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A large contribution of methylsiloxanes to particulate matter from ship emissions

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ABSTRACT

The chemical and stable carbon isotopic composition of the organic aerosol particles (OA) emitted by a shuttle passenger ship between mainland Naples and island Capri in Italy were investigated. Various methylsiloxanes and derivatives were found in particulate ship emissions for the first time, as identified in the mass spectra of a thermal desorption – proton transfer reaction – mass spectrometer (TD-PTR-MS) based on the natural abundance of silicon isotopes. Large contributions of methylsiloxanes to OA (up to 59.3%) were found under inefficient combustion conditions, and considerably lower methylsiloxane emissions were observed under cruise conditions (1.2% of OA). Furthermore, the stable carbon isotopic composition can provide a fingerprint for methylsiloxanes, as they have low $\delta^{13}\text{C}$ values in the range of $-44.91\text{‰} \pm 4.29\text{‰}$. The occurrence of methylsiloxanes was therefore further supported by low $\delta^{13}\text{C}$ values of particulate organic carbon (OC), ranging from -34.7‰ to -39.4‰ , when carbon fractions of methylsiloxanes in OC were high. The $\delta^{13}\text{C}$ values of OC increased up to around -26.7‰ under cruise conditions, when carbon fractions of methylsiloxanes in OC were low. Overall, the $\delta^{13}\text{C}$ value of OC decreased linearly with increasing carbon fraction of methylsiloxanes in OC, and the slope is consistent with a mixture of methylsiloxanes and fuel combustion products. The methylsiloxanes in ship emissions may come from engine lubricants.

1. Introduction

Methylsiloxanes are cyclic or linear oligomers or polymers composed of $-\text{Si}(\text{CH}_3)_2-\text{O}-$ units (Rücker and Kümmerer, 2015). They have been widely used in personal care products (e.g. cosmetic, skin- and hair-care products) (Wang et al., 2009; Lu et al., 2011), household products (Wang et al., 2013), and industrial applications (Andriot et al., 2007). Volatile methylsiloxane (VMS) are small molecular oligomers, either in cyclic form (e.g., $(\text{Me}_2\text{SiO})_n$, $n = 3-6$, where Me stands for $-\text{CH}_3$, referred to as D₃–D₆) or in linear form (e.g., $\text{Me}-(\text{Me}_2\text{SiO})_n-\text{SiMe}_3$, $n = 1-5$, referred to as L₂–L₆). They are considered environmental contaminants (Rücker and Kümmerer, 2015), which can be taken up by organisms and are found in blood, fat, and breast milk of humans (Flassbeck et al., 2001), as well as in aquatic species and mammals

(Warner et al., 2010; Fairbrother and Woodburn, 2016). Exposure to VMS may lead to direct or indirect toxic effects, such as neuro and pulmonary damage (Meyers et al., 2013), endocrine disruption, connective tissue disorders, adverse immunologic responses, and liver damage (Lieberman et al., 1999; He et al., 2003; Quinn et al., 2006; Horii and Kannan, 2008).

VMS have been found in the gas phase in various indoor environments (e.g., offices (Pieri et al., 2013), classrooms (Tang et al., 2015), hair salons (Tran and Kannan, 2015), residential homes (formed by heating silicones in an oven; Katz et al., 2021), industries and residential areas (Xu et al., 2015)) and outdoor air (Genualdi et al., 2011; Okan et al., 2021), including some remote areas, such as the Arctic (Krogseth et al., 2013) and the Tibetan Plateau in China (Wang et al., 2018). The main source of VMS is believed to be the evaporation from personal care,

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household, and industrial products.

Oligomeric methylsiloxanes have also been found in the particle phase, such as indoor air particles (Brown et al., 2021) and dust (Lu et al., 2010; Guo et al., 2019), as well as atmospheric nanoparticles (Bzdek et al., 2014) and outdoor aerosols (Xu et al., 2022). The oxidation of VMS is considered the potential route that can lead to methylsiloxane-containing secondary aerosols through the gas-to-particle conversion (Wu and Johnston, 2017; Milani et al., 2021). To date, significant primary emissions of methylsiloxanes in the particle phase have not been reported. As a consequence, methylsiloxanes in the particle phase have received much less attention than gaseous VMS.

However, it is plausible that mobile sources may directly emit methylsiloxanes, because of the possible presence of polydimethylsiloxanes (PDMS) in engine lubricants and fuels. PDMS are large Me-(Me₂SiO)_n-SiMe₃ polymers, which are non-volatile, water-insoluble, with no confirmed toxicity (Stringer, 1994; Kuo, 1999). They are commonly used for lubricating products in industry and transportation (Andriot et al., 2007) due to low surface tension, high thermal stability, smooth texture (Hori and Kannan, 2008) and defoaming properties (Mortier et al., 2010). PDMS are also widely used as antifoam additives in crude oil (Blázquez et al., 2014; Chen et al., 2019; Liu et al., 2021), fuel oils (Grabowski, 1996), and engine oils (Centers, 1993; Yang et al., 2021). At high temperatures, PDMS can decompose into fragments, including VMS (Fuentes et al., 2007). Since the lubricating oils for engines enter the combustion chamber (Supporting Information Section S1), methylsiloxanes originating from lubricants might be emitted by mobile sources such as cars and ships. While combustion products of liquid fossil fuels are generally considered the main constituents of ship emissions, a recent study indicates that unburned lubricating oil can strongly contribute to particulate matter in ship exhaust (Eichler et al., 2017). However, ship emissions have not yet been considered a potential source of methylsiloxanes in coastal air and aerosols.

In this study, we investigated particulate matter emitted by a shuttle passenger ship between mainland Naples and island Capri in Italy under different cruise conditions. In particular, we analyzed the detailed chemical composition of the ship-emitted organic aerosols by thermal desorption – proton transfer reaction – mass spectrometry (TD-PTR-MS). The methylsiloxanes and derivatives were identified in the mass spectra using a new method based on Si isotope abundance.

In addition, the stable carbon isotopic composition of particulate matter was investigated. Carbon has two stable isotopes, ¹²C and the minor isotope ¹³C, which approximately constitute 98.93% and 1.07% of all carbon atoms. In general, the ratio of ¹³C/¹²C is slightly variable between different carbon reservoirs, with typical differences in the % range. In particular, the ratios of ¹³C/¹²C are significantly higher in crude oil (fuel oils and base oil in lubricating oils, e.g., (Yao et al., 2022a)) than in methylsiloxanes analyzed to date (Pieri et al., 2013). ¹³C/¹²C ratios could therefore provide supplementary evidence for the presence of methylsiloxanes.

2. Materials and methods

2.1. Sampling of particulate matter from ship exhaust

The measurement campaign was performed on a high-speed passenger hydrofoil (2000 kW power; 1200 kg fuel consumption for round trip) shuttling between mainland Naples and island Capri in the Gulf of Naples, South Italy (Chianese et al., 2021). Particulate matter of 10 μm or smaller in diameter (PM₁₀) was collected from the exhaust stack on quartz filters with a portable pump (Air monitoring System-AMS Analytica) and a PM₁₀ selective head. Filters were sampled with a flow of 30 L/min for 10 min and stored in petri dishes, which were sealed with parafilm and kept at -20 °C until analysis. A total of 30 filters were collected, and 5 filters were selected for detailed chemical and isotopic analysis in this study. The filters were collected under different

operating conditions, including standby in Naples, exit from the harbor, docking maneuvers, standby in Capri, and offshore cruise conditions.

2.2. Analysis of organic and elemental carbon concentrations and isotopic compositions

The filter samples of particulate matter from ship emissions were measured for different carbon fractions and related δ¹³C values using a thermal-optical analyzer (TOA, Sunset Laboratory Inc.) coupled with an isotope ratio mass spectrometer (IRMS) (Yao et al., 2022b). The δ¹³C value is calculated as the relative deviation of the ¹³C/¹²C ratio (R¹³) of the sample from the ratio of international primary standard Vienna Pee Dee Belemnite (VPDB).

$$\delta^{13}\text{C} = \frac{R_{\text{Sample}}^{13}}{R_{\text{VPDB}}^{13}} - 1 \quad (1)$$

Since typical variations in R¹³ are very small, δ¹³C is usually reported in ‰. Organic carbon (OC), elemental carbon (EC), and total carbon (TC) concentrations of particulate carbonaceous matter were determined using the EUSAAR_2 protocol (Cavalli et al., 2010). In EUSAAR_2 protocol, OC is first thermally desorbed from the filter in Helium through several temperature steps (up to 650 °C). During this stage, some of the OC undergoes pyrolysis and pyrolyzed carbon (pOC; a measurement artefact) is formed, which remains on the filter. In a second stage of the analysis, pOC and EC are combusted in He/O₂ through several temperature steps (up to 850 °C). The desorbed OC (dOC) and pOC add up to OC. A separation between pOC and EC is achieved by monitoring the light absorption of the filter samples using a laser. During the analysis in He, the light absorption increases due to the formation of pOC, and it decreases again when pOC and EC are combusted in He/O₂. pOC is defined as the carbon fraction combusted from the start of the He/O₂ phase until the time when the light absorption returns to the starting value. In the ¹³C analysis by TOA-IRMS, selected carbon fractions were converted to CO₂ with a CeO₂ catalyst in the Sunset analyzer. The CO₂ was automatically collected in a liquid nitrogen trap, purified, concentrated, and injected into IRMS for ¹³C analysis (Dusek et al., 2013; Zenker et al., 2020; Yao et al., 2022b).

For the ¹³C analysis of TC, all carbon evolved during the entire EUSAAR_2 protocol was collected for ¹³C analysis, resulting in the isotopic signature of TC (δ¹³C_{TC}). For the ¹³C analysis of EC, only the carbon that evolved after the optical OC/EC split time of the EUSAAR_2 protocol was collected and the corresponding isotopic signature was further referred to as δ¹³C_{EC}. δ¹³C_{OC} was calculated by isotope mass balance (Eq. (2)), using the measured carbon concentrations and δ¹³C values of TC and EC. A Monte Carlo approach was used to estimate the propagated uncertainties.

$$\delta^{13}\text{C}_{\text{OC}} = (\text{TC} \times \delta^{13}\text{C}_{\text{TC}} - \text{EC} \times \delta^{13}\text{C}_{\text{EC}}) / \text{OC} \quad (2)$$

To investigate δ¹³C_{OC} in more detail, three temperature steps (200 °C, 350 °C, 650 °C; 5 min each) were used to desorb different fractions of OC under a flow of He for subsequent ¹³C analysis (OC_{200°C}, OC_{350°C}, OC_{650°C}, with corresponding δ¹³C_{OC200°C}, δ¹³C_{OC350°C}, δ¹³C_{OC650°C}) (Zenker et al., 2020). Since more volatile organic compounds tend to evaporate at lower temperatures, the desorbed OC roughly corresponds to classes of compounds with higher, medium, and lower volatilities. More details on data correction and quality control can be found in Supporting Information Section S2.

2.3. Chemical analysis

The ship emissions samples were analyzed for the chemical composition using a thermal desorption – proton transfer reaction – mass spectrometry (TD-PTR-MS) (Holzinger et al., 2010a; Holzinger et al., 2010b; Materić et al., 2017; Materić et al., 2019). A filter piece (with size depending on the amount of carbon on the filter) was put in a quartz

vial, and organic compounds were thermally desorbed at four temperature steps (125, 200, 275, and 350 °C) with 3 min for each step. The concentrations desorbed at 125 °C and 200 °C were combined as 200 °C step, and the concentrations desorbed at 275 °C and 350 °C were combined as 350 °C step, which can be correlated with ^{13}C results.

The flow rate through the glass vial was 89 mL/min, and ~ 40 mL/min of this flow was sub-sampled into the PTR-MS. The drift tube and inlet line were controlled to 120 °C and 180 °C, respectively, to prevent condensation of organic compounds. The organic molecules were ionized by H_3O^+ through proton transfer reaction and detected by a time of flight mass spectrometer with a mass resolution of ~ 4000 at full width half maximum. The raw data were processed by the PTRwid software (Holzinger, 2015), including peak identification and peak integration, resulting in a concentration for each ion reported as ppb in the carrier gas. The total concentration of each ion (in ng/cm² of filter material) was calculated for each temperature step, as described in a previous study (Timkovsky et al., 2015). Three different procedural blanks were analyzed. For each ion, the average concentrations of the procedural blanks (in ng/cm² of filter material) were subtracted from the sample. A 3σ detection limit was applied for detecting individual peaks. The total OA mass concentration was calculated as the sum of the concentrations of all molecules desorbed from filter samples and detected by PTR-MS minus the blank. Finally, the concentrations were converted to the unit of mg/m³ in the ship exhaust.

A unified mass list gave the m/z ratio with ± 2 sigma (95% confidence interval) for each ion, and provides possible molecular formulas for organic compounds that fall into this uncertainty range. The most probable molecular formula for each m/z ratio was selected based on the rules and priorities described in the Supporting Information Sections S3–S8 (Holzinger et al., 2010a; Masalaite et al., 2017).

2.4. Qualitative and quantitative analysis of methylsiloxanes

Identification of different methylsiloxane species with TD-PTR-MS is difficult, because the mass resolution does not allow the direct separation of methylsiloxane peaks from potential compounds with similar m/z . However, it is possible to identify methylsiloxanes based on their isotope peaks in the mass spectra. For the elements C, O, H, and N, higher isotopes have very low abundances ($\sim < 1\%$, Table S4), whereas for Si, the abundance of higher isotopes is significantly larger: ^{29}Si ($m/z = 28.976$, 4.685%) and ^{30}Si ($m/z = 29.974$, 3.092%). Taking advantage of the higher natural abundance of Si isotopes, we identified and quantified silicon-containing organics, as demonstrated in the example of D_5 ($\text{C}_{10}\text{H}_{30}\text{O}_5\text{Si}_5$) in the following steps. It is important to note that, unlike IRMS, the PTR-MS cannot resolve differences between isotopic ratios in the order of thousandths of isotopic abundances (‰). Instead, the analysis described in detail below identifies high abundance of $m/z + 1$ and $m/z + 2$ peaks of certain ions that can only be explained by the presence of silicon atoms.

(1) Main peaks and isotope peaks of methylsiloxanes. According to the natural abundances of C, H, O, and Si isotopes, the m/z and relative abundance of the main and isotope peaks of methylsiloxanes can be calculated. For example, D_5 has a main peak at m/z 371.102 with relative abundance 0.5918, and a first isotope peak corresponding to molecules containing either ^{29}Si , ^{13}C , ^2H , or ^{17}O with m/z 372.101–372.106 and relative abundance 0.2155. The remainder of the relative abundance (0.1927) is other isotope peaks. The natural abundance ratio between the first isotope peak and the main peak $(M + 1)/M$ of D_5 is calculated as 0.3641. The complete information of typical cyclic VMS (cVMS, $(\text{Me}_2\text{SiO})_n$; $n = 3\text{--}6$, $\text{D}_3\text{--}\text{D}_6$) and of their derivatives found in this study, as well as their main and isotope peaks can be found in the Supporting Information Section S3.

(2) Identification of methylsiloxanes based on the mass ratio of the isotope peak to the main peak. A peak potentially corresponding to D_5 was found in the PTR-MS mass spectra at m/z 371.105. At the mass resolution of the PTR-MS, other possible compounds at this m/z are:

$\text{C}_{11}\text{H}_{18}\text{O}_{12}\text{N}_2\text{H}^+$ (371.094), $\text{C}_{16}\text{H}_{18}\text{O}_{10}\text{H}^+$ (371.098), $\text{C}_{15}\text{H}_{18}\text{O}_9\text{N}_2\text{H}^+$ (371.109), $\text{C}_{13}\text{H}_{22}\text{O}_{12}\text{H}^+$ (371.119). These CHO or CHON compounds have much lower $(M + 1)/M$ ratios than methylsiloxanes, ranging from 0.1329 to 0.1789 (Table S11). Hydrocarbons, which are also common in ship exhaust, can be distinguished from methylsiloxanes based on their molecular weight at the mass resolution of the PTR-MS (e.g. $\text{C}_{27}\text{H}_{46}$, $m/z = 371.368$). By comparing the $(M + 1)/M$ ratios and the natural ratios, methylsiloxanes are distinctly different from other organic compounds with similar m/z . In our example, the observed $(M + 1)/M$ ratio of m/z 371.105 (0.368–0.379, Table S12) is very close to the natural ratio of D_5 (0.3641). This allows identification of the peak in question as methylsiloxane.

(3) Methylsiloxane quantification. In addition to the methylsiloxanes mentioned above, methylsiloxane fragments with one missing $-\text{CH}_3$ were identified in the mass spectra. These fragments are likely formed during ionization in the PTR-MS. Moreover, methylsiloxane diols ($\text{HO}-(\text{Me}_2\text{SiO})_n\text{-H}$) formed through hydrolysis (Varaprath et al., 2000; Guallar-Hoyas et al., 2012; Ai et al., 2014) and cVMS silanols with methyl replaced by hydroxyl through oxidation (Latimer et al., 1998) were identified. Similar to cVMS, these compounds were identified as Si-containing compounds, based on their isotope peaks, see Supporting Information Sections S3.2–S3.4. To determine the total concentration of methylsiloxanes, the mass concentrations of all siloxane peaks and their fragments were considered.

Due to the high abundance of the isotope peaks, it is important to consider the first and second isotope peaks in the quantification of methylsiloxanes, the latter corresponding mainly to molecules containing one atom of ^{30}Si and ^{18}O , or two different or identical atoms of ^{29}Si and ^{13}C . For D_5 , the main peak accounts for 59.2%, the first and second isotope peaks together account for an intensity fraction of 35.5% and the rest of the isotope peaks account for 5.3%. Since interfering CHON compounds are usually present at the second isotope peak in our case, the natural isotope abundances of methylsiloxanes and the measured $(M + 1)/M$ ratios (Table S10) can be used to estimate the total amount. The calculation steps and details can be found in Supporting Information Section S7.

3. Results

3.1. ^{13}C analysis of OC and EC

The TC shown in Fig. 1a indicates the total particulate carbonaceous emissions for each cruise condition. Under constant fuel consumption, lower TC generally represents higher combustion efficiency. The modified combustion efficiency is defined as the molar emission ratio $\Delta\text{CO}_2 / (\Delta\text{CO} + \Delta\text{CO}_2)$ (Ward and Radke, 1993), where ΔCO_2 and ΔCO refer to the molar concentrations of CO_2 and CO emitted from combustion. Previous studies have shown that combustion efficiency is correlated with EC/TC ratios, e.g., (Vernooij et al., 2022), and a higher percentage of EC in TC indicating higher combustion efficiency. Therefore, the percentage of EC in TC is another indicator of combustion condition (Fig. 1c). The Exit sample was taken when the ship left the harbor under acceleration and has the lowest percentage of EC in TC, indicating low combustion efficiency. On the other hand, the Offshore sample was taken under constant cruise condition and has the highest percentage of EC in TC, indicating high combustion efficiency. The Exit sample also has the highest TC (42.4 mg/m³), which is reasonable considering the inefficient combustion and higher fuel consumption during acceleration. The Offshore sample has much lower TC (10.5 mg/m³), but the lowest TC was observed in the Dock sample (2.7 mg/m³) which means more efficient combustion during deceleration, likely due to adequate air supply, reduced fuel supply, and good engine condition after a long journey.

The $\delta^{13}\text{C}$ values of OC and EC and their mass fractions in TC under different cruise conditions are shown in Fig. 1b and 1c. Except for the Offshore sample, the OC fractions have very low $\delta^{13}\text{C}$ values, especially

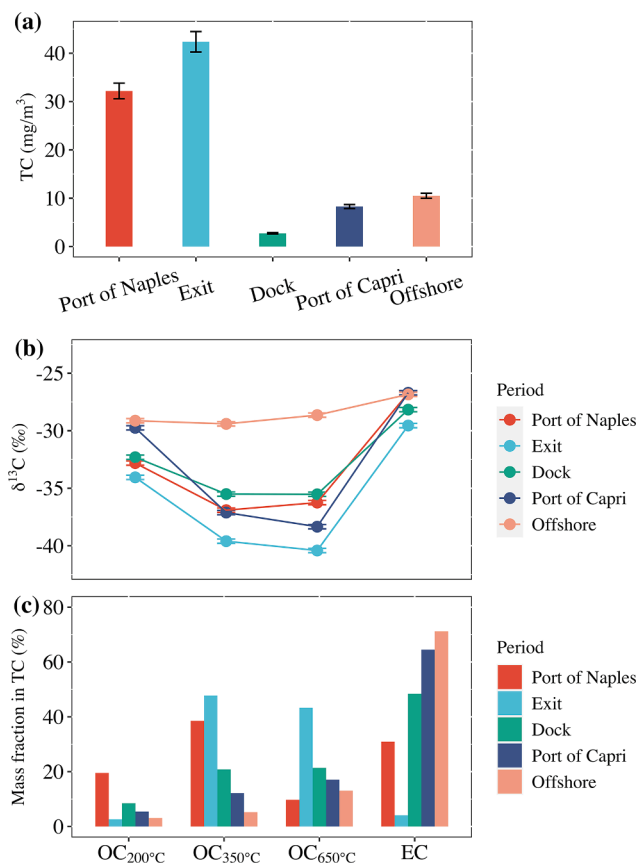


Fig. 1. Different carbon fractions of particulate matter in ship emissions and their isotopic compositions. (a) TC concentrations under different cruise conditions, including standby at Port of Naples (red), Exit from the port (light blue), Dock maneuvers (green), standby at Port of Capri (dark blue), and Offshore cruise conditions (pink). Error bars refer to the measurement precision. (b) $\delta^{13}\text{C}$ values and (c) mass fractions of OC and EC in TC. Error bars refer to the measurement precision of ^{13}C analysis. $\text{TC} = \text{OC} + \text{EC} = \text{OC}_{200^\circ\text{C}} + \text{OC}_{350^\circ\text{C}} + \text{OC}_{650^\circ\text{C}} + \text{pOC} + \text{EC}$. $\text{OC}_{200^\circ\text{C}}$, $\text{OC}_{350^\circ\text{C}}$, and $\text{OC}_{650^\circ\text{C}}$ refer to OC desorbed at different temperature steps. pOC refers to the pyrolyzed carbon that formed during analysis when OC was desorbed in an inert atmosphere. pOC as a measurement artifact was not analyzed for ^{13}C . Mass fractions of desorbed OC and EC do not add up to 100%, since pOC is not shown in this figure. Data see Table S1.

$\delta^{13}\text{C}_{\text{OC}_{350^\circ\text{C}}}$ (-35.5‰ to -39.6‰) and $\delta^{13}\text{C}_{\text{OC}_{650^\circ\text{C}}}$ (-35.5‰ to -40.4‰). In contrast, $\delta^{13}\text{C}_{\text{EC}}$ is similar during all cruise conditions (data in Table S1). The averaged $\delta^{13}\text{C}_{\text{EC}}$ is $-26.8\text{‰} \pm 0.1\text{‰}$ for Offshore and standby cruise conditions (Port of Naples and Port of Capri), which is typical for combustion emissions of liquid fossil fuels (Yao et al., 2022a). Large differences in $\delta^{13}\text{C}$ values between OC and EC (up to -10‰) are unlikely to be caused by isotope fractionation during the combustion process, which is usually much smaller (Widory, 2006; Yao et al., 2022a). Therefore, it is likely that organic compounds with very low $\delta^{13}\text{C}$ values are present in ship emissions, a hypothesis that will be explored in the following sections.

3.2. Methylsiloxanes and derivatives

Organic mass spectra of the Exit sample (typical for inefficient combustion) and the Offshore sample (typical for normal cruise conditions) are compared in Fig. 2, normalized to the peak at $m/z = 93.037$. For the Offshore sample, the peaks are mainly found at low molecular weights ($m/z < 200$). However, for the Exit sample (as well as the other samples taken under inefficient combustion, see Figure S2), there are peaks at higher molecular weight ($m/z > 200$). In addition, these peaks

repeat at regular intervals of 74 m/z units.

To investigate the high molecular weight peaks ($m/z > 200$) in detail, the mass spectrum of OA desorbed from the Exit sample at 350°C is shown in Fig. 3a, where the arrows indicate the peaks corresponding to the m/z of several methylsiloxanes. The peaks identified as methylsiloxanes and derivatives are shown separately in Fig. 3b. The main peaks in the mass spectrum meet the theoretical m/z values of typical methylsiloxanes, and for most of the peaks the $(M + 1)/M$ ratios are close to the expected natural ratios for siloxanes (Table S12). This provides strong evidence for the presence of methylsiloxanes in particulate matter emitted by ships. These methylsiloxanes of ship emissions might originate from PDMS as antifoam additives in fuel oils or lubricating oils.

The identified compounds are mainly small cVMS, $(\text{Me}_2\text{SiO})_n$; $n = 3-6$, D_3-D_6 ; $n = 1-2$, fragments of one and two Me_2SiO units, labelled as D_1-D_2 , methylsiloxane diols formed in hydrolysis, oxidized products with $-\text{CH}_3$ replaced by $-\text{OH}$, and fragments that lost one $-\text{CH}_3$ during ionization. Example structures of detected methylsiloxanes are indicated in Fig. 3c. Isomerism is possible since all methylsiloxane compounds were identified by mass spectra only. For example, $\text{C}_{10}\text{H}_{30}\text{O}_5\text{Si}_5$ can be a cycle of five Me_2SiO units, known as D_5 , but it can also be an isomer made of a cycle of four siloxane units bearing an OSiMe_3 side chain. However, isomerism needs further investigation and will not be further discussed in this study.

Additionally, during ionization, positively charged fragments of these cVMS might be formed by loss of one $-\text{CH}_3$ (indicated as $\text{D}_1\text{f}-\text{D}_6\text{f}$). Diols of methylsiloxanes ($\text{HO}-(\text{Me}_2\text{SiO})_n-\text{H}$) might be formed by hydrolysis (Varaprath et al., 2000; Guallar-Hoyas et al., 2012; Ai et al., 2014). Diols with n ranging from 1 to 6 were identified in the mass spectra of ship emissions, including monomer dimethylsilanediol ($n = 1$, $\text{Me}_2\text{Si}(\text{OH})_2$, DMSD), dimer diol ($n = 2$, labelled as D_2w), oligomer diols ($n = 3-6$, labelled as $\text{D}_3\text{w}-\text{D}_6\text{w}$). The highest peak ($m/z = 93.037$) in Fig. 3b is the hydrolyzed monomer, DMSD, which indicates that hydrolyzed fragments are very common. It is not certain, if hydrolysis happened during the combustion in the ship engine resulting in particle-phase oligomer diols, which fragmented during analysis, or if the diols were produced from cVMS during ionization in the PTR-MS.

Finally, oxidized methylsiloxanes (silanols) with one $-\text{CH}_3$ replaced by one $-\text{OH}$ were found in the mass spectra, including the monomer $\text{CH}_4\text{O}_2\text{Si}$ (labelled as D^{OH} , formed from D_1) and further $\text{DD}^{\text{OH}}-\text{D}_5\text{D}^{\text{OH}}$ (formed from D_2-D_6). Previous studies indicate that $\text{D}_4\text{D}^{\text{OH}}$ is a product from D_5 and OH radicals (Latimer et al., 1998; Alton and Browne, 2020), and the latter can be formed photochemically in the atmosphere. Due to the lower vapor pressure, oxidized cVMS can be found in the particle phase. In the present study, oxidation of PDMS and their fragments likely happened during engine combustion.

The origin of the observed cVMS in the mass spectra of particulate matter needs to be further clarified. During the engine operation, PDMS might break down into fragments of various molecular sizes. However, based on partition equilibrium, small molecular cVMS usually are present in the gas phase rather than the particle phase (Latimer et al., 1998; Donahue et al., 2006; Wu and Johnston, 2017). Previous studies either did not detect small molecular cVMS in the particle phase (Brown et al., 2021) or detected much smaller amounts than in this study, e.g., (Guo et al., 2019; Guo et al., 2020), where $> 99\%$ of D_4-D_6 was in the gas phase. Therefore, most detected cVMS are likely generated during filter analysis (thermal desorption of the filter samples and ionization in PTR-MS) from larger particulate-phase methylsiloxanes. However, based on our analysis, we also cannot rule out the possibility that some cVMS were originally present in the particle phase.

To better understand the origin of the detected cVMS and their derivatives, commercially available PDMS samples were analyzed in the PTR-MS using the same analytical procedure as for ship emissions samples. The analysis of the PDMS with a viscosity of 5 cSt is shown in Figure S3, which produced similar fragments in the mass spectra as observed from ship emissions samples. All types of methylsiloxane peaks shown in Fig. 3 were identified except for the oxidized methylsiloxanes.

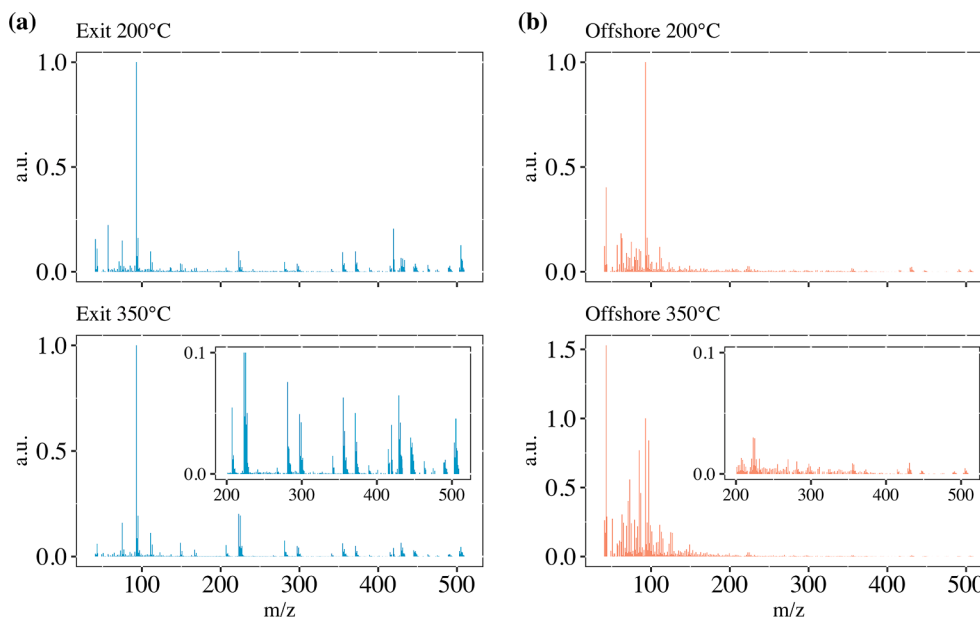


Fig. 2. The mass spectra of ship-emitted aerosol desorbed at 200 °C and 350 °C under (a) Exit from the harbor and (b) Offshore cruise conditions. The y-axis scale is normalized to the peak at $m/z = 93.037$ (the highest peak in most cases, except for Offshore 350 °C) for comparison. Other cruise conditions can be found in Figure S2.

The occurrence of D_1 – D_5 indicates that PDMS can be broken into cVMS during analysis. The occurrence of D_5f and D_6f means that this fragmentation likely occurs during PTR-MS ionization. The occurrence of methylsiloxane diols indicates that hydrolysis can happen during proton transfer reaction in the PTR-MS, because the PDMS samples were processed without contact with H_2O . However, the oxidized methylsiloxanes in ship emissions are likely produced during engine combustion, as they are not generated in the analytical procedure. These comparisons support our hypothesis that the methylsiloxanes of ship emissions originate from PDMS in antifoam additives in fuel oils or lubricating oils.

3.3. Contribution of methylsiloxanes to emitted organic aerosols

Mass fractions of methylsiloxanes in desorbed organic aerosols (dOA) and carbon fractions of methylsiloxanes in desorbed organic carbon (dOC) measured by the PTR-MS (Fig. 4a) were calculated based on the method described in Section 2.4. The contribution of methylsiloxanes to dOA is higher than to dOC because the carbon fraction in methylsiloxane molecules is usually lower than that in fuel oil molecules. The contribution of methylsiloxanes to dOA in ship emissions is very high under Exit, Dock, and Standby conditions (28.2%–59.3%), but much less under Offshore conditions (1.2%). This difference can be explained by the combustion efficiency of methylsiloxanes from engine lubrication. Lubricating oil with high thermal stability usually consists of large molecules, including base oil derived from crude oil fractionation (Mortier et al., 2010; Eichler et al., 2017) and additives (potentially antifoam PDMS additives in our case) (Andriot et al., 2007; Yang et al., 2021). These molecules are not easily combusted, especially under conditions of inefficient combustion, and therefore contribute to the emitted aerosols. To estimate concentrations in the exhaust plume, we assume that $OC_{200^\circ C}$ and $OC_{350^\circ C}$ in Fig. 1 are roughly equivalent to dOC obtained by PTR-MS. Then the carbon concentrations of methylsiloxanes can be estimated to be 0.006–9.2 mg/m³ (Table S13) in the exhaust plume, by multiplying the carbon fraction of methylsiloxanes in dOC obtained by PTR-MS and the OC fractions obtained by the Sunset thermal-optical analyzer.

A previous study has shown that cVMS have very low $\delta^{13}C$ values (Pieri et al., 2013), averaged to be $-43.93\% \pm 3.67\%$ (commercial D_3 – D_6 , see Table S2b). To verify low $\delta^{13}C$ values also in PDMS, some

PDMS samples from different manufacturers were analyzed in this study, and the averaged $\delta^{13}C$ value is $-45.88\% \pm 4.90\%$ (Table S2a). The averaged $\delta^{13}C$ values of cVMS and PDMS were combined as $-44.91\% \pm 4.29\%$ for methylsiloxanes based on the method described in Supporting Information Section S2. The low $\delta^{13}C$ values of methylsiloxanes may be caused by industrial raw materials, as well as by industrial synthesis. Methylsiloxanes (and other compounds containing Si–C bonds) are synthesized via Müller-Rochow direct process (Rochow, 1945), which involves copper-catalyzed reactions of elemental silicon and alkyl halides (usually CH_3Cl in the highest yield, made from methanol). Natural gas, a common raw material of industrial methanol, is known to have very low $\delta^{13}C$ values (Widory, 2006; Menoud et al., 2022). On the other hand, the $\delta^{13}C$ value of regional crude oil can be estimated as $-28.5\% \pm 1.1\%$ (Table S3) (Yao et al., 2022a), which serves an estimate of the $\delta^{13}C$ value of fuel oil combustion products.

The hypothesis that methylsiloxanes are responsible for the low $\delta^{13}C$ values can be substantiated by the correlation between the carbon fractions of methylsiloxanes in dOC and the corresponding $\delta^{13}C_{OC}$ values ($\delta^{13}C_{OC200^\circ C}$, $\delta^{13}C_{OC350^\circ C}$), as shown in Fig. 4b. The results show that $\delta^{13}C$ values of OC have a linear dependence on the carbon fractions of methylsiloxanes in dOC (slope = -16.7 ± 4.4 , intercept = -30.0 ± 1.2 , $R^2 = 0.647$, p-value = 0.005). The regression line roughly intercepts the $\delta^{13}C$ values of crude oil and of pure methylsiloxanes as end members (i.e. at 0% and 100% methylsiloxanes in OC). It also indicates that considerable methylsiloxanes in ship emissions contributed to the very low $\delta^{13}C$ values. With this evidence, the differences in $\delta^{13}C$ values in Fig. 1b under different cruise conditions can be roughly explained by the combustion efficiency, but not strictly. The $\delta^{13}C$ values in the two standby conditions (Port of Naples and Port of Capri) are similar and both lower than in the Offshore cruise condition. However, the combustion efficiency was obviously higher in the Port of Capri after a long journey indicated by lower TC concentration (Fig. 1a) and by a higher percentage of EC in TC (Fig. 1c). One possible explanation is that methylsiloxane emissions may depend not solely on combustion conditions but also on engine operational parameters, fuel supply, and lubrication, which requires further investigation.

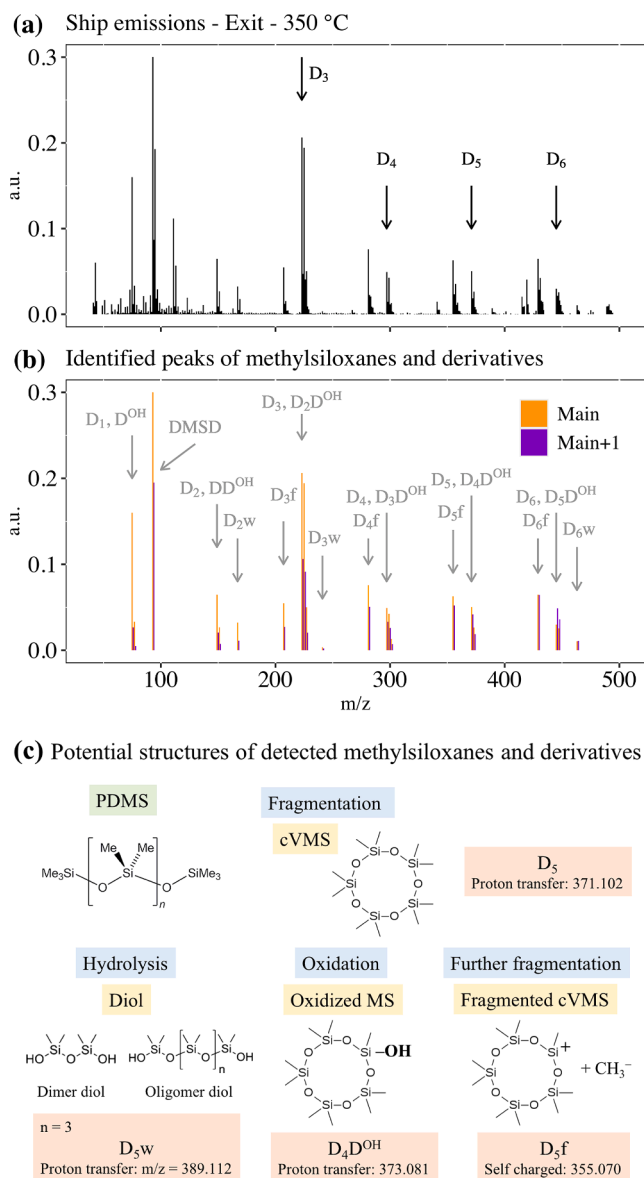


Fig. 3. (a) Mass spectrum of ship-emitted aerosols under exit condition desorbed from the filter sample between 200 and 350 °C. (b) The peaks of the above mass spectrum that can be attributed to methylsiloxanes and derivatives based on the methods described in Section 2.4. The Main and Main + 1 (i.e., first isotope) peak are shown in orange and purple bars. The mass spectra are normalized to the highest peak ($m/z = 93.037$) and y-axis scale is truncated at $y = 0.3$. (c) Example structures of detected methylsiloxanes (yellow), which could be formed from PDMS (green) during engine combustion, thermal desorption, or ionization. Possible pathways for each compound are further discussed in the text.

4. Discussion

Considerable amounts of methylsiloxanes (up to 59.3% of OA mass) were identified and quantified in organic aerosol particles emitted from one ship. This finding is corroborated by two independent lines of evidence, (i) the natural abundance of Si isotopes investigated by TD-PTR-MS, and (ii) the very low $\delta^{13}\text{C}$ values of the emitted OC investigated by IRMS. This shows for the first time that primary particulate emissions from combustion processes can contain methylsiloxanes.

As products of engine combustion, considerable amounts of methylsiloxanes and derivatives in particulate matter suggest that VMS and other fragments may also be emitted in the gas phase at the same time,

which is more harmful to human health (Hori and Kannan, 2008; Meyers et al., 2013). Besides, our samples were collected in the very concentrated exhaust plume, and a fraction of the detected particle-phase methylsiloxanes might evaporate upon dilution and further be converted to harmful VMS.

Since in this study only one ship was investigated, more studies are needed to confirm that ships are an important source of particulate and gas-phase methylsiloxanes. If confirmed, methylsiloxanes in some remote areas, such as the Arctic (Krogseth et al., 2013), may be related to ship emissions rather than long-distance atmospheric transport. Since lubricant oils emitted from engines previously have not been considered as a source of methylsiloxanes, other vehicles may be possible emitters as well, which needs further and urgent investigation.

The toxicity of methylsiloxanes in particulate matter is still under investigation. PDMS has shown no signs of toxicity in animal experiments by oral intake, dermal contact and inhalation (Stringer, 1994; Kuo, 1999). While secondary photochemical aerosols from OH oxidation of D₅ were found to be not highly toxic to lung cells under 4 h exposure (King et al., 2020), potential health effects of methylsiloxanes combustion products, such as oxidized methylsiloxanes and their co-products with fuel oils, need to be further investigated.

5. Conclusions

Particularly low $\delta^{13}\text{C}$ values of OC were found in some ship emissions samples from Italy in this study, which indicates the presence of special compounds other than fuel combustion residues. The chemical compositions of the selected samples were therefore analyzed using PTR-MS, and methylsiloxanes and derivatives were found in the mass spectra based on natural abundance of silicon isotopes. With the mass spectrometry method of identification and quantification of silicon-containing compounds developed in this study, various methylsiloxanes and derivatives were recognized in mass spectra of ship emissions. The origin of the analyzed methylsiloxane fragments and derivatives remains unclear, as they can be produced during PTR-MS analysis, except for oxidized methylsiloxanes, which were likely formed during engine combustion of PDMS contained in fuel oils or lubricating oils. It is further demonstrated that the carbon fraction of methylsiloxanes in the desorbed OC is linearly related to the corresponding $\delta^{13}\text{C}$ value. Since methylsiloxanes have very low $\delta^{13}\text{C}$ values, this implies that the low $\delta^{13}\text{C}$ value of OC in ship emissions can be explained by the presence of methylsiloxanes. The methylsiloxanes and SiO₂ from ship emissions can be an emerging contamination for coastal residents, and their contribution to gas phase and particulate pollutants needs urgent investigation. Possible methylsiloxanes and SiO₂ emissions from other combustion sources, such as other engine powered vehicles, also need urgent investigation.

CRedit authorship contribution statement

Peng Yao: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Visualization, Data curation, Writing – original draft, Writing – review & editing. **Elena Chianese:** Resources, Validation, Investigation, Writing – review & editing. **Norbertas Kairys:** Validation, Investigation, Data curation. **Rupert Holzinger:** Methodology, Validation, Investigation, Writing – review & editing. **Dušan Materić:** Validation, Investigation, Writing – review & editing. **Carmina Sirignano:** Resources, Validation, Investigation. **Angelo Riccio:** Resources, Validation, Investigation, Writing – review & editing. **Haiyan Ni:** Validation, Investigation, Data curation. **Ru-Jin Huang:** Validation, Investigation, Funding acquisition, Writing – review & editing. **Ulrike Dusek:** Conceptualization, Methodology, Validation, Investigation, Writing – review & editing, Supervision, Project administration, Funding acquisition.

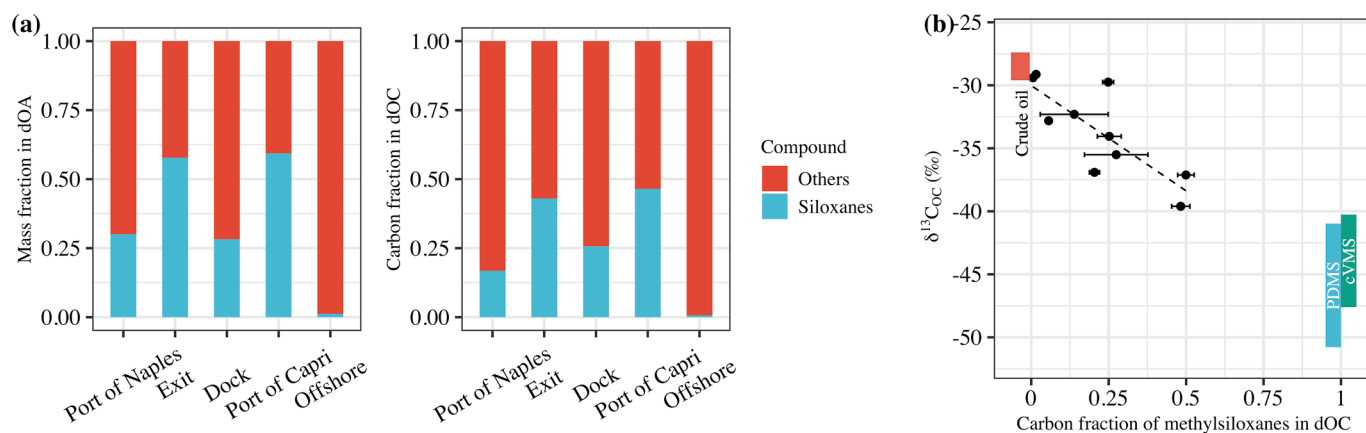


Fig. 4. (a) Mass fractions of methylsiloxanes in desorbed organic aerosols (dOA) and carbon fractions of methylsiloxanes in desorbed organic carbon (dOC) measured by the PTR-MS under different cruise conditions. Data see Table S13. (b) The correlation between carbon fractions of methylsiloxanes in dOC and corresponding $\delta^{13}C_{OC}$ values. The black dots refer to carbon fractions desorbed at 200 °C and 350 °C under different cruise conditions. The black dashed line is the linear regression line to the data. The red rectangle refers to the $\delta^{13}C$ value of regional crude oil, estimated to be $-28.5\text{‰} \pm 1.1\text{‰}$ (Table S3). The blue rectangle refers to the $\delta^{13}C$ value of pure PDMS determined in this study, averaged to be $-45.88\text{‰} \pm 4.90\text{‰}$ (Table S2a). The green rectangle refers to $\delta^{13}C$ value of cVMS summarized from the literature (Pieri et al., 2013), averaged to be $-43.93\text{‰} \pm 3.67\text{‰}$ (Table S2b). The rectangles corresponding to carbon fraction of 0 (pure crude oil) or 1 (pure methylsiloxanes) have been shifted on the x-axis to avoid overlapping.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting Information

Supporting Information to this article can be found online at <https://doi.org/10.1016/j.envint.2022.107324>.

References

- Ai, G., Sun, T., Dong, X., 2014. Evaluation of hydrolysis and alcoholysis reactions in gas chromatography/mass spectrometry inlets. *J. Chromatogr. A* 1356, 283–288. <https://doi.org/10.1016/j.chroma.2014.06.036>.
- Alton, M.W., Browne, E.C., 2020. Atmospheric Chemistry of Volatile Methyl Siloxanes: Kinetics and Products of Oxidation by OH Radicals and Cl Atoms. *Environ. Sci. Technol.* 54, 5992–5999. <https://doi.org/10.1021/acs.est.0c01368>.
- Andriot, M., Chao, S.H., Colas, A., Cray, S., de Buyl, F., DeGroot, J.V., Dupont, A., Easton, T., Garaud, J.L., Gerlach, E. and Gubbels, F., 2007. Silicones in industrial applications. In: *Silicon-based Inorganic Polymers*, De Jaeger, R. and Gleria, M., New York: Nova Science Publishers, 61–161.
- Blázquez, C., Emond, E., Schneider, S., Dalmazzone, C., Bergeron, V., 2014. Non-Aqueous and Crude Oil Foams. *Oil Gas Sci. Technol. – Rev. d'IFP Energies Nouv.* 69, 467–479. <https://doi.org/10.2516/ogst/2013186>.
- Brown, W.L., Day, D.A., Stark, H., Pagonis, D., Krechmer, J.E., Liu, X., Price, D.J., Katz, E. F., DeCarlo, P.F., Masoud, C.G., Wang, D.S., Hildebrandt Ruiz, L., Arata, C., Lunderberg, D.M., Goldstein, A.H., Farmer, D.K., Vance, M.E., Jimenez, J.L., 2021. Real-time organic aerosol chemical speciation in the indoor environment using extractive electrospray ionization mass spectrometry. *Indoor Air* 31, 141–155. <https://doi.org/10.1111/ina.12721>.
- Bzdek, B.R., Horan, A.J., Pennington, M.R., Janecek, N.J., Baek, J., Stanier, C.O., Johnston, M.V., 2014. Silicon is a Frequent Component of Atmospheric Nanoparticles. *Environ. Sci. Technol.* 48, 11137–11145. <https://doi.org/10.1021/es5026933>.
- Cavalli, F., Viana, M., Yttri, K.E., Genberg, J., Putaud, J.-P., 2010. Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol. *Atmos. Meas. Tech.* 3, 79–89. <https://doi.org/10.5194/amt-3-79-2010>.
- Centers, P.W., 1993. Behavior of Silicone Antifoam Additives in Synthetic Ester Lubricants. *Tribol. Trans.* 36, 381–386. <https://doi.org/10.1080/10402009308983173>.
- Chen, J., Huang, X., He, L., Luo, X., 2019. Foaming of Oils: Effect of Poly (dimethylsiloxanes) and Silica Nanoparticles. *ACS Omega* 4, 6502–6510. <https://doi.org/10.1021/acsomega.9b00347>.
- Chianese, E., Tirimberio, G., Appolloni, L., Dinoi, A., Contini, D., Di, A., Palmisani, J., Cotugno, P., Valeria, D., Ulrike, M., Gennaro, D., Angelo, C., 2021. Chemical characterisation of PM₁₀ from ship emissions: a study on samples from hydrofoil exhaust stacks. *Environ. Sci. Pollut. Res.* <https://doi.org/10.1007/s11356-021-17035-y>.
- Donahue, N.M., Robinson, A.L., Stanier, C.O., Pandis, S.N., 2006. Coupled Partitioning, Dilution, and Chemical Aging of Semivolatile Organics. *Environ. Sci. Technol.* 40, 2635–2643. <https://doi.org/10.1021/es052297c>.
- Dusek, U., Meusinger, C., Oyama, B., Ramon, W., de Wilde, P.A., Holzinger, R., Röckmann, T., 2013. A thermal desorption system for measuring $\delta^{13}C$ ratios on organic aerosol. *J. Aerosol Sci.* 66, 72–82. <https://doi.org/10.1016/j.jaerosci.2013.08.005>.
- Eichler, P., Müller, M., Rohmann, C., Stengel, B., Orasche, J., Zimmermann, R., Wisthaler, A., 2017. Lubricating Oil as a Major Constituent of Ship Exhaust Particles. *Environ. Sci. Technol. Lett.* 4, 54–58. <https://doi.org/10.1021/acs.estlett.6b00488>.
- Fairbrother, A., Woodburn, K.B., 2016. Assessing the Aquatic Risks of the Cyclic Volatile Methyl Siloxane D4. *Environ. Sci. Technol. Lett.* 3, 359–363. <https://doi.org/10.1021/acs.estlett.6b00341>.
- Flassbeck, D., Pfeleiderer, B., Grümping, R., Hirner, A.V., 2001. Determination of Low Molecular Weight Silicones in Plasma and Blood of Women after Exposure to Silicone Breast Implants by GC/MS. *Anal. Chem.* 73, 606–611. <https://doi.org/10.1021/ac000738z>.
- Fuentes, M.J., Font, R., Gómez-Rico, M.F., Martín-Gullón, I., 2007. Pyrolysis and combustion of waste lubricant oil from diesel cars: Decomposition and pollutants. *J. Anal. Appl. Pyrolysis* 79, 215–226. <https://doi.org/10.1016/j.jaap.2006.12.004>.
- Genualdi, S., Harner, T., Cheng, Y., MacLeod, M., Hansen, K.M., van Egmond, R., Shoeib, M., Lee, S.C., 2011. Global Distribution of Linear and Cyclic Volatile Methyl Siloxanes in Air. *Environ. Sci. Technol.* 45, 3349–3354. <https://doi.org/10.1021/es200301j>.
- Grabowski, W., OSI Specialties Inc, 1996. Efficient diesel fuel antifoams of low silicon content. U.S. Patent 5,542,960.
- Guaillar-Hoyas, C., Turner, M.A., Blackburn, G.J., Wilson, I.D., Thomas, C.L.P., 2012. A workflow for the metabolomic/metabonomic investigation of exhaled breath using thermal desorption GC–MS. *Bioanalysis* 4 (18), 2227–2237.
- Guo, J., Zhou, Y., Cui, J., Zhang, B., Zhang, J., 2019. Assessment of volatile methylsiloxanes in environmental matrices and human plasma. *Sci. Total Environ.* 668, 1175–1182. <https://doi.org/10.1016/j.scitotenv.2019.03.092>.
- Guo, J., Zhou, Y., Sun, M., Cui, J., Zhang, B., Zhang, J., 2020. Methylsiloxanes in plasma from potentially exposed populations and an assessment of the associated inhalation exposure risk. *Environ. Int.* 143, 105931. <https://doi.org/10.1016/j.envint.2020.105931>.
- He, B., Rhodes-Brower, S., Miller, M.R., Munson, A.E., Germolec, D.R., Walker, V.R., Korach, K.S., Meade, B.J., 2003. Octamethylcyclotetrasiloxane exhibits estrogenic activity in mice via ER α . *Toxicol. Appl. Pharmacol.* 192, 254–261. [https://doi.org/10.1016/s0041-008x\(03\)00282-5](https://doi.org/10.1016/s0041-008x(03)00282-5).
- Holzinger, R., 2015. PTRwid: A new widget tool for processing PTR-TOF-MS data. *Atmos. Meas. Tech.* 8, 3903–3922. <https://doi.org/10.5194/amt-8-3903-2015>.

- Holzinger, R., Kasper-Giebl, A., Staudinger, M., Schauer, G., Röckmann, T., 2010a. Analysis of the chemical composition of organic aerosol at the Mt. Sonnblick observatory using a novel high mass resolution thermal-desorption proton-transfer-reaction mass-spectrometer (hr-TD-PTR-MS). *Atmos. Chem. Phys.* 10, 10111–10128. <https://doi.org/10.5194/acp-10-10111-2010>.
- Holzinger, R., Williams, J., Herrmann, F., Lelieveld, J., Donahue, N.M., Röckmann, T., 2010b. Aerosol analysis using a Thermal-Desorption Proton-Transfer-Reaction Mass Spectrometer (TD-PTR-MS): a new approach to study processing of organic aerosols. *Atmos. Chem. Phys.* 10, 2257–2267. <https://doi.org/10.5194/acp-10-2257-2010>.
- Horii, Y., Kannan, K., 2008. Survey of Organosilicone Compounds, Including Cyclic and Linear Siloxanes, in Personal-Care and Household Products. *Arch. Environ. Contam. Toxicol.* 55, 701–710. <https://doi.org/10.1007/s00244-008-9172-z>.
- Katz, E.F., Lunderberg, D.M., Brown, W.L., Day, D.A., Jimenez, J.L., Nazaroff, W.W., Goldstein, A.H., DeCarlo, P.F., 2021. Large Emissions of Low-Volatility Siloxanes during Residential Oven Use. *Environ. Sci. Technol. Lett.* 8, 519–524. <https://doi.org/10.1021/acs.estlett.1c00433>.
- King, B.M., Janecek, N.J., Bryngelson, N., Adamcakova-Dodd, A., Lersch, T., Bunker, K., Casuccio, G., Thorne, P.S., Stanier, C.O., Fiegl, J., 2020. Lung cell exposure to secondary photochemical aerosols generated from OH oxidation of cyclic siloxanes. *Chemosphere* 241, 125126. <https://doi.org/10.1016/j.chemosphere.2019.125126>.
- Krogseth, I.S., Kierkegaard, A., McLachlan, M.S., Breivik, K., Hansen, K.M., Schlabach, M., 2013. Occurrence and Seasonality of Cyclic Volatile Methyl Siloxanes in Arctic Air. *Environ. Sci. Technol.* 47, 502–509. <https://doi.org/10.1021/es3040208>.
- Kuo, A.C.M., 1999. Poly (dimethylsiloxane). *Polym. data Handb.* 411–435.
- Latimer, H.K., Kamens, R.M., Chandra, G., 1998. The atmospheric partitioning of decamethylcyclopentasiloxane (D5) and 1-hydroxynonamethylcyclopentasiloxane (D4TOH) on different types of atmospheric particles. *Chemosphere* 36, 2401–2414. [https://doi.org/10.1016/S0045-6535\(97\)10209-0](https://doi.org/10.1016/S0045-6535(97)10209-0).
- Lieberman, M.W., Lykissa, E.D., Barrios, R., Ou, C.N., Kala, G., Kala, S.V., 1999. Cyclosiloxanes produce fatal liver and lung damage in mice. *Environ. Health Perspect.* 107, 161–165. <https://doi.org/10.1289/ehp.99107161>.
- Liu, N., Sun, H., Xu, L., Cai, Y., 2021. Methylsiloxanes in petroleum refinery facility: Their sources, emissions, environmental distributions and occupational exposure. *Environ. Int.* 152. <https://doi.org/10.1016/j.envint.2021.106471>, 106471.
- Lu, Y., Yuan, T., Wang, W., Kannan, K., 2011. Concentrations and assessment of exposure to siloxanes and synthetic musks in personal care products from China. *Environ. Pollut.* 159, 3522–3528. <https://doi.org/10.1016/j.envpol.2011.08.015>.
- Lu, Y., Yuan, T., Yun, S.H., Wang, W., Wu, Q., Kannan, K., 2010. Occurrence of Cyclic and Linear Siloxanes in Indoor Dust from China, and Implications for Human Exposures. *Environ. Sci. Technol.* 44, 6081–6087. <https://doi.org/10.1021/es101368n>.
- Masalaite, A., Holzinger, R., Remeikis, V., Röckmann, T., Dusek, U., 2017. Characteristics, sources and evolution of fine aerosol (PM₁) at urban, coastal and forest background sites in Lithuania. *Atmos. Environ.* 148, 62–76. <https://doi.org/10.1016/j.atmosenv.2016.10.038>.
- Materić, D., Ludewig, E., Xu, K., Röckmann, T., Holzinger, R., 2019. Brief communication: Analysis of organic matter in surface snow by PTR-MS – implications for dry deposition dynamics in the Alps. *Cryosph.* 13, 297–307. <https://doi.org/10.5194/tc-13-297-2019>.
- Materić, D., Peacock, M., Kent, M., Cook, S., Gauci, V., Röckmann, T., Holzinger, R., 2017. Characterisation of the semi-volatile component of Dissolved Organic Matter by Thermal Desorption – Proton Transfer Reaction – Mass Spectrometry. *Sci. Rep.* 7, 15936. <https://doi.org/10.1038/s41598-017-16256-x>.
- Menoud, M., VanderVeen, C., Lowry, D., Fernandez, J., Bakkalogi, S., France, J., Fischer, R., Maazallahi, H., Stanisavljevic, M., Necki, J., Vinkowich, K., Lakomic, P., Rinne, J., Korben, P., Schmidt, M., Defratyka, S., Yver-Kwol, C., Anderson, T., Chen, H., Rockmann, T., 2022. Global inventory of the stable isotopic composition of methane surface emissions, augmented by new measurements in Europe. *Earth Syst. Sci. Data* [preprint], 1–31. [10.5194/essd-2022-30](https://doi.org/10.5194/essd-2022-30).
- Meyers, V.E., García, H.D., McMullin, T.S., Tobin, J.M., James, J.T., 2013. Safe human exposure limits for airborne linear siloxanes during spaceflight. *Inhal. Toxicol.* 25, 735–746. <https://doi.org/10.3109/08958378.2013.845629>.
- Milani, A., Al-Naiema, I.M., Stone, E.A., 2021. Detection of a secondary organic aerosol tracer derived from personal care products. *Atmos. Environ.* 246. <https://doi.org/10.1016/j.atmosenv.2020.118078>, 118078.
- Mortier, R.M., Fox, M.F., Orszulik, S.T., 2010. *Chemistry and Technology of Lubricants: Third Edition*. Springer Netherlands, Dordrecht. 10.1007/978-1-4020-8662-5.
- Okan, F., Odabasi, M., Yaman, B., Dumanoglu, Y., 2021. Development of a New Passive Sampling Method for the Measurement of Atmospheric Linear and Cyclic Volatile Methyl Siloxanes. *Environ. Sci. Technol.* 55, 4522–4531. <https://doi.org/10.1021/acs.est.1c00227>.
- Pieri, F., Katsoyiannis, A., Martellini, T., Hughes, D., Jones, K.C., Cincinelli, A., 2013. Occurrence of linear and cyclic volatile methyl siloxanes in indoor air samples (UK and Italy) and their isotopic characterization. *Environ. Int.* 59, 363–371. <https://doi.org/10.1016/j.envint.2013.06.006>.
- Quinn, A.L., Regan, J.M., Tobin, J.M., Marinik, B.J., McMahon, J.M., McNett, D.A., Sushynski, C.M., Crofoot, S.D., Jean, P.A., Plotzke, K.P., 2006. In Vitro and In Vivo Evaluation of the Estrogenic, Androgenic, and Progestagenic Potential of Two Cyclic Siloxanes. *Toxicol. Sci.* 96, 145–153. <https://doi.org/10.1093/toxsci/kfl185>.
- Rochow, E.G., 1945. The Direct Synthesis of Organosilicon Compounds. *J. Am. Chem. Soc.* 67, 963–965. <https://doi.org/10.1021/ja01222a026>.
- Rücker, C., Kümmerer, K., 2015. Environmental Chemistry of Organosiloxanes. *Chem. Rev.* 115, 466–524. <https://doi.org/10.1021/cr500319v>.
- Stringer, D.A., 1994. Linear Polydimethylsiloxanes (viscosity 10–10,000 Centistokes): CAS No. 63148-62-9. European Centre for Ecotoxicology and Toxicology of Chemicals.
- Tang, X., Misztal, P.K., Nazaroff, W.W., Goldstein, A.H., 2015. Siloxanes Are the Most Abundant Volatile Organic Compound Emitted from Engineering Students in a Classroom. *Environ. Sci. Technol. Lett.* 2, 303–307. <https://doi.org/10.1021/acs.estlett.5b00256>.
- Timkovsky, J., Chan, A.W.H., Dorst, T., Goldstein, A.H., Oyama, B., Holzinger, R., 2015. Comparison of advanced offline and in situ techniques of organic aerosol composition measurement during the CalNex campaign. *Atmos. Meas. Tech.* 8, 5177–5187. <https://doi.org/10.5194/amt-8-5177-2015>.
- Tran, T.M., Kannan, K., 2015. Occurrence of cyclic and linear siloxanes in indoor air from Albany, New York, USA, and its implications for inhalation exposure. *Sci. Total Environ.* 511, 138–144. <https://doi.org/10.1016/j.scitotenv.2014.12.022>.
- Varaparth, S., Seaton, M., McNett, D., Cao, L., Plotzke, K.P., 2000. Quantitative Determination of Octamethylcyclotetrasiloxane (D4) in Extracts of Biological Matrices by Gas Chromatography-Mass Spectrometry. *Int. J. Environ. Anal. Chem.* 77, 203–219. <https://doi.org/10.1080/03067310008032683>.
- Vernooij, R., Dusek, U., Popa, M.E., Yao, P., Shaikat, A., Qiu, C., Winiger, P., van der Veen, C., Eames, T.C., Ribeiro, N., van der Werf, G.R., 2022. Stable carbon isotopic composition of biomass burning emissions – implications for estimating the contribution of C3 and C4 plants. *Atmos. Chem. Phys.* 22, 2871–2890. <https://doi.org/10.5194/acp-22-2871-2022>.
- Wang, D.-G., Norwood, W., Alae, M., Byer, J.D., Brimble, S., 2013. Review of recent advances in research on the toxicity, detection, occurrence and fate of cyclic volatile methyl siloxanes in the environment. *Chemosphere* 93, 711–725. <https://doi.org/10.1016/j.chemosphere.2012.10.041>.
- Wang, R., Moody, R.P., Koniecki, D., Zhu, J., 2009. Low molecular weight cyclic volatile methylsiloxanes in cosmetic products sold in Canada: Implication for dermal exposure. *Environ. Int.* 35, 900–904. <https://doi.org/10.1016/j.envint.2009.03.009>.
- Wang, X., Schuster, J., Jones, K.C., Gong, P., 2018. Occurrence and spatial distribution of neutral perfluoroalkyl substances and cyclic volatile methylsiloxanes in the atmosphere of the Tibetan Plateau. *Atmos. Chem. Phys.* 18, 8745–8755. <https://doi.org/10.5194/acp-18-8745-2018>.
- Ward, D.E., Radke, L.F., 1993. Emissions measurements from vegetation fires: A comparative evaluation of methods and results. In: Crutzen, P.J., Goldammer, J.G., eds. *Fire in the Environment: The Ecological, Atmospheric, and Climatic Importance of Vegetation Fires*. Dahlem Workshop Reports: Environmental Sciences Research Report 13. Chichester, England: John Wiley & Sons. 53–76.
- Warner, N.A., Evensen, A., Christensen, G., Gabrielsen, G.W., Borgå, K., Leknes, H., 2010. Volatile Siloxanes in the European Arctic: Assessment of Sources and Spatial Distribution. *Environ. Sci. Technol.* 44, 7705–7710. <https://doi.org/10.1021/es101617k>.
- Widory, D., 2006. Combustibles, fuels and their combustion products: A view through carbon isotopes. *Combust. Theory Model.* 10, 831–841. <https://doi.org/10.1080/13647830600720264>.
- Wu, Y., Johnston, M.V., 2017. Aerosol Formation from OH Oxidation of the Volatile Cyclic Methyl Siloxane (cVMS) Decamethylcyclopentasiloxane. *Environ. Sci. Technol.* 51, 4445–4451. <https://doi.org/10.1021/acs.est.7b00655>.
- Xu, J., Harrison, R.M., Song, C., Hou, S., Wei, L., Fu, P., Li, H., Li, W., Shi, Z., 2022. PM_{2.5}-bound silicon-containing secondary organic aerosols (Si-SOA) in Beijing ambient air. *Chemosphere* 288. <https://doi.org/10.1016/j.chemosphere.2021.132377>, 132377.
- Xu, L., Shi, Y., Liu, N., Cai, Y., 2015. Methyl siloxanes in environmental matrices and human plasma/fat from both general industries and residential areas in China. *Sci. Total Environ.* 505, 454–463. <https://doi.org/10.1016/j.scitotenv.2014.10.039>.
- Yang, Z., Liao, Y., An, M., Ren, H., Hao, X., Song, X., Liu, Z., 2021. Composition characteristics of siloxane derived waste lubricating oil and its effect on low-rank coal flotation. *Fuel* 305. <https://doi.org/10.1016/j.fuel.2021.121555>, 121555.
- Yao, P., Huang, R.-J., Ni, H., Kairys, N., Yang, L., Meijer, H.A.J., Dusek, U., 2022a. ¹³C signatures of aerosol organic and elemental carbon from major combustion sources in China compared to worldwide estimates. *Sci. Total Environ.* 810. <https://doi.org/10.1016/j.scitotenv.2021.151284>, 151284.
- Yao, P., Ni, H., Paul, D., Masalaite, A., Huang, R.-J., Meijer, H.A.J., Dusek, U., 2022b. An automated method for thermal-optical separation of aerosol organic/elemental carbon for ¹³C analysis at the sub-µgC level: A comprehensive assessment. *Sci. Total Environ.* 804. <https://doi.org/10.1016/j.scitotenv.2021.150031>, 150031.
- Zenker, K., Sirignano, C., Riccio, A., Chianese, E., Calafapietra, C., Prati, M.V., Masalaite, A., Remeikis, V., Mook, E., Meijer, H.A.J., Dusek, U., 2020. ^{δ13}C signatures of organic aerosols: Measurement method evaluation and application in a source study. *J. Aerosol Sci.* 145. <https://doi.org/10.1016/j.jaerosci.2020.105534>, 105534.