

Proceeding Paper

Seasonal Variations and Composition of Soluble Ions in PM_{2.5} at an Urban Location in Kenitra, Morocco [†]

Bassma El Gouch ^{1,*}, Bouchaib Ihssane ^{1,2}, Mounia Tahri ³, Fatiha Zahry ³, Ghassan Acil ³, Taoufik Saffaj ¹ and Abdelfettah Benchrif ^{3,*}

¹ Laboratory of Applied Organic Chemistry, Faculty of Sciences and Technologies, Sidi Mohamed Ben Abdellah University, Fes 80000, Morocco; bouchaib.ihssane@usmba.ac.ma (B.I.); taoufiq.saffaj@usmba.ac.ma (T.S.)

² Physio-Chemical Laboratory of Inorganic and Organique Materials (LPCMIO), Materials Science Center (MSC), Ecole Normale Supérieure, University Mohammed V, Rabat 10001, Morocco

³ National Centre for Nuclear Energy, Science, and Technology (CNESTEN), Rabat 10001, Morocco; tahri@cnesten.org.ma (M.T.); zahry@cnesten.org.ma (F.Z.); acil.ghassan@gmail.com (G.A.)

* Correspondence: elgouchbassma@gmail.com (B.E.G.); abenchrif@gmail.com (A.B.)

[†] Presented at the 6th International Electronic Conference on Atmospheric Sciences, 15–30 October 2023; Available online: <https://ecas2023.sciforum.net/>.

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 in a period of 24 h 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⁻, SO₄²⁻, F⁻, NO₃⁻, NH₄⁺, Na⁺, Ca²⁺, 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⁺ > SO₄²⁻ > Cl⁻ > NO₃⁻ > K⁺ > NH₄⁺ > F⁻. The predominant constituents of water-soluble ions in PM_{2.5} were detected to be secondary inorganic species (NH₄⁺, SO₄²⁻, and NO₃⁻), 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 [NO₃⁻]/[SO₄²⁻] 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: PM_{2.5}; water-soluble ions; seasonal variations; urban aerosols; ion chromatography



Citation: El Gouch, B.; Ihssane, B.; Tahri, M.; Zahry, F.; Acil, G.; Saffaj, T.; Benchrif, A. Seasonal Variations and Composition of Soluble Ions in PM_{2.5} at an Urban Location in Kenitra, Morocco. *Environ. Sci. Proc.* **2023**, *27*, 20. <https://doi.org/10.3390/ecas2023-16341>

Academic Editor: Patricia Quinn

Published: 27 November 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

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], as are the associated energy structures [4].

Considerable limitations exist regarding the available information on 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.

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

The vials were immersed in an ultrasonic bath for 45 min 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, Dionex®, Sunnyvale, CA, USA) 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⁺, NH₄⁺, K⁺).

A 4 mm diameter AS11 column was used coupled with a DIONEX model DX-600 ion chromatography (IC) system that was additionally equipped with a reagent-free system to analyze the main inorganic anions (SO₄²⁻, NO₃⁻, Cl⁻, F⁻).

Blank filters were gathered and subjected to testing using identical preservation procedures to 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/m³), are comparable to the mean PM_{2.5} values obtained by Benchrif et al. [5] at an urban site in Tetouan, Morocco (17.9 µg/m³). 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/m³). 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/m³).

Comprised of 18% of the PM_{2.5} concentration, the average mass concentration of total WSIs was measured to be 3.2 µg/m³. In Brindisi, Italy [8], the most common components were secondary inorganic ions, making up a significant part of the sample (38%, 6.7 µg/m³). Similar patterns were seen in Tetouan [5] and Marseille, France [9], where these ions made up 28% (5.1 µg/m³) and 27% (5.4 µg/m³) 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/m³) was the highest, followed by SO₄²⁻ (0.69 ± 0.30 µg/m³), Cl⁻ (0.55 ± 0.41 µg/m³), NO₃⁻ (0.52 ± 0.41 µg/m³), K⁺ (0.33 ± 0.25 µg/m³), NH₄⁺ (0.23 ± 0.17 µg/m³), and F⁻ (0.10 ± 0.08 µg/m³).

Furthermore, the sequence of mass concentration levels over the four seasons was as follows: autumn > winter > summer > spring. Figure 1 exhibits seasonal variation in the total concentration of the seven WSIs. In winter, compared to other seasons, the concentrations of the three primary secondary ions (SO₄²⁻, NH₄⁺, and NO₃⁻) constituted 44% of the overall water-soluble ions. The contribution of SO₄²⁻ to total WSIs (21.35%) was the highest, followed by NO₃⁻ (15.93%) and NH₄⁺ (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].

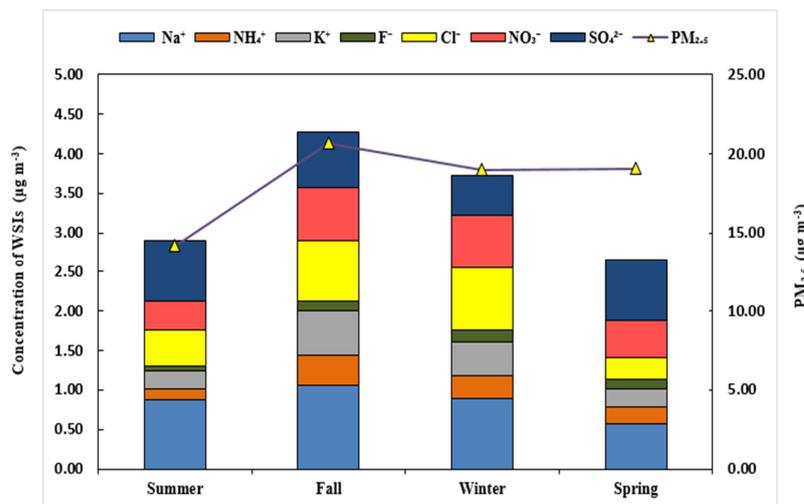


Figure 1. Seasonal variation in WSIs in PM_{2.5} during sampling periods.

3.2. Analysis of the 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 [12–14] indicated that it may be applied to investigate the significance of ionic contributions to the aerosol mass concentration. Figure 2 illustrates the ion balance calculated from detected anions and cations in PM_{2.5}. It shows good correlation ($r = 0.7$) between the cations and anions, and the derived slope of the linear regression lines reaches 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 weakly acidic [15].

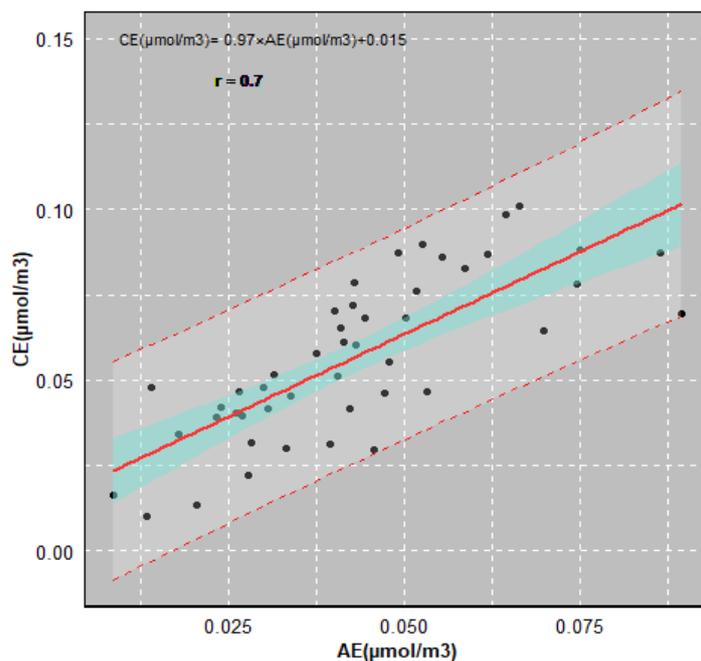


Figure 2. The ion balance of water-soluble anions and cations in Kenitra over the year.

3.3. $\text{NO}_3^-/\text{SO}_4^{2-}$ Concentration Equivalent Ratio

In this study, the annual average $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ mass ratio was 0.8, which was below unity, suggesting the predominance of stationary source emissions over mobile emissions in Kenitra [16]. This $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ ratio exhibited seasonal variations, as illustrated in Figure 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 $\text{PM}_{2.5}$.

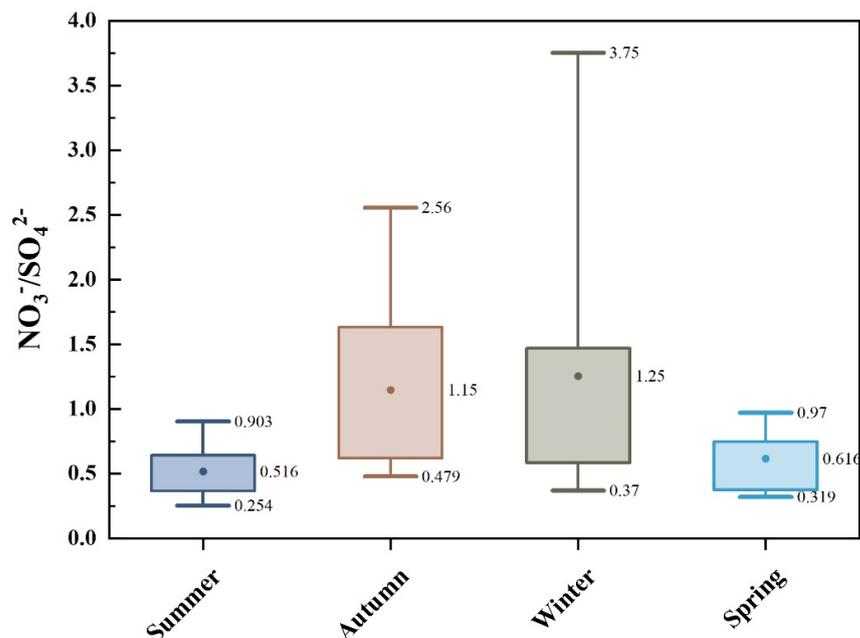


Figure 3. Seasonal variations in $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ ratio. The dots in the box plots represent the mean values, and the upper and lower borders of the dashed vertical lines represent the minimum and maximum values.

4. Conclusions

From 2020 to 2021, this research examined $\text{PM}_{2.5}$ characteristics in Kenitra City. The results demonstrated a significant proportion of WSIs in $\text{PM}_{2.5}$. The following ions showed up in this order: $\text{Na}^+ > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{K}^+ > \text{NH}_4^+ > \text{F}^-$. Secondary aerosols, namely NO_3^- , SO_4^{2-} , and NH_4^+ , contributed around 44% of total $\text{PM}_{2.5}$. The ion balance between anions and cations was properly maintained. The average AE/CE value, which is almost equal to unity, indicated the neutral nature of $\text{PM}_{2.5}$ aerosols. The average $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ ratio was 0.8, pointing to stationary sources being one of the primary pollution contributors in Kenitra.

Author Contributions: Conceptualization, A.B. and B.E.G.; methodology, A.B. and B.E.G.; validation, B.I., A.B. and M.T.; formal analysis, B.E.G.; resources, F.Z. and G.A.; writing—original draft preparation, B.E.G.; writing—review and editing, M.T. and A.B.; supervision, B.I., A.B. and T.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The datasets produced and/or analyzed in the current study can be provided by the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare that there are no competing financial interests that could inappropriately influence the contents of this manuscript.

References

1. Sun, K.; Qu, Y.; Wu, Q.; Han, T.T.; Gu, J.W.; Zhao, J.J.; Sun, Y.L.; Jiang, Q.; Gao, Z.Q.; Hu, M.; et al. Chemical characteristics of size-resolved aerosols in winter in Beijing. *J. Environ. Sci.* **2014**, *26*, 1641–1650. [[CrossRef](#)]
2. Xue, J.; Griffith, S.M.; Yu, X.; Lau, A.K.H.; Yu, J.Z. Effect of nitrate and sulfate relative abundance in PM_{2.5} on liquid water content explored through half-hourly observations of inorganic soluble aerosols at a polluted receptor site. *Atmos. Environ.* **2014**, *99*, 24–31. [[CrossRef](#)]
3. Ding, L.; Zhao, W.; Huang, Y.; Cheng, S.; Liu, C. Research on the Coupling Coordination Relationship between Urbanization and the Air Environment: A Case Study of the Area of Wuhan. *Atmosphere* **2015**, *6*, 1539–1558. [[CrossRef](#)]
4. Cheng, H.R.; Gong, W.; Wang, Z.W.; Zhang, F.; Wang, X.M.; Lv, X.P.; Liu, J.; Fu, X.X.; Zhang, G. Ionic composition of submicron particles (PM_{1.0}) during the long-lasting haze period in January 2013 in Wuhan, central China. *J. Environ. Sci.* **2014**, *26*, 810–817. [[CrossRef](#)]
5. Benchrif, A.; Tahri, M.; Guinot, B.; CHakir, E.; Zahry, F.; Damnati, B.; Baghdad, B.; Bounakhla, M.; Cachier, H.; Costabile, F. Aerosols in Northern Morocco-2: Chemical Characterization and PMF Source Apportionment of Ambient PM_{2.5}. *Atmos. Environ.* **2018**, *174*, 140–147. [[CrossRef](#)]
6. Almeida, S.M.; Pio, C.; Freitas, M.C.; Reis, M.A.; Trancoso, M.A. Approaching PM_{2.5} and PM_{2.5–10} source apportionment by mass balance analysis, principal component analysis and particle size distribution. *Sci. Total Environ.* **2006**, *368*, 663–674. [[CrossRef](#)]
7. Pérez, N.; Pey, J.; Querol, X.; Alastuey, A.; López, J.M.; Viana, M. Partitioning of major and trace components in PM₁₀–PM_{2.5}–PM₁ at an urban site in Southern Europe. *Atmos. Environ.* **2008**, *42*, 1677–1691. [[CrossRef](#)]
8. Genga, A.; Ielpo, P.; Siciliano, T.; Siciliano, M. Carbonaceous particles and aerosol mass closure in PM_{2.5} collected in a port city. *Atmos. Res.* **2017**, *183*, 245–254. [[CrossRef](#)]
9. Salameh, D.; Detournay, A.; Pey, J.; Pérez, N.; Liguori, F.; Saraga, D.; Bove, M.C.; Brotto, P.; Cassola, F.; Massabò, D.; et al. PM_{2.5} chemical compositions in five European Mediterranean cities: A 1-year study. *Atmos. Res.* **2015**, *155*, 102–117. [[CrossRef](#)]
10. Willison, M.J.; Clarke, A.G.; Zeki, E.M. Chloride aerosols in central northern England. *Atmos. Environ.* **1989**, *23*, 2231–2239. [[CrossRef](#)]
11. Penner, J.E. Carbonaceous Aerosols Influencing Atmospheric Radiation: Black Carbon and Organic Carbon. In *Aerosol Forcing of Climate*; Charlson, R.J., Heintzenberg, J., Eds.; Wiley: Hoboken, NJ, USA, 1995; pp. 91–108.
12. Hueglin, C.; Gehrig, R.; Baltensperger, U.; Gysel, M.; Monn, C.; Vonmont, H. Chemical characterization of PM_{2.5}, PM₁₀, and coarse particles at Switzerland's urban, near-city, and rural sites. *Atmos. Environ.* **2005**, *39*, 637–651. [[CrossRef](#)]
13. Cheng, Y.; Lee, S.C.; Ho, K.F.; Chow, J.C.; Louie, P.K.K.; Cao, J.J.; Hai, X. Chemically-speciated on-road PM_{2.5} motor vehicle emission factors in Hong Kong. *Sci. Total Environ.* **2010**, *408*, 1621–1627. [[CrossRef](#)]
14. Orsini, D.A.; Ma, Y.L.; Sullivan, A.; Sierau, B.; Baumann, K.; Weber, R.J. Refinements to the Particle-Into-Liquid Sampler (PILS) for ground and airborne measurements of water-soluble aerosol composition. *Atmos. Environ.* **2003**, *37*, 1243–1259. [[CrossRef](#)]
15. Hu, M.; Wu, Z.J.; Slanina, J.; Lin, P.; Liu, S.; Zeng, M. Acidic gases, ammonia and water-soluble ions in PM_{2.5} at a Pearl River Delta, China coastal site. *Atmos. Environ.* **2008**, *42*, 6310–6320. [[CrossRef](#)]
16. Zhao, Z.Z.; Wang, Q.Y.; Li, L.; Han, Y.M.; Ye, Z.L.; Pongpiachan, S.; Liu, S.X.; Tian, R.X.; Cao, J.J. Characteristics of PM_{2.5} at a high-altitude remote site in the Southeastern margin of the Tibetan Plateau in premonsoon season. *Atmosphere* **2019**, *10*, 645. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.