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Residual Status of Chlorpyrifos and Octachlorodipropylether in Ambient Air and Polished Rice Stock in Houses Five Years after Application for Termite Control

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Indoor exposure to chlorpyrifos and 2,3,3,3,2',3',3',3'-octachlorodipropylether (OCDPE, a synergist, commercial name S-421 in Japan) of residents living in two houses (B and F) treated for termite control, was investigated by examining the residual levels in ambient air and in polished rice stock in houses through five years after their application. Chlorpyrifos and OCDPE levels detected in the air of the dining room of house B ranged from 0.007 to 0.11 $\mu g/m^3$ and from 0.12 to 0.79 $\mu g/m^3$, respectively. Chlorpyrifos and OCDPE levels detected in the air of a Japanese-style room in house F ranged from 0.07 to 0.41 $\mu g/m^3$ and from 0.008 to 0.046 $\mu g/m^3$, respectively. The estimated combined daily intake of chlorpyrifos from air and rice, was around 3 μg in house B and 4 μg in house F, below the recommended reference dose (RfD) of 3 $\mu g/kg/d$ from all sources. The estimated combined daily intake of OCDPE from air and rice was approximately 48 μg in house B and 0.5 μg in house F. Termiticide concentration in both air and rice depended on the season, being high in summer and lower in winter. Chlorpyrifos and OCDPE levels in the indoor air in the breathing zone did not decrease during the five years after their application for termite control.

Key words —— chlorpyrifos, octachlorodipropylether (S-421), indoor air pollution, rice pollution, termite control, human exposure

INTRODUCTION

Chlorpyrifos is one of the most widely used compounds in insect control programs in the indoor environment worldwide. Recent studies[1–4] indicate that broadcast spraying of chlorpyrifos in the indoor environment may pose considerable health risk for habitants, especially for children. In Japan, chlorpyrifos has been used extensively for almost twelve years to control termites in wooden buildings, as a major substitute for chlordane, whose use was banned in September 1986. Termiticides move to nontarget areas from their site of application and airborne termiticides poses some health risks. Nagami *et al.*,[5] Katsura *et al.*[6] and Yoshida[7,8] reported that chlorpyrifos levels in the air inside dwellings were below 0.26 $\mu g/m^3$ from one to three years after application for termite control in Japan. Wright *et al.*[9] determined chlorpyrifos levels in the ambient air of houses in the U.S.A. which had been treated with chlorpyrifos for termite control, and data through two years ranged from 0.10 to 8.54 $\mu g/m^3$, showed no ambient air level above the National Academy of Sciences (NAS) proposed guideline level of 10 $\mu g/m^3$. Though reported the chlorpyrifos levels in the indoor air of Japanese houses were one order of magnitude lower than those reported by Wright *et al.*,[9] pollution of the air inside dwellings is equally of great concern in Japan and the U.S.A.

2,3,3,3,2',3',3',3'-Octachlorodipropylether (OCDPE, commercial name S-421 in Japan) is a synergist for pyrethroid and organophosphorus insecticides widely used in commercial household pesticides,[10] and is commonly detected in household dust.[11] OCDPE was reported to be present in the ambient air of houses that have been treated with chlorpyrifos for termite control.[6,8]

When polished rice was exposed to air under the sink in the kitchen of chlorpyrifos- and

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OCDPE-treated houses, airborne termiticides were adsorbed and the levels did not decrease during two years after their application.[7,8]

Few data has been published on airborne levels of chlorpyrifos and OCDPE in houses for three or more years after their application in Japan. This paper reports the residual status of chlorpyrifos and OCDPE present in both ambient air and polished rice stock in two houses over a five year period after application for termite control in Osaka.

MATERIALS AND METHODS

Chlorpyrifos was purchased from Wako Pure Chemical Industries (Osaka, Japan), OCDPE was from Riedel-de Haen (Hannover, Germany). Silica gel 40 (Art 10180, 70-230 mesh) for column chromatography was from Merck (Darmstadt, Germany). Reagents used for the analysis were all of special analytical grade for pesticide residues (Wako Pure Chemical Industries, Osaka, Japan).

Construction of house B[8] was completed in September 1994, and it was treated with pyridaphenthion, chlorpyrifos and OCDPE in June 1994, in the course of the construction. Air samples were taken in the dining room (1F, 1.5 m height), underneath the kitchen sink where a rice stocker was placed, and in the crawl space under the kitchen floor. Sampling periods were in March, July, September and December of each year after the termiticide treatments.

House F was built several decades before. Chlorpyrifos and OCDPE were applied at the time of reconstruction of the bath room in October 1993, which had been damaged by termites. Air samples were taken in the Japanese-style room (1F, 1.5 m height), on the floor of the kitchen where a rice stocker was placed, and in the crawl space close to the bath room. Samples were collected in November 1993, April, July and December 1994, October 1995, November 1996, October 1997 and October 1998.

Air sampling was the same as reported in the previous paper.[7] Air samples were collected with an air pump (Shibata MP-2N, Tokyo, Japan) equipped with a collection tube (ORBO-49P, SUPELCO, Bellefonte, PA, U.S.A.). The air was pumped at 1.0 l/min for 8 h through the collection tube. After sampling, termiticides were extracted with solvent and analyzed by GC. Recoveries for air sampling tubes were conducted by injecting varying amounts of chlorpyrifos and OCDPE (0.1 to 5.0 μg in each) on 6 collection tubes and pulling air at a flow rate of 1.0 l/min for 8 h. Glass fiber filter, polyurethane foam plug and resin were removed from the tube and transferred to a 10 ml test tube. The emptied tube was rinsed with 5 ml acetone+hexane (1 : 1), and the rinsing solvent was transferred into the test tube containing the filter, resin and foam plug. The test tube was shaken vigorously and placed in an ultrasonic bath for 10 min, and the extract was filtered into another 10 ml sample vial. This procedure was repeated twice with 2 ml of solvent for 5 min. The combined extracts were evaporated to dryness under a gentle stream of nitrogen and the residue was dissolved in hexane.

Polished rice (100 g) was placed in a paper dish (18 cm i.d., 1.5 cm depth) and was exposed to air near a rice stocker underneath the kitchen sink (house B) or on the floor of the kitchen (house F) for a week. Analytical procedures for chlorpyrifos and OCDPE in polished rice were as described before.[7]

Quantitative analysis of chlorpyrifos and OCDPE was performed with a Hewlett Packard GC-5792 with electron-capture detection, capillary column and a splitless injection system. A 30 m × 0.32 mm i.d. DB-17 fused silica capillary column (film thickness 0.5 μm, J&W Scientific, Folsom, CA, U.S.A.) was temperature-programmed from 180 to 280℃ at 4℃/min. The detector and injector port temperatures were 330 and 200℃, respectively. Carrier gas (argon+methane : 95 : 5) velocity was 30 cm/sec and make up gas (nitrogen) was 60 ml/min. The sample size injected was 2 μl.

RESULTS AND DISCUSSION

Recoveries for air sampling tubes were from 90.2% to 110.1%, with an average recovery of 100.4% (CV% of 6.9%) for chlorpyrifos, and were from 87.5% to 106.6% with an average recovery of 94.2% (CV% of 7.5%) for OCDPE. Polished rice grains were fortified at a level of 0.02 μg/g and carried through the analytical procedure with rice samples. Recoveries from the polished rice (n=6) averaged 100.3% (CV% of 5.0%) for chlorpyrifos and averaged 94.0% (CV% of 5.3%) for OCDPE.

Changes in chlorpyrifos and OCDPE levels detected in the ambient air of house B for five years after their application are shown in Fig. 1. No pyridaphenthion (below 0.01 $\mu g/m^3$) was detected in the air of the dining room of house B during these five years, even though it was used

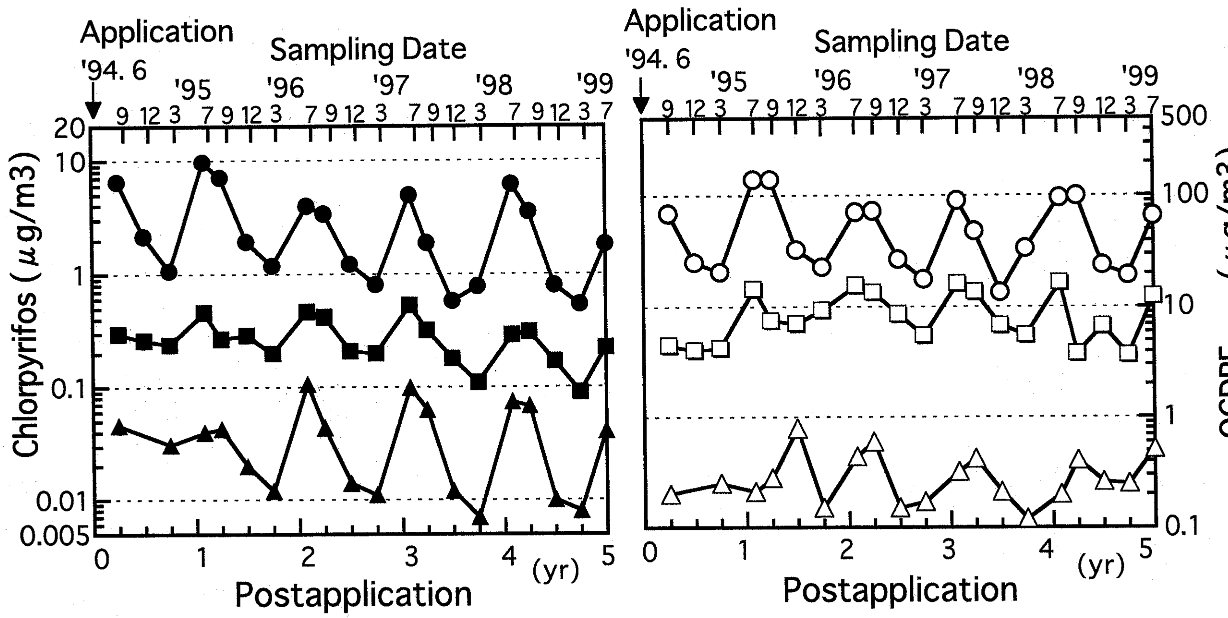

Fig. 1. Concentration of Chlorpyrifos and Octachlorodipropylether Detected in the Ambient Air of House B Five Years after Application for Termite Control

Ordinate indicates the concentration of chlorpyrifos (closed symbols) or OCDPE (2,3,3,3,2',3',3',3'-octachlorodipropylether, open symbols) in the air. -●- and -○-, crawl space; -■- and -□-, under the kitchen sink; -▲- and -△-, dining room. Air was pumped at 1.0 l/min for 8 h.

mainly for termite control.[8] Pyridaphenthion is hard to vaporize because of its very low vapor pressure (1.1×10^{-8} mmHg, 25℃), compared to that of chlorpyrifos (1.9×10^{-5} mmHg, 20℃) and OCDPE (0.6×10^{-6} mmHg, 20℃). Chlorpyrifos and OCDPE levels detected in dining room air ranged from 0.007 to 0.106 μg/m^3 and from 0.12 to 0.79 μg/m^3, respectively. Much more OCDPE was found in the air than chlorpyrifos. Termiticide levels in the air underneath the kitchen sink were one order of magnitude higher than those in the breathing zone, and two orders of magnitude more termiticide was present in the crawl space than in the breathing zone. Termiticide concentration in the air depended on the season, being high in summer and lower in winter. The respirable termiticide concentration in the indoor air of house B was found to maintain the same level for five years.

Figure 2 shows the contamination of termiticides in the ambient air of house F for five years after their application. The OCDPE level in the air of the crawl space decreased dramatically during the year after treatment. Chlorpyrifos level detected in the air of the Japanese-style room and the kitchen varied between 0.07 and 0.41 μg/m^3 and between 0.09 and 0.20 μg/m^3 for five years, respectively. OCDPE levels in the ambient air of house F were one order of magnitude lower than chlorpyrifos.

In general, termiticides are considered to be effective for five years after their application. From the data described above, a sufficient quantity of the drug for termite control seems to have remained in the house for five years. Wright *et al.*[12,13] reported that chlorpyrifos levels in the air of kitchens and bed rooms for four years after application, ranged from 1 to 9 μg/m^3,[12] and for eight years after ranged from <0.1 to 0.7 μg/m^3.[13] Chlorpyrifos levels present in ambient air were shown to decrease significantly between four and eight years after application. On the basis of their findings, termiticide levels in houses B and F will decrease rapidly within two or three years.

There is no indoor exposure guideline for chlorpyrifos in Japan. Chlorpyrifos levels inside the dwellings studied here showed no air level above the National Academy of Science (NAS, U.S.A.) proposed guideline level of 10 μg/m^3. However, using the Floride-Pinella exposure guideline (24 h exposure to chlorpyrifos at 0.48 μg/m^3),[1] chlorpyrifos levels in the indoor air of houses treated with termiticides in Japan may exceed this guideline on a summer day, even though the levels in Japan are generally lower than in the U.S.A.

Indoor air pollution by chlorpyrifos is a

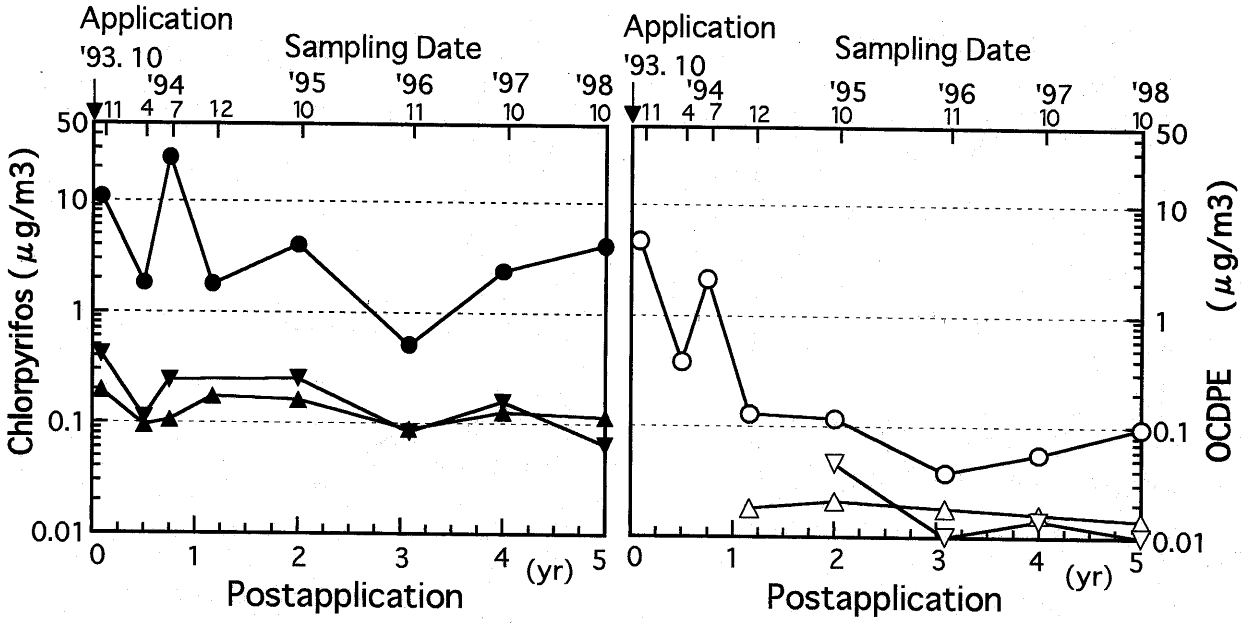

Fig. 2. Concentration of Chlorpyrifos and Octachlorodipropylether Detected in the Ambient Air of House F Five Years after Application for Termite Control

Ordinate indicates the concentration of chlorpyrifos (closed symbols) or OCDPE (2,3,3,3,2',3',3',3'-octachlorodipropylether, open symbols) in the air. -●- and -○-, crawl space; -▼- and -▽-, Japanese-style room; -▲- and -△-, kitchen. Air was pumped at 1.0 l/min for 8 h.

great concern in the U.S.A. because infants have a higher risk of exposure to chlorpyrifos from playing toys and residential surfaces that have accumulated chlorpyrifos after broadcast spraying. Davis and Ahmed[4] reported that based on the findings of the studies by Gurunathan *et al.*,[3] the estimated chlorpyrifos exposure levels from indoor spraying for children are approximately 21—119 times above the recommended reference dose (RfD) of 3 μg/kg/d from all sources. Household dust represents a possibly significant route of indoor exposure to pesticides for residents.[2,14,15] We reported[11] that chlorpyrifos levels in the dust of houses treated with chlorpyrifos for termite control were two orders of magnitude higher than dust from non-treated houses in Osaka. We also reported that chlorpyrifos concentrations in the dust sucked into a vacuum cleaner were 5.1 μg/g from house B (July 1995; one year after treatment) and 4.6 μg/g from another house (July 1995; eight years after treatment), and below 0.01 μg/g from non-treated houses. To prevent exposure of residents to termiticides in indoor air, it is necessary to clean rooms to reduce household dust, which accumulates pesticides. Furthermore, it is necessary to minimize the termiticide level in indoor air with adequate ventilation, in order to protect children from intake of termiticides from toys which accumulate the airborne material.

When polished rice was exposed to air in a termiticide-treated house, airborne termiticides were readily adsorbed on to it. Chlorpyrifos and OCDPE levels in the polished rice stock in house B ranged from 0.006 to 0.024 μg/g and from 0.22 to 0.87 μg/g, respectively (Fig. 3). The concentration depended on the season, being high in summer and lower in winter, reflecting the concentrations in ambient air. The pollution level of rice in house B did not decrease through five years. Figure 4 shows the change of termiticide levels in polished rice stock in house F. Contaminant levels in rice decreased for two years after the application to below 0.01 μg/g and maintained the same level up to the current time.

Daily intake of chlorpyrifos from inhalation of chlorpyrifos-polluted air in house B was estimated to be 0.75 μg, assuming that the breathing amount was 15 m^3 per day and the chlorpyrifos concentration of air was 0.05 μg/m^3. Daily intake of chlorpyrifos from rice in house B was also estimated to be 2.4 μg, assuming that the concentration of chlorpyrifos in the polished rice was 0.02 μg/g and the intake of polished rice was 300 g/d, and that the remaining percentage of chlorpyrifos in polished rice after the cooking process was 40%.[7] The total chlorpyrifos intake from air and rice in house B was thus around 3 μg/d.

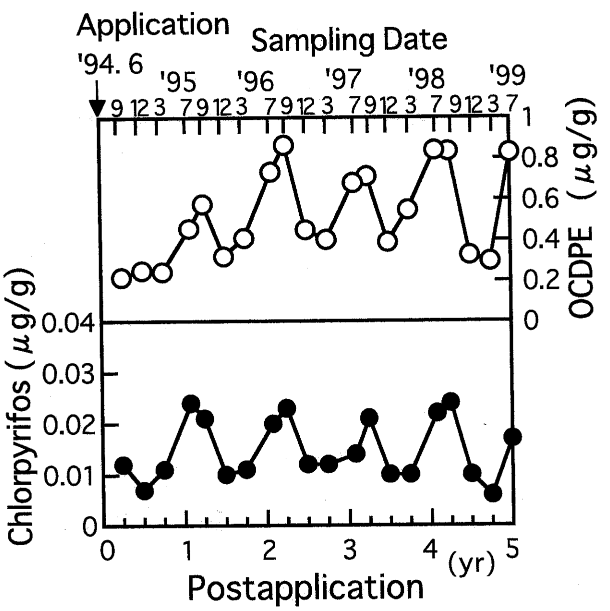

Fig. 3. Adsorption of Chlorpyrifos and Octachlorodipropylether on Polished Rice in House B

Ordinate indicates the concentration of chlorpyrifos (-●-) or OCDPE (2,3,3,3,2',3',3',3'-octachlorodipropylether, -○-) in polished rice which was placed in a paper dish and exposed to air near a rice stocker underneath the kitchen sink for a week.

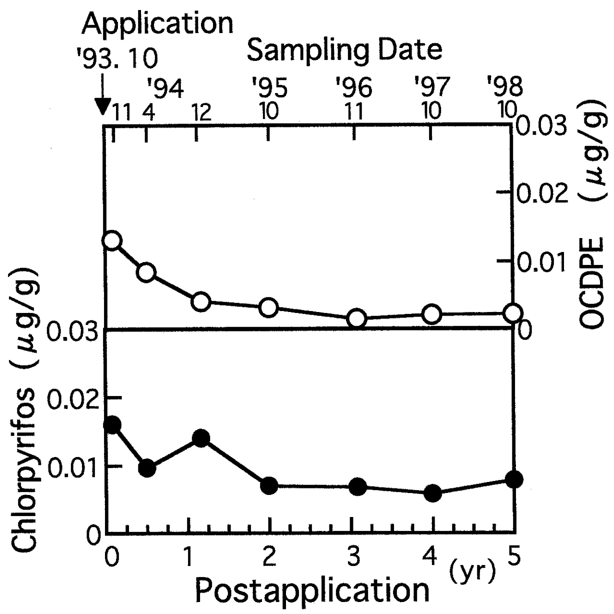

Fig. 4. Adsorption of Chlorpyrifos and Octachlorodipropylether on Polished Rice in House F

Ordinate indicates the concentration of chlorpyrifos (-●-) or OCDPE (2,3,3,3,2',3',3',3'-octachlorodipropylether, -○-) in polished rice which was placed in a paper dish and exposed to air near a rice stocker on the kitchen floor for a week.

Similarly the daily intake of chlorpyrifos in house F was estimated to be around 4 μg/d in all, 3 μg from air (0.2 μg/m^3 × 15 m^3) and 1.2 μg from rice (0.01 μg/g × 300 g/d × 40%). The estimated daily intakes of chlorpyrifos in houses B or F are less than the RfD of 3 μg/kg/d from all sources.

Daily intake of OCDPE in house B was estimated to be 4.5μg (0.3 μg/m^3 × 15 m^3) from inhalation, and 43.5 μg (0.5 μg/g × 300 g/d × 29%[8]) from rice. The total OCDPE intake from air and rice in house B was approximately 48 μg/d. Similarly the daily intake of OCDPE in house F was estimated to be 0.5 μg/d in all, 0.3 μg from air (0.02 μg/m^3 × 15 m^3) and 0.2 μg from rice (0.002 μg/g × 300 g/d × 29%).

Dietary intake of organophosphorus pesticides in Osaka, previously analyzed in our institute,[16] were 0.12 μg of chlorpyrifos (analyzed in 1993) and 0.11 μg of fenitrothion (analyzed in 1994). Those of organochlorine compounds (analyzed in 1995)[17] were 0.55 μg for PCBs, 0.65 μg for total DDT, 0.40 μg for total HCH, and 0.32 μg for total chlordane. These levels were for a control group living in a house which was not treated with termiticides. Occupants living in termiticide-treated houses would uptake the above levels of contaminants from meals and also be exposed to a considerable extent to termiticides in addition. Konishi *et al.*[18] and Yakushiji *et al.*[19] reported that foods prepared in houses which had undergone termite treatment with chlordane were contaminated with chlordane at levels from two to twenty times higher than that in foods cooked in non-treated houses. In order to minimize the termiticide intake from meals for the occupants living in termiticide-treated houses, it is important to prevent food, especially polished rice, which is the staple food in Japan, from contamination by termiticides. Yoshida[7,8] reported that when polished rice was separated from termiticide-polluted air by use of a plastic container, the uptake of termiticides by rice was practically nil after a one-week exposure to termiticide-polluted air underneath the kitchen sink or even in the crawl space. The separation of foodstuffs from termiticide-polluted air by packing in a container is effective to prevent the uptake of termiticides.

Taguchi and Yakushiji[20] reported that chlordane levels in the milk of breast-feeding women who live in chlordane-treated houses were statistically higher than those in the control group. They concluded that chlordane treatment of a house increased the contaminant level in breast milk. We intend to investigate chlorpyrifos and OCDPE levels in milk samples of breast-feeding women living in houses treated with them for termite control.[21,22)]

Chlorpyrifos and OCDPE levels in indoor air in the breathing zone were found not to decrease significantly during five years after application for termite control. Further investigation is required until there is no pollution in the house.

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REFERENCES

1) Lemus R., Abdelghani A.A., Akers T.G., Horner W.E., *Rev. Environ. Health*, **12**, 91—97 (1997).

2) Lewis R.G., Fortman R.C., Camann D.E., *Arch. Environ. Contam. Toxicol.*, **26**, 37—46 (1994).

3) Gurunathan S., Robson M., Freeman N., Buckley B., Roy A., Meyer R., Bukowski J., Lioy P.J., *Environ. Health Perspect.*, **106**, 9—16 (1998).

4) Davis D.L., Ahmed A.K., *Environ. Health Perspect.*, **106**, 299—301 (1998).

5) Nagami H., Uno M., Onji Y., Itou S., Sasaki M., *Eisei Kagaku*, **37**, 332—336 (1991).

6) Katsura E., Ogawa H., Kojima H., Fukushima A., *Jpn. J. Toxicol. Environ. Health*, **42**, 354—359 (1996).

7) Yoshida S., *J. Food Hyg. Soc. Japan*, **35**, 287—291 (1994).

8) Yoshida S., *J. Food Hyg. Soc. Japan*, **37**, 260—265 (1996).

9) Wright C.G., Leidy R.B., Dupree H.E. Jr., *Bull. Environ. Contam. Toxicol.*, **40**, 561—568 (1988).

10) Nakamura Y., Kaneko M., Mori K., Kan T., Watanabe Y., *Ann. Rep. Tokyo Metr. Res. Lab. P. H.*, **41**, 78—84 (1990).

11) Yoshida S. Taguchi S., Fukushima S., *Jpn. J. Toxicol. Environ. Health*, **43**, 64—67 (1997).

12) Wright C.G., Leidy R.B., Dupree H.E. Jr., *Bull. Environ. Contam. Toxicol.*, **46**, 686—689 (1991).

13) Wright C.G., Leidy R.B., Dupree H.E. Jr., *Bull. Environ. Contam. Toxicol.*, **52**, 131—134 (1994).

14) Roinestad K.S., Louis J.B., Rosen J.D., *J. AOAC. Int.*, **76**, 1121—1126 (1993).

15) Uno M., Onji Y., Sasaki M., Tanigawa K., *Eisei Kagaku*, **30**, 207—210 (1984).

16) Kuwabara K., Matsumoto H., Murakami Y., Imaida M., Hori S., *J. Food Hyg. Soc. Japan*, **38**, 372—380 (1997).

17) Kuwabara K., Matsumoto H., Murakami Y., Hori S., *J. Food Hyg. Soc. Japan*, **38**, 286—295 (1997).

18) Konishi Y., Yakushiji T., Taguchi S., Nishimune T., Tanaka R., *J. Food Hyg. Soc. Japan*, **31**, 238—243 (1990).

19) Yakushiji T., Konishi Y., Taguchi S., Nishimune T., Tanaka R., *J. Food Hyg. Soc. Japan*, **32**, 78—85 (1991).

20) Taguchi S., Yakushiji T., *Arch. Environ. Contam. Toxicol.*, **17**, 65—71 (1988).

21) Yoshida S., Moriguchi Y., Konishi Y., Taguchi S., Yakushiji T., *Jpn. J. Toxicol. Environ. Health*, **38**, 52—56 (1992).

22) Miyazaki T., *Bull. Environm. Contam. Toxicol.*, **29**, 566—569 (1982).