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Seasonal Variations and Composition of Soluble Ions in PM2.5 at an Urban Location in Kenitra, Morocco †

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Abstract: : A comprehensive study was executed within the urban vicinity of Kenitra city, covering the period from 2020 to 2021. During this study, 60 effective $PM_{2.5}$ samples were collected for 24 hours using a dichotomous sampler and Nuclepore track-etched polycarbonate filters with a diameter of 37 mm. Ion chromatography was employed to identify the composition of our samples, including Cl^-, SO_4^{2-}, F^-, NO_3^-, NH_4^+, Na^+, Ca^{2+}, and K^+. The results showed that the average mass concentration (± standard deviation) of the seven ions in $PM_{2.5}$ was 3.2 ± 1.3 μg/m³, constituting approximately 18% of the total mass concentration. Among the ions, the concentrations followed the order of $Na^+ > SO_4^{2-} > Cl^- > NO_3^- > K^+ > NH_4^+ > F^-$. The predominant constituents of water-soluble ions in $PM_{2.5}$ were detected to be secondary inorganic species (NH_4^+, SO_4^{2-}, and NO_3^-), contributing an average of 44% to the total $PM_{2.5}$ ions. Throughout the four seasons, the concentrations of these three ions exhibited variability, with the greatest levels observed in spring, followed by summer, fall, and winter. The ratio of $[NO_3^-]/[SO_4^{2-}]$ was found to be almost equal to unity, indicating that the primary sources of nitrogen and sulfur in the Kenitra atmosphere were prioritized from stationary sources (typically associated with power plants, industrial and commercial activities, and other large-scale facilities).

Keywords: PM2.5; water-soluble ions; seasonal variations; urban aerosols; Ion chromatography

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1. Introduction

The degradation of urban air quality has evolved into a significant public health and environmental protection issue. It is irrefutable that air pollution hurts human health, as indicated by the increase in premature deaths and associated respiratory and cardiovascular diseases. As a result of its accelerated economic prosperity, the Moroccan city of Kenitra generates a significantly higher quantity of air pollutants. Particulate matter (PM) with aerodynamic diameters of less than 2.5 μm ($PM_{2.5}$) has elicited significant interest from both academia and society, as a measurement for monitoring the prevailing air quality in residential areas.

Numerous investigations have revealed that the origins, material compositions, and processes governing the formation of $PM_{2.5}$ in the atmosphere are highly intricate [1,2]. However, due to the variations in regional geographic characteristics and climatic variables, $PM_{2.5}$'s components are various [3], and energy structures [4].

Considerable limitations exist regarding the available information on the chemical $PM_{2.5}$ and the sources of its emissions in the Kenitra area. To collect water-soluble inorganic ions and analyze them employing ion chromatography, ambient $PM_{2.5}$ samples were obtained in a city environment in Kenitra, Morocco.

2. Materials and Methods

To provide comprehensive and verifiable results, the method used in this study was both skillful and interdisciplinary, incorporating many methodologies. Measurements were carried out over one year (2020-2021) to obtain long-term data on the levels of specific materials.

The Nuclepore track-etched polycarbonate filters were employed to gather the $PM_{2.5}$ samples were subjected to ion analysis. One-half of every sample filter was placed in a 15 ml container of MilliQ water which typically has a resistivity below 18 Ω for this study.

The vials were immersed in an ultrasonic bath for 45 minutes to release the aerosols from the filters and transfer them to the solution. Next, a 4 mm diameter CS12 column connected to an ion chromatograph (IC) (Dionex model DX-600) furnished with a reagent-free system (automatic eluent production and self-regenerating suppression) was employed for the analysis of the primary soluble inorganic cations (Na^+, NH_4^+, K^+).

A 4 mm diameter AS11 column was used coupled with a Dionex model DX-600 ion chromatography (IC) that was additionally equipped with a reagent-free system to analyze the main inorganic anions (SO_4^{2-}, NO_3^-, Cl^-, F^-).

Blank filters were gathered and subjected using identical preservation procedures as the samples, nonetheless, they revealed an absence of noteworthy contamination throughout the processes of collection, handling, or transportation.

3. Results and Discussion

3.1. Seasonal Variation Characteristics of Water-Soluble Ions and $PM_{2.5}$

The levels of $PM_{2.5}$ recorded at our sampling location in Kenitra, Morocco (17.2 μg/m^3) are comparable to the mean $PM_{2.5}$ obtained by Benchrif et al. [5] at an urban site in Tetouan, Morocco (17.9 μg/m^3). Notably, the $PM_{2.5}$ mass concentrations in Kenitra exhibited a similar range to those observed in suburban areas of Lisbon, Portugal, as reported by Almeida et al. [6] (14 μg/m^3). Nonetheless, the mass concentration of $PM_{2.5}$ at our sample location is notably less than the concentrations reported by Pérez et al. [7] in Barcelona, Spain (29 μg/m^3).

Comprised of 18% of the $PM_{2.5}$ concentration, the average mass concentration of total WSI was measured to be 3.2 μg/m^3. In Brindisi, Italy [8], the most common components were secondary inorganic ions, making up a significant part (38%, 6.7 μg/m^3). Similar patterns were seen in Tetouan [5] and Marseille, France [9], where these ions made up 28% (5.1 μg/m^3) and 27% (5.4 μg/m^3) of the $PM_{2.5}$ particles, respectively. This aligns closely with our study's conclusions. The mean concentration of Na^+ (0.85 ± 0.32 μg/m^3) was the highest followed by SO_4^{2-} (0.69 ± 0.30 μg/m^3), Cl^- (0.55 ± 0.41 μg/m^3), NO_3^- (0.52 ± 0.41 μg/m^3), K^+ (0.33 ± 0.25 μg/m^3), NH_4^+ (0.23 ± 0.17 μg/m^3) and F^- (0.10 ± 0.08 μg/m^3).

Furthermore, the sequence of mass concentration levels over the four seasons was as follows: autumn > winter > summer > spring. Figure 2 exhibits the seasonal variation of the total concentration of the seven WSI. In winter, compared to other seasons, the concentrations of the three primary secondary ions (SO_4^{2-}, NH_4^+, and NO_3^-) constituted 44% of the overall water-soluble ions. The contribution of SO_4^{2-} to total WSI (21.35%) was the highest, followed by NO_3^- (15.93%) and NH_4^+ (7.03%). Observations revealed that Na^+ concentrations were higher in autumn than in other seasons. In addition, K^+ and Cl^- levels peaked in autumn, followed by winter, and showed their lowest values in summer, reflecting the phenomenon of combustion and sea salts [10,11].

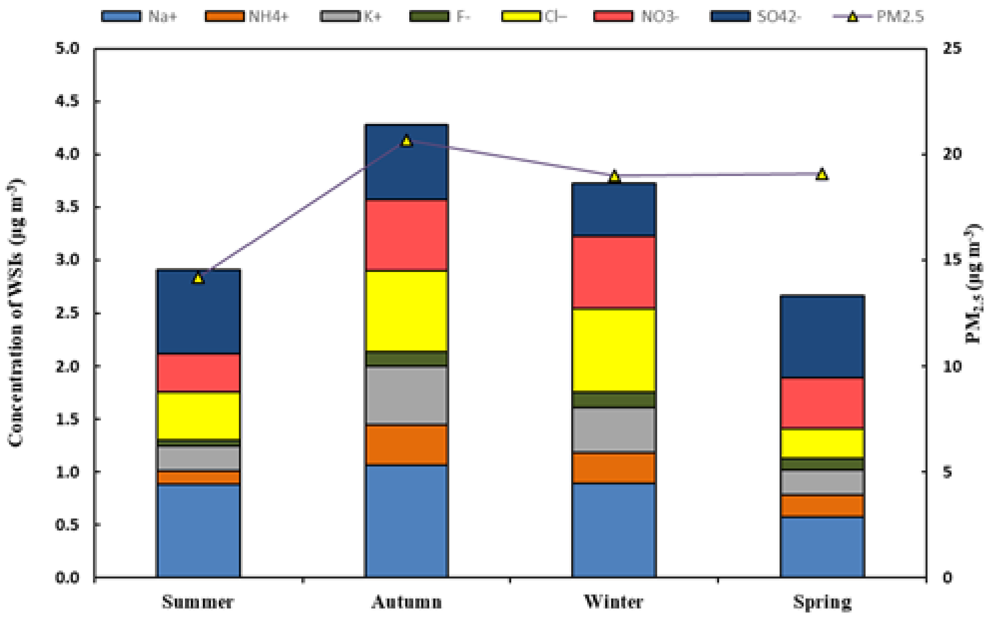

Figure 1. Seasonal variation during sampling periods in WSI in $PM_{2.5}$.

3.2. Analysis of ion balance of Water-Soluble Ions

The anion equivalent (AE) and cation equivalent (CE) can be calculated according to the following formula :

$$AE = \frac{Cl^-}{35.5} + \frac{NO_3^-}{62} + \frac{SO_4^{2-}}{48} + \frac{F^-}{19} \quad (1)$$

$$CE = \frac{Na^+}{23} + \frac{NH_4^+}{18} + \frac{K^+}{39} \quad (2)$$

Ion balance is often used to assess the acid-base balance of WSIs in aerosols. However, some studies [12,13,14] indicated that it may be applied to investigate the significance of ion's contributions to the aerosol mass concentration. Figure 3 illustrates the ion balance calculated from detected anions and cations in $PM_{2.5}$. It showed a good correlation ($r = 0.7$) between the cations and anions and the derived slope of the linear regression lines reached 0.97. These results suggest that the investigated ions had a clear relationship, the major ionic components were measured, and the $PM_{2.5}$ was either neutral or weak acidic [15].

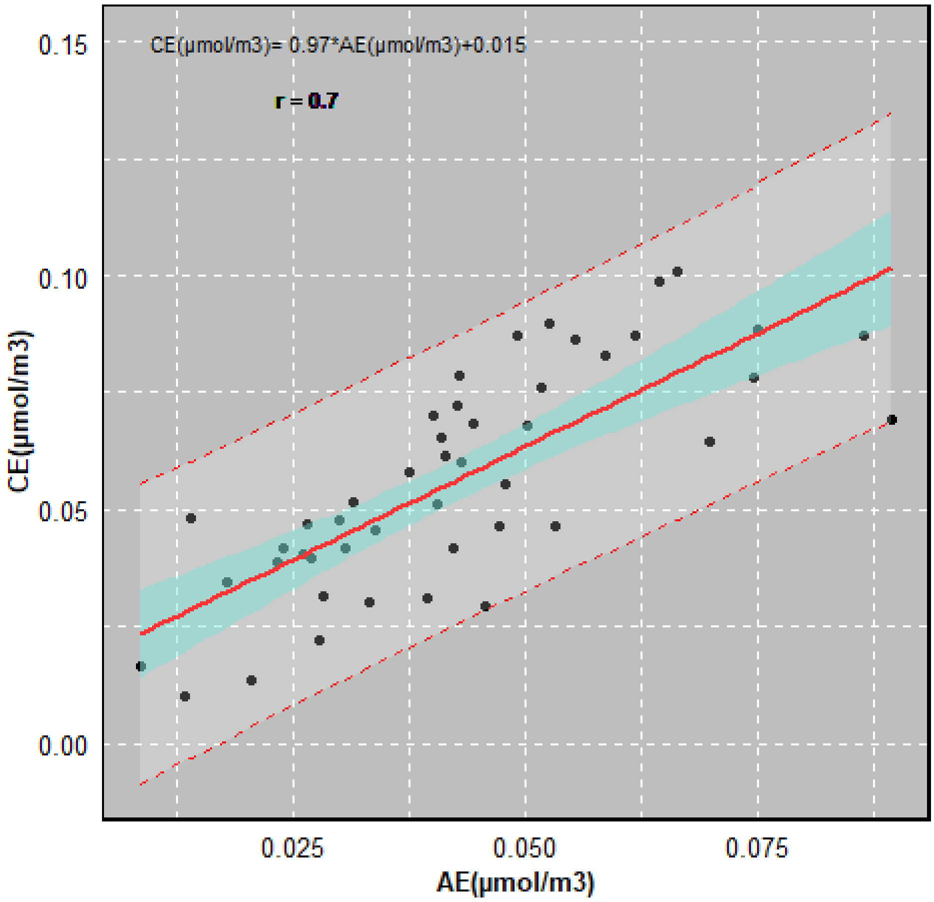

Figure. 2. The ion balance of water-soluble anions and cations in Kenitra over the year

3.3. NO_3^-/ SO_4^{2-} Concentration Equivalent Ratio

In this study, the annual average [NO_3^-]/[SO_4^{2-}] mass ratio was 0.8, which was below unity, suggesting the predominance of stationary source emissions over mobile emissions in Kenitra [16]. This [NO_3^-]/[SO_4^{2-}] ratio exhibited seasonal variations, as illustrated in Fig.3. The highest average ratio was noted during winter (1.25), while the lowest occurred in summer (0.52), potentially attributed to the relatively warmer summer temperatures facilitating the decomposition of NO_3^- in PM2.5.

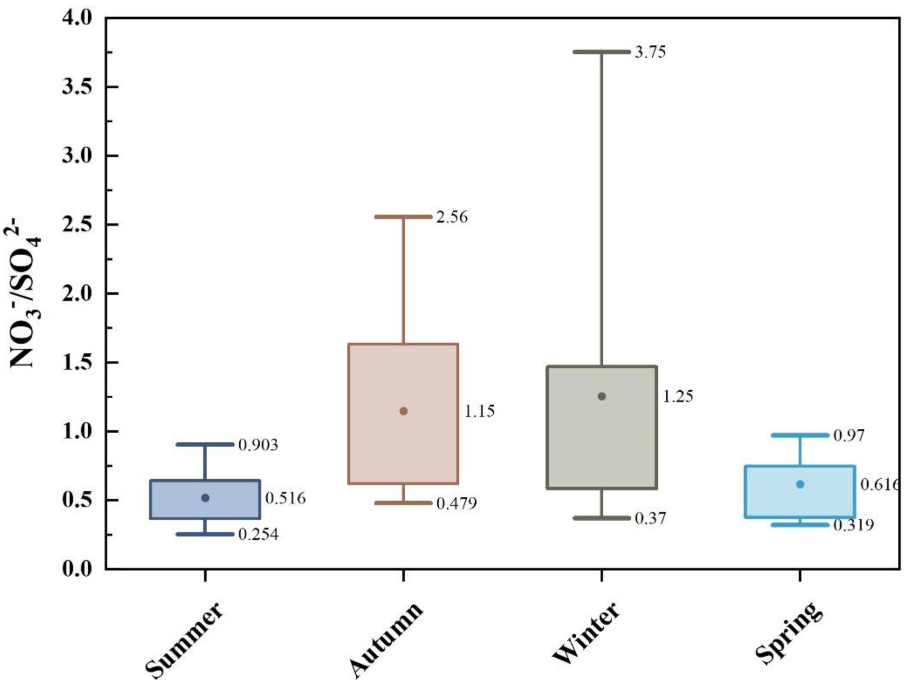

Figure 3. Seasonal variations in $[NO_3^-]/[SO_4^{2-}]$ ratio. The dot in the box plot represent the mean values, and the upper and lower borders of the dashed vertical lines represent the minimum and maximum values.

4. Conclusions

From 2020 to 2021, this research examined $PM_{2.5}$ characteristics in Kenitra City. The results demonstrated a significant proportion of WSI in $PM_{2.5}$. The following ions showed up in this order: $Na^+ > SO_4^{2-} > Cl^- > NO_3^- > K^+ > NH_4^+ > F^-$. Secondary aerosols, namely NO_3^-, SO_4^{2-}, and NH_4^+, contributed around 44% of total $PM_{2.5}$. The ion balance between anions and cations was properly maintained. The average AE/CE value, which is almost equal to the unity, indicated the neutral nature of $PM_{2.5}$ aerosols. The average $[NO_3^-]/[SO_4^{2-}]$ ratio was 0.8 pointing out stationary sources being one of the primary pollution contributors in Kenitra.

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