Nano Silica Application for Inducing Rice Resistance and the Possibility for Ytterbium Rare Earth Elements Green Mining

Sulis Dyah Candra and Titik Musriati

Faculty of Agriculture, Panca Marga University - Jl Yos Sudarso 107 Dringu Probolinggo 67271, East Java, Indonesia.

Corresponding author: sulis.d.candra@gmail.com

Abstract. There is a growing body of literature that recognizes the importance and usage of Silicon (Si) in plants to increase growth and productivity as well as plant resistance. Si in the form of Nano Silica particle recently becomes more frequently prescribed for inducing plant resistance and is essential for a range of technologies. This research examines the role of Nano Silica in rice for plant-induced resistance. This study set out to assess the effect of hydrophilic fumed Nano Silica application with the frequency of 1x, 2x, 3x, and 4x application respectively, through Randomized Block Design with three replications. SEM-EDX and XRF analysis were also used to identify the rice microanalysis appearance and microelement contents. Based on the observations, the Nano Silica frequencies showed a distinctive decrease of damage intensity at the 3x and 4x applications. The research also shows that the rice husk increase of metal-like surface appearance as more Nano Silica frequency was applied. Based on the finding it is proposed that Nano Silica induced plant resistance through the modification of surface layer or stronger physical barrier against pathogens or pests and stronger plant tolerance against environmental stress. The most unexpected observation to emerge from the data was that the emergence of Ytterbium (Yb), known as a Rare Earth Elements (REE) at the 3x and 4x Nano Silica applications. This indicates that the result of the Nano Silica application provides important insights and opportunities to advance the understanding of the Nano Silica application on Rice for the purpose of acquiring Ytterbium from farmland. Nano Silica can play an important role as a new method in addressing the Ytterbium green mining, which would be very advantageous to support renewable energy resources.

1. Introduction

In recent years, there has been an increased recognition to the usage of silicon (Si), especially in a form of nanomaterial/ Nano Silica in agriculture fields, that Si could increase the growth, yield and induced resistance against pest and pathogen. Although Si exist as the second most abundant mineral, due to the desilication process, Si in the soil was continually lost, e.g. because of the leaching (Meena et al., 2014).

It is very important to maintain Si levels in plants according to their needs so as not to inhibit the potential for plant growth and prevent production decline or stagnation. Si is a beneficial elements that could induce plant resistance system of plant against disease, insects and unfavorable weather conditions (Snyder et al., 2006), as well as supporting plant in dealing with biotic and abiotic pressure conditions, help maintain water balance, photosynthetic activity and leaf toughness (Bhavya et al., 2011).

Si able to create a physical barrier in the cuticle of the leaves and help increase plant resistance to pest and disease attacks, thus inducing the defense mechanism (Singh, 2015). The application of Si nutrients can also reduce the pests' ability to eat, number of viral pathogen vectors, and the risk of virus infection in plants (Schumann et al., 2018). While the form of silicone hemicellulose bonds has the potential to increase the mechanical ability and regeneration of cell walls in rice plants (He et al., 2015). Root application of Si can reduce the drastic effects of saline stress by supporting the sustainability of photosynthesis, protecting it from oxidative stress due to salt reducing free radicals that interfere with plant resistance (Parveen, 2012).

On rice plant, the application of Si have a significant effect in: maximum number of tillers, grain dry weight (Yohana et al., 2013), plant height, leaf angle, number of productive tillers (Ningsari, 2017) and increase rice yields (Husnain et al., 2012). The use of nano-agricultural products becoming increasingly feasible with experimental results which show great potential to reduce the impact of traditional agrochemicals on the environment, while significantly increasing crop yields and crop quality (Gomez et al., 2021). Nano Silica (Synonyms: Nano SiO_2, Nano-silicon, Silica nanoparticles, SiNPs) is an amorphous synthesized silica powder with diameters at the nano size (between 10–100 nm) consisting of silica particles (Laane, 2018). Foliar Nano Si sprays tend to decrease biotic stress and stimulate increase in growth and yield (Laane, 2018). The application of Nano Si was also proven to affect the increase of plant height and number of rice tillers (Sabatini et al., 2017), number of leaves, leaf area index, leaf area duration, total dry matter, crop growth rate, grain yield and straw yield (Soumya et al., 2020).

This study aims to experimentally investigate the performance of Nano Si in rice based on the ability to decrease pest intensity, and to acknowledge the result of microanalysis appearance as well as the micro element contents in rice grain. It is assumed that at the optimum Nano Si application could increase rice resistance against pest through mechanical defense.

2. Materials and Methods

The experiment conducted from May to August 2019 at Probolinggo, located on 7°47'17.2"S 113°30'41.1"E with altitude of 86 meter above sea level. The rice used in this experiment was Ciherang variety as the favorite variety among local farmers. The rice was planted using 25 days germinated rice seed. An AEROSIL® 200 hydrophilic fumed Nano Silica with specific surface area of 200 $m^2.g^{-1}$, containing 99.8% labotratory grade SiO2, were applied with the concentration of 25 ppm. The fertilizers used in the agricultural practices were: 120 kg of Urea, 50 kg of SP36 and 50 kg of KCl.

The plant growth observation includes the pest intensity percentage (absolute) and yield as dry weight ($g.plant^{-1}$). The pest intensity observation performed from 60 DAP at the intervals of 7 days, which were conducted after each Nano Silica application (1^{st} observation: 60 DAP), 2^{nd} observation: 67 DAP, 3^{rd} observation: 74 DAP, and 4^{th} observation: 81 DAP). Pest intensity percentage rate to measure damages that occurs permanently to rice plant, was calculated as stated in equation (1):

$$Pest\ Intensity = \frac{(n \div N)}{100\%} \qquad (1)$$

n = number of samples of plants that caused absolute damaged; and
N = number of plant samples observed.

Randomized Block Design with three repetitions were carried out on the Nano Silica frequency as treatment: N_1= 1x application; N_2= 2x applications; N_3= 3x applications; N_4 = 4x applications. The Anova analysis continued by the 5% Least Square Design analysis to see the differences between each treatment.

The Scanning Electron Microscope Energy-Dispersive X-ray (SEM-EDX) spectroscopy analysis were held to analyze the rice husk outer surface microscopic appearances affected by the Nano Silica application. The SEM Phenom were used to examine physical structures and the morphology of sample material with magnification of up to 1,000 times. The X-Ray Fluorescence (XRF) spectrometer analysis using PANalytical MiniPal 4 Energy-dispersive X-ray fluorescence, were also performed to determine the nutrient content contained in the rice due to Nano Si.

3. Results and Discussion

Soil and weather analysis were also presented to support the data, as served in Table 1 for soil analysis result, Figure 1 for Precipitation (%) and Rainfall (mm), also Figure 2 for Solar Energy (kWh) and Average Temperature (°C). From the soil analysis result show that the soil was dominated by Clay (50%) with the pH tendency of normal to acid, and most essential nutrients and organic content were low. The precipitation probability and average rainfall throughout the field experiment tend to be in alignment of showing decrease supply as the rice grow. The solar energy otherwise showing slight increase overtime, while the temperature tend to be colder.

Table 1. The Soil Analysis Result

pH 1:1		C Org	N total	C/N	P Olsen	K	Na	Ca	Mg	KTK	Sand	Silt	Clay
H_2O	KCl 1N	… % …			mg kg^{-1}	NH4OAC1N pH:7					… % …		
6.6	5.6	0.97	0.11	8	10.69	0.20	0.30	15.03	1.74	38.53	12	38	50

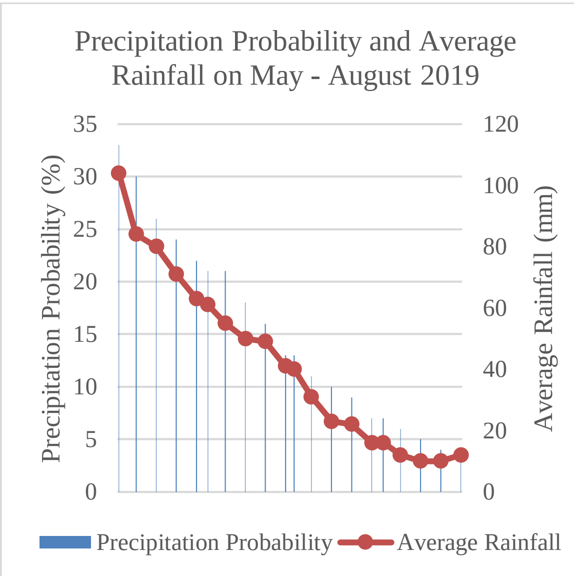

Figure 1. Precipitation (%) and Rainfall (mm) in Probolinggo during the experiment.

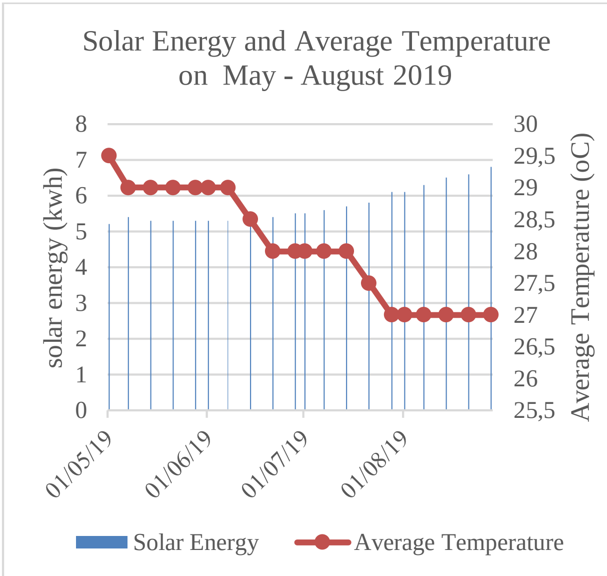

Figure 2. Solar Energy (kWh) and Average Temperature (°C) in Probolinggo during the experiment.

3.1 Analysis of Variance on Rice Plant

Based on the observations, the nano-silica frequencies showed a distinctive differences in terms of decreased damage intensity by pest on plants. The result show that especially shown on 74 DAP, the N_3 and N_4 (3 and 4 time nano silica application) could significantly decrease rice plants damages intensity (12.77 and 14.9 % respectively) compared to N_1 and N_2 (17.43 and 17.9 % respectively). While the results on the first, second and fourth pest intensity observation were not statistically significant (at 60, 67 and 81 DAP respectively).

According to the Directorate of Food Crop, the score scale for the damaged plants of all crops in the experiments shows in the range of moderate damages if the pest intensity value 25-50% at the end of observation. In this experiment, most damages were caused by Rice blast as the main threat to rice plant production loss. Indonesia mainly counting on rice production as main staple food to cover for the majority of its citizens, and currently still in the struggle to achieve national food security. In most lowincome countries, blast represents is a clear threat to food security (Cruz-Mireles et al., 2021). The calculated yield loss potential from rice blast is up to 3.65 ton ha^{-1}, which is equivalent to 61% the Ciherang variety average yield (Suganda et al., 2016).

Blast entry to plant by forming a melanin-pigmented dome-shaped appressorium (Cruz-Mireles et al., 2021). According to the field experiment result, it is proposed that with the application of Nano silica could decrease the blast entry to plant surface. Nano silica can be turned smart by crafting a surface coating (Nayfeh, 2018), as nano silica particles could accumulates on the surface of the rice cells (Cui et al., 2017). In this function, nano silica is a form of novel pesticide formulations that could be used to control pest (Debnath et al., 2011).

The rice plant dry weight of the N_1 (1x Nano Si application), N_2 (2x Nano Si application), N_3= (3x Nano Si application), and N_4 (4x Nano Si application) are 41.72, 57.52, 58.23, and 39.17 gram respectively, with the highest result acquired by N_3 and followed by N_2,as shown in Figure 4.

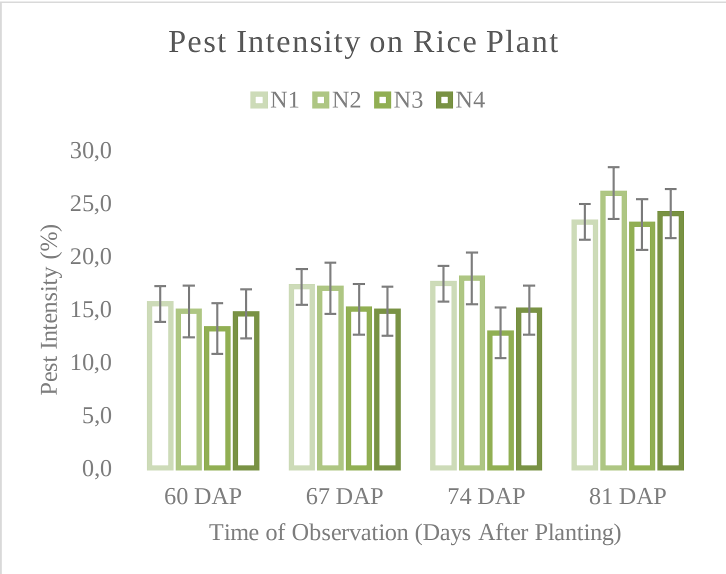

Figure 3. Pest Intensity (%) at Different Nano Silica Application on Rice Plant

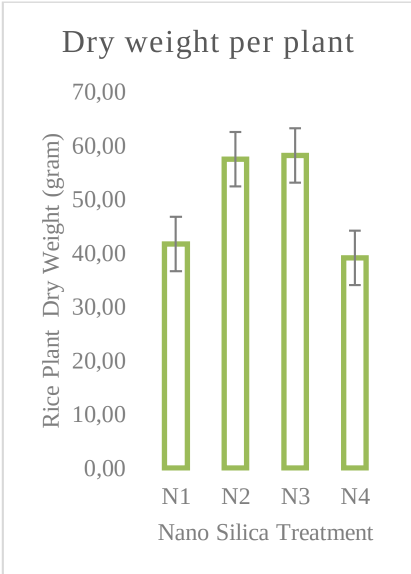

Figure 4. Rice Dry Weight per plant at Different Nano Silica Application

3.2 SEM-EDX Analysis on Rice Grain

The results of SEM-EDX analysis of rice husk showed physical differences in the metallic appearance from the surface layer of rice husks, which showed an increase in intensity as more frequent the applications of nano-silica (most visible at N_3 and N_4).

In the 50x magnification, visually the rice husk shows brighter effect/ higher light reflectance with the higher frequency of application. While in the 350x magnification, the rice husk shows the increase of metal-like surface as the frequency gets higher.

Bigger difference could be seen on the 1.000x magnification. Although most surface shows the existence of silica deposits, at the lower frequency (N_1 and N_2) shows that some pathogen still could attach itself to the husk surface, yet at the N2, the pathogen seems unable to pass through deeper. At higher concentration (N_3 and N_4), the husk surface seems to be cleaner from any pathogens, the scale seems stiffer/ harder, and the metallic shine becomes more visible on the surface. This could be explained as nano-silica is a highly hydrophilic and possess a good potential for surface modifications (Nakamura et al., 2007).

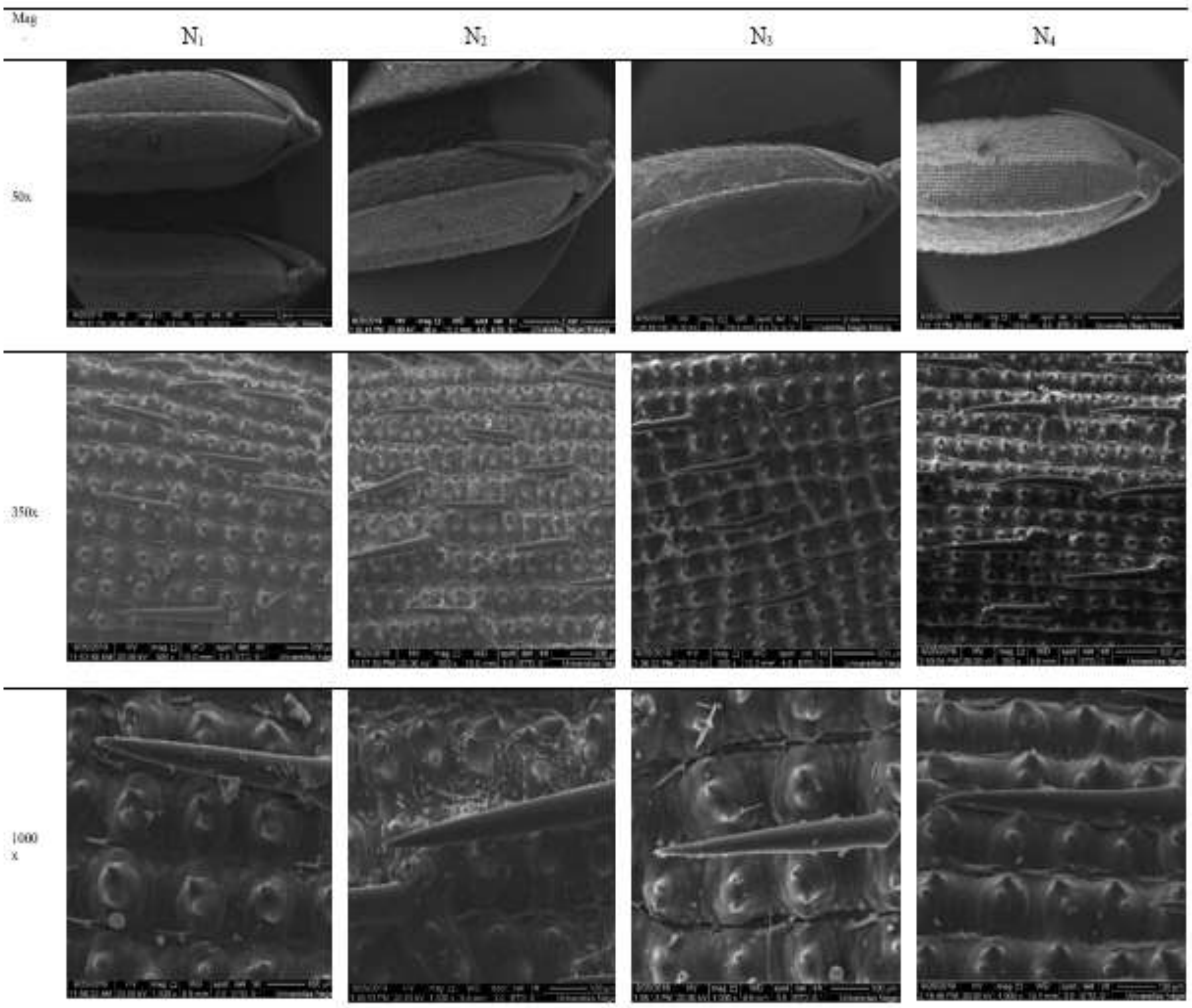

Figure 5. SEM-EDX Analysis on Rice Husk Surface on Different Nano-Silica Application (N_1= 1x application; N_2= 2x applications; N_3= 3x applications; N_4 = 4x applications).

3.3 XRF Analysis on Rice Grain

XRF analysis on rice grain showed the availability of Si, P, K, Ca, Mn, Fe, Ni, Cu, Zn, Eu, and Re on each treatment with relatively low differences. The Silicon content was ranging from 71.40 to 77.90 %; the Phosphorus content was ranging from 2.40 to 3.70 %; the Potassium content was ranging from 11.10 to 19.90 %; the Calcium content was ranging from 3.79 to 5.60 %; the Manganese content was ranging from 0.15 to 0.62 %; the Ferrum content was ranging from 0.22 to 0.56 %; the Nickel content was ranging from 0.10 to 0.43 %; the Cuprum content was ranging from 0.08 to 0,31 %; the Zinc content was ranging from 0.06 to 0.25 %; the Europium content was ranging from 0.40 to 0.50 %; the Rhenium content was ranging from 0.30 to .40 %; and the Ytterbium content was ranging from to 0.00 to 0.43 %. The Si foliar sprays was proven to reduce infections of rice blast incidence, but did not increase Si absorption or its accumulation by the plant (Buck et al., 2008).

The only prominent result that emerged from XRF data was that the presence of Ytterbium (Yb), which known as the Rare Earth Element (REE) at a higher frequency of Nano Si applications (as shown in Table 2). REE are widely used in high technologies such as computer, telecommunication, nuclear, outer space sophisticated instruments (Wahyudi, 2015), wind turbines, batteries, catalysts, electric cars

(Haque et al., 2014), medical devices, military defence systems, and are especially indispensable in emerging clean energy (Zhou et al., 2017).

The experiment results support the previous research which has shown a relationship between Si and Yb, both of which are found to be interconnected and beneficial for plants' yield quality (Aubert et al., 2001). The research of Yb direct effect for plant are still limited, but other rare earth elements of lanthanum (La) and cerium (Ce) were already been used to enhance plant growth, the mixture had been used on a large-scale in China as foliar sprays or seed treatment of agricultural and horticultural crop species (Marschner, 2003). In the material science, the usage of both Si and Yb latest example are the environmental barrier coating system of a pore-free ytterbium monosilicate (Yb_2SiO_5) and ytterbium disilicate (YbDS; $Yb_2Si_2O_7$) to protect SiC structures from high temperatures in vapor-rich exposure (Richards et al., 2015).

Table 2. Concentration of Components (%) in Rice Grain based on XRF Analysis of Nano Silicon Application

Concentration (%)	Si	P	K	Ca	Mn	Fe	Ni	Cu	Zn	Eu	Re	**Yb**
N_1	77.90	3.30	11.10	5.27	0.62	0.50	0.13	0,27	0.10	0.50	0.30	0.00
N_2	71.60	2.40	19.90	3.79	0.46	0.31	0.12	0.25	0.06	0.40	0.40	0.00
N_3	71.40	3.70	16.60	5.44	0.50	0.56	0.10	0.31	0.09	0.50	0.40	**0.43**
N_4	73.70	3.40	15.10	5.60	0.15	0.22	0.43	0.08	0.25	0.40	0.30	**0.30**

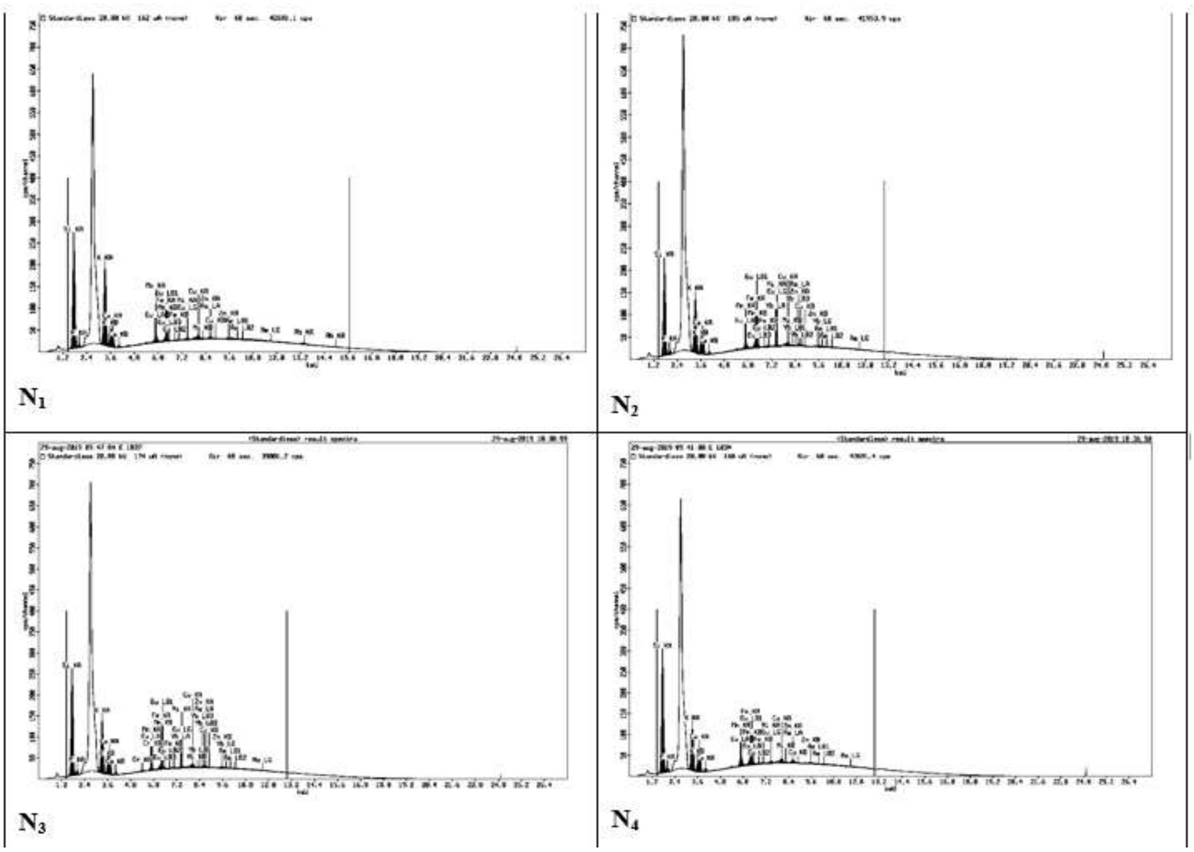

Figure 6. XRF Analysis on Peak Concentration of Nutrition at Different Nano-Silica Application (N_1= 1x application; N_2= 2x applications; N_3= 3x applications; N_4 = 4x applications).

4. Conclusion

The Nano Silica application could increase plant rice resistance, with better performance shown from 3x applications. Thus it is recommended to use 3x Nano Si applications to achieve increased rice resistance against pest through mechanical defence by stronger physical appearance. On the SEM analysis of 3x and 4x Nano Si application, showing the rice husk surface of becoming more metallic-like, and also the unpredicted existence of Ytterbium (Yb). It is proposed to be a relation between Si application and Yb content in plant, which is also play favourable role for rice plant productivity. It is recommended to conduct further research on Nano Si application for Ytterbium green mining, by using rice or other Si accumulator plants to acquire rare earth element from soil, to support clean energy and sustainable environment.

Acknowledgement

This experiment was supported by the Directorate of Research and Community Service Director General of Higher Education, Indonesian Ministry of Research and Technology.

References

Aubert, D., Stille, P., & Probst, A. (2001). REE fractionation during granite weathering and removal by waters and suspended loads: Sr and Nd isotopic evidence. *Geochimica et Cosmochimica Acta*, *65*(3), 387–406. https://doi.org/10.1016/S0016-7037(00)00546-9

Bhavya, H. K., Nache, G. V., Jaganath, S., Sreenivas, K. N., & Prakash, N. B. (2011). Effect of Foliar Silicic Acid and Boron Acid in Bangalore Blue Grapes. *Proceedings of the 5th International Conference on Silicon in Agriculture*, 7–8.

Buck, G. B., Korndörfer, G. H., Nolla, A., & Coelho, L. (2008). Potassium silicate as foliar spray and rice blast control. *Journal of Plant Nutrition*, *31*(2), 231–237. https://doi.org/10.1080/01904160701853704

Cruz-Mireles, N., Eseola, A. B., Osés-Ruiz, M., Ryder, L. S., & Talbot, N. J. (2021). From appressorium to transpressorium - Defining the morphogenetic basis of host cell invasion by the rice blast fungus. *PLOS Pathogen*, *17*(7), 1–7. https://doi.org/10.1371/journal.ppat.1009779

Cui, J., Liu, T., Li, F., Yi, J., Liu, C., & Yu, H. (2017). Silica nanoparticles alleviate cadmium toxicity in rice cells: Mechanisms and size effects. *Environmental Pollution*, *228*, 363–369. https://doi.org/10.1016/j.envpol.2017.05.014

Debnath, N., Das, S., Seth, D., Chandra, R., Bhattacharya, S. C., & Goswami, A. (2011). Entomotoxic effect of silica nanoparticles against Sitophilus oryzae (L.). *Journal of Pest Science*, *84*(1), 99–105. https://doi.org/10.1007/s10340-010-0332-3

Gomez, A., Narayan, M., Zhao, L., Jia, X., Bernal, R. A., Lopez-Moreno, M. L., & Peralta-Videa, J. R. (2021). Effects of nano-enabled agricultural strategies on food quality: Current knowledge and future research needs. *Journal of Hazardous Materials*, *401*(January). https://doi.org/10.1016/j.jhazmat.2020.123385

Haque, N., Hughes, A., Lim, S., & Vernon, C. (2014). Rare earth elements: Overview of mining, mineralogy, uses, sustainability and environmental impact. *Resources*, *3*(4), 614–635. https://doi.org/10.3390/resources3040614

He, C., Ma, J., & Wang, L. (2015). A hemicellulose-bound form of silicon with potential to improve the mechanical properties and regeneration of the cell wall of rice. *New Phytologist*, *206*(3), 1051–1062. https://doi.org/10.1111/nph.13282

Husnain, H., Rochayati, S., & Adamy, I. (2012). Pengelolaan Hara Silika pada Tanah Pertanian di Indonesia. In Wigena (Ed.), *Prosiding Seminar Nasional Teknologi Pemupukan dan Pemulihan Lahan Terdegradasi* (pp. 237–246). Badan Penelitian dan Pengembangan Pertanian, Kementerian Pertanian. https://balittanah.litbang.pertanian.go.id/ind/index.php/publikasi-mainmenu-78/art/661-silika153

Laane, H. M. (2018). The effects of foliar sprays with different silicon compounds. *Plants*, *7*(2). https://doi.org/10.3390/plants7020045

Marschner, H. (2003). *Mineral Nutrition of Higher Plants* (2nd ed.). Academic Press.

Meena, V. D., Dotaniya, M. L., Coumar, V., Rajendiran, S., Ajay, Kundu, S., & Subba Rao, A. (2014). A case for silicon fertilization to improve crop yields in tropical soils. *Proceedings of the National Academy of Sciences India Section B - Biological Sciences*, *84*(3), 505–518. https://doi.org/10.1007/s40011-013-0270-y

Nakamura, M., Shono, M., & Ishimura, K. (2007). Synthesis, characterization, and biological applications of multifluorescent silica nanoparticles. *Analytical Chemistry*, *79*(17), 6507–6514. https://doi.org/10.1021/ac070394d

Nayfeh, M. (Ed.). (2018). Nanosilicon. In *Fundamentals and Applications of Nano Silicon in Plasmonics and Fullerines* (pp. 205–285). Elsevier. https://doi.org/10.1016/b978-0-323-48057-4.00009-8

Ningsari, O. (2017). *Frekuensi Aplikasi dan Konsentrasi Ekstrak Abu Sekam Berpelarut Asap Cair sebagai Pupuk Silikon terhadap Pertumbuhan Tanaman Padi* [Universitas Jember]. https://repository.unej.ac.id/bitstream/handle/123456789/84908/Oktavia Ningsari - 101510501085_.pdf

Parveen, N. (2012). *Influence of silicon on growth and some physiological attributes of maize (Zea mays L .) under salt stress*. University of Agriculture, Faisalabad.

Richards, B. T., Zhao, H., & Wadley, H. N. G. (2015). Structure, composition, and defect control during plasma spray deposition of ytterbium silicate coatings. *Journal of Materials Science*, *50*(24), 7939–7957. https://doi.org/10.1007/s10853-015-9358-5

Sabatini, S. D., Budihastuti, R., & Suedy, S. W. A. (2017). Pengaruh Pemberian Pupuk Nanosilika terhadap Tinggi Tanaman dan Jumlah Anakan Padi Beras Merah (Oryza sativa L.var. indica). *Buletin Anatomi Dan Fisiologi*, *2*(2), 128–133.

Schumann, A. W., Vashisth, T., & Spann, T. M. (2018). *Mineral Nutrition Contributes to Plant Disease and Pest Resistance* (Issue 3, pp. 1–5). University of Florida. https://edis.ifas.ufl.edu/publication/hs1181

Singh, D. P. (2015). Plant nutrition in the management of plant diseases with particular reference to wheat. In *Recent Advances in the Diagnosis and Management of Plant Diseases* (pp. 273–284). Springer India. https://doi.org/10.1007/978-81-322-2571-3_20

Snyder, G. H., Glade, B., Matichenkov, V. V, & Datnoff, L. E. (2006). Silicon. In A. V. Barker & D. J. Pilbeam (Eds.), *Handbook of Plant Nutrition* (First, pp. 551–568). CRC Press. https://doi.org/10.1201/9781420014877

Soumya, K., Girijesh, G. K., Veeranna, H. K., Dushyanthkumar, B. M., & Salimath, S. B. (2020). Effect of Nano Zinc and Silicon on Crop Growth and Yield of Rice (Oryza sativa L.). *International Journal of Current Microbiology and Applied Sciences*, *9*(10), 1112–1120. https://doi.org/10.20546/ijcmas.2020.910.133

Suganda, T., Yulia, E., Widiantini, F., & Hersanti. (2016). Intensitas penyakit blas (Pyricularia oryzae Cav .) pada padi varietas Ciherang di lokasi endemik dan pengaruhnya terhadap kehilangan hasil [Disease intensity of blast disease (Pyricularia oryzae Cav.) of Ciherang rice variety at the endemic location and. *Jurnal Agrikultura*, *27*(3), 154–159. https://doi.org/10.24198/agrikultura.v27i3.10878

Wahyudi, T. (2015). Element-Bearing Minerals , Rare Earth Elements and Cerium Oxide Compound. *Indonesian Mining Journal*, *18*(2), 92–108. https://doi.org/10.30556/imj.Vol18.No2.2015.293

Yohana, O., Hanum, H., & Supriadi. (2013). Pemberian Bahan Silika Pada Tanah Sawah Berkadar P Total Tinggi Untuk Memperbaiki Ketersediaan P Dan Si Tanah, Pertumbuhan Dan Produksi Padi (Oryza Sativa L.). *Jurnal Agroekoteknologi Universitas Sumatera Utara*, *1*(4). https://doi.org/10.32734/jaet.v1i4.4510

Zhou, B., Li, Z., & Chen, C. (2017). Global potential of rare earth resources and rare earth demand from clean technologies. *Minerals*, *7*(11). https://doi.org/10.3390/min7110203