ANNUAL MASS BALANCE OF DIOXINS IN A JAPANESE PADDY FIELD

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Introduction

Paddy fields are the main form of cultivation of rice (*Oryza sativa* L.), which is a primary food in Japan. However, Japanese paddy soils are contaminated with polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (co-PCBs), which are collectively called "dioxins" in this paper. These compounds are impurities (byproducts) in the production of the agricultural chemicals chloronitrophen (CNP) and pentachlorophenol (PCP) [1]. The average dioxins concentration in Japanese paddy soils in 2001 is 46.5 pg-TEQ/g [2]. This concentration is higher than the average concentration in nonagricultural soils. Rice does not appear to absorb these compounds from the soil via its roots, and dioxins are barely detectable in brown rice[3]. Therefore, the anxiety over the safety of rice for human consumption has almost disappeared. However, new fears have arisen over the possibility that dioxins flow out together with soil suspension from paddy fields and accumulate in coastal sediments[4]. It is thus important to retain these soils within paddy fields so that any dioxins in the soil will not migrate and increase dioxins. In an administrative press, the half-life of dioxins in paddy soil was estimated as 25 years.[1] This value demonstrates that dioxin levels in paddy soil decrease only slowly, although the annual balance of dioxins in these soils was not investigated in that study. As a result, it is not known whether current soil-management approaches are suitable or whether new cultivation methods, such as the use of organic fertilizer from livestock-breeding wastes, will be appropriate management techniques. To fill this information gap, we examined the annual balance of dioxins in a Japanese paddy soil with respect to the following components:

Factors that increasing dioxins levels—atmospheric deposition, input of dioxins in rice plant parts, and input in irrigation.

Factors that decreasing dioxins levels—leaching, decomposition, and volatilization.

Materials and Methods

Atmospheric deposition: We collected dioxins in atmospheric deposition of dioxins using a deposition collector (Shibata, Tokyo, Japan) equipped with a glass-fiber filter and polyurethane foam. The glass-fiber filter was changed every 2 weeks, and the polyurethane foam was changed every 4 weeks, from 5 June 2003 to 25 May 2004. The filter and foam were combined to provide the sample used for dioxin analysis.

Cultivation of rice: We sowed seeds of the "Nihonbare" rice cultivar in seedling trays on 8 April 2003 and transplanted the seedlings into a paddy field at the National Institute for Agro-Environmental Sciences (NIAES) at a density of 20 plants/m^2. We provided fertilizer at 4 kg N/10 a at the start of the experiment, and 4 kg N/10 a on 20 June and 7 August, respectively. The concentration of dioxins in the paddy field soil was 61,000 pg/g (82 pg-TEQ/g). Cultivation from 8 May to 7 October was in flooded and then from 20 June to 7 August as dry culture. We sampled the plant above 5 cm from the soil at 7 October, separated into head and leaves/stem.

Sampling of the paddy water: We installed flux meters at the paddy drains to measure water fluxes, and briefly used a water sampler to measure the concentration of suspended solids. We used these measurements to calculate the concentration of dioxins in outflow from the paddy.

Soil sampling: We sampled the paddy soil at a depth of 15 cm before paddling.

Dioxins analysis

1. Atmospheric deposition: Dioxins in the glass-fiber filter and in the polyurethane foam were Soxhlet-extracted with toluene. We purified and fractionated the extracts by chromatography, using silica-gel and activated-carbon columns.

2. Plant samples: We crushed leaf samples (100 g fresh weight) in dry ice, then added *n*-hexane and acetone (150 mL each), and passed the slurry through a glass-fiber filter (Kiriyama Glass Works, Tokyo, Japan). We then washed the filtrate with water, treated it with conc. sulfuric acid, and evaporated, purified, and fractionated the organic layer. Purification and fractionation were carried out as described above.

3. Soil samples: Dioxins in the soil samples were Soxhlet-extracted with toluene for 18 h. The extracts were then purified and separated by chromatography, as described above. All samples were analyzed by means of high-resolution gas chromatography combined with high-resolution mass spectrometry (HRGC/HRMS; HP6890/VG Autospec Ultima, Micromass Technologies Ltd., Manchester, UK). The HRGC/HRMS instrument was equipped with either an SP-2331 column (Supelco, Bellefonte, PA, USA) or a DB-5 column (J&W Scientific, Folsom, CA, USA).

Results and Discussion

1. Factors That Increase Dioxins Levels

Atmospheric deposition: Dioxin input from the atmosphere was 2.0 ng-TEQ/m^2/year (total dioxins, 490 ng/m^2/year; PCDDs, 340 ng/m^2/year; PCDFs, 79 ng/m^2/year; dioxin-like PCBs, 65 ng/m^2/year).

Input in rice plant parts: The dioxins concentration of leaf/stem of rice was 4.3 pg-TEQ/g. The yield was 700 g/m^2. Dioxins input to the paddy soils in the form of rice leaves and stems was 3.0 ng-TEQ/m^2/year (eq. 1). Paddy chaff accounted for an additional 0.35 ng-TEQ/m^2, and brawn rice equaled < 0.001 ng-TEQ/m^2, but these components were not added to the paddy field.

4.3 pg-TEQ/g ´ 700 g/m^2 = 3.0 ng-TEQ/m^2 (1)

Concentration ´ Source amount (actual measurement value) = Dioxins amount

Input in irrigation: The concentration of irrigation was 0.25 pg-TEQ/L [5]. Dioxins input in irrigation equaled 0.30 ng-TEQ/m^2 (eq. 2)

0.25 pg-TEQ/L ´ 1,200 mm = 0.3 ng-TEQ/m^2 (2)

Concentration ´ Source amount (average value) = Dioxin amount

No dioxins were calculated in agricultural chemicals, including fertilizer. Therefore, the total increase in dioxin levels equaled 5.3 ng-TEQ/m^2.

2. Factors That Decrease Dioxin Levels

Decomposition and volatilization of dioxins is impossible to measure. We calculated the amounts remaining in the soil on the basis of the half-lives of these chemicals. The quantity of dioxins in the paddy soil equaled 12 300 ng-TEQ/m^2 (eq. 3). With a half-life of 25 years for dioxins, we calculated a disappearance rate constant (*K*) equal to 0.0277 (eq. 4). As a result, the annual decrease in dioxin levels equaled 341 ng-TEQ/m^2 (eq. 5).

82 pg-TEQ/g ´ 0.15 m ´ 1.0 g/m^3 = 12,300 ng-TEQ/m^2 (3)

Concentration ´ Sampling depth ´ Specific gravity = Dioxin amount

K = 0.693/25 years = 0.0277/year (4)

12,300 ng-TEQ/$m^{2´}$ 0.0277/year = 341 ng-TEQ/m^2-year (5)

Drainage during flooding: The decrease in dioxin levels during flooding as a result of drainage equaled 1.8 ng-TEQ/m^2.

True decrease: The annual decrease in dioxins levels was adjusted using an increase factor. Therefore, the true amount of the decrease was 346 ng-TEQ/m^2 (eq. 6).

341 ng-TEQ/m^2 + 5.3 ng-TEQ/m^2 = 346 ng-TEQ/m^2 (6)

The true amount of the decrease thus equaled 346 ng-TEQ/m^2, which includes a drainage amount of 1.8 ng-TEQ/m^2 and decomposition and volatilization amount of 344 ng-TEQ/m^2.

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The results of these calculations are summarized in Fig. 1, with the ratio of each amount to the total remaining in the soil shown in parentheses. The amount remaining in the soil was 12,300 ng-TEQ/m^2 (100%), thus the total increase of 5.3 ng-TEQ/m^2 accounted for only 0.040% of the total, and the total decrease of 346 ng-TEQ/m^2 accounted for 2.8% of the total.

The quantity of dioxins that originated in agricultural chemicals (CNP and PCP) were provisionally calculated as a function of the dioxins remaining in the soil. From 1972 to 1981, dioxin impurities from CNP product were 9,000 ng-TEQ/m^2 (eq. 7) [6], 5.1 ng-TEQ/m^2 from 1982 to 1994 (eq. 8) [6]. From 1965 to 1975, dioxin impurities from PCP product were 6,100 ng-TEQ/m^2 (eq. 9) [6]. Total dioxins from agricultural chemicals were estimated about 15,100 ng-TEQ/m^2. Remaining dioxins concentration of paddy field soil used this experiment was 12,300, this value is almost equaled from agricultural chemicals as estimated value. Therefore, we seem to be that most of the dioxins in Japanese paddy field soil originated impurities of agricultural chemicals.

(0.28–0.30 g/m^2) ´ 3 000 ng-TEQ/g = 9 000 ng-TEQ/m^2 (CNP 1972–1981) (7)

Average amount of use ´ concentration in products = amount of dioxins

(0.28–0.30 g/m^2) ´ 1.3 ng-TEQ/g = 5.1 ng-TEQ/m^2 (CNP 1982–1994) (8)

Average amount of use ´ concentration in products = amount of dioxins

0.75 g/m^2´ 740 ng-TEQ/g = 6 100 ng-TEQ/m^2 (PCP 1965–1975) (9)

Average amount of use ´ Concentration in products

= Amount of dioxins (Average (phenol method and HCB)

Total = 15,100 ng-TEQ/m^2

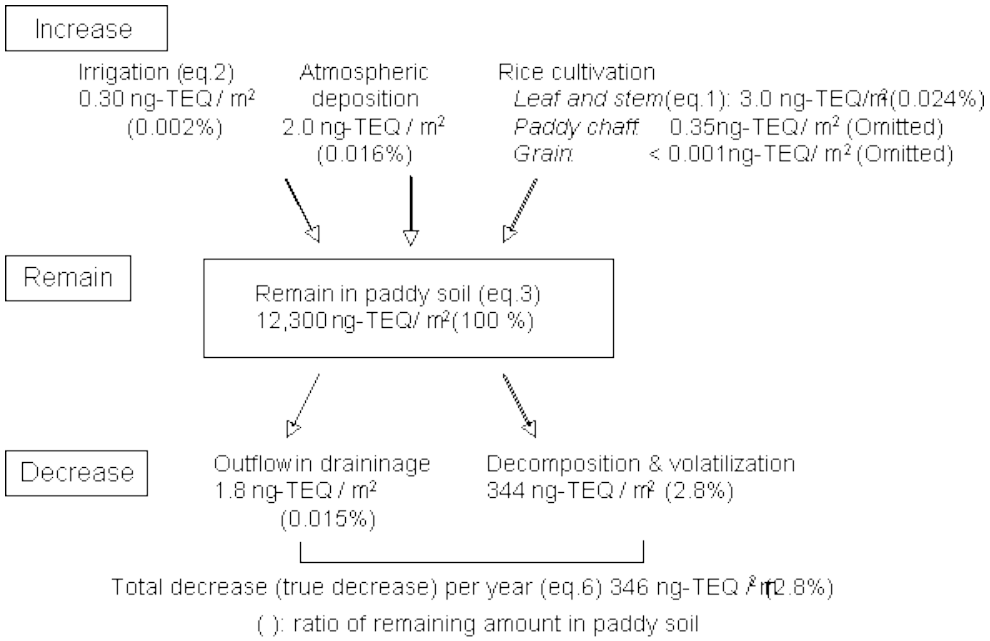

Figure 1. Summary of inputs and outputs from the paddy soil. Numbers in parentheses represent the ratio of each value to the total remaining in the paddy soil.

We think about that there will be little influence of the above-mentioned factors that are responsible for decreasing dioxin levels, even if the current inputs are decreased (e.g., in rice plant parts) because of the high cumulative amount already present in the soils. Dioxin levels will nonetheless decrease slowly in the future as a result of decomposition and volatilization.

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