

Acidic Wet Deposition in Bandung City Indonesia

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Abstract. Acidic deposition (acid rain) has been known to cause negative impact to environment. Measurement of rain chemical composition was done in March to August 2016 to investigate temporal variation of atmospheric deposition in Bandung City. Rainwater samples are collected at four sampling sites. The chemical properties of the rain determined were pH and ionic concentrations of SO_4^{2-} , NO_3^- , Cl^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+ and NH_4^+ . The rainwater was typically acidic with the range of mean pH between 5.29 – 5.56 and mean electric conductivity value range between 16.37 – 19.96 $\mu\text{S}/\text{cm}$. Temporal variation showed higher SO_4^{2-} , NO_3^- and NH_4^+ concentration in August when rainfalls were the lowest (214.88 mm). Similar temporal variation for the mean pH (5.98) and electric conductivity (25.36 $\mu\text{S}/\text{cm}$) in August. Ca^{2+} highest concentration was observed in June. Generally, the the major component of precipitation chemistry were SO_4^{2-} and NO_3^- , Ca^+ and NH_4^+ , for anion and cations, respectively. The largest proportions of the total anions in all sampling sites was SO_4^{2-} ranged from 32% (Lembang) to 37% (Buah Batu) followed by NO_3^- (13 – 15%) and Cl^- (4 – 7%). For cations, NH_4^+ dominated with proportion ranged between 21 – 27% and subsequently Ca^{2+} (13 – 19%) and followed by Na^+ , Mg^+ , K^+ and H^+ . The Neutralizing Factor (NF) results reveal that Ca^{2+} and NH_4^+ are the dominant neutralization substances in the rainwater. However it should be noted that reduced nitrogen (NH_4^+) act as mobile nitrogen that further will acidify the environment, particularly to soil ecosystem downstreams.

1 Introduction

There are two meanings of wet deposition terms determined by The World Meteorological Organization (WMO). Firstly, wet deposition is a process of scavenging of any gases and/or particles from the atmosphere by liquid (i.e., water droplets) and solid (i.e., ice crystals) phases. The process involves removal of any species by droplets/ice crystals within clouds (i.e., in-cloud scavenging), and by falling drops/snowflakes (i.e., below-cloud scavenging). Second, wet deposition is the mass of material deposited from the atmosphere to the underlying surface in precipitation (over unit of area during unit of time) [1].

Acid deposition in the general is precipitation with a pH level of less than 5.6 and thus is considered to be acidic, and when it falls on the Earth it is considered to be "acid deposition." Acid deposition from atmospheric precipitation can makes soils, lakes and ponds become acidic. Sulfur dioxide and nitrogen oxides, typical air pollutants are transformed into sulfuric and nitric acid compounds in the atmosphere, with resultant changes of their properties. These acid compounds are carried by the wind as fine particles (aerosols) on sunny days. They

dissolve in rain drops on rainy days or within clouds, then fall to the Earth's surface, making the environment acidic. Research has detected this transport on a continental scale, with effects extending beyond national borders [2].

Acid rain is a mild combination of mainly sulfuric and nitric acid. Sulfurous acid and nitrous acid are less stable and are present only in very low amounts. Sulfuric acid and nitric acid are the main acids present in acid rain. The problem occurs when rainwater combines with gaseous oxides of sulfur, nitrogen, and phosphoric and hydrochloric acid mists. The latter two and sulfur are released into the atmosphere from automobile exhausts, industries and electric power plants [3].

Nitrogen deposition has had a detrimental impact on temperate ecosystems resulting in soil acidification and a reduction in plant biodiversity. Soils release base cations during acidification process, such as calcium and magnesium, neutralizing the increase in acidity, if base cations have been depleted, aluminium was released from the soils, often reaching toxic levels was superseded by iron release into soil water [4].

Preliminary study evaluation of air quality in Bandung City showed factor characteristic of airborne

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particulate matter samples were attributed to sea salt, soil dust, vehicular emissions and biomass burning and industrial emissions. Many scale factories are located in and around the city with several pocket of slum areas, lacking waste disposal system, rapid growth of industry, residential area, population and motor vehicle has caused air pollutant problem in Bandung City [5].

Wet deposition is the most effective scavenging process to removing particulate and gaseous air pollutant from atmosphere in Bandung City. We present the precipitation chemistry and wet deposition that occurred at four sampling sites in Bandung City from February to August 2016. Weekly bulk precipitation chemistry samples were analyzed for the anion of SO_4^{2-} , NO_3^- , Cl^- and for the cations of Ca^{2+} , Mg^{2+} , Na^+ , K^+ and NH_4^+ in addition to pH and conductivity measurement.

2 Material and Method

Rain water samples were collected on a weekly basis in four sampling stations from March 2016 to August 2016. These stations were distributed in Bandung City. The locations of the sampling sites were chosen in order to represent various geographical conditions and expected pollution levels and are presented in Figure 1.

Three of the sampling sites are placed in urban areas. The first installed in an altitude of 1271 m asl at Lembang farming area. The second was installed at an altitude of 803 m asl in Coblong area and the third was installed at an altitude of 742 m asl in Sumur Bandung. The fourth was installed at an altitude of 642 m asl at Buah Batu area.



Fig. 1. Sampling site

2.1. Sampling Equipment and Methods

The rainwater samples was collected manually using a polyethylene bottle (1000 mL) with a polyethylene funnel (12 mm in diameter) and put on a stainless steel cylinder. The funnel equipped with a filter plug (1 mm mesh) to protect large debris. The inside wall of canister painted with black color to diminish light levels around the collecting bottle and to inhibit biological growth [6].

Rainwater sampling was collected on a weekly basis from March to August 2016. The bulk collector bottle was replaced with a clean one and funnels were rinsed with deionized water. Samples bottle were placed in a

cool box with blue ice and were transported from the sampling sites to the laboratory.

2.2 Laboratory Analysis Method

Upon arrival at the laboratory, samples were immediately weighed for volume determination, followed by pH measurement (Sartorius Professional Meter PP-20) and electric conductivity (Agilent Technologies 3200 C). The pH meter and conductivity meter were calibrated before measurement. Samples were sealed from the atmosphere and stored in the dark at 4°C in the refrigerator until analysis. Major ions (SO_4^{2-} , NO_3^- , Cl^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+ and NH_4^+) were analysis using ion chromatograph DIONEX ICS 500 DP.

2.3 Quality Assurance

2.3.1 Ionic Balance (IB)

The accuracy of laboratory analysis was determined using ion balance analysis. Ionic Balance is the sum of major anions in a water sample that is theoretically should equal to sum of major cations. In reality, factors such as the presence of unknown ions that have not been analyzed, analytical error or measurement precision could cause differences in ion balance (IB) was calculate by Equation 1 [6]:

$$IB = (\sum_{anions} - \sum_{cations}) / (\sum_{anion} + \sum_{cations}) \times 100 \% \quad (1)$$

It is suggested that the difference between ions were $IB \pm 8\%$ if sum ions $> 100 \mu\text{eq/L}$, $IB \pm 15\%$ if sum ions $50 - 100 \mu\text{eq/L}$ and $IB \pm 30\%$ if sum of ions $< 50 \mu\text{eq/L}$ [2].

2.3.2 Precipitation Weight Mean (PWM) Concentration

In order to determine the influence of air pollution to rainwater chemistry, precipitation weighted mean (PWM) concentration was calculated to eliminate the effect of rainwater amount for each ion analyzed. PWM is carried out by summing the product of ion concentration and the precipitation amount, obtained from rainwater sampler, for each data pair and dividing the result by the sum of precipitation amount for a certain period [6].

$$C_{w,j} = \sum C_{j,k} \cdot P_k / \sum P_{k_s} \quad (2)$$

where :

$C_{w,j}$: precipitation weighted concentration for ion j (meqL^{-1})

$C_{j,k}$: ion j concentration in precipitation of time k (meqL^{-1})

P_k = precipitation amount of time k (mm time^{-1})

3 Result and Discussion

3.1. Precipitation Chemistry

Generally SO_4^{2-} and NO_3^- for anion and Ca^{2+} and NH_4^+ for cations, were found as major component in precipitation chemistry, at all sampling sites (Table 1). Table 1 present mean, minimum and maximum of pH, conductivity and concentration of major ions in rainwater in Bandung City. Mean concentration of SO_4^{2-} ranged from 39.90 $\mu\text{eq/L}$ (at Lembang) to 78.76 $\mu\text{eq/L}$ (at Sumur Bandung) and mean concentration of NO_3^- ranged from 19.47 (at Lembang) to 27.41 $\mu\text{eq/L}$ (at Sumur Bandung). Mean concentration of Ca^{2+} ranged from 31.43 $\mu\text{eq/L}$ (at Coblong) to 51.61 $\mu\text{eq/L}$ (at Lembang) and NH_4^+ ranged from 29.07 $\mu\text{eq/L}$ (at Lembang) to 49.70 $\mu\text{eq/L}$ (at Sumur Bandung).

Gaseous pollutant such as SO_2 and NO_x are released into the atmosphere when fuels such as oil and coal are burnt. SO_2 and NO_x are the major causative agents (precursors) of acid deposition. The high concentrations of alkaline ions (mainly Ca^{2+} , NH_4^+) in the atmosphere have played an important role to neutralize the acidity of rainwater, but it is worth noting that the emission of NO_x from the automobile exhaust is increasing and becoming the important precursor of acid rain [7].

We observed that the lowest mean rainwater pH value in Buah Batu was 5.28 which was less than pH value of 5.6 of unpolluted rainwater at equilibrium with atmospheric CO_2 [8]. Carbonic acid is a weak acid, it brings down the pH of the rainwater to 6.0 – 5.2. With pH levels ranging between 6.0 – 5.2, rainwater is acidic, but still not dangerous. This is a reversible reaction. Sometimes, the pH level can even become as low as 2. This phenomenon of acidic rainwater precipitation, is called acid rain.

The mean electric conductivity in rainwater samples ranged from 15.67 $\mu\text{S/cm}$ at Buah Batu – 19.37 $\mu\text{S/cm}$ at Sumur Bandung. The common range of electric conductivity for precipitation sample is from < 0.5 to 100 mS/cm [2]. Precipitation conductivity is mainly contributed by water soluble ions, the value being related to the total sum of anions and cations in the rainwater. Low precipitation conductivity is an indicator of good atmospheric environmental quality [9].

In term of ionic balance, more than 65% of the data is characterized by positive ionic balance value, which means the sum of anions in the samples exceeds that of cations. The chemical determination of heavy metals, aluminum, mercury, and organic compounds will aid in the characterization of precipitation if the ion balance not meet criteria [2].

3.2 Temporal Variation of Precipitation Chemistry

Monthly variation of precipitation chemistry is shown in Figure 2. Higher SO_4^{2-} and NO_3^- anions concentration were observed in August (89.41 $\mu\text{eq/L}$ and 35.69 $\mu\text{eq/L}$) and cation NH_4^+ (77.76 $\mu\text{eq/L}$) when the lowest rainfall was observed (214.88 mm). But cation Ca^{2+} highest concentration (94.27 $\mu\text{eq/L}$) was observed in June (521.67 mm).

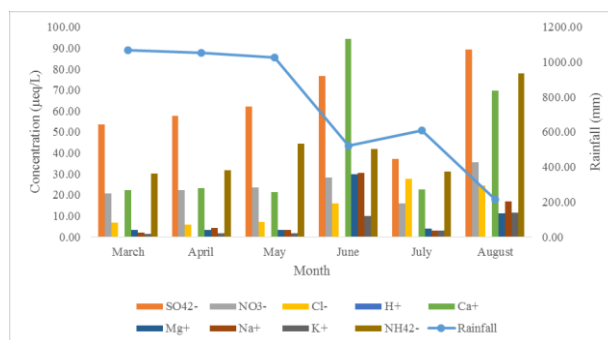


Fig. 2. Temporal variation of precipitation chemistry in Bandung City.

3.3 Temporal Variation of pH and Electric Conductivity

Temporal variation of pH and electric conductivity presented in Figure 3. Data show mean pH (5.98) and mean electric conductivity (25.36 $\mu\text{S/cm}$) were slightly higher in less rainy periods in August. This can be explained by the fact that, in drought periods, the atmosphere is considerably more polluted, so the wet scavenging process carries a higher load of compounds which increases both measured parameters.

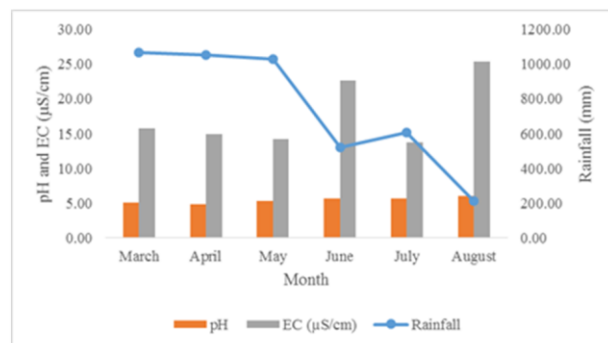


Fig. 3. Temporal variation of pH and electric conductivity in Bandung City

Table 1. Mean, minimum and maximum of pH, conductivity ($\mu\text{S}/\text{cm}$) and concentration ($\mu\text{eq}/\text{L}$) of major ions in rainwater collected four site from March to August 2016 (n = the number of samples)

	Lembang n=24		Coblong n = 24		Sumur Bandung n = 24		Buah Batu n = 24	
	Mean	Min-Max	Mean	Min-Max	Mean	Min-Max	Mean	Min-Max
SO_4^{2-}	39.90	9.22-81.84	64.70	18.00-135.38	78.76	32.35-192.33	65.36	20.82-125.97
NO_3^-	19.47	0.00-67.70	27.22	11.12-67.61	27.41	14.16-55.29	22.62	9.01-41.68
Cl^-	13.59	2.23-71.62	13.29	3.39-77.26	11.69	3.95-39.26	9.80	3.33-30.42
Ca^+	51.61	4.41-827.8	31.43	7.65-91.81	45.67	15.69-204.97	44.34	16.64-132.60
Mg^+	21.77	0.49-440.44	5.26	0.58-18.91	6.72	2.30-28.53	6.34	2.43-16.20
Na^+	23.46	0.07-398.37	5.98	0.13-26.19	6.84	0.87-29.25	6.14	0.74-25.03
K^+	9.09	0.61-76.33	3.93	0.51-29.04	2.89	0.97-48.36	3.50	0.87-15.79
NH_4^+	29.07	0.00-70.66	49.22	16.30-206.16	49.70	23.06-86.45	37.75	0.00-88.45
H^+	0.01	0.00-0.04	0.01	0.00-0.06	0.01	0.00-0.04	0.01	0.00-0.02
pH	5.63	4.36-7.71	5.41	4.24-6.79	5.38	4.10-6.29	5.28	4.68-6.36
Cond.	17.88	4.94-134.90	17.71	5.34-50.45	19.37	12.84-40.41	15.67	5.61-27.7

2.4 Precipitation-weight Mean Concentrations (PWM)

The proportion of Precipitation Weight Mean (PWM) concentrations in the rainwater sample shown the most anion components of rainwater sample in all sampling sites was SO_4^{2-} , which contributed for 32% (at Lembang) – 37% (at Buah Batu) to the total anions, followed by NO_3^- (13 – 15%) and Cl^- (4 – 7%). Both NH_4^+ (21 – 27%) and Ca^{2+} (13 – 19%) were the major cations components, followed by Na^+ , Mg^{2+} , K^+ and H^+ .

Precipitation Weight Mean (PWM) concentrations in the rainwater sample for each sampling site location as shown in Figure 4, Figure 5, Figure 6, and Figure 7.

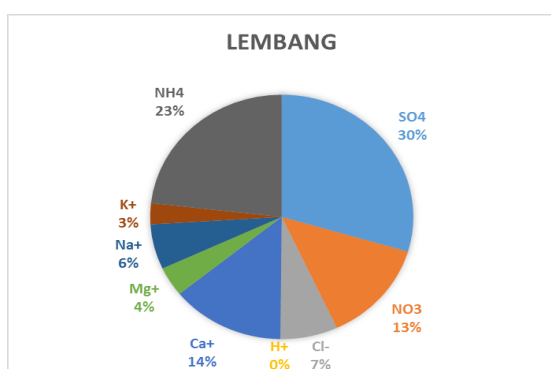


Fig. 4. Precipitation Weight Mean (PWM) concentration in Lembang

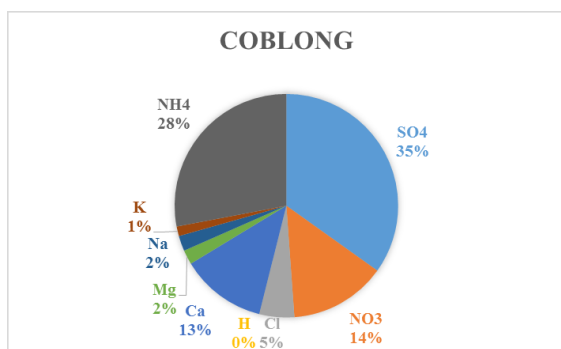


Fig. 5. Precipitation Weight Mean (PWM) concentration in Coblong

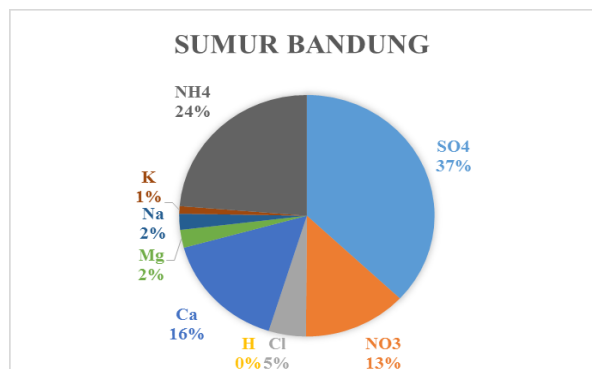


Fig. 6. Precipitation Weight Mean (PWM) concentration in Sumur Bandung

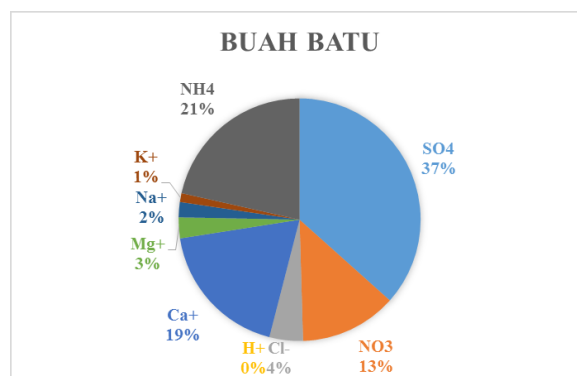


Fig. 7. Precipitation Weight Mean (PWM) concentration in Buah Batu

2.5 Neutralizing Factor (NF)

Neutralization factors (NF) can be used to evaluate the neutralization of precipitation by Ca^{2+} , Mg^{2+} and NH_4^+ , which are calculated by the following Equation 3 [10,11,12,13,6] :

$$NF_{Xi} = [X_i^{2+}] / [SO_4^{2-} + NO_3^-] \quad (3)$$

where X_i is the chemical component of interest, with all the ions expressed in $\mu eq/L$.

The NF values for Ca^{2+} , Mg^{2+} and NH_4^+ in rainwater of the study area are 0.87, 0.37 and 0.49 (at Lembang); 0.34, 0.06 and 0.54 (at Coblong); 0.43, 0.06 and 0.47 (at sumur Bandung) and 0.50, 0.07 and 0.43 (at Buah Batu). The results reveal that Ca^{2+} and NH_4^+ are the dominant neutralization substances in the rainwater.

2.6 Sources of Emission

To identify the sources of emission which affects the quality of atmospheric precipitation was used to quantifies the sources emissions [14]. The result found ratio $\text{SO}_4^{2-}/\text{NO}_3^-$ were 2.05 (at Lembang), 2.38 (at Coblong), 2.87 (at Sumur Bandung) and 2.89 (at Buah Batu). The results showed that sulfuric emissions still dominated, however the ratio is not as high as the one found in cities affected by industry. Ratio $\text{SO}_4^{2-}/\text{NO}_3^-$ at Dhanbad City, known as coal city in India was 16.94 due the fact that the site are located beside or in industrialized urban areas [14]. SO_2 and NO_x come from electric power generation that relies on burning fossil fuels, like coal [3].

Nitrate and sulfate are the major component of acid rain and their concentrations are increasing rapidly in the atmosphere growing to anthropogenic activities such as the burning of coal and petroleum fuels. Nitrogen in precipitation is present mainly as ammonium (NH_4^+) and nitrate (NO_3^-). NH_3 emissions sources from soils, oceans, and animal excreta. Sulfate in precipitation in different areas study were sea-salt sulfate, emissions of SO_2 from industrialized areas and local sources as coal combustion and biogenic sulfur [15].

2.7 Wet Deposition Rate

Wet deposition rate for certain study periods were present in **Table 2**. The highest wet deposition rate of anion due to SO_4^{2-} with mean ranged between 15.90 kg/ha in Lembang to 45.45 kg/ha in Sumur Bandung. For cations, wet deposition rate of Ca^{2+} ranged between 8.58 kg/ha in Lembang to 11.60 kg/ha in Buah Batu. NH_4^+ has significant rate for cation in all sampling sites with range values between 4.60 kg/ha in Lembang to 10.77 kg/ha in Sumur Bandung.

Calcium is a major neutralising agent that may play an important role in the precipitation chemistry in Bandung City. Calcium in rainwater may be contributed from soil dust, coal combustion and cement factories [16]. The neutralization capacity of soil dust from desert and semi-arid areas northern China was largely related to the calcite (CaCO_3) content of the soil, so precipitation pH in this part of China has remained high despite the high sulfur emissions and large quantities of sulfuric acid in the precipitation. The chemical composition of the anthropogenic emitted calcium dust are not known, but is likely a combination of CaCO_3 , CaO and CaSO_4 [17].

Table 2. Wet deposition rate (kg/ha)

Sampling Site	Rainfall (mm)	Anion (kg/ha)			Cations (kg/ha)				
		Cl	NO_3^-	SO_4^{2-}	Ca	Mg	Na	K	NH_4^+
Lembang	829.88	4.00	10.02	15.90	8.58	2.20	4.48	2.95	4.35
Coblong	1155.61	5.44	19.51	35.91	7.28	0.74	1.59	1.78	10.26
Sumur Bandung	1201.52	4.98	20.42	45.45	11.00	0.98	1.89	3.36	10.77
Buah Batu	1304.94	4.53	18.30	40.97	11.60	1.01	1.84	1.79	8.89

4 Conclusions

The total amount of wet precipitation measured during the sampling period (March to August 2016) for Bandung City were ranged between 214.99 mm – 1067.32 mm. The mean pH showed that samples had their majority acidic properties. This acidity was directly associated with SO_4^{2-} and NO_3^- , where SO_4^{2-} that were found to be the main contributor to this characteristic.

On the other hand, the neutralization process mainly originated from the presence of Ca^{2+} and NH_4^+ . Cation wet deposition rate of Ca has highest. Calcium is a major neutralising agent that may play an important role in the precipitation chemistry in Bandung City. Ammonium (NH_4^+) came the second and showed significant rate for cation in all sampling site. There are not many agricultural areas in the city of Bandung. It is suggested that ammonia is originated from decomposition process of waste and wastewater mix in open channel in Bandung City are. However, this is still need further investigation.

This paper is part of the research “Prediksi Dampak Kesehatan Lingkungan Deposisi Basah Logam Berat di Wilayah Perkotaan Bandung” funded by Riset KK dan Inovasi ITB 2017.

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