CHARACTERIZATION OF INDONESIAN LOCAL SILICON MATERIAL AND EVALUATION OF CONTROLLING FACTORS FOR SOIL SILICON AVAILABILITY

（インドネシア産ケイ素資材の特性付けと土壌のケイ酸可給度の制御因子の評価）

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THE UNITED GRADUATE SCHOOL OF AGRICULTURAL SCIENCES, TOTTORI UNIVERSITY

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Approval Sheet

This thesis enclosed herewith, "**Characterization of Indonesian Local Silicon Material and Evaluation of Controlling Factors for Soil Silicon Availability**", prepared and submitted by **Linca Anggria** in partial fulfillment of the requirement for the award of the degree of Doctoral of Philosophy, is hereby approved as to style and contents.

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I dedicate this work for my father Sutopo Samani and my mother Nurhayani. The reason of what I become today. Thanks for your great support and continuous care.

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Chapter 1

General Introduction

1.1. Rice production and consumption in Indonesia

Rice is the major staple food in Indonesia. Indonesia is the third largest producer of rice in the world, but the domestic rice production is not enough to meet the demand and feed the people. According to ADB (2012), the total rice consumption was 39.55 million tons in 2011 which grows at 0.90% per year solely due to population growth.

Rice production in 2014 was estimated at 70.61 million tons of milled rice but decreased by 0.94% compared to 2013. The decline in estimated production occurred due to a decrease in harvested area by around 0.48% and productivity by 0.47%. Estimated decreases of rice production in 2014 were relatively large in the province of Central Java, West Java, South Sumatera, North Sumatera and West Nusa Tenggara. Meanwhile, the estimated increases of rice production in 2014 are relatively large in the province of South Sulawesi, East Java, Lampung, East Nusa Tenggara and South Kalimantan (BPS, 2014).

1.2. Silicon

Silicon (Si) is an ubiquitous element and the second most abundant in the crust of the earth after oxygen (Liang et al., 2015). Silicon is a beneficial element for rice plants and usually taken up in larger amounts than essential nutrients such as N (nitrogen), P (phosphorus) and potassium (K) (Ma & Takahashi, 2002). Although Si is abundant in the soil but it is primarily in an inert form and consequently unavailable for plant uptake (Tubana & Heckman, 2015). Rice plant obviously requires Si to maintain healthy growth and high productivity. Although Si is recognized as a non-essential element for rice plant, rice plant uptakes Si ranging from

230 to 470 kg Si ha^{-1}, two times higher than N uptake (Savant et al., 1997). Silicon is deposited on the cell wall of epidermal cells of leaves, hulls, and stems, forming a silica-cuticle double layer and a silica-cellulose double layer (Yoshida, 1965; Raven, 2003). The deposition of Si enhances the strength and rigidity of cell walls and thus increases rice resistance to leaf and neck blast, sheath blight, brown spot, leaf scald and stem rot (Epstein, 1994; Ma & Takahashi, 2002; Ma, 2003; Datnoff & Rodrigues, 2005;) and decreases the incidence of powdery mildew in several crops (Fauteux et al., 2005). Silica also alleviates many abiotic stresses including chemical stress (high salt, metal toxicity, nutrient imbalance) and lodging, drought, radiation, high temperature and freezing. An awareness of Si deficiency in soil is now recognized as being a limiting factor for crop production (Ma & Yamaji, 2006). Silica indirectly improves P utilization in plants (Ma & Takahashi 1990). Solubility of silica minerals in soil is different and is affected by soil pH and the amounts of clay, minerals, organic matter and Fe/Al oxides/hydroxides (Tubana & Heckman, 2015).

Rice can be considered as Si accumulator and can be able to accumulate Si above 10% of shoot dry weight (Yamamoto et al., 2012). Plants absorb Si exclusively as monosilicic acid, also called orthosilicic acid (H_2SiO_4), by diffusion and also by the influence of transpiration-induced root absorption known as mass flow (Datnoff & Rodrigues, 2005).

Available Si in rice fields in the whole of Java Island in Indonesian decreased by approximately 17-22 % during the period 1970-2003 (Darmawan et al., 2006). The lower soil Si content was found to be severe in intensive rice field where enormous Si uptake is not followed by sufficient Si replenishment (Husnain et al., 2008). Soil is always at risk of Si depletion due to the large amounts of Si removal by plants. Husnain et al. (2009) found that dissolved silica in irrigation water which is a main Si source to rice field decreased through Si trapped by diatoms in dams in the Citarum watershed.

1.3. Silicon materials

Many sources of Si have been evaluated for use in agriculture. The source of Si for rice plants is derived from soil, irrigation water and plant residues, such as straw and rice husks. Soil derived from the parent material of volcanic ash contains higher Si (Imaizumi, 1958) than soils derived from alluvium material, particularly soil in lowlands. As plants accumulate Si, there is possibility of using crop residues as Si source. Rice (Oryza sative, *L.*) hulls and sugarcane (Saccarum *spp.*) bagasse have considerable Si concentrations (Gascho, 2001). Rice husk is one of the by-products obtained during milling of rice. It is generally reported that in rice husk, silica is predominantly in inorganic linkages, but some of the silica is also bonded covalently to the organic compounds (Prasad & Pandey, 2012). Rice husk contains about 20% ash which can be retrieved as amorphous, chemically reactive silica (Ghosh & Bhattacherjee, 2013).

Baggase is the main waste from the milling process of the sugar cane industry. Bagasse ash is rich in silica that is an economically viable raw material for silica gel (Affandi, et.al., 2009). In Indonesia, a continuous rice-cropping system with 3 crops per year on average is commonly practiced which yields abundant straw after harvest (Husnain, 2009). Rice straw residue contains numerous nutrient and particularly high in silica (SiO_2) and potassium (K) (Ma & Takahashi, 1991).

Recently, the most common forms of silicate materials used as fertilizer are various industrial by products, for example, slag from iron and alloy manufacturing that consist of calcium silicate which could meet the demand of Si. Furthermore, a nominee source material must be accessible distance from the place of application to avoid costs that are greater than potential benefits (Gascho, 2001).

Numerous studies have reported beneficial effects of Si on rice growth and production based on both pot and field experiments. However, Si fertilizer has never been used in Indonesia and other inorganic fertilizer is expensive. Meanwhile, to import silicate fertilizer from other countries are relatively expensive for farmers, for this reason, it is desirable to explore cheap and abundant local materials as Si source.

1.4. Objectives of the study

The objectives of this study are to:

- Characterize Si availability of material in acid, neutral and alkaline condition by chemical extraction method and plant growth.
- Evaluate Si release from different materials used as soil fertilizers under submerged conditions in relation with soil chemical properties and other controlling factors.
- Evaluate the interaction between Si with Ca and Mg in terms of Si solubility.
- Examine the effect of steel slag application on rice growth and yield in different soil types.
- Improve solubility of Si from industrial waste material using two different techniques.

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CHAPTER 2

Characterization of Si Local Material Using Chemical Extractions and Rice Plant Growth

2.1. Introduction

Silicon (Si) is the second most common element of the earth's crust (Wedepohl, 1995). Silica minerals undergo chemical and physical weathering, thus release Si in solution which is either combined with other elements to form clay minerals or released toward the streams and oceans or absorbed by vegetation (Guntzer et al. 2012).

The form of Si absorbed by plant root is silicic acid (Datnoff et al., 2001). According to Matichenkov and Bocharnikova (2001), monosilicic acid, polysilicic acid, organo-silicon compound and complex compounds with organic and inorganic substances are mobile Si. By replacing phosphorus (P) from calcium (Ca), aluminum (Al) and magnesium (Mg) phosphates, monosilicic acid can control the mobility of phosphates and can transform plant-unavailable P into plant-available (Matichenkov & Ammosova, 1996).

The beneficial effects of Si applications to increase available soil P was affirmed by several researchers. According to Raleigh (1953), application of Si increased P uptake on soil deficient in P. While, Si is also beneficial to the plant when available P is high, by reducing P uptake and thereby reducing inorganic P within the plant (Ma & Takahashi, 1990). Although inorganic P is necessary for metabolism and storage but high concentrations inhibit enzyme reactions that create abnormal osmotic pressure in the cell (Yoneyama, 1988). According to Tubana and Heckman (2015), Si fertilizer increased the amount of Si release in the soil solution. Furthermore, Si adsorbed onto the slightly soluble phosphates of Al, Ca, Fe, and Mg by desorption of the phosphate anion. It seems possible to reduce the amount of fertilizer P by application of Si.

Plant takes up and utilizes N for photosynthesis of which chlorophyll meters are widely used to guide N management by monitoring leaf N status in agricultural systems (Xiong et al., 2015). Due to a synergistic effect, applied Si has the potential to increase the optimum rate of N, thus helping to enhance yields (Elawad & Green, 1979).

Currently, many materials are being evaluated as Si sources for use in agriculture, and the most important of those materials must have much Si readily soluble in the soil solution (Gascho, 2001). Rice straw contains about 86% of the total Si storage in rice plants (Klotzbucher et al., 2015). However, farmers commonly burn or take out rice straw from rice fields after the harvest for animal feed. As continual removal of Si through harvested products, Si status of agricultural soil becomes decreased. Furthermore, nutrients not replenished by fertilization are possibly getting decreased season to season.

Silicon from natural sources have potential to mitigate environmental stresses and soil nutrient depletion for maintaining sustainable agriculture (Guntzer et al. 2012). Rice is a Si-accumulator that has physic-chemical functions for plant growth (Nguyen et al., 2014). Baggase is the main waste from the milling process of the sugar cane industry. Burning of baggase in the boiler produces bagasse ash as a combustion product and bagasse ash is rich in silica (Affandi, et.al., 2009). In Indonesia, it is estimated that every hectare of sugarcane plant is capable of producing 100 tons of bagasse. The potential national bagasse that can be available of the total area of sugarcane plants reached 39,539,944 tons per year (Ministry of Environment, 2005). The silicon rich material from plant biomass as potential sources of bioavailable Si was evaluated such as bamboo leaf. Bamboo is also considered as Si accumulator with Si content from 3 to 410 mg SiO_2 g^{-1} (DM) (Ding et al., 2008; Li et al., 2006). Indonesia has 37.93 million bamboo tree and mostly in Java Island (Central of Inventory & Forestry Statistics, 2004).

Soil derived from the parent material of volcanic ash contains high Si (Imaizumi, 1958). Wollastonite ($CaSiO_3$) is the best known Si fertilizer source. However, its relatively expensive (Haynes et al., 2013). Silicon sources such as slag, fly ash, bottom ash from industrial waste are of great interest for Si fertilizer in paddy field. Haynes et al. (2103) reported that industrial waste materials such as slag, processing mud and fly ash increased soil pH and EC. Steel slag are non-metallic by products from iron and steel manufacturing that consist of Ca, Mg, and Al silicates in various combinations. At high temperatures, slag is formed when limestone reacts with silicon dioxide and other impurities of iron ore (Teir et al., 2005).

Currently, there are varieties of methodologies for extracting different forms of Si from different materials, for examples HCl, NaOH, Na_2CO_3 and water. However, before applying any type of extraction method, it is essential to consider the various Si materials and soil types which may be different. Inorganic Si materials from industrial by product are mainly different in chemical, physical and biological properties with organic Si materials. The purpose of this study was to characterize Si availability of material in acid, neutral and alkaline condition by chemical extraction method and plant growth.

2.2. Materials and Methods

2.2.1. Fertilizer materials used

There are two kinds of materials namely organic and inorganic material. The organic materials include rice husk-ash (RHA), rice husk-burnt (RHB), rice husk-ash (RHA), rice husk-heated (RHH), media of mushroom (MM), cacao (*Theobroma cacao,* L.*)* shell - biochar (cacao SB), rice (*Oryza sativa*, L.) straw compost (RSC), bagasse, elephant grass, vetiver grass, bamboo leaf, sugarcane leaf and palm nut shell-biochar (palm nut SB). While the inorganic materials include fy ash, steel slag, silica gel, Japanese silica gel (JSG), volcanic ash, bottom ash, electric furnace slag (EFS) and Japanese silica fertilizer (JSF) were used. All materials were ground into fine powder in agate grinding jars, using a mixer mill (MM 200, Retsch GmbH, Haan, Germany).

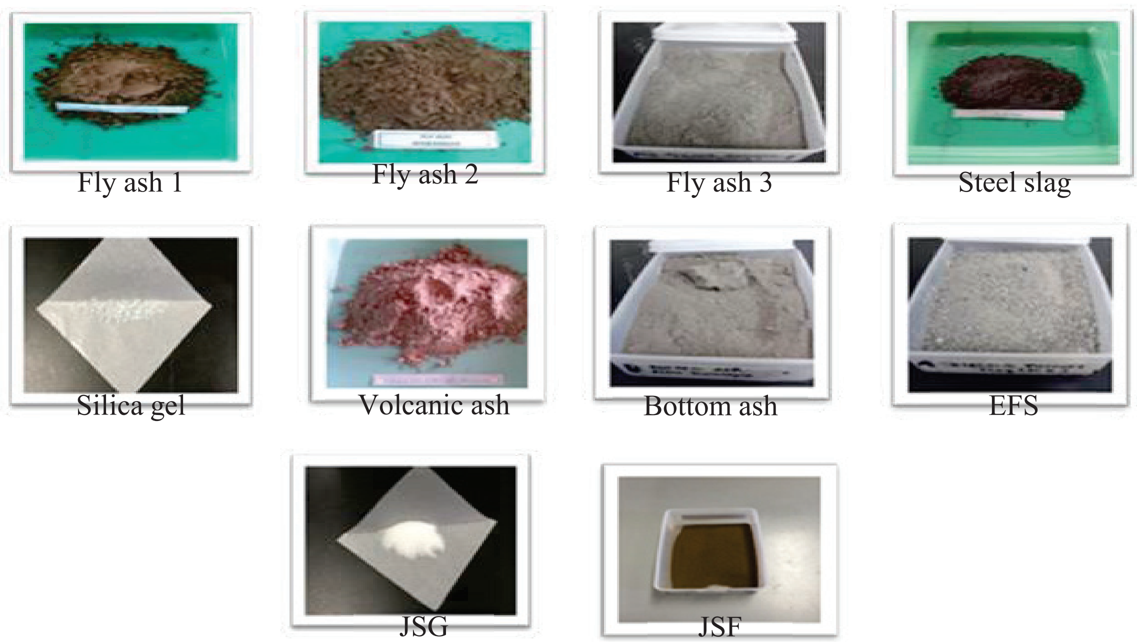

Figure 1. Inorganic materials

Figure 2. Organic materials

2.2.2. Analysis of material

Silicon was extracted from materials with six extraction method, namely : (1) Na_2CO_3/NH_4NO_3 (10 g L^{-1}/16 g L^{-1}) (1:100 ratio continuous shaking 1h, filter) (Pereira et al., 2003), (2) 0.04 M sodium phosphate buffer (pH 6.2) (1:30 ratio, 5 minutes shake, incubated at 40°C for 24 h, 5 minutes shake, filter) (modified in ratio from Kato and Sumida, 2000), (3) 0.5 M HCl (1:150 ratio for 1h, filter) (Savant et al., 1999), (4) 0.1 M citric acid (1:50 ratio, 2h shake, rest O/N, 1h shake, filter) (Acquaye & Tinsley, 1965), (5) 0.01 M $CaCl_2$ (1:30 ratio, continuous shaking for 16h, filter) (modified in ratio from Haysom and Chapman, 1975), and (6) acetate buffer (pH 4.0) with ratio of 1:30, for intermittent shaking for 5h at 40°C (modified in ratio from Imaizumi & Yoshida, 1958). Silicon concentrations in supernatant were determined by colorimetric analysis with Spectrophotometer UV 1800 Shimadzu at the wavelength of 810 nm.

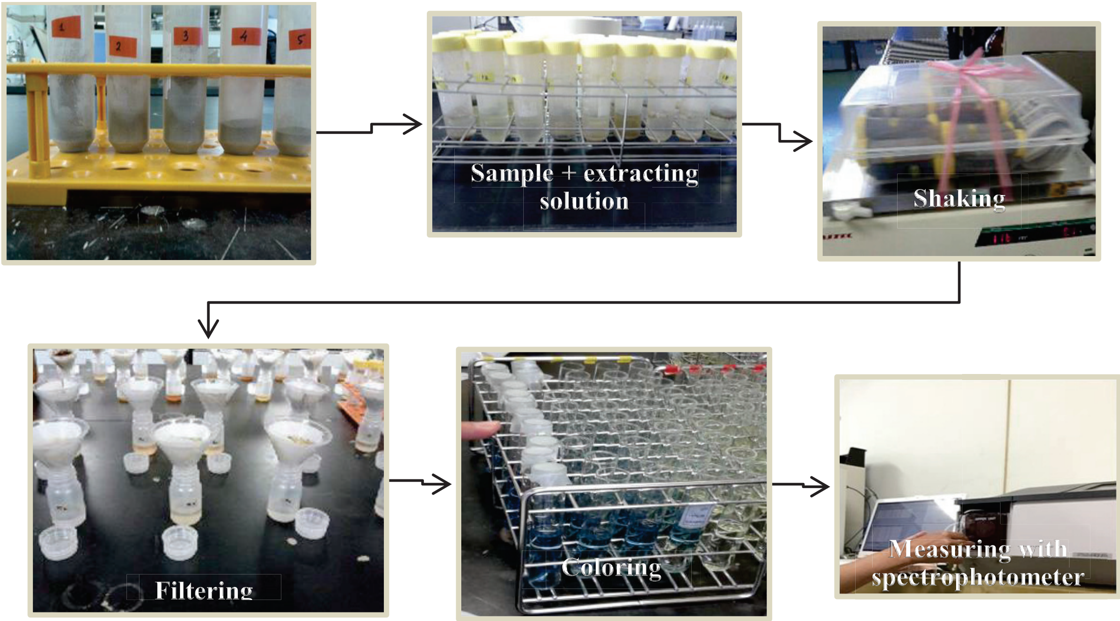

Figure 3. Na_2CO_3/NH_4NO_3, sodium phosphate, HCl, citric acid, and $CaCl_2$ extractable-Si

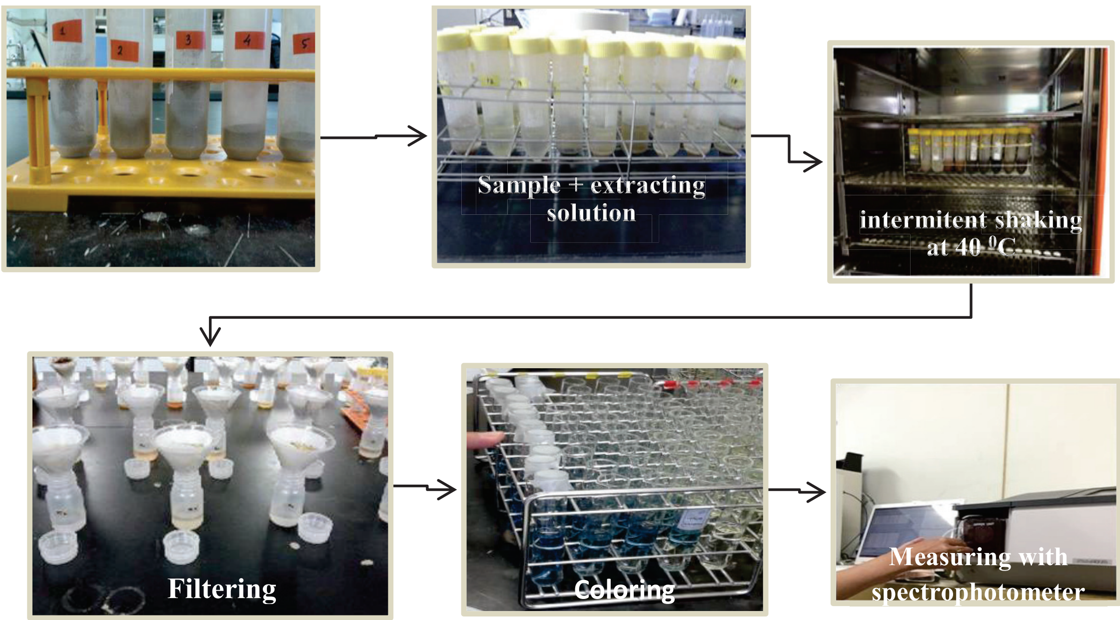

Figure 4. Acetate buffer extractable-Si

2.2.3. Greenhouse experiment

The soil sample was air dried and passed through a 2 mm sieve. Exchangeable potassium (K), sodium (Na), calcium (Ca) and magnesium (Mg) were extracted with 1 M ammonium acetate pH 7.0 and measured by Inductively Coupled Plasma Spectroscopy (ICPE-9000 Shimadzu, Kyoto Japan). Available Si was extracted by acetate buffer (pH 4.0) with ratio of 1:10, for intermittent shaking for 5h at 40^oC, determined using the silicate molybdenum blue method (Imaizumi & Yoshida, 1958). Soil pH (H_2O) was determined on 1:2.5 (w/v) soil: water suspensions with pH meter (D-51, Horiba). Total carbon (C) and nitrogen (N) were assessed using dry combustion methods (Sumigraph NC-22 Analyzer).

Seeds of Koshihikari variety were sterilized against nematodes, fungi and bacteria with fungicides (suporutakkuu sitaana) and air dried for overnight. The soaked seeds were kept in incubator for 4 days at 20^oC and on the fifth day, the temperature was increased to 32^oC to enhance uniform germination. The seeds were planted out in the nursery box, covered with black polythene and put in the growth chamber with temperature 25^oC by day and 20^oC at night for 1 week. The nursery box was transferred to the pool for the remaining 3 weeks.

A pot experiment was carried out under greenhouse conditions at Shimane University on June 2, 2016 to July 10, 2016. The experiment was set up in completely randomized design with ten treatments and three replicates. The soils used for experiment were collected from Japan. 400 gram of soils and 1 gram of fine powder Si materials (fly ash 3, steel slag, silica gel, RHA, RHB, MM, cacao SB, and RSC), except JSG (it was not fine powder) were weighed into each pot and mixed thoroughly. All Si materials and 0.88 g KH_2PO_4 and 0.95 g $(NH_4)_2SO_4$ per pot were applied one day before transplanting. One seedling of rice (*Oryza sativa* L.) was sown in each pot. Conventional continuous flooding system was used in this experiment.

2.2.4. Parameter observation

2.2.4.1. Water surface sampling and laboratory analysis

Silicon, P and pH of water surface were measured at day 7, 17, 24 and 34. The supernatant was obtained after filtration (paper filter Advantec No.6). Silicon and P concentrations in supernatant were determined by colorimetric analysis with spectrophotometer UV 1800 Shimadzu. The wavelength used for the Si detection was 810 nm and for P detection was 720 nm.

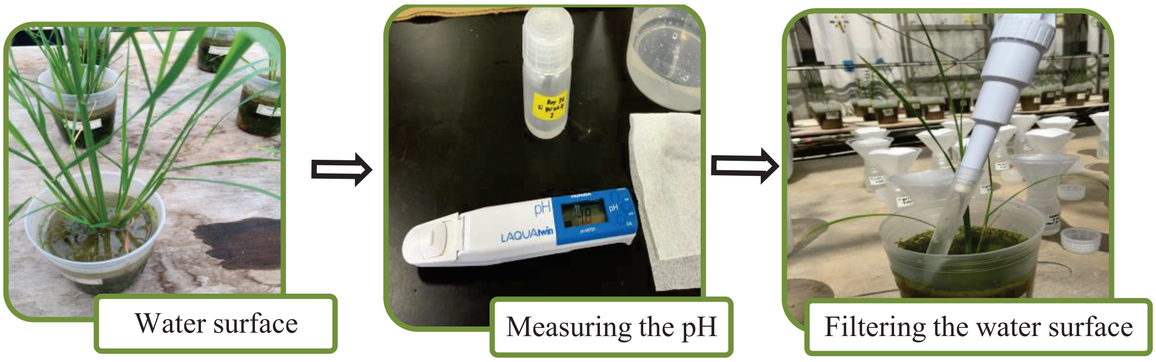

Figure 5. Measuring pH and filtering of water surface

2.2.4.2. Plant growth observation and analysis

The tiller number and plant height were recorded at 16, 21, 36 day after transplanting (DAT). Plant height was measured from the ground to the tip of the highest plant leaves. The number of tillers was obtained by calculating the number of tillers that grew from the main stem of rice plants.

The stomata imprint sampling at 36 DAT were observed (Fig. 6) using non-destructive method according to Kusumi (2013). A clear nail varnish was used as glue. Y leaves or flag leaves were selected for observation. Y leaf is the 2^{nd} leaf from the top. Imprints have been taken from upper (adaxial) surfaces. The widest (middle) region of mature leaf blade has been selected as a target area. A drop of clear nail varnish was applied evenly to the surface of the rice leaf with a long size approximately 2 cm. Then press the accelerator (isolative) on the leaf for about 30 seconds and remove the isolative from the leaf gently. Make sure that the imprint adhered on the isolative. Then put on a glass slide and give some short of ID code signifying the samples and observed with microscope Olympus BX 51.

Figure 6. Stomata imprint sampling on leaves of rice

One method of estimating plant N content is to measure the leaf chlorophyll content. The chlorophyll contents of the leaves of 34 DAT were estimated with Minolta SPAD (soil and plant analytical development) chlorophyll meter (Konica Minolta-Japan) with three times sampling per pot (Fig. 7). The chlorophyll content, calculated from average SPAD values.

This tool for assessing leaf chlorophyll in a fast, accurate and non-destructive manner of leaf chlorophyll concentration. SPAD readings are calculated based on two transmission values: the transmission of red light at 650 nm, which is absorbed by chlorophyll, and the transmission of infrared light at 940 nm, at which no chlorophyll absorption occurs (Xiong et al., 2015).

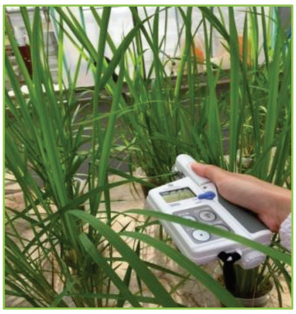

Figure 7. SPAD value on leaves of rice

Plants were harvested after 37 DAT, separated into straw and root. The dry weight of these tissues recorded after being dried. Straw plant samples were oven dried 60 - 70°C for one day after which they were grinded with a grinding machine into fine particles in agate grinding jars, using a mixer mill (MM 200, Retsch GmbH, Haan, Germany).

Fine samples were oven-dried 12 hours at 80^{o}C. The total Si uptake by straw plant samples (Fig. 8) were determined by HNO_3 at 160^{o}C for 4 hours and HF digestion method using Teflon vessel and measured by spectrophotometer UV 1800 Shimadzu (Koyama & Sutoh, 1987).

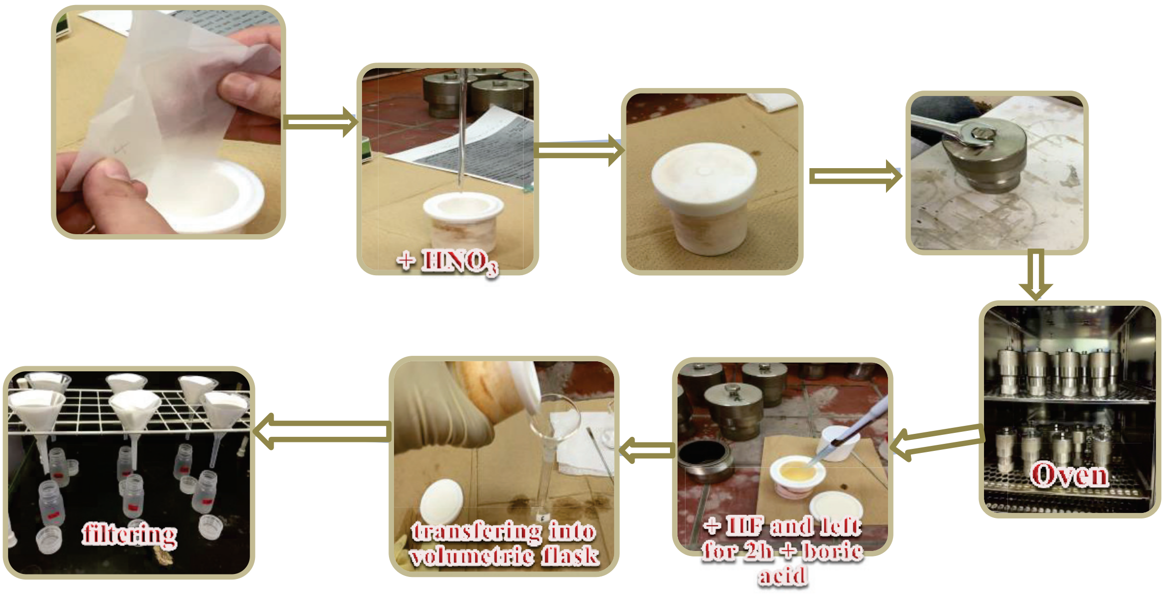

Figure 8. Silicon plant analysis

2.2.5. Statistical analysis

IBM package SPSS 22 was used to analyze the data. A one way ANOVA was carried out to compare the means of different treatments at the 5% level using Duncan's test. The Pearson correlations were determined to confirm the relationships between extractable Si materials with plant Si uptake. We made several combination until we got the significant correlations.

2.3. Results and discussion

2.3.1. Properties of soil

The soil had pH of 5.0 with textural classes of clay loam. In general, the soil chemical soil properties were low. Exchangeable Ca and Mg were 4.7 and 1.0 $cmol_c kg^{-1}$, respectively. Total C and N content of 15.0 and 1.0 g kg^{-1}. The available Si concentration was 138.1 mg SiO_2 kg^{-1}. According to Sumida (1992), those were classified to be below critical level of available silica for rice (300 mg SiO_2 kg^{-1}).

2.3.2. Properties of material

Generally, all of the inorganic materials were alkaline (Table 1) with JSF having the highest pH (12.37) and silica gel was the lowest (6.78). JSF and fly ash 3 had the highest C and N content (20.20 and 2.62 g kg^{-1}). The highest Ca and Mn content were in JSF, while the lowest Ca and Mn were fly ash 3 and volcanic ash, respectively. Among fly ash materials, fly ash 1 and 2 were low in C content, but high Ca content compared to fly ash 3. It might be due to the difference in coal source, degree of coal pulverization or design of boiler unit. As the color of two fly ashes (1 and 2) was cream, it is indicative of a high Ca and low C content. While, fly ash 3 had grey to black color indicating high C and low Ca content. Where, high Ca fly ashes usually contain a smaller amount of unburned C (<1%) (Fang, 1991; Ramezanianpour, 2014).

The organic materials varied with RHA having the highest pH (10.74) and elephant grass was the lowest (5.22). MM had high Ca content (7.67 %) because in mushroom cultivation, the media was added with $CaCO_3$ neutralize acid that was released by mushroom. The lowest and highest Mg content were cacao SB and RHH (0.18 and 15.6 g kg^{-1}). The lowest carbon content was 3.70 g kg^{-1} for RHA due to this material in ash form. Meanwhile sugarcane leaf was the highest C (465.10 g kg^{-1}). RSC had highest Fe and Mn content (16.30 and 1.83 g kg^{-1}, respectively) than other materials.

Preventing heavy metal pollution from materials applied to soil is critical because plant will uptake and it can enter the food chain leading to genotoxic effects to DNA (Chakraborty & xMukherjee, 2009). However, heavy metal content of all materials (Table 1) were below the regulatory limit of Environmental Protection Agency [EPA] (1993) with max concentration of Cu = 4300, Zn = 7500, Cd = 85, and Ni = 420 mg kg^{-1}.

Table 1. Chemical composition of materials

Materials	pH	TC	TN	Ca	Mg	Fe	Mn	Cu	Zn	Cd	Ni
		------------------------- g kg^{-1} ---------------------------						------------- mg kg^{-1} --------------			
Fly ash 1	9.76	2.20	0.02	40.73	10.90	115.44	3.08	81.25	71.35	35.08	99.59
Fly ash 2	11.42	1.40	0.02	41.52	10.46	117.50	2.83	81.15	63.73	35.35	99.08
Fly ash 3	7.73	107.60	2.62	18.37	9.01	29.61	0.34	30.73	102.27	18.42	47.17
Steel slag	9.80	1.40	0.02	198.11	34.82	281.65	9.61	147.08	46.12	67.04	113.56
Silica gel	6.78	-	-	-	-	-	-	-	-	-	-
JSG	8.50	-	-	-	-	-	-	-	-	-	-
Volcanic ash	7.61	0.70	0.06	24.27	1.20	24.09	0.33	29.21	150.49	10.46	18.17
Bottom ash	9.22	9.40	0.11	34.43	14.18	50.39	0.72	40.36	52.36	20.06	76.08
EFS	9.46	7.70	0.04	157.21	59.46	151.67	11.59	120.93	942.28	56.44	109.85
JSF	12.37	20.20	0.06	238.00	18.10	70.24	22.80	-	-	-	-
RHA	10.74	3.70	0.05	3.43	0.79	0.37	0.59	2.21	38.11	1.05	3.46
RHB	7.61	427.40	7.83	1.95	0.99	2.49	0.55	3.82	38.73	1.60	4.29
RHH	7.10	416.40	3.09	0.73	0.18	0.07	0.17	n.d.	15.24	n.d.	1.11
MM	8.62	360.10	7.38	76.69	2.69	1.60	0.25	6.83	27.04	6.83	15.18
Cacao SB	10.50	423.50	10.81	22.28	15.60	4.19	1.20	54.39	317.85	8.07	27.62
RSC	9.51	222.60	14.32	14.36	4.34	16.30	1.83	26.59	87.76	9.66	18.65
Bagasse	7.33	442.30	3.48	18.64	1.50	15.02	0.21	86.27	47.60	7.36	19.06
Elephant grass	5.22	427.10	24.04	6.04	2.53	0.22	0.06	6.15	35.48	1.39	7.15
Vetiver grass	6.07	445.60	15.02	6.32	2.44	0.23	0.06	4.86	14.54	1.40	6.37
Bamboo leaf	6.55	409.30	18.46	4.62	2.35	0.47	0.16	6.62	23.12	1.33	4.38
Sugarcane leaf	6.15	465.10	18.58	4.39	0.96	0.13	0.04	2.92	27.54	0.70	3.88
Palm nut SB	7.15	416.20	15.99	4.42	1.38	7.16	0.34	31.69	37.70	3.35	38.70

n.d.: not detected, -: not determined, JSG=Japanese silica gel, JSF=Japanese Si fertilizer, EFS=electric furnace slag, RHA=rice husk-ash, RHB=rice husk-burnt, RHH=rice husk-heated, MM=media of mushroom, cacao SB=cacao shell-biochar, RSC=rice straw compost, palm nut SB=palm nut shell-biochar.

2.3.3. Extractable Si in materials

Plants are only able to absorb Si in the form of monosilicic acid, thus we used the ammonium molybdate method that reacts only with monosilisic acid and does not determine Si in the polysilicic acid form (Snyder, 2001).

The materials vary in term of extractable Si due to different sources of material. Table 2 illustrates the diversity of extractant that have been used, which inorganic materials were higher with 0.5N HCl (1.595 – 25.362 g Si kg^{-1}, respectively) than other extractant methods. Although, Silica gel and JSG ($SiO_2.xH_2O$) were inorganic material but Si content was low with 0.5N HCl (2.705 and 0.789 g Si kg^{-1}, respectively) due to silica gel was made by neutralizing water glass, gelling and dehydrating which silica gel is not dissolved in HCl (Ma & Takahashi, 2002). For steel slag, the results are in line with Haynes et al. (2013). They found that Si was higher in steel slag with HCl method compared to Na_2CO_3/NH_4NO_3 method.

Generally, this study showed that Si content in material by citric acid extractable was lower than 0.5N HCl extractable (Table 2). In line with Wang et al. (1995) who reported that Si concentration extracted by 2% citric acid was lower than 0.5 M HCl.

By comparing the fly ash and steel, the Si concentration in 0.5N HCl-extractable Si was lower in fly ash. It was possible as fly ash is made up of highly insoluble, glass-like particles and consists of amorphous ferro-aluminosilicate and quartz. In contrast, steel slag consist of Si as semicrystalline larnite [$Ca_2(SiO_4)$] which is sparingly soluble (Haynes et al., 2013).

In general, of the six extraction methods, Si concentration was higher in the order of 0.5N HCl > citric acid > acetate buffer (pH 4.0) > sodium phosphate > Na_2CO_3/NH_4NO_3 > $CaCl_2$ for inorganic materials. While organic materials, concentration of Si was higher in the order of Na_2CO_3/NH_4NO_3 > $CaCl_2$ > sodium phosphate > citric acid > 0.5N HCl.

Table 2. Quantities of extractable Si in materials

Materials	Acetate buffer	Citric acid	0.5N HCl	Sodium phosphate	$CaCl_2$	Na_2CO_3/NH_4NO_3
	------------------------------ g Si kg^{-1} --------------------------------					
Fly ash 1	4.662	7.374	7.677	1.978	0.019	0.077
Fly ash 2	4.645	7.275	7.573	1.403	0.031	0.163
Fly ash 3	4.173	7.412	8.418	1.105	0.018	0.793
Steel slag	4.612	6.522	16.143	2.22	0.019	0.146
Silica gel	-	1.326	2.705	0.675	1.762	6.54
JSG	1.745	1.317	0.789	2.328	1.691	6.771
Volcanic ash	0.15	1.587	1.595	1.405	0.011	0.073
Bottom ash	4.577	6.45	13.376	0.396	0.053	0.178
EFS	7.458	6.584	20.618	1.335	-	0.131
JSF	3.536	5.843	25.362	2.695	0.022	3.838
RHA	-	0.377	0.289	0.358	1.937	2.768
RHB	0.061	0.111	0.079	0.27	0.569	1.582
RHH	0.088	0.05	0.032	0.41	0.341	4.964
MM	-	0.119	0.074	0.531	1.234	1.471
Cacao SB	1.322	1.852	3.739	0.578	0.098	0.161
RSC	0.746	1.003	1.233	0.309	1.197	2.08
Bagasse	0.041	0.154	0.132	0.281	0.148	1.474
Elephant grass	0.464	0.101	0.152	0.672	0.199	5.378
Vetiver grass	0.223	0.129	0.076	0.324	0.771	5.509
Bamboo leaf	0.218	0.13	0.082	0.711	1.031	6.951
Sugarcane leaf	0.627	0.148	0.134	1.55	0.455	5.586
Palm nut SB	0.173	0.466	0.472	0.283	0.116	0.209
Min	0.00	0.05	0.03	0.27	0.00	0.07
Max	7.46	7.41	25.36	2.7	1.94	6.95
Mean	1.8	2.56	5.03	0.99	0.53	2.58
Std deviation	2.25	3.01	7.44	0.76	0.65	2.58

JSG=Japanese silica gel, JSF=Japanese Si fertilizer, EFS=electric furnace slag, RHA=rice husk-ash, RHB=rice husk-burnt, RHH=rice husk-heated, MM=media of mushroom, cacao SB=cacao shell-biochar, RSC=rice straw compost, palm nut SB=palm nut shell-biochar.

The greatest proportion of Si from organic materials were extracted by Na_2CO_3/NH_4NO_3 method (1.471 – 2.768 g Si kg^{-1}), other than cacao SB, but was notably ineffective at extracting Si from inorganic materials. It is possible that alkaline solution dissolves organic matter that covers Si and thus Si may release from organic matter. According to Pereira et al (2003), this extraction method was developed with the specific aim of dissolving the water-insoluble $CaSiO_3$. The alkaline-extractable method is based on the fact that the solubility of amorphous Si increases with increasing pH values (Iler, 1979).

2.3.4. Green house experiment

The effect of Si on the growth of the rice plants was studied from both aspects: the release of Si at different time and Si uptake by plants. Beside Si, we also observed P in soil solution. The Si uptake ability was compared among the materials during 37 DAT under the same condition.

Silicon

The Si release pattern during 34 DAT was similar for all the materials (Fig. 9a), which was higher in the beginning of observation. Both inorganic and organic materials produce unstable concentrations of Si which sharply decreased from day 7 to 17, and then slightly increased on day 24. It may indicate the continuous dissolution of Si from material and soil. Most of the treatments, the lowest Si concentration was on day 34. Another possibility is rapid polymerization that occurs at high solution concentrations, increasing soil pH and in the presence of oxides and hydroxides of Al and Fe (Berthelsen & Korndorfer, 2005). In line with Marxen et al. (2016) who reported that Si concentration in soil solution after 10 DAT was decrease for treatment with silica gel or rice straw compared to without plant growth.

The amount of Si concentration in soil solution was higher for inorganic materials application compared to organic materials on the first 7 DAT, except steel slag (< 0.5 mmol L^{-1}). It might be possible that decomposition of organic materials (MM, cacao SB, and RSC) started slowly. Marxen et al. (2016) reported Si concentrations in soil solution increased when the organic matrix surrounding the phytoliths was decomposed and the surface of phytoliths become exposed to the soil solution.

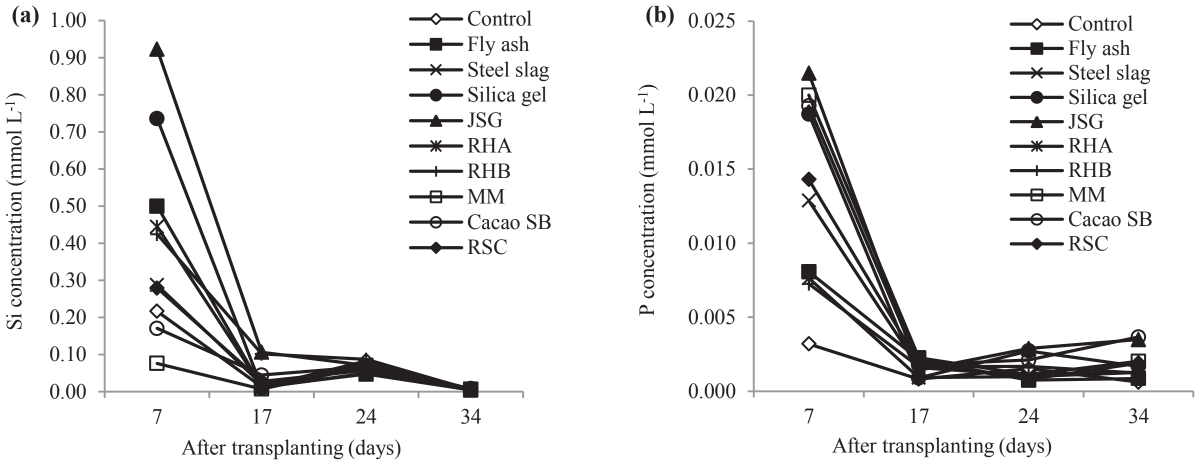

Figure 9. Release pattern of Si (a) and phosphorus (b) in soil solution during 34 days of experimental time

Phosphorus

Silicon material applications to the soil not only supply Si, but also raise P concentration. The P release pattern was the same with Si release pattern (Fig. 9b) which was higher in the first 7 DAT. According to Ma and Takahashi (1991), both Si and P may produce beneficial effects on the growth of rice plants especially in acid soils deficient in P. Silicic acid had indirect effect to improve P on the rice growth by decreasing Mn uptake. In this experiment, although the P concentration was around 10 times lower compared to Si concentration (Table 3), but the Si effect can be held responsible mainly for an increase P supply from the soil.

The amount of Si and P concentration in soil solution (Table 3) with added material was higher than control, except MM and cacao SB for Si concentration. It means, almost all materials increased Si and P in soil solution. For MM and SB, it was not only due to sampling loss but also to active Si absorption by the rice plant (Kato & Owa, 1997). Victoria et al. (2001) reported a positive interaction of Si and P of rice yield on soils with low in both Si and P. The highest amount of Si concentration in soil solution by inorganic and organic material application was JSG and RHB, respectively.

Table 3. Cumulative concentration of Si and P in water surface during 34 DAT

Treatments	Si	P
	mmol L^{-1}	
Control	0.319	0.006
Fly ash	0.565	0.012
Steel slag	0.375	0.017
Silica gel	0.806	0.024
JSG	1.107	0.029
RHA	0.539	0.011
RHB	0.618	0.012
MM	0.159	0.025
Cacao SB	0.290	0.027
RSC	0.371	0.019

According to Jones and Handreck (1967), activity of Al ions in solution are reduced by monosilicic acid and then preventing those ions from precipitating the phosphate. Reaction in the release of phosphates into soil solution (Mathicnekov & Bocharnikova, 2001):

$$2Al(H_2PO_4)_3 + 2Si(OH)_4 + 5H^+ = Al_2Si_2O_5 + 5H_3PO_4 + 5H_2O$$

$$2FePO_4 + Si\ (OH)_4 + 2H^+ = Fe_2SiO_4 + 2H_3PO_4$$

pH

The change in soil solution pH during the plant growth period was presented in figure 10. Most of the treatment increased soil solution pH, except silica gel that was slightly decreases at 34 DAT. The highest soil solution pH at 34 DAT was obtained from steel slag, JSG, MM and cacao SB (6.0 – 6.9) and the lowest soil pH resulted from silica gel (4.4) compared to control (5.0).

The pH of soil solution did not increase for control, fly ash, and RSC after 24 DAT. It might be due to excess Si concentration in soil solution which increases until the solubility curve is reached, but then decreases as the pH continue to decrease because the remaining un-dissolved Si removes more OH^- ions from solution (Helmuth et al., 1993).

According to Tubana and Heckman (2015), application of fly ash and steel slag increased soil pH (>1 unit). Flooding an acid soil lead to increase soil pH between 6.5 and 7 (Ponnamperuma, 1984). Furthermore, Kogel-Knabner et al. (2010) reported the pH in paddy soil solution is neutral under flooded conditions. The increase in pH of acid soil is due to reduction of Fe (III) to Fe (II). Furthermore, Haynes et al. (2013) reported that industrial waste material such as slag and fly ash increased soil pH.

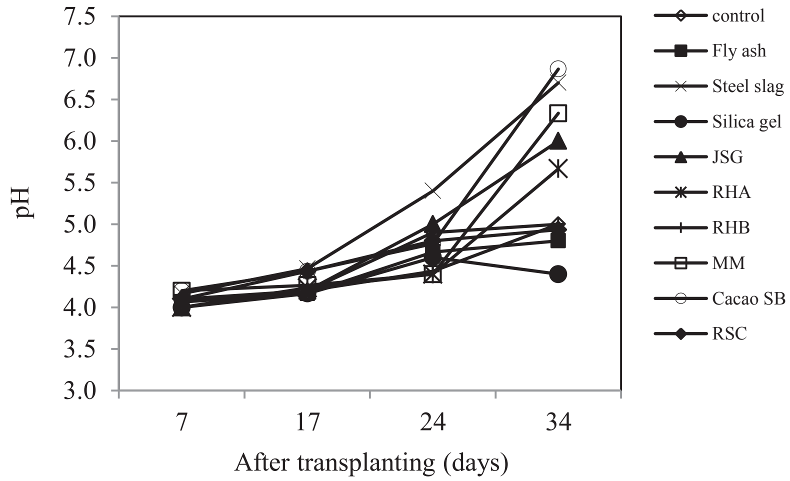

Figure 10. Effects of applications of various Si materials on pH of soil solution

The increasing pH in soil solution was at contrast with Si concentration that tends to decrease during plant growth. Our results are partly in line with previous studies; Gocke et al. (2013) showed that for wheat plant, Si concentration in solution with silica gel application was higher at pH 4.5 compared to pH 7. According to Beckwith & Revee (1963), concentration of Si in soil solution may increase when pH value decreases from 7 to 2. Haynes (2014) suggested that the effect of pH on Si availability in soil needs more understanding about the competing and interacting processes involved.

2.3.4.1. Plant growth

Plant height

The significant difference among treatments on plant height is shown in figure 11 with the letter indicating significant difference. Cacao SB, silica gel, Japanese Si gel and RHB significantly increased plant height on 36 DAT. Fallah (2012) reported that plant height increased under Si application. This was corroborated by Pati et al. (2016), who observed significant increase in plant height with Si fertilization.

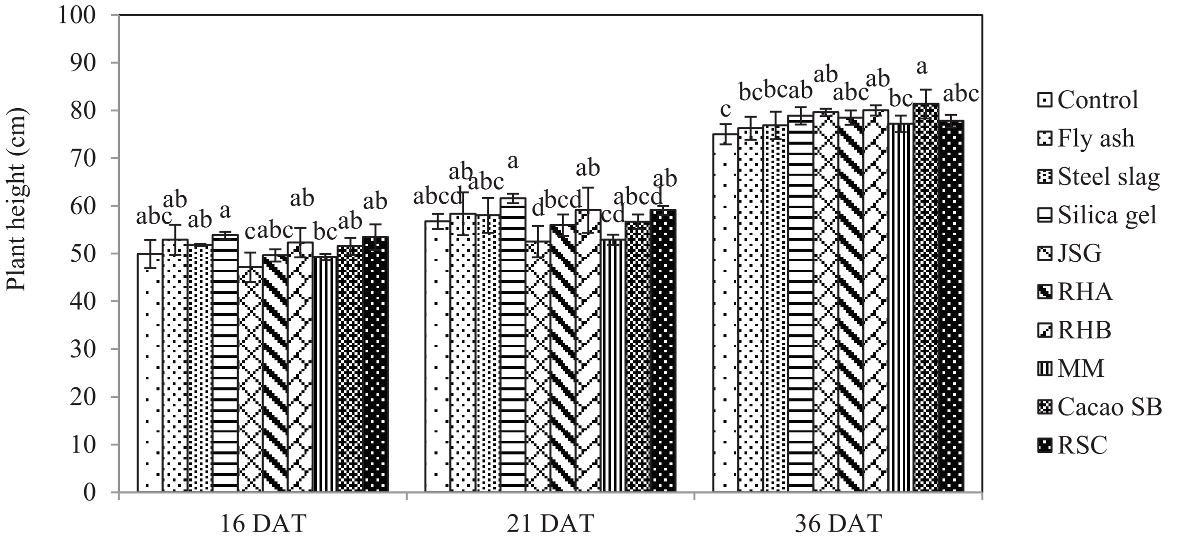

Figure 11. Impact of silicon material on plant height

Silica gel and JSG was similar with Silicon that release in water surface, which was higher than other treatment. This clearly shows application of Silica gel and JSG increase plant height. Meanwhile for RHB and cacao SB, we could not find that material increase plant height as silicon in water surface was not in line with plant height (Fig. 9A).

Tiller number

It is interesting to note that Si materials hardly affected the tiller number (Fig. 12). However, the highest tiller number was obtained with JSG application at 36 DAT. Tamai and Ma

(2008) reported that Si does not affect tiller number. Agostinho (2016) also reported that there is no significantly increased on tiller number with foliar or soil application of Si. On the other hand increase tiller number of rice plant was recorded by Yasari et al. (2012); Gholami and Falah (2013).

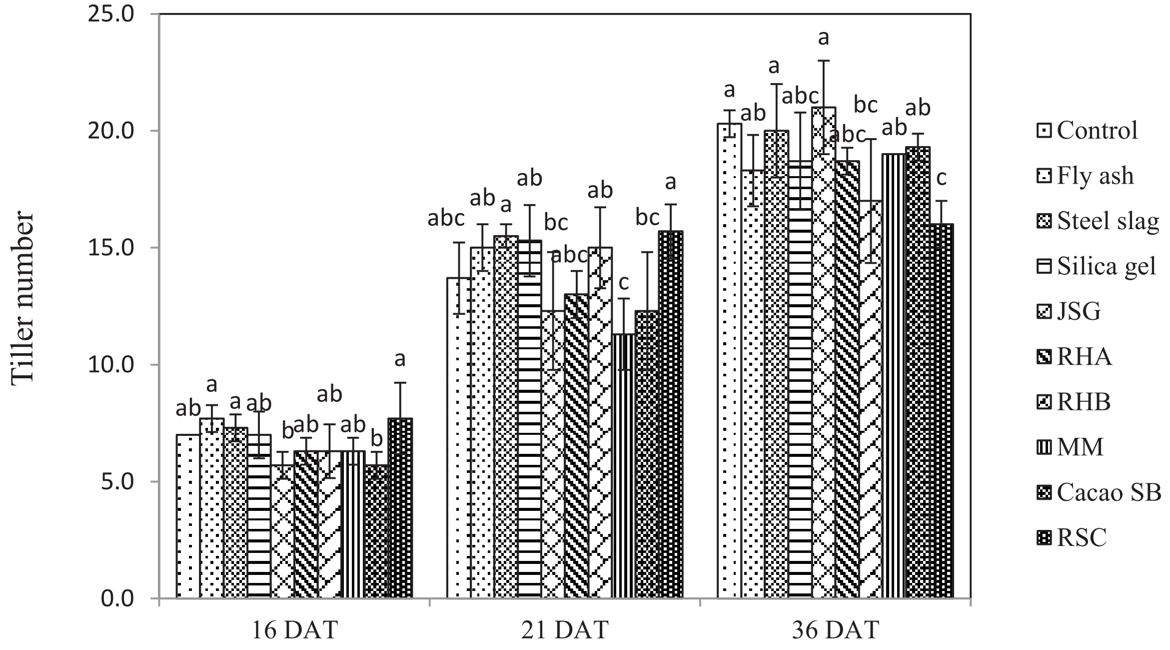

Figure 12. Impact of silicon material on tiller number

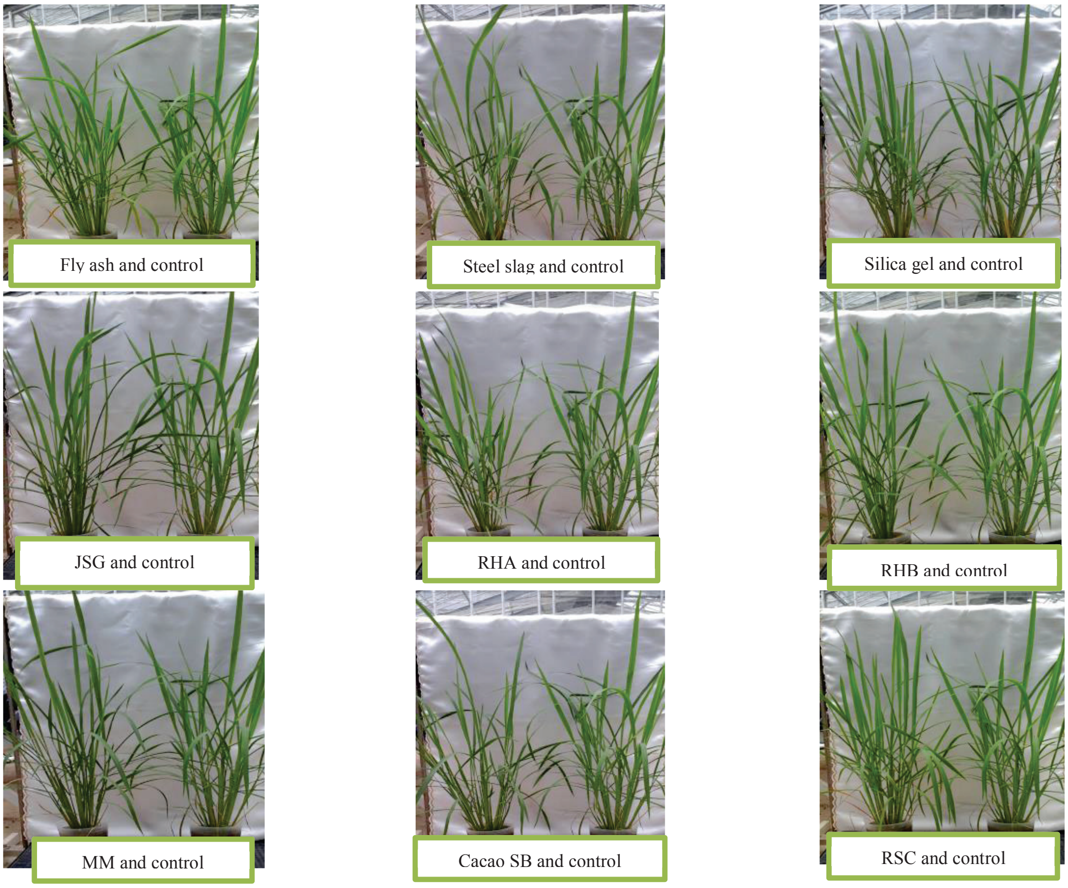

Figure 13. Plant growth at 36 DAT

2.3.4.3. Plant Si uptake and biomass

As Si accumulates at the places of respiratory water losses and consequently Si concentrates in leaves (Gocke et al., 2013), thus we analyze Si concentration in above ground biomass. Plant Si uptake by straw was significantly affected by JSG and steel slag application compared to control (Fig. 14).

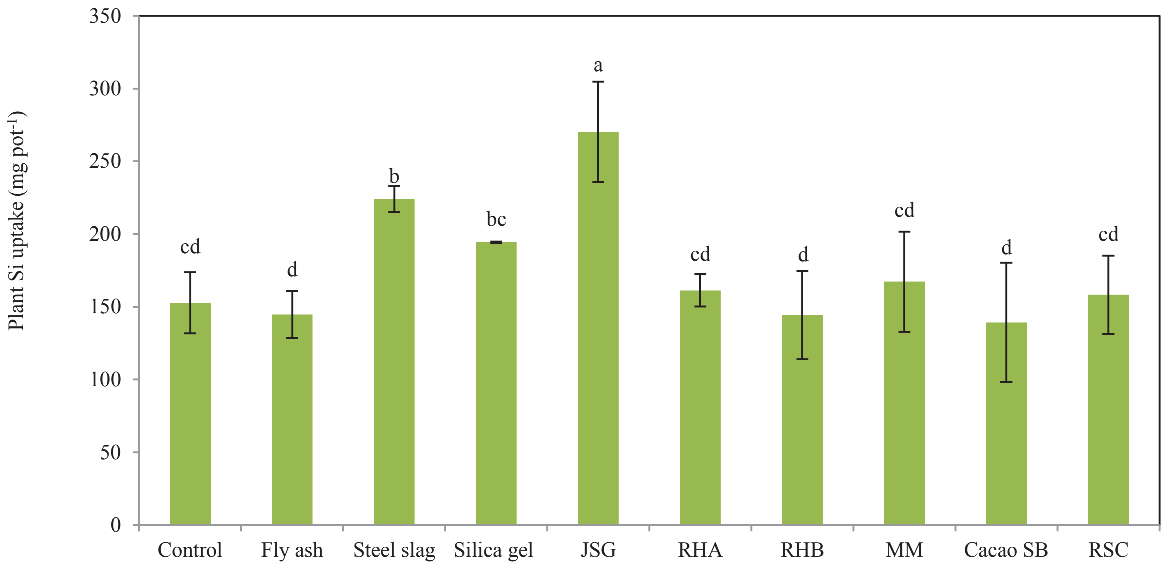

Figure 14. Plant Si uptake

The greatest uptake occurred from JSG treatment. Beside those materials, silica gel and MM increase plant Si uptake but not significant compared to control. As silica gel and JSG were easier to dissolve into solution (Table 3), resulted in more Si uptake by plants. These data suggest that the plant Si uptake accelerated the release of dissolved Si from both silica gels and soil. It might be similar with experiment by Marxen et al. (2016) who reported that decreased Si concentrations in soil solutions was the reason for the accelerated weathering of straw and soil minerals as they used in experiment.

As local material, steel slag was also high Si uptake. But it was not like both silica gels, steel slag in soil solution was lower. It might be because Si uptake by plant was more for steel slag and Si release from steel slag need longer time or the weathering of Si from steel slag was slower compared to silica gel. Steel slag that consists of calcium silicate increased the soil solution pH up to 6.7 on day 34. This effect results in stimulating the ammonification of organic nitrogen. Thus, extra nitrogen may dilute the Si content via promoted growth and then it is possible that the application of steel slag as silicate fertilizer affect the formation of

Si bodies indirectly through nitrogen nutrition (Ma & Takahashi, 1993). Meanwhile, plant biomass was not significantly affected by application of Si materials (Fig. 15).

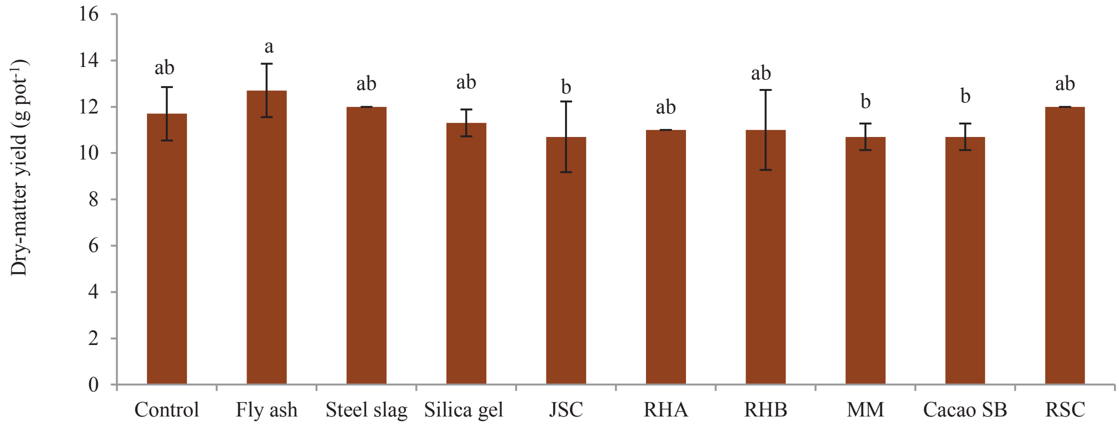

Figure 15. Dry matter yield

2.3.5. Extractable Si material, relationship to plant-Si uptake

Concentrations of different extractable Si in material vary considerably within the study (Table 2). From six, we used five extractants (Na_2CO_3/NH_4NO_3, sodium phosphate, 0.5N HCl, citric acid, and $CaCl_2$) to test the release of Si in relationship with plant Si uptake.

Silicon taken up by the plants is related to Na_2CO_3/NH_4NO_3, sodium phosphate, and 0.5N HCl-extractable Si in materials (Fig. 16). Liang et al. (2015) noted the best extracting for available Si in solid fertilizer was Na_2CO_3/NH_4NO_3. However, we suggest that in our study, the Si uptake is driven by Si availability with several extractants, because of the widely different forms in which Si is present in the different materials.

Table 4. Categorized method of various materials

Na_2CO_3/NH_4NO_3	Sodium phosphate	0.5N HCl
Silica gel	Fly ash	Fly ash
JSG	Steel slag	Steel slag
RHA	JSG	Cacao SB
RHB		RHB
MM		
RSC		

Furthermore, we try to classify methods for determining available Si content of various materials based on relationship between extractable Si (Table 4) and plant Si uptake into three categories: (1) 0.5N HCl-extractable Si is closely related to plant Si uptake with application of fly ash, steel slag, cacao SB, and RHB (Fig. 16a). (2) Fly ash and steel slag are also related to sodium phosphate which is in the same group with JSG (Fig. 16b). (3) Na_2CO_3/NH_4NO_3-extractable Si is related to plant Si uptake with application of silica gel, JSG, RHA, RHB, MM, and RSC (Fig. 16c).

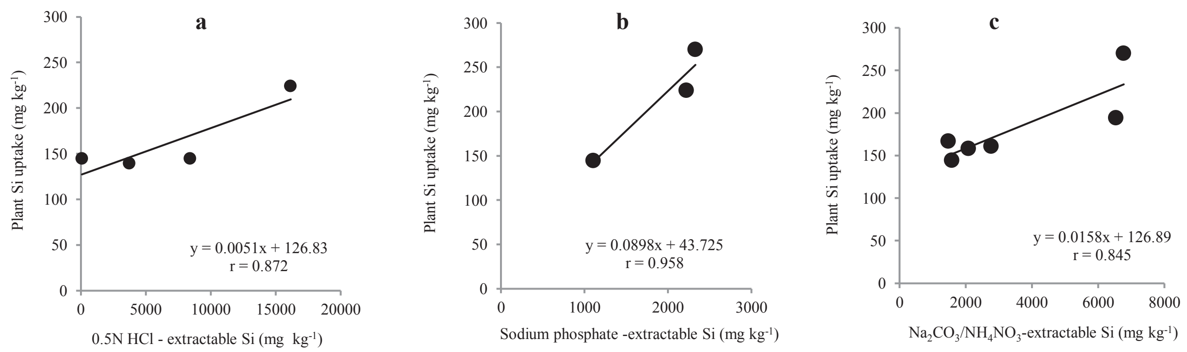

Figure 16. Relations between Si concentration in extractable and plant Si uptake

It has been reported that it is difficult to select a universally suitable method for all types of materials (Liang et al., 2015). Therefore, we assume that those categories of extractable Si, can provide information on plant available Si, which is important to assess the Si-supplying capacity of the fertilizer.

However, materials only reacted with the soil for 36 days prior to extraction and analysis of available Si. This condition was apparently not long enough to measure the potential Si-supplying power of all materials.

2.3.6. Stomatal density

Stomatal density is defined as the number of stomata per unit leaf area (Tanaka et al., 2013). In our study, stomatal density was not significantly affected by Si materials application (Table 5). This is in line with Putra et al., (2012) that reported stomatal density (abaxial and adaxial) was not influenced by silicon fertilizer or combination of silicon and NPK fertilizer. Another study on silicon decrease of transpiration rate was performed by Gao et al. (2006) using maize plants in which stomatal density of the plant leaves in which -Si application was similar to that of +Si application.

Table 5. Stomatal density in rice leaf

Treatments	Stomatal density (mm^{-2})
Control	334
Fly ash	304
Steel slag	334
Silica gel	323
JSG	323
RHA	299
RHB	339
MM	349
Cacao SB	312
RSC	368

2.3.7. SPAD

The data regarding photosynthetic revealed that application of material increased SPAD value. The highest SPAD-value of the leaf was RHA (42.8). In line with Isa et al. (2010) who reported silicic acid treatment markedly enhanced the SPAD values of leaf and Ahmed et al. (2011) who reported that chlorophyll content was increased due silicon application. Farooq et al. (2015) pointed out that Si application increased SPAD value in saline and non-saline conditions.

Table 6. SPAD value at 34 DAT

	SPAD value
Control	38.7
Fly ash	40.1
Steel slag	41.0
Silica gel	41.3
JSG	42.6
RHA	42.8
RHB	41.1
MM	42.3
Cacao SB	41.9
RSC	41.0

2.4. Conclusions

Extractable Si material analysis combined with green house experiment for getting information about better extraction method and Si source material for rice plant showed that various sources of Si materials had different extractable Si. In inorganic materials, the Si concentration was high with 0.5N HCl, except silica gel. In contrast, organic materials extracted by Na_2CO_3/NH_4NO_3 had high Si concentration, except cacao SB.

Tiller number and plant biomass were not affected by Si material application. Of the materials used here, steel slag and Japanese silica gel (JSG) affected Si uptake by rice plant. Thus, steel slag as local Si material is an option to increase rice yields.

Based on the results there is no universally accepted method to evaluate plant-available Si in materials. Thus, 3 categories of extractable Si: (1) Na_2CO_3/NH_4NO_3 for silica gel, JSG, RHA, RHB, MM, and RSC, (2) sodium phosphate for fly ash and steel slag, and (3) 0.5N HCl for fly ash, steel slag, cacao SB, and RHB.

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CHAPTER 3

Silicon Release from Local Materials in Indonesia under Submerged Condition

3.1. Introduction

Silicon is not recognized as an essential element, but as a beneficial element, Si enhances diseases resistance, alleviates metal toxicity, improves nutrient balance, prevents lodging and enhanced drought tolerance of rice (Ma & Yamaji, 2006). Silicate minerals liberate dissolved Si (DSi) as monosilicic acid (H_4SiO_4) by chemical weathering (Cornelis et al., 2011). Furthermore, Si is taken up by the roots in the form of H_4SiO_4 (Ma & Yamaji, 2006). However, the soluble Si content of tropical soils, such as highly weathered mineral (Ultisols and Oxisols) is generally less than that in most temperate soils as a result of Si leaching (Foy, 1992). While desilification and fertilization processes are extremely active in red soil (Liang et al., 2015). However, in sandy soil that consists mostly of quartz (SiO_2), the chemical decomposition of this mineral is complex (Marafon & Endres, 2013). One of the most important factors that influence the solubility of Si in soil is redox potential. Low soil Eh as flooding condition, normally leads to an increase in available Si concentration (Liang et al., 2015). The solubility of Si containing mineral is affected by pH, where the soil pH regulates the solubility and the mobility of Si (Tubana & Heckman, 2015). Silica concentration is lowest at pH 8-9 and Si concentration in soil solution may rise sharply when pH value decreases from 7 to 2 (Beckwith & Reeve, 1963).

Most of the land in Indonesia is acidic due to high level of leaching of basic cations. There are about 102,000,000 ha of acidic soil with Ultisols and Oxisols the dominat soils, beside Entisols, Inceptisols and Spodosols (Subagyo et al., 2000; Mulyani et al., 2009). These soils have been used for rice production in Indonesia. Although Si is very abundant element in soil with the range from 25 to 35 %, repeated cropping can reduce the levels of plant-available Si to the point that supplemental Si fertilization is required for maximum production (Datnoff & Rodrigues, 2005). In Indonesia, lower soil Si content was found to be severe in intensive rice field where enormous Si uptake is not followed by sufficient Si replenishment (Husnain et al., 2008). In present, the most common forms of silicate materials used as fertilizer are various industrial by products (Haynes, 2014). Slag from iron and alloy manufacturing that consist of calcium silicate which could be used to meet the demand of Si. Fly ash from coal combustion where the dust-collection system removes the fly ash from the combustion gases before they are discharged in the atmosphere is high in Si content (Ramezanianpour, 2014). These Si rich materials from industrial wastes are also applied to increase soil pH (Haynes et al., 2013).

Besides industrial wastes, potential organic sources of silicate material have been assessed for use as an agricultural amendment. As plants accumulate Si, there is possibility of using crop residues as Si source. For example, rice (*Oryza sativa* L.) husk and sugarcane (*Saccarum* spp.) bagasse have considerable Si concentration (Gascho, 2001). Biogenic amorphous silica is a natural constituent from unicellular organism, compost and crop residue (Rabovsky, 1995; Tubana & Heckman, 2015). However, the demand of Si from crop residues for agriculture is insufficient from plant residues. To address this issue, it is desirable to explore cheap and abundant local materials as Si source.

In Indonesia, there are some potential sources as silicate fertilizer from industrial by product and plant material-based silica. Factories that produce slag as by product of steel with crude steel production was 4.7 million ton on 2011 (Ministry of Industry Republic of Indonesia, 2014). Production of coal in Indonesia is around 437 million ton (Ministry of Energy and

Mineral Resources, 2014) with fly and bottom ash as waste. Indonesia is the world's third largest cocoa bean producer (FAO, 2010) so it is also possible to use cacao shell and leaf as source of Si fertilizer. Considering the large amount of Si accumulated in rice straw and husk, straw compost and husk burning are an interesting Si source for plants.

Emphasis should be made not only on Si content but also on its solubility. The release of Si from the local materials into soil solution varies in different combination of materials and soils. Factors controlling dissolution of Si include iron (Fe), calcium (Ca), manganese (Mn), pH, particle size of the materials and presence of organic matter (Makabe et al., 2013; Kendrick, 2006). The factors that cause variation Si release from material and soil should be evaluated to improve use of material as Si source. Therefore, the objective of this study is to evaluate Si release from different local materials used as soil fertilizers under submerged conditions in relation with soil chemical properties and other controlling factors.

3.2. Materials and Methods

The Si release from the local materials was characterized through laboratory incubation experiments.

3.2.1. Si Source Materials

Eleven materials were collected from Indonesia and Japan. There are two groups of materials, namely (1) five inorganic materials (fly ash from coal company in South Sumatera, steel and electric furnace slag/EFS were obtained from Banten, silica gel, Japanese silica fertilizer (JSF) is a slag-based silicate fertilizer). (2) Six organic materials (elephant grass (*Pennisetum purpureum*), rice (*Oryza sativa* L.) straw compost/RSC, rice husk-biochar/RHB, cacao (*Theobroma cacao* L.) shell-biochar (cacao SB), media of mushroom/MM and rice husk-ash/RHA from West Java**.** The geographic and climatic condition of South Sumatera is 1°0′-

4°0′S and 102°0′-106°0′E (Badan Pusat Statistik (BPS), 2015), Banten is 5°7′50″-7°1′1″S and 105°1′11″-106°7′12″E (Banten, 2016). West Java is 5°50′-7°50′S and 104°48′-108°48′E (Jawa Barat, 2016), with rainfall of about 3409,3573 and 2682 mm on 2013 in South Sumatera, Banten and West Java, respectively (Badan Meteorologi Klimatologi dan Geofisika (BMKG), 2000-2013). The elephant grass and media of mushroom were air-dried for 2-3 days. Materials were ground into fine powder in agate grinding jars, using a mixer mill (MM 200, Retsch GmbH, Haan, Germany).

Samples were oven-dried 12 hours at 80^{o}C. Total element (Ca, Mg, K, Na, Fe Mn, Cu, Zn, Cd and Ni) composition of materials was measured by ICP after digestion in Teflon vessel with HNO_3 at 160^{o}C for 4 hours and diluted with distilled water up to 25 ml after kept resting overnight (Koyama & Sutoh, 1987). Total carbon (C) was assessed using dry combustion methods (Sumigraph NC-22 Analyzer).

Available Si (Table 1) was extracted from materials with 0.5 M HCl (1: 150 ratio for 1h shake at 110 rpm) (Savant el al., 1999) and Na_2CO_3/NH_4NO_3 (10 g L^{-1}/16 g L^{-1}) (1:100 ratio for 1h shake at 110 rpm) (Pereira et al., 2003). The concentration of Si in all extracts was determined using the molybdenum blue method and measured by Spectrophotometry UV 1800 Shimadzu. The wavelength use for the Si detection was 810 nm. pH (H_2O) was determined on 1: 30 (w/v) soil: water suspensions with pH meter (D-51, Horiba).

3.2.2. Soil Samples

Two types of soil were used, a red clayey soil (Ultisol) and a sandy soil (Entisol) with textural classes of clay loam and fine sand, respectively. Red clayey soil is slightly acidic (pH 5.7) and relatively rich in available Fe and Mn (72.5 and 52.2 mg kg^{-1}). Exchangeable Ca and

Mg were 4.3 and 2.4 $cmol_c kg^{-1}$, respectively. Sandy soil is neutral in pH (7.3), has high content of exchangeable Ca (26.4 $cmol_c\ kg^{-1}$, 1M ammonium acetate extractable Ca) and available Fe (136.4 mg kg^{-1}). The available Si concentration of red clayey and sandy soil was 267.1 and 129.3 mg $SiO_2\ kg^{-1}$, respectively. According to Sumida (1992), those were classified to be below critical level of available silica for rice (300 mg $SiO_2\ kg^{-1}$). We expected the difference of these properties to influence the dynamics of dissolved Si from the local materials.

The soil sample was air dried and passed through a 2 mm sieve. Exchangeable Ca and Mg were extracted with 1 M ammonium acetate pH 7.0 and measured by Inductive Coupled Plasma Spectroscopy (ICPE-9000 Shimadzu, Kyoto Japan). Available Si was extracted by acetate buffer pH 4 with ratio of 1:10, for intermittent shaking for 5h at 40 °C, determined using the silicate molybdenum blue method (Imaizumi & Yoshida, 1958). Soil pH (H_2O) was determined on 1:2.5 (w/v) soil: water suspensions with pH meter (D-51, Horiba). The contents of available Fe and Mn were obtained by extraction with 0.1 N HCl and quantified using the ICP.

3.2.3. Incubation Experiment

Under submerged condition, the soil was incubated with Si materials as treatment. The experiment was replicated three times. Air dried soil of 10 g was placed in a 50 mL centrifuge plastic tube, 1 g of organic material and 40 mL of distilled water (DW) were added into the tube. For inorganic material (steel slag, fly ash, EFS and JSF) 0.02 g of 30% 0.5 M HCl and silica gel 0.02 g of 30% Na_2CO_3/NH_4NO_3 as silicon dioxide (SiO_2) were added to the centrifuge tube containing 10 g of soil, and then 40 mL of distilled water was added. The tube was covered and mixed thoroughly, incubated at 30^{o}C for 70 days. After incubation, the redox potential (Eh) and pH of soil solution were measured with Eh meter and pH meter (TOA HM-14P and D-51 Horiba, respectively) without disturb the soil. The supernatant was obtained after filtration (paper filter Advantec No. 6). Silica, Ca, Mg, Fe and Mn concentrations in supernatant were measured using ICPE-9000 Shimadzu. To resume the incubation, residue on the filter paper was washed back into tube with distilled water and distilled water was added up to a total volume of 40 mL base on the weight (Makabe et al., 2013). The soil solution was replaced with distilled water at day (d) 7, 14, 21, 42, 49, 56, 63 and 70 assuming field water replacement by drainage / leaching and irrigation in the field.

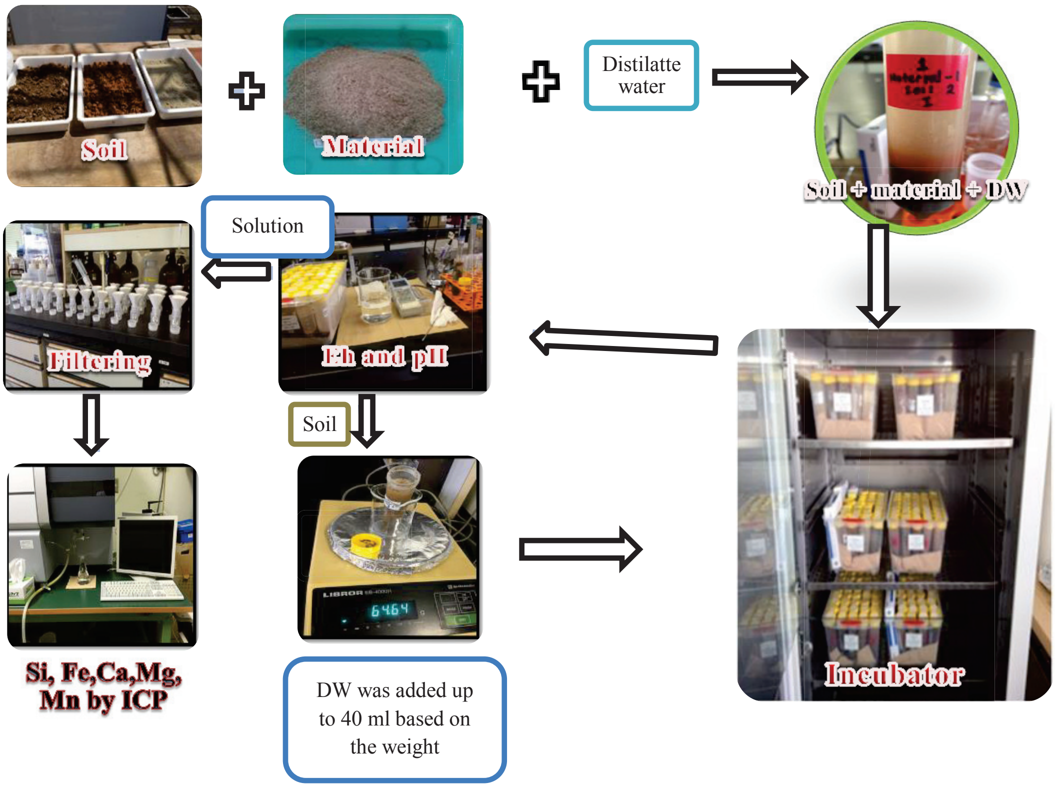


Figure 1. Flow chart of incubation experiment

3.2.4. Data Analysis

The release of Si in the soil solution after the incubation experiment is symbolized the concentration of Si (mmol L^{-1}). The net release of Si and the other elements (ΔSi, ΔCa, ΔFe, ΔMg, ΔMn) from the materials was estimated based on the difference between the concentration of elements in samples with materials and without material (control). A correlation analysis was conducted to identify relationship between the Si and other elements. Statistical analyses were done using the statistical package SPSS 22.

3.3. Results and Discussion

3.3.1. Chemical Composition of Si Material Sources

The chemical composition of 11 materials used in this study is shown in Table 1.

Table 1. Chemical composition of materials

Material	pH	Si		TC	Ca	Mg	Fe	Mn	Cu	Zn	Cd	Ni
		Na_2CO_3/NH_4NO_3	HCl 0.5 M									
		------------ mmol kg^{-1} ------------		------------ mg kg^{-1} ------------								
Steel slag	9.8	5.2	801.0	1400.0	198105.2	34818.5	281649.6	9605.1	147.1	46.1	67	113.6
Silica gel	6.8	234.3	96.6	-	11013.9	3283.6	6124.5	102.9	-	-	-	-
Fly ash	7.7	28.3	300.1	107802.6	18368.1	9006.0	29612.9	341.9	30.7	102.3	18.4	47.2
EFS	9.5	4.7	412.5	7700.0	157214.1	59459.2	151671.3	11589.5	120.9	942.3	56.4	109.9
JSF	12.4	137.1	975.0	20259.0	240126.9	18261.8	8606.2	23003.8	-	-	-	-
RSC	9.5	74.3	44.0	222578.3	14364.9	4340.8	16297.7	1833.5	26.6	87.8	9.7	18.7
RHB	7.6	56.5	2.8	427394.4	1952.0	991.5	2489.0	552.5	3.8	38.7	1.6	4.3
RHA	10.7	98.8	10.3	3650.4	3429.4	793.3	372.6	592.5	2.2	38.1	1.1	3.5
Cacao SB	10.5	5.7	133.5	423490.9	22278.9	15601.3	4189.9	1198.3	54.4	317.9	8.1	27.6
Elephant grass	5.2	192.1	5.4	427055.8	6043.3	2528.2	216.8	59.9	6.2	35.5	1.4	7.2
MM	8.6	52.5	2.6	360115.7	76687.3	2692.8	1594.9	246.3	6.8	27	6.8	15.2

Note. -: not determined, TC: total carbon, EFS: electric furnace slag, JSF: Japanese Si fertilizer, RSC: rice straw compost, RHB: rice husk-biochar, RHA: rice husk-ash, cacao SB: cacao shell-biochar, MM: media of mushroom.

Inorganic materials were alkaline in nature with JSF having the highest pH, except silica gel. According to Savant et al. (1997), the amount of H_4SiO_4 in soil solution is affected by pH and the soil pH regulates the solubility and the mobility of Si (Tubana & Heckman, 2015). Among the elements, Ca, Mg, Mn and Fe were reported to relate to soil Si availability (Makabe et al., 2013; Hansen et al., 1994). Among all the materials used, JSF had highest Ca and Mn content. The highest Fe and Mg content were found in steel slag and EFS, as chemical composition of EFS was $CaSiO_3/MgSiO_3$, while steel slug was $CaSiO_3$ (Tubana & Heckman, 2015). The lowest Ca, Mn, Mg and Fe content were found in silica gel.

The chemical composition of organic materials indicated that RHA had the highest pH (10.7) and elephant grass had the lowest (5.2). Carbon content in organic materials ranged from 222578.3 to 427394.4 mg kg^{-1}, except RHA material. MM had higher Ca content than the other organic materials because in mushroom cultivation, the media was added with $CaCO_3$ to neutralize acid that was released by mushroom. Cacao SB had high content of Mg (15601.3 mg kg^{-1}). RSC compost had the highest Fe and Mn and the lowest was elephant grass. Among materials, except JSF as reference, the available Si content was highest in steel slag.

Concentration of Si was higher with 0.5 M HCl than Na_2CO_3/NH_4NO_3 (alkaline) solution for inorganic materials (300.1-975.0 mmol Si kg^{-1}), except silica gel. For organic material, Si concentration was high with Na_2CO_3/NH_4NO_3 solution (52.5-192.1 mmol Si kg^{-1}), except cacao SB. Concerning about heavy metal pollution by material application, Cu, Zn, Cd and Ni contents of all the materials were below the regulatory limit of Environmental Protection Agency (EPA) (1993); Cu = 4300, Zn = 7500, Cd = 85, and Ni = 420 mg kg^{-1}.

3.3.2. Release Pattern of Si from Materials (Δ Si) for 70 Days Incubation

The temporal changes in Si concentrations in the soil solution show that Si release rate and pattern for soil and materials differed. The Si release pattern was different between two type of soil and eleven materials. Release of Si from the materials in red clayey soil during 70 days of incubation is shown in figure 2a**.** Concentration of Si in soil solution from silica gel was stable and reached different peaks 42-56 days after flooding. Silica release from steel slag in red clayey soil started after day 49 and then increased rapidly until the end of incubation. It may indicate continuous dissolution of Si from steel slag. The dissolution pattern of Si from steel slag was different to dissolution pattern of silicate slag fertilizer reported by Makabe et al. (2013), where Si dissolution increased rapidly during the first 22 days in weakly acidic solution.

In contrast, fly ash released Si on the first 49 days then remained not detected (n.d.). A slightly higher peak of Si release from silica gel and fly ash at day 42 was probably because the soil solution was not changed for three weeks after day 21, this condition resulted in high Si in soil solution. Meanwhile, EFS and JSF did not apparently release Si throughout the incubation period in red soil. It was probably that the bond between Si and the other elements such as Fe-O-Si, CaO-SiO_2-H_2O (Hansen et al., 1994; Flint & Wells, 1934) in these materials was too strong to release Si in the red soil incubation condition.

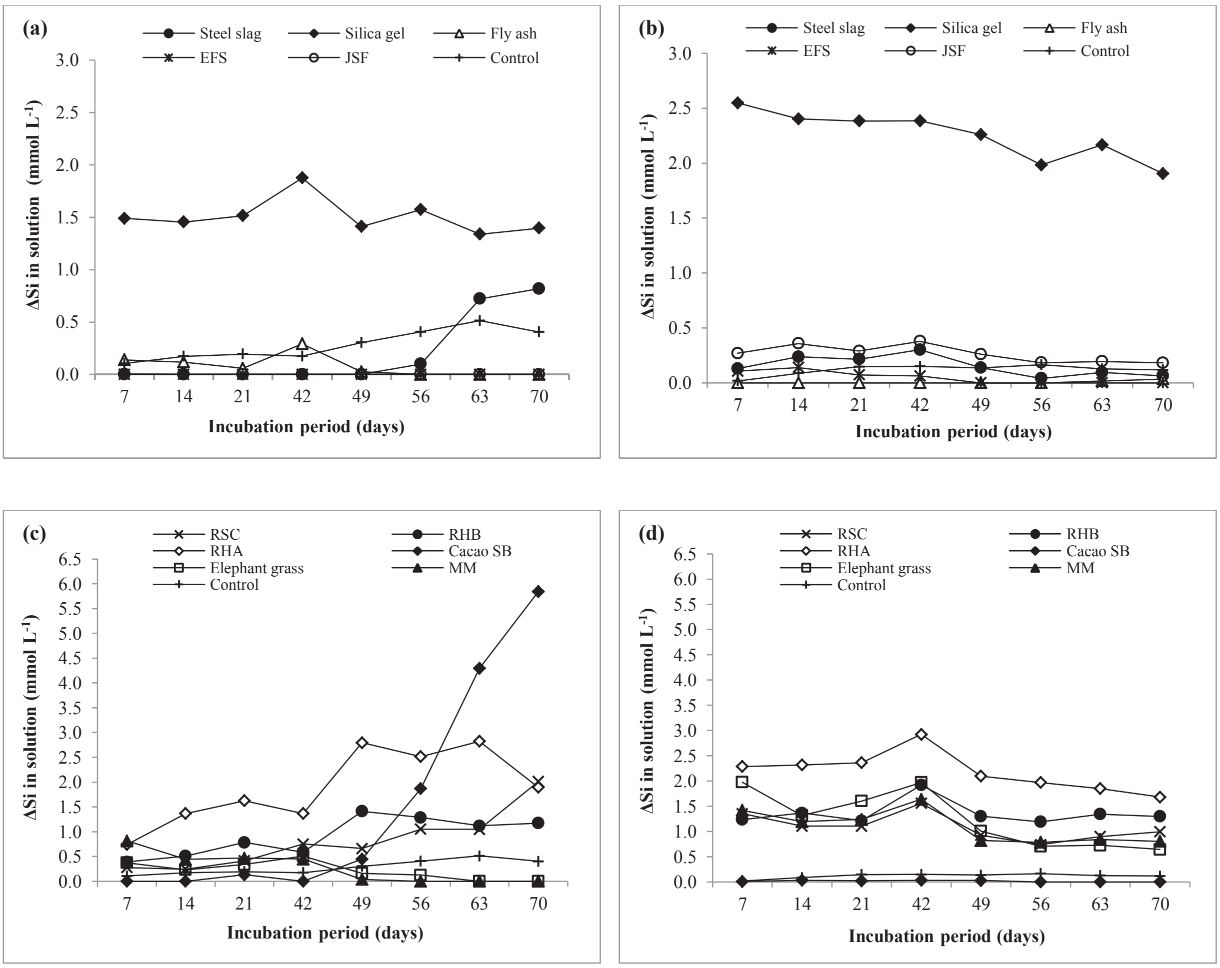


Figure 2. Release pattern of Si from the materials (Δ Si): (a) red clayey and (b) sandy soils with inorganic materials; (c) red clayey and (d) sandy soils with organic materials

Figure 2c shows release of Si from organic materials in red clayey soil. Silica concentration in soil solution with added RSC tends to increase as incubation period increased. Release of Si from RHB and RHA had similar pattern, where the release of Si was started from day 7. Silica release from cacao SB started on day 21 up to the end of incubation time. Release of Si from MM is described by an initially fast release on day 7 followed by a progressively slight release until 42 days of incubation. Silica release rates from elephant grass tended to be slightly higher on 56 days of incubation.

The effect of EFS application gradually becomes less pronounced and not detected toward the end of experiment in sandy soil (Figure 2b). Concentration of Si in sandy soil with steel slag application increased during first weeks of incubation time. Silica concentration reached the maximum value after 42 days of incubation and then gradually decreased. Silica release from JSF was high during first 49 days, then decreased. The rate of Si concentration from silica gel decrease with the time of incubation. We recorded that Si release from fly ash in sandy soil solution was less (n.d.-0.03 mmol L^{-1}) than red clayey soil, which Si release was only during the last 14 days of incubation.

Si release from silica gel was higher in sandy soil than red clayey soil. As silica gel is made by neutralizing water glass. Thus, according to Bunker et al. (1988) that the tetrahedral SiO_4 sites common to all silicates glasses were susceptible to nucleophilic attack primarily by OH^- to form a reactive five-coordinated intermediate which can be decomposed to rupture the Si-O-Si bond. Therefore, a significant quantity of OH^- could improve the formation of a five-coordinated intermediate which could lead to a great dissolution of the silica gel. Moreover, as Si concentration was higher with alkaline solution (Table 1).

Figure 2d show release of Si from organic material in sandy soil solution. Silica release from RSC and MM had similar rate, where Si concentration in sandy soil solution was high in the first 42 days of incubation. Slightly different with RSC and MM, Si release was high for 49 days after submerged with added cacao SB and elephant grass. Silica release rates from RHB were fluctuating, with the highest Si concentration on day 42 (1.92 mmol Si L^{-1}). The fact that Si release from RHA was highest on day 42, then decreased until the end of incubation.

3.3.3. The Amounts of Si Release and Coexisting Element from the Materials for 70 Days Incubation

The cumulative amounts of Si and the element expected interact on with Si release from materials during the 70 days of incubation are listed in table 2.

Table 2. Silicon and other elements release from materials and soil during 70 days.

Materials or soil	Red clayey soil					Sandy soil				
	Si	Ca	Mg	Fe	Mn	Si	Ca	Mg	Fe	Mn
	mmol kg^{-1}					mmol kg^{-1}				
Steel slag	508.32	377.43	126.72	80.15	0.20	375.97	196.65	n.d	0.15	0.77
Silica gel	1158.74	3.34	10.67	20.63	2.79	1733.00	82.31	4.16	0.39	0.01
Fly ash	79.33	185.16	77.80	0.06	n.d.	6.40	201.61	50.17	0.44	n.d
EFS	n.d.	861.84	471.59	36.35	0.41	64.22	108.13	n.d	0.08	0.43
JSF	n.d.	2050.13	340.69	0.82	2.09	852.50	2217.51	n.d	n.d	0.31
RSC	280.88	192.04	124.31	37.44	25.72	377.73	208.35	169.49	4.01	9.83
RHB	304.86	10.26	6.16	9.01	0.42	456.12	39.84	34.83	0.02	2.82
RHA	611.29	21.47	28.97	8.68	0.55	706.72	n.d	n.d	0.22	0.49
Cacao SB	659.98	52.48	129.25	11.26	1.84	6.61	n.d	63.24	0.30	0.20
Elephant grass	77.59	321.31	208.95	269.13	77.24	442.99	1441.29	309.08	12.13	0.68
MM	98.20	1527.00	226.20	28.28	42.77	388.21	1599.20	227.12	1.02	1.18
Soil	9.66	0.80	0.63	0.91	0.03	3.78	9.50	5.59	0.18	n.d

Note. n.d.: not detected, EFS: electric furnace slag, JSF: Japanese Si fertilizer, RSC: rice straw compost, RHB: rice husk-biochar, RHA: rice husk-ash, cacao SB: cacao shell-biochar, MM: media of mushroom.

The amount of Si release in red clayey and sandy soils ranged from n.d.-1158.74 mmol Si kg^{-1} and 3.78-1733.00 mmol Si kg^{-1}, respectively. The highest Si release in both red clayey and sandy soil was silica gel. Release of Si from red clayey soil (control) was higher than sandy soil, while Si concentration from soil was lower compared to that in the materials.

According to Marxen et al. (2016), Si concentrations in the soil solution from rice straw increased only when the organic matrix surrounding the phytoliths was decomposed and the surface of the phytoliths became exposed to soil solution. The release of Si was higher from RHA than RHB due to higher available Si content in RHA (Table 1), beside that C content in RHB was higher than RHA. According to Xiao et al. (2014), C and Si form in biochar result in the mutual protection between C and Si. Silica in biochar becomes difficult to dissolve, reflecting the protection of Si by C.

Organic materials in this research were high in Si concentration with alkaline solution, except cacao SB, which was high in acid solution. The results were similar to the initial Si concentrations in organic materials (Table 1). It is possible that alkaline solution dissolves organic matter that covers Si and thus Si may release from organic matter. According to Molina (2014), alkaline solution dissolved protoplasmic and structural components from fresh organic tissues.

Release of Ca, Mg, Mn and Fe were different among the materials and two soil types. In red clayey soil, released amounts of Ca and Mg were the highest from JSF (2050.13 mmol kg^{-1}) and EFS (471.59 mmol kg^{-1}), it might be due to high Ca and Mg content in both of materials (Table 1). While the lowest of Ca and Mg were silica gel and RHB (3.34 and 6.16 mmol kg^{-1}, respectively) due to Ca and Mg content was low in both materials. The highest Fe and Mn were released from elephant grass (269.13 and 77.24 mmol kg^{-1}, respectively).

Calcium and Mg release from soil (red clayey soil) was lower than in the materials. Red clayey soil has lower Fe solubility compared to in the materials, except fly ash and JSF.

For sandy soil, Ca release was the highest with JSF application due to its high Ca content. Manganese release was the highest with RSC (9.83 mmol kg^{-1}), while Fe and Mg release was the highest from elephant grass.

Calcium release was lower in soil (sandy soil) than in the materials, except RHA and cacao SB. The release of Mg from soil (sandy soil) was lower than in the materials, except steel slag, silica gel, EFS, JSF and RHA. Almost the same with Mg, Fe concentration from sandy soil was also lower than materials, except steel slag, EFS and JSF. Furthermore, Mn concentration from materials was higher than sandy soil, except fly ash. Kato and Owa (1997) reported that the application of the slags increase the Ca concentration in soil solution. Eight of eleven materials had higher Si release in sandy soil than red clayey soil. According to Dematte et al. (2011), the chemical decomposition of clay mineral is complex, which made sandy soils more responsive on Si release than red clayey soils to the material application.

3.3.4. Effects of pH and Eh

It is generally stated that Si availability depends on soil types (Wei et al., 1997). In detail, pH, Eh and the type of coexisting metals influence the adsorption of monosilicic acid by oxides (Tubana & Heckman, 2015; Liang et al., 2015).

The increase of pH and decrease of Eh (Table 3) in red clayey soil solution due to added of materials and also effect of submergence. In sandy soil solution, the trend of pH and Eh was different with red clayey soil solution. Steel slag, EFS, JSF, RHA and cacao SB tend to increase soil solution pH. Where steel slag, EFS, JSF, cacao SB, elephant grass and MM decrease soil solution Eh.

Table 3. Mean pH and Eh values of red clayey and sandy soil solution during 70 days of incubation

Material	Red clayey soil				Sandy soil			
	Mean of pH	Δ pH	Mean of Eh	Δ Eh	Mean of pH	Δ pH	Mean of Eh	Δ Eh
			---------- mV ---------				---------- mV ----------	
Steel slag	6.3	0.9	155.9	-28.3	9.8	1.2	-33.8	-14.9
Silica gel	4.8	-0.6	256.5	72.3	8.3	-0.4	21.8	40.7
Fly ash	6.1	0.7	140.9	-43.3	8.6	-0.1	-7.6	11.3
EFS	7.2	1.7	68.0	-116.2	10.2	1.5	-67.6	-48.7
JSF	6.9	1.5	100.9	-83.3	11.0	2.3	-90.8	-71.9
RSC	6.5	1.1	-19.1	-203.4	6.9	-1.8	-13.2	5.7
RHB	5.6	0.2	171.3	-12.9	7.8	-0.9	43.3	62.3
RHA	6.4	1.0	161.3	-22.9	9.4	0.7	-9.8	9.1
Cacao SB	8.0	2.6	-7.7	-191.9	9.8	1.1	-77.3	-58.3
Elephant grass	5.9	0.5	-43.2	-227.4	6.4	-2.3	-92.8	-73.9
MM	6.7	1.3	-91.9	-276.1	6.9	-1.8	-71.9	-53

Note. Δ pH means the change in pH from control (5.4 and 8.7 for red clayey and sandy soil solution, respectively); Δ Eh means the change in Eh from control (184.2 and 18.9 for red clayey and sandy soil solution, respectively). EFS: electric furnace slag, JSF: Japanese Si fertilizer, RSC: rice straw compost, RHB: rice husk-biochar, RHA: rice husk-ash, cacao SB: cacao shell-biochar, MM: media of mushroom.

3.3.4.1. Red Clayey Soil

The mean value of differences (Δ) during the entire incubation period for soil solution pH ranged from -0.6 to 2.6 units. Where, the increase in soil solution pH was 0.2 to 2.6 units. The soil solution pH was elevated by addition of all the materials, other than silica gel. The lowest soil solution pH was found in silica gel (4.8) and a maximum increase was obtained in cacao SB (8.0). Among inorganic material, the highest pH was gained with EFS application (7.2). Soil solution pH with added steel slag, fly ash, RSC and RHA were almost the same (6.1-6.5). Meanwhile, JSF and MM were close in soil solution pH (6.9 and 6.7, respectively). RHB and elephant grass increased soil solution pH with almost the same value (5.6 and 5.9, respectively).

According to Ponnamperuma (1972) that submerging soil cut off oxygen supply, where aerobic organisms use up the oxygen present in the soil. Kashem and Singh (2001) reported oxygen is reduced at Eh > 300 mV and Mn^{4+} at Eh of 200 mV. We observed that Eh decrease with increasing pH, especially with organic material treatment. Kashem and Singh (2001) reported that organic material had contributed to low and negative values of Eh resulting into higher increase in pH values.

Decreases in Eh were observed for the soil samples with addition of Si materials after submergence, except for soil with silica gel, where the values rose to 256.5 mV. The submerged condition with the addition of steel slag and fly ash result almost the same value of Eh (155.9 and 140.9 mV, respectively). The negative Eh was found in soil solution with RSC, cacao SB, elephant grass and MM (-7.7 to -91.9 mV). We observed RHB and RHA had almost the same in soil solution Eh (171.3 and 161.3 mV, respectively), it might be because both material were rice husk.

Even though, steel slag and EFS from steel company but the Eh of soil solution Eh with EFS (68.0 mV) was lower than steel slag. It was probably due to Mn content in EFS was higher that influenced Eh. Whereas, soil solution Eh with JSF application was higher than EFS (100.9 mV), but it was also probably due to high Mn content in original material.

3.3.4.2. Sandy Soil

It is obvious from Table 3 that the increased in sandy soil solution pH occurred following additions of steel slag, EFS, JSF, RHA and cacao SB with the highest increase of 2.3 units was JFS. Soil pH decreased with addition of silica gel, fly ash, RSC, RHB, elephant grass and MM with incubation time. The largest decreasing -2.3 units of pH was elephant grass.

Steel slag, EFS, RHA and cacao SB increased pH around 9.4-10.2. Meanwhile, RSC, elephant grass and MM decreased pH close to neutral (6.4-6.9). Silica gel and fly ash were almost the same in lowering soil solution pH (8.3 and 8.6, respectively) whereas pH 7.8 in soil solution was obtained with RHB application.

The Eh in soil solution with additional of steel slag, EFS, JSF, cacao SB, elephant grass and MM markedly decreased after submergence and the maximum negative value of 92.8 mV was observed for soil solution with elephant grass application. Elephant grass, cacao SB and MM as organic matter increased microbial activity in sandy soil thus decreasing soil solution Eh.

The Eh change was not as large as observed in red clayey soil. Meanwhile, Eh increased with addition of silica gel, fly ash, RSC, RHB and RHA. The highest soil solution Eh was obtained after added RHB (43.3 mV). Interactive the effect of submergence with RSC, RHB and RHA had the same result, which soil solution Eh was not decrease with those material. The same trend was probably due to the same source from rice plant.

3.3.5. Characteristics of Si Release from the Materials

Generally, soil pH regulates the solubility and the mobility of Si (Tubana & Heckman, 2015). The Eh of soils controls the stability of various oxidized components such as Mn IV and Fe III in submerged soils (Sahrawat, 2005). Reduction in Eh was accompanied with an increase in the solubility of the soil Si, where Si increase in soil solution was attributed to the release from ferric silica complexes under anaerobic conditions (Ponnamperuma, 1965). This is in line with Snyder et al. (2006) who reported that Si release such as monosilicic acid and polysilicic acid that have high chemical activity can react with Fe in the formation of slightly soluble silicate. Makabe et al. (2013) reported that Si concentration had significantly negative correlation with Ca in soil solution.

Figure 3 revealed some significant correlations between Si release with Ca or Eh changes for each material. We characterized the materials as below.

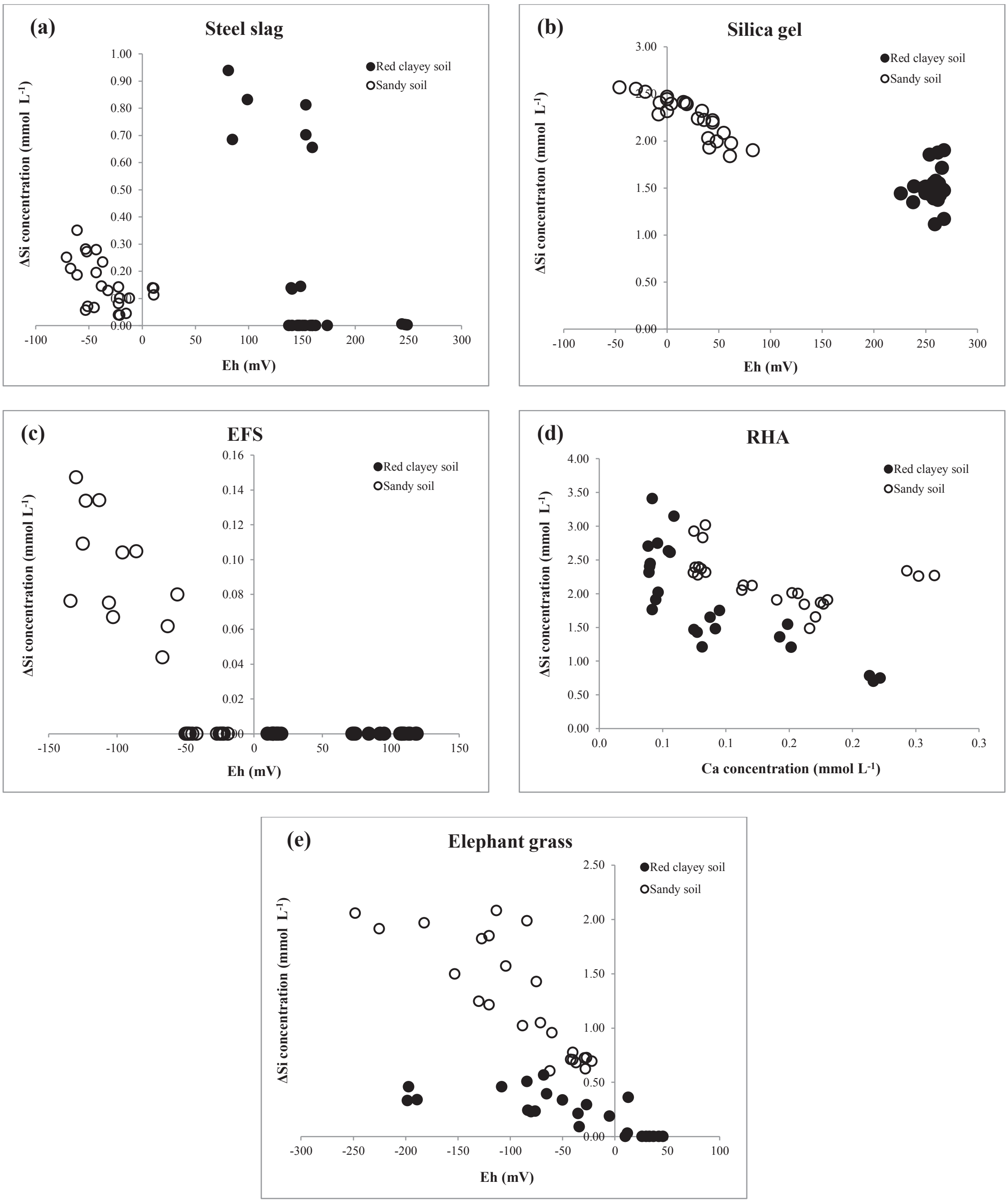


Figure 3. Correlations coefficient of Si concentration from material and other elements in soil solution

3.3.5.1. Steel Slag

Si release from steel slag in red clayey soil showed positive correlation with Fe release and negative one with Eh change in soil solution (Figure 3a). At conditions in which pH of soil solution was weak alkaline, Si was not affected by pH, but was negatively correlated with Eh. This indicated that Si release of the steel slag was basically controlled by dissolution of the slag with lowering Eh. Steel slag contains Si as calcium silicate form and the slag dissolution and Si release proceeded by following two steps, i) Ca and Mg are dissolved by ion exchange reaction with hydrogen ion in water (first step), ii) Si-O-Si and/or Al-O-Si chemical bonds are cleaved by hydrolysis (second step) (Kato & Owa, 1996). Kato and Owa (1996) also reported that lowering pH increase Si release and in contrast high Ca content in soil or soil solution decreased it. Beside, Liang et al. (2015) reported that low soil Eh at flooding condition, normally leads to an increase in available Si concentration. Lower Eh of sandy soil (Table 3) probably led to release of Si from the beginning of incubation. However, total amount of Si released from the steel slag was higher in red clayey soil, which was due to lower pH and lower exchangeable Ca content of the red clayey soil.

3.3.5.2. Silica Gel

Silica gel released highest concentration of Si among all the materials in both acid and weak alkaline conditions. We observed that Si release from silica gel in sandy soil solution condition was higher than in red clayey soil by 40% (Table 2). It seemed that high pH and low Eh (Figure 3b) in soil solution increased Si release from silica gel.

3.3.5.3. Fly Ash

Fly ash is made up of highly insoluble, glass-like particles, consisting of amorphous ferro-aluminosilicate and quartz (Haynes et al., 2013). The total amount of Si released from fly ash was higher in red clayey soil, which was due to lower pH in soil solution (Table 3).

3.3.5.4. Electric Furnace slag and Japanese Si Fertilizer

EFS consist of $CaSiO_3$/$MgSiO_2$ (Tubana & Heckman, 2015), where Si release was affected by reduction of Eh and pH in soil solution. EFS and JSF did not aparently release Si in red clayey soil solution (Table 2), which is possibly due to specific range of pH and relatively high Eh comparing with sandy soil condition. According to Meyer (1999), Si solubility is lowered at pH range of 6.5-7.5. Thus, soil pH, 7.2 and 6.9 for EFS and JSF (Table 3), respectively in red soil suppressed Si release from the materials.

3.3.5.5. Rice Straw Compost

RSC stably released Si in both soil conditions, although it was higher in sandy soil than in red clayey soil. Exchangeable Ca and Mg in red clayey soil might suppress Si release, but exchangeable Ca or Mg in sandy soil seemed not to influence the Si release. It was confirmed as an effective soil Si amendment.

3.3.5.6. Rice Husk-Biochar and Rice Husk-Ash

Silicon in rice husk was concentrated and increased in its availability by ashing (Table 1). The release of Si from RHA looked negatively affected by Ca (Figure2d). Thus, we assume Si in RHA was changed in Ca bind form and Ca in soil or material itself might suppresse Si release. While Ca did not suppresse Si release from RHB. Eh was a possible factor influencing Si release from RHB as the release of Si was higher with low Eh in sandy soil (Table 3).

3.3.5.7. Cacao SB

The results of this study revealed that there was an inverse relationship between Ca and Si concentration in red clayey soil solution. Higher pH and exchangeable Ca content in sandy soil tended to reduce Si release from cacao SB. This is more likely because Ca binds Si in cacao SB which might hardly dissolve under higher pH and Ca condition. It seems there is a higher potential to release Si in acidic and low exchangeable Ca soil condition.

3.3.5.8. Elephant Grass and Media of Mushroom

Silicon release of elephant grass (Figure 3e) and MM was negatively correlated with Eh change. Elephant grass and MM had relatively high potential to reduce soil Eh but they also enhance release of Fe and Mn especially in red clayey soil (Table 2). Eh of soil control the solubility of Fe and Mn oxides (Patra & Neue, 2010). Solubilitzation of Fe and Mn possibly influence Si release from elephant grass and MM.

3.3.6. Prospectives of Local Materials as Silicon Fertilizers

Most of the land areas in Indonesia are acidic soil, of which area is around 102,000,000 ha. The dominant acidic soil types are Ultisols and Oxisols, and some belong to Entisols, Inceptisols and Spodosols (Subagyo et al., 2000; Mulyani et al., 2009). In order to discuss the possibility to use examined materials in the present study for Si amendments in Indonesian paddy fields, we focused on the results found in red clayey soil as most of the land area in Indonesia are acidic soil. Overall Si materials, release of Si into red clayey soil solution were high for steel slag, cacao SB, RSC and also RHB as local Si materials. These can be candidates of Si amendments of paddy soil in Indonesia. The amount of Si release from EFS, elephant grass and MM were relatively low. Therefore, we assume these materials are not effective to improve paddy soil available Si in Indonesia. Although silica gel could be of course a good Si fertilizer as it was used in Japan, it is presently expensive for Indonesian local farmers.

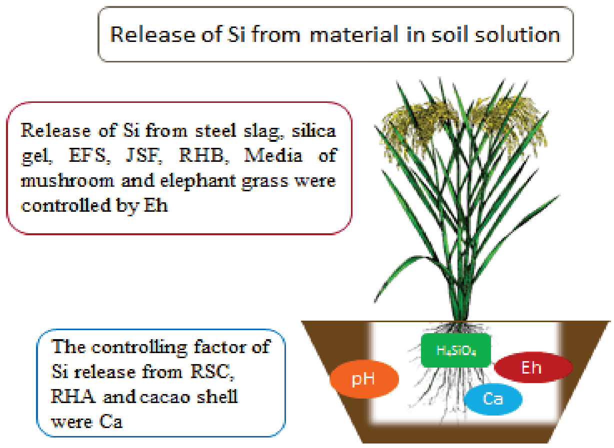
In terms of availability of these materials in Indonesia, steel slag is promising. Rice straw is the biggest waste in Indonesia with the amount of 55 million ton per year (Setiarto, 2013). So far in Indonesia, there has been no research on Si content in rice straw and straw compost. Thus we cannot give recommendation which is better between rice straw and rice straw compost. Generally, agricultural waste in Indonesia is burned to accelerate land preparation. Based on our result that rice straw compost release high Si, thus farmers can sell the rice straw compost to increase income. Furthermore we suggest to make rice straw as compost.

Rice husk is also available throughout Indonesia. For the use of rice straw and husk, it is easy to collect and use in rice producing areas as farmers' groups exist. Besides, its function as Si amendment, i.e. Si release, can be easily improved by burning in paddy fields as the present study exhibited.

Cacao production for some regions in Indonesia such as Sumatera, Java and Sulawesi were 0.36; 0.40 and 0.46 ton ha^{-1} on 2013 (Tree crop estate statistics of Indonesia, 2014). Cacao shell waste has not been optimally used in Indonesia (Murni et al., 2012), thus its agricutural use is recommendable.

3.4. Conclusions

EFS, Fly ash and organic materials under submerged condition in paddy fields, improved Si availability. Besides, the addition of local materials such as steel slag reduces the soil Eh. Local materials such as steel slag, rice straw and husk, and cacao shell could be used as Si amendments in paddy fields in Indonesia. Additionally, other materials with relatively low Si release (i.e. elephant grass and MM) could be used to improve the availability Si in soil.



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CHAPTER 4

Effect of Calcium and Magnesium on Solubility of Silicon in Soil Solution

4.1. Introduction

Silicon (Si) is a tetravalent mettaloid and an ubiquitous element in soil (Liang et al., 2015). According to Haynes (2014), concentration of Si in soil solution (the intensity) is one of the important key parameters in relation to the plant-availability of Si. Silicate can be adsorbed to the surfaces of variable charged soil colloids such Fe and Al hydrous oxides. The amount of Si adsorbed onto the slightly soluble phosphates of Ca, Mg, Fe, Al and dissolved Si in the soil solution increased with Si fertilization (Tubana & Heckman, 2015). Silicon in soil solution in the form of H_4SiO_4, is present at concentrations normally ranging from 0.1 to 0.6 mM (Epstein, 1999). Monosilicic acid is absorbed by plant roots along with other elements occurring in soil solution (Kamenik et al., 2013).

The soil pH regulates the solubility and mobility of Si (Tubana & Heckman, 2015). Increasing pH and Ca concentration in the solution reduces the dissolution of Si from slag silicate fertilizer (Kato & Owa, 1996). According to Roy (1969), additions of $CaCO_3$ to soils reduced silica concentration in soil solutions.

Monosilicic acid can interact with Fe and Mn to form slightly soluble silicates (Snyder et al., 2006). Fertilization with silica gel is an option to improve Si for growing of rice plants on soils with low levels of plant-available Si (Marxen et al., 2016). The release of Si from silica gel into soil solution must vary in different soil type. Factors controlling dissolution of Si include iron (Fe), calcium (Ca), manganese (Mn), pH, and particle size of the materials and presence of organic matter (Makabe et al., 2013; Kendrick, 2006). In the present study, we examined the interaction between Si and Ca, Mg in terms of Si solubility and investigate behavior of Si in soil solution in relation with Fe, Mn, Eh, and pH.

4.2. Materials and Method

Japanese silica gel (JSG) and red clayey soil were collected from Japan. Silica gel was ground into fine powder in agate grinding jars, using a mixer mill (MM 200, Retsch GmbH, Haan, Germany). The soil sample was air dried and passed through a 2 mm sieve. Exchangeable Ca, K, Mg and Na (Ex. Ca, K, Mg, Na) were extracted with 1 M ammonium acetate pH 7.0 and measured by Inductively Coupled Plasma Spectroscopy (ICPE-9000 Shimadzu, Kyoto Japan). The contents of available Fe and Mn were obtained by extraction with 0.1 N HCl and quantified using the ICP. Available Si was extracted by acetate buffer (pH 4.0), soil water ratio of 1:10, with intermittent shaking for 5 h at 40^{o}C, determined using the silicate molybdenum blue method (Imaizumi and Yoshida, 1958). Soil pH (H_2O) was determined on 1:2.5 (w/v) soil: water suspensions with pH meter (D-51, Horiba).

Incubation experiment

Under submerged condition, the soil was incubated with JSG, Ca and Mg as treatment (Fig. 1). The experiment was replicated three times. The soil sample was air dried and passed through a 2 mm sieve. 10 g of air dried soil was added with 0.39 g of JSG was placed in a 50 mL centrifuge plastic tube. 40 ml Ca or Mg (0, 5, 10, and 15 mg L^{-1}) solution was added into the tube and mixed thoroughly (Table 1).

Table 1. Treatments

Treatments	
T0	Soil + DW
T1	Soil + Silica gel + DW
T2	Soil + Silica gel + 5 mg Ca L^{-1}
T3	Soil + Silica gel + 10 mg Ca L^{-1}
T4	Soil + Silica gel + 15 mg Ca L^{-1}
T5	Soil + Silica gel + 5 mg Mg L^{-1}
T6	Soil + Silica gel + 10 mg Mg L^{-1}
T7	Soil + Silica gel + 15 mg Mg L^{-1}

Note. DW: distilled water

The tube was covered with plastic Para film, incubated at 30^{o}C for 29 days. After incubation, the redox potential (Eh) and pH of soil solution were measured with Eh meter and pH meter (TOA HM-14P and D-51 Horiba, respectively) without disturbing the soil. The supernatant was obtained after filtration (paper filter Advantec No. 6). Silica, Ca, Mg, Fe, and Mn concentrations in supernatant were measured using ICPE-9000 Shimadzu. To resume the incubation, residue on the filter paper was washed back into tube with distilled water and distilled water was added up to a total volume of 40 mL base on the weight (Makabe et al., 2013). The soil solution was replaced with distilled water at day (d) 8, 15, and 29 assuming field water replacement by drainage / leaching and irrigation in the field.

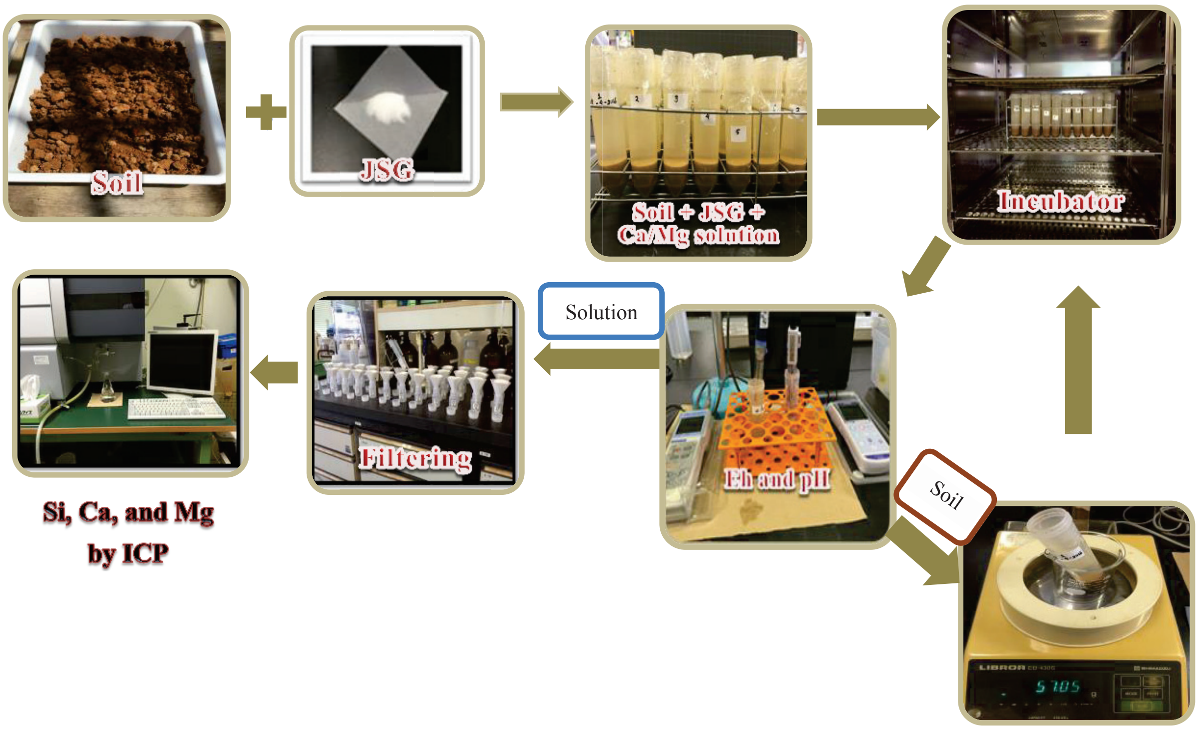

Figure 1. Flow chart of incubation experiment

4.3. Results and Discussion

4.3.1. Properties of soils

The soil is slightly acidic (pH 5.7) and relatively rich in available Fe and Mn (72.5 and 52.2 mg kg^{-1}). Exchangeable Ca, Mg, K, and Na were 4.3, 2.4, 0.7, and 0.3 $cmol_c kg^{-1}$, respectively. The extractable Si concentration was 267.1 mg SiO_2 kg^{-1}. According to Sumida (1992), it was classified to be below critical level of available Si for rice (300 mg SiO_2 kg^{-1}), but above deficiency criteria (<86 mg SiO_2 kg^{-1}) by Doberman and Fairhurst (2000).

4.3.2. Solubility of Si, Ca, Mg, Fe and Mn in soil solution

Regardless of silica gel, Ca, and Mg application, there was different on Si, Ca, Mg, Fe and Mn concentration in soil solution (Fig 2 and 3). On the first 8 days of incubation, Si release into soil solution (Fig 2b and 3b) was higher for T1 (1.336 mmol L^{-1}) compared to other treatments. This is possible because Ca and Mg decreased Si release into soil solution for T2 – T4 (1.163 – 1.335 mmol L^{-1}) and T5 – T7 (1.255 – 1.276 mmol L^{-1}), respectively.

As could be expected, soil solution was higher in Ca and Mg concentration for T4> T3> T2 > T1> T0 and T7> T6> T5> T1> T0 (Fig 2a and 3a), respectively. It seems that Ca and Mg affected solubility of Si into soil solution with binding of Si as $CaSiO_3$ or $MgSiO_3$ in soil/solid phase. While, part of excess Ca release in soil solution due to high doses of Ca. In submerged condition and by the time of incubation, it is possible silica will be released into soil solution through the following reaction mechanism (Flint & Wells, 1934):

$$\text{Soil} + \text{water} \leftrightarrow \text{soil solution}$$

$$MgSiO_{3(s)} + 3\,H_2O \leftrightarrow Mg_2{}^{+}{}_{(aq)} + H_4SiO_{4(aq)} + 2OH^{-}{}_{(aq)}$$
$$\textit{or}\ MgOH^{+}{}_{(aq)} + H_4SiO_{4(aq)} + OH^{-}{}_{(aq)}$$

In this research, most of Fe concentrations in soil solution were lower on day 8 compared to other days, specifically Fe was lower for T2 to T4 (Fig 2c) and T5 to T7 (Fig 3c) compared to T0 and T1. This might be explained that Ca and Mg reduced Fe concentration in soil solution. In contrast, Mn concentration was higher for treatment with Ca and Mg application (Fig 2d and 3d, respectively).

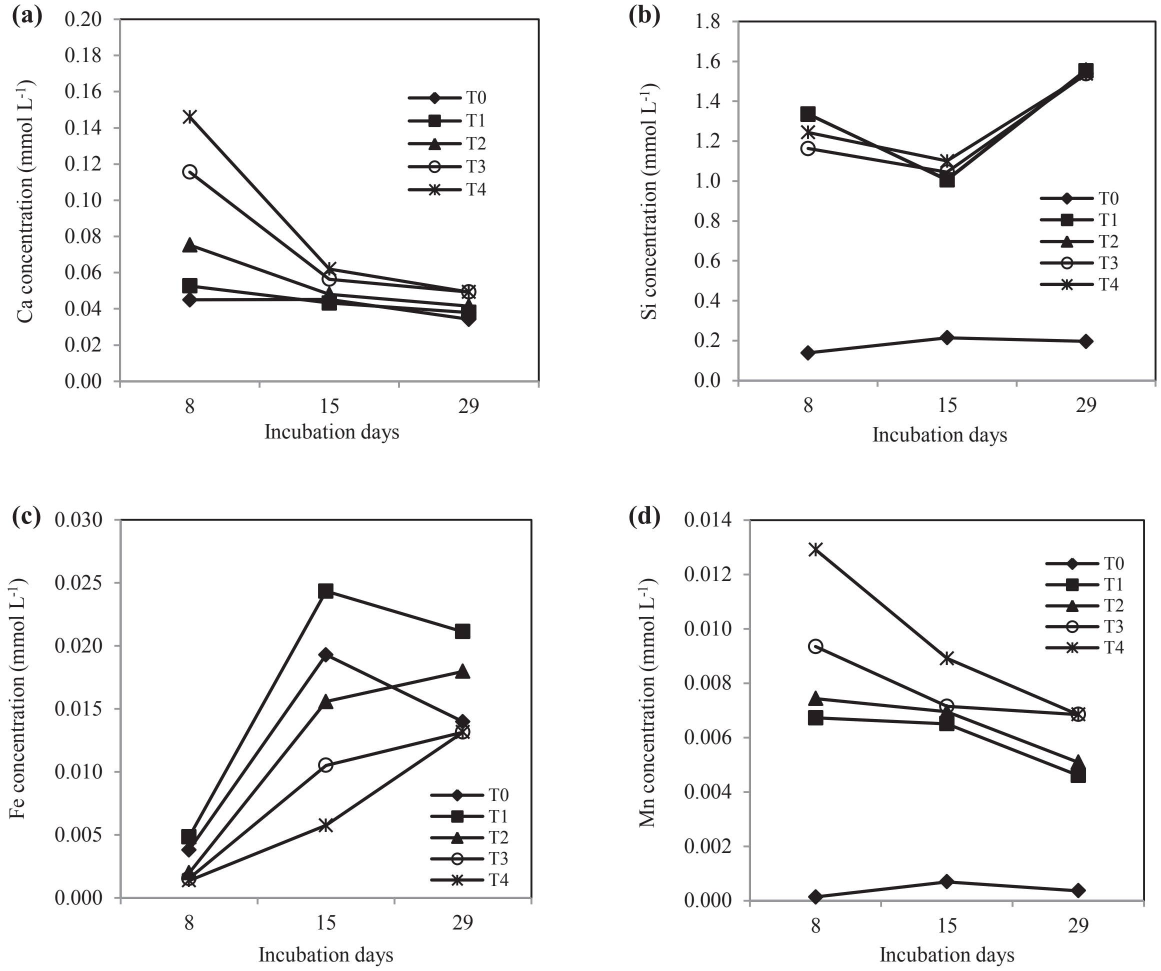

Figure 2. Release pattern of calcium (a), silicon (b), iron (c), and manganese (d) during 29 days of experimental time

Silicon concentration decreased from day 8 to day 15 for T1 to T7 and then increased on day 29, except T0. Low Si concentration on day 15 was probably due to replacement of soil solution with distilled water and was not strong enough to release Si that is adsorbed by soil into soil solution, although the Si existed in easily releasable form (Makabe et al., 2013). Concentration of Si increased again on day 29, it might be due to the soil Si and Si from silica gel that adsorbed by the soil could enter the soil solution when concentration of Si in soil solution decreases (Kato and Owa, 1997). According to Ponnamperuma (1972), the Si concentration in the solutions of submerged soils increases slightly after flooding. The release of Si after flooding may be due to reduction of hydrous oxides of Fe (III) sorbing Si and action of CO_2 on aluminosilicates (Briker & Godfrey, 1967).

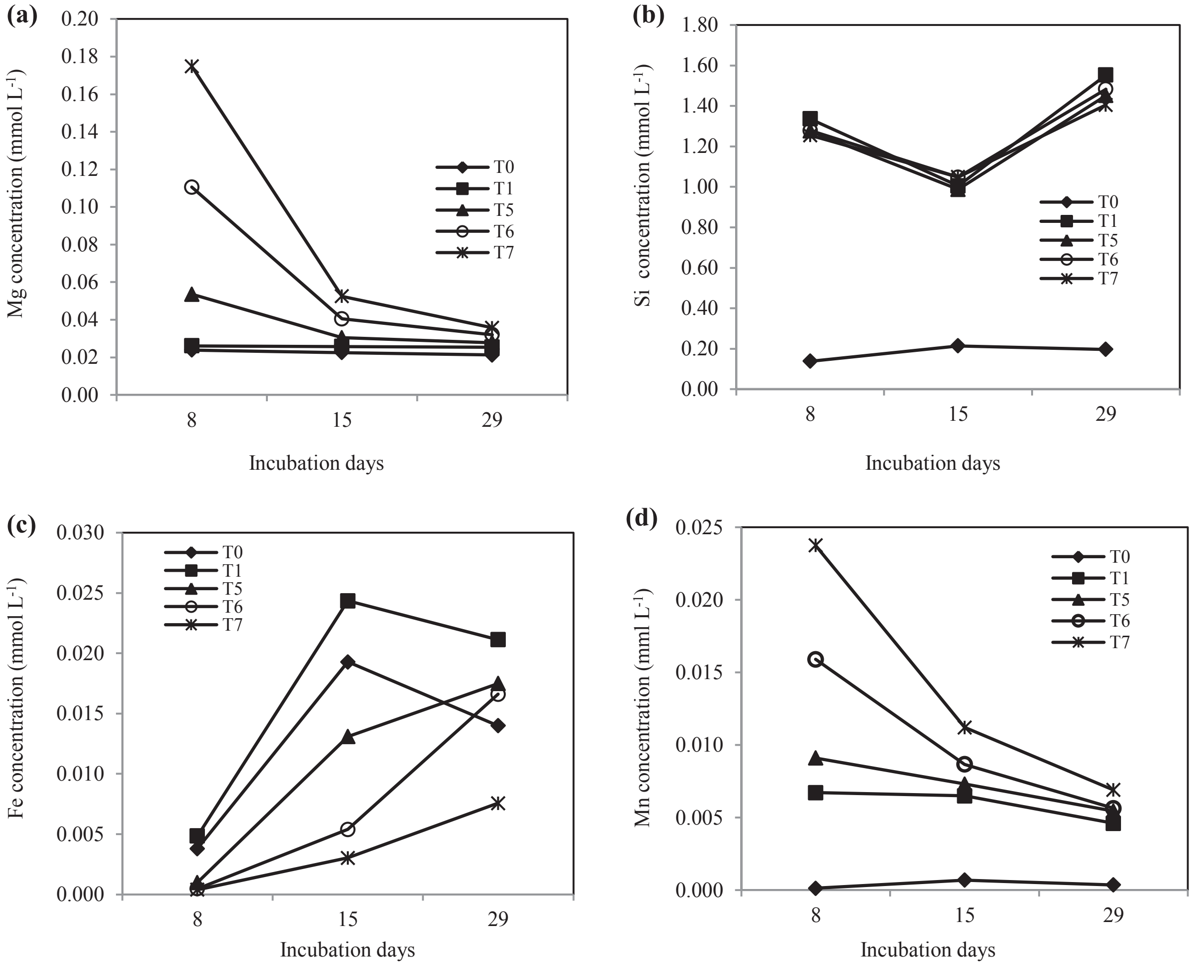

Figure 3. Release pattern of magnesium (a), silicon (b), iron (c), and manganese (d) during 29 days of experimental time

Furthermore, the release pattern of Ca and Mg were higher on the first 8 days and sharply decreased, thus slightly decreased on day 29. We assume that the soil solution replacement with distilled water thus reduced Ca and Mg concentration. However, the Ca and Mg concentration in soil solution was higher for T2 - T4 and T5 - T7, respectively compared to other treatments.

Iron concentration increased during incubation day (Fig 2c and 3c), except T0 and T1 in which Fe was higher on day 15 and then decreased. The release pattern of Mn was similar for T1 to T4, in which concentration of Mn tend to decreased during incubation days. In addition, Ca and Mg application decreased Fe concentration for T2 to T7.

Meanwhile, silica gel, Ca and Mg application increased Mn concentration for T1 to T7. This result related to pH of soil solution which was lower compared to control (T0). It was probably due to silica gel application and submerged condition. As similar with the result in chapter 3, which silica gel decreased soil solution pH. From the viewpoint of this result, it is important to note that Mn increased due to mean pH of soil solution was lower for T1 to T7 (Table 3). Husson (2013) reported that solubilization of Mn^{2+} ions is a function of both pH and Eh. In this experiment, pH was the dominant factor for dissolution of Mn. According to Schwab and Lindsay (1982), higher Mn bioavailability corresponds to a decrease in Eh.

4.3.4. The Amounts of Si, Ca, Mg, Fe, Mn concentration, mean pH and Eh during incubation

The amounts of Si concentration in supernatant (Table 2) for treatment with Ca application (T3 and T4) was lower than soil solution with T1 and T2.

Table 2. Cumulative concentration of Si and other elements in supernatant during 29 days.

Treatments	Si	Ca	Mg	Fe	Mn
		------------ mmol L^{-1} -----------			
T0	0.550	0.125	0.068	0.037	0.001
T1	3.893	0.134	0.077	0.050	0.018
T2	3.900	0.165	-	0.036	0.019
T3	3.745	0.221	-	0.025	0.023
T4	3.881	0.257	-	0.020	0.029
T5	3.715	-	0.112	0.032	0.022
T6	3.810	-	0.183	0.022	0.030
T7	3.708	-	0.263	0.011	0.042

Note. -: not determined

Meanwhile, Si concentration of the control (T1) without Mg application was higher than with Mg application (T5 – T7), indicating that these systems were affected by Mg. Solubility of Si (3.708 mmol L^{-1}) was lowest by high application of Mg (T7). The amount of Ca and Mg concentration in supernatant was higher for T4 and T7 (0.257 and 0.263 mmol L^{-1}, respectively).

The finding that Fe concentrations in soil solution were similar to Si concentration, which the lower Fe T7 (0.011 mml L^{-1}) and the highest was T1 (0.050 mmol L^{-1}). Meanwhile for Ca application, Fe and Si concentration was lower for T4 and T3 (0.020 and 3.745 mmol L^{-1}, respectively). An explanation for this finding might be that Eh was higher in soil solution with Ca and Mg application compared to control (T0 and T1) (Table 3).

The mean of pH in soil solution was lower for T2 to T7 than T1 or T0. It was similar with Si concentration. The explanation for these results might be that as alkali is consumed, the pH decreases, the concentration of Ca^{2+} increases, and then the concentration of Si in solution decreases. While, if alkali concentrations remain high, Ca concentrations are very low, and the loosened Si structure imbibes more liquid and hydroxyl ion that continue the process of dissolution of the Si (Helmuth et al., 1993).

Table 3. Mean pH and Eh values of soil solution during 29 days

Treatments	T0	T1	T2	T3	T4	T5	T6	T7
pH	5.1	4.8	4.7	4.7	4.6	4.6	4.6	4.6
Eh (mV)	254	281	297	301	310	309	313	317

It clearly shows that Ca and Mg increased Eh in soil solution. For this reason, Fe and Si solubility was low in soil solution under less reduction condition. Ponnamperuma (1972) proposed reduction of Fe has important chemical consequences such as Fe and Si concentration increase. Snyder et al. (2006) reported that Si release such as monosilicic acid and polysilicic acid that have high chemical activity can react with Fe in the formation of slightly soluble silicate.

$$2Fe_2SiO_4 + 4H^+ = 2Fe_2^+ + 2H_4SiO_4$$

4.3.5. Relationship between solubility of Si with Ca, Fe, Mn, pH and Eh

The results indicated that Si concentration was significantly and positively correlated with Fe (r = 0.99) and Mn concentration (r = 0.81) in solution for soil without silica gel and Ca application (T0). The higher correlation coefficient of Si with Fe compared to Mn might be due to its greater concentration in soil compared with Mn, suggesting that Fe is the dominant absorbent. Furthermore, Si concentration in soil solution of T0 was significantly and negatively correlated with Eh (r = 98) and pH (r = 71). Those results indicate that Fe, Mn, Eh, and pH are the limiting factor of Si release in soil solution for soil without Si and Ca application (control).

Silicon in soil solution was not significantly correlated with Fe, Mn, Ca, Mg, pH or Eh in soil solution for treatment T1, T3, T5, and T7. On the other hand, soil solution with T2 showed significantly negative correlation between Si and pH (r = 0.76). These data suggest that pH affected dissolution of Si when silica gel and 5 mg Ca L^{-1} was applied in soil. We found that by applying silica gel and 15 mg Ca L^{-1} (T4) or 10 mg Mg L^{-1}(T6), release of Si in soil solution was controlled by Fe (r = 0.74 and 0.68, respectively).

So far we found no relationship between Si and Ca or Mg concentration in soil solution. However, Ca and Mg application reduced Si concentration in soil solution. Makabe et al. (2013) reported that Si and Ca were significantly and negatively correlated in soil solution during incubation.

4.4. Conclusions

Results showed that Ca and Mg in the Si materials and soils could inhibit Si release in soil solution. Solubility of Si was negatively and positively correlated with pH and Fe concentration in the soil solution, respectively, which indicated these were also the controlling factors of the Si release.

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CHAPTER 5

Relationships between Soil Properties and Rice Growth with Steel Slag Application in Indonesia

5.1. Introduction

Rice is the major staple food in Indonesia and the third in the world in regards to total rice production. The production of lowland rice is highly concentrated in Java, followed by Sumatera and Sulawesi. The average yield of rice grain is higher in Java (5 ton ha^{-1}) than in other regions (4 ton ha^{-1}). The share of harvested area and production of rice in Java from 1998 to 2002 has been nearly constant at around 51 percent. However, presently, Indonesia became the world's 7^{th} largest rice importer over the past 5 years; on average requiring over 1.1 million tons of imports per year as a result of increasing population. Of the top ten global rice producing nations, only the Philippines and Indonesia also rank in the top ten of all rice importers (FAS-USDA, 2012; FAO, 2005).

Rice is cultivated more than 2 seasons per year in Indonesia. This intensive rice cultivation may degrade soil fertility and decline the yield. There have been several works on nutrient-balance studies majorly focusing on macronutrients such as nitrogen (N), phosphorus (P) and potassium (K). Arafah & Sirappa (2003) working on Inceptisol in South Sulawesi with low N, available P and exchangeable K content, found that N fertilizer was needed for increasing the growth and yield of rice. Nitrogen and K significantly influenced rice yields and biomass production in Jakenan-Central Java (Boling et al., 2004). According to Abdulrachman et al. (2006) from 21 cropping seasons (or 10.5 years of intensive cropping), they indicated that with balanced fertilization of N, P, and K grain yield averaged 5.5 ton ha^{-1} in the dry season and 6.5 ton ha^{-1} in the wet season. They also found that in West Java, farmers believed that the natural supply of K in the soil is sufficient for high rice yields and have never applied fertilizer K to their rice fields, but fertilizer K application increased the yield by 10 ton ha^{-1} across the 21 seasons. Sofyan et al. (2004) made a map of the nutrient status of N, P, K, Ca and Mg in rice field in Java and other islands for better fertilizer management in Indonesia. However, rice growth also depends on the other nutrients such as micronutrients and silica (Si). Repeated cropping and the constant application of chemical fertilizers have probably depleted micronutrients.

Silica is present in plants in amounts equivalent to those of such macronutrient element as calcium (Ca), magnesium (Mg) and P (Epstein, 1999). Rice plant obviously required Si to maintain healthy growth and high productivity. Although Si is recognized as the non-essential element for rice plant, rice plant uptakes Si ranging from 230 to 470 kg Si ha^{-1}, two times higher than N uptake (Savant et al., 1997). Silica increases rice resistance to leaf and neck blast, sheath blight, brown spot, leaf scald and stem rot (Datnoff & Rodrigues, 2005) and decreases the incidence of powdery mildew in several crops (Fauteux et al., 2005). Silica also alleviates many abiotic stresses including chemical stress (high salt, metal toxicity, nutrient imbalance) and lodging, drought, radiation, high temperature and freezing. An awareness of Si deficiency in soil is now recognized as being a limiting factor for crop production (Ma & Yamaji, 2006). Silica indirectly improves the P utilization efficiency of plant (Ma & Takahashi 1990). The effect of silica on the growth of rice plant is most remarkable at the reproductive stage (Ma et al., 1989).

Available Si in rice fields in the whole of Java in Indonesian decreased by approximately 17-22 % during the period 1970-2003 (Darmawan et al., 2006). With regard to mineral composition, many Indonesian soils contain low Si and high iron, aluminum and manganese (De Datta, 1981). The lower soil Si content was found to be severe in intensive rice field where enormous Si uptake is not followed by sufficient Si replenishment (Husnain et al., 2008). Soil is always at risk of Si depletion due to the large amounts of Si removal by plants. Husnain et al. (2009) found that dissolved silica in irrigation water, which is a main Si source to rice field, decreased through Si trap by diatoms in dams in the Citarum watershed. This phenomenon could be accelerated by N and P enrichment caused by chemical fertilizer usage in uplands and fish culture in the dams. This Si depletion in rice fields might be a reason for the recent fluctuation and stagnancy in rice productivity in Indonesia. Hence, there is need to study the actual effect of available Si in relation to this fluctuation in rice yield.

In the presence study, we selected representative rice producing sites in Lampung, Central and West Java Province and examined the relationships between soil properties, rice growth and yield, and further evaluated the effect of Si application on rice growth and yield in different soil types. We used local steel slag, which is the most common material as the Si amendment.

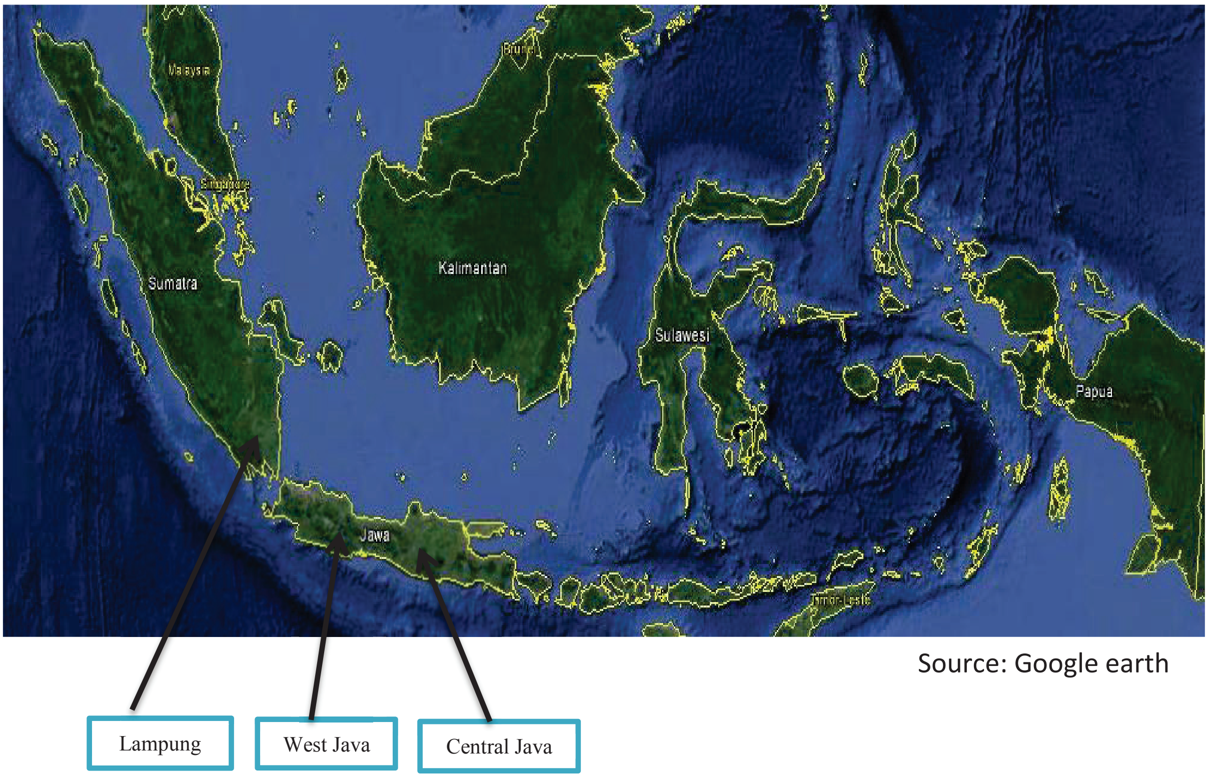
5.2. Materials and methods

5.2.1. Site selection for soil sampling

Ten sites were selected to collect representative soil samples from main rice production areas as show in table 1.

Table 1. Location and fertilizer doses of study sites

Site No	Village	Regency	Province	Coordinates		SP-36	KCl	Urea	
								Basal	Top dressing
						----------- kg/ha ------------			
Site 1	Bolo Agung	Pati	Central Java	06°51'34.0" S	111°01'26.0" E	75	50	150	150
Site 2	Dari	Sragen	Central Java	07°43'81.8" S	110°89'98.1" E	50	100	150	150
Site 3	Rancaekek	Bandung	West Java	06°54′53.08″S	107°36′35.32″E	50	50	150	150
Site 4	Bojong Kulon	Cirebon	West Java	06°37'46.2"S	108°22'05.2"E	50	50	150	150
Site 5	Hegarmanah	Cianjur	West Java	06°48'24.9"S	107°11'09.6"E	50	50	150	150
Site 6	Batukarut	Bandung	West Java	07°02'54.3"S	107°36'09.8"E	50	100	150	150
Site 7	Majangsari	Garut	West Java	07°03'14.3" S	107°56'03"E	100	50	150	150
Site 8	Sinar Galih	Garut	West Java	07°15'8.1"S	107°52' 21.4" E	50	50	150	150
Site 9	Samarang	Garut	West Java	07°12'50.4"S	107°50'04"E	75	250	150	150
Site 10	Taman Bogo	Taman Bogo	Lampung	05°00'20.7"S	105°29'27.5"E	50	100	125	125



Source: Google earth

Figure 1. Location of study sites

Phosphorus and K fertilizer was applied regarding to extraction 2 g soil with 2 ml of P and K solution (concentrations of 0, 20, 40, 80 and 160 mg P_2O_5 kg^{-1} and 0, 20, 40, 80 and 160 mg

K_2O kg^{-1}). Thereafter incubated for several days until dry, 10 ml of 25% HCl was added to the soil, shaken for 5 hours and filtered. The P and K in supernatant were measured by using spectrophotometer UV-Vis (Hitachi U-2010) and atomic absorption spectrophometer (AAS Varian AA 55, Australia). Based on the result, we calculated the amount of SP 36 and KCl. Urea was applied based on recommendation from ISRI (Indonesian Soil Research Institute), where Lampung was lower of urea application than other location due to the production in that area was 5-6 ton ha^{-1}. While in Java Island, the production is > 6 ton ha^{-1}.

The rice production in Kayen (site 1) and Plupuh (site 2) in Central Java are 5.6 and 6.0 ton/ha, respectively (CBS Central Java, 2013). West Java is one of the central rice productions with a contribution of 17.6% to the national rice production (Iskandar, 2011). The rice production in Karang Tengah, Banjaran, Rancaekek, Susukan, Blubur Limbangan, Bayongbong and Samarang in 2013 ranged from 5.8 to 7.0 ton ha^{-1} (CBS West Java, 2009-2013). Rice productivity in Cianjur tended to fall from 5.43 ton ha^{-1} in 2003 to 5.25 ton ha^{-1} in 2007 (Ruli et al., 2010). Taman Bogo in Lampung is the site that has been degraded in soil quality which is characterized by relatively acidic soil (pH 4.17).

5.2.2. Soil and Si fertilizer (steel slag) analyses

Soil samples were analyzed by standard methods (Indonesian Soil Research Institute, 2009). The soil samples were air-dried and crushed to pass through 2 mm sieve. The pipet method was used to evaluate the textural class of the soil (ISRI, 2009; Chintala et al., 2010). Total carbon (TC) content was assessed using Walkley-Black method (Black, 1965). Exchangeable Ca, Mg, K and Na were measured using 1 M NH_4 acetate at pH 7.0 and Ca, Mg, K, and Na in the extracts were analyzed by flame AAS (ISRI, 2009). The pH was measured in 1: 5 soil : water ratio. Available P was measured using Bray 1 method. Total nitrogen (TN) content was obtained by Kjedahl method. The available Si in soils was determined using the acetate buffer method. Soil samples were extracted in 1 mol L^{-1} acetate buffer (pH 4.0) at ratio 1:10 incubated for 5 h at 40^{o}C with occasional shaking (Imaizumi & Yoshida, 1958). The concentration of Si in supernatant was determined by colorimetric analysis with Spectrophotometer UV-Vis.

As Si fertilizer, we used steel slag that was collected from Krakatau steel company in Banten Province, Indonesia. The material was analyzed by the same method with soil analysis for available Si (Imaizumi & Yoshida, 1958) and by HNO_3 digestion method with the determination by Inductive Coupled Plasma Spectroscopy (Shimadzu ICPE 9000, Kyoto Japan) for the other elements (Koyama & Sutoh, 1987). The chemical composition of steel slag was 1541 mg SiO_2 kg^{-1} of avail. Si, 19.8 % Ca, 0.04 % K, 3.48 % Mg, 0.11% Na, 28.16 % Fe and 0.96 % Mn.

Figure 2. Steel slag

5.2.3. Experimental Design

A pot experiment was carried out under greenhouse conditions at the Indonesian Soil Research Institute. The experiment was set up in completely randomized design with three replicates. The soils used for experiment were collected from farmer's fields. They were collected from several points in the field using hoe at the depth of 0 – 15 cm (top soil). The soil was air dried and crushed with 2 mm sieve. Five kilogram of soils was weighed into each pot. The Puddling of soils was performed by saturating with water and stirred by hand to form slurry.

Husnain (2013) reported that applying 160 – 200 kg ha^{-1} silica fertilizer produced higher yield in three sites farmer fields (Lampung, South Sulawesi and West Sumatera), with Si fertilizer application done at the rate of: 0, 20, 50, 100, 200 and 300 kg Si ha^{-1}. Steel slag, single fertilizer SP 36 and KCl were applied one day before transplanting. Urea was applied twice; 50% at 6 DAT (day after transplanting) and 50% at 35 DAT. Conventional continuous flooding system was used in this experiment. From transplanting up to 7 days after transplanting (DAT) water was added until 2 cm from soil surface. From 7 DAT to 15 days before harvest, the pot would be drain until harvest. Seeds of INPARI -15 varieties were soaked in water for 24 hours before transferring into seedling pot filled with 3 kg soil as seedling growing media in the nursery.

Figure 3. Rice transplanting

5.2.4. Plant growth observation and sampling

After transplanting, the tiller number and plant height were recorded at 70 day after transplanting (DAT). Plant height was measured from ground level to the tip of the top most of the leaf. The tiller numbers were obtained by counting the number of tillers that grow from the main stem of rice plants. Rice plants were harvested at maturity, separated into straw and grain. Then washed thoroughly with distilled water. The dry weight of these tissues recorded after being oven-dried at 60 - 70°C for 2 days.

Figure 4. Plant growth observation

5.2.5. Statistical analysis

The effects of the treatment, soil and the treatment-soil interaction on plant height, tiller number, grain and straw were analyzed using a two-way analysis of variance (ANOVA) at $p < 0.05$. One-way ANOVA was carried out to analyze the effects of the treatment and soil on straw and grain yield. Correlation analyses were conducted to identify significant relationships between the soil properties with tiller number, plant height, straw and grain yield. Effect of soil properties on the yield was analyzed by principle component analysis (PCA) and multiple regression analysis. All statistical analyses were done using the statistical package SPSS 22.

5.3. Results and Discussion

5.3.1. General soils properties

Table 2 shows the soil properties, reference values of tropical Asia paddy fields (Kyuma, 2004) and deficiency criteria by International Rice Research Institute (Doberman & Fairhurst, 2000) of selected parameters.

Table 2. Selected properties of the soil

Site No	Sand	Silt	Clay	pH (1 : 5) H$_2$O	pH (1 : 5) KCl	TC	TN	C/N	Available P	Exchangeable K	Exchangeable Ca	Exchangeable Mg	Exchangeable Na	CEC	BS	Available Si
	-------------%------------					---g kg^{-1}---			mg P_2O_5 kg^{-1}	--------------------cmol$_c$kg^{-1}-------------------					%	mg SiO_2 kg^{-1}
Site 1	39.9	37.1	23.0	5.2	4.6	13.2	0.7	17.6	20.5	0.28	7.00	1.18	0.15	17.74	48.52	65
Site 2	8.3	27.7	63.9	6.0	5.1	9.8	0.7	14.8	12.8	0.14	22.85	10.62	0.29	34.12	99.38	838
Site 3	4.7	28.0	66.8	5.7	5.2	33.7	2.4	14.2	41.5	0.52	16.42	6.04	0.43	33.43	70.04	761
Site 4	8.8	31.4	59.8	6.7	6.0	17.2	1.1	15.5	18.5	0.39	17.32	9.66	0.27	41.72	66.26	852
Site 5	6.2	36.3	57.6	6.0	5.1	21.0	1.4	15.1	8.9	0.36	11.92	7.22	0.36	27.28	72.79	940
Site 6	22.0	13.6	63.8	5.3	4.6	28.9	2.1	14.0	11.7	0.04	6.65	2.91	0.20	23.29	42.07	494
Site 7	10.0	19.7	70.3	5.5	4.5	11.5	0.8	14.3	3.7	0.76	8.65	6.57	0.09	27.78	57.86	836
Site 8	29.6	22.3	48.0	5.7	4.8	16.0	0.8	19.2	60.3	0.56	8.97	5.32	0.44	33.56	45.55	966
Site 9	49.1	15.9	35.0	5.6	4.9	21.8	1.5	14.2	3.8	0.29	6.80	7.48	0.35	25.60	58.33	749
Site 10	55.3	21.0	23.7	4.5	4.0	9.3	0.6	16.3	15.1	0.05	0.91	0.19	0.23	6.12	22.64	414
Mean	23.4	25.3	51.2	5.6	4.9	18.3	1.2	15.5	19.7	0.34	10.75	5.72	0.28	27.06	58.34	691
CV	81.3	32.1	34.9	10.3	10.9	44.8	52.0	11.0	91.0	68.1	60.0	59.7	41.3	36.7	35.6	41.0
Tropical asia (n=529)[a]	23.3	30.5	41.2	5.6			1.7	11.5	30	0.4	9.3	5.6	1.5			237
Deficiency criteria[b]										< 0.2	< 1	< 1				< 86

Note. a: Kuyuma (2004) ; b: Doberman & Fairhurst (2000)

The soil textural classes were clayey, except for site 1 classified as loam and sites 9 and 10 classified as sandy clay loam. Soil samples were acidic to neutral (pH 4.5 - 6.7). Mean TC content was comparable with that in tropical Asia (20.7 g kg^{-1}). However, it showed high variation ranging from 9.3 to 33.7. According to Sofyan et al. (2004) most of rice soils in Indonesia have organic C less than 20 g kg^{-1}. Nitrogen content was also low compared with the average in tropical Asia. The average C/N ratio was 15.5, exceeded the mean value in tropical Asia. The exchangeable Ca was the dominant cation and exchangeable K exceeded the deficiency criteria of 0.2 cmol$_c$kg^{-1} in most sites, except sites 2, 6 and 10. The exchangeable Mg exceeded the deficiency criteria of 1 cmol$_c$ kg^{-1}, except site 10 was lower than 1 cmol$_c$ kg^{-1}. The averages were higher than those in tropical Asia at 5.6 cmol$_c$ kg^{-1}.

The soil pH was 5.6 on average and ranged from 4.5 to 6.7. This acidic soil condition was due to high rainfall in most parts of Indonesia, which led to particularly high level of leaching of basic cation and form acidic complexes through the adsorption of clay and humus on the form H^+ and Al^{3+}, they making the soil acidic (Subagyo et al., 2000; Chintala et al.,2010; Chintala et al., 2012). The available P content ranged from 3.7 to 60.3 mg P_2O_5 kg^{-1}, with site differences possibly reflecting differences in the cumulative amount of phosphorus fertilizers applied in the paddy fields. Available Si ranged from 65 to 940 mg SiO_2 kg^{-1} and exceeded the deficiency criterion of 86 mg SiO_2 kg^{-1}, except site 10 (65 mg SiO_2 kg^{-1}). The correlation analysis of 10 sites attribute, which represent soil properties is shown in table 3.

Table 3. Correlations coefficient of among soil properties

	pH-H_2O	pH-KCl	Sand	Silt	Clay	C	N	Available	Exchangeable				CEC	BS
								P	K	Ca	Mg	Na		
pH-KCl	0.95***													
Sand	-0.73**	-0.63**												
Silt	0.36	0.43	-0.39											
Clay	0.61*	0.47	-0.91***	-0.08										
C	0.19	0.29	-0.29	-0.15	0.37									
N	0.17	0.26	-0.32	-0.21	0.43	0.98***								
Available P	0.06	0.14	-0.04	0.11	0.00	0.21	0.08							
Exchangeable :														
K	0.36	0.26	-0.42	0.11	0.39	0.04	-0.02	0.31						
Ca	0.80***	0.77***	-0.78***	0.43	0.64**	0.10	0.13	0.12	0.16					
Mg	0.89***	0.77***	-0.65**	0.14	0.63**	0.03	0.06	-0.11	0.31	0.83***				
Na	0.35	0.40	-0.12	0.08	0.09	0.45	0.38	0.62*	0.10	0.32	0.33			
CEC	0.93***	0.87***	-0.74**	0.19	0.70**	0.26	0.23	0.29	0.49	0.81***	0.85***	0.41		
BS	0.75***	0.65**	-0.72**	0.41	0.58*	0.06	0.11	-0.12	0.17	0.91***	0.86***	0.26	0.70**	
Available Si	0.69**	0.53*	-0.57*	-0.10	0.65**	0.12	0.12	0.17	0.50	0.51	0.78***	0.55*	0.71**	0.52

Note. *, **,***: Correlation is significant at the 5, 1 or 0.1 % level, respectively.

The pH-H_2O was positively correlated with clay, exchangeable Ca, exchangeable Mg, CEC, base saturation (BS) and available Si. The pH-KCl showed positive correlation with exchangeable Ca, exchangeable Mg, CEC, BS and available Si. Sand was negatively correlated with clay, exchangeable Ca, exchangeable Mg, CEC, BS and available Si. There was positive correlation of clay with exchangeable Ca, exchangeable Mg, CEC, BS and available Si. The available P was positive correlation with exchangeable Na. High positively correlated of exchangeable Ca with exchangeable Mg, CEC and BS. The exchangeable Mg was positively correlated with CEC, BS and available Si. CEC showed positive correlation with BS and available Si. The exchangeable Na was positively correlated with available Si.

The available Si content of soil was possitively correlated with pH due to Si as an element whose amounts in available forms in the soil depend on soil pH. According to Szulc et al. (2015), the soil pH may have indirectly affected the increase in the availability of Si by limiting exchangeable Al. The possitive correlation of available Si and clay was also reported by Takahashi & Sato (2000).

The PCA grouped the estimated soil properties variables into four main components in which PC1 accounted for about 49.32% of the variation; PC2 for 15.64% and PC3 for 10.69% (Table 4).

Table 4. Factor loadings, eigenvalues and cumulative contribution ratio of total variance

Variables	Component		
	1	2	3
pH-H_2O	0.94	-0.14	0.03
pH-KCl	0.87	-0.04	0.10
Sand	-0.85	0.04	0.24
Silt	0.30	-0.43	0.32
Clay	0.78	0.15	-0.40
C	0.31	0.87	-0.22
N	0.31	0.84	-0.37
Available P	0.17	0.42	0.79
Exchangeable : K	0.43	0.00	0.30
Ca	0.89	-0.23	-0.02
Mg	0.89	-0.25	-0.09
Na	0.45	0.51	0.55
CEC	0.95	0.02	0.11
BS	0.83	-0.31	-0.15
Available Si	0.76	0.07	0.13
Eigenvalue	7.40	2.35	1.60
Cumulative percent of variance	49.32	64.96	75.64

Note. *, **,***: Correlation is significant at the 5, 1 or 0.1 % level, respectively.

The variables, which contributed to PC1 were clay, pH, exchangeable Ca, exchangeable Mg, CEC, BS and available Si. While, sand texture contributed negatively to PC1. The rice soils in study sites were mainly characterized with this PC1 which explained about 50 % of the variance. As an easy soil evaluation method in the fields, soil texture and pH could be practical indicators of the soil properties contributing to PC1. Variables which contributed to PC2 were TC and TN suggesting organic matter accumulation. PC3 was characterized by available P.

5.3.2. Relationships between soil properties and rice growth and yield

As in table 5, tiller number was positively correlated with exchangeable Na content. Meanwhile, plant height, straw and grain yield were positively correlated with several parameters.

Table 5. Correlations matrix of plant growth parameters and soil properties

	Tiller number	Plant height	Straw	Grain
Plant height	0.19			
Straw yield	0.80***	0.65**		
Grain yield	0.61 *	0.77***	0.81***	
pH-H_2O	0.14	0.79***	0.51	0.76***
pH-KCl	0.35	0.69**	0.59*	0.79***
Sand	0.15	-0.69**	-0.24	-0.47
Silt	0.06	0.09	0.08	0.43
Clay	-0.18	0.70**	0.22	0.31
TC	0.51	0.53*	0.51	0.47
TN	0.46	0.50	0.47	0.39
Available P	0.35	0.18	0.25	0.33
Exchangeable : K	0.04	0.53*	0.53*	0.41
Ca	0.04	0.64**	0.30	0.52*
Mg	0.07	0.75***	0.48	0.60**
Na	0.74**	0.49	0.66**	0.75***
CEC	0.12	0.85***	0.52*	0.70**
BS	-0.04	0.68**	0.30	0.51
Available Si	0.19	0.70**	0.55*	0.62**

Note. *, **,***: Correlation is significant at the 5, 1 or 0.1 % level, respectively.

Among the plant growth and yield parameters, we found that tiller number was significantly correlated with straw and grain yields. Plant height was significantly correlated with straw and grain yield. In other words, rice yield is supported by tiller number and plant height.

The correlation analysis in the preceding section revealed that some of the soil variables were highly interrelated. In order to simplify the relationship and to assess the major factors as the determinants of plant growth and yield, we also performed multiple regression analyses. Table 6 presents the stepwise regression analysis and the order of entry of variables into the model at the 5 % significance level.

Table 6. Stepwise multiple regression equations

Plant factor	Model	R^2
Tiller number	Y = 27.256 x exchangeable Na + 9.881	0.54
Plant height	Y = 0.611 x CEC + 83.628	0.73
Straw	Y = 37.942 x exchangeable Na + 15.160	0.43
Grain	Y = 7.888 x pH-KCl + 31.444 x exchangeable Na - 20.572	0.84

We could extract variable CEC as indicator to predict plant height. Exchangeable Na was the factor to predict tiller number and straw. Grain yield could be predicted by pH-KCl and exchangeable Na. As the soil pH correlated with the many of other parameters as shown in Table 3 and in the result of PCA (Table 4), it seems understandable that the soil pH could be an indicator of grain yield. It was very unique that exchangeable Na could be an indicator of plant growth (tiller number), straw and grain yield. However, we could not clarify why exchangeable Na showed such high correlation with the plant growth and the yield. Although it may be related with soil parameters other than those examined in the present study, we have not had concrete idea.

5.3.3. Effect of Si application on rice growth and yield

We analyzed the effect of soil, treatment and soil-treatment interaction on rice growth and yield by using two-way ANOVA (Table 7).

Table 7. Results of two-way ANOVA for tiller number, plant height, straw and grain yield of rice exposed to variations in soil type and silica application. Shown are the degrees of freedom (df), F-statistic (F), and probability of type I error (P) with soil type and Si addition analyzed as fixed effects. NS = P > 0.05.

	Tiller number			Plant height			Straw			Grain		
Source	df	*F*	P	df	*F*	P	df	*F*	P	df	*F*	P
Soil	9	144.484	.000	9	102.145	.000	9	175.813	.000	9	120.323	.000
Treatment	5	2.153	.064	5	4.809	.001	5	4.339	.001	5	8.229	.000
Soil x Treatment	45	.781	.824	45	1.712	.013	45	6.526	.000	45	3.359	.000

Soil type was significant, while treatment and interaction soil-treatment were not significant on tiller number. The soil types, Si treatment and interaction soil-treatment were significant at 5 % level on the plant height, straw and grain yield. Application of Si increased straw of sites 1,7 and 10 around 68, 68 and 10 %, respectively. The grain yield increased in sites 1, 6, 7 and 10 with percentage was 19, 42, 22 and 41, respectively.

5.3.3.1. Tiller number

Regardless of treatment, there were no significant on tiller number (Table 7). These findings are in line to Ahmad et al. (2013), where productive tiller was lower in Si application than control. While, in opposition to results of Hosseini et al. (2011) who reported higher SiO_2 fertilization level (10 g SiO_2) resulted in the higher number of tiller and Yasari et al. (2012) who found tiller number was larger when 250 kg Si ha^{-1} was applied than without Si. The tiller number was not affected by Si application and probably due to soil properties. The tiller number was significant in soil type, as show in figure 5 with the letter indicating significant difference.

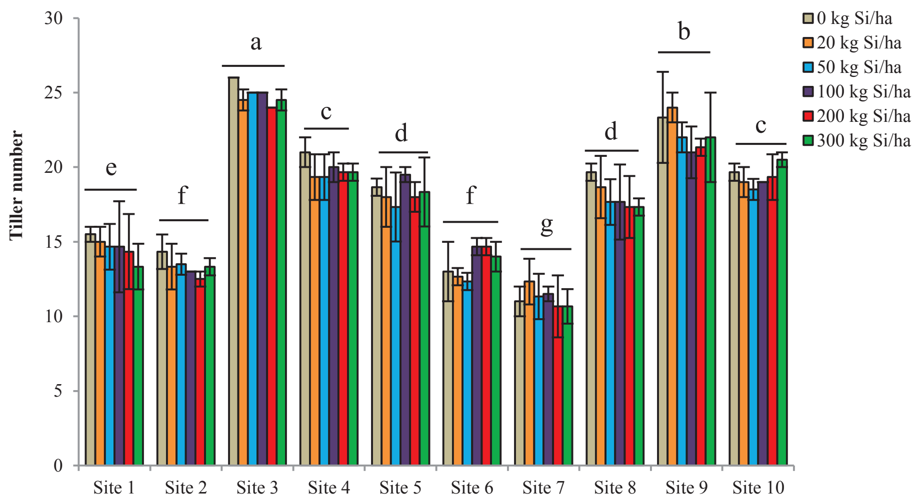


Figure 5. The effect of added silica on tiller number

Between sites 5 and 8 were not significantly different due to avail. Si in the original soil which was almost the same (940 and 966 mg SiO_2 kg^{-1}). The tiller number of sites 2 and 6 were not significant as these sites had the same clay content (64 %). Sites 4 and 10 were not significantly different, probably because exchangeable Na of these sites were almost the same (0.27 and 0.23 $cmol_c$ kg^{-1}, respectively). Tiller number in site 1 was low due to low CEC and available Si (17.74 $cmol_c$ kg^{-1} and 65 mg kg^{-1}, respectively) than other sites except site 10 for CEC.

The highest number of tillers was produced from site 3 and the lowest tiller number was site 7. The high tiller number in site 3 was due to soil properties in which TC, TN and available P were high; meanwhile site 7 had low available P and TN. Nitrogen content probably affected the tiller number, as Islam et al. (2013) found tiller number significantly higher with N application than control. The results are in conformity with Pramanik & Bera (2013), where N level increasing of effective tillers hill of rice due to favorable root growth and higher mobility of N in soil solution and its absorption by plant root. Moreover, available Si in original soil was also high in site 3. According to De Datta (1981), Si makes soil P available to rice.

5.3.3.2. Plant height

The significant difference among soil types on plant height were show in figure 6 with the letter indicating significant difference.

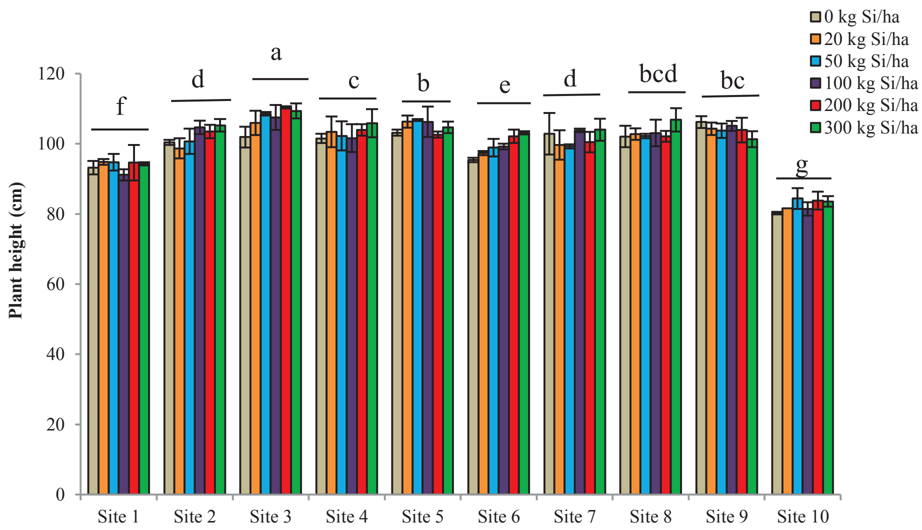


Figure 6. The effect of silica on plant height

Based on site, the highest plant height was site 3 and the lowest was site 10 and followed by sites 1 and 6, probably because these three sites had low available Si, pH and BS compared to other sites. Fallah (2012) reported that plant height increased under Si application, as plant height in site 3 was high due to high available Si. Regardless of the treatments, our results indicate that rice plants exposed to Si enrichment significantly increased plant height with additional of 300 kg ha^{-1} compared to control (Table 8).

Table 8. Effect of Si application on plant height

	0	20	50	100	200	300
Doses	kg Si ha^{-1}					
Plant height	99.2 c	100.6 bc	100.7 b	100.8 b	100.5 bc	102.3 a

Note. Values with different letter within same column show significant differences at $p<0.05$ level between treatments according to the Duncan's multiple range test

These findings are in accordance with earlier reports by Wattanapayapkul et al. (2011), where increasing the rate of Si application significantly increased plant height. According to Moghadam & Heidarzadeh (2014) and Hosseini et al. (2011), plant height was significantly increased with Si application. Support for this result also comes from Okuda & Takahashi (1961) observed that the plant height was higher when Si was added at later growth stage (after panicle initiation stages). Further, Increase in plant height of Si treatments might owe to increased cell division, elongation and expansion caused by silicon (Jawahar et. al., 2015). Yavezadah et al. (2008) reported that deposition of Si on plant tissues caused erectness of leaves and stems resulted increase in plant height.

5.3.3.3. Straw and grain yield

Yields of rice in relation to the amount of steel slag applied are shown in figure 7 and 8 with the letter indicating significant difference.

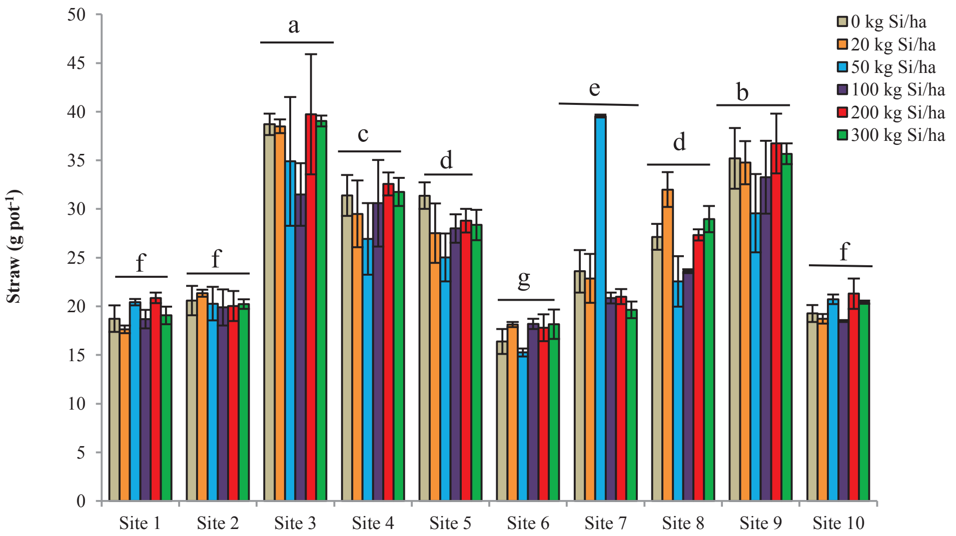


Figure 7. Response of straw yield to Si application

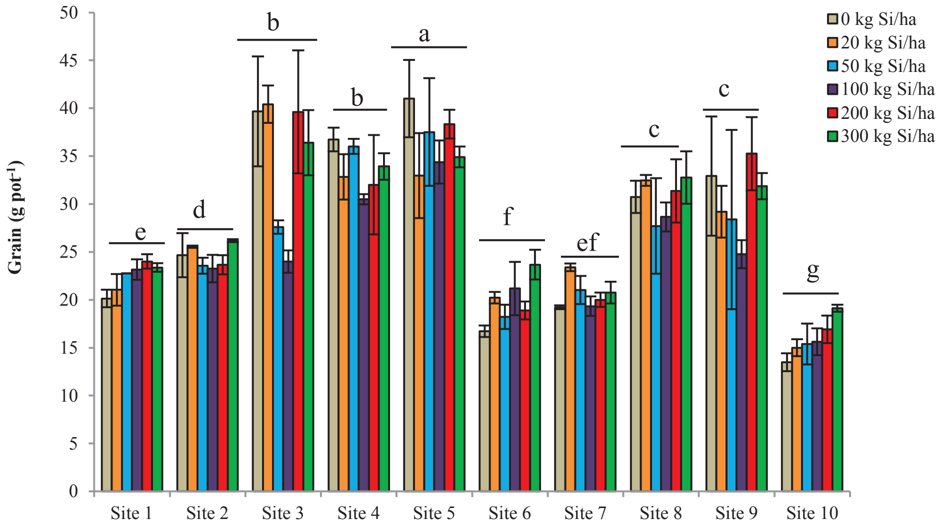


Figure 8. Response of grain yield to Si application

These results indicated that soil properties affected straw and grain yield. The highest yield of straw and grain were from sites 3 and 5, respectively. It was similar with tiller number and plant height, where available Si, TC, TN and were high in site 3. Hence, grain yield was high in site 5 due to high TN, TC and available Si. The lowest straw and grain yield were sites 6 and 10, respectively. As sites 6 and 10 had lower available Si than other sites. Besides that, site 10 had low available Si, TN, TC, CEC and BS.

Furthermore, as a two-way ANOVA was not effective in determining the overall contributions of soil and treatment for each soil sample. Than it is more appropriate with one-way ANOVA. Table 9 show results of statistical one-way ANOVA data of straw and grain yield.

Table 9. Results of one-way ANOVA for straw and grain yield of rice exposed to variations in soil type and silica application.

Gram	Doses (kg Si ha^{-1})	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Straw	0	18.7 c	20.6 a	38.7 ab	31.4 a	31.4 a	16.4 ab	23.6 b	27.1 b	35.2 ab	19.3 bc
	20	17.6 c	21.4 a	38.5 ab	29.5 a	27.5 b	18.1 a	22.9 b	32.0 a	34.8 ab	18.7 c
	50	20.4 ab	20.3 a	34.9 ab	26.9 a	25.0 b	15.3 b	39.6 a	22.6 c	29.6 b	20.7 a
	100	18.7 c	20.0 a	31.5 b	30.6 a	28.0 ab	18.2 a	20.9 bc	23.6 c	33.3 ab	18.5 c
	200	20.9 a	20.0 a	39.7 a	32.6 a	28.8 ab	17.8 a	21.0 bc	27.3 b	36.7 a	21.3 a
	300	19.1 bc	20.2 a	39.1 ab	31.8 a	28.4 ab	18.2 a	19.6 c	29.0 b	35.7 a	20.4 ab
Grain	0	20.1 b	24.7 ab	39.7 a	36.7 a	41.0 a	16.7 c	19.2 b	30.8 a	32.9 ab	13.5 c
	20	21.1 b	25.5 ab	40.4 a	32.8 ab	33.0 b	20.2 b	23.4 a	32.5 a	29.2 ab	15.0 bc
	50	22.8 a	23.6 b	27.6 b	36.0 a	37.5 ab	18.2 bc	21.0 b	27.7 a	28.4 ab	15.4 bc
	100	23.2 a	23.3 b	24.0 b	30.5 b	34.4 ab	21.2 ab	19.3 b	28.7 a	24.8 b	15.6 bc
	200	24.0 a	23.7 b	39.6 a	32.0 ab	38.3 ab	18.9 bc	20.0 b	31.4 a	35.3 a	16.9 ab
	300	23.4 a	26.2 a	36.4 a	33.9 ab	34.9 ab	23.7 a	20.8 b	32.8 a	31.9 ab	19.1 a

Note. Values with different letter within same column show significant differences at $p<0.05$ level between treatments according to the Duncan's multiple range test

In general, both straw and grain yields of sites 2, 3, 4, 5, 8 and 9 did not respond to Si application. Meanwhile sites 1, 6, 7 and 10 responded to added Si. Straw and grain yield of site 5 was not significantly different with control. Straw and grain of site 3 was not significantly different between Si treatments and control. However, the highest straw was treatment 200 kg Si ha^{-1} and grain was treatment 20 kg Si ha^{-1} in site 3. The results showed site 2, either straw or grain yield were not significant difference between control and Si treatments. However, the highest straw and grain yield was obtained by 20 and 300 kg Si ha^{-1}, respectively.

Straw dry weight was significantly increased with 20 kg Si ha^{-1} for site 8 but decreased with high Si treatment (50 - 300 kg ha^{-1}), while there was no significant difference between control and Si treatments of grain yield. Straw and grain were not significantly different between control and Si treatments of site 9. However, the highest grain and straw yield was found in 200 kg Si ha^{-1} which was higher than control. In this case, we assume that sites 3, 4, 5 and 9 had similar reason. In which TN of those sites were higher compared to other sites. High N in soil induce the number of stalks and leaves, creating unfavorable conditions to yielding, such as shading and lodging (Barbosa 1987 & 1991). When plants receive too much N, they also become more attractive to insects and diseases. In this research, added Si into soil was used to restore conditions caused by high N in the soil. Besides TN, exchangeable Na was also higher in sites 2, 3, 4, 5, 8 and 9 compared to other sites (Table 2). Sodium probably induced the level of soil salinity. Thus Si application was also used to reduce salinity. Silica has been shown to be effective in mitigating soil salinity according to Liang et al. (2007).

The beneficial effect of Si treatment in increased straw and grain of sites 1, 6 and 10 seemed to be the results of lower initial available Si in soil. Indicating low available Si in soil made plants respond to Si application. The adequate Si supply might have improved the photosynthetic activity that enables the rice plant to accumulate sufficient photosynthates. Hence, resulted in increased dry matter production. These factors coupled with efficient translocation of photosynthates resulted in more number of filled grains and straw as reported by Jawahar et al. (2015). These finding were corroborated by the results of Makabe-Sasaki et al. (2013) who found the amount of dissolved Si in soil solution is increased by slag silicate fertilizer (SSF). Moreover, the grain yield response to Si application may be due to increased leaf erectness, decreased mutual shading caused by dense planting.

Although straw yield of site 6 was not significantly different between treatment and control, the highest straw was 100 kg Si ha^{-1}. While, Si application significantly increased the grain yield which the highest was 300 kg Si ha^{-1}. Treatment of 50 and 20 kg Si ha^{-1} significantly increased straw and grain, respectively in site 7. Site 7 had low pH and high clay (70%), as phyllosilicates are clay minerals that are an important source of silicic acid in agricultural soils (Mark, 1995). However, the solubility of Si from original soil was probably low due to high clay content bind Si, then Si was not in soil solution and less Si was extracted by rice plants. By adding steel slug, soil pH increased and Si might be release into soil solution. According to Kato & Owa (1997), the application of the slags increased the soil solution pH when large alkalinity of the applied slag was high. Therefore, Si from steel slag would be directly used by plant. In other words, plants respond to Si application. Furthermore, available P content in soil was also low (3.7 mg P_2O_5 kg^{-1}), where with high Si content had a beneficial indirect effect on plant growth. The Si caused a decrease in Fe and Mn uptake when P was low, thus promoted P availability within plant (Ma & Takahashi, 1990).

The effect of Si treatments in straw and grain yield of site10 was significant. Whereas at 50 kg Si ha^{-1} enhanced the straw and 200 kg Si ha^{-1} increased grain yield. Salman et al. (2012) reported straw had significant effect under silicon treatment (5% probability level), where the maximum straws yield was observed for 300 kg Si ha^{-1}. Among the different level of Si, application of 300 kg/ha recorded maximum grain yield of rice, which was closely followed by 200 kg Si ha^{-1}. Increasing levels of Si increased the grain yield. The response of plant with Si application also due to the available Si, pH and exchangeable Ca in this site was low compared to other sites.

Figure 9. Harvesting

5.4. Conclusions

Among the different sites, tiller number and plant height were highest in the site with high available Si content. Silica enrichment significantly increased plant height with additional of 300 kg Si ha^{-1} compared to control. Soils responded to the applied Si in achieving higher grain yields over the control due to its low available Si content. The increase grain yield was high with 50 – 300 Si kg ha^{-1} for site 1, 6 and 10. In contrast, although grain yield of some soil with high available Si content was higher than soil with low available Si but these soils did not respond significantly to Si application. This indicates that other soil properties such as pH-KCl and exchangeable Na affected the grain yield while CEC serves as indicator to predict plant height in this experiment. Exchangeable Na was the factor to predict tiller number and straw. It was very unique that exchangeable Na could be an indicator of tiller number, straw and grain yield.

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CHAPTER 6

Production of High Purity Silica from Materials

6.1. Introduction

Globally, industrial waste such as fly ash, bottom ash and slag in the power thermal energy, steel and coal industry has been potential for environmental stresses. This environmental impact has encouraged research into new products that are beneficial for agriculture. One innovative idea for recycling the industrial waste is to use it to produce high purity Si as fertilizer.

The commercial use of fly ash as a fertilizer in crop production is uncommon in most countries, including Indonesia. As coal ashes may contain non-essential elements that adversely affect soil, crop and groundwater quality (Adriano et al., 1978, 1980; Page et al., 1979). Despite the potential and negative effect on environmental quality, production of coal in Indonesia is around 437 million ton (Ministry of Energy and Mineral Resources, 2014) with fly and bottom ash as waste that is likely to remain a serious issue. Fly ash is a fine particulate residue that is removed from the dust-collection system. The diameter of fly ash particles from <1 µm up to 150 µm (Ramezanianpour, 2014). According to Adriano et al (1980), fly ash is a glassy material with a very high available Si content which is produced from coal combustion. In general, fly ash from the combustion of subbituminous coals contains more calcium (Ca), less iron (Fe) and contains very little unburned carbon (C) than fly ash from bituminous coal (Ramezanianpour, 2014).

Silica is polymers of silicic acid consisting of inter linked SiO_4 units in a tetrahedral fashion with the general formula SiO_2 or $SiO_2.xH_2O$. In nature, it exists as sand, glass, quartz, etc.

(Vansant et al., 1995; Le at al., 2013). According to Barby (1976), silica is divided by two class classification, natural silica and synthetic silica. The synthetic silica (mostly amorphous) consist of colloidal silica, silica gels (hydrogels, xerogels, and aerogels), pyrogenic silica (aerosils, arc silicas, and plasma silicas), and precipitates.

There are various methods to prepare pure silica from different materials. Le at al. (2013) synthesized nanoparticles from rice husk via sol-gel method. Affandi et al. (2009) synthesized silica xerogels from bagasse ash. The sol-gel technique is the most common method for silica synthesis that involves simultaneous hydrolysis and condensation reaction. A sol of sodium silicate or silicon alkoxide gets converted into a polymeric network of gel by that process (Le et al., 2013). Another method for Si purification is treatment with acid solution (HCl). According to Poykio et al. (2014), HCl is one of the common partial extractants which extracts labile metals, but has little effect on breaking up the silicate lattice and residual phase metals, hence leaving metals bound to these phases untouched. The research has mainly focused on improve solubility of Si from industrial waste material using two different techniques as pre-treatment.

6.2. Materials and method

Four materials were selected to produce high purity Si, namely: (1) Bottom ash, (2) Fly ash 1, (3) fly 2 and (4) fly ash 3. The flow chart of high purity Si production is shown in Fig. 1 and 2. Silicon was extracted from materials with 2 extraction method, namely: (1) Na_2CO_3/NH_4NO_3 (10 g L^{-1}/16 g L^{-1}) (1:100 ratio continuous shaking 1h, filter) (Pereira et al., 2003), (2) 0.5 M HCl (1:150 ratio for 1h, filter) (Savant et al., 1999)._ Silicon concentrations in supernatant were was determined by colorimetric analysis with Spectrophotometer UV 1800 Shimadzu. The wavelength use for the Si detection was 810 nm.

6.2.1. High purity of Si (technique 1)

High purity of Si from materials was prepared using technique 1 (figure 1). (1) The acid washing step was to elute metal components from materials. (2) The material sample was dispersed in 2N HCl and the dispersion was boiled up of white vapor. (3) The material residues were filtered through filter paper Advantec No. 6 and washed by distilled water and until pH 6 – 7 or several times. (4) The residues were dried at 105^{o}C for 16h as high purity of Si.

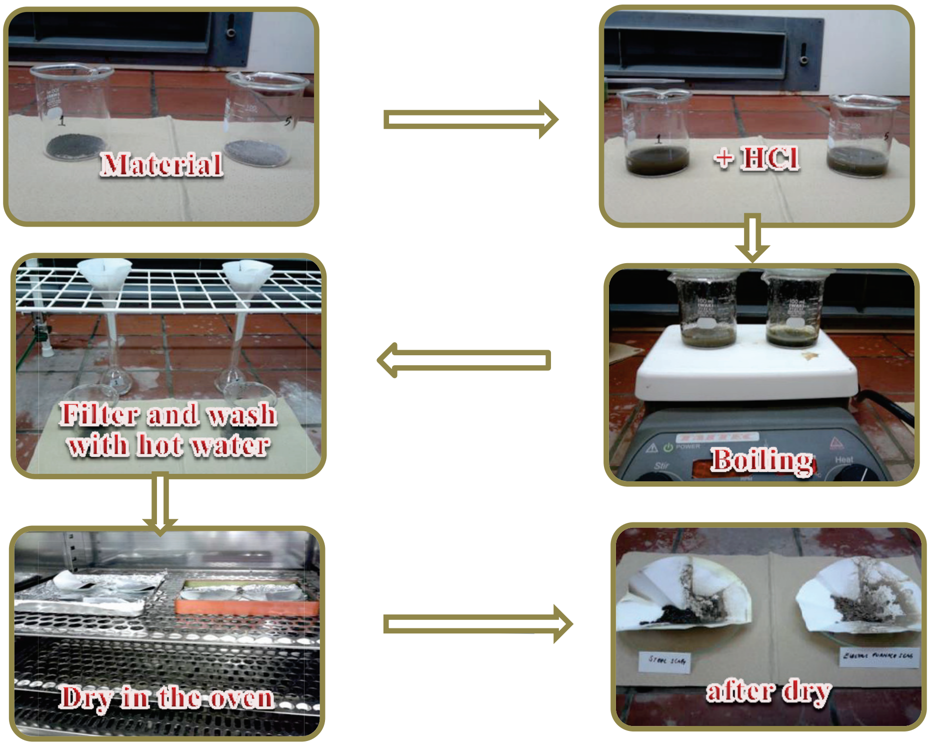

Figure 1. The flow diagram of technique 1

6.2.2. Sol-gel (technique 2)

The flow diagram of silica synthesis is shown in Fig. 2. Silica gels were prepared using alkaline and acid solution with 3 different steps. These steps were (1) pretreatment of fly ash and bottom ash using hot water washing to remove impurities. (2) Silica was extracted from fly ash and bottom ash using 2N NaOH solution producing sodium silicate. During silica extraction, the mixture of materials and NaOH solution was boiled for 1h with constant stirring. After cooling, the solution was filtered through filter paper Advantec No. 6. (3) The filtrate was sodium silicate which was added with 2N HCl to produce soft silica gels. (4) Filter and wash with hot water until pH of solution was neutral. (5) The silica gels in filter paper were dried at 105°C for 1h.

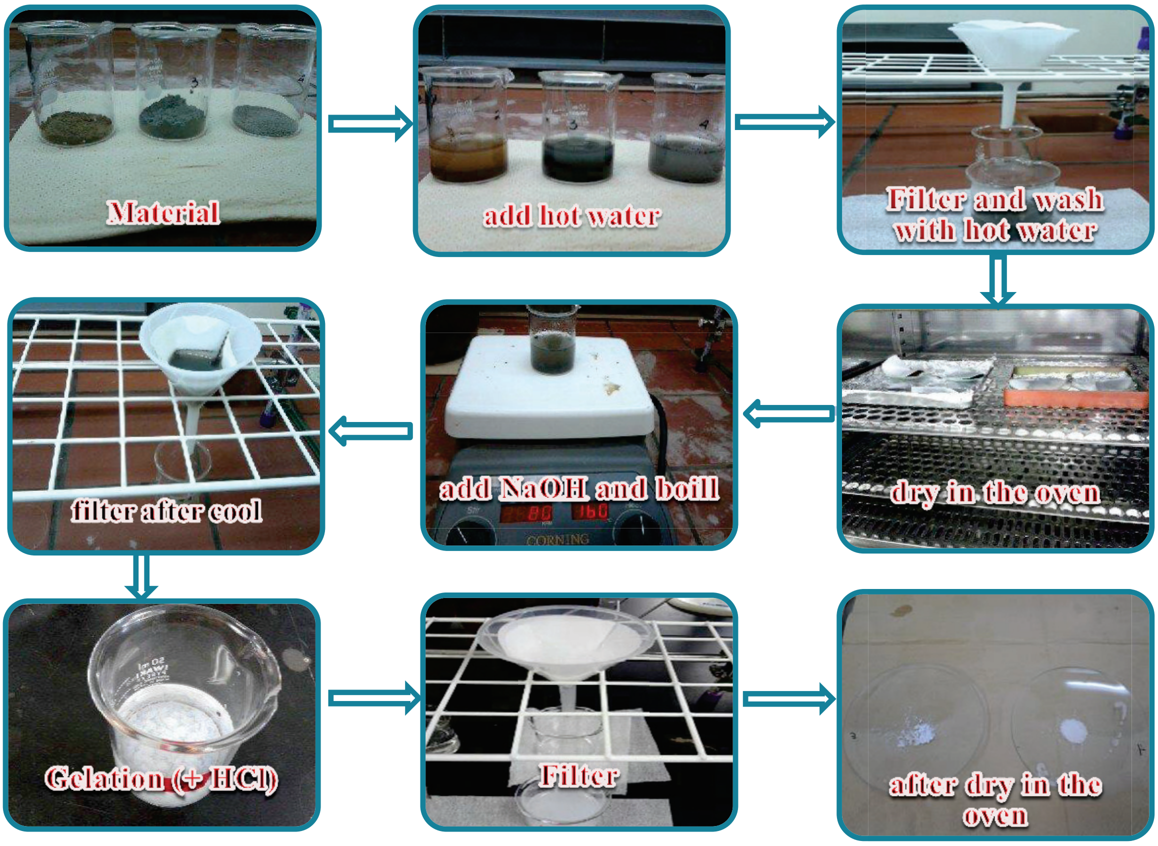

Figure 2. The flow diagram of technique 2

Silica was extracted after treatment with 2 extraction method, namely: (1) Na_2CO_3/NH_4NO_3 (10 g L^{-1}/16 g L^{-1}) (1:100 ratio continuous shaking 1h, filter) (Pereira et al., 2003) and 0.5 M HCl (1:150 ratio for 1h, filter) (Savant et al., 1999).

6.3. Results and discussion

6.3.1. Silica concentration

The silica content of materials was characterized by two different extractants. From table 1, it is shown that pre-treatment by technique 1 produced silica with higher concentration compared to without pre-treatment by Na_2CO_3/NH_4NO_3 extraction. It was probably due to HCl in technique 1 was used to elute metal components from material (Kim et al., 2010), while Si was not soluble in acid, was filtered out and dried into high purity Si. Furthermore, Si content in material after pre-treatment was higher with alkaline extractants compared to acid extractants. The hot water was used to wash the carbon residues from materials (Kalapathy, et al., 2000).

Table 1. The silica content of materials by two different extractable Si.

Material	Pre-treatment				Without pre-treatment	
	Technique 1		Technique 2			
	HCl 0.5 N	Na_2CO_3/NH_4NO_3	HCl 0.5 N	Na_2CO_3/NH_4NO_3	HCl 0.5 N	Na_2CO_3/NH_4NO_3
	---------- mg SiO_2 kg^{-1} ----------					
Bottom ash	260	6745	75957	9873	28664	381
Fly ash 1	335	6926	51075	3221	16451	165
Fly ash 2	238	7811	46331	2266	16229	349
Fly ash 3	1051	6878	86448	2618	18039	1699

After pre-treatment with method 2, in which is the materials changed into silica slurry formation, concentration of Si was increased as shown in table 2. Concentration of silica by two different methods was higher compared than original materials (without treatment).

In technique 2, prior silica extraction, materials were washed hot water to remove sulphur (S). According to Poykio et al. (2014) that water extraction most effectively released S from fly ash and bottom ash. Furthermore, Si is soluble in alkaline solution as expressed in Eq. (1)

$$\text{Material} + NaOH \rightarrow NaSiO_3 + H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Parameter in determining quality of silica gel preparation is gelation pH (Kalapathy et al., 2000). In this experiment, pH of silica gel after adding HCl was around 1 - 4. This condition was the same with titration method, which is sodium silicate solution, was titrated with HCl and was stopped at certain pH condition. The soft silica gel was gently broken after filtering and washing by distilled water to make slurry. According to Affandi et al. (2009), sodium silicate that was formed and water purification showed great promise for high purity of silica gel production. In the preparation of silica gel, gelation pH is critical parameter. The experiment demonstrated that precipitation of amorphous silica from solutions due to salinity (Eq. 2). According to Angcoy Jr. (2006), increased salinity increased both silica polymerization and deposition rates. Silica polymerization is regarded as a precursor to the precipitation of silica gel (Iler, 1979). In saline solutions, the presence of ions reduces the repulsive forces allowing the polymer to aggregate and form gel (Angcoy Jr, 2006).

$$Na_2SiO_3 + 2HCl \rightarrow 2NaCl + SiO_2 + H_2O \quad \text{.........................} \quad (2)$$

Hydrochloric acid solution was added gradually into the suspension in order to initiate the hydrolysis-condensation reaction (Le at al., 2013) at pH < 4. According to Affandi et al. (2009), in acidification reaction, Si starts to precipitate when the pH decreases less than 10.

Sodium silicates are slightly basic, and when neutralized with acid, hydrolysis will occur and silanol (Si-OH) groups will form. Silica sols are formed by the mixing of silicate salt with an acid or liquid alkoxide with water. Particles of colloidal size are formed by condensation. The small three-dimensional siloxane networks are gradually formed as condensation proceeds. The condensation reaction may be influenced by the addition of electrolyte or change of the pH as the factors which control the growing of the particles or the linkage of particles to from chains (Vansant et al., 1995). According to Affandi et al. (2009), in the absence of salts, electrostatic interaction between charged particles limits the aggregation process to form a three-dimensional, porous silica network. Furthermore, the size of primary particles increase and decrease in number as a results of Oswald ripening process (figure 3)

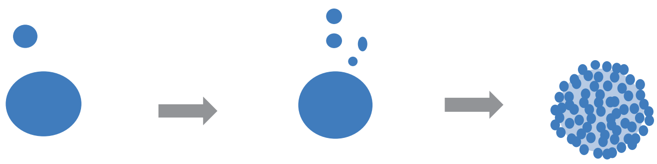

Figure 3. Oswald ripening process

6.3.2. The amount of silica material

The Si material after treatment showed different quantity (Table 2). The amount of material reduced after treatment by two techniques. The decreased in Si material was higher with technique 2 compared with technique 1. The quantity of material was produced by technique 1 was 74 – 82 % and technique 2 was 3.0 – 4.8 % from raw material. It was possible as material by treatment technique 2 through several stages of purification such hydrolysis, gelation, and drying. During those stages, it might be more Si lost from material. Another possibility that during synthesis of Si gel, the raw material was not through an aging process. Aging process is when the gel in contact with the pore-filling liquid, its structure and properties keep changing as a function of time (Vansant et al., 1995). Le at al. (2013) reported that gel mixture was aged at 60°C for 8 h. As also Affandi et al. (2009) reported that the soft gel was aged for 8 – 40 h.

Table 2. The amount of materials before and after treatment

Material	Technique 1		Technique 2	
	before	after	before	after
	------------- g -------------			
Bottom ash	5	3.9	5	0.18
Fly ash 1	5	3.7	5	0.23
Fly ash 2	5	3.8	5	0.15
Fly ash 3	5	4.1	4	0.19

6.4. Conclusions

In order to improve the Si availability of fly ash and bottom ash, silica gel was produced from these materials by Sol-gel technique and then extracted with HCl and Na_2CO_3/NH_4NO_3 to determine the silica content in the silica gel. Sol-gel technique of fly ash and bottom ash increased Si concentration and Si release than those in initial ones. Although the improvement method was found to be effective, it is needed to be tested in a pilot scale to evaluate the economic feasibility.

6.5. References

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CHAPTER 7

Summary

Rice is the main staple food in Indonesia in which Indonesia ranks third in rice production in the world. However, the domestic rice production is not enough to meet the demand. Although Silicon (Si) is a beneficial element for rice plant, Si fertilizer has never been used in Indonesia. Therefore, soil available Si in rice fields in Java Island has decreased by approximately 17-22 % during the period 1970-2003 (Darmawan et al., 2006). Application of Si fertilizer is recommendable, but not accessible to local farmers. For this reason, it is desirable to explore cheap and abundant local Si containing materials as Si fertilizer sources. In the present study, Si availability of 18 local materials, namely rice husk-burnt (RHB), rice husk-ash (RHA), rice husk-heated (RHH), media of mushroom (MM), cacao (*Theobroma cacao,* L.*)* shell - biochar (cacao SB), rice (*Oryza sativa*, L.) straw compost (RSC), bagasse, elephant grass, vetiver grass, bamboo leaf, sugarcane leaf and palm nut shell-biochar (palm nut SB), fly ash, steel slag, silica gel, volcanic ash, bottom ash, electric furnace slag (EFS), from different sources in Indonesia were determined by extraction and incubation methods and compared with Japanese silica gel (JSG) and Japanese silica fertilizer (JSF) as reference. The bioavailability was also examined by pot experiments of rice cultivation in the greenhouse. Based on the results of these experiments, factors of materials and soils controlling Si release from the materials were also discussed. In addition, methods to improve availability of Si of fly ash and bottom ash were also examined.

In general, Si release examined by incubation method was lower in organic materials than in inorganic materials. Release of Si from silica gel was the highest among the materials tested both in red and sandy soils. However, its use was not realistic as it is imported and costly. Among the local materials such as steel slag, RSC and RHB, and cacao SB could be used as

Si amendments in paddy fields in Indonesia. Of the six extractable Si studied, Si concentration was higher in the order of 0.5N HCl > citric acid > acetate buffer pH 4.0 > sodium phosphate > Na_2CO_3/NH_4NO_3 > $CaCl_2$ for inorganic materials. The Si of the inorganic materials was more extractable in acid solution, while for organic materials, the Si was more extracted in alkaline solution with the order of Na_2CO_3/NH_4NO_3 > $CaCl_2$ > sodium phosphate > citric acid > 0.5N HCl.

In the incubation experiment, JSG was used to test the interaction between Si solubility with the application of Ca and Mg. Results showed that Ca and Mg in the Si materials and soils could inhibit Si release in soil solution. Solubility of Si was negatively and positively correlated with pH and Fe concentration in the soil solution, respectively, which indicated these were also the controlling factors of the Si release.

In the pot experiment examining bioavailability of Si in the local materials with paddy soil which was analyzed to be acidic, steel slag and JSG significantly increased silica uptake by rice plant compared with control. The amount of Si taken up by the plants at 37 DAT was closely related to the amount of Si extracted from the materials by Na_2CO_3/NH_4NO_3, sodium phosphate and 0.5N HCl depending on the types of the materials. Based on the results, there is no generally accepted method to evaluate plant-available Si in materials. Three methods could be proposed to evaluate bioavailable Si as follows: (1) Na_2CO_3/NH_4NO_3 for silica gel, JSG, RHA, RHB, MM, and RSC, (2) sodium phosphate for fly ash and steel slag, and (3) 0.5N HCl for fly ash, steel slag, cacao SB, JSG, RHA, RHB, and MM.

In another pot experiment to examine the effect of steel slag application on plant growth parameters with 10 soils collected from different sites in Indonesia, three of the soils were identified to have low available silica (<500 mg SiO_2 kg^{-1}). Steel slag applied at the rate of 300 kg Si ha^{-1} significantly increased plant height for all the soils. In grain yield, the rice grown in three soils with lower available Si responded to steel slug application of 50 – 300 Si kg ha^{-1}, while rice in the other seven did not respond.

In order to improve the Si availability of fly ash and bottom ash, silica gel was produced from these materials by Sol-gel technique and then extracted with HCl and Na_2CO_3/NH_4NO_3 to determine the silica content in the silica gel. Sol-gel technique of fly ash and bottom ash increased Si concentration and Si release than those in initial ones. Although the improvement method was found to be effective, it is needed to be tested in a pilot scale to evaluate the economic feasibility.

Based on the results obtained in the present study, steel slag could be the most realistic Si fertilizer source among the inorganic materials tested because of its high Si release potential and the abundance in Indonesia. For the organic materials, RSC and RHB showed relatively high Si release and are available everywhere, indicating that these can be effective Si sources in Indonesia.

Characterization of Indonesian Local Silicon Material and Evaluation of Controlling factors for Soil Silicon Availability

インドネシア産ケイ素資材の特性付けと土壌のケイ酸可給度の制御因子の評価

米はインドネシアの主食であり、インドネシアは世界第 3 位の米生産国である。しかし、国内生産量は需要を満たしていない。ケイ素(Si)は稲植物にとって有用元素であるが、インドネシアでは Si 肥料は使用されていない。このため、Java 島の稲作地では 1970 年から 2003 年にかけて土壌の可給態 Si がおよそ 17-22％減少している (Darmawan et al., 2006)。Si 肥料の施用が推奨されるが、地域の農民には入手ができない。よって、Si 肥料の原料として安価で豊富な在地の Si 含有資材を探索する事が望ましい。本研究では、18 種のインドネシア在地の資材、もみ殻炭化物 (RHB), もみ殻灰(RHA) , 加熱もみ殻 (RHH), 菌床残渣(MM), カカオ殻炭(cacao SB), 稲わら堆肥 (RSC), バガス（サトウキビ茎残渣）, elephant grass, vetiver grass, 竹葉, サトウキビ葉, ココナツ殻炭 (palm nut SB), フライアッシュ, 鉄鋼スラグ, シリカゲル, 火山灰, ボトムアッシュ, 電気炉スラグ (EFS)について、いくつかの抽出方法と培養法により可給態 Si を測定し、日本製のシリカゲル(JSG)と Si 肥料(JSF) と比較した。Si の生物利用度についてもガラス室での稲ポット栽培試験で評価した。これらの試験結果に基づき、資材からの Si 放出を制御する（資材と土壌中の）要因についても考察した。また、フライアッシュとボトムアッシュの Si 可給度改善の方法についても検討した。

培養法による Si 放出量は概して、無機資材よりも有機物資材の方で低くなった。シリカゲルからの Si 放出量が赤土と砂土の両方ともに最も大きかった。しかし、シリ

カゲルの利用は輸入品で高価なため現実的ではない。6 種の Si 抽出方法の比較の結果、Si 抽出量は無機物資材では 0.5N HCl > citric acid > acetate buffer pH 4.0 > sodium phosphate > Na_2CO_3/NH_4NO_3 > $CaCl_2$ の順、酸性溶液で高くなった。一方有機物資材ではアルカリ溶液で高く、Na_2CO_3/NH_4NO_3 > $CaCl_2$ > sodium phosphate> citric acid> 0.5N HCl の順であった。

JSGのSi溶解度とCaとMg施用の関係評価を培養試験で実施した結果、CaとMgは資材と土壌中のSiの土壌溶液への放出を阻害した。また、Siの溶解度は、土壌溶液のpHと正の相関を、Fe濃度と負の相関を示し、これらも資材からのSi溶解の制御因子である事が示された。

酸性土壌を用いたポット試験の結果、鉄鋼スラグと JSG 施用区で稲の Si 吸収量が対象区に比べて有意に増加した。移植後 37 日(DAT)の植物の Si 吸収量と、Na_2CO_3/NH_4NO_3, sodium phosphate と 0.5N HCl による Si 抽出量の関係は資材の種類に応じて異なり、次の 3 つの植物の Si 利用可能度の評価方法が提案できた。(1) Na_2CO_3/NH_4NO_3 は,シリカゲル JSG, RHA, RHB, MM, RSC, (2) sodium phosphate はフライアッシュと鉄鋼スラグ, (3) 0.5N HCl は フライアッシュと鉄鋼スラグ,および cacao SB, JSG, RHA, RHB, と MM である。

インドネシアの 10 土壌 うち 3 土壌は低可給態 Si(500 mg SiO_2 kg^{-1})を用いた鉄鋼スラグの施用効果を確認したポット試験の結果、300 kg Si ha^{-1} の施用はすべての土壌において草丈生長を増加した。籾収量について、可給態 Si レベルの低い 3 土壌で育っ

た稲は 50 – 300 Si kg ha^{-1} の鉄鋼スラグ施用に応答したが、その他の 7 土壌の稲は応答しなかった。

フライアッシュとボトムアッシュの Si 可給度の改善のために、Sol-gel 法によるシリカゲル生成を行い、HCl and Na_2CO_3/NH_4NO_3 抽出により Si 含量の測定を行った。その結果、フライアッシュ、ボトムアッシュとも Si 含量および可給度を向上させることができた。この処理は効果的であるが、経済的な実現可能性は実証規模での試験が必要である。

本研究で得られた結果より、無機物資材では高い Si 放出特性と豊富さより鉄鋼スラグがインドネシアでは最も現実的な Si 肥料資源と考えられた。有機物資材では、RSC と RHB の Si 放出が比較的高く、そしてインドネシアのいずれの地域でも利用可能であることから、有効な Si 資源であることが示された。

List of Publications

1. Relationships between Soil Properties and Rice Growth with Steel Slug Application in Indonesia. Linca Anggria, Husnain, Antonius Kasno, Kuniaki Sato and Tsugiyuki. Masunaga. Journal of Agricultural Science, Canadian Center of Science and Education. Vol. 8 (5), 1-14, 2016.

   (Chapter 5)

2. Silicon Release from Local Materials in Indonesia under Submerged Condition. Linca Anggria, Husnain, Kuniaki Sato and Tsugiyuki Masunaga. Journal of Agricultural Science, Canadian Center of Science and Education. Vol. 8 (12), 72-85, 2016.

   (Chapter 3).