Comprehensive Analysis of VOCs in an Industrial Harbor City: Spatiotemporal Distribution, Health Risk, and Potential Sources

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Abstract

Volatile organic compounds (VOCs) measurements during the worst air quality season of 2020-2022 were conducted at three distinct sites within Kaohsiung Harbor, Taiwan's largest harbor and a significant hub in Asia. Air VOCs samples were collected continuously in 24h by canister and analyzed by GC/MS with pre-concentration systems according to USEPA Method TO-15. The source apportionment was defined by diagnostic ratio analysis and positive matrix factorization (PMF) model while ozone formation potentials (OFP) were estimated by maximum incremental reactivity method. Health risk was estimated by unit risks and reference concentration for cancer and non-cancer risk, respectively. The results indicate a decrease in average total VOC (TVOC) concentrations (ppbv) over the study period: 37.9 ± 4.5 in 2020, 23.3 ± 9.9 in 2021, and 23.3 ± 2.6 in 2022. Dominant VOC components were C2-VOCs and aromatics, which made up more than 50% of TVOCs. According to diagnostic ratio analysis, local anthropogenic emissions, such as industrial and ship/vehicle emissions around harbor area, were main causes. Four sources were identified by positive matrix factorization (PMF), with industrial activities (33.7%), followed by vehicle and ship emissions (30.6%), solvent usages (21.1%), and fuel evaporations (14.6%). OFP results indicated that toluene was primary OFP contributor, accounting for an average of 30.4%, followed by C2-VOCs at 16.2% and m/p-xylene at 12.5%, collectively contributing nearly 60% to OFP. These OFP contributors were significantly attributed to vehicle/ship emissions and solvent usages. Cumulative non-carcinogenic hazard indices were less than 1 indicates an acceptable non-carcinogenic health concern. Notably, only 1,2-dichloroethane exceeded the threshold of 1.0 × 10⁻⁶ for carcinogenic risk throughout the three-year observation period, while 1,3-butadiene indicated a high risk only in 2020. Industrial emissions could mainly contribute to carcinogenic risks in Kaohsiung Harbor and the surrounding area. The results are conducive to developing control strategies for VOC emissions to reduce human exposure risk to ambient air.

Keywords: Carcinogenic risks, Green port, Ozone formation, Pollution sources, Volatile organic compounds.
Port activities, including freight transport, significantly contribute to air pollution, impacting port city air quality and human health (Obiweluozo et al., 2022; Poulsen et al., 2018; Tichavska et al., 2019). For instance, Liu et al. (2016) noted that ship emissions in East Asia cause over 24,000 premature deaths annually. As a result, International Maritime Organization (IMO) introduced emission control areas with stricter fuel sulfur content limits (IMO, 2020). However, adopting low-sulfur oil policies could increase VOCs levels in harbor areas (Huang et al., 2018; Wu et al., 2020; Yeh et al., 2023). Ambient VOCs, crucial in forming tropospheric ozone and secondary organic aerosols (Hui et al., 2019; Koppmann, 2020), pose health risks like irritation, nervous system impairment, asthma, and cancer (Dehghani et al., 2018; Sahu et al., 2017). Despite their impact, VOC monitoring is often overlooked due to analytical complexity (Sarmiento et al., 2023). Port air quality and health concerns necessitate increased attention. Thus, exploring VOC pollution is crucial for effective harbor control policies, sustainability, and eco-friendly practices in port cities.

In harbor area, VOC-related studies mainly focused on ship emissions and ambient air VOCs. Previous studies performed on ships mainly concentrate on characteristics of VOC emissions. For instance, Huang et al. (2018) tested a Handysize class bulk carrier under at-berth, maneuvering and cruising conditions, and Xiao et al. (2018) tested 20 ships at berth and found that aromatics dominated VOC emissions. Meanwhile, ambient VOCs at harbor studies have mainly involved emission source profiles and characteristics of VOCs. Many studies were conducted in harbor cities such as Japan (Ohura et al., 2006), France (Roukos et al., 2009), Turkey (Mentese & Akca, 2020; Thera et al., 2019), Greece (Liakakou et al., 2022), etc. The results indicated that VOC characteristics vary in different regions due to geographical, meteorological, industrial, and sampling factors.
The origins of VOCs are complicated. Some common source apportionment methods, such as diagnostic ratio and receptor model, were applied to identify source of VOCs. Benzene-to-toluene (B/T) and xylene-to-benzene (X/B) ratios are frequently employed to assess air mass aging and VOC sources based on photochemical reactivity estimates (Li et al., 2020; Liu et al., 2008). In detail, B/T ratios below 0.4 and X/B ratios exceeding 1.1 suggest young air parcels, often from local sources (Liu et al., 2008). Additionally, receptor models, especially Positive Matrix Factorization (PMF), have been crucial in identifying primary VOC sources due to their efficiency and quantitative capabilities (Miller et al., 2002).

Tropospheric ozone formation, influenced by VOCs, is crucial for climate change (Solomon et al., 2007) and impacts human health and ecosystems (Karlsson et al., 2017; Shiraiwa et al., 2017). VOCs are known precursors for photochemical O₃ formation, assessed by O₃ formation potential (OFP) (Le et al., 2023; Yuan et al., 2022a) based on their structure and chemical reactivity. Continuous logistic activities in harbor may significantly contribute to NOx formation, potentially limiting O₃ formation due to VOC concentration. Monitoring and regulating VOC emissions are essential to address this issue, highlighting the importance of OFP assessment.

Understanding the presence and impact of VOCs is crucial for ensuring harbor air quality and evaluating associated health risks. In particular, inhalation exposure to VOCs poses a cancer risk, given the presence of high-cancer-risk compounds like benzene, toluene, ethylbenzene, xylene, and formaldehyde in harbor areas (Ohura et al., 2006; Santiago et al., 2021; Sarmiento et al., 2023). Estimating potential health risk of individual VOCs and identifying high-risk compounds are essential steps to protect harbor workers and nearby residents. The OFP and health risk of VOCs are closely related to source (Wu et al., 2020). Thus, identifying and characterizing high-risk compounds and their origins in harbor area is necessary to assist in developing specific control policies for district, prioritizing well-being of community.
Kaohsiung Harbor, a critical global industrial port in southern Taiwan, faces emissions from industrial activities and ships (Ju et al., 2021; Yuan et al., 2022b), posing a detrimental impact on human beings (Obiweluozo et al., 2022; Tichavska et al., 2019). However, many previous studies conducted in Kaohsiung City mainly focus on VOC in urban area (Hong et al., 2006; Kuo et al., 2015) and VOC emissions from industrial sector (Chen et al., 2005; Lin et al., 2004), while less studies investigated in harbor area. Most of previous studies in this harbor mainly focus on particulate matters, NOx, SOx, O3, CO, and particular hydrocarbons instead of VOCs (Lai et al., 2011; Lin et al., 2007; Lin et al., 2005; Liu et al., 2008; Tseng et al., 2021; Yuan et al., 2022b). A recent study by Le et al. (2023) explored VOC variations across the four seasons of 2020 at Kaohsiung Harbor, identifying winter as the most polluted period due to the influence of Northern winds and the geographical blocking of central mountains. However, the study did not assess the associated human health risks. Few studies have investigated VOCs in this harbor area, and none have assessed human health risks. Thus, it is vital to delve into the characteristics of VOCs and their risk to human beings in this harbor area.

This study was conducted to assess the characteristics of VOC emissions from Kaohsiung Harbor, identify sources of these VOCs within harbor, estimate O3 formation potentials and inhalation health risk of VOCs. Air samples were collected from three locations near industrial and shipping operations during pollution-prone periods from 2020 to 2022. The results of this study are expected to offer valuable knowledge about air quality in harbor area and support the successful execution of environmentally friendly portal city air quality management strategy.

2 METHODOLOGY
2.1 Site and Sampling Strategy

This research focused on Kaohsiung Harbor, located near industrial complexes in Taiwan Island's southwest coast. This harbor, a major contributor to Taiwan's cargo throughput, spans 28.9 kilometers with 124 piers. Stationary sources around Kaohsiung Harbor are industrial sectors, including refineries, petrochemical manufacturing industrial parks, steel mills, metallic parts manufacturing processes, coal-fired power plants, semiconductor manufacturers, shipyards, ship architecture industries, etc. (Fig. 1). Other critical mobile sources around harbor include motorcycles, cars, heavy-duty trucks, ships, and airplanes. With many sources contributing, Kaohsiung City has claimed Taiwan's worst air quality in the past decades.

Three specific sites were selected within Kaohsiung Harbor area, identified as Qihou (E1), Zhongdao (KEPZ), and Zhonghe (E2), as indicated in Figure 1. Site E1 (22° 34' N, 120° 16' E) is situated at harbor's northern entrance (entrance no.1), serves mainly cruise and small merchant ships. Site KEPZ (22° 36' N, 120° 18' E), is inside Kaohsiung Export Processing Zone, adjacent to the chemical manufacturing areas by the harbor and pier where bulk ships load and unload, positioned at the middle section of harbor. Site E2 (22° 33' N, 120° 19' E) is entrance no.2 at the southernmost portion of harbor and can serve giant merchant ships up to 22,000 TEU. Industrial pollution significantly impacts this site since it is close to many industrial facilities and Linhai Industrial Zone (Fig. 1). These sampling sites were chosen to investigate various aspects of VOC pollution, including its spatiotemporal variations and potential sources.

VOCs sampling canisters were placed on the building rooftops with a height of roughly 7 to 10 meters and simultaneously sampled VOCs in the most polluted period Fall to Winter from 2020 to 2022. Specifically, measurement of VOCs was conducted in November 2020, October 2021, and December 2022. Each sampling campaign involved continuous 24-hour collection of VOCs over 7 to 10 days. The 24-hour sampling was extended from 9:00 am to 9:00 am the next morning to
explore spatiotemporal variations in VOCs and identify possible sources within this industrial harbor.

Fig. 1. VOC sampling locations and nearby pollution sources in Kaohsiung Harbor.

2.2 VOC Sampling and Analytical Methods

The TO-15 method as described by USEPA was used to analyze VOCs (USEPA, 2019). Briefly, interferences were removed by passing air samples via three traps within the Entech 7100A pre-concentrator after being diluted with nitrogen gas. Then, samples were introduced into a GC/MS system (Agilent 6890/5973, USA) to analyze VOCs. The carrier gas employed was helium, and a DB-VRX capillary column (60 m x 250 µm x 1.4 µm, Agilent Technology Inc., USA) was utilized. Two standard gases were used: photochemical assessment monitoring system (PAMS), which included 55 compounds, and urban air toxics monitoring program (UAT), which included 59 compounds. LINDE Group of North America supplied these standards. The two standards had 13 compounds in common, and they are adopted for relative percent deviation (RPD) quality...
control. Additionally, m-xylene and p-xylene were categorized as m/p-xylene, whereas acetylene, ethane, and ethene were grouped as C_2-VOCs. Compounds with values below the Method Detection Limit (MDL) were reported as non-detects to accurately reflect their absence in the samples. Approximately 75% of detected species in our measurements were above the MDL, indicating a robust dataset that supports our conclusions. Detailed quality assurance and quality control (QA/QC) information for certain compounds is included in Table S1.

2.3 Health Risk Assessment

This research employed the health risk assessment approach suggested by USEPA to evaluate potential dangers posed by certain harmful air VOCs that people may inhale (USEPA, 2009). Reference Concentrations (RfC) and Inhalation Unit Risks (IUR) are used to assess non-cancer and cancer risks, respectively. The RfCs and IURs are sourced from established databases like the California Office of Environmental Health Hazard Assessment (OEHHA) and Integrated Risk Information System (IRIS), which provide vetted risk assessment values based on extensive toxicological research. It's worth noting that this methodology has gained global recognition as a widely used method for assessing human health risks (Chen et al., 2016; Dodson et al., 2007; Zhang et al., 2022a). Data collection occurred during pollution-prone periods from 2020 to 2022. We extrapolated short-term exposure measurements to estimate lifetime risks under the following assumptions: steady-state exposure, assuming measured levels represent long-term exposure; consistent exposure levels over a lifetime, barring significant changes in policies or behaviors; and using a typical human lifespan of 74.8 years for risk calculations, applying time-weighting factors for different life stages. This health risk assessment comprised two components: one for cancer risk and another for non-carcinogenic risk. To quantify the risk of cancer, we utilized a measure known as cancer hazard over a lifetime (Risk, dimensionless). We employed the hazard index (HI, dimensionless) for non-cancer health risks. Below, description of evaluation method is provided:
The chronic exposure concentration (EC, μg m\(^{-3}\)):

\[
EC = \frac{CA \times ET \times EF \times ED}{ED \times 365 \times 24} \tag{1}
\]

The carcinogenic risk:

\[
Risk = IUR \times EC \tag{2}
\]

The hazard quotient (HQ, dimensionless) of non-carcinogenic risk:

\[
HQ = \frac{EC}{RfC \times 1000 \mu g \, m^{-3}} \tag{3}
\]

HI is determined by summing the HQs of all compounds:

\[
HI = \sum HQ_i \tag{4}
\]

where CA (μg m\(^{-3}\)) is concentration of air pollutant; ET (8 h day\(^{-1}\)) is time of exposure; EF (365 days year\(^{-1}\)) is frequency of exposure; ED (74.8 years) is exposure duration of a lifetime; IUR (μg m\(^{-3}\))\(^{-1}\) is inhalation unit risk; RfC (μg m\(^{-3}\)) is reference concentration. We based the 8-hour daily exposure assumption on standard occupational guidelines for an 8-hour workday. Our study targets workers in industrial settings exposed to ambient air pollution, aligning with occupational health standards. Focusing our cancer risk assessment on port workers ensures our estimates are relevant and tailored to their specific exposure scenarios.
A reference value of one or less (HI ≤ 1) was considered an acceptable non-carcinogenic health concern, while HI > 1 indicated that negative non-carcinogenic risks were more likely to occur ([USEPA, 2009]). Meanwhile, carcinogen risks estimated to be less than or equal to $1 \times 10^{-6}$ is generally deemed negligible, while a risk predicted to be equal to or greater than $1 \times 10^{-3}$ is considered significant (Rodricks et al., 1987).

2.4 Source Apportionment

Diagnostic ratios and Positive Matrix Factorization (PMF) model were employed in this study to discover source of VOCs. Ratios involving BTEX compounds (benzene, toluene, ethylbenzene, and xylene) for diagnostic analysis were used to evaluate the age of air masses, and PMF version 5.0 ([USEPA, 2014]), widely used in previous studies (Pinthong et al., 2018; Ji et al., 2022), was utilized to determine the source factors of VOCs in this study. PMF extracts factors from different sources based on the weighted least square method. PMF generates purely constrained non-negative factor loading and factor scores resulting in less rotational ambiguity. To obtain the weights, weighted least squares are used to fit the stated error estimates of the data matrices' elements. Two data sets, one comprising compound concentrations and other containing uncertainty values, were utilized as inputs for this analysis. Equation (5) displays the formula for calculating uncertainty (u). If the compound shows concentrations lower than method detection limit (MDL), its concentration and uncertainty will be substituted with $\frac{MDL}{2}$ and $\frac{5 \times MDL}{6}$, respectively.

$$u = \sqrt{(Error \ Fraction \times \ concentration)^2 + (0.5 \times \ MDL)^2} \quad (5)$$

Error fraction was set at 0.1 in accordance with Chang et al. (2011). PMF analysis did not include compounds whose signal-to-noise ratio was less than 0.5 or whose data percentage fell below detection limit by more than 30%. Only 28 compounds were included in model as a result.
Three to eight source criteria were examined to determine the best source kinds. Several diagnostic parameters were evaluated to determine the optimal factor number: (1) the accuracy of error estimation, represented by $Q_{\text{true}}/Q_{\text{exp}}$ and $Q_{\text{true}}/Q_{\text{robust}}$ (USEPA, 2014; Brown et al., 2015); (2) error diagnostics including displacement (DISP), bootstrap (BS), and BS-DISP methods (USEPA, 2014; Brown et al., 2015); and (3) robust physical validity. More details of the PMF model analysis in this study are presented in the Supplementary. Factors were categorized into sources using the USEPA Speciate database version 5.2 (USEPA, 2022). First, compounds making a substantial contribution (> 50%) to each factor were cross-referenced with database to identify potential origins. Subsequently, all probable origins for each compound were gathered, and these origins were utilized to designate a certain source of the factor. Additionally, prior research conducted in this region was consulted for reference.

3 RESULTS AND DISCUSSION

3.1 Variation of Total VOC Concentrations

Figure 2 illustrates the spatial distribution of total VOC concentrations in Kaohsiung Harbor, Taiwan, over a period of three years, highlighting variations across different sampling locations. In 2020, the highest VOC values were found in site E2, followed by KEPZ and E1 (Fig. 2). However, a shift occurred in 2021 and 2022, with the highest VOC concentrations observed in KEPZ, followed by E2, while E1 exhibited the lowest concentrations throughout the three years. These variations can be attributed to several potential reasons. Primarily, the substantial contribution of industrial activities in E2 and KEPZ likely accounts for the elevated VOC emissions evident in these regions (Le et al., 2023). KEPZ consistently showed declining VOC concentrations, while E2 experienced a significant decrease in 2021 and a slight increase in 2022. The changes at E2 could result from the disruptive impact of the COVID-19 pandemic on industrial activities during 2021. E1 experienced a decline in 2021 due to reduced tourism activities amid pandemic...
restrictions, followed by a resurgence in 2022. KEPZ remained heavily polluted as its import/export operations faced fewer disruptions than industrial and tourism sectors.

Fig. 2. Spatial distribution of total VOCs over three sampling periods at three sites.

Variations in VOC concentrations correlated with emission origins near the sampling locations (Fig. 1). Site E2 experienced high VOC levels due to industrial activities and ship/vehicular exhausts nearby. At KEPZ, near the Kaohsiung Export Processing Zone, bulk carriers, machinery, and heavy-duty trucks contributed to elevated VOC concentrations. Meanwhile, main pollution origins near site E1 were the exhausts from ships and vehicles. The levels of air pollutants assessed at three ambient air quality monitoring stations around the harbor sampling locations are illustrated in Fig. S2. Sulfur dioxide (SO$_2$) is a measure of emissions from sulfur-containing fuel burning and ship emissions. (Winnes & Fridell, 2009; Zhang et al., 2022b). Site E2 exhibited higher SO$_2$ levels than the other two locations, indicating the higher contribution of ship emissions at E2. Meanwhile, NO$_2$ and NOx indicate emissions originating from both ship
and vehicular exhausts (Ramacher et al., 2020). The concentrations of NO\textsubscript{2} and NO\textsubscript{x} were higher at E2 and KEPZ compared to E1. Additionally, the number of large ships arriving and departing at site E2 was higher than at site E1. Thus, the elevated VOC concentrations at E2 and KEPZ were due to industrial and higher mobile source activities, while lower VOCs at site E1 were mainly influenced by ship and vehicular activities.

Meteorological conditions, including wind patterns and atmospheric stability, may influence the dispersion and transport of VOCs, contributing to variations in observed concentrations across harbor. Meteorological data in Table S2 were also collected for investigation of their effects on VOC concentrations. Wind profiles throughout three-year sampling periods (Fig. S1) indicated that northerly, northeasterly, and northwesterly winds were predominant. This wind direction can flow pollutants to the downwind area of site E2; however, the wind was characterized by weak wind speeds, mainly below 3.6 m/s, which may not affect the downwind site. Pearson correlation between meteorological conditions and VOCs was further performed to confirm their relationship (Table S3). The results indicated a weak positive correlation between VOCs and wind speed ($r = 0.13$), which is similar to all other conditions ($r < 0.13$). A weak correlation between VOCs and meteorological conditions, including wind profiles, suggests that local anthropogenic sources, especially at sites KEPZ and E2, significantly contribute to the spatial distribution of VOCs in Kaohsiung Harbor area, with site E1 having lower emissions.

### 3.2 VOC Functional Group Distribution

Over a three-year observation period, characteristics of VOCs at three distinct locations remained remarkably stable, with minimal changes (Fig. 3). C\textsubscript{2}-VOCs consistently dominated, contributing significantly at all sites. Aromatic compounds consistently ranked as the second-largest contributor, followed by alkanes and ketone compounds. These four groups accounted for over 85.4% of total VOCs across three locations. Specifically, C\textsubscript{2}-VOCs were the primary
contributors to VOC concentrations at all three sites, with average fractions of 32.5%, 21.1%, and 45.7% in 2020, 2021, and 2022, respectively. Aromatics were another significant contributor, with average fractions of 19.9%, 31.6%, and 27.7% in 2020, 2021, and 2022, respectively. Aromatics have the most significant potential for ozone generation (Zou et al., 2015), and certain aromatic compounds pose carcinogenic risks. Alkenes and ketones, while contributing less, significantly impact VOC composition and atmosphere by forming secondary pollutants through high photochemical reactions (Jia et al., 2016). The stable VOC pattern over three years emphasizes a need for continuous monitoring and understanding of sources. Controlling C2-VOCs and aromatics is crucial to minimize the area's secondary pollutant formation and human health risks.

![Functional group distribution of VOCs over three sampling periods at three sites.](image)

**Fig. 3.** Functional group distribution of VOCs over three sampling periods at three sites.

In detail, Table S4 provides insights into the top 10 species of VOCs detected at three sites over a period of three years. This analysis reveals consistent findings across these sampling campaigns. C2-VOCs, toluene, and acetone consistently ranked among the top three contributors. At E2 site, m/p-xylene was detected constantly over three sampling times, suggesting a consistent
emission source of this compound. In contrast, at KEPZ site, m/p-xylene and ethyl acetate were detected, indicating the presence of multiple VOC sources at this location. Interestingly, at E1 site, chloromethane was the only compound detected consistently over three sampling campaigns. This finding suggests that the emission source of chloromethane at E1 may differ from industrial sites, highlighting the importance of considering diverse locations when studying VOC emissions.

Furthermore, Fig. S3 illustrates BTEX concentrations at three sampling sites over three sampling periods. The data consistently indicated the same patterns across three sampling times, with the highest concentrations observed at KEPZ, followed by E2 and E1. Notably, toluene was dominant compound among the BTEX group, contributing to the highest concentration. The elevated BTEX concentration at KEPZ may be attributed to industrial processes nearby, chemical storage tanks from chemical plant (as shown in Fig. 1), and increased vehicle activities associated with this area's import and export processes. A more in-depth discussion of the sources of VOCs will be conducted in the source apportionment section (section 3.5). Overall, the results emphasize the recurring presence of certain VOCs, such as C2-VOCs, toluene, acetone, m/p-xylene, ethyl acetate, and chloromethane, at sampled sites. Similarly, Thera et al. (2019) reported that toluene was a primary contributor to VOCs, followed by acetone, n-butane, and m/p-xylene in Besiktas harbor of Turkey.

This study compared the field measurements of VOCs in Kaohsiung Harbor and those recorded in other harbor cities (Table 1). Similar to other harbors, the significant origins of VOCs are local anthropogenic sources, influenced mainly by industrial and related vehicle/ship activities (Liakakou et al., 2022; Ohura et al., 2006; Sarmiento et al., 2023; Thera et al., 2019). Due to the complexity of VOC measurements, some studies designed to focus and quantify only concentration and characteristics of BTEX compounds, comprising benzene, toluene, ethylbenzene, m/p-xylene, o-xylene (Roukos et al., 2009; Santiago et al., 2021; Sarmiento et al., 2023). Table 1 presents the
top 5 VOC compounds detected in each harbor study, consistently identifying toluene as a significant contributor to VOCs in harbor areas despite varying local sources. Furthermore, some studies conducted risk assessments of VOCs, mirroring our findings. Non-cancer risks were generally not a cause for concern, while cancer risks were elevated for specific aromatic, halogenated, and aldehyde compounds (Ohura et al., 2006; Santiago et al., 2021; Sarmiento et al., 2023). For instance, benzene, carbon tetrachloride, formaldehyde, and acetaldehyde posed cancer risks at Shimizu Harbor, Japan (Ohura et al., 2006), while benzene, ethylbenzene, and 1,2-dichloroethane were reported as carcinogenic at Fortaleza, Brazil (Santiago et al., 2021), Paranaguá Port, Latin America (Sarmiento et al., 2023); and Kaohsiung harbor, Taiwan (this study), respectively.

In general, relatively few studies have explored VOC characteristics and related risks within harbor locations, especially when compared to industrial, urban, suburban, and rural investigations. VOC emissions in harbor areas are often attributed to a combination of industrial discharges and emissions from ships and heavy-duty trucks. Kaohsiung Harbor is close to industrial and metropolitan zones. As a result, the origins of emissions and the chemical transformation processes in this region are notably more complex than what is typically observed in urban and suburban areas. Given these complexities, a comprehensive exploration of VOCs and their risks within industrial harbor areas necessitates further in-depth investigation. Future studies must focus on this issue to develop a deeper grasp of the topic.
Table 1. The VOC characteristic across sampling sites and other harbor regions.

<table>
<thead>
<tr>
<th>Sampling Sites</th>
<th>Sampling year</th>
<th>Type of Sampling Areas</th>
<th>Main sources</th>
<th>Top 5 VOCs</th>
<th>Risk concern</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Besiktas Port, Turkey</td>
<td>2014</td>
<td>Urban</td>
<td>Mixed regional emissions</td>
<td>Methanol, Acetone, Toluene, n-Butane, Acetaldehyde</td>
<td>-</td>
<td>Thera et al. (2019)</td>
</tr>
<tr>
<td>Kilitbahir Harbor, Turkey</td>
<td>2018</td>
<td>Roadway/Fishing Harbor</td>
<td>Traffic-related emissions</td>
<td>Toluene, m,p-Xylene, 4-Chlorotoluene, n-Hexane, Benzene</td>
<td>-</td>
<td>Mentese and Akca (2020)</td>
</tr>
<tr>
<td>Canakkale Harbor, Turkey</td>
<td>2018</td>
<td>Roadway/Urban/Harbor</td>
<td>Traffic-related emissions</td>
<td>Toluene, m,p-xylene, 4-Chlorotoluene, n-Hexane, Benzene</td>
<td>-</td>
<td>Mentese and Akca (2020)</td>
</tr>
<tr>
<td>Piraeus Port, Greece</td>
<td>2019</td>
<td>Urban/Harbor</td>
<td>Fugitive emission</td>
<td>n-Hexane, Toluene, Benzene, n-Heptane, 2,2-dime-butane</td>
<td>-</td>
<td>Liakakou et al. (2022)</td>
</tr>
<tr>
<td>Shimizu Harbor, Japan</td>
<td>2000</td>
<td>Industrial/Harbor</td>
<td>Vehicle exhaust and industrial activity</td>
<td>Toluene, m,p-Xylene, Ethylbenzene, Acetaldehyde, Formaldehyde</td>
<td>Benzene, Carbon tetrachloride, Formaldehyde, Acetaldehyde</td>
<td>Ohura et al. (2006)</td>
</tr>
<tr>
<td>Fortaleza, Brazil *</td>
<td>2015</td>
<td>Coastal/Harbor</td>
<td>Influenced by meteorology</td>
<td>Benzene, Toluene, Ethylbenzene, m,p-Xylene, o-Xylene</td>
<td>Benzene</td>
<td>Santiago et al. (2021)</td>
</tr>
<tr>
<td>Paranaguá Port, Latin America *</td>
<td>2018-2019</td>
<td>Harbor</td>
<td>Fresh emission</td>
<td>Benzene, Toluene, Ethylbenzene, m,p-Xylene, o-Xylene</td>
<td>Ethylbenzene</td>
<td>Sarmiento et al. (2023)</td>
</tr>
<tr>
<td>Dunkirk Port, France **</td>
<td>2007</td>
<td>Rural/Harbor</td>
<td>Industrial and urban sources</td>
<td>Benzene, Toluene, Ethylbenzene, m,p-Xylene, o-Xylene</td>
<td>-</td>
<td>Roukos et al. (2009)</td>
</tr>
<tr>
<td>Location</td>
<td>Year</td>
<td>Type</td>
<td>Emission Source</td>
<td>Compounds</td>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>----------</td>
<td>---------------</td>
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</tr>
<tr>
<td>Kaohsiung Harbor (E1), Taiwan</td>
<td>2020-2022</td>
<td>Island/ Harbor</td>
<td>Industrial and ship/vehicle emission</td>
<td>C₂-VOCs, Toluene, Acetone, Ethyl Acetate Chloromethane</td>
<td>This study</td>
<td></td>
</tr>
<tr>
<td>Kaohsiung Harbor (KEPZ), Taiwan</td>
<td>2020-2022</td>
<td>Urban/ Harbor</td>
<td>Industrial and ship/vehicle emission</td>
<td>C₂-VOCs, Toluene, Acetone, n-Decane, Ethyl Acetate</td>
<td>This study</td>
<td></td>
</tr>
<tr>
<td>Kaohsiung Harbor (E2), Taiwan</td>
<td>2020-2022</td>
<td>Industrial/ Harbor</td>
<td>Industrial and ship/vehicle emission</td>
<td>C₂-VOCs, Toluene, Acetone, Isopentane, m,p-Xylene</td>
<td>This study</td>
<td></td>
</tr>
</tbody>
</table>

Note: *: these studies only measured BTEX compounds.

**: this study identified 174 VOC compounds, but only BTEX concentration was quantified.
3.3 Source Apportionment

3.3.1 Diagnostic ratios

Previous studies used diagnostic ratios like benzene-to-toluene (B/T) to assess VOC origins and air mass aging (Kumar et al., 2018; Li et al., 2020). In particular, B/T values exceeding 0.5 indicate a source related to vehicle exhaust emissions (Nelson & Quigley, 1984). Conversely, B/T values below 0.5 indicate contributions from other sources, with values below 0.1 suggesting strong industrial sources nearby (Kumar et al., 2018; Niu et al., 2012). In this study, B/T ratios (Table 2) varied between 0.1 – 0.2, suggesting a mixed source of industrial and vehicular emissions, with a dominant industrial contribution. A previous study by Chen et al. (2005) at Kaohsiung discovered that the petrochemical sector and vehicle emissions are primary producers of VOCs. Thus, the higher contribution of industrial activities compared to vehicle exhaust/shipping transport could be related to improvements in vehicle exhaust control in Kaohsiung harbor.

Another critical diagnostic ratio is xylene-to-ethylbenzene (X/E) ratio (Yurdakul et al., 2018), which helps assess the age of VOCs in the atmosphere based on the differential reactivity of xylene and ethylbenzene with OH radicals (Elbir et al., 2007; Yurdakul et al., 2013). An X/E value significantly below 3 suggests a greater likelihood of reactions involving xylene and OH radicals, shorter VOC persistence in the surrounding air, and the presence of aged air masses (Yurdakul et al., 2018). Table 2 reveals that the average X/E values consistently exceeded 3, indicating relatively fresh air pollutants in harbor. Calculated B/T ratios were below 0.4, and X/B ratios exceeded 1.1, suggesting that air parcels at three harbor locations were relatively fresh. Therefore, the dominant origins of VOCs in this harbor are likely to be local industrial operations and ship/vehicle emissions.
Table 2. Diagnostic ratios at three sampling sites during the three years of sampling.

<table>
<thead>
<tr>
<th>Sampling Periods</th>
<th>Sampling locations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E2</td>
</tr>
<tr>
<td></td>
<td>B/T</td>
</tr>
<tr>
<td>2020</td>
<td>0.2</td>
</tr>
<tr>
<td>2021</td>
<td>0.3</td>
</tr>
<tr>
<td>2022</td>
<td>0.2</td>
</tr>
</tbody>
</table>

3.3.2 Source apportionment by PMF

Figure 4 shows four distinct factors that PMF model identified. Factor one contributed to 30.6% of TVOCs. Aromatic compounds, C2-VOCs, n-decane, and n-undecane contributed more than 50% in this factor. These compounds, commonly found in gasoline as reported in the SPECIATE database (version 5.2) from USEPA (2022), were also linked to vehicular emission in the study of Cai et al. (2010). Aromatics and alkanes were also reported as the primary VOC emissions from ships at berths (Huang et al., 2018; Xiao et al., 2018). Specifically, ethylene, n-nonane, n-decane and n-undecane, identified as distinctive markers of ship emissions in studies by Wu et al. (2020) and Xiao et al. (2018). Furthermore, n-nonane emerged as a predominant species in gasoline and diesel vehicle exhaust across various cities (Liu et al., 2023; Song et al., 2018). Thus, factor 1 was classified as vehicle and ship emissions in the nearby region.

Factor two counted for 33.7% of TVOCs and was characterized by significant percentages of acetone, 2-butanone, 1-butene, dichloromethane, dichlorofluoromethane, chloromethane, and C2-VOCs. Acetone is used as a solvent or ingredient in various manufacturing sectors. 1-butene and C2-VOCs can come from refinery plants (Chiang et al., 2007) and petrochemical industries (Mo et al., 2015), respectively, the primary industrial sector around the harbor area. C2-VOCs and
chloromethane could also indicate coal and biomass burning (Li et al., 2014; Liu et al., 2022), a primary process in the nearby coal-fired power plant. Halogenated VOCs were primarily attributed to industrial and commercial origins and discharges from wastewater treatment facilities (Yang et al., 2019), which were prevalent close to the harbor, such as the United Sewage Treatment Plant. Thus, factor 2 was attributed to industrial activities.

Factor three represented 14.6% of TVOCs and featured notable percentages of pentane, n-nonane, cyclohexane, n-propylbenzene, and 2-methoxy-2-methyl-propane. These compounds were commonly found in gasoline, as reported in the SPECIATE database (version 5.2) from USEPA (2022). Among them, pentane, which contributed almost 90% to this factor, emitted through gasoline evaporation associated with traffic emissions (Bari et al., 2015). Furthermore, 2-methoxy-2-methyl-propane was a typical gasoline additive (McCarthy et al., 2013). Thus, this factor was identified as fuel evaporations.

Factor four comprised 21.1% of TVOCs and was characterized by a notable percentage of isopentane, ethyl acetate, and toluene. Isopentane could relate to chemical manufacturing volatilization (USEPA, 2022), which can be found easily in the harbor area. Ethyl acetate is a solvent and an organic raw material for coatings and plastics (Nguyen et al., 2021), primarily deriving from its extensive usage as an industrial solvent, particularly within the sector of petrochemicals (Yang et al., 2019). Toluene was particularly important because they were the most common VOCs in urban and industry (Shuai et al., 2018), originating from the painting and petrochemical industry (Marč et al., 2015). The results corresponded with local origins such as the Taiwan International Shipbuilding Corporation, Dalin refinery plant, China Petrochemical Development Corporation. Thus, this factor was categorized as solvent usages.
Fig. 4. Sources of VOCs in Kaohsiung harbor based on PMF model.
3.4 Ozone Formation Potential

VOCs and NOx act as precursors in photochemical atmospheric reactions that create ozone (Doak et al., 2021). The potential for ozone formation (OFP, $\mu g \text{ O}_3 \text{ m}^{-3}$) can be computed using the values of maximum incremental reactivity (MIR, $\mu g \text{ O}_3 \mu g \text{ VOC}^{-1}$) as the following equation.

$$\text{OFP}_i = \sum (C_{\text{VOC}_i} \times \text{MIR}_i)$$ (6)

where $\text{VOC}_i$ is the individual VOC concentration ($\mu g \text{ VOC m}^{-3}$), and values of MIR$_i$ were developed and updated by Carter (2010).

![Ozone formation potential](image)

**Fig. 5.** The contribution groups to ozone formation potential during three-year sampling at the Kaohsiung Harbor.
Figure 5 shows the formation potential of ozone trends in the harbor during three-year sampling. The average OFP values in 2020, 2021, and 2022 were within the range of $262.8 \pm 42.3$, $195.7 \pm 104.7$ and $206.8 \pm 36.0 \mu g O_3 m^{-3}$, respectively. During three years, the highest OFP values were consistently observed at KEPZ, followed by E2 and E1. This spatiotemporal variation of OFP indicated a similar trend with TVOC concentration. Pearson correlation analysis between individual VOC concentration and its contribution to OFP also shows a strong correlation ($r=0.88-0.90$). These findings are similar to the study of Le et al. (2023), who also observed a significant correlation between VOC concentration and OFP.

Notably, during three-year sampling period, aromatic compounds emerged as the primary contributors to OFP in Kaohsiung Harbor (Fig. 5). Although $C_2$-VOCs and alkanes were frequently detected in the area, elevated OFP was mainly attributed to aromatic compounds like toluene, xylene, and 1,2,4-trimethylbenzene. Specifically, average contribution for three years highlighted toluene as the primary OFP contributor, accounting for an average of 30.4%. A study by Yuan et al. (2022a) supported toluene as the most promising photochemical precursor for ozone formation in Kaohsiung City. The contribution of toluene was followed by $C_2$-VOCs at 16.2% and m/p-xylene's at 12.5%, collectively contributing nearly 60% to OFP. $C_2$-VOCs, comprising ethane, ethene, and acetylene, have different MIR values (0.28, 9.00, and 0.95, respectively). In research in New Taipei City, Taiwan, Chang et al. (2016) found that ethane had the highest contribution to TVOC concentrations, followed by ethene and acetylene. In this study, despite acetone significantly contributing to TVOC concentrations, its impact on OFP was minimal. This indicates that presence in high concentrations might not considerably affect ozone formation. Therefore, to accurately assess OFP, it is essential to analyze and calculate ethane, ethene, and acetylene.
separately. Monitoring aromatic compounds, particularly toluene, and m/p-xylenes, along with C2-VOCs, is crucial to mitigate ground-level ozone formation in the study area.

### 3.5 Health Risk Assessment

**Fig. 6.** The carcinogenic risk (a) and non-carcinogenic risk (b) results of VOCs in ambient air during three years in Kaohsiung harbor.

According to the U.S. EPA health risk assessment approach, the suggested safety threshold for carcinogenic risk in the general adult population is $1.0 \times 10^{-6}$, regarded as acceptable. The top 6 carcinogenic risk compounds were presented in Fig. 6a. The carcinogenic risk assessment revealed that the carcinogenic risk values for the six most prominent compounds fell within the range of $2.2 \times 10^{-9}$ to $3.4 \times 10^{-6}$ in the study area. Notably, only 1,2-dichloroethane exceeded the threshold of $1.0 \times 10^{-6}$ for carcinogenic risk throughout the three-year observation period (Fig. 6a), while 1,3-butadiene indicated a high risk only in 2020. The preceding analysis indicates that these VOCs carry specific carcinogenic risks and could harm human health. Therefore, particular attention must be paid to 1,2-dichloroethane, a compound frequently employed in the production of vinyl chloride and as a solvent, as well as 1,3-butadiene, a dangerous chemical mainly utilized in the manufacturing of synthetic rubber and plastics. Their potential source could be plastic and
rubber manufacturing, petrochemical material manufacturing, and chemical plants, primarily located at the export processing zone and Linhai Special Industrial Complex, as indicated in Fig. 1. Taking precautions to prevent prolonged exposure is essential, especially when air pollution incidents occur. The government should enhance and regulate industrial emission sources that emit large amounts of 1,2-dichloroethane and 1,3-butadiene to protect human beings in the study area.

Regarding the consideration of the synergism effect in this health risk assessment, it is important to note that the current analysis primarily focused on evaluating individual carcinogenic risks of each VOC independently. Synergism, where the combined impact of multiple chemicals may be greater than the sum of their individual effects, was not explicitly accounted for. This is a critical consideration because interactions between different chemicals can significantly alter the overall risk profile. Incorporating synergistic effects requires comprehensive interaction data for the compounds in question, which is often not readily available. The complexity and variability of potential interactions between multiple VOCs further complicate this analysis. Thus, future studies should aim to include synergistic interactions to provide a more comprehensive risk assessment.

The Hazard Quotient (HQ) is a numerical value used to assess the risk of non-carcinogenic health effects from exposure to hazardous substances. In health risk assessments, the HQ helps to determine whether the exposure level to a specific chemical is likely to cause adverse health effects. If the HQ is less than or equal to 1, it suggests that the exposure is unlikely to cause harmful non-carcinogenic effects. If the HQ exceeds 1, there may be a potential risk of adverse health effects, and further evaluation or mitigation measures may be necessary. In this study, HQ as an indicator for non-carcinogenic risk is shown in Fig. 6b. The outcomes of non-carcinogenic risk evaluation indicated that the hazard quotient (HQ) values for the six most prominent VOCs ranged from $1.9 \times 10^{-6}$ to $3.2 \times 10^{-5}$. These values are significantly below 1, indicating that the non-
carcinogenic health risks from these VOCs are minimal. Moreover, the cumulative non-
carcinogenic hazard index (HI) did not surpass 1 during the last three years in any sampling period.

This suggests that the non-carcinogenic risks remained at a relatively low level and within
acceptable safety margins. Nevertheless, despite the relatively low non-carcinogenic risk, it is
important to note that the absence of non-carcinogenic risk cannot be conclusively asserted due to
limited sampling duration VOCs. Other than cancer risk is concerned by 1,2-dichloroethane and
1,3-butadiene, non-cancer risk is generally not an emerging concern.

4 CONCLUSIONS

This study analyzed VOCs in Kaohsiung Harbor during the severe air pollution period from
2020 to 2022. It investigated VOC characteristics, sources, ozone formation potential, and health
risks. During three sampling periods, the dominant VOC at the harbor were C2-VOCs, toluene,
and acetone. The most polluted site varied throughout time, possibly due to changes in industrial
and port activities. A comparison of the criteria air pollutants concentration at three sampling sites
suggested that site E2 experienced higher ship emissions, while site KEPZ had a significant
contribution from vehicle exhaust. Meteorological factors like wind speed and precipitation had
minimal impact on VOC variations during the sampling periods. Additionally, industrial activity
(33.7%) and vehicle/ship emissions (30.6%) accounted for more than 60% of VOCs in this harbor.
Furthermore, there was a significant positive relationship between VOCs and OFP; toluene was
the most potential contributor. For the health risk assessment, compounds like 1,2-dichloroethane
and 1,3-butadiene were identified as carrying significant cancer risks. The carcinogenic risk values
for these compounds ranged from $2.2 \times 10^{-9}$ to $3.4 \times 10^{-6}$, with 1,2-dichloroethane consistently
exceeding the safety threshold of $1.0 \times 10^{-6}$ throughout the three-year observation period. This
indicates a potential health risk requiring regulatory attention and mitigation. Meanwhile, the HQ
values indicated low non-carcinogenic risks for the VOCs studied. Despite these low non-carcinogenic risks, continued monitoring and assessment are essential, considering the limitations of the sampling duration and potential for other unassessed risks. Some concerned compounds such as toluene, 1,2-dichloroethane, and 1,3-butadiene likely originate from industrial activities like metal smelting, coking, plastic/rubber production, and petrochemical manufacturing in the export processing zone and Linhai Industrial Zone. Government authorities must enhance regulations on industrial emissions, mainly from significant sources of VOCs, to reduce ozone formation and health risks. A comprehensive VOC control strategy is vital for improving air quality and visibility, especially during winter in Kaohsiung. Compared to other areas, the sources of VOCs in industrial harbors like Kaohsiung Harbor require further in-depth investigation and discussion for effective solutions.

**STUDY LIMITATIONS**

The limitations of this study should be acknowledged. While diagnostic ratios are useful for identifying VOC sources, their effectiveness can be compromised by atmospheric reactions and varying environmental conditions, leading to potential misidentification. PMF relies heavily on the quality and representativeness of the input data, and any inaccuracies can affect the results. PMF outputs can also vary based on the selection of factor numbers and initial conditions, necessitating further validation with independent datasets and complementary methods. The calculation of OFP offers insights into VOC contributions to ozone formation but is based on theoretical reactivity scales that may not fully capture real atmospheric interactions. Practical application of OFP requires consideration of local meteorology, VOC mix, and existing background ozone levels. Our health risk assessment focused on individual carcinogenic and non-carcinogenic risks of specific VOCs, using methods like Hazard Quotient (HQ) and Incremental
Carcinogen Risk (ICR). However, it did not account for synergistic effects of multiple VOCs, and the limited sampling duration may not fully reflect long-term exposure trends. Additionally, variability in population exposure patterns was not thoroughly addressed. These limitations highlight the need for comprehensive approaches in future studies, including longer sampling periods, more detailed exposure assessments, consideration of synergistic interactions, and validation of PMF results with independent datasets.

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