A Comparison of Visible Spectroscopy and Atomic Absorption Spectroscopy Techniques to Determine Silicon Availability in Sugarcane Growing Clayey Soils

การเปรียบเทียบเทคนิควิสิเบิลสเปกโทรสโกปีและอะตอมมิกแอบซอร์พชันสเปกโทรสโกปี เพื่อวัดความเป็นประโยชน์ของซิลิคอนในดินปลูกอ้อยที่เป็นดินเหนียว

Karuna Poomsong, Saowanuch Tawornpruek* and Worachart Wisawapipat
กรุณา พุ่มทรง เสาวนุช ถาวรพฤกษ์* และ วรชาติ วิศวพิพัฒน์

Department of Soil Science, Faculty of Agriculture, Kasetsart University, Bangkok 10900, Thailand
ภาควิชาปฐพีวิทยา คณะเกษตร มหาวิทยาลัยเกษตรศาสตร์ กรุงเทพฯ 10900
**Corresponding author: Email: agrsnt@ku.ac.th*

(Received: 11 November 2022; Accepted: 10 February 2023)

บทคัดย่อ: ซิลิคอนเป็นธาตุเสริมประโยชน์สำหรับพืช โดยทั่วไปการวิเคราะห์ความเป็นประโยชน์ของซิลิคอนในดินจากปริมาณซิลิคอนในสารสกัดดินด้วยด้วยเทคนิควิสิเบิลสเปกโทรโกปี และอะตอมมิกแอบซอร์ชันสเปกโทรโกปี วัตถุประสงค์ของการศึกษานี้คือเพื่อเปรียบเทียบการวิเคราะห์ซิลิคอนในสารละลายสกัดโดยวิธีโมลิบดีนัมบลูคัลเลอริเมตริก และอะตอมมิกแอบซอร์พชันสเปกโทรสโกปีในดินปลูกอ้อยที่เป็นดินเหนียวจำนวน 36 ตัวอย่าง การประเมินซิลิคอนที่เป็นประโยชน์ในสารละลายสกัดทั้ง 5 ชนิด ได้แก่ สารละลาย Mehlich I กรดอะซิติก 0.5 โมลาร์ แอมโมเนียมอะซิเตท 0.5 โมลาร์ (pH 4.8) แคลเซียมคลอไรด์ 0.01 โมลาร์ และโพแทสเซียมคลอไรด์ 0.01 โมลาร์ ผลการศึกษาพบว่าสารละลายสกัดที่พบปริมาณซิลิคอนที่เป็นประโยชน์ที่มีอยู่ในดินสูงสุดคือ สารละลาย Mehlich I ตามด้วยกรดอะซิติก 0.5 โมลาร์, แอมโมเนียมอะซิเตต 0.5 โมลาร์ (pH 4.8), แคลเซียมคลอไรด์ 0.01 โมลาร์, และน้อยที่สุดคือ โพแทสเซียมคลอไรด์ 0.01 โมลาร์ ทั้งการวิเคราะห์ด้วยเทคนิควิสิเบิลสเปกโทรโกปีและอะตอมมิกแอบซอร์พชันสเปกโทรสโกปี ความสัมพันธ์ระหว่างการวิเคราะห์ทั้งสองพบความสัมพันธ์สูงในทุกสารละลายสกัด ได้แก่ Mehlich I (R^2 = 0.9803), แอมโมเนียมอะซิเตต 0.5 โมลาร์ (pH 4.8) (R^2 = 0.9869) แคลเซียมคลอไรด์ 0.01 โมลาร์ (R^2 = 0.8902) โพแทสเซียมคลอไรด์ 0.01 โมลาร์ (R^2 = 0.7406) และกรดอะซิติก 0.5 โมลาร์ (R^2 = 0.7287) ซิลิคอนที่สกัดด้วยสารละลายสกัดที่แตกต่างกันมีความสัมพันธ์กันระหว่างสารละลายสกัดที่เป็นกรด ได้แก่ (Mehlich I, กรดอะซิติก 0.5 โมลาร์ และแอมโมเนียมอะซิเตต 0.5 โมลาร์) และสารละลายสกัดเกลือที่เป็นกลาง ได้แก่ (แคลเซียมคลอไรด์ 0.01 โมลาร์ และโพแทสเซียมคลอไรด์ 0.01 โมลาร์) ผลการวิจัยชี้ให้เห็นว่าสารละลายสกัดทั้ง 5 ชนิดนี้ มีลักษณะเฉพาะของความสามารถในการสกัดซิลิคอนในดินและปัจจัยพีเอชของสารละลายสกัดส่งผลต่อปริมาณซิลิคอนที่เป็นประโยชน์ในดิน เทคนิควิสิเบิลและอะตอมมิกแอบซอร์พชันสเปกโทรสโกปีมีความเหมาะสมในการวัดความเป็นประโยชน์ของซิลิคอนในดินปลูกอ้อยที่เป็นดินเหนียว

คำสำคัญ: ซิลิคอนที่เป็นประโยชน์ สารละลายสกัด อัลตราไวโอเลต-วิสิเบิล อะตอมมิกแอบซอร์พชันสเปกโทรสโกปี

Abstract: Silicon (Si) is a beneficial element for plants, Si availability assessment is determined from Si content in soil extracts using visible spectroscopy (Vis) and atomic absorption spectroscopy (AAS). Different chemical extractants are developed to assess plant-available Si. The objective of this study was to compare Si determination in soil extracts by the molybdenum blue colorimetric method and Atomic Absorption Spectroscopy (AAS) in 36 samples of sugarcane growing soils. Five extractants included Mehlich I, 0.5 M acetic acid, 0.5 M ammonium acetate (pH 4.8), 0.01 M calcium chloride, and 0.01 M potassium chloride. The concentration of extractable Si was found to be maximum by Mehlich-I, followed by 0.5 M acetic acid, 0.5 M ammonium acetate (pH 4.8), 0.01 M calcium chloride, and least by 0.01 M potassium chloride, as determined by both Vis and AAS. The correlation between Vis and AAS determinations was highly correlated in all extractants: Mehlich-I (R^2 = 0.9803), 0.5 M ammonium acetate (pH 4.8) (R^2 = 0.9869), and 0.01 M calcium chloride (R^2 = 0.8902), 0.01 M potassium chloride (R^2 = 0.7406), and 0.5 M acetic acid (R^2 = 0.7287). Si extracted by different extractants was correlated between acid extractants (Mehlich I, 0.5 M acetic acid, and 0.5 M ammonium acetate) and neutral salt extractants (0.01 M calcium chloride and 0.01 M potassium chloride). The results suggest that these five extractants characterize different pools of Si-supplying capacity of the soil, and the efficiency of the extractants is significantly influenced by the extraction pH conditions. The Vis and AAS techniques are both suitable for determining Si availability in sugarcane growing clayey soils.

Keywords: Available Si, Extractants, UV-Vis, AAS

Introduction

Silicon (Si) is the second most abundant element in the Earth's crust. It is responsible for the formation of silicate minerals but it is mostly inert and only slightly soluble (Savant *et al*., 1999). Si fractions in soils are classified as adsorbed, liquid, and solid. Si concentration in the liquid phase is strongly influenced by solid-phase solubility (Tubana *et al*., 2016). Although Si is not an essential nutrient for plants, it is beneficial for induced resistance to biotic and abiotic stresses (Guntzer *et al*., 2012; Majumdar and Prakash, 2020). As a result, Si has been regarded as agronomically essential to long-term crop production. Notably, members of the grass family, such as sugarcane, accumulate a significant amount of Si in their tissues and harvested components (Tubana *et al*., 2016). In terms of sugarcane cultivation, Thailand is the world's fourth-largest producer and the world's second-largest leading sugar-exporting country (Office of the Cane and Sugar Board, 2019). Sugarcane (*Saccharum officinarum* L.) absorbs Si from soil solutions more efficiently than any other mineral nutrient (Meyer and Keeping, 2000), and obtains it in the form of monosilicic acid (H_4SiO_4). Although agricultural soils are mostly made up of silicate minerals, many soils have a limiting factor for crop production and an insufficient supply of plant-available Si (Ma and Yamaji, 2006). A review found that the soil-available Si in clayey soils was higher than in sandy soils (Crusciol *et al*., 2018a; Crusciol *et al*., 2018b). After multiple harvests, Si concentrations in the soil will inevitably be reduced as the same areas have been used for cropping for several decades (Tubana *et al*.,

2016). As a result, the current study focused on sugarcane growing in clayey soils and considered whether Si could improve crop yields as well as provide other benefits.

The numerous soil Si extractants combined with issues surrounding the solubility and availability of Si in agricultural soils necessitate additional research. Because total Si content is unrelated to soluble Si in soils, analysis of soil-available Si is one of the most commonly used methods for determining whether or not Si deficiency will occur in the soil at a locale. To evaluate plant-available Si, various chemical extractants are being developed. Calcium chloride, which only extracts the easily soluble Si fraction, was found to have the highest correlation to sugarcane yield (Crusciol *et al*., 2018b; Haysom and Chapman, 1975); acetic acid is one of the extractants used on a large scale (Crusciol *et al*., 2018a). Phonde *et al.* (2014) discovered a correlation between cane yields and naturally available soil Si extracted with 0.5 M ammonium acetate. In further investigations to verify Ca and Mg extraction in normal soil testing analysis, potassium chloride should be examined for Si extraction. (Crusciol *et al*., 2018a); one of the most basic versions of universal extractants used to extract plant nutrients in soil samples is dilute double acid (Mehlich I) (Mylavarapu *et al*., 2002). Different analytical techniques have been proposed to determine Si in chemical extracts and water samples, including the ultraviolet-visible (UV-Vis) and atomic absorption spectrometry (AAS) (Yang *et al*., 2015) or by ICP (Wang *et al*., 2004). A Vis method uses a light absorption spectrometer based on the molybdenum blue at lower Si concentrations and its higher sensitivity. In addition, dissolved Si can also be determined by AAS using a nitrous oxide–acetylene flame (Liang *et al*., 2015). AAS is still used to measure Si due to its precision, accuracy, and high sensitivity. The cost of analysis is lower than ICP. The objective of this study was to compare Si determination in soil extracts by the molybdenum blue colorimetric method and atomic absorption spectroscopy (AAS) in 36 samples of sugarcane growing soils for development method application in routine analysis laboratories.

Materials and Methods

Sampling sites

The soil sampling sites were selected from sugarcane plantation areas in Khlong Hat District, Sa Kaeo Province, with 36 clayey soil samples collected. There are Thap Phrik (Tpk), Klang Dong (Kld), Wang Nam Yen (Wyn) and Wang Saphung (Ws) soil series. The soil sampling method involved collecting a composite sample at a depth of 0 - 30 centimeters.

Physical and chemical properties analysis

Soil samples from the study areas were air-dried and ground to pass through a stainless sieve of 2 mm. All samples were analyzed for the basic physical and chemical properties of soil. The ranges of basic physical and chemical properties of the soils were: pH 5.58 - 8.13, organic matter 33.05 - 62.08 g kg^{-1}, Bray II-available phosphorus 0.00 - 0.04 g kg^{-1}, exchangeable potassium 0.03 - 0.27 g kg^{-1}, exchangeable calcium 1.38 - 10.39 g kg^{-1}, and exchangeable magnesium 0.28 - 1.18 g kg^{-1}. The texture of the soil samples ranged from clay loam to clay, though the majority was clay (%clay 27.09 - 58.61). pH was based on soil: water 1 : 1 (Thomas, 1996), with organic matter determined by Walkley and Black Titration (Walkley and Black,

1934), available phosphorus by the Bray II method (Bray and Kurtz, 1945) and extractable K, Ca, and Mg by 1 M NH_4OAc pH 7.0 (Pratt, 1965), while soil texture was determined by a pipette method (Day, 1965; Kilmer and Alexander, 1949).

Methods for extraction of soil-available Si

Extractable Si was extracted using the conventional method; five Si extractants are shown in Table 1. The Si extracted from the soil solution was separated into two experiments to compare the method with the Vis and AAS. For all analyses of Si in soil, plastic laboratory vessels were used and washed successively in a 5 % HNO_3 and a 0.1 M NaOH for greater than or equal to 5 hours each and then rinsed with deionized water after each bath.

Determination of soil Si availability

The Vis analysis for Si was carried out with a Lambda 265 (UV-Vis; Lambda 265; PerkinElmer; USA) using a modified molybdenum blue method developed by Duboc *et al.* (2019). The developed color method is suitable for analyzing water samples and chemical extracts. Such water samples often contain greater concentrations of phosphate, sodium hydroxide, suspended materials, and other impurities. Specifically, an aliquot of sample extract containing 1 ml was added to a marked 10-ml centrifuge tube, deionized water 7.75 ml, acidified molybdate with 0.50 ml, and then mixed by hand vortexing. After 10 ± 3 min, 0.5 mL of 20 % tartaric acid was added and then mixed by hand vortexing. After 5 ± 1 min, 0.25 ml of the 1-amino 2-naphthol-4-sulphonic acid reducing agent was added to the solution and then mixed by hand vortexing. After allowing 1 hour for color development, absorbance was measured at a wavelength of 630 nm. Standard curves were prepared as 0.0, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 mg Si L^{-1}. The AAS analysis for Si was carried out with a Varian 240 (AAS; AA240; Varian; Palo Alto, CA, USA). Flames were produced by a nitrous oxide - acetylene. The wavelength of 251.6 nm was used for the AAS analysis of solution Si. Method validation was reported with a percentage of recovery by spiking a known amount of Si standard. Analytical solutions were prepared using an appropriate dilution of 1000 µg mL^{-1} Si atomic absorption spectroscopic standard (PerkinElmer; USA) into each extract of selected soil samples and measuring the difference between the spiked sample and the original sample.

Table 1. Five extraction methods for determination of soil-available Si

No.	Extractant	Soil: solution ratio	pH	Period (h)	References
1	Mehlich I (0.05 M HCl, 0.0125 M H_2SO_4)	1 : 10	1.27	1	Modified from Mylavarapu *et al.* (2002)
2	0.5 M Acetic acid	1 : 10	2.54	1	Korndörfer *et al.* (2004); Snyder (2001)
3	0.5 M NH_4OAc	1 : 10	4.84	1	Fox *et al.* (1967)
4	0.01 M $CaCl_2$	1 : 10	5.46	1	Korndörfer *et al.* (2004)
5	0.01 M KCl	1 : 10	5.67	1	Crusciol *et al.* (2018b)

Statistical data analysis

The relationships among available Si in soil using various extractants for Si assessment in clayey soils and comparing the Si determination in these extracts by the molybdenum blue colorimetric method and atomic absorption spectrometry (AAS) were tested using Statistica software.

Results and Discussion

Comparison of soil Si determined by Vis and AAS in different extractants

The correlation between Vis and AAS determinations was highly correlated in all extractions: Mehlich-I (R^2 = 0.9803), 0.5 M ammonium acetate (pH 4.8) (R^2 = 0.9869), and 0.01 M calcium chloride extractions (R^2 = 0.8902), 0.01 M potassium chloride (R^2 = 0.7406), and 0.5 M acetic acid (R^2 = 0.7287). Linear regressions indicated that the amount of soil Si estimated by Vis analysis was slightly higher than that by AAS analysis in all extractions (Figure 1).

Ammonium molybdate reacts exclusively with monosilicic acid to form a colored complex, enabling an alternative to the molybdenum blue method to determine only monosilicic acid (Govett, 1961). Consequently, it has been utilized to study the kinetics of monosilicic acid release from non-monosilicic species by observing the time-dependent color development of the Si-Mo complex (Wada and Wada, 1980; Xu and Harsh, 1993). Si determination can be incorporated into routine soil testing using AAS analysis, which is more expeditious.

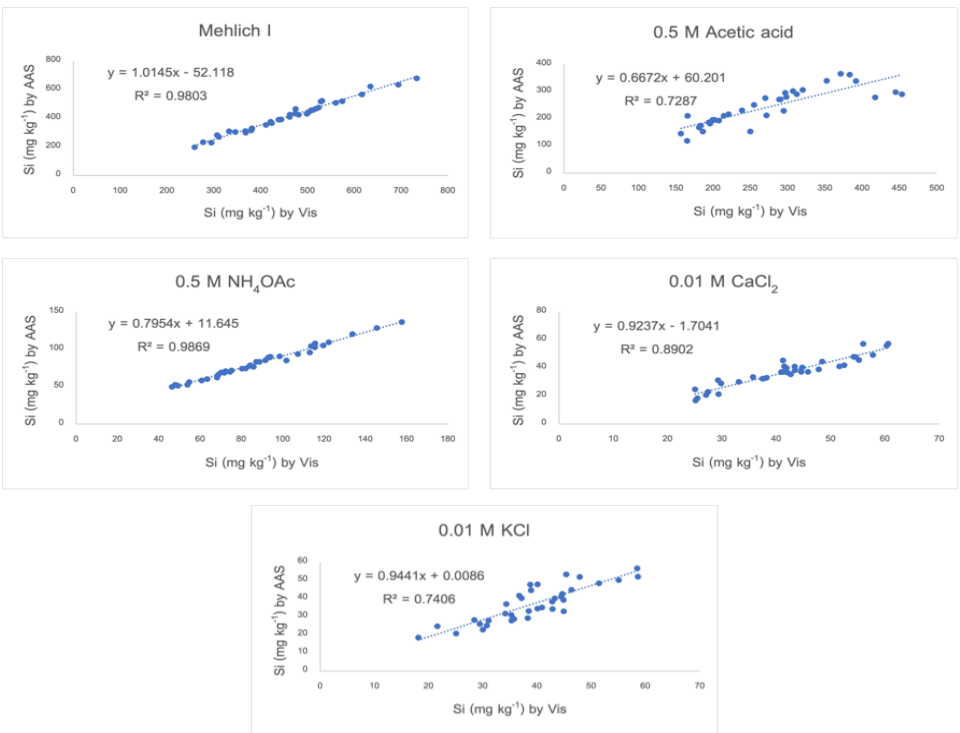

Figure 1. Correlation of soil Si determined by Vis and AAS in different extractants

Mehlich I may have been able to extract more Si than the four extractants and depolymerize all of the non-monomeric Si in the solution. According to the strong correlation between the slopes of the linear regression for Mehlich I, extractable Si that was discovered by AAS and Vis was close to a ratio of 1 : 1. This outcome was in line with earlier research that found high acidity to be the most crucial element in maintaining the stability of monomeric Si (Iler, 1979). A further indication that these reagents were suitable to extract or preserve labile monosilicic acids in solutions was the high correlation between AAS and Vis methods for 0.5 M NH_4OAc, which showed relationships that were slightly less than 1 : 1. The correlation between Vis and AAS determinations in the 0.5 M acetic acid and 0.01 M potassium chloride methods suggests that special care must be taken with soil samples containing a high concentration of soil-available Si.

The spike recovery of extract samples determined by AAS and Vis is shown in Table 2. The recovery of Si in spiked soil samples was between 89.8 - 102.2 % for Vis and 65.5 - 77.2 % for AAS determination. A Vis determination with a return percentage close to 100 percent is regarded as highly accurate. In all extractions, spike recovery by the AAS-Si was lower than spike recovery by the Vis-Si because the samples were diluted before analysis.

Overall, these results demonstrated that both AAS and Vis determinations for Si analysis exhibited minor matrix effects in the various extractions. The Vis and AAS techniques are both suitable for determining Si availability in sugarcane-growing clayey soils. However, Vis also has limitations due to color measurement. The reaction must take one hour for the color to develop. This procedure could potentially interfere with other substances. The Vis utilizes more chemicals but it is less susceptible to tool deterioration than AAS, which requires more equipment and gas to operate the tool. The AAS should be determined using the flame technique because this method has the added benefits of being both dependable and time-efficient. Each element has a characteristic absorption wavelength. However, nitrous oxide must be used as the oxidant instead of air for elements such as Si that form refractory oxides.

Table 2. Spike recovery for Si determination by Vis and AAS in five different extractants

Extractants	Vis (%)	AAS (%)
Mehlich I	102.2	76.9
0.5 M Acetic acid	97.5	77.2
0.5 M NH_4OAc	89.8	65.5
0.01 M $CaCl_2$	98.9	71.8
0.01 M KCl	98.6	72.0

Relationship between available Si in soils extracted with different extractants

The Si extraction pool of five extractants from the soil, expressed by overall means of soil Si over 36 samples, is shown in Figure 2. The highest extractable was found in Mehlich I, followed by 0.5 M acetic acid, 0.5 M ammonium acetate, 0.01 M calcium chloride and 0.01 M potassium chloride, respectively. Meanwhile, a similar tendency was found in AAS determination.

The Si content of the acid extractant (Mehlich I, 0.5 M acetic acid, and 0.5 M NH_4OAc) was greater than that of the neutral salt extractant (0.01 M $CaCl_2$ and 0.01 M KCl). In general, Si extractors that use acidic solutions perform better than neutral ones because Si can be extracted more efficiently from the soil when the pH of the extractant is low (Narayanaswamy and Prakash, 2010). Consequently, Mehlich I extracted more available Si from all soils than other extractants. It could be concluded that the extraction conditions and soil composition (particularly primary silicates, clay minerals, and amorphous components) have a significant effect on the efficiency of the extractants (Berthelsen and Kordorfer, 2005; Sailaja *et al.*, 2019). Wang *et al.* (2004) also demonstrated similar results and reported that various extractants possessed the characteristics of soil Si-supplying capacity pools.

A similar trend was observed in neutral salt extractants (0.01 M $CaCl_2$ and 0.01 M KCl). The plant-available Si contents extracted by these two extractants were found to be positively correlated with each other, as shown in Figure 3.

This relationship implies that both methods could extract the same soil Si-species. If it does not change the pH of the soil solution, the salt that promotes ionic strength stabilization ($CaCl_2$) should be a good Si extractant. The 0.01 M $CaCl_2$ is a diluted neutral salt that should be capable of extracting soluble Si, which represents the more labile forms in soils, primarily monomeric silicic acid. Although the chemical process involved has not been studied extensively and little has been done to gain a better understanding of the kinetics of ion release from the solid phase to the solution phase, the extractant, 0.01 M $CaCl_2$, simulates the ionic strength of the solution (Crusciol *et al.*, 2018a). Poor correlations between 0.01 M $CaCl_2$ and 0.01 M KCl and other acid extractants

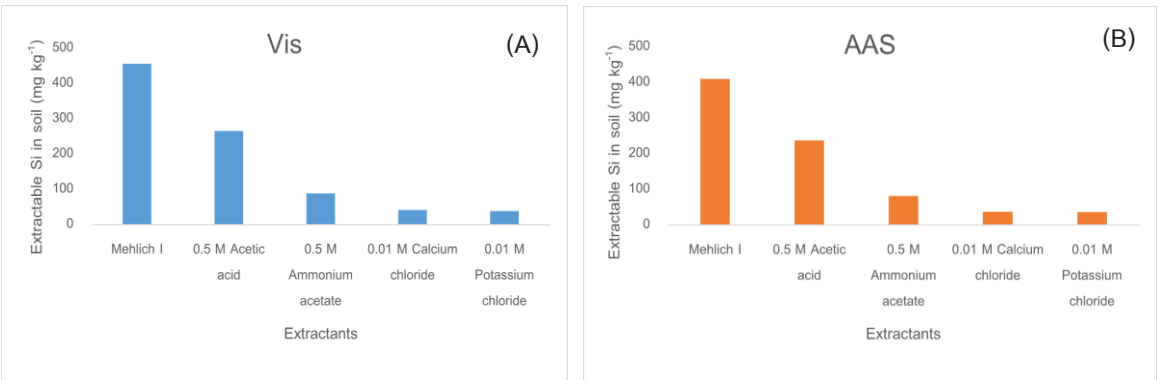

Figure 2. Comparison of mean extractable Si for 36 soils by five extractants using Vis (A) and AAS (B) methods

suggest that the 0.01 M $CaCl_2$ extraction (Table 3 and 4), like the KCl extraction procedure, may only reflect a transient status of soil soluble Si. A lower linear correlation was observed between 0.01 M $CaCl_2$ and 0.01 M KCl between Mehlich I, 0.5 M acetic acid, and 0.5 M NH_4OAc extractions, as shown in Tables 3 and 4. These methods may extract three different forms of Si. Melhich I extracted specifically adsorbed Si, while 0.5 M acetic acid and 0.5 M NH_4OAc dissolved some exchangeable Si. At the same time, 0.01 M $CaCl_2$ and 0.01 M KCl extracted more easily soluble Si. These findings suggested that the Si removed by these extractants could be divided into two categories, including acid extractants (Mehlich I, 0.5 M acetic acid, and 0.5 M NH_4OAc) and neutral salt extractants (0.01 M $CaCl_2$ and 0.01 M KCl). Soil extraction with 0.01 M $CaCl_2$ and 0.01 M KCl reflects a primarily transient pool of soluble Si for a specific soil condition. Some researchers have used this extraction, particularly on moist samples, to characterize mobile forms of Si, with monosilicic acid being the dominant form, along with polysilicic acids and both inorganic and organic Si complexes (Ma and Takahashi, 2002; Matichenkov *et al*., 2000). Because the polymerization and depolymerization of soluble Si are heavily influenced by soil pH, salt concentration, and dry-wet cycles (Iler, 1979), it is doubtful that this method can provide a reasonable Si nutritional status for the soil over the course of a growing season. The second category of Mehlich I, 0.5 M acetic acid and 0.5 M NH_4OAc extractants, removes Si that is either mobile or loosely bound, as well as some fractions in amorphous forms (Matichenkov *et al*., 2000; Savant *et al*., 1999). Mehlich I extracts extremely high levels of Si. It should be noted that Mehlich I, as a multi-element extractant, has been widely used by many researchers and laboratories for the routine testing of soil available P, K, Ca, Mg, and even certain micronutrients (Mylavarapu *et al*., 2002). Nonetheless, Mehlich I has not been compared to other extractants in terms of predicting plant-available Si.

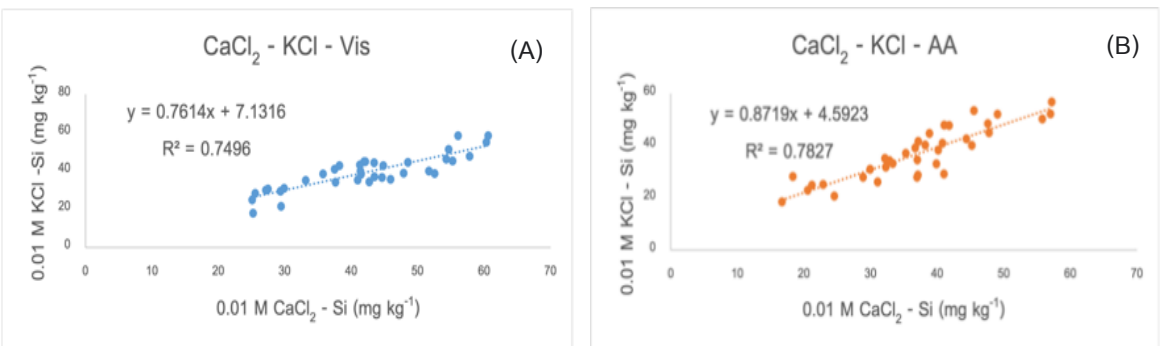

Figure 3. A significant linear correlation documented between calcium chloride (A) and potassium chloride (B) extractions

Table 3. A linear correlation between soil Si extracted by five extractants using Vis

Y\X	Mehlich I	Acetic acid	NH_4OAc	$CaCl_2$
Acetic acid	y = 0.3954x + 85.421 R^2 = 0.2875*			
NH_4OAc	y = 0.1866x + 3.5582 R^2 = 0.5926*	y = 0.2304x + 27.426 R^2 = 0.4912*		
$CaCl_2$	y = 0.0226x + 31.754 R^2 = 0.0597	y = 0.01x + 39.387 R^2 = 0.0064	y = -0.028x + 44.526 R^2 = 0.0054	
KCl	y = 0.0304x + 25.285 R^2 = 0.1401*	y = 0.0195x + 33.968 R^2 = 0.0313	y = 0.0339x + 36.134 R^2 = 0.0103	y = 0.7614x + 7.1316 R^2 = 0.7496*

* Indicates the significance of values at $P < 0.05$

Table 4. A linear correlation between soil Si extracted by five extractants using AAS

Y\X	Mehlich I	Acetic acid	NH_4OAc	$CaCl_2$
Acetic acid	y = 0.2903x + 118.32 R^2 = 0.2663*			
NH_4OAc	y = 0.1369x + 25.955 R^2 = 0.5224*	y = 0.232x + 27.06 R^2 = 0.4746*		
$CaCl_2$	y = 0.0311x + 24.364 R^2 = 0.1243*	y = 0.0355x + 28.692 R^2 = 0.0513	y = 0.0236x + 35.186 R^2 = 0.0026	
KCl	y = 0.0243x + 27.009 R^2 = 0.0778	y = 0.0372x + 28.141 R^2 = 0.0578	y = -0.0196x + 38.572 R^2 = 0.0018	y = 0.8719x + 4.5923 R^2 = 0.7827*

* Indicates the significance of values at $P < 0.05$

To further explain the difference in extractability, the measured pH in the pure extractants used in this study followed the order Mehlich I (1.27) < 0.5 M acetic acid (2.54) < 0.5 M NH_4OAc (4.84) < 0.01 M $CaCl_2$ (5.46) < 0.01 M KCl (5.67). These orders corresponded to the total amount of extractable Si found in this study. Previously, it was demonstrated that a high concentration of H^+ dissolved aluminosilicates and released Si into a solution (Beckwith and Reeve,

1964; Wang *et al*., 2004). However, the solubility of crystalline or amorphous Si was essentially constant at solution pH 2-8.5, so the kinetic factor would prevent the dissolved Si from reaching a new equilibrium with a solid phase (e.g., quartz or amorphous Si) (Iler, 1979). As a result, an inverse relationship between soil solution pH and Si concentration has frequently been observed (Wang *et al*., 2004). Thus, Mehlich I extracts more soil Si than any other extractant tested in this study. The extraction of more Si by Mehlich I than 0.5 M acetic acid and 0.5 M NH_4OAc suggests that factors other than acidity may dominate soil Si extractability. According to Iler (1979), certain anions affect the dissolution of silicate minerals or the displacement of strongly adsorbed Si. Acidity and anions could have an additive effect on Si release from soils. The combined effect of dilute double acid could explain why Mehlich I (0.05 M HCl, 0.0125 M H_2SO_4) extracted the most soil Si, followed by 0.5 M acetic acid and 0.5 M NH_4OAc extractions.

According to Haynes (2014), the pH of the extractant solution can easily lead to an overestimation of the soluble Si content when acetic acid is used. Some acetates (CH_3COO^- NH_4^+) and acetic acid (CH_3COOH) are used to remove soluble Si and certain exchangeable Si from soils (Sailaja *et al*., 2019). Because AAS and UV-Vis determinations of soil-extractable Si yield comparable results, which suggest that non-monosilicic soluble species and/or colloidal Si may precipitate out of the aqueous phase during 0.5 M NH_4OAc extraction. The polymerization of monomeric Si and coagulation of soluble polysilicic acids as well as colloidal Si increased with increasing salt concentration, particularly between pH 3.5 and 5.5 (Iler, 1979). To prevent clay mineral destruction during the extraction of soluble and exchangeable Si, the pH should be adjusted to 4.5 - 4.8, as suggested by Ayres (1966), Cheong and Halais (1970), and Fox *et al.* (1967).

Conclusion

The correlation between Vis and AAS determinations was highly correlated in all extractions: Mehlich-I (R^2 = 0.9803), 0.5 M NH_4OAc (pH 4.8) (R^2 = 0.9869), and 0.01 M $CaCl_2$ extractions (R^2 = 0.8902), 0.01 M KCl (R^2 = 0.7406), and 0.5 M acetic acid (R^2 = 0.7287). Linear regressions indicated that the amount of soil Si determined by Vis analysis was slightly higher than that by AAS analysis in all extractions. The Vis and AAS techniques are both suitable for determining Si availability in sugarcane-growing clayey soils. However, the benefit of this study is its ability to determine the amount of Si available for all types of soil globally, and those methodologies have been applied to soil samples to extract the soil-available Si and identify the crop Si requirement. Melhich I extracted specifically adsorbed Si, while acetic acid and NH_4OAc dissolved some exchangeable Si as well. Calcium chloride and potassium chloride extracted more easily soluble Si. The lower pH of the extractant has a higher Si extraction power from the soil. The Si extraction pool from soil was found to be the maximum in Mehlich I, followed by 0.5 M Acetic acid, 0.5 M NH_4OAc, 0.01 M $CaCl_2$, and the least by 0.01 M KCl. The results suggest that these five extractants characterize different pools of Si-supplying capacity in the soil and that the efficiency of the extractants is significantly influenced by the extraction pH conditions. More

research is needed to determine the relationship between available Si in soil using various extractant solutions and the Si yield of sugarcane, as well as to identify the most suitable Si extractant in the soil and how to manage the availability of Si in soil. Mehlich I and KCl could be alternative methods for extracting Si because they are frequently used to determine available plant nutrients in routine soil analysis and are relatively inexpensive. Further, the KCl method has additional advantages over others as it is easy to prepare and does not require a concentration of acids, thus reducing risk for the operator.

References

Ayres, A.S. 1966. Calcium silicate slag as a growth stimulant for sugarcane on low-silicon soils. Soil Science 101(3): 216-227.

Beckwith, R.S. and R. Reeve. 1964. Studies on soluble silica in soils. II. The release of monosilicic acid from soils. Australian Journal of Soil Research 2: 33-45.

Berthelsen, S. and G.H. Kordorfer. 2005. Methods for silicon analysis in soil, plant, and fertilizers. pp. 85-91. *In*: Proceedings of the third International Conference on Silicon in Agriculture, Federal University of Uberlandia, Uberlandia in Brazil.

Bray, R.H. and L.T. Kurtz. 1945. Determination of total, organic, and available forms of phosphorus in soils. Soil Science 59(1): 39-46.

Cheong, Y.W.Y. and P. Halais. 1970. Needs of sugar cane for silicon when growing in highly weathered Latosols. Experimental Agriculture 6(2): 99-106.

Crusciol, C.A.C., D.P. de Arruda, A.M. Fernandes, J.A. Antonangelo, L.R.F. Alleoni, D.M. Fernandes and J.M. McCray. 2018a. Methods and extractants to evaluate silicon availability for sugarcane. Scientific Reports 8(1): 1-14.

Crusciol, C.A.C., D.P. de Arruda, A.M. Fernandes, J.A. Antonangelo, L.R.F. Alleoni, D.M. Fernandes and J.M. McCray. 2018b. Evaluation of soil extractants for silicon availability for sugarcane. Journal of Plant Nutrition 41(17): 2241-2255.

Day, P.R. 1965. Particle fractionation and particle-size analysis. pp. 545-567. *In*: C.A. Black, D.D. Evans, L.E. Ensminger, J.L. White and F.E. Clark (eds.). Methods of Soil Analysis Part 1: Physical and Mineralogical Properties, Including Statistics of Measurement and Sampling. American Society of Agronomy, Inc., Madison, Wisconsin.

Duboc, O., A. Robbe, J. Santner, G. Folegnani, P. Gallais, C. Lecanuet, F. Zehetner, P. Nagl and W.W. Wenzel. 2019. Silicon availability from chemically diverse fertilizers and secondary raw materials. Environmental Science & Technology 53(9): 5359-5368.

Fox, R.L., J.A. Silva, O.R. Younge, D.L. Plucknett and G.D. Sherman. 1967. Soil and plant silicon and silicate response by sugarcane. Soil Science Society of America Journal 31(6): 775-779.

Govett, G.J.S. 1961. Critical factors in the colorimetric determination of silica. Analytica Chimica Acta 25(1): 69-80.

Guntzer, F., C. Keller and J.-D. Meunier. 2012. Benefits of plant silicon for crops: A

review. Agronomy for Sustainable Development 32(1): 201-213.

Harvey, D.T. 2000. Modern Analytical Chemistry. McGraw-Hill, New York. 817 p.

Haynes, R.J. 2014. A contemporary overview of silicon availability in agricultural soils. Journal of Plant Nutrition and Soil Science 177(6): 831-844.

Haysom, M.B.C. and L.S. Chapman. 1975. Some aspects of the calcium silicate trials at Mackay. pp.117-122. *In*: Proceeding of the Queensland Society of Sugar Cane Technologists. Mackay, Queensland.

Iler, R.K. 1979. The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica. John Wiley & Sons, NewYork. 866 p.

Kilmer, V.J. and L.T. Alexander. 1949. Methods of making mechanical analyses of soils. Soil Science 68(1): 15-24.

Korndörfer, G.H., H.S. Pereira and A. Nolla. 2004. Silicon analysis: Soil, plant and fertilizer. Technical Bulletin 2. GPSi/ICIAG/UFU, Uberlandia. 34 p.

Liang, Y., M. Nikolic, R. Bélanger, H. Gong and A. Song. 2015. Silicon in Agriculture: From Theory to Practice. Springer, Dordrecht. 235 p.

Ma, J.F. and E. Takahashi. 2002. Soil, Fertilizer, and Plant Silicon Research in Japan. Elsevier, Amsterdam. 97 p.

Ma, J.F. and N. Yamaji. 2006. Silicon uptake and accumulation in higher plants. Trends in Plant Science 11(8): 392-397.

Majumdar, S. and N.B. Prakash. 2020. An overview on the potential of silicon in promoting defence against biotic and abiotic stresses in sugarcane. Journal of Soil Science and Plant Nutrition 20: 1969-1998.

Matichenkov, V.V., E.A. Bocharnikova, D.V. Calvert and G.H. Snyder. 2000. Comparison study of soil silicon status in sandy soils of south Florida. pp. 132-137. *In*: Proceedings of the Soil and Crop Science Society of Florida.

Meyer, J.H. and M.G. Keeping. 2000. Review of research into the role of silicon for sugarcane production. pp. 29-40. *In*: Proceedings of the South African Sugar Technologists' Association.

Mylavarapu, R.S., J.F. Sanchez, J.H. Nguyen and J.M. Bartos. 2002. Evaluation of mehlich-1 and mehlich-3 extraction procedures for plant nutrients in acid mineral soils of Florida. Communications in Soil Science and Plant Analysis 33(5-6): 807-820.

Narayanaswamy, C. and N.B. Prakash. 2010. Evaluation of selected extractants for plant-available silicon in rice soils of southern India. Communications in Soil Science and Plant Analysis 41(8): 977-989.

Office of the Cane and Sugar Board. 2019. Sugancane cultivated area report year 2018/2019. (Online). Available: http://www.ocsb.go.th/upload/journal/fileupload/923-1854.pdf (October 1, 2020).

Phonde, D.B., P.S. Deshmukh, K. Banerjee and P.G. Adsule. 2014. Plant available silicon in sugarcane soils and its relationship with soil properties, leaf silicon and cane yield. An Asian Journal of Soil Science 9(2): 176-180.

Pratt, P.F. 1965. Potassium. pp.1022-1030. *In*: C.A. Black, D.D. Evans, L.E. Ensminger,

J.L. White and F.E. Clark (eds.). Methods of Soil Analysis Part 2: Chemical and Microbiological Properties. American Society of Agronomy Inc., Madison, Wisconsin.

Sailaja, V., K. Rajamani and B.H. Kumara. 2019. Research review on extracting methods of silicon from soil. International Journal of Chemical Studies 7(6): 477-481.

Savant, N.K., G.H. Korndörfer, L.E. Datnoff and G.H. Snyder. 1999. Silicon nutrition and sugarcane production: A review. Journal of plant nutrition 22(12): 1853-1903.

Snyder, G.H. 2001. Methods for silicon analysis in plants, soils, and fertilizers. Studies in Plant Science 8: 185-196.

Thomas, G.W. 1996. Soil pH and soil acidity. pp.475-490. *In*: D.L. Sparks, A.L. Page, P.A. Helmke, R.H. Loeppert, P.N. Soltanpour, M.A. Tabatabai, C.T. Johnston and M.E. Sumner (eds.). Methods of Soil Analysis Part 3: Chemical Methods. Soil Science Society of America, Inc., Madison, Wisconsin.

Tubana, B.S., T. Babu and L.E. Datnoff. 2016. A review of silicon in soils and plants and its role in US agriculture: History and future perspectives. Soil Science 181(9/10): 393-411.

Wada, S-I and K. Wada. 1980. Formation, composition and structure of hydroxy-aluminosilicate ions. European Journal of Soil Science 31(3): 457-467.

Walkley, A. and I.A. Black. 1934. An examination of the Degtjareff methods for determining soil organic matter, and a proposed modification of the chromic acid titration method. Soil Science 37(1): 29-38.

Wang, J.J., S.K. Dodla and R.E. Henderson. 2004. Soil silicon extractability with seven selected extractants in relation to colorimetric and ICP determination. Soil Science 169(12): 861-870.

Xu, S. and J.B. Harsh. 1993. Labile and nonlabile aqueous silica in acid solutions: Relation to the colloidal fraction. Soil Science Society of America Journal 57(5): 1271-1277.

Yang, H., C. Li, C. Wei, M. Li, X. Li, Z. Deng and G. Fan. 2015. Molybdenum blue photometry method for the determination of colloidal silica and soluble silica in leaching solution. Analytical Methods 7(13): 5462-5467.