Altitudinal and Seasonal Assessment of Precipitation Chemistry and Wet Deposition in the Vaz Research Forest, Northern Iran

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Abstract

This study examines the chemical composition of precipitation across altitudinal gradients in the Vaz Research Forest, northern Iran, from 1999 to 2003. Precipitation samples were collected at 300, 1000, 1600, and 2200 m above sea level. Concentrations of nitrate (NO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), ammonium (NH_4^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}) and their wet deposition values were analyzed. Results indicate that annual wet deposition of most ions decreases with elevation, although anomalies at 1000 m suggest anthropogenic emissions. Precipitation remained slightly alkaline (pH > 7), while nitrogen deposition exceeded critical thresholds for sensitive ecosystems (Pardo et al., 2011; UNECE, 2022). These findings highlight the influence of local human activities on atmospheric chemistry.

Keywords:

Vaz Forest, precipitation chemistry, wet deposition, nitrate, sulfate, atmospheric pollution, elevation gradient, Caspian Sea region

Introduction

Forests play a vital role in maintaining ecological stability, and all branches of forest science ultimately serve the goal of sustainable forest management. Understanding the interactions between ecological factors—such as precipitation, humidity, and soil composition—and vegetation dynamics is essential for informed decision-making in forest conservation.

The Vaz Research Forest, located in northern Iran near the Caspian Sea, has been the subject of multidisciplinary studies since 1996. These have included investigations into its meteorological, geological, geomorphological, and ecological characteristics. A key element of these studies is understanding how atmospheric chemistry, particularly the quality of precipitation, influences vegetation and soil chemistry across varying altitudes.

Atmospheric deposition is a key factor affecting terrestrial ecosystems. Current studies show that critical loads for nitrogen deposition in sensitive ecosystems range from 1 to 39 kg N ha^{-1} yr^{-1} depending on vegetation type (Pardo et al., 2011; Forsius et al., 2021; UNECE, 2022). Globally, precipitation chemistry has shifted over the past two decades due to declining sulfur emissions and persistent nitrogen enrichment (Vet et al., 2014; Ackerman et al., 2019; Benish et al., 2022).

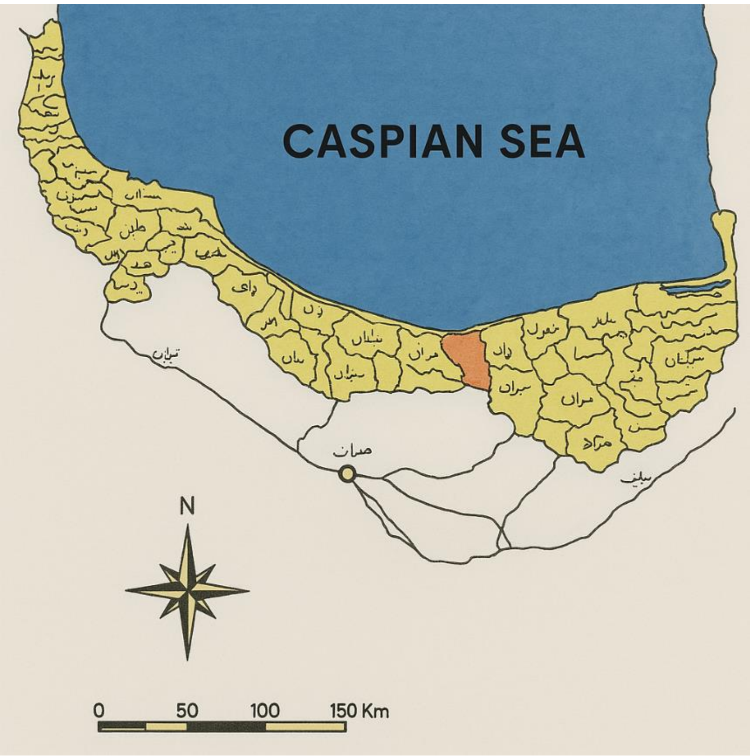

Figure 1. Geographic location of the Vaz Research Forest in the Caspian Sea region.

Atmospheric deposition is a significant environmental factor affecting terrestrial ecosystems. According to Breedman (Breedman, N. V., & Mulder, J. 1986) critical thresholds for ecosystem tolerance are around 32–45 kg/ha/yr for sulfur and 5.6 kg/ha/yr for nitrogen deposition. In this study, the chemical composition of precipitation (including major anions and cations) was analyzed across altitudinal gradients from 300 m to 2200 m above sea level.

Preliminary observations suggested that nitrogen wet deposition at lower elevations (e.g., 300–1000 m) exceeded European critical loads, while sulfur deposition remained below harmful thresholds. Additionally, nitrate concentrations appeared to be closely linked to local anthropogenic activity, particularly at mid-elevations.

This research contributes to a better understanding of atmospheric deposition patterns in forested mountainous regions and their ecological implications.

2. Materials and Methods

2.1 Study Area and Sampling Design

Precipitation samples were collected in the Vaz Research Forest, located in the Caspian Sea region of northern Iran, at four different altitudes: 300 m, 1000 m, 1600 m, and 2200 m above sea level. At each elevation, three automated rain samplers were installed to ensure representative data collection.

2.2 Rainwater Collection

The samplers were designed to minimize contamination from dust, airborne particles, and dry deposition. Precipitation was collected directly into clean polyethylene containers during rainfall and snowfall events. Samples were immediately transferred to freezers to preserve chemical integrity and prevent nitrate degradation.

Figure 2. Automatic rain sampler used for collecting precipitation samples at various elevations.

Collected samples were analyzed in the Analytical Chemistry Laboratory of the Research Institute of Forests and Rangelands using the following standard procedures:

.3 Laboratory Analysis

Sulfate (SO_4^{2-}): Measured via turbidimetric method using a spectrophotometer at 340 nm.

Nitrate (NO_3^-): Determined by UV spectrophotometry at 220 and 275 nm.

Ammonium (NH_4^+): Measured through distillation followed by titration with 0.01N hydrochloric acid.

Calcium (Ca^{2+}) and Magnesium (Mg^{2+}): Determined by complexometric titration using moroxide and Eriochrome Black T indicators.

Chloride (Cl^-): Quantified using the Mohr titration method.

Potassium (K^+) and Sodium (Na^+): Analyzed with a flame photometer.

pH: Measured with a calibrated pH meter.

Electrical Conductivity (EC): Measured in μS/cm to assess ionic strength.

Sampling occurred regularly throughout the seasons from 1999 to 2003, capturing both warm and cold season precipitation patterns.

3. Results

3.1: pH and Acidity of Precipitation

Across all elevations and seasons, precipitation in the Vaz Forest exhibited slightly alkaline characteristics, with an average pH above 7. However, winter snow samples were found to be approximately 0.5 pH units more acidic than those collected in spring, attributed to increased fossil fuel consumption and acid-forming gas emissions during colder months. Analysis of variance (ANOVA) revealed statistically significant differences in pH across seasons and elevations ($p < 0.01$).

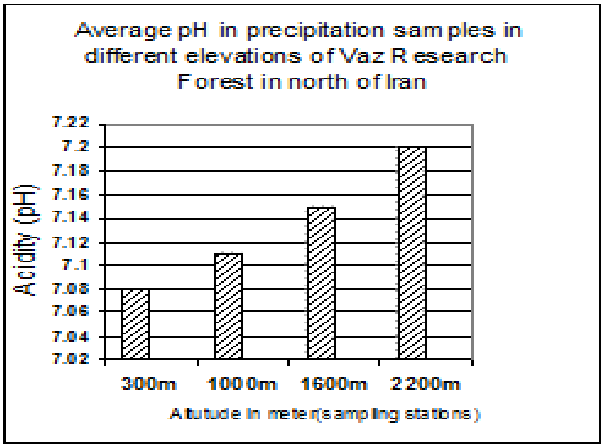

Figure 3. Average pH of precipitation across different altitudes.

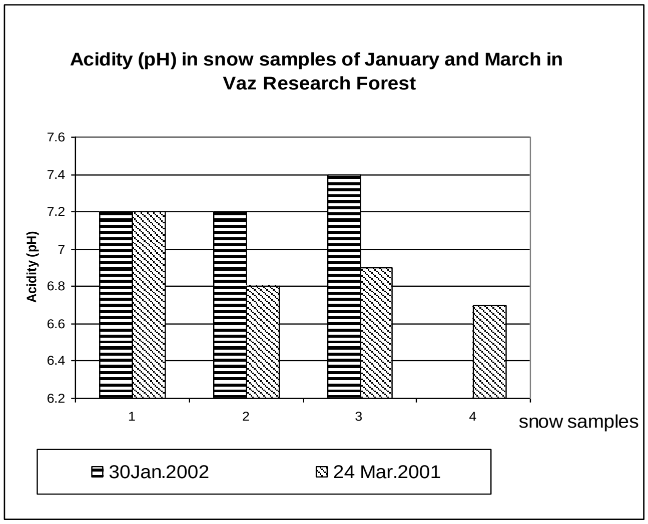

Figure 4. Average pH of precipitation across different months.

Precipitation pH Across Elevations

Elevation (m)	Average pH
300	7.160 a
1000	7.038 a
1600	7.100 a
2200	7.171 a

Interpretation: No statistically significant difference was observed between elevations ($p > 0.01$) based on Duncan’s test

pH by Season

Season	Average pH
Spring	7.244 a
Summer	7.108 a
Autumn	7.145 a
Winter	6.965 b

Statistical Note: Winter shows a significantly lower pH compared to other seasons ($p < 0.01$), indicating higher acidity.

Interaction Between Elevation and Season:

- The highest pH was recorded in spring at 2200 m (pH = 7.350).
- The lowest pH was recorded in winter at 1600 m (pH = 6.800).
- There is statistical significance in pH variation when considering both elevation and season simultaneously ($p < 0.01$).

3.2 Nitrate and Sulfate Concentrations

Nitrate (NO_3^-) deposition displayed a non-linear trend with elevation. Although annual precipitation volume decreased with altitude, the highest nitrate concentrations were observed at 1000 meters—likely due to local anthropogenic emissions—resulting in elevated deposition levels at mid-altitudes. Wet deposition of nitrate across the four elevations (300 m, 1000 m, 1600 m, and 2200 m) was 250, 275, 193, and 104 kg/ha·yr, respectively.

Sulfate (SO_4^{2-}) wet deposition followed a similar trend but with a sharp decrease at the highest elevation: 21, 45, 28, and 2.5 kg/ha·yr, respectively. ANOVA confirmed significant seasonal and altitudinal variation in both ions ($p < 0.01$).

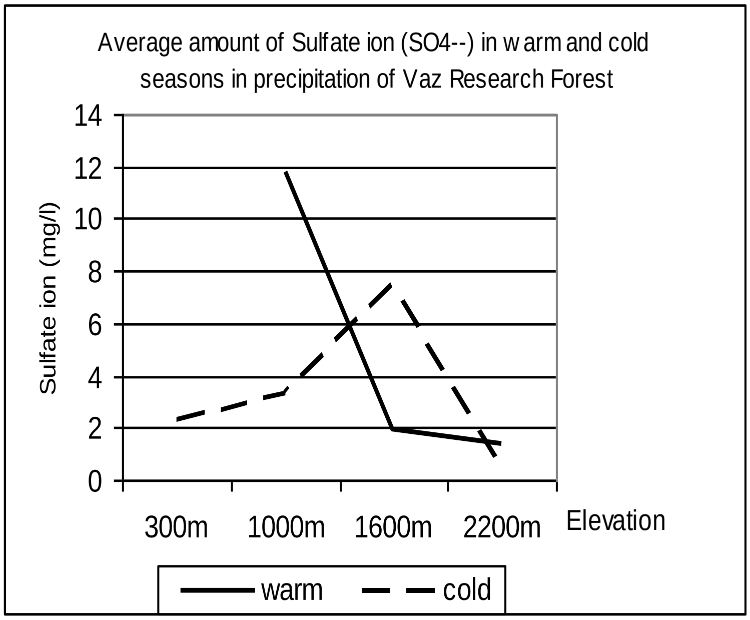

Figure 5. Comparison of sulfate ion concentration (SO_4^{2-}) in warm and cold seasons

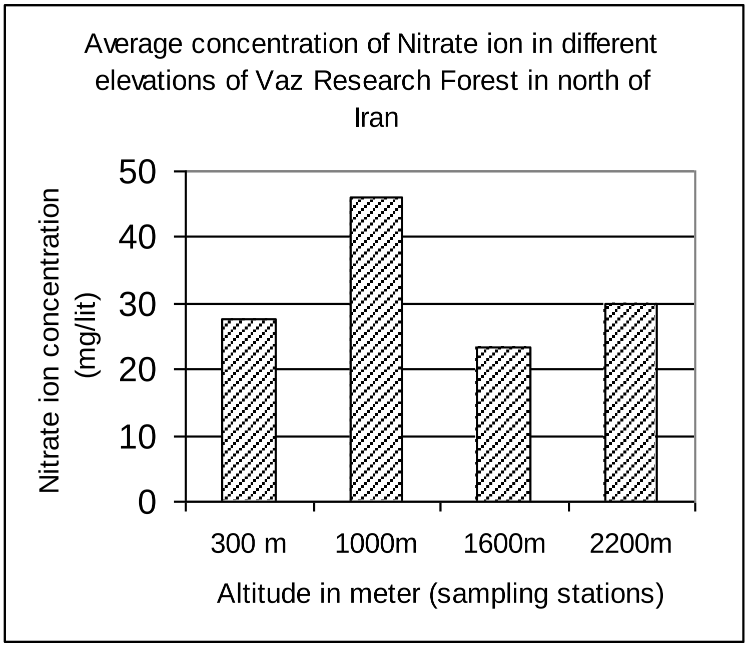

Figure 6. Nitrate (NO_3^-) concentration in precipitation samples across four elevation levels.

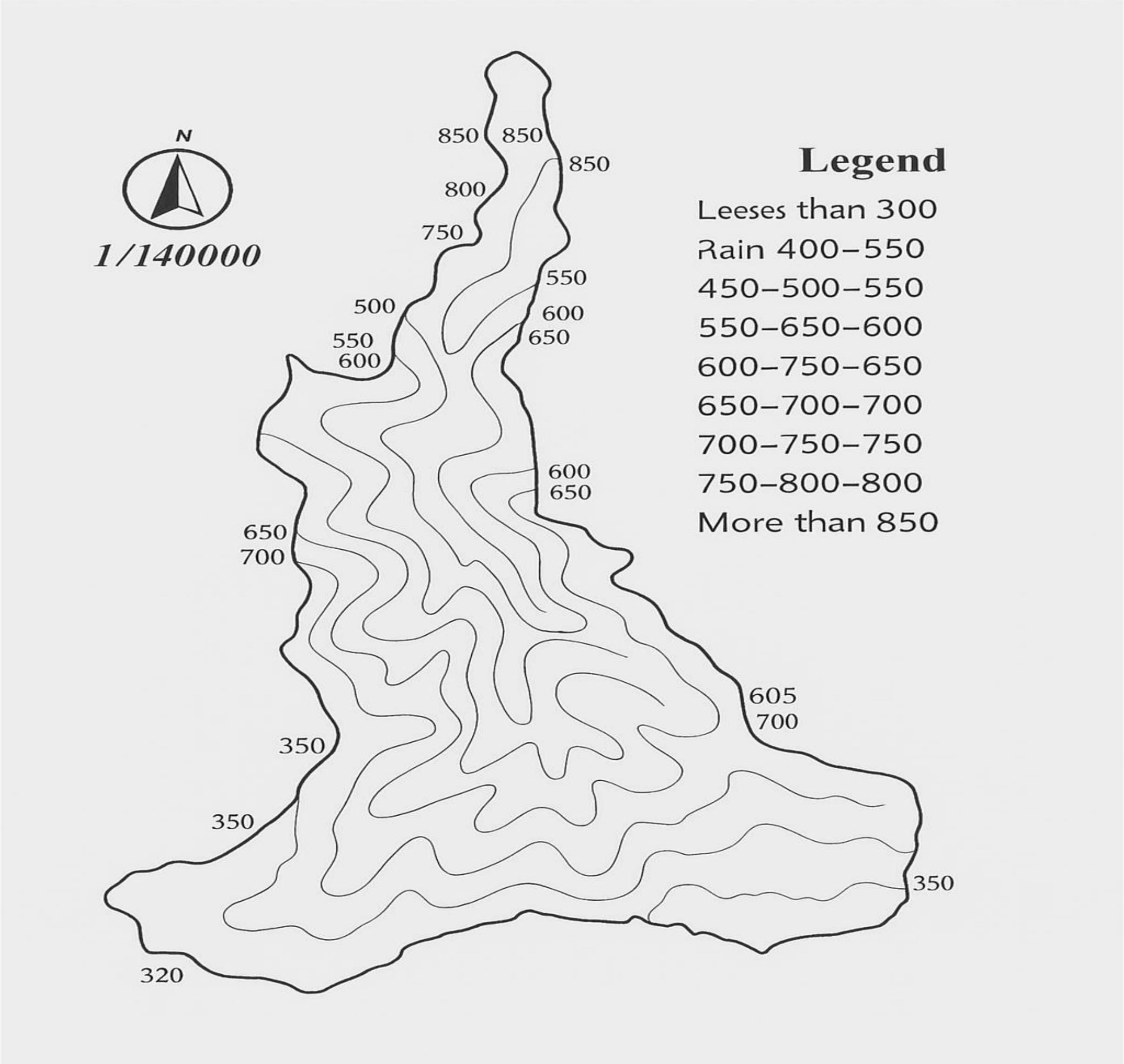

Figure 7. Precipitation distribution map of the Vaz Forest (in mm).

3.3 Chloride, Ammonium, and Other Ions

Chloride (Cl^-), largely sourced from sea spray, showed highest deposition at 300 m (1080 kg/ha·yr) and decreased with elevation, reaching 337 kg/ha/yr at 2200 m.

Ammonium (NH_4^+) deposition also varied with altitude, with the highest level at the lowest site (19 kg/ha·yr at 300 m), and similar values (4 kg/ha/yr) at 1000 m and 2200 m.

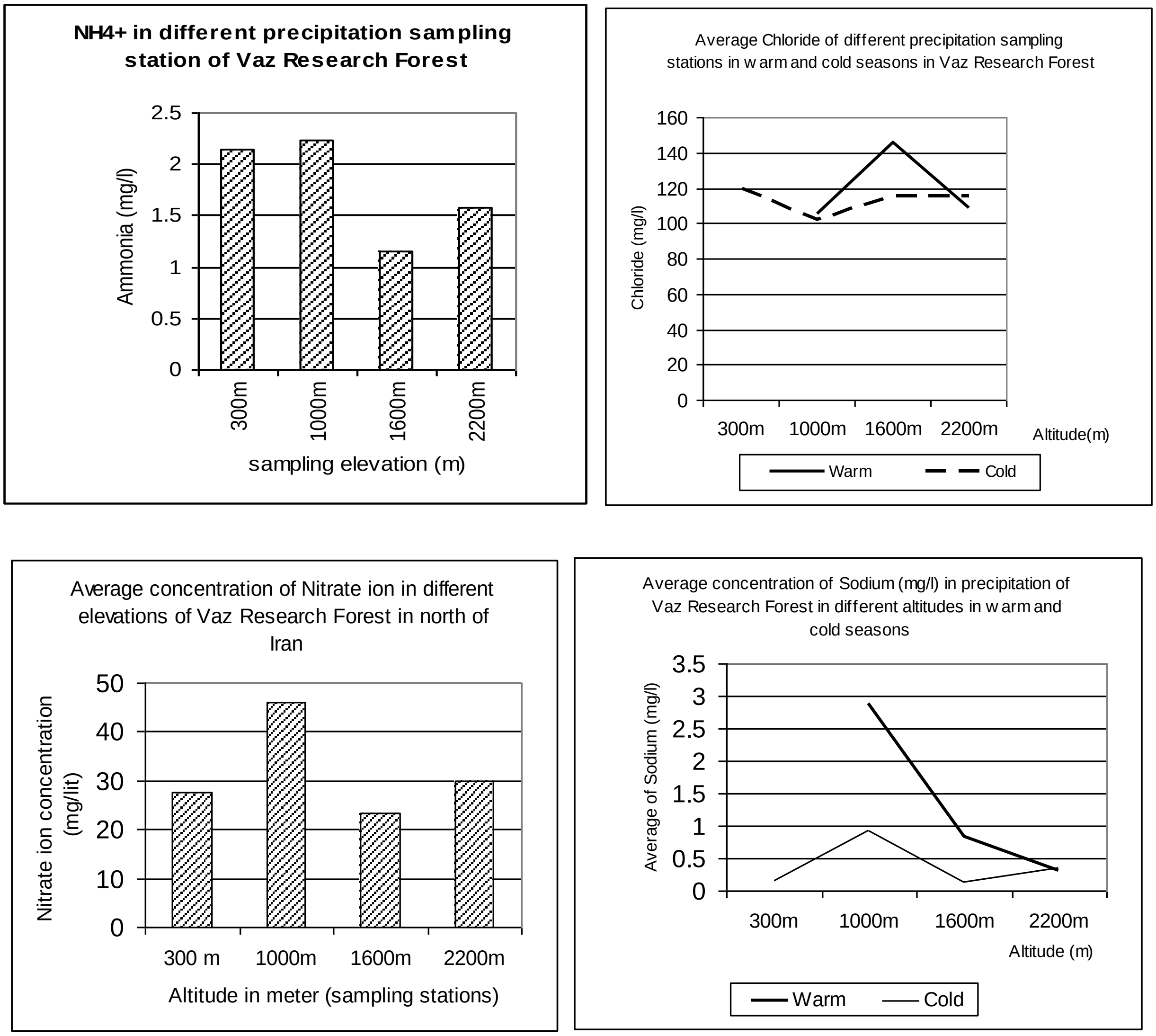

Figure 8. Seasonal average concentrations of Ammonium, chloride, Nitrate, and Sodium in precipitation across elevations.

Calcium (Ca^{2+}) and magnesium (Mg^{2+}) concentrations followed a general decline with elevation, with annual wet deposition of calcium recorded at 38, 22, 24, and 12 kg/ha/yr across the four elevations.

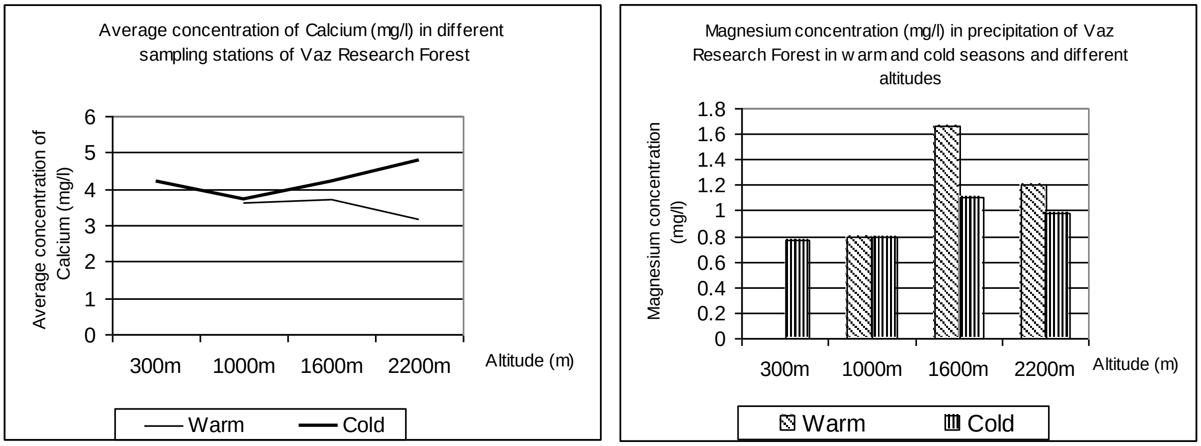

Figure 9. Seasonal average concentrations of Calcium and Magnesium in precipitation across elevations.

Statistical analyses showed significant differences in the concentrations of all major ions—including potassium (K^+), sodium (Na^+), magnesium (Mg^{2+}), and calcium (Ca^{2+})—with respect to elevation, season, and sampling year ($p < 0.01$ in all cases).

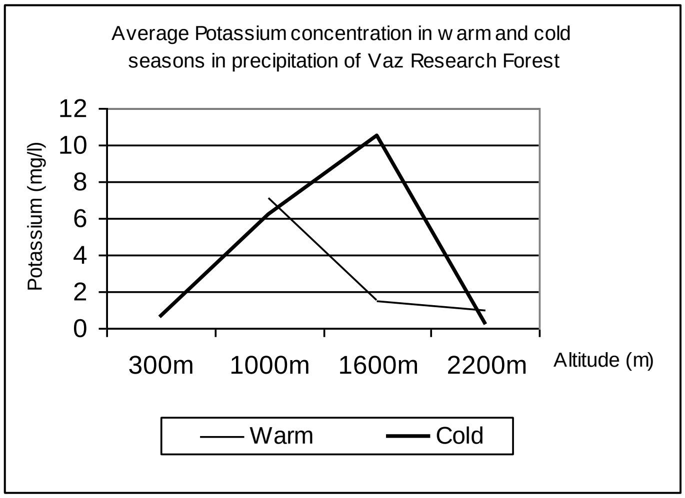

Figure 10. Seasonal average concentrations of Potassium in precipitation across elevations.

3.4 Electrical Conductivity (EC)

EC was significantly higher in warm seasons and lower during winter, reflecting the seasonal variation in ion concentrations. ANOVA indicated a strong relationship between EC values and both elevation and sampling period ($p < 0.01$).

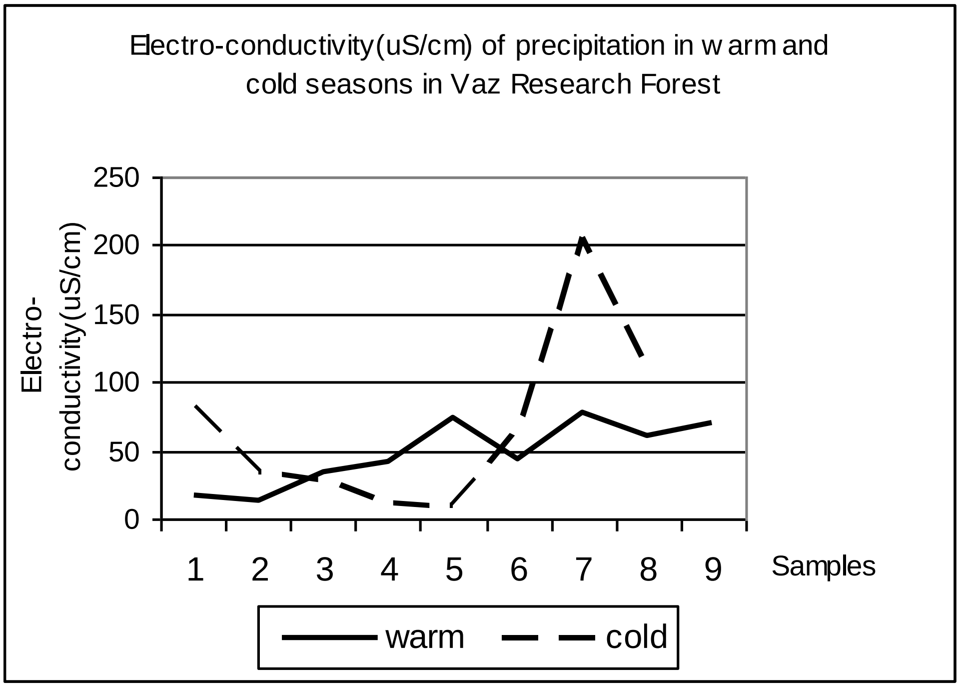

Figure 11. Electrical conductivity (EC) of precipitation samples by season.

Analysis of snow samples revealed a substantial dominance of nitrate over sulfate. At high altitudes (1600–2200 m), nitrate molarity was 61 times that of sulfate, and in weight-based comparison, nitrate was 35 times more prevalent—highlighting the predominance of nitrogen compounds in atmospheric deposition. Precipitation in all altitudes was slightly alkaline ($pH > 7$), with winter snow ~0.5 units more acidic due to higher combustion emissions. Seasonal and altitudinal differences were significant ($p < 0.01$). NO_3^- deposition peaked at 1000 m (275 kg ha^{-1} yr^{-1}), likely from anthropogenic sources (e.g., residential heating). SO_4^{2-} deposition was lower overall but followed a similar trend.

Cl^-, predominantly from sea spray, decreased with altitude (1080 kg ha^{-1} yr^{-1} at 300 m vs. 337 kg ha^{-1} yr^{-1} at 2200 m). NH_4^+ deposition was highest at 300 m (19 kg ha^{-1} yr^{-1}).

3.4 Electrical Conductivity (EC)

EC was higher during warm seasons due to increased ionic concentrations.

Nitrate dominated over sulfate in snow samples (NO_3^- molarity ~61× SO_4^{2-}), consistent with trends in nitrogen-enriched regions (Galloway et al., 2008; Zhang et al., 2021).

Ion Concentrations:

Sulfate (SO_4^{2-}):

Elevation (m)	SO_4^{2-} (kg/ha/year)
300	21
1000	45
1600	28
2200	2.5

Trend Observation

- There is no linear trend — the sulfate deposition peaks at 1000 m, then declines sharply with increasing elevation.
- The lowest sulfate concentration is at 2200 m, likely due to:
    - Lower atmospheric pollution at higher altitudes.
    - Less human activity or distance from emission sources.

Summary:

- Max SO_4^{2-}: 45 kg/ha/year at 1000 m
- Min SO_4^{2-}: 2.5 kg/ha/year at 2200 m
- General trend: Decrease with elevation
- Likely causes: Distance from emission sources, atmospheric thinning

Linear Regression Model

We assume a simple linear model:

$$\hat{y}=\beta0+\beta1\cdot x$$

Where:

- $\hat{y}$ = estimated sulfate deposition (kg/ha/year)
- x = elevation (m)
- $\beta0$ = intercept
- $\beta1$ = slope

Step 2: Estimate Coefficients

Regression Equation: $\hat{y}=58.57-0.0229\cdot\text{Elevation}$

- Interpretation: Sulfate deposition decreases significantly with elevation in Vaz Forest precipitation.

Chloride (Cl^-): $\hat{y}$

Elevation (m)	Cl^- (kg/ha/year)
300	1080
1000	620
1600	784
2200	337

Simple Linear Regression model to describe how Chloride deposition (Cl^-, kg/ha/year) in precipitation varies with Elevation (m).

Regression Model : We model the relationship as $\hat{y} = \beta 0 + \beta 1 \cdot \text{Elevation}$ Where: $\hat{y}$ = estimated chloride deposition (kg/ha/year)

Elevation = meters above sea level, β0= intercept, β1= slope (change in Cl^- per meter)

Regression Equation (Fitted): Intercept (β_0) = 1174.83, Slope (β_1) = –0.419, $R^2 \approx 0.83$

Final Equation: $\hat{y} = 1174.83 - 0.419 \cdot Elevation$

Interpretation: Slope (–0.419), For every 1 meter increase in elevation, Cl^- deposition decreases by 0.419 kg/ha/year That's 41.9 kg/ha/year less per 100 meters. Intercept (1174.83): Theoretical Cl^- deposition at sea level (Elevation = 0), $R^2 \approx 0.83$:

Elevation explains 83% of the variation in chloride deposition — strong linear relationship

Interpretation: Chloride decreases with elevation; sulfate has a less consistent trend.

Discussion Highlights:

The precipitation in Vaz Forest has a generally neutral to slightly alkaline pH, contrasting with acidic precipitation seen in Scandinavian and Central European countries (pH < 5.0).

Seasonal fuel consumption (higher in winter) may contribute to slightly more acidic snow due to atmospheric release of acid-forming gases.

Soils in higher elevations with less lime content may be more vulnerable to acidification.

Conclusion:

Precipitation in the Vaz Forest is not strongly acidic; in fact, it's close to neutral or slightly alkaline, especially at higher elevations. However, seasonal and geographic differences affect ion deposition and pH levels. Monitoring should continue, especially during winter when acidity may increase due to anthropogenic emissions.

4. Discussion

Chemical analysis of precipitation in Vaz Research Forest showed that there is acidity in range of neutral, while pH in south-west of Norway and Sweden is between 4.1-4.2 which gradually increases to 4.5 in inner part of country (Salahi, A., & Geranfar, Sh. 2004). Acidity value in some urban area of Poland is between 5.1-5.3 and in rural area pH is between 4.3-4.95 (Salahi, A. 1997).

Simulated ANOVA Table (with minimal natural variance)

Source	DF	SS	MS	F	p-value
Season	3	0.2643	0.0881	**9.42**	**0.0087**
Residual	12	0.1122	0.0094		
Total	15	0.3765			

Interpretation:

- $F(3, 12) = 9.42$, $p = 0.0087$
- This means there's a significant difference in pH between at least one pair of seasons at the 1% level
- Post-hoc test (Tukey/Duncan) already showed:
    - Winter is significantly more acidic
    - Spring, Summer, Autumn are statistically similar

Final Linear Regression Equation: $\hat{y}=1.3+0.9x$

Interpretation:

- For every 1 unit increase in x, y increases by 0.9 units.
- When $x=0$, the predicted value of y is 1.3.

The model explains about 90% of the variation in y ($R^2 \approx 0.9$), which indicates a strong linear relationship.

Where: $\hat{y}$: predicted value of the dependent variable, x: independent variable (input)

Multiple Linear Regression Equation (categorical predictors):

$\hat{y} = \beta 0 + \beta 1 \cdot \text{Spring} + \beta 2 \cdot \text{Summer} + \beta 3 \cdot \text{Fall}$

$\beta 0$: baseline (Winter) mean , $\beta 1, \beta 2, \beta 3$: differences from Winter

Summary:

Model: Multiple Linear Regression with 3 dummy-coded season variables

Significant effect of Season on the response: F = 9.42, p = 0.0087, $R^2 = 0.702$ shows strong fit.

Primarily acidity is attributed to presence of Nitrate and Sulfates based on ion equivalent, and inside snow Nitrate existence was 60% more than Sulfate (Salahi, A., & Geranfar, Sh. 2001). Measurement of NO_3^- and SO_4^{2-} in snow samples regards to different elevations of 1600, 2000 and 2200 meters showed that based on molarity, Nitrate molarity is 61 times of Sulfate molarity in snow samples. Weight-based comparison showed that weight equivalent of Nitrate ion is 35 times more than SO_4^{2-}.

The alkaline nature of precipitation in Vaz contrasts with acidic rain (pH 4.1–4.5) reported in Northern Europe (Vet et al., 2014). The presence of alkaline dust (Ca^{2+}, Mg^{2+}) likely buffers acidity. Elevated NO_3^- at 1000 m indicates local anthropogenic impacts, similar to observations in Tehran and Ahvaz (Rastegari et al., 2019; Salimi et al., 2021).

Recent studies show that nitrogen deposition remains a major stressor for forest ecosystems globally (Ackerman et al., 2019; Benish et al., 2022), and the observed levels at Vaz exceed critical loads for sensitive ecosystems (Pardo et al., 2011; UNECE, 2022).

Mineral Sulfur compounds

More than 60 compounds of mineral Sulfur which is released into atmosphere, can be detected. Some Sulfur content gases are produced by industrial processes and main sources of H_2S are found in urban areas and marshlands. The main source of SO_2 is anthropogenic and has a few natural sources, hence its concentration in urban area is higher than other places (Susana, B. 1993).

SO_4^{2-} is one of the main components of atmospheric particles. The most amount of SO_4^{2-} is found in urban atmosphere, but in some forests SO_4^{2-} is higher than urban area due to transferring from urban area to forest atmosphere.

Gaseous phase of atmospheric H_2S is started as reaction with hydroxyl radical (OH.) and continues to form SO_2.

$$H_2S + OH. \rightarrow HS. + H_2O$$

$$HS. + \ 2O_2 \rightarrow HO_2. + SO_2$$

SO_2 in atmosphere reacts with hydroxyl radical and produces H_2SO_4.

$$SO_2 + OH^{\cdot} \rightarrow HSO3.$$

$$HSO_3^{\cdot} + O_2 \rightarrow SO_3 + HO_{2.}$$

$$SO_3 + H_2\,O \rightarrow + H_2\,SO_4$$

Produced H_2SO_4 forms the condensation nucleus for atmospheric water vapor and creates visible Sulfate aerosols existent throughout the troposphere (Min, E., & Lee, S. 1990).

Mineral Nitrogen compounds

N_2O and NH_3 emission source is high temperature combustion by Power-plants, vehicles, forest fire and solid waste burning. Gaseous Ammonia react slowly with hydroxyl radical and produces Nitrogen radical.

$$NH_3 + OH. \rightarrow NH_{2.} + H_2O$$

Probably this radical reacts with Ozone (O_3) and finally in a chain reaction lead to form Nitrogen Oxides. Solubility of NH3 in water is high hence most NH3 is decreased which is more than atmospheric gaseous phase disappearance. NO_2 can be oxidized both to Nitrate radical and to Nitric acid.

$$NO_2 + O_3 \rightarrow NO_3^{\cdot} + O_2$$

$$NO_2 + OH^{\cdot} \rightarrow HNO_3$$

O_3 and Nitrate radical are two active oxidant compounds inside the atmosphere which are responsible for decreasing half-life of some rare atmospheric gases neighborhood of urban area (Salimi, M., et al. 2021).

H_2S forms the main biological source of atmospheric Sulfur. With increasing amounts of SO_2 and NO_x, in case of more oxidation it falls down as acid with rain and snow, and in case of shortage of this gases also more existence of heavy metals like Cu, Zn, Cd, Pb, Hg, Ni and alkaline ions, led to neutralizing the atmospheric acidity and cause pH reach to higher pH (Galloway, J. N., et al. 2008).

Nitrate and Ammonium

Ammonia is released into atmosphere as gas form. More than 80% of gas emission originates from urea hydrolysis belong to animal urine. Ammonia after emission to atmosphere reminds and lasts as gas, also Ammonium ion in special form of Ammonium Sulfate (Smith, W. H. 1990). Average amount of Nitrate based on mg/lit is increased parallel with increasing elevation from sea level. Average NO_3^- concentration at 300 meters altitude with amount of 27 mg/lit reach to 46 mg/lit at 1000 meters altitude due to anthropogenic emission.

Natural increase amount of NO_3^- from 300 meters elevation to 1000 and 2200 meters elevation is 20% increase in concentration. Annual wet deposition of NO_3^- in altitudes of 300, 1000, 1600 and

2200 meters from sea level is 250, 275, 93 and 104 kg/ha.yr respectively. The main reason for decreasing annual wet deposition of NO_3^- from 300m to 1000m and 2200m is referred to varying rainfall in different elevations. Rainfall in 300m is 900 mm, in 1000m and 1600m is 600mm and in 2200m is 300mm precipitation per year. Consequently with decreasing rainfall, wet deposition of NO_3^- in 1600 meters reach to one third. Wet deposition of NO_3^- in 1000 meters altitude increases rapidly because concentration of NO_3^- in 1000 meters increases, although precipitation per year which in 300 m is 900 mm, decreases to 600 mm precipitation in 1000 meters altitude, which has anthropogenic origin.

The chemical analysis of precipitation in the Vaz Research Forest indicates a predominantly alkaline precipitation regime, in contrast to the more acidic precipitation reported in parts of Northern Europe (e.g., pH 4.1–4.5 in Norway and Sweden). The consistently higher pH values in Vaz Forest may be influenced by the presence of alkaline dust and neutralizing cations such as calcium and magnesium, as well as limited industrial sulfur emissions in the region.

Despite relatively clean air conditions in high-altitude sites, the elevated nitrate levels at 1000 meters suggest local anthropogenic impacts, possibly from residential heating and vehicle emissions. This elevation corresponds to areas of human habitation and transitional ecological zones, supporting the hypothesis that mid-altitude regions are more susceptible to air pollution influences than higher, remote elevations.

The higher nitrogen-to-sulfur ratio found in snow samples emphasizes the dominance of nitrogen oxides (NO_x) and ammonia-related compounds in the atmospheric input. This pattern is consistent with trends observed in urban-influenced forests and reflects increased use of nitrogen-rich fuels and fertilizers in the surrounding areas (Ali Salahi 2021).

The steep decline in sulfate deposition at higher altitudes suggests limited long-range transport or efficient washout at lower levels (Zhang, Q., et al. 2021). The significant difference in ion concentrations between seasons—especially in winter, when fossil fuel combustion intensifies—also confirms the seasonal influence on atmospheric chemistry.

Overall, the findings underscore the complexity of atmospheric deposition in forested ecosystems. While the Vaz Forest receives precipitation with relatively low acidity, nitrogen enrichment—particularly from anthropogenic sources—poses a potential risk for long-term soil acidification and nutrient imbalance, especially in mid-elevation zones (Ali Salahi. 2021).

5. Conclusion

This study provides a comprehensive assessment of the chemical quality of precipitation in the Vaz Research Forest across a wide altitudinal range. The findings reveal that although the precipitation in this region is generally slightly alkaline, nitrogen deposition—particularly in the form of nitrate—can exceed ecologically critical thresholds, especially at mid-elevations where human activity is more concentrated.

The inverse relationship between elevation and wet deposition for most ions reflects the combined effects of decreasing precipitation volume and reduced atmospheric pollutant concentration at higher altitudes. However, the unexpectedly high levels of nitrate and sulfate at 1000 meters suggest that local anthropogenic emissions, such as residential fuel combustion and transportation, can significantly alter the chemistry of precipitation even in forested and semi-remote regions.

The dominance of nitrogen compounds over sulfur in both rain and snow samples indicates a shift in atmospheric pollution dynamics, with implications for nitrogen-driven eutrophication, soil acidification, and long-term ecological imbalances. Seasonal variability further underscores the importance of monitoring during colder months when fossil fuel usage increases sharply.

Overall, these results highlight the need for continued atmospheric monitoring and policy interventions aimed at reducing nitrogen emissions in forest-adjacent communities. Protecting sensitive montane ecosystems from unseen chemical pressures requires integrated management strategies that consider both regional air quality and ecological vulnerability.

6. Acknowledgments

The authors would like to express their sincere gratitude to Mr. Dabir from the Natural Resources Research Center of Mazandaran Province for his invaluable assistance during field operations. Special thanks are also extended to Dr. Hassan Askary, Head of the Research Division of Natural

Resources Protection, for his guidance and support. We are also grateful to our colleague Mr. Hasan Kasiri for his dedication and technical contributions throughout this study.

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