Concentrations and Composition of Atmospheric Nitroaromatic Compounds over the Yellow Sea in Summer

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Abstract. Five $PM_{2.5}$ samples were collected over the Yellow Sea from July 13 to 17, 2024, and analyzed for 11 nitroaromatic compounds (NACs). The total NAC concentrations ranged from 0.18 to 1.54 ng/m³, with an average of 0.82 ng/m^3. 5-Nitrosalicylic acid (5NSA), 4-nitrophenol (4NP), and 5-nitroguiacol (5NG) were the dominant species. Sample Q4 showed the highest concentration (1.54 ng/m^3), while Q5 the lowest (0.18 ng/m^3). Meteorological data indicated average temperature of 24.6°C, relative humidity of 90.0%, and wind speed of 7.7 m/s. High humidity and low wind speed favored the partitioning of NACs into the particle phase. This study provides the first baseline data on atmospheric NACs over the Yellow Sea in summer, offering insights into the sources and secondary formation of organic aerosols in this region.

1 Introduction

Nitroaromatic compounds (NACs) are important light-absorbing components of organic aerosols, with significant impacts on climate and human health[1]. They contribute substantially to brown carbon (BrC) absorption in the ultraviolet–visible range, affecting radiative forcing and atmospheric photochemistry. Moreover, several NACs are known to be cytotoxic and mutagenic, posing potential risks to both marine and terrestrial ecosystems. They originate from incomplete combustion of fossil fuels and biomass, as well as secondary formation via photochemical oxidation of volatile organic compounds (e.g., phenols with OH and NO_3 radicals)[2, 3]. Recently, aqueous-phase nitration of phenols under acidic conditions has been recognized as an additional important pathway[2]. The Yellow Sea is a semi-enclosed sea heavily influenced by surrounding industrial, port, and shipping emissions. Rapid economic development around the Bohai Rim region has led to elevated atmospheric pollutant levels, yet marine atmo-spheric chemistry over this sea remains understudied. In particular, seasonal patterns of NACs are poorly characterized, and summer conditions, characterized by high temperature, strong solar radiation, and high humidity, may favor secondary formation processes. However, studies on atmospheric NACs over this region are still scarce[1]. To fill this knowledge gap, we collected $PM_{2.5}$ samples during a summer cruise, analyzed the concentrations and composition of NACs, and combined with meteorological parameters to explore their sources and influencing factors, providing scientific support for air pollution control in the region.

2 Sampling and Analysis

2.1 Sample Collection

$PM_{2.5}$ samples were collected using a high-volume sampler (flow rate ~1.05 m^3/min) over the Yellow Sea (120°52′–124°00′E, 34°00′–36°29′N) from July 13 to 17, 2024. A total of five filter samples (Q1–Q5) were obtained. Sampling durations ranged from 12 to 20 hours, and stop sampling when stopping the ship to prevent the sample from being polluted. The corresponding start and stop times for each sample are presented in Table 1. This table provides a clear summary of the temporal boundaries associated with the data collection process for all samples. Each sample recorded meteorological parameters including temperature, relative humidity, wind speed, wind direction, and pressure.

Table 1. Sampling record.

Sample	Start time	End time
Q1-July 13	Jul 13 8:17	Jul 13 23:39
Q2- July 14	Jul 13 23:39	Jul 15 2:36
Q3- July 15	Jul 15 3:22	Jul 16 4:20
Q4- July 16	Jul 16 5:04	Jul 17 3:11
Q5- July 17	Jul 17 4:30	Jul 17 22:05

Aerosol samples were collected using Pall quartz fiber filters. These filters are specifically chosen for their high thermal resistance and low trace organic background, making them suitable for subsequent carbonaceous analyses. After sampling, each filter was wrapped in aluminum foil for preservation. The foil wrapping was performed immediately after sampling to prevent contamination from ambient particulates and to avoid loss

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of volatile components. Both the filters and aluminum foil were pre-baked at 500 °C to remove organic residues prior to use. This pre-baking temperature is sufficiently high to oxidize and eliminate any residual organic carbon without compromising the structural integrity of the quartz fibers or the foil. The sealed filter samples were stored at −20 °C until chemical analysis. Such sub-freezing storage effectively inhibits microbial activity and chemical degradation, thereby preserving the original composition of the collected aerosols.

2.2 Nitroaromatic compounds Analysis

Filters were extracted by ultrasonication, concentrated under nitrogen, and analyzed using high-performance liquid chromatography-mass spectrometry (HPLC-MS) for 11 NACs, including 4-nitrophenol (4NP), 2-methyl-4-nitrophenol (2M4NP), 3-methyl-4-nitrophenol (3M4NP), 2,6-dimethyl-4-nitrophenol (2,6DM4NP), 4-nitrocatechol (4NC), 4-nitroguaiacol (4NG), 5-nitroguaiacol (5NG), 3-nitrosalicylic acid (3NSA), 4-nitrosalicylic acid (4NSA), 5-nitrosalicylic acid (5NSA) and 4-nitrophenyl sulfate (4NPS). Table 2 listed the names, $[M-H]^-$ and retention times of the 11 NACs. The recovery rate of NACs standard was between 75 and 100%. Each NAC could be detected and field blank values were below detection limits for all target compounds.

Table 2. Nitroaromatic Compounds Quantified in This Study.

Components	[M-H]⁻	Retention time/min
4NP	138	10.76
2M4NP	152	16.31
3M4NP	152	19.67
2,6DM4NP	166	28.56
4NC	154	8.30
4NG	168	12.52
5NG	168	11.42
3NSA	182	8.47
4NSA	182	12.17
5NSA	182	10.83
4NPS	218	6.87

3 Results and discussion

3.1 Meteorological Conditions

During the sampling period, the Yellow Sea was under the influence of a subtropical high, with mostly clear to partly cloudy skies and occasional fog. Average temperatures ranged from 24.1 to 25.2°C (mean 24.6°C). Relative humidity was high, between 86.3% and 91.4% (mean 90.0%). Wind speeds varied from 5.5 to 11.7 m/s (mean 7.7 m/s), with prevailing southerly to southeasterly winds (mean relative wind direction ~300°). The combination of high humidity and low wind speed favored the accumulation of NACs in the particle phase[1]. Notably, pressure dropped to 1003 hPa during the late period of Q5 (evening of July 17), indicating a weak cold front passage that caused rapid pollutant removal, explaining the extremely low concentration in Q5. The above results are shown in Fig. 1.

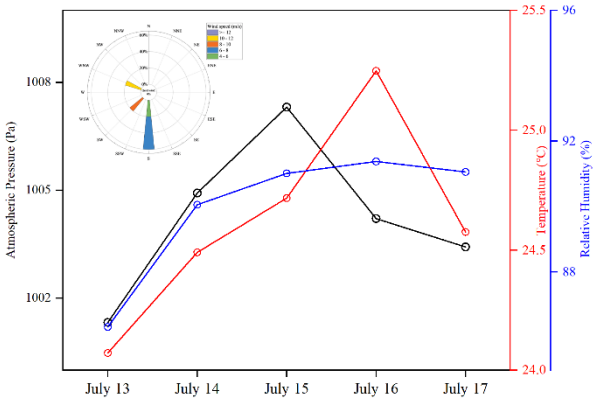

Figure 1. Sample corresponding meteorological data.

3.2 Concentrations and Composition of Nitroaromatic Compounds

3.2.1 Total Concentration Levels

Total NAC (∑NACs) concentrations in the five $PM_{2.5}$ samples are shown in Fig. 2. ∑NACs ranged from 0.18 to 1.54 ng/m³, with an average of 0.82 ng/m³. Sample Q4 exhibited the highest concentration (1.54 ng/m³), while Q5 the lowest (0.18 ng/m³).

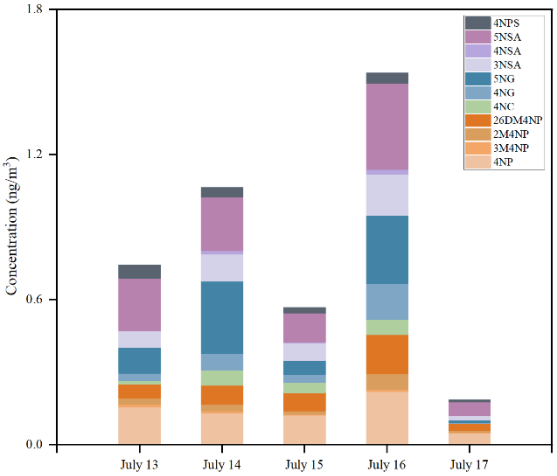

Figure 2. NACs concentration in each sample.

Compared to other regions, the ∑NACs over the Yellow Sea in summer were higher than those over the East China Sea (0.35 ng/m³)[1], but lower than those at urban sites in the North China Plain (e.g., Beijing, summer average 1.2 ng/m³)[4, 5], reflecting the influence of continental emissions but with dilution over the sea. Long-term trends in northern China also show significant levels of nitrated PAHs in rural coastal areas[6]. The observed concentrations are comparable to those reported in the Yellow Sea during summer (0.5–1.0 ng/m³), suggesting that the Yellow Sea is moderately polluted by NACs. The high concentration in Q4 (1.54 ng/m³) exceeded the summer mean of many coastal sites, possibly due to stagnant meteorological conditions and local accumulation. In contrast, Q5's extremely low value

(0.18 ng/m³) is among the lowest reported for Chinese coastal waters, highlighting the strong scavenging effect of the cold front. Furthermore, the wide variability (coefficient of variation ~70%) indicates that NAC levels over the Yellow Sea are highly sensitive to synoptic weather patterns and air mass origins. These findings underscore the need for high-time-resolution measurements to capture episodic pollution events.

3.2.2 Compositional Characteristics

The relative contributions of the 11 NACs in each sample are summarized in Fig. 3. Overall, 4NP, 5NG and 5NSA were the three most abundant compounds, together accounting for more than 60% of ∑NACs. 5NSA dominated in Q1, Q3, Q4 and Q5(21%–30%), 5NG contributed the highest in Q2 (28%), while 4NP reached up to 26% in Q5. In Q5, 4NP and 5NSA remained dominant, but total concentrations were extremely low. 2M4NP, 2,6DM4NP, and 3NSA also made moderate contributions (5%–16%). In contrast, 3M4NP, 4NG, and 4NSA were minor (<3%). This compositional pattern suggests that secondary formation (e.g., nitration of phenolic compounds) is likely the dominant source of NACs over the Yellow Sea, while direct biomass burning emissions play a smaller role[2, 3].

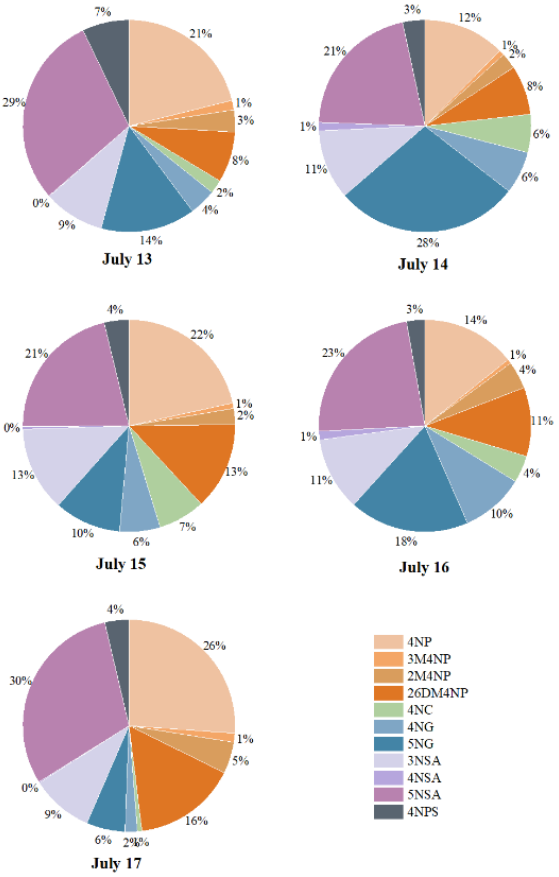

Figure 3. Relative contribution of different NAC in each sample.

Similar secondary dominance has been observed in Chinese megacities during summer[5]. Compared with typical biomass burning tracers such as levoglucosan or K^+ (not measured in this study), the contribution of primary combustion-derived NACs is relatively low. For instance, 4NP, which can be emitted directly from combustion, accounted for only 12%–26% of ∑NACs, and its abundance was generally lower than that of secondary oxygenated species like 5NSA and 5NG across most samples. This further supports the conclusion that secondary formation, rather than primary biomass burning, dominates the NAC budget over the Yellow Sea in summer. Notably, the high abundance of 5NSA, a dihydroxybenzoic acid derivative, points to the nitration of salicylic acid, which is emitted from both biogenic sources and combustion processes. This compound is rarely emitted directly from biomass burning, and its strong presence therefore implies secondary aqueous-phase formation under humid conditions, consistent with the high relative humidity (>90%) observed during our cruise[7]. 5NG, a typical product of guaiacol nitration, is often used as a tracer for biomass burning under certain conditions, but its high proportion in Q2 (28%) might also indicate secondary aqueous-phase formation. The significant contribution of 4NP, which can be formed from both photochemical oxidation of benzene and direct emissions, further supports mixed sources. Compared to winter studies[6], our summer samples show a higher fraction of oxygenated NACs (e.g., 5NSA, 4NC), consistent with enhanced secondary processing under warm, humid, and photochemically active conditions. For instance, the average ratio of 5NSA to 4NP in our samples (0.8) is more than twice that reported for winter in northern China, further highlighting the role of summer photochemistry and aqueous-phase reactions[8]. This compositional fingerprint provides valuable evidence for the predominance of secondary formation pathways over the Yellow Sea in summer. Collectively, these findings reinforce that secondary nitration of phenolic compounds, rather than primary biomass burning, drives the NAC budget in this marine atmosphere during the warm season.

3.2.3 Variation Among Samples

In Fig. 4, Samples Q1 and Q2 were collected in the southern part of the sea (34°–36 °N), close to the Shandong and Jiangsu coasts, and thus more influenced by anthropogenic emissions from land, resulting in higher total concentrations (0.74 and 1.06 ng/m³). Coastal proximity likely increased precursor aromatics (e.g., benzene, toluene) for nitrophenol formation. Q3 and Q4 mainly traversed the central and northern Yellow Sea (35°–36°N); Q4 reached the peak concentration (1.54 ng/m³), likely due to stagnant, humid conditions and local accumulation on July 16. Stagnant air masses reduce dilution and allow prolonged aqueous-phase processing, which can further promote the nitration of phenolic compounds. Q5 showed a sharp drop to 0.18 ng/m³, partly because of the cold front scavenging and partly because the sampling area moved northward (above 36 °N) where emissions are weaker. The northward shift also brought the sampling region into a more remote marine environment with lower anthropogenic influence, further explaining the marked decrease in NAC concentrations.

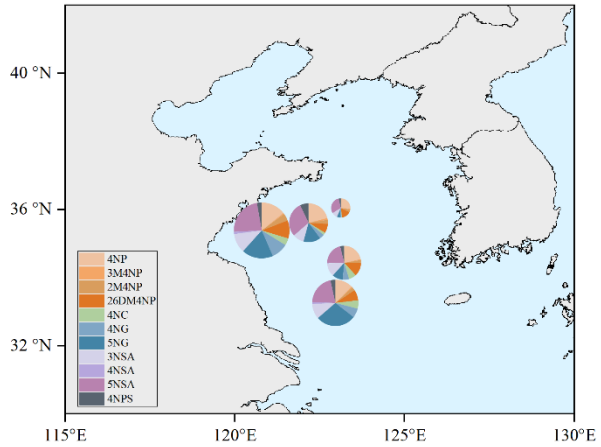

Figure 4. Spatial distribution of samples.

The influence of marine biological emissions on organic aerosol composition in the Yellow Sea has also been reported[9]. Spatial variation reveals a clear south-to-north gradient, with southern sites (closer to Shandong Peninsula) exhibiting higher NAC loads. This pattern aligns with the distribution of industrial activities and population density along the Bohai coast. For example, the cities of Qingdao, Weifang, and Yantai host numerous petrochemical plants and coal-fired power plants, which emit large amounts of volatile organic compounds (VOCs) and NO_x that serve as precursors for secondary NAC formation[10]. Temporal evolution within the cruise shows that Q2 (collected overnight and early morning) had elevated 5NG, possibly due to nighttime chemistry involving NO_3 radicals. NO_3 radicals are formed via the reaction of NO_2 with O_3 and are known to efficiently oxidize methoxyphenols such as guaiacol, leading to nitrocatechol and nitrosyringol derivatives; this pathway is particularly active in the absence of sunlight and can explain the 5NG peak in Q2. In contrast, Q3 and Q4, collected during daytime, showed higher proportions of 4NP and 5NSA, consistent with photochemical production. Under sunlight, hydroxyl radicals (•OH) dominate the oxidation of benzene and phenol, ultimately yielding nitrophenols and nitrosalicylic acids through a series of reactions with NO_2. The dramatic decrease from Q4 to Q5 (by a factor of 8.6) cannot be explained solely by spatial change; the passage of a cold front caused strong winds and precipitation that effectively washed out particulate NACs. Such meteorological events can overshadow source differences and should be carefully considered in marine atmospheric studies. Overall, the variability from sample to sample highlights the combined control of source strength, transport distance, and weather dynamics on NAC concentrations over the Yellow Sea.

Although only five $PM_{2.5}$ samples were collected over five days, this study represents a baseline dataset for atmospheric NACs over the Yellow Sea in summer. The limited sample size is offset by the wide spatial coverage (120°52′–124°00′E, 34°00′–36°29′N) and the inclusion of diverse meteorological conditions (e.g., stagnant humid periods vs. cold front passage). These samples capture both typical summer pollution accumulation and rapid scavenging events, providing valuable preliminary insights into the magnitude, composition, and controlling factors of NACs in this region. Future studies with larger sample sizes are needed to confirm seasonal trends.

4 Conclusions

Total nitroaromatic concentrations in $PM_{2.5}$ over the Yellow Sea in summer 2024 ranged from 0.18 to 1.54 ng/m³ (average 0.82 ng/m³), representing moderate pollution levels compared to other Chinese coastal seas—higher than over the East China Sea but lower than urban sites in the North China Plain, indicating a clear land-to-sea gradient. The dominant compounds were 5NSA, 4NP, and 5NG, together accounting for over 60% of the total. The high abundance of oxygenated species (e.g., 5NSA, 4NC, 5NG) suggests that secondary formation via photochemical and aqueous-phase nitration of phenolic precursors is the dominant source, rather than primary biomass burning emissions, consistent with recent studies in Chinese megacities during summer. Meteorological conditions played a critical role: high humidity (>90%) and low wind speed (~7.7 m/s) favored gas-to-particle partitioning and accumulation, leading to the peak concentration in Q4; conversely, the passage of a cold front caused rapid scavenging, reducing concentrations by nearly an order of magnitude in Q5. This study provides the first baseline dataset on atmospheric NACs over the Yellow Sea in summer. Future work should focus on high-resolution online measurements, source apportionment using isotopic or receptor models, and assessment of the radiative forcing and health impacts of NACs in this rapidly developing coastal region.

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