



# Reliable VOC Monitoring in Industrial Coastal Areas: Uncertainty Quantification and Variability in the Berre Basin

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**Abstract.** Continuous measurements of 23 volatile organic compounds (VOCs) were deployed at three sites surrounding the lake of Berre industrial basin (southern France). This dataset was used to characterize VOC variability in a complex industrial environment and to establish a robust methodological framework for long-term monitoring. The sites, located near major Seveso-classified industrial platforms, exhibit distinct chemical signatures driven by contrasting source influences, mesoscale circulations, and topographic effects. The monitoring strategy relied on dual online GC-FID systems and was supported by an extensive quality assurance and quality control (QA/QC) program, including routine calibration, assessments of linearity, repeatability, blank correction, and environmental influences. A comprehensive uncertainty calculation scheme was developed by combining elements of the NF EN 14662-3 Benzene standard with the ACTRIS network's standard operating procedure (GAW report No.281, WMO, 2023) and implemented within the Incert'R R-based tool to enable automated uncertainty estimation for each VOC concentration. The resulting expanded uncertainties, calculated for a reference concentration of 5  $\mu\text{g m}^{-3}$ , ranged from 9 % to 25 % depending on the compound. Except for 1,2-dichloroethane (25 %), all VOCs exhibited uncertainties below 20 %, while benzene showed an uncertainty of 9 %, well below the 25 % limit required by the benzene standard. Overall, these uncertainty levels confirm the reliability of the dataset for interpreting concentration patterns across the three sites. Having established this, the analysis of VOC concentrations reveals pronounced spatial and temporal contrasts across the sites: Berre-l'Étang is strongly affected by land-sea breeze recirculation, leading to recurrent morning and evening peaks and exceptionally high values during industrial maintenance periods, while Lavéra shows frequent episodic enhancements dominated by chlorinated and light hydrocarbon compounds. Port-de-Bouc records lower and less structured concentrations, consistent with more intermittent plume impacts. These findings highlight the importance of combining high time-resolution measurements with harmonized QA/QC procedures and systematic uncertainty estimation to reliably detect high variability of VOC concentration in industrial regions. The resulting dataset provides a rigorous basis for subsequent source-apportionment analyses and for improving emission inventories and atmospheric modelling in one of Europe's most industrially impacted coastal areas.



## 1. Introduction

35 Volatile organic compounds (VOCs) play a crucial role as precursors in the formation of tropospheric ozone and secondary aerosols, making them key contributors to air quality degradation. Among these compounds, non-methane hydrocarbons (NMHCs) are released into the atmosphere from various anthropogenic sources – including vehicular traffic, domestic heating, solvent use, and industrial processes – as well as from natural biogenic emissions (Panopoulou et al., 2018; Thera et al., 2019; Wang et al., 2020). A subset of VOCs, particularly aromatic compounds, raises specific toxicological concerns due to their chronic health impacts and their relevance in air-quality regulation. Among these species, benzene is the only VOC with an established annual limit value in the European Union ( $5 \mu\text{g m}^{-3}$ ) due to its proven carcinogenicity (Group 1 carcinogen, IARC), mainly linked to hematological effects such as leukemia (Directive 2024/2881/EU, 2024; Khalade et al., 2010). In contrast, while not regulated as strictly, toluene, ethylbenzene, and xylenes are also classified as hazardous air pollutants and have been associated with neurotoxic and irritative effects under chronic exposure (Thetkathuek et al., 2015). Once released, NMHCs undergo photochemical reactions that generate secondary pollutants such as ozone and secondary organic aerosols (SOAs), significantly contributing to urban and industrial air pollution (Atkinson, 2000; Goldstein and Galbally, 2007). These pollutants pose serious threats to both health and climate stability (Lelieveld et al., 2015).

45 The relative importance of VOC sources has evolved significantly in recent years. As transport-related emissions have strongly decreased in many European cities due to stricter regulations, other sources – particularly solvent use and industrial activities – have become increasingly significant contributors to ozone formation (Li et al., 2024; McDonald et al., 2018). This shift has intensified regulatory focus on non-traffic VOC sources. Current European air quality legislation, including Directive 2024/2881/EU on ambient air quality, establishes target values for ozone mandates monitoring of precursor substances, including specific VOCs, in regions exceeding ozone thresholds (Directive 2024/2881/EU, 2024). Additionally, the Industrial Emissions Directive (Directive 2024/1785/EU, 2024) and the National Emission reduction Commitments Directive (Directive 2016/2284/EU, 2016) impose emission limits and control measures on industrial VOC sources.

55 Accurate and continuous VOC monitoring is therefore essential – not only for regulatory compliance but also to support health risk assessment and the design of effective emission reduction strategies, particularly in heavily industrialized areas where multiple and variable sources coexist (Derwent et al., 2007). While sectoral contributions to ozone formation have been well characterized in northwestern Europe, their applicability to other regions – such as Southern and Eastern Europe – remains uncertain due to differing environmental conditions (Ge et al., 2024; Kilian et al., 2024; Real et al., 2024). Beyond the transport and solvent use sectors, emissions from fossil fuel extraction and distribution represent the next most significant contributor to VOC-related ozone production (Xu et al., 2025).

60 The Fos-Berre region in the South of France is an industrial hotspot and hosts major metallurgical and petrochemical industries, spread over three large industrial complexes (Berre l'Étang, Martigues Lavéra, and Fos-sur-Mer), known for their high VOC emissions. This area features a particularly high industrial density featuring 56 high-risk industrial sites (SEVESO upper tier under the SEVESO III EU directive), making it the second-largest concentration of such sites in France. Notably, the



65 petrochemical plant in Lavéra produces 25 % of France's chlorine and 40 % of its vinyl chloride monomer (VCM) (Producer's data: *KEM ONE*)

The region's VOC dynamics are strongly influenced by specific orographic and meteorological conditions, particularly land-sea breeze regimes that advect relatively clean marine air during the nighttime while favoring inland pollutant advection and accumulation during the day. Under mistral conditions, the atmospheric boundary layer can exceed 1 000 m, while during thermally driven breezes, it typically remains between 300-600 m, significantly affecting pollutant dispersion and  
 70 accumulation (Riandet et al., 2023).

In response to these challenges, three monitoring stations operated by French regional network (AtmoSud) have been continuously monitoring 23 VOCs in the Berre-Fos area since January 2022. The stations are strategically located near industrial complexes and in residential areas, including one adjacent to a school. Site selection was guided by prior research, including the Scenarii study (<https://www.atmosud.org/etude/scenarii>), which, used spatially resolved emission inventories  
 75 coupled with atmospheric dispersion modelling to identify potential hotspots of carcinogenic, mutagenic, and reprotoxic (CMR) compounds such as 1,3-butadiene, 1,2-dichloroethane (1,2-DCE), benzene, and vinyl chloride monomer (VCM). Since the results were derived from modelled emission data rather than direct observations, in situ measurements were necessary to provide an observational basis for assessing ambient VOC levels and to better constrain the interpretation of exposure in a complex industrial environment.

80 The selection of an analytical method for VOC monitoring depends on the target compounds and objective. Proton Transfer Reaction Mass Spectrometry (PTR-MS) excels in real-time measurements with high time resolution (sub second), the separation of VOCs of equal  $m/z$  is not possible without chromatographic coupling. Gas Chromatography-Mass Spectrometry (GC-MS), though highly specific and a reference method, is complex, costly with time-consuming data processing. GC-MS methods offer high sensitivity and spatial coverage but lack temporal immediacy. On-line Gas Chromatography with Flame  
 85 Ionization Detection (GC-FID), provides a cost-effective, stable solution suitable for long-term monitoring, despite limitations in resolving coeluting compounds and a lower time resolution (30 min -hourly). To ensure reliability, challenges such as coelution, matrix effects, retention time drift, and species-specific calibration must be addressed through robust QA/QC frameworks and harmonized protocols. The only strictly regulated VOC, benzene, benefits from well-established European standards (NF EN 14662-3) ensuring strong metrological traceability, most other VOCs lack equivalent regulatory references,  
 90 highlighting the need for harmonized protocols addressing a broad range of compounds and concentration ranges.

This study proposes a methodological framework for VOC using GC-FID, selected for its operational stability, broad detection capabilities and suitability for long term monitoring in complex industrial environments. The framework was built on the European regulation for benzene measurements (NF EN 14662-3) and research-standard procedures (GAW report No.281, WMO, 2023) to establish high-quality, harmonized practices across the three monitoring sites. A key contribution is the  
 95 development and application of a dedicated module within the R-based Incert-R software tool—originally not designed for VOCs—that enables automated calculation of measurement uncertainty. This uncertainty quantification is further used to assess whether observed concentration contrasts between sites reflect genuine spatial gradients or fall within the analytical



noise of the measurement system. The technical challenges and solutions for the implementation of QA/QC procedures under real-world industrial monitoring conditions are discussed.

## 100 2. Material and Methods

### 2.1. Study area

The study area is located in the south of France, more precisely on the Mediterranean coast in the Provence-Alpes-Côte d'Azur region, around a brackish lake called the lake of Berre (l'Étang de Berre), home to major metallurgical and petrochemical industries, as shown on Fig. 1. The area includes three major industrial complexes (Fos-sur-Mer, Martigues Lavéra and Berre-  
105 l'Étang, Fig. 1(A-C)) known to be major VOC emitters, but also account for up to 50 % of regional industrial SO<sub>2</sub> emissions (AtmoSud, 2022). The zone has a complex local topography, marked by the presence of vast stretches of water, the Mediterranean Sea and the lake of Berre, next to abrupt reliefs and this can create local accumulation phenomena, favoring the stagnation of pollutants under certain conditions. In addition, the strong variability of wind directions and wind speed and meteorological conditions, result in unstable air pollution dynamics, requiring continuous monitoring to better understand and  
110 anticipate its environmental and health impacts. Continuous measurements of VOCs were started on the three sites described in detail below in December 2021 and continue until this day. Here, we will only discuss the development of the method and measurements for 2022 for Martigues-Lavéra and Berre-l'Étang, and for 2023 for Port de Bouc.



**Figure 1: Map of France (in upper right corner) and a zoom on the study zone around the lake of Berre with the exact locations of the three observation sites indicated by the green pins and letter with (A) Port-de-Bouc (PDBL), (B) Martigues-Lavéra (MLVR) and (C) Berre-l'Étang (BETG). The red shaded zones are the locations of industrial complexes (© Google Earth 2026).**

The Port de Bouc site (Fig.1, (A)) is unique because of its proximity to the industrial port of Fos-sur-Mer on the Mediterranean Sea, an area of heavy maritime traffic. The industrial complexes nearby include petrochemical facilities, fuel storage depots and large metallurgical installations located to the N-NW and all classified as Seveso upper-tier industrial sites (DREAL PACA : Base de données des installations classées, 2025). Port activity, with ship movements and the unloading of chemical and petroleum cargoes, generates additional emissions of fine particles, sulfur oxides ( $\text{SO}_x$ ) and VOC, as evidenced in a field campaign in 2011 at the Fos-sur-Mer site. Elevated levels of particles are consistent with observations reported in industrial and port areas, frequently accompanied by significant spikes in sulfur dioxide ( $\text{SO}_2$ ), suggesting the contribution of industrial combustion sources and maritime fuel emissions (Dron et al., 2017). Moreover, VOC such as benzene, toluene, and naphthalene showed abrupt increases during specific meteorological conditions like thermal breezes, independent of particulate or  $\text{SO}_2$  trends, indicating diverse and intermittent emission sources (Dron et al., 2017).

The second site, located in Lavéra, an industrial district within the municipality of Martigues, lies directly on the Mediterranean coast and just 4 to 5 km east of the main industrial platform of Fos-sur-Mer. Lavéra hosts one of the largest petrochemical complexes in southern Europe including a major producer of chlorochemicals, all classified as Seveso upper-tier industrial sites (DREAL PACA, 2021). These industries emit substantial amounts of VOCs,  $\text{NO}_x$ , and  $\text{SO}_2$ . VOCs such as benzene, toluene, and 1,3-butadiene are monitored near Lavéra, with benzene levels occasionally approaching or exceeding the annual target



value of  $5 \mu\text{g m}^{-3}$  set by European Directives. These pollutants are prioritized in regional air quality action plans due to their toxicity and chronic exposure risks for nearby populations (Legrand, 2018).

The Berre-l'Étang industrial complex, bordering the lake, is dominated by major oil refineries and petrochemical installations. Among them are major installations classified as Seveso upper-tier sites. Given the industrial density of the area and the proximity of populations, a dedicated air quality monitoring station was established in 2015, located approximately 3-4 km SW of the core industrial area to monitor the downwind dispersion of emissions. This station, part of the Scenarii project, identified persistently elevated 1,3-butadiene concentrations, relative to regional background levels, confirming this location as a hotspot for carcinogenic VOCs (AtmoSud, 2020).

In the same area, significant associations between background  $\text{SO}_2$  concentrations. ( $\sim 6 \mu\text{g m}^{-3}$ ) and increased lung-cancer incidence, and between particulate cadmium exposure ( $\sim 0.21\text{-}0.25 \mu\text{g m}^{-3}$ ) and insulin-metabolism disruption among the elderly were evidenced (Pérez et al., 2022).

Overall, annual benzene concentrations remained below the regulatory annual limit of  $5 \mu\text{g m}^{-3}$ . In the Fos–Berre area, annual mean concentrations were typically within the low  $\mu\text{g m}^{-3}$  range, approximately  $0.5\text{--}2.8 \mu\text{g m}^{-3}$  depending on the station over 2012–2022, with most values close to or below the annual quality objective of  $2 \mu\text{g m}^{-3}$  (AIRPARIF, 2020; Sekar et al., 2019). Nevertheless, passive sampling campaigns conducted near industrial facilities showed localized campaign-mean concentrations close to, and in one case slightly above, the  $5 \mu\text{g m}^{-3}$  annual reference value, highlighting the persistence of local benzene hotspots and the need for continued monitoring (AtmoSud, 2022).

These observations underline the complex mixture of pollutants affecting air quality in the Fos-Berre basin, especially in zones directly exposed to combined industrial and port activities and highlight the public-health relevance of VOCs (notably benzene and 1,3-butadiene) in the area in addition to other pollutants.

## 2.2. Meteorological conditions:

Among the three VOC monitoring stations, only the Berre-l'Étang site is equipped with an in-situ meteorological station located at the same site as the VOC analyzer. For the other two stations, meteorological characterization of the study area was based on data from the official French meteorological administration (Météo France) station in Marignane, situated between the two main industrial hubs of Berre and Lavéra. Additional data from the nearby AtmoSud station in Martigues – La Gâtasse were also used to complement the analysis. The dataset covers the entire year of 2022 and provides insight into wind regimes and atmospheric parameters that influence the dispersion and accumulation of VOCs in the study area.

The annual wind rose for Marignane shows a clear predominance of north to northwestern winds (mistral), with average speeds reaching up to  $8 \text{ m s}^{-1}$ . Secondary southeastern wind regimes are observed, associated with lower wind speeds from sea breezes and certain synoptic situations. The mistral, a regional strong and dry N-NW wind regime, promotes the rapid dispersion of pollutants towards the Mediterranean Sea, while southeasterly winds can transport industrial emissions inland. Data from the AtmoSud station in Berre-l'Étang and Martigues-La Gâtasse enable the observation of more specific local-scale phenomena. At Berre, the wind rose reveals a clear alternation between north to northwest (mistral and nocturnal land breeze) and south to



southeast (diurnal sea breeze) wind directions, a direct consequence of the proximity of the lake and sea, which promotes a regular diurnal-nocturnal circulation pattern. In contrast, the wind rose for Martigues-La Gâtasse shows a less structured and directional distribution, dominated by winds from the west to the northwest, with a secondary contribution from the east to the southeast. Compared with Berre, the large distribution at Martigues-La Gâtasse suggests a less pronounced influence of coastal topography and surrounding relief, resulting in locally circulating wind regime (Supplementary Information Fig. S1).

Daily mean temperatures range from approximately 9 °C in winter to over 28 °C in summer, with maximum values frequently exceeding 35°C. Relative humidity is predominantly between 60 % and 80 %, with pronounced minima during summer and peaks approaching 100 % during humid episodes. Precipitation, mainly concentrated in autumn and spring, can exceed 40 mm day<sup>-1</sup> during intense events (Supplementary Information Fig. S2).

### 2.3. Measurement strategy

In this study, only non-methane hydrocarbons (NMHCs) are considered. Unless otherwise specified, the term VOCs refers to NMHCs throughout this work. GC-FID offers a cost-effective solution with stable and linear response and a reasonable time resolution for long-term monitoring (30 mins to hourly). Therefore, GC-FID represents an attractive solution for continuous monitoring in industrial environments. However, its inability to resolve certain coeluting compounds and its variable detection efficiency depending on compound structure, limit its applicability for complex VOC mixtures (Bachelier et al., 2024). This technique is very sensitive (LoD in ppt range) in particular for non-oxygenated species. However, to ensure successful implementation in a long-term monitoring scheme, several technical challenges need to be addressed, including coelution issues, matrix effects, retention time drift, and the need for species-specific calibration. Indeed, coelution of initially separated VOCs can occur when the chromatographic separation deteriorates due to column aging, unstable operational conditions, or insufficient maintenance, compromising the identification and the quantification accuracy. Retention time drift caused by changes in humidity, temperature, pressure, or column contamination can complicate peak alignment and reduce reproducibility. Loss of sensitivity due to contamination of the trap, detector aging, or heavy compound accumulation, requires annual replacement of the thermal desorption trap and full system revalidation. These requirements underscore the necessity of robust quality assurance and quality control (QA/QC) frameworks and comprehensive approaches to measurement uncertainty estimations.

Each monitoring site is equipped with two on-line compact Gas Chromatography coupled to a Flame Ionization Detector (GC-FID) analyzers (airmoVOC, Chromatotec, Bordeaux, France). One instrument measures C<sub>2</sub>-C<sub>6</sub> VOCs, and the other targets C<sub>6</sub>-C<sub>20</sub> species, allowing the measurement of a total of 68 VOCs, among which only 23 were retained for the present study. These include alkanes, alkenes, and aromatics such as BTEX (Benzene, toluene, ethylbenzene and xylenes), as well as halogenated compounds including 1,2-DCE and vinyl chloride monomer (VCM). It needs to be noted that there is an unresolved co-elution for methyl-cyclopentane and 1,2-dichloromethane on our system, which will be reported as 1,2-DCE in the rest of the discussion. The concentrations of 1,2-DCE should thus be considered with this limitation in mind.



Ambient air is drawn through the system's sampling line by vacuum pumps and directed to the air handling and calibration unit (airmoCAL, Chromatotec, Bordeaux, France), which distributes the total sample flow, 50 mL min<sup>-1</sup> to the two GC-FID analyzers. No dilution of the sample flow is applied. For the C<sub>2</sub>-C<sub>6</sub> compounds, the samples pass through a Nafion® dryer before entering a Peltier-cooled three-phase trap (Carbotrap C, Carboback B, Carboxen) maintained at approximately -10 °C for preconcentration. Inorganic gases are not retained, while VOCs are trapped. After 10 minutes of sampling at 10 mL min<sup>-1</sup>, thermal desorption is performed at 220 °C. Desorbed compounds are separated on a Plot Al<sub>2</sub>O<sub>3</sub>/Na<sub>2</sub>SO<sub>4</sub> and detected by FID at 170 °C.

For C<sub>6</sub>-C<sub>20</sub> compounds, sampling last 30 minutes at a flow rate of 40 mL min<sup>-1</sup> is performed using a dual-phase trap maintained at 60 °C. The desorption is performed at 380 °C, separation on a MXT 30 CE column, and detection by FID at 200 °C. After each injection, hydrogen is used to backflush the trap in the reverse direction to prevent memory effects.

Compounds are identified by their retention time and quantified using a base sensitivity (BS) factor referenced to butane (C<sub>2</sub>-C<sub>6</sub>) and benzene (C<sub>6</sub>-C<sub>20</sub>) for the C<sub>2</sub>-C<sub>6</sub> and C<sub>6</sub>-C<sub>20</sub> analyzers respectively. Compound-specific response factors (RFs) are modified only for VOCs included in the certified gas mixture. For all other VOCs, the default response factors supplied by the manufacturer are used.

#### 2.4. Quality assurance and quality control (QA/QC)

Quality assurance (QA) and quality control (QC) are crucial steps in guaranteeing the correct operation of the instrument and ultimately the validity of the data obtained. Efficient QA/QC frameworks enhance the overall reliability, consistency, and reproducibility of results, ensuring data integrity throughout the entire analytical process. Such procedures enable the determination of the uncertainties associated with measurements of VOCs at measurement sites, with the aim of rigorously assessing the quality of the data produced. The QA/QC approach taken here englobes several parameters, namely the calibration of the instruments, blank controls and controls of the linearity, repeatability and drift of the measurements and the determination of the limit of detection.

A complete calibration approach was applied, including calibration of the BS of the instruments and the compound-specific RFs, as detailed in the supplementary information (Fig. S3).

The base sensitivity is calibrated annually, with the first calibration performed in June 2021, using a certified gas mixture containing 3 VOCs, n-hexane, n-butane and benzene (NPL, U.K.), each at 10 ppb. The reference compound for the C<sub>2</sub>-C<sub>6</sub> instrument is n-butane and, for the C<sub>6</sub>-C<sub>20</sub> instrument, benzene is the reference compound. The analyzer's sensitivity is calibrated using these two reference compounds, whose response factor is set to 1. No dilution is applied during this process. Six consecutive injections are performed, and the BS is determined by averaging the last three injections. The BS value is changed in the software if it differs by more than 100 ua ng<sup>-1</sup> from the previous value.

The RF are recalibrated monthly using appropriate standard gas mixtures (BTEX and 1,3-butadiene). All compounds are introduced at 10 ppb, except for m/p-xylene, which is introduced at 20 ppb, again without any dilution. Six injections are performed, and the RF is determined by averaging the last three injections.



To ensure the correct identification of the compounds, retention times RT are verified on a monthly basis using previously mentioned gas mixtures, a canister with 48 VOCs (full details in SI) and the permeation tubes present in the AirmoCal. Each weekly calibration sequence with the permeation tubes is systematically followed by a blank injection using ultrapure air generated by a catalytic system (airmoPURE, Chromatotec, Bordeaux, France). This blank is injected directly into the internal injection system – bypassing the sampling line – and therefore serves to verify the absence of contamination within the airmoPURE unit and the airmoCAL unit. Compound peak areas are corrected by subtracting the corresponding value obtained from the blank immediately preceding each measurement. Instrument stability is monitored by tracking the peak areas and retention times obtained over all previous tests. This enables early detection of any drift potentially caused by degradation or malfunction of key components such as the trap, column, or FID.

A control chart is implemented to ensure data quality over long time period. Therefore, every five days, a control gas mixture with a known concentration of BTEX + 1,3-butadiène (around 10 ppb) was injected into the analyzer, and the corresponding response was recorded. Data validation is submitted to two strict criteria: (i) if three successive points deviated by more than  $\pm 5\%$ , corrective maintenance was scheduled within 7 days; (ii) if a single point exceeded  $\pm 10\%$ , immediate maintenance was required.

## 2.5. Development of a new approach for uncertainty calculation

Once the QA/QC framework is established, the uncertainties associated with measurements of VOCs can be determined, to assess the quality of the data produced. In this study, the uncertainty estimation methodology for AirmoVOC GC-FID analyzers combines elements from the NF EN 14662-3 benzene standard (obtained from the MCERT certification) and the ACTRIS network's standard operating procedure (GAW report No.281, WMO, 2023). The NF EN 14662-3 framework incorporates uncertainty components associated with the environmental operating conditions of the instrument, including the surrounding temperature and water vapor of the sampled air, thereby accounting for potential variations in analyzer performance under real atmospheric conditions. It describes all the characteristics and performance criteria required for the regulatory measurement of benzene. In parallel, the ACTRIS SOP addresses uncertainty sources related to the analytical process itself, such as blank measurements, calibration procedures, ensuring traceability and intercomparability of results across observation networks. The integration of terms from both approaches provides a comprehensive representation of measurement uncertainty encompassing both environmental influences on instrument stability and analytical factors affecting analytical accuracy. Several parameters used in the uncertainty calculation are also monitored for data validation and will be discussed here.

**Repeatability of the measurements:** The relative standard deviation ( $\sigma_{rel}$ ) is determined once per year by analyzing the NPL cylinder (BTEX + 1,3-butadiene) or the control mixture at concentrations between 10 and 20 ppb. Using this gas mixture, six successive analyses are performed. The five last repeats are used to calculate the standard deviation and its ratio to the mean is calculated.



**Impact of sample filter and sampling line:** Annual tests are performed to evaluate both the sampling line and particle filter (a stainless-steel particle filter with a 2-micron filtration threshold). For the first test, six injections are carried out using the calibration line with the filter in place, followed by six injections without the filter, using a certified gas mixture; the deviation must remain below 3 % (NF EN 14662-3). For the sampling-line test, six injections are performed through the calibration line and six through the sampling line; acceptable losses must remain below 2 %, and the sampling lines are cleaned or replaced annually.

**Linearity of the measurements:** Linearity of measurements assesses how well the analytical response scales proportionally to the analyte concentration, which is essential for valid quantitative determination. In accordance with standard NF EN 14662-3, linearity is assessed at four points, including the blank and must respect a linearity residual of less than 5 % or 0.5  $\mu\text{g m}^{-3}$ . The frequency of this assessment depends on the maximum residual. If the residual is between 2 % and 5 %, the test is carried out every year, while if the residual is less than 2 %, the assessment is spaced out to three years.

In this study, the first linearity test was carried out in May 2022 on six VOCs listed in Table 1. As an example, for benzene — the only regulated VOC in Europe — six consecutive injections were performed at each concentration tested (4, 21, 38, and 0  $\mu\text{g m}^{-3}$ ). The average of the last five measurements in each series was used. Subsequently, the residual was calculated as the difference between the measured values and the theoretical values obtained from the linear regression. The results (Table 1) show that the maximum residual of the linearity varies between 1.9 % and -5 %. The highest linearity deviation at -5 % is obtained for m,p-xylene, and the lowest value for 1,3-butadiene at 1.9 %.

**Table 1: Linearity assessment for a selection of six VOCs at the Berre l'Étang station**

| Compound      | Maximum residual (%)* | Maximum residual ( $\mu\text{g m}^{-3}$ )* | Repeatability ( $\mu\text{g m}^{-3}$ ) |
|---------------|-----------------------|--------------------------------------------|----------------------------------------|
| 1,2-DCE       | 3.6%                  | 0.20                                       | 0.056                                  |
| Benzene       | 2.4%                  | 0.10                                       | 0.002                                  |
| Toluene       | 2.6%                  | 0.13                                       | 0.002                                  |
| m,p-xylene    | -5.0%                 | -0.59                                      | 0.007                                  |
| o-xylene      | 3.8%                  | 0.22                                       | 0.004                                  |
| 1,3-butadiene | 1.9%                  | 0.06                                       | 0.021                                  |

\*The maximum residual was obtained for the concentration of 4  $\mu\text{g m}^{-3}$  for each compound.

When the maximum linearity deviations are compared with the repeatability of one concentration, as described in the paragraph above, a clear distinction emerges between compounds. For toluene and m,p-xylene, the absolute linearity residuals (0.13 and -0.59  $\mu\text{g m}^{-3}$ , respectively) largely exceed their standard deviations (0.002 and 0.007  $\mu\text{g m}^{-3}$ ) by factors of approximately 65 and 84, respectively, indicating that the observed deviations cannot be attributed to random analytical noise alone. This large linearity deviation is consistent with a systematic error of the calibration function rather than simple scatter around the regression line. Several physicochemical mechanisms may account for such error : (i) partial breakthrough of the pre-



concentration trap at higher loadings, leading to incomplete analyte retention and a progressive underestimation of the response at elevated concentrations; (ii) non-linear thermal desorption kinetics, whereby heavier aromatic compounds such as toluene and xylenes may desorb incompletely or unevenly across the concentration range and lead to negative or positive deviations; and (iii) incipient saturation of the detector at the upper end of the working range. These observations underscore the importance of examining both the magnitude and the sign of linearity residuals, as a monotonic pattern with concentration – as observed for toluene and m,p-xylene – constitutes stronger evidence of a structural analytical limitation than residuals of comparable magnitude to repeatability.

#### Determination of the detection Limit (LoD):

To determine the LoD, we applied the method used in the ACTRIS approach (GAW report No.281, WMO, 2023), consisting in carrying out 3 successive measurements of low concentration gas mixtures, then calculating the standard deviation of the 3 measurements. This standard deviation is then multiplied by the student's t-test ( $t_{1-\alpha}$ ) corresponding to a probability of 5 %. For 3 repetitions,  $t_{1-\alpha} = 2.92$ . In this study, the FID was considered to be linear, a canister containing the 23 VOCs at concentrations between 500 ppt and 1 ppb was used to perform this test.

Further parameters intervening in the uncertainty determination are specific for the two different approaches used here. The benzene standard (NF EN 14662-3) defines all the elements for measuring benzene in ambient air; part 3 (NF EN 14662-3 12-2015) focuses on automatic measurement of this pollutant. The benzene standard assesses uncertainties related to sample gas pressure, ambient temperature of the lab, electrical voltage supplied to the analyzer, analyzer memory effect, absolute humidity of the sampled air, drift and linearity of the analyzer, all of which seem relevant to assess in the context of this study.

The ACTRIS approach considers all compounds measured by the analytical chain in the calculation of uncertainties, unlike the benzene standard, which only determines uncertainties for benzene specifically. The ACTRIS approach includes uncertainties linked to blank and integration errors, which are not present in the benzene standard approach.

Equation (2) shows the resulting terms for the calculation of uncertainties, based on a combination of both approaches, as used in this work. A detailed description can be found in both approaches used (GAW report No.281, WMO, 2023 and (Ambient air quality - Standard method for the measurement of benzene concentrations - Part 3 : automated pumped sampling with in situ gas chromatography, 2026) and (MCERT, 2022).

$$U(c) = 2 \times u(c) \quad (1)$$

$$u^2(c) = u_{prec}^2(c) + u_{cal}^2(c) + u_{int}^2(c) + u_{blank}^2(c) + u_{gp}^2(c) + u_{st}^2(c) + u_v^2(c) + u_{H2O}^2(c) + u_m^2(c) + u_{d,t}^2(c) + u_l^2(c) + u_{lp}^2(c) + u_{fp}^2(c) \quad (2)$$

With :

- $U(c)(\mu\text{g m}^{-3})$ : Absolute expanded uncertainty ( $k=2$ )
- $u(c)(\mu\text{g m}^{-3})$ : Standard uncertainty of the compound
- $u_{prec}(\mu\text{g m}^{-3})$ : Standard uncertainty of the precision
- $u_{cal}(\mu\text{g m}^{-3})$ : Standard uncertainty of calibration
- $u_{int}(\mu\text{g m}^{-3})$ : Standard uncertainty due to the peak integration



- $u_{blank}$  ( $\mu\text{g m}^{-3}$ ): Standard uncertainty of the blank
- $u_{gp}$  ( $\mu\text{g m}^{-3}$ ): Standard uncertainty due to variations in the pressure of the sampled gas
- $u_{st}$  ( $\mu\text{g m}^{-3}$ ): Standard uncertainty due to variations in surrounding temperature of the lab
- $u_v$  ( $\mu\text{g m}^{-3}$ ): Standard uncertainty due to variations in electrical voltage of the lab
- $u_{H_2O}$  ( $\mu\text{g m}^{-3}$ ): Standard uncertainty due to the presence of water vapor in the sampled air
- $u_m$  ( $\mu\text{g m}^{-3}$ ): Standard uncertainty due to the memory effect
- $u_{d,l}$  ( $\mu\text{g m}^{-3}$ ): Standard uncertainty due to long-term drift
- $u_l(c)$  ( $\mu\text{g m}^{-3}$ ): Standard uncertainty of linearity
- $u_{lp}(c)$  ( $\mu\text{g m}^{-3}$ ): Standard uncertainty due to the sampling line
- $u_{fp}(c)$  ( $\mu\text{g m}^{-3}$ ): Standard uncertainty due to the impact of the particle filter

Table 2 reports the detection limits, maximum concentrations, and mean concentrations with associated uncertainties for the VOCs monitored at Berre-l'Étang and Martigues-Lavéra in 2022, and at Port-de-Bouc in 2023. The uncertainties were calculated over the monitoring period considered at each station. Overall, the results show substantial compound-to-compound variability in absolute uncertainty, particularly at the Berre-l'Étang station. Ethylene exhibits by far the highest mean uncertainty for the average concentration obtained for the whole period, with  $5.9 \pm 4.5 \mu\text{g m}^{-3}$ , leading to a high relative uncertainty (76 %) on its average concentration. Propene, cyclohexane and 1,2-DCE also show rather elevated mean uncertainties around  $1 \mu\text{g m}^{-3}$  ( $1.2 \mu\text{g m}^{-3}$ ,  $1.0 \mu\text{g m}^{-3}$  and  $0.8 \mu\text{g m}^{-3}$  resp.). This leads to a high relative uncertainty for the mean concentration only in the case of propene (92 %). Despite this variability, most uncertainties are well below  $1.0 \mu\text{g m}^{-3}$  ( $\leq 0.5 \mu\text{g m}^{-3}$  for 16 VOCs)

The elevated uncertainties observed for ethylene and propene can be attributed to specific instrumental issues. In particular, baseline values were occasionally abnormally high following monthly maintenance operations on one of the VOC analyzers. To better estimate the blank contribution subtracted from ambient measurements, the baseline was therefore interpolated. As detailed in the Supplementary Information (Fig. S4), this correction approach treats the error associated with the estimated blank as a conservative upper-bound uncertainty. In these cases, the uncertainty associated with blank subtraction becomes a major additional term in the overall uncertainty budget.

In contrast, compounds such as benzene, acetylene and vinyl chloride monomer show lower mean uncertainties at Berre-l'Étang, generally below  $0.5 \mu\text{g m}^{-3}$  for mean concentrations of  $1.9 \mu\text{g m}^{-3}$  for benzene and  $1.7 \mu\text{g m}^{-3}$  for both acetylene and vinyl chloride monomer, indicating more stable measurements under the same operating conditions. Benzene is of particular interest because it is the only regulated VOC among the compounds listed in this table, with an annual limit value defined for ambient air in European air-quality legislation.

At Martigues-Lavéra, mean concentrations for quantified compounds range from  $0.3$  to  $8.2 \mu\text{g m}^{-3}$ , while mean uncertainties range from  $0.04$  to  $1.5 \mu\text{g m}^{-3}$ . The highest uncertainty is observed for 1,2-DCE, followed by isopentane and n-pentane, for which the relatively high mean concentrations partly explain the larger absolute uncertainties. At Port-de-Bouc, mean concentrations range from  $0.1$  to  $3.4 \mu\text{g m}^{-3}$ , with mean uncertainties ranging from  $0.1$  to  $1.9 \mu\text{g m}^{-3}$ . The unusually high uncertainty associated with 1-butene, despite its low mean concentration, suggests that the uncertainty budget is mainly driven by blank correction.



Overall, these results highlight the importance of determining specific uncertainties for each compound as well as each instrument. They also demonstrate the need for targeted corrections for compounds that are particularly sensitive to instrumental baseline fluctuations or blank contamination.

**Table 2: Overview of the detection limits, maximum concentrations, and mean concentrations with associated uncertainties for VOCs measured at the three measurement sites for 2022 (Berre-l'Étang, Martigues-Lavéra) and first trimester of 2023 (Port-de-Bouc)**

| VOC            | Berre-l'Étang 2022 (n=7152) |                      |                       | Martigues-Lavéra 2022 (n=7879) |                      |                       | Port-de-Bouc 2023 (n=3911) |                      |                      |
|----------------|-----------------------------|----------------------|-----------------------|--------------------------------|----------------------|-----------------------|----------------------------|----------------------|----------------------|
|                | DL                          | Max±Uncertain        | Mean±Uncertain        | DL                             | Max±Uncertain        | Mean±Uncertain        | DL                         | Max±Uncertain        | Mean±Uncertain       |
|                | µg m <sup>-3</sup>          | y µg m <sup>-3</sup> | ty µg m <sup>-3</sup> | µg m <sup>-3</sup>             | y µg m <sup>-3</sup> | ty µg m <sup>-3</sup> | µg m <sup>-3</sup>         | y µg m <sup>-3</sup> | y µg m <sup>-3</sup> |
| ethane         | 0.1                         | 100±15               | 2.6±0.6               | 0.07                           | ND                   | ND                    | 0.12                       | ND                   | ND                   |
| ethylene       | 0.12                        | 1600±200             | 5.9±4.5               | 0.13                           | 215±30               | 2.2±0.4               | 0.12                       | 104±14               | 1.8±0.3              |
| propane        | 0.18                        | 414±60               | 3.8±0.7               | 0.19                           | 377±52               | 2.4±0.4               | 0.17                       | ND                   | ND                   |
| propene        | 0.15                        | 75±11                | 1.3±1.2               | 0.14                           | 199±27               | 1±0.2                 | 0.17                       | ND                   | ND                   |
| isobutane      | 0.26                        | 70±10                | 1.6±0.3               | 0.24                           | 89±12                | 1.6±0.2               | 0.12                       | ND                   | ND                   |
| n-butane       | 0.24                        | 153±15               | 3.3±0.4               | 0.23                           | 120±10               | 3.8±0.4               | 0.21                       | 91±12                | 3±0.4                |
| acetylene      | 0.11                        | 246±36               | 1.7±0.3               | 0.11                           | ND                   | ND                    | 0.11                       | 26±4                 | 0.4±0.1              |
| trans-2-butene | 0.27                        | 87±13                | 0.4±0.2               | 0.24                           | 78±10                | 0.5±0.1               | 0.21                       | 45±6                 | 0.6±0.1              |
| 1-butene       | 0.19                        | 38±6                 | 0.5±0.2               | 0.21                           | 95±10                | 0.5±0.3               | 0.19                       | 16±3                 | 0.3±1.9              |
| VCM            | 0.27                        | 570±80               | 1.7±0.3               | 0.26                           | 1440±215             | 2.6±0.6               | 0.11                       | 90±13                | 0.6±0.1              |
| isopentane     | 0.3                         | 69±10                | 2.6±0.5               | 0.28                           | 710±97               | 8.2±1                 | 0.25                       | 485±65               | 3.4±0.5              |
| n-pentane      | 0.27                        | 360±52               | 2.1±0.4               | 0.25                           | 165±23               | 4.8±0.7               | 0.08                       | 130±15               | 1.6±0.2              |
| 1,3-butadiene  | 0.19                        | 152±17               | 2.7±0.3               | 0.07                           | 60±6                 | 0.4±0.1               | 0.07                       | 50±5                 | 0.5±0.4              |
| cis-2-pentene  | 0.33                        | 85±13                | 0.4±0.2               | 0.34                           | 46±6                 | 0.3±0.2               | 0.13                       | 30±4                 | 0.1±0.1              |
| 2-methylpenta  | 0.31                        | 44±8                 | 0.5±0.2               | 0.23                           | 200±35               | 0.9±0.2               | 0.39                       | 150±21               | 0.7±0.2              |
| ne             |                             |                      |                       |                                |                      |                       |                            |                      |                      |
| 1,2-DCE        | 0.41                        | 311±77               | 3.1±0.8               | 0.41                           | 235±55               | 6.1±1.5               | 0.41                       | 78±20                | 1.6±0.5              |
| benzene        | 0.07                        | 95±7                 | 1.9±0.2               | 0.18                           | 119±9                | 1.2±0.1               | 0.05                       | 145±10               | 0.6±0.1              |
| cyclohexane    | 0.06                        | 218±29               | 7.3±1                 | 0.17                           | 62±8                 | 0.6±0.1               | 0.07                       | 24±3                 | 0.3±0.2              |
| toluene        | 0.41                        | 210±20               | 3.8±0.5               | 0.3                            | 29±3                 | 1.3±0.2               | 0.13                       | 59±6                 | 1.2±0.1              |
| ethylbenzene   | 0.35                        | 450±40               | 2.1±0.2               | 0.02                           | 9±1                  | 0.4±0.04              | 0.14                       | 12±1                 | 0.3±0.1              |
| m,p-xylene     | 0.39                        | 1300±150             | 5.7±0.7               | 0.29                           | 17±2                 | 1.1±0.2               | 0.08                       | 50±6                 | 1±0.1                |
| styrene        | 0.73                        | 44±6                 | 0.7±0.3               | 0.73                           | 23±3                 | 0.5±0.3               | 0.73                       | 21±3                 | 0.4±0.3              |
| o-xylene       | 0.07                        | 588±86               | 2.1±0.4               | 0.13                           | 17±3                 | 0.5±0.1               | 0.11                       | 29±4                 | 0.4±0.1              |

ND: not detected; DL: detection limit

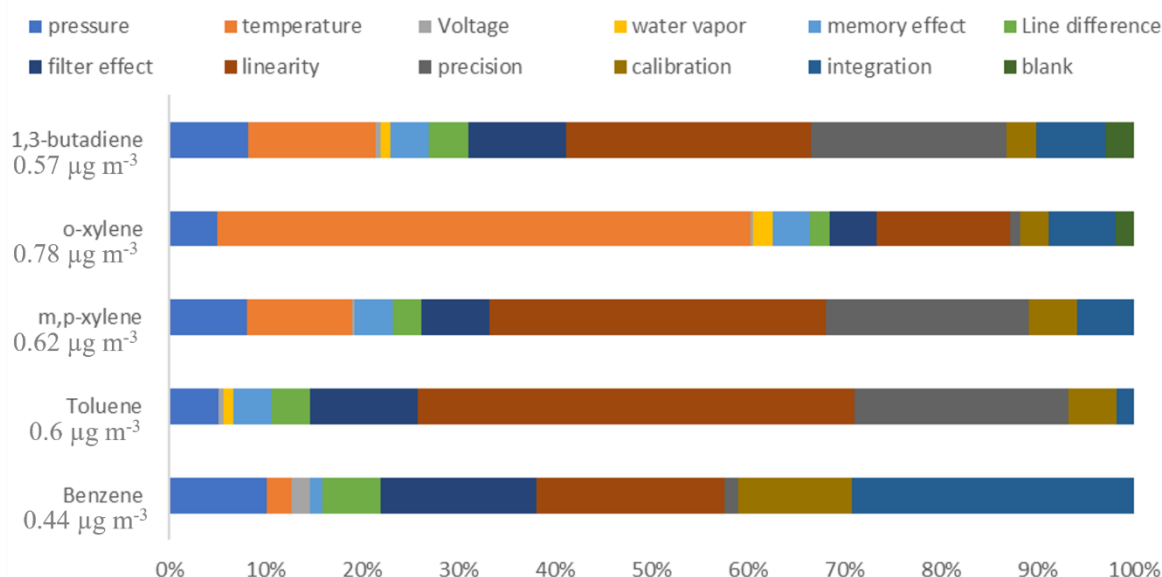
Figure 2 illustrates the contribution of the different uncertainty terms to the overall uncertainty for 5 VOCs. These 5 compounds were all included in the same certified gas mixture but exhibited contrasted contributions of the different uncertainty



components, making them relevant examples to illustrate the variability of the uncertainty composition among VOCs. For instance, the contribution of linearity ranges from 9 % to 37 % depending on the compound. This variability evidence that the linearity uncertainty proved to be substantial for some VOCs, despite often considered as negligible in GC-FID applications.

365 The influence on the sampling setup, notably the sampling line and particle filter, was also evaluated. Often perceived as technical details, such factors play a decisive role in measurement quality and must be strictly controlled to limit their impact. In this study, the uncertainty contribution to the total uncertainty from the sampling line remained below 6 %, while that associated with the use of a particle filter ranged between 7 % and 16 %.

External parameters, such as voltage delivered, and of the environmental conditions of the analyzer, including temperature  
370 ( $T^{\circ}\text{C}$ ), pressure (P), and absolute humidity, were also investigated. Figure 2 clearly shows that temperature-related uncertainty presents a major component of the total uncertainty, reaching its highest value for o-xylene at 56 %. This elevated contribution is directly linked to the temperature sensitivity coefficient applied for o-xylene, which was taken from the MCERT certification report for the Chromatotec GC FID analyzer. Across the two instrument units tested in that report, the coefficient for o-xylene at the calibration value ranges from 0.24 %  $\text{K}^{-1}$  (series 1) to 0.42 %  $\text{K}^{-1}$  (series 2), representing a factor of approximately 1.75  
375 between the two units – the largest inter-instrument variability observed within the compound set. For the remaining VOCs, the coefficients at the calibration value ranged from 0.00 to 0.18 %  $\text{K}^{-1}$  across both series, remaining substantially lower than those observed for o-xylene. This variability suggests that the coefficient itself carries a degree of uncertainty, and consequently, the 56 % temperature-related uncertainty contribution for o-xylene should be interpreted with caution. Pressure-related uncertainty also proved significant in some cases, such as 10 % for benzene. These findings emphasize the need for  
380 continuous monitoring of such parameters to minimize total measurement uncertainty. Overall, the uncertainty analysis performed for these compounds allowed for the identification of specific contributions from each parameter to the total uncertainty budget. The results underline that, beyond calibration, maintaining tight control over environmental conditions and the technical specification of the instrumentation is essential to ensure measurement reliability and accuracy.



**Figure 2: Relative contributions of different errors to the expanded uncertainty for five VOCs measured at a concentration of 5 µg m<sup>-3</sup> at the Berre-l'Étang station. The expanded uncertainty value (µg m<sup>-3</sup>) for each compound is indicated on the left side of the corresponding bar.**

This uncertainty calculation has been automated to allow an online determination of the uncertainties based on an R based tool, Incert'R. Incert'R was developed by three French regional air quality monitoring networks. Its primary goal is to enable the calculation of measurement uncertainties at various possible aggregation levels (e.g., quarter-hour, hour, day, month – rolling average) for automatic measurements of gases and particles within the framework of air quality monitoring. As part of this work, a new module dedicated to VOCs has been added. This extension allows for the real-time storage of VOC concentration data from multiple stations, with an associated uncertainty value for each concentration.

The tool operates by first inserting all uncertainty-related terms, outlined in Section 2.5, into Structured Query Language (SQL) tables. Once the database is populated using Incert'R and SQL table, it can be processed using the Incert'R package, which includes the complete set of uncertainty calculation equations in R. Then the VOC database can be connected to generate CSV output files containing time-based VOC concentration data along with their corresponding uncertainties. All files necessary for installing and running the tool are available at the following website: <http://sourceforge.net/projects/incetr/>

### 3. Results and discussions:

#### 3.1. Overview of VOC concentrations

To further explore the chemical signature of each site, we compare the maximum and mean concentrations for all quantified VOCs at the three stations as shown in Table 2. The results presented in this section are based on hourly data covering the full year 2022 for Berre-l'Étang and Martigues-Lavéra. For Port-de-Bouc, however, only the period from 1 January to 30 June



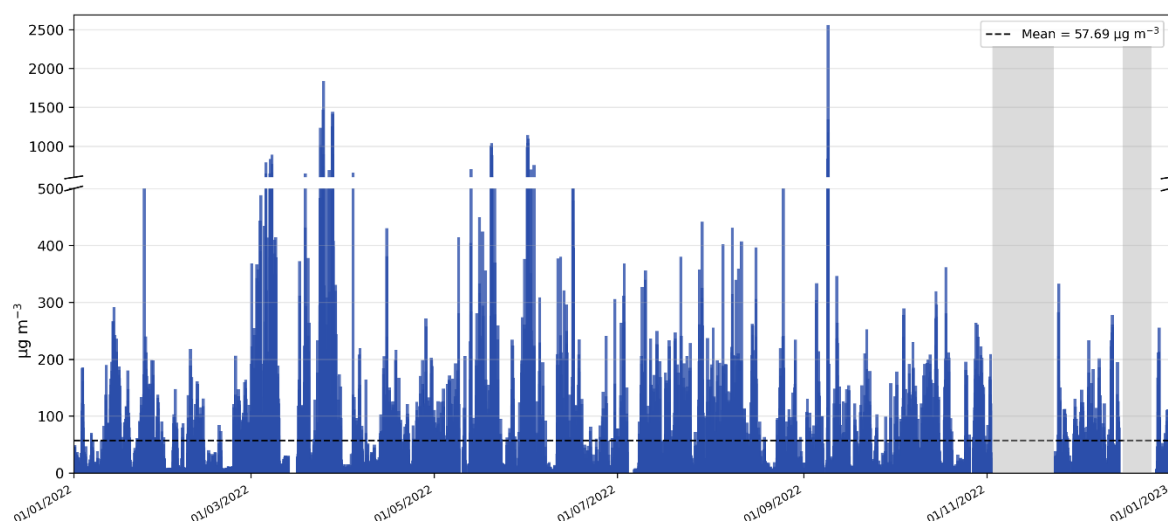
2023 was considered, as the 2022 dataset cannot be exploited because of analyzer-related problems. Where the minimum value was below the detection limit, the value was replaced by DL/2.

405 At Berre-l'Étang, several VOCs reached high maximum concentrations, especially reactive olefins and chlorinated compounds, confirming the site's strong and recurrent exposure to nearby industrial sources. Ethylene reached an extreme value of  $1\,600\ \mu\text{g m}^{-3}$ , a peak recorded during the major shutdown of the Berre industrial platform (01 March-30 June), when maintenance operations generated substantial and atypical releases of VOCs. Outside this shutdown period, ethylene levels generally remained within  $50\ \mu\text{g m}^{-3}$  and  $100\ \mu\text{g m}^{-3}$ , highlighting the exceptional character of these events. Other VOCs also

410 exhibited unusually high hourly peaks during this industrial maintenance phase, including aromatic species such as m,p-xylene ( $1\,300\ \mu\text{g m}^{-3}$ ) and toluene ( $210\ \mu\text{g m}^{-3}$ ), as well as lighter hydrocarbons such as n-butane ( $153\ \mu\text{g m}^{-3}$ ), indicating a broad and mixed emissions signature associated with purging and restart operations. Chlorinated compounds followed the same patterns, with vinyl chloride monomer (VCM) and 1,2-DCE peaked at  $570\ \mu\text{g m}^{-3}$  and  $311\ \mu\text{g m}^{-3}$ , respectively. However, several species reached their highest hourly maxima outside the maintenance period, including o-xylene ( $588\ \mu\text{g m}^{-3}$ ),

415 ethylbenzene ( $450\ \mu\text{g m}^{-3}$ ) and propane ( $414\ \mu\text{g m}^{-3}$ ), confirming that intense pollution episodes also occur during routine operations. These values are consistent with short-term industrial releases transported toward the station under the dominant N and NNE winds, which represent the prevailing circulation pattern throughout the year at this site. Figure 3 illustrates this pattern directly, presenting the full-year 2022 time series of total VOC concentrations at Berre-l'Étang. The concentrations remain close to the annual mean (dashed line) most of the time, punctuated by short but sharp excursions; most prominently

420 during the March-June maintenance shutdown; that visually confirms the episodic, wind-driven nature of the exposure described above. The broad variability, reflected in the contrast between minimum and maximum hourly values, supports the idea of episodic but intense exposures occurring whenever wind direction and atmospheric stability favor plume advection from the industrial area.



**Figure 3: Time series of the total concentration of 23 VOCs measured at Berre-l'Étang site from 1 January to 31 December 2022. The dashed line represents the mean concentration over the study period. The broken y-axis is used to display both the main concentration range and the highest short-term peaks. Gray shaded bands indicate periods of analyzer maintenance.**

Despite overall lower concentrations, maximum concentrations of several species were higher at Martigues-Lavéra than at Berre-l'Étang (Table 2). The most pronounced enhancement was observed for vinyl chloride monomer (VCM), which reached 1 440  $\mu\text{g m}^{-3}$ , representing the highest value in the entire 2022 dataset and reflecting the strong influence of chlorinated-chemical and PVC related industrial activities located near the station. Substantial maxima were also recorded for isopentane (710  $\mu\text{g m}^{-3}$ ) and 1,2-DCE (235  $\mu\text{g m}^{-3}$ ), indicating episodic but significant releases associated with fuel-handling operations and chlorinated-solvent production units. Elevated spikes were further observed for several light hydrocarbons and reactive olefins, notably ethylene (215  $\mu\text{g m}^{-3}$ ), propene (199  $\mu\text{g m}^{-3}$ ), 2-methylpentane (200  $\mu\text{g m}^{-3}$ ), n-pentane (165  $\mu\text{g m}^{-3}$ ) and n-butane (120  $\mu\text{g m}^{-3}$ ), illustrating the contribution of mixed petrochemical, storage and combustion-related emissions. Aromatic VOCs, although lower in magnitude than at Berre, also exhibited significant maxima such as benzene (119  $\mu\text{g m}^{-3}$ ), consistent with emissions from solvent and fuel processing. These pronounced hourly peaks are strongly modulated by the multidirectional wind regime characteristic of Lavéra, with dominant winds from NW, N, NE, ESE and W-WNW frequently placing the monitoring station downwind of multiple industrial units. In addition, local topography, notably a hill SE of the station, can promote wind deflection and recirculation, enhancing plume transport toward the site even under non-dominant conditions. As a result, Martigues-Lavéra experiences frequent and short pollution events, producing elevated maxima driven by both complex airflow patterns and the spatial concentration of petrochemical and chlorinated-chemical emission sources. The resulting chemical fingerprint, enriched in C5 hydrocarbons, chlorinated VOCs, olefins and selected aromatics, clearly reflects the multiplicity and intensity of industrial processes impacting this site.

At Port-de-Bouc, which is more distant from major point sources than the other two sites, VOC concentrations were generally lower over the January-June 2023 period. Despite this overall decrease, several species exhibited notable hourly maxima (Table



2), including isopentane ( $485 \mu\text{g m}^{-3}$ ) and benzene ( $145 \mu\text{g m}^{-3}$ ). The latter showed some of the highest episodic peaks among the three stations, although such outliers occurred less frequently than at Berre-l'Étang or Martigues-Lavéra. Chlorinated compounds such as vinyl chloride monomer (VCM,  $90 \mu\text{g m}^{-3}$ ) and 1,2-DCE ( $78 \mu\text{g m}^{-3}$ ) were consistently detected above the detection limit but remained at lower levels than at the other two sites. However, the elevated hourly peaks occasionally  
 450 observed for these species systematically coincided with E wind. Under these conditions, the plumes impacting Lavéra can be advected westward and intermittently reach Port-de-Bouc, generating short enhancements. This behavior is characteristic of coastal industrial environments where rapid changes in wind direction control the spatial extent of plume dispersion (Chen et al., 2013).

Although the three monitoring stations are located within a radius of less than 20 km (with 16 km between Berre-l'Étang and  
 455 Martigues-Lavéra, 18 km between Berre-l'Étang and Port-de-Bouc, and 4 km between Martigues-Lavéra and Port-de-Bouc) and all situated in the vicinity of large industrial platforms, the observed VOC concentrations display pronounced spatial contrasts in both variability and chemical composition. These differences arise not only from the distance to the dominant emission sources but also from site-specific wind regimes, topographic influences, and the chemical reactivity of the VOCs during transport. The distinct chemical fingerprints confirm that each station captures a unique combination of sources and  
 460 transport processes, underlining the importance of spatially resolved VOC monitoring in complex industrial environments. Such spatial complexity and the episodic nature of concentration peaks place stringent demands on measurement robustness, making the explicit reporting of uncertainty bounds a necessary condition for meaningful inter-site comparison. At high concentration levels, absolute uncertainties scale accordingly and can reach several tens to several hundreds of  $\mu\text{g m}^{-3}$ , such that only differences exceeding the combined uncertainties of both instruments can be interpreted as genuine spatial gradients.  
 465 For the majority of VOCs, the differences in maximum concentrations between stations are sufficiently large to remain unambiguously resolved. The most striking example is VCM, whose maximum at Martigues-Lavéra ( $1\,440 \pm 215 \mu\text{g m}^{-3}$ ) (Max  $\pm$  uncertainty) exceeds that at Berre-l'Étang ( $570 \pm 80 \mu\text{g m}^{-3}$ ) by approximately  $870 \mu\text{g m}^{-3}$  — far exceeding the combined uncertainty of  $\sim 295 \mu\text{g m}^{-3}$  — and unambiguously reflects the dominant influence of chlorinated-chemical production at the Lavéra platform. Similarly, isopentane ( $710 \pm 97$  vs.  $69 \pm 10 \mu\text{g m}^{-3}$ ) and ethylene ( $1\,600 \pm 200$  vs.  $215 \pm 30 \mu\text{g m}^{-3}$ ) display inter-  
 470 site differences of several hundred  $\mu\text{g m}^{-3}$  that are robust with respect to their associated uncertainties, and can therefore be attributed confidently to contrasting source types and intensities at each site.

In contrast, for 1,2-DCE, the maximum concentrations at Berre-l'Étang ( $311 \pm 77 \mu\text{g m}^{-3}$ ) and Martigues-Lavéra ( $235 \pm 55 \mu\text{g m}^{-3}$ ) differ by only  $76 \mu\text{g m}^{-3}$ , while the combined uncertainty reaches approximately  $95 \mu\text{g m}^{-3}$ . This case illustrates a situation where an apparent inter-site contrast in peak values is not statistically resolved, and where conclusions on differential source  
 475 influence must be drawn with caution — all the more so given that 1,2-DCE already carries one of the highest individual uncertainties in the dataset (Section 2.5).

For benzene, the gradient in maximum hourly concentrations across the three sites —  $95 \pm 7 \mu\text{g m}^{-3}$  at Berre-l'Étang,  $119 \pm 9 \mu\text{g m}^{-3}$  at Martigues-Lavéra, and  $145 \pm 10 \mu\text{g m}^{-3}$  at Port-de-Bouc — is progressive and directionally consistent. Inter-site differences ( $\sim 25$ – $50 \mu\text{g m}^{-3}$ ) remain above the combined measurement uncertainties ( $\sim 12$ – $16 \mu\text{g m}^{-3}$ ), confirming a robust



spatial gradient. Notably, the highest episodic benzene peaks occur at Port-de-Bouc despite its generally lower mean concentrations, pointing to occasional but intense plume advection from the Martigues-Lavéra platform under easterly winds, as discussed in Section 3.2.

These examples demonstrate that the uncertainty framework established in Section 2.5 is an operational tool for objectively assessing whether concentration contrasts between sites carry genuine physical meaning.

### 3.2. Spatial and temporal variabilities:

Hourly VOC data from the three monitoring stations in the Berre industrial basin were analyzed (supplementary information Fig. S5). The average diurnal profile of VOC concentrations for 2022 at the Berre l'Étang station reveal a diurnal dynamic, typical of sites influenced by alternating land-sea breeze regimes. This station shows the highest concentrations, with a pronounced peak in the early morning ( $\approx 03:00-07:00$ ,  $> 100 \mu\text{g m}^{-3}$ ), dominated by light alkanes (ethane, propane; isobutane, n-butane) followed by unsaturated hydrocarbons (ethylene, propene) and aromatic compounds (benzene, toluene, xylenes). This morning peak corresponds to the end of nocturnal land breeze, which transports pollutant-laden air masses originating from the industrial area located to the NNW of the monitoring station promoting their advection. Around midday ( $\approx 11:00-14:00$ ), concentrations decrease under the combined influence of the increased height of the boundary layer and the sea breeze (S/SE) that places the site outside the direct influence of emission from the northern industrial platform. Nevertheless, VOC levels are persistently observed above the LoD, reflecting the contribution of other local and regional sources as well as background concentrations. In the evening, concentrations increase again, linked to the weakening of the sea breeze and the re-establishment of the land breeze, combined with increased atmospheric stability. Some alkanes such as n-butane and isopentane, and other VOCs as VCM show relatively high levels throughout the day, reflecting continuous emissions, whereas reactive olefins show a larger variability, due to the combined influence of local sources and photochemical processes.

Compared to the other stations, Berre-l'Étang shows in particular large contributions of cyclohexane ( $52\ 307 \mu\text{g m}^{-3}$ ; 13 %), m,p-xylenes ( $40\ 473 \mu\text{g m}^{-3}$ ; 10 %) and ethylene ( $42\ 450 \mu\text{g m}^{-3}$ ; 11 %). The latter is a reactive species, explaining its very low concentration during the day (mean daytime concentration:  $3.62 \mu\text{g m}^{-3}$ , compared with  $8.13 \mu\text{g m}^{-3}$  at night). Long-lived species as ethane and propane show no marked diurnal profile typical for species present in the regional background.

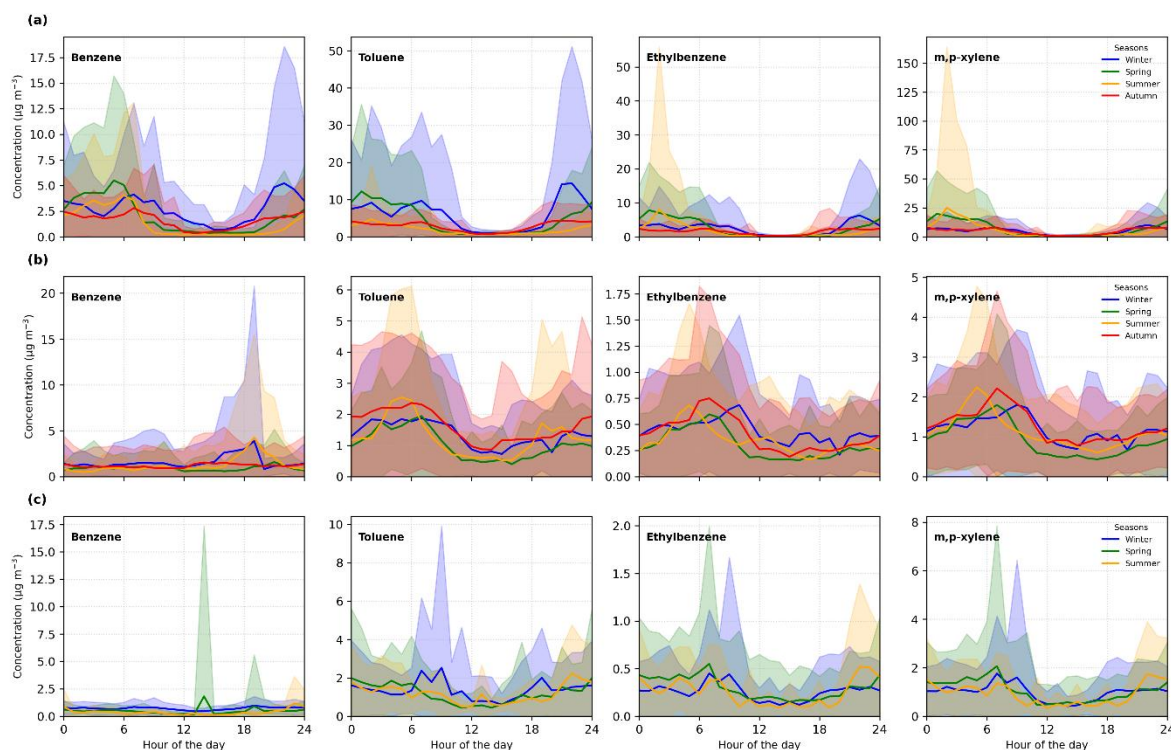
At the Martigues-Lavéra station, the 2022 average diurnal profile of VOCs shows total concentrations ranging from 30 to  $45 \mu\text{g m}^{-3}$ , with a pronounced late-evening peak ( $\approx 20-21$  h) exceeding  $45 \mu\text{g m}^{-3}$ . The chemical composition at Lavéra is dominated by light alkanes (propane, ethane, isobutane, n-butane), followed by aromatic compounds (benzene, toluene, xylenes), light olefins (ethylene, propene), and notably high concentrations of VCM and 1,2-DCE, both characteristic of local petrochemical production processes and of particular concern due to their toxicity. The relatively stable daytime concentrations, combined with the sharp evening maximum, indicate a continuous advection from the industrial sector, followed by reduced mixing-layer height and weakened horizontal ventilation at the end of the day, favors local VOC accumulation. Unlike Berre l'Étang station, where the diurnal variability is strongly modulated by alternating land-sea breezes, the Lavéra site shows a more stable profile, consistent with a more continuous influence of nearby industrial emissions. Wind



direction therefore appears less as a driver of the mean diurnal cycle than as a factor modulating the intensity of specific concentration enhancements.

515 Port-de-Bouc, although geographically close to industrial sources, shows the lowest concentrations of the three stations, with summed average diurnal VOC concentration ranging from 12 to 24  $\mu\text{g m}^{-3}$ . However, the analysis is based on measurements collected during the first six months of 2023, whereas the datasets for Berre l'Étang and Lavera correspond to 2022. This restriction was motivated by the high variability of temperature inside the Port-de-Bouc station, which caused significant variations in VOC retention times and increased uncertainty on the identification of the compounds. Therefore, the data was  
520 only validated for the six months once a better air conditioning of the station was effective. To verify that using different reference years does not bias the interpretation, a comparison was performed for some VOCs. At Berre l'Étang, benzene and VCM averaged at 2.22 and 1.53  $\mu\text{g m}^{-3}$  resp. during the first semester of 2022, compared to 1.11 and 1.64  $\mu\text{g m}^{-3}$  resp. for the same period in 2023. The slightly higher benzene values in early 2022 are consistent with the major industrial shutdown and maintenance period that temporarily increased several VOC concentrations. At Lavéra, benzene and toluene averaged 1.17  
525 and 1.11  $\mu\text{g m}^{-3}$  in the first trimester of 2022, versus 0.94 and 1.10  $\mu\text{g m}^{-3}$  for the corresponding period in 2023. Despite these operational variations, the concentrations remain of the same order of magnitude between 2022 and 2023 at both sites, supporting the comparability of the datasets across stations. In Port de Bouc, the average diurnal concentrations show two distinct maxima: one during the early night (00:00–02:00) and another in the late evening (20:00–22:00). Concentrations are lowest during the early afternoon (12:00–15:00). The chemical composition is dominated by n-butane, isopentane, and n-  
530 pentane, followed by cyclohexane, ethylene, and trans-2-butene, with notable contributions from aromatics such as benzene, toluene, and xylenes. Here too, VCM and 1,2-DCE are observed, indicating that this station is also influenced by the emitting industrial activities. Midday minima are consistent with stronger convective mixing and potentially reduced upwind industrial influence. The night-time double-peak pattern likely reflects intermittent exposure governed by wind variability and atmospheric stability rather than continuous emission input; the hydrocarbon mix observed at this station points to a significant  
535 contribution from petrochemical sources.

Each station exhibits a distinct diurnal profile and chemical signature shaped by its specific geographic setting and dominant atmospheric dynamics.



**Figure 4: Averaged hourly concentrations of the BTEX compounds for the year 2022 separated by season, winter (blue), spring (green), summer (orange) and autumn (red) for the three stations (a) Berre-l'Étang, (b) Martigues Lavéra, (c) Port-de-Bouc. Solid lines represent the seasonal mean diurnal concentration, and shaded areas represent the mean  $\pm$  one standard deviation ( $\sigma$ ).**

Aromatic VOCs, in particular BTEX, were selected for focused analysis in this study due to their toxicological significance, regulatory relevance, and widespread presence in urban air monitoring networks (Fig. 4).

BTEX compounds are widely used as proxies for anthropogenic VOC sources, including vehicular emissions, fuel evaporation, industrial processes, and solvent use (Derwent et al., 2007). Their chemical reactivity and health implications are well described, making them particularly suitable for a spatiotemporal assessment.

The highest concentrations of BTEX for the stations were observed at Berre-l'Étang for m,p-xylenes during the spring and summer nighttime, with a remarkable peak around 2 am, shared by the other species, which may reflect specific nighttime emissions dynamics or accumulation processes during the warm season. Notably, benzene concentrations at the Berre-l'Étang station occasionally exceeded  $5 \mu\text{g m}^{-3}$  during winter mornings, surpassing the EU annual limit on an hourly basis. In comparison, the Martigues-Lavéra station showed more moderate BTEX levels, with toluene reaching up to  $2\text{--}2.5 \mu\text{g m}^{-3}$  during early morning hours in spring and summer, while the other BTEX species generally remained below  $2 \mu\text{g m}^{-3}$ . The amplitude of the diurnal variation was markedly reduced compared to Berre-l'Étang station. Both stations are influenced by industrial emissions, but the frequency of plume impacts differs substantially due to contrasting wind regimes. As a result, Lavéra exhibits smoother temporal patterns, and its seasonal variations are also less pronounced. Finally, the Port-de-Bouc station recorded the lowest BTEX concentrations among the three sites, with values rarely exceeding  $2 \mu\text{g m}^{-3}$ . As shown by



the irregular diurnal patterns, Port-de-Bouc is less directly impacted by industrial plumes or heavy traffic, contrasting clearly with the more polluted environment of Berre l'Étang.

### 3.3. Comparison with other sites:

Mean concentrations of selected VOCs at the three study sites are compared with published data from five urban or suburban sites in Europe and Asia in Table 3. Despite differences in measurement periods and local meteorological conditions, the GC-FID instrumentation used across all studies ensures analytical comparability.

**Table 3: Comparison of mean concentrations  $\pm$  standard deviations, where available, of selected VOCs measured in this study with values reported in previous studies conducted at European and Chinese sites ( $\mu\text{g m}^{-3}$ )**

| Studies          |                                       | Current work                             |                                 | Dufresne et al., 2025                 | Badol et al., 2008           | Zhang et al., 2017        | Jia et al., 2016                    | Shao et al., 2016               |
|------------------|---------------------------------------|------------------------------------------|---------------------------------|---------------------------------------|------------------------------|---------------------------|-------------------------------------|---------------------------------|
| Analysis details |                                       | GC-FID                                   |                                 | TD-GC-FID                             | GC-FID                       | GC-FID                    | GC-FID                              | GC-FID                          |
| VOCs             | Berre-l'Étang (01/01/2022–31/12/2023) | Martigues-Lavéra (01/01/2022–31/12/2023) | Port-de-Bouc (01/01–30/06/2023) | Marseille Longchamp (03/2019–08/2020) | Dunkerque (09/2002–08/2003)  | Beijing (04/2014–01/2015) | Downtown Lanzhou (01/01–31/12/2013) | Nanjing (15/05–31/08/2013)      |
|                  | suburban (industrial influence)       | suburban (industrial influence)          | urban (industrial influence)    | urban background                      | urban (industrial influence) | Urban                     | petrochemical-industrial            | suburban (industrial influence) |
| ethylene         | 5.9 $\pm$ 4.8                         | 2.2 $\pm$ 0.4                            | 1.8 $\pm$ 0.3                   | 0.9 $\pm$ 1.2                         | 3.6                          | 6.1 $\pm$ 6.1             | --                                  | 4.5 $\pm$ 2.8                   |
| propene          | 1.3 $\pm$ 0.3                         | 1 $\pm$ 0.2                              | --                              | 0.2 $\pm$ 0.3                         | 1.9                          | 3.2 $\pm$ 2.9             | 4.3                                 | 3 $\pm$ 1.7                     |
| isopentane       | 2.6 $\pm$ 0.5                         | 8.2 $\pm$ 0.2                            | 3.4 $\pm$ 0.5                   | 0.7 $\pm$ 0.7                         | 2.8                          | 0.2 $\pm$ 0.4             | 4.7                                 | 3.2 $\pm$ 3.1                   |
| n-pentane        | 2.1 $\pm$ 0.4                         | 4.8 $\pm$ 1                              | 1.6 $\pm$ 0.2                   | 0.3 $\pm$ 0.3                         | 1.6                          | 1.4 $\pm$ 1.7             | 2.6                                 | 1.9 $\pm$ 0.5                   |
| VCM              | 1.7 $\pm$ 0.3                         | 2.6 $\pm$ 0.5                            | 0.6 $\pm$ 0.1                   | 0.14 $\pm$ 0.4                        | --                           | 0.9 $\pm$ 1.8             | --                                  | --                              |
| 1,3-butadiene    | 2.7 $\pm$ 0.4                         | 0.4 $\pm$ 0.1                            | 0.5 $\pm$ 0.5                   | 0.06 $\pm$ 0.09                       | 0.1                          | 0.3 $\pm$ 0.2             | --                                  | --                              |
| 1,2-DCE          | 3.1 $\pm$ 0.9                         | 6.1 $\pm$ 1.6                            | 1.5 $\pm$ 0.6                   | --                                    | --                           | 2.9 $\pm$ 2.8             | --                                  | --                              |
| benzene          | 1.9 $\pm$ 0.3                         | 1.2 $\pm$ 0.1                            | 0.6 $\pm$ 0.1                   | 0.2 $\pm$ 0.2                         | 1.7                          | 4.1 $\pm$ 3.2             | 6.3                                 | 7.6 $\pm$ 7.4                   |
| cyclohexane      | 7.3 $\pm$ 1                           | 0.6 $\pm$ 0.1                            | 0.3 $\pm$ 0.2                   | 0.2 $\pm$ 0.2                         | 0.3                          | 0.3 $\pm$ 0.3             | 10.3                                | 2.9 $\pm$ 1.1                   |
| toluene          | 3.8 $\pm$ 0.5                         | 1.3 $\pm$ 0.2                            | 1.2 $\pm$ 0.2                   | 0.5 $\pm$ 0.4                         | 4.1                          | 6.1 $\pm$ 4.3             | 3.9                                 | 6.4 $\pm$ 5.8                   |
| ethylbenzene     | 2.1 $\pm$ 0.3                         | 0.4 $\pm$ 0.04                           | 0.3 $\pm$ 0.1                   | 0.1 $\pm$ 0.1                         | 0.7                          | 2.7 $\pm$ 2.1             | 2.5                                 | 7.2 $\pm$ 4.9                   |
| m,p-xylene       | 5.7 $\pm$ 0.7                         | 1.1 $\pm$ 0.2                            | 1 $\pm$ 0.1                     | 0.3 $\pm$ 0.4                         | 2.3                          | 5.6 $\pm$ 4.4             | 3.7                                 | 2.5 $\pm$ 1.5                   |

VCM: vinyl chloride monomer; 1,2-DCE: 1,2-dichloroethane; (--): not reported.

Overall, concentrations at the three study sites are consistent with, or exceed, those reported at other industrially influenced sites, reflecting the petrochemical character of the étang de Berre basin. Several compounds stand out. Cyclohexane at Berre-l'Étang (7.3  $\mu\text{g m}^{-3}$ ) is markedly elevated relative to all reference sites except Lanzhou (10.3  $\mu\text{g m}^{-3}$ ), suggesting a shared petrochemical-industrial emission profile. Vinyl chloride monomer (VCM) and 1,2-dichloroethane (1,2-DCE), absent or



negligible at most reference sites, are detected at significant concentrations across all three study sites, pointing to specific industrial point sources — likely PVC-related activities — with no equivalent at the comparison locations. Notably, Beijing also reports detectable VCM ( $0.9 \pm 1.8 \mu\text{g m}^{-3}$ ) and 1,2-DCE ( $2.9 \pm 2.8 \mu\text{g m}^{-3}$ ) concentrations, likely attributable to the chemical industry and plastic manufacturing activities documented in that urban area, yet levels at Berre-l'Étang and Lavéra remain significantly higher, reinforcing the specificity of chlorinated compound emissions in the study area. Lavéra exhibits the highest isopentane and n-pentane levels among all sites, consistent with refinery fugitive emissions. Conversely, benzene concentrations at the study sites are substantially lower than those observed at Chinese urban sites (Beijing, Lanzhou, Nanjing), where vehicle exhaust and coal combustion are dominant sources. Similarly, toluene remains moderate compared to Chinese and Dunkerque sites, indicating that solvent usage and traffic contribute less to the aromatic fraction here than petrochemical and halogenated compound sources. The urban background site of Marseille-Longchamp (Dufresne et al., 2025) systematically shows the lowest concentrations across all species, confirming the strong industrial imprint specific to the lake de Berre corridor.

#### 4. Conclusion:

Continuous measurements of 23 VOCs at three sites around the lake of Berre, supported by a rigorous QA/QC framework and automated uncertainty estimation, demonstrate the feasibility of high-quality long-term monitoring in a complex industrial environment. The expanded uncertainties calculated at a reference concentration of  $5 \mu\text{g m}^{-3}$  ranged from 9 % to 25 % across compounds, with benzene well below the 25 % limit imposed by the NF EN 14662-3 standard. When applied to extreme hourly concentrations, these uncertainties scale to absolute values of several tens to hundreds of  $\mu\text{g m}^{-3}$ , yet inter-site differences for most VOCs remain sufficiently large to be unambiguously resolved — as demonstrated for VCM, isopentane, and ethylene — while cautioning against over-interpretation of apparent gradients for analytically challenging compounds such as 1,2-DCE. This operational use of the uncertainty framework — moving beyond its conventional metrological role — represents a methodological contribution in its own right, directly applicable to any multi-site monitoring network dealing with episodic industrial emissions.

Each monitoring station exhibits a distinct chemical fingerprint shaped by its specific industrial environment and local atmospheric dynamics. Berre-l'Étang is strongly influenced by land-sea breeze recirculation and recorded exceptional concentration peaks during the industrial maintenance period, with ethylene reaching  $1\,600 \pm 200 \mu\text{g m}^{-3}$  and m,p-xylene  $1\,300 \pm 150 \mu\text{g m}^{-3}$ . Martigues-Lavéra is dominated by chlorinated and light hydrocarbon compounds, with VCM peaking at  $1\,440 \pm 215 \mu\text{g m}^{-3}$ , reflecting the intensity of nearby petrochemical and PVC-related activities. Port-de-Bouc records the lowest and least structured concentrations, consistent with its greater distance from point sources and intermittent plume exposure driven by wind direction. Across all three sites, annual benzene concentrations remained below the EU regulatory limit of  $5 \mu\text{g m}^{-3}$ , despite frequent short-lived hourly exceedances.



600 The harmonized QA/QC framework developed here — combining the NF EN 14662-3 benzene standard with the ACTRIS  
approach (GAW report No.281, WMO, 2023) and implemented within the Incert'R tool — ensures metrological traceability  
across the full set of monitored compounds and provides a transferable methodology for other industrial monitoring networks  
in Europe. The resulting dataset, with explicit compound-specific uncertainty bounds, meets the requirements for advanced  
source-apportionment analyses using positive matrix factorization (PMF), which will form the basis of subsequent work aimed  
605 at refining regional emission inventories and supporting forecasting tools for ozone and secondary aerosol pollution in the  
Marseille industrial corridor.

### Code and data availability

The Incert'R uncertainty-calculation tool, including the VOC module developed for this study, is open source and freely  
available at <http://sourceforge.net/projects/incerttr/>. The VOC concentration and associated uncertainty dataset for the three  
610 monitoring stations discussed in this study is available from the corresponding author upon request and from DOI xxxx  
(ongoing deposit of the data on Easy Data)

### Author contributions

ZB, LT, SS, GG and NL designed the study. CC, ZB carried out the measurements, CC, ZB, GG did the data processing and  
ZB the uncertainty calculations, and ZB prepared the manuscript with contributions from all co-authors. The manuscript was  
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### Competing interests

The authors declare that they have no conflict of interest.

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