



Enhanced emission of intermediate-volatility/ semi-volatile organic matter in gas and particle phases from ship exhausts with low-sulfur fuels

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Received: 5 November 2024 – Discussion started: 14 November 2024

Revised: 3 March 2025 – Accepted: 25 March 2025 – Published: 10 July 2025

Abstract. The widespread utilization of low-sulfur fuels in compliance with global sulfur limit regulations has significantly mitigated the emissions of sulfur dioxide (SO₂) and particulate matter (PM) on ships. However, significant uncertainties still persist regarding the impact on intermediate-volatility/semi-volatile organic compounds (I/SVOCs). Therefore, onboard tests of I/SVOCs from three ocean-going vessels (OGVs) and four inland cargo ships (ICSs) with low-sulfur fuels ($< 0.50\% \text{ m/m}$) in China were carried out in this study. Results showed that the emission factors of total I/SVOCs were 881 ± 487 , 1181 ± 421 , and 1834 ± 667 mg per kg fuel for OGVs with heavy fuel oil (HFO), marine gas oil (MGO), and ICSs with no. 0 diesel, respectively. The transition from low-sulfur-content ($< 0.50\% \text{ m/m}$) to ultra-low-sulfur-content ($< 0.10\% \text{ m/m}$) fuels had evidently enhanced the emission factor of I/SVOCs, with unignorable contributions from particle-phase I/SVOCs, thereby further amplifying the secondary organic aerosol formation potential (SOAFP). Fuel type, engine type, and operating conditions comprehensively influenced the emission factor level, compositions, and volatility distribution of I/SVOCs. Notably, a substantial proportion of fatty acids had been identified in ship exhausts, necessitating heightened attention. Furthermore, organic diagnostic markers of hopanes, in conjunction with the C_{18:0}-to-C_{14:0} acid ratio, could be considered potential markers for HFO exhausts. The findings suggest that there is a need to optimize the implementation of a global policy on ultra-low-sulfur oil in the near future.

1 Introduction

Ship transportation plays a critical role in global trade, as it accounts for over 80 % of the total cargo transport worldwide due to its substantial carrying capacity and cost-effectiveness (Zhang et al., 2016, 2021). Consequently, the expansion of the global economy has led to an increasing impact on air quality, human health, and various other aspects due to the emission of gaseous and particulate pollutants from ship exhausts (Zhang et al., 2018a, 2014; Liu et al., 2022). Over the past 2 decades, extensive studies have been carried out on the characteristics of various vessel pollutants, including sulfur dioxide (SO_2), nitrogen oxide (NO_x), particulate matter (PM), carbon dioxide (CO_2), and volatile organic compounds (VOCs) (Davis et al., 2001; Liu et al., 2022). Results show that shipping emissions are responsible for 2 %–5 % of fine particulate matter ($\text{PM}_{2.5}$) (Kramel et al., 2021); CO_2 from ships accounts for around 3 % of the total global CO_2 emission (Faber et al., 2020), while the NO_x from ships contributes approximately 15 % of the total global atmospheric NO_x emissions (Faber et al., 2020). Besides, the employment of high-sulfur fuel (HSF, $\geq 0.50 \text{ \% m/m}$) has resulted in a significant emission of SO_2 from ship exhausts, which accounts for approximately 14 % of global anthropogenic SO_2 emissions (Zhou et al., 2019). Specifically, the consumption of heavy fuel oil constitutes 70 % of total ship fuel usage (International Maritime Organization, 2016), which is primarily responsible for the majority of SO_2 emissions associated with global shipping. This has considerable effects on coastal regions and the marine environment.

Given all this, the International Maritime Organization (IMO; additional abbreviations and their corresponding full names are provided in Table S1 in the Supplement) has been continuously revising the International Convention for the Prevention of Pollution from Ships (MARPOL) since 1997, progressively imposing stricter sulfur limits on marine fuels. Following the guidelines of Annex VI to the MARPOL, the limit for sulfur content in ship fuels has been set at 0.50 % (m/m) since 2020 globally, or alternative measures such as exhaust scrubbers must be employed (International Maritime Organization, 2016). In designated Sulfur Emission Control Areas (SECAs, including the North Sea, the Baltic Sea, North America, and the United States Caribbean), this limit has been further restricted to below 0.10 % (m/m) since 2015. In certain SECAs, the utilization of exhaust scrubbers as an alternative treatment method to low-sulfur fuel is not even acceptable. Numerous countries are undergoing a transition in their shipping practices, shifting from high-sulfur fuels to low-sulfur or ultra-low-sulfur alternatives (Liu et al., 2019; Zhang et al., 2024, 2021). Within China, emission standards vary across regions, with specific requirements tailored to each area. Typically, the fuel oil regulations of China have been able to mandate that vessels maintain sulfur content at below either 0.50 % (m/m) in SECAs since 2019 or 0.10 % (m/m) in inland areas and specific control regions

since 2020 when utilizing fuel. In brief, the global mandatory use of ultra-low-sulfur-content fuel ($< 0.1 \text{ \% m/m}$) or alternative measures is an inevitable trend in the near future.

Previous studies have indicated that the low-sulfur-fuel regulation is an effective measure for reducing SO_2 and PM mass emission in many countries. For example, Lehtoranta et al. (2019) demonstrate that the change of fuel from high sulfur to lower sulfur has significantly decreased the PM emissions. The global shipping emissions have been quantified by Sofiev et al. (2018) using the Ship Traffic Emissions Assessment Model (STEAM). Their finding reveals a positive correlation between the implementation of a reduced sulfur fuel strategy and reductions in both SO_2 and PM levels. However, even though studies have shown that the low-sulfur-fuel policy may reduce emissions of PM and SO_2 , it could lead to an increase in VOCs and intermediate-volatility organic compounds (IVOCs) (Sofiev et al., 2018; He et al., 2022a; Shen et al., 2023; Liu et al., 2022). The impact of fuel quality on organic compounds, such as VOCs and intermediate-volatility/semi-volatile organic compounds (I/SVOCs), remains uncertain.

VOCs are a topic of growing interest due to their crucial role as common precursors of secondary organic aerosols (SOAs) and ozone (O_3) (Shen et al., 2023; Hui et al., 2019). Additionally, the aging process of VOCs and the resulting intermediates also play pivotal role in SOA formation (He et al., 2023; Srivastava et al., 2022). Recently, numerous studies have unveiled a substantial gap between measured SOAs and theoretical calculated SOAs, with the primary cause being attributed to the neglect of I/SVOCs (Fang et al., 2021; Knote et al., 2015). For example, the study conducted by An et al. (2023) integrates an emission inventory of I/SVOCs into the Community Multiscale Air Quality (CMAQ) modeling system to simulate the characteristics of primary organic aerosols (POAs) and SOAs originating from various sources within the Yangtze River Delta (YRD) region. Their findings reveal a significant 148 % increase in predicted SOA concentrations. Wu et al. (2019) employ the Weather Research and Forecasting Model coupled with Chemistry (WRF-Chem) to organize the 2010 I/SVOC emission inventory in the Pearl River Delta (PRD) region of China, revealing a substantial 161 % increase in SOA concentration. However, there is still a significant dearth of measured I/SVOCs from various sources, leading to substantial uncertainty in the estimation of inventory and estimation of SOAs. Clarifying the contribution of I/SVOCs from different sources to SOA formation is crucial for a comprehensive understanding of their role in atmospheric processes and their impact on air quality (He et al., 2024; Srivastava et al., 2022).

In recent years, several studies have reported measured data of organic compounds with varying volatility emitted from ships. Although progress has been achieved in shipping I/SVOC measurement, a comprehensive understanding of their characteristics and their contribution to SOA formation remains incomplete, particularly in light of increas-

ingly stringent global emission control regulations. Previous studies mainly focus on gas-phase VOCs and IVOCs, which might underestimate the emissions of particle-phase I/SVOCs (Huang et al., 2018a; Zhang et al., 2018b, 2024). Particulate I/SVOCs can also form SOA after being transferred to the gaseous state through evaporation and undergoing atmospheric oxidation (Srivastava et al., 2022; Liu et al., 2022). In addition, the qualitative analysis of particle-phase I/SVOCs in ship exhaust focuses more on detecting and evaluating of *n*-alkanes and 16 polycyclic aromatic hydrocarbons (PAHs) based on limited previous studies, with little emphasis on other species of I/SVOCs (Liang et al., 2022; Perrone et al., 2014). In brief, there is a lack of simultaneous measurement data on detailed low-volatility organic compounds in gas and particle phases, which could be beneficial to the accurate evaluation of SOA and O₃ formation potentials. Moreover, the effects resulting from the implementation of low-sulfur-fuel policies on shipping I/SVOC emission characteristics remain unclear, particularly regarding the utilization of ultra-low-sulfur fuels ($\leq 0.1\%$, *m/m*). There is an urgent need to update emission factors and component profiles of full-volatility particulate organic compounds, as this is crucial for reducing uncertainties in I/SVOCs inventory estimation and providing fundamental data for formulating optimal emission control policies for ships, considering their comprehensive impacts on various pollutants.

Therefore, typical ocean-going vessels (OGVs) and inland cargo ships (ICSs) with different types of fuels in China were selected for onboard measurement in this study. Gas-phase and particle-phase I/SVOCs were collected synchronously from ship exhausts with different low-sulfur fuels under different engine conditions. A comprehensive analysis was conducted on the emission factor, volatility, profile, and influence factors of I/SVOCs. Besides, the SOA formation potential (SOAFP) of I/SVOCs from the test ships was also estimated based on the measured data.

2 Material and methods

2.1 Test ships and fuels

Onboard tests of seven typical Chinese cargo ships have been carried out in this study, including three large ocean-going vessels and four small inland cargo ships. Detailed comprehensive parameters of the test ships can be found in Table S2 in the Supplement. The OGVs were equipped with two types of engines: one was a two-stroke main engine (ME) and the other was a four-stroke auxiliary engine (AE). Meanwhile, the ICSs only had one four-stroke main engine. Low-sulfur-content heavy fuel oil (HFO) and ultra-low-sulfur marine gas oil (MGO) were used as fuels of OGVs, while no. 0 diesel with ultra-low sulfur content was used for ICS engines. The detailed parameters of fuels used in this study are shown in Table 1. It should be acknowledged that all those fuels complied with the latest regulations issued by both IMO and

China. The engines tested in this study were not equipped with any aftertreatment devices.

2.2 Sampling system

Real-world measurements of pollutants from vessels under different operating conditions were conducted by a combined sampling system in this study. Vessel exhaust in sampling was passed through a dilution system followed by various connected samplers (Fig. S1 in the Supplement). Detailed information was described in previous studies (Zhang et al., 2016, 2024). Briefly, two separate sampling pipes were utilized to direct emissions from the main engine and auxiliary engine stacks, respectively. A flue gas analyzer probe (Testo 350, testo, Germany) was then inserted into the sampling pipe to directly measure gaseous pollutants for on-line data collection (CO₂, O₂, CO, NO, NO₂, SO₂). Another probe was used to extract flue gas for dilution. PM samples (total suspended particles) were collected using particulate samplers, while gas samples were obtained by employing polyurethane foam. In this study, the dilution ratios varied from 1 to 10 according to operating conditions. A total of 64 sets of gas-phase and particle-phase I/SVOCs samples were collected in this study, involving various engine types, fuels, and operating modes (Table S3 in the Supplement). Offline samples were wrapped in prebaked aluminum foil and stored at -20°C until analysis. Additionally, all samples were analyzed within 2 weeks of sampling.

2.3 Chemical analysis

Organic matter in gas-phase and particle-phase samples in this study was analyzed by gas chromatography–mass spectrometry (GC–MS, Agilent GC 7890B/MS 5977B, HP-5MS). Prior to analysis, the organic fraction was subjected to the analytical method of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) derivatization and spiked with internal standard (tridecane, $3.024\text{ ng }\mu\text{L}^{-1}$). The qualitative analysis was conducted using the National Institute of Standards and Technology (NIST) standard organic mass spectral library queries, in conjunction with their standard compound retention time. Detailed information of analysis and detection process has been described elsewhere (Li et al., 2020, 2016).

A total of 76 specific I/SVOC species were identified and quantified in this study, including 24 *n*-alkanes (C₁₂–C₃₆), 16 polycyclic aromatic hydrocarbons (PAHs), 8 oxygenated polycyclic aromatic hydrocarbons (OPAHs), 17 acids (13 fatty acids and 3 benzoic acids), and 11 hopanes. Detailed information about the identified I/SVOC species is presented in Table S4 in the Supplement. Furthermore, the quantification of branched alkanes (b-alkanes) and unresolved complex mixtures (UCMs) was conducted using a procedure described by previous studies (Zhao et al., 2016, 2014). Given the good linear relationship between carbon number and

Table 1. Parameters of the fuels used in the test ships. N.D. stands for not detected.

	Unit	OGV1 /HFO	OGV1 /MGO	OGV2 /HFO	OGV2 /MGO	OGV3 /HFO	OGV3 /MGO	ICS /no. 0 diesel
Gross calorific value	MJ kg ⁻¹	44.21	45.76	42.62	45.72	43.08	45.64	
Net calorific value	MJ kg ⁻¹	41.45	42.75	40.28	42.71	40.61	42.66	
Kinematic viscosity	(50 °C), mm ² s ⁻¹	44.04						
Kinematic viscosity	(20 °C), mm ² s ⁻¹		5.216	152.3	4.724	161.1	5.363	
Moisture	%m	0.03	N.D.	0.09	N.D.	0.12	N.D.	
Ash	%m							
Sulfur (S)	%m	0.50	0.03	0.43	0.02	0.43	0.05	N.D.
Carbon (C)	%m	86.62	80.80	82.4	79.6	69.9	66.5	85.5
Hydrogen (H)	%m	11.33	8.15	9.68	12.3	11.3	10.61	
Nitrogen (N)	%m	N.D.	N.D.	0.39	N.D.	2.36	N.D.	
Oxygen (O)	%m	0.36	N.D.	1.53	0.59	1.34	0.73	
Vanadium (V)	mg kg ⁻¹			N.D.	0.20	4.00	N.D.	
Nickel (Ni)	mg kg ⁻¹			16.0	0.10	15.0	N.D.	
Sodium (Na)	mg kg ⁻¹			6.00	0.10	8.00	0.10	
Lead (Pb)	mg kg ⁻¹			N.D.	0.30	N.D.	N.D.	
Zinc (Zn)	mg kg ⁻¹			2.00	0.40	8.00	0.20	
Aluminum + silicon (Al + Si)	mg kg ⁻¹			8.00	0.80	12.0	0.90	

volatility of *n*-alkanes, the relative response factor (RRF) of *n*-alkanes was used as the surrogate for b-alkanes and UCMs to estimate their concentrations. The volatility classification of each substance is distinguished based on its carbon number. Generally, compounds with carbon numbers of 12–22 (C₁₂–C₂₂) are classified as IVOCs, while those with carbon numbers of 23–36 (C₂₃–C₃₆) are considered SVOCs (Zhao et al., 2014; Fujitani et al., 2020).

2.4 Emission factor

Fuel-based emission factors were provided and discussed in this study using the carbon balance method. It is assumed that, under ideal conditions, all carbon in the fuel will undergo complete conversion into carbon present in CO₂, CO, organic carbon (OC), and elemental carbon (EC) following combustion. OC and EC were analyzed using an OC/EC analyzer (Model 4, Sunshine Lab). The CO₂ emission factor was derived using the following formula:

$$EF_{CO_2} = \frac{c_F \times \Delta(CO_2)}{\Delta(cCO_2) + \Delta(cCO) + \Delta(cOC) + \Delta(cEC)}, \quad (1)$$

where EF_{CO_2} is the emission factor of CO₂ (g per kg fuel); $\Delta(CO_2)$ indicates the CO₂ mass level after adjustment for environmental background (g m⁻³); c_F is the carbon content of fuel (g per kg fuel); and $\Delta(cCO_2)$, $\Delta(cCO)$, $\Delta(cOC)$, and $\Delta(cEC)$ represent the mass carbon concentrations of CO₂, CO, OC, and EC following the deduction of the background (g m⁻³), respectively.

$$EF_x = \frac{\Delta X_x}{\Delta CO_2} \times \frac{M_x}{M_{CO_2}} \times EF_{CO_2}, \quad (2)$$

where EF_x (g per kg fuel) represents the emission factor for species *x*; ΔX_x and ΔCO_2 (mol m⁻³) are the concentrations of species *x* and CO₂ after background correcting; and M_x and M_{CO_2} express the molecular weights of species *x* and CO₂, respectively.

2.5 SOA formation potential

The organic compounds in this study were categorized into two classes based on volatility: bins 12–22 were defined as IVOCs and bins 23–36 were defined as SVOCs, corresponding to C₁₂–C₂₂ and C₂₃–C₃₆, respectively. The equation utilized for the estimation of SOA production via IVOCs in this study is as follows:

$$\Delta SOA_{IVOCs} = \sum_j [HC_j] (1 - e^{-k_{OH,j}[OH]\Delta t}) \times Y_j, \quad (3)$$

where $[HC_j]$ represents the concentration of IVOC species involved in the reaction, Y_j is the yield coefficient of IVOC species, and k_{OH} is the OH reaction rate constant of precursor *j* at 25 °C (cm³ molec.⁻¹ s⁻¹); $[OH]$ is the OH concentration (molecules cm⁻³), which is assumed in this study to be 1.5×10^6 molecules cm⁻³; Δt is the photochemical age (h); and Y_j is the SOA mass yield of precursor *j*. The OH reaction rate constants (cm³ molec.⁻¹ s⁻¹) and SOA yields used in this study are the same as those in Zhao et al. (2016), which reacted (Δt) after 48 h photo-oxidation at the OA concentration of 9 µg m⁻³; the specific values of Y_j and k_{OH} under different environmental conditions were obtained from the simulation study of the smoke chamber (Tables S5 and S6 in the Supplement).

The equation for estimating SOA yield based on SVOCs is as follows:

$$\Delta\text{SOA}_{\text{SVOCs}} = \sum_j (\Delta X_j \cdot Y_j), \quad (4)$$

where ΔX_j is the reaction mass of the compound in the j interval after partitioning, based on its saturation concentration, and Y_j is the respective SOA yield. The study employed a conservative calculation method and identified the UCM as the n -alkane component with the lowest SOA yield. Additionally, the yield coefficients of C_{23} and higher, which were not included in the relevant parameters, were cautiously replaced with those of C_{22} .

2.6 Quality assurance and quality control

PAHs stipulated by EPA in the United States were used for recovery experiments, and the recovery rate of PAHs was 82 %–115 %. Before conducting GC–MS measurements, n -hexane was injected prior to each measurement in order to ensure a stable baseline and clean column. Subsequently, standard samples were introduced into the instrument for calibration purposes. The quantitative error of the target compound concentration was ensured to be less than 5 % by randomly re-testing one sample after every 20 samples. Moreover, the calibration of target compounds was performed through simultaneous measurement of blank samples to eliminate any potential experimental contamination.

3 Results and discussion

3.1 Emission factors for total I/SVOCs ($\text{EF}_{\text{I/SVOCs}}$)

Figure 1 presents the total $\text{EF}_{\text{I/SVOCs}}$ in gas and particle phases for OGVs and ICSs under different engine types and fuels. Obviously, OGVs had lower I/SVOC emission factors than ICSs. The average total emission factors for total IVOCs (EF_{IVOCs}) of OGVs and ICSs were 512 ± 292 and 784 ± 517 mg per kg fuel, respectively, while the average total emission factors for total SVOCs (EF_{SVOCs}) of OGVs and ICSs were 520 ± 268 and 1050 ± 817 mg per kg fuel, respectively. The ICSs with no. 0 diesel exhibited the highest level of IVOC emissions (784 ± 587 mg per kg fuel), followed by OGVs with MGO (651 ± 367 mg per kg fuel), while OGVs with HFO showed the lowest levels (373 ± 218 mg per kg fuel). When it came to SVOCs, ICSs with no. 0 diesel (1050 ± 817 mg per kg fuel) were still the highest, followed by OGVs with MGO (530 ± 170 mg per kg fuel), and OGVs with HFO (509 ± 365 mg per kg fuel) still showed the lowest level. It could be seen that the switch of fuels from HFO to MGO had enhanced the emission of IVOCs and SVOCs.

Recently, IVOCs from ships have gained more and more attention. The average EF_{IVOCs} in this study exhibited a comparable yet slightly diminished level when compared to previous onboard measurement results obtained from OGVs. For instance, Huang et al. (2018a) quantified the IVOCs

from an OGV and showed that the total EF_{IVOCs} value was 1003 mg per kg fuel. The average EF_{IVOCs} value from low-sulfur fuel was 2.4 times higher than that from high-sulfur fuel. The IVOC data measured from the same tested OGVs in this study were also provided by Liu et al. (2022), revealing EF_{IVOCs} of 1830.5 and 1494.4 mg per kg fuel for MGO and HFO, respectively. It is worth noting that the EF_{IVOCs} measured in this study were lower compared with results from Liu et al. (2022), which was mainly due to different analysis methods. The thermo desorption–gas chromatography/mass spectrometry (TD-GC/MS) method was employed for the analysis of IVOCs extracted from adsorption tubes in the study conducted by Liu et al. (2022). In order to maximize the identification of species, this study employed organic solvent extraction coupled with the BSTFA derivatization method; however, it is important to note that this approach may potentially underestimate the total IVOCs. Other studies also reported EF_{IVOCs} from different ship engines with different fuels. For instance, Lou et al. (2019) conducted a study on the gaseous IVOCs emitted from a main ship engine using HFO and demonstrated that the EF_{IVOCs} ranged from 20.2 to 201 mg per kg fuel on average. Moreover, Su et al. (2020) conducted a series of tests on fuels of waste cooking oil (WCO) and MGO at the auxiliary engine test bench. They found that the total EF_{IVOCs} of MGO and WCO were 2.33 ± 0.43 and 1.47 ± 0.17 mg per kg fuel, respectively, at 75 % engine load. The findings from these studies have demonstrated that the emission of IVOCs from ships can be influenced by a multitude of influence factors, encompassing vessel types, fuel compositions, and navigation conditions. However, limited research has been conducted on the comprehensive emission factors of SVOCs and their constituents emitted from ships, which also need more attention due to their non-negligible contribution to SOA and O_3 formation (Robinson et al., 2007).

Figure 1 also illustrates the gas–particle partitioning of I/SVOCs from ship exhausts in this study under low dilution ratios. Results showed that almost all I/SVOCs in the gas phase had higher emission levels compared to the particle phase except for SVOCs in HFO MEs. Previous studies focused on gaseous I/SVOC emissions of ship exhausts and indicated that the gas-phase I/SVOCs played a crucial role in atmospheric chemical reactions and aerosol formation processes (Liu et al., 2022; Lou et al., 2019). However, the contribution of I/SVOCs from particles still could not be ignored. For example, the contribution of particle-phase I/SVOCs to the total I/SVOCs could reach 16 %–50 % in this study. Previous study has shown that they could continue to contribute to the formation of SOA and O_3 largely through evaporation and oxidation in the atmosphere (Drozd et al., 2021). Even though particle-phase reactions generally occur more slowly than gas-phase reactions due to limitations imposed by oxidant diffusion and absorption into aerosols (An et al., 2023), it still could be implied that particle-phase I/SVOCs were similarly important precursors of SOA and O_3 . The emis-

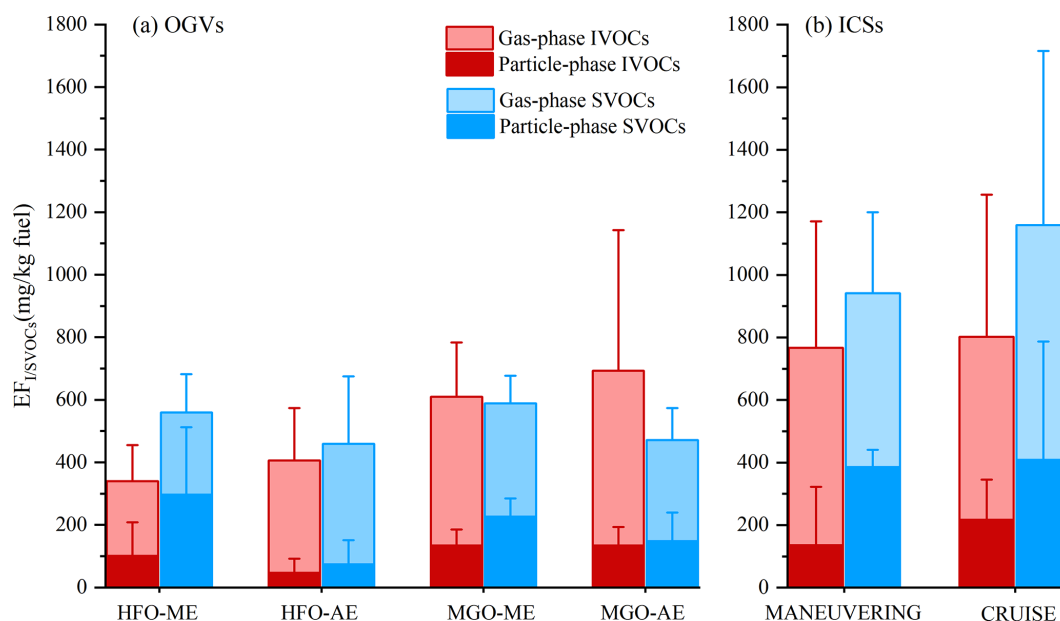


Figure 1. Emission factors of I/SVOCs in the gas phase and the particle phase for (a) OGVs and (b) ICSs.

sions of total I/SVOCs from ships in gas and particle phases should be thoroughly considered, as this could potentially enhance the accuracy of simulation results for the formation of SOA and O₃.

3.2 Influence factors of I/SVOCs

The EFs for I/SVOCs emitted from ship exhausts exhibited significant variations under real-world conditions, as illustrated in Fig. 1. In order to explore the impact of low-sulfur-fuel policy on I/SVOCs, EF_{I/SVOCs} with different oil products (HFO, MGO, and no. 0 diesel) were given and discussed in this study (seen in Fig. 2a). Besides, EF_{I/SVOCs} across diverse engine types (main engine (ME) and auxiliary engine (AE)) and various operating conditions (25 %–90 % operating modes of OGVs, cruise and maneuvering of ICSs) were also investigated (seen in Fig. 2b and c). Results showed that fuel type had a considerable impact on the emission of I/SVOCs (Fig. 2a). EF_{I/SVOCs} with no. 0 diesel presented the highest levels, followed by MGO, while HFO had the lowest EF_{I/SVOCs}. The mean EF_{I/SVOCs} of no. 0 diesel, MGO, and HFO were 1834 ± 667 , 1181 ± 421 , and 881 ± 487 mg per kg fuel, respectively. It was a noteworthy observation that a decrease in sulfur content of the fuel corresponded to an increase in EF_{I/SVOCs} levels, as demonstrated by this study. Furthermore, relevant studies have also shown that the transition from high-sulfur to low-sulfur fuels resulted in an elevation of emission factors for both VOCs and IVOCs. For instance, Wu et al. (2020) reported a 15-fold increase in EF_{VOCs} following the transition from high-sulfur ($> 0.5\% m/m$) to low-sulfur fuels, subsequent to the implementation of the low-sulfur policy. Zhang et al. (2021),

Huang et al. (2018a), and Liu et al. (2022) also found negative correlations between sulfur content in fuel and IVOC emissions from ships. The study by An et al. (2023) in the Yangtze River Delta region found that both I/SVOCs and non-methane hydrocarbons (NMHCs) with low-sulfur oil had higher emission factors, which resulted in a high SOA formation potential. This meant that the use of lower-sulfur-content fuels contributed to a significant reduction in SO_x and PM emissions and mitigated their impact on the environment. It also could lead to higher emissions of full-volatility organics during combustion, which had negative impacts on the formation of SOA and O₃ that further affected human health.

Fuel compositions could directly affect the emission characteristics of I/SVOCs. During the combustion of fuel, the generation of I/SVOCs could involve complex processes, such as pyrolysis of organic matter, dehydrogenation, oxygenation, and incomplete combustion (Akherati et al., 2019; Zhao et al., 2014). A large portion of I/SVOCs derived directly from incomplete combustion of fuel (Zhang et al., 2016; Liu et al., 2022). The main components of no. 0 diesel are typically hydrocarbons, including alkanes, cycloalkanes, and aromatic hydrocarbons. These components are mostly within the range of I/SVOCs, mainly composed of complex hydrocarbons ranging from C₁₂ to C₂₂ (Alam et al., 2018). The similar compositions of no. 0 diesel to I/SVOCs might be the primary reason for its highest emission levels. MGO and HFO both belong to marine fuel oil (Corbin et al., 2018). MGO is a kind of light marine diesel, while HFO refers to the black, viscous residue left after distilling lighter fractions such as gasoline, kerosene, and diesel from crude oil, or a blend of the black, viscous residue with lighter fractions

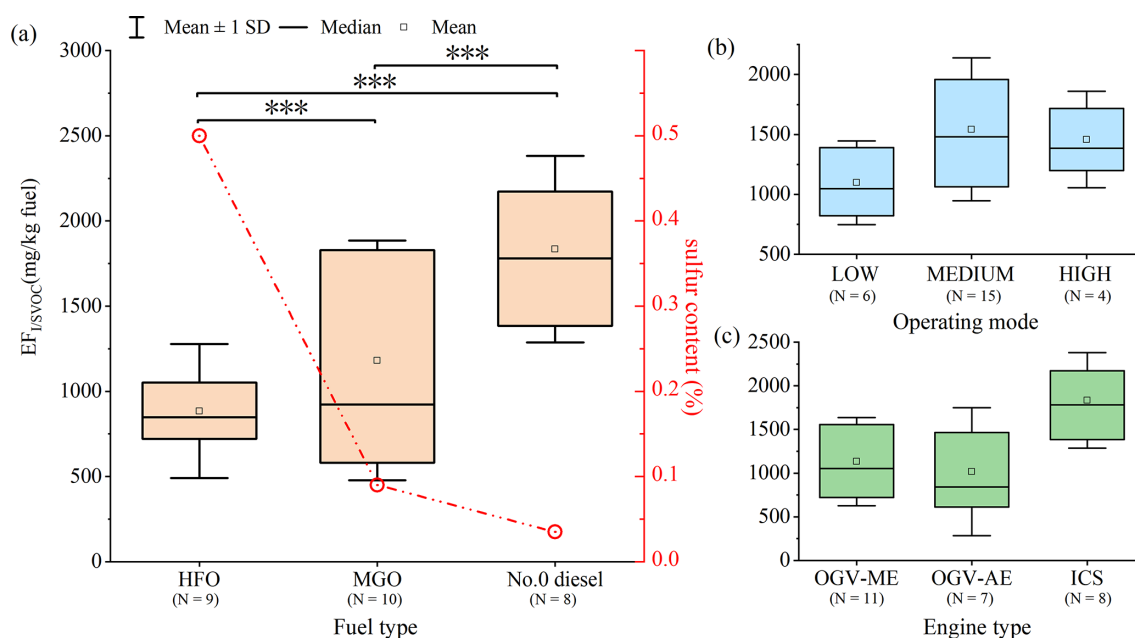


Figure 2. Box-whisker plots of total $EF_{I/SVOCs}$ for the tested ships under (a) different fuel types, (b) different operating modes, and (c) different engine types. N represents the number of samples. Significant differences between samples were determined using an independent samples T test. The error bars represent the standard deviation of the measured values, while *** indicates a significance level of $p < 0.001$.

(Schüppel and Gräbner, 2024). HFO is categorized into HSF and low-sulfur fuel (LSF). HSF were generally utilized before low-sulfur standards were introduced, while LSF have been adopted since these standards were enacted, enabling compliance with stricter environmental regulations through reduced sulfur content. Unless otherwise specified, HFO in this study refers to LSF HFO. Referring to the measured organic compositions of MGO and HFO from Liu et al. (2022), it could be seen that MGO had higher n -alkanes but lower PAHs compared with HFO. This was also one main reason for the higher $EF_{I/SVOCs}$ for MGO than HFO. Moreover, sulfides play a catalytic role in combustion, reducing the ignition temperature of the fuel (Ju and Jeon, 2022). The ignition point of low-sulfur fuel is comparatively higher than that of high-sulfur fuel, thereby necessitating elevated temperatures and increased oxygen input to achieve complete combustion (Dinamarca et al., 2014; Drozd et al., 2019). Therefore, the incomplete combustion might be enhanced for low-sulfur fuel at similar engine loads (Zhao et al., 2015), leading to greater production of I/SVOCs for low-sulfur fuel. To further elucidate the impact of reduced sulfur content on combustion efficiency, we calculated the modified combustion efficiencies (MCEs) for various fuel types (Fig. S2 in the Supplement). The results indicated a notable decline in MCE values as the sulfur content decreased, suggesting that incomplete combustion was a key factor contributing to the elevated levels of I/SVOCs in low-sulfur fuels.

The operating condition was another important factor that affected ship I/SVOC emissions. During actual navigation of

OGVs, the operating modes were ranging from engine load of 25 % to 90 %. In this study, the operating modes were categorized into three distinct levels: low mode for engine loads below 50 %, medium mode for loads between 50 % and 75 %, and high mode for loads exceeding 75 %. As for the ICSs, because the time for departure and docking could be neglected compared with long-distance cargo transportation, cruise and maneuvering were selected according to the actual operating conditions. The engine operating load was higher in cruise mode (classified as high mode) compared with maneuvering (medium mode). It could be seen from Fig. 2b that the average emission factors (EFs) of I/SVOCs in this study followed a relatively ascending order across operating modes: 1098 ± 305 mg per kg fuel in low, 1542 ± 465 mg per kg fuel in medium, and 1457 ± 276 mg per kg fuel in high operating modes, respectively, revealing significantly elevated emissions at both medium and high loads compared to low-load conditions. This trend was consistent with PM emission patterns reported by Zhang et al. (2021) but notably diverged from the characteristics of ship-emitted IVOCs, which reached their lowest value under medium-load conditions in prior studies (Zhao et al., 2014; Huang et al., 2018b). This discrepancy could be attributed to the dominance of SVOCs over IVOCs in this study. Operating modes affect the combustion state in engines and the air–fuel ratio during the combustion process, thereby influencing exhaust emissions (Shrivastava and Nath Verma, 2020). The air–fuel ratio exhibits a decreasing trend with increasing engine load, which induces more pronounced incomplete combustion within the

cylinder, thereby establishing a direct causative relationship with elevated total I/SVOC emissions. (Zhang et al., 2021; Watson et al., 1994). The high operating mode is associated with reduced fuel diffusion and combustion time, leading to a partial oxygen deficiency within the cylinder, thereby resulting in an increased generation of I/SVOCs (Zhao et al., 2016; Liu et al., 2022). The investigation of methodologies for optimizing engine design and control systems to achieve enhanced combustion efficiency under different operating conditions, thus reducing emissions, is of great significance.

Engine type also led to a difference in I/SVOC emissions from ships. There were two types of engines on the OGVs, which were low-speed engines (LSEs) for the main engines (ME) and medium-speed engines (MSEs) for the auxiliary engines (AEs), while there was only one type engine on the ICSs as the main engines, which were high-speed engines (HSEs) (seen in Table S1). The findings indicated that there were no statistically significant differences in the $EF_{I/SVOCs}$ among various engines. Typically, medium-speed engines exhibit lower combustion efficiencies than low-speed engines, leading to higher I/SVOC emissions (Wu et al., 2020; Liu et al., 2022). However, as AEs, the MSEs used in this study were almost operated in medium loads that always presented the lowest pollutants as described above, which resulted in the lowest I/SVOC emissions as well. This finding suggested that the influence of operating conditions offset that of the engine type, ultimately resulting in similar levels of $EF_{I/SVOCs}$ for the MSE compared to the LSE. $EF_{I/SVOCs}$ for ICSs with high-speed engines presented the highest level (1370 ± 382 mg per kg fuel). As previously mentioned, high-speed engines typically exhibit lower combustion efficiencies compared to other engine types (Wu et al., 2020), while the utilization of low-sulfur fuel also results in elevated levels of $EF_{I/SVOCs}$. Therefore, both the engine type and fuel type used for ICSs jointly caused the highest $EF_{I/SVOCs}$ in this study. In summary, fuel types determine emission compositions, while engine type and operating conditions affect combustion efficiency and reaction paths. These factors interact, thereby leading to varying degrees of incomplete combustion, ultimately resulting in complex I/SVOC emissions.

3.3 Chemical compositions and profiles of I/SVOCs

3.3.1 Chemical compositions of I/SVOCs

The chemical compositions (speciated I/SVOCs and UCM) of I/SVOCs emitted from OGVs and ICSs under various operating conditions are presented in Fig. 3. The speciated I/SVOCs included *n*-alkanes, branched alkanes (b-alkanes), (O)PAHs, hopanes, and acids. In general, UCM and b-alkanes dominated the total I/SVOCs from ship exhausts, contributing 83.4 % to 89.8 % of the total I/SVOCs (speciated + UCMs). The emissions of acids and *n*-alkanes were also noteworthy, accounting for an average of 6.51 % and 4.61 % of the total I/SVOCs, respectively. Previous studies also have

noted the relatively high proportion of *n*-alkanes in I/SVOCs from shipping emission sources (Huang et al., 2018a; He et al., 2022a). However, there are limited data available on organic acids, particularly those emitted by shipping activities. PAHs, hopanes, and benzoic acids collectively contribute only about 1 % to the overall emissions, indicating their relatively minor role. However, even though these substances only constituted a small proportion of the overall emissions, the environmental and health effects still demanded in-depth research and vigilance due to their strong toxicity and bio-accumulative nature (He et al., 2022b; Mochida et al., 2003).

It is noteworthy that both the EFs and proportions of fatty acids in the total I/SVOCs were found to be remarkably high in this study, as previously mentioned. This finding aligns with the results reported by Huang et al. (2018a) and Wang et al. (2023), where *n*-fatty acids were identified as a significant component of chemical compositions derived from an OGV exhaust. However, there is still very little research on fatty acids from shipping emissions. Fatty acids are a category of organic compounds with carboxyl groups and relatively long carbon chains, playing essential physiological roles within organisms. Prolonged exposure to elevated levels of fatty acid pollutants has been linked to the development of respiratory, immune, and cardiovascular disorders (He et al., 2022a, b). Studies have indicated that fatty acids can constitute a substantial portion of the organic matter in atmospheric aerosols, especially in marine aerosols (Hu et al., 2023; Mochida et al., 2003; Kawamura et al., 2017). For example, research in the North Pacific has shown that fatty acids could account for 10 % to 30 % of organic carbon (Mochida et al., 2003, 2002). In addition, low-molecular-weight fatty acids ($C_{14:0}$ – $C_{19:0}$) have been increasing in the North Pacific in recent years (Hu et al., 2023). The content of fatty acids in marine aerosols was relatively high, yet their specific sources were often attributed to biomass burning and biological emissions in the past (Hu et al., 2023; Kawamura et al., 2010). It could be inferred from the results in this study that shipping emissions might be one significant potential contributor to the fatty acids in marine aerosols. Besides, the EFs of fatty acids were found to be higher in ship exhausts fueled by MGO and no. 0 diesel compared to HFO, which aligns with the findings of Huang et al. (2018a), indicating that the average EF of *n*-fatty acids from LSF was 6.7 times greater than that from HSF. Consequently, the forthcoming implementation of a globally uniform ultra-low-sulfur oil policy may potentially lead to an elevated release of fatty acids, particularly in coastal and inland regions. Given studies on acid pollutants from ship exhausts are relatively scarce or have been overlooked due to limitations in sampling and detection methods, further investigation is warranted to enhance the comprehension of the characteristics and influences of acidic emissions derived from ship exhausts.

As mentioned above, the total $EF_{I/SVOCs}$ of ship exhausts were significantly influenced by fuel type. The average emission factors of the primary chemical compositions

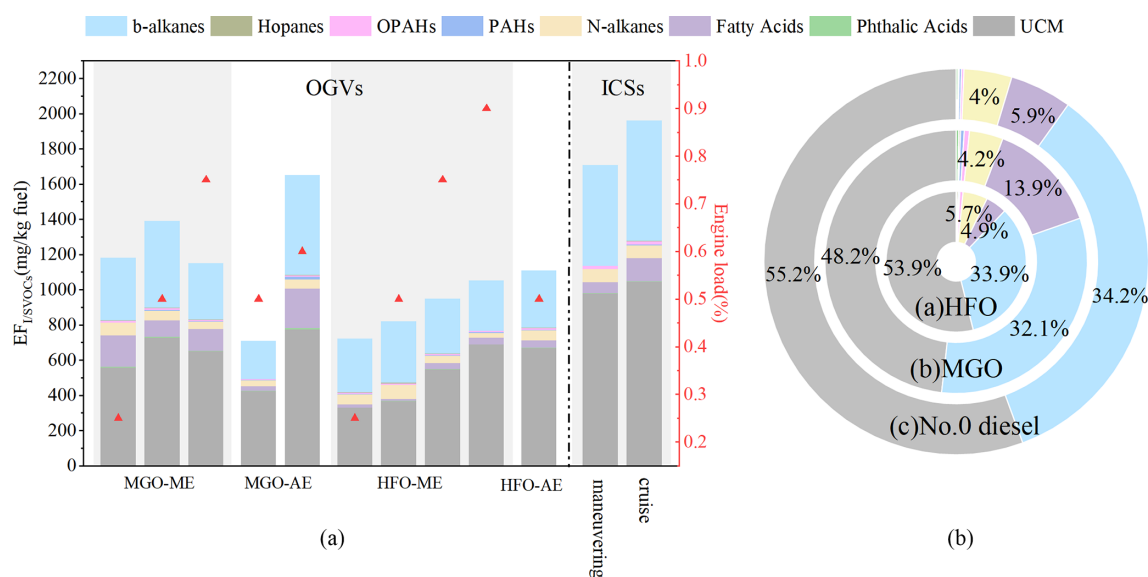


Figure 3. Chemical compositions of I/SVOCs from the tested ships: (a) emission factors (mg per kg fuel) and (b) fractional contributions (%). The red triangles represent the engine load.

of I/SVOCs under various fuel conditions are presented in Table 2. Results demonstrated that the EFs of the majority of organic compounds in ship emissions exhibited an upward trend as the sulfur content in fuels decreased. Specifically, emission factors of UCM, branched alkanes, and (O)PAHs for no. 0 diesel were much higher than the other two fuels, with HFO having the lowest values, while in terms of *n*-alkanes, the average total EFs of *n*-alkanes in these fuel types were 72.9 ± 28.1 mg per kg fuel (no. 0 diesel), 50.1 ± 15.1 mg per kg fuel (HFO), and 49.2 ± 11.2 mg per kg fuel (MGO), respectively, indicating a slight deviation from the findings of Liu et al. (2022) regarding the higher EF_{*n*-alkanes} in MGO compared to HFO. This might be explained by the fact that not only *n*-alkanes in IVOCs but also SVOCs were detected in this study. Compared with IVOCs ranging from C₁₂ to C₂₂, SVOCs (C₂₂–C₃₆) from HFO had higher emission factor values due to the higher carbon chains than MGO (details are also shown in Sect. 3.4), which offset the higher EF_{*n*-alkanes} caused by IVOCs (seen in Fig. 1). Besides, compared with the other two types of fuels, MGO emitted higher emission factor level of acids. MGO is a blend of straight-run light distillate diesel and secondary processed diesel from crude oil (Ahn et al., 2021), which may contain a considerable amount of impurities that could be a reason for its higher content of acidic substances. However, hopanes from HFO presented the highest emission factor level, which was one rare category of organic matter that decreased with the improvement of fuel quality. The details will be discussed in Sect. 3.3.2.

3.3.2 Profiles of I/SVOCs

Detailed profiles of organic compounds from ship exhausts are of great significance for source identification. The profile characteristics of the identified organic compounds, including fatty acids, *n*-alkanes, PAHs, OPAHs, and hopanes measured from the three types of ships in this study, are presented in Fig. 4. Results showed that fatty acids with 11–18 carbon numbers (C_{11:0}–C_{18:0} and C_{18:1}) were the main acids emitted from ships, especially *n*-C₁₄ and *n*-C₁₈. In addition, results showed that HFO had a significantly lower proportion of dodecanoic (C_{12:0}) and tetradecanoic (C_{14:0}) compared with no. 0 diesel and MGO, while the proportion of octadecanoic (C_{18:0}) in no. 0 diesel was lower than other fuels. The C_{18:0}-to-C_{14:0} ratios of HFO, MGO, and no. 0 diesel were 3.7 ± 1.0 , 0.3 ± 0.2 , and 0.1 ± 0.4 , respectively. This C_{18:0}-to-C_{14:0} ratio decreased significantly with the decrease in sulfur content of the fuel. Besides, the average proportion of fatty acids containing an even number of carbons ($88.05\% \pm 3.7\%$) in this study was significantly higher than that of fatty acids with an odd number of carbons. Previous studies have demonstrated a robust distribution of fatty acids with even-numbered carbon chains in marine aerosols, exhibiting distinct peaks at *n*-C₁₆ and *n*-C₁₈ (Hu et al., 2023; Kawamura et al., 2017; Mochida et al., 2002), thereby providing further evidence that ship exhaust emissions constitute a significant source of fatty acids in marine aerosols. Given the limited availability of studies on single-source acids, it is imperative to gather additional evidence regarding acid pollution resulting from ship transportation emissions. This will enhance our comprehension of the magnitude of the issue and the environmental and human health implications associated with these emissions.

Table 2. Average emission factors of main chemical compositions of I/SVOCs under different fuels (mg per kg fuel).

Fuel type	UCM	Branched alkanes	Acids	<i>n</i> -Alkanes	(O)PAHs	Hopanes
HFO	492 ± 137	299 ± 17.5	27.7 ± 10.6	50.1 ± 15.1	9.47 ± 3.1	2.99 ± 1.01
MGO	608 ± 109	379 ± 112	129 ± 57.7	49.2 ± 11.2	12.9 ± 5.3	2.41 ± 0.88
No. 0 diesel	1010 ± 134	628 ± 55.7	99.5 ± 33.9	72.9 ± 28.1	21.4 ± 3.3	1.88 ± 0.82

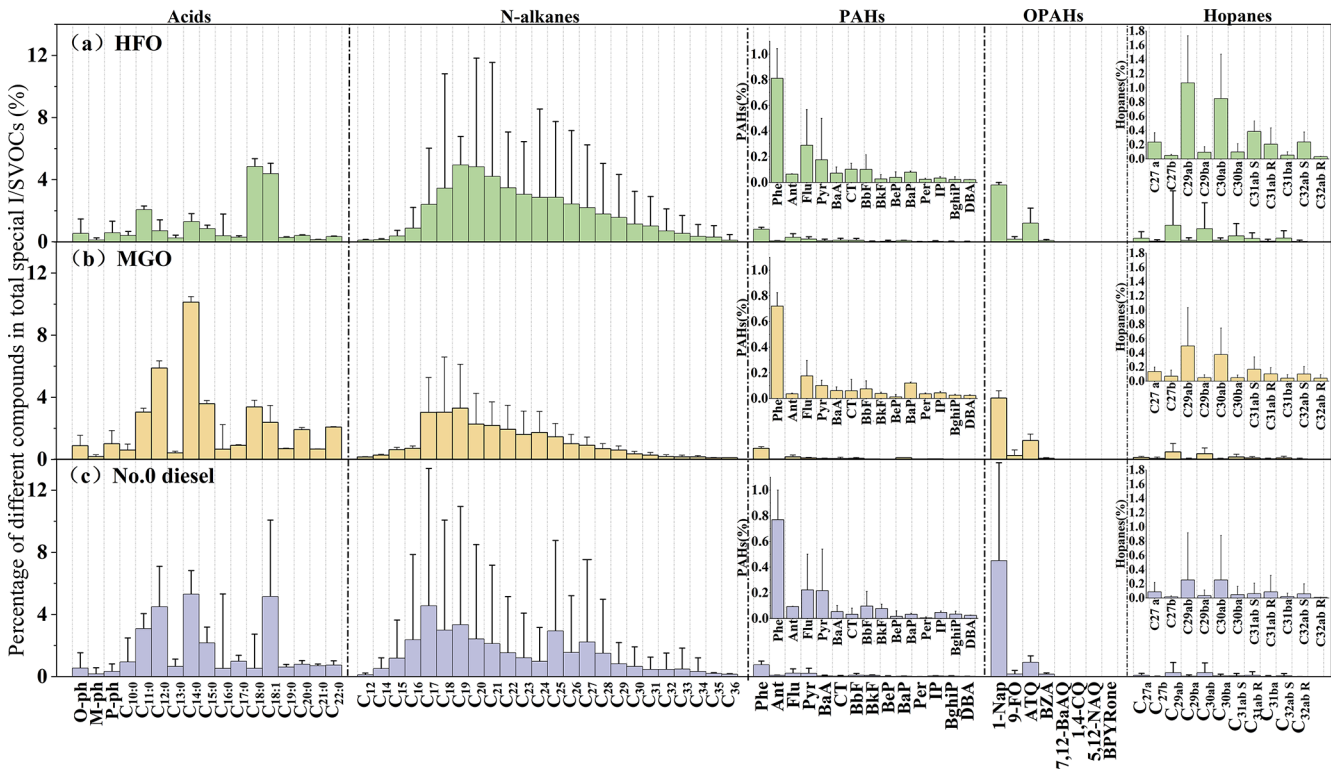


Figure 4. Profiles of I/SVOCs in ship exhausts under different fuels.

The *n*-alkane profiles of the three types of fuels in this study (depicted in Fig. 4) clearly indicated that low-carbon-number *n*-alkanes exhibit dominance. *n*-Nonadecane (C₁₉) exhibited the highest compositions for both HFO and MGO, while no. 0 diesel exhibited a peak at heptadecane (C₁₇), which was mainly caused by the characteristic of fuel compositions. Significant variations were observed in the emissions of *n*-alkanes from other non-internal combustion engine sources, such as high composition of *n*-octacosane (C₂₉) and apparent odd-carbon advantages in biomass emissions (Hu et al., 2023; Perrone et al., 2014), as well as high compositions of C₂₃ and C₂₁ for coal combustion (Duan et al., 2010; Xie et al., 2009).

The PAH profiles associated with different fuel types in this study exhibited similar patterns to those observed by Liu et al. (2022), wherein low-molecular-weight PAHs were found to constitute a relatively higher proportion. The major compounds in this study were phenanthrene (Phe), pyrene (Pyr), fluorene (Flu), chrysene (Chr), and benzo[a]pyrene

(Bap), aligning with the conclusions of previous studies (Zhang et al., 2016, 2014). PAHs from no. 0 diesel had a higher proportion of Pyr and lower proportion of Bap compared with the other two types of fuels. Besides, high proportions of 1-naphthaldehyde (1-Nap) and anthraquinone (ATQ) in OPAHs were also revealed from ship exhausts in this study, with 1-NAP for no. 0 diesel having the highest level. Most of the PAHs and OPAHs emitted in this study were low-molecular-weight tricyclic and tetracyclic substances, accounting for 94.7 % to 96.9 % of total OPAHs + PAHs, and 6.6 % ± 2.1 %, 6.7 % ± 1.7 % and 10.1 % ± 5.9 % of the total speciated I/SVOC profile in HFO, MGO, and no. 0 diesel, respectively. The present study observed a positive correlation between the decrease in sulfur content and an increase in OPAHs + PAHs, with smaller ring numbers emitted from ship exhausts, while, conversely, larger-ring compounds exhibited a negative relationship. Specifically, 1-Nap accounted for a significantly higher proportion of OPAHs + PAHs in no. 0 diesel (70.4 % ± 1.2 %) than in MGO (47.9 % ± 7.3 %)

and HFO ($36.6\% \pm 15.2\%$). As the sulfur content decreased, both the emission factor level and proportion of 1-Nap exhibited an increasing trend.

Hopanes are found mainly in coal, fuel oils, and lubricants and are generally regarded as molecular markers of fossil fuel combustion sources due to their stable chemical property (Cass, 1998). In this study, C_{29ab} and C_{30ab} were the main hopanes emitted from ships, accounting for $67.1\% \pm 5.5\%$ of the total hopanes. In addition, C_{31abS} , C_{31abR} , and C_{32abS} also showed unignorable contributions in ship emissions. Different from *n*-alkanes and (O)PAHs, among the fuels, hopanes presented the highest proportions from exhausts of HFO, followed by MGO, while no. 0 diesel showed the lowest levels. This finding was consistent with the results reported by Sippula et al. (2014), which demonstrated that HFO operation yields higher concentrations of hopanes compared to diesel fuel. The primary reason for this disparity was attributed to the presence of hopanes in HFO, whereas lubrication oil served as the sole source of these compounds during diesel fuel operation (Kleeman et al., 2008). Given vanadium and nickel cannot continue to be typical tracers of ship exhausts with low-sulfur-content HFO (Yu et al., 2021), organic diagnostic characteristics such as hopanes coupled with the ratio of $C_{18:0}$ to $C_{14:0}$ could be considered potential markers of HFO exhausts.

3.4 Volatility distribution of I/SVOCs

The volatility distribution of I/SVOCs from ships is shown in Fig. 5; 24 bins were divided using *n*-alkanes as an indicator. It should be noted that the effective saturation concentration (C^*) of *n*-alkanes in each bin was used as a surrogate value to discuss the volatility distribution of I/SVOCs (Zhao et al., 2016, 2014). The employed experimental method of solvent extraction in this study should be acknowledged for its potential to underestimate highly volatile organic compounds. However, in the meantime, this method could also effectively identify and quantify as many I/SVOC species as possible. Figure 5 shows the proportion of I/SVOCs in each volatile bin to further investigate the effects of different factors on I/SVOCs. Obviously, fuel type had an apparent impact on the overall trend of the volatility distribution of $EF_{I/SVOC}$, with similar volatility profiles of identical fuels (Fig. 5a), while operating mode and engine type also affected the volatility distributions of I/SVOCs (Fig. 5b). For example, for both HFO MEs and MGO MEs of OGVs, there were maximum values in bin 29. The range and magnitude of this maximum region increased with engine load, reaching its peak at 50 % engine load and subsequently declining at 75 % engine load (Fig. 5b). The higher emissions of I/SVOCs in low-speed and high-speed loads might be significantly influenced by the increase in these low-volatility components.

In order to figure out the volatility distributions of detailed chemical compositions of I/SVOCs from different fuels, the average volatility distributions of UCM, *b*-alkanes,

n-alkanes, PAHs, acids, and hopanes based on the volatility basis set (VBS) framework are given in Fig. 6. Results revealed that the volatility distributions of UCM exhibited distinct bimodal characteristics, with peak values occurring at $\log C^* = -3$ to -2 and $\log C^* = 3$ to 4. Notably, the concentration was more pronounced in the low-volatility region. Moreover, the bimodal characteristic of UCM in no. 0 diesel was more pronounced compared to HFO and MGO. Additionally, HFO exhibited a higher proportion of low-volatility UCM relative to no. 0 diesel and MGO. The volatile distributions of *n*-alkanes exhibited a bimodal structure, with peaks occurring at $\log C^* = -4$ to -2 and $\log C^* = 5$ to 6, respectively. Furthermore, from HFO to MGO and finally to no. 0 diesel, the VBS peak of *n*-alkanes progressively shifted towards the higher-volatility range. This shift could be attributed to the distinct characteristics of these fuels, where MGO and no. 0 diesel had lower boiling points and contained fewer carbon atoms in their hydrocarbon chains compared to HFO (Liu et al., 2022). The volatility distributions of other specific I/SVOCs were consistent with their molecular sizes. (O)PAHs emitted from ships were predominantly small molecules with high volatility, primarily enriched in the $\log C^*$ range of 4 to 5. Acids were mainly concentrated in the higher-volatility bins ($\log C^* = 0$ to 5), whereas hopanes exhibited a primary concentration in the lower-volatility intervals. The compositions and physicochemical properties of different fuel types vary, leading to differences in the volatile organic compounds they contain. Consequently, the type of fuel played a significant role in determining the distribution of volatile fractions for each individual I/SVOC component. The composition and combustion efficiency of fuel are important factors affecting the emission and distribution of I/SVOCs.

3.5 SOA formation potential of I/SVOCs

I/SVOCs have been proposed as crucial precursors of SOA (Murphy et al., 2017; Hu et al., 2023). However, most previous studies about ship exhausts have focused on the contribution of gas-phase IVOCs on SOA (Huang et al., 2018b; Liu et al., 2022), and the contributions from IVOCs and SVOCs in the particle phase have been neglected. The comprehensive assessment of ship exhaust emissions, encompassing gas-phase and particle-phase I/SVOCs, was crucial for evaluating the overall impact on the environment. This became particularly important in light of the implementation of low-sulfur-fuel policies, which had resulted in increased emissions of full-volatility organic compounds. Therefore, the SOAFP of I/SVOCs from ships with different fuels was estimated (shown in Fig. 7). Results showed that in terms of the total SOAFP evaluated from both IVOCs and SVOCs, no. 0 diesel and MGO with the lower sulfur content showed higher values, which could reach as high as 634 and 418 mg per kg fuel, respectively. In comparison, the SOAFP from HFO only had a lower value of 354 mg per kg fuel. For

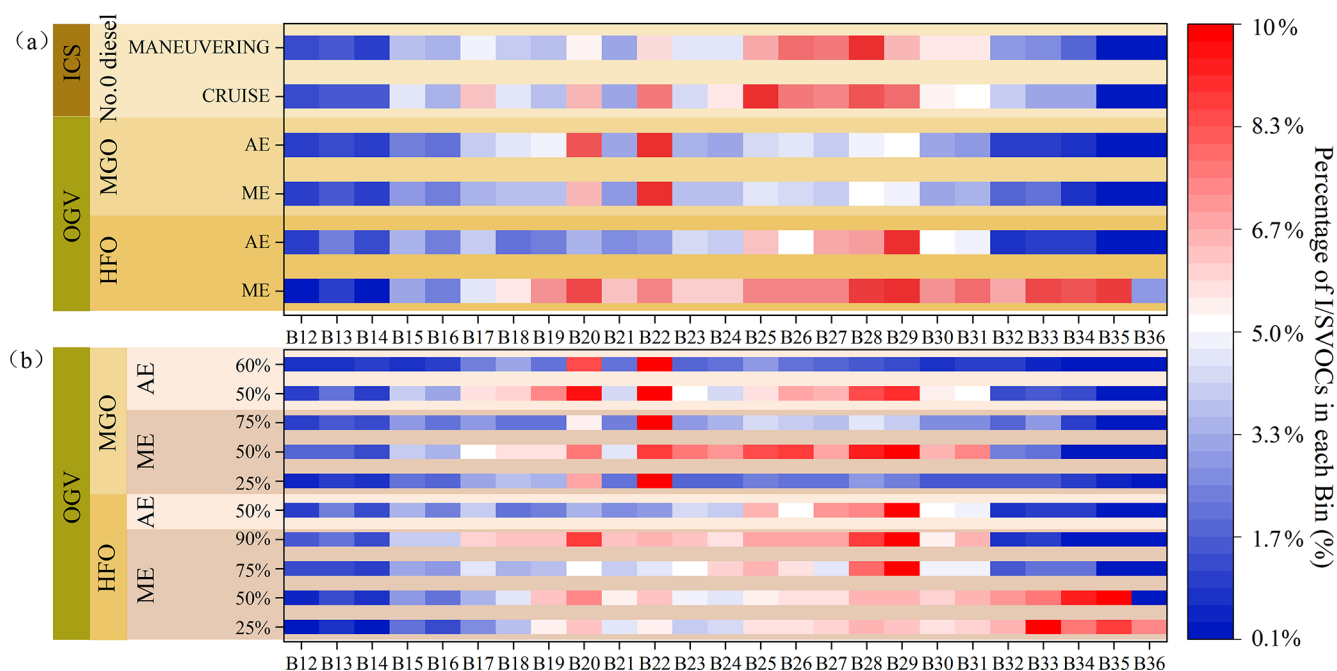


Figure 5. Split-bar heat plot of the I/SVOCs proportions in each volatile bin under (a) different fuel types for different engines and (b) different operating conditions (25 %–90 % operating modes) for OGVs.

IVOCs, the use of low-sulfur no. 0 diesel and MGO could lead to higher SOAFP that reached 234 and 157 mg per kg fuel, respectively, while HFO exhibited a significantly lower SOAFP level of only 101 mg per kg fuel. As for SVOCs, the SOAFP values of those three fuels were 400 mg per kg fuel for no. 0 diesel, 261 mg per kg fuel for MGO, and 253 mg per kg fuel for HFO. Previously, there has been limited research on SVOCs and their SOAFP, resulting in a scarcity of relevant comparative studies. Compared to diesel vehicles (430 ± 574 mg per kg fuel), gasoline vehicles (39 ± 79 mg per kg fuel), and non-road machinery (424 ± 138 mg per kg fuel) reported in previous IVOC studies (Zhao et al., 2015, 2016; Qi et al., 2019), SOA emissions of total I/SVOCs from ships using no. 0 diesel exhibit significantly higher formation potential (634 mg per kg fuel). This discrepancy highlights critical knowledge gaps in current assessments, where the scarcity of research on SVOCs and their SOAFP has led to incomplete comparisons. Results from this study indicate that SOAFP could be enhanced with the decrease in sulfur content – the same as I/SVOC emission factors. The major contribution to the total SOAFP was observed from b-alkanes and UCM, accounting for 81.1 %–87.8 %, but the significance of acids, particularly IVOCs, should not be overlooked. Besides, SOAFP values from SVOCs were higher than those of IVOCs, regardless of the types of fuels, which further indicated the importance of SVOCs. However, due to the analysis method of I/SVOCs, the emission factor and SOAFP were underestimated in this study. More real-world measurements of chemically identifiable full-volatility organic matter

should be carried out to figure out their emission characteristics and SOAFP, especially for the ultra-low-sulfur marine fuels, which could provide the basis for the further establishment of ship emission policies.

4 Conclusions and atmospheric implications

The results revealed that $EF_{I/SVOCs}$ of ICSs were higher than OGVs. Furthermore, a decreasing sulfur content in fuel was found to be associated with an increasing trend in $EF_{I/SVOCs}$. Fuel quality, engine type, and engine load all exerted significant influences on the emissions, compositions, and volatility distributions of I/SVOCs. Besides, the most predominant I/SVOC components were UCM and b-alkanes, followed by acids and *n*-alkanes. Notably, a significant presence of fatty acids was detected in ship exhausts, warranting further attention, particularly towards fatty acids ranging from C_{11} – C_{18} carbon numbers. It also found that organic diagnostic markers of hopanes, in conjunction with the $C_{18:0}$ -to- $C_{14:0}$ acid ratio, could be considered potential markers for HFO exhausts. Moreover, the transition from low-sulfur-content to ultra-low-sulfur-content fuels also enhanced the secondary organic aerosol formation potential.

The findings of this study, along with previous research, suggest that a decrease in sulfur content in fuels leads to a significant increase in emissions of full-volatility organics from OGVs. This further exacerbates the SOAFP, which poses serious environmental and health risks, particularly in densely populated coastal areas. Therefore, there is a need

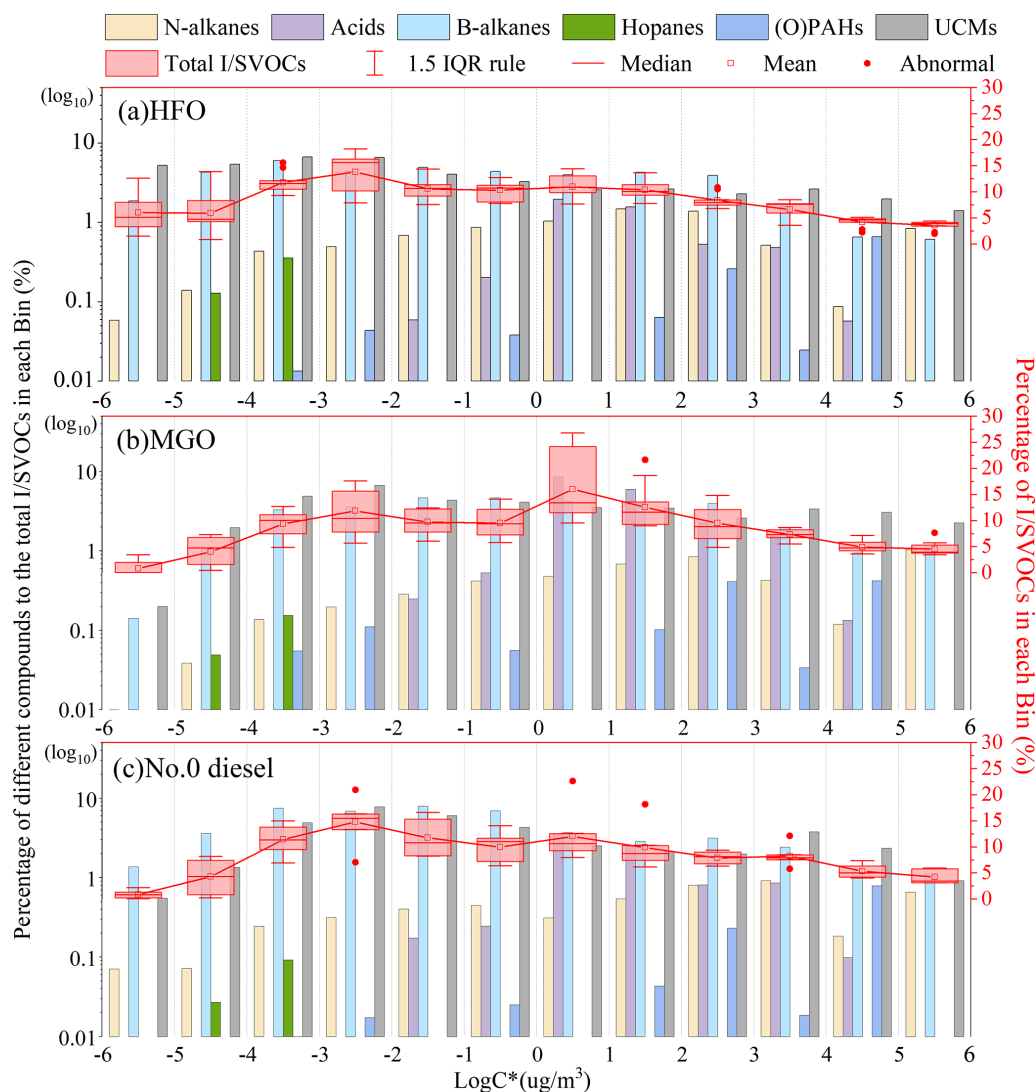


Figure 6. The volatility distributions of I/SVOCs based on the volatility basis set (VBS) framework from different fuels.

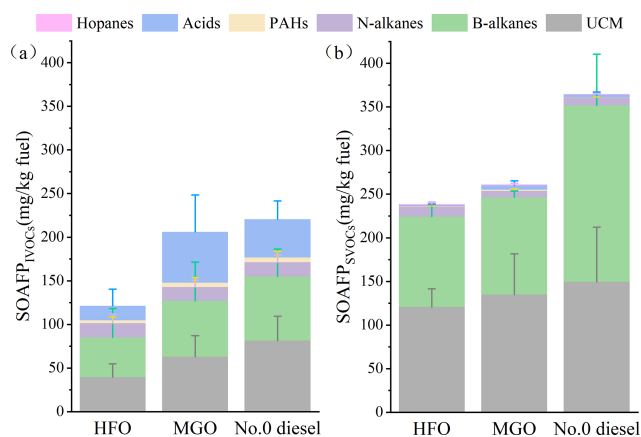


Figure 7. SOAFP from (a) IVOCs and (b) SVOCs.

for optimization of the implementation of an ultra-low-sulfur oil policy. Due to data limitations, previous emission inventories for ships often underestimated the emissions of organic matter, particularly from I/SVOCs. This underestimation has led to an incomplete assessment of the contribution of ship emissions to air quality, particularly in terms of SOA formation. Specifically, according to existing emission inventories based on previous studies, the total IVOC emissions from non-road mobile sources amount to 238 Gg, with ships contributing 6.16 % (14.7 Gg) of this total (Zhao et al., 2022). Assuming these ships use low-sulfur fuel (with a sulfur content below 0.5 % (*m/m*)) and applying the emission factors from this study for re-estimation, the unconsidered SVOCs would lead to an underestimation of 11.9 Gg pollutant emissions. If the sulfur content of the fuel is further reduced to 0.1 % ultra-low-sulfur fuel oil (with a sulfur content below 0.1 % (*m/m*)), the revised IVOC emissions from ships would

be 17.7 Gg, and SVOC emissions would be 23.6 Gg, representing a 64 % increase in total emissions compared to using low-sulfur fuel.

Moreover, high proportions of acidic substances in I/SVOCs from ships were found in this study, which extended the profiles of ship exhaust emissions. It also could be inferred that organic diagnostic characteristics, such as hopanes, in combination with the ratio of $C_{18:0}$ to $C_{14:0}$ could be considered potential markers for HFO exhausts. However, there was still a limitation in this study that the experimental method used might lead to the underestimation of highly volatile organic compounds. Besides, more than half of the I/SVOCs still could not be identified in this study. An improved experimental method needs to be considered to identify more full-volatility organic substances with greater precision and accuracy in a future study. Future research can obtain more comprehensive and accurate organic component emission data by using advanced methods such as comprehensive two-dimensional gas chromatography–mass spectrometry (GC $\times$ GC–MS) and Orbitrap mass spectrometry. Considering the proven effectiveness of after-treatment systems, such as diesel oxidation catalyst (DOC), diesel particulate filter (DPF), and selective catalytic reduction (SCR), in reducing emissions of full-volatility organic compounds (Reşitoğlu et al., 2015; Nadanakumar et al., 2021; Biswas et al., 2009; Yashnik and Ismagilov, 2023; Hamada and Haneda, 2012), these systems could be regarded as potential measures to mitigate the elevated levels of I/SVOCs emitted by ships.

Data availability. Datasets are available upon request to the corresponding author, Fan Zhang (fzhang@geo.ecnu.edu.cn).

Supplement. The supplement related to this article is available online at <https://doi.org/10.5194/acp-25-7053-2025-supplement>.

Author contributions. FZ, GW, YZ, and YC conceptualized and designed the study. BX, ZL, XW, YW, YH, MC, and YuC performed the measurements. FZ, RL, CW, LZ, and GW analyzed the data. BX wrote the manuscript draft. All the authors reviewed, edited, and contributed to the scientific discussion in the paper.

Competing interests. The contact author has declared that none of the authors has any competing interests.

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Financial support. This research has been supported by the National Natural Science Foundation of China (grant nos. 42377096, 42130704, and U23A2030).

Review statement. This paper was edited by Arthur Chan and reviewed by four anonymous referees.

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