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Spatial-temporal Variations of Chemical Components and Trends of Acid Rain in Vietnam: A Case Study of Hanoi, Hoa Binh and Ho Chi Minh Cities

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Abstract

Acid rain poses a worldwide environmental concern, impacting ecosystems and human health, even within Vietnam. This research delves into its occurrence across a range of urban and rural settings in the country. This study evaluated the acid rain in Hanoi, Hoa Binh in 2000-2020 and Ho Chi Minh in 2014-2020. Irregular acid rain, influenced by human activities and atmospheric convection, is observed in the study areas. Interestingly, while serving as pivotal growth centers with similar developmental levels and emissions, Hanoi encounters a more frequent occurrence of acid rain compared to Ho Chi Minh City. Notably, even in the rural vicinity of Hoa Binh, the prevalence of acid rain exceeds that observed in Ho Chi Minh City. The primary contributor to acidity in rainwater is nss *(non-sea-salt)*-SO_4^{2-}, with NH_4^+ acting as the neutralizing agent and both predicted to increase in concentration in Hanoi and Hoa Binh. Conversely, NO_3^- serves this role and shows an upward trend in Ho Chi Minh. Overall, the results obtained from an extended evaluation period using the EANET database and diverse city characteristics indicate a worrisome escalation of acid rain in Vietnam.

1. Introduction

Acid rain has been widely recognized as a significant environmental concern, particularly during the 1980s (Grennfelt *et al.,* 2020). Studies on the acidity of rainfall have played a crucial role in assessing rainwater composition and understanding the primary atmospheric components involved. The international alarm regarding acid rain has grown due to widespread ecological degradation of marsh ecosystems, and damage to historical monuments (Gurgen, 2017). Acid rain driven from air pollution which detrimental impacts on human health and the natural environment for plants, while also causing physiological, psychological, and economic harm to society. (Almetwally *et al.,* 2020). Keresztesi *et al.* (2019) conducted a study examining the chemical composition of rainfall in 27 European nations from 2000 to 2017, focusing on wet deposition and source contributions. They found that the physical and chemical properties of rainfall are controlled by dominant atmospheric circulation and locations with diverse pollution sources, with sulfates, nitrates, ammonium, and potassium being the primary acidifying factors. In a separate study, Kline *et al.* (2016) utilized the Seasonal Mann-Kendall test to evaluate long-term changes in acid-neutralizing capacity in surface water within the Appalachian river basin in the USA. Results showed decreasing trends in K^+, Mg^{2+}, and Ca^{2+} concentrations, while Na^+ concentrations increased. Furthermore, Ossohou *et al.* (2020) conducted a study in Sub-Saharan Africa in 2020, evaluating the

long-term trend of atmospheric inorganic nitrogen deposition from 2000 to 2015 using observational and model data. Their findings indicated that NH_3^+ had the most significant contribution to dry deposition, followed by HNO_3 and NO_2. The seasonality of N-pNO3 (nitrogen deposition from particulate NO_3^-) was more noticeable than that of N-pNH4+ (nitrogen deposition from particulate NH_4^+, with the highest levels observed during the dry season and the lowest values during the rainy season.

Industrialization and modernization have brought significant economic and social changes to Vietnam, but they have also led to environmental challenges, notably acid rain. Acid deposition has garnered attention in recent national environmental reports and is a matter of concern for scientists and managers. The annual Vietnam Environmental Status Report indicates that air quality in many urban centers and industrial zones is polluted, leading to the occurrence of acid rain (MONRE, 2019). According to research conducted across Vietnam, there have not been many comprehensive studies on acid rain and acid deposition. Existing studies have mainly focused on wet deposition, ion correlation in rainfall, or cation fusion ability in rainwater (Anh, 2018; Pham *et al.,* 2022). Acid rain studies contribute to a comprehensive assessment of environmental changes amidst the growing complexity and challenges in solving environmental problems. Such research explores various avenues to evaluate the quality of air, water, and soil environments, which significantly impact socioeconomic aspects in modern society.

The study examines acid rain monitoring data from three stations: urban sites Ha Noi and Ho Chi Minh City, which represent Vietnam's economic progress, and the rural site Hoa Binh, a transforming northern province with economic breakthroughs, including industrialization (Figure 1). Despite rapid urban development in Ha Noi and Ho Chi Minh City, characterized by skyscrapers and extensive boulevards (GSO, 2020), both cities grapple with worsening pollution.

They host nearly 6 million and over 8 million motorbikes daily, respectively, along with transit from other regions (MONRE, 2020). Many older vehicles in circulation fail emission standards, are poorly maintained, and use inefficient fuel, leading to high concentrations of harmful emissions and dust in exhaust gases. This contributes to rising air pollution in these cities. In contrast, Hoa Binh, a northern mountainous province with an agricultural-based economy undergoing innovation, exhibits greater acidity compared to Ha Noi and Ho Chi Minh City. This phenomenon stems not only from local sources but also from convection currents influenced by socio-economic development in adjacent regions and prevailing wind patterns (Pham *et al.,* 2016).

Previous research in Vietnam has examined ion concentrations and their impact on flora and fauna (Lan *et al.,* 2006; Anh, 2018; Pham *et al.,* 2016, 2022). Anh TKN analyzed pollutant concentrations and wet deposition trends using 2000 - 2018 data (Anh *et al.,* 2019). Ngan (2019) utilized hydrometeorological monitoring data from temporary stations for the period 2005 - 2017 to assess NO_3^- and nss-SO_4^{2-} deposition variations by season and year. Urgent research is needed for Hanoi, Hoa Binh and Ho Chi Minh City to evaluate and address acid rain's environmental and human health implication.

This study aims to evaluate acid rain components and trends in distinct Vietnamese regions: Hanoi, Hoa Binh, and Ho Chi Minh cities. By using the data of chemical compositions of rainwater in these major cities, this research seeks to gain insights into the prevalence and distribution of acid rain. Additionally, it aims to predict trends in acidity content to better understand changes in acid precipitation patterns. Through an analysis of the deposition trend of ions in rainwater up to 2020, considering both the slope and concentration of ions, this study aims to provide authorities with valuable information to develop accurate and responsive measures for addressing acid rain and its associated issues.
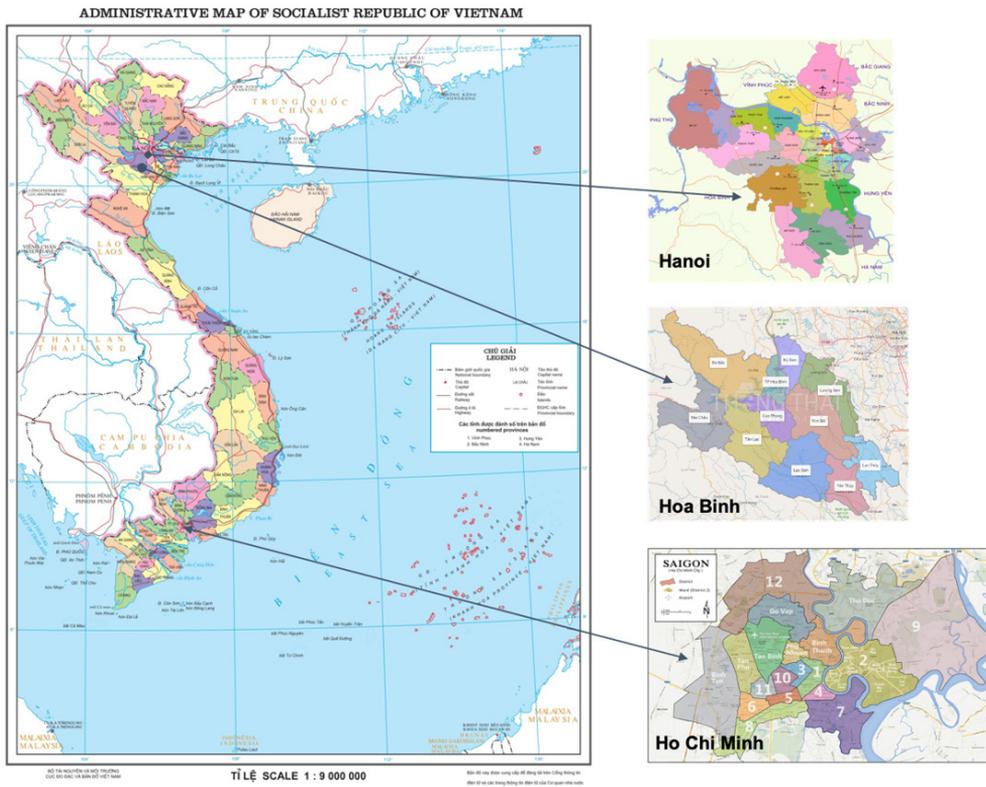
Figure 1. Location of research areas (Hanoi, Hoa Binh, Ho Chi Minh city)

2. Methodology

2.1 Research data

This study utilized data from the Acid Deposition Monitoring Network in East Asia (EANET), a regional network that employs standardized monitoring methods. The dataset spans from 2000 to 2020 for Hanoi and Hoa Binh stations and from 2014 to 2020 for the Ho Chi Minh station, which joined EANET in 2014. Chemical data were analyzed to ascertain air pollutant characteristics in wet deposition and the underlying formation mechanisms. The research employed diverse methodologies, including frequency assessment of acid rain, acidity determination, ion concentration in rainwater, concentration and deposition trend analysis. Noteworthy parameters assessed for acid rain include pH, SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Ca^{2+}, Na^+, Mg^{2+}, K^+, and H^+.

2.2 Research methods

To ensure data quality and reliability, the collected data underwent screening and analysis, which included the calculation of ionic balance as an indicator of constituent measurement completeness. Rainwater indicators such as components change the pH value, average concentration, deposition, neutralization factor, correlation coefficient and acid rain frequency were computed using Excel. The Seasonal Mann Kendall method was executed through XLSTAT software (https://www.xlstat.com/en/) for assessing acid rain trends. XLSTAT software by Addinsoft, the leading data analysis and statistical solution for Microsoft Excel, provides advanced analytical capabilities, enhancing the rigor and insights of the study.

Calculation of acid rain frequency (percentage)

$$F = (M/12) \; x \; 100$$

where:

F: frequency of acid rain (%)

M: the number of months that have $pH < 5.6$; $pH < 5.0$; $5 < pH < 5.6$

Evaluation of the components change the pH value

Various ions contribute to both the acidity and neutralization of rainfall. Correlation coefficient calculations reveal stronger associations between H^+ ions and SO_4^{2-}, NO_3^- ions than other ions. Additionally, cations Ca^{2+} and NH_4^+ exhibit substantial correlations with all other cations (Keresztesi *et al.,* 2020). Thus, the primary components altering rainwater pH are SO_4^{2-}, NO_3^-, Ca^{2+}, and NH_4^+.

$A = NO_3^-/nss\text{-}SO_4^{2-} > 1$, indicating that NO_3^- is the main component causing acid rain, whereas when this ratio is less than 1, it is SO_4^{2-}.

$B = NH_4^+/nss\text{-}Ca^{2+} > 1$, showing that NH_4^+ is the main component of neutralizing rainwater acids, whereas when this ratio is less than 1, it is $nss\text{-}Ca^{2+}$.

$C = (NH_4^+ + nss\text{-}Ca^{2+})/(NO_3^- + nss\text{-}SO_4^{2-})$ is the neutral value, when this ratio is high, the pH value will increase and vice versa.

Wet deposition flux

$$Dw = C \; x \; P$$

where:

Dw: amount of wet deposition ($\mu mol/m^2/$month)

P: total monthly rainfall (mm)

C: average monthly concentration ($\mu mol/L$)

Neutralization factor (NF)

The neutralization factor NF was generally used to identify the relative neutralization effect of different alkaline species of NH_4^+ and Ca^{2+} (Roy *et al.,* 2016). Studies on the capacity of rainfall to neutralize acids frequently utilize the formula $(NH_4^+ + nss\text{-}Ca^{2+})/(NO_3^- + nss\text{-}SO_4^2)$, which does not address other cations and defaults to only two cations. Acids in rainfall are mostly neutralized by NH_4^+ and Ca^{2+} (Keresztesi *et al.,* 2020).

$$NF_i = \frac{[Xi]}{[SO_42-]+[NO_3-]}$$

where: $[X_i]$ is the concentration of the alkaline component (Ca^{2+}, NH_4^+, Mg^{2+}, Na^+, K^+) expressed in $\mu eq/L$.

Correlation coefficient

The correlation coefficient (ρxy) is calculated to determine the correlation relationship between chemical ions in rainwater (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Ca^{2+}, Na^+, Mg^{2+}, K^+ and H^+) and determined by the following formula (Ho *et al.* 2009):

$$\rho_{xy} = \frac{\frac{1}{n}\sum_i^n (x_i - \mu_x)(y_i - \mu_y)}{\sigma_x \sigma_y}$$

This calculation allows to determine the relationship between ions in rainwater and the main components that change the pH value in rainwater in study area.

Non-parametric Seasonal Mann-Kendall test method

The Seasonal Mann-Kendall method, is commonly used to assess trends in seasonal data series and the analysis of the climatological time series, for example: temperature and precipitation (Anie, 2018; Gavrilov *et al,* 2018; Neel, 2019), atmospheric deposition (Camarero *et al,* 2017), and in the hydrological time series (Satish *et al,* 2019). This approach compares the relative sizes of the sequence's elements, not their values, it can cope with missing values and values below the detection limit. In this study, the non-parametric Seasonal Mann-Kendall test is employed to analyze change trends in cation and anion concentrations and depositions within the study areas. According to the SMK test, two hypotheses were tested: the null hypothesis that there is no trend in the time series; and the alternative hypothesis that there is a significant trend in the series. The probability p-value is a measure of confidence in the hypothesis. If p-value is lower than 5%, the significant trend should be accepted (Salehi S *et al,* 2019).

XLSTAT software was used to calculate the p-value and hypothesis testing.

3. Results and Discussion

3.1 Rainwater pH, ions concentrations and compositions

Figure 2 presents annual average pH variations in precipitation across three sites. Hanoi experienced acid rain primarily in its dry season, with an average pH of 5.74 (range: 4.95 to 6.53). In 2019, severe pollution was evident with a pH of 4.95, and 75% of rain exhibited acidity (pH < 5). This corresponded with increased industrial activity in 2019 in Hanoi at 8.5% (World Bank, 2019). Besides, the massive number of vehicles on the road also caused sulfur dioxide and nitrogen oxide emissions. A high density of private fossil fuel vehicles, of which motorbikes account for more than 90%, puts a strain on traffic infrastructure, causing traffic congestion as well as air and noise pollution in metropolitan areas (Duc *et al.,* 2021). For Hoa Binh, the average pH was 5.42 (range: 5.04 to 6.04), with acid rain frequency peaking at 83% (pH < 5.6) and 33% (pH < 5) in 2019. Ho Chi Minh station had a slightly acidic mean pH of 5.97 (range: 5.76 to 6.11), with three acid rain-free years (2014 - 2016). The rise in car usage in 2017 (VRA, 2018) correlated with the appearance of acid rain in 2017 (25% at pH < 5.6). The prevailing acidic pH frequency across the three stations implies a pronounced anthropogenic impact, aligning with major ion concentrations. Lower pH values correspond to elevated acidic ion concentrations compared to alkaline ions. This observation concurs with Zhang *et al.* (2007) findings.

Overall, the northern region recorded higher precipitation acidity, with a total average pH of 5.74 in Hanoi and 5.72 in Hoa Binh, compared to the southern region, which had a pH of 5.97 in Ho Chi Minh. Vietnam maintains a relatively higher pH value, averaging 5.79 across all three locations. However, this pH level still indicates lower acidity compared to certain other nations, including China with a pH of 5.12, Indonesia with a pH of 5.02, Korea with a pH of 4.99, Malaysia with a pH of 4.94, and Japan with a pH of 4.82 (EANET, 2020).
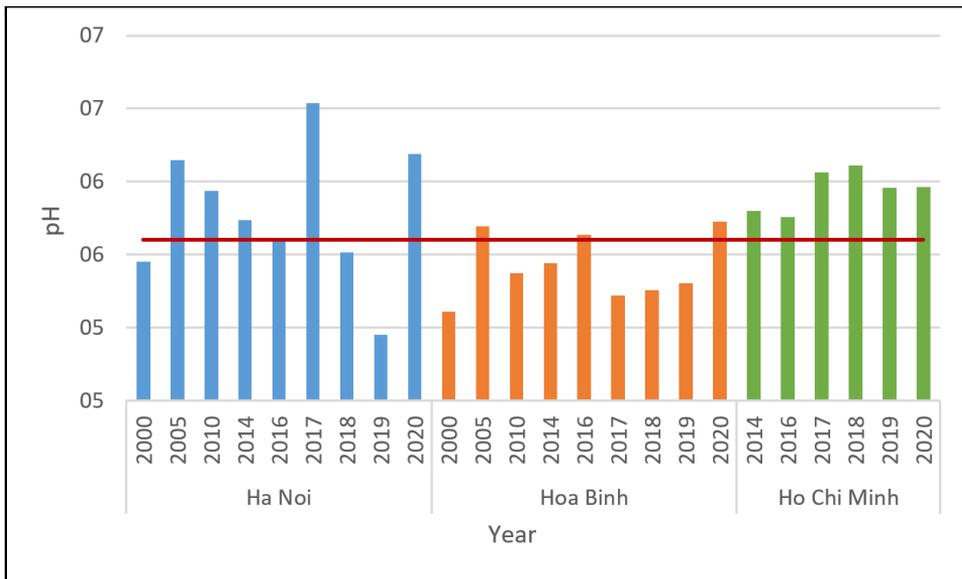
Note: Red line indicates the pH = 5.6

Figure 2. Annual average pH variation of precipitation at three sites

Table 1. Average concentrations (µmol/L) of measured ionic species and pH in rainwater sample at three different locations (Hanoi, Hoa Binh, Ho Chi Minh) from 2000 to 2020, along with minimum (Min.) and maximum (Max.)

Variable	Hanoi			Hoa Binh			Ho Chi Minh		
	Min	Avg	Max	Min	Avg	Max	Min	Avg	Max
pH	4.95	5.74	6.53	5.04	5.42	6.04	5.76	5.97	6.11
SO_4^{2-}	14	37.8	86	13.6	20.9	39.8	19.2	28	47.6
NO_3^-	5.1	28.9	77.6	8.8	17.9	42.4	4.9	12.3	18.3
Cl^-	6.6	16.8	48.3	4.2	9.4	22.1	36.3	42.6	52
NH_4^+	20.3	54.1	98.8	8	28.6	56.9	20.7	27.8	38.4
Na^+	4.2	11.5	26.4	2.1	5	12.7	13.5	20.5	34.6
K^+	1.6	4	8.1	1.5	2.8	7.1	6.6	9.8	12
Ca^{2+}	10.7	27.9	83	9.3	15.7	43.6	12.1	22.5	44.3
Mg^{2+}	2.2	5.1	8.6	1.4	3	5.6	6.9	10.8	17.9
H^+	0.3	2.4	11.2	0.9	4.4	9.1	0.8	1.1	1.7

At the Hanoi site, cation mean concentrations (µmol/L) followed the order $NH_4^+ > Ca^{2+} > Na^+ > Mg^{2+} > K^+ > H^+$, while anion abundance ranked as $SO_4^{2-} > NO_3^- > Cl^-$. Similarly, at the Hoa Binh site, cations exhibited the sequence $NH_4^+ > Ca^{2+} > Na^+ > Mg^{2+} > K^+ > H^+$, and anions followed $NO_3^- > SO_4^{2-} > Cl^-$. At the Ho Chi Minh site, cation mean concentrations resembled $NH_4^+ > Ca^{2+} > Na^+ > Mg^{2+} > K^+ > H^+$, whereas anions ranked $Cl^- > SO_4^{2-} > NO_3^-$.

Anions, particularly SO_4^{2-}, play a significant role in rainwater acidity, with a notably high average concentration of 37.8 µmol/L observed at the Hanoi station (Table 1). Hanoi's pollutant levels surpass those of other regions, particularly exceeding those of Ho Chi Minh City. In 2022, survey data revealed prevalent use of liquefied petroleum gas in Ho Chi Minh City's industries, while coal remained the primary fuel for Hanoi-based firms (Bang *et al.,* 2022). Urban aerosol SO_4^{2-} is mainly linked to coal combustion (Zhang *et al.,* 2013; Luo *et al.,* 2019), and biomass fuel utilization significantly escalates SO_x emissions. Rapid urbanization, industrialization, and vehicular combustion, emitting SO_2 and NO_x, are central in urban rain acidity (Shivashankara *et al.,* 2012; Gonzalez *et al.,* 2012). This pattern aligns with Hanoi's situation, where industries like paper, cement, and construction materials contribute to substantial air pollutants. Hanoi and Ho Chi Minh City share similar air pollution source distributions (Hien *et al.,* 2002).

Hoa Binh station recorded SO_4^{2-} ranging from 13.6 to 40.0 µmol/L, averaging 20.9 µmol/L. Notably, within a 10 km radius, the presence of the Hoa Binh sugar company, cement factory, and burgeoning mining activities for construction materials were observed (Pham *et al.,* 2016). Chemical fertilizers like ammonium sulfate and urea are widely used for cultivation, particularly for short-term crops like beans, peanuts, maize, and industrial crops such as tea and oranges (Pham *et al.,* 2016). Nearby cement production facilities using fossil fuels contribute to increased SO_2 concentrations, notably affected by prevailing wind directions (Cam Hoang, 2017). Agricultural urea usage elevates atmospheric NO_x and SO_2 when combined with ammonium sulfate fertilizers. Livestock emissions constitute the primary NH_3 source (Gu *et al.,* 2014), impacting eutrophication and acidification (Fangmeier *et al.,* 1994). NH_4^+ concentration is influenced by anthropogenic sources, including agriculture, human/animal waste and nearby vegetation (Khan *et al.,* 2018). Economic restructuring in 2020 (HBSO, 2021), emphasizing agriculture, forestry, and fishery, increased NH_4^+ fourfold from 12.0 µmol/L (2019) to 41.2 µmol/L (2020). Hoa Binh's SO_4^{2-} and NO_3^- concentrations causing acidity are lower than Hanoi and Ho Chi Minh, yet acid rain frequency surpasses those stations. The low pH might result from unmeasured HCO_3^- ions and organic acids in rainwater, warranting further investigation.

In Ho Chi Minh city, Cl^- exhibited the highest concentration with an average of 42.6 μmol/L (range: 36.3 μmol/L to 52.0 μmol/L). Atmospheric Cl^- originates from natural sources like seawater, wildfires, dust storms, and volcanic eruptions (Liss & Johnson, 2014), as well as anthropogenic sources, including coal combustion, biomass burning, and industrial emissions (Zhang *et al.,* 2013; Christian *et al.,* 2010; Arsene *et al.,* 2011). Ho Chi Minh City's traffic congestion, attributed to over 7.6 million motorcycles and 0.7 million cars during rush hour, leads to substantial vehicular exhaust emissions, which are a primary cause of its air pollution (Hien *et al.,* 2019). Transportation sources contributed overwhelmingly, accounting for 97% and 93% of total NO_x and SO_2 emissions, respectively. Industries contributed 22% and 5% of total SO_2 and NO_x emissions, with textiles, food, and metal manufacturing being key contributors (Ho *et al.,* 2019). Notably, port activities significantly contributed to air pollution, with seaports contributing 15% of total SO_2 and 11.5% of NO_x emissions in 2017, particularly those using "dirty" marine oil and heavy oil for power generation (Ho *et al.,* 2019)

3.2 Wet deposition of major ions

Wet deposition, influenced by factors like precipitation and chemical composition, varied across Hanoi, Hoa Binh, and Ho Chi Minh during the study period. Ammonium had the highest fluxes, except in Ho Chi Minh, where chloride had higher rates. $NH4^+$ deposition peaked in July in Hanoi (13.09 μmol/m²/month), March in Hoa Binh (20.56 μmol/m²/month), and September in Ho Chi Minh (10.94 μmol/m²/month). Sulphate also exhibited notable wet deposition, with Hanoi reaching 9.60 μmol/m²/month in August, Hoa Binh at 5.45 μmol/m²/month, and Ho Chi Minh at 11.61 μmol/m²/month, all in September. Hanoi experiences its highest precipitation in summer (July-August) and the least in winter (December-January). This leads to air quality deterioration, especially concerning fine particulate matter, in drier months due to sources like traffic, rice burning, and regional transportation

(Thanh *et al.,* 2015). Across the stations, the monthly wet deposition fluxes of major ions for acidic species varied with precipitation amount, leading to substantial differences in annual anion-to-cation deposition rates. Deposition generally heightened in summer, corresponding with increased rainy season precipitation from May to October.

3.3 Acid neutralization

3.3.1 Factors influence the pH of rainfall

Rainwater acidity primarily hinges on acidic ion concentrations, like NO_3^- and SO_4^{2-}. Past research has noted that rainwater acidity can be influenced by basic ion levels, such as Ca^{2+} and NH_4^+ (Zhang *et al.,* 2012). Thus, SO_4^{2-}, NO_3^-, Ca^{2+}, and NH_4^+ constitute the primary pH-affecting components in rainwater. The concentration ratios of rainwater chemical components at Hanoi, Hoa Binh, and Ho Chi Minh stations are provided in the calculation result.

Calculation reveal that the average ratio $A = NO_3^-/nss\text{-}SO_4^{2-}$ at Hanoi station from 2000 to 2020 remains below 1 in all periods underscoring $nss\text{-}SO_4^{2-}$ as a key pH-reducing contributor. The annual mean ratio $B = NH_4^+/nss\text{-}Ca^{2+}$ at Hanoi station indicates neutral NH_4^+ influence in rainwater during dry seasons, while wet seasons predominantly exhibit ratios exceeding 1, emphasizing NH_4^+ role in acidity neutralization. Ratio $C = (NH_4^+ + nss\text{-}Ca^{2+})/(NO_3^- + nss\text{-}SO_4^{2-})$ consistently exceeds 1, signifying cationic capacity ($NH_4^+ + nss\text{-}Ca^{2+}$) to neutralize anionic acidity ($NO_3^- + nss\text{-}SO_4^{2-}$). Except for 2019, the C ratio was lower than 1 (0.78), so the concentration of the cationic component was insufficient to neutralize the acidic component. This explains the high frequency of acid rain (75%) in Hanoi in 2019.

Average ratio A at Hoa Binh station (2000-2020) fluctuates around 1, highlighting alternate $nss\text{-}SO_4^{2-}$ and NO_3^- contributions to pH reduction. The annual mean ratio B during dry seasons at Hoa Binh station exceeds 1 in most years, except 2000 and 2008, highlighting NH_4^+ ions' neutral role in rainwater. Similarly, wet seasons exhibit ratios exceeding 1, stressing NH_4^+ role in acidity neutralization.

Ratio C mostly surpasses 1, indicating the ability of cationic components to neutralize anionic acidity. Except 2019, the ratio C was lower than 1 (0.72), this explains the high-frequency of acid rain (83%) in Hoa Binh this year.

Average ratio A at Ho Chi Minh station (2014 - 2020) consistently exceeds 1, identifying NO_3^- as primary pH-reducing contributor. The annual mean ratio B illustrates that nss-Ca^{2+} ions play a neutral role in rainwater during dry seasons, as all values are below 1. Wet seasons similarly exhibit ratios below 1, emphasizing nss-Ca^{2+} role in neutralizing acidity. Ratio C consistently exceeds 1 (except 2019), signifying cationic (NH_4^+ + nss-Ca^{2+}) neutralization of anionic acidity (NO_3^- + nss-SO_4^{2-}). Infrequent acid rain aligns with above-mentioned neutralizing contribution.

3.3.2 Capacity of acid neutralization of ions in rainwater's chemical composition

Table 2 presents NFs for the ions. Notably, NH_4^+ exhibits the highest NF across all sites, trailed by Ca^{2+}, with K^+ displaying the lowest NF. This suggests NH_3 surpasses $CaCO_3$, predominantly neutralizing acidic constituents. NH_4^+ values in Hanoi, Hoa Binh, and Ho Chi Minh range from 0.45 to 0.96, equivalent to European studies (Keresztesi, 2019), where NF(NH_4^+) ranges from 0.03 to 1.25.

Hanoi and Ho Chi Minh City experience severe environmental contamination due to substantial emissions from fertilizers, industries, factories, hospitals, animal waste, and untreated effluents. Although Hoa Binh's rural, mountainous context revolves around agriculture and small-to-medium industries, the high frequency of acid rain reveals its dependence on atmospheric circulation beyond local emissions.

3.4 Trend of ions in rainwater

3.4.1 Trend of ions concentration

In order to analyze the causes of the trend in ions concentration, the study conducted analysis of the ions concentration, which are presented in Table 3. P-value is the maximum probability to observe outcome and must be less than 5% for a statistical test to achieve significance.

At Hanoi station, H^+ ion concentration shows an annual decrease of -11.1%/ year, indicating declining acid rain frequency due to reduced H^+ concentration. NO_3^- ion concentration increase at 28%/year. Similarly, nss-SO_4^{2-}, SO_4^{2-}, nss-Ca^{2+}, and Ca^{2+} concentrations rise at 10.9%, 10.7%, 19.9%, and 19.6%/year, respectively, all with $p < 0.05$ significance.

H^+ ion concentration at Hoa Binh declines annually at -12.9% ($p = 0.003$), suggesting reduced acid rain due to lower H^+ content. NO_3^- ion concentration rise at 28.22%/year. Similarly, Ca^{2+} and nss-Ca^{2+} concentrations increase at 12.7% and 11.3%/year, respectively. Concentrations of SO_4^{2-}, nss-SO_4^{2-}, Cl^-, NH_4^+, Na^+, K^+, and Mg^{2+} have p-values exceeding 0.05.

At Ho Chi Minh station, NO_3^- ion concentration decreases at -24.8%/year ($p = 0.003$). Similarly, Ca^{2+} and nss-Ca^{2+} concentrations decrease at -23.7% and -23.3%/year, respectively. Cl^-, Na^+, and Mg^{2+} concentrations also decrease at -25%, -23.7%, and -20%/year. Concentrations of SO_4^{2-}, nss-SO_4^{2-}, NH_4^+, K^+, and H^+ have p-values exceeding 0.05.

Table 2. Value of neutralization factors for ions in precipitation

Station	NF (Ca^{2+})	NF (NH_4^+)	NF (Na^+)	NF (K^+)	NF (Mg^{2+})
Hanoi (2000 – 2020)	0.22	0.49	0.10	0.03	0.04
Hoa Binh (2000 – 2020)	0.25	0.45	0.09	0.04	0.05
Ho Chi Minh (2014 – 2020)	0.65	0.96	0.64	0.32	0.34

Table 3. Level of change in concentration, p-value at three stations.

Variable	Mean			Kendall's tau			p-value (Two-tailed)		
	Hanoi	Hoa Binh	Ho Chi Minh	Hanoi	Hoa Binh	Ho Chi Minh	Hanoi	Hoa Binh	Ho Chi Minh
SO_4^{2-}	88.9	18.7	29.5	0.107	0.057	-0.022	**0.014**	0.198	0.799
$nss\text{-}SO_4^{2-}$	87.3	41.5	28.2	0.109	0.03	-0.004	**0.013**	0.493	0.05
NO_3^-	67.4	36.7	13.2	0.28	0.282	-0.248	**< 0.0001**	**< 0.0001**	**0.003**
Cl^-	39	18.7	46.5	0.014	-0.035	-0.25	0.751	0.423	**0.003**
NH_4^+	118.5	59.1	29.9	0.074	0.077	-0.044	0.096	0.079	0.603
Na^+	25	10.3	22.2	0.07	0.04	-0.212	0.109	0.365	**0.012**
K^+	8.9	6.1	10.3	0.131	0.036	0.01	**0.003**	0.413	0.912
Ca^{2+}	60.5	31.8	23.2	0.196	0.127	-0.237	**< 0.0001**	**0.004**	**0.005**
$nss\text{-}Ca^{2+}$	59.9	29.6	22.3	0.199	0.113	-0.243	**< 0.0001**	**0.01**	**0.004**
Mg^{2+}	10.3	5.4	11.6	0.052	-0.03	0.2	0.233	0.502	**0.019**
H^+	3.7	7.1	1.2	-0.111	-0.129	-0.082	**0.011**	**0.003**	0.339

Note that the values in bold are acceptable as $p < 0.05$

3.4.2 Trend of ions deposition

Table 4 displays average annual ion deposition values, change in deposition, and p-values at the three stations. For each ion, calculations using SMK were performed, and results with p-value > 0.05 are considered statistically insignificant and are excluded. Ions with p-value < 0.05 were analyzed to determine their deposition trends.

At Hanoi station, NO_3^- deposition, the fastest increasing trend with 32.7%/year. This is due to an increase in emissions as well as the contribution of air pollution from nearby locations. According to emissions data from 2000 to 2012, NO_x emissions increased from 439.58 x 10^6 – 945.5 x 10^6 kg with an average annual increase of 6.66% (Ngan, 2020). Air pollution from the Northeast area affects the North of Vietnam. For NO_2 in Northern Vietnam originating from neighboring nations with 22.31%, 15.66%, 10.78%, and 11.13%, respectively, in January, February, June, and August (Son, 2013). The deposition levels of $nss\text{-}SO_4^{2-}$ and SO_4^{2-} were 15.9% and p-value at 0. SO_4^{2-} deposition in Hanoi has been increasing modestly throughout the years, which can also be explained by the increase in SO_2 concentration in the atmosphere as well as the current increase in air pollution. SO_2 emissions from 2000 – 2020 increased from 324.15 x 10^6 – 745.55 x 10^8 kg, the average increase in the air from the

Northeastern region affecting the North of Vietnam is quite large 55% for SO_2 (Anh *et al.,* 2019). In the north, dry deposition rate of SO_4^{2-}, which is an origin of neighboring countries of thorns from 12.63 – 28.61% (An *et al.,* 2016). The tendency of NH_4^+ ion deposition increases for 12.6%/year. The trend of NH_3 deposition over the years tends to increase sharply in recent years in Hanoi, which can be explained by the formation of NH_4^+ mainly due to agricultural activities, while currently agricultural activities is decreasing. Deposition of $nss\text{-}Ca^{2+}$ and Ca^{2+} has an average increase of 23.5%/year and 23.6%/year, respectively. Similarly, K^+ and Na^+ deposition tend to increase with the corresponding values of 16.6%/year and 10.3%/year. Mg^{2+} and Cl^- deposition also tend to increase average concentration at 7.8%/year and 6.8%/year, respectively, however do not reach the level of significance (p > 0.05). Ion H^+ is calculated through pH, H^+ can represent acid level, the average value of total H^+ ion deposition is 326.8 µmol/l. The total amount of H^+ ion deposition tends to decrease significantly over time with -4.4%/year at Hanoi station. Deposition value tends to decrease, which means that acid rain in these localities tends to decrease and vice versa.

At Hoa Binh station, NO_3^- deposition, the fastest increasing trend at 2.11%/year. Likely Hanoi, the NO_3^- deposition trend of Hoa Binh can be explained by the rising emissions and

Table 4. Level of change in deposition, p-value at three stations

Variable	Mean			Kendall's tau			p-value (Two-tailed)		
	Hanoi	Hoa Binh	Ho Chi Minh	Hanoi	Hoa Binh	Ho Chi Minh	Hanoi	Hoa Binh	Ho Chi Minh
SO_4^{2-}	5037.2	3172.2	5228.3	0.159	0.06	0.098	**0**	0.156	0.197
nss-SO_4^{2-}	4942.9	3125.1	4999.6	0.161	0.062	0.102	**0**	0.146	0.177
NO_3^-	3879.5	2713.2	2280.5	0.327	0.211	0.017	**< 0.0001**	**< 0.0001**	0.828
Cl^-	2298.2	1518.5	8342.8	0.068	-0.007	0.065	0.108	0.868	0.389
NH_4^+	7378.9	8697.7	5633.3	0.126	0.063	0.093	**0.003**	0.137	0.22
Na^+	1563.3	781.4	3792.9	0.103	0.089	0.032	**0.015**	**0.036**	0.675
K^+	546.2	433.5	1905.9	0.166	0.072	0.106	**< 0.0001**	0.088	0.16
Ca^{2+}	3692.8	2422.3	4036.6	0.235	0.087	0.026	**< 0.0001**	**0.039**	0.733
nss-Ca^{2+}	3659	2405.4	3954.8	0.236	0.088	0.025	**< 0.0001**	**0.037**	0.744
Mg^{2+}	685.1	460.6	2017.2	0.078	0.003	0.122	0.065	0.944	0.108
H^+	326.8	670.4	218.4	-0.044	-0.033	0.052	0.299	0.44	0.492

Note that the values in bold are acceptable as p < 0.05

pollutants from neighboring places, NO_2 pollution from neighboring nations affects the north of Vietnam. The deposition levels of nss-SO_4^{2-} and SO_4^{2-} were 6.0% and 6.2% with p-value were not significant enough (p > 0.05). The tendency of NH_4^+ ion deposition increases for 6.3%/year, which is lower than value in Hanoi, but does not meet the significance threshold (p > 0.05). Deposition of nss-Ca^{2+} and Ca^{2+} has an average increase of 8.8%/year and 8.7%/year, respectively. Similarly, K^+, Na^+ and Mg^{2+} deposition tend to increase with the corresponding values of 7.2%/year (p > 0.05), 3.6%/year and 94.4%/year. The average value of total H^+ ion deposition is highest at 670.4 µmol/l, and deposition of ion H^+ tends to decrease at 3.3%/year.

Unlike the Hanoi and Hoa Binh stations, the trend of ions deposition in rainwater at Ho Chi Minh station tends to increase. It can be seen that there is an incompatible between the trend of H^+ and the trends of cations NH_4^+, Ca^{2+}, K^+, and Mg^{2+}.

4. Conclusion

Irregular acid rain, influenced by human activities and convection currents, occurs in both urban and rural areas. In 2019, Hanoi and Hoa Binh exhibited frequencies of 75% and 83%, respectively, while Ho Chi Minh City showed a peak of 25% in 2017 and none from 2014 to 2016. In conclusion, acid rain is more prevalent in both Hanoi and Hoa Binh, the urban and rural areas, respectively, than in Ho Chi Minh City. The dominant ion concentration in rainwater is NH_4^+, followed by SO_4^{2-} and NO_3^-.

Deposition in the three stations rises during the summer, coinciding with the May to October rainy season. Maximum values were recorded for SO_4^{2-} in Hanoi and Hoa Binh. At Ho Chi Minh station, the highest value observed was for Cl^-.

The main components that change the pH value of rainwater in the study area are nss-SO_4^{2}, NO_3^-, nss-Ca^{2+}, NH_4^+. At Hanoi and Hoa Binh station, the main components involved in reducing the pH value of rainwater is nss-SO_4^{2-} ions, the key component in neutralizing rainwater acid is NH_4^+ which plays a key role in neutralizing acidity in rainwater. At Ho Chi Minh station, NO_3^- is the main contributor to decrease the pH value and ion nss-Ca^{2+} plays a key role in neutralizing acidity in rainwater.

Annual EANET data trends for the three stations were examined. For ion concentration, Hanoi and Hoa Binh experienced negative trend in H^+ which declined acid rain frequency, and NO_3^- was of decreasing trend in Ho Chi Minh city. Some ions displayed rising or declining deposition trends, while others lacked statistical significance. Amongst the three stations, NO_3^- had the most pronounced increase: 37.2%/year in Hanoi and 21.1%/year in Hoa Binh. H^+ ion deposition trends revealed two patterns: decrease in the north Hanoi and Hoa Binh and increase in the south Ho Chi

Minh. However, Ho Chi Minh's insufficient data length impacts trend assessment.

Acid rain, a consequence of economic advancement, requires effective monitoring to mitigate its effects and foster sustainable growth. Vietnam, among the nation most vulnerable to climate shifts, demonstrated its commitment during the 2021 United Nations Climate Change Conference (COP 26). The government endorsed Notice No 30/TB-VPCP, outlining strategies to achieve net-zero emissions by discontinuing coal-fired power projects and transitioning to clean energy, as per Decision 888 in 2022. The notice delineates eight priority areas, encompassing renewable energy, greenhouse gas reduction, electric mobility, and sustainable forestry management. However, the implications of acid rain on health and the environment remain unclear, necessitating comprehensive investigation to prompt mitigation strategies. Therefore, conducting a thorough investigation into its significant impacts is imperative to facilitate the prompt formulation of adaptation and mitigation strategies, aimed at curtailing adverse repercussions. Subsequently, leveraging an extended data chronology, forthcoming research could analyze acid rain and deposition patterns, assessing evolving deposition levels within the region and the nation.

Acknowledgment

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