A study of the relationship between the oxidation-reduction layer and the denitrification activity in paddy soil

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Abstract
The characteristics of oxidation-reduction (redox) layers were reviewed under natural conditions. This study was carried out a field survey from 2014 to 2015. The survey was conducted in a paddy field. Soil temperatures, air temperatures, and T-N concentrations of water had been measured. The dissolved oxygen (DO) concentrations of redox layers in flooded soil were measured per 0.2 mm with a special DO concentration sensor through surface to 6 cm depths of soils. Based on the DO concentration results, the soil of the oxidized layers where the concentration was over 1 mg L^{-1} was sampled, along with reduced layer of less than 0 mg L^{-1}. The denitrification activities of redox layers were measured by acetylene blocking technique.
The DO concentrations in paddy field soil have a seasonal change and changed in a thin layer. A positive correlation is observed between the thickness of the oxidized layer and soil surface temperature in the range of 12 ~ 24 °C. The oxidized layer denitrification activities are little, denitrification of paddy fields is dependent on the reduced layer.

Key Words
Denitrification activity, nitrogen removal, oxidized layer thickness

Introduction
In the agricultural sector, excessive fertilization causes a variety of nitrogen pollution problem. One of the main causes of eutrophication in closed water areas is the nitrogen load outflow. The nitrogen removal of paddy fields/wetlands is a nitrogen pollution countermeasure. Paddy fields and wetlands contribute to nitrogen removal. Denitrification is a process of nitrate reduction that may ultimately produce molecular nitrogen (N_2). Kuroda et al. (1976) found that both reductive and oxidative conditions are present in a thin soil layer of paddy field and the thickness of the oxidized layer will influenced nitrification. When dissolved oxygen (DO) is consumed in the presence of easily decomposable organic matter in the soil, then the soil becomes a reduced state (Sadao E, 2012). On the other hand, the DO concentration in flooding water has diurnal variation and the oxidative condition in the daytime becomes oversaturated (Kasubuchi, 2010). The formation of oxidative soil layers and reductive soil layers may affect the denitrification of the paddy field soil.
The study of the redox reaction often uses redox potential (Eh) (Takai and Chiang, 1967; Yamane, 1982; Daisuke and Tatsuaki, 2007). Eh evaluates the redox state in a potential difference using a platinum electrode and a comparison electrode. Therefore the difference of processing or contact area of a sensor is easy to cause a measurement deviation. For this reason, using a DO concentration sensor to measure the redox state of soil layer is desirable.
In this research, characteristics of seasonal changes of oxidation-reduction layers in paddy field soil had been studied. Seasonal variation in the oxidized layer thickness and its influence on denitrification had been studied. We have investigated the seasonal variation in the thickness of oxidized layer and its influence on a denitrification. A DO concentration sensor was used to measure the redox state of soil layer. We measured denitrification activity using the acetylene blocking technique (Toda and Hidaka, 1996).

Methods
Site description
This research was under taken at the O area in Ami town, Ibaraki prefecture in Japan. The land-use is a typical geological formation (known as "Yatsuda" in Japanese in Kanto Plain). It has fields and forests on a plateau and a wetland (or a paddy field) in lowlands. The difference in elevation between the groundwater table and the surface of the vegetable field is about 7 m. This site has been maintained as an experimental paddy field for studies of the nitrogen removal for more than 20 years. The research plot is a non-vegetation plot with all year irrigation. The plot size is 25 m * 1.4 m. Depth of flooding is 5~ 6 cm. The experiment

dates were on July 24, August 19, September 18 and October 30, 2014, and June 4, July 9, August 27, October 15, 2015, respectively. Measurements were taken at about AM 9:00 o'clock.

Soil sampling
Soil samples were collected 3 points by undisturbed sample. Each sample was measured the DO concentration every 0.2 mm in soil samples by a DO concentration sensor (Unisense comp.). Based on the DO concentration results, oxidized layers and reduction layers were collected. The DO concentration border of oxidized layer and reduction layer is 0 mg L^{-1}. DO concentration is curvilinear in soil with increasing depth. In order to prevent contamination during soil sampling, the soil of oxidized layers where the DO concentration was above 1 mg L^{-1} was sampled, along with reduced layer of less than 0 mg L^{-1} in this study. Then denitrification activities of oxidized layers and reduction layers were measured by the acetylene blocking technique. Soil temperatures were measured every 1 cm from soil surface.

Water sampling
Inlet water, midpoint water and outlet water were sampled on every survey date. We measured water temperatures, EC, pH, DO concentrations onsite and T-N concentrations in a laboratory.

Results
DO concentrations of soil
The depth of the DO concentration where was 0 mg L^{-1} is shown in Figure 1. Average values of depth were 20.7 mm, 16.0 mm, 43.3 mm, 30.1 mm, 51.3 mm, 64.4 mm, 84.1 mm and 30.5 mm to the survey date days, respectively. The DO concentrations changed in range of 10 ~1.5 mm in soil layer and became deepest between August and September. It because of the temperature rise made biological activity became brisk from August to September. In this study, we consider these depths as "the oxidized layer thickness".

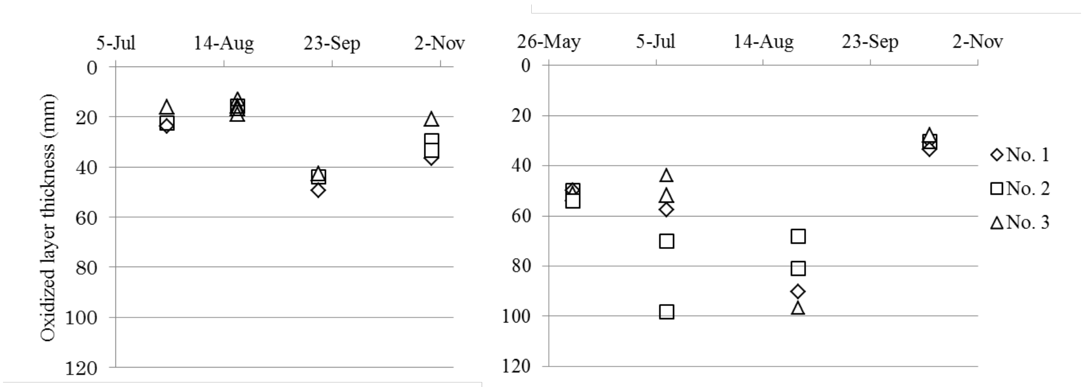
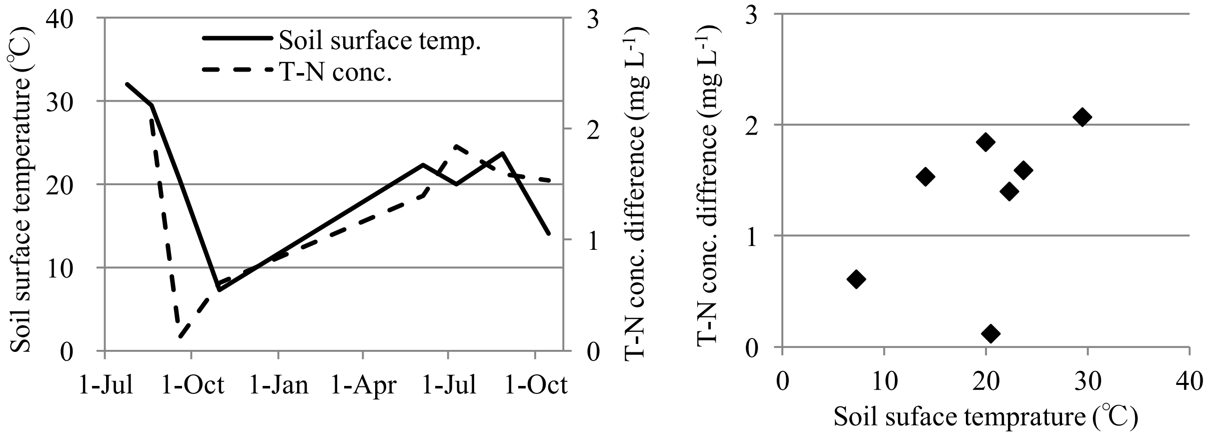


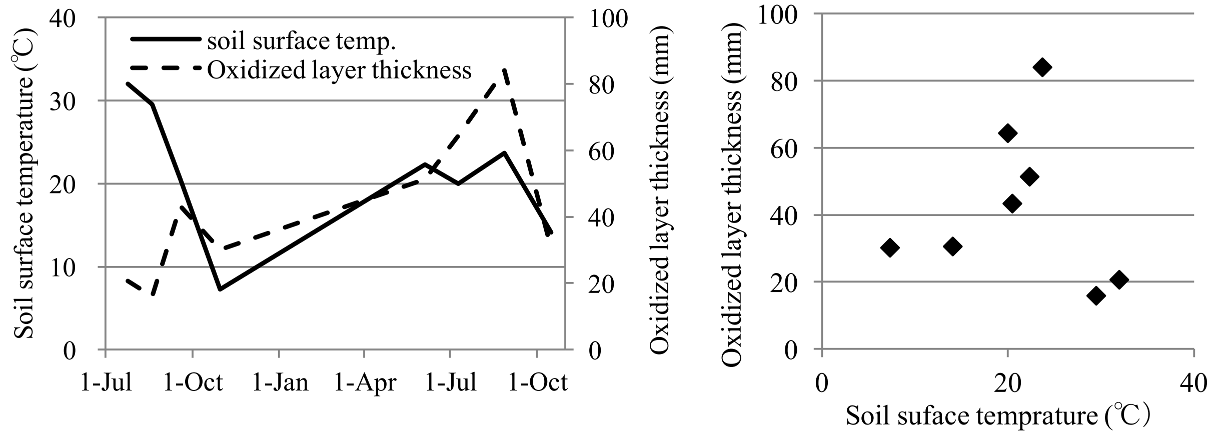
Figure 1. The results of the DO concentration measurement on each survey day. Plots show depth where the DO concentration was 0 mg L^{-1}. From right of water flow direction, three soil samples were named "No. 1" ~ "No. 3", respectively.

Water qualities and soil properties
The relationship between soil surface temperature and the T-N concentration difference is shown in Figure 2. As the soil surface temperature increase, the larger T-N concentration difference became. It shows nitrogen removal is dependent on the soil surface temperature. Also, the relationship between soil surface temperature and the oxidized layer thickness is shown in Figure 3. A positive correlation is observed between the thickness of oxidized layer and soil surface temperature in the range of 12 ~ 24 °C.



(a) (b)

Figure 2. The relationship between soil surface temperature and the T-N concentration difference. (a) The soil surface temperature and the T-N concentration difference (the difference between inlet water and midpoint water) on each survey day. (b) The correlation diagram of soil surface temperature and the T-N concentration difference.



(a) (b)

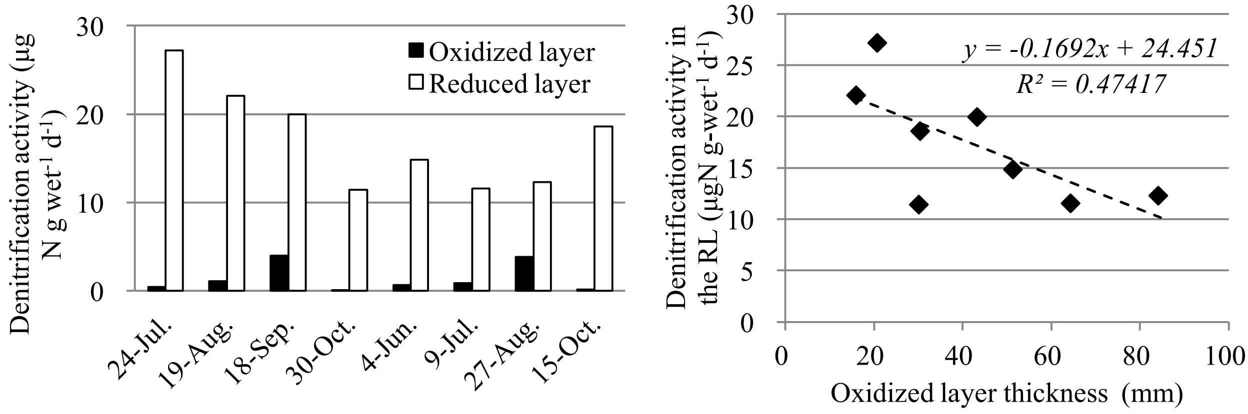
Figure 3. The relationship between soil surface temperature and the oxidized layer thickness. (a) The soil surface temperature and the oxidized layer thickness on each survey day. (b) The correlation diagram of soil surface temperature and the oxidized layer thickness.

Denitrification activity

Changes in denitrification activity of oxidized and reduced layer are shown in Figure 4. The highest denitrification activity was 4.0 μg N g-wet^{-1} d^{-1} at September 2014, and the smallest was 0.1 μg N g-wet^{-1} d^{-1} at October 2014 in the oxidized layer. Also, in the reduced layer, they were 27.2 μg N g-wet^{-1} d^{-1} at July 2014 and 11.5 μg N g-wet^{-1} d^{-1} at October 2014, respectively.

The denitrification activity of the oxidized layers rose from August to September and dropped in October. Denitrification activity in the reduced layer was lower from August to October and higher than denitrification activity of the oxidized layers.

Figure 4-(b) shows the correlation diagram of the reduced layer denitrification activities and the oxidized layer thickness. It shows that a negative correlation is observed between the denitrification activity of the reduced layer and oxidized layer thickness.



(a) (b)

Figure 4. (a) The denitrifications of oxidized layer and reduced layer on each survey day. (b) The correlation diagram of the reduced layer denitrification activities and the oxidized layer thickness.

Conclusion

In this study, characteristics of seasonal changes of oxidation-reduction layers in paddy field soil had been studied. As a result, research has shown as follows.

1) The DO concentrations in paddy field soil have a seasonal change and changed in a thin layer.

2) A positive correlation is observed between the thickness of oxidized layer and soil surface temperature in the range of 12 ~ 24 °C.

3) Denitrification in paddy fields is dependent on the reduced layer.

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