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Chemical Composition of Rainwater at Selected Sites on Upolu Island, Samoa

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Abstract

The study involved analysis of rainwater samples at four sites on Upolu Island, Samoa from November 2019 to April 2020. A total of 48 rainwater samples were analysed in order to determine the major cations (Na^+, Mg^{2+}, Ca^{2+}, K^+) and anions (Cl^-, SO_4^{2-}, NO_3^-) in wet precipitation from the four sites. The average pH of the rainwater was 6.89, perhaps due to neutralization. Only 50% of the rain samples had a pH above 5.6. This shows strong inputs of alkaline species to rainwater samples in some sites. The average pH of samples higher than 5.6 is due to high loadings of sodium ions. The rainwater samples are dominated by Na^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-}. The principal cations and anions, in decreasing order, are $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ and $Cl^- > SO_4^{2-} > NO_3^-$. The correlation study and the comparison of major ion composition with other sites revealed that rainwater ion composition is strongly influenced by marine sources rather than anthropogenic and terrestrial sources.

Keywords

Atmosphere, Pollutants, Sources, Concentration, Anions, Cations, Samoa

1. Introduction

Chemical species in the atmosphere may be deposited onto the Earth's surface in two ways: 1) wet deposition (water-based particles in liquid or solid form—rain, snow, ice) and 2) dry deposition (dry species including gases such as sulfur dioxide and solid particles (aerosols). The primary anthropogenic polluting emissions gases are SO_2 (sulfur dioxide) and NOx (nitrogen oxides). These pollutants may be dissolved and transported by the rainwater to ground. Acid rain has huge effects on the aquatic and marine ecosystems, soil, buildings as well as human health. [1] have reported that more than 90% of the total amount of pollutants present in the atmosphere is percolated by wet deposition, being the prime cleansing mechanism to alleviate pollutants from the air. Thus, rainwater can be a way to reduce the atmospheric amount of pollutants and concurrently a source of contamination for water, soil and terrestrial vegetation [2] [3]. During the past several years the world has been seriously affected by acid rain. The seriously affected areas are mainly in the economically developed countries and have been a major problem in many urban and rural regions. In India several studies have generally highlighted the alkaline nature of rainwater due to soil derived particles in the atmosphere and chemical composition of rainwater has been carried out at urban and rural locations [4]. There are mounting evidences on the impact of acid rain on the aquatic and marine ecosystems, terrestrial and human health as well. [5] [6] reported that chemical characteristics of rainwater in urban areas are contributed to the local pollution sources, whereas in rural areas, it indicates the degree of impact of anthropogenic as well as natural sources. Climatic conditions may also affect the levels of trace substances in rainwater. Over the last thirty years, rainwater chemistry has been imperiled to intense research and numerous researches on the chemical composition, long and short-term trends of precipitation have been conducted globally [7]-[12]. The chemical composition of rainwater varies from site to site and region to regions depending on the influence of source points and anthropogenic sources. A baseline data on the ionic characteristics and nature of rainfall in Samoa has been documented over the last ten years ago. However, systematic observations of the chemical composition of precipitation are needed to investigate the changes and other characteristics of atmospheric pollution in Samoa after this period. The objectives of this study are to 1) study the chemical deposition and rainwater quality in the selected sites and 2) report on the chemical composition of rainwater trend in the last ten years. Samoa has undergone tremendous growth and commercial development over the last ten years with a population of 195,843 [13]. The majority of the population (~78%) reside on Upolu Island and 19% of the population live in the Apia urban area. Most of the population in Samoa are using readily available, untreated rainwater for both consumption and other domestic purposes. [14] reported that most of the ions originated mainly from the ocean with smaller contributions to potassium and magnesium levels from continental matter. Most sulfate ions also had a marine origin and regression analysis indicated non-marine sources such as the oxidation of biogenic sulfur-containing compounds. Thus, the result from this study will provide more insight of the level of atmospheric pollution in rainwater through the determination of chemical composition of rainwater in Samoa in ten years.

2. Methodology

2.1. Study Area

Four sites were selected for sampling (**Figure 1**), Alafua (13.8652˚S, 171.7965˚W),

Figure 1. Sampling locations [Source: Meteorology Office, MNRE].

Fagalii (13.8453˚S, 171.7411˚W), Tiapapata (13.8972˚S, 171.7808˚W) and Malie (17.5707˚N, 3.9962˚W). The Alafua sampling site is within the urban area of Upolu. It is located on a more inclined slope with an elevation of 40 m above sea level. The nearest road is about 10 m away from where the samples were collected. It is one of the busiest main roads every day. Fagalii with the elevation of 36 m above sea level is the most northerly of the four sites and the site is near to the domestic airport which has been permanently closed over a year now. The domestic airport is surrounded by residential homes and few tall trees and grass cover. There is no industrial activity in the vicinity of this location. Tiapapata has the highest elevation of 444 m above sea level. The area has more bushy cover and is generally cooler compared to the other three sites. It is more isolated in terms of location of residential homes compared to the other three sampling site. The Malie sampling site is within the rural area of Upolu island with an elevation of 12 m above sea level. It is one of the most southerly of the four sites. The sampling site is surrounded by residential homes and the nearest road is more than 15 m away from the sampling site. This road has busy traffic every day from the international Faleolo airport to the Capital, Apia. There is no industrial activity within the location but few open burnings of vegetation were undertaken about 500 - 1000 m from this site.

2.2. Sampling Collection

A total of 48 rainwater samples were collected between the months of November 2019 and April 2020. Samples were manually collected with the use of a polyethylene film with a diameter of 25 cm that were placed approximately 1.5 m above the ground. The least expensive and best method of collecting rainwater samples for inorganic analyses is the use of polyethylene bottles [15]. These materials also ensure that sufficient water quantities are collected for analysis, they prevent evaporation and minimise dry deposition [16]. Glass materials are avoided as glass is prone to breakage and can act as an ion exchanger through adsorption-desorption [17] [18] thereby influencing the accuracy of the results. After collection and weighing, samples were transported to the laboratory for chemical analysis and stored at 4˚C. All samples were filtered through a 0.45 μm filter prior to storage in order to determine only the dissolved chemical elements in atmospheric precipitation.

2.3. Sampling Analyses

Sample pH and hardness were determined with a potentiometer (Digmed DM 20) using a glass electrode combined with an Ag/AgCl (sat) reference electrode. Sample hardness were measured by titration with EDTA in NH_4Cl/NH_4OH buffer pH 10 using Eriochrome Black-T as the indicator. A radiometer (Digmed DM 31) conductivity meter and platinum electrode were used for conductivity measurements. Major ions were determined using a capillary electrophoresis system with an automatic sampler and a spectrophotometric detector (CE Hewlett-Packard) equipped with a DAD UV-Vis detector. Indirect detection was performed for cations at 214 nm and at 375 nm for anions [19]. In order to determine the quality of sample analyses by capillary electrophoresis, a rainwater standard reference material (CRM 409—Commission of the European Communities) were analysed.

3. Results and Discussion

3.1. Rain Quantity

There were 48 rainwater samples collected in the months of November 2019 - April 2020. It was recorded that the largest number of monthly events occurred in January (19) followed by December (18) and February (18), March

(17), November (16) and April (15). The highest rainfall was during January (2020) (450 mm) followed by February (380 mm) and December (2019) (375) as shown in **Figure 2**. The average rainfall was found to be 344 mm (stdev = 77 mm).

3.2. Variation of pH

The pH of rainwater samples ranged from 6.30 to 8.02. In this study, the volume-weighted mean pH (VWM) value was 6.89 (stdev = 0.94). In comparison with other results (pH = 6.5) reported in Samoa by [14], the results are not similar. The pH of natural precipitation is controlled by dissolved CO_2, due the interaction between water droplets and carbon dioxide [20]. Precipitation pH is modified by the addition of both acidic and alkaline components [21]. **Figure 3** shows the temporal variation of mean pH.

The frequency distribution of pH is shown in **Figure 4**. A 50% of the 48 rain samples showed a pH above 5.6, indicating that rainfall with above–background acidity is not common in all sampling sites. However, the abundance of pH

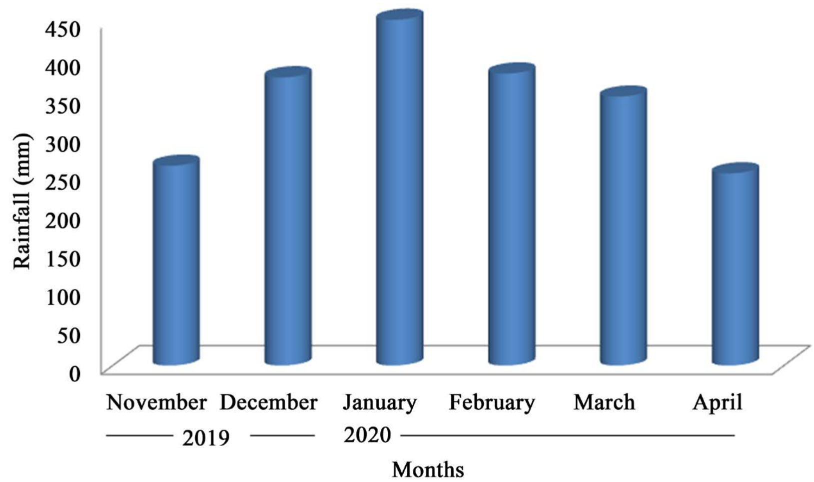

Figure 2. Monthly variation of rainfall occurrence during the months of November 2019-April 2020.

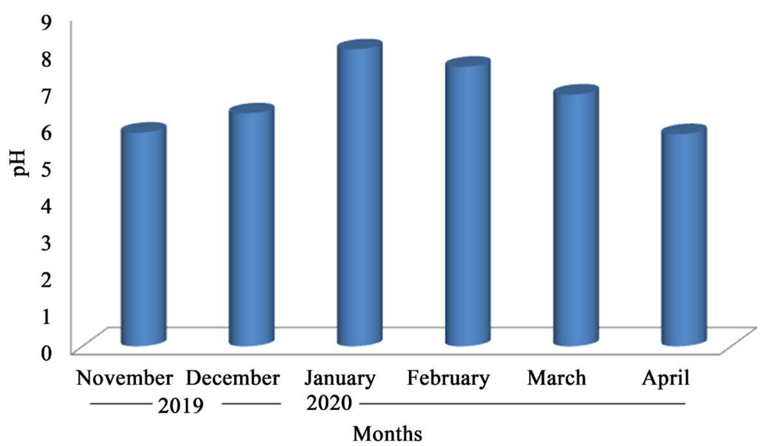

Figure 3. Monthly average pH.

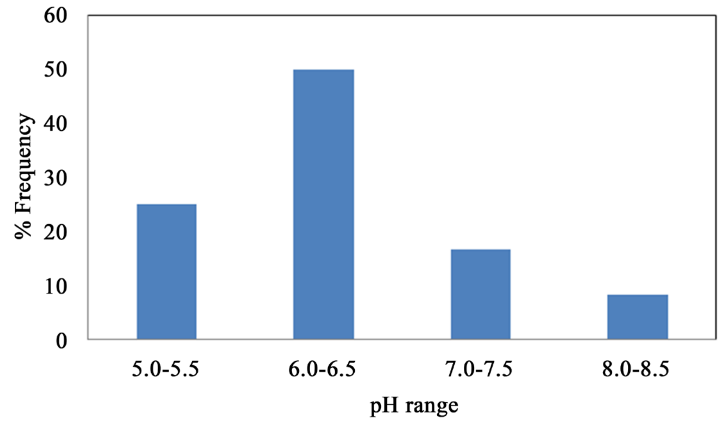

Figure 4. Frequency distribution of pH.

values above 5.6 indicates the presence of alkaline substance in the rainwater [22].

Alkaline precipitation has been reported in different parts of the world. In India, previous studies have recorded pH values ranging from 6.23 to 6.85 [23]. [24] reported an alkaline volume-weighted mean of 7.11. Another study, in the urban area of Varanasi district, India, reported alkaline pH values due to the dominance of soil-derived particles [25]. Thus, the VWM pH of 6.89 for our samples likely reflects an intense impact of alkaline soil dust on rainwater composition.

3.3. Chemical Composition

The variation of monthly mean concentration of major cations and anions in rainwater is illustrated in **Table 1**. Volume weighted mean concentrations of cations can be ordered in descending order as $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ with values ranging from 198 to 11 μeq/L. The corresponding order of anions volume VWM concentration was Cl^-, SO_4^{2-} and NO_3^-, with values ranging from 122 to 10 μeq/L.

Na^+ and Cl^- concentrations are large because the samples were collected from Malie which is located on the north coast of Upolu island. The high concentration of cations observed in November may be due to the small volume of rainfall recorded compared to other months. The lesser amount of rainwater is likely to generated greater concentrations of ionic species in rainwater due to reduced removal mechanism of suspended particles by wet deposition [26]. The smaller amount of rainwater is expected to produce higher concentrations of chemical species in rainwater due to reduced removal of suspended particles by wet deposition [27].

3.4. Comparison with Other Sites

The volume-weighted mean concentrations in rainwater for this study and other sites reported worldwide are shown in **Table 2**. The pH of the present study (6.89) is higher than the reported pH value of 6.5. Most of the ions originated

Table 1. Major ions in rainwater.

	Major ions in rainwater		
	Max	Min	SD
Na^+	198	22	49.44
K^+	95	18	25.44
Mg^{2+}	98	15	26.04
Ca^{2+}	87	7	26.36
Cl^-	122	18	25.70
NO_3^-	59	10	14.54
SO_4^{2-}	76	23.2	12.94

Table 2. Volume weighed mean concentrations of major ions in rainwater (μeq/L) from different regions.

	Volume weighed mean concentrations of major ions in rainwater							
	pH	Cl^-	NO_3^-	SO_4^{2-}	K^+	Mg^{2+}	Na^+	Ca^{2+}
This study (2019)	6.89	43.1	32.4	41.8	36.0	40.7	70.5	31.7
Wazhou, China (2018)	5.00	15.1	35.1	156.9	20.1	9.9	24.4	62.1
Hyderabad, India (2014)	6.00	21.5	28.7	38.9	2.28	4.29	25.6	158.6
Minas Gerais State, Brazil (2014)	6.22	17.3	16.2	14.2	7.12	24.1	25.0	39.6
Faatoia, Samoa (2007)	6.50	46.5	0	3.8	1.8	9.9	45.7	5.0

mainly from the ocean with smaller contributions to potassium and magnesium levels from continental matter [14]. Most sulfate ions also had a marine origin and regression analysis indicated non-marine sources such as the oxidation of biogenic sulfur-containing compounds. The dry season showed higher ion concentrations than the wet season although the variations were minimal.

Table 2 above shows volume-weighted mean concentrations in rainwater for this study and other results reported for the different regions and selected sites worldwide. In this study Na^+ and Cl^- are the most abundant ions with the highest concentrations of about 198 and 122 μeq/L and mean concentrations of 70.5 and 43.1 μeq/L respectively.

3.5. Sources Contribution

The correlation between ions was calculated for all samples and presented in Table 3 below.

The levels of Na^+ were strongly correlated to those of Cl^- (r = 0.92) followed by SO_4^{2-} (r = 0.89), Mg^{2+} (r = 0.84) and Ca^{2+} (r = 0.81) indicating their origin from similar sources. The strong correlation between the levels of the cations and that of the sulfate ion is also suggestive of neutralization processes between acids and alkaline species in rainwater [28]. Assuming that all Na^+ ions arise from marine sources, the high correlation between the levels of Na^+ and Cl^- and

Table 3. Pearson Correlation Coefficient for concentrations of major ions.

	Pearson Correlation Coefficient						
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
Na^+	1	0.02	0.84	0.81	0.92	0.05	0.89
K^+		1	0.06	0.42	0.32	0.11	−0.23
Mg^{2+}			1	0.82	0.75	0.66	−0.12
Ca^{2+}				1	0.51	0.27	−0.38
Cl^-					1	0.64	0.87
NO_3^-						1	0.78
SO_4^{2-}							1

the slight increase in the Na^+/Cl^- rainwater ratio suggests that most of the Cl- ions also originated from the ocean, with only small amounts possibly arising from other sources. Another potential source of Cl^- is HCl emitted from industrial activity [23] or HCl generated from the reactions between NaCl aerosols and industrial sources.

4. Conclusion

A study on the chemical composition of rainwater was carried out over a six-month period at selected sites on Upolu Island. The analyses revealed a strong correlation between Na^+ and other ionic species. The average pH of the rainwater was 6.89. Only 50% of the rain samples had a pH above 5.6. This shows strong inputs of alkaline species to rainwater samples in some sites. The average pH of samples higher than 5.6 is due to high loadings of sodium ions. The rainwater chemistry is dominated by Na^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-}. The principal cations and anions, in decreasing order, are $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ and $Cl^- > SO_4^{2-} > NO_3^-$. The cation Na^+ correlated strongly with Mg^{2+} and Ca^{2+}, suggesting a common natural source of crustal origin. The monthly variation in ionic deposition is influenced by rainfall rate and ionic species concentration. The comparative study of the major ion composition with other sites revealed that rainwater ion composition is strongly influenced by marine sources rather than anthropogenic and terrestrial sources.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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