HISTORICAL TREND OF DIOXIN AND AGROCHEMICALS IN RICE STRAW AND THEIR IMPACT ON MEAT AND DAIRY PRODUCTS

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Introduction

Dioxin and dioxin-like PCB impurities in agrochemicals used previously in paddy fields have flawn out and ultimately precipitated and accumulated in sediments in Japanese bays and lakes. Earlier we reported that the maximum impurities flew out during the 1960s and the 1970s[1,2]. Meanwhile total daily intake (TDI) study[3] revealed Japanese dioxins daily intake has decreased since 1977, especially polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/DFs) from dairy products and meat and egg products. Besides, polychlorinated biphenyls (co-PCBs) from fishes and shellfishes also showed similar trend. In this study, pesticides and congener specific pattern of PCDD/DFs and co-PCBs in old rice straws were measured in order to find out straw exposure level. In addition, we estimated the daily PCDD/DFs intake from dairy products, meat and eggs originated from impurities in straws.

Methods and Materials

Straw

Five old straws including firs were taken from the bottoms of each “tatami mat” (rush mat) which was used in floor of a house in Kashima, Ibaragi Prefecture, Japan. These mats were made up of rice straws in selected paddy fields by only one tatami maker in this area. The renewal report of mats shows that each straw was harvested in the years; 1954, 1962, 1970, 1974, and 1981. Straws harvested in the same paddy fields during 2000 were also sampled in addition. All these 6 straws were divided into three parts, stem/leaves, bottom shoot part, and firs. Firs were divided into unpolished rice and rice hull by hand. Altogether, three parts of straws in each 6 periods were investigated.

Analysis

Flowcharts of analytical procedure are shown in Fig. 1 and Fig. 2. Pesticides (DDTs, pentachlorophenol (PCP), chloronitrofen (CNP)) were analyzed using HRGC-HRMS (HP6890GC-Finnigan MAT-95XL) .The DB-5MS column (J&W, 60m×0.32 mm (i.d.), film thickness of 0.25 mm) was used and the temperature program was 170 °C (1 min), ramped at 20 °C/min to 210 °C and increased at 5 °C/min to 260 °C, next at 1 °C/min to 265 °C then at 20 °C/min to 300 °C (10 min). Dioxins were analyzed using HRGC-HRMS (HP6890GC-Micromass Autospec Ultima). Two chromatographic columns were used for dioxin analysis by GC-MS. One was the fused silica capillary column DB-17HT (J&W, 60 m × 0.32 mm (i.d.), film thickness of 0.15 mm) with a temperature program of 150 °C (3 min) , ramped at 20 °C/min to 200 °C, then at 3 °C/min to 280 °C. The other was DB-5MS (J&W, 60 m × 0.25 mm (i.d.), film thickness of 0.25 mm) with a temperature program of 130 °C (1 min) , ramped at 30 °C/min to 200 °C, then at 4 °C/min to 300 °C (11.7 min). Co-PCBs were also analyzed using HRGC-HRMS (HP6890GC-Micromass Autospec Ultima). The column DB-5MS

(J&W, 60 m × 0.25 mm (i.d.), film thickness of 0.25 mm) was employed with a temperature program of 150 °C (1 min) , ramped at 20 °C/min to 185 °C, next at 2 °C/min to 245 °C (3min), then at 6 °C/min to 290 °C. In all cases, the mass spectrometer was operated at over 10,000 resolution in a single-ion monitoring mode.

Reslts and Discussion

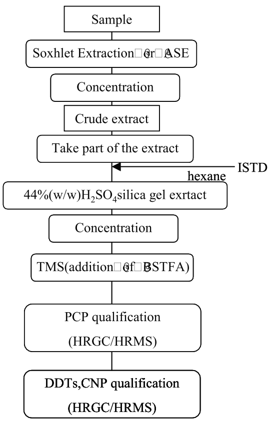

Figure 1. Analytical procedure of pesticides

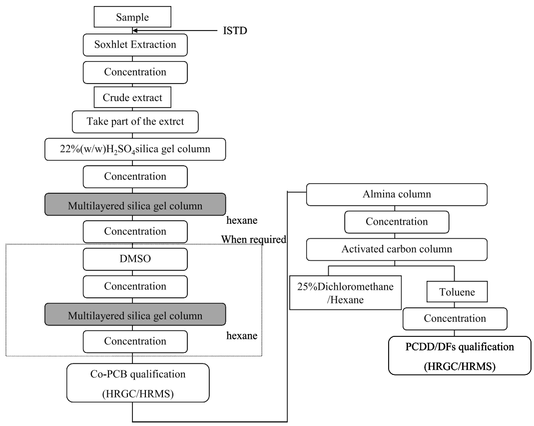

Figure 2. Analytical procedure of dioxins

The trend of dioxins in straws

Fig. 3 shows the trends of dioxins concentration (sum of PCDD/DFs and sum of co-PCBs) and WHO-toxic equivalent (TEQ). The trend of dioxins concentration was similar to that of WHO-TEQ in straws. In general, greatest concentrations and TEQs were noticed in 1970 samples respectively, 4300 pg/g dry weight and 6.1 pg WHO-TEQ/g dry weight. These levels were approximately 10 times and 6 times (respectively, PCDD/DFs and TEQs) greater than the samples collected in 2000. Notably TEQ profiles were similar in entire period of study with approximately 25 % contributed by PCDDs, approximately 34 % contributed by PCDFs and approximately 41 % contributed by co-PCBs. On the other hand, contributions of PCDD/DFs and co-PCBs to total concentration were found to be variable. The highest constituent was co-PCBs (48-82 % in total concentration) and the lowest was PCDFs (2-11 %).

Fig. 4 shows the trends of DDTs concentration in straws, amount of domestic active ingredient consumption, and amount of pesticides involving DDTs sprayed over 10 are paddy field in Kanto Region. Particularly the study location, Kashima is located in Kanto Region. DDTs were used as insecticides in Japanese paddy fields from 1930's and prohibited in 1971. Our present study comprehended that straw collected in 2000 contained DDTs (390 pg/g dry weight). The major constituents of DDTs were *o,p'*-DDT, *p,p'*-DDT and *p,p'*-DDE in entire period of study.

PCP (Fig. 5) was used as herbicides in paddy fields during the 1960s and the beginning of 1970s. However, complete regulation has been implemented in 1990. Based on our results, straws contained considerable PCP in all years. The concentration of the latest samples (in the year 2000) was 190 pg/g dry weight. Collectively all these observations suggested the possibility of prolonged persistency of DDTs and PCPs in soils in paddy fields and adherence to straws.

Eventually, CNP (Fig. 6) came into extensive use as paddy field herbicides in Japan during the 1970s as a replacement for PCP and was prohibited in 1994. Based on our analysis, the straw in 1970

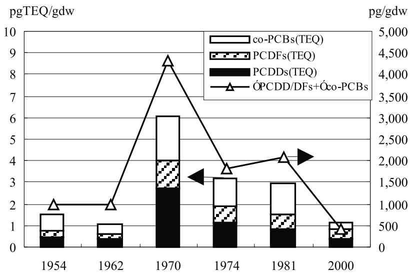

Figure 3. Trend of dioxin concentration and WHO-TEQ in straw

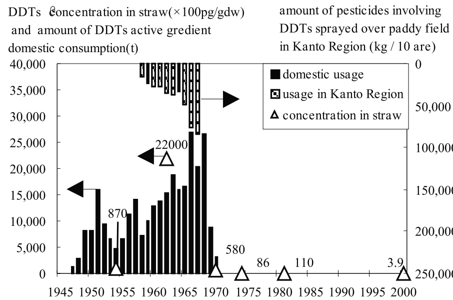

Figure 4. Trends of DDTs concentration in straw, amount of domestic DDTs active ingredient consumption, amount of pesticides involving DDTs sprayed over 10 are of paddy field in Kanto Region

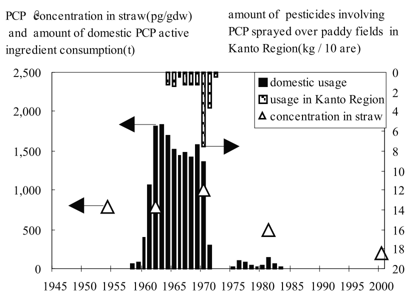

Figure 5. Trends of PCP concentration in straw, amount of domestic PCP active ingredient consumption, amount of pesticides involving PCP sprayed over 10 are of paddy field in Kanto Region

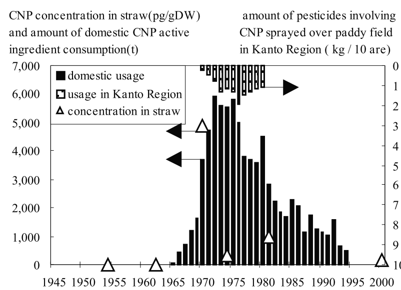

Figure 6. Trends of CNP concentration in straw, amount of domestic CNP active ingredient consumption, amount of pesticides involving CNP sprayed over 10 are of paddy field in Kanto Region

contained the greatest CNP concentration though this period was the beginning of usage in Kanto Region. Considerably, CNP was not detected in samples collected in 2000 which is reverse to DDTs and PCP trends. This result could be attributed to higher biodergadation of CNP in the environment, but amino-CNP wasn't detected in straw in all periods.

The Estimation of source apportioning of PCDD/DFs in straw

Source apportioning of PCDD/DFs in rice straw was estimated by multiple regression analysis. The congener profiles of three sources, such as dioxin impurities from PCP, CNP and air depositions from combustion[4] were used as independent variables and concentrations of congeners of PCDD/DFs in straws for dependent variables. To increase the accuracy, each homologue was analyzed independently and the result was shown in Fig. 7. Estimated concentrations of PCDD/DFs were in good agreement in all the year. We also propose that impurities of pesticides were found to be main sources of PCDD/DFs in straws, over approximately 76 % of PCDD/DF concentrations. Besides, trends of estimated concentrations of pesticides were similar to those of consumptions of pesticides. Estimated air deposition, however, was main source of TEQ in samples. One of this reason was assumed to be dilution by growing of straw after spray of pesticides over straw scions and high toxicity of air deposition.

Estimation of daily intake of PCDD/DFs from straw via dairy products and beef

Straws have been used as roughages for lactating cows and beef cattle in Japan. Therefore it is expected that straws are one of the routesof PCDD/DFs to dairy products and beef. Japanese intake of

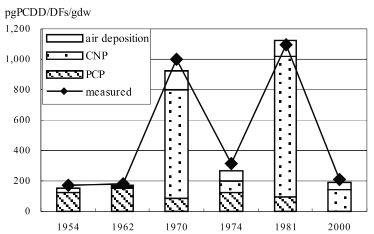

Figure 7. Result of source apportioning of PCDD/DFs in straw

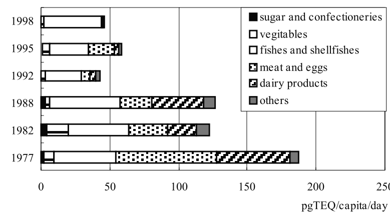

Figure 8. Trend of Japanese PCDD/DFs daily intake

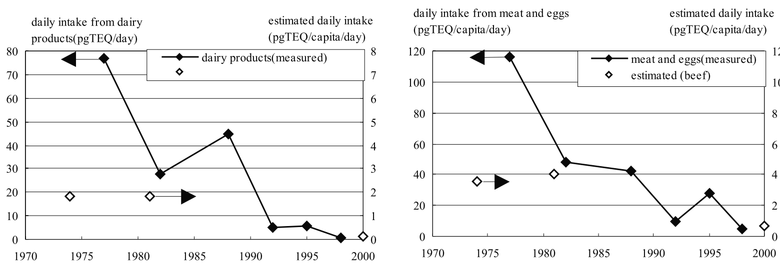

Figure 9. Trends of estimated daily intake of PCDD/DFs in straw from dairy products and beef

PCDD/DFs decreased in 1998 when compare to the levels in 1977 (Fig. 8) in terms of dairy products and meat and eggs. Based on these discussion, it is anticipated that decrease of PCDD/DFs in straw influenced the intake of PCDD/DFs via dairy products and beef. The calculated total daily intake estimations based on dairy products (sum of milk, cheese and butter) and beef calculated by Michael's model[5] are shown in Fig. 9. The estimated intake trend through dairy products and beef decreased corresponding to those of PCDD/DFs in straw. The decrease of estimated trends accounted for only 2.2% of observed decrease of daily intake through dairy products during 1977-98 (1.7 pg TEQ/capita/day) and 2.6% of observed decrease of intake through beef (2.9 pg TEQ/capita/day). Present result indicated that change of PCDD/DF concentrations in straws observed in this study was not enough to explain the decrease of Japanese PCDD/DFs intake from dairy and beef.

Acknowledgment

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References

1. Shigeki Masunaga, Yuan Yao, Isamu Ogura, Satoshi Nakai, Yutaka Kanai, Masumi Yamamuro, and Junko Nakanishi (2001) Environmental Science and Technology 35[10], 1967
2. Shigeki Masunaga, Yuan Yao, Hideshige Takada?Takeo Sakurai?and Junko Nakanishi (2001) Geochemical Journal 35[4] , 159
3. Ministry of Health and Welfare (1999) About investigation of dioxin daily intake from Food in 1999 (Total diet study)
4. Shigeki Masunaga, Takumi Takasugi, Junko Nakanishi (2001) Chemosphere, Vol. 44, 873
5. Michael S. (1997) Chemosphere, Vol. 34, 1263