

## Investigation of Chemical Composition of Fine Particles in Istanbul with Ion Chromatography

*İstanbul'daki İnce Partiküllerin Kimyasal Bileşiminin İyon Kromatografisi ile İncelenmesi*

Rosa M. FLORES <sup>1</sup>

<sup>1</sup>Environmental Engineering Department, Faculty of Engineering, Marmara University, Istanbul, Turkey

### Abstract

This study quantitatively investigates the chemical composition of highly-time resolved fine particulate matter (PM<sub>2.5</sub>) in the Beşiktaş district of Istanbul, focusing on sulfate, nitrate, phosphate, ammonium, and nitrite using ion chromatography. PM<sub>2.5</sub> samples were collected during the daytime and nighttime in winter, spring, summer, and fall of 2017, allowing analysis of diurnal and seasonal variations. Water soluble ion (WSI) concentrations in PM<sub>2.5</sub> were notably lower than those recorded in heavily polluted cities such as Beijing and Delhi and were comparable to Seoul. Ammonium exhibited pronounced peaks, reaching as high as 367.8 ng/m<sup>3</sup> during nighttime (19:00-07:00), attributed to enhanced gas-to-particle partitioning under stable atmospheric conditions. Phosphate exhibited moderate diurnal variability, typically peaking in early morning (07:00-09:00) and late afternoon (15:00-19:00), with maximum concentrations recorded at 196.2-197.2 ng/m<sup>3</sup>, suggesting continuous contributions from combustion sources, dust resuspension, and semi-volatile organophosphate esters (OPEs). Suggestions to decrease the WSI precursors are also provided in order to decrease secondary inorganic aerosol levels in Istanbul.

**Keywords:** ion chromatography, PM<sub>2.5</sub>, water soluble ions, nitrate, sulfate

### Öz

Bu çalışma, İstanbul'un Beşiktaş ilçesinde yüksek zaman çözünürlüğüne sahip ince partikül madde (PM<sub>2.5</sub>) içerisindeki kimyasal bileşimi niceliksel olarak incelemektedir. İyon kromatografisi kullanılarak sülfat, nitrat, fosfat, amonyum ve nitrit iyonlarına odaklanılmıştır. PM<sub>2.5</sub> örnekleri, 2017 yılı boyunca kış, ilkbahar, yaz ve sonbahar mevsimlerinde, gündüz ve gece saatlerinde toplanarak günlük ve mevsimsel değişimlerin analizi yapılmıştır. PM<sub>2.5</sub> içindeki suda çözünebilir iyon (WSI) konsantrasyonları, Beijing ve Delhi gibi yüksek kirliliğe sahip şehirlerde kaydedilen seviyelerden önemli ölçüde daha düşük olup, Seoul ile benzerlik göstermektedir. Amonyum, gece saatlerinde belirgin yüksek seviyeler göstererek 367,8 ng/m<sup>3</sup>'e kadar ulaşmıştır ve bu durum durağan atmosfer koşullarında gaz-partikül dönüşümünün artmasıyla açıklanmaktadır. Fosfat, orta derecede günlük değişkenlik göstermiş olup, sabah erken saatlerde (07:00-09:00) ve öğleden sonra (15:00-19:00) 196,2-197,2 ng/m<sup>3</sup> değerleriyle konsantrasyonları zirve yapmıştır ve bu durumun yanma kaynakları, toz yeniden süspansiyonu ve yarı uçucu organofosfat esterleri (OPE'ler) gibi sürekli kaynaklardan gelen katkılardan kaynaklandığı göstermektedir. İstanbul'daki ikincil inorganik aerosol seviyelerini düşürmek amacıyla WSI öncüllerini azaltmaya yönelik öneriler de sunulmaktadır.

**Anahtar Kelimeler:** iyon kromatografisi, PM<sub>2.5</sub>, suya çözünebilir iyonlar, nitrat, sülfat

## I. INTRODUCTION

The regulation of particulate matter (PM) emission is critical to enhancing air quality since PM constitutes individual particles distinguished by their aerodynamic diameters. PM<sub>10</sub> denotes particulate matter that has diameters less than 10 µm, while PM<sub>2.5</sub>, otherwise known as fine particles, involves particles with a diameter less than 2.5 µm. The term PM<sub>10-2.5</sub> includes particles between a diameter of 2.5 and 10 µm, and ultrafine particles (UFP) less than 0.1 µm. Indicators such as PM<sub>2.5</sub> and PM<sub>10</sub>, are commonly used in air quality research [1]. Health-wise, the fine particles are more hazardous as they have the potential to penetrate deep into the respiratory tract, become embedded in the lungs, and result in respiratory and cardiovascular illnesses. World Health Organization suggests PM<sub>2.5</sub> as a better marker of air pollution than PM<sub>10</sub> due to its larger surface area, over which it can trap toxic chemicals, avoid nasal filters, and reach deep into the lungs [2]. Rising ambient pollution levels, for example, coarse PM, have been linked with rising respiratory morbidity (PM<sub>10</sub> and PM<sub>2.5</sub>). Coarse PM emissions are considerably influenced by domestic heating, combustion events, and natural aerosols [3].

In particles with a diameter of 2.5 micrometers or less ( $PM_{2.5}$ ), water-soluble ions (WSI) are predominant constituents, including sulfate ( $SO_4^{2-}$ ), nitrate ( $NO_3^-$ ), ammonium ( $NH_4^+$ ), phosphate ( $PO_4^{3-}$ ), and chloride ( $Cl^-$ ) [4].  $SO_4^{2-}$  and  $NO_3^-$  mainly arise from the photochemical transformation of sulfur dioxide ( $SO_2$ ) and nitrogen dioxide ( $NO_2$ ), leading to the formation of secondary aerosols in the atmosphere [5].

Ionic elements play a critical role in determining PM levels in different regions, with  $SO_4^{2-}$ ,  $NO_3^-$ , and  $NH_4^+$  being the principal WSIs in  $PM_{2.5}$  [5]. Although past studies have analyzed PM content, the day and night variations in particulate composition, especially water-soluble ions, remain less explored despite these ions being key chemical elements of  $PM_{2.5}$  in addition to carbon. Analyzing the ionic makeup of fine and coarse particles is essential to evaluate air quality events during both day and night [5].

Among the ionic species,  $SO_4^{2-}$ ,  $NO_3^-$ , and  $NH_4^+$  are found in both fine and coarse particulates. Sulfate and ammonium are found in  $PM_{2.5}$ , mainly due to atmospheric chemical reactions and combustion processes. Industrial emissions from fossil fuel combustion are primary sources of  $SO_2$ , with additional input from natural phenomena such as volcanic eruptions and sectors such as transportation, which includes trains, ships, and other vehicles using high sulfur fuels [6]. Vehicle  $SO_2$  emissions tend to be higher during the day, aligning with higher levels of hydroxyl radicals (OH) that promote photochemical interactions [3].

Nitrate ( $NO_3^-$ ) and nitrite ( $NO_2^-$ ) are naturally found in soils and water as part of the nitrogen cycle, usually existing as highly water-soluble compounds bonded with sodium and potassium ions. Nitrite is rapidly transformed into nitrate, an important element of atmospheric aerosols. Natural nitrate sources include the breakdown of organic matter, while human-induced sources include fertilizers and industrial discharges. Moreover, human and animal waste significantly contributes to atmospheric ammonia ( $NH_3$ ) [7]. It has been reported that the majority (89.7%) of ammonia emissions in Turkey originates from the agriculture sector [8]. The presence of  $NO_3^-$  in  $PM_{2.5}$  largely results from chemical reactions in the atmosphere, notably the reaction between nitric acid ( $HNO_3$ ) and ammonia ( $NH_3$ ), creating ammonium nitrate ( $NH_4NO_3$ ).  $NO_3^-$ ,  $NH_4^+$ , and  $Cl^-$  levels generally increase at night because  $NH_4NO_3$  and  $NH_4Cl$  are more unstable during the day due to higher temperatures and photochemical processes [5]. Cooler nighttime temperatures diminish the thermal decomposition of ammonium salts, leading to elevated nighttime concentrations of  $NH_4^+$  [3].

Chloride aerosols are recognized as a significant component of atmospheric particulate matter, with contributions from both natural and human activities

[9-11]. In regions with forests and agricultural activity, potassium chloride (KCl) constitutes approximately half of the fine particle concentration resulting from biomass burning [12]. Since water-soluble ions (WSI) play an important role in  $PM_{2.5}$  generation, a complete investigation of their composition and diurnal and seasonal changes is necessary for the optimization of air quality management and pollution control.

Fine  $PM_{2.5}$  particles have been associated with respiratory and cardiovascular diseases, as well as neurological disorders [13]. Additional health effects may arise depending on the specific chemical composition of the particles. Inorganic salts such as the major ions studied in this work, have the ability to interact with water and are known to initiate smog formation, impair visibility, and contribute to complex air pollution [14]. Exposure to ammonium sulfate and ammonium nitrate has been associated with decreases in body weight, as well as pneumotoxic and immunotoxic effects, and has more recently been linked to reproductive toxicity in both humans and animals [15]. A comprehensive review of the health effects of secondary inorganic aerosols has been provided by Sokan-Adeaga et al. [16].

Water soluble ions have been scarcely studied in Istanbul. Szigeti et al. [17] investigated the major anions sulfate, nitrate, and chloride, as well as the ammonium cation in the fine aerosol fraction  $PM_{2.5}$  over one year, with a low time resolution of 96h for 4 consecutive workdays in 2011. Daily concentrations of water soluble ions have been also investigated in the coarse aerosol  $PM_{10}$  fraction in 2010 [18] and between 2007 and 2009 [19]. Given the importance of investigating diurnal variations of water soluble ions in the fine aerosol fraction, our previous study [20] reported weekly averaged diurnal variations of water soluble ions over 4 seasons. The present study provides a more comprehensive analysis on a day-to-day basis. Overall, 300 samples have been analysed and reported in this study.

## II. MATERIALS AND METHODOLOGY

### 2.1. Sample and Analysis

The sampling and analysis have been performed according to Mertoglu et al., [20]. Briefly, a week-long sampling campaign was conducted in Beşiktaş, Istanbul, across four seasons.  $PM_{2.5}$  samples were collected using filter papers at various intervals throughout the day (7:00–9:00, 9:00–11:00, 11:00–13:00, 13:00–15:00, 15:00–17:00, and 17:00–19:00). Additionally, a 12-hour nighttime sample was collected. After sampling, the filter papers were folded in half, wrapped in aluminum foil, and stored in a refrigerator. Each filter paper was then cut into 16 pieces, resulting in 32 small sections due to the folding. These pieces were placed into test tubes containing 10 mL of deionized water, along with a blank control. The

test tubes were then subjected to sonication for 60 minutes at 5°C, facilitating the dissolution of water-soluble ions through vibration. Following sonication, turbidity was observed in the samples, necessitating centrifugation. The test tubes were centrifuged six times for four minutes each to remove turbidity. After centrifugation, the samples were prepared for analysis by filtering them through a 0.22 µm filter using a syringe. The filtered samples were divided into two small conical vials, sealed, and wrapped in aluminum foil before being refrigerated until analysis. The samples were then analyzed using an ion chromatography device to quantify nitrite, nitrate, ammonium, sulfate, and phosphate concentrations. Both anion and cation measurements were recorded.

### III. RESULTS AND DISCUSSION

#### 3.1. Diurnal variation of WSI in Winter 2017

Figure 1 presents the aerosol concentrations measured in Winter1 sampling campaign between January 28 and February 4, 2017. On January 28, 2017, over a 24-hour period, including 2-hour and 12-hour intervals. Among the analyzed ions, sulfate exhibited the highest concentration, followed by ammonium, phosphate, nitrate, and nitrite. The peak sulfate concentration was recorded at 241.0 ng/m<sup>3</sup> on this date. In contrast, nitrite had the lowest concentration, with a minimum value of 1.4 ng/m<sup>3</sup>, particularly during the nighttime period. Nitrate concentrations ranged between 31.0 ng/m<sup>3</sup> and 45.5 ng/m<sup>3</sup>, while phosphate reached a maximum of 71.6 ng/m<sup>3</sup>. Ammonium also exhibited relatively high concentrations, with a peak value of 115.1 ng/m<sup>3</sup>

On January 29, 2017, sulfate was identified as the ion with the highest concentration among those analyzed, succeeded by phosphate, ammonium, nitrate, and nitrite. The sulfate concentrations measured were 157.0 ng/m<sup>3</sup> and 81.6 ng/m<sup>3</sup>. Phosphate reached a peak concentration of 76.7 ng/m<sup>3</sup>, while ammonium concentrations ranged from 8.0 ng/m<sup>3</sup> to 50.0 ng/m<sup>3</sup>. Nitrite exhibited the lowest concentration, with a minimum of 1.4 ng/m<sup>3</sup>, particularly during the 12-hour nighttime period. Nitrate concentrations fluctuated between 12.0 ng/m<sup>3</sup> and 36.8 ng/m<sup>3</sup>. In general, the concentrations of all ions measured were reduced during nighttime, except for ammonium, which displayed elevated levels during this period.

On January 30, 2017, during a complete 24-hour cycle, which included both 2-hour and 12-hour segments, ions were ranked by concentration as follows: sulfate, phosphate, ammonium, nitrate, and nitrite. Sulfate exhibited the highest concentration at 123.3 ng/m<sup>3</sup>, while nitrite was the least concentrated at 1.9 ng/m<sup>3</sup>. Nitrate concentrations ranged from 6.2 ng/m<sup>3</sup> to 13.1 ng/m<sup>3</sup>, with the lowest values recorded at night.

Phosphate peaked at a concentration of 73.9 ng/m<sup>3</sup>, and ammonium concentrations reached a maximum of 27.1 ng/m<sup>3</sup> based on the 12-hour average during nighttime.

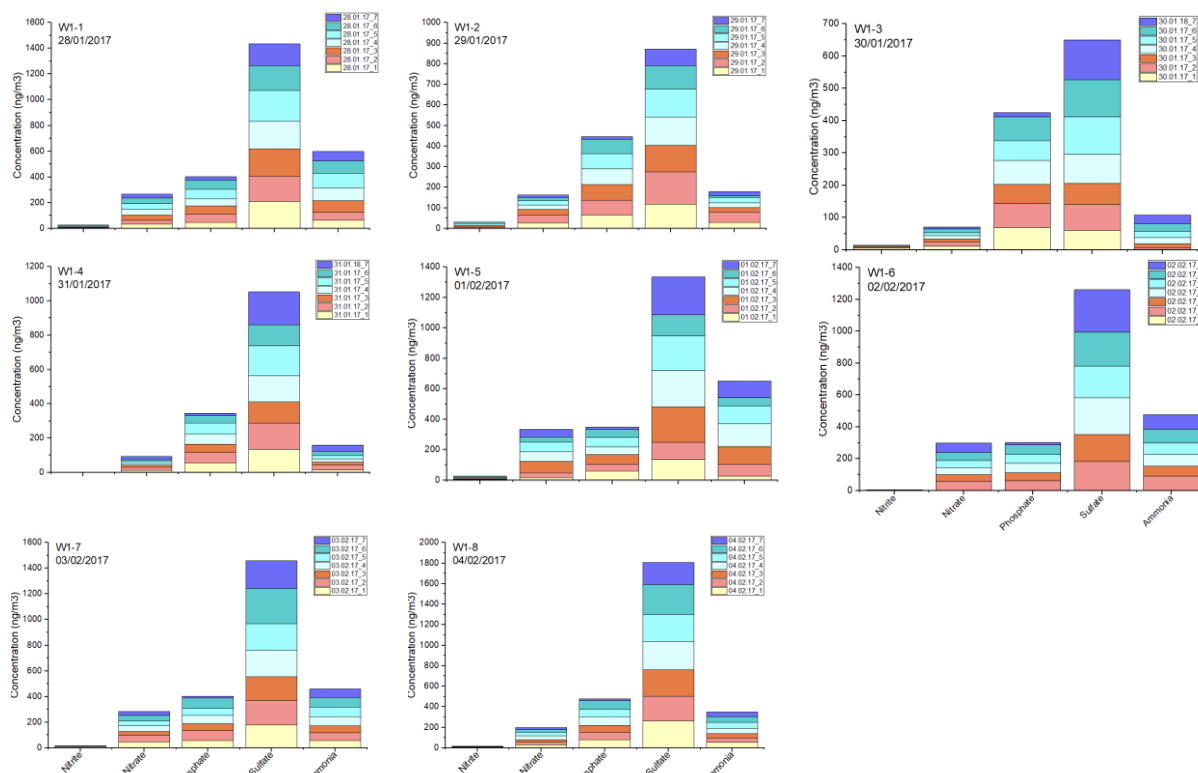
On January 31, 2017, among the ions examined, sulfate showed the greatest concentration, succeeded by phosphate, ammonium, nitrate, and nitrite. Sulfate concentrations measured between 123.0 ng/m<sup>3</sup> and 190.5 ng/m<sup>3</sup>. The range for phosphate concentrations extended from 12.3 ng/m<sup>3</sup> to 66.4 ng/m<sup>3</sup>. Ammonium levels peaked during nighttime at 38.3 ng/m<sup>3</sup>, with the minimum concentration recorded at 14.1 ng/m<sup>3</sup>.

On February 1, 2017, sulfate ions were found to have the greatest concentration among the ions analyzed, followed sequentially by ammonium, phosphate, nitrate, and nitrite ions. Measured sulfate concentrations spanned from 113.3 ng/m<sup>3</sup> to 249.8 ng/m<sup>3</sup>. The concentrations of nitrate and phosphate were similar, with phosphate levels ranging from 13.9 ng/m<sup>3</sup> to 61.7 ng/m<sup>3</sup>. Ammonium concentrations fluctuated between 25.5 ng/m<sup>3</sup> and 116.2 ng/m<sup>3</sup>, with nighttime measurements showing the peak concentration.

On February 2, 2017, among the ions examined, sulfate was found in the highest concentrations, followed in order by ammonium, phosphate, nitrate, and nitrite. Sulfate concentrations varied between 168.2 ng/m<sup>3</sup> and 265.8 ng/m<sup>3</sup>. Ammonium concentrations exhibited a nighttime peak of 94.1 ng/m<sup>3</sup>, with the lowest observed value at 61.9 ng/m<sup>3</sup>. Phosphate levels were in the range of 14.9 ng/m<sup>3</sup> to 60.6 ng/m<sup>3</sup>. Notably, nitrate and phosphate concentrations were similar, with nitrate levels spanning from 41.4 ng/m<sup>3</sup> to 59.5 ng/m<sup>3</sup>.

On February 3, 2017, Sulfate was found to have the highest concentration among the studied ions, with ammonium, phosphate, nitrate, and nitrite showing lower levels. The concentration of sulfate was observed to range from 179.1 ng/m<sup>3</sup> up to 276.0 ng/m<sup>3</sup>. Ammonium was found in quantities ranging from 52.5 to 75.0 ng/m<sup>3</sup>. Phosphate levels were encountered between 14.0 ng/m<sup>3</sup> and 81.9 ng/m<sup>3</sup>, while nitrate concentrations varied from 30.2 to 49.8 ng/m<sup>3</sup>. Nitrite was the ion with the lowest concentration, having a minimum observed value of 4.9 ng/m<sup>3</sup>.

On February 4, 2017 sulfate was detected at the highest concentration, succeeded by phosphate, ammonium, nitrate, and nitrite. The sulfate concentrations measured spanned from 215.8 to 291.7 ng/m<sup>3</sup>. Phosphate levels ranged from 17.4 to 85.1 ng/m<sup>3</sup>, whereas ammonium concentrations varied between 41.7 and 60.0 ng/m<sup>3</sup>. Nitrate concentrations were found to range from 23.0 to 37.5 ng/m<sup>3</sup>, with nitrite exhibiting the lowest levels observed.



**Figure 1.** Diurnal variation of WSI in Winter 1 sampling campaign in 2017

### 3.2. Diurnal variation of WSI in Spring 2017

Figure 2 presents the aerosol concentrations measured in Spring sampling campaign between May 3 and May 9, 2017.

On May 3, 2017. Among the analyzed ions, sulfate exhibited the highest concentration, followed by phosphate, ammonium, nitrate, and nitrite. Nitrate and phosphate concentrations were closely aligned, showing similar trends throughout the day. The sulfate concentration ranged from 231.0 ng/m<sup>3</sup> to 419.3 ng/m<sup>3</sup>, while ammonium levels varied between 31.9 ng/m<sup>3</sup> and 79.4 ng/m<sup>3</sup>. Nitrate concentrations fluctuated between 29.7 ng/m<sup>3</sup> and 48.1 ng/m<sup>3</sup>, and phosphate levels ranged from 14.8 ng/m<sup>3</sup> to 87.6 ng/m<sup>3</sup>. Among all measured ions, nitrite had the lowest concentration, recorded at 3.0 ng/m<sup>3</sup>.

Among the analyzed ions on May 4, 2017, sulfate exhibited the highest concentration, followed by phosphate, ammonium, nitrate, and nitrite. Nitrate and phosphate concentrations were closely aligned, showing similar variations throughout the day. The sulfate concentration ranged from 66.0 ng/m<sup>3</sup> to 394.3 ng/m<sup>3</sup>, while ammonium levels peaked at 71.2 ng/m<sup>3</sup>. Nitrate concentrations fluctuated between 7.6 ng/m<sup>3</sup> and 45.7 ng/m<sup>3</sup>, whereas phosphate levels ranged from 8.6 ng/m<sup>3</sup> to 72.1 ng/m<sup>3</sup>.

On May 5, 2017 sulfate exhibited the highest concentration, followed by ammonium, phosphate, nitrate, and nitrite. The sulfate concentration ranged from 255.9 ng/m<sup>3</sup> to 429.3 ng/m<sup>3</sup>, while ammonium levels varied between 54.0 ng/m<sup>3</sup> and 127.7 ng/m<sup>3</sup>. Nitrate concentrations fluctuated between 22.5 ng/m<sup>3</sup> and 54.6 ng/m<sup>3</sup>, whereas phosphate levels ranged from 9.8 ng/m<sup>3</sup> to 88.8 ng/m<sup>3</sup>. Nitrite had the lowest recorded concentration, measured at 1.9 ng/m<sup>3</sup>.

On May 6, 2017 sulfate exhibited the highest concentration, followed by ammonium, phosphate, nitrate, and nitrite. The sulfate concentration ranged from 89.2 ng/m<sup>3</sup>

On May 7, 2017 sulfate exhibited the highest concentration, followed by phosphate, ammonium, nitrate, and nitrite. The sulfate concentration ranged from 126.7 ng/m<sup>3</sup> to 1148.3 ng/m<sup>3</sup>, while ammonium levels varied between 25.4 ng/m<sup>3</sup> and 149.2 ng/m<sup>3</sup>. Nitrate concentrations fluctuated between 23.1 ng/m<sup>3</sup> and 162.1 ng/m<sup>3</sup>, whereas phosphate levels ranged from 17.0 ng/m<sup>3</sup> to 196.2 ng/m<sup>3</sup>. Nitrite had the lowest recorded concentration, measured at 1.2 ng/m<sup>3</sup>.

Among the analyzed ions on May 8, 2017, sulfate exhibited the highest concentration, followed by phosphate, nitrate, ammonium, and nitrite. Ammonium and nitrate concentrations were closely aligned, showing similar variations throughout the day. The sulfate concentration ranged from 174.8 ng/m<sup>3</sup> to 349.0

ng/m<sup>3</sup>, while ammonium levels varied between 4.0 ng/m<sup>3</sup> and 41.5 ng/m<sup>3</sup>. Nitrate concentrations fluctuated between 20.2 ng/m<sup>3</sup> and 51.8 ng/m<sup>3</sup>, whereas phosphate levels ranged from 13.9 ng/m<sup>3</sup> to 104.3 ng/m<sup>3</sup>. Nitrite had the lowest recorded concentration, measured at 1.1 ng/m<sup>3</sup>.

On May 9, 2017, sulfate exhibited the highest concentration, followed by phosphate, nitrate, ammonium, and nitrite. The sulfate concentration ranged from 171.6 ng/m<sup>3</sup> to 309.9 ng/m<sup>3</sup>, while ammonium levels varied between 19.9 ng/m<sup>3</sup> and 53.5 ng/m<sup>3</sup>. Nitrate concentrations fluctuated between 26.9 ng/m<sup>3</sup> and 55.5 ng/m<sup>3</sup>, whereas phosphate levels ranged from 11.5 ng/m<sup>3</sup> to 106.8 ng/m<sup>3</sup>. Nitrite had the lowest recorded concentration, measured at 1.3 ng/m<sup>3</sup>.

### 3.3. Diurnal variation of WSI in Summer 2017

Figure 3 presents the aerosol concentrations measured in summer sampling campaign between July 6 and July 12, 2017.

On July 6, 2017, sulfate was observed to have the highest concentration, followed in descending order by phosphate, nitrate, ammonium, and nitrite. The concentration of sulfate spanned from 63.5 to 155.9 ng/m<sup>3</sup>, whereas ammonium levels ranged between 2.2 ng/m<sup>3</sup> and 14.4 ng/m<sup>3</sup>. Nitrate concentrations exhibited variability, ranging from 8.5 to 17.1 ng/m<sup>3</sup>, while phosphate concentrations ranged from 10.1 ng/m<sup>3</sup> to 103.9 ng/m<sup>3</sup>. Nitrite was recorded at the lowest concentration of 0.9 ng/m<sup>3</sup>.

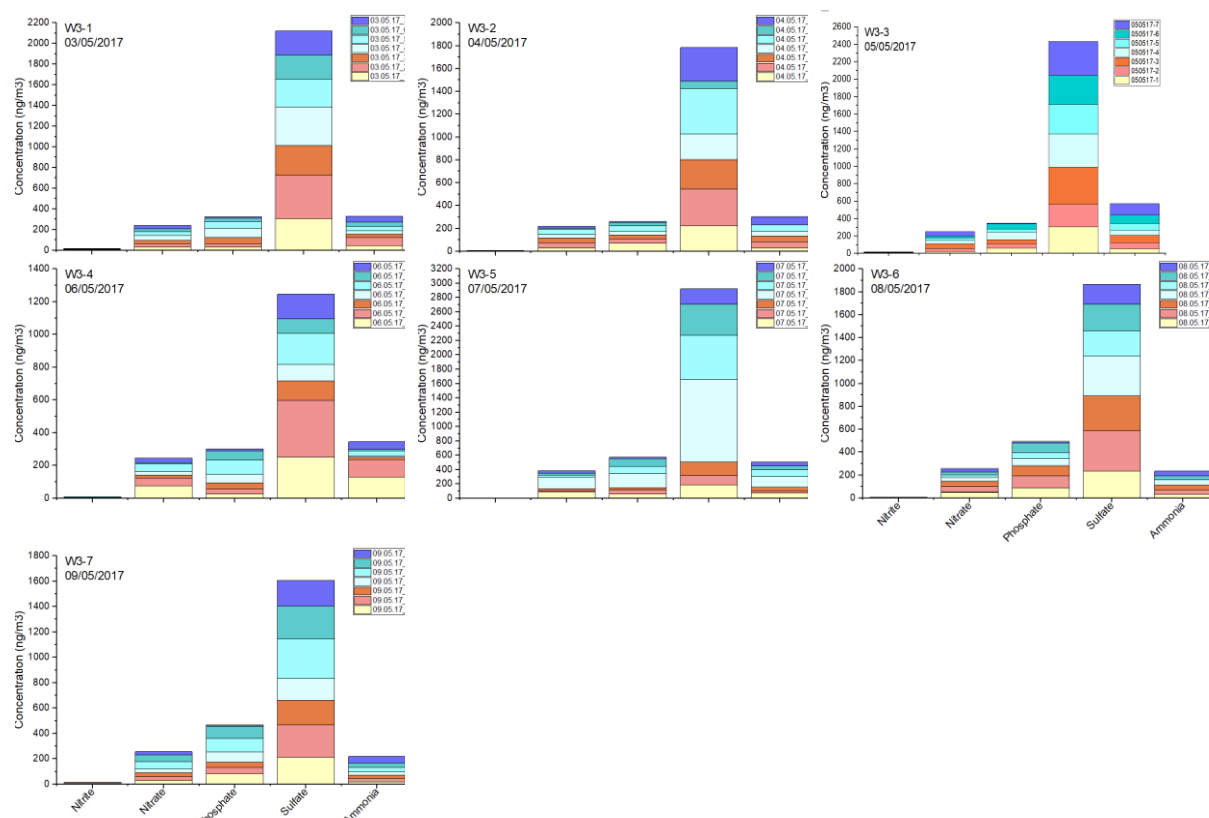
On July 7, 2017, sulfate remained the prevailing ion with the highest concentration, succeeded by phosphate, nitrate, ammonium, and nitrite. Sulfate concentrations ranged from 1.2 to 147.5 ng/m<sup>3</sup>, with

ammonium reaching a peak of 18.6 ng/m<sup>3</sup>. The maximum concentration for nitrate was 14.3 ng/m<sup>3</sup>, whereas phosphate levels fluctuated between 2.9 ng/m<sup>3</sup> and 73.3 ng/m<sup>3</sup>. Nitrite was measured as having the least concentration at 0.8 ng/m<sup>3</sup>.

On July 8, 2017, sulfate continued to exhibit the highest concentration, sequentially followed by phosphate, nitrate, ammonium, and nitrite. On this day, phosphate concentrations increased relative to the prior day. The range of sulfate concentration was from 37.3 to 84.2 ng/m<sup>3</sup>, and ammonium levels peaked at 5.9 ng/m<sup>3</sup>. The recorded nitrate concentrations varied between 7.0 and 18.3 ng/m<sup>3</sup>, while phosphate concentrations ranged from 9.2 to 71.0 ng/m<sup>3</sup>. Nitrite continued to show the lowest concentration, measured at 1.6 ng/m<sup>3</sup>.

On July 9, 2017, sulfate still presented the highest concentration, succeeded by phosphate, ammonium, nitrate, and nitrite. The concentration of sulfate ranged from 134.4 to 278.0 ng/m<sup>3</sup>, whereas ammonium levels varied between 21.2 and 36.8 ng/m<sup>3</sup>. Nitrate concentrations fluctuated between 9.0 and 33.2 ng/m<sup>3</sup>, while phosphate levels were observed to range from 13.8 to 74.2 ng/m<sup>3</sup>. Nitrite exhibited the lowest recorded concentration, measured at 1.7 ng/m<sup>3</sup>.

On July 10, 2017, sulfate again demonstrated the highest concentration, followed by phosphate, nitrate, ammonium, and nitrite. The sulfate concentration spanned from 79.2 to 191.0 ng/m<sup>3</sup>, while ammonium levels fluctuated between 8.9 and 21.1 ng/m<sup>3</sup>. Nitrate concentrations varied from 7.1 to 25.5 ng/m<sup>3</sup>, whereas phosphate levels ranged between 10.2 and 72.6 ng/m<sup>3</sup>. Nitrite was consistently recorded with the lowest concentration at 1.7 ng/m<sup>3</sup>.



**Figure 2.** Diurnal variation of WSIs in Spring sampling campaign in 2017

On July 11, 2017, sulfate maintained the highest concentration, followed by phosphate, ammonium, nitrate, and nitrite. The sulfate concentration was observed to range from 84.7 to 131.5 ng/m<sup>3</sup>, while ammonium levels varied from 14.2 to 22.1 ng/m<sup>3</sup>. Nitrate concentrations were recorded between 7.0 and 14.2 ng/m<sup>3</sup>, with phosphate levels ranging from 9.8 to 47.6 ng/m<sup>3</sup>. Nitrite, once again, recorded the lowest concentration at 1.2 ng/m<sup>3</sup>.

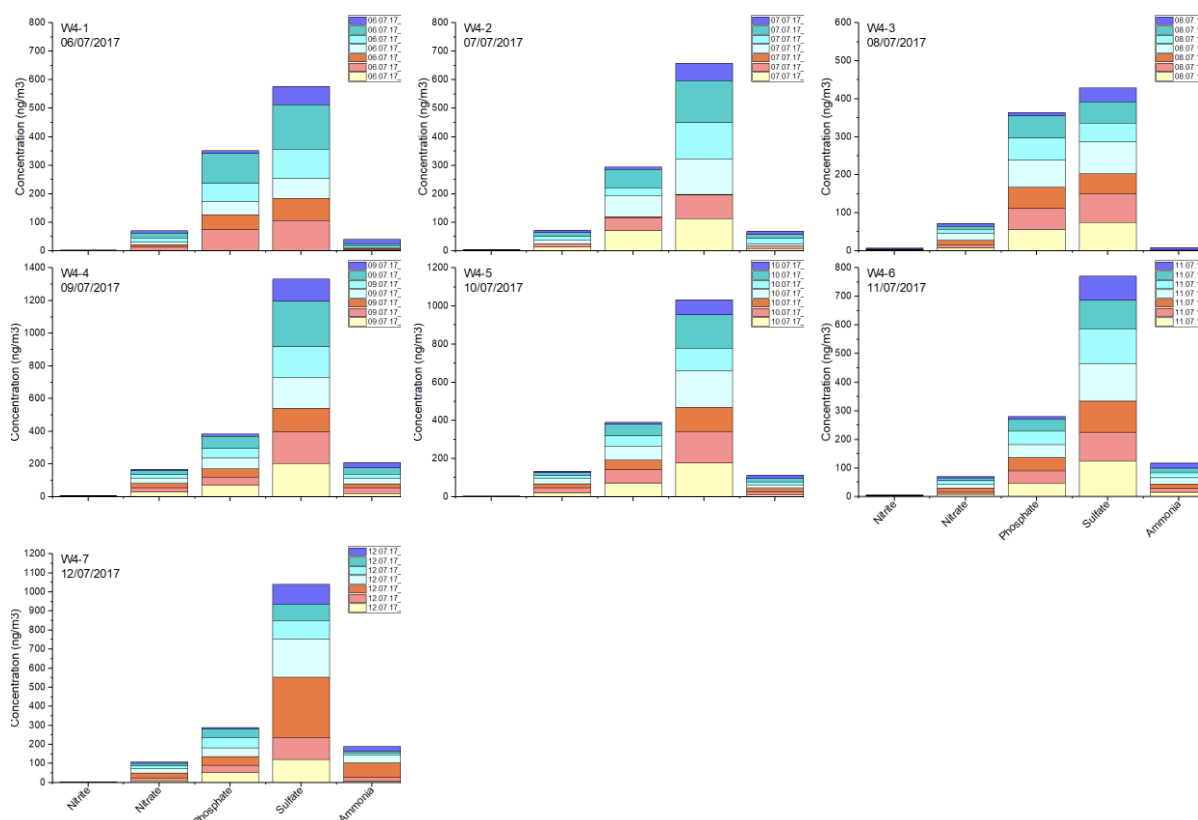
On July 12, 2017, sulfate sustained the highest concentration, followed by phosphate, ammonium, nitrate, and nitrite. Concentrations of sulfate varied from 84.6 to 317.7 ng/m<sup>3</sup>, while ammonium levels ranged from 8.2 to 75.3 ng/m<sup>3</sup>. Nitrate concentrations fluctuated between 8.5 and 17.1 ng/m<sup>3</sup>, whereas phosphate levels ranged from 7.9 to 53.5 ng/m<sup>3</sup>. Nitrite

consistently reported the lowest concentration, at 1.2 ng/m<sup>3</sup>.

### 3.4. Diurnal variation of WSI in Fall 2017

Figure 4 presents the aerosol concentrations measured in Fall sampling campaign between October 20 and October 26, 2017.

On October 20, 2017 sulfate had the highest concentration, followed by ammonium, nitrate, phosphate, and nitrite. The sulfate concentration ranged from 10.1 ng/m<sup>3</sup> to 425.3 ng/m<sup>3</sup>, while ammonium levels peaked at 154.9 ng/m<sup>3</sup>. Nitrate concentrations fluctuated between 5.5 ng/m<sup>3</sup> and 105.1 ng/m<sup>3</sup>, whereas phosphate levels ranged from 2.5 ng/m<sup>3</sup> to 40.4 ng/m<sup>3</sup>. Nitrite had the lowest recorded concentration, at 1.6 ng/m<sup>3</sup>.



**Figure 3.** Diurnal variation of WSIs in Summer sampling campaign in 2017

On October 21, 2017 sulfate had the highest concentration, followed by ammonium, nitrate, phosphate, and nitrite. The sulfate concentration ranged from 441.7 ng/m<sup>3</sup> to 1118.1 ng/m<sup>3</sup>, while ammonium levels peaked at 367.8 ng/m<sup>3</sup>. Nitrate concentrations fluctuated between 63.2 ng/m<sup>3</sup> and 179.7 ng/m<sup>3</sup>, whereas phosphate levels ranged from 8.7 ng/m<sup>3</sup> to 50.6 ng/m<sup>3</sup>. Nitrite had the lowest recorded concentration, at 1.6 ng/m<sup>3</sup>.

On October 22, 2017 sulfate had the highest concentration, followed by ammonium, nitrate, phosphate, and nitrite. The sulfate concentration ranged from 11.5 ng/m<sup>3</sup> to 424.0 ng/m<sup>3</sup>, while ammonium levels peaked at 141.3 ng/m<sup>3</sup>. Nitrate concentrations fluctuated between 12.6 ng/m<sup>3</sup> and 70.1 ng/m<sup>3</sup>, whereas phosphate levels ranged from 11.5 ng/m<sup>3</sup> to 60.9 ng/m<sup>3</sup>. Nitrite had the lowest recorded concentration, at 1.8 ng/m<sup>3</sup>.

On October 23, 2017, sulfate had the highest concentration, followed by ammonium, phosphate, nitrate, and nitrite. The sulfate concentration ranged from 241.0 ng/m<sup>3</sup> to 458.1 ng/m<sup>3</sup>, while ammonium levels peaked at 103.0 ng/m<sup>3</sup>. Nitrate concentrations

fluctuated between 5.5 ng/m<sup>3</sup> and 105.1 ng/m<sup>3</sup>, whereas phosphate levels ranged from 8.3 ng/m<sup>3</sup> to 76.3 ng/m<sup>3</sup>.

On October 24, 2017 sulfate had the highest concentration, followed by phosphate, ammonium, nitrate, and nitrite. The sulfate concentration ranged from 58.6 ng/m<sup>3</sup> to 408.7 ng/m<sup>3</sup>, while ammonium levels peaked at 71.4 ng/m<sup>3</sup>. Nitrate concentrations fluctuated between 5.1 ng/m<sup>3</sup> and 38.2 ng/m<sup>3</sup>, whereas phosphate levels ranged from 9.5 ng/m<sup>3</sup> to 64.0 ng/m<sup>3</sup>.

On October 25, 2017 sulfate had the highest concentration, followed by phosphate, ammonium, nitrate, and nitrite. The sulfate concentration ranged from 104.9 ng/m<sup>3</sup> to 170.5 ng/m<sup>3</sup>, while ammonium levels peaked at 29.8 ng/m<sup>3</sup>. Nitrate concentrations fluctuated between 4.8 ng/m<sup>3</sup> and 16.1 ng/m<sup>3</sup>, whereas phosphate levels ranged from 9.6 ng/m<sup>3</sup> to 53.3 ng/m<sup>3</sup>.

On October 26, 2017, sulfate had the highest concentration, followed by phosphate, ammonium, nitrate, and nitrite. The sulfate concentration ranged from 59.1 ng/m<sup>3</sup> to 112.3 ng/m<sup>3</sup>, while ammonium levels peaked at 29.3 ng/m<sup>3</sup>. Nitrate concentrations fluctuated between 6.2 ng/m<sup>3</sup> and 15.5 ng/m<sup>3</sup>, whereas phosphate levels ranged from 6.8 ng/m<sup>3</sup> to 49.1 ng/m<sup>3</sup>.

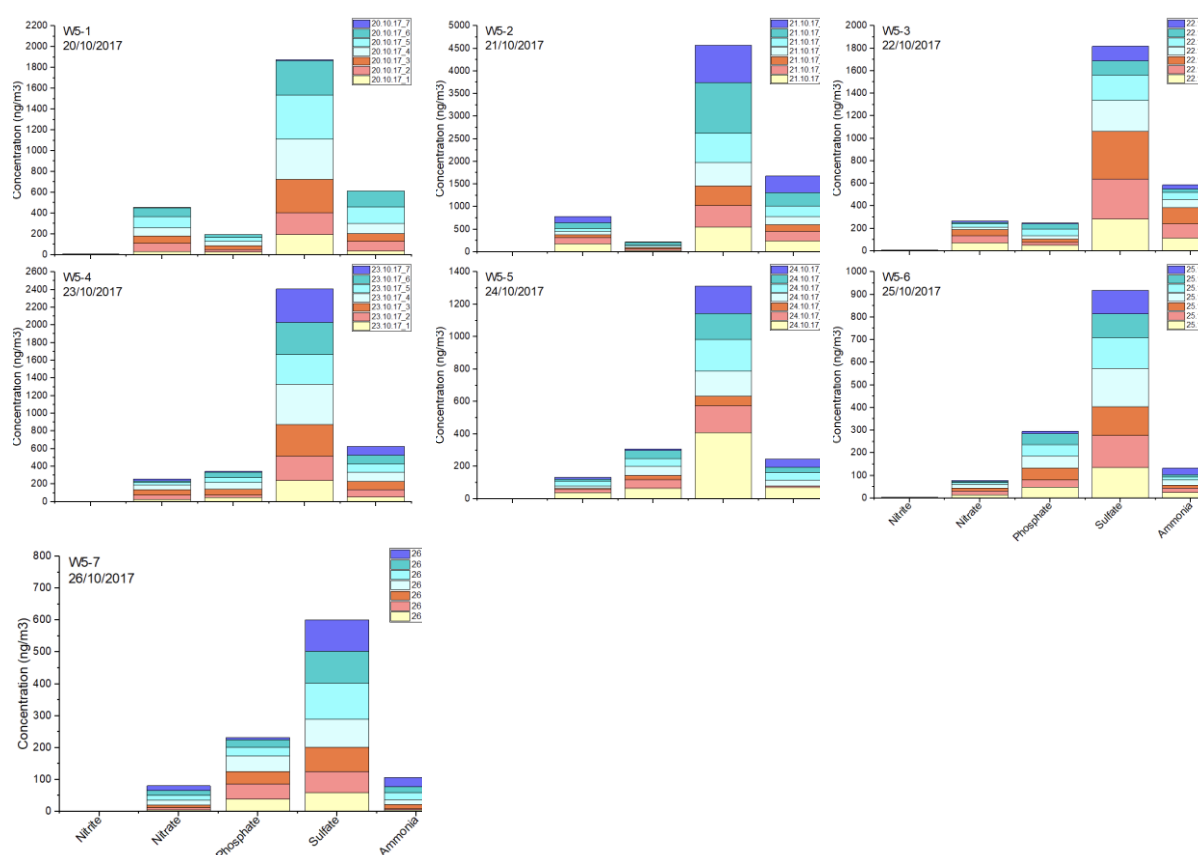


Figure 4. Diurnal variation of WSIs in Fall sampling campaign in 2017

### 3.5. Seasonal Variations

A figure like this was provided by Mertoglu et al., [20] however the analysis was performed according to seasons, rather than according to WSI.

Figure 5 presents the box plots containing all the high-time resolution WSI concentrations during all sampling campaigns. The minimum, average, and maximum concentrations as well as the dispersion of the data can be easily observed.

In Winter1, nitrite exhibited the lowest concentration, with an average of  $5.2 \text{ ng/m}^3$ , a maximum of  $9.0 \text{ ng/m}^3$ , and a minimum of  $1.4 \text{ ng/m}^3$ , showing low variance, which remained consistent across all seasons. Nitrate concentrations were lower compared to phosphate and sulfate, with an average of  $31.1 \text{ ng/m}^3$ , a maximum of  $73.7 \text{ ng/m}^3$ , and a minimum of  $6.2 \text{ ng/m}^3$ . Phosphate concentrations had an average of  $57.3 \text{ ng/m}^3$ , with a maximum of  $85.1 \text{ ng/m}^3$  and a minimum of  $12.3 \text{ ng/m}^3$ . Sulfate recorded the highest maximum concentration at  $297.7 \text{ ng/m}^3$ , while its average and minimum concentrations were  $179.4 \text{ ng/m}^3$  and  $60.4 \text{ ng/m}^3$ , respectively. Ammonium levels showed significant variation, with an average concentration of  $54.3 \text{ ng/m}^3$ , a maximum of  $151.9 \text{ ng/m}^3$ , and a minimum of  $0.9 \text{ ng/m}^3$ .

In Spring, nitrite ion had an average concentration of  $3.0 \text{ ng/m}^3$ , with a maximum of  $8.4 \text{ ng/m}^3$  and a minimum of  $1.1 \text{ ng/m}^3$ . Nitrate concentrations

decreased in spring compared to Winter2, with an average of  $37.9 \text{ ng/m}^3$ , a maximum of  $162.1 \text{ ng/m}^3$ , and a minimum of  $7.6 \text{ ng/m}^3$ , showing low daily variance. Phosphate had an average concentration of  $56.5 \text{ ng/m}^3$ , ranging from  $8.6 \text{ ng/m}^3$  to  $196.2 \text{ ng/m}^3$ . Sulfate continued to increase in average concentration, reaching  $285.3 \text{ ng/m}^3$ , which was significantly higher than other ion concentrations during spring. The maximum recorded sulfate concentration was  $1148.3 \text{ ng/m}^3$ , while the minimum was  $66.0 \text{ ng/m}^3$ . Ammonium had the lowest seasonal average among all ions, measuring  $51.2 \text{ ng/m}^3$  in spring.

In Summer Nitrite concentrations continued to decrease, with an average of  $1.7 \text{ ng/m}^3$ , a maximum of  $3.1 \text{ ng/m}^3$ , and a minimum of  $0.9 \text{ ng/m}^3$ . Nitrate had an average concentration of  $14.9 \text{ ng/m}^3$ , with a maximum of  $37.9 \text{ ng/m}^3$ . Phosphate concentrations averaged  $49.2 \text{ ng/m}^3$ , ranging from  $2.9 \text{ ng/m}^3$  to  $103.9 \text{ ng/m}^3$ . Sulfate had the lowest average concentration in summer, measuring  $125.0 \text{ ng/m}^3$ , which was significantly lower than in other seasons. The maximum recorded sulfate concentration was  $317.7 \text{ ng/m}^3$ , while the minimum was  $1.2 \text{ ng/m}^3$ . Despite the overall decrease in sulfate levels, it still had the highest average concentration among all ions during summer. Ammonium had an average concentration of  $16.3 \text{ ng/m}^3$ , with a maximum recorded value of  $75.3 \text{ ng/m}^3$ .

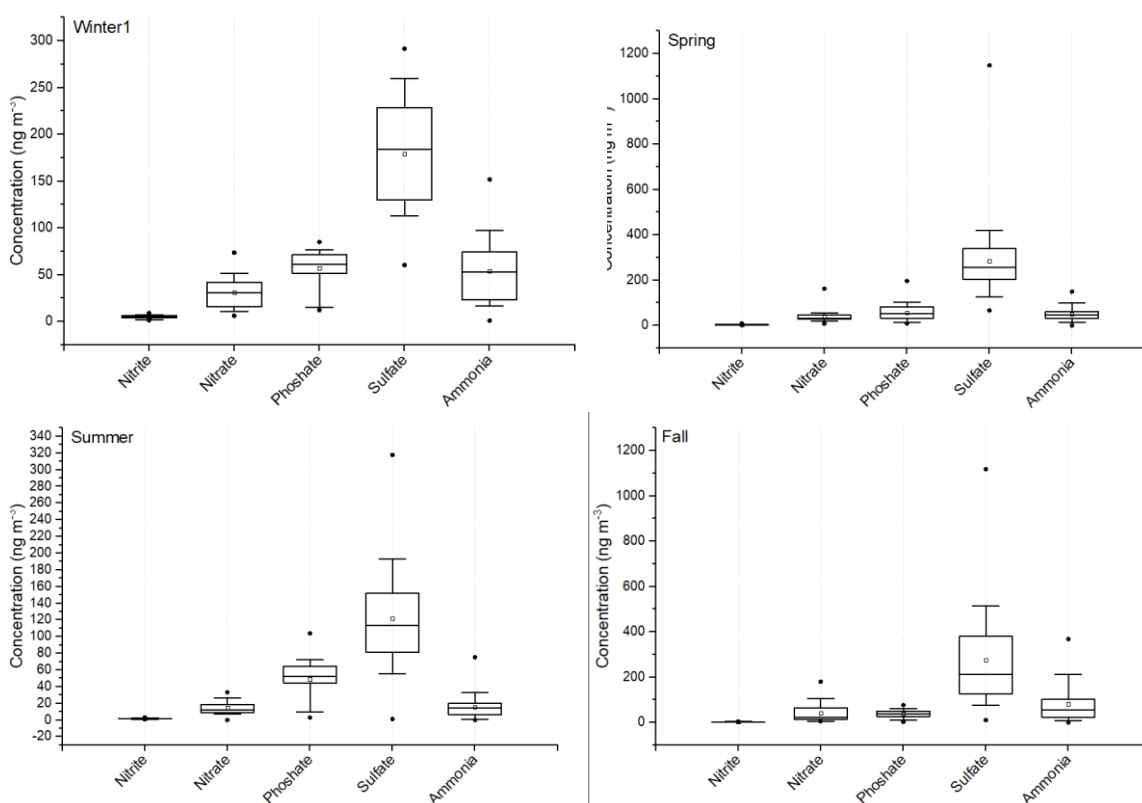
In Fall Nitrite had an average concentration of 2.3 ng/m<sup>3</sup>, with a maximum of 4.3 ng/m<sup>3</sup> and a minimum of 1.6 ng/m<sup>3</sup>. Nitrate had an average concentration of 42.0 ng/m<sup>3</sup>, ranging from 4.6 ng/m<sup>3</sup> to 179.9 ng/m<sup>3</sup>. Phosphate had the lowest seasonal average in fall, measuring 37.5 ng/m<sup>3</sup>, with a minimum concentration of 2.5 ng/m<sup>3</sup> and a maximum of 76.3 ng/m<sup>3</sup>. Sulfate had a significantly higher average concentration compared to other ions in fall, reaching 275.7 ng/m<sup>3</sup>.

As seen in Figure 5, Sulfate also had the highest variability, with a maximum concentration of 1118.1 ng/m<sup>3</sup> and a minimum of 10.1 ng/m<sup>3</sup>. Ammonium had an average concentration of 81.4 ng/m<sup>3</sup>, with the highest recorded ammonium concentration for all seasons at 367.8 ng/m<sup>3</sup>.

### 3.6. Comparison with other regions in the world

As a result of this study, sulfate exhibited the highest water-soluble ion (WSI) concentration. Sulfate levels were observed to reach their peak during spring and autumn, which can be attributed to rising temperatures and increased relative humidity, both of which enhance sulfate formation.

In general, high WSI concentrations in winter and autumn were primarily associated with increased emissions from biomass combustion, traffic, and industrial activities, particularly for residential heating. Conversely, higher concentrations in summer were mainly due to the photochemical production of secondary inorganic substances, driven by higher temperatures and increased exposure to sunlight.



**Figure 5.** Seasonal variation of WSIs in 2017 in Istanbul

The WSI concentrations obtained in this study were compared with those recorded in other urban cities worldwide and rural areas in Turkey (Table 1). Among the selected studies, the highest concentrations were observed in Beijing, China, particularly during the summer months. In contrast, NO<sub>2</sub> levels were found to be highest in Kocaeli during summer, likely due to increased emissions from transportation (land, sea, and air) and industrial activities. Overall, fuel combustion, industrial air pollution, and transportation emissions were identified as key contributors to the WSI concentrations observed in this study. However, the concentrations in Istanbul are among the lowest

compared to other regions in the world and are comparable to those found in Seoul. These low concentrations in Istanbul may be attributed to the location of industrial areas far from both the urban centers and the sampling site, as well as to the dominant wind direction from the NE, which transports air masses from the Black Sea that contain low concentrations of the investigated WSIs.

Phosphate may originate from various sources including agricultural activities, biomass burning, fossil fuel combustion, mineral dust, and most recently, it has also been associated with vehicle emissions as

discussed by Mertoglu et al. [20]. This highlights the importance of determining its diurnal variations. In our study we found that phosphate concentrations were among the lowest of the investigated WSIs. This may partly explain the limited research on phosphate, which could also be influenced by the analytical methods used to determine its concentration. For example, a study by Salam et al. [21] in Bangladesh reported that most phosphate concentrations were below the detection limit. In their work, Salam et al., [21] collected daily PM<sub>2.5</sub> samples using a low volume sampler and 47 mm filters. In our work we developed a method using high-time resolution sampling with a high-volume sampler and 20x25 cm quartz fiber filters to ensure sufficient mass was collected for determining the low concentrations and their diurnal variations.

### 3.7. Summary of Findings and Implications for Air Quality

The analysis of Winter (3.1), Spring (3.2), Summer (3.3), and Fall (3.4) of 2017 provides insights into the

diurnal fluctuations of key water-soluble ions (WSI) in PM<sub>2.5</sub>, including sulfate (SO<sub>4</sub><sup>2-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), nitrite (NO<sub>2</sub><sup>-</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), and phosphate (PO<sub>4</sub><sup>3-</sup>). In general, it was found that these variations are influenced by emission sources, meteorological conditions, and atmospheric chemical processes. Supplementary material includes Figures 1-4 based on percentages to facilitate discussion and findings in this section.

#### 3.7.1. Sulfate (SO<sub>4</sub><sup>2-</sup>)

Diurnal variations were driven by photochemical reactions. Highest concentrations observed in daytime (exact time varies from season to season between 9:00 and 19:00) due to photochemical oxidation of sulfur dioxide (SO<sub>2</sub>) in the presence of sunlight, forming sulfate aerosols [22, 23]. Lowest concentrations were observed at night (consistently between 19:00-07:00 and 07:00-09:00), as photochemical activity declines, reducing the conversion of SO<sub>2</sub> into SO<sub>4</sub><sup>2-</sup>.

**Table 1.** Comparison of WSI concentrations in the literature

Location	Location Type	Time Average	Parameters (ng m <sup>-3</sup> )					Reference
			SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	NO <sub>2</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	
Amasra	Rural	Annual (1995-1997)	665	2310	821	-	-	[24]
Ankara	Urban	Annual (1993)	471	1140	-	-	-	
Antalya	Rural	Annual (1992-1993)	1280	4240	871	-	-	
Çubuk, Ankara	Rural	Annual (1993-2000)	1720	3910	2500	-	-	
Kocaeli	Urban	Winter	-	-	-	43000	-	[25]
		Summer	-	-	-	46000	-	
Seoul	Urban	Winter	87.07	219	189.8	-	-	[26]
		Spring	120.8	222.2	217.1	-	-	
		Summer	130.9	180	204.9	-	-	
		Fall	91.18	168.5	217.1	-	-	
Beijing -2017	Urban	Winter	13310	11930	6960	-	-	[27]
		Summer	25560	12510	14340	-	-	
Beijing-2019	Urban	Daily(3-12 Nov. 2014)	5500	13400	3900	-	-	[28]
Delhi	Urban	Annual (Dec.2011-Nov2012)	19100	8900	5800	-	-	[29]
Barcelona	Urban	Annual (2011-2012)	2800	1000	1000	-	-	[7]

**Table 1.** Comparison of WSI concentrations in the literature (cont.)

Location	Area	Winter 2014	5790	8850	567	-	-	[30]
		Shanghai	Urban	Autumn 2014	7900	7560	4780	
Istanbul - 2017	Urban	Winter	181.5	29.7	56.2	2.0	39.4	This work
		Spring	265.0	34.7	56.8	1.4	38.3	
		Summer	103.2	11.5	16.5	0.7	32.1	
		Fall	263.8	37.1	84.1	0.7	25.3	

#### Seasonal evolution:

The highest concentrations were observed in spring and autumn, when moderate temperatures and humidity enhance sulfate formation [31]. Lower concentrations were found in winter, due to weaker photochemical activity and lower oxidation rates. Summer levels were lower than expected, possibly due to increased atmospheric dispersion and removal via wet deposition [32].

#### 3.7.2 Nitrate ( $NO_3^-$ ).

Diurnal variations were dominated by traffic emissions. Highest concentrations found consistently in the morning and early afternoon, mostly between -9:00-15:00 which coincide with the highest traffic density as reported by Flores et al. [33]. On the contrary, the lowest concentrations found at night due to decrease in  $NH_3$  emissions from traffic [34].

Some of the lowest concentrations were also found in midday, when elevated temperatures cause volatilities of the semi-volatile ammonium nitrate or nitrate volatilization back into nitric acid ( $HNO_3$ ) gas [35]

#### Seasonal variation:

Winter and Fall showed the highest nocturnal nitrate peaks, attributed to increased  $NO_x$  and VOC emissions from traffic and residential heating sources and stable atmospheric conditions [36]. Higher nighttime  $NO_x$  concentrations (132.6 and 146.2 ppb) were observed in Fall and Winter, respectively, compared to daytime concentrations (100.7 and 111.3 ppb) [33], while low boundary layer heights below 300 m were observed at night in Fall and Winter [37]. Spring had moderate levels, while summer had the lowest nitrate concentrations, likely due to increased temperatures and low relative humidity [20] favoring  $NO_3^-$  volatilization [38].

#### 3.7.3. Nitrite ( $NO_2^-$ )

Concentrations were driven by primary emissions and limited secondary formation. There were variations on a day to day and season to season basis. Concentrations were undetectable in several samples due to its chemical instability. For this reason, diurnal patterns were less pronounced. High nitrite concentrations were typically found in the afternoon and at night. Particulate nitrite and nitrous acid (HONO) are important intermediates; thus, nitrite concentrations may be due

nocturnal heterogenous reactions of  $NO_2$  produced from traffic and enhanced with high relative humidity. In addition, since HONO accumulates at night, high particle nitrite concentrations may be due to the gas/particle partitioning between particulate nitrite and HONO [39, 40]. Lowest typical in the morning between 09:00-11:00 and 11:00-13:00, as sunlight promotes formation of  $NO_3^-$  particles through oxidation reactions involving ozone ( $O_3$ ), hydroxyl radicals (OH), or hydrogen peroxide ( $H_2O_2$ ) [23]

#### Seasonal variation:

Due to its limited stability, nitrite concentrations were low compared to other WSIs. The highest concentrations were found in winter, possibly associated with increased fossil fuel combustion for residential heating [41, 42]. For instance, lower concentrations found in spring, summer, and fall, due to enhanced oxidation and atmospheric mixing.

#### 3.7.4. Ammonium ( $NH_4^+$ ).

Concentrations were mainly driven by neutralization of acidic aerosols. Two distinct trends were observed: Day peaks found variable between 11:00-15:00, driven by oxidation of precursor ammonia gas ( $NH_3$ ) with  $NO_x$  mainly emitted from traffic and possibly also due to regional transport with an expanded boundary layer [43, 44]. Peaks observed at nighttime were due atmospheric conditions favoring the formation of ammonium particles from gas/particle partitioning and accumulation [44].

#### Seasonal variation:

Higher concentrations were found in Winter and Fall, correlating with increased acid-neutralization processes from  $SO_4^{2-}$  and  $NO_3^-$  [43]. Lowest concentrations found in summer, likely due to the volatilization of ammonium nitrate and ammonium sulfate to form ammonia gas at higher temperatures [44].

#### 3.7.5. Phosphate ( $PO_4^{3-}$ )

Variability in the concentrations were due to combustion and dust resuspension. Among all WSIs, phosphate exhibited moderate diurnal variation, with peaks in the morning 07:00-9:00 and in the afternoon 15:00-19:00, possibly due to the gas/particle partitioning of semi-volatile organophosphate esters (OPEs) used as flame retardants, plasticizers,

defoamers, floor waxes paints, among others or by dust transport and dust resuspension [45, 46].

Seasonal variation:

Phosphate exhibited the lowest dispersion indicating continuous apportionment from sources during the various seasons. Concentrations were slightly higher in summer and spring, likely due to natural sources such as soil resuspension and biomass burning. Lower concentrations found in winter fall, except for occasional spikes possibly related to lower atmospheric transport due to low boundary layer heights [47] and anthropogenic combustion emissions [46, 48] possibly for residential heating during the cold season [49].

### 3.7.6. Key Implications for Air Quality and Atmospheric Chemistry

Winter and Fall exhibited the highest overall WSI concentrations, primarily due to emissions from residential heating, and traffic, combined with limited atmospheric dispersion.

Photochemical activity is enhanced in Spring and summer, promoting sulfate formation while reducing nitrate retention due to higher temperatures.

Nitrate's volatility in warm conditions reinforces the importance of controlling NO<sub>x</sub> emissions to limit formation of nitrate particle formation in summer. Ammonium trends confirm its role in aerosol neutralization, forming ammonium sulfate and ammonium nitrate, with stronger concentrations in winter and fall.

Phosphate's lack of seasonality suggests continuous contributions from sources such as OPEs or dust resuspension.

## IV. CONCLUSIONS

Investigation of water-soluble ions (WSIs) in fine particulate matter (PM<sub>2.5</sub>) in Istanbul demonstrated pronounced seasonal and diurnal variations. Sulfate (SO<sub>4</sub><sup>2-</sup>) consistently showed the highest concentrations, particularly during spring and fall, attributable to increased photochemical oxidation and elevated humidity; on the contrary, winter levels were reduced due to decreased photochemical activity. Nitrate (NO<sub>3</sub><sup>-</sup>) concentrations reached their maximum during winter and fall, driven by traffic emissions and residential heating, yet were significantly lower in the summer months due to volatilization.

**Table 2.** Overview of WSI concentration diurnal trends

Time of Day	Sulfate (SO <sub>4</sub> <sup>2-</sup> )	Nitrate (NO <sub>3</sub> <sup>-</sup> )	Nitrite (NO <sub>2</sub> <sup>-</sup> )	Ammonium (NH <sub>4</sub> <sup>+</sup> )	Phosphate (PO <sub>4</sub> <sup>3-</sup> )
Early Morning (7-9 AM)	Moderate	Low	Low	Peak (traffic emissions)	Moderate
Midday (11 AM - 3 PM)	Peak (photochemical oxidation)	Lowest (volatilization)	Lowest	moderate	Peak (resuspension, industrial sources)
Evening (5-7 PM)	Declining	Increasing	Moderate	Increasing	Stable
Night (7 PM - 7 AM)	Lowest	Peak (stable conditions, condensation)	Peak (combustion emissions)	Peak (less thermal decomposition)	Lower

Ammonium (NH<sub>4</sub><sup>+</sup>) exhibited increased concentrations at night, especially in winter and fall, as stable atmospheric conditions facilitated gas-to-particle partitioning. Phosphate (PO<sub>4</sub><sup>3-</sup>) showed moderate diurnal variability, with peaks occurring in the morning and late afternoon, likely due to combustion sources and dust resuspension. Nitrite (NO<sub>2</sub><sup>-</sup>) concentrations remained consistently low throughout all seasons due to the chemical instability of the compound and rapid oxidation. Diurnal trends indicated a pronounced daytime peak for sulfate, driven by photochemical oxidation of sulfur dioxide (SO<sub>2</sub>), whereas nitrate and ammonium concentrations were typically elevated during nighttime due to atmospheric stability and lower temperatures promoting condensation. Compared to other urban areas worldwide, Istanbul's WSI concentrations were significantly lower than those observed in highly polluted megacities such as Beijing and Delhi, where sulfate and nitrate levels are significantly elevated due to more intense industrial

and traffic-related emissions. On the other hand, WSI concentrations in Istanbul are in line with those recorded in Seoul, showing the impact of industrial and transport activities with relatively less emission intensities than those in Beijing and Delhi. Even though the WSI concentrations found in Istanbul are low compared to other urban areas, it is still necessary to reduce the levels of PM<sub>2.5</sub> for health and environmental protection.

For the improvement in Istanbul's air quality, efforts are needed to reduce emissions from WSI precursors. Stricter controls on sulfur dioxide (SO<sub>2</sub>) emitted from industries and fossil fuel combustion, especially at peak times, are essential. For managing nitrate pollution, which increases in the cold season, a reduction in vehicular nitrogen oxide (NO<sub>x</sub>) emissions is recommended through the implementation of cleaner fuels and improved traffic management. The higher nighttime ammonium concentrations highlight the

necessity for improved regulation of ammonia (NH<sub>3</sub>) emissions from traffic, industrial activities, particularly the agricultural sector, and coal combustion. Phosphate emissions, associated with combustion, dust resuspension, and OPEs, can be diminished through enhanced emission control and the transition to higher-quality fuels. Given that WSI concentrations increase during winter and fall due to stable atmospheric conditions, pollution control measures should be seasonally adapted, with more stringent control during these periods. Continuous monitoring of PM<sub>2.5</sub> chemical speciation is recommended to evaluate the effectiveness of mitigation strategies. By implementing comprehensive air quality strategies, WSI levels and PM<sub>2.5</sub> can be reduced in Istanbul.

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### REFERENCES

- [1] Kan, H., S.J. London, G. Chen, Y. Zhang, G. Song, N. Zhao, L. Jiang, and B. Chen, (2007). Differentiating the effects of fine and coarse particles on daily mortality in Shanghai, China. *Environ Int*, 33 (3), 376-384.
- [2] Song, Y., Y. Zhang, and W. Dai, PM<sub>2.5</sub> Sources and Their Effects on Human Health in China: Case Report☆, in *Encyclopedia of Environmental Health (Second Edition)*, J. Nriagu, Editor. 2019, Elsevier: Oxford. p. 274-281.
- [3] Wang, H. and D. Shooter, (2002). Coarse–fine and day–night differences of water-soluble ions in atmospheric aerosols collected in Christchurch and Auckland, New Zealand. *Atmos Environ*, 36 (21), 3519-3529.
- [4] Ocskay, R., I. Salma, W. Wang, and W. Maenhaut, (2006). Characterization and diurnal variation of size-resolved inorganic water-soluble ions at a rural background site. *J Environ Monit*, 8 (2), 300-306.
- [5] Hsu, Y.-C., M.-H. Lai, W.-C. Wang, H.-L. Chiang, and Z.-X. Shieh, (2008). Characteristics of Water-Soluble Ionic Species in Fine (PM<sub>2.5</sub>) and Coarse Particulate Matter (PM<sub>10-2.5</sub>) in Kaohsiung, Southern Taiwan. *J Air Waste Manage Assoc*, 58 (12), 1579-1589.
- [6] ATSDR, (1998). Toxicological Profile for Sulfur Dioxide. U.S. Department Of Health and Human Services Public Health Service Agency for Toxic Substances and Disease Registry.
- [7] Salameh, D., A. Detournay, J. Pey, N. Pérez, F. Liguori, D. Saraga, M.C. Bove, P. Brotto, F. Cassola, and D. Massabò, (2015). PM<sub>2.5</sub> chemical composition in five European Mediterranean cities: a 1-year study. *Atmospheric Research*, 155 102-117.
- [8] İrde, Ç., (2024). Ministry of Environment, Urbanization and Climate Change. Türkiye's Informative Inventory Report IIR 2024.
- [9] Carslaw, K., O. Boucher, D. Spracklen, G. Mann, J. Rae, S. Woodward, and M. Kulmala, (2010). A review of natural aerosol interactions and feedbacks within the Earth system. *Atmospheric Chemistry and Physics*, 10.
- [10] Duce, D.J.E.I.R.A., On the global flux of atmospheric sea salt. 1988.
- [11] Laskin, A., R.C. Moffet, M.K. Gilles, J.D. Fast, R.A. Zaveri, B. Wang, P. Nigge, and J. Shutthanandan, (2012). Tropospheric chemistry of internally mixed sea salt and organic particles: Surprising reactivity of NaCl with weak organic acids. *Journal of Geophysical Research: Atmospheres*, 117 (D15).
- [12] Pratt, A., M. Johnson, E. Magalhaes, L. You, X. Diao, and J. Chamberlin, (2011). Yield Gaps and Potential Agricultural Growth in West and Central Africa. *Research monograph* 170.
- [13] Sangkham, S., W. Phairuang, S.P. Sherchan, N. Pansakun, N. Munkong, K. Sarndhong, M.A. Islam, and P. Sakunkoo, (2024). An update on adverse health effects from exposure to PM<sub>2.5</sub>. *Environmental Advances*, 18 100603.
- [14] Hong, X., K. Yang, H. Liang, and Y. Shi, (2022). Characteristics of Water-Soluble Inorganic Ions in PM<sub>2.5</sub> in Typical Urban Areas of Beijing, China. *ACS Omega*, 7 (40), 35575-35585.
- [15] Bae, J.-W., H.J. Kwon, S.-H. Kim, L. Ma, H. Im, E. Kim, M.O. Kim, and W.-S. Kwon, (2020). Inhalation of ammonium sulfate and ammonium nitrate adversely affect sperm function. *Reprod Toxicol*, 96 424-431.
- [16] Sokan-Adeaga, A., G. Ana, M. Sokan-Adeaga, E. Sokan-Adeaga, and M. Oseji, (2019). Secondary inorganic aerosols: Impacts on the global climate system and human health. *Biodiversity Int J*, 3 (6), 249-59.
- [17] Szigeti, T., V.G. Mihucz, M. Óvári, A. Baysal, S. Atilgan, S. Akman, and G. Záray, (2013). Chemical characterization of PM<sub>2.5</sub> fractions of urban aerosol collected in Budapest and Istanbul. *Microchem J*, 107 (0), 86-94.
- [18] Theodosi, C., U. Im, A. Bougiatioti, P. Zarrmpas, O. Yenigun, and N. Mihalopoulos, (2010). Aerosol chemical composition over Istanbul. *Sci Total Environ*, 408 (12), 2482-2491.

- [19] Koçak, M., C. Theodosi, P. Zarnpas, U. Im, A. Bougiatioti, O. Yenigun, and N. Mihalopoulos, (2011). Particulate matter (PM10) in Istanbul: Origin, source areas and potential impact on surrounding regions. *Atmos Environ*, 45 (38), 6891-6900.
- [20] Mertoglu, E., H.D. Amantha, and R.M. Flores-Rangel, (2022). Chemical characterization of water-soluble ions in highly time-resolved atmospheric fine particles in Istanbul megacity. *Environmental Science and Pollution Research*, 29 (50), 76456-76471.
- [21] Salam, A., M. Assaduzzaman, M.N. Hossain, and A.N.A. Siddiki, (2015). Water soluble ionic species in the atmospheric fine particulate matters (PM<sub>2.5</sub>) in a Southeast Asian mega city (Dhaka, Bangladesh). *Open Journal of Air Pollution*, 4 (3), 99-108.
- [22] Zhou, L., Z. Liang, B.R. Go, R.A.I. Cuevas, R. Tang, M. Li, C. Cheng, and C.K. Chan, (2023). Sulfate formation via aerosol-phase SO<sub>2</sub> oxidation by model biomass burning photosensitizers: 3,4-dimethoxybenzaldehyde, vanillin and syringaldehyde using single-particle mixing-state analysis. *Atmos. Chem. Phys.*, 23 (9), 5251-5261.
- [23] Seinfeld, J.H. and S.N. Pandis, *Atmospheric chemistry and physics: from air pollution to climate change*. 2016: John Wiley & Sons.
- [24] Türküm, A., H. Pekey, B. Pekey, and G. Tuncel, (2008). Investigating relationships between aerosol and rainwater compositions at different locations in Turkey. *Atmospheric Research*, 89 (4), 315-323.
- [25] Türküm, A., (2018). Kocaeli atmosferinde uçucu organik bileşiklerin ve inorganik gazların dağılımları, kaynakları ve sağlık risklerinin belirlenmesi.
- [26] Shon, Z.-H., K.-H. Kim, S.-K. Song, K. Jung, N.-J. Kim, and J.-B. Lee, (2012). Relationship between water-soluble ions in PM<sub>2.5</sub> and their precursor gases in Seoul megacity. *Atmos Environ*, 59 540-550.
- [27] Liu, Z., Y. Xie, B. Hu, T. Wen, J. Xin, X. Li, and Y. Wang, (2017). Size-resolved aerosol water-soluble ions during the summer and winter seasons in Beijing: Formation mechanisms of secondary inorganic aerosols. *Chemosphere*, 183 119-131.
- [28] Xu, W., Liu, X., Liu, L., Dore, A. J., Tang, A., Lu, L., ... & Zhang, F., (2019). Impact of emission controls on air quality in Beijing during APEC 2014: Implications from water-soluble ions and carbonaceous aerosol in PM<sub>2.5</sub> and their precursors. *Atmos Environ*.
- [29] Dumka, U., S. Tiwari, D. Kaskaoutis, P. Hopke, J. Singh, A. Srivastava, D. Bisht, S. Attri, S. Tyagi, and A. Misra, (2017). Assessment of PM<sub>2.5</sub> chemical compositions in Delhi: primary vs secondary emissions and contribution to light extinction coefficient and visibility degradation. *Journal of Atmospheric Chemistry*, 74 (4), 423-450.
- [30] Ye, X., Tao, Y., Liu, Y., Wang, R., Li, Q., Yang, X., & Chen, J., (2019). Size-fractionated water-soluble ions during autumn and winter: Insights into volatile ammonium formation mechanisms in Shanghai, a megacity of China. *Atmos Environ*.
- [31] Wang, S., J. Nan, C. Shi, Q. Fu, S. Gao, D. Wang, H. Cui, A. Saiz-Lopez, and B. Zhou, (2015). Atmospheric ammonia and its impacts on regional air quality over the megacity of Shanghai, China. *Sci Rep*, 5 15842.
- [32] Duan, J., R.J. Huang, Y. Li, Q. Chen, Y. Zheng, Y. Chen, C. Lin, H. Ni, M. Wang, J. Ovadnevaite, D. Ceburnis, C. Chen, D.R. Worsnop, T. Hoffmann, C. O'Dowd, and J. Cao, (2020). Summertime and wintertime atmospheric processes of secondary aerosol in Beijing. *Atmos. Chem. Phys.*, 20 (6), 3793-3807.
- [33] Flores, R.M., (in review). Characteristics, Evolution, and Sources of OC and EC fractions with Insights into Secondary Organic Aerosol Formation at a Traffic Site in Istanbul.
- [34] Kim, M.J. Sensitivity of Nitrate Aerosol Production to Vehicular Emissions in an Urban Street. *Atmosphere*, 2019. 10.
- [35] Schaap, M., G. Spindler, M. Schulz, K. Acker, W. Maenhaut, A. Berner, W. Wiedprecht, N. Streit, K. Müller, and E. Brüggemann, (2004). Artefacts in the sampling of nitrate studied in the "INTERCOMP" campaigns of EUROTRAC-AEROSOL. *Atmos Environ*, 38 (38), 6487-6496.
- [36] Fu, X., T. Wang, J. Gao, P. Wang, Y. Liu, S. Wang, B. Zhao, and L. Xue, (2020). Persistent Heavy Winter Nitrate Pollution Driven by Increased Photochemical Oxidants in Northern China. *Environ Sci Technol*, 54 (7), 3881-3889.
- [37] Flores, R.M., E. Mertoğlu, H. Özdemir, B.O. Akkoyunlu, G. Demir, A. Ünal, and M. Tayanç, (2020). A high-time resolution study of PM<sub>2.5</sub>, organic carbon, and elemental carbon at an urban traffic site in Istanbul. *Atmos Environ*, 223 117241.
- [38] Chiu, Y.T.T. and A.G. Carlton, (2024). Aerosol Thermodynamics: Nitrate Loss from Regulatory PM<sub>2.5</sub> Filters in California. *ACS EST Air*, 1 (1), 25-32.
- [39] Zhang, Z., C. Ye, Y. Wu, T. Zhou, P. Chen, S. Kang, C. Zhang, Z. Jiang, and L. Geng, (2025). On the presence of high nitrite (NO<sub>2</sub><sup>-</sup>) in coarse particles at Mt. Qomolangma. *EGUsphere*, 2025 1-25.

- [40] Wang, L., L. Wen, C. Xu, J. Chen, X. Wang, L. Yang, W. Wang, X. Yang, X. Sui, L. Yao, and Q. Zhang, (2015). HONO and its potential source particulate nitrite at an urban site in North China during the cold season. *Sci Total Environ*, 538 93-101.
- [41] Chen, J., X. Wang, J. Zhang, M. Li, H. Li, Z. Liu, Y. Bi, D. Wu, X. Yin, R. Gu, Y. Jiang, Y. Shan, Y. Zhao, L. Xue, and W. Wang, (2022). Particulate organic nitrates at Mount Tai in winter and spring: Variation characteristics and effects of mountain-valley breezes and elevated emission sources. *Environ Res*, 212 113182.
- [42] Jeon, J.-W., S.-W. Park, Y.-J. Han, T. Lee, S.-H. Lee, J.-M. Park, M.-S. Yoo, H.-J. Shin, and P.K. Hopke, (2024). Nitrate formation mechanisms causing high concentration of PM<sub>2.5</sub> in a residential city with low anthropogenic emissions during cold season. *Environ Pollut*, 352 124141.
- [43] Wang, Q., Y. Miao, and L. Wang, (2020). Regional Transport Increases Ammonia Concentration in Beijing, China. *Atmosphere*, 11 (6), 563.
- [44] Kutzner, R.D., J. Cuesta, P. Chelin, J.E. Petit, M. Ray, X. Landsheere, B. Tournadre, J.C. Dupont, A. Rosso, F. Hase, J. Orphal, and M. Beekmann, (2021). Diurnal evolution of total column and surface atmospheric ammonia in the megacity of Paris, France, during an intense springtime pollution episode. *Atmos. Chem. Phys.*, 21 (15), 12091-12111.
- [45] Wang, Y., M. Bao, F. Tan, Z. Qu, Y. Zhang, and J. Chen, (2020). Distribution of organophosphate esters between the gas phase and PM<sub>2.5</sub> in urban Dalian, China. *Environ Pollut*, 259 113882.
- [46] Richon, C., J.C. Dutay, F. Dulac, R. Wang, and Y. Balkanski, (2018). Modeling the biogeochemical impact of atmospheric phosphate deposition from desert dust and combustion sources to the Mediterranean Sea. *Biogeosciences*, 15 (8), 2499-2524.
- [47] Flores, R.M., H. Özdemir, B.O. Akkoyunlu, A. Ünal, and M. Tayanç, (2020). Seasonal variation of carbonaceous PM<sub>2.5</sub> in an Istanbul traffic site. *Atmospheric Pollution Research*, 11 (12), 2110-2118.
- [48] Dong, S., H. Zhang, P. Krishnan, S. Jia, C. Huang, F. Wang, L. Luo, F. Wang, H. Meng, Y. Zhu, R. Li, and M. Tang, (2023). Sources and solubility of aerosol phosphorus at a coastal site in northern China: Coarse versus fine particles and spring versus winter. *Atmos Environ*, 315 120127.
- [49] Flores, R.M., H. Özdemir, A. Ünal, and M. Tayanç, (2022). Distribution and sources of SVOCs in fine and coarse aerosols in the megacity of Istanbul. *Atmospheric Research*, 271 106100.