

Measurement of Rainwater Chemical Composition in Malaysia based on Ion Chromatography Method

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Abstract—Air quality in Setapak district of Kuala Lumpur was studied by analysing the rainwater chemical composition using ion chromatography method. Twelve sampling sites were selected and 120 rainwater samples were collected in the period of 10 weeks. The results of this study were compared to the earlier published data and the evaluation showed that the NO_3^- ion concentration increased from 0.41 to 3.32 ppm, while SO_4^{2-} ion concentration increased from 0.39 to 3.26 ppm over the past two decades that is mostly due to rapid urban development of the city. However, it was found that the chemical composition for both residential and industrial areas does not have significant difference. Most of the rainwater samples showed alkaline pH (pH > 5.6). The possible factors for such alkaline pH in rainwater samples are assumed to be the marine sources, biomass burning and alkaline character of soil particles.

Keywords—acid deposition; atmospheric pollution; deposition fluxes; trajectories

I. INTRODUCTION

MALAYSIA has developed quite rapidly over the past 20 years. However, such rapid growth has led to serious environmental concerns especially in the capital city, Kuala Lumpur. In the southern Kuala Lumpur, a variety of both natural and industrial activities contribute to the occurrence of acidic precipitations. In addition, rapid housing development and increase of vehicles number also resulted in the raised concern over the air quality. Besides that, due to geographic location of Malaysia, the long-ranged source such as marine source and biomass burning affect the country's atmospheric pollution. A study by [1] showed that in 1996, the total $\text{NO}_x + \text{SO}_x$ ion concentration in Klang Valley (Kuala Lumpur) locations were increased by a factor of ~10 due to anthropogenic activities in comparison to the three 'remote' tropical location sites: Tanah Rata in the Cameron Highlands of Malaysia, Bukit Koto Tabang on the island of Sumatra in Indonesia, and Charles Point/Katherine in the Northern Territory of Australia. In addition, the studies conducted in Petaling Jaya showed that the average pH (1982 – 1991) decreased by 1996 [1, 2]. Besides that, the studies showed steady increment in the SO_4^{2-}

and NO_3^- ion concentrations from 1982 to 1996. Both studies pointed out that sulphur species of power generation processes as the main contributor to the acidity of the rainwater. It is believed that comparative evaluation of air quality is important for various locations in Kuala Lumpur. This article presents the wet deposition analysis of three months study period, between April and June 2009. Setapak district was chosen as study area as it is one of the biggest suburbs that mostly occupied by residential, constructions and some light industry zones. The sources of the wet deposition compositions are traced using trajectories analysis. This study focuses on the rainwater composition chemistry over Malaysia and pollutants contributing sources. It also provides an overall comparison of the changes in air quality in Malaysia in the past decades.

II. EXPERIMENTAL

A. Sampling Sites

Setapak (3.21°N, 101.73°E) is a major suburb in Kuala Lumpur, Malaysia. It is located in the north-eastern part of Kuala Lumpur and has an area of 160 km². Twelve sites were selected in Setapak to collect the rainwater samples for this study. The sites are located in residential areas, adjacent to the highways and industrial zones. The residential areas are represented by R1 to R6, while the highways and industrial zones are represented by I1 to I6. Sampling sites I1, I2 and I3 are located within the light industrial area, while sampling sites I4, I5 and I6 are located nearby the busy roads.

B. Sampling sites details



Fig. 1 Map of sampling points in the study area

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TABLE I
LOCATION OF SAMPLING POINTS AND CODE NAMES

Code	Location	Latitude & Longitude	Description
Residential			
R 1	Tmn Melati	N03°13. 376' E101°43 .537'	Contains many houses, shops, 2 petrol stations and a railway station (LRT) while construction works carrying within the area.
R 2	Tmn Ibu Kota	N03°12. 822' E101°43 .062'	Surrounds by many houses, few shop lots, 2 petrol stations, a recreation park and Muslim cemetery. Night market is nearby in this area.
R 3	Genting Kelang	N03°11. 762' E101°42 .548'	Highly population centralised area. Consists of 5 condominiums, many shop lots, 2 schools and a Chinese temple.
R 4	Tmn Sri Rampai	N03°11. 824' E101°43 .919'	Recreation park for sporting area or playground uses. Commercial area is beside this area. Weekly night market occupies here.
R 5	Tmn Wangsa Melawa ti	N03°12. 277' E101°44 .605'	An oxidation pond located in front of this area. Another side is facing a commercial centre, Carrefour shopping mall and a petrol station.
R 6	Tmn Wangsa Maju Section 2	N03°12. 436' E101°44 .310'	Highly population centralised area mainly establishes by condominiums and shop lots, 2 schools, 1 railway station (LRT) and 1 mosque close by.
Industrial Area			
I 1	Leng Seng Omnib us	N03°11. 764' E101°42 .886'	Bus and maintenance centre, surrounds by residential houses and commercial centre such as bank, restaurants, clinic and etc.
I 2	PKNS Industri al Zone	N03°12. 025' E101°43 .443'	Industrial area contains steel manufacturing, vehicle service centre and other light industry works.
I 3	PKNS Industri al Zone 2	N03°11. 763' E101°43 .383'	Some neighboring extents have under construction project. A newly operating concrete batching plant and an international school are located in this area.
I 4	Jln Genting Kelang	N03°12. 007' E101°43 .060'	A busy roadway at all the time. While night time is carried widening and upgrading roadway. Construction work is right beside the sampling point.
I 5	Jln Genting Kelang Crossro ad	N03°12. 498' E101°43 .668'	Congested crossroad during on-off duty hours. A railway station (LRT), a Tamil temple and a recreation park with play ground are nearby.
I 6	MRR2	N03°12. 954' E101°44 .244'	Heavily vehicle flow during most the time. It has along with housing area, shops, a college and a university.

C. Sample collection

The rain precipitations in the Setapak area were collected weekly using homemade plastic bottle sampler. The dimensions of the plastic bottle sampler were 90mm in diameter and 230 mm in height. A plastic funnel was fixed at the sampler opening and the sampler remained open to the atmosphere during the sampling period. The mouth of the funnel was covered with a mesh (~1 mm) to prevent large particles fall into the container to prevent contamination of the rainwater sample. The outer surface of the container was

wrapped with a layer of aluminium foil to prevent the exposure of the collected rainwater samples to the direct sun light. The samplers were placed at about 2 m height from the ground on the lamp posts. The sampling period was 10 weeks, from 29th March to 7th June 2009.

D. Analytical procedures

After collection, the rainwater samples were transferred to a 100 ml polyethylene bottle and placed in a container with ice to transport samples to the laboratory. The samples were kept in the darkness at temperature of 4°C if they were not tested immediately. Major concentrations of F⁻, NO₂⁻, PO₄²⁻, SO₄²⁻, Cl⁻, Br⁻ and NO₃⁻ anions were evaluated using METROHM 881 Compact Ion Chromatograph (IC) Pro with 858 autosampler. The IC was equipped with 150mm/4.0mm Metrosep A Supp 5 anion column with Na₂CO₃ and NaHCO₂ as eluent. The injection volume was 20 ml and flow rate was 0.7 ml/min. The rainwater samples are expected to have low or none concentration of F⁻, NO₂⁻, PO₄²⁻ and Br⁻. In addition, pH, conductivity and TDS levels of the rainwater samples were tested using Scientific Accument Waterproof Hand-held Meters and Turbidimeter TN-100, Eutech Instruments. 50 mL of the rainwater samples were filtrated using 0.45µm pore size filter paper. This filtrated rainwater samples were tested for anions concentrations while the remaining infiltrated rainwater samples were tested for pH, conductivity, TDS and turbidity level. To maintain the accuracy of the results, rainwater samples were tested two times. The pH and turbidity equipment was calibrated before each time.

III. RESULTS AND DISCUSSION

A. Ions concentration

The average chloride ion concentration of rainwater samples from Setapak area ranged between 1.44 and 2.27 ppm. High concentration of chloride ion can be associated with the local and long range biomass burning spots as biomass burning produces minor amount of CH₃Cl that contribute to the chloride ion concentration.

The lowest and highest mean concentrations of nitrate ion were 2.81 and 4.03 ppm, respectively. Rainwater samples collected from sampling site R5 have the highest concentration of nitrate ions. The possible source of nitrate ions is from the vehicle emissions on the expressway. In addition, the mean nitrate concentration of the sampling sites R1 and I6, next to the expressway, were found to be sufficiently high, 3.48 ppm and 3.65 ppm, respectively. It is probable that the vehicles from the expressway greatly influenced the air quality at sampling sites R1, R5 and I6.

The average concentrations of sulphate ions ranged from 2.69 ppm to 4.17 ppm. Rainwater samples collected from sampling site I4 had the highest concentration of sulphate ions. The possible factor is presence of construction sites nearby the sampling site I4. Rainwater samples collected from sampling sites R2, R3, R4 and I5 had low concentrations of nitrate and sulphate ions. The possible factor is geographical location that is away from the major industrial processes and heavy vehicle emissions. Besides that, sampling sites R2, R4 and I5 share a

common feature, they are located close to the green park. [3] stated that urban trees can have significant effects on reducing air pollutants. It is believed that the park's greenery played significant role in reducing the air pollutants such as NO_x and SO_2 originated from vehicle emissions and industrial processes. The major anions concentrations in rainwater for residential (R1-R6) and industrial (I1-I6) sites are summarised in Table 2. All sites showed similar levels of nitrate and sulphate ions presence. It is believed that both anions are of anthropogenic origin since the distance between the sampling locations is relatively short. However, the concentrations of nitrate and sulphate anions for industrial area were slightly higher compared to the data for the residential area. Concentrations of fluoride, chloride and nitrite ions at the residential sites were found to be greater compared to the concentrations of the same ions at the industrial sites. The order of anion concentrations decreased as follows: $\text{NO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{PO}_4^{3-} > \text{F}^- > \text{NO}_2^-$.

Figure 2 displays the fractional contributions of anion species. Among all measured ions, nitrate is the major species, 37.4% to the total mass of anions. Sulphate is the second significant contributor and it accounts for 36.8% followed by chloride (21.5%); while nitrite, fluoride and phosphate ions were present at relatively low concentrations.

Bivariate plots in Figure 3 are used to identify the relationship between NO_3^- and SO_4^{2-} levels for the industrial and residential sites. It is observed that the N/S mole ratio for the residential sites is twice higher than N/S mole ratio, which is 1.1 reported for Petaling Jaya (Malaysia) in 1996 [1]. This indicates steady increment of the NO_x emissions over the past few years compared to the increment in SO_2 emissions, which are probably due to the increase of the number vehicles. Malaysia's statistics department released data on the number of registered vehicles that reached 15 millions in year 2007, which is approximately 31% growth since year 2002 [4]. Next, the N/S mole ratio for the industrial sites is found to be lower compared to the N/S mole ratio for residential sites. This clearly shows the greater presence of NO_x emissions in the residential areas relatively to the SO_2 presence in the industrial areas.

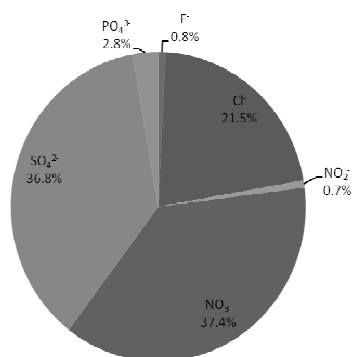


Fig. 2 Fractional contribution of anion species

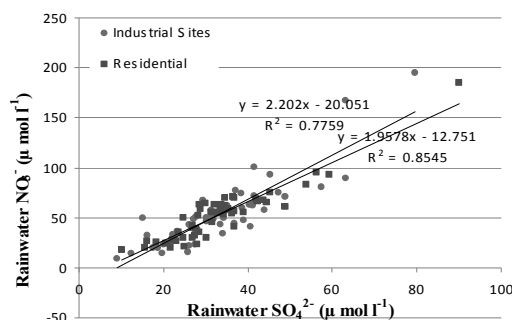


Fig. 3 Bivariate plot of wet-only weekly rainwater NO_3^- concentration versus rainwater SO_4^{2-} concentration.

B. pH

The average pH of rainwater for industrial and residential sites calculated are 6.0 and 5.6, respectively. Figure 4 shows the percentage of pH distribution frequency for 31 rain events. In total, 74 out of 120 rainwater samples showed alkaline range of pH, around pH 5.6 that is indicative of equilibrated atmospheric CO_2 dissolved in the cloud water [5]. These pH values mostly ranged between pH 6 to 7 (40%), while about 20% of rainwater samples were below pH 5. It is probable that most of the rainwater samples were affected by the particulate matter presence that contains such neutralising ions as Ca^{2+} and NH_4^+ . The particulate matter (PM_{10}) was found to have an ascendant trend for the industrial and urban land use after year 2002. However, its concentration was close to the acceptable level according to the Malaysian Air Quality Recommended Guideline [6]. However, the pH values tend to vary from alkaline range to acidic range within the sampling period as can be observed in Figure 5, the pH changes of rainwater indicate moderate fluctuations of alkali and acidic species presence.

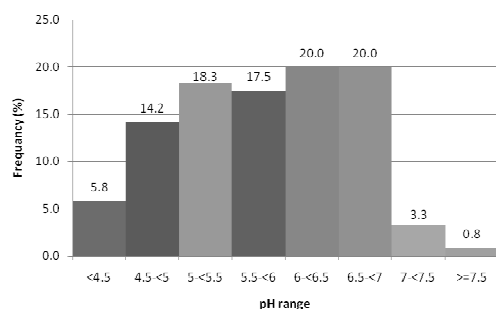


Fig. 4 Frequency distribution of pH

Generally, the rainwater samples from sampling site I4 were the most alkaline with the pH value of 6.5. This is probably associated with the vicinity of the construction works to the sampling sites. The construction processes such as land filling and excavation produce large amount of particulate matter that is mostly of alkaline character, and thus increase of rainwater pH is observed. For instance, the rainwater from sampling site I3 had an average pH of 6.3 due to the impact of the concrete batching plant located there. In addition, the concrete batching plant also affected the rainwater composition of the sampling site I2 which is located just 1 km away from the batching plant.

The mean pH of the rainwater samples for sampling sites R1 and I6 is 5.8 and 5.6, respectively. This indicates the impact of the NO_x of vehicle emissions originated of the expressway on the increase of the acidity of rainwater samples collected there.

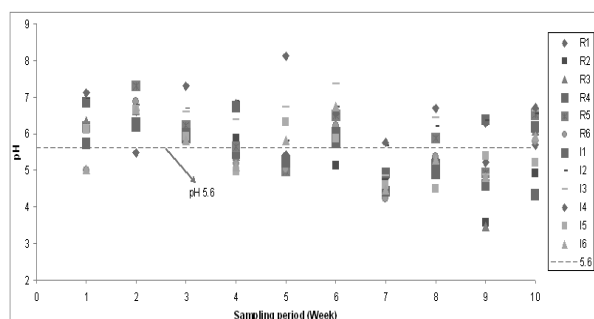


Fig. 5 Variation of rainwater pH (30th March and 7th June 2009)

C. Trajectories

Backward trajectories were calculated for certain rain events occurred in Setapak area during the study period. The calculations were done using the NOAA HYSPLIT (Hybrid Single Particle Lagrangian Integrated) Model [7] to trace the origin of the air masses for the rain events. Two-dimensional trajectories were calculated 72 hours before the time of the arrival at altitude of 1000 m and 3000 m AMSL (above mean sea level) and as arrival time at 10 UTC (1800) local time.

Generally, it is observed that the trajectories come from five directions: east, south-east, west, south-west and north-west. The main directions of the backward trajectories are east and south-east before mid-April 2009. It is possible to explain the highest concentration as compared to backward trajectories,

because the most important emission sources are the biomass burning spots in the Philippines situated at the east. According to [8], high concentrations of Ca^{2+} , NH_4^+ , Na^+ , Cl^- and Mg^{2+} could be due to the forest fires. Singapore Meteorological Services Division recorded high hotspot counts in the Philippines during that period.

After mid-April, the backward trajectories directions changed to the west, south-west and north-west. The source of high chloride ion concentration could be associated to the biomass burning in Sumatra situated at the south-west. High hotspot counts in Sumatra were recorded during that period. In addition, high concentrations of chloride ions are mostly attributed to the marine source as the wind carried the sea salt travelling across the Malacca Straits and South East China Sea region. Overall, 33 trajectories were generated. Figure 6 shows an example of four trajectories chosen at random.

D. Deposition flask

Deposition flux represents the rate of ionic element deposition across a unit area. The deposition flux for chloride, nitrate and sulphate ions is shown in Table 3. The deposition fluxes for nitrate and sulphate ions show high level for sampling sites R1 and R5 due to their geographical location that is close to the expressway. Emissions of the vehicles are the main factor of the high nitrate and sulphate ions presence. The main factor of the high wet deposition flux of SO_4^{2-} at sampling sites I1 and I2 is the industrial process; while high NO_3^- and SO_4^{2-} deposition flux for sampling site I4 can be associated to the construction activities in the vicinity to the sampling site.

It is reasonable that wet deposition fluxes for NO_3^- and SO_4^{2-} ions at sampling sites R1, R3, R4 and R6 are low as the sites are located in the residential areas, away from the influence of the anthropogenic sources. Though a concrete batching plant is next to the sampling site I3, the fluxes for NO_3^- and SO_4^{2-} are far below the fluxes of the industrial sampling sites I1 and I2. This suggests that the concrete batching plant did not contribute much NO_x and SO_x to the atmosphere. However, the concrete batching plant is the possible contributor of the particulate matter that is harmful to the human health. Lastly, the sampling site R5 located at a busy junction showed low wet deposition flux. The air nearby the sampling site I5 appeared to be purified by the greenery in the park that is close to the junction.

E. Comparison with other countries

The volume-weighted mean of pH and major anions concentration for all rainwater samples is compared with values from several rapidly developing and neighbouring countries as shown in Table 4. The observed pH values of this study are close to the pH values reported for Nakorn Pathom, Thailand; such alkaline pH was due to presence of the alkaline particles (including Ca^{2+} and NH_4^+) suspended in the air and it played important role in changing rainwater acidity [9].

TABLE III
 NOMINAL WEEKLY WET DEPOSITION FLUXES
 FOR NO_3^- AND SO_4^{2-}

Site	R1	R2	R3	R4	R5	R6
NO_3^-	109.5	76.7	71.1	89.3	127.5	81.3
SO_4^{2-}	115.8	83.3	82.2	87.4	116.8	85.5

Site	I1	I2	I3	I4	I5	I6
NO_3^-	90.0	100.2	92.4	106.7	80.0	98.4
SO_4^{2-}	102.6	117.6	80.9	131.5	84.2	89.3

IV. CONCLUSION

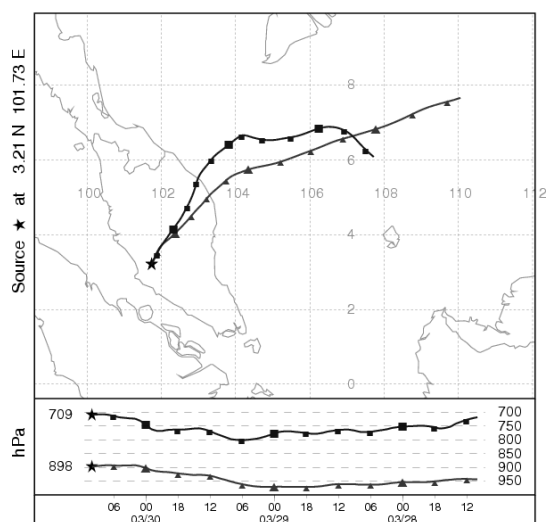
The rainwater chemical composition for residential and industrial areas in Setapak was investigated. It was observed that the nitrate and sulphate ions concentrations have increased over the past two decades mostly due to rapid economic development of Malaysia. The NO_3^- concentration increased from 0.41 to 3.32 ppm while SO_4^{2-} concentration has increased from 0.39 to 3.26 ppm. However, it was found that the chemical composition of the collected samples for both residential and industrial areas does not have significant differences. In this study, the rainwater composition was dominated by NO_3^- and SO_4^{2-} attributed to vehicle emissions, light industrial and construction processes. The average pH of the rainwater samples collected in Setapak was 5.8, which is slightly higher than average rainwater of pH 5.6. Besides that, the measured pH was much higher compared to study carried out in Singapore during Nov 1999 - Dec 2000 period, and in Petaling Jaya, Malaysia between 1981 - 1991 period. The main factors of such high pH are assumed to be the marine sources and forest fires based on the trajectories analysis. Lastly, the rainwater samples collected from sampling sites R2, R4 and I5 had lower ions concentrations compared to rainwater samples of other sites due to the greenery park areas presence.

Chloride concentration is much higher compared to other countries, except Jordan. Excluding for Jordan, nitrate concentration is much higher relatively to the data for other countries. According to numerous studies, increase in vehicles number and traffic density results in higher presence of NO_3^- ions, especially during dry seasons [10]-[12]. The concentration of sulphate is quite low as compared to data reported for China, Romania, Jordan and Singapore. However, nitrate and chloride ions concentrations are found to be higher in rainwater analyzed in this study compared to Singapore's data.

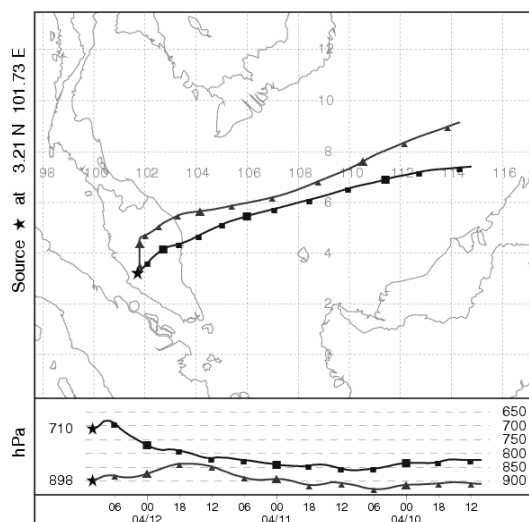
Overall, NO_3^- and SO_4^{2-} concentrations in rainwater increased from 0.41 to 3.32 ppm and 0.39 to 3.26 ppm, respectively, over the past two decades. It is evident that quite rapid development of Malaysia over the past two decades has resulted in the increased level of environmental concerns over the air quality, especially in the capital city.

TABLE IV
 VOLUME WEIGHTED OF MAJOR ANIONS CONCENTRATION IN RAINWATER AT SELECTED COUNTRIES

Site	China	India	Mexico	Romania	China	Jordan	Thailand	Singapore	Malaysia	This Study
Anion (ppm)	Jinhua	Roorkee	Rancho Viejo	Iasi	Shen Zhen	Ghore El-Safi	Nakorn Pathom	NUS campus	Petaling Jaya	Setapak
	Jan 2004~ Dec 2004	Monsoon Season (2001& 02)	2001~ 2002	Apr 2003~ Dec 2006	1986~ 2006	Oct 2006~ May 2007	Apr 2003~ Oct 2006	Nov 1999 ~ Dec 2000	1982~ 1991	Apr 2009~ Jun 2009
pH	4.54	7.05	4.50	5.92	5.02	6.91	6.00	4.2	4.65	5.79
F ⁻	0.17				0.09					0.07
Cl ⁻	0.30	1.93	0.36	1.33	1.34	5.05	0.44	1.21		1.87
NO ₃ ⁻	1.94	2.26	1.66	3.00	1.37	4.17	0.94	1.39	0.41	3.32
SO ₄ ²⁻	4.57	1.00	2.69	3.62	3.57	5.40	1.35	4.01	0.39	3.26
PO ₄ ²⁻							0.003			0.61
Area Type	urban	urban	rural	urban	urban	rural	rural	coastal	urban	urban
Reference	[10]	[13]	[15]	[14]	[12]	[11]	[9]	[8]	[2]	



(a)



(b)

Fig. 6 Backward trajectories samples

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