

PROFILE OF NITRATE CONCENTRATION IN GROUNDWATER IN WINONGO WATERSHED AREA OF YOGYAKARTA CITY, INDONESIA

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ABSTRACT

The mostly occurring case of anthropogenic source for nitrate contamination in groundwater especially in developing countries is domestic sewage. Hence, many cases of the presence of nitrate in groundwater are always correlated with the poor quality of wastewater management system. Since 2008 Yogyakarta area in Indonesia has improved its wastewater management system which should also improve the groundwater quality. This paper will discuss the recent condition of groundwater quality in Yogyakarta City area which focused on nitrate and its association to contamination from sewage after the improvement of sewage management system. Chloride concentration was measured and its ratio to nitrate was calculated to examine this association. Analysis of 32 groundwater samples showed the range of nitrate-N concentration from 3.6 to 42.56 with average of 9.97 mg/L. Meanwhile, chloride concentration ranged from 15.82 to 35.85 with average of 23.79 mg/L. The ratio of N to Chloride exceeds 1 only at 1 sampling to the same cluster. This indicates that the nitrate in groundwater in this study may not originated from domestic sewage. Hence, the effort to improve wastewater management systpoint. In addition, Hierarchical Cluster Analysis showed that nitrate and chloride did not belongem has given positive impact to groundwater quality.

Keywords: nitrate concentration, groundwater, watershed

1. INTRODUCTION

In many developing countries including Indonesia, groundwater is still the main source of drinking water as it is considered the best in quality [1]. However, over the past several decades, groundwater quality has been deteriorated globally due to both natural and anthropogenic causes. The natural source includes hydrogeology condition, natural fertilization, bacterial production, and atmospheric deposition. Meanwhile the increasing use of fertilizer in agriculture and the release of untreated sewage and industrial wastewater become the main source of groundwater pollution from anthropogenic source [2].

Among few chemicals which cause adverse health effect to human through drinking water consumption, nitrate is one of the most prevalent [3]. Due to its high water solubility and poor adsorption qualities, nitrate is quickly dissolved in groundwater, resulting in water contamination [4,5]. WHO recommended the maximum concentration of 50 mg/L as nitrate or 10 mg/L as nitrate-N in drinking water. Epidemiological study reported the absence of negative health effect at concentration below this value. Adverse health effect

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DOI: <https://doi.org/10.20885/icsbe.vol4.art50>



associated with high concentration of nitrate in drinking water are methemoglobinemia and thyroid dysfunctions especially in kids and pregnant woman. In addition, reduction of nitrate to nitrite may result in the formation of carcinogenic N-nitrosamines [6]. To address this issue, nitrate has been one of parameters which is periodically examined for groundwater quality monitoring in Indonesia including in Yogyakarta area. Many studies reported the increasing concentration of nitrate in groundwater in Yogyakarta area in relation to urbanization. Study conducted by [7] compared nitrate concentration in groundwater in Yogyakarta City area since 1970s until 2005 and found the increasing average concentration from 1.2 mg/L in 1970s-1980s, 2.8 mg/L in 1985, 2.1 mg/L in 1990, 12.9 mg/L in 1997 and 31.5 mg/L in 2005. This study presented the indication of the source of nitrate was from sewage due to the nitrate and chloride ratio around 2-2.5 : 1. This indication was supported by the fact that domestic wastewater system in the area was still limited. Coverage of centralized sewerage system in the area was only 9% of the population [7], while the rest were treated in communal or on-site system or just release to the environment without proper treatment. In recent years, the government of Yogyakarta continuously improves the service coverage of its wastewater system through various efforts such as upgrading the capacity of the centralized wastewater treatment plant in Sewon, construction of additional sewerage connection and communal wastewater treatment system. This paper will discuss the recent condition of groundwater quality in Yogyakarta City area which focused on nitrate and its association to contamination from sewage as improvement have been made to better handle wastewater from domestic sector. Chloride concentration was measured and its ratio to nitrate was calculated to examine this association.

2. MATERIAL AND METHODS

2.1 Study Area

Study area is part at the western part of Yogyakarta City. It covered the areas of 5 subdistricts (Kecamatan) including Wirobrajan, Ngampilan, Gondomanan, Kraton, and Mantrijeron. This area was among the most densely populated in Yogyakarta City with the highest population density of 18.841 persons/km² in Ngampilan subdistrict [8]. At the centre of the study area is one of the tourism centres in Yogyakarta City, where many non-domestic activities were taking place including hotels, marketplaces and home industries. For this study, total of 32 (thirty-two) samples were taken from households dug wells in which their locations are presented in Figure 1.

2.2 Sample collection and laboratory analysis

Groundwater samples were collected in January 2022 during rainy season. Parameters of temperature, pH and electrical conductivity (EC) were measured on site, while nitrate-N and chloride concentration were analysed at the laboratory by following reference methods below.

Table 1. Reference method for laboratory analysis

Parameter	Reference method
Nitrate-N	SNI 01.3554:2006 on Analysis of the quality of packaged drinking water
Chloride	SNI 6989.19.2009 on Chloride analysis using argentometry method

2.3 Statistical analysis and map works

Statistical analysis was performed by using R program version 4.0.3 [10]. Basic R package “base” was used to present summary statistics [10]. For Hierarchical Cluster



Analysis (HCA), “Euclidian” and “Ward.D2” were used as distance measuring and clustering method respectively, as available in “stats” package [10]. To ensure comparability among datasets, standardization was performed before HCA. Dendrogram visualization of HCA was performed by using “factoextra” Package [11]. Map works was produced by using QGIS open-source software version 3.16 Hannover ([12]. Basic maps were provided by Indonesia Geospatial Portal [13].

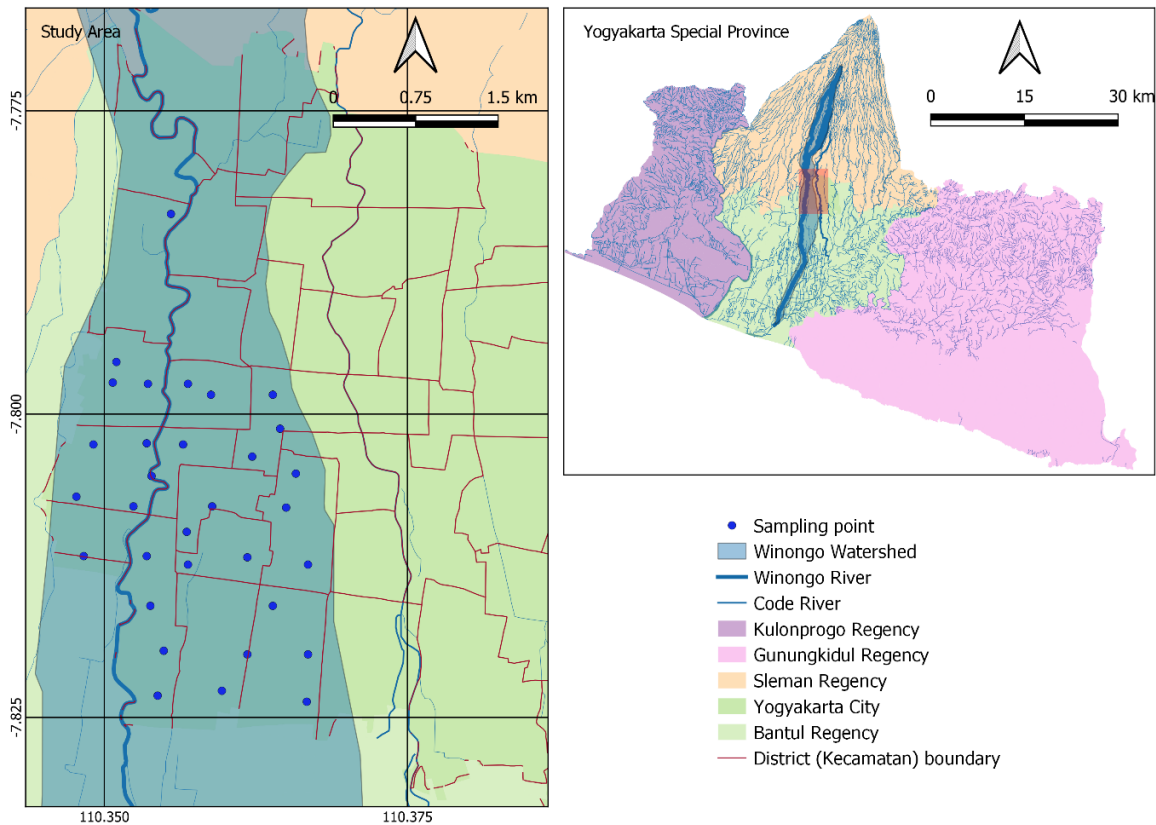


Figure 1. Study area and sampling points

3. RESULTS AND DISCUSSION

3.1. Results of Laboratory Analysis

Result of analysis of 32 groundwater sample in Yogyakarta City area is summarized in Table 2. Temperature and pH were within the acceptable range compared to the standard. EC is an indicator of amount of dissolved solid or salinity in water. It may also become indicator of water pollution [14]. Land usage patterns and pollution are primarily accountable for the variations in EC or TDS [1]. A positive correlation with TDS and EC indicates salinity. This parameter is important to determine suitability for irrigation [15]. According to WHO, maximum allowable limit for EC is 1.5 mS/cm [16]. No samples in this study exceed this value.

Distribution of nitrate in water samples across 32 sampling points are plotted in map and presented in Figure 2. According to Regulation of the Indonesian Ministry of Health No. 32/2017, maximum concentration of Nitrate-N in water for hygiene and sanitation purposes should not exceed 10 mg/L. Of the 32 sampling points, 10 exceed this standard. Concentration of nitrate in samples ranged from 3.60 to 42.56 mg/L and percentage of samples exceeded standard was 31 %. Figure 2 shows that high concentration of nitrate was observed in the middle section of the study area.



Table 2. Summary statistics of all measured parameters

Parameters	Unit	Mean	Min	Max	Std.Dev	Standard*
Temperature	°C	27.30	21.00	32.00	1.59	± 3 **
pH	-	7.77	6.60	8.83	0.52	6.5-8.5
EC	μ.S/cm	500.88	402.00	581.00	49.73	-
Nitrate-N	mg/L	9.97	3.60	42.56	7.13	10.00
Chloride	mg/L	23.79	15.82	35.85	5.73	250***

* Regulation of the Indonesian Ministry of Health No.32/2017

**from ambient temperature

***WHO guideline for drinking water quality 2022

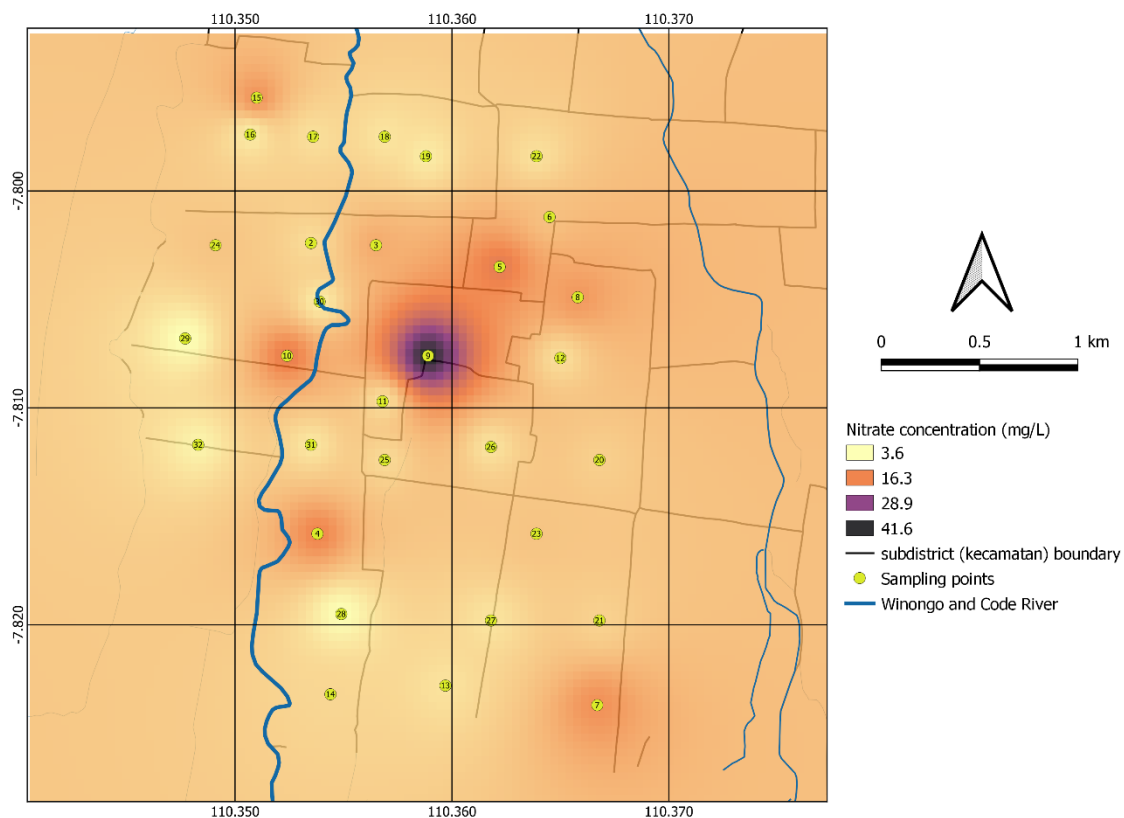


Figure 2. Distribution of nitrate-N in study area

For chloride, concentration in samples ranged from 15.82 to 35.85 mg/L. No standard available at local level for this parameter so that WHO guideline was used instead as reference. Concentration of 250 mg/L is suggested not over the health concern but more to the aspect of taste threshold as concentration above this value is likely to be detected by its salty taste. As presented in Figure 3, high concentration was observed at the top and the middle section of study area.



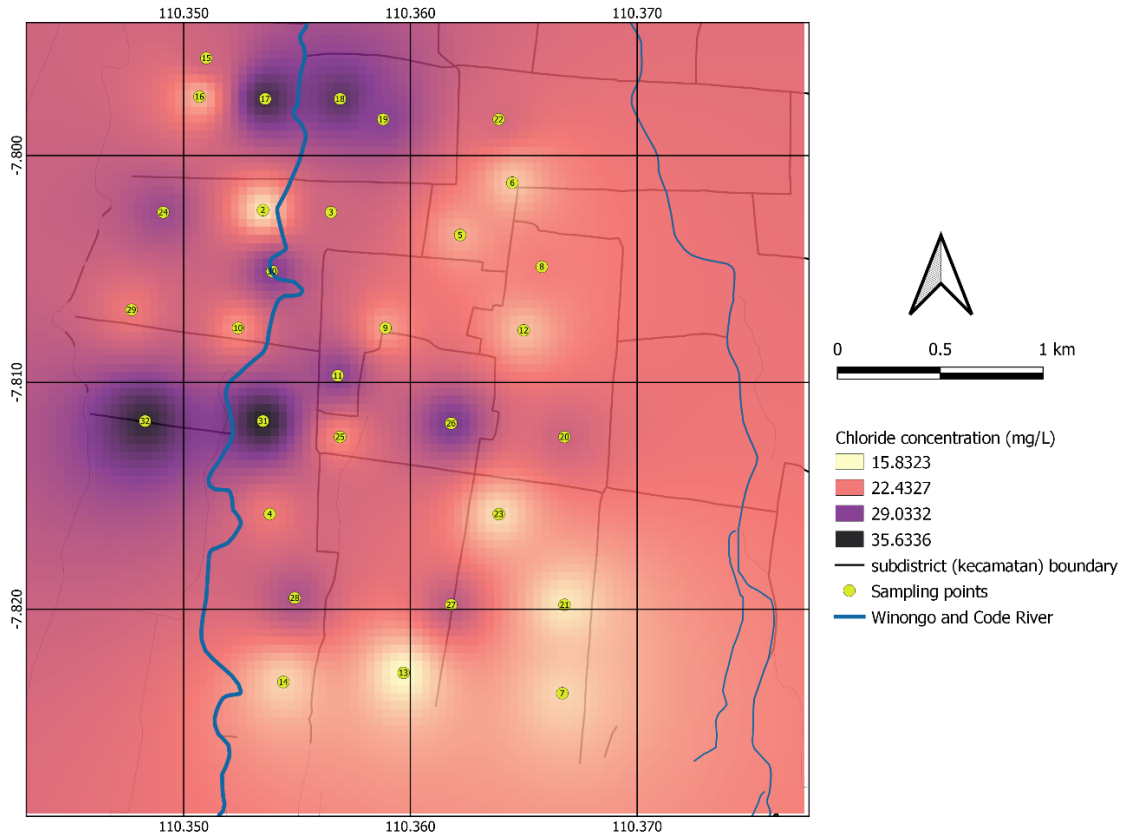


Figure 3. Distribution of chloride in study area

3.2. Cluster analysis

Cluster analysis has been applied in many studies to identify and analyse interrelationship among variables including in the analysis of the fate and distribution of nitrate in groundwater [17]. Other than concentration of nitrate-N, other parameters considered in this study are temperature, pH, EC and chloride concentration. Hierarchical Cluster Analysis (HCA) resulted in 2 dendrograms showed interrelationship among samples and parameters as presented in Figure 4 and Figure 6.

HCA generated 4 sample clusters. Figure 5 presented distribution of samples according to these clusters. No specific spatial grouping was observed on the distribution of each cluster. The 3 clusters with many sampling points not specifically distributed in certain areas. However, the yellow cluster has feature of relatively high nitrate-N, grey cluster with high EC, red cluster with high Chloride and blue cluster which consists of only 1 sampling point has a distinguished very high concentration of nitrate-N.

Cluster analysis was conducted to observe relationship among parameters. HCA generated 3 clusters. Parameters in one cluster may indicate the possible common source. The first cluster consists of EC and pH. EC in groundwater is a measure of the concentration of total ions in water including hydrogen ions which is the basis of the pH measurement [18]. As both belongs to the same cluster, hydrogen ion indicated by pH value had positive contribution to conductivity. The second cluster put together temperature and Nitrate-N concentration and left chloride at different cluster with only single member. In general, the 5 parameters had relatively similar height. The height axis in cluster dendrogram represent distance between parameters and/or clusters [19]. The more the height, the more they are dissimilar. In this study, the 5 parameters showed relatively high height indicating low strength of relationship.



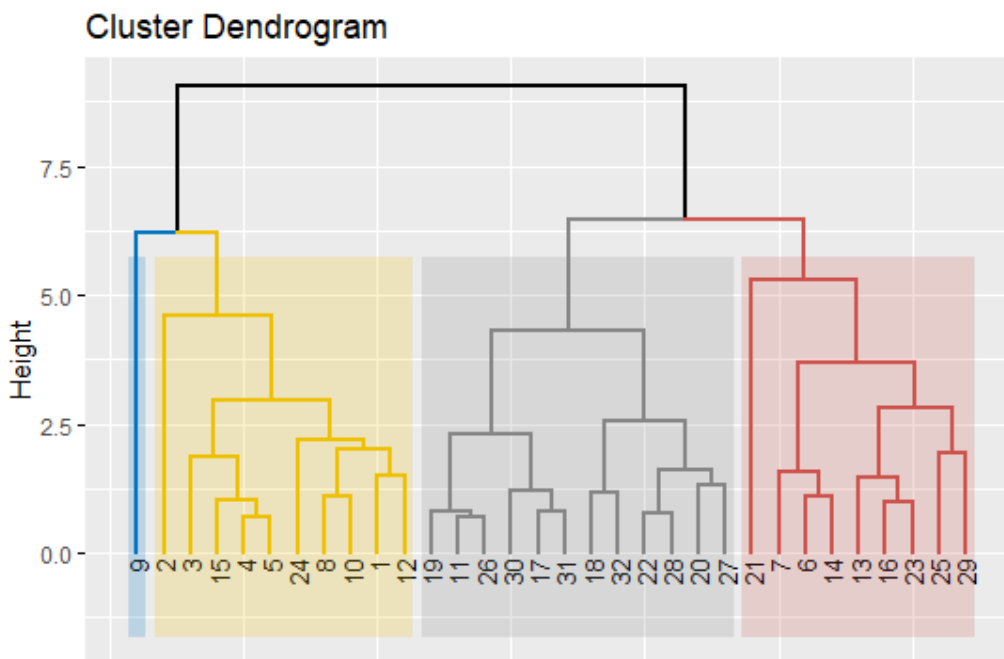


Figure 4. Cluster dendrogram for samples

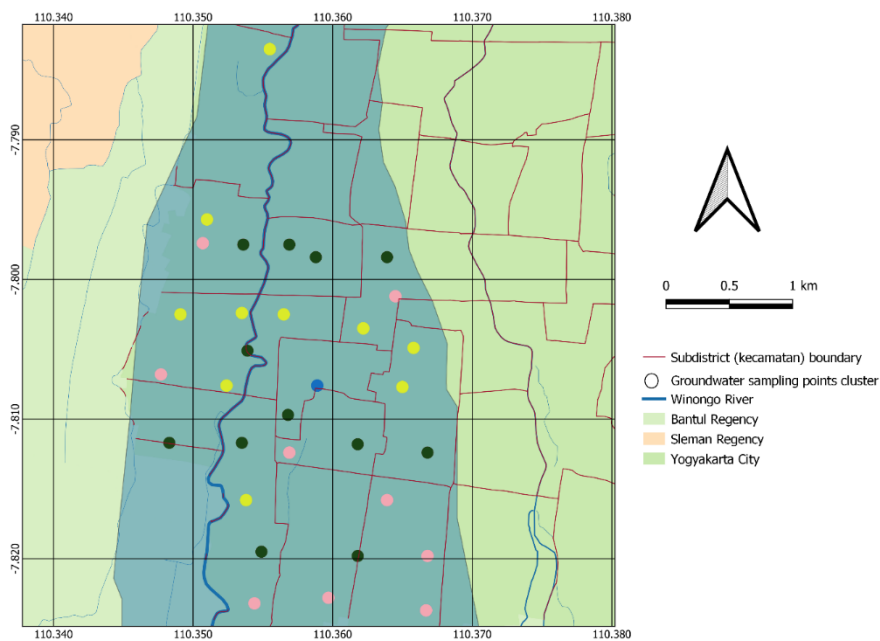


Figure 5. Distribution of samples according to cluster analysis (showed by different dot colours)



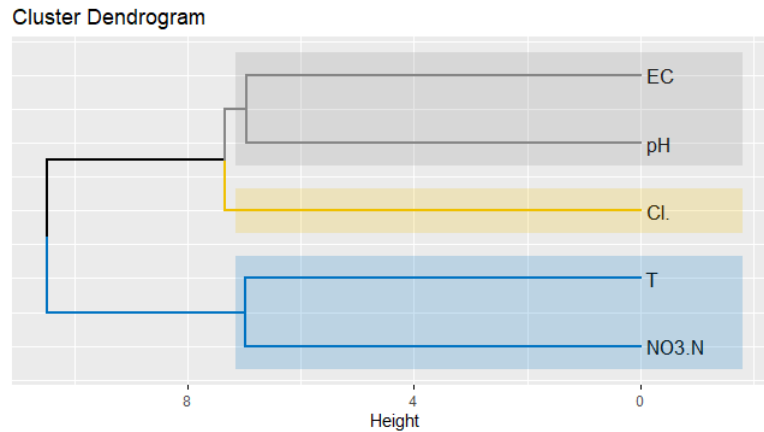


Figure 6. Cluster dendrogram for parameter

3.3. Indication of sewage contamination

Nitrate concentration in groundwater may indicate contamination from untreated sewage. According to study conducted by [7], nitrate concentration detected in groundwater samples from Yogyakarta City area in 2005 was probably from this source. It is indicated with its ratio to Chloride which is around 2-2.5:1. This indication was supported by the fact that the coverage area of the existing wastewater treatment system connected to Sewon plant was still very low. However, since 2008, local government tried to improve the service coverage of wastewater treatment system in Yogyakarta area by increasing the capacity of wastewater treatment plant in Sewon and its connected sewerage system from 8.300 in 2008 to 26.050 house connections in 2021 [20]. This effort was expected to also improve the groundwater quality as one of the sources of its contamination was reduced.

Laboratory analysis of groundwater samples from study area showed nitrate-N concentration ranged from 3.60 to 42.56 mg/L with the percentage of samples exceeded the standard of 10 mg/L was 31 %. Some studies used the threshold 1 or 3 mg/L to indicate the possibility of anthropogenic contamination with surface origin [17,21]. All sampling points exceed this theoretical threshold indicating the anthropogenic sources. One of prominent anthropogenic source of nitrate concentration in groundwater is untreated sewage.

Figure 7 presents the map of existing sewerage connection to wastewater treatment plant in Sewon ([20]. Pipe network is presented with blue line and sampling area is indicated by red rectangle. Sewerage connection served most of sampling area especially at the east side of Winongo River. In addition to this, communal and individual wastewater treatment system covered areas without connection to this sewerage system. Hence in total, wastewater treatment service had covered 97% of this area [22]. Good wastewater treatment system should prevent various contaminant from sewage reaching out to soil or groundwater environment.

To further examine possible source of nitrate from sewage, the ratio of nitrate-N to chloride in samples were calculated. The ratio of 2-2.5:1 suggests positive indication of sewage contamination. The ratio of each sampling point is presented in Figure 8. The range of nitrate to chloride ration in samples is 0.36 to 2.07 with average of 0.46. Only one sampling point has ratio above 1, which is at the sampling point 9 located in the centre of sampling area. This result may indicate that the source of nitrate in groundwater was not from sewage. The result of cluster analysis in the previous section supports this



finding as nitrate and chloride do not belong to the same cluster indicating source differences.

Other than domestic sewage, nitrate and chloride in groundwater may be from industrial waste, livestock waste or the use of fertilizer. Considering the study area which was a highly urban area with many home industries, industrial waste was the most possible source of nitrate contamination.

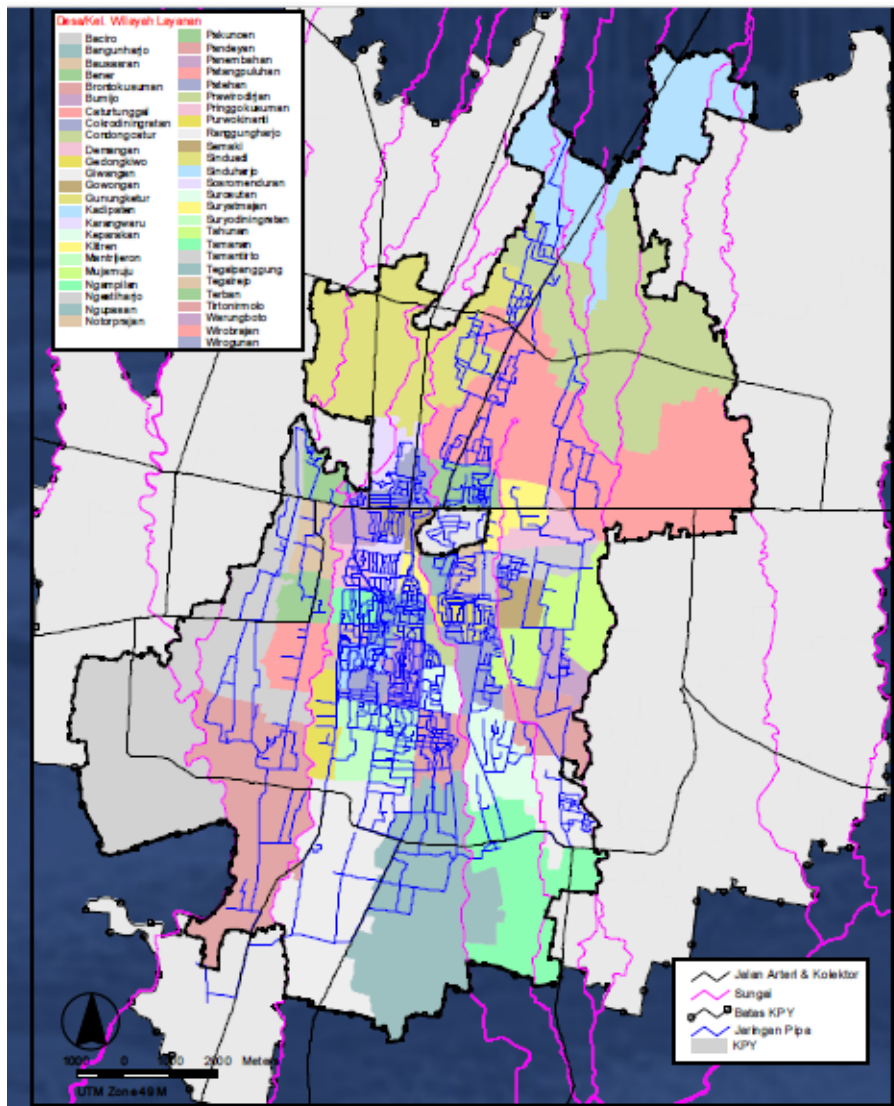


Figure 7 Coverage of existing sewerage connection in Yogyakarta Urban Area

4. CONCLUSION

Analysis of 32 groundwater samples from study area located in Winongo Watershed of Yogyakarta City showed the concentration of nitrate-N and chloride within the range of 3.60 to 42.56 mg/L and 15.82 to 35.85 mg/L respectively. The possible relationship among parameters was examined using cluster analysis showing that both belong to different cluster. To examine the possible source from domestic sewage, ratio of nitrate-N to chloride was calculated and compared to the theoretical ratio of 2-2.5:1 for sewage contamination. The ratio ranged from 0.36 to 2.07 with the average of 0.46. Only 1 sampling point had ratio above 1 which indicated that the source of nitrate was from other



than domestic sewage. The improvement of domestic wastewater treatment system in the area has prevent considerably contamination of soil and groundwater by sewage. This finding suggests other source of nitrate in groundwater in study area. As many home industries were operated in the area, this anthropogenic sector may be the source of nitrate contamination in groundwater in study area.

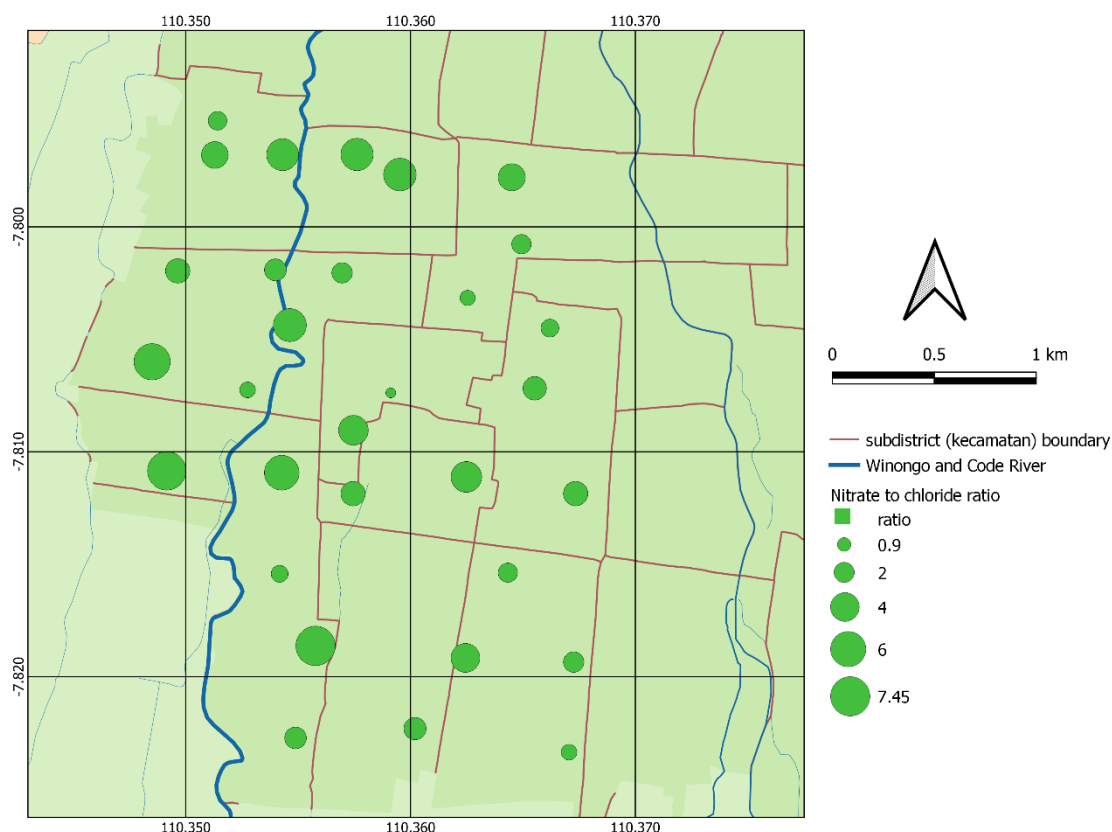


Figure 8 Chloride to nitrate-N ratio of samples

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