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釩在臺灣不同類型土壤的分佈與有效性評估

Assessment of vanadium distribution and availability in different types of soil in Taiwan

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釩在臺灣不同類型土壤的分佈與有效性評估
Assessment of vanadium distribution and availability in different types of soil in Taiwan

本論文係吳卓穎君（r05623038）在國立臺灣大學農業化學學系完成之碩士學位論文，於民國 108 年 06 月 25 日承下列考試委員審查通過及口試及格，特此證明

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摘要

2001 到 2017 年間，全球工業中釩的需求量增加超過一倍，如此迅速成長的釩需求也成為環境品質以及人類健康的潛在威脅。然而，關於釩的地質化學方面的知識仍十分薄弱。因此，本研究欲利用 17 個採集自臺灣不同母質 (板岩、砂頁岩互層、安山岩、玄武岩以及蛇紋岩) 之土壤剖面進行釩全面性的探討，包含其來源、潛在移動性、剖面中的分佈以及生物有效性。結果顯示，由 ICP-AES 測定氫氟酸消化後之供試土樣中總釩濃度為 35.4-475 mg/kg 其平均值為 182 mg/kg，其中，玄武岩母質的土樣中總釩濃度遠高於其餘土樣。此外，風化程度並未對總釩濃度有顯著影響。攜帶式 X 射線螢光光譜儀之測定結果顯示其在土樣中釩的快速檢測具有高度實用性。BCR 序列萃取結果指出，供試土樣中的釩主要固定於礦物晶格中，然而鐵錳氧化物結合態的釩也佔有可觀的比例。利用 DCB 萃取法以及電子探針顯微分析儀，本研究更進一步證實釩在母質以及風化後的土壤中皆具有高度親鐵性。釩的 X 射線吸收近邊緣結構圖譜顯示在供試土樣中釩的主要化學物種 V(IV) (VO^{2+}) 和 V(V) ($H_2VO_4^-$)，此兩者皆可有效地被 $NaHCO_3$ 所萃取。以小白菜 (*Brassica rapa* var. chinensis) 進行之盆栽試驗顯示 $NaHCO_3$ 土壤釩萃取量和植物地上部之釩吸收量呈顯著正相關，此結果同時證明，釩潛在的生物有效性可由包含土壤總釩濃度以及土壤酸鹼值之多變因回歸等式計算而出。

關鍵字：生物有效性；電子探針顯微分析儀；土壤母質；序列萃取；X 射線吸收近邊緣結構圖譜

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Abstract

The global vanadium (V) demand in industry increased over 100% from 2001 to 2017, thus the burgeoning V demand leads to potential risks to environment quality and human health. However, there is still a knowledge gap in pedogeochemical aspect of V. This study attempted to explore the sources, fractionation, profile distribution, and bioavailability of V from 17 soil pedons with 94 horizon samples in Taiwan. These pedons were derived from different parent materials including slate, sandstone interstratified with shale, andesite, basalt, and serpentine. The total V content was measured by using ICP-AES followed with HF-digestion and portable x-ray fluorescence (pXRF). The total V content by ICP-AES in the soils ranged from 35.4 to 475 mg/kg with an average level of 182 mg/kg. Moreover, the total V content in the basalt-derived soils was much higher than those of other parent materials. Nevertheless, the weathering degree of soil did not clearly affect the V level among soils. Furthermore, the pXRF showed high practicality in rapid V determination. The Commission of the European Communities Bureau of Reference (BCR) selective sequential extraction (SSE) method indicated V was primarily fixed in the mineral lattices. However, the Fe/Mn-oxide-bound fraction was remarkably observed. The siderophilic affinity of V in parent materials and derived soils was further confirmed by the dithionite-citrate-bicarbonate (DCB)-extractable Fe and element mapping conducted with electron probe X-ray microanalyzer (EPMA). V(IV) (VO^{2+}) and V(V) ($H_2VO_4^-$) were the dominant species of V in the soils demonstrated by the V K-edge X-ray absorption near edge structure (XANES) spectra, while both can be efficiently extracted by $NaHCO_3$ extraction to predict a better bioavailability of V than $CaCl_2$, HCl, and EDTA. The plant assay conducted with Chinese cabbage (*Brassica rapa* var. chinensis) revealed the soil $NaHCO_3$ extractable V positively and significantly correlated with the plant shoot uptake of V, supporting the potentially bioavailable V can be computed by using multivariate regression equation considering the soil total V and pH.

Key words: bioavailability; EPMA; parent material; sequential extraction; XANES.

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Chapter 1 Background

According to the LARGO Resources (2018), global vanadium (V) demand in industry increased over 100% from 2001 to 2017 while the global V market will has an 11.24% growth during the period 2017-2021. This increase of global V demand could lead to potential leakage of V into environment. For instance, Hernandez et al. (2012) reported that the soil V content in the industrial area was much higher than that in the agricultural area of Salamanca in central Mexico. Several studies documented an excessive intake of V caused the reduced number of red blood cells, interruption of neural system and growth retardation in animals while photosynthetic pigments and protein reduction, membrane damage and DNA degradation in plants (Imtiaz et al., 2016; Park et al., 2016; Poggioli et al., 2001). Considering the biological toxicity of V abovementioned and the potential environmental risk, V geochemistry has received numerous attentions than before. However, most of the studies were conducted in temperate climatic zone with limited soil diversity.

Taiwan locates on the plate boundary belt. The arc-continent collision between the Philippine Sea plate and the Eurasian plate as well as the constantly volcanic activity gave us diverse geographic regions and highly geologic diversity. Moreover, Taiwan is run across by the Tropic of Cancer which divides the island into tropical and subtropical climatic zone and with more than 2500 mm of rainfall every year generally. Therefore, Taiwan contains 11 of the 12 soil orders in Soil Taxonomy (Chen et al., 2015). Additionally, the control standards of heavy metal contamination in soil in Taiwan are only for As, Hg, Cd, Cr, Cu, Ni, Pb, and Zn revealing V is still less concerned. To provide the fundamental information for soil V in Taiwan and to fulfill the knowledge

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gap of soil V in tropical and subtropical climatic zone, Taiwan is the suitable site to start a comprehensive research, which includes resources, geochemical fractions, species distribution and bioavailability for soil V.

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Chapter 2 Introduction

2.1. Chemical characteristics of vanadium

V is an element belonging to group VB and with atomic number 23 in the chemical period table. V was first discovered by Andrés Manuel del Río, a Spanish-Mexican mineralogist in 1801. It is a silvery grey, ductile and hard transition metal. Being one of the transition metals, V has variable oxidation state from -1 to +5, however, only V(III), V(IV) and V(V) species can participate in reactions in biosphere (Huang et al., 2015).

2.2. Application of vanadium in industry

According to Metal Bulletin 28th International Ferroalloys Conference, about 92% of global V consumption is in steel industries producing high strength low alloy steel (HSLA steel). Nitrides and carbides of V are added to steels in order to give better toughness, hardening response and high wear resistant. There is a wide application of HSLA steels in engineering, such as railways, architectural structures and petroleum pipelines (Bayer and Becherer, 1989). About 4% of V demand is from titanium alloys for aerospace purposes. The addition of V to titanium alloys provides the solid solubility which raises the yield strength after the heat treatment is carried out. V also been used in petro chemistry, catalysts, pollution control applications as well as ceramic pigments, special glasses and other chemical industry applications which account for about 3% of the total consumption (Horie et al., 2010). And about 1% of the global V usage is from producing V redox batteries (Perron, 2001).

2.3. Biological toxicity of vanadium

Dobritskaya (1969) found out the content of V can reach 12 mg/kg in certain species of legume, proving V takes part in catalysis of nitrogen fixation while replacing molybdenum during nitrogen fixation. Nevertheless, being an analogue of phosphate, V can inference phosphate metabolism causing membrane rupture and synthesis inhibition of protein and chlorophyll (Lin et al., 2009; Somasundaram et al., 1994). Two genotypes of chickpea: C-44 (tolerant to V stress) and Balkasar (sensitive to V stress) were used to investigate the different responses of V toxicity between tolerant and sensitive lines. The results of Balkasar pointed out an inducing DNA degradation depending on levels of V as well as significant reducing of soluble proteins and photosynthetic pigments, increasing in ion leaching and antioxidant enzyme activities such as superoxide dismutase, catalase and peroxidase (Imtiaz et al., 2018). To observe the effects of soil V on plants growth under different time scales, 4 soils from Denmark, Sweden and Belgium were amended with $NaVO_3$. V toxicity to tomato and barley plant was evaluated in freshly spiked soils and the relatively aged soils which were equilibrated for 330 days after spiking. Suppression in root elongation of both plants occurred in freshly spiked soils and aged soils. However, aged treatments gave rise to less suppression on roots growth while the root elongation ratio between 2 treatments could reach 2.3. In addition, at the same added V content, shoot V contents of freshly spiked treatments were significantly higher than aged treatments indicating the growth inhibition was proportional to V contents in plants. The results suggested that V aging processes reduced the toxicity of V by decreased its bioavailability and mobility (Baken et al., 2012).

In northern Sweden, 23 heifers died of acute V toxicity in 10-day period. The farm

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used basic slag as fertilizer, which was a by-product of steel manufacturing industry containing about 3% of V, and the heifer were fed with fresh hay. First round of signs of illness appeared at 11 days after the fertilizer application including black diarrhea, lethargy, dehydration, spontaneous abortions, pulmonary lesions, and neurological disturbances. (Frank et al., 1996). The other team gave rats water solution of $VOSO_4$ (300 mg/L) as drinks 3 days before giving birth and up to the 100th day of the extra uterine life. In the offspring with V treatment, growth retardation occurred during the lactation period and after weaning. Moreover, lethality was higher in the V-treated rats during the weaning (Poggioli et al., 2001). On the other hand, a study used isolated mitochondria of rats showed different contents of $NaVO_3$ induced significant progresses in reactive oxygen species (ROS) formation, ATP depletion, glutathione (GSH) oxidation, mitochondrial outer membrane rupture, mitochondrial swelling and cytochrome c release before the mitochondrial potential collapse happened. The symptoms mentioned above caused mitochondrial respiratory complex I、II and III interference which led to V-induced liver toxicity (Hosseini et al., 2013). Park et al. (2016) added V oxide nanoparticles (VO NPs) into the drink water for mice. The results pointed out that S-V_2O_5 and S-V_2O_3 nanoparticles could be easily accumulated in animal tissues with the accumulated level in the order of heart > liver > kidney > spleen. In addition, tissue levels of redox reaction-related elements and electrolytes were altered in the heart of treated mice as well as the reduction of total protein and albumin levels.

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2.4. Vanadium in soils

2.4.1. Natural background

V is widely presented in lithosphere that around 65000 tons of V enters the environment each year naturally (Galloway et al., 1980). The average content of V in earth's crust is 135 mg/kg while there are only few minerals that V forms, which are vanadinite, $Pb_5Cl(VO_4)_3$, roscoelite, $KV_2(OH)_2(AlSi_3O_{10})$, mottramite, $Pb(Cu,Zn)(VO_4)(OH)$ and patronite, of variable composition: VS_2, VS_4, and V_2S_5 (Kabata-Pendias, 2011). Minerals link V circulating in the Earth's interior to weathering and biogeochemical processes at the surface (Huang et al., 2015). That is the content of V in soil is inherited from the parent materials which consisted by vanadium-containing minerals. The size and charge enable V to substitutes Fe in minerals (Huang et al., 2015). Like octahedral sites of titaniferous magnetite, which is produced as a byproduct of ion and titanium mining, are occupied by V(III) mostly with minor V(IV) (Balan et al., 2006), thus V tends to be concentrated in mafic igneous rocks than in felsic rocks (Hurlbut and Klein, 1977). Additionally, around 92% of V found in basic rocks such as basalt, gabbro, amphibolites, and eclogites with V contents ranged from 200 to 300 mg/kg, and 7% in acid and neutral rocks such as granites with V contents ranged from 5 to 80 mg/kg (Nriagu, 1998; World Health Organization, 1988).

V incorporates in the structure of clay minerals such as micas, smectites, illite, kaolinite and chlorite as well as Fe-Mn hydrous oxides (Algeo and Maynard, 2008; Brumsack, 2006; Condie, 1993; Morford et al., 2005). V(IV) can substitute Al(III) in octachedral sites of clay minerals as VO^{2+} form (Gehring et al., 1994); V(III) is reported to exchange the Fe(III) in Fe-oxides and goethite (Taylor and Giles, 1970) because of the similarity between ionic radius of V^{3+} (64.0 pm) and Fe^{3+} (64.5 pm) (Aide, 2005). V

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also occurs in carnotite, roscoelite, vanadinite, patronite, bravoite, and davidite. (Baroch, 2006; Lide, 2008).

The abundance of soil V ranges from 69 mg/kg to 320 mg/kg, which is 5th abundant among all transitional metals and 22nd among all discovered elements. Table 1 lists V contents in the soil from different countries showing a great diversity of V levels. As mentioned, V in soils originated from the weathering of parent materials might be one of the explanations for the uneven distribution of V contents in Table 1. Takeda et al. (2004) determined the contents of 57 elements in 514 soil samples collected from 78 sampling sites by using microwave assisted hydrogen fluride digestion method. To evaluate the influence of parent materials, the total elemental contents were sorted, based on a lithological group. The results showed that Andisols containing relatively high amount of mafic elements, therefore the levels of V, magnesium, iron, cobalt and copper reached the highest in Andisols while decreased as rock type shifted from mafic toward felsic.

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Table 1 V content in the soil from different regions.

Region	Content (mg/kg)	Reference
Belgian	69	Cappuyns and Slabbinck (2012)
Canada	31.7-180.1	Mermut et al. (1996)
China	0.48-4994.6	Yang et al. (2017)
Denmark	31	Baken et al. (2012)
Egypt	37.4-122.1	Shaheen and Rinklebe (2018)
Finland	12.0-13.0	Reijonen et al. (2016)
Germany	20.7-133.1	Shaheen and Rinklebe (2018)
Greece	23-158	Tsadilas and Shaheen (2010)
Hungary	15.2-42.0	Ovari et al. (2001)
Ireland	52.2	Zhang et al. (2008)
Italy	58	Manta et al. (2001)
Italy	34-276	Cicchella et al. (2015)
Italy	54-239	Guagliardi et al. (2018)
Japan	94-250	Takeda et al. (2004)
Lithuania	38	Gregorauskiene et al.(2000)
Northern England	103	Rawlins et al. (2002)
Poland	18.39	Dudka and Market (1992)
Portugal	32	Ferreira et al. (2001)
Russia	79-91	Protasova and Kopayeva (1985)
South Africa	2200.0-3505.0	Panichev et al. (2006)
Spain	6.01	Granero and Domingo (2002)
Spain	15.2-144.9	Tume et al. (2006)
Sri Lanka	29.3-810	Chandrajith et al. (2005); Jayawardana et al. (2015)
Sweden	27-58	Baken et al. (2012)
Thailand	210-591	Wisawapipat and Kretzschmar (2017)
Turkey	74	Yay et al. (2008)
USA	36-150	Govindaraju (1994)

2.4.2. Anthropogenic sources

Galloway et al. (1980) estimated about 200000 tons of V addition into the environment was caused by human's activities. The total content of V in soil is the summation of the natural background which as mentioned above: highly depends on the parent materials, weathering and leaching processes and the input from various anthropogenic sources. In the past few years the number of refinery plants and smelt plants burgeoned along with the rapid development in industry. In the wastes released from those plants, around 30-40% of V is discharged into the environment by gas emission, dust, waste water and slag making V contents much higher than the natural background value in uncontaminated area (Hope, 1997; Jiao and Teng, 2008). Teng et al. (2011) collected soil samples from different parts of Panzhihua City, which is one of the industry centers in China, for V contents analyses. The results showed an upward trend of the bioavailability of V in soils from urban park and agricultural toward smelting and mining area, in which the V contents were 9.9-25.2 mg/kg, 9.8-26.4 mg/kg, 41.7-132.1 mg/kg, and 18.0-83.6 mg/kg, respectively (Teng et al., 2011). Application of certain phosphate fertilizers and soil amendments containing rock phosphate, superphosphate, and basic slag containing considerable V: 10-1000 mg/kg, 50-2000 mg/kg, and 1000-5000 mg/kg, respectively (van Zinderen Bakker and Jaworski, 1980) may increase the contents of V in soils as well. However, not only human activities may cause the contamination of V into the environment. The torrents caused by Hurricane Katrina, one of the worst natural catastrophes in American history, demolished several oil tanks and oil refineries in central-east America (Adams et al., 2007). Su et al. 2008 reported the V content in soils and sediments from New Orleans and the Louisiana Delta pre-Katrina and post-Katrina were 5.17 mg/kg and 33.7 mg/kg, respectively. This significantly

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pollution-increased was caused by flood water which carried V from leached crude oil into the city.

2.4.3. Geochemical fractions of V in soils

Geochemical fractionations of V in soils are critical to understand the potential mobilization and bioavailability during the pedogenesis. Shaheen and Rinklebe (2018) found that the residual fraction was dominant while the potential mobile fractions, which represents all the non-residual fractions (carbonate-, Fe/Mn oxides-associated and OM-bounded fractions) that can become mobile if the pH or Eh of the soil change, accounted 4.4-64.7% by using the BCR SSE method in Fluvisols, Luvisols, and Gleysols from Gemmany and Egypt. However, in soils with high weathering degree, the dominant fraction was crystalline Fe oxide binding fraction (23-54%), followed by the acid soluble fraction (2-36%), and the residual fraction (10-38%) (Wisawapipat and Kretzschmar, 2017). The dominance of V in the residual fractions also in agreement with the results reported by Teng et al. (2009) conducted with the soils from mining area in China.

Khan et al. (2013) compared the time required and contents of dissolved V between conventional sequential extraction (CSE) and ultrasonic assisted extraction (USE) protocols using modified BCR sequential extraction method as extraction strategy. Their results showed the time consumption of USE was much lower than CSE which were 40 min and 16 h, respectively. However, the V contents were found no significant difference. Besides, the total content of V was obtained with digestion method using 2 acid mixtures: H_2O_2–HF–HNO_3–H_2SO_4 and $HClO_4$–HF–HNO_3–H_2SO_4 were also compared, and the results pointed out H_2O_2–HF–HNO_3–H_2SO_4 released higher amounts of V (3-4%) than obtained by the other mixture. For safety reason, Xu et

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al. (2016) developed a new eight-step sequential extraction scheme which avoided using very strong oxidants, acid and toxic reagents as well as reduces the extraction temperature. Considering V(III) and V(IV) may incorporate into the lattice of soil minerals, Xu et al. (2016) refined Fe and Al (hydr)oxides-associated fraction into 3 fractions based on different crystallinity. Excluding the residue fraction, 55-77% of soil V can be obtained with this sequential extraction scheme.

2.4.4. Sorption of vanadium

V is considered to be well-retained by oxides, clay minerals and organic matters after released into soils from primary minerals or added via anthropogenic processes (Larsson, 2014). Larsson et al. (2017) found from 26 mineral soils that added V sorption closely related to oxalate-extractable Fe and Al while minor contributions from organic-complex form. Similar results have been reported by Burke et al. (2012) that amorphous Al-oxyhydroxides showed observable ability on V sorption. V is considered to be easily absorbed by clay minerals, especially together with Fe cations (Kabata-Pendias, 2011). Wisawapipat and Kretzschmar (2017) addressed that in highly weathered soil samples, V(V) absorbed to kaolinite, goethite, ferrihydrite, gibbsite while V(IV) substituted in the structure of kaolinite.

Organic matters play an important in V sorption as well. V can form complexes with a large amount of organic compounds including fulvic and humic acids through oxygen groups (Cheshire et al., 1977; Wehrli and Stumm, 1988). Wehrli and Stumm (1988) found V(IV) tended to form relatively strong complexes with organic compounds comparing to V(V). Moreover, V can be stabilized against reduction processes by binding to humic substance under circumstantial pH values (Lu et al., 1998)

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2.4.5. Vanadium speciation in soils

V(V) species are dominant under oxidizing conditions at low pH values, and both oxidizing and reducing conditions when pH value greater than 8 (Figure 1). Francavilla and Chasteen (1975) observed the content of VO^{2+} in solution decreased while the pH value increasing from pH 2 to pH 6 because of the formation of $(VOOH)_2^{2+}$ as well as $VO(OH)_2$ and the increased pH causing condensation of VO^{2+} to $V_{10}O_{28}^{6-}$. VO^{2+} and its hydrolyzed species $VOOH^+$ show a great stability under the both oxidizing and reducing conditions when pH value less than 7 and exist under pH values above 7 only if associated with organic or inorganic ligands. V(III) species only exist under strongly reducing conditions which is relatively insoluble and could be easily oxidized to V(IV) or V(V) in the presence of low content of O_2 or when the pH value is larger than 10 (Francavilla and Chasteen, 1975; Lu et al., 1998; Imtiaz et al., 2015).

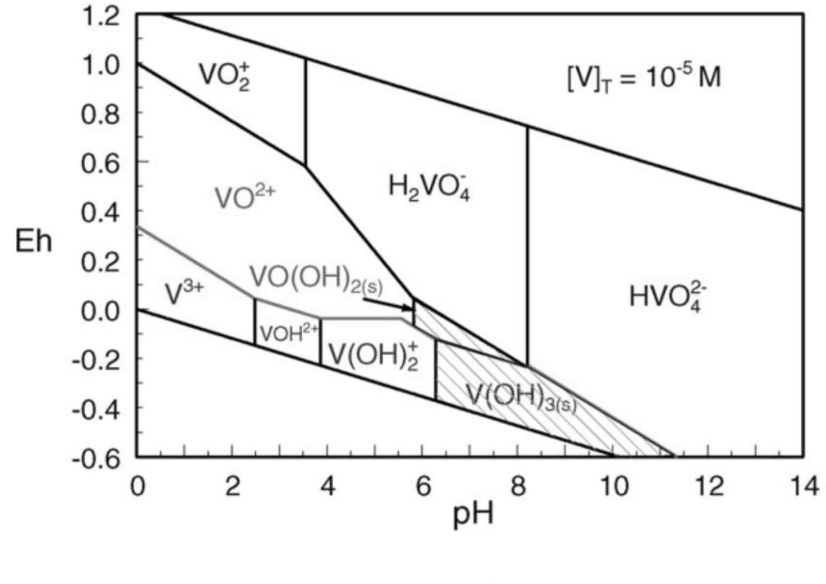

Figure 1 Eh-pH predominance for soluble and solid species of V (Huang et al., 2015).

Various analysis methods have been utilized to determine the valence of V species which could be used to predict the toxicity and solubility of V in the environment. Most chemical analysis concentrated on distinguish V(IV) and V(V) species by using chelating agents and spectrophotometry. Bosque-Sendra et al. (1998) used ECR (eriochrome cyanine R) to form complex compounds with V(IV), and then the determination was done by UV/Vis spectrophotometer. On the other hand, V(V) was analyzed after reduction with ascorbic acid. A similar research was conducted in 2003 using chrome azurols and benzydodecyldimethylammonium bromide to form ternary complex compounds with V(IV). Meanwhile V(V) was reduced by using mesity oxide. The determination was done by UV/Vis spectrophotometer as well while the results showed the sensitivity of this method was as high as ICP-AES (Poledniok and Buhl, 2003). The methods mentioned above displayed outstanding results in both recovery and sensitivity. However V species respond rapidly toward pH and Eh, excessive addition of reagents can easily change the former composition. Therefore, it is more commonly to use synchrotron X-ray absorption spectroscopy (XAS), which is a nondestructive method that can be performed on the soil sample without chemical pretreatments reflecting the original condition.

The XAS measurement of V was conducted at V K-edge with the excitation energy 5465 eV (Shaheen et al., 2019). X-ray absorption near edge structure (XANES) analysis has been used to study the characteristics of electron of target elements such as charge density, electron structure, oxidation state and electron occupation in d orbital of transition metals, XANES can also indicate the symmetry of the soil mineral lattice containing target elements. The V speciation in soil samples can be determined by using linear combination fitting (LCF) of several known standard reference spectra. Alternations in the valence state of V from trivalent to pentavalent result in 2 major

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shifts in the XANES spectra: (1) an increase at a pre-edge feature at nearly 5470 eV, and (2) 1-2 eV increase in the absorption edge position along with every unit increase in V valence state (Wong et al., 1984; Chaurand et al., 2007). Balan et al. (2006) pointed out that in titanomagnetite V occurred mostly as V(III) with minor V(IV) while V(V) species mostly formed during the weathering process by using XANES. The results also pointed out both V(III) and V(IV) occurred in the octahedral site of the spinel structure.

Larsson et al. (2015) conducted a long-term transformation of V species in a soil of pine forest stand in southern Sweden. The forest was covered by converter lime originated from the Swedish Steel company since 1984 and the V speciation and total content of the converter lime at that time cannot be determined. The results obtained with XANES show that V(IV) was the predominant species in the mor layer. Further, Fe/Al-(hydr)oxides were mean sorbents for V(V) in the mineral soils. Burke et al. (2012) revealed that V(V) dominated in red mud samples polluted with As and Cr. Wisawapipat and Kretzschmar (2017) exposed the predominance of V(IV) and V(V) in a primarily octahedral or tetrahedral coordination by comparing V K-edge XANES spectra from 10 highly weathered soil samples along with various reference components.

2.4.6. Bioavailability of soil vanadium

The essential of V for alga species and certain bacteria has been addressed, that V is a specific catalyst of the N_2 fixation. However it is not yet considered as an essential element for higher plants (Kabata-Pendias, 2011). V content in various food plants are shown in Table 2. To date, most studies focused on the relation between total V content and plant growth deficiency (Xiao et al., 2012; Hou et al., 2013).

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Table 2 V in food plants (µg/kg).

Plant	Range	Reference
Asparagus	52-128	Kabata-Pendias (2011)
Barley	0.9-7.6	Kabata-Pendias (2011)
Beetroot	46000	Owolabi et al. (2016)
Chillies	146000	Owolabi et al. (2016)
Cucumber	35-56	Kabata-Pendias (2011)
Lemon grass	22000	Owolabi et al. (2016)
Lettuce leaves	280-710	Kabata-Pendias (2011)
Onion bulbs	22-58	Kabata-Pendias (2011)
Pea	54	Welch and Cary (1975)
Potato	458-606	Kabata-Pendias (2011)
Rosemary	33000	Owolabi et al. (2016)
Spinach	533-840	Kabata-Pendias (2011)
Sweet basil	1840	Akoumianaki-Ioannidou et al. (2016)
Tea	170-250	Filik and Aksu (2012)
Thyme	44000	Owolabi et al. (2016)
Wheat grain	7-10	Kabata-Pendias (2011)
Wild mushroom	50-2000	Kabata-Pendias (2011)
Winter wheat grain	0.6-7.8	Kabata-Pendias (2011)

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As mentioned in section 2.4.4 Fe/Al/Mn (hydr)oxides, soil organic matter and clay minerals also been reported to be the sorbents of V affecting the mobility (Shaheen et al., 2019). Sequential extraction method aims to fractionate V into the operationally defined phases in order to reveal the solubility and mobile, while extraction using chelating agent or weak acid/base simulating plants' uptake mechanism can help to understand the bioavailability of V in soils for ecological risk assessment. V is considered to be less bioavailable than Cd in 3 herbaceous index plant extracted by HCl and H_2SO_4 (Martin et al., 1996). Teng et al. (2011) evaluated the extractable soil V by conducting single extractions with HOAc, $NaNO_3$, EDTA and HCl. These results were later compared to total V to evaluate the extraction efficiency of V. The final outcomes were: EDTA 0.27–4.09% > HCl 0.06–0.28% > $NaNO_3$ 0.13–0.72% > HOAc 0.01–1.33%, where EDTA was considered as the most powerful reagent.

Larsson et al. (2013) found that the bioavailability and toxicity of added soil V decreased as the sorption increased by using isotherm experiments and plant assay. Besides using chemical extraction strategy, many researchers use diffusive gradients in thin films (DGT) to measure bioavailable heavy metal in past few years. The working model of DGT is similar to plant's heavy-metal-uptake-mechanism, hence the results can be considered as bioavailable V. However DGT had only been apply to the determination of V in water samples by now. An in situ determination of V(V) by DGT using anion exchange resin as a binging layer was carried out in the Piracicaba River, Brazil (Luko et al., 2017).

The bioavailable fraction of elements usually relates with the soil properties, such as pH, texture, OC or the content of other elements, which means the bioavailability might be predicted by specific soil properties to reduce the time consuming in ecological evaluation (Meers et al., 2007). Meers et al. (2007) compared Cd

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extractability using 13 common single extraction methods with 28 soils, and revealed a multivariate regression functions for Cd extractability as a function of soil parameters (total Cd content, pH, CEC). Similar results had been reported by van der Ent et al. (2019) in ultramafic soils. Although, the bioavailability of soil V is well-known to be related with speciation, sorption condition and the total V content in the soil, the bioavailability of soil V as well as the prediction equation has seldom been considered.

2.5. Aims of this study

This study aims to analyze the total content, solubility, species distribution, and bioavailability of V in soil from different parent materials throughout Taiwan. Therefore, the objectives were (1) to investigate total and labile V contents through soil profiles with different parent materials, (2) to reveal relationship between these V and soil properties, and (3) to indicate the spatial distribution, speciation, and bioavailability of released V from soil weathering.

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Chapter 3 Materials and methods

3.1. Sample source

Totally 94 horizon samples were collected from 17 soil profiles in Taiwan with different parent materials including slate, sandstone interstratified with shale, andesite, serpentinite, and basalt (Table 3). Pedons 1 to 4 were derived from slate alluvium while the soil classification of these pedons is Dystrudept, Paleustalf, Plinthaquult, and Paleudult, respectively. The studied areas of these pedons are constantly for agricultural use locating in both northern and southern Taiwan in which belongs to 2 of 5 geologic provinces in Taiwan: Coastal Plain and Western Foothill. Pedons 5 to 7 were derived from sandstone interstratified with shale alluvium while the soil classification of these pedons is Ustifluvent, Endoaquept, and Haplorthod, respectively. These pedons were collected from 2 studied areas; one of these studied areas is constantly for agricultural use locating in southern Taiwan belonging to Western Foothill. Another studied area is a conifer-broadleaf forest without human inference locating in the high mountain area belonging to Central Range. Pedon 8 was derived from andesite and the soil classification of this pedon is Hapludand. This pedon was collected from a conifer-broadleaf forest without human inference in the Tatun Volcano Group which is a group of volcanic cones composed largely of andesitic flows and pyroclastic deposits (Chen et al., 2015). Pedons 9 to 14 were derived from basalt while the soil classification of these pedons is Ustorthent, Ustorthent, Dystrudept, Haplustalf, Haplustalf, and Haplustalf, respectively. These pedons were collected from 2 studied areas; one of these studied areas is in a small area covered by basaltic rock in the Tatun Volcano Group with the vegetation is conifer-broadleaf forest. Other 5 pedons were collected from both forest and agricultural areas on the Penghu Islands, which is a series of islands and islets representing a volcanic area of fissure eruptions. This studied area is marked by low flat-topped tablelands composing by basalt flows and tuffs with minor sand and clay intercalations (Chen et al., 2015). Pedons 15 to 17 were derived from serpentine while the soil classification of these pedons is Humudept, Hapludert, and Hapludalf, respectively. These pedons were collected form eastern Taiwan composing by metamorphic rocks. The vegetation of the studied areas is broad-leaved forest with slight human inference.

Table 3 Geographic information and classification of the studied profiles.

Pedon code	Location	Parent material	Land use	Soil classification[1]
1	N 22°35'40.9", E 120°34'10.0"	Slate alluvium	Agriculture	Dystrudept
2	N 23°14'20.4", E 120°19'00.4"	Slate aged alluvium	Agriculture	Paleustalf
3	N 24°58'06.4", E 121°07'38.7"	Slate aged alluvium	Agriculture	Plinthaquult
4	N 22°39'24.0", E 120°36'31.7"	Slate aged alluvium	Agriculture	Paleudult
5	N 22°46'10.1", E 120°17'59.9"	Sandstone interstratified with shale alluvium	Agriculture	Ustifluvent
6	N 22°34'41.2", E 120°21'54.0"	Sandstone interstratified with shale alluvium	Agriculture	Endoaquept
7	N 23°30'37.6", E 120°48'30.3"	Sandstone interstratified with shale	Forest	Haplorthod
8	N 25°09'42.6", E 121°33'29.8"	Andesite	Forest	Hapludand
9	N 23°34'12.6", E 119°30'27.9"	Basalt	Forest	Ustorthent
10	N 23°39'24.4", E 119°35'52.1"	Basalt	Agriculture	Ustorthent
11	N 25°11'36.0", E 121°30'50.0"	Basalt	Forest	Dystrudept
12	N 23°33'40.3", E 119°37'02.2"	Basalt	Agriculture	Haplustalf
13	N 23°34'17.0", E 119°36'02.2"	Basalt	Agriculture	Haplustalf
14	N 23°34'55.9", E 119°38'43.5"	Basalt	Agriculture	Haplustalf
15	N 23°02'17.13", E 121°11'59.80"	Serpentine	Forest	Humudept
16	N 23°02'09.62", E 121°11'32.32"	Serpentine	Forest	Hapludert
17	N 22°47'29.04", E 121°09'23.13"	Serpentine	Forest	Hapludalf

[1] Keys to Soil Taxonomy (Soil Survey Staff, 2014)

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3.2. Soil sampling

Selection of sampling sites was based on geology, landforms, topography, climate and natural vegetation. The collection of soil pedons was referred to the manual published by United States Department of Agriculture (Soil Survey Staff, 2014). That is, the profile was dig until showing the C horizon, or to the depth that was sufficient for pedogenesis study. The profile was cleaned immediately after digging to expose the fresh surface presenting the origin state of that profile. Field morphological characteristics of the studied profiles were described in fields according to the U.S. Soil Survey Manual (Soil Survey Staff, 2014). Soil samples (about 2 kg) were collected from each horizon and well-labeled, then were air-dried, ground and passed through a 2 mm sieve for laboratory analysis.

3.3. Physical and chemical analysis

3.3.1. Water content

Water contents of studied samples were evaluated by following the Gravity method (Gardner, 1986). W_1 g soil sample was placed in a weighted beaker (W g), and then was oven-dried at 105°C for 24 h. The sample was weighted again (W_2 g) after it reached the room temperature in a desiccator. The water content was calculated with following equation: $\theta_{WW}\%=[((W_1-W_2))/((W_1-W))]\times 100\%$

3.3.2. Particle size analysis

The particle size was determined following the pipette method (Gee and Bauder, 1986). 12 g of air-dried soil sample was placed into a 250 mL centrifuge tube with 50 mL DI water and 10 mL 1 M NaOAc (adjusted to pH 5) well-mixed; centrifuged for about 10 min at 1500 rpm then remove the supernatant. The residual was washed with 50 mL of DI water until the supernatant was clear then was centrifuged for about 10 min at 1500 rpm then the supernatant was removed.

After the removal of carbonates, the sample was transferred into a 600 mL beaker and added 5 mL 30% H_2O_2 then was heated to 90℃ until the solution was nearly removed. Mentioned act was repeated until the reactions was completed, and then keep heating to reduce the volume of the solution for 1 h.

After the removal of organic matters, 50 mL sodium-citrate-bicarbonate buffer was added (1 L 0.3M $Na_3C_6H_5O_7$ mixed with 125 mL 1M $NaHCO_3$) into the sample, and then 1 g $Na_2S_2O_4$ was added for 3 times while heating in a 85℃ water bath for 20 min. 10 mL saturated NaCl was added into the sample when it reached the room temperature. The sample was centrifuged for about 10 min at 1500 rpm then removed the supernatant. The residual was washed with 50 mL 10% NaCl and 50 mL DI water then the supernatant was removed.

After the removal of Fe-oxides, the sample was washed into a 250 mL beaker, and then oven-dried at 105°C. The sample was weighted before washed into mixed cup with DI water, and then 10 mL 5% $(NaPO_3)_6$ was added. The sample was later mixed for 15 min by the blender machine. After that, the sample was poured through a 325-mesh (< 44 μm) sieve into a 1 L sedimentation cylinder, and then the sand (particle size > 44 μm) was transferred into a beaker with DI water. The weight of the sand particle was recorded after been oven-dried.

Added DI water to the sedimentation cylinder mentioned above to make up to 1 L volume and waited for few hours until the sample reached the equilibration. The sample was later well-mixed thoroughly with a hand stirrer for at least 30 s, and waited until the silt precipitated completely. 25 mL sample was withdrawn within 12 s by using a pipette

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from 10 cm below the liquid level, and then the weight of this sample was record after been oven-dried. Multiply this weight by 40 to get the weight of clay.

3.3.3. Soil pH

The soil sample was well-mixed with DI water with a 1 to 1 ratio (w/w). The pH value was measured with glass electrode after the sample stood for 1 h (Thomas, 1996).

3.3.4. Organic C (OC)

The OC content was evaluated following Walkley-Black wet chemical oxidation method (Nelson and Sommers, 1996). The 0.50 g soil sample (<150 μm) was placed into a 500 mL Erlenmeyer flask with 10 mL 1 N $K_2Cr_2O_7$ and 20 mL concentrated sulfuric acid well-mixed. 200 mL DI water, 10 mL 85% H_3PO_4 and 2 drops of o-phenanthroline indicator were added into the sample after it stood for 30 min. the sample was later titrated with 0.5 N $(NH_4)_2Fe(SO_4)_2$ until the solution changed to a dark green color. The OC content was calculated with following equation:

$$OC\% = 10 \times (1 - V_s/V_b) \times (1.0\ N) \times (12/4000) \times 1.3 \times (100/W)$$

V_s: titration volume of sample (mL)

V_b: titration volume of blank (mL)

W: sample weight (g)

1.3: convert factor for the recovery of this method

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3.3.5. Total element content

(1) Portable X-ray Fluorescence Spectrometer (pXRF)

Olympus Delta Premium 2000 pXRF was used to determine total V content in the studied samples. The voltage of these pXRF is 40 kV with Rh anode and the detector is large-area silicon drift detector. Nearly 3 g of soil sample (<150 µm) was placed in a transparent zipper bag for pXRF analysis. The detection program was as followed: Beam 1 (40 kV) excites and detects the elements with higher atomic number for 60 s (displayed by pXRF); Beam 2 (15 kV) excites and detects the elements with lower atomic number for 100 s (displayed by pXRF). The actual detection time was 230 s. Each sample was measured for 3 times and the average value was calculated.

(2) Microwave associated HF digestion method

0.4 g soil sample (<150 µm) was well-mixed with 2 mL HF and 6 mL concentrated HNO_3 in a Teflon tube. The digestion program was as followed: Raise to 180 ± 5 ℃ in 5.5 min and remains 180 ± 5 ℃ for 9 min while the pressure reaching the maximum value within 5 to 15 min. After the heating progress and met the room temperature, the sample was transferred into a 25 mL volumetric flask. The Teflon tube was washed with pure water twice and the solution was collected into the mentioned volumetric flask (US EPA SW-846 3052). The samples were kept in polyethylene bottles at 4℃ before V was analyzed with ICP-AES (Optima 8000, PerkinElmr, USA) and Si, Fe, and Mn were analyzed with AAS (Z-2300) after been filtered with 0.45 µm millipore.

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3.4. Geochemical fractions

The BCR SSE modified by Rauret et al. (1999) was conducted with four selected soil pedons including pedon 2, 3, 10, and 13 representing different parent materials and with different soil properties. The extraction procedure is as follows:

(1) F1 (Acid soluble): 2 g soil was extracted using 40 mL 0.11 M HOAc in a 100 mL centrifugation tube with a 16 h shaking period at 25℃.

(2) F2 (Fe/Mn oxides bounding): Residue from F1 was extracted using 40 mL 0.5 M $NH_4OH \cdot HCl$ (pH 1.5, adjusted by HNO_3) in a 100 mL centrifugation tube with a 16 h shaking period at 25℃.

(3) F3 (Organic matter bounding): Residue from F2 was extracted using 10 mL of 30%, w/v, H_2O_2 in a 100 mL centrifugation tube with a 1 h shaking period at 25℃, and 1 h heating period at 85℃; an additional 10 mL of H_2O_2 for 1 h at 85 ℃ with occasional agitation to reduce the volume to less than 1 mL, and 45 mL of 1 M CH_3COONH_4 (pH 2) was added and shacked for 16 h at 25℃.

(4) F4 (Residual): Residual from F3 was transferred into a Teflon tube and digested with 2 mL HF and 6 mL concentrated HNO_3.

After each extraction step, the sample was centrifuged under 4000 rpm for 20 min to get the supernatant. The residual was washed with 20 mL DI water with a 15 min shaking period, and then centrifuged under 4000 rpm for 15 min. The suspension of washing procedure was deposed before starting next extraction step. The supernatant of each extraction step was filtered with 0.45 μm millipore and stored in polyethylene bottles at 4°C before analyzed with ICP-AES (Optima 8000, PerkinElmr, USA).

3.5. Dithionite–citrate–bicarbonate (DCB) extraction of Fe, Al, Mn and V

Dithionite–citrate–bicarbonate (DCB) extraction method was used to determinate pedogenic Fe oxides (Mehra and Jackson, 1960). 1.0 g air-dried soil sample was well-mixed with 40 mL 0.3M $Na_3C_6H_5O_7 \bullet 2H_2O$ and 5 mL 1M $NaHCO_3$ in a 100 mL polyethylene bottle. The sample was heated at 80℃ water bath for 15-20 min while adding 1 g $Na_2S_2O_4$. The mentioned process was repeated until the sample showed a grayish color. Note that the heating temperature should not above 80℃ in order to avoid the degradation of dithionite and the formation of FeS. When the sample met the room temperature, 10 mL saturated NaCl solution was added then the sample was centrifuged at 4000 rpm for 10 min to get the supernatant. The supernatant was filtered with 0.45 μm millipore and stored in polyethylene bottles at 4℃ before analyzed for Fe, Al, Mn, and V with ICP-AES (Optima 8000, Perlin Elemr).

3.6. Spatial distribution of soil vanadium

According to FitzPatrick (1970) the sampling site of thin sections should avoid rocks, thick plant roots and holes in case to maintain the native state of soil profile. Kubiena box was gently hit into the soil profile with a wooden hammer or hands then dig out carefully with a trowel in order to get an undisturbed soil block. After air drying, vertically oriented thin sections were prepared by Spectrum Petrographics, Inc., Washington, USA for micromorphological studies.

Thin section from pedon 9 deriving from basalt parent material was selected and observed using back-scattered electron imaging with a scanning electron microscope. The elemental compositions of thin sections were obtained using electron Probe X-ray

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Micro-Analyzer (EPMA) (JEOL JXA 8230) equipping with 5 wavelength-dispersive spectrometers operating at 15 kV and 107 nA bean current. The EPMA analysis was conducted at Research Facility Center for Science and Technology of University of Tsukuba, Japan. Analysis condition was modified from Hseu and Iizuka (2013).

3.7. Valence of soil vanadium

The soil sample from pedon 10 derived from basalt parent material was ground and passed through a 100-mesh (< 150 µm) sieve for XANES analysis. The reference standard compounds were prepared using solid V_2O_3, V_2O_4, and V_2O_5, which were ground and pass through a 100-mesh (< 150 µm) sieve. The standards and soil sample were mounted on plastic sample holders and sealed with transparent tape for XANES analysis (Hseu and Iizuka, 2013). The XANES experiment was conducted at the National Synchrotron Radiation Research Center of Taiwan. The X-ray absorption V spectra were obtained using BL-17C1 beam line. The electron storage ring was operated with energy of 1.5 GeV and a current of 120-200 mA. The energy of the incoming X-ray beam was tuned of 5315-5765 eV for V K-edge. Data was collected in transmission mode for V standards and the fluorescence mode for the soil sample. The normalization of XANES spectra were plotted using Athena.

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3.8. Bioavailability of soil vanadium

3.8.1. Single extraction

In order to investegt the bioavailable V in soils, we selected 4 single extracting reagents with different extraction mechanism while targeting different V specie:

(1) $CaCl_2$ is known to exchange cation in soils. 2 g soil sample was extracted using 20 mL 0.01 M $CaCl_2$ in a 100 mL centrifugation tube with a 3 h shaking period at 25℃, and then centrifuged at 3000 rpm for 10 min (Novozamsky et al., 1993).

(2) EDTA acts as a chelator targeting cation. 2 g soil sample was extracted using 20 mL 0.05 M EDTA in a 100 mL centrifugation tube with a 1 h shaking period at 25℃, and then centrifuged at 3000 rpm for 10 min (Wear and Evans, 1968).

(3) HCl can provide an acidic environment that increases the solubility of heavy metals targeting the cations as well. 2 g soil sample was extracted using 20 mL 0.1 N HCl in a 100 mL centrifugation tube with a 1 h shaking period at 25℃, and then centrifuged at 3000 rpm for 10 min (Baker and Amacher, 1982).

(4) $NaHCO_3$ has been reported had a great extraction efficiency of As which has similar anion structure with V. 2 g soil sample was extracted using 20 mL 0.5M $NaHCO_3$ in a 100 mL centrifugation tube with a 20 h shaking period at 25℃, and then centrifuged at 3000 rpm for 10 min (Woolson et al., 1971).

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The supernatants of each extraction method were filtered with 0.45 µm millipore and stored in polyethylene bottles at 4°C before analyzed with ICP-AES (Optima 8000, PerkinElmr, USA).

3.8.2. Pot experiment

To evaluate the bioavailability of soil V, Chinese cabbage (*Brassica rapa* var. chinensis) was chosen to conduct the plant assay due to the following reasons: (1) Chinese cabbage is a well domesticated yet common vegetable specie in Taiwan, and (2) the differentiation of above-ground part is relatively simple and entirely edible. In addition, 13 soil samples coded as P1 to P13 were collected from the surface soil of 10 selected pedons (pedon 1, 3, 4, 9, 10, 12, 14, 15, 16, 17) with different properties, such as parent material, degree of weathering, pH value, texture and land use in order to obtain bioavailability of soil V with representative**.** Three additional surface soils coded as P11, 12 and 13 in the pot experiments acting as a replacement of the surface soils of pedon 8, 11 and 13, respectively, because of the similarity in the soil properties while the original profiles were unavailable for conducting the pot experiments (Appendix 1).

All pot experiments were performed at a nature light green house of Department of Agricultural Chemistry, National Taiwan University. Air-dried soil sample (3 kg) were rewetted to a moisture content of 60% of field capacity in a Wagner 1/5000 a pot with a diameter of 16 cm and a height of 19 cm while the drainage hole was sealed with robber plug. Seeds of Chinese cabbage (*Brassica rapa* var. chinensis) were sown in plug trays with cultivatable soil, and then transplanted into the pots after the seedlings reached 3 leaves age. Each pot was irrigated daily to maintain moisture content of roughly 60% field capacity in the soil. Only shoots were collected, washed with DI water, oven-dried

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at 65℃ and grinded with grinder for analysis. Chinese cabbage plants were harvested after 45 days while only above-ground parts were collected. The plant shoot samples were rinsed carefully with DI water, oven-dried at 70℃ for 2 days, and then ground to powder by grinder. The dry weight of the each plant could be found in appendix 2.

3.8.3. Vanadium content in plant shoot

0.2 g of ground plant material and 5 mL concentrated HNO_3 were placed into a 100 mL digestion tube and stood overnight for completely reaction. The sample and 1 mL 30% H_2O_2 were heated at 60℃ for 1 h, then at 80℃ for 20 min. The mentioned process was repeated until for 2 times, and then gradually heated the sample to 120℃ for 3 h. After the heating progress and met the room temperature, the sample was transfer into a 50 mL volumetric flask. Total V content in plant materials were analyzed with ICP-MS (7700 series, Agilent Technologies, USA) after been filtered with 0.45 μm Millipore (Meharg and Rahman, 2003).

3.10. Quality assurance and quality control

The R^2 of calibration line was larger than 0.995 while certified soil reference materials: NIST 2710a was used to ensure the digestion efficiency of microwave associated HF digestion method which the recoveries were large than 90% for V and ranged from 50-120% for Si, Fe, and Mn. The calibration line of pXRF was built by certified soil reference materials: NIST 2709a, 2710a, and 2711a under the geochem mode. In addition, pXRF was calibrated by using stainless steel 316 before started the sample determination. The total V contents obtained by microwave associated HF digestion method were used to calculate the recovery of BCR SSE method (70-97%). Certified plant reference material: NIST 1573a tomato leaves was used to ensure the digestion efficiency of HNO_3/H_2O_2 digestion method for plant materials which the recoveries were large than 60%.

3.11. Statistical analysis

Statistical analyses were performed using the statistical software R. The linear correlations between different data were evaluated using Pearson correlation coefficient, and a $P < 0.05$ was considered to be significant. If the sample size less then $n=25$, then Wilcoxon signed rank tests were also conducted to corroborate the results. Levels of statistical significance are expressed as $^{*}P < 0.05$, $^{**}P < 0.01$ and $^{***}P < 0.001$. Multivariate regression was used to reveal the equation between bioavailable V and selected soil properties, and a $P < 0.001$ was considered to be significant.

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Chapter 4 Results and discussions

4.1. Soil physical and chemical characteristics

The selected physical and chemical characteristics of the studied soils show an enormous diversity among pedons (Table 4). The sand content ranged from 2.36 to 70.7% while the value rising as the depth increased on account of that surface soil has higher weathering degree than subsoil. In addition, the clay content ranged from 9.70 to 78.3% while Bt horizons presented notable accumulation of illuvial clay indicating the higher weathering degree and the leaching process in some pedons. For instance, in pedon 13 (Haplustalf), clay content considerably amplified in Bt1 to Bt4 horizons. The pH value was in the range of 3.6-8.5 while pH value of soils with felsic and (ultra)mafic parent material had the average value 6.2±1.7 and 7.2±0.9, respectively. Moreover, the pH values of pedon 1 (Dystrudept) were clearly lower than that of pedon 4 (Paleudult) corresponding to the effect of both parent material and weathering degree. Soil organic carbon (OC) content (0.08-18%) gave similar tendency among each pedon as well, that upper horizons tended to contain more abundant OC content while the OC content decreased as the depth increased. Nevertheless, pedons 7 and 16 didn’t follow the same pattern of other pedons, because the OC content in Bhs/Bt horizons of pedon 7 (Haplorthod) were much higher than in upper horizon and 2A horizons of pedon 16 contained higher OC content than upper horizons. The total Si, Fe, and Mn ranged from 132-483 g/kg, 12.6-38.1 g/kg, and < 0.003-0.33 g/kg, respectively in soils with felsic parent materials (pedon 1 to 8) and 137-268 g/kg, 24.3-81.2 g/kg, and 0.08-7.88 g/kg, respectively in soils with mafic and ultramafic parent materials (pedons 9 to 17), demonstrating the major differences in the elemental composition of felsic and (ultra)mafic rocks while the elements slightly increasing with the increase in the depth

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in all samples showing the characteristic of geogenic backgrounds of each elements in the studied soils.

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Table 4 Selected physicochemical characteristics of the studied soils.

Pedon	Depth	Horizon	Sand	Clay	pH	OC[1]	Si	Fe	Mn	V
	cm		-------%-------			%	--------g/kg--------			mg/kg
1	0-15	Ap1	14	35	5.9	1.80	428	25.2	0.09	107
	15-30	Ap2	16	31	6.1	0.67	452	25.0	0.13	104
	30-45	BA	23	27	6.4	0.58	444	23.0	0.09	99.2
	45-65	Bt1	19	24	6.7	0.41	437	30.3	0.26	93.0
	65-100	BC	46	23	7.0	0.25	386	27.0	0.33	103
2	0-14	Ap1	15	44	5.9	2.20	128	23.3	0.08	95.5
	14-30	Ap2	11	46	7.4	0.80	161	29.4	0.20	105
	30-60	Bt1	4.7	50	7.9	0.56	158	31.6	0.20	120
	60-85	Bt2	3.4	46	8.0	0.37	141	33.1	0.20	126
	85-100	Bt3	20	38	7.9	0.23	158	27.7	0.22	94.9
3	0-24	Ap	4.8	49	5.6	1.70	159	21.7	0.07	95.9
	24-47	Bt1	3.7	64	6.2	0.57	153	21.7	0.04	123
	47-69	Bt2	1.9	62	6.1	0.43	158	21.1	0.04	108
	69-100	Bt3	3.4	70	5.9	0.43	132	34.7	0.03	131
4	0-20	Ap	12	54	4.7	0.83	423	32.0	0.08	103
	20-40	Bt1	11	53	4.3	0.75	424	27.2	0.06	103
	40-55	Bt2	13	54	4.5	0.75	304	30.6	0.07	102
	55-75	Bt3	12	52	4.3	0.89	412	30.4	0.06	106
	75-105	Bt4	8.8	56	4.4	0.51	348	31.4	0.08	103
5	0-15	Ap1	41	14	7.9	0.73	402	19.4	0.11	54.9
	15-28	Ap2	45	16	8.4	0.55	363	18.3	0.10	54.5
	28-55	AC	43	17	8.2	0.42	483	19.2	0.12	54.4
	55-80	C1	40	16	8.3	0.35	437	21.5	0.13	61.0
	80-100	C2	71	12	8.3	0.18	406	16.5	0.10	47.1
6	0-20	Ap	17	35	6.2	1.40	396	24.7	0.06	81.1
	20-35	BA	14	37	7.4	0.79	428	24.2	0.18	81.0
	35-55	Bt1	6	50	8.5	0.38	353	30.0	0.21	110
	55-75	Bt2	13	42	8.1	0.26	332	26.1	0.17	95.4
	75-100	BC	36	30	7.9	0.19	401	26.0	0.20	89.7

Table 4 (continued)

Pedon	Depth	Horizon	Sand	Clay	pH	OC[1]	Si	Fe	Mn	V
	cm		-------%-------			%	--------g/kg--------			mg/kg
7	0-20	A	66	10	3.6	11.0	478	8.5	< 0.003	35.4
	20-25	E	68	10	4.0	1.00	530	12.6	< 0.003	54.6
	25-35	Bhs/Bt1	57	23	3.8	3.30	444	42.5	< 0.003	129
	35-40	Bhs/Bt2	51	28	4.0	4.50	417	45.3	< 0.003	133
	40-45	C	58	20	4.3	2.70	383	38.1	0.03	103
8	0-20	A1	30	35	3.8	18.0	246	24.6	0.11	122
	20-35	A2	24	39	4.2	13.0	272	24.1	0.11	134
	35-60	Bw1	24	39	4.4	13.0	286	23.9	0.08	129
	60-98	Bw2	32	36	4.6	9.00	341	27.6	0.11	154
9	0-10	A	43	34	8.0	3.10	179	64.6	1.16	306
	10-22	CA	46	33	8.3	1.10	157	72.7	1.46	412
	22-35	C	55	34	8.1	0.86	164	56.6	1.58	410
10	0-15	A	41	43	7.7	3.00	175	55.3	1.22	241
	15-26	AC1	64	22	8.1	1.00	170	81.2	1.61	273
	26-36	AC2	61	27	8.2	0.66	130	74.4	2.28	316
	>36	AC3	37	48	8.0	0.73	170	55.9	3.47	340
11	0-10	A	11	55	4.0	6.40	173	52.1	0.61	354
	10-25	Bw1	12	47	4.2	3.40	172	54.1	0.63	369
	25-35	Bw2	11	53	4.5	2.60	179	55.7	0.54	392
	35-50	Bw3	16	49	5.0	1.90	184	57.2	0.63	391
	50-65	BC	17	47	5.1	1.40	153	58.5	0.68	385
	65-90	C1	25	39	5.3	1.10	152	59.8	0.54	362
	>90	C2	28	32	5.2	0.79	159	58.7	0.71	374
12	0-11	A	28	27	7.9	4.20	175	52.3	1.03	258
	11-22	BA	50	13	8.2	1.30	161	41.9	1.63	298
	22-40	Bt1	13	39	8.1	1.00	255	61.3	0.41	210
	40-75	Bt2	18	27	7.9	0.45	239	61.8	0.46	223
	75-105	Bt3	17	31	7.9	0.49	235	61.2	0.44	259
	105-140	Bt4	13	31	7.7	0.45	252	62.2	0.59	269
	140-180	BC	30	17	7.6	0.17	268	62.4	0.08	276
	180-210	C	40	5.0	7.6	0.08	255	66.0	0.57	355

Table 4 (continued)

Pedon	Depth	Horizon	Sand	Clay	pH	OC[1]	Si	Fe	Mn	V
	cm		-------%-------			%	--------g/kg--------			mg/kg
13	0-10	A	40	40	7.7	4.10	163	58.2	0.85	287
	10-20	BA	56	33	8.2	0.84	146	75.4	1.04	475
	20-40	Bt1	22	60	7.9	0.93	146	64.0	0.47	328
	40-63	Bt2	15	58	7.8	0.52	137	49.4	0.22	244
	63-80	Bt3	7.8	68	7.8	0.50	164	45.8	0.63	284
	80-100	Bt4	2.4	78	7.8	0.39	170	65.4	1.53	358
14	0-15	Ap	72	15	8.0	4.50	198	33.6	0.59	186
	15-25	AB	71	19	8.5	1.10	210	49.1	0.54	219
	25-50	BA	37	37	8.2	1.20	217	50.3	0.29	239
	50-70	Btv	52	23	8.1	0.43	170	58.5	7.88	418
	70-90	Bt	30	45	8.0	0.54	199	52.6	1.10	290
	90-120	BC	28	41	8.1	0.34	224	55.3	0.91	262
	>120	C	47	27	8.1	0.20	215	53.0	0.88	258
15	0-17	A1	11	36	6.1	2.60	192	53.3	1.53	90.5
	17-30	A2	12	41	5.4	1.80	206	56.5	2.29	121
	30-40	AB	12	56	5.7	1.40	190	46.9	1.98	122
	40-60	Bw1	5.6	74	5.5	1.10	172	49.8	1.49	152
	60-75	Bw2	12	69	5.7	0.70	184	70.3	1.21	140
	>75	C	14	64	6.0	0.63	190	85.4	1.37	134
16	0-15	A1	43	34	6.5	2.00	198	36.6	0.84	106
	15-35	A2	37	43	6.7	1.50	155	41.6	0.83	99.7
	35-58	Bw	22	49	6.7	2.60	163	43.2	0.78	112
	58-73	2A1	20	47	6.6	3.00	173	54.7	1.24	111
	73-90	2A2	9.0	67	6.5	2.20	186	41.2	0.59	148
	90-118	2Bss1	7.7	66	6.5	1.40	183	43.9	0.50	179
	118-145	2Bss2	10	62	5.9	0.79	144	31.4	0.52	153
	>145	2C	12	60	6.5	0.75	184	40.6	0.52	173

Table 4 (continued)

Pedon	Depth	Horizon	Sand	Clay	pH	OC[1]	Si	Fe	Mn	V
	cm		-------%-------			%		--------g/kg--------		mg/kg
17	0-30	A	24	43	6.7	1.10	193	41.6	0.78	92.9
	30-42	BA1	20	47	6.8	2.00	221	50.6	0.90	89.4
	42-70	BA2	22	52	6.9	2.10	230	52.0	1.04	88.9
	70-90	Bt1	18	43	7.1	1.40	208	40.9	0.97	95.0
	90-120	Bt2	25	50	7.3	0.69	197	24.3	1.13	82.8
	120-140	BC	30	49	7.4	0.51	217	28.9	1.38	77.9
	>140	C	36	44	7.5	0.44	203	26.6	1.35	69.5

[1] Organic carbon

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4.2. Total vanadium contents

The total soil V content ranged from 35.4 to 475 mg/kg with an average level of 182 mg/kg while differing widely between the studied profiles but varying slightly with soil depth showing the characteristics of geogenic backgrounds of V in uncontaminated soils (Figure 2). However, V in the Bhs/Bt horizon was much higher than in the A and E horizons in pedon 7 revealing a distinct enrichment in total V content from 35.4 mg/kg to 133.3 mg/kg, which was a consequence of the considerable downward migration of V from top soil caused by strong leaching processes in Spodosols (Berrow et al., 1978). The vertical migration abovementioned of V might be a consequence of the leached clay, OC or Fe. In addition, the enrichment of V content in subsoil of pedon 12 (BA horizon) and pedon 13 (Btv horizon) might be resulted from leaching process together with Fe (Table 4).

Total V content in the soils with felsic parent materials including slate, sandstone interstratified shale, and andesite were lower than 100 mg/kg, while the soils with mafic parent materials (basalt and serpentine) were demonstratively higher in total V (Figure 2). This variation of V was also supported by the positive and significant ($P < 0.001$) correlation between total V and Fe content while negative and significant ($P < 0.001$) correlation between total V and Si content in Figure 3a and b. A similar result to this study in the tendency of soil V, Fe, and Si was reported by Takeda et al. (2004) that the level of soil V increased as rock type shifted from felsics toward mafics. However, the basalts derived soils contained higher V than serpentine soils (Figure 2b), because V is mildly incompatible during mantle partial melting (Huang et al., 2015). Huang et al. (2015) indicated that total V content in peridotites forming serpentinites after serpentinization, range from few mg/kg to around 100 mg/kg, which is lower than that

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in mid-ocean ridge basalts, ocean island basalts and island arc basalts.

The OC content was relatively low and the variety with soil depth was irregular in comparison with total V content in studied soils, thus no significant relationship between them was observed in Figure 3d. Figure 3e and f reveal that clay content and pH value poorly correlated with total V content as well. The abovementioned data of OC, clay, and pH correlated with total V show that parent material controls the vertical distribution of V rather than these soil properties.

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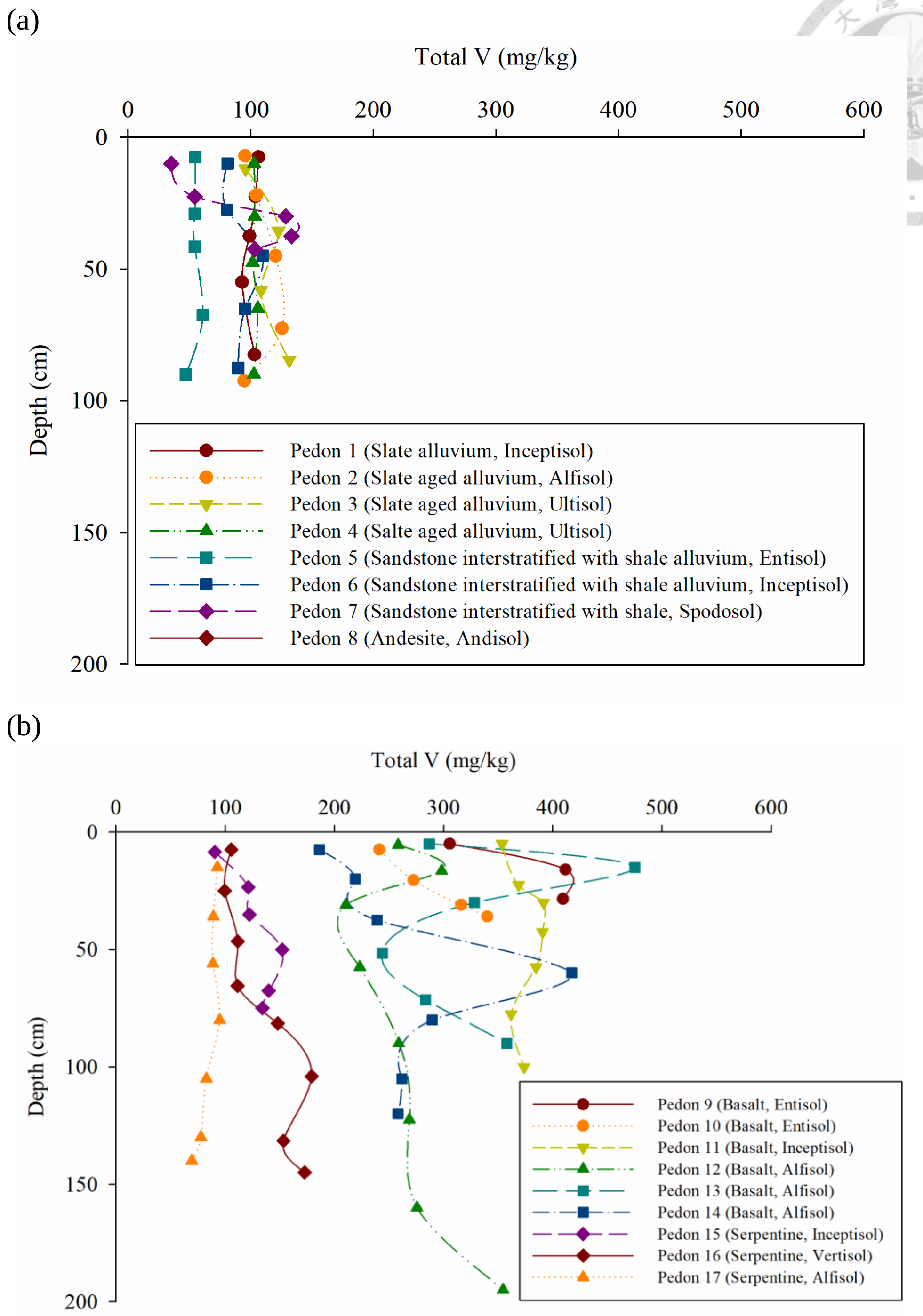

Figure 2 Total V content obtained with ICP-AES in the studied profiles from different parent materials: (a) felsic (b) mafic and ultramafic.

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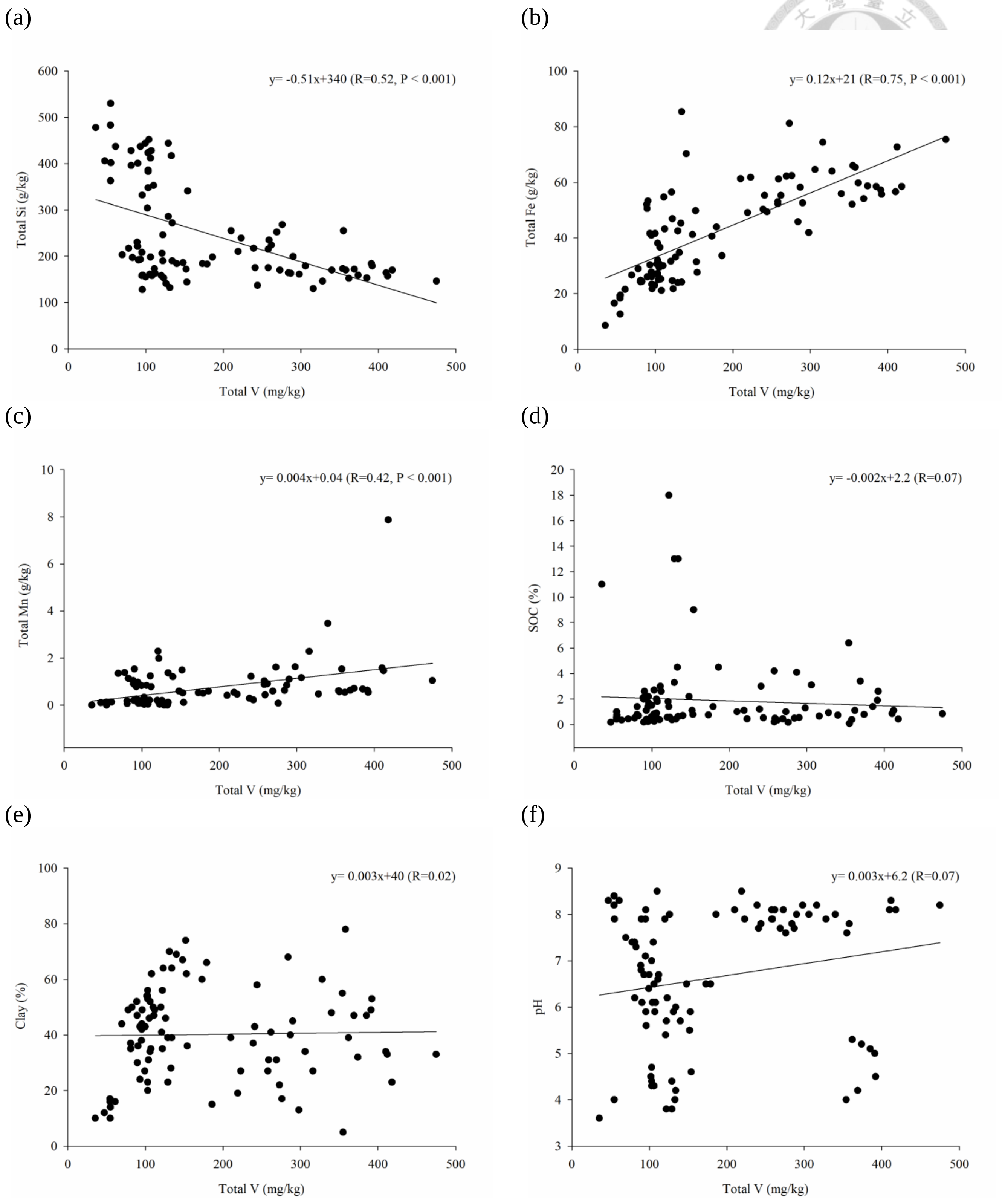

Figure 3 Relationship between total V content and selected physicochemical characteristics of studied soils: (a) total Si content, (b) total Fe content, (c) total Mn content, (d) SOC content, (e) clay content, and (f) pH value (n=94).

According to United States Environmental Protection Agency (EPA) method 6200, pXRF is a standard in-situ analytical method for soil V. However, the pros and cons about pXRF application on soil V had rarely been mentioned. Our results revealed a positive correlation (R=0.81) between 2 methodologies in most samples (Figure 4). However, in soil samples derived from serpentine, total V was below the detection limit while Ti was significantly underestimated by pXRF comparing to ICP-AES after microwave associated HF digestion (R=0.93, data not shown). The reason of great variation of soil V measurement was the spectral inference between V, Ti, and Cr. The energy of K_α and K_β of V are 4.95 keV and 5.43 keV respectively while K_α of Cr is 5.42 keV and K_β of Ti is 4.93 keV. These similarities of transition energies caused a misjudgment to pXRF detector called K_α /K_β inference (Pattle Delamore Partners, 2013). In addition, each result of pXRF was an average value of several measurements, thus during the measuring the signal of Ti as well as Cr might be considered as the signal of V broadening the signal peak of V which also gave rise to deviation of V measurement. Although high background level of Ti and Cr in the serpentine soil samples were observed, for instants, 0.71-3.49 g/kg and 0.24-2.05 g/kg respectively in this study, V might be clearly underestimated or below the detection limit. Despite of this weakness, pXRF is still a feasible strategy for rapid screening of soil V.

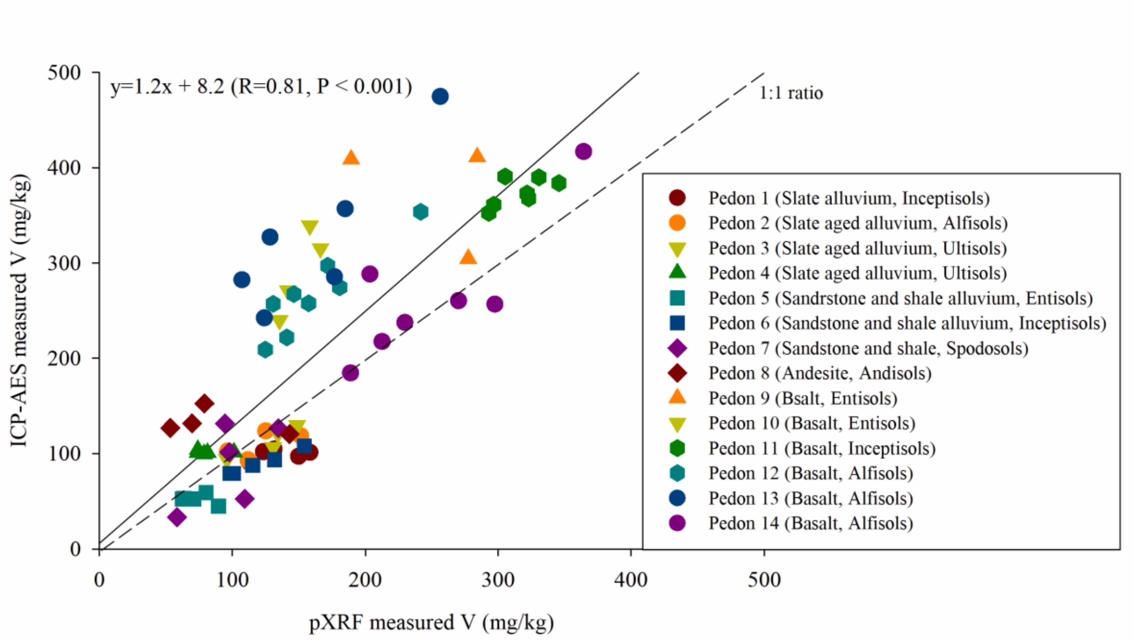

Figure 4 Relationship between total V content obtained with ICP-AES and pXRF for all horizon samples.

4.3. Geochemical fractions of vanadium

Specific sequential extraction (SSE) aims to demonstrate that soil samples consist of a different distribution of the main V-bearing phases, which are of relevance for considering the potential bioavailability and risk to the environment (Wisawapipat and Kretzschmar, 2017). The fraction distribution showed a similar tendency among pedons: residual fraction (fraction 4) was the dominant fraction and followed by reducible fraction (fraction 2), oxidisable fraction (fraction 3), and acid soluble fraction (fraction 1) (Table 5). The data showed that about < 0.01-0.12%, 0.79-6.57%, < 0.01-2.17% and 95.1-99.1% of total soil V was distributed in acid soluble fraction, Fe/Mn oxide bounded fraction, oxidisable fraction and residual fraction indicating less than 5.0 % of total V had been released from parent materials in all cases.

The residual fraction increased with the decreasing depth in spite that released V was limited. F3 represents the organic-matter-binding form of V which was most abundant in the surface soil and decreased with the increasing depth. The difference of F3 between surface and subsurface soils was caused by that organic matter accumulated majorly in the upper horizon and soil organic matter had been reported as one of the primary sorbents of V in soils (Shaheen et al., 2019). Moreover, the F2 content was much higher than F1 and F3 in all peodns while highly and positively related to total Fe and Mn distribution (Figure 5). Thus, we assumed that the released V associates with pedogenic Fe after weathering.

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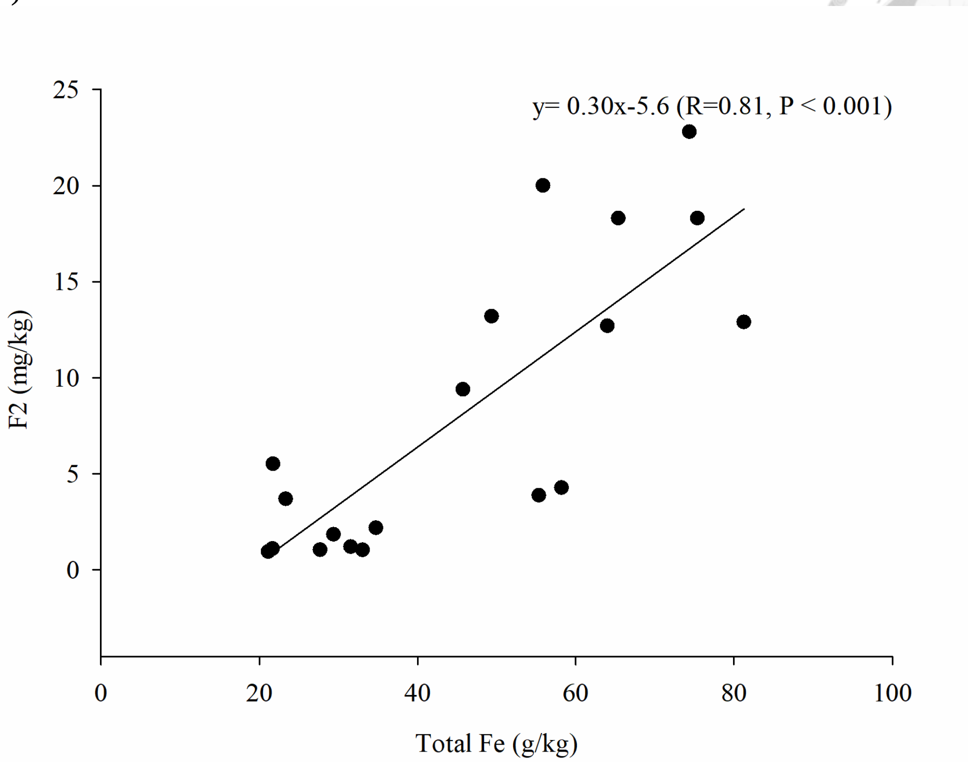
Table 5 Chemical fractions (mg/kg) of V and their proportions of total V in selected pedons; recovery (%) was obtained by sum of V content in each fraction divided by the V total content.

Pedon		F1	F2	F3	F4	Recovery
2	Ap1	0.02 (0.03%)	3.69 (4.28%)	0.54 (0.63%)	82.1 (95.1%)	90.4
	Ap2	0.01 (0.01%)	1.84 (1.97%)	0.03 (0.03%)	91.6 (98.0%)	89.2
	Bt1	0.01 (0.01%)	1.2 (1.06%)	< 0.001 (< 0.01%)	111 (98.9%)	93.1
	Bt2	< 0.001 (< 0.01%)	1.03 (0.89%)	< 0.001 (< 0.01%)	116 (99.1%)	93.2
	Bt3	0.01 (0.02%)	1.04 (1.22%)	0.02 (0.02%)	84.4 (98.7%)	90.1
3	Ap	0.10 (0.12%)	5.51 (6.57%)	1.82 (2.17%)	76.5 (91.1%)	87.5
	Bt1	0.06 (0.06%)	1.10 (1.00%)	0.24 (0.22%)	109 (98.7%)	90.0
	Bt2	0.06 (0.06%)	0.94 (0.91%)	0.26 (0.25%)	102 (98.8%)	95.2
	Bt3	0.07 (0.06%)	2.18 (1.84%)	0.24 (0.20%)	116 (97.9%)	90.1
10	A	< 0.001 (< 0.01%)	3.87 (2.08%)	28.7 (15.5%)	153 (82.5%)	76.9
	AC1	< 0.001 (< 0.01%)	12.9 (5.75%)	2.36 (1.05%)	210 (93.2%)	82.7
	AC2	< 0.001 (< 0.01%)	22.8 (8.57%)	0.07 (0.03%)	244 (91.4%)	84.4
	AC3	< 0.001 (< 0.01%)	20.0 (6.84%)	< 0.001 (< 0.01%)	272 (93.2%)	85.9
13	A	< 0.001 (< 0.01%)	4.27 (1.86%)	33.3 (14.5%)	192 (83.6%)	80.0
	BA	< 0.001 (< 0.01%)	18.3 (4.49%)	24.7 (6.07%)	364 (89.4%)	85.6
	Bt1	< 0.001 (< 0.01%)	12.7 (5.52%)	0.05 (0.02%)	217 (94.5%)	70.0
	Bt2	0.01 (0.01%)	13.2 (6.42%)	< 0.001 (< 0.01%)	192 (93.6%)	84.1
	Bt3	0.02 (0.01%)	9.39 (4.14%)	< 0.001 (< 0.01%)	217 (95.9%)	79.8
	Bt4	0.02 (0.01%)	18.3 (6.25%)	< 0.001 (< 0.01%)	274 (93.7%)	81.6

Note: F1: acid soluble, F2: bound to Fe/Mn oxides, F3: bound to organic matter, and F4: residual

(a)



(b)

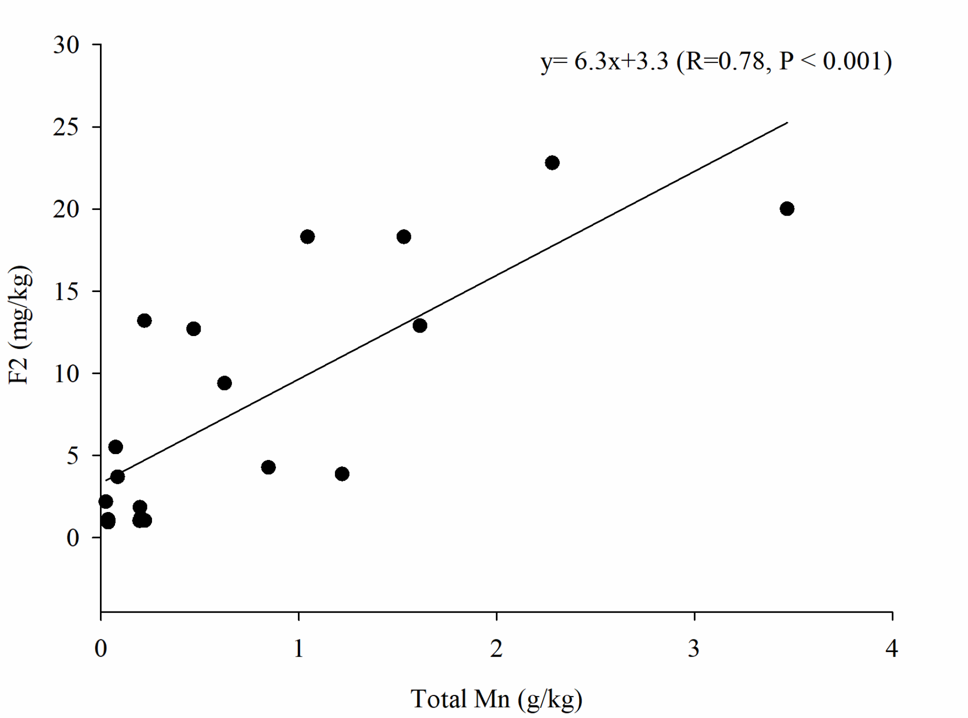


Figure 5 Relationship between the F2 fraction of BCR extraction method and total (a) Fe and (b) Mn.

DCB extraction, which was designed specifically for extracting free Fe oxides, was conducted in order to confirm our hypothesis. DCB-extractable V ranged from 1.16 to 204 mg/kg while Fe_d obviously accumulated in the Bt horizons (Table 6). In addition, V_d significantly ($P < 0.01$) and positively correlated with Fe_d, revealing that the weathered V was retained by pedogenic Fe oxide (Table 7). The positive correlation between Fe_d and V_d and the dominance fraction of BCR extraction method gave solid evidence that V tended to be sequestered by Fe after V was released from mineral lattices.

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Table 6 DCB extracted elements in the studied pedons (n=94).

Pedon code	Horizon	Fe$_d$	Mn$_d$	Al$_d$	V$_d$
			-------------g/kg-------------		mg/kg
1	Ap1	12.4	0.20	0.98	3.85
	Ap2	12.9	0.36	0.82	3.25
	BA	10.3	0.24	0.52	1.32
	Bt1	20.0	0.92	0.77	1.16
	BC	15.1	0.89	1.25	1.23
2	Ap1	14.4	0.15	1.00	9.42
	Ap2	18.1	0.49	1.57	10.4
	Bt1	19.9	0.49	2.19	8.89
	Bt2	19.5	0.48	2.17	6.81
	Bt3	16.4	0.49	1.86	6.08
3	Ap	17.5	0.13	2.39	26.0
	Bt1	20.4	0.07	4.43	39.2
	Bt2	16.4	0.06	3.55	27.7
	Bt3	31.1	0.04	4.70	39.6
4	Ap	36.5	0.24	8.78	24.2
	Bt1	37.2	0.22	8.89	22.5
	Bt2	37.9	0.22	9.12	23.5
	Bt3	36.6	0.20	8.80	22.3
	Bt4	37.8	0.25	9.05	23.3
5	Ap1	6.57	0.18	0.37	2.64
	Ap2	7.20	0.19	0.42	2.50
	AC	6.86	0.18	0.40	2.34
	C1	9.73	0.24	0.77	3.89
	C2	7.50	0.16	0.53	1.77
6	Ap	9.74	0.16	0.46	11.4
	BA	11.6	0.35	0.61	7.34
	Bt1	12.6	0.29	1.88	3.20
	Bt2	8.80	0.23	1.32	0.73
	BC	10.5	0.45	1.53	1.45
7	A	5.68	0.02	1.33	10.6
	E	12.3	0.01	0.62	28.9
	Bhs/Bt1	56.4	0.08	3.70	73.3
	Bhs/Bt2	48.8	0.05	6.22	65.6
	C	37.4	0.11	8.57	40.8

Table 6 (continued)

Pedon code	Horizon	Fe_d	Mn_d	Al_d	V_d
		-------------g/kg-------------			mg/kg
8	A1	15.7	0.03	10.5	22.6
	A2	18.7	0.03	13.0	24.8
	Bw1	18.6	0.03	17.1	25.5
	Bw2	22.9	0.03	16.3	29.6
9	A	52.4	1.15	4.47	99.2
	CA	51.9	1.40	4.19	102
	C	56.0	1.98	5.89	111
10	A	48.9	0.92	4.16	90.4
	AC1	50.0	1.61	3.91	79.9
	AC2	58.1	1.62	4.59	96.0
	AC3	70.5	3.95	6.23	125
11	A	46.6	1.03	8.37	132
	Bw1	52.4	1.10	9.23	144
	Bw2	53.4	1.01	9.27	149
	Bw3	53.0	0.96	8.87	145
	BC	53.0	1.04	8.51	151
	C1	53.6	1.12	7.75	148
	C2	52.6	1.21	7.23	152
12	A	54.7	1.49	5.40	88.3
	BA	62.4	1.65	5.98	101
	Bt1	57.4	0.60	6.55	83.2
	Bt2	55.5	0.68	5.58	79.6
	Bt3	61.5	0.71	5.87	113
	Bt4	69.4	1.03	6.01	127
	BC	62.3	1.47	4.74	107
	C	62.1	1.16	4.41	150
13	A	49.3	0.59	3.77	116
	BA	61.8	0.73	4.57	148
	Bt1	69.9	0.74	6.62	150
	Bt2	73.9	0.34	6.93	158
	Bt3	63.7	0.28	6.31	144
	Bt4	64.0	0.34	6.70	204

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Table 6 (continued)

Pedon code	Horizon	Fe_d	Mn_d	Al_d	V_d
		-------------g/kg-------------			mg/kg
14	Ap	14.3	0.63	1.51	34.8
	AB	17.5	0.54	1.86	43.2
	BA	34.7	0.74	3.56	91.1
	Btv	48.4	7.36	6.24	115
	Bt	49.7	1.74	6.94	130
	BC	41.4	1.18	5.94	112
	C	32.6	1.10	3.96	99.2
15	A1	59.0	2.11	2.86	28.8
	A2	79.9	2.33	4.60	42.5
	AB	97.3	2.21	5.94	53.3
	Bw1	122	1.72	8.49	72.5
	Bw2	106	1.74	6.60	70.4
	C	100	1.76	6.37	64.5
16	A1	33.5	0.98	2.23	43.5
	A2	38.1	1.09	2.14	40.5
	Bw	50.7	1.41	2.97	50.8
	2A1	53.0	1.76	2.94	46.2
	2A2	60.1	1.13	4.99	89.2
	2Bss1	55.4	0.91	5.41	113
	2Bss2	44.1	0.94	3.97	106
	2C	42.7	0.94	3.68	104
17	A	56.6	1.28	2.47	27.7
	BA1	58.7	1.30	2.35	24.8
	BA2	56.7	1.32	2.38	23.1
	Bt1	64.2	1.31	2.61	29.7
	Bt2	53.1	1.32	2.54	29.8
	BC	46.0	1.58	2.27	27.0
	C	38.8	1.56	1.90	25.6

Table 7 Linear correlation matrix between DCB extracted elements of soil horizon sample (n=94).

	Fe_d	Mn_d	Al_d	V_d
Fe_d	1.00			
Mn_d	0.50	1.00		
Al_d	0.36	0.05	1.00	
V_d	0.62**	0.33**	0.42**	1.00

** : significance at $P < 0.01$

4.4. Spatial distribution of soil vanadium

Both the BCR SSE and DCB selective extraction data supported that labile V significantly correlated with Fe oxides in studied soils. By far, the results stand by our hypothesis mentioned above was from destructive analysis. Thus, EPMA was utilized to conduct element mapping in order to obtain more understandable in situ results.

Several spots in the soil thin sections with lighter color representing high heavy metal content were randomly selected to conduct the quality analysis. Element composition mapping were only performed on the spots showing distinct V peak in the quality analysis (data not shown). Figure 5a representing the soil matrix shows the overlaps among the hotspots of Fe and V, whereas Mn appeared to show weaker signals in most part of the sample. Figure 5b representing the Fe concretion shows the overlaps among the hotspots of Fe and V as well. Meanwhile, the overlaps of the hotspots of Si and Al occurred to have the lowest abundance of Fe and V also in the agreement with the results from section 4.2 that felsic-parent-material derived soils had lower V content (Figure 3).

The elemental distribution in these mapping further verified the study hypothesis: V tends to associate with Fe in both parent materials and weathered soil particles presenting the considerable siderophilic affinity.

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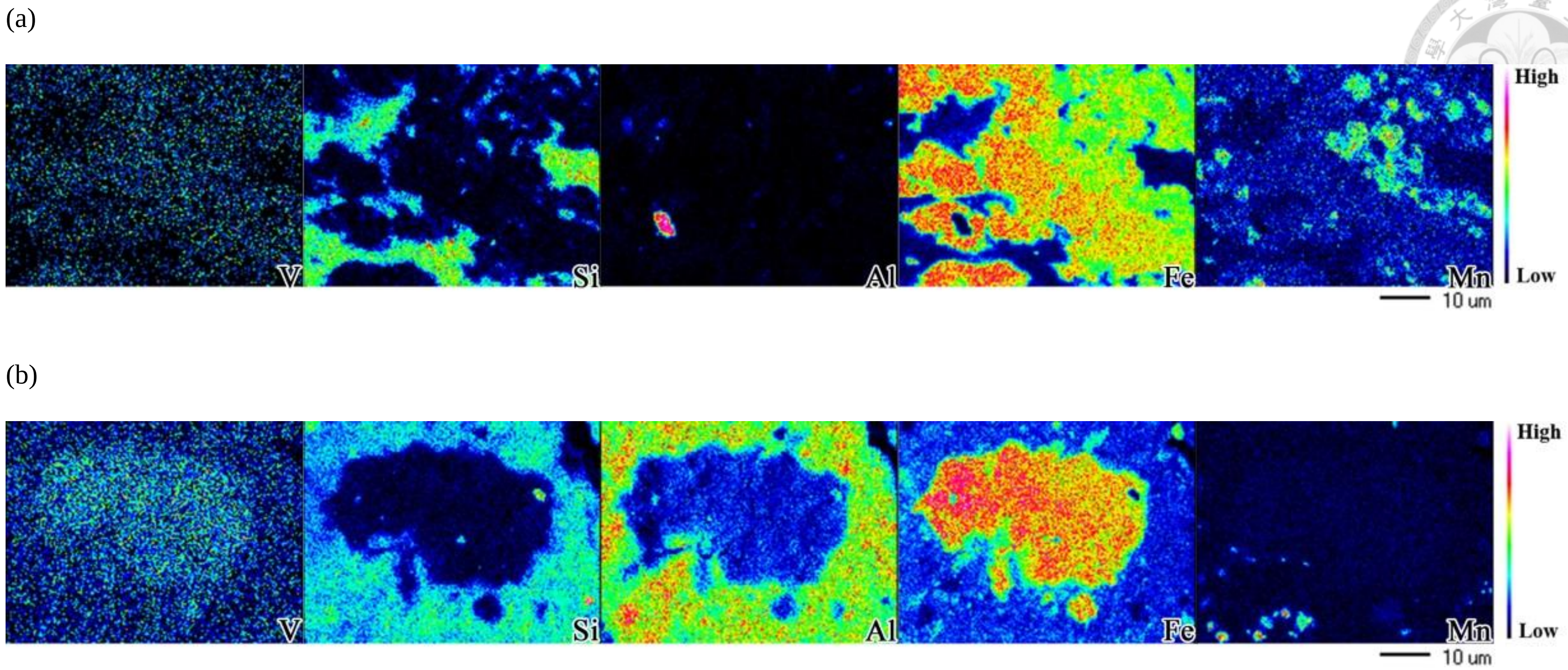

Figure 6 Elemental mappings obtained by EPMA of (a) soil matrix and (b) Fe concretion.

4.5. Valence of soil vanadium

Several analytical techniques have been utilized to determine the valence and coordination condition of V species bound to soils. Typically, the sequential extraction methods are used to quantify the affinity for V bound to soil particles, such as minerals, organics, and biochar discriminating total V pool into different geochemical fractions (Shaheen et al., 2019). However, sequential extraction methods are unable to provide quantitative information about specific binding environment or the valence of soil V, although V species can be determined by using a sensitive spectrophotometric method combining chelators, and reductants (Poledniok and Buhl, 2003). XANES analysis is a more common method to differentiate the species of soil V.

The V K-edge XANES spectra of three reference compounds and an averaged spectrum for the soil sample expressing the notably differences in pre-edge depending on the oxidation state of V (Wisawapipat and Kretzschmar, 2017). The V_2O_4 and V_2O_5 compounds had a strong pre-edge peak with a centroid at nearly 5470 eV corresponding to 1s to 3d transitions. Wisawapipat and Kretzschmar (2017)indicated that this intense pre-edge geature is the sign of the asymmety of the V coordination environment: distorted octahedral (O_h), tetrahedral (T_d) or square pyramidal (P_y) (Figure 6). On the other hand, V_2O_3 spectra had a much weaker and broader pre-edge feature showing the high coordination symmetry (Figure 6). The soil sample had a strong pre-edge peak at appromaximately 5470 eV likewise V_2O_4 and V_2O_5 compounds had (Figure 6). The rising peak appeared at nearly 5485 eV which as known as the edge energy (EE*) representing the trasiton from 1s to 4p. Generally, EE* shows a sytematic shift to higher energy with the increasing oxidation state (Bianconi et al., 1991). However, most studies addressed the oxidation state of V is rather difficult to identified basing on the

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EE* because of the overlap of EE* value for different oxidation state of V (Chaurand et al., 2007).

The linear combination fitting (LCF) between reference standard compounds and studied sample indicating the dominant species of V in soil were V(IV) and V(V). The pH value of the studied soil ranging from 3.8 to 8.5 (Table 4) and all soils were well drained, thus eliminated the possibility for V(III) species occurring in the studied soils since they only exist under strongly reducing conditions. Hence, based on the V K-edge XANES spectra (Figure 6) and the results of LCF, we demonstrated the dominant V species in the studied soils were VO^{2+} (cation) and $H_2VO_4^-$ (anion) shown in Figure 1.

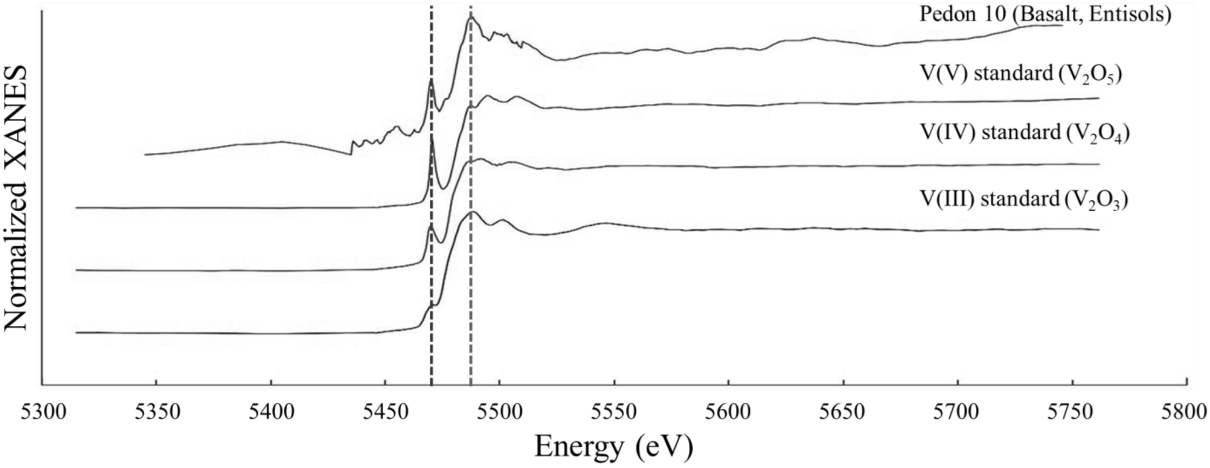

Figure 7 Normalized V K-edge XANES spectra of pedon 10 and reference standard compounds.

4.6. Bioavailability of soil vanadium

An increased number of studies measured the effect of soil V on plant growth. Most of these studies focused on the total V content only (Xiao et al., 2012; Hou et al., 2013), which pointed out similar increase in the plant growth inhibition along with the increasing total V (Tian et al., 2015). However, the evaluation of metal bioavailability based only on total soil content is insufficient to predict the actual ecological impact (Meers et al., 2007). Tian et al. (2015) evaluated the uptake of V by rape (*Brassica juncea* L.) in spiked soils; Teng et al. (2011) measured the extractable V with HOAc, $NaNO_3$, EDTA and HCl. The studies relating to bioavailable V abovementioned were rather scattered.

The extractable V with $CaCl_2$, EDTA, HCl, and $NaHCO_3$ ranged from 0.01%-0.48%, 0.08%-3.65%, <0.005%-2.43%, and <0.002%-3.11%, respectively (Table 8). In section 4.3, the results of BCR SSE revealed nearly 5%, which was the sum of F1, F2 and F3, of total V had potential mobility corresponding to the value of extractable V mentioned above.

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Table 8 Extracted V content (mg/kg) by different single extractions. Extractable V (%) was obtained by dividing the extracted V content with total V content.

Pedon code	Horizon	Extracted V				Extractable V			
		$CaCl_2$	EDTA	HCl	$NaHCO_3$	$CaCl_2$	EDTA	HCl	$NaHCO_3$
1	Ap1	0.06	0.33	0.72	0.27	0.05	0.31	0.67	0.25
	Ap2	0.03	0.11	0.38	0.19	0.03	0.11	0.37	0.18
	BA	0.02	0.27	0.34	0.04	0.02	0.27	0.34	0.04
	Bt1	0.02	0.26	0.14	0.16	0.02	0.28	0.15	0.17
	BC	0.02	0.26	0.22	0.10	0.02	0.25	0.21	0.10
2	Ap1	0.03	0.25	1.68	0.54	0.03	0.26	1.76	0.57
	Ap2	0.02	0.62	0.62	0.31	0.02	0.59	0.59	0.30
	Bt1	0.02	0.68	0.43	0.30	0.02	0.57	0.36	0.25
	Bt2	0.01	0.74	0.26	0.23	0.01	0.59	0.21	0.18
	Bt3	0.02	0.63	0.35	0.25	0.02	0.66	0.37	0.26
3	Ap	0.02	0.81	2.34	1.24	0.02	0.84	2.43	1.29
	Bt1	0.01	0.99	0.45	0.35	0.01	0.80	0.37	0.28
	Bt2	0.02	0.45	0.47	0.39	0.02	0.42	0.44	0.36
	Bt3	0.01	0.43	1.19	0.70	0.01	0.33	0.91	0.53
4	Ap	0.02	0.62	0.48	0.41	0.02	0.60	0.46	0.39
	Bt1	0.02	0.43	0.46	0.35	0.02	0.42	0.45	0.34
	Bt2	0.02	0.44	0.44	0.37	0.02	0.43	0.43	0.36
	Bt3	0.02	0.46	0.42	0.38	0.02	0.43	0.40	0.36
	Bt4	0.02	0.39	0.49	0.22	0.02	0.38	0.48	0.21
5	Ap1	0.05	0.47	1.23	0.33	0.09	0.86	2.24	0.60
	Ap2	0.03	0.86	0.92	0.23	0.06	1.58	1.69	0.42
	AC	0.02	0.80	0.68	0.13	0.04	1.47	1.25	0.24
	C1	0.03	0.74	0.47	0.12	0.05	1.21	0.77	0.20
	C2	0.02	0.52	0.42	0.07	0.04	1.10	0.89	0.15
6	Ap	0.02	0.40	2.90	0.78	0.02	0.49	3.58	0.96
	BA	0.03	1.08	1.25	0.42	0.04	1.33	1.54	0.52
	Bt1	0.02	1.15	< 0.005	0.15	0.02	1.05	< 0.005	0.14
	Bt2	0.03	0.42	< 0.005	0.09	0.03	0.44	< 0.005	0.09
	BC	0.04	0.18	0.28	0.17	0.04	0.20	0.31	0.19
7	A	0.17	0.42	0.87	1.10	0.48	1.19	2.46	3.11
	E	0.05	1.22	0.37	0.71	0.09	2.23	0.68	1.30
	Bhs/Bt1	0.05	0.80	0.33	0.55	0.04	0.62	0.26	0.43
	Bhs/Bt2	0.05	0.85	0.20	0.31	0.04	0.64	0.15	0.23
	C	0.05	0.58	0.12	0.17	0.05	0.56	0.12	0.17
9	A	0.05	0.38	< 0.005	2.13	0.01	0.12	< 0.005	0.70
	CA	0.05	0.41	< 0.005	2.33	0.01	0.10	< 0.005	0.57
	C	0.05	0.46	0.42	2.60	0.01	0.11	0.10	0.63

Table 8 (continued)

Pedon code	Horizon	Extracted V				Extractable V			
		$CaCl_2$	EDTA	HCl	$NaHCO_3$	$CaCl_2$	EDTA	HCl	$NaHCO_3$
10	A	0.04	4.42	< 0.005	2.78	0.01	1.83	< 0.005	1.15
	AC1	0.03	0.49	< 0.005	2.59	0.01	0.18	< 0.005	0.95
	AC2	0.06	0.51	< 0.005	2.47	0.02	0.16	< 0.005	0.78
	AC3	0.03	0.43	0.06	2.19	0.01	0.13	0.02	0.64
11	A	0.05	0.92	1.22	0.73	0.01	0.26	0.34	0.21
	Bw1	0.03	1.28	1.51	0.57	0.01	0.35	0.41	0.15
	Bw2	0.03	1.63	1.45	0.63	0.01	0.42	0.37	0.16
	Bw3	0.03	1.82	1.43	0.65	0.01	0.47	0.37	0.17
	BC	0.02	2.20	1.41	0.71	0.01	0.57	0.37	0.18
	C1	0.02	2.65	1.38	0.81	0.01	0.73	0.38	0.22
	C2	0.02	2.64	1.48	0.93	0.01	0.71	0.40	0.25
12	A	0.03	2.91	< 0.005	1.32	0.01	1.13	< 0.005	0.51
	BA	0.03	0.67	< 0.005	1.18	0.01	0.22	< 0.005	0.40
	Bt1	0.04	3.16	0.44	0.68	0.02	1.50	0.21	0.32
	Bt2	0.04	2.45	0.29	0.56	0.02	1.10	0.13	0.25
	Bt3	0.04	5.26	0.32	0.95	0.02	2.03	0.12	0.37
	Bt4	0.05	4.64	0.34	0.85	0.02	1.72	0.13	0.32
	BC	0.05	5.80	0.30	0.76	0.02	2.10	0.11	0.28
	C	0.05	7.44	0.76	1.31	0.01	2.10	0.21	0.37
13	A	0.07	0.47	< 0.005	2.35	0.02	0.16	< 0.005	0.82
	BA	0.06	0.38	< 0.005	2.14	0.01	0.08	< 0.005	0.45
	Bt1	0.06	5.67	0.40	1.30	0.02	1.73	0.12	0.40
	Bt2	0.09	8.81	3.64	1.36	0.04	3.61	1.49	0.56
	Bt3	0.07	5.23	2.68	1.21	0.02	1.84	0.94	0.43
	Bt4	0.06	13.07	3.24	2.93	0.02	3.65	0.91	0.82
14	Ap	0.09	0.59	0.03	2.35	0.05	0.32	0.01	1.26
	AB	0.04	0.36	< 0.005	1.70	0.02	0.16	< 0.005	0.78
	BA	0.04	0.40	< 0.005	2.05	0.02	0.17	< 0.005	0.86
	Btv	0.04	7.02	0.05	2.48	0.01	1.68	0.01	0.59
	Bt	0.04	9.62	0.05	2.39	0.01	3.32	0.02	0.82
	BC	0.03	8.89	0.09	2.34	0.01	3.39	0.03	0.89
	C	0.03	8.09	0.28	2.81	0.01	3.14	0.11	1.09
15	A1	0.02	0.34	0.06	< 0.003	0.02	0.38	0.07	< 0.002
	A2	0.02	0.39	0.03	< 0.003	0.02	0.32	0.02	< 0.002
	AB	0.02	0.45	0.03	< 0.003	0.02	0.37	0.02	< 0.002
	Bw1	0.02	0.70	0.03	< 0.003	0.01	0.46	0.02	< 0.002
	Bw2	0.02	0.99	0.05	0.04	0.01	0.71	0.04	0.03
	C	0.02	1.05	0.06	0.06	0.01	0.78	0.04	0.04

Table 8 (continued)

Pedon code	Horizon	Extracted V				Extractable V			
		$CaCl_2$	EDTA	HCl	$NaHCO_3$	$CaCl_2$	EDTA	HCl	$NaHCO_3$
16	A1	0.02	1.37	0.59	0.57	0.02	1.29	0.56	0.54
	A2	0.02	1.38	0.30	0.44	0.02	1.38	0.30	0.44
	Bw	0.02	0.85	0.21	0.24	0.02	0.76	0.19	0.21
	2A1	0.03	0.55	0.10	0.09	0.03	0.50	0.09	0.08
	2A2	0.02	0.96	0.27	0.20	0.01	0.65	0.18	0.14
	2Bss1	0.05	1.95	0.56	0.49	0.03	1.09	0.31	0.27
	2Bss2	0.03	3.39	0.55	0.75	0.02	2.22	0.36	0.49
	2C	0.01	3.69	0.65	0.81	0.01	2.13	0.38	0.47
17	A	0.02	0.53	0.11	0.04	0.02	0.57	0.12	0.04
	BA1	0.02	0.49	0.07	0.01	0.02	0.55	0.08	0.01
	BA2	0.02	0.48	0.06	0.02	0.02	0.54	0.07	0.02
	Bt1	0.02	0.67	0.07	0.04	0.02	0.71	0.07	0.04
	Bt2	0.02	0.85	0.07	0.11	0.02	1.03	0.08	0.13
	BC	0.02	1.02	0.07	0.17	0.03	1.31	0.09	0.22
	C	0.01	1.06	0.08	0.19	0.01	1.53	0.12	0.27

Figure 7 demonstrates that $NaHCO_3$ showed a moderate relationship ($0.5 < R < 0.7$), $CaCl_2$ and EDTA showed weak relationship ($0.3 < R < 0.5$), and HCl showed no relationship ($R < 0.3$) with total V content (Moore et al., 2013). In addition, EDTA and $NaHCO_3$ extractable V, which had not only higher extracting efficiency than the other two extractions (Table 8), but also positively and significantly ($P < 0.001$) correlated with total V content. These results revealed that the extractable EDTA and $NaHCO_3$ extractable V highly affected by total V. Moreover, the extractable V was also positively and significantly ($P < 0.001$) correlated with pH value (Table 9). The valence of soil V is sensitive with pH that under oxidation condition V(IV) (VO^{2+}) can be transformed rapidly to V(V) ($H_2VO_4^-$) as increasing pH value (Figure 1), which is close to the extracting condition providing by $NaHCO_3$ pointing out $NaHCO_3$ can extract both dominant V species in the studied soils while EDTA can mainly extract VO^{2+} only. These results revealed that 0.5M $NaHCO_3$ is a suitable extracting reagent for evaluating extractable V in soils.

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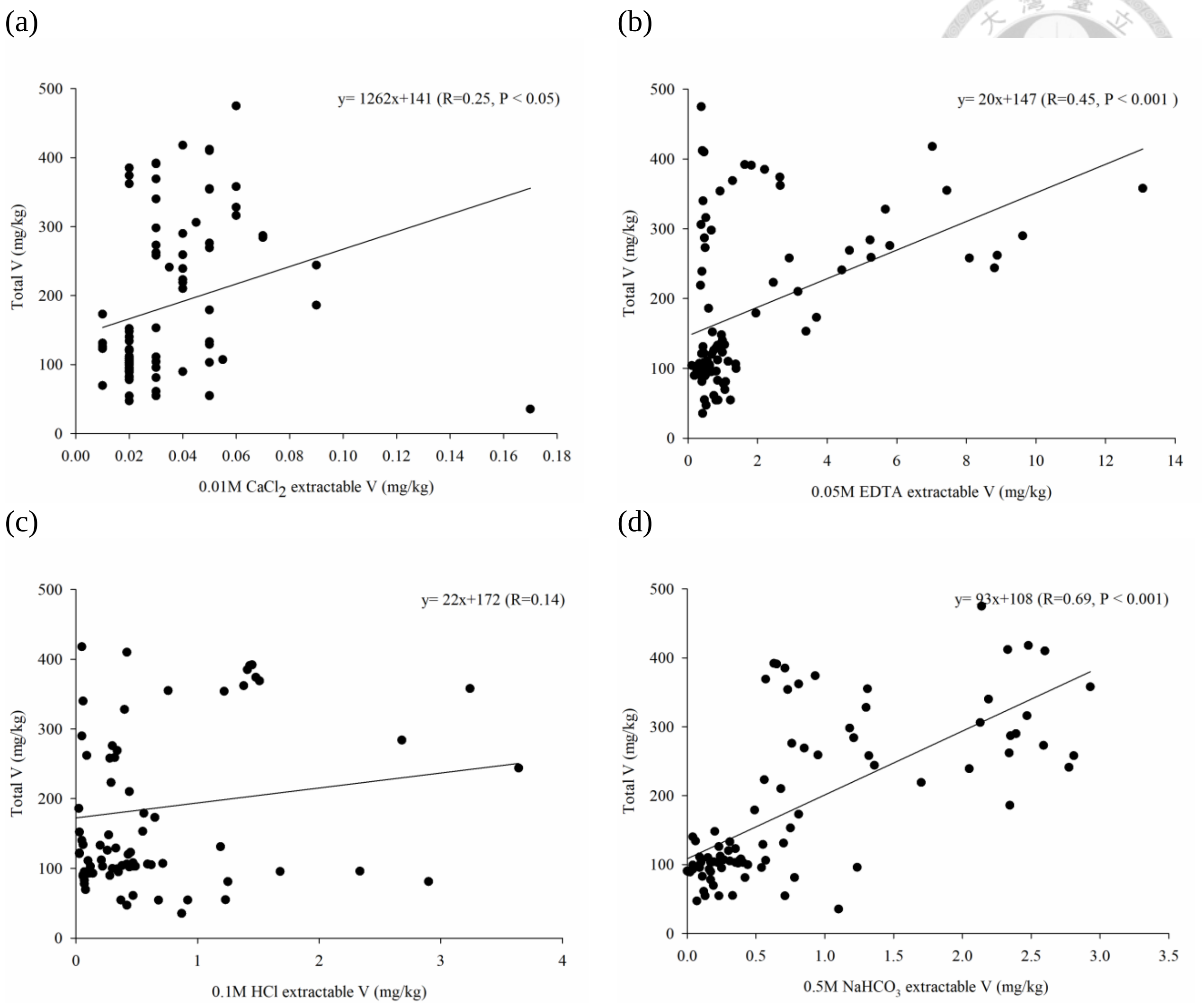

Figure 8 Relationship between total V content and V extracted with different single extractions (n=88).

Table 9 Linear correlation matrix between selected soil properties and V extracted with different single extractions (n=90).

	V-$CaCl_2$	V-EDTA	V-HCl	V-$NaHCO_3$
Total V content	0.25*	0.45***	0.15	0.69***
Clay	-0.30**	0.11	0.24*	-0.15
pH	0.02	0.27**	-0.18	0.40***
OC	0.57***	-0.21*	0.004	0.06

*, ** and *** Significant at $P < 0.05$, < 0.01 and 0.001

Figure 8 presents the linear relationships between V uptake per plant and in the soils extractable V. The $NaHCO_3$ extractable V showed a strong relationship ($R > 0.7$) with the V uptake per plant while $CaCl_2$ and EDTA showed a moderate relationship ($0.5 < R < 0.7$), and HCl showed none relationship ($R < 0.3$) (Moore et al., 2013). In addition, EDTA and $NaHCO_3$ extractable V were positively related to plant uptake of V at $P < 0.05$ and 0.01 confidence levels, respectively. We found that $NaHCO_3$ extractable V was significantly affected by total V content in last section. Moreover, the $NaHCO_3$ extractable V highly related to plant V indicating bioavailable V content can be well evaluated by this soil extraction.

By combining these results with the data obtained by BCR SSE, DCB extraction and EPMA, we can further address: the soil V was released from the mineral lattices, and then associated with Fe oxides by the mechanisms of absorption or incorporation with VO^{2+} form or been up taken by plants with $H_2VO_4^-$ form during the weathering process.

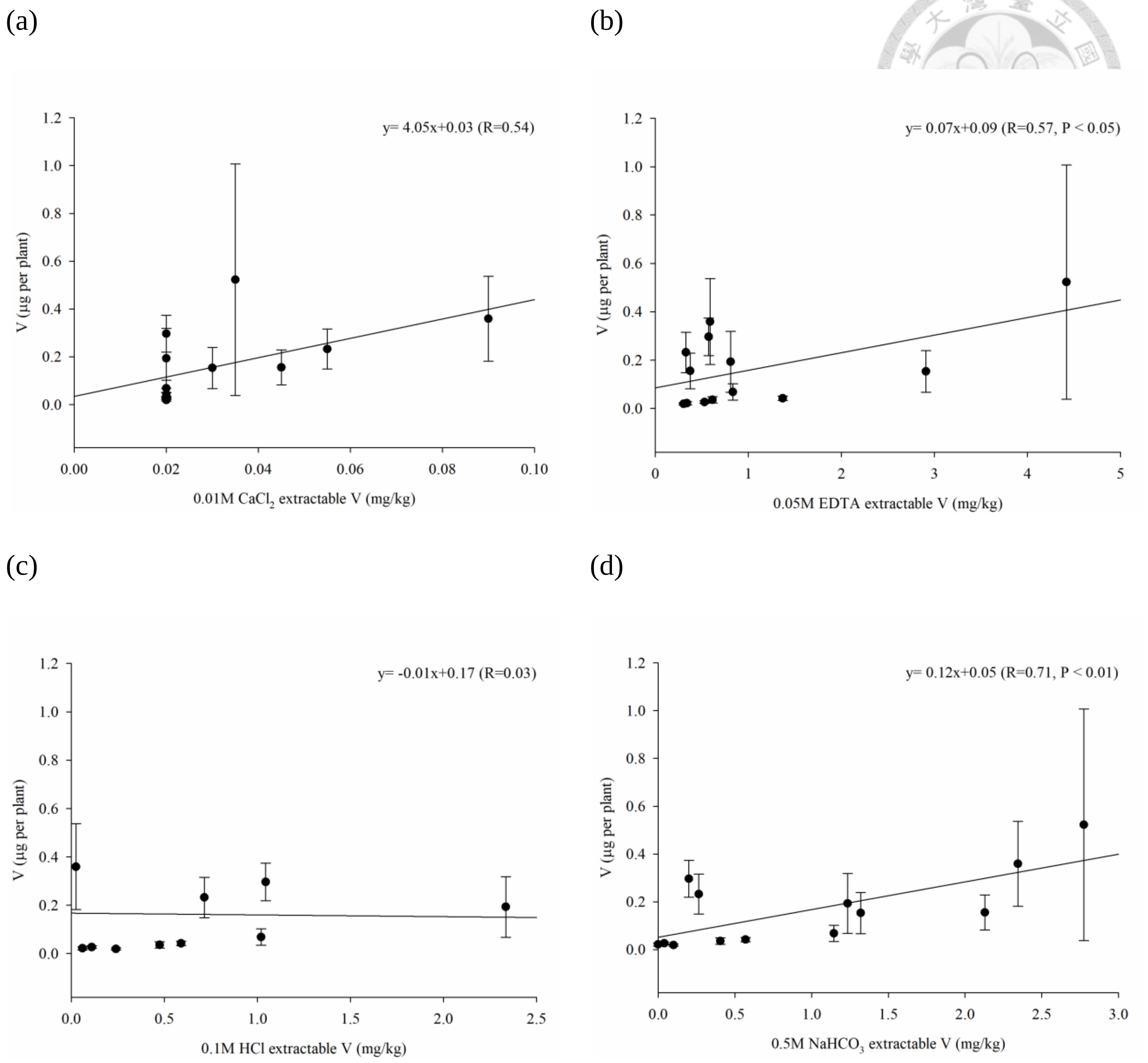

Figure 9 The relationship between V content in Chinese cabbage and V extracted with different single extractions (n=13); Error bars represent the standard deviation of triplicates.

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4.7. Multivariate regression of independent parameters

Meers et al. (2007) mentioned that multivariate regression can express extractable metal contents as a function of general soil properties. In section 4.6, we found that $NaHCO_3$ extractable V positively correlated with total V as well as pH value. Thus these soil properties were selected as the parameters to build the multivariate regression with extractable V. The equation ($n=90$, $p < 0.001$) is as follow:

$$\log(V_{extractable}) = 1.6 \times \log(V_{total}) + 0.12 \times pH - 4.8$$

In this equation only the $NaHCO_3$ was considered because of its considerable extraction efficiency in both extractable V and bioavailable V. Hence, this equation can be utilized in prediction of extractable soil V, which can shorten the time consuming and indicate the bioavailability of soil V to plant.

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Chapter 5 Conclusions

This is a first study that focused on various aspects of soil V including the sources, geochemical fractions, spatial distribution, speciation, and bioavailability. Our results indicated that the total V content ranged from 35.4 to 475 mg/kg with an average value 182 mg/kg in uncontaminated soils from Taiwan, while the soils developed from mafic parent materials had the highest total V content. The pXRF showed high practicality in rapid soil V evaluation, but the application in serpentinite soils still requires spectrum calibration.

The SSE results of BCR approach revealed the dominant geochemical fraction was the residual fraction following by Fe/Mn bounded fraction. DCB extraction data and EPMA element mapping further addressed the incorporation of V and Fe in soil particles showing that V has considerable siderophile affinity in both parent materials and weathered soils. According to the LCF results for V K-edge XANES spectra and Eh-pH predominance figure for V, VO^{2+} and $H_2VO_4^-$ were the dominant specie in studied soils. In addition, the correlation between the results of plant assay and single extractions demonstrated that $NaHCO_3$ is a suitable extraction method for evaluating both extractability of soil V and V uptake in plant. Moreover, the extractable V can be predicted by using the equation considering soil properties (total V and pH value). This study being the pioneer in the V research in Taiwan provided a comprehensive picture of V in soil for future studies. Our results not only can fill the knowledge gap of V in pedogeochemistry aspect, but also offer an information foundation agricultural application, and ecosystem assessment.

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Appendix 1

Selected physicochemical characteristics of the studied soils.

Sample code	Sand	Clay	pH	OC	Fe	Mn	V
	%			%	g/kg		mg/kg
P11	44	40	4.7	1.9	23.3	0.06	58.3
P12	12	65	4.1	0.9	31.9	0.29	63.0
P13	25	24	6.8	2.1	32.7	0.28	19.3

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Appendix 2

Dry weight (g) of Chinese cabbage in studied soils; 3 replicated plant samples were measured in each soil sample.

Sample code	Dry weight	Sample code	Dry weight
P1	2.99	P8	0.09
	2.26		0.07
	1.97		0.07
P2	0.71	P9	0.09
	1.03		0.08
	0.77		0.24
P3	0.16	P10	0.2
	0.17		0.33
	0.13		0.28
P4	1.41	P11	0.06
	1.70		0.73
	0.64		0.27
P5	1.85	P12	0.08
	2.37		0.09
	1.82		0.10
P6	0.44	P13	1.40
	1.46		3.27
	1.14		2.35
P7	2.44		
	1.02		
	1.06		