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journal or publication title	Journal of Integrated Field Science
volume	5
page range	13-16
year	2008-03
URL	<a href="http://hdl.handle.net/10097/40359">http://hdl.handle.net/10097/40359</a>

## Relationship between the content of expansible 2:1 type clay minerals in paddy soils and the amount of ammonium nitrogen in the ponding water by a laboratory experiment

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**Keywords:** nitrogen outflow, ammonium adsorption, readily available fertilizer, smectite, vermiculite, ponding water

Received 10 December 2007; accepted 7 January 2008

### *Abstract*

From the viewpoint of ammonium-nitrogen (N) transportation from paddy fields to rivers, estimation of ammonium-N in the ponding water is important for soil management to reduce N outflow from paddy fields. The relationship between the content of expansible 2:1 type clay minerals (i.e. smectite and vermiculite) and the amount of ammonium-N in the ponding water was investigated by a laboratory incubation experiment. Eighteen soils including fifteen alluvial soils and three volcanic ash soils from north-eastern Japan were used; the clay content in soils was 116-476 g kg<sup>-1</sup>; the content of expansible 2:1 type clay minerals in soils was 0-395 g kg<sup>-1</sup>. The experimental condition corresponded to the condition of paddy fields just before transplanting, where readily available N fertilizer was incorporated to plow layers (0.15 m) at a rate 5 g N m<sup>-2</sup> as basal fertilizer and submerged water depth was 0.06 m. The concentration and the amount of ammonium-N in the ponding water was 1.4-7.5 mg L<sup>-1</sup> and 0.08-0.45 g m<sup>-2</sup>. The amount of ammonium-N significantly related to the amount of clay in the calculated plow layer with a depth of 0.15 m (R<sup>2</sup>=0.42). On the other hand, the amount of expansible 2:1 type clay minerals in the calculated plow layer more strongly related to ammonium-N than the amount of clay (R<sup>2</sup>=0.55). These results were

attributed to the fact that expansible 2:1 type clay minerals have larger amount of negative charge site per clay and higher selectivity in ammonium adsorption than other clay minerals. From these results it was considered that paddy soils rich in clay fraction or expansible 2:1 type clay minerals could adsorb larger ammonium and mitigate ammonium-N runoff through the ponding water.

### *1. Introduction*

From the viewpoint of environment concern, nitrogen (N) outflow through the ponding water drainage from paddy fields is a serious problem, especially after application of readily available nitrogen fertilizer (Takamura et al., 1976; Asano et al., 1976). In a paddy field soon after basal fertilization and puddling, substantial part of total N in the ponding water was particle N (i.e. organic N and adsorbed ammonium-N in soil colloids), and dissolved ammonium-N occupied only about 20 % of total N, because large amount of suspended solids remain in the ponding water (Sato & Taguchi, 2000). However, the ponding water is usually drained several days after puddling for transplanting using machine. Dissolved ammonium-N was about 50 % of total N in the ponding water five days after puddling, when sedimentation of most suspended solids had been finished (Sato & Taguchi,

2000). Therefore, estimation of ammonium-N in the ponding water is important for soil management to reduce N outflow from paddy fields. It is reported that the percentage of adsorbed ammonium in soils ranges from 85 to 95 % in paddy fields (Okajima & Imai, 1973; Toriyama & Ishida, 1987). The residual ammonium-N is dissolved in the soil solution and ponding water. Clay minerals were main materials that adsorb ammonium ion in soils. Especially, expansible 2:1 type clay minerals (i.e. smectite and vermiculite) have high cation exchange capacity that is due to substantial isomorphic substitution and to the presence of fully expanded interlayers that promote exchange of ions, compared to the other clay minerals (Sparks, 1995). Smectite (Reid-soukup & Ulery, 2002) and vermiculite (Malla, 2002) have high adsorption selectivity of ammonium, compared to the other clay minerals. Ammonium adsorption selectivity is high in smectitic and low in allophanic soils (Okamura & Wada, 1984; Egashira *et al.*, 1998). Therefore, it is considered that the content of smectite and ver-

miculite in soils strongly affects ammonium-N in the ponding water. However, no report that investigated the relationship between them is found. In the study, the relationship between the content of expansible 2:1 type clay minerals in paddy soils and the amount of ammonium-N in the ponding water was investigated by a laboratory incubation experiment.

## 2. Materials and Method

Eighteen soils were collected from northeastern Japan (thirteen soils from Miyagi Prefecture; two soils from Yamagata Prefecture; a soil from Akita, Niigata and Tochigi Prefecture, respectively). The soils used in this study were fifteen alluvial soils and three volcanic ash soils (Table 1). Clay content was determined by a pipette method (Nakai, 1997). Clay mineralogical composition of clay fraction was identified by X-ray diffraction (Rigaku Co. Ltd, Miniflex). Relative contents of the clay minerals were evaluated by using X-ray diffraction peak areas, according to the method of Egashira *et al.* (1995). Total contents of

**Table 1** Properties of tested soils.

		In dry soil (g kg <sup>-1</sup> )						In calculated plow layer (kg m <sup>-2</sup> )				
		Smectite & Clay Vermiculite in clay <sup>1)</sup>	Smectite & Vermiculite in soil	Total C	Total N	Acid oxalate extractable		Dry soil <sup>2)</sup>	Clay	Smectite & Vermiculite	Total C	
						Fe	Al					
Alluvial soils	Tsuruoka	116	357	41	25.7	2.4	2.2	3.5	113	13.2	4.7	2.9
	Aotsuka	262	672	176	31.2	2.7	8.8	1.5	95	24.8	16.7	3.0
	Ishikoshi I	262	716	187	20.8	1.9	12.9	2.5	90	23.5	16.8	1.9
	Fujishima	264	595	157	37.8	3.3	10.8	2.8	79	20.7	12.4	3.0
	Tajiri	292	651	190	20.3	1.8	11.8	1.6	82	23.8	15.5	1.7
	Ishikoshi II	315	743	234	22.7	2.1	12.5	1.6	89	28.1	20.9	2.0
	Nakada	327	749	245	15.4	1.4	14.2	1.7	90	29.5	22.1	1.4
	Furukawa	359	928	333	36.5	3.2	15.7	1.7	81	29.0	26.9	2.9
	Hasama	385	764	294	23.6	2.2	13.2	1.6	78	29.8	22.8	1.8
	Iijima	388	697	270	30.7	2.9	11.1	1.7	73	28.5	19.9	2.3
	Kiyosato	411	961	395	39.3	4.0	16.7	3.3	74	30.5	29.3	2.9
	Ohgata	476	679	323	41.6	4.3	7.3	2.5	61	29.0	19.7	2.5
	Minamikata muck	345	465	161	70.6	4.9	14.3	3.4	74	25.4	11.8	5.2
	Toyosato muck	347	373	129	51.4	4.3	8.5	2.9	76	26.4	9.9	3.9
	Nakada muck	373	416	155	73.0	5.4	12.1	2.7	69	25.9	10.8	5.1
Volcanic ash soils	Naruko	126	401	51	46.7	3.7	5.4	9.1	103	13.0	5.2	4.8
	Sikama	211	530	112	68.8	5.2	10.0	20.0	79	16.8	8.9	5.5
	Mohka	341	0	0	106.6	8.1	14.2	29.8	76	25.7	0.0	8.0

1) Evaluated using X-ray diffraction peak areas, according to Egashira *et al.* (1995).

2) Dry weights in plow layers with depth of 0.15 m.

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carbon (C) and N were determined by a dry combustion method (Sumitomo chemical Co. Ltd., NC-80S). Acid oxalate (pH 3.0) extractable iron and aluminum were determined by atomic adsorption spectrometry, according to the method of Ito (1997).

Moist soils without drying after collection from paddy fields were taken into glass bottles (volume, 100 mL; base area, 0.0010 m<sup>2</sup>) to adjust the sedimentation height to 50 mm (±2 mm). The weight of used soils per each bottle ranged from 20.3 to 37.9 g (dry soil). Ammonium chloride was added at a rate 1.67 g N m<sup>-2</sup>. Deionized water was added to dip the soil clods, and the bottles were shaken for 30 minutes. Water level was adjusted to 70 mm from the bottom, and the bottles were incubated at 20 °C for 5 days. This experimental condition corresponded to the condition of paddy fields just before transplanting, where readily available N fertilizer was incorporated to plow layer (0.15 m) at a rate 5 g N m<sup>-2</sup> as basal fertilizer under submerged water depth of 0.06 m. After the incubation, the ponding water with a depth of 0.02 m in the bottle was taken by using a pipette and filtered with a membrane filter (0.45 μm). The concentration of ammonium in the ponding water was determined by the indophenol blue photometric method (Scheiner, 1976).

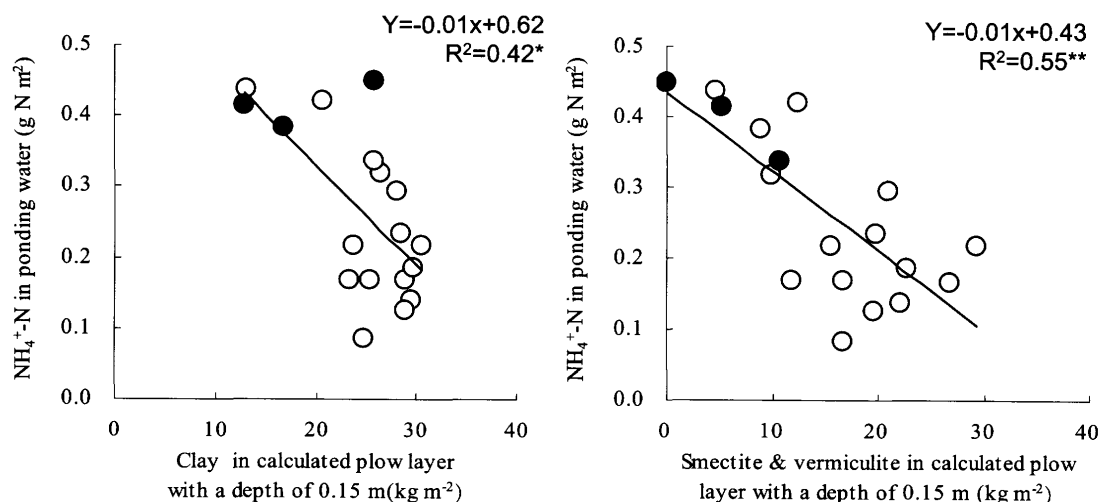
### 3. Results and Discussion

Table 1 shows some chemical and clay mineralogical properties of tested soils. The clay content in soils was 116-476 g kg<sup>-1</sup>. The content of expansible 2:1 type clay minerals was 0-395 g kg<sup>-1</sup>. The contents

of total clay and expansible 2:1 type clay minerals correspond to 13-30 kg m<sup>-2</sup> and 0-29 kg m<sup>-2</sup>, respectively, when the laboratory experimental condition is extended to the field condition with plow layer depth of 0.15 m. Acid oxalate extractable aluminum was large in three volcanic ash soils, and Mohka soil is dominant in allophanic clay.

Fig. 1 shows the relationship between the amount of clay, and expansible 2:1 type clay minerals in the calculated plow layer with a depth of 0.15 m (the calculated plow layer, hereafter) and the amount of ammonium-N in the ponding water. The concentration and amount of ammonium-N in the ponding water were 1.4-7.5 mg L<sup>-1</sup> and 0.08-0.45 g m<sup>-2</sup>. 3-9 % of added ammonium-N (5 g N m<sup>-2</sup>) was dissolved in the ponding water. There was a significant negative relationship between the amount of clay in the calculated plow layer and the amount of ammonium-N in the ponding water (R<sup>2</sup>=0.42). The result indicated that soils with larger amount of clay had higher negative charge and adsorbed larger amount of ammonium ion. However, the amount of ammonium-N in the ponding water showed much variation in soils with the similar amount of clay. The variation of the amount of ammonium-N in the ponding water is considered to be due to ammonium adsorption capacity with the different clay minerals and ammonium adsorption by humus in the soils.

As shown in Fig. 1 (right side), the amount of expansible 2:1 type clay minerals in the calculated plow layer showed closer correlation with the amount of ammonium-N in the ponding water than those of



**Fig. 1** Relationship between clay, expansible 2:1 type clay minerals (smectite and vermiculite) in the calculated plow layer and NH<sub>4</sub><sup>+</sup>-N in surface water. Asterisks mean the relationship was significant (n=18; \* p<0.01; \*\* P<0.001). ○ : alluvial soil, ● : volcanic ash soil.

clay ( $R^2=0.55$ ). These results were attributed to the fact that expansible 2:1 type clay minerals had larger amount of negative charge site per clay (Sparks, 1995) and higher selectivity in ammonium adsorption than the other clay minerals (Reid-soukup & Ulery, 2002; Malla, 2002).

Soil organic matter (SOM) also possesses ammonium adsorption ability because of its negative charge. However, coefficient of determination ( $R^2$ ) between the amount of C in the calculated plow layer and ammonium-N in the ponding water was no more than 0.22, although the relationship was significant ( $p<0.05$ ). It is considered that a substantial part of the relationship was indirect, because there was a significant relationship between the amount of C and expansible 2:1 type clay minerals in the calculated plow layer ( $R^2=0.50$ ). Therefore, the effect of ammonium adsorption of SOM on the amount of ammonium-N in the ponding water was not clarified in the study.

From these results obtained by the laboratory experiment conducted under the condition similar to paddy fields, it was considered that paddy soils rich in clay fraction or expansible 2:1 type clay minerals could adsorb larger ammonium and mitigate ammonium-N runoff through the ponding water drainage from paddy fields.

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