REDUCTION OF DIOXIN OUTFLOW FROM PADDY FIELDS BY APPLICATION OF NEUTRAL SALTS AS FLOCCULATION AIDS

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Abstract
The herbicides pentachlorophenol (PCP) and 2,4,6-trichlorophenyl 4-nitrophenyl ether (CNP), containing dioxin as impurities were commonly used in Japanese paddy fields from the 1960s to 1970s. The residual dioxin in soils flow out together with suspended solids (SS) in drainage from the fields when paddy soil is puddled and dispersed. Thus, we studied to prevent the dioxin discharge from paddy fields by promoting settlement of SS through the use of soil flocculation aids. Yellow soil in paddy fields is easily dispersed by puddling, leading to high concentrations of SS in the drainage. We applied calcium chloride and potassium chloride to a paddy field (Yellow soil) as a flocculation aid at puddling time. The SS concentration in the paddy water was reduced to 3-12％ of that in the control plot by this procedure. The SS particle-size distribution, measured by the laser scattering, showed the proportion of coarse-grained SS was higher when the flocculation aids were applied. With application of flocculation aids, the dioxin concentrations in paddy water had decreased to between 2％ and 11％ of that of the control plot after puddling. Application of these flocculation aids did not significantly affect soil properties and rice yield.

Introduction

Pentachlorophenol (PCP) and 1, 3, 5-trichloro-2-(4-nitrophenoxy) benzene (CNP) were commonly used as herbicides in paddy fields in Japan during the 1960s and 1970s. While isomers with a high chlorine content, such as OCDD/F and HpCDD/Fs, became mixed mainly with PCP as impurities, isomers with low chlorine content, such as 1, 3, 6, 8-TeCDD and 1, 3, 7, 9-TeCDD, became mixed with the latter [1, 2, 3]. Although registration of these herbicides has already expired, dioxin mixed remains in soil in paddy fields. Dioxin that strongly adheres to suspended solids (SS), however, flows out from paddy fields into rivers, lakes, marshes and oceans at the time of puddling or when the water level rises, and concerns exist regarding intake of dioxin by consumers of fish and shellfish originating from polluted waters and bottom mud [3, 4].

On the other hand, it has been reported that almost no dioxin is transferred from soil in paddy fields to unpolished rice [5]. Also, dioxin gradually decomposes in soil, although its half-life is several decades [3]. Thus, prevention of the spread of dioxin from paddy fields is considered to be one of the solutions to dioxin problems in paddy fields. Based on these backgrounds, the object of this study is to verify the effect on the control of dioxin discharge from rice paddies by promoting settlement of suspended solids using soil flocculation aids at the time of puddling.

Materials and Methods

(1) Screening of the most appropriate flocculation aids:
Eight g of a field-moist yellow soil (fine texture), containing 1.5 g of water, collected from a paddy field was placed in six test tubes and 15 ml of purified water was added to each tube to produce a solid-liquid ratio of 1:2.5. Various chemicals, a mineral flocculation aid (Aquaflock), porous calcium silicate, aluminum sulfate, calcium sulfate, calcium chloride and potassium chloride within a range of 0 to 80 mg were added to the respective tubes as flocculation aids, and each mixture was shaken for 30 minutes. After test tubes were left upright for one hour, 2 ml of supernatant fluid was collected from each one from a depth of 2.5 cm, and the transmittance (wavelength: 660 nm) was measured using a spectrophotometer (U-2001, HITACHI Ltd, Japan).

(2) Application of flocculation aids to paddy fields:
Soil puddling that is mechanically mixing of paddy soil with pooled irrigation water was conducted after spreading 3 kg per 100 m^2 of calcium chloride or potassium chloride as flocculation aids on paddy fields (fine-textured yellow soil) of approximately 3000 m^2 in each plot. Paddy water was collected 1, 3 and 24 hours later by draining water from the outlet of the paddy field to measure pH, EC, weight of suspended solids (SS),

grain-size distribution of SS (laser scattering method, LA-920 manufactured by HORIBA Ltd.). Dioxin concentration in paddy water sampled at 3 hrs after the puddling was analyzed according to the method described by Japanese Industrial Standards Committee [6].

(3) Changes of soil chemical properties with the application of the flocculation aids:
Soils were sampled from the experimental paddy fields, air-dried at approximately 25℃ and passed through a 2 mm mesh sieve. Soil pH was determined by means of the glass-electrode method (Horiba, PH81, Japan) with a ratio of soil to either water or 1 mol L^{-1} KCl of 1:2.5. Exchangeable cations and cation exchange capacity of soils were determined by ammonium acetate method7 with minor modification [7].

(4) Paddy rice cultivation:
Paddy rice cultivar, Koshihikari, was transplanted and cultivated in the experiment paddy fields after the puddling. Mature rice was harvested by hand, taking two 1.65 m^2 quadrilaterals in each plot. Air-dried shoot material and brown rice yield were measured.

Results and Discussion
(1) Screening of flocculation aids:
Soil was more likely to be flocculated by ionic materials, such as aluminum sulfate, calcium sulfate, calcium chloride and potassium chloride, and the transmittance of supernatant fluid increased dramatically by adding 0.15 mg of flocculation aid per gram of dry soil (Fig. 1). The dosage of 0.15 ml per gram of dry soil is equivalent to application of 1.5 to 3 kg per 100 m^2 of paddy field on the assumption that the plowed soil layer of the paddy field is 10 to 20 cm and the apparent specific gravity of the field soil is 1.
Calcium chloride and potassium chloride were screened as the most appropriate flocculation aids taking into consideration the autumn decline of paddy rice due to generation of hydrogen sulfide and the safety of aluminum, and given that the effect of other flocculation aids was relatively low.

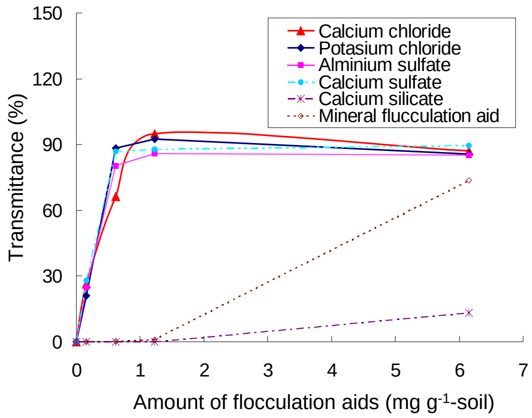
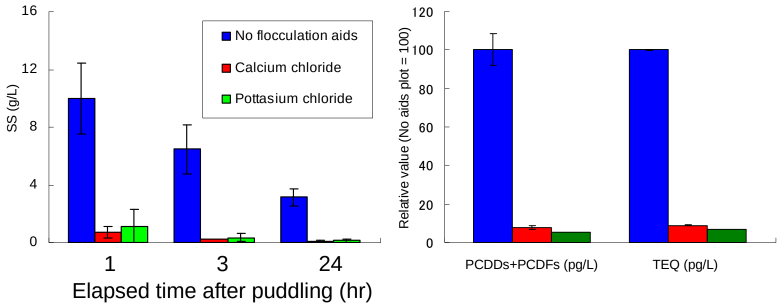


Fig. 1 Effect of various flocculation aids added to yellow soil on the soil particle settlement.

(2) Application of flocculation aids to paddy fields:
The SS concentration in paddy water was 5 to 11% lower in plots where flocculation aids were applied compared with the non-application plot (Fig. 2-a). According to the SS particle-size distribution measured by the laser scattering method, the rate of coarse-grained SS was high in the plots where flocculation aids were applied. It is thought that gathered and flocculated particles formed large masses and promoted settling due to the fact that these flocculation aids dissolved in paddy water, increased the ionic strength and decreased the inter-particle repulsion by narrowing the diffuse double layer of the soil particle surface (Fig. 3). With the application of flocculation aids, the dioxin concentration in paddy water also decreased to between 5 and 9% of that of the non-application plot 3 hours after soil puddling (Fig. 2-b). Because this rate of decrease virtually corresponded with changes in the SS concentration and almost no dioxin was contained in the liquid phase, it was presumed

that promotion of settling of SS decreased the dioxin concentration.



(2-a) (2-b)

Fig.2. (a&b) Changes of suspended soilid contents (SS) (2-a) and dioxin concentrations (2-b) in the paddy water with the application of flocculation aids.

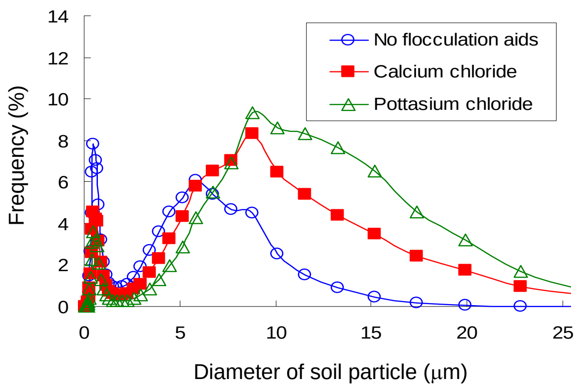


Fig. 3. Relationships between application of flocculation aids and diameter of soil particle (floc), after 1hr of the application.

(3) Changes of soil chemical properties with the application of the flocculation aids:

While the exchangeable potassium concentration increased with the application of potassium chloride during the cultivation period, no significant changes were observed in other soil properties by application of flocculation aids. Thus, the application of the flocculation aids could not have crucial adverse effects on soil chemical properties.

Table 1 Changes of soil chemical properties by the application of flocculation aids. (Relative value: pre-application=100)

Flocculation aids	pH (H2O)	pH (KCl)	(Exchangeable form) Ca	K	Mg	CEC
No aids	103.7	101.5	96.7	68.6	91.1	90.8
$CaCl^2$	101.9	99.5	96.5	78.3	93.7	98.6
KCl	96.1	96.2	96.1	126.7	90.5	90.2

(4) Paddy rice cultivation:

Application of flocculation aids did not significantly affect growth such as stem length and straw weight, and rice yield (Fig. 4). From the above results, it was found that flocculation aids did not adversely affect soil or paddy rice, and that this method could be applied to actual fields.

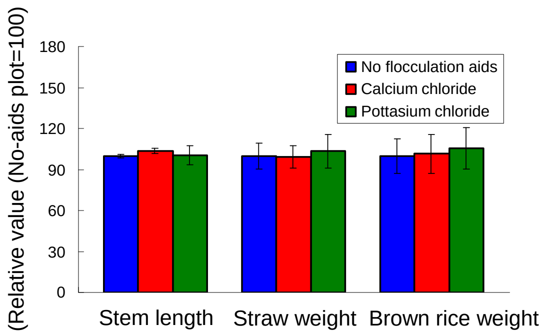


Fig.4. Changes of growth and yield of rice with the application of flocculation aids.

Conclusion

We found that flocculation aids did not adversely affect soil or paddy rice, and that this method could be cost effective and applied to prevent dioxin outflow from paddy fields.

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