Elimination of BHC Residues in the Polishing and Cooking Processes of Brown Rice

Yong-Hwa Kim, Hye-Nam Kim, Sang-Soon Kim* and Su-Rae Lee

Environmental Chemistry Laboratory, Korea Atomic Energy Research Institute, Seoul

(Received January 10, 1979)

玄米의 搗精 및 炊飯 과정중 BHC 殘留分의 除去

金容華。金惠男・金尚淳*。李瑞來

韓國原子力研究所 環境化學研究室 (1979년 1월 10일 수리)

Abstract

In order to investigate the effect of polishing, washing and cooking processes on the residue level of BHC in rice grain, brown rice samples having a 0.3 ppm total BHC content were subjected to various treatments and residue analysis. The results are summarized as follows:

- The conventional polishing process of brown rice decreased the residue level down to 8 and 20% for 100 and 70% polished rice, respectively.
- 2) The washing procedure decreased the level to 34 and 31% for 100 and 70% polished rice, respectively.
- 3) The cooking processes with a conventional kettle and an automatic electric cooker decreased the residue level to 86 and 77% in 100% polished rice, and 69 and 41% in 70% polished rice, respectively.
- 4) By summation of the above results in sequence, it was concluded that the residue levels of BHC in cooked rice were 2.3 and 4.3% of original residue in the brown rice for 100 and 70% polished rice, respectively.

Introduction

BHC, one of the organochlorine pesticides still used in this country, is of great concern to food and environmental scientists because of its potential hazards from contamination of food materials and environment. In spite of its confined usage for the control of rice stem borer nowadays, the government is planning to ban its production effective July 1979, due to worry in excess for its acculmuation in the

ecosystem.

Our previous study⁽¹⁾ showed that the residue level in collected rice samples produced in Korea was far below the tolerance limit (0.2 ppm) set for brown rice in Japan. It was, therefore, suggested that the use of BHC would not pose much problem as far as it is applied to a definite crop according to the safeuse standard (a pre-harvest interval regulation scheme). Moreover, the tolerance limit was set for brown rice which is usually eaten after polishing, washing and boiling processes.

^{*} Sook-Myung Women's University (淑明女子大學校 食品營養學科)

Various studies to eliminate or reduce the organochlorine pesticide residues in food materials during their processing and cooking procedures were reported by several workers.

Liska(2) reported that spray-drying destroyed more than 80% of lindane residues in raw milk, but sterilization caused little change. Seidler et al. (3) studiedthe fate of 14C- and 36Cl-labeled lindane during baking and showed that only 6.5% of the activity was lost by evaporation. On studying the effectiveness of heat treatment and storage to reduce the residue levels in lindane-fortified spinach and apricot, Elkins et al. (4) noted a decrease of 33% in the processed spinach and 13% in apricot. Kawakita et al. (5) reported that the losses of BHC residues in milk upon heating at 80°C for 15 and 60 minutes were 7 and 18%, respectively, those in beef upon boiling and roasting for 10 minutes were 57 and 48%, respectively, and that in beet tops upon boiling in water for 5 minutes and squeezing was 50%. Nikonorow and Zimak (6) found that boiling of eggs for 10 minutes had no effect on the BHC residues. Noren (7) noted the reduction of about half of the BHC level in boiling of lentil (Lens esculenta) for 45 minutes. Yadrick et al. (8) investigated the effectiveness of curing and cooking to reduce the dieldrin residue level in bacon and found that cooked bacon contained 20 to 53% of the dieldrin originally present in the uncured pork samples and most of the losses were attributed to the fat lost during cooking, although heat destruction, codistillation, and/or aeration may have occurred. McCaskey et al.9), Liska et al. (10), and Ritchey et al. (11) have reported reductions in residue levels of many chlorinated hydrocarbons contained in chicken tissues.

Ritchey et al. (11) suggested that leaching of fat during cooking was very effective in reducing the pesticide residue levels. Reports in regard to the eff ect of polishing on the removal of BHC residues from rice are very scarce but those by Kanesawa. (12,13) On the fate of BHC residues during rice cooking, only two reports by Takeda et al. (14) and Mukherjee et al. (15) are available. But their results are so controversial that it is difficult to conclude the whole picture of BHC reduction in practical rice processing. It is assumed that the controversy might have original

nated from the difference in their experimental methods. Takeda et al. used the sample collected from market containing BHC residues of 0.004 ppm near the detection limit whereas Mukherjee et al. fortified the sample with 1% standard BHC solution to make a final concentration of 100 ppm which is not obtainable under conventional agricultural practices. It is of prime importance that test samples having a residue level sufficient for analysis in a state of natural contamination should be used to study its behavior or removal in various processing steps of food materials.

This study was, therefore, undertaken in order to elucidate the elimination of BHC residues by polishing, washing and cooking processes of rice grains which were harvested after application of a commercial BHC preparation under conventional agricultural practices. The results showed that the BHC residues originally present in the brown rice were reduced remarkably before ingestion and this effect should be taken into account in establishing the tolerance limit of pesticide residues in food.

Materials and methods

1. Brown rice sample

Rice grain was harvested from three experimental field lots $(15 \times 15 \text{ m})$ which had been sprayed with commercial BHC of 6% granular formulation at the dose of 3 kg/10 a on August 9, 1977 at the second generation time of rice stem borer, as described in the previous report⁽¹⁾. The harvested grain was dehusked with a dehuller (Chyota Co., Japan) to obtain brown rice samples.

2. Polishing procedure

Brown rice was polished with a laboratory mill, Model McGill Miller No.2 (H. T. McGill Inc.) having a polishing capacity of 150 g grains. For 70 and 100% polished rice, the polishing time was adjusted to 40 and 140 seconds, respectively. The yields of rice bran from 70% and 100% polishings were 6.2% and 9.8% by weight, respectively.

3. Washing procedure

Polished rice was washed with the same weight of distilled water three times in a 500 ml Erlenmeyer

flask with an aluminum-lined cap. Every washing process was conducted by shaking 14 min with a wrist action shaker (Burrell Corp.) at a medium shaking capacity and followed by decantation to remove the washings, which were then combined for the analysis of BHC residues.

4. Cooking procedure

1) Conventional kettle cooking

Washed rice (50 g, based on polished raw rice) was drained on a sieve and transferred to a small aluminum pot (13 cm diameter × 6 cm height). To this was added 1.6 times volume of water (80 ml) and cooked on a hot plate with 1 kw capacity for about 15 min after boiling. Cautions were taken to make a little charring at the bottom of the pot. The boiled rice was allowed to cool at room temperature for 30 min and a portion of it equivalent to 20 g raw rice was taken for BHC analysis.

2) Cooking with an electric cooker

Washed rice from 20 g polished rice and 1.6 times volume of water were put to an automatic electric cooker (Toshiba RC-6 LH model, indirect-heating type). After cooking, it was allowed to cool for 30 min and used for the residue analysis.

3) Cooking with model cooking devices

To elucidate the vaporization of BHC residues during cooking, two types of model cooking devices were designed; that is, one to imitate the conventional kettle cooking and the other for steam cooking as shown in Figs. 1 and 2. For the conventional cooking, 3 times volume of water was added to reduce the charring and heated for 10-15 min. For steam cooking, a strong current of steam was passed through the

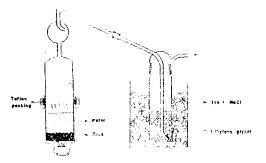


Fig. 1. A model device of conventional kettle cooking for residue analysis

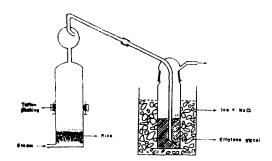


Fig. 2. A model device of steam cooking for residue analysis

washed rice for 10-15 min.

5. Chemical analysis of BHC residues

1) Brown rice, polished rice and rice bran samples

Extraction, purification and quantitation were the same as those in the previous report⁽¹⁾ except the concentration step just before the injection into the gas chromatograph. That is, the final extract was concentrated to the smallest volume by means of dry air current and made up to 2 ml with hexane. The 2 ml aliquot was transferred to a vial and 3 μ l aliquot was subjected to gas chromatographic analysis.

2) Water washings

Water washings from brown rice were extracted and determined according to the FDA method(16) (Reg. Sec. 212.13 a) as described below. Combined water washings from 20 g of polished rice were transferred to a blendor jar and made to 100 ml volume with redistilled water. To this was added 200 ml acetonitrile, blended for 2 min and filtered through a Büchner funel fitted with filter paper (Toyo 5 C) with suction. Residues on the funnel were washed three times with 25 ml acetonitrile, dried at room temperature and analyzed for BHC content according to the method 1) described above. Half a portion of the filtrate in the suction flask was transferred to a 1 L separatory funnel and 50 ml petroleum ether was added and shaken 1 min. To this were added 5 ml NaCl solution and 300 ml redistilled water and then the mixture was shaken again for 1 min.

After separation of the layers, the aqueous layer was extracted with two 50 ml portions of petroleum ether. Three combined petroleum ether extracts were

washed with two 50 ml portions of water. Washings were discarded and the organic solvent layer was dehydrated by passing through an anhydrous sodium sulfate column. The florisil column purification and gas chromatographic analysis were the same as the method 1).

3) Boiled rice sample

Fifty ml of redistilled water was added to 50 g boiled rice (equivalent to 20 g polished raw rice), blended for 2 min and 200 ml acetonitrile was added, followed by blending again for 2 min and filtration. Next steps were the same as described in the method 2). When acetonitrile was added directly to the boiled rice, it was very difficult to make a homogeneous sample, owing to the hardening phenomena of granules.

4) Water sample

The methed of EPA (Section 10, A) (17) was employed as described below. A 50 ml water sample was transferred to a 250 ml separatory funnel and 20 ml of 15% methylene chloride in hexane was added and shaken for 2 min. This extraction procedure was repeated twice more and the three combined extracts were passed through an anhydrous sodium sulfate column, The eluate was concentrated with a K-D concentrator and analyzed directly with the gas chromtograph.

5) Vapor sample

Vapor was analysed according to the method of EPA (Section 8, B) (17) as described below. The vapor generated during the cooking was trapped in 100 ml ethylene glycol and it was transferred to a 500 ml separatory funnel and 350 ml water was added. To this was added 60 ml hexane, shaken for 2 min and let layers separate. This extraction procedure was repeated twice. The combined hexane extract was passed through an anhydrous sodium sulfate column, cencentrated with a K-D concentrator, dried to the smallest volume with dry air and made up to 2 ml with hexane. It was then subjected to gas chromatographic analysis.

Results and discussion

1. Recovery test of BHC residues

As the experiment was dealt with various kinds of

samples differing in physical and/or chemical properties, it was necessary to test the recovery of BHC in different samples. The results are shown in Table 1. Though the recovery differs from isomer to isomer, the average recovery for total BHC does not deviate so widely from the usual recovery data indicated in the FDA manual (Table 201-A) (16) which defines a recovery higher than 80% as complete. It is seen that the lower the residue level is, the higher the recovery is, so that the recovery may give rise to more than 100% as Kanesawa's study (3) also showed.

All the data in this report were not corrected for recovery and expressed on the "as it is" basis. Therefore, the addition of BHC residues of two separates after processing might not coincide arithmetically with that of original material. The percentage of BHC residue in a fraction after processing to the original one was, thus, obtained by dividing with the arithmetic sum of the two separated fractions. All the analyses were run in triplicate and the accuracy of analysis in terms of relative standard deviation was below 20% in brown rice, polished rice, and bran, below 30% in washed rice and below 50% in cooked rice.

2. Fate of BHC residues in polishing process

The fate of BHC residues in the polishing process of brown rice is shown in Table 2. The residue rates of total BHC originally present in the brown rice were only 20 and 8% in 70 and 100% polishing processes, respectively and they were nearly identical for 4 different isomers. These experimental results appear more reasonable than Kanesawa's (13) in that the

Table 1. Recovery test of BHC isomers added to various samples (Unit: % of added BHC)

Test sample (BHC added*)	α	β	γ	δ	Aver- age
Polished rice (0.5 μg)	90	80	80	75	81
Water washings(0.5 μg)	68	92	74	65	75
Boiled rice (0.5 μg)	64	115	72	52	76
Distilled water (0.5 μg)	71	96	85	97	87
Distilled water (1 μg)	70	81	80	83	79
Vapor** (0.3 μg)	81	100	101	104	97
Vapor (1μg)	66	81	77	85	77

^{*} Quantity of BHC isomers of equal concentrations added to unit weight of sample for one run of analysis

^{**} trapped in ethylene glycol

(Unit: ppm)

Table 2. Fate of BHC residues in the polishing process of brown rice

Rice sample	α	β	r	δ	Total
Browm rice	0. 165	0.019	0.030	0.086	0.300
70% polished rice (% residue*)	0.032(21)	0.004(23)	0.005(19)	0.012(16)	0.053(20)
100% polished rice (% residue*)	0.017 (9)	0.003(15)	0.003 (9)	0.006 (5)	0.029 (8)
Rice bran from 70% polishing (% removal)	1.770(79)	0.207(77)	0.316(81)	0.942(84)	3. 235(80)
Rice bran from 100% polishing(% removal)	1.636(91)	0.156(85)	0.265(91)	1.000(95)	3.057(92)
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* % residue based on brown rice = $\frac{\text{ppm in polished rice} \times K}{\text{ppm in polished rice} \times K + \text{ppm in rice bran} \times (1-K)} \times 100$

K: experimentally obtained degree of polishing as fraction; i.e., 0.902 for 100% and 0.938 for 70% polished rice

Table 3. Fate of BHC residues in the washing process of polished rice

(Unit: ppm based on raw rice)

Sample	α	β	7	δ	Total
70% polished rice	0. 032	0.004	0.005	` ' 1	0.053
Washed rice (% residue)	0. 0060(22)	0.0017(41)	0.0022(32)		0.0207(31)
Water washings (% removal)	0. 0213(79)	0.0024(59)	0.0046(68)		0.0464(69)
100% polished rice	0. 017	0.003	0.003	' 1	0. 029
Washed rice (% residue)	0. 0035(30)	0.0013(25)	0.0014(33)		0. 0093(34)
Water washings (% removal)	0. 0080(70)	0.0038(75)	0.0029(67)		0. 0177(66)

recovery of total BHC partitioned into the polished rice and bran was more than 83% whereas it was only 35% in Kanesawa's.

It was also observed that the % residue of BHC in the polished rice was far less than the % transfer of oil into the polished rice from the brown rice. Therefore, there leaves an unanswered question why the partition coefficient of BHC residues into the polished rice and bran is different from that of oil, in spite of the oil-soluble property of BHC. There are possibilities that "free and bound lipid" concept in starchy foods (18,19) or "bound residue" concept in residue analysis (20,21) is applicable differently to polished rice rich in starch and rice bran rich in crude fiber. This question could be confirmed by other sophisticated methods such as radioactive tracer techniques.

3. Elimination of BHC residues in washing process

The fate of BHC isomers in the washing process of polished rice is shown in Table 3. The removal rate of total BHC by washing was about 65~70% for the two polished rice. This result is nearly the

same with Mukherjee et al.'s. (15) and suggests the significance of washing rice grains before cooking in order to diminish the hazards from BHC residues if any.

4. Elimination of BHC residues in cooking process

The residue rates of BHC after cooking by a conventional kettle and an electric cooker are shown in Table 4. The β -and γ -isomers were not detectable or negligible since their contents were quite low even before cooking. Generally, it would be very difficult to detect the agronomically contaminated BHC in rice if the grains are passed through the processes of polishing and washnig. However, it was possible in this experiment to demonstrate that the cooking process of rice exhibited a small effect on the elimination of BHC residues. The removal effect was greater in 70% polished rice than in 100% polished and in automatic electric cooker than in conventional kettle cooking.

In order to confirm these removal or residue effects, a model cooking device was employed to trap the vaporized BHC during cooking. The results are shown

Table 4. Elimination of BHC residues in the cooking process of rice by home cookers

(Unit: ppm based on raw rice)

Rice sample	α	β	7	δ	Total
70% polished, washed rice Conventional kettle cooking (% residue) Electric rice cooker (% residue)	0.0060 0.0050(83) 0.0033(55)			0. 0108 0. 0086 (80) 0. 0043 (40)	
100% polished, washed rice Conventional kettle cooking (% residue) Electric rice cooker (% residue)	0.0035 0.0014(40) 0.0019(54)			0.0031 0.0060(194) 0.0047(152)	

ND: non-detectable

TR: $\alpha, \gamma, \delta < 0.0006$ ppm, $\beta < 0.0013$ ppm

Table 5. Fate of BHC residues in the cooking process of rice by a model cooking device

(Unit: ppm based on raw rice)

Sample	α	β	γ	δ	Total
70% polished, washed rice Boiled rice (% residue) Vapor in trap (% removal)	0.0060 0.0113(71) 0.0046(29)	0.0017 TR ND	0.0022 0.0033 (66) 0.0017 (34)	1	0. 0207 0. 0257(79) 0. 0069(21)
100% polished, washed rice Boiled rice (% residue) Vapor in trap (% removal)	0.0035 0.0031(52) 0.0029(48)	TR ND ND	0.0014 0.0007(100) ND	0.0031 0.0049(89) TR	0. 0093 0. 0088(72) 0. 0035(28)

Table 6. Effect of boiling on the removal of BHC residues in rice bran by a model cooking device

(Unit: ppm based on rice bran)

Sample	α	β	γ	δ	Total	
Rice bran Vapor in trap (% vaporized)	1.770 1.317(74)	0.207 0.034(16)	0.316 0.222(70)	0. 942 0. 261(28)	3. 235 1. 830(57)	

in Table 5. About 20~30% portion of BHC present in the washed rice was vaporized along with the vapor during cooking. As the concentration of BHC residues remaining in the polished rice was so low that it was almost impossible to know the vaporization property of four individual isomers from the biological material. Therefore, rice bran samples containing much more BHC residues than the polished rice were cooked in the same model cooking device to know this property more clearly. As shown in Table 6, the vaporization property of each isomer was apparent; that is, α and r-isomers were more apt to vaporize than β - and δ -isomers were. This kind of vaporization property might be one of the factors reflected in the selective bioaccumulation of BHC isomers through the long food chain in the nat ural ecosystem. It should be noticed that a larger

portion of BHC residues was vaporized from rice bran than from washed rice grain. However, the vaporization rate of BHC from rice bran as obtained here was not employed in summing up the elimination levels of BHC in various steps of rice processing in spite of the low relative standard deviation in the rice bran analysis since the physical state of BHC in rice bran may be different from that in rice grain.

The effect of steam cooking on the fate of BHC residues by a model cooking device is shown in Table 7. Steam cooking of rice eliminated slightly more BHC than the conventional cooking by direct heating. Though the effect of cooking time was not observed in detail in this experiment, most of the BHC residues must have been vaporized earlier than 15 minutes.

A summation of all the results in sequence is shown

Table 7. Effect of steam cooking on the fate of BHC residues by a model cooking device

(Unit: ppm based on raw rice)

Sample	α	β	r	δ	Total
70% polished rice	0.0060	0.0017	0.0022	0.0108	0.0207
Steamed rice, 15 min (% residue)	0.0063(54)	TR	0.0016(39)	0.0066(89)	0.0158(64)
Vapor in trap (% removal)	0.0054(46)	ND	0.0025(61)	0.0008(11)	0.0087(36)
Steamed rice, 30 min (% residue)	0.0109(60)	ND	0.0021(48)	0.0039(70)	0.0169(60)
Vapor in trap (% removal)	0.0073(40)	ND	0.0023(52)	0.0017(30)	0.0113(40)
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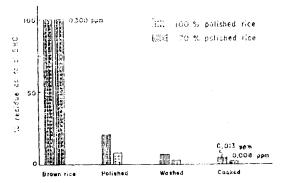


Fig. 3. Elimination of BHC residues in the processing of rice

in Fig. 3. It could be concluded that the residue rates of BHC originally present in the brown rice at the level of 0.3 ppm were 8 and 20% in the polished rice, 2.7 and 6.2% in the washed rice and 2.3 and 4.3% in the boiled rice for 100 and 70% polished samples, respectively. It was also observed that physical processes such as polishing and washing procedures played a major role in the elimination of BHC residues.

This result might interpret the status of BHC problem for contaminated rice in Korea. Our previous study⁽¹⁾ reported that the amount of BHC in the rice samples harvested after application of commercial BHC at the first generation time of rice stem borer according to the recommended safe-use standard was 0.02 ppm. Since this study revealed that more than 90% of the residue was eliminated by polishing, washing and cooking processes, cooked rice from such a contaminated lot would contain less than 0.002 ppm. Such a concentration of BHC is only one hundredth of 0.2 ppm which is the tolerance limit for brown rice in Japan. Thus, it is thought that the BHC contamination of foodstuffs in Korea does not render much problem as far as it's usage is confined

to the first generation time of rice stem borer. It is strongly suggested that not only a total diet survey for BHC residues but also this kind of study to assess the effect of processing on the fate of pesticide residues should be undertaken to establish the tolerence limit and to settle down the argument on the hazards of pesticide residues in foodstuffs consumed in this country.

요 약

BHC를 살포하여 재배한 玄米(BHC 잔류량 0.3 ppm) 의 搗精, 洗米 및 炊飯중 BHC 殘留量을 분석하여 그 의 행방을 추적한 결과는 다음과 같다.

- 1) 현미의 搗精중 BHC는 10분도미에서 8%, 7분도 미에서 20%가 찬류하였다.
- 2) 쌀의 洗滌중 10분도미에서는 34%, 7분도미에서 는 31%가 잔류하였다.
- 3) 재래석 炊飯과 전기밥솥에 의한 취반중 10분도미에서는 각각 86%, 77%, 7분도미에서는 각각 69%, 41%가 잔류하였다.
- 4) 전체적으로 보아 현미로부터 밤으로의 BHC 移行率은 10분도미에서 2.3%, 7분도미에서 4.3%에 불과하였다. 따라서 현미의 調理, 加工중 발생되는 BHC의除去量을 잔류농약 許容量설정에 反映하여야 될 것이다.

This work was supported in part by the Research Contract No. 1656/R2/RB from the International Atomic Energy Agency.

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