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DANGEROUS HEAVY METAL POLLUTION AND NITRATE AND PHOSPHATE CONCENTRATION CONTAINED IN THE SEAWEED THALLUS

(Kappaphycus Alvarezii and Gracilaria Verrucosa)

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ABSTRACT

Kappaphycus alvarezii seaweed is a key local commodity in Central Sulawesi. However, since 2012, its production has drastically decreased, especially in mining exploration centers such as the coastal waters of Morowali Regency and Palu Bay. Mining activities, including nickel mining in Morowali, gold mining in Poboya, and other mining operations in Palu, have led to changes in land use, transforming areas into mining concessions. This situation raises significant concerns as both mining commodities and seaweed are crucial regional assets for driving the local and national economy. Mining activities have resulted in a substantial reduction in the area of *Kappaphycus alvarezii* cultivation in Morowali Regency, decreasing from 78,420 ha in 2011 to 8,410 ha in 2014. Data from the Central Sulawesi Provincial Fisheries Service reveals a significant decline in dry *Kappaphycus sp* production from 2016-2020, reaching 383,360 – 59,129 tons/year, with no production expected in 2021. Similarly, E. spinosum and *Gracilaria sp* production have also experienced declines from 2018-2021. The results of the research show that the nickel content in the thallus of seaweed along the Morowali waters is very high and can be dangerous and is thought to be the cause of the extinction of the seaweed.

Keywords: Seaweed, Mining, Exploitation, Extinction

1. INTRODUCTION

Seaweed cultivation has been a longstanding practice in Indonesia, utilizing species such as *Kappaphycus alvarezii*, Gracilaria sp., and others [1]. As a non-food source and main commodity (e.g., carrageenan and agar), Eucheuma sp. holds promising economic prospects for coastal communities, boasting advantages like easy cultivation, a relatively short growing season, and low production costs (Ya'laa et al., 2022).

The potential of seaweed is evident through increased production and profitable investment. Environmental conditions and qualifications support suitable habitats for seaweed cultivation, with local participation indicating strong community support. The government must secure policies, allocate funds, and establish partnerships with local banks to ensure the sustained growth of seaweed cultivation in regions like the Salabangka Islands (Ya'laa et al., 2022).

The physical characteristics of water play a pivotal role in determining the suitability of an area for seaweed cultivation. This research employs an ecological approach by simultaneously cultivating seaweed and milkfish, recognizing the interconnectedness of environmental factors. Seaweed growth is highly dependent on oceanographic parameters such as physical, chemical, and biological aspects (Ya'la et al., 2022).

Figure 1. Conditions of Mining and Water Activities

Figure 2. Conditions of Mining Activities

Numerous companies operating in Central Sulawesi contribute to water pollution, particularly in areas like Morowali Regency, where nickel mining has rapidly transformed the landscape. This occurs at vital points identified as nickel mining hotspots in Bahodopi Selatan Bungku and gravel mining in Palu Bay. The high mining activities along the coast have altered sea water quality, impacting the production of E. cottonii (Yala & Sulistiawati, 2017).

The mining sector significantly contributes to the country's foreign exchange, accounting for 36% of state income in 2008 [4]. Additionally, it serves as a substantial source of employment. However, the unchecked mining expansion in Morowali Regency, Central Sulawesi, has led to the destruction of protected forest areas over the past dozen years. Mangrove forests along Tambayoli Beach, Tamainusi, and Tandoyondo have been cleared for use as a nickel loading port. From an environmental standpoint, coal mining is deemed the most destructive compared to other natural resource exploitation activities (Fitrawan et al., 2021).

2. METHODS

2.1. Research sites

The research location consists of 4 stations, namely station 1 South Bungku waters, Station 2 Moschino waters and station 3 Bahonsuai waters.

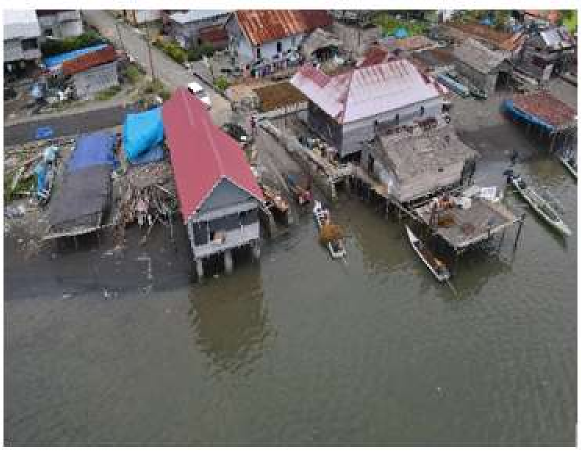

Figure 3. South Bungku waters

Figure 4. Witaponda Waters

Figure 5. The waters of Bumi Raya

2.2. Sampling Location Map

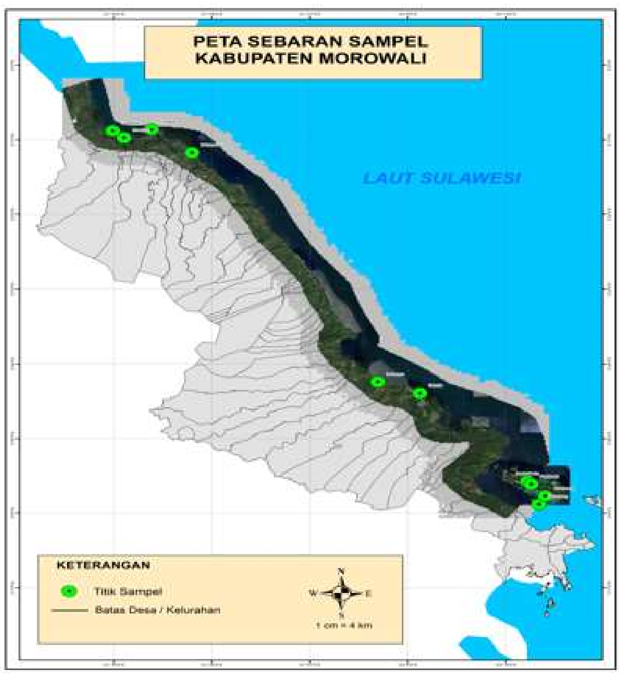

Figure 6. Location of Seaweed Sampling

2.3. Measurement of Heavy Metals in Seaweed Thallus

Table 1. Materials used in research and their functions 7

No	Material	Function
1	HNO3 is concentrated	Reagents
2	APDC 4%	Reagents
3	Aquadest	Tool calibration
4	Heavy Metal Standards	Heavy metal guide
6	MIBK Solvent (Methyl ISO butyl ketone)	Reagents
7	Sodium Borohydride Potassium Iodide 10%	Reagents
8	Water sample	For sample materials

2.4. Research Procedure

1) Seaweed samples were taken at each station at each station with three repetitions, seaweed sampling was carried out based on SNI
2) Seaweed samples taken in dry conditions were obtained from cultivators along the waters of Morowali District.
3) Then the sample was given 1 drop of formalin for 200 grams of dried seaweed.
4) Analyzing the heavy metal content in seaweed was carried out using the Association of Official Analytical Chemists (AOAC) international modification 2005: 999.10 method, using Flame Atomic Absorption Spectrophotometry (FAAS) and Graphite Furnace Atomic Absorption Spectroscopy (GFAAS). A total of 0.5 grams of test seaweed and CRM was weighed then added with HNO acid and then extracted using microwave digestion. The resulting digestion solution was then measured for the total metal concentration of copper (Cu), zinc (Zn), iron (Fe), cadmium (Cd) and lead (Pb) usingFAAS and GFAAS. The parameters in this method study include linearity, detection limit, accuracy and precision (Anonim, 2012).

3. RESULT AND DISCUSSION

Data from the Central Sulawesi Provincial Fisheries Service In 2011-2015, dry Kappaphycus sp production in Central Sulawesi ranged from 220,160 – 460,166 tons/year. However, from 2016-2020, there was a significant decline, plummeting to 383,360 – 59,129 tons/year, and in 2021, there was no production. Similarly, E. spinosum production witnessed a decline from 36,420-9,385 dry tons between 2018-2021. Gracilaria sp production also decreased from 2014-2021, ranging from 57,146.6 - 2,792 dry tons/year. This data contrasts sharply with research findings by Konda and Meiyasa (2023), which suggest continuous seaweed production growth from 2,321,408 tonnes in 2021 to 2,224,478 tonnes in 2022 (KKP, 2021). Meanwhile, seaweed production data in East Nusa Tenggara in 2020 was around 2,158,903 tons, and in East Sumba in 2020, it was approximately 29,738 tons.

3.1. Content of Total N, Total P and Heavy Metals in Grass auat *Kappaphycus alvarezii* in South Bungku Waters (Station 1):

Mining is essentially an effort to develop potential mineral and energy natural resources for economic and optimal utilization, benefiting people through exploration, exploitation, and utilization of mining products. This effort relies on various resources, especially energy and mineral resources, supported by quality human energy resources, mastery of science and technology, and management capabilities (Prihantini, 2015).

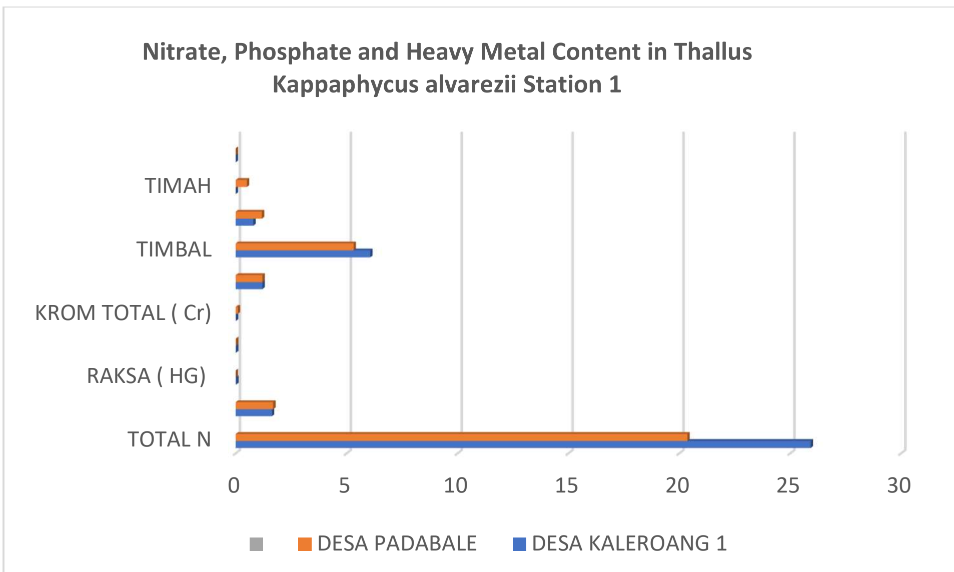

Figure 7. Nitrate, Phosphate and Heavy Metal Content in Thallus *Kappaphycus alvarezii* Station 1

The research results on heavy metal content in the South Bungku Waters of Kaleroang Village showed the highest value of Total N at 27.42 ppm, Total P at 1.81, and lead (Pb) at around 6.06 ppt. In Padabale Village waters, Total N was recorded at 20.36 ppm, Total P at 1.69 ppm, and Lead (Pb) at 5.4 ppm, with Cadmium (Cd) at 1.18 ppm. In comparison, heavy metal contamination from Mangili and Wula-Waijule waters is significantly lower than that reported by Siaka et al. (2016), indicating low lead and copper contamination in seaweed from Pandawa coastal waters (13.27-51.32 mg/kg lead and 0.06-0.20 mg/kg copper) (Konda & Meiyasa, 2023). Another study (NABILAH, 2017) on the heavy metal mercury (Hg) concentration in *Kappaphycus alvarezii* seaweed in Bluto and Saronggi waters, Sumenep, ranged from 0.1 ppm – 0.06 ppm. The Hg concentration in the waters around Bluto and Saronggi ranged from 0.0731 – 0.1138 ppm, and in sediment in waters, it was 0.002 – 0.003 ppm (NABILAH, 2017).

3.2. Total N, Total P and Heavy Metal Content in *Kappaphycus Alvarezii* Seaweed Thallus in Wita Ponda Waters (Station 2):

One type of seaweed with economic value is *Kappaphycus alvarezii* and *Gracilaria sp.* Seaweed, acting as a biofilter, absorbs compounds from the water. Pollutants, especially heavy metals, can compromise seaweed quality. The influx of heavy metals into the waters leads to their accumulation in the seaweed thallus, resulting in bioaccumulation and biomagnification.

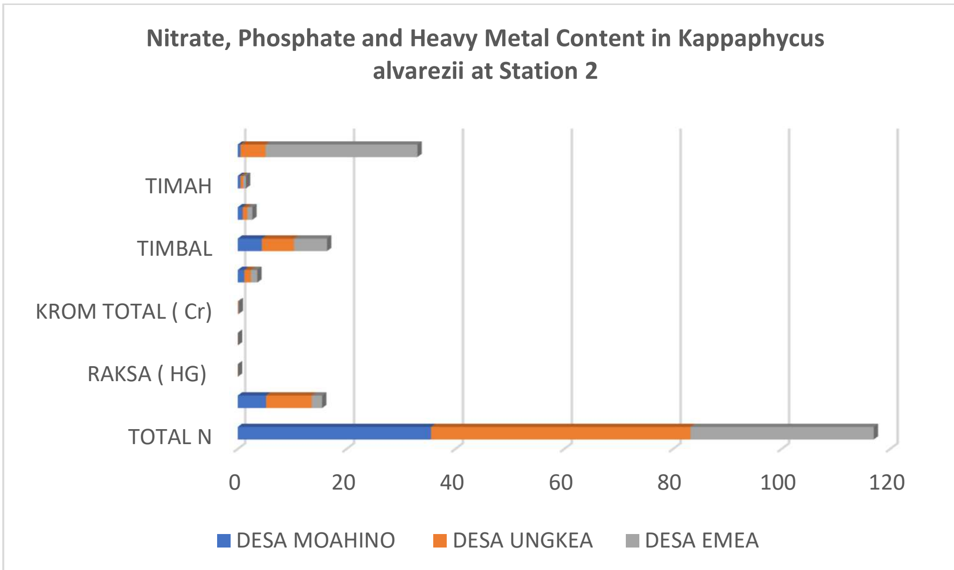

Figure 8. Nitrate, Phosphate and Heavy Metal Content in Thallus *Kappaphycus alvarezii* Station 2

Seaweed heavy metal analysis is essential due to its connection to seaweed use, particularly as food. It is crucial to understand the elevated levels of buried metals as part of observing consumption safety and addressing water pollution. The review of food safety is an integral element in community food security.

The contents of Total N, Total P, and heavy metals in the Wita Ponda waters of Moschino Village include Total N 34.82 ppm, Total P 5.32 ppm, Lead 4.42 ppm. Ungkea Village waters include Total N 47.68 ppm, Total P 8.37 ppm, Lead 5.89 ppm, nickel 4.61 ppm. Emea Village waters include a total of 33.78 ppm, a total of 1.93 ppm, Lead 6.09 ppm, and nickel 27.90 ppm.

Concentrations of heavy metals (Fe, Zn, Cu, Cd, Ni, Pb, Cr, As) were determined in seven seaweeds of environmental and commercial relevance (Ulva rigida C. Ag., Gracilaria gracilis (Stackhouse) Steentoft, L. Irvine and Farnham, Porphyra leucosticta Thuret, Grateloupia doryphora (Montagne) Howe., Undaria pinnatifida (Harv.) Suringar, Fucus virsoides J. Agardh, Cystoseira barbata (Good. et Wood.) Ag.) were collected at four sampling locations in the Venice lagoon, in spring and autumn 1999. High levels of contamination, especially Pb, were detected in Ulva and to a lesser extent in Gracilaria sp. Brown seaweed, especially Cystoseira, is heavily contaminated with Arsenic. A decrease in Zn and Cd concentrations was observed from the inside of the central lagoon, near the industrial area, to the direction of the lagoon opening to the sea (Caliceti et al., 2002).

Competitive ability for N uptake by four types of intertidal seaweed, Stictosiphonia arbuscula (Harvey) King et Puttock, Apophlaea lyallii Hook. F. and Harvey, Scytothamnus australis Hook. F. et Harvey, and Xiphophora gladiata (Labillardière) Montagne ex Harvey, from New Zealand described by NO3−, NH4+, and urea uptake kinetics. This is the first study to report the kinetics of N uptake by a number of Southern Hemisphere intertidal seaweeds in relation to season and zonation. Species growing at the highest coastal positions had higher NO3− and urea uptake at high and low concentrations and had unsaturated NH4+ uptake in summer and winter. Although there is evidence of feedback inhibition of Vmax for NO3− uptake by Stictyosiphon arbuscula growing at the lower vertical limit of its range, this figure is relatively high compared to species growing lower on the coast. Our results highlight the superior competitive ability of N uptake in certain intertidal kelps, and consistent with our previous findings, we can conclude that intertidal kelps in southeastern New Zealand are adapting to maximize N gain in potentially N-limiting environments (Omar et al., 2017).

3.2. Total N, Total P and Heavy Metal Content in *Kappaphycus Alvarezii* Seaweed Thallus in Bumi Raya Waters (Station 3)

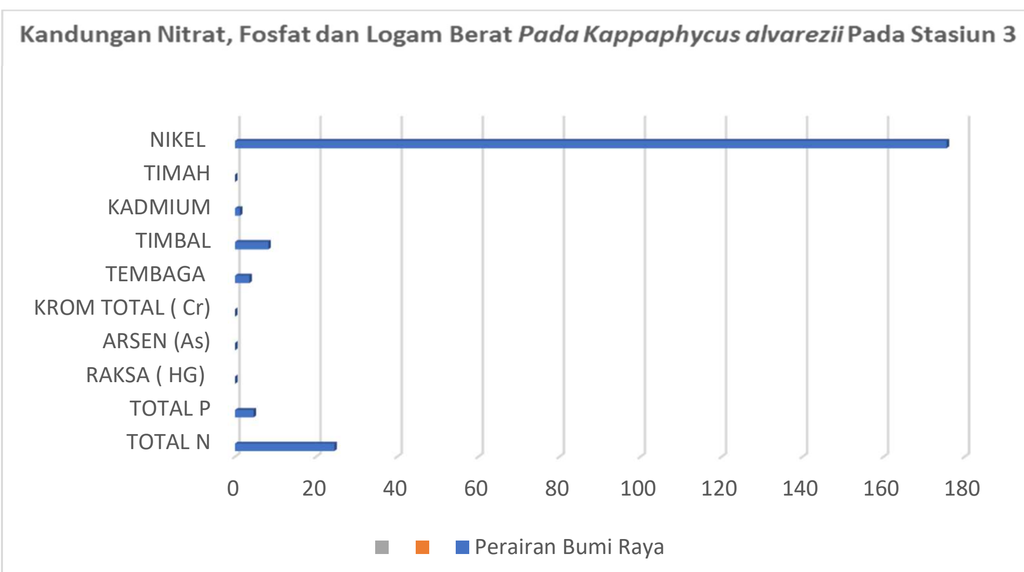

Figure 9. Nitrate, Phosphate and Heavy Metal Content in Tallus *Kappaphycus alvarezii* Station 3

Figure 9 illustrates the content of Total N, Total P, and heavy metals in the waters of Bumi Raya Bahonsuai Village, with Total N at 26.46 ppm, Total P at 5.53 ppm, Lead at 8.21 ppm, and nickel reaching the highest value at 175.54 ppm. The primary cause of nitrate enrichment is attributed to excessive fertilizer use on the soil surface and uncontrolled discharge of wastewater into the soil and river basins (Shrimali and Singh, 2001). Nitrate uptake rate and storage capacity were also determined in laboratory experiments. The seasonal growth of the seaweed Ulva rigida correlates with the seasonal trend of nitrogen concentration in the water column. The biomass of U. rigida exhibited exponential growth during spring, reaching a peak of around 300–400 g dry mass (DM) m−2. As biomass increases, U. rigida depletes nitrate in the water column. Thallus nitrate reserves also decreased from 100 mol N (g DM)−1 to barely detectable levels, and total thallus nitrogen decreased from 4% to 2.5% DM and 1.25% DM in 1991 and 1992, respectively. During summer, the decomposition of U. rigida increases, leading to an elevation in the concentration of organic nitrogen in the water column. Uptake experiments revealed an inverse relationship between thallus nitrate content and nitrate uptake rate, indicating a physiological response to a eutrophic environment where nitrate is supplied in large quantities for most of the year (Naldi & Viaroli, 2002).

3.3. Total N, Total P and Heavy Metal Content in *Gracilaria Verrucosa* Seaweed Thallus in Wita Ponda Waters (Station 4)

Seaweed is one of the fisheries commodities that needs special attention regarding the quality of seaweed to get high quality jelly. *Gracilaria verrucosa* is the most important type of seaweed as a source of agar (*agarophyte*) which is mostly used both for direct consumption and for industrial needs.

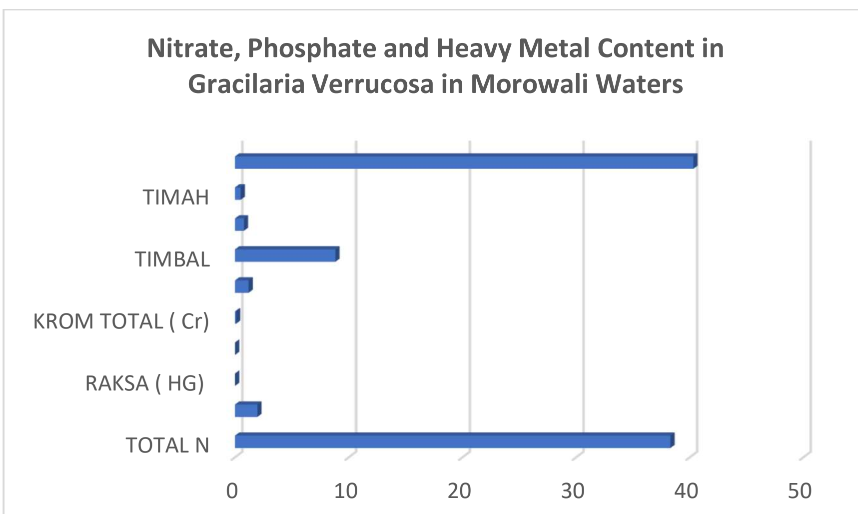

Figure 10. Nitrate, Phosphate and Heavy Metal Content in *Gracilaria verrucosa* Thallus Station 3

Based on Figure 10, it reveals the highest heavy metal content, namely nickel at 40.32 ppm, lead at 8.83 ppm, and Total N around 38.30 ppm. Meanwhile, the content of other heavy metals ranges from 0-0.79 ppm. The nickel content is exceptionally high in the seaweed type *Gracilaria verrucosa*. The significant negative impact of nickel mining is environmental damage. The nickel extraction process involves extensive excavation, chemical usage, and large water consumption, leading to deforestation, soil erosion, water pollution, and habitat degradation. Forests, serving as homes for diverse animal and plant species, face irreversible loss of biodiversity. Additionally, air pollution is a notable consequence, with the nickel processing process emitting toxic gasses like sulfur dioxide and nitrogen dioxide. These emissions contribute to increased local air pollution, adversely affecting air quality and the health of surrounding communities. Inhaled harmful particles can cause respiratory problems, eye irritation, and serious illnesses, including cancer.

Seaweed Gracilaria sp. exhibits the ability to absorb heavy metals such as Pb, Cu, and Cd. This ability is attributed to the polysaccharides present in Gracilaria's cell walls, allowing it to bind heavy metal ions and form complex compounds with organic substances in the thallus (Yulianto et al., 2006; Raya & Ramlah, 2012). According to Suardika et al. (2017), seaweed effectively cleans pollutants from industrial waste, absorbing 95% of heavy metals in water discharged from industries (Amanda et al., 2021). Waste from industrial and agricultural activities negatively impacts marine ecosystems, and heavy metal Cu, with its high potential for toxicity, is effectively absorbed by Gracilaria gigas cell walls (Yulianto et al., 2006).

4. CONCLUSION

In the thallus of *Kappaphycus alvarezii* seaweed in South Bungku Waters, the total nitrate content ranges from 20.36 to 27.42 ppm, and the lead and cadmium content in the seaweed thallus ranges from 6.06 ppm to 5.31 ppm. In the thallus of *Kappaphycus alvarezii* seaweed in Witaponda waters, the total nitrate content ranges from 34.83 to 47.68 ppm, total phosphate from 1.93 to 8.37 ppm, lead content from 4.42 to 6.09 ppm, and the highest content is nickel ranging from 0.5 to 29.9 ppm. The nickel content is very high and has become toxic to seaweed growing in these waters. In the thallus of *Kappaphycus alvarezii* seaweed in Bumi Raya waters, the total nitrate content ranges from 4.56 to 34.49 ppm, and the lead and copper content ranges from 8.21 ppm to 3.53 ppm. The nickel content is exceptionally high, reaching 175.54 ppm. In the thallus of the seaweed *Gracilaria verrucosa* in Witaponda waters, the total nitrate content ranges from 38.30 to 1.97 ppm, lead content at 8.83 ppm, and nickel content reaches 40.32 ppm. The nickel content in the thallus of seaweed along the Morowali waters is exceptionally high and poses a potential danger, thought to be the cause of the seaweed's extinction.

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