氏 名(国籍) 森川 クラウジオ 健 治

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学位論文題目
Exchangeable Al and crop growth in acidified Andosols
(酸性化した黒ボク土における交換性 Al と作物の生
育)

論文審査委員 (主 査) 教授 Ξ 枝 Æ 彦 巳 教授 南 條 Æ 教授 戓 分 牧 衛 論文内容要旨

I. Introduction

Soil acidity is one of the most serious environmental stresses that limit the root growth of many crops. Acid soils are widely distributed in the world, comprising of approximately 40% of the world's arable land (Wright, 1989). Strongly acidic soils are mainly distributed in developing countries where the increase of food production is an actual necessity. On the other hand, the recent increases of acid precipitation and heavy application of fertilizers have also been increasing the soil acidity in developed countries. Strongly acidic soil is comprised of Oxisols, Utisols, Psaments, Spodosols, Andosols, Histosols and Sulfic Fulvents. Crop growth is seriously inhibited in these soils and aluminium toxicity is the principal problem.

Andosols are widely distributed in Japan and divided into two groups according to soil colloidal composition: allophanic Andosol and non-allophanic Andosol. Saigusa and Matsuyama (1998), reported that allophanic Andosols were mainly distributed in the areas having thick depositions of Holocene and/or Late Pleistocene tephras and occupied 4.51 million ha or 69.9% of the total land areas of Andosols in Japan. On the other hand, non-allophanic Andosols were scattered in the areas having poor deposition of these tephras and occupied 1.95 million ha or 30.1% of the total Andosols. In contrast to allophanic Andosols, non-allophanic ones have a clay fraction dominated by 2:1 minerals and mostly contain large amounts of KCl exchangeable Al. Consequently, crop production on non-allophanic Andosols is often severely restricted by Al toxicity. According to Saigusa et al. (1980) and Shoji et al. (1980), in natural leaching condition, allophanic Andosol have only variable charges at a pH higher than 5 and do not show critical pH for root elongation, while non-allophanic Andosol have a critical pH of about 5 due to the Al³⁺ retained in the constant charge of chloritized 2:1 minerals. The recent heavy application of fertilizers, to increase the quality of tea, has been acidifying allophanic Andosols and high amounts of M KCl extractable Al were reported (Kasahara, 1998; Nakae, 1999). However, the origin of M KCl extractable Al of allophanic Andosols is unclear and requires more studies.

Considering the discussion above, the objectives of this work were as follows:

- 1. To evaluate the effect of simulated acid rain and heavy application of fertilizers on acidification of allophanic and non-allophanic Andosols and their effect on crop growth.
- 2. To investigate the origin of M KCl extractable Al in strongly acidified allophanic

Andosols used for tea garden.

- 3. To evaluate the effect of continuous application of low-acidulent fertilizers and controlled release fertilizers on both acidification of Andosols and crop growth.
- 4. To evaluate the effect of Si containing materials on amelioration of Al toxicity of barley (*Hordeum vulgare* L.) grown in acid Andosols.

II. Effect of simulated acid rain and heavy application of fertilizer on acidification of allophanic and non-allophanic Andosols and their effect on crop growth

The effects of simulated acid rain and heavy application of fertilizers on acidification of allophanic Zao Andosol and non-allophanic Kawatabi Andosol (Table 1) were studied. Two studies were carried out. One was carried out using a 21 cm height and 16.5 cm diameter column, and a rain simulator machine. The other, was done using a stirred-flow reaction system to determine the SO_4^{2-} adsorption capacities of Andosols. For both allophanic and non-allophanic Andosols, the amount of soil extractable SO₄²⁻ increased with depth, but the amount of SO_4^{2-} extracted in Zao soil was much higher than that in Kawatabi soil (Figure 1). The rates of acidification of Kawatabi soil due to acid inputs were higher than that of Zao soil (Figure 2). The amount of M KCl extractable aluminium were higher than that of water extractable Al and increased when soil pH decreased (Figure 2, 3). A significant (P<0.05) reduction of root growth of barley was found in fertilizer treatments of Kawatabi soil (Figure 4). Amounts of SO42adsorbed in Zao soil were much higher than those in Kawatabi soil (Figure 5). Kawatabi soil was more sensitive to acid inputs and adsorbed lower sulfate than Zao soil. The amount of M KCl extractable Al in Zao soil was lower than that in Kawatabi soil. However, in both soils they increased with the decrease of soil pH. It was suggested that if soil pH of Zao soil decreased to lower values, the amount of M KCl extractable aluminium could be increased to toxic levels for crop growth.

III. Origin of M KCl extractable Al in strongly acidified allophanic Andosols used for tea garden

To determine the origin of M KCl extractable Al from allophanic Andosols following three samples were used: one collected from the inter row of allophanic Andosol of Fuji tea garden strongly acidified by heavy application of fertilizer, one collected from C-horizon of allophanic Andosol, rich in allophane and imogolite

minerals, of Utsunomiya University (Allo/Imo sample) and acidified to pH4.0 (Table 2), and one from an amorphous synthetic precipitate. All samples were continuously extracted with H₂O and M KCl solution using a stirred flow-through reaction vessel system (Figure 6) for 60 minutes. As shown in Figure 7, X-ray diffraction analysis revealed that synthetic precipitate was an amorphous material. The chemical composition of synthetic precipitate was shown in Table 3. Amounts of Al and SO₄²⁻ extracted by M KCl solution during 60 minutes in Fuji soil, Allo/Imo samples and synthetic precipitate were higher than those extracted by deionized water. On the other hand, the amounts of Si extracted by both water and M KCl were almost the same for all samples (Table 4). The reduction of pyrophosphate extractable aluminium by continuous KCl extraction of Fuji soil sample was 44% of total Al extracted for 60 minutes by KCl solution (Figure 8). Ion activities for Al^{3+} , H^+ calculated for each extract were not completely fit with a solubility line for gibbsite (Figure 9). Except for KCl extracts of Fuji Andosol, the relations between ion activities (pAl + pOH + pSO₄ vs 2pH+pSO₄) of all extracts were near the solubility line of synthetic precipitate (Figure 10). Therefore, origin of aluminium in KCl extract from Fuji soil was not due to the dissolution of allophane materials. Part of Al in KCl extract of allophanic Fuji soils was from an organic pool and the remains were probably due to the amorphous aluminium sulfate precipitates and gibbsite. On the other hand, the origin of KCl extractable aluminium in Allo/Imo sample was mainly due to amorphous aluminium sulfate precipitates and gibbsite.

IV. Methods to reduce the aluminium toxicity of Andosols

IV-I. Effect of continuous application of low-acidulent fertilizer and controlled release fertilizers on both acidification of Andosols and crop growth

Pot and field experiments were conducted to evaluate the effect of low acidulent fertilizer (LAF) and controlled release fertilizer (CRF) on the reduction of Andosol acidification from fertilizer application in comparison with the continuous application of readily soluble ammonium based fertilizer (RSF). In both experiments, Komatsuna (*Brassica campestris* var. Maruha) was used as test plant. For the pot experiment, after three successive Komatsuna cultivations, barley (*Hordeum vulgare* L. var. Shunrai) was grown for 7 days to evaluate the degree of soil acidification. The amount of fertilizer corresponding to 150 kg N.ha⁻¹ soil was applied in each Komatsuna

culture for both experiments.

Pot experiment: In RSF treatments, soil 0.01 M NaOH extractable SO_4^{2-} increased whereas soil pH decreased. On the other hand, no significant changes on amounts of SO₄²⁻ and only a little decrease of soil pH were found in LAF treatments (Figure 11). The concentration of aluminium in soil solution and amount of soil exchangeable aluminium increased significantly in RSF5 treatment (Figure 12). For all crops, fresh weight of Komatsuna of RSF6 treatment and LAF6 treatments were not significantly different (P<0.05). On the other hand, fresh weights of Komatsuna plants at second and third crops of RSF5 treatments were lower than that of LAF5 treatments (Figure 13). Root growths of barley seedlings were drastically reduced in RSF treatment (Figure 14). Field experiment: The input of NO_3^- and SO_4^{2-} ions to soils through atmospheric precipitation was 5.4 and 6.2 kg.ha⁻¹, respectively, during the experimental period (Table 5). Sulfate ions were not accumulated in the soils from LAF and CRF treatments. However, SO₄²⁻ was accumulated and lowered soil pH remarkably in RSF treatment (Figure 15). Fresh weights of Komatsuna plants in RSF and CRF treatments were bigger (P<0.0) than that of LAF treatment at first and second crops. On the other hand, at the third crop the highest fresh weight was found in CRF treatment and no significant differences (p<0.05) were found between RSF and LAF treatments (Figure 16). It was concluded that acidification of Andosol was reduced, and Al toxicity was alleviated by use of both low acidulent fertilizer and controlled release fertilizers.

IV-II. Effect of Si materials on amelioration of Al toxicity of barley (*Hordeum vulgare* L.) grown in acid Andosols

Two experiments were carried out. One was to evaluate the effect of silicon on aluminium toxicity of barley (*Hordeum vulgare* L. cv. Shunrai) and the other was to investigate the Si adsorption capacity of Andosols. Both Kawatabi and Kitakami Andosols were used (Table 6). The treatments of the first experiment were established as follows: virgin soil (named Virg) = non treated soil; lime treatment (named L) = the virgin soil with the addition of CaCO₃ to increase the soil pH to 6.5; porous hydrated calcium silicate treatments at 0.5, 1 and 2.5 g.kg⁻¹ of soil (named PS1, PS2, PS3); silica gel treatments at 0.5, 1 and 2.5 g.kg⁻¹ of soil (named SG1, SG2 and SG3); and, three solutions of sodium metasilicate (named SS1, SS2, SS3). Namely, 236, 473 and 1182 mg of sodium metasilicate were dissolved in 1 liter of deionized water and the pH of solutions was adjusted at 5.0. In the Si adsorption experiment, a series of 20 ml of

metasilicate solutions containing various amounts of silicon (0-3 mmol.1⁻¹) were added to 4 g of the soil sample and the Si adsorption capacity of the Andosols was evaluated. The pHs of both soils increased in L and PS treatments, decreasing the amount of exchangeable Al to a negligible level. However, SS and SG treatments had no effects on both soil pH and amount of exchangeable Al (Figure 17). More than half of Si applied in SS treatment was adsorbed in the soils (Table 7). Regardless of treatments, only 0.2 and 1.8% of Si in the soil solution of Kawatabi and Kitakami soils, respectively, were AlH₃SiO₄⁺² forms (Table 8 and 9). Aluminium toxicity of barley seedlings was ameliorated on L and PS treatments (Figure 18). Kitakami soil adsorbed more silicon than Kawatabi soil (Figure 19). According to these results, it was concluded that amelioration of aluminium toxicity by porous hydrated calcium silicate was due to the increase in soil pH rather than to the increase of silicon concentration in soil solution. Silicon amelioration on aluminium toxicity in hydroponics has been reported. However, Al and Si interaction in a soil system is very complex and if present, may not be as clear-cut as those in hydroponics.

Based on the description above, general conclusions of this work were as follows:

- 1. Kawatabi soil was more sensitive to acid inputs and adsorbed lower sulfate than Zao soil. The amount of M KCl extractable Al from Zao soil was lower than that of Kawatabi soil. However, in both soils it increased with a decrease of soil pH.
- 2. Part of Al in KCl extracts of Fuji soil can be explained by changes on organic pools of Al and remains may be due to the dissolution of amorphous aluminium sulfate precipitates and gibbsite. On the other hand, main part of Al in M KCl extracts of Allo/imo sample could be explained by dissolution of amorphous aluminium sulfate precipitates and gibbsite.
- 3. Komatsuna plants absorbed part of SO_4^{2-} applied as RSF fertilizers, but the main part of that remained in the soil, leading to a decrease of soil pH. On the other hand, the use of LAF and CRF decreased the acidification rate of Andosols.
- 4. Ameliorations of aluminium toxicity of barley seedlings by porous hydrated calcium silicate were probably due to the increase of soil pH rather than the increase of silicon concentration in soil solution.

Soil	pН	OM	EC	EC Exchangeable cations (
5011	H_2O	%	dS/m	Ca	Mg	K	Na	
Zao	5.99	4.0	0.072	3.8	0.6	1.3	1.7	
Kawatabi	6.01	16.2	0.034	10.0	0.2	0.9	1.8	

Table 1 - Chemical properties of soils before simulated acid rain and fertilizer treatments.



Fig. 1 - Effect of simulated acid rain and fertilizer on soil 0.01 M NaOH extractable SO_4^{2-}

 \blacktriangle C (control rain)

 \triangle AR (acid rain)

• C+F (C add fertilizer)

• AR+F (AR add fertilizer)



Fig. 2 - Effect of simulated acid rain and fertilizer on soil pH(H₂O)

С -∆· AR ► C+F -O· AR+F



Fig. 3 - Effect of simulated acid rain and fertilizer on soil H₂O and M KCl extractable Al

- AR +F (H₂O) - C +F (H₂O) - - AR +F (KCl) - C + F (KCl)



Fig. 4 - Root growth of barley in soil samples from different depths.

1-5cm depth 5-10cm depth 10-15cm depth 15-20cm depth





▲ Z	ao soil	0	Kawatabi	soil
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Table 2 - Effect of KCl extraction on OM, Alp, Alo, Sio, Fep, Feo, and allophane content of soil samples

<u> </u>		OM	Alp	Al _o	Sio	Fep	Feo		Allophane
Sample		%			mg.kg ⁻¹		- Alp/Alo	%	
	Before	10.1	12110	73820	30513	3505	21860	0.16	21.7
Fuji soil	KCl	9.8	11520	71580	30127	3575	21380	0.16	21.4
-	H ₂ O	10.3	12105	71200	29677	3770	21140	0.17	21.1
<u>,,,, ,, ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,</u>	Before	tr. ^(a)	nd ^(b)	118281	63854	420	12281	nd ^(b)	45.3
Allo/Imo	KCl	tr.	nd	107438	63725	335	12969	nd	45.2
	H ₂ O	tr.	nd	111688	62054	400	12875	nd	44.1

^(a) trace; ^(b) not determined

Table 3 - Chemical composition of synthetic aluminium

S	ulfate prec	ipitate.							
Al	Si	SO4 ²⁻		Malan notio					
	g.kg ⁻¹		÷		IVI	olar I	alle		
6.4	15.8	194.4		1	:	2.4	:	8.6	



Fig. 6 - Schematic representation of sample collection/kinectic flow-through system.



Fig 7 - X-ray diffraction patterm for the synthetic precipitate.

Table 4 - Changes of pH in extract and amount of Al, Si and SO_4^{2-} displaced by H_2O

or MKCl solutions.

Sample	Evitus stant	pl	H	pН	Al	Si	SO ₄ ²⁻
Sample	Extractant	Initial	Final	range		mg.kg ⁻¹	
Enii soil	H ₂ O	4.27	4.40	+ 0.13	377	137	1684
ruji soli	KCl	4.09	4.48	+ 0.39	1341	140	7114
A110/Imo	H ₂ O	4.22	4.39	+ 0.17	4113	898	6588
Ano/mio	KCl	4.20	4.81	+ 0.61	5425	872	16565
Precipitato	H ₂ O	4.68	4.53	- 0.15	88	179	5456
Precipitate	KCl	4.44	4.92	+ 0.48	934	197	7903



Fig. 8 - Difference between amounts of pyrophosphate extractable Al from Fuji soil before (Alpb) and after (Alpa) KCl extraction and total amount of Al extractated by KCl (Al_{KCl}) during 60 minutes.



Fig. 9 - Activities of Al³⁺as a function of extracts pH and stability lines of (---) microcrystalline gibbsite and (---) crystalline gibbsite

 $\blacktriangle KCl extract \bigcirc H_2O extract$



Fig. 10 - Ion activities and solubility lines of synthetic precipitate in the (---) KCl and (---) H₂O extracts

A KCl extract \bigcirc H₂O extract





-O- LAF6 (initial soil pH of 6) -D- RSF6 (initial soil pH of 6)

- LAF5 (initial soil pH of 5) - RSF5 (initial soil pH of 5)



Fig. 12 - Effect of fertilizer treatments on concentration of Al in the soil solution and exchangeable aluminium of soil with initial pH of 5 (pot experiment).

🕒 LAF5 📥 RSF5 🥅 LAF5 🌌 RSF5



Fig. 13 - Effect of fertilizer treaments on fresh weight of komatsuna (pot experiment)

LAF5

RSF5

LAF6 RSF6



Fig. 14 - Effect of fertilizer treaments on root length of barley seedlings (pot experiment)

Table 5 - Total precipitation, mean rain pH and concentrations of NO_3^- and SO_4^{2-} , and

to	total deposition of NO_3^- and SO_4^{2-} during the experimental period.											
R	ain	concentratio	on (mg. l^{-1})	deposition (kg.ha ⁻¹)								
mm	pH	NO ₃ -	SO4 ²⁻	NO ₃	SO4 ²⁻							
663	4.92	1.8	2.2	5.38	6.22							



Fig. 15 - Effect of fertilizer treaments on soil 0.01M NaOH extractable SO_4^{2-} and soil pH (Field experiment)





RSF LAF CRF





Exchangeable Al ---- Soil pH

Table	6 -	Chemie	cal pro	operties	of	soils	used	for	Si	treatments	3.
	-								· • •		•

	pH	OM	Excl	Al saturation				
5011	H_2O	%	Al	Ca	Ca Mg		Na	%
Kitakami	5.16	1.5	179.9	16.0	160.0	4.0	146.0	49.5
Kawatabi	4.56	19.3	441.2	200.0	16.0	tr.	26.0	79.8

^(a) Ca, Mg and K determined with 0.05 M NH₄Ac; Al with M KCl

Table 7 - Adsorption of Silicon in the soils of silicon solution treatments.

Turnet	Kawatabi soil	Kitakami soil				
I reatment	Si adsorption (%)					
Virg	0.0	0.0				
SS1	59.2	76.8				
SS2	69.7	86.4				
SS3	79.5	92.8				

					H ₄ SiO ₄					
Treat./soil			Al	3+	AlH ₃ SiO ₄ ²⁺		others		μΜ	
		рп	[] ^(a)	{ } ^(b)	[]	· · · { }	[]	{ }	[]	
Virg		. 4.6	126	72	2.4	1.26	32.7	27	148	
L		6.7	0.0	0	0.0	0.0	0.0	0	4	
PS	1	4.9	44	25	3.8	2.9	40	33	356	
•	2	5.1	1.3	1	0.2	0.17	1	1	550	
	3	5.7	0.0	0	0.0	0.0	0	0	890	
SS	1	4.7	107	60	3.3	2.6	53	43	207	
	2	4.7	118	65	4.5	3.5	58	47	256	
	3	4.7	91	48	5.1	3.88	44	35	385	
SG	1	4.6	107	61	2.7	2.12	41	34	207	
	2	4.5	137	77	3.5	2.71	39	32	267	
	3	4.9	73	42	7.7	5.99	66	55	433	

Table 8 - Activity and concentration of Al species and H₄SiO₄ after Si treatments according MINTEQA program. (Kawatabi soil)

^(a) activity; ^(b) concentration

					Al speci	es (µM)			H ₄ SiO ₄
Trea	t./soil	ъU	A	1 ³⁺	AlH ₃ SiO ₄ ²⁺		others		μΜ
		pm	[] ^(a)	{ } ^(b)	[]	{}	[]	{}	[]
Virg		5.3	3.2	2.3	0.3	0.3	13.2	12.1	140
L		6.9	0.0	0.0	0.0	0.0	0.0	0.0	40
PS	1	5.4	2.3	1.7	0.3	0.3	14.3	13.3	170
	2	5.5	1.4	1.0	0.2	0.2	8.3	7.7	200
	3	5.6	0.0	0.0	0.0	0.0	0.0	0.0	260
SS	1	5.3	5.8	4.0	0.6	0.5	23.6	21.6	149
	2	5.1	7.9	5.5	0.5	0.4	15.6	14.1	150
	3	5.1	6.7	4.5	0.5	0.4	12.8	11.5	180
SG	1	5.1	7.9	5.5	0.5	0.5	15.6	14.1	160
	2	5.3	3.8	2.7	0.5	0.4	15.7	14.4	190
	3	5.3	4.6	3.2	0.7	0.6	18.7	17.2	229

Table 9 - Activity and concentration of Al species and H₄SiO₄ after Si treatments according MINTEQA program. (Kitakami soil)

^(a) activity; ^(b) concentration



Fig. 18 - Effect of Si treatments on root length of barley seedlings.





論 文 審 査 結 果 要 旨

酸性土壌は世界の約46億ha(農業利用可能地の42%)を占めている。そのうち作物の生育を著しく阻害する"強い酸性土壌"は34億ha(同31%)に達するといわれている。このAl過剰害が問題となる強い酸性土壌の多くは、食糧増産を急務とする発展途上国に分布している。一方、アメリカやわが国などの先進国においては酸性雨や多肥による土壌の強酸性化が顕在化しており、酸性土壌のAl過剰害の土壌学的、栽培管理学的、あるいは植物栄養生埋学的改善は緊急を要する最も重要な課題の1つである。

我が国には黒ボク土が広く分布し,弱酸性のアロフェンを主体とするアロフェン質黒ボク土と強酸性 の2:1と2:1:1型中間種紘物を主体とする非アロフェン質黒ボク土に分けられている。アロフェ ン質黒ボク土では自然条件下ではAl過剰害は問題とならないが,酸性雨および多肥による強酸性化とAl 過剰害が報告されている。そこで本論文では1)酸性雨と多肥による黒ボク土の酸性化過程,2)強酸性 化したアロフェン質黒ボク土のKCl抽出Alの起源,3)黒ボク土における施肥法とAl過剰害軽減法を検討 した。

まず第1に酸性雨および多肥による黒ボク土の酸性化過程を人工降雨装置下で降雨条件と施肥条件を 変えて詳細に検討した。その結果,自然条件下では交換性AIが検出されず,AI過剰害が問題とならない アロフェン質黒ボク土でも酸性雨と多肥で土壌が強酸性化し,KCI抽出AIが出現し,耐酸性の弱い大麦 の生育を著しく阻害することが明らかとなった。また我が国で記録された強さの酸性雨と多肥の影響を 検討したところ,黒ボク土の酸性化は酸性雨より多肥の影響の方がより大きい事が明らかにされた。ま た土壌の酸性化はアロフェン質黒ボク土より非アロフェン質黒ボク土で顕著であった。

第2に、強酸性化したアロフェン質黒ボク土の見かけの交換性Al(KCI抽出Al)の起源を明らかにす るために、有機物を多量に含む富士茶園土壌、有機物を含まない宇都宮黒ボク土C層、合成硫酸アルミ ニュウム沈殿物について連続抽出槽を用いた溶解実験で溶液論的に検討した。その結果、アロフェン質 富士茶園黒ボク土のKCI抽出Alの一部は腐植複合体Alであり、また残りは硫酸アルミニュウム沈殿物と ギブサイト由来Alと考えられた。これに対して、有機物を含まない宇都宮黒ボク土C層からのKCI抽出 Alは大部分が硫酸アルミニュウム沈殿物とギブサイト由来Alであった。

第3に,酸性化しやすい非アロフェン質黒ボク土における施肥形態として低酸根肥料と肥効調節型肥料を用いて酸性化軽減効果を慣行の化成肥料と比較検討した。その結果,施肥と栽培の繰り返しにより 化成肥料区ではSO4²が集積。SO4²はコマツナの栽培によって一部分が吸収されたものの,大部分は土 壌中に残留してpHの低下を引き起こした。これに対して,低酸根肥料と肥効調節型肥料の連続施用は酸 根の付加が見られず,普通化成肥料に比べて非アロフェン質黒ボク土の酸性化(Al害)を著しく軽減した。

また水耕栽培で示されたケイ酸資材によるAI過剰害の軽減効果を実際の非アロフェン紫黒ボク土でケ イ酸カルシウム、シリカゲル、水ガラス溶液を用いて検討したところ、ケイ酸資材のAI害軽減効果はケ イ素の効果と言うよりpH上昇効果によることを明らかにした。

このように本研究は黒ボク土における施肥と酸性雨による酸性化過程,酸性化した黒ボク土のKC1抽 出AIの起源,黒ボク土における酸性化を軽減する施肥法を明らかにしたものでその農業的意義は極めて 大きく,審査員一同は学位(農学)に値するものと判断した。