

## ACID RAIN AND WELL WATER ACIDIFICATION RATE IN INDUSTRIAL AREA

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**Abstrak.** In the area of Cibinong-Citeureup Bogor has many industries, dusty and there are has been acid rain. About 75.63 % people in this area take well water for drinking. It was studied impact of acid rain for well water degradation in order to know the trend and rate of well water pH change. Preliminary research was done in order to make sure the effect of acid rain to well water using soil column leaching simulation. The main research was done by pH monitoring of acid rain and well water in the specific location. The pH of acid rain was monitored in the first 30 minutes on 12 locations, and the well water pH was measured. The acidity (pH) was measured using pHmeter electronic. The rate of pH change was calculated by first order reaction. The result showed that the well water acidity has uptrend (the pH to be lower). The acid rain has a little impact to the acidity of well water ( $r = 0.68$ ). The rate of acidity of well water has constant value,  $k = 0.004$  year<sup>-1</sup>.

**Keywords:** acid rain; pH; acidity; leaching; well water

### I. INTRODUCTION

The Cibinong-Citeureup Bogor area is an industrial area with dense transportation. The number of large-medium manufacturing industries reaches 423 with two cement industries and 45 mining/quarrying industries, the total number of businesses reaches 3,598 companies including service businesses, and employs a total of 149,698 workers. The population density in four sub-districts, namely Gunung Putri Sub-district, Citeureup Sub-district, Cibinong Sub-district and Klapanunggal Sub-district, respectively reaches 5,345; 2,594; 5,828; and 786 people km<sup>-2</sup>, or an average of 3,638 people km<sup>-2</sup>. Based on data from the Bogor Regency PDAM in the four sub-districts, there are 23,334 households of drinking water customers from 195,121 households. The number of families subscribing to PDAM water only reached 11.96%, and as many as 88.04% of the population consumed groundwater/well water, springs, and river water, which used well water reaching 75.63% (BPS Bogor Regency [1]). The data shows that most families rely on groundwater/well water as a source of water for daily needs including drinking water needs. The domestic water needs of a household can reach 60 liters per day per person. Well water as a source of drinking water must meet the quality of drinking water according to PerMenKESNo.492/MENKES/PER/IV/2010. Three requirements that must be met are physical, chemical, and biological parameters. Physically, clean water is clear, odorless, and tasteless, with a normal temperature below ambient air temperature. Chemically, the chemical constituent content of drinking water must be below the established standard quality value, especially for acidity (pH) in the range

of 6.5-8.5. The acidity of well water can be affected by various things including the soil, and the quality of water input that seeps into the ground. The largest well water input is rainwater. The quality of rainwater that falls around the well affects the quality of the well water.

Rainwater quality monitoring in cities relatively close to the research area showed the occurrence of acid rain with a tendency for rainwater pH to continue to decline. Based on the Eanet report, Serpong experienced the highest intensity of acid rain (pH 4.63) and did not show any significant pH changes for 8 years. Jakarta experienced high intensity acid rain and the pH continued to decline (average pH 5.18). The city of Bandung has an average annual rainwater pH for 7 years of around 4.99. Acid rain has also occurred in Cisarua-Bogor with a frequency of occurrence of 72% (Budiwati et al. [2]). Observations of rainwater in various places in the Bogor district area showed that the quality of rainwater has an average pH of 5.09 (Diapari [3]). The monitoring data shows that the Bogor area and its surroundings have experienced continuous acid rain. A case study of acid rain in the Cibinong-Citeureup Bogor Industrial Area shows that acid rain occurs with high intensity, reaching a pH of 4.7 concentrated in areas around the industrial center with a radius of several km. The intensity of acid rain decreases with increasing distance from the industrial center up to a radius of 10 km and returns to normal (pH > 5.6) at a distance > 20 km (Sutanto et al. [4]). A total of 24 wells from residents distributed in the Citeureup-Cibinong industrial area of Bogor Regency in 1995 had an average pH of 5.09 with a range of 3.99–7.15 (Komala et al. [5]). In 2000, the average pH of the residents' well water was 4.63 with a nitrate concentration of

0.25 ppm and sulfate of 4.85 ppm (Sutanto et al., [6]), and in 2001 the average pH was measured at 4.11 with a nitrate content of 6.19 ppm and sulfate of 5.44 ppm (Iryani [7]). Changes in the decline in the quality of well water in this area, namely the tendency for a decrease in pH values and the possibility of increasing levels of nitrate, sulfate and metals in well water, are possible due to the high acid rain that occurs in this area. The objectives of this study are: (1) evaluation and monitoring of the acidity of rainwater and well water; (2) seeking a correlation between the acidity of rainwater and well water; (3) determining the equation that connects the pH of rainwater and well water; (4) determining the equation for the rate of acidification of well water in the Cibinong-Citeureup industrial area, Bogor Regency.

## II. RESEARCH METHODS

The research area is the Cibinong-Citeureup Industrial Area, Bogor Regency at latitude: 106o50'34"-106o54'46" East Longitude and 6o25'20"- 6o31'50" South Latitude. The research area is 100 km<sup>2</sup>. In accordance with the research objectives, the research methods are described separately to answer each specific research objective. Two preliminary studies were conducted, first: simulation of the effect of rainwater acidity and its effect on well water acidity using leachate columns, and the second preliminary study: Daily temporal effect on well water acidity. The second preliminary experiment aims to see the daily temporal effect on well water pH. 5 wells were sampled at different locations at 8, 10, 11, 13, 16, and 19 and the pH was measured directly. Evaluation and Monitoring of Acid Rain Data Collection Method [8]. Acid rain monitoring is carried out by sampling rainwater in the research area. There are 12 sampling points or locations and they are distributed in the research area. Analyzed Parameters. Rainwater analysis includes physical parameters, namely temperature and electrical conductivity and chemistry including pH. Observations of temperature, electrical conductivity, and pH were carried out directly in the field using a pH meter and digital conductometer. Data Analysis Method. The rainwater data obtained was evaluated by comparing it with control rainwater data and rainwater data from three previous studies. Determining the Correlation of Rainwater Acidity with Well Water Acidity. The results of the analysis of physical and chemical parameters of well water and rainwater were each grouped to obtain a data series. Determining the Equation that Connects Rainwater Acidity and Well Water Data Collection Method and pH Measurement. Then Determining the Rate of Well Water Acidification

## III. RESULTS AND DISCUSSION

The results of observations of pH in leachate depend on the acidity level of artificial rainwater. Figure 1 shows the pattern of changes in leachate acidity at various acidities of artificial rainwater that is flowed into the leach column. In artificial rainwater flow pH 4.5 (Curve A) causes the leachate

pH to fluctuate between 6.94, 6.83, 7.12, and back to 6.94. This shows that the soil has the ability to neutralize the pH of artificial rainwater (pH<sub>air</sub>). Fluctuations in leachate pH can be caused by the non-linear nature of the soil buffer [9]. In artificial rainwater flow pH 4.0 (Curve B) initially causes the leachate pH to become 7.01, then the pH tends to decrease to 6.83. This can be caused by the soil buffer capacity decreasing due to some of the base cations that act as buffers being leached. In the flow of artificial rainwater pH 3.5 (Curve C), initially the pH of the leachate was 6.61 and then fluctuated and finally became 6.59.

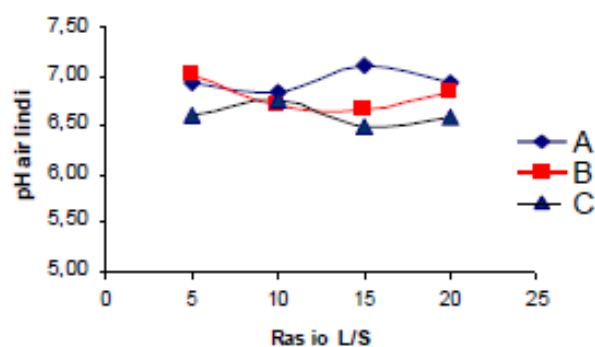


Figure 1. Pattern of changes in leachate pH in column experiments due to increasing L/S values at various pH of artificial rainwater. Artificial Rainwater A = pH 4.5; B = pH 4.0; and C = pH 3.5.

The lower the pH of the artificial rainwater, the faster the pH of the leachate decreases [10]. However, because the nature of the soil buffer capacity is not linear, fluctuations in the pH of leachate are obtained where it can be seen that at pH 4.5 artificial rainwater, initially the rainwater is neutralized to pH > 7, then with the continuous flow of artificial rainwater the soil can no longer neutralize the rainwater so that the pH of the leachate continues to decrease with the equation  $pH_{air} = 0.0585 \ln(L/S) + 6.8161$ . The ability of the soil to neutralize rainwater pH is due to the soil having base cations that can be exchanged with acid cations (especially H<sup>+</sup> ions). The ability to neutralize acid by the soil is expressed in terms of ANC (anion neutralizing capacity), in units of meq L<sup>-1</sup>, which is the difference between the number of base anions and cations with acid anions and cations. Calculations based on soil data at the Gunung Putri research location and referring to the ANC calculation according to Rose et al. [11] obtained a fairly high ANC value of 15.04 mmol L<sup>-1</sup>. At an artificial rainwater pH of 4.0, the change in leachate pH (pH<sub>air</sub>) decreased more sharply with the equation:  $pH_{air} = 7.2045 (L/S) - 0.0244$ . At an artificial rainwater pH of 3.5, it caused a different pattern of leachate pH changes. Artificial rainwater cannot be completely neutralized but leachate only reaches pH 6.76 then drops to around pH 6.59 following the equation  $pH_{air} = 6.7565(L/S) - 0.0091$ . This very small change pattern can be caused by the almost achieved equilibrium or equality between the acid strength and the soil's ability to withstand the rate of acidification due to acid rain. The acidity of leachate will be constant or stable when

the ratio of rainwater to soil volume (L/S) reaches 10 (Sloot et al. [12]). The addition of artificial rainwater volume exceeding L/S>10 will not significantly change the pH of leachate. If we take into account the soil volume of 5 kg, the L/S ratio reaches 10 when the leachate reaches 50 liters

Table 1. Results of leachate pH calculation based on the graph equation in Figure 1

L/S	pH Rainwater		
	4,5	4	3,5
1	6,82	7,20	6,76
3	6,88	7,01	6,69
6	6,92	6,90	6,65
8	6,94	6,85	6,63
10	6,95	6,81	6,62

Calculation of leachate pH with this equation at the L/S ratio = 10, obtained pH = 6.95 (Curve A), pH = 6.81 (Curve B), and pH = 6.62 (Curve C) as presented in Table 1. The leachate pH data at the L/S ratio of 10 is plotted against the pH of artificial rainwater, a graph is obtained with a line equation stating the relationship between pH al and pH ah. The relationship between the two is directly proportional, meaning that the higher the pH of artificial rainwater, the higher the pH of leachate. The relationship is strong following the equation  $pH_{al} = 1.3155Ln(pH_{ah}) + 4.9765$  and 99% can be explained ( $R^2 = 0.99$ ).

*Temporal Observation Results of Well Water pH*

The results of well water pH observations at various sampling times in areas that often experience high intensity acid rain are presented in Table 2. The variation in pH over time is in a very small range between 0.011 to 0.085 (average  $\pm 0.061$  units) possibly due to temperature variations or carbon dioxide solubility. Meanwhile, the measurement error of the tool in this case the pH meter used has 2 digits behind the comma with a tolerance of the measurement value is  $\pm 0.05$ . The % RSD value is in the range of 0.25 to 2.47, with an average of 1.43%. From this % RSD data, the value of which is <3% explains that the pH of well water is not affected by the time in one day of observation.

Table 2 Observation data of well water pH at various times in a day

time sampling	Well Location				
	1	2	3	4	5
08.00-09.00	4,24	4,30	4,01	4,78	4,37
10.00-11.00	4,24	4,17	4,05	4,80	4,34
13.00-14.00	4,10	4,11	3,92	4,92	4,36
16.00-17.00	4,30	4,12	4,04	4,75	4,36
19.00-20.00	4,24	4,20	3,93	4,69	4,36
Average	4,22	4,18	3,99	4,79	4,36
Minimum	4,1	4,11	3,92	4,69	4,34
Maksimum	4,3	4,3	4,05	4,92	4,37
deviationStandard	0,07	0,076	0,061	0,085	0,011
%RSD	1,75	1,83	1,53	1,77	0,25

Description: 1 = Kranggan Puspasari; 2 = Kranggan G. Putri 1; 3 = Kranggan G Putri 2; 4 = Tlajung Udik; 5 = Ps. Average SD = 0.061 and average RSD = 1.43%

The results of mapping the distribution of acid rain with a pH isopleth map (Sutanto et al.[16]) show that there are areas that continuously experience high-intensity acid rain and there are also areas that only occasionally experience high-intensity acid rain. Areas that often experience high-intensity acid rain are Cibinong Village (partially), Kranggan Village (partially), Puspasari Village, Gunung Putri Village (partially), Citeureup Village, West Karanga Asem Village (partially), and East Karang Asem. Areas that rarely experience high-intensity acid rain include: Sentul Village, Klapanunggal (Narogong), Wanaherang, Tajur, West Cibinong, and Cilangkap Village, Bogor Regency.

*Evaluation and Monitoring of Acid Rain and Well Water Acidity*

Changes in rainwater acidity (pH) at each location in the research area in areas that often experience high intensity acid rain, on average changed from 4.86 to 4.40. The average pH decrease occurred over 10 years by 0.46 pH units. Although this pH change is not apparent ( $P = 0.315$ ). The lower the pH, the higher the levels of pollutants that cause acid. Data on dust levels in this area are between 200-315  $\mu\text{g m}^{-3}$ , and NO<sub>2</sub> levels reach 700  $\mu\text{g m}^{-3}$ , while SO<sub>2</sub> levels are relatively small, and dust levels reach 555.6  $\mu\text{g m}^{-3}$  (DTRLH [13]). NO<sub>2</sub> pollutants react with rainwater to form acid rain. The higher the levels of NO<sub>2</sub> pollutants, the higher the acidity of rainwater, the lower the pH of rainwater. Areas that rarely experience high intensity acid rain include Wanaherang Village, Cibinong, Sentul, and Narogong Klapanunggal. In this area, the pH of acid rain is relatively stable at around five and even tends to increase. The average pH of rainwater in this area increased from 5.12 to 5.52. The levels of NO<sub>2</sub> pollutants in this area range from 16.34  $\mu\text{g m}^{-3}$  to 26.12  $\mu\text{g m}^{-3}$ , and the levels of SO<sub>2</sub> pollutants range from 15  $\mu\text{g m}^{-3}$  to 94.90  $\mu\text{g m}^{-3}$ , and the levels of dust range from 17.12  $\mu\text{g m}^{-3}$  to 118.87  $\mu\text{g m}^{-3}$  (DTRLH [13]). Figure 2 shows the differences in the patterns of changes and levels of acidity of rainwater in areas that often and rarely experience high intensity acid rain. Figure 2 Graph of changes in rainwater pH in the research area in areas that often (a) and rarely (b) experience high intensity acid rain.

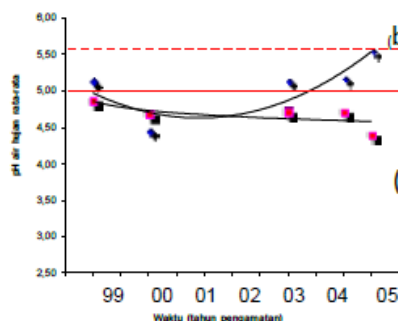


Figure 2 Graph of changes in rainwater pH in the research area in areas that often (a) and rarely (b) experience high intensity acid rain.

### Well Water Acidity

Well water quality monitored is which presents series of well water pH data at various sampling locations in areas that often experience high intensity acid rain. It appears that the pH of well water varies greatly, and the most extreme lowest measured pH = 3.46 is well water in Puspanegara II. There were only 2 wells that had a well water pH >5.0, the rest of the well water had a pH below 5. At the end of all well water had a pH <5.0. The low pH of well water is closely related to the low pH of rainwater in this area, and the low pH of rainwater is closely related to the high levels of pollutants that cause acid rain including levels. Areas that rarely experience high intensity acid rain in the research area were identified from the results of acid rain mapping. The value of the terminated coefficient  $R^2 = 0.46$ , or the value of the linear correlation coefficient  $r = 0.68$ . The correlation coefficient (r) of 0.68 explains that there is a direct relationship between the pH of well water and the pH of rainwater.

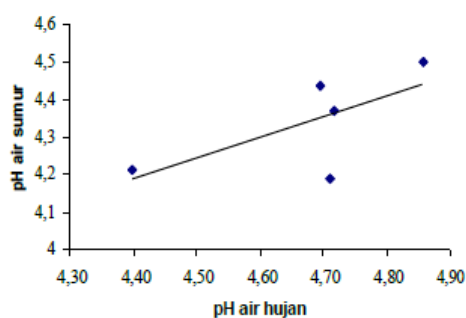


Figure 4 Graph of the relationship between the acidity level of rainwater and the acidity of well water in areas that often experience high-intensity acid rain.

Well water in the research area is shallow well water with a depth of between 10 and 15 m. The depth of this well has not reached the rock layer where water can presented in Table 3, which presents series data on well water pH in stored for quite a long time, but the existence of well water is very dependent on rainwater. Thus, rainwater is the main input for well water, and therefore the quality of rainwater affects the quality of well water. The results of the pH plot against time obtained a correlation coefficient of  $r = 0.48$ , meaning that the pH of well water in areas that rarely experience high-intensity acid rain cannot be said to be influenced by the pH of rainwater. This can be caused by two things, first in areas that rarely experience acid rain have the opportunity to neutralize the acidity of rainwater by the soil better because the time available for neutralization is quite long compared to areas that continuously experience high intensity acid rain [14], and second, the input of acid from the atmosphere (nitrate and sulfate) is slightly less than in areas with high intensity acid rain, the ANC value is high, so the acidity of rainwater is not strongly correlated with the acidity of well water.

### Mathematical Relationship Between Well Water pH and Rainwater pH

The plot between the acidity of rainwater and well water in areas that often experience high intensity acid rain in

the Cibinong-Citeureup industrial area, Bogor Regency produces a curve that describes the relationship between changes in the acidity of well water and the acidity of rainwater. The relationship between the acidity levels of rainwater and well water is directly proportional. The dependence of well water pH on rainwater pH follows the equation  $pH_{\text{as}} = 2.39e0.128(pH_{\text{ah}})$  with  $R^2 = 0.46$  or  $r = 0.68$ . Although the relationship between the pH of well water and rainwater is not very strong, there are other factors that affect the acidity of well water besides the acidity of rainwater, for example the hydrolysis of aluminum ions in well water. The average Al content in well water is 0.806 mg L<sup>-1</sup> (Appendix 10). Hydrolyzed aluminum ions produce H<sup>+</sup> ions which can acidify well water, In areas that rarely experience high intensity acid rain, the relationship between well water pH and rainwater pH is weak  $r=0.48$ . This can be caused by low acid input from rainwater, the ANC value is quite high and so has better buffer properties than soil in areas with continuous high acid rain.

## IV. CONCLUSION

The results of the study can be concluded that in areas that continuously experience high intensity acid rain, the acidity of rainwater continues to increase, reaching an average pH of 4.40. The acidity of well water tends to increase, reaching an average pH of 4.60. The acidity level of well water is directly proportional to the acidity level of rainwater with a relationship that is not too strong ( $r = 0.68$ ). The equation for the rate of acidification according to the first order reaction with a rate constant value,  $k = -0.004 \text{ year}^{-1}$ . In areas that rarely experience high intensity acid rain, the pH of well water does not depend on the pH of rainwater ( $r = 0.48$ ).

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