



Odor-active volatile organic compounds along the seafront of Thessaloniki, Greece. Implications for sources of nuisance odor

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HIGHLIGHTS

- Total mean VOCs concentrations were highest at the west site of the seafront.
- The main contributors to total odor pollution in both seasons were mercaptans.
- Most VOCs exhibited lower concentrations at the seafront in comparison to inland sites.

GRAPHICAL ABSTRACT



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ABSTRACT

Volatile organic compounds (VOCs) have long been associated with odor nuisance at urban sites close to emission sources. Sulfur containing volatile organic compounds (VOSCs) in particular, constitute a major category of malodorous compounds since some of them are characterized by intense odor and low odor thresholds. VOSCs have both, anthropogenic and biogenic sources. The purpose of this study was to assess the concentration levels of a variety of VOCs (mercaptans, sulfides, thiophenes, aromatics and aldehydes) along the seafront of the city of Thessaloniki, northern Greece, a city with frequent citizen complaints for nuisance odor. 1-Hour sampling on adsorption tubes was carried out concurrently at 3 sites along the seafront of the city (EAST, CENTER and WEST) three times during the day in winter and summer 2020. VOCs analysis, performed on a Thermal Desorption - Gas Chromatography/Mass Spectroscopy (TD-GC/MS) system. Diurnal and seasonal variations, and correlations with prevailing meteorological conditions were investigated. Concentrations found along the seafront were compared to previous data from inner-city sites affected by urban and/or industrial activities. Most VOCs were found at lower concentrations at the seafront in comparison to inner-city sites demonstrating better air quality. Typical biogenically-deriving VOSCs such as carbonyl sulfide and dimethyl sulfide were found at the seafront either at higher or at similar levels with inner city thus suggesting negligible contribution from biogenic sources. Odor activity values were further calculated and assessed. Odor nuisance at all seafront sites was significantly higher in winter, being in both seasons maximum at the WEST seafront that is closer to port activities, polluted creek estuaries and industrial facilities. Mercaptans were identified as the major contributors to odor pollution followed by aldehydes. The new findings described in this study might contribute to the better understanding of the odor pollution from VOCs at coastal urban sites.

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1. Introduction

Odor nuisance in urban regions is a worldwide-recognized issue. Indeed, odor emissions are a common source of complaints, affecting the quality of life of humans (Conti et al., 2020).

Volatile organic compounds (VOCs) have long been associated with odor nuisance at urban sites close to emission sources (Gallego et al., 2008). Volatile Organic Sulfur Compounds (VOSCs) in particular, including mercaptans, and other reduced sulfur organic compounds such as sulfides and disulfides, are the main sub-category of VOCs responsible for odor episodes, as they are characterized by a particularly strong, penetrating and repulsive odor. VOSCs have a low molecular weight and therefore easily escape into the gas phase. In addition to odor nuisance, VOSCs play an important role in the sulfur cycle participating in biological, chemical and geochemical processes. They play an important role in atmospheric chemistry, since their presence has impact on air quality (contribute to acid deposition), climate change (contribute to cloud condensation nuclei CCN) and human health (Chasteen and Bentley, 2004; Li and Shooter, 2004; Sanchez et al., 2018).

Natural sources of VOSCs to the atmosphere include anaerobic reduction of sulfates and decomposition of organic matter in surface waters and soils. Carbonyl sulfide is the most abundant reduced sulfur trace gas in the atmosphere with an average tropospheric life time of 2–6 years and known sources including oceans, anaerobic soils, marshes, precipitation, and volcanoes (Du et al., 2017). Dimethyl sulfide is the most abundant volatile biogenic sulfide emanating from the oceans, lakes, salt marshes and estuaries, vegetation, soils and freshwater wetlands. Since its production is common among algae of marine or saline habitat, dimethyl sulfide has been found to be the major sulfur gas in coastal waters, with lesser amounts of carbonyl sulfide and carbon disulfide (Turner and Liss, 1985). Once released in the atmosphere, dimethyl sulfide rapidly reacts with radicals (OH and NO_3^-) thus its tropospheric lifetime is about 12 days (Du et al., 2017).

However, the primary emission sources of VOSCs into the atmosphere are anthropogenic (Ras et al., 2008; Vassilakos et al., 2002). The majority of relevant research concerns the identification of VOSCs in ambient air close to municipal solid waste treatment plants (Gallego et al., 2012; Rodríguez-Nava et al., 2012), landfills (Borrás et al., 2016; Liu et al., 2018), sewer networks (Wang et al., 2015), wastewater treatment plants (Ras et al., 2008; Fisher et al., 2018; He et al., 2018; González et al., 2019; Gallego et al., 2016), oil refineries (Besis et al., 2020), petrochemical plants (Gallego et al., 2019), and viscose plants (Brunekreef and Harssema, 1980) where a strong odor is observed.

Measurements of VOSCs in Greece are rather scarce limited in areas close to industrial sources. Methyl mercaptan, carbon disulfide and carbonyl sulfide were found at high concentrations close to an oil refinery (Vassilakos et al., 2002; Vasilakos et al., 2005), while dimethyl trisulfide, dimethyl sulfide and dimethyl disulfide were found in and close to a rendering plant (Sazakli and Leotsinidis, 2021). A broad array of VOSCs including 8 mercaptans, 7 sulfides and 5 thiophenes were detected in the west part of the city of Thessaloniki, in northern Greece that has diachronically been faced odor nuisance episodes (Besis et al., 2020). Concentrations of mercaptans found in this area, that is adjacent to a large-scale petroleum refining and petrochemical process complex, were significantly higher than those measured at other sites of the city suggesting influence from wastewater and petroleum sludge management activities in the oil refinery (Besis et al., 2020).

It is worth to note that exempting benzene, toluene, ethylbenzene, and xylenes (BTEX), that have been previously measured in downtown Thessaloniki (Kelessis et al., 2006; Kourtidis et al., 2002), only little is known about the occurrence of VOSCs in the air of the city (Besis et al., 2020). In the past, the malodorous episodes that the city occasionally experienced were assumed to be due to hydrogen sulfide since its annual mean concentration ($8 \mu\text{g m}^{-3}$) at an urban traffic site (at the crossroads of two main roads), was found to be higher than the WHO

recommendation for odor annoyance ($7 \mu\text{g m}^{-3}$, WHO, 2000) (Kourtidis et al., 2008).

The purpose of this study was to measure and assess the levels of odorous VOCs in the seafront of the city of Thessaloniki, a city with frequent citizen complaints for nuisance odor, and explore potential sources. For this purpose, VOC sampling was carried out at three sites along the seafront of the city during winter and summer of 2019–2020. A total of 56 VOCs were identified, including 20 VOSCs (mercaptans, sulfides, thiophenes), 23 aromatic hydrocarbons and 13 oxygenated VOCs (aldehydes). Diurnal and seasonal variations, and correlations with prevailing meteorological conditions were investigated. Results were compared to those previously found at inner sites of the city of Thessaloniki and literature values. Odor activity values were further calculated and assessed in order to identify the compounds that contribute mostly to odor nuisance and their potential sources.

2. Materials and methods

2.1. Study area

Thessaloniki ($40^\circ 62' \text{E}$, $22^\circ 95' \text{N}$) is the second largest city in Greece with estimated population more than one million inhabitants, the majority of which are concentrated in the center and the northwest districts ($16,000 \text{ inhabitants km}^{-2}$). The city lies on the northern fringe of Thermaikos gulf, the Thessaloniki bay ($15\text{--}30 \text{ m depth}$), and is surrounded to the east by Sheikh Su Forest ($\sim 490 \text{ m altitude}$) (Fig. 1).

The complex topography and intense ground characteristics of the greater Thessaloniki area create a local air flow field. Prevailing winds are S-SW mainly during summer, NW mainly during winter until spring, and NE. N-NW and N-NE winds are dry and often very strong. In contrast, S-SW winds are weak (rarely exceed 1.4 m/s) contributing to the creation of a local sea breeze, that is especially felt at the coastal area although its intensity substantially decreases at inner sites of the city due to problematic urban planning. Usually, the sea breeze starts at 09:00 h in summer and 10:00 h in winter lasting up to 22:00 h and 17:00 h, respectively.

Major industrial activities with potential VOCs emissions are located to the west and northwest of the city including a big oil refinery and petrochemical process complex, polypropylene and PVC plants, a thermal natural gas-burning power plant, a natural gas metering station, petroleum and petroleum products storage tanks, and liquefied petroleum gas (LPG) facilities (Fig. 1). Other potential sources of VOCs located close to the west part of Thessaloniki include Dendropotamos creek, a pantorriotic recipient of stormwater and some untreated municipal and industrial effluents, and the crude oil pipeline where tankers unload crude oil for transportation to the oil refinery, and the port of the city (Fig. 1).

Far enough, on the west coast of Thermaikos gulf lies one of the most important ecosystems in Greece, a wetland complex which includes a system of river estuaries, marshes, lagoons and salt flats. The Kalochori lagoon and the wetland of Gallikos river are at a distance of about 3–5 km from the port of the city (Fig. 1). The water circulation pattern (Poulos et al., 2000), in combination with nutrient overloading from wastewater and the surface run-off of nearby areas featuring intense agricultural activities, has been considered to be highly associated to the spring bloom of diatoms that usually appears in the gulf (Nikolaidis and Evangelopoulos, 1997). The worst algae blooms in recent years occurred on June 26th 2017 along the port of Thessaloniki and was associated with high air temperatures an unpleasant odor.

The seafront of the city extends over 10 km. It is theoretically divided into two segments, the old and the new seafront. The old seafront, considerably narrower than the new one, is an important infrastructure in the city center extending parallel to one of the main road axes of the city that serves a traffic flow of over 60,000 vehicles daily (Vougias and Tsakalidis, 2015). The new seafront is a linear place with a length of 3 km, consisting of a long walk along the waterfront and several



Fig. 1. Map of the city of Thessaloniki and the surroundings (WEST, CENTER, EAST: sampling sites on the city's seafront; 1. Port of Thessaloniki; 2. Estuary of Dendropotamos creek; 3. Crude oil pipeline; 4. Oil refinery; 5. Wastewater treatment plant; 6. Kalochori lagoon; 7. Gallikos river wetland).

green spaces (Amprasi et al., 2020). Both seafront segments include pedestrian and bicycle paths, so high pedestrian and bicycle flow rates are observed during the spring and early summer months, especially in the evening after the sunset.

2.2. Sampling and analysis

Three sampling sites were selected along the seafront of Thessaloniki denoted as WEST, CENTER, and EAST (Fig. 1). The selection of sampling sites was based mainly on the following factors: absence of obstacles to the sea side, absence of nearby emission sources, accessibility, and representativeness of a large part of the seafront of the city.

Sampling of VOCs was carried out concurrently at the three sites using identical fixed pumps (Air Samplers Micro PNS, Umwelttechnik MCZ GmbH, Bad Nauheim, Germany) in the winter season, and portable pumps Gillian GILAIR-Plus Personal Air Sampling Pump, Sensidyne, USA ($1\text{--}5000 \text{ cm}^3 \text{ min}^{-1}$) in the summer season. For the collection of the compounds of interest, adsorption - thermal desorption columns (Markes International Limited, Llantrisant, UK) inert-coated stainless steel tubes were used, packed with a carefully optimized combination of weak and strong inert sorbents (Tenax/Sulficarb), making them perfect for profiling a wide range of compounds over a wide volatility range including reactive sulfur. Sampling was performed at a constant air flow of 50 mL min^{-1} that is the theoretical optimum flow rate for 1/4 inch o.d. tubes, (US EPA, 1999), for a period of 1 h.

Two 5-day sampling campaigns were carried out in winter (January–February 2020) and summer (July 2020) and 90 samples were collected. During each campaign, three air samples were collected during the day: in the morning (10:00–11:00), at midday (13:00–14:00), and in the afternoon (17:00–18:00).

After collection, sampled tubes were transported to the laboratory in a clean, airtight portable refrigerator, and stored in the fridge (at 4°C) until ready for analysis (within 24 h) (US EPA, 1999). Analysis was

performed in a thermal desorption - gas chromatography/mass spectrometry system (TD-GC/MS) consisting of a gas chromatograph/mass spectrometer (GC/MS-QP2020, Shimadzu, Japan) and a sulfur/labile thermal desorption unit (UNITY-xr, Markes International Limited, Llantrisant, UK) as described in Besis et al. (2020). Briefly, the primary thermal desorption of VOCs was performed at 200°C at a He (99.999% or higher purity) flow rate of 50 mL min^{-1} for 3 min. The cold trap (U-T6SUL-26, Markes International Limited, Llantrisant, UK) connected in line was maintained at -10°C . After primary desorption, the cold trap was rapidly heated from -10°C to 200°C and maintained at this temperature for 3 min (secondary desorption). Analytes were then injected into the capillary column (MEGA-624 MS PLUS, $60 \text{ m} \times 0.25 \text{ mm} \times 1.4 \mu\text{m}$) for chromatographic separation via the transfer line at 200°C . The column oven temperature started at 40°C for 1 min, increased to 230°C at a rate of 6°C min^{-1} , and then was maintained at 230°C for 15.10 min. Helium (99.999%) carrier gas flow the analytical column was approximately 1.5 mL min^{-1} (total program time 47.8 min). Electron impact source was obtained with electron energy of 70 eV. Mass spectral data were acquired over a mass range of 42–300 amu. Ion source and interface temperature were set at 230°C and 240°C , respectively.

The TD-GC/MS system was calibrated using liquid custom standards (mixtures and individual compounds in MeOH, toluene, or isooctane). The GC/MS variables were optimized for the simultaneous determination of 56 odor-active compounds including 8 mercaptans, 5 thiophenes, 7 sulfides, 23 aromatics, and 13 aldehydes.

2.3. Quality assurance and control

The Markes' Calibration Solution Loading Rig (CSLR), that has been specifically designed for loading sorbent tubes with liquid-phase standards, was used. Standard solution was prepared so that the mass of analytes introduced in the injection volume matches the expected

masses that will be collected during field monitoring. The liquid calibration standard (1.0 µL) was injected through the injector septum using a precision syringe, and onto the sampling end of the attached tube. The solution vaporized in the carrier gas flow (nitrogen, 50 mL min⁻¹ for 3–5 min) and was passed onto the sorbent tube in the vapor phase. A sufficient volume of carrier gas was required to pass through the tube so that most of the carrier solvent (e.g., methanol) passes through the sorbent and away to vent while the compounds of interest are still quantitatively retained. Then, the tube was placed directly in the tube oven for analysis.

The qualitative identification of VOCs was based on retention time and the match of the ion ratios of the target qualifier ions, using the MS data of the NIST-14 mass spectra library (NIST/EPA/NIH, NIST MS Search version 14d). A chromatographic peak was assigned to a specific VOC when the retention time was the same as that of the standard compound by ±2 s. The mass spectrum obtained from the various members of a class of isomers was particularly characteristic, thus facilitating the identification of the various members.

Quantification of VOCs was conducted by the external standard method using 4-point calibration curves (excluding the blank) that were constructed for each one of the 56 identified compounds. The standard concentrations covered, at least, the range of concentrations encountered during the analysis of real samples. Calibration curves were tested on a daily basis. Limits of detection (LOD) were calculated as signal-to-noise ratio of 3 and the limits of quantification (LOQ) as three times the LOD. Method detection limits (MDL) were calculated considering the volume of air samples (3000 mL). The performance characteristics of the TD-GC/MS analysis of the 56 targeted VOCs are provided in Table S1 while Fig. S1 shows a chromatogram of the standard mixture. The studied compounds showed repeatabilities (% relative standard deviation values) ≤25% (Ribes et al., 2007), accomplishing the EPA performance criteria (US EPA, 1999).

2.4. Odor activity values

To evaluate the contribution of each VOC in the produced odor, the odor activity value (OAV) of each compound was calculated, which is the ratio of the compound's concentration in air to its odor threshold value (OTV) based on literature data (Nagata, 2003). In that way, the most odorant compounds can be identified, as they produce the higher OAVs. Total odor was calculated as the sum odor activity of individual compounds (Σ OAVs).

2.5. Statistical treatment and mapping software

Statistical analysis of concentration data was carried out by employing SPSS version 25 (IBM Company, Chicago, IL, USA).

Concentrations identified as NDs are observations with no signal detected and these values were considered equal to 0 in statistical analysis. Concentrations between 0 and LOD identified as <LOD were substituted by LOD/2. We performed sensitivity analysis for the 4 compounds (tert-Butylmercaptan, isobutyl mercaptan, n-Butyl mercaptan, 3-Methylbenzothiophene) exhibited values below LOD at a percentage higher than 25%, using two different values (0 and LOD) and their distributions were compared to the distribution of the data set with LOD/2 by means of the Mann Whitney U test. Results are provided in Table S1b.

The Mann-Whitney U test was also used to assess spatial/seasonal differences. Associations among the different classes of VOCs and between VOCs and meteorological parameters were assessed by Spearman rank correlation analysis. Multiple linear regression analysis was further used for estimating the relationships between VOC levels (dependent variable) and independent variables including meteorological parameters, sampling site and time of sampling. Statistical significance was set at the 95% level ($P < 0.05$). Arc-GIS software (ArcGIS for Desktop Advanced, Version 10.1. Redlands, CA) was used to illustrate sampling locations on map and the spatial distribution of VOCs.

3. Results and discussion

3.1. Concentration levels and composition patterns

All targeted VOCs including 8 mercaptans, 5 thiophenes, 7 sulfides, 23 aromatics and 13 aldehydes were identifiable in the air samples from the coastal front of Thessaloniki, except 2-propyl mercaptan. The percentage of observations below LOD for each compound are reported in Table S1a.

The mean, median, 5th percentile and 95th percentile concentrations of individual compounds measured in winter and summer are provided in the Supplementary Material (Table S2).

The sum concentrations of each VOC sub-class in winter and summer are illustrated in Fig. 2. Apparently, sulfides were the predominant sub-class of VOCs along the seafront, followed by mercaptans, whereas thiophenes were detected at very low concentrations only. Among the non-sulfur VOCs, aldehydes appeared to be at comparable levels with aromatics in winter, however, showing clear prevalence in summer.

The average profiles of each VOC class, i.e., the percent contribution of each compound to the sum of their concentrations, are shown in Fig. 3. Sec-butyl-mercaptan prevailed Σ_8 Mercaptans across the whole seafront (50–61%) in winter followed by tert-butyl-mercaptan and 1-propyl-mercaptan. In summer, sec-butyl-mercaptan continued to prevail at the West (49%), whereas tert-butyl-mercaptan dominated by far at the East and the Center (72–84%). Concerning Σ_5 Thiophenes, similar profiles were observed along the seafront sites with 2-methyl-thiophene prevailing in winter (70–79%), and 3-methyl-benzothiophene in summer (65–90%). The Σ_7 Sulfides profile at all sites was by far dominated by carbonyl sulfide (70–78% in winter, 82–90% in summer). The aromatic profile also showed a recurring pattern along the seafront sites with toluene dominating Σ_{23} Aromatics (56–79%) with lower contributions from benzene (3–11%) and m,p-xylene (7–10%). Finally, nonanal and decanal appeared to be the most prevalent aldehydes in winter and summer accounting for 29–39% and 42–47% to Σ_{13} Aldehydes, respectively.

In general, the chemical profiles of VOCs at the seafront are quite similar to those previously reported for the west city, close to the industrial facilities, or other non-impacted sites within the city (Besis et al., 2020). However, some differences could be attributed to diurnal variations since, in the current study, the profiles are averages of three samples during the day, whereas the profiles previously reported were based mainly on early morning samples.

3.2. Diurnal and seasonal variations

Diurnal variations of the concentrations of VOCs along the seafront during winter and summer are shown in Fig. 4.

Apparently, the diurnal pattern of VOCs varies across sites and seasons. During the winter period, mercaptans at the EAST and CENTER peaked at midday, while at the WEST they peaked in the morning. Aromatics peaked at all sites in the morning coinciding with traffic rush hours, whereas aldehydes peaked later, at midday and the afternoon, suggesting contribution from photochemical formation. During the summer period, all VOCs classes exhibited similar diurnal variation at the EAST and CENTER peaking at midday and in the afternoon, in contrast to the WEST, where the corresponding peaks of mercaptans, aromatics, sulfides and aldehydes appeared earlier. The diurnal variation of VOCs suggests that emissions and meteorological conditions (wind speed and direction) are important variables that control the atmospheric abundance, especially during stagnant weather conditions that favor the development of land-sea breeze circulations.

The highest winter/summer ratios (28, 47 and 6 at East, Center and West, respectively) were observed for Σ_5 thiophenes which showed statistically significant differences ($P < 0.05$) at all seafront sites. This suggests release preferably from wintertime sources and accumulation due to more stagnant atmospheric conditions during this season, and/or enhanced decomposition under summertime conditions. Likewise, the

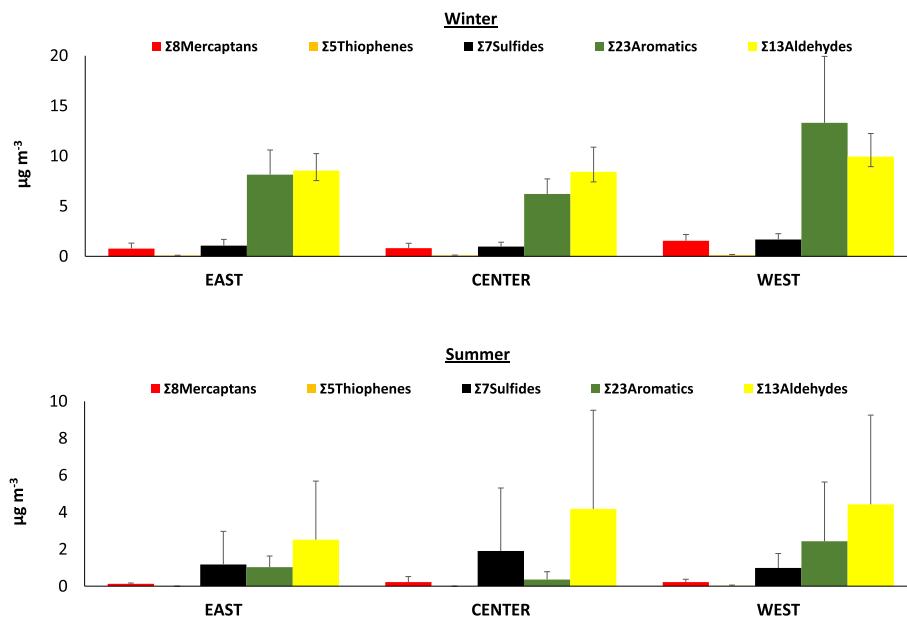


Fig. 2. Sum concentrations of each VOC class in winter and summer (mean \pm SD) ($n = 90$).

concentrations of Σ_8 Mercaptans were higher in winter than in summer at all three seafront sites (winter/summer ratios 6, 4 and 3 at EAST, CENTER and WEST, respectively) although differences were statistically significant ($P < 0.05$) only at the EAST and the CENTER. Given that mercaptans often occur at lower concentrations in summer due to enhanced photodecomposition by reaction with OH (daytime) and/or NO_3 (nighttime) (Berresheim et al., 1995), and/or lost via conversion into other forms (e.g., DMDS) under aerobic conditions (Wilber and Murray, 1990), the higher concentrations in winter found in this study suggest release from wintertime sources.

In contrast to mercaptans and thiophenes, Σ_7 Sulfides exhibited insignificant ($P > 0.05$) seasonality at the seafront sites (winter/summer ratios 0.9, 0.5 and 1.7 at the EAST, CENTER and WEST, respectively). The winter/summer ratios of carbonyl sulfide, in particular, were 0.7, 0.4 and 1.6 at the EAST, CENTER and WEST, respectively. This is in agreement to other studies reporting no significant seasonal variations for carbonyl sulfide in marine air (Mihalopoulos et al., 1992; Turner and Liss, 1985). Dimethyl sulfide also exhibited small seasonal variations (winter/summer ratios 2, 0.8 and 1.8 at the EAST, CENTER and WEST, respectively) in contrast to other studies that found up to 40 times higher concentrations in June, approximately contemporaneous with the plankton bloom (Turner and Liss, 1985).

Σ_{23} Aromatics showed significantly ($P < 0.05$) higher concentrations in winter at all three seafront sites (winter/summer ratios 8, 17 and 5 at EAST, CENTER and WEST, respectively). This seasonal pattern, that is consistent with previous findings for aromatics in the western part of the city (Besis et al., 2020), and for BTEX in the commercial center (Kelessis et al., 2006), is attributable to their emission from wintertime combustion sources and their high reactivity with OH radicals in summer.

Finally, aldehydes also showed relatively higher concentrations in winter than in summer at all three seafront sites (winter/summer ratios 3, 2 and 2 at EAST, CENTER and WEST, respectively), but the differences were statistically significant only at EAST. The relatively low winter/summer ratios could be attributed to the fact that aldehydes can be photochemically formed through reactions of alkenes with OH and NO_3 in summertime (Yang et al., 2018).

3.3. Spatial variations

The mean total VOCs concentrations (Σ_{56} VOCs) along the seafront followed the order: WEST ($26.6 \mu\text{g m}^{-3}$) > EAST ($18.6 \mu\text{g m}^{-3}$) >

CENTER ($16.5 \mu\text{g m}^{-3}$) in winter, and WEST ($8.37 \mu\text{g m}^{-3}$) > CENTER ($6.67 \mu\text{g m}^{-3}$) > EAST ($4.85 \mu\text{g m}^{-3}$) in summer. The higher concentrations at the WEST seafront might suggest stronger influence from local anthropogenic activities such as the harbor, the unloading of tankers with crude oil, and vehicular traffic, as well as potential transport from the lagoon and the natural ecosystems located at short distance to the west.

Nevertheless, according to the Mann-Whitney U test, statistically significant differences ($P < 0.05$) were observable only in winter and only between WEST and CENTER for Σ_8 Mercaptans ($1.55 \mu\text{g m}^{-3}$ vs. $0.816 \mu\text{g m}^{-3}$), and for Σ_{23} Aromatics ($13.3 \mu\text{g m}^{-3}$ vs. $6.22 \mu\text{g m}^{-3}$). In contrast, no significant spatial differences were observable for any VOCs sub-class in summer ($P > 0.05$).

3.4. Comparison with inner-city sites

To the best of our knowledge, there are no literature values concerning the occurrence of odorous VOCs at the seafront of coastal cities. The concentrations found in the present study along the seafront of Thessaloniki are in general at similar or lower levels with those reported for other urban and industrial sites. Specifically, concentrations of mercaptans are lower than those found near landfills in Spain (Borrás et al., 2016). Also, concentrations of mercaptans, thiophenes and sulfides are lower than those found in the delta of polluted streams in Turkey, where malodor episodes were frequent (Muezzinoglu, 2003). Concentrations of sulfides are at similar levels compared to those reported for urban and industrial areas of Spain (Borrás et al., 2016; Gallego et al., 2019; Ribes et al., 2007), and the Brazil's coastal front (Nunes et al., 2005). Aromatics were found at similar levels with urban sites in Spain (Gallego et al., 2019), Turkey (Yurdakul et al., 2013), southern China (Hong et al., 2019), Argentina (Massolo et al., 2010), and Canada (Bari and Kindzierski, 2018; Xu et al., 2016), but significantly lower than those reported for industrial sites in the Yangtze River Delta region, China (Jia et al., 2021) and in coastal cities of China (Tong et al., 2013). Finally, the concentrations of aldehydes were also at similar levels like those reported for urban and industrial sites in Spain (Gallego et al., 2019; Ribes et al., 2007) (Table S4).

Fig. 5 presents the average concentrations found along the seafront in comparison to those previously found at inner-city sites of the city of Thessaloniki (Besis et al., 2020). Although direct comparison should be made with much cautiousness due to the different sampling period and frequency at each site, the seafront sites appear to have lower

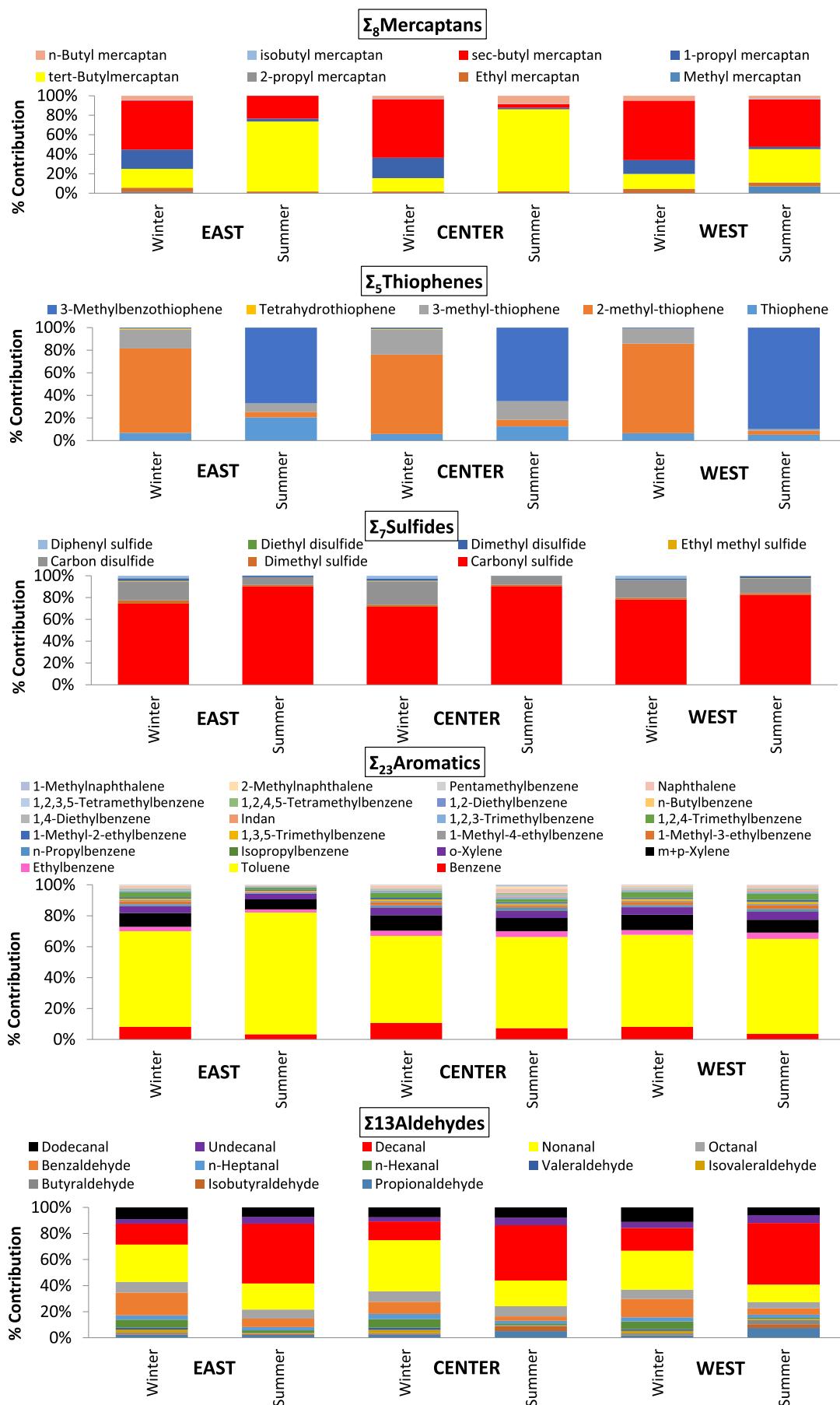


Fig. 3. Mean profiles of VOCs classes at the three seafront sampling sites during winter and summer.

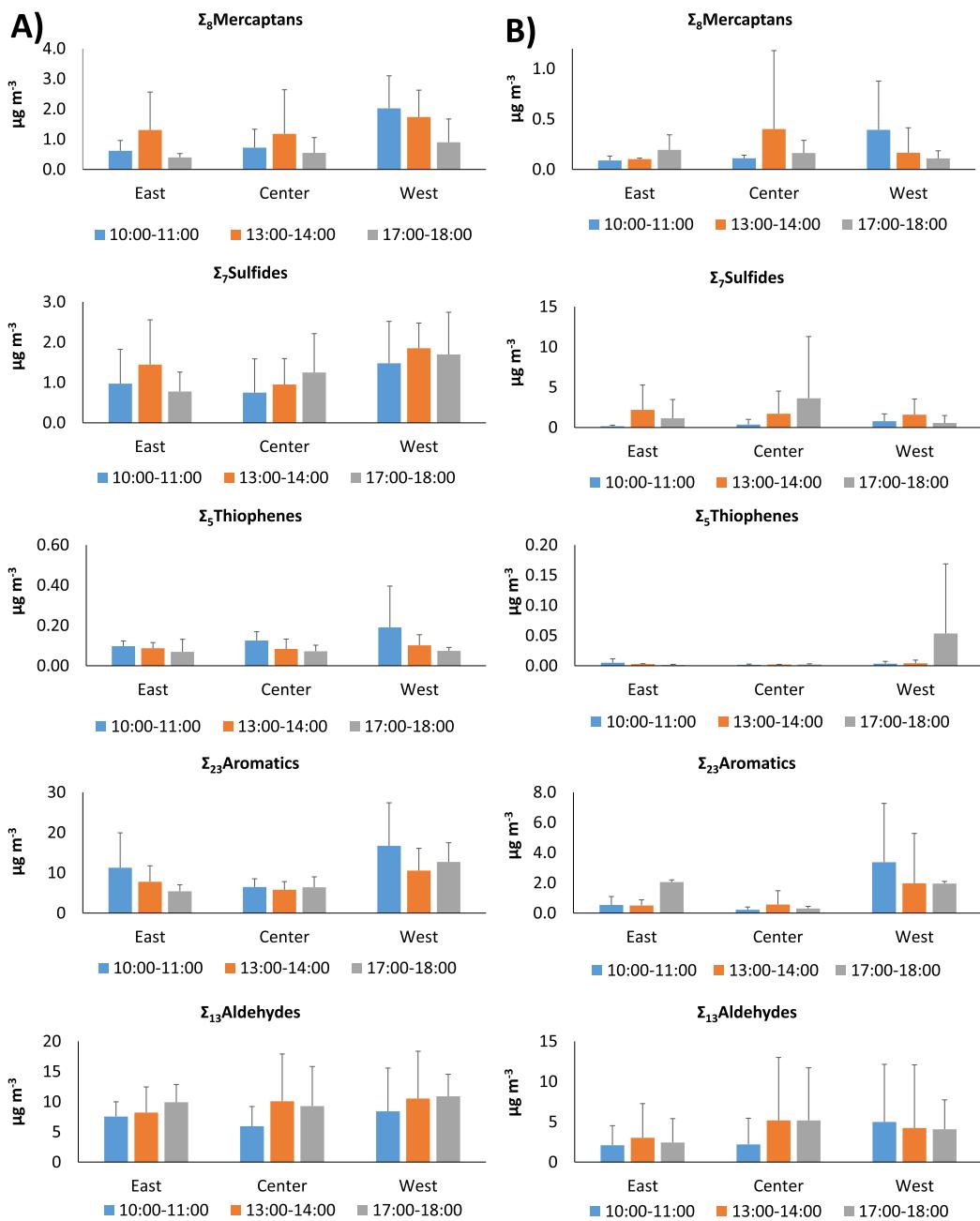


Fig. 4. Diurnal variations of the coastal concentrations of VOCs (mean \pm SD) during winter (a) and summer (b) ($n = 90$).

concentrations in comparison to the corresponding inner-city sites for most VOC classes, e.g. sulfides at all sites (particularly at the west), aromatics at the center and the west, aldehydes at all sites, mercaptans and thiophenes at the west. This might be attributed to emissions from inner-city sources, urban and industrial, in combination to the more stagnant atmospheric conditions prevailing within the urban agglomeration that do not favor dispersion of pollutants.

The largest difference between the seafront and the inner-city areas was observed for carbonyl sulfide ($\sim 1 \mu\text{g m}^{-3}$ on average at the seafront vs. $3.71, 6.50$ and $12.9 \mu\text{g m}^{-3}$ on average at the east, center and west inner-city, respectively). It has been reported that the surface waters of the Mediterranean Sea are supersaturated in carbonyl sulfide with respect to the atmosphere, therefore they could be sources of carbonyl sulfide to the atmosphere (Mihalopoulos et al., 1992). However, in the current study, carbonyl sulfide seems to be released from anthropogenic rather than biogenic sources. Dimethyl sulfide was found at

similar levels at the seafront and at inner-city thus suggesting negligible contribution from biogenic sources.

Only mercaptans appeared to be slightly higher at the CENTER and EAST seafront in comparison to the corresponding inner-city sites thus suggesting potential influence from sources located in the sea sector.

3.5. Odor pollution

Total odor activity values (Σ OAVs) are presented in Fig. 6 (left column) along with their allocation to the measured VOC subclasses. It is worth noting that, in contrast to concentrations, OAVs can help better understand the odor perceived by people (Seo et al., 2014).

Odor pollution varied along the seafront following the order WEST (25.5 ± 11.2) > EAST (13.1 ± 5.7) > CENTER (12.1 ± 4.6) in winter, and CENTER (4.68 ± 4.68) \approx WEST (3.74 ± 2.87) > EAST (1.61 ± 0.66) in summer. At all sites, total odor was significantly higher in

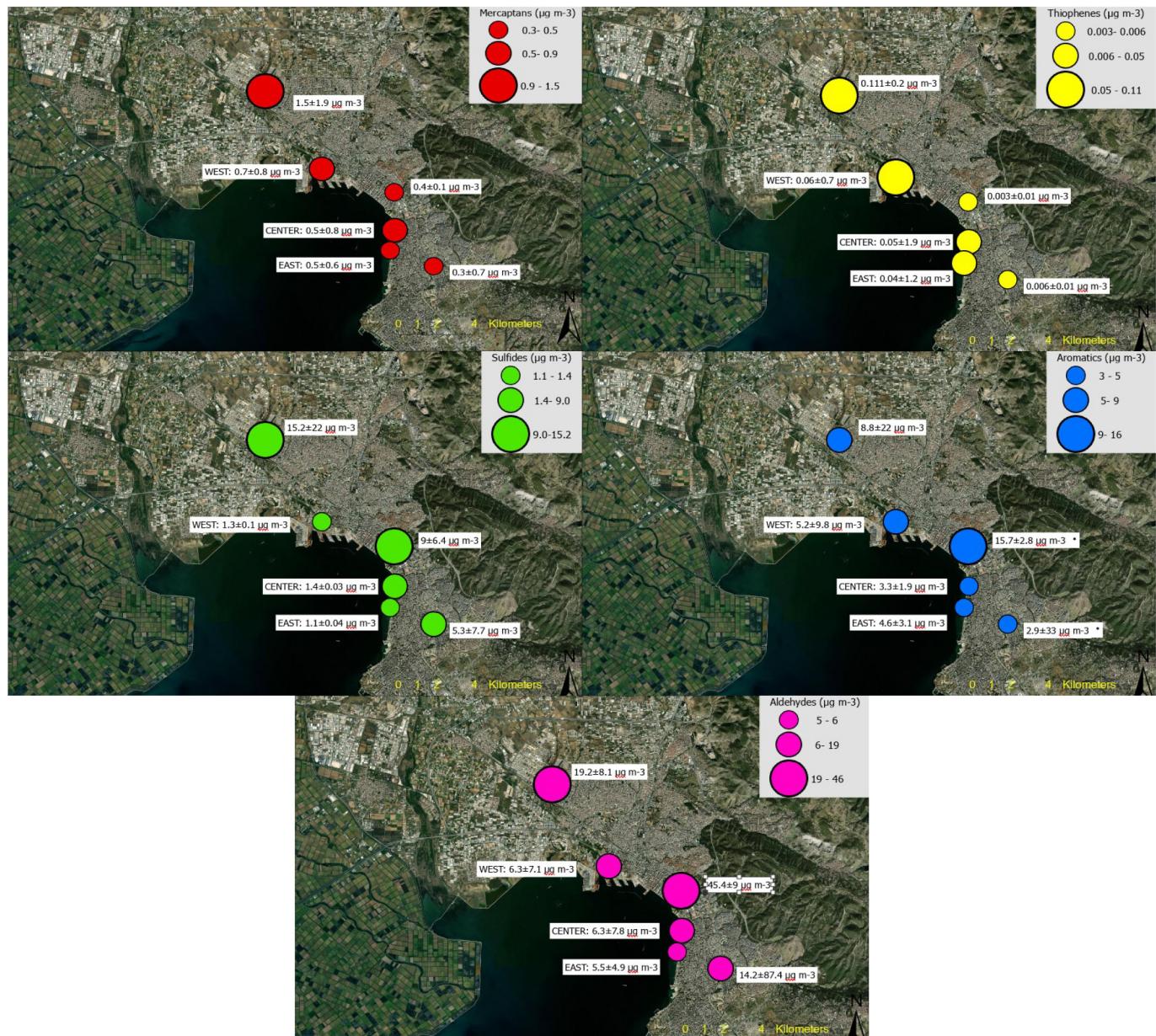


Fig. 5. Sum concentrations of VOC classes at the seafront and inland city sites (mean \pm SD) (*: Σ_{22} Aromatics, toluene is not included) (seafront n = 90; inner city east n = 10; inner city center n = 10; inner city west n = 312, Besis et al., 2020).

winter than in summer with winter/summer ratios 8, 3 and 7 at the EAST, CENTER and WEST, respectively. The main contributors to total odor in both seasons appeared to be mercaptans (69–91% of Σ OAVs) followed by aldehydes (9–30% of Σ OAVs). This specifies that the VOC subclasses found at high concentrations in the air do not necessarily contribute the most to odor nuisance, moreover, it reveals the odor pollution role of aldehydes in addition to their ozone formation potential and their adverse health effects on humans.

The odor activity values allocated to individual compounds are presented in Fig. 6 (right column). Apparently, sec-butyl mercaptan and n-butyl mercaptan were the dominant odorants in winter with decreasing contributions from ethyl mercaptan, tert-butyl mercaptan, nonanal and octanal. Correspondingly, the dominant odorants in summer were mercaptans (tert- and sec-butyl mercaptans at EAST, tert- and n-butyl mercaptans at CENTER, tert-, sec-, and n-butyl mercaptans at the WEST), with lower contributions from ethyl mercaptan, nonanal and octanal.

3.6. Correlation with meteorological factors and multiple regression analysis

Meteorological conditions prevailing during each sampling were obtained from the meteorological station of the Region of Central Macedonia located within the city at a distance of about 1 km from the seafront and at an altitude of ~60 m a.s.l.

Prevailing meteorological conditions during the two sampling campaigns are summarized in Table 1. Air temperature and wind speed exhibited similar seasonal variations with lower values in the cold season, in contrast to relative humidity. Likewise, air temperature and wind speed exhibited similar diurnal variations with lowest values in the morning and highest in the afternoon, whereas relative humidity exhibited the opposite diurnal trend.

Spearman rank correlation coefficients between the sum concentrations of the various VOC classes and meteorological factors are given in Table S3. Significant negative correlation with wind speed were

observed for thiophenes and aromatics at all sites, as well as for mercaptans at EAST and CENTER, and for aldehydes at EAST. This observation, which is in agreement with previous findings in the western inner part of the city (Besis et al., 2020), highlights the role of stagnant weather conditions. Significant negative correlations were also found with temperature for mercaptans, thiophenes, and aromatics at all sites, whereas for aldehydes only at the EAST. In contrast to other VOCs, sulfides did not show any correlation with meteorological factors.

Multiple regression analysis was performed to infer causal relationships of VOC levels and the values of covariates such as meteorological conditions (sampling temperature, relative humidity, wind speed and direction), sampling site and time of sampling. The results of the

regression are given in Table S5a, b, c, d, e. The F-statistic was statistically significant ($P < 0.001$) in all regressions except for sulfides that means that the independent variables in the regression model improve the fit. Nevertheless, R-squared indicated that the regression model could explain a relatively small proportion of the variance of each depended variable (25.9%, 32.7%, 10.1%, 47.1% and 25.4% for mercaptans, thiophenes, sulfides, aromatics and aldehydes, respectively) suggesting a weak relationship mainly for thiophenes.

Two independent variables appeared to have a statistically significant effect (positive) on aromatics levels: sampling site and relative humidity. For thiophenes, the unique independent variable with significant effect (negative) was sampling temperature. Sampling site and sampling temperature appeared to have a statistically significant effect

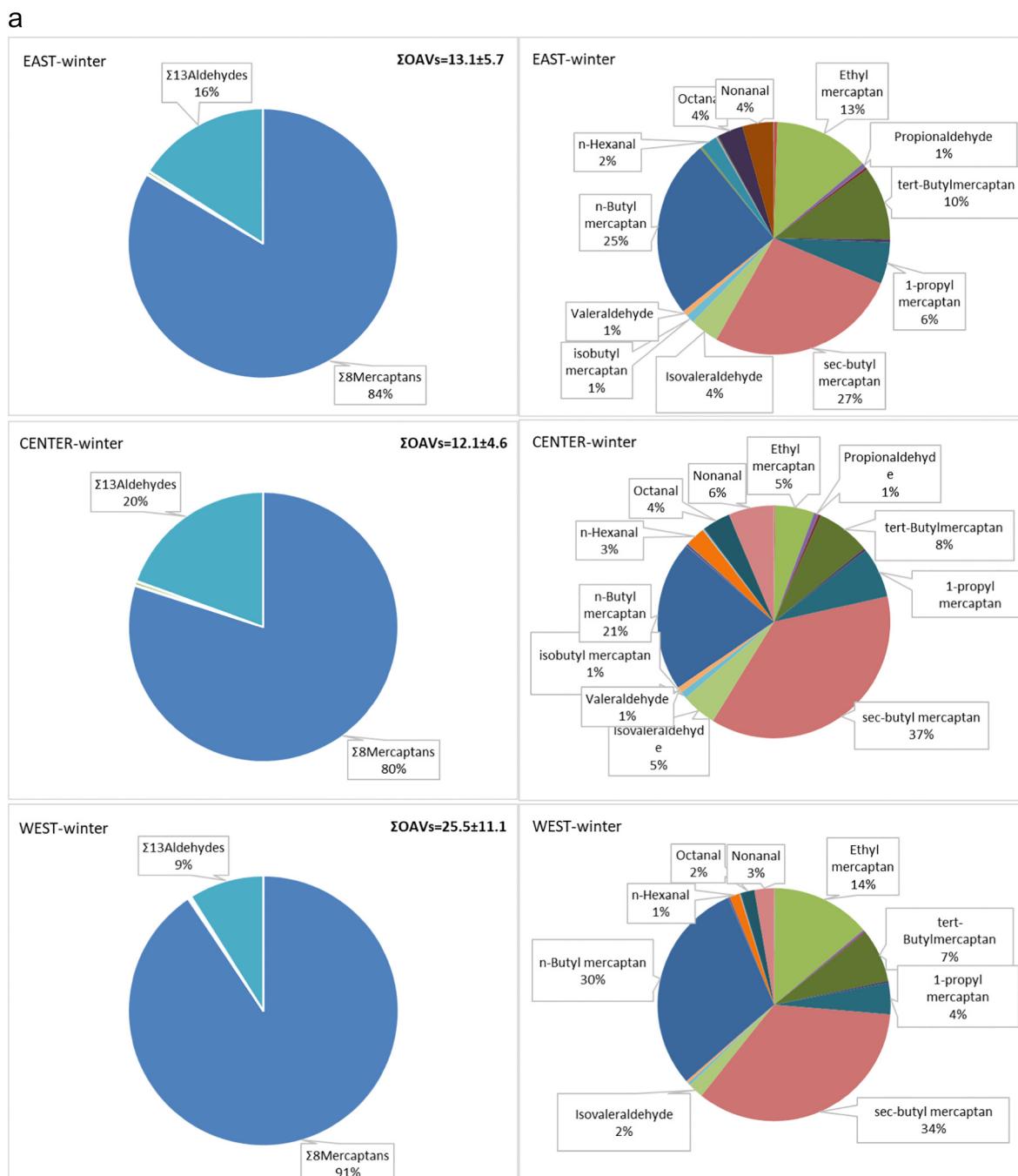


Fig. 6. Odor activity values (OAVs) attributable to VOC subclasses and individual compounds across the seafront in winter (a) and in summer (b).



Fig. 6 (continued).

(positive and negative, respectively) on mercaptan levels. Finally, for aldehydes, sampling temperature and wind speed indicated a negative effect, whereas sampling time a positive effect.

In order to evaluate the correlation of the concentrations of VOCs with wind direction, pollution rose graphs for each VOC subclass were created (Fig. 7). High concentrations of most VOCs were related to

Table 1

Average meteorological data during the cold and the warm sampling campaigns.

| Sampling period | Cold | | | Warm | | |
|-----------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Sampling hour | 10:00–11:00 | 13:00–14:00 | 17:00–18:00 | 10:00–11:00 | 13:00–14:00 | 17:00–18:00 |
| Temp (°C) | 11.3 | 15.4 | 15.8 | 26.8 | 30.4 | 32.4 |
| RH (%) | 86.9 | 64.8 | 64.5 | 57.3 | 43.0 | 43.1 |
| WS (m/s) | 1.0 | 1.3 | 1.5 | 1.8 | 2.3 | 2.8 |
| WD | SSW (60%) | SSW (100%) | SW (40%) | SSW (80%) | SSW (60%) | SSW (60%) |
| | NW (20%) | | SSW (20%) | N (20%) | SW (20%) | |
| | NE (20%) | | S (20%) | | NW (20%) | W (40%) |
| | | | NNE (20%) | | | |

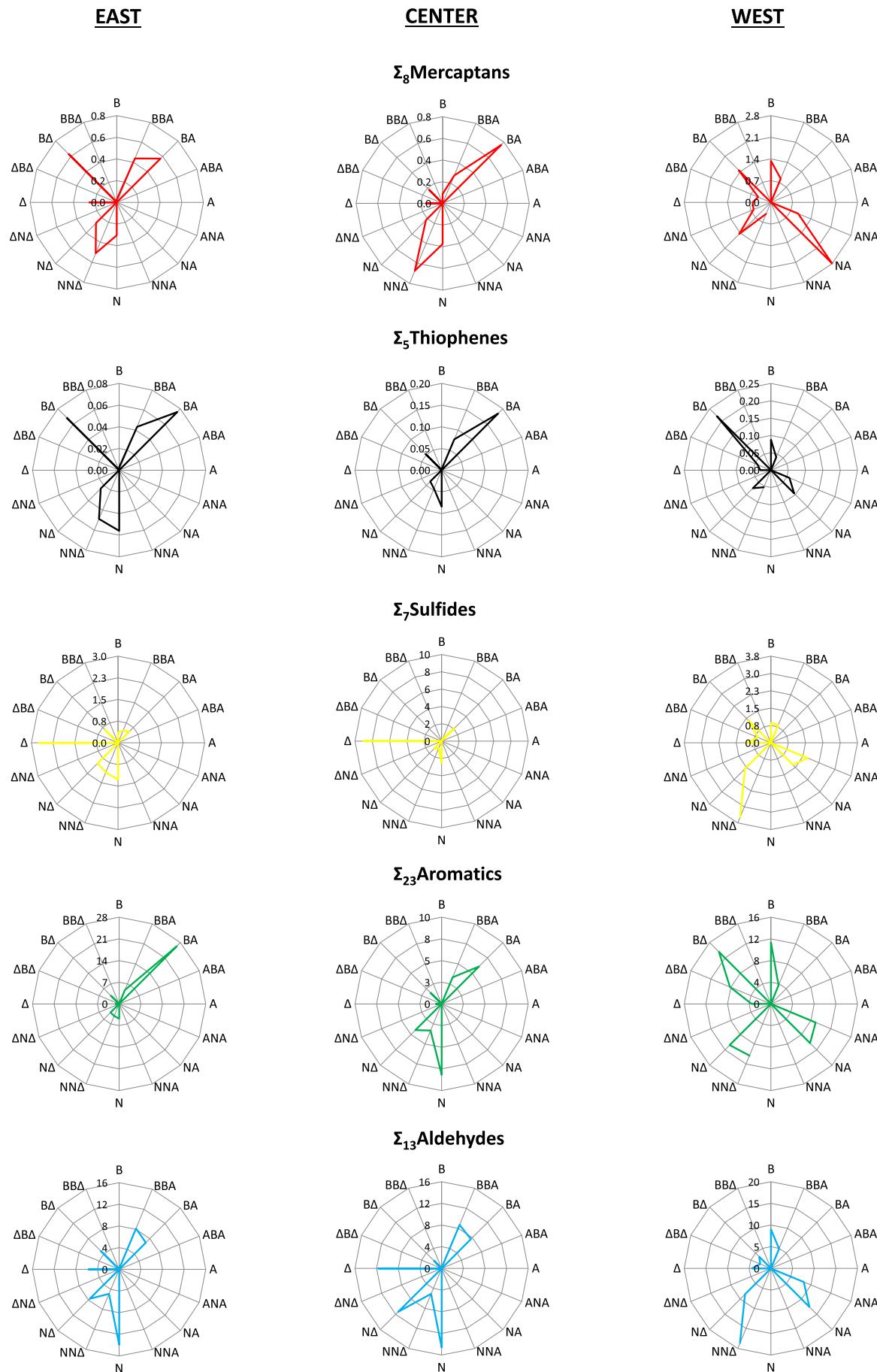


Fig. 7. Pollution rose graphs for the average concentrations of VOCs at the seafront sites.

SSW/SW and NE winds that coincide with the directions of the sea and the land breeze, respectively. Additional peak concentrations of mercaptans and thiophenes at the EAST with NW winds might suggest influence from the city sector. Correspondingly, the highest concentrations of sulfides at the EAST and CENTER were related with W winds, that were frequent during summer afternoons, implying some influence from the sea sector.

At the WEST seafront site, the highest concentrations of mercaptans and thiophenes were related with S winds suggesting potential influence from port activities, while peak concentrations of mercaptans and sulfides with W winds might suggest anthropogenic and biogenic influences from polluted areas and activities located in this direction (e.g. the estuary of Dendropotamos creek, the crude oil pipeline of the oil refinery, Fig. 1).

At all sites, aromatics were related with winds from the city sector, however a strong relation with S winds was also observed at the CENTER suggesting influence from port activities. Aldehydes also showed their highest concentrations with S winds at all sites suggesting potential photochemical formation from vehicle emissions at the EAST and CENTER, and vehicle plus ship emissions at the WEST. In addition, it has been suggested that saturated and unsaturated aldehydes may be photochemically synthesized at the air-sea interface, however it is not known yet how the interplay of sea-land breeze circulation and sea-air chemical exchange affects the air quality of coastal cities.

4. Conclusions

The concentrations of 56 VOCs, including mercaptans, thiophenes, sulfides, aromatics and aldehydes, were determined along the seafront of the city of Thessaloniki during the winter and summer 2020.

Sulfides (dominated by carbonyl sulfide) were the major sub-class of the sulfur containing VOCs along the seafront, followed by mercaptans (dominated by sec- and tert-butyl-mercaptans), whereas thiophenes were detected at very low concentrations. Among the non-sulfur VOCs, aldehydes (dominated by decanal and octanal) appeared to be at comparable levels with aromatics (dominated by toluene, benzene and xylenes) in winter, however, showing clear prevalence in summer.

Although the difference was statistically significant only in winter, the mean total VOCs concentrations (Σ_{56} VOCs) were in both seasons highest at the WEST site of the seafront suggesting stronger influence from nearby activities that, in addition to vehicular traffic, include petroleum and petroleum products storage tanks, the crude oil pipeline of the oil refinery, as well as polluted creek estuaries and lagoons.

Most VOCs sub-classes (thiophenes, mercaptans, aromatics, aldehydes) exhibited higher concentrations in winter, in contrast to sulfides that did not show noticeable seasonality. The diurnal variation of VOCs suggested that their atmospheric abundance is influenced by emissions and meteorological conditions especially during stagnant weather conditions that favor the development of land-sea breeze circulations.

Odor nuisance, significantly higher in winter, varied along the seafront being highest at the WEST in winter, and at the WEST and the CENTER in summer. The main contributors to total odor pollution in both seasons appeared to be mercaptans (69–85%) followed by aldehydes (15–30%). This indicates that the VOC subclasses found at high concentrations in the air do not necessarily contribute the odor nuisance.

Most VOCs exhibited lower concentrations at the seafront in comparison to inner-city sites demonstrating better air quality. Correlation with wind direction indicated relation of most VOCs with the directions of the sea and the land breeze that recycles pollutants from the city to the sea and vice versa. However, other sources were also assumed as likely to affect particularly the WEST seafront including port activities, polluted creek estuaries and industrial facilities.

4.1. Limitations of the study

This study has potential limitations regarding sample size, equipment and statistical treatment of analytical data that could be addressed in future research.

First, the total number of samples (90) was probably inadequate to provide answers to all survey questions set including spatial, seasonal and diurnal variations. Second, the time coverage of the two sampling campaigns is relatively small, 5 days, which might not be representative of a whole season. The limited time duration of the sampling campaigns, particularly in summer, is probably the reason that no any odor event from the sea associated with phytoplankton blooming was identified although such events are usual in summer months (June-July) almost every year. Therefore, an odor event – targeted sampling along the seafront of the city is recommended in future research for accurate assessment of the relative contribution of biogenic sources to odor nuisance.

Another limitation of the study is the statistical treatment of data that for certain VOCs that exceeded a large percentage of concentration values below the LODs particularly in the summer campaign. Following the simplistic practice commonly used in the vast majority of environmental studies, values between zero (i.e. with no signal detected) and LOD were substituted by LOD/2. Alternative to substitution statistical approaches, such as maximum likelihood estimation (MLE), Regression on order statistics (ROS), Tobit regression, Kaplan-Meier estimator, etc., would probably better perform to data sets with multiple nondetects (Helsel, 2005; Shoari and Dube, 2018), however they were not available in the statistical package used in this study.

CRediT authorship contribution statement

Athanasiос Besis: Conceptualization, Methodology, Investigation, Writing – original draft, Supervision. **Eleni Georgiadou:** Formal analysis, Investigation, Writing – original draft. **Constantini Samara:** Conceptualization, Methodology, Writing – original draft, Supervision, Project administration.

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. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2021.149388>.

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