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The Effect of SO$_2$ and NO$_2$ from Transportation and Stationary Emissions Sources to SO$_4^{2-}$ and NO$_3^-$ in Rain Water in Semarang

S. Sudalma$^{a, b}$, P. Purwanto$^{a, c}$ and Langgeng Wahyu Santosod$^d$$^*$

$^a$Doctorate Program in Environment Studies Diponegoro University, Semarang 50241, Central Java, Indonesia
$^b$Occupational Health and Safety Office, Semarang 50263, Central Java, Indonesia
$^c$Department of Chemical Engineering, Diponegoro University, Semarang 50275, Central Java, Indonesia
$^d$Faculty of Geography Gadjah Mada University, Yogyakarta 55281, Indonesia

Abstract

Semarang is the central of economic growth in the Central Java; grow as the city of industry, trade, services and education. One of the impacts of urban development is air pollution and acid rain. This study aims to analyse the impact of emissions of SO$_2$ and NO$_2$ emissions from stationary sources and mobile sources of the content of SO$_4^{2-}$ and NO$_3^-$ in the rain. Research method using Gaussian distribution models to determine the contribution of SO$_2$ and NO$_2$ emissions from 98 industrial stacks and transport activity of 43 major roads in the city of Semarang and its correlation with SO$_4^{2-}$ and NO$_3^-$ in the rain at points monitored. Location of monitoring conducted at 13 monitoring points includes residential areas, industrial areas and areas with dense transport. Number of samples rainwater 131 samples during the period February - May 2013. SO$_2$ emissions from stationary sources and transportation caused 1.1 to 1.9%. Whereas NO$_2$ impact of emission sources in Semarang on nitrates in rain water was 27.1% of rain events during the period January - June 2013.

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* Corresponding author. Tel.: +85-225145990.
E-mail address: dalma.chem.gm88@gmail.com
1. Introduction

Each nation seeks to increase the economic growth through investment and industrialization. Economic activity requires a driver in the form of energy. Currently almost all of the energy as an economic powerhouse is a fossil fuel (coal and oil) to meet the power plant, industrial and transportation [1-3]. Economic growth in Asia in two decades led to the energy consumption of fossil fuels is expected to double. It is estimated that in 2030 the consumption reached 6.3 Btoe (billions tons of oil equivalent) caused by urbanization, industrialization and population growth[4]. The use of fossil fuels can be a driver of increased emissions of SO2, NO2 and other pollutants and can cause environmental problems such as air pollution and acid rain [2 - 6]. Industry growth by 1% resulting in an increase in total pollutant emissions by 11.8% [7].

The main source of anthropogenic SO2 is the use of coal and petroleum as an energy source. Coal containing sulphur and coal quality is determined by the content of sulphur, low-sulphur coal (<1% S), medium sulphur (1-<3% S) and high sulphur (≥ 3% S) in the form of pyrite (FeS2) and organic sulphur [8]. Burning of pyrite forming SO2 and only a small percentage (1-2%) to form SO3 [9]. In addition to using coal, most industrial uses heavy oil fractions as fuel. Fly ash is being emitted in addition to containing sulphur also contain metal ions that can be hydrolysed which act as agents strong acids [10].

NO2 is the source of high temperature combustion in motor vehicles using either gasoline or diesel fuel. Nitrogen oxide emissions from the burning of the majority (85-97%) in the form of NO. The atmospheric NO rapidly oxidized by ozone to form NO2 [11, 12]. NO2 emissions from motor vehicles are estimated using the ratio (ratio) between a mixture of nitrogen oxides (NO + NO2) with a total oxidants (O3 + NO2). NO2 emissions from motor vehicles less than 10% in the 1990s and increased to 20% in 2009. The increase in primary NO2 emissions due to the use of a catalyst in a motor vehicle. In the period 1994 - 2004 Conversion of NO to NO2 through photochemical reactions contributed as much as 51%, while the primary emissions by 31%. In the period 2005 - 2009, the contribution of the chemical conversion dropped from 54% in 2005 to 43% in 2009. The primary NO2 emissions increased from 32% to 44%. The increase in primary NO2 fraction caused by the use of catalysts in modern diesel engines. NO3 in the atmosphere occurs chemical equilibrium is affected by meteorological circumstances. Fraction NO emissions quickly in a matter of seconds to minutes oxidized by O3 to NO2. On the afternoon with the help of sunlight, NO2 is converted to NO and O3 [13].

Pollutants in the atmosphere experienced displacement of sources spread in the environment [14]. Displacement caused by wind is called advection (advection). In fact, the movement of pollutants is not purely due to advection. In displacement, pollutants have spread (dispersion), occurs distribution of pollutants vertical and horizontal direction and there is mixing with the air led to a dilution or react with other compounds [15]. Transport of pollutants influenced by meteorological circumstances [14] as well as the lifetime of pollutants [16]. The shorter lifetime of chemical species, then the distance deployment / transportation are getting shorter, while the longer lifetime of pollutants distance spreading farther and engage in global transport of pollutants [16]. Sulphur dioxide (SO2) is a gas that has a long lifetime and the rate of reaction with other species walked slowly so that the distribution of SO2 and SO3 cause the formation of secondary pollutants such pollutants are SO42- spread away from the source of emission [2, 17, 18].

Acid rain is rain water that has a pH below 7. In the absence of pollution in the atmosphere, the pH of rain water can reach 5.6 due to the formation of CO2 - H2CO3. Although the amount of CO2 in the atmosphere is abundant but H2CO3 much weaker than H2SO4 and HNO3, [9, 19]. In the industrial area, the pH of rain water can reach 4.3 caused by emissions of NO2 and SO2 [19 - 23]. The degree of acidity (pH) of rain water is also influenced by particles in the atmosphere and rainfall intensity [24]. SO42- and NO3- formation as a major component of acid rain is influenced by the position of geography, topography, sources of emissions (SO2 and NOx), meteorology and climatology [9, 25, 26].

Semarang is the capital city and a center of economic growth in central Java develop as a city of industry, commerce, services and education. The average industrial growth in the city of Semarang in the last 5 years at 1.4% with the use of coal and petroleum as an energy source. The development of industrial zones in the region, especially in the border area development. South: Srondol Kulon. East: Terboyo Industrial Area, Muktiharjo, Banjardowo and Plamongan cider. West: Regional Industrial Monument, Temple, Tambakaji and Jatibarang.

The purpose of this research is to examine the impact of emissions of SO2 and NO2 from mobile sources and mobile sources of emissions to SO42- and NO3- in rainwater in Semarang period February - May 2013.
2. Method

The study was conducted with laboratory analysis $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ in the period rainwater month period from February to May 2013 at the 13 monitoring location were spread in Semarang city covers an area of residential areas, industrial areas and areas with dense transport. $\text{SO}_4^{2-}$ analysis using SNI 6989.20-2004 and $\text{NO}_3^-$ analysis using the SNI 6989.74-2004. The addition of $\text{SO}_2$ and $\text{NO}_2$ at points monitored from transportation activities and emission sources do not move during rain events is calculated based on the emission of $\text{SO}_2$ and $\text{NO}_2$, wind direction, wind speed and atmospheric stability [27]. The addition of $\text{SO}_2$ and $\text{NO}_2$ of transport activity was calculated based on the density of vehicles and motor vehicle emission factor according MoE No. 12/2010 of 43 main roads include highways, arterial roads and collector roads using Gaussian distribution model of the line source. The addition of $\text{SO}_2$ and $\text{NO}_2$ of 100 emission sources do not move calculated using the Gaussian distribution model of a point source [27]. Source of Data $\text{SO}_2$ and $\text{NO}_2$ emission source does not move from RKL-RPL (environmental management plan - environmental monitoring plan) firms in the city of Semarang. Atmosphere state data in the form of wind direction, wind speed, solar radiation, air temperature and precipitation derived from the Meteorology and Geophysics Agency (BMKG) Semarang. Atmospheric stability is determined by the data intensity of sunlight and wind speed [27] with the data source from BMKG Semarang. $\text{SO}_4^{2-}$ theoretical calculations and $\text{NO}_3^-$ in rain water using a washout coefficient [28].

3. Results and Discussion

Physical condition of Semarang City has a varied surface, hilly areas, lowlands and coastal areas with an altitude of 0 up to 348 meters above sea level. Condition of the land slopes Semarang City is divided into four (4) types of slope, namely: Slope I (0-2%) include Sub Genuk, Pedurungan, Gayangsari, East Semarang, Semarang North, Monument and some Tembalang region. Slopes II (2-5%) covering Western District of Semarang, Semarang South, Candisari, Gajahmungkur, Gunungpati and Ngalian. III slopes (15-40%) covers an area of around Kaligarang and time Kreo (Sub Gunungpati), Wonoploomon (District Mijen), some districts and Sub Banyumanik, Candisari. IV slopes (> 50%), covering some districts Banyumanik (southeast) and part of Gunungpati.

The predominant wind direction daily in Semarang in January came from the north to the west, the moon February - March dominant wind direction is from the Northwest. End of April to mid-May dominant wind direction is from the east. Mid-May to the end of June the wind much going evolving from the northwest, north, northeast, and east to southeast. Daily atmospheric stability in Semarang in January-February 2013 in the category tend not stable (Class B). March-June 2013 in the category tend atmospheric stability unstable, very unstable (Class AB).

Total $\text{SO}_2$ emissions from 100 stationary sources and 43 main roads in Semarang is 28.75 tons/day and total emissions of $\text{NO}_2$ is 39.09 tons/day. Pollutants $\text{SO}_2$ and $\text{NO}_2$ emissions from sources spread following the direction of the wind [27].

Concentration of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ in rain water are presented in Table 1 and Table 2. Sulphate and nitrate in rainwater is an accumulation of the effects of pollutant transport and reaction products of oxidation of $\text{SO}_2$ and $\text{NO}_2$ in the atmosphere dissolves in rain water. Differences $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ concentrations at each monitoring location due to differences in the distance to the source of emissions, concentrations of $\text{SO}_2$ and $\text{NO}_2$ in the atmosphere and precipitation [17, 29].

<table>
<thead>
<tr>
<th>Monitoring Sites</th>
<th>M</th>
<th>MD</th>
<th>VR</th>
<th>SD</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beringin</td>
<td>3.81</td>
<td>2.82</td>
<td>7.89</td>
<td>2.81</td>
<td>1.00</td>
<td>8.25</td>
</tr>
<tr>
<td>Candisari</td>
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<td>2.79</td>
<td>2.57</td>
<td>1.60</td>
<td>1.00</td>
<td>5.87</td>
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<tr>
<td>Kandri</td>
<td>2.43</td>
<td>1.98</td>
<td>2.54</td>
<td>1.59</td>
<td>1.00</td>
<td>5.60</td>
</tr>
<tr>
<td>Wijaya Kusuma Industrial Park</td>
<td>2.86</td>
<td>2.33</td>
<td>3.22</td>
<td>1.79</td>
<td>0.93</td>
<td>6.68</td>
</tr>
<tr>
<td>Kramas</td>
<td>5.34</td>
<td>5.44</td>
<td>6.69</td>
<td>2.58</td>
<td>2.00</td>
<td>7.26</td>
</tr>
<tr>
<td>Meteseh</td>
<td>1.69</td>
<td>1.50</td>
<td>0.99</td>
<td>0.99</td>
<td>0.98</td>
<td>2.98</td>
</tr>
<tr>
<td>Mijen</td>
<td>4.16</td>
<td>4.66</td>
<td>7.49</td>
<td>2.74</td>
<td>1.00</td>
<td>6.33</td>
</tr>
<tr>
<td>Ngaliyan</td>
<td>2.82</td>
<td>2.44</td>
<td>2.37</td>
<td>1.54</td>
<td>2.00</td>
<td>4.31</td>
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<tr>
<td>Sendang Mulyo</td>
<td>9.16</td>
<td>5.52</td>
<td>53.40</td>
<td>7.30</td>
<td>3.00</td>
<td>26.00</td>
</tr>
<tr>
<td>Sta. BMKG</td>
<td>2.74</td>
<td>4.88</td>
<td>10.83</td>
<td>3.29</td>
<td>1.00</td>
<td>10.00</td>
</tr>
</tbody>
</table>
Table 2. Concentration of NO$_3^-$ (mg.l$^{-1}$) in the rainfall, mean (M), median (MD), variance (VR), std. Deviation (SD), minimum (Min), maximum (Max).

<table>
<thead>
<tr>
<th>Monitoring Sites</th>
<th>M</th>
<th>MD</th>
<th>VR</th>
<th>SD</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bringin</td>
<td>0.59</td>
<td>0.30</td>
<td>0.33</td>
<td>0.58</td>
<td>0.14</td>
<td>1.88</td>
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<tr>
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<td>0.56</td>
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<td>1.49</td>
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<td>0.28</td>
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<td>0.32</td>
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<td>0.32</td>
<td>0.3</td>
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<tr>
<td>Kramas</td>
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<td>0.3</td>
<td>0.18</td>
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<tr>
<td>Meteseh</td>
<td>0.19</td>
<td>0.19</td>
<td>0.01</td>
<td>0.09</td>
<td>0.03</td>
<td>0.36</td>
</tr>
<tr>
<td>Ngaliyan</td>
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<td>0.18</td>
<td>0.01</td>
<td>0.08</td>
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<tr>
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<td>0.76</td>
<td>0.87</td>
<td>0.21</td>
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<td>0.57</td>
<td>0.53</td>
<td>0.73</td>
<td>0.25</td>
<td>2.52</td>
</tr>
<tr>
<td>Sta. Maritim Tanjung Mas</td>
<td>0.43</td>
<td>0.46</td>
<td>0.05</td>
<td>0.22</td>
<td>0.16</td>
<td>0.78</td>
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<tr>
<td>Tlogosari</td>
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<td>0.64</td>
<td>0.80</td>
<td>0.49</td>
<td>2.89</td>
</tr>
<tr>
<td>Wonodri Sendang</td>
<td>0.83</td>
<td>0.68</td>
<td>0.51</td>
<td>0.71</td>
<td>0.17</td>
<td>2.64</td>
</tr>
</tbody>
</table>

Bivariate correlation analysis is used to measure the degree of association between the dependent variable (sulfate ions in rainwater) with free variables (precipitation and SO$_2$). In this correlation is the total concentration of SO$_2$ from stationary sources and mobile sources. The results of the Pearson correlation between sulfate in rainwater with rain and SO$_2$ are:

i. The correlation between sulfate precipitations
   Pearson correlation level $r = -0.266$ showed weak correlation levels ($r = 0.201$ to $0.400$). Toward a negative correlation indicates when rainfall greater the concentration of sulfate in rainwater getting smaller.
   The significance of $p = 0.003$ ($p < 0.005$) showed a significant relationship.

ii. The correlation between the sulfate emissions of SO$_2$ from stationary sources
   $r = 0.023$ indicates that both variables have a weak correlation ($r < 0.02$).
   $p = 0.779$ showed that the correlation between the two variables was not significant ($p > 0.005$).
   So that the SO$_2$ from the industry has little effect on sulfate in rainwater.

iii. The correlation between sulfates by the addition of SO$_2$ from mobile sources of emissions of SO$_2$
   $r = 0.113$ indicates that both variables have a very weak correlation ($r < 0.02$).
   $p = 0.215$ showed that the correlation between the two variables was not significant ($p > 0.005$).
   Thus, SO$_2$ from mobile sources have little effect on sulfate in rainwater.

Bivariate correlation analysis is used to measure the degree of association between nitrate ions in rainwater with precipitation and NO$_2$ from stationary sources of NO$_2$ emissions from mobile sources of emissions. The results of the Pearson correlation between nitrates in rain water by rainfall and NO$_2$ emissions from these sources are:

i. The correlation between nitrates with rainfall
   $r = -0.181$ indicates the level of correlation is very weak ($r < 0.200$). Toward a negative correlation indicates when rainfall greater the concentration of sulphate in rainwater getting smaller.
   $p = 0.041$ ($p > 0.005$) shows the correlation between the two variables are not significant.

ii. The correlation between sulphate by addition of NO$_2$ from stationary sources of emissions.
   $r = 0.035$ indicates that both variables have a very weak correlation ($r < 0.02$).
   $p = 0.693$ showed that the correlation between the two variables was not significant ($p > 0.005$).
   Thus, NO$_2$ from the industry has little effect on nitrate in rain water.

iii. The correlation between sulphate by addition of NO$_2$ from mobile sources of emissions
contribution of SO2 in the air Semarang from background concentrations, emissions of stationary sources and coefficient showed that sulphate derived from emission sources in Semarang of 1.1 to 1.9%. This means that the transport chemicals in wet deposition of sulphur in rainwater showed that in 2001-2005, and the results showed due to the spread of pollutants from outside the study area (Semarang). The magnitude of the impact of the global transport of pollutants is calculated based on the difference between the concentrations of sulphate and nitrate in rain water measured by the concentration of sulphate and nitrate are formed from SO2 and NO2 in air using a washout coefficient showed that sulphate derived from emission sources in Semarang of 1.1 to 1.9%. This means that the contribution of SO2 in the air Semarang from background concentrations, emissions of stationary sources and mobile sources of emissions to sulphate in rainwater by 1.1 to 1.9 %. Kuribayashi (2012) use the model to calculate the transport chemicals in wet deposition of sulphur in rainwater showed that in 2001-2005, and the results showed that wet deposition of sulphur is less than 2.1%. Whereas NO2 impact of emission sources in Semarang on nitrates in rain water is 27.1 % [17].

4. Conclusion

SO2 emissions from stationary sources and transportation caused 1.1 to 1.9 %. Whereas NO2 impact of emission sources in Semarang on nitrates in rain water was 27.1 % of rain events during the period January - June 2013 saturated with SO4$^{2-}$ and 58.02% saturated with NO3$^{-}$ especially at locations close to the emission source.

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