관개기간 중 농경지로부터의 용존 유기물의 유출

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Outflow of Dissolved Organic Matter from Agricultural Fields in an Irrigation Period

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Abstract

The aim of this study is to quantify and characterize the dissolved organic carbon (DOC) from paddy fields and crop fields in Tottori, Japan. DOC and ultraviolet (UV) absorption were measured in the filtrated water of each sample. The DOC concentration and the SUVA (specific UV absorption) of biodegradation analysis samples were determined around 50 days after their incubation. In the Fukui paddy fields, DOC concentration varied seasonally from 1.1 to 10.1 mg Cl^{-1}, becoming higher during heavy runoffs in April, a non-agriculture period. Variations in DOC concentration did not always correspond to rainfall, though. The Obadake paddy fields showed a DOC concentration pattern similar to that of the Fukui paddy fields. The daily DOC discharge per area in the Fukui (up), Fukui (down), Obadake (south) and Obadake (north) paddy fields influent from paddy fields were 0.02, 0.0161, 0.0135 and 0.0027 kg a^{-1} day^{-1}, respectively. These differences resulted from differences in agricultural types and customs of farmers according to paddy fields and other kinds of fields. Also, the SUVAs [which are indirect means to evaluate humic substances (hydrophobic fractions)] of the studied influent waters from paddy fields were generally lower than those of the influent waters from crop fields. Nonbiodegradable DOC accounted for 50.2 - 98% and 46.8 - 85.5% of the total DOC in the paddy fields and in the crop fields, respectively.

keywords : Dissolved organic carbon (DOC), Paddy field, Non-biodegradable

1. Introduction

Dissolved organic matter (DOM) is ubiquitous in global aquatic systems, with its mass concentrations ranging from 0.5 to 100 mg Cl^{-1} of organic carbon (Thurman, 1985). Its important functions include serving as an electron donor in metal complexation, sorption of xenobiotics, and adsorption onto mineral phases and onto activated carbon. DOM is partially oxidized during microbial utilization and water treatment, in which it may also become a substitute for chlorine, which would lead to a suite of products with toxic relevance (Frimmel, 1998). Application of organic waste materials in agriculture has received considerable attention in recent years (Iakimenko et al., 1996). For example, these organic waste materials have been applied to agricultural lands for a good harvest before seeding of plants in the spring. Many pollution sources from agricultural lands such as paddy fields and crop fields are affected by the geology and geography of watersheds, the water quality in watersheds, and human influences such as the use of fertilizers and water management. Runoffs of fertilizer contents (such as phosphorus and nitrogen) from paddy fields to lakes and streams cause waterblooms in water systems. The study discussed herein relates the DOC of non-point sources such as agricultural lands, forests and animal farms with some studies of other water systems. These studies have evaluated the DOC export budget, the transformation of DOC in forests (Cronan, 1985; Trumbore et al., 1992), and the role of hydrology on the concentration and fluxes of DOC (Hinton et al., 1997). There is little information, however, about DOC concentrations, loading and characteristics in agricultural lands such as paddy fields, crop fields and animal farms. We thus researched on DOC from paddy fields, which are very important sources of non- point pollution in aquatic

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systems. The objective of the study described herein is to evaluate the quantity of dissolved organic matter (such as DOC) from paddy fields and crop fields and to show their characteristics by determining biodegradation for the rapidly and slowly degradable organic matter and ultraviolet adsorption properties for the presumption of humic substances.

2. Method and materials

The study areas are located around Koyama Lake in the Tottori prefecture, Japan. The surface water and drain water of four paddy fields in these areas were investigated from April 2003 to September 2003 (Fig. 1).

Paddy field samples were obtained from surface and drain water, and crop field samples, only from surface water. The samples collected in 1 L polycarbonate bottles were immediately placed in an icebox and brought back to the laboratory, where they were filtered through precombusted (450°C for 4 hr) Whatman GF/F filters (with an effective pore size of 0.7 um). The filtrates were stored at 3°C or frozen in 500 mL polycarbonate bottles until they were analyzed. All the polycarbonate bottles had been washed previously in HCl and then placed in an ultrasonic bath filled with Milli-Q water for 30 min. DOC was analyzed using a total organic carbon analyzer (TOC-V from Shimadzu) with a Pt catalyst on quartz wool. UV absorption was measured with a Shimadzu UV-2500

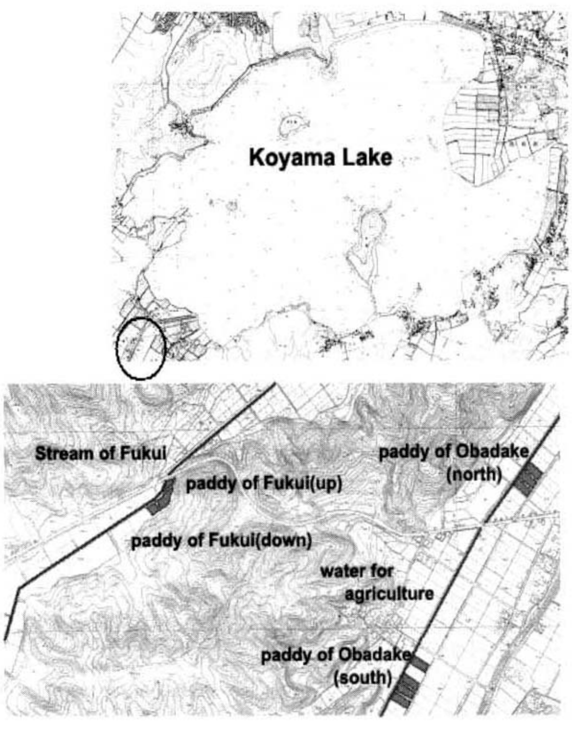

Fig. 1. Map of the study areas.

UV/Vis. spectrometer at 254 nm using a quartz cell with a 1-cm path length. UV absorption at 254 nm has been used effectively to determine concentrations of organic carbon in drinking water for the purpose of monitoring DBP (Disinfection By-Product) precursors (Edzwald et al., 1985) such as AHSs (Aquatic Humic Substances). The filtrates of the samples taken from May 2003 to September 2003 were incubated in sterile 300 mL glass bottles in the dark at 20°C. The sorptive losses to the bottles could be neglected because there was almost always less than a 0.1 mg Cl^{-1} difference in the blank test. Analysis samples of about 30 mL were taken and DOC concentrations were determined around 50 days after the incubation began.

3. Results and Discussion

3.1. DOC Variations in Paddy Fields and Crop Fields

In Fukui and Obadake, the rainfall pattern was not concentrated on heavy showers occurring several times during the summer, but was instead regular from April to September, with the exception of August (Fig. 2). In the Fukui paddy fields, the flow rate of surface water increased during early summer (June and July) and decreased in later months (April, May and August). These increases in flow rates during early summer were due to the rainfall, agricultural events and agricultural water management. Flow rates of others months were regularly influent, however, responding to agricultural water management (or agricultural events) and unaffected by rainfall (Fig. 2).

In the Fukui paddy fields, the monthly average DOC

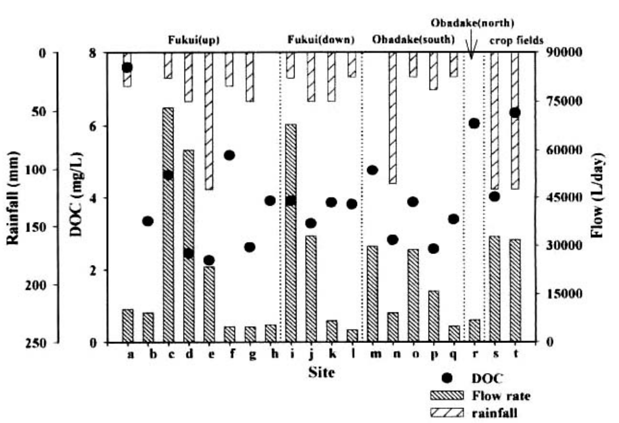

Fig. 2. Variations of rainfall, flow rate and DOC concentration in agricultural fields (Surface flow: a-Apr., b-May, c-Jun., d-Jul., e-Aug.; Drain flow: f-Apr., g-Jul., h-Sep. / Surface flow: i-Jun., j-Jul.; Drain flow: k-Jul., l-Sep. / Surface flow: m-May, n-Aug., o-Sep.; Drain flow: p-Apr., q-Sep. / Surface flow: r-May / Surface flow: s-crop1_Aug., t-crop2_Aug.).

concentrations varied seasonally (or according to agricultural events) from 1.77 to 7.59 mg Cl^{-1}, increasing during the first heavy runoff in April, a non-agricultural period. In the Obadake paddy fields, variations in flow rate and DOC concentration showed a pattern similar to that of the Fukui paddy fields, but the Obadake fields' flow rate and the DOC concentration differed from those of the Fukui paddy fields during the sampling periods (Fig. 2). These results were due to the different agricultural types (water management) and customs of farmers. The distinct increase in the DOC occurred only in the first heavy rainfalls of the season, but not in all heavy rainfalls (Choi et al., 2002; Parks et al., 1997; Kim et al., 2000). These results show that much of the organic matter, such as mineral soils and composts, that were accumulated in the paddy fields during the dry season were washed away in the first heavy rainfall. On the other hand, the average DOC concentration in the paddy fields' surface water in May and June (3.35 and 4.63 mg Cl^{-1}, respectively) was higher than in other months (2.26-2.45 mg Cl^{-1}), except for April, which was affected by rainfall (Fig. 2). The paddy fields are filled with water and then tilled extensively in preparation for transplanting young rice plants from late April to late May. Many paddy fields located around the lake or stream are used for agricultural activity. Imai et al. indicated in 2001 that paddy fields may be an important source of organic matter (such as DOC) for local water systems (such as rivers and lakes) from April to May. The DOC concentration in the drain water in the Fukui paddy fields in April (5.19 mg Cl^{-1}) was higher than in the Obadake paddy fields in April (2.57 mg Cl^{-1}) (Fig. 2). The flow rate in the Obadake paddy fields in April (15,824 L day^{-1}) was higher, however, than in the Fukui paddy fields in the same month (4,787 L day^{-1}) (Fig. 2). This result shows that the correlation between DOC and flow rate was not good. Besides, the DOC concentration (5.19 mg Cl^{-1}) in the drain water in the paddy fields of Fukui (up) in April was lower than the DOC concentration (7.59 mg Cl^{-1}) in the surface water in the same site and time. Because of adsorption and decay processes in soil, the DOC of interstitial waters decreases with the waters' depth. Another factor is the decrease of organic carbon in the soil horizons. Thurman reported in 1985 that interstitial waters of soil have a DOC range of from 2 to 30 mg Cl^{-1}, have low ionic strength and contain low concentrations of inorganic ions. Antwelier and Drever determined in 1983 the DOC in interstitial waters from podozols near Jackson Hole, Wyoming, USA. It can be hypothesized that DOC in interstitial waters affect water systems around the watershed (Stream, Lake, etc.). In the crop fields, DOC concentration was measured from 3.227 to 10.26 mg Cl^{-1}. Crop1 had a higher DOC concentration (avg. 4.01) than crop2 (avg. 6.34), but their flow rates (crop1: 32,718, crop2: 31,717 L day^{-1}) did not differ significantly (Fig. 2). This difference in DOC concentration may be due to differences in the agricultural types of crop 1 and crop 2. The crop 2 fields grew various vegetables and demanded much organic fertilizer such as excrements of farm animals, compared with the crop 1 fields that grew mainly beans and did not demand much organic fertilizer.

Table 1. Summary of unit per area of dissolved organic carbon in paddy fields(Unit : kg · a^{-1} · day^{-1})

site	Fukui (up)	Fukui (down)	Obadake (south)	Obadake (north)
Surface	0.0167	0.0143	0.0112	0.0027
Drain	0.0033	0.0018	0.0023	-
Sum	**0.02**	**0.0161**	**0.0135**	**0.0027**

Surface / Drain: surface / drain (= underground) flow water from paddy fields

The recorded discharges of daily DOC units per area were 0.02, 0.0161 and 0.0135 kg a^{-1} day^{-1} in Fukui (up), Fukui (down) and Obadake (south), respectively (Table 2). These results show that DOC discharge was low in paddy fields where good agricultural practices were applied, usage and traditional custom but was high in paddy fields of poor agricultural practice and traditional custom. The results from Fukui (up) were higher compared with those from Fukui (down) and Obadake (south). In all the paddy fields, the unit per area of DOC of surface flow was significantly higher than drain flow (Table 2). This demonstrated that the drain flow of the daily discharge of DOC per area in paddy fields was 11-17% of the total DOC discharge, but these values differed with the areas of the paddy fields (Table 2).

3.2. Characteristics of Organic Matter in Paddy Fields and Crop Fields

In all samples from Fukui (up)-S, except for one sample taken on June 27, a slow decrease in DOC was observed during the incubation periods. A sample taken on June 27 and evaluated based on the difference between its initial and final DOC had 58% total DOC (Fig. 3). The May 31 sample decreased by 2% from the first day to the final day during the incubation periods, and only a negligible DOC decrease was observed. In the samples taken in May, June and July, the ratios of biodegradation were 2-27%, 58%, and 17-36%, respectively, indicating that most DOC contents of these samples are non-biodegradable DOC (Fig. 3). Kalbitz et al. reported in 2003 that the labile

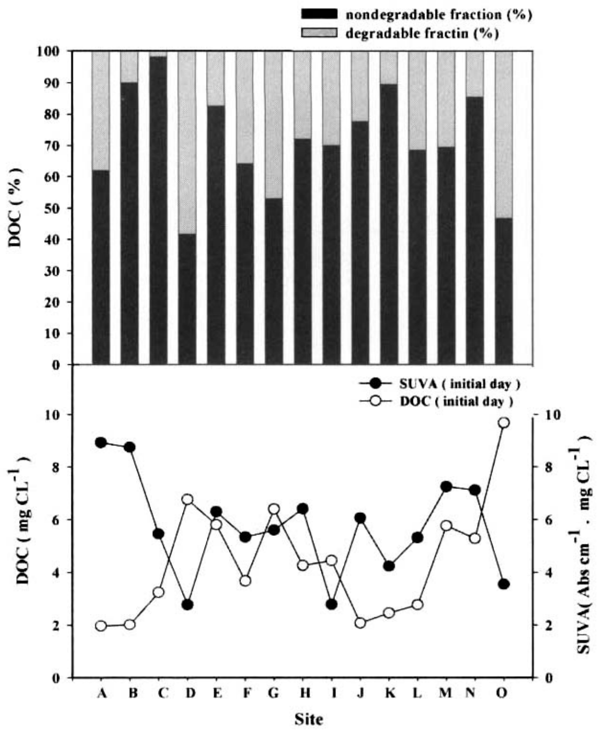

Fig. 3. Proportion (%) of biodegradable DOC and relation with DOC and SUVA. (A: Fukui (U) - S (23 May-a), B: Fukui (Up) - S (23 May-b), C: Fukui (Up) - S (31 May), D: Fukui (Up) - S (27 Jun.), E: Fukui (Up) - S (5 Jul.), F: Fukui (Up) - S (18 Jul.), G: Fukui (Down) - S (27 Jun.), H: Obadake (South) - S (20 May-a), I: Obadake (South) - S (20 May-b), J: Obadake (South) - S (5 Jul.), K: Obadake (South) - D (5 Jul.), L: Obadake (South) - S (9 Aug.), M: Obadake (North) - S (21 May), N: Crop field (St. 1) - S (6 Aug.), O: Crop field (St. 2) - S (6 Aug.))

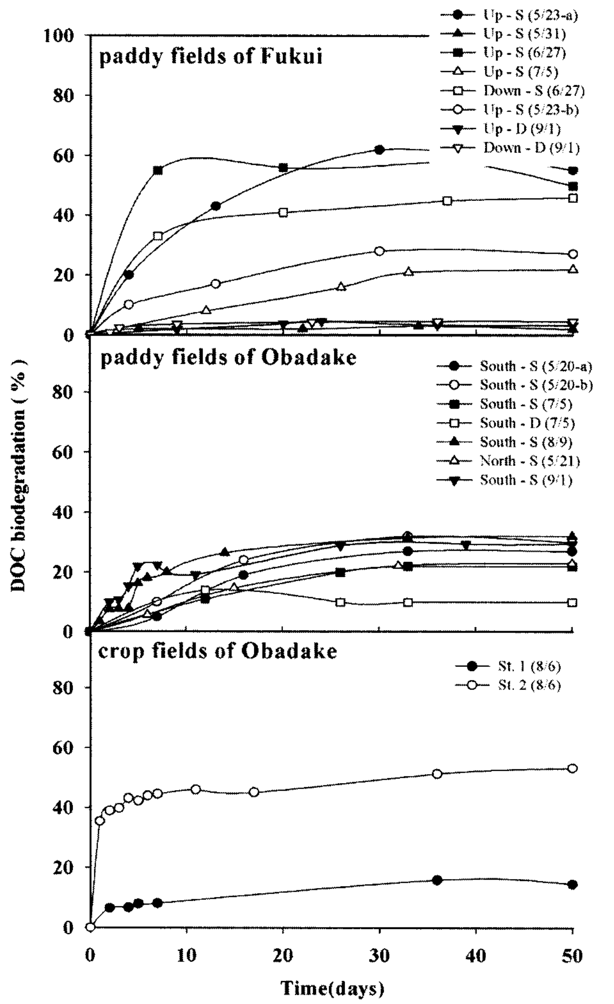

Fig. 4. Dynamics of DOC biodegradation in different DOM sources.

DOC of DOM extracted from agricultural soils and forests of less humified organic material (such as straw and litter) and fermentation layers of forest floors represented 14-25% and 59-88% of tot al DOC, respectively.

In Fukui (up) and Fukui (down), the DOC concentration similarly decreased with time in two areas, and the ratios of the remaining DOC concentration in Obadake (south) - S, Obadake (south) - D and Obadake (north) - S after biodegradation for 50 days were 78%, 72% and 90%, respectively (Fig. 4). The ratio of the biodegradation of crop 1 (14.5%) was lower than of crop 2 (53.2%) (Fig. 3). This difference may be due to differences in the agricultural types and fertilizer quantities of crop 1 and crop 2. Crop 1 showed a high volume of organic matter (high DOC) but low SUVA (Fig. 3) because it consisted mainly of beans and used almost no fertilization. In contrast, crop 2 consisted of various vegetables and demanded much organic fertilizer such as excrements of farm animals and many portions of organic matters decomposed by bacteria. These reported data show that the ratio of biodegradation of the allochthonous DOM sources (such as paddy fields and crop fields) by incubation was almost always low but differed according to agricultural practices, usages and traditional customs of farmers as well as geological features.

The 17 samples were classified according to the paddy fields of Fukui and Obadake and the crop fields of Obadake (Fig. 4). In all DOM samples, after 50 days of incubation at 20°C, 2.0-53.2% of the DOC was biodegraded (Fig. 4). In most samples, a high degradation rate during the initial days (< about 10 days) and a lower degradation rate in the later days were found. The paddy fields of Fukui had the highest extent and degradation rate of all other DOM solutions. In these samples, 2.0-55.3% of the total DOC was degraded within about 50 days (Fig. 4). The Obadake paddy fields of DOM solutions with a low extent and rate of degradation were comprised from surface flow and drain flow. Within these solutions, 10-32% of the total DOC was degraded after 50 days

(Fig. 4). In the Obadake crop fields, the ratios of the DOC degradation of crop 1 and crop 2 were 14.5% and 53.2%, respectively, and the crop field of crop 2 was higher than of crop 1 (Fig. 4).

This difference is a result of the differences in the types of plants, the farmers' customs or types, and the soil conditions, etc., according to the agricultural area. Besides the portion of the DOC that was degraded, the size and degradation constants of the DOC also depend on the origin of the DOM. In this study, the percentage of the DOC degradation (2-50% of the total DOC) of samples from paddy fields was similar to that of samples from the forests in the study of Qualls and Haines (1992). They found that 33% of the litter DOM was degraded after 134 days. Kalbitz et al. reported in 2003 that the percentage of DOC degradation from spruce and beech litter and from the fermentation layer of the spruce forest was 61-93%. In this study, the ratio of the degradation of DOC from paddy fields was high. As Kalbitz et al. reported in 2003, this reflects a different litter composition and a faster turnover of organic matter in agricultural soils compared to forest soils. The proportions of non-degradable DOC in Fukui (up) - D (9/1), Fukui (down) - D (9/1) and Obadake (south) - D (7/5) were 95.3%, 96.7% and 89.7%, respectively (Fig. 4). The non-degradable DOC in the drain water was higher than in the surface water. This may be due to the complex DOM with metal ions such as Al and Fe. Laboratory experiments carried out by several authors (McDowell et al., 1984; Jardin et al., 1989; Dalva et al., 1992) showed that solution pH, amorphous Fe and Al oxides, organic matter and clay minerals are important control factors in DOC adsorption. Binding of Al and Fe to DOM influences the mobility of Al, Fe and DOM in several ways. When insoluble complexes are formed, both DOM and metals are obviously immobilized (Kalbitz et al., 2000). When soluble metal-DOM complexes are formed, the influence on the mobility is less clear. Al and Fe can occupy the same functional groups on DOM molecules that are also involved in sorption of DOM to solid soil components (Kaiser et al., 1997). In the underground soil of paddy fields (= drain flow), organic carbon decreased with the soil's depth as well as with complex DOC and metal ions. The agricultural DOM samples of crop fields 1 and 2 showed different ratios of DOC biodegradation. These differences may have been due to agricultural practices, fertilization, and the types of plants in crop 1 and crop 2 of the two crop fields. In particular, the initial DOC was highest in all the samples and the ratio of biodegradation was also high due to the fact that crop field 2 was produced using manure as fertilizer. In 2003, Kalbitz et al. also found increased biodegradation of organic C after the addition of manure.

4. Conclusion

DOC concentration in paddy fields was highest during the first heavy rainfall of the dry season (April 2003). This result appears to have been due to accumulated composts and organic soil during the dry season. The descending order of daily DOC discharges per area (Kg a^{-1} day^{-1}) in paddy fields was Fukui (Up) - Fukui (Down) - Obadake (South) - Obadake (North). This was a result of the differences in agricultural practices, usages and traditional customs. The proportions of the daily discharges of DOC per area in the drain water of paddy fields to the total DOC discharge were high (15-57%). Therefore, an influent from drain water may be a very important source among non-point sources included mainly in paddy fields. UV absorption increased with increasing DOC concentrations, and had a strong correlation with SUVA, which is used as an indirect means to evaluate humic substances and DOC. The SUVA of the paddy fields was lower than the influent water from the crop fields. The higher SUVA in the paddy fields might have been caused by humic substances in muddy soils and compost. The structural characterization of the DOM can be indirectly completed through the determination of its biodegradable DOC content. The non-biodegradable DOC accounted for 50.2-98% and 46.8-85.5% of the total DOC in the paddy fields and the crop fields, respectively. These differences in degradation in various DOM sources are due to the size and degradation constants of DOC and also depend on the origin of the DOM.

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