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REVIEW

Method to Evaluate "Uplandization" in Converted Field from a Paddy Based on Crystallinity of Free Iron Oxides

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Abstract

"Uplandization" is the process that changes the physical and chemical properties in a paddy field into those of an upland field. There is a transitional period when a paddy field is converted to an upland field. We propose a new method to evaluate the degree of "uplandization" based on changes in crystallinity of free iron oxides. The iron oxides influence soil physical and chemical properties such as soil microstructure or phosphate retention. Iron crystallinity is evaluated by the amount of iron extraction over 120 min by 1 mol L^{-1} pH 3.0 sodium acetate buffer, at solution to soil of 100 to 1 (Fe_{ac}). Fe_{ac} decreases in proportion to the period after conversion to upland cultivation. Fe_{ac} is significantly correlated with phosphate retention properties and iron reducibility of soils under submerged conditions, but acid-oxalate-extracted iron, which is used to extract amorphous free iron generally, is not. For this reason, Fe_{ac} is considered to be more suitable for evaluation of the history of uplandization.

Discipline: Soils, fertilizers and plant nutrition
Additional key words: redox reaction, phosphate sorption, soil microstructure

Introduction

Upland fields converted from paddy fields (UFP) are fields used to produce crops other than rice in paddy fields. Paddy soil, without submerging and puddling, naturally dries, oxidizes and develops new soil structure[10]. Soils in UFP have unique physical and chemical properties engendered by their transitional status from paddy to upland soil. Elucidating the changes in UFP chemical and physical properties is necessary for suitable UFP management. Naganoma and Moroyu[9] proposed an index of "uplandization" based on changes in soil microstructure; the degree of uplandization (DU) that takes a value between 0 and 1. The equation is:

DU = (Sediment volume of continuous paddy soil – Sediment volume of UFP) / (Sediment volume of continuous paddy soil – Sediment volume of continuous upland soil)

Because soil drying decreases sediment volume[5] and submergence increases sediment volume by reduction of free iron oxides[13] in soils, the DU might reflect the history of the soil moisture and redox condition.

When paddy soil is oxidized, ferric oxides are formed by oxidization and hydration of soluble Fe^{2+}, exchangeable Fe(II), and free ferrous oxides. During oxidization, other chemicals may suppress crystalization of ferric oxides, resulting in production of unstable amorphous ferric oxides[3]. Such iron oxides have the following properties: (1) highly reactive with phosphate[11,13]; (2) easily reducible under submerged conditions[12]; (3) gradually decrease in amount concomitant with the period of upland cultivation[12,14]. It is likely that this unstable fraction of ferric oxides affects physical and chemical properties of UFP soil, such as ion sorption properties, destabilization of soil structure by reduction of soil, and others.

Generally, such reactive ferric oxide is considered to be an amorphous free iron oxide that has high surface

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area[2], thus acid-oxalate extractable iron (Fe_o) has been used to estimate the amount of this iron oxide fraction[7]. However, Fe_o is almost constant with the period of upland cultivation because Fe_o constitutes almost all free iron oxides in UFP[12]. Some researchers[11, 14] have tried to use a milder extractant for evaluation, but they have not conducted comprehensive studies to find more suitable conditions for specific iron evaluation in UFP.

This study is intended to: (1) develop a method to measure free iron oxides mentioned above; (2) investigate the possibility of the method to evaluate the degree of uplandization in UFP.

Materials and Methods

1. Soils

Soils were sampled from the plow layer in 7 UFPs of the Hokuriku Research Center, National Agriculture Research Center. One of them had 6 sub-plots that were converted to an upland field for 0–5 y. Three samples were obtained from each field except for the one field that had sub-plots; from this field, one sample was obtained from each sub-plot. Soils used in this study are classified as *clayey, montmorillonitic, mesic, typic Epiaquepts* containing 0.38 kg kg^{-1} clay and 0.011 kg kg^{-1} free iron[4].

2. Methods

Sodium acetate buffer was selected to extract ferric oxides. Concentration and pH of acetate buffer, shaking period, and ratio of extractant to soil were examined. Examination was conducted by comparing results of continuous paddy field and UFP sample soil over 5 y. In addition, we examined temperature during shaking and the effect of drying and period of storage after drying the soil. The amount of iron in the extractant was determined by colorimetry using the o-phenanthroline method[7] after reduction by 0.1 kg L^{-1} of hydroxylammonium-chloride. Phosphorus retention[1], Fe_o, and active ferrous iron[6] extracted from submerged conditions that were incubated for 7 days at 30°C were used to examine properties of iron extracted by the method developed in this study. Phosphate retention was measured using 1:5 soil to solution ratio for soils from sub-plots and 1:25 for all others.

Results and Discussion

1. Condition for extraction

More iron was extracted with the lower pH, the higher concentration of acetic acid, the longer period of shaking, and the higher ratio of extractant to soil (Fig. 1). The ratio of the amount of extracted iron in continuous

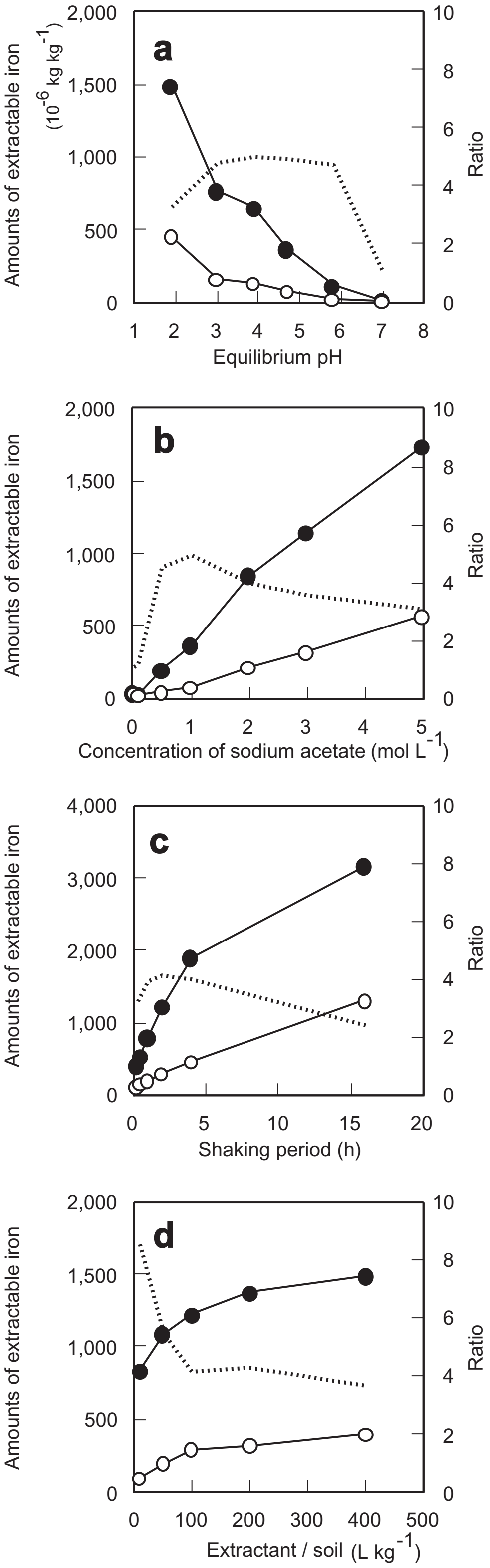

Fig. 1. Effect of extracting conditions on amount of extracted iron

●: continuous paddy field. ○: upland field converted from a paddy field 5 y before. ----: ratio of the amount of extracted iron between ● & ○ . For each condition except the examined one, we used pH 3.0, 1 mol L^{-1} sodium acetate buffer, 2 h shaking period, and 100 L kg^{-1} ratio of extractant to soil.

paddy field to UFP over 5 y was calculated. The highest values were obtained at pH from 3.0 to 6.0; 1 mol L^{-1} concentration of extractant; 1 h shaking time; and the ratio of extractant to soil was better if lower (Fig. 1). The ratio of extractant to soil of 100 L kg^{-1} was considered to be acceptable because the extracted amount was relatively stable around this ratio. Moreover, in cases where the ratio is lower, the ratio and concentration of extractant could deviate from a selected value because water that is contained in wet soil could affect the ratio. The extractant of pH 3.0 was selected because the amount of extracted ferric iron is high and relatively stable at this pH. There is the additional advantage that active ferrous iron can be determined by the proposed method simultaneously. pH 3 is close to pH 2.8, which is used in a method to extract active ferrous iron[6]. Other conditions like shaking period, component of extractant, and ratio of soil to extractant are identical.

2. Effect of temperature during extraction, air drying of soil, and period of storage after drying

The higher temperature during shaking increased the amount of extracted iron (Fig. 2). As temperature increased from 15 to 29°C, the amount of extracted iron increased to 1.5 times more than that at 15°C. The temperature during shaking must be kept constant.

The amount of extracted iron showed no significant difference between the dried samples and wet samples (Fig. 3). Storage for 1 y in a dried condition showed no significant change in the amount of extracted iron, but storage for 6 y significantly increased the amount extracted (Fig. 3). The use of samples stored in a dried condition should be limited to 1 y. The reason for the increase of extracted iron in samples stored for 6 y is unclear.

3. Proposed method to extract iron oxides

The suggested method to extract iron oxide is as follows: 1.0 g as oven dried basis of wet or air-dried soil sample is added to 100 mL of 1 mol L^{-1} sodium acetate previously adjusted to pH 3.0. The resulting suspension is shaken for 120 min at room temperature. After shaking, the suspension is filtered immediately and the iron concentration in the filtrate is determined. Active ferrous iron[6] can be determined at the same time using this filtrate by colorimetry[7]. The amount of extracted iron (Fe_{ac}) is expressed as extracted iron amount per unit of soil weight (oven dried basis).

4. The chemical characteristics of Fe_{ac}

Fe_{ac} was more suitable for evaluation of reactivity of iron oxide with phosphate in UFP than Fe_o. There was a highly significant correlation between Fe_{ac} and phosphate retention (Fig. 4a). The correlation between Fe_o and phosphate retention was not significant (Fig. 4b). Subplots whose period from conversion were different

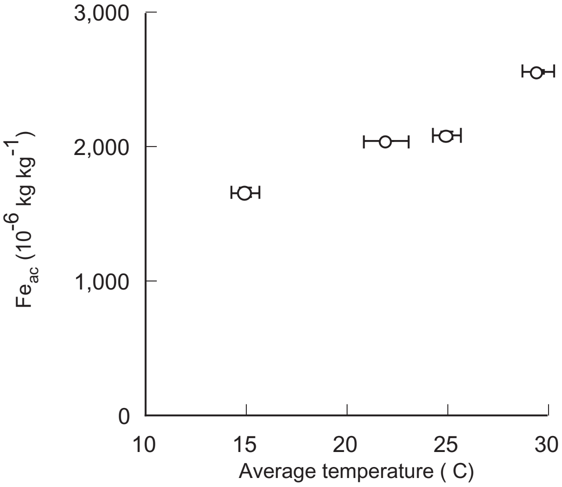

Fig. 2. Effect of temperature during shaking on Fe_{ac}
Error bars show SD.

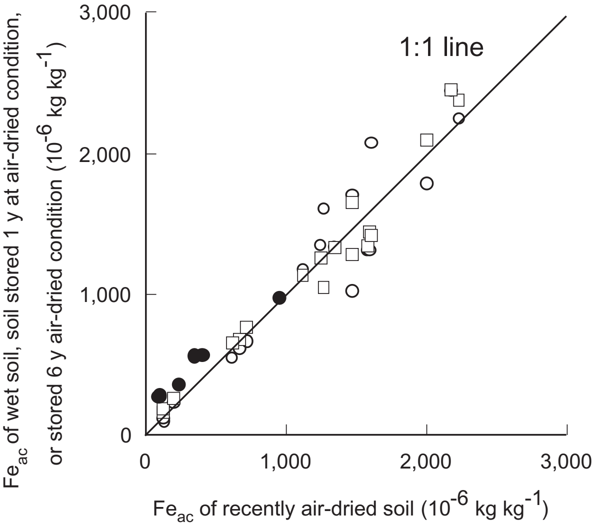

Fig. 3. Relationship between Fe_{ac} of recently air-dried soil (x-axis) and Fe_{ac} of wet soil, Fe_{ac} after 1 y storage at air-dried condition, or Fe_{ac} after 6 y storage at air-dried condition (y-axis)

○: wet soil. □: stored 1 y at air-dried condition. ●: stored 6 y at air-dried condition. Wilcoxon signed rank test showed that there is no significant difference between Fe_{ac} of recently air-dried soil and Fe_{ac} of wet soil ($n = 18, p<0.95$) and 1 y storage ($n = 18, p<0.35$). There was a significant difference between Fe_{ac} of recently air-dried soil and 6 y storage ($n = 6, p<0.028$).

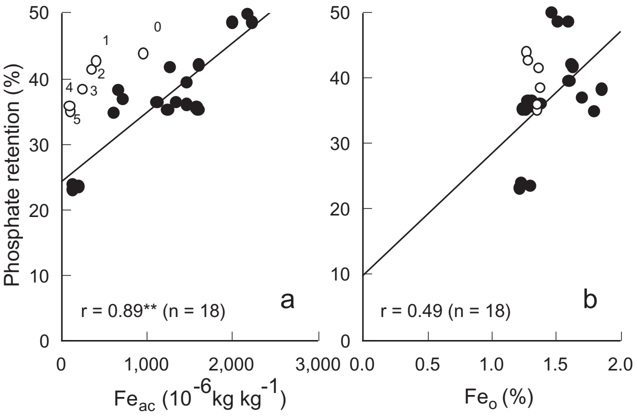

Fig. 4. Relationship between Fe$_{ac}$, Fe$_o$ and phosphate retention

Open circles indicate sub-plots with different periods from conversion. Solution to soil ratio was 5 for phosphate retention (solution to soil ratio of others was 25). Years after conversion are indicated by numerals next to open circles.

**: significant correlation at $p<0.01$ for closed circles.

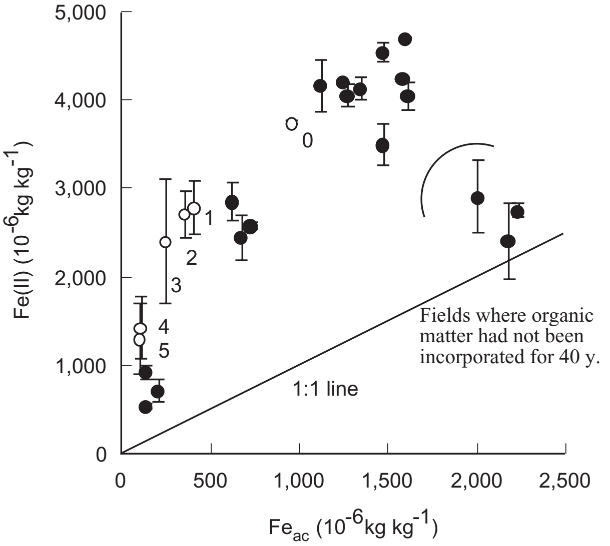

Fig. 5. Amount of active ferrous iron (Fe(II)) in soil incubated under submerged conditions and Fe$_{ac}$

Error bars indicate a duplicate difference. Incubation was for 7 days at 30°C. Open circles indicate sub-plots with different periods from conversion. Years after conversion are indicated by numerals next to open circles.

showed that Fe$_o$ did not change in relation to the period of conversion, but Fe$_{ac}$ was related to the period of conversion (Fig. 4a). The reason that the results of sub-plots were slightly different from others is ascribed to the difference in the soil to solution ratio.

A higher amount of active ferrous iron was formed when the soil with a higher amount of Fe$_{ac}$ was incubated under a flooded condition (Fig. 5). When a longer period elapsed under upland condition, a lower amount of active ferrous iron was formed by flooding. Our results also show that Fe$_o$ did not change by cultivation period (Fig. 4), but that the reducibility of iron was significantly changed. Preferential reduction of amorphous to crystalline iron oxides by bacterial activity had been observed by Munch and Ottow[8]. Our results indicated that preferential reduction of iron exists within the amorphous fraction, Fe$_o$. We think Fe$_{ac}$ can evaluate the tendency toward preferential reduction within the Fe$_o$ fraction. On the other hand, the amount of active ferrous iron formed was relatively low in a field where organic matter had not been incorporated for 40 y (Fig. 5). In this field, microbial activity could be a factor limiting iron reduction in soil.

The results showed that determination of Fe$_{ac}$ can indicate specific properties of iron oxides in UFP.

5. Usage of Fe$_{ac}$

The Fe$_{ac}$ probably complements the DU[9]. The DU value cannot indicate changes in UFP chemical properties, such as phosphate retention, because DU is an index based on the soil microstructure. The DU of any air-dried soil is one. However, there could exist two soils with equal DU but they could have different iron reducibility. The difference in reducibility effects soil chemistry and soil microstructure[12]. This disadvantage of DU can be ascribed to the fact that DU does not fully reflect the change in UFP iron oxide.

Results shown in this paper and in Takahashi et al.[12] suggest that Fe$_{ac}$ could reflect a history of soil moisture environment in UFP. Takahashi et al.[12] showed that the total amount of the Fe$_{ac}$ fraction gradually decreased after conversion to upland conditions whereas free iron oxides fluctuated between ferrous iron and ferric iron. Our results indicate that rapid air-drying of soil did not change Fe$_{ac}$ (Fig. 3) and that a flooded condition generated a greater amount of ferrous iron than Fe$_{ac}$ (Fig. 5). According to Furukawa[3], rapid oxidization of soil ferrous iron produces unstable ferric oxides. Increases in such an unstable iron fraction should be reflected in Fe$_{ac}$ as mentioned above. These considerations suggest that Fe$_{ac}$ decreases slowly under aerobic conditions and increases when the soil is submerged. We consider both Fe$_{ac}$ and DU should be used to determine changes in UFP physical and chemical properties. Yanai et al.[15] provide a typical example of using Fe$_{ac}$ to examine history of soil management.

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