JPII 11(1) (2022) 129-141

Jurnal Pendidikan IPA Indonesia

http://journal.unnes.ac.id/index.php/jpii

CHLORINE CONCENTRATION AND PHYTOPLANKTON DIVERSITY IN THE STREAMS AROUND TONDANO WATERSHED, NORTH SULAWESI, INDONESIA

S. Wantasen*[1], J. N. Luntungan[2], R. Koneri[3]

[1,2]Agriculture Faculty, Universitas Sam Ratulangi, Indonesia
[3]Department of Biology, Faculty of Mathematics and Natural Sciences, Universitas Sam Ratulangi, Indonesia

DOI: 10.15294/jpii.v11i1.31601

Accepted: August 13th 2021. Approved: March 30th 2022. Published: March 31st 2022

ABSTRACT

The use of chlorine in agriculture and settlements increases and impacts surrounding waters, such as watersheds: The land area is a unit with rivers and tributaries that function to accommodate, store and distribute water from rainfall to the sea naturally. The environmental condition of the Tondano watershed is important to study in terms of chlorine distribution, considering that residential and agricultural activities in the watershed can cause residues in the aquatic environment, which harm the environment, especially phytoplankton. This study aims to examine the concentration of chlorine and its impact on the phytoplankton diversity in the Tondano watershed, North Sulawesi, Indonesia. Using the composite method, water quality sampling to calculate chlorine concentration was carried out at 17 river locations using the composite method, while six river stations represented phytoplankton sampling. Chlorine concentration was measured using UV-VIS spectrophotometry, while plankton sampling used a plankton net with a mesh size of 40 μm and a net mouth diameter of 20 cm. The results show that the highest chlorine concentration was found in the Tondano Hilir River (0.05 mg/L), followed by the Kakas River downstream (0.04 mg/L). Chlorine concentration distribution in other rivers has the same concentration (0.03 mg/L). Quality standard Chlorine according to Government Regulation number 22/2021 Appendix VI Class II is 0,03 mg/L. The highest number of species and index of phytoplankton species diversity was found in the Hulu Panasen River, while the highest species abundance was found in the Tondano River downstream. The correlation analysis of species diversity index with chlorine concentration did not show a significant relationship with the diversity of phytoplankton, but aquatic ecosystems have experienced moderate ecological pressure.

Keywords: chlorine; diversity; phytoplankton; Tondano watershed

INTRODUCTION

The physical and environmental conditions of the Tondano watershed are important to study in terms of the spatial distribution of chlorine, considering that residential and agricultural activities in the watershed can cause residues in the waters of Lake Tondano and Tondano River, which empties into Manado Bay. Government Regulation of the Republic of Indonesia Number 26 of 2008 concerning the National Spatial Planning (RTRWN) stipulates that the Tondano watershed is designated as a national strategic area from the point of view of the importance of the function and carrying capacity of the environment and a national strategic river area. The Tondano River, which has its upstream in Lake Tondano, has an important role in supporting the lives of the people of Manado City, Tondano, and its surroundings, namely as a source of drinking water for the community, raw water sources for the local water company in Manado, and Tondano, a source of power plants (hydroelectric power plant) Tanggari and Tonsealama, sources of

***Correspondence Address**
E-mail: swantasen@unsrat.ac.id

irrigation water, inland fisheries and tourism objects (Sittadewi, 2008). This condition causes the Tondano watershed to experience environmental degradation due to the entry of wastewater from these activities, such as chlorine, which can cause residues in the aquatic environment (Wantasen et al., 2020).

The chlorine sources are the outlets of irrigation canals, rivers, and settlements drainage outlets. River pollution increases when rivers pass through areas contaminated with chlordecone/organochlorine pesticides (Della Rossa et al., 2017). Chlorine residues impact aquatic biota such as phytoplankton because aquatic organisms accumulate toxic substances in their organs (Da Costa et al., 2014), and the effect depends on the time, frequency, and duration of the application (Levillain et al., 2012). Data from the Agricultural Extension Center (BPP) Kakas in June 2021 shows that the time, frequency, and dose of KCl fertilizers and pesticides are high according to the growing season. The location of the Tondano River, which crosses the settlements, also receives input of wastewater containing chlorine from the settlement drainage.

The use of chlorine materials, named the chemical compound chlorine ($CaCl_2$), increases clean water treatment. The use of chlorine at a low percentage can be used as a water purifier, bleach clothes, larvae killer, disinfectant for drinking water and industry. In agriculture, chlorine is used for pesticides and inorganic KCl fertilizers. Irrigation and fertilization contribute significantly to the precipitation of chlorine (Hassaan & El Nemr, 2020). The remaining free chlorine distribution is influenced by the location of the injection position, the dose, and the time of injection—the further away from the chlorine source, the less the residual chlorine spread. The chlorine concentration decreases with increasing distance from the source (Bassey, 2017). The dangers of chlorine concerning the ecological effects of pesticides are biomagnification, bioconcentration, and bioaccumulation (Jayaraj et al., 2016; Hassaan & El Nemr, 2020). Organochlorine pesticides belong to chlorinated hydrocarbon derivatives with high toxicity, slow degradation, and bioaccumulation.

Organochlorine pesticides have high persistence and are toxic, harmful to aquatic organisms (Jayaraj et al., 2016; García-Espinoza et al., 2018; Pan et al., 2019). The toxicity of the effluent under inadequate dichlorination conditions is mainly due to residual chlorine, especially monochloramines. Disinfectants (NH_2Cl) can pose a significant risk to aquatic life (Zhang et al., 2018) and have adverse effects on human health, such as disinfectant by-products that are suspected of causing cancer (Tsitsifli & Kanakoudis, 2018). The condition of the Tondano River, which receives input from the irrigation channel/ moor outlet, the settlement drainage channel outlet carries residual chlorine in chlorite ions, chlorate, and chlorophenol compounds.

Chlorophenol compounds are toxic to aquatic life and cause histopathological changes, mutagenic, and carcinogenic effects (Igbinosa et al., 2013). When chlorine gas is dissolved in water, it will hydrolyze rapidly to produce hypochlorous acid $Cl_2 = H_2O$ ......> $HClO + H^+ Cl^-$. The HClO ratio depends on pH 6-9 and climate. The role of climate produces heterogeneity of pollution because these compounds are sensitive to sunlight and are not easily decomposed (Sharma et al., 2018; Mottes et al., 2020). Pesticides have become an important part of agriculture to protect cultivated crops from pests but pose a risk to the environment. Spatially, the largest source is from pest control activities (Li et al., 2011; Özkara et al., 2016; Mahmood et al., 2016).

Chlorine that enters water bodies such as watersheds will impact the biota that lives in them, such as phytoplankton. Phytoplankton has an important role in aquatic ecosystems and is a producer of oxygen (O_2) through photosynthesis and absorbs carbon dioxide (CO_2) in producing food. Phytoplankton productivity contributes to almost half of the global net primary productivity (Sriwijayanti et al., 2019). Phytoplankton as primary production is a source of food for all populations in the waters (Sardet, 2015; Rowe et al., 2017). Phytoplankton of the types of Bacillariophyceae, Chlorophyceae, and Chynophyceae as indicators to determine the level of pollution of waters (Hou et al., 2018; Yusuf, 2020) and Chlorination in power station cooling water systems: Effect on biomass, abundance, and physiology of natural phytoplankton communities (Vannoni et al., 2021).

Several studies on the distribution of chlorine in waters and the relationship between water quality and phytoplankton have been carried out, including analysis of free chlorine (Cl_2) levels and their impact on public health along the Cidanau river, Cilegon (Hayat, 2020), evaluation and analysis of the distribution pattern of residual free chlorine in the distribution network of Lulut River WTP PDAM Bandarmasih (Sofia & Riduan, 2017), and analysis of the relationship between water quality and the diversity index of plankton and benthic in the Cirata reservoir (Prasiwi & Wardhani, 2018).

Research on chlorine concentration and its relationship with air quality and phytoplankton diversity in the Tondano watershed, North Sulawesi, has never been studied and published. This research is vital because the current community activities along the Tondano watershed can discharge chlorine into the river body. These activities are in the form of agricultural and residential activities in the watershed. The presence of chlorine impacts air quality because chlorine causes residues in the aquatic environment and will impact biota, such as phytoplankton that lives in it. Air quality conditions influence phytoplankton diversity. Air quality conditions are indicated by certain types of phytoplankton, such as Bacillariophyceae, Chlorophyceae, and Chynophyceae. The analysis was conducted to determine the relationship between air quality and the correlation of phytoplankton diversity. In addition, a spatial analysis was carried out to determine the distribution of chlorine and phytoplankton in the Tondano watershed. Chlorine concentration and phytoplankton biodiversity will indicate the condition of the waters of the Tondano watershed. In addition, locations that have experienced ecological stress that can be identified spatially can help policymakers identify target locations for environmental management. This study aims to examine the concentration of chlorine and the diversity of phytoplankton in the Tondano watershed, North Sulawesi.

METHODS

A water sampling for testing the chlorine concentration was conducted at 17 stations in the Tondano watershed, North Sulawesi. The river stations are located in the Tondano watershed (upstream and downstream): Noongan River is the upper part of the watershed, Kakas River, Tikala River, and Tondano River are rivers that flow through settlements, and Panasen River flows through agricultural land/rice fields and horticulture. Water sampling was carried out using the composite method (Hadi, 2015). Chlorine concentration data were analyzed using the UV-VIS Spectrophotometry method and compared with the Quality Standards according to Government Regulation (PP) Number 22 of 2021 Attachment VI Implementation of Environmental Protection and Management (P3LH). Class II is water whose designation can be used for water recreation infrastructure/facilities, freshwater fish cultivation, animal husbandry, water for irrigating crops, or other designations that require the same water quality as that user.

Phytoplankton sampling was only conducted at six river stations: Panasen River upstream, Panasen River downstream, Noongan River upstream, Kakas River downstream, Tikala River downstream, and Tondano River downstream. Phytoplankton samples were taken using a plankton net with a mesh size of 40 m and a net mouth diameter of 20 cm. Phytoplankton samples were taken as much as 50 L from each station, then filtered with a plankton net (Prasiwi & Wardhani, 2018). The filtering results were put into a 100 ml sample bottle labeled and preserved with Lugol. Furthermore, the phytoplankton samples were observed and identified in the laboratory (Lestari et al., 2021). Identifying phytoplankton species, the sample was observed under a microscope and then identified using the identification book from Borja (2012). Identification is made by matching the sample with the image in the identification book. In detail, this research method is presented in a flow chart (Figure 1).

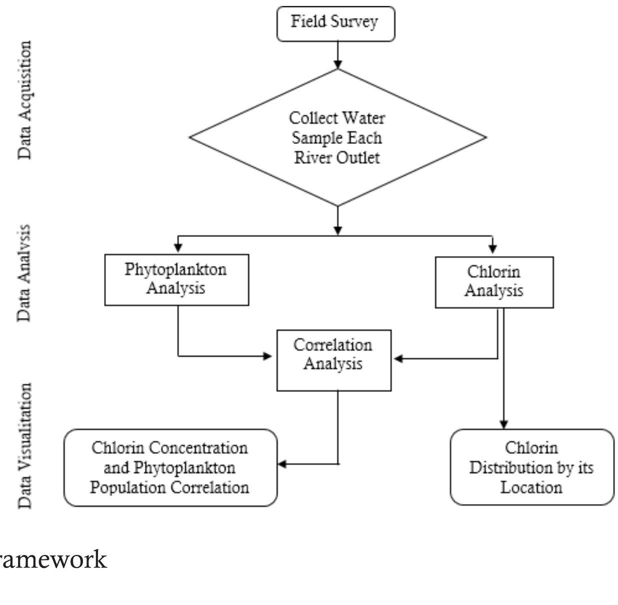

Figure 1. Research Framework

The study begins with a field survey and sampling of water quality at the river outlet. The next stage is the analysis of water quality data with chlorine parameters using analysis of phytoplankton diversity and the correlation between the two parameters. The final stage in this research is the visualization of chlorine distribution data on water quality and phytoplankton diversity. Chlorine distribution mapping in 17 rivers was processed in ArcGIS desktop 10.7.1 (Bajjali, 2018). The abundance of phytoplankton was analyzed using the formula: E= c × A/fa × V; where: E = phytoplankton density (ind/ltr), c = total observed individuals, A = phytoplankton concentrate volume, fa = phytoplankton sample volume, and V = sample volume (Clesceri et al., 1989). The species diversity index (Shannon-Wiener diversity (H'), the species evenness index (Pielou evenness (J) and the correlation between species abundance, number of species, diversity index, and species evenness index with chlorine content were analyzed using Paleontological Statistics software (PAST software v. 2.12) (Koneri et al., 2021).

RESULTS AND DISCUSSION

Chlorine concentration measurement results show that the highest chlorine was found in the Tondano River downstream at 0.05 mg/L, followed by the Kakas River downstream at 0.04 mg/L. Panesan River upstream 1 and downstream 1 have the same concentration of 0.03 mg/L. The other thirteen rivers had the same chlorine concentration (0.02 mg/L) (Figure 2).

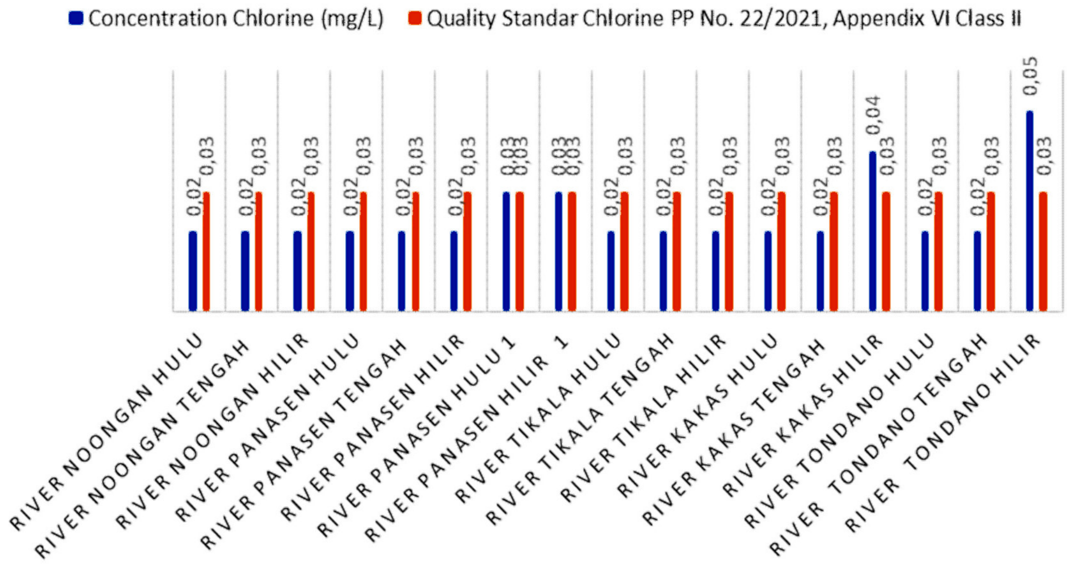

Figure 2. Chlorine Concentration and Quality Standard (Government Regulation No. 22/2021 Class II)

The results of this study indicate that the concentration of chlorine fluctuates in the upstream, middle, and downstream rivers. High concentrations exceeding the quality standard and threshold were found in four of the seventeen sites studied. These locations are the Tondano River downstream, Kakas River, Panasen River downstream 1, and Panasen River downstream 2 (Quality Standards according to PP No. 22 of 2021 Appendix VI chlorine concentration is 0.03 mg/L).

Figure 2 shows that 23.53% of the chlorine concentration does not meet the quality standard (Government Regulation Number 22/2021 Class II), whose distribution is shown in Figure 3.

Chlorine distributed in the Tondano watershed has a high concentration in the lower reaches of the Tondano and Kakas rivers. Both rivers cross dense residential areas and rice fields or moor. River flows carry domestic and agricultural waste from their catchment areas.

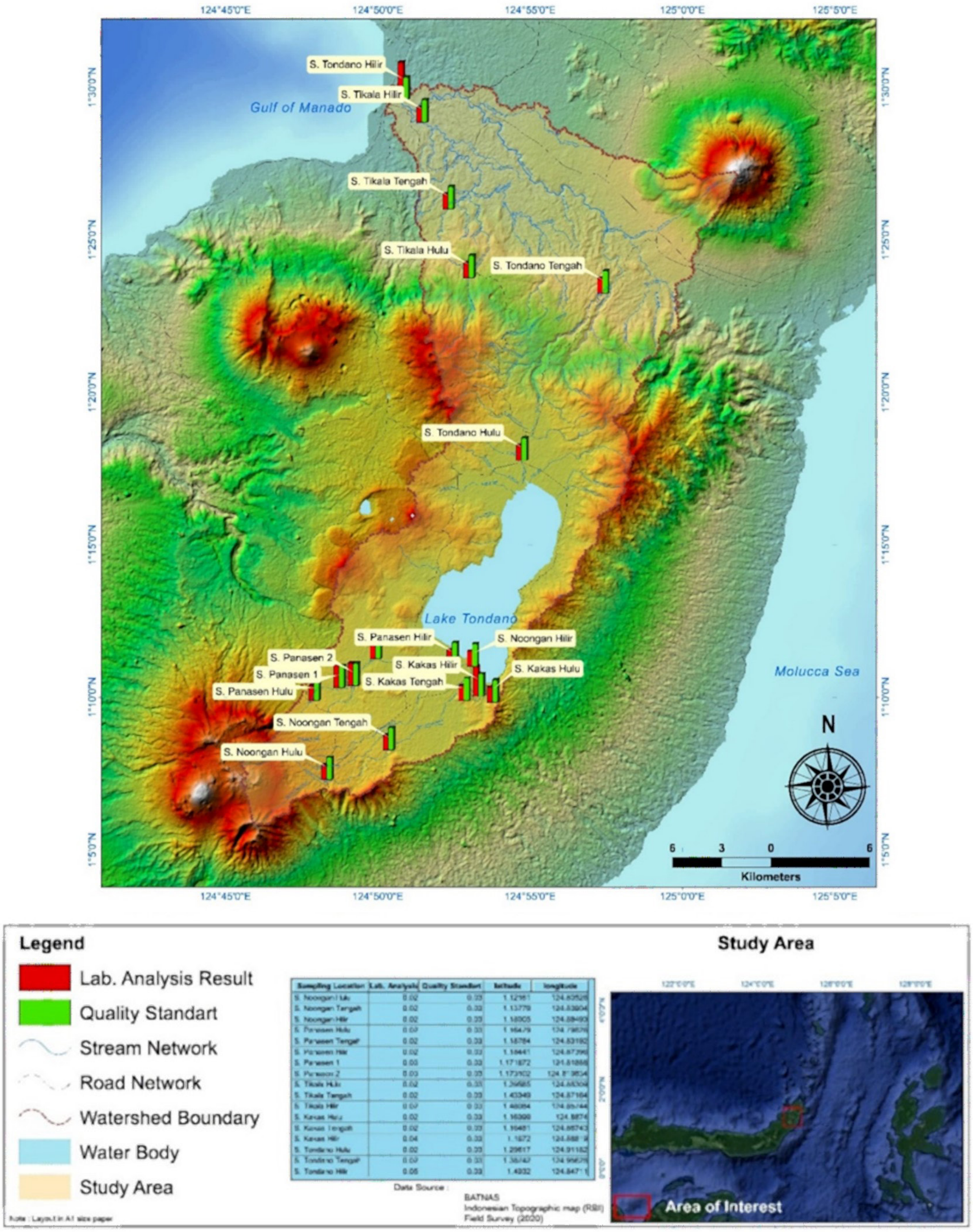

Figure 3. Chlorine Distribution in the Upstream and Downstream of the Tondano Watershed

The results obtained were six classes, 37 species, and 594 individual phytoplankton. The most common class found was Bacillariophyceae (38.9%) and Cyanophyceae (22.4%), while the class with the least number was Trebouxiophyceae which was only found in 2% (Table 2 and Figure 3). Navicula sp is the most common species (6.57%), then Anabaena sp. obtained as much as 6.23%. The species with the least number of individuals found were *Hydrophycea* sp. and *Merismopedia* sp., each as much as 0.34% (Table 1).

Table 1. Class, Species, and Number of Individual Phytoplankton Found in 6 Research Stations (SKR: Kakas River Downstream, SNU: Noongan River Upstream, SPR: Panasen River Downstream, SPU: Panasen River Upstream, STIR: Tikala River Downstream, STOR: Tondano River Downstream)

Class	Species	Location/Number of Individuals						∑	%
		SKR	SNU	SPR	SPU	STIR	STOR		
Conjugatophyceae	*Mougeotia* sp.	4	9	0	0	0	0	13	2,19
Bacillariophyceae	*Cymbella* sp.	0	6	0	0	10	12	28	4,71
Bacillariophyceae	*Diatoma* sp.	0	0	6	2	0	0	8	1,35
Bacillariophyceae	*Eunotia* sp	0	10	0	0	9	5	24	4,04
Bacillariophyceae	*Gomphonema* sp.	7	5	2	6	0	9	29	4,88
Bacillariophyceae	*Gyrosigma* sp.	0	9	0	2	5	9	25	4,21
Bacillariophyceae	*Melosira* sp.	11	8	5	0	0	0	24	4,04
Bacillariophyceae	*Navicula* sp.	0	10	6	6	2	15	39	6,57
Bacillariophyceae	*Nitzchia* sp.	12	7	3	0	0	7	29	4,88
Bacillariophyceae	*Pinnularia* sp.	5	0	0	0	3	2	10	1,68
Bacillariophyceae	*Surirella* sp.	6	3	0	0	0	0	9	1,52
Bacillariophyceae	*Synedra* sp.	4	2	0	0	0	0	6	1,01
Cholorophyceae	*Microspora* sp.	0	0	2	2	0	0	4	0,67
Cholorophyceae	*Oedogonium* sp.	0	3	0	0	5	7	15	2,53
Cholorophyceae	*Pediastrum* sp.	9	16	0	0	0	0	25	4,21
Cholorophyceae	*Peridinium* sp.	0	0	2	2	0	0	4	0,67
Cholorophyceae	*Staurastrum* sp.	5	0	10	0	7	6	28	4,71
Cholorophyceae	*Tetraspora* sp.	0	0	0	8	6	5	19	3,20
Cholorophyceae	*Ulothrix* sp.	0	0	14	0	0	0	14	2,36
Cholorophyceae	*Zynegma* sp.	0	0	0	4	0	0	4	0,67
Cyanophyceae	*Anabaena* sp.	7	0	8	8	3	11	37	6,23
Cyanophyceae	*Aphanocapsa* sp.	0	0	10	7	0	0	17	2,86
Cyanophyceae	*Coleosphaerium* sp.	9	4	0	0	0	14	27	4,55
Cyanophyceae	*Fragillaria* sp.	0	0	0	7	0	0	7	1,18
Cyanophyceae	*Hydrophycea* sp.	0	0	2	0	0	0	2	0,34
Cyanophyceae	*Merismopedia* sp.	0	0	0	2	0	0	2	0,34
Cyanophyceae	*Oscillatoria* sp.	0	0	4	6	0	0	10	1,68
Cyanophyceae	*Phormidium* sp.	0	0	6	8	0	0	14	2,36
Cyanophyceae	*Protococus* sp.	0	0	0	8	0	0	8	1,35
Cyanophyceae	*Rivularia* sp.	0	0	2	7	0	0	9	1,52
Fragilariophyceae	*Asterionela* Sp.	0	0	0	0	9	5	14	2,36
Fragilariophyceae	*Tabellaria* sp.	0	0	0	6	4	3	13	2,19
Trebouxiophyceae	*Botryococcus* sp.	0	0	0	0	7	5	12	2,02
Xanthophyceae	*Tribonema* sp.	5	0	0	0	15	8	28	4,71
Zygnemophyceae	*Closterium* sp.	0	0	8	0	0	0	8	1,35
Zygnemophyceae	*Gonatozygon* sp	10	0	0	0	5	7	22	3,70
Zygnemophyceae	*Tetmemorus* sp.	0	0	2	5	0	0	7	1,18
	Grand Total	94	92	92	96	90	130	594	100,00

The highest number of phytoplankton species was found in the Panasen Hulu River (18 species), while the least in the Kakas Hilir and Noongan Hulu rivers, each with 13 species (Figure 4a). The Tondano Hilir River had the highest abundance of 130 individuals, while the lowest abundance was the Lower Tondano River (90 individuals) (Figure 4b). The highest species diversity index was found in the Panasen Hulu River (2.78), while the lowest was in the Noongan Hulu River (2.43) (Figure 4c). The Kakas Hilir River has the highest species evenness index (0.94) compared to other rivers (Figure 4d).

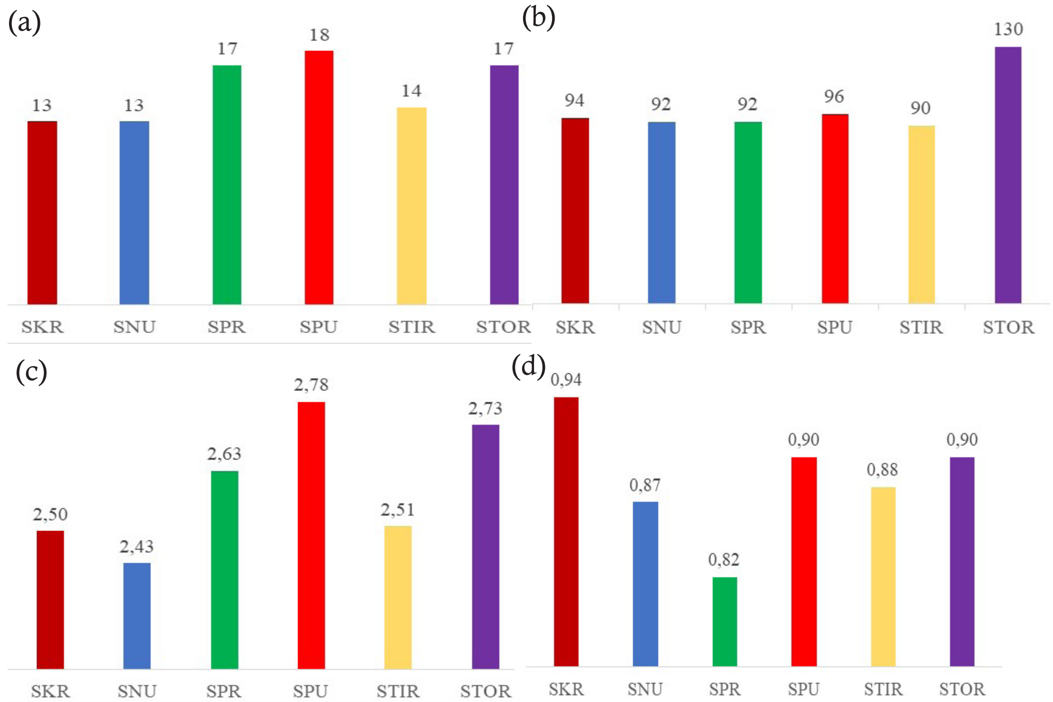

Figure 4. Diversity of Phytoplankton Species at Six Observation Stations for Species Number (A), Species Abundance (B), Species Diversity Index (C), And Species Evenness Index (D) (SKR: Kakas River Downstream, SNU: Noongan River Upstream, SPR: Panasen River Downstream, SPU: Panasen River Upstream, STIR: Tikala River Downstream, STOR: Tondano River Downstream)

The results of the correlation analysis between species diversity and chlorine concentration have different values and show a positive correlation. The correlation between species and chlorine is 0.14, while the number of species is 0.78. The correlation between the species diversity index and chlorine is 0.27, while the evenness index is 0.36 (Table 2).

Table 2. Correlation between Wealth, Abundance, Dominance, Diversity, and Evenness of Phytoplankton with Chlorine

		Number of Species	Species Abundance	Diversity Index	Evenness Index
Chlorine	Pearson Correlation	0.14	0.78	0.27	0.36
	Sig.	0.79	0.07	0.60	0.49

Note: The sign** indicates a very significant correlation at =0.01 and * shows a significant correlation at =0.05

The high chlorine concentration in the Panasen River is caused by KCl fertilizer, pesticides in rice fields, and horticultural fields. Upstream of the Tondano watershed is dominated by wetland agriculture with an area of about 2,924 ha of rice fields (Luntungan, 2014). The active ingredients in pesticides include organochlorines (Bassey, 2017). Chlorine input can be obtained by precipitation of fertilizer salts (David et al., 2016). In addition, it can also be from certain pollutants such as chlorinated hydrocarbons produced from municipal and industrial waste (Azizullah et al., 2011). Domestic waste that contains chlorine, such as preservatives, disinfectants, solvents, bleach, household, and industrial cleaners, creates residual chlorine in the water bodies of the Tondano river.

Residential activities cause a high chlorine concentration in the Tondano and Kakas river downstream. Waste containing household waste, human waste discharged directly into natural sewers or water bodies, and open agricultural land (Iglesias & Garrote, 2015). The leaching to a lower soil profile (Singh & Singh, 2012) and its persistence in the soil are influenced by organic matter (Zhao et al., 2013). Nutrient uptake of N, P, K decreases due to exposure to pesticides can form oxidative microbiological reactions of compounds that degrade cells resulting in the death of soil microorganisms.

The main problem in the Tondano River watershed is domestic and agricultural waste residue. The dominant agricultural waste residues are derived from the residual leached nutrients (leaching) during fertilization in agricultural activities. Agricultural waste residues include chlorine. Around 77% of the water catchment area (DTA) of the Tondano watershed is used for intensive agricultural cultivation, and the rest is in the form of forests, settlements, swamps, and solfatara (Luntungan, 2014). The land used for agricultural cultivation is a mixed garden, 1,856 ha or 17.73% of the total research area, rice fields are about 2,924 ha or 27.95%, and upland about 3,231 ha or 27.95% of the research area.

A decrease in river water quality is a decrease in water quality due to the leaching of nutrients, some of which will become residue (Pereira et al., 2019) carried into rivers, causing a decrease in river water quality (Da Costa et al., 2014). Chlorine is beneficial for human life and can be toxic to the environment and human health. The nature of chlorine as a solid oxidizing agent makes it easy for chlorine to bind with other compounds to form toxic compounds, such as organochlorine compounds, which have carcinogenic effects (Hassaan & El Nemr, 2020). Chlorine and its compounds are widely used for water disinfection because they are available in gas, liquid, or powder form and are also inexpensive and easy to apply because of their relatively high solubility (7000 mg/L). They leave residues in solution, which are temporarily harmful to humans, protect the distribution system, are highly toxic to most microorganisms, stop metabolic activity (Erlangga & Setiawan, 2018). Microbiological reactions in water and earth and the metabolism of pesticides consumed by organisms can ultimately interfere with the reproduction and growth of organisms (Gill & Garg, 2014).

Chlorine can exhibit high acute toxicity to aquatic organisms with a toxicity value of less than or equal to 1 mg L-1. The toxicity of chlorinated effluents in aquatic systems depends on added chlorine and the concentration of residual chlorine remaining in the solution (Da Costa et al., 2014). Organochlorine insecticides are absorbed by plankton, algae, invertebrates, plants, and fish in the food chain, causing pesticides' concentration in the food chain to increase over time (Kibria, 2016). Chloride in ion Cl- is one of the major inorganic anions or negative ions in salt water and fresh water. It comes from the dissociation of salts such as sodium chloride or calcium chloride in water (Alkhateeb, 2014). Chlorine is reactive. It quickly combines with other chemicals in the environment to form secondary compounds. It is toxic to aquatic life and can cause histopathology, mutagenicity, and carcinogenicity, including high acute toxicity (Emmanuel et al., 2004; Igbinosa et al., 2013). These compounds are known for their high toxicity, slow degradation, and bioaccumulation.

The trend that has occurred during the last seven years is that the analysis data of Chlorine concentration is above the quality standard in March, June, and November. The results of interviews with farmers show that fertilization and pesticide use are generally carried out in March and November (Wantasen et al., 2020). Domestic waste, which currently contains many chlorine products such as household appliances, medical devices, paper, drugs and pharmaceutical products, refrigerants, cleaning sprays, solvents, and various other products, also contributes to the chlorine concentration in the aquatic environment. The use of pesticides affects the balance of the ecosystem/changes the food chain (Hassaan & El Nemr, 2020).

The research results on the Panasen River's water quality show that the parameters analyzed generally meet Government Regulation Number 22 of 2021 Appendix VI: chlorine 0.03 mg/L, except that the chlorine parameter does not meet the quality standard requirements. Chlorine analysis results ranged from 0.03 to 0.26 mg/l (Wantasen et al., 2019). The main source of chlorine can come from fertilizers and pesticides whose concentrations fluctuate depending on fertilization and pesticide spraying, namely in March and November. The agricultural intensification program harms water resources because it causes a decrease in water quality. The use of fertilizers and pesticides that are not following the needs of agricultural intensification will cause residues/pollution in the aquatic environment. Land use and water pollution in the Tondano Hulu watershed are needed to protect aquatic ecosystems. Upstream and in the middle of the Tondano watershed, there is a relatively large area of agricultural land. In its cultivation activities, pesticides are often used, which impacts the quality of the waters of the upstream, middle, and finally downstream of Tondano watersheds (Wantasen et al., 2020).

There is a relationship between the concentration of Chlordecone pesticide residues in Galion River water from upstream to downstream and its tributaries. The location upstream of the Galion River is not contaminated, while the concentration increases to the middle and downstream (Della Rossa et al., 2017). Chlorine distribution follows the Noongan River, Kakas River, Panasen River, Tikala River, and Tondano River. The waters of the Tondano River estuary and the surrounding waters have a high potential for water resources, in the form of potential fishery resources, tourism, settlements, ports, transportation facilities, and many others, which will be affected if there is a decrease in water quality or pollution in these waters.

Pesticides that reach water bodies are quickly absorbed and accumulate in the sediments, plankton, algae, aquatic invertebrates, aquatic vegetation, and fish (Ogunfowokan et al., 2012). Excessive chlorine can affect salinity and is toxic to plants (Chen et al., 2010), weakening the accumulation of nutrients in the topsoil (Li et al., 2014). Chlorine affects microbes that convert nutrients into nutrients that are not available to plants. Toxic chlorine leaves residues in humans through the food chain and bioaccumulation in tissues (Badawi et al., 2000; Kibria, 2016; Choudhary et al., 2018). It causes the risk of cancer (Jayaraj et al., 2016). Organochlorines are a group of widely used chlorinated compounds belonging to the dangerous persistent organic pollutant group. Chlorine affects the function and activity of biota, changing microbial communities (Wang et al., 2010; Atashgahi et al., 2018; Medo et al., 2020) affects the growth/availability of nutrients for plants in terms of absorption. The effect of chlorine on biota activity and nutrient availability, chemically microbes will convert some nutrients into insoluble forms to become unavailable to plants (Nogueira et al., 2020). Active ingredients pesticides can affect the balance of adsorption complexes in the soil. It affects the balance of nutrients and soil acidity levels to affect the availability of nutrients that plants can absorb.

The water supply management sector is responsible for solving this problem by complete monitoring and using sufficient chlorine so that no more water is harmful to the health of residents (Abid et al., 2014). The government must monitor the use of chlorine and water quality as a whole according to its standards to minimize the effects of various harmful effects on living things (Abid et al., 2014). Therefore, it is necessary to manage a watershed system that can provide high land productivity, watershed sustainability, improvingcommunity welfare (Asdak, 2018). With surface water analysis being able to distinguish contaminated/polluted watersheds from those that are not polluted, the control of fertilizer and pesticide residues in the watershed environment, especially the Tondano watershed, is under control (Rochette et al., 2020).

Bacillariophyceae was the most dominant class found in the study, followed by *Chlorophyceae* and *Cyanophyceae*. River waters are generally dominated by phytoplankton from the *Bacillariophyceae*, *Chlorophyceae*, and *Cyanophyceae* classes. According to Widigdo and Wardiatno (2013), the class of phytoplankton often found in large amounts of water is the Class *Bacillariophyceae*. The *Cyanophyceae* class is also dominantly found because this class can bind nitrogen free from the air so that *Cyanophyceae* will grow faster than other classes. Several genera of the *Cyanophyceae* group that is thread-shaped have special cells called heterocyst that can bind free nitrogen from the air so that these species can survive in waters with low nitrogen concentrations (Widigdo & Wardiatno, 2013). *Bacillariophyceae* and *Cyanophyceae*. *Chlorophyta* is green algae that, if they are numerous and dominate the waters, will make the waters look greenish, while *Bacillariophyta* is phytoplankton, better known as diatoms. The dominance of the number and types of *Chlorophyta* can indicate that water is eutrophication (Mujiyanto et al., 2011).

Bacillariophyceae is a group of algae that, qualitatively and quantitatively, are abundant in various types of waters, both in plankton and periphyton. The *Bacillariophyceae* class is a cosmopolitan phytoplankton class, resistant to extreme conditions, easy to adapt, and has very high reproductive power. Abundant phytoplankton was found to be a genius with high tolerance; besides, it is supported by water conditions that contain sufficient nutrients needed for developing phytoplankton, namely phosphate and nitrate from household and industrial waste.

The diversity index is an index that expresses community structure and ecosystem stability. The diversity index value at the six observation stations ranged from 2.43-2.78. Diversity at all research sites is classified in moderate species diversity. Yunandar et al. (2020) stated that the diversity index value ranges from 0-1, indicating that the area has high ecological pressure and low species diversity index. The range 1-3 indicates a moderate diversity index, for diversity values more significant than three indicate the state of an area experiencing low ecological pressure and a high species diversity index. These results suggest that the diversity of phytoplankton species in the Tondano watershed has moderate distribution, average productivity, balanced ecosystem conditions, and moderate ecological pressure.

Based on the classification of the diversity index, it can be said that the diversity of phytoplankton in the Tondano River watershed is classified as moderate. It indicates that the waters have experienced moderate disturbances and affect the diversity and abundance of phytoplankton. Several factors that can affect the diversity of phytoplankton in water are currents, nutrient content, predators, temperature, brightness, turbidity, pH, dissolved gases, and chlorine levels that enter the waters.

The species evenness index (E) is used to see the level of each community formed whether there is a balance and describes the distribution of individuals between different species obtained from the relationship between diversity (Dea, 2000). The evenness of species at six stations varied with index ranging from 0.82 to 0.94. Based on this value, it can be said that the evenness of phytoplankton species at the six observation stations is high. Balqis et al. (2021) state that if the E value is > 0.75, then the evenness of the species is classified as high, meaning that the density or presence of biota is evenly distributed, whereas if the E value is < 0.75, the evenness is low, and the distribution of species is uneven, or some species dominate. The species evenness index is strongly influenced by the distribution of individuals of the species because even though a community has many types if the distribution of individuals is not evenly distributed, the evenness of species is low. Differences strongly influence the distribution of phytoplankton species in nutrients such as phosphate and nitrate and chlorine levels in the waters of the Tondano River watershed.

The correlation between species diversity and chlorine concentration shows different values. According to Clarke and Ainsworth (1993), the standard for grouping correlation numbers is: If the value of r = 0: There is no correlation between two variables; r > 0–0.25: very weak correlation; r > 0.25 – 0.5 : sufficient correlation; r > 0.5 – 0.75 : strong correlation; r > 0.75 – 0.99: very strong correlation and if r = 1 : perfect correlation. Based on these values, it can be said that the correlation between the number of species and the chlorine concentration is very weak, while the species diversity index and species evenness index show a sufficient correlation. There is a powerful correlation between the abundance of phytoplankton and the chlorine concentration, but the value is not significant. It means that the diversity of phytoplankton species in the Tondano watershed does not significantly affect the phytoplankton diversity, but there is already ecological pressure. There is no significant effect because the chlorine concentration in each river has not shown too high compared to the quality standard according to Government Regulation Number 22 of 2021, with a chlorine concentration of 0.03 mg/L. In contrast, those above the quality standard are only two rivers, the Tondano River downstream and the Kakas River downstream.

CONCLUSION

Chlorine distribution from upstream to downstream of the Tondano watershed was observed from 17 river stations. There were two rivers with chlorine distribution at the threshold to exceed the quality standard (0.03 mg/l). The dominant phytoplankton found were from the *Bacillariophyceae*, *Chlorophyceae*, and *Cyanophyceae* classes, while the most abundant species was *Navicula* sp. The diversity of phytoplankton species which includes the number of species, species abundance, species diversity index, and species evenness index in the Tondano River watershed, is categorized as moderate and aquatic ecosystems are experiencing moderate ecological pressure. However, the impact of chlorine distribution on phytoplankton species diversity has no significant effect.

REFERENCES

Abid, K., Alamgir, A., Zahid, Y., Mahar, K., Arif, S., Zehra, W., ... & Sherwani, S. K. (2014). Chlorine status and drinking water quality in public institutions of Karachi, Pakistan. *American-Eurasian Journal of Agricultural & Environmental Science*, *14*(11), 1317-1321.

Alkhateeb, R. (2014). Influence of Chloride Concentration on Water Quality. *International Journal of Applied Engineering Research and Development (IJAERD)*, *4*(1), 63–68.

Asdak, C. (2018). *Hidrologi Dan Pengelolaan Daerah Aliran Sungai*. Gadjah Mada University Press.

Atashgahi, S., Liebensteiner, M. G., Janssen, D. B., Smidt, H., Stams, A. J. M., & Sipkema, D. (2018). Microbial synthesis and transformation of inorganic and organic chlorine compounds. *Frontiers in Microbiology*, *9*, 3079.

Azizullah, A., Khattak, M. N. K., Richter, P., & Häder, D. P. (2011). Water pollution in Pakistan and its impact on public health—a review. *Environment international*, *37*(2), 479-497.

Badawi, A. F., Cavalieri, E. L., & Rogan, E. G. (2000). Effect of chlorinated hydrocarbons on the expression of cytochrome P450 1A1, 1A2 and 1B1 and 2-and 4-hydroxylation of 17β-estradiol in female Sprague–Dawley rats. *Carcinogenesis*, *21*(8), 1593–1599.

Bajjali, W. (2018). Watershed delineation. In *ArcGIS for environmental and water issues* (pp. 235–245). Springer.

Balqis, N., El Rahimi, S. A., & Damora, A. (2021). Keanekaragaman dan kelimpahan fitoplankton di perairan ekosistem mangrove Desa Rantau Panjang, Kecamatan Rantau Selamat, Kabupaten Aceh Timur. *Jurnal Kelautan Dan Perikanan Indonesia*, *1*(1), 35–43.

Bassey, G. I. (2017). Residual chlorine decay in water distribution network. *Journal of Scientific Research and Engineering Studies (IJSRES)*, *3*(3), 1-6

Borja, V. M. (2012). *Marine phytoplankton of the Western Pacific*. Kouseisha Kouseikaku.

Chen, W., He, Z. L., Yang, X. E., Mishra, S., & Stoffella, P. J. (2010). Chlorine nutrition of higher plants: progress and perspectives. *Journal of Plant Nutrition*, *33*(7), 943–952.

Choudhary, S., Yamini, N. R., Yadav, S. K., Kamboj, M., & Sharma, A. (2018). A review: Pesticide residue: Cause of many animal health problems. *Journal of Entomology and Zoology Studies*, *6*(3), 330-333.

Clarke, K. R., & Ainsworth, M. (1993). A method of linking multivariate community structure to environmental variables. *Marine Ecology-Progress Series*, *92*, 205.

Clesceri, L. S., Greenberg, A. E., & Trussell, R. R. (1989). Chlorophyll Method 10200H. *Standard Methods for the Examination of Water and Wastewater, 17th Ed. American Public Health Associate, Washington, DC*, 31–39.

Da Costa, J. B., Rodgher, S., Daniel, L. A., & Espíndola, E. L. G. (2014). Toxicity on aquatic organisms exposed to secondary effluent disinfected with chlorine, peracetic acid, ozone and UV radiation. *Ecotoxicology*, *23*(9), 1803–1813.

David, M. B., Mitchell, C. A., Gentry, L. E., & Salemme, R. K. (2016). Chloride sources and losses in two tile-drained agricultural watersheds. *Journal of Environmental Quality*, *45*(1), 341–348.

Dea, D. G. B. (2000). Teknik pengambilan contoh dan analisis data biofisik sumberdaya pesisir. *Pusat Kajian Sumberdaya Pesisir Dan Lautan. Fakultas Perikanan Dan Ilmu Kelautan. Institut Pertanian Bogor. Bogor*.

Della Rossa, P., Jannoyer, M., Mottes, C., Plet, J., Bazizi, A., Arnaud, L., Jestin, A., Woignier, T., Gaude, J.-M., & Cattan, P. (2017). Linking current river pollution to historical pesticide use: Insights for territorial management?. *Science of the Total Environment*, *574*, 1232–1242.

Emmanuel, E., Keck, G., Blanchard, J.-M., Vermande, P., & Perrodin, Y. (2004). Toxicological effects of disinfections using sodium hypochlorite on aquatic organisms and its contribution to AOX formation in hospital wastewater. *Environment International*, *30*(7), 891–900.

Erlangga, Y. Y., & Setiawan, H. (2018). Perancangan mesin pengolah air bersih bergerak dengan menggunakan sistim modular untuk penanggulangan keadaan darurat air. *Machine: Jurnal Teknik Mesin*, *4*(1), 21–28.

García-Espinoza, J. D., Mijaylova-Nacheva, P., & Avilés-Flores, M. (2018). Electrochemical carbamazepine degradation: effect of the generated active chlorine, transformation pathways and toxicity. *Chemosphere*, *192*, 142–151.

Gill, H. K., & Garg, H. (2014). Pesticide: environmental impacts and management strategies. *Pesticides-Toxic Aspects*, *8*, 187.

Hadi, A. (2015). Pengambilan sampel lingkungan. *Erlangga, Jakarta*.

Hassaan, M. A., & El Nemr, A. (2020). Pesticides pollution: Classifications, human health impact, extraction and treatment techniques. *The Egyptian Journal of Aquatic Research*, *46*(3), 207-220.

Hayat, F. (2020). Analisis Kadar Klor Bebas (Cl2) dan Dampaknya Terhadap Kesehatan Masyarakat di Sepanjang Sungai Cidanau Kota Cilegon. *Jurnal Kesehatan Masyarakat Mulawarman (JKMM)*, *2*(2), 64–69.

Hou, Z., Jiang, Y., Liu, Q., Tian, Y., He, K., & Fu, L. (2018). Impacts of environmental variables on a phytoplankton community: A case study of the tributaries of a subtropical river, Southern China. *Water*, *10*(2), 152.

Igbinosa, E. O., Odjadjare, E. E., Chigor, V. N., Igbinosa, I. H., Emoghene, A. O., Ekhaise, F. O., Igiehon, N. O., & Idemudia, O. G. (2013). Toxicological profile of chlorophenols and their derivatives in the environment: the public health perspective. *The Scientific World Journal*, *2013*.

Iglesias, A., & Garrote, L. (2015). Adaptation strategies for agricultural water management under climate change in Europe. *Agricultural Water Management*, *155*, 113–124.

Jayaraj, R., Megha, P., & Sreedev, P. (2016). Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. *Interdisciplinary Toxicology*, *9*(3–4), 90.

Kibria, G. (2016). Pesticides and its impact on environment, biodiversity and human health-A short review.

Koneri, R., Nangoy, M., & Wakhid, W. (2021). Richness and diversity of insect pollinators in various habitats around Bogani Nani Wartabone National Park, North Sulawesi, Indonesia. *Biodiversitas Journal of Biological Diversity*, *22*(1), 288-297.

Lestari, H. A., Samawi, M. F., Faizal, A., Moore, A. M., & Jompa, J. (2021). Diversity and abundance of phytoplankton in the coastal waters of South Sulawesi. *HAYATI Journal of Biosciences*, *28*(3), 199–211.

Levillain, J., Cattan, P., Colin, F., Voltz, M., & Cabidoche, Y.-M. (2012). Analysis of environmental and farming factors of soil contamination by a persistent organic pollutant, chlordecone, in a banana production area of French West Indies. *Agriculture, Ecosystems & Environment*, *159*, 123–132.

Li, H., Mehler, W. T., Lydy, M. J., & You, J. (2011). Occurrence and distribution of sediment-associated insecticides in urban waterways in the Pearl River Delta, China. *Chemosphere*, *82*(10), 1373–1379.

Li, Y., Li, J., & Zhang, H. (2014). Effects of chlorination on soil chemical properties and nitrogen uptake for tomato drip irrigated with secondary sewage effluent. *Journal of Integrative Agriculture*, *13*(9), 2049–2060.

Luntungan, J. N. (2014). *Dinamika spasial penggunaan lahan pertanian berdasarkan citra penginderaan jauh: Tinjauan dalam rangka menuju pertanian lestari didaerah aliran sungai (DAS) Noongan dan Panasen kabupaten Minahasa Sulawesi Utara*. Universitas Gadjah Mada.

Mahmood, I., Imadi, S. R., Shazadi, K., Gul, A., & Hakeem, K. R. (2016). Effects of pesticides on environment. In *Plant, soil and microbes* (pp. 253–269). Springer.

Medo, J., Hricáková, N., Maková, J., Medová, J., Omelka, R., & Javoreková, S. (2020). Effects of sulfonylurea herbicides chlorsulfuron and sulfosulfuron on enzymatic activities and microbial communities in two agricultural soils. *Environmental Science and Pollution Research*, *27*(33), 41265–41278.

Mottes, C., Deffontaines, L., Charlier, J. B., Comte, I., Della Rossa, P., Lesueur-Jannoyer, M., Woignier, T., Adèle, G., Tailame, A.-L., & Arnaud, L. (2020). Spatio-temporal variability of water pollution by chlordecone at the watershed scale: what insights for the management of polluted territories? *Environmental Science and Pollution Research*, *27*(33), 40999–41013.

Mujiyanto, D. W., Tjahjo, H., & Sugianti, Y. (2011). Hubungan Antara Kelimpahan Fitoplankton dengan Konsentrasi N: P pada Daerah Keramba Jaring Apung (KJA) di Waduk Ir. H. Djuanda. *Jurnal Limnotek*, *18*(1), 15–25.

Nogueira, L. M., Buzetti, S., Filho, M. C. M. T., Galindo, F. S., & Mello, T. F. (2020). Residual effect of KCl coated by polymeters incorporated in a corn crop. *IDESIA (Chile)*, *38*(1), 39–46.

Ogunfowokan, A. O., Oyekunle, J. A. O., Torto, N., & Akanni, M. S. (2012). A study on persistent organochlorine pesticide residues in fish tissues and water from an agricultural fish pond. *Emirates Journal of Food and Agriculture*, 165–184.

Özkara, A., Akyıl, D., & Konuk, M. (2016). Pesticides, environmental pollution, and health. In *Environmental health risk-hazardous factors to living species*. IntechOpen.

Pan, L., Zhang, X., Yang, M., Han, J., Jiang, J., Li, W., Yang, B., & Li, X. (2019). Effects of dechlorination conditions on the developmental toxicity of a chlorinated saline primary sewage effluent: Excessive dechlorination is better than not enough. *Science of the Total Environment*, *692*, 117–126.

Pereira, D. G. C., Santana, I. A., Megda, M. M., & Megda, M. X. V. (2019). Potassium chloride: impacts on soil microbial activity and nitrogen mineralization. *Ciência Rural*, *49*.

Prasiwi, I., & Wardhani, E. (2018). Analisis Hubungan Kualitas Air Terhadap Indeks Keanekaragaman Plankton dan Bentos Di Waduk Cirata. *Rekayasa Hijau: Jurnal Teknologi Ramah Lingkungan*, *2*(3).

Rochette, R., Bonnal, V., Andrieux, P., & Cattan, P. (2020). Analysis of surface water reveals land pesticide contamination: an application for the determination of chlordecone-polluted areas in Guadeloupe, French West Indies. *Environmental Science and Pollution Research*, *27*(33), 41132–41142.

Rowe, M. D., Anderson, E. J., Vanderploeg, H. A., Pothoven, S. A., Elgin, A. K., Wang, J., & Yousef, F. (2017). Influence of invasive quagga mussels, phosphorus loads, and climate on spatial and temporal patterns of productivity in Lake Michigan: A biophysical modeling study. *Limnology and Oceanography*, *62*(6), 2629–2649.

Sardet, C. (2015). *Plankton: wonders of the drifting world*. University of Chicago Press.

Sharma, P. P., Yadav, V., Rajput, A., & Kulshrestha, V. (2018). Synthesis of chloride-free potash fertilized by ionic metathesis using four-compartment electrodialysis salt engineering. *ACS Omega*, *3*(6), 6895–6902.

Singh, N., & Singh, S. B. (2012). Sorption-desorption behavior of metsulfuron-methyl and sulfosulfuron in soils. *Journal of Environmental Science and Health, Part B*, *47*(3), 168–174.

Sittadewi, E. H. (2008). Fungsi strategis Danau Tondano, Perubahan ekosistem dan masalah yang terjadi. *Jurnal Teknologi Lingkungan*, *9*(1), 5-66.

Sofia, E., & Riduan, R. (2017). Evaluasi dan analisis pola sebaran sisa klor bebas pada jaringan distribusi ipa sungai lulut pdam bandarmasih. *Jukung (Jurnal Teknik Lingkungan)*, *3*(2), 10-24.

Sriwijayanti, L. A., Setiawan, R. Y., Firdaus, M. R., Fitriya, N., & Sugeha, H. Y. (2019). Community structure of phytoplankton in the surface and thermocline layers of Sangihe and Talaud waters, Indonesia. *International Journal of Bonorowo Wetlands*, *9*(2), 51-58.

Tsitsifli, S., & Kanakoudis, V. (2018). Disinfection impacts to drinking water safety—A review. *Multidisciplinary Digital Publishing Institute Proceedings*, *2*(11), 603, 1-7.

Vannoni, M., Créach, V., Lozach, S., Barry, J., & Sheahan, D. (2021). Chlorination in power station cooling water systems: Effect on biomass, abundance and physiology of natural phytoplankton communities. *Aquatic Toxicology*, *239*, 105954.

Wang, Y. S., Chen, W. C., Lin, L. C., & Yen, J. H. (2010). Dissipation of herbicides chlorsulfuron and imazosulfuron in the soil and the effects on the soil bacterial community. *Journal of Environmental Science and Health Part B*, *45*(5), 449-455.

Wantasen, S., Luntungan, J. N., & Tarore, A. E. (2020). Spatio-temporal distribution of chlorine in the upper Tondano Watershed North Sulawesi Indonesia. *IOP Conference Series: Earth and Environmental Science*, *535*(1), 12029.

Wantasen, S., Luntungan, J. N., Tarore, A. E., & Lumingkewas, A. (2019). Water quality of the Panasen River in the upstream of the Tondano Watershed in a five-year period (2014-2018). *Journal of Physics: Conference Series*, *1321*(3), 32115.

Widigdo, B., & Wardiatno, Y. (2013). Dinamika komunitas fitoplankton dan kualitas perairan di lingkungan perairan tambak udang intensif: sebuah analisis korelasi. *Jurnal Biologi Tropis*, *13*(2), 160-184.

Yunandar, D., Effendi, H., & Setiawan, Y. (2020). Plankton biodiversity in various typologies of inundation in Paminggir peatland, South Kalimantan, Indonesia on dry season. *Biodiversitas Journal of Biological Diversity*, *21*(3), 1012-1019

Yusuf, Z. H. (2020). Phytoplankton as bioindicators of water quality in Nasarawa reservoir, Katsina State Nigeria. *Acta Limnologica Brasiliensia*, *32*, 1-11

Zhang, Q., Gaafar, M., Yang, R.-C., Ding, C., Davies, E. G. R., Bolton, J. R., & Liu, Y. (2018). Field data analysis of active chlorine-containing stormwater samples. *Journal of Environmental Management*, *206*, 51–59.

Zhao, C., Xie, H., Zhang, J., Xu, J., & Liang, S. (2013). Spatial distribution of organochlorine pesticides (OCPs) and effect of soil characters: a case study of a pesticide producing factory. *Chemosphere*, *90*(9), 2381–2387.