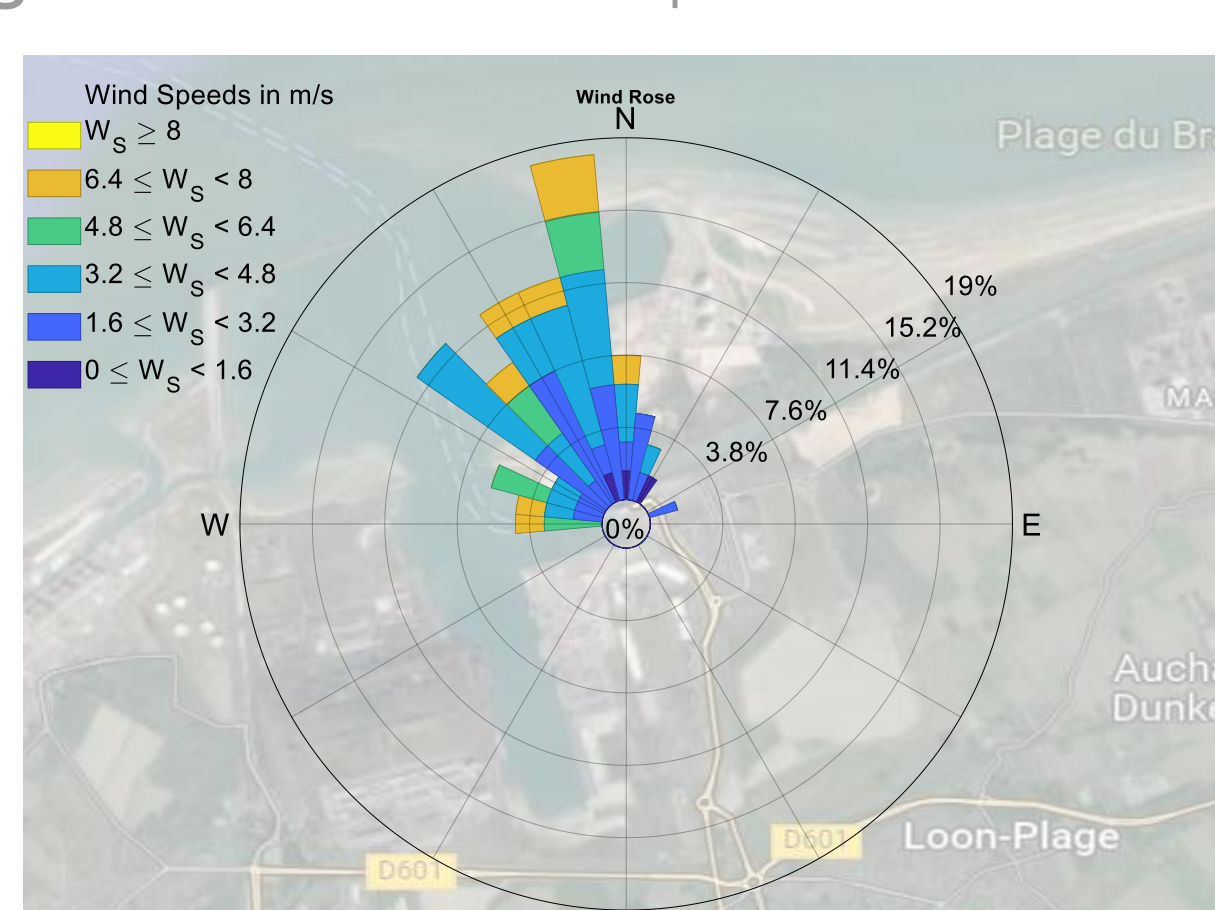


- Yet no speciation is used in emission factors for atmospheric modelling

What are the VOC emitted by the ships and their contribution in shipping emissions ?

4. Emission factors

Fig. 6 Wind rose of September 15th to 19th



- 67 peaks of ferry ships plumes were identified based on video recording, AMS correlation and SO_2 gradients

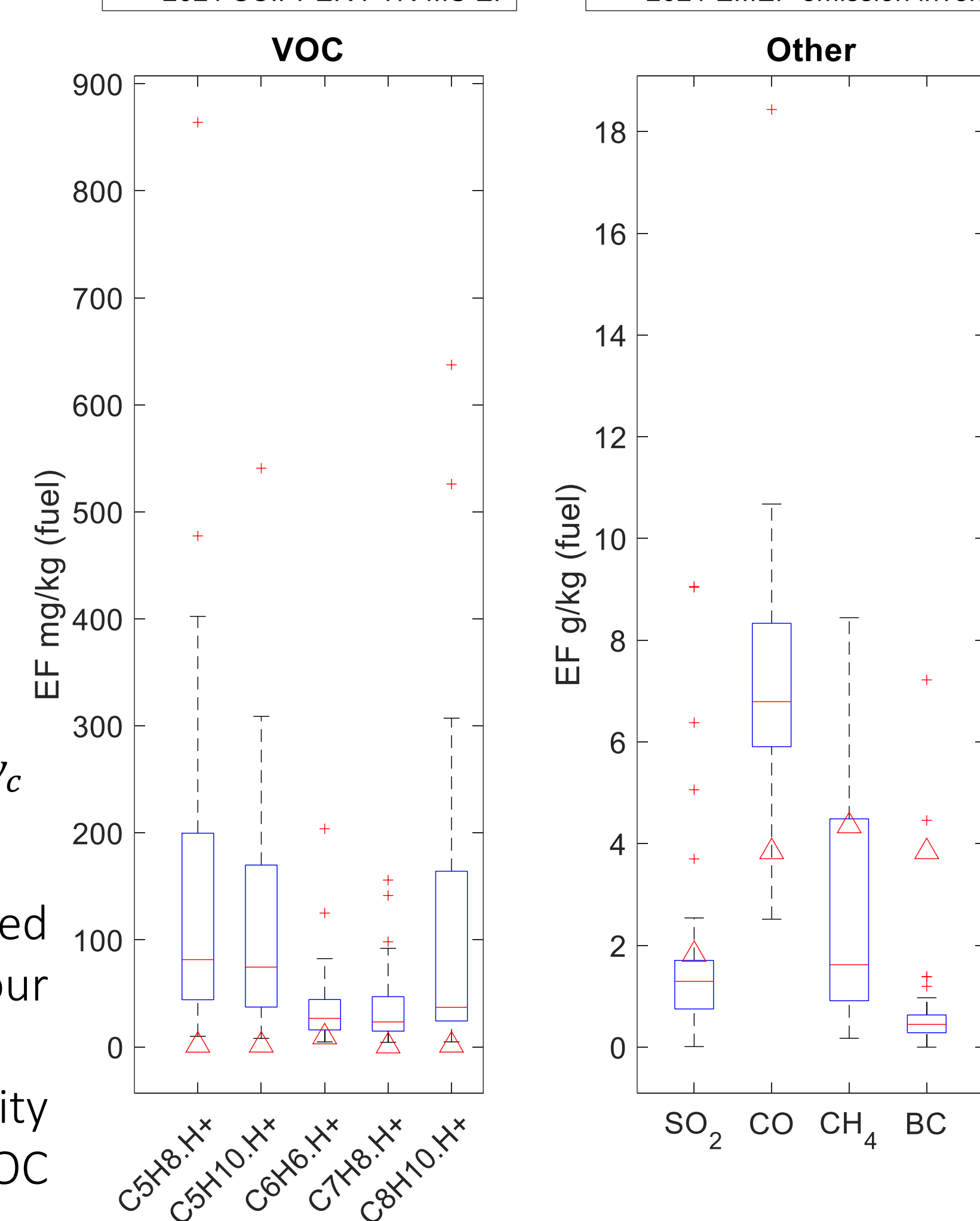
$$EF_i (\text{g} \cdot \text{kg}^{-1}) = \frac{\Delta x_i (\mu\text{g} \cdot \text{m}^3)}{\Delta \text{CO}_2 (\text{mg} \cdot \text{m}^3)} \cdot \frac{M_C}{M_{\text{CO}_2}} \cdot w_c$$

- Background concentration is defined as the 2nd percentile of a one-hour interval on both sides of the peak
- Good reproduction of low-reactivity gases EF but low consistency of VOC possibly

- Impact of distance and representativity

Fig. 7 Calculated emission factors

△ 2021 SCIPPER PTR-MS EF △ 2021 EMEP emission inventory



3. Field campaign

- Measurement site of September 2022 : Dunkirk harbour (northern France)

- PTR-MS for the measurements of $> 300 \text{ m/z}$ VOCs, completed with $\text{CO}/\text{CH}_4/\text{CO}_2$ monitor, AMS, auxiliary meteorological data and harbour office entries

Fig. 4 Measurement site

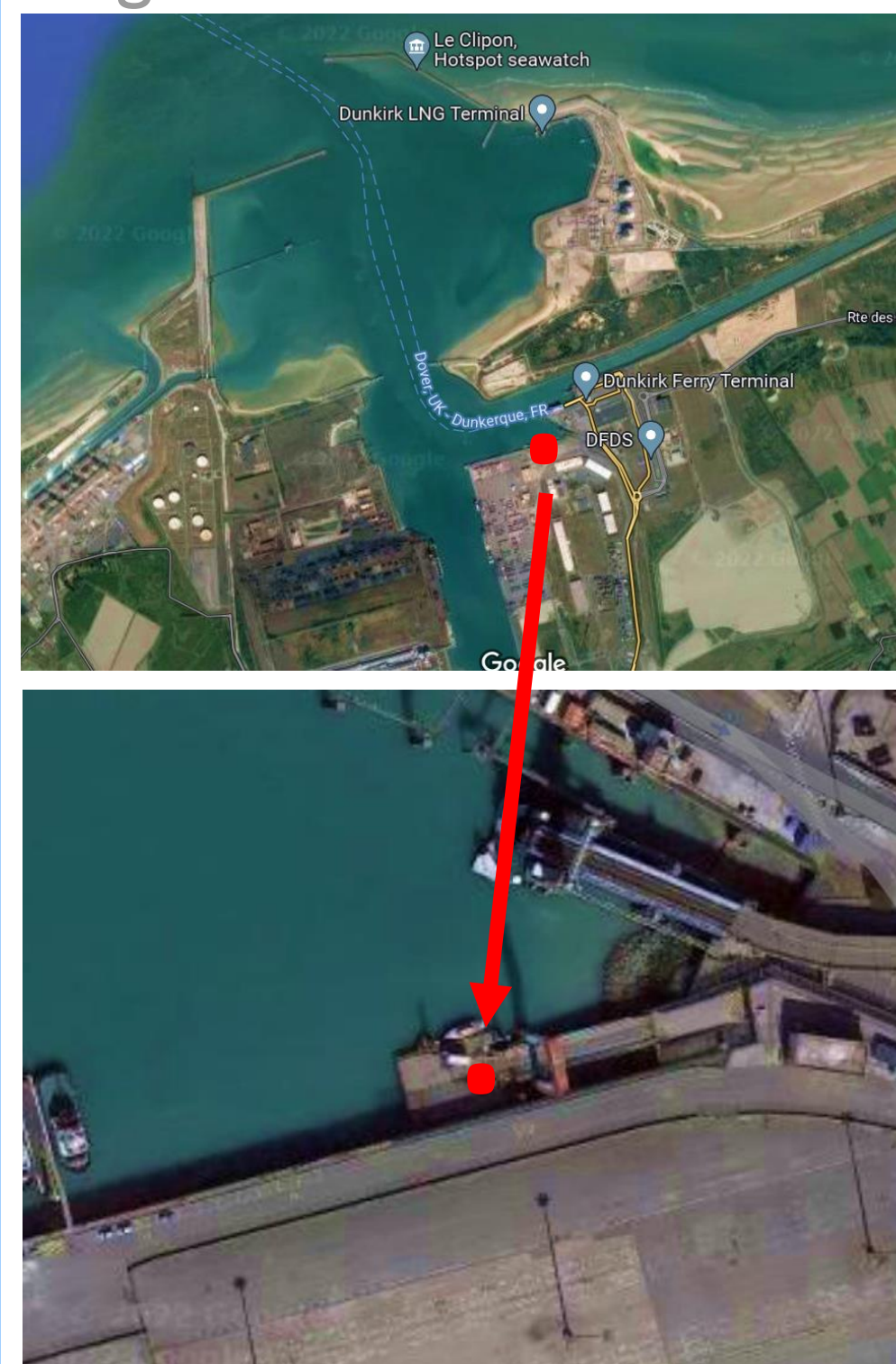
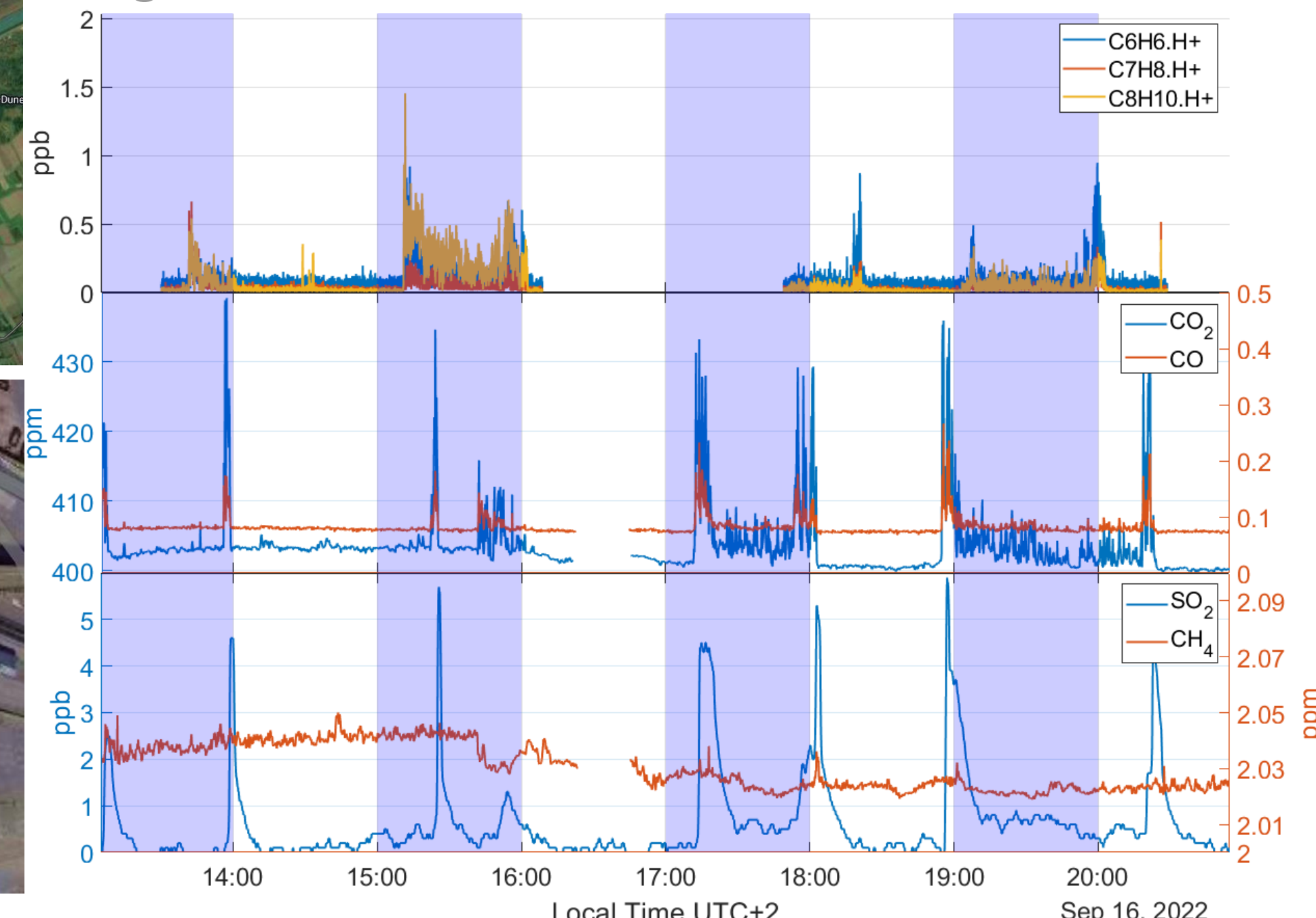


Fig. 5 Partial time series



- Good correlation of peaks with the presence of ship in the harbour
- Same behaviour from September 15th and 19th
- Period of reference to calculate emission factors of shipping in Dunkirk

5. Conclusion and perspectives

- Good consistency of EF of SO_2 , CO and CH_4 Emission Factors with EMEP emission inventory guidebook of 2021 taken from the SCIPPER Project
- Lower PTR-MS m/z emission factors compared to low-reactivity gases, but greater than previous on-board measurement at the stack
- Our dataset allows us to calculate emission factors in real condition focusing on the harbour, with a higher population and diversity of ships compared to previous exhaust emission measurements of one ship

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