Bull. Environ. Contam. Toxicol. (1995) 55:510–516

Bulletin of Environmental Contamination and Toxicology

Occurrence of Butyltin Residues in Certain Foodstuffs

K. Kannan,* S. Tanabe, R. Tatsukawa

Department of Environment Conservation, Ehime University, Tarumi 3-5-7, Matsuyama 790, Japan

Received: 10 October 1994/Accepted: 20 February 1995

Organotin compounds are used in a variety of consumer and industrial products including marine antifouling paints, agricultural pesticides, wood preservatives and as stabilizers in poly(vinyl chloride) (PVC) plastic (Evans and Karpel 1985; Crowe 1987). Annual world consumption of organotins is growing rapidly, from 35,000 tons in 1986 (Maguire 1987) to 50,000 tons in 1992. Among a wide variety of organotin compounds, octyltin, butyltin and phenyltin derivatives are permitted for use as stabilizers in plastic products which contact food (Ainsworth 1992). In addition to antifouling uses of tributyltin, its application as disinfectant in waxes, polishes, sprays and in laundry washes may cause contamination of sewage effluents and sludge. Industrial discharges of tributyltin, used as a slimicide in the paper industry and for textile and lumber treatment and in cooling water treatment, are further sources of sewage sludge contamination. Since sludge is used as a fertilizer in agriculture, butyltin species could be transferred to soils (but the biological availability of butyltins in sludge has not been established) (Maguire 1991). Recent studies have shown the presence of butyltins in a wide variety of household textiles including diaper cover, sanitary panty, socks, etc. (Nakashima et al. 1990; Yamada et al. 1993). Despite the diverse application of butyltin compounds, studies on food contamination and human exposure are meager.

Only a few studies have reported the contamination of food products from non-agricultural usage of butyltins. Fish and fish products (Short and Thrower 1986; Davies and McKie 1987; Ishizaka et al. 1989; Alzieu et al. 1989; Cullen et al. 1990; Forsyth and Cléroux 1991; Suzuki et al. 1992; Batley et al. 1992), beers and wines (Forsyth et al. 1992a, b) and fruit juices (Forsyth et al. 1992c) were shown to be contaminated with butyltin residues. Similarly, meat products such as poultry and turkey contained considerable levels of dibutyltin (DBT), originating from its use as an anthelmintic to control intestinal worms in chicken (Epstein et al. 1991).

---

*Present address: Skidaway Institute of Oceanography, #10 Ocean Science Circle, Savannah, Georgia 31411
Correspondence to: K. Kannan

These studies suggested the presence of butyltins in animal origin foodstuffs, and recommended the need for monitoring a wide variety of food items to elucidate major exposure routes to humans.

Butyltin compounds are highly toxic to several aquatic organisms (such as bivalve mollusks), affecting growth and shell formation (Alzieu et al. 1989). In mammals, the most obvious effect was immune reduction (Snoeij et al. 1988). Although, organotin compounds are considered to be less persistent than chlorinated hydrocarbons, they accumulate in biota to the extent of causing adverse health effects. So far no known adverse human-health effect due to the exposure of organotin contaminated foods has been documented. However, intake of foods containing high concentrations may exert toxic effects in humans. More information is needed on food contamination by butyltins to understand the major sources of human exposure. Based on immune function studies, Penninks (1993) established a tolerable daily intake of 0.25 µg TBT/kg bw/day. The present study provides preliminary results on the analysis of certain farm and animal origin foods for mono-(MBT), di-(DBT) and tributyltin (TBT) residues.

MATERIALS AND METHODS

Rice was collected from Atherton, Australia; sunflower oil, peanut oil, cheese and butter were from local markets in Sydney, Australia; fish representing, rubberlip morwong (*Nemadactylus douglasii*), shovelnose ray (*Aptchotrema rostrata*) and blue groper (*Achoerodus viridis*) caught off coastal waters of Sydney and greenspotted kingfish (*Caranx papuensis*) from Honiara, the Solomon Islands, were also examined for the presence of butyltin residues. Among meat products, chicken liver and muscle and goat liver were obtained from a butcher shop in Bombay, India; Duck liver was taken from Ho Chi Minh, Vietnam; Pork liver and muscle were collected in Magadan, Russia. Samples were collected during 1989-90 except for those samples from Magadan which were purchased in 1993. Meat and fish were preserved in 10% formalin and stored at 4ºC until analysis. Examination of formalin, to check whether butyltins are extracted from tissues, showed that the levels were below the limits of detection suggesting that formalin preservation did not affect the concentration of butyltins in tissues.

Details of butyltin analysis are described elsewhere (Kannan et al. 1994). Briefly, samples were acidified with 1N HCl and extracted with 0.1% tropolone-acetone. The extract was passed through a 35 g Na_2SO_4 packed glass column to remove moisture and concentrated using a rotary evaporator. The extract was then propylated by adding *n*-propyl magnesium bromide (ca. 2 mol/L in THF solution, Tokyo Kasei Kogyo

Co. Ltd., Japan) as a Grignard reagent. The derivatized extract was passed through a 20 g Florisil packed dry column to remove lipids and then passed through a 6 g Florisil packed wet column for final clean-up.

A gas chromatograph-flame photometric detector (Hewlett-Packard 5890 series II) with a moving needle type injection system and a tin mode filter at 610 nm was used for quantification. A fused silica capillary column coated with 0.25 µm of DB-1 was used. The column oven temperature was programmed from 80ºC (1 min hold) to 160ºC at a rate of 15ºC/min and then at a rate of 5ºC/min to a final temperature of 260ºC and then held for 5 min. Helium was the carrier gas while hydrogen, air and nitrogen were used for operating flame photometer. Injector and detector temperatures were maintained at 200 and 270ºC, respectively. Butyltin trichloride, dibutyltin dichloride and tributyltin chloride of known amounts (0.1 µg) were spiked into cod muscle (caught off the Pacific Ocean and contained below detectable levels of butyltins), passed through the whole analytical procedure and used as an external standard. Concentrations were estimated by comparing peak heights of butyltins in samples with those in external standards. The detection limits of MBT, DBT and TBT were 3.0, 1.0 and 1.0 ng/g, respectively. Recoveries of MBT, DBT and TBT were 81, 108 and 98%, respectively, on average of three analysis.

RESULTS AND DISCUSSION

Mono-, di- and tributyltin were not detected in most of the foods (Table 1). Total butyltin concentration in all farm products (rice, peanut oil and sunflower oil) was <3.5 ng/g. Although reports regarding the use of phenyltin and cyclohexyltin derivatives for the control of agricultural pests are available (Crowe 1987; Forsyth et al. 1992b), not much is known about the usage of butyltins in agriculture. The major sources of butyltin contamination in agricultural products could be the irrigation water flowing through PVC pipes and the use of non-food grade PVC products in storage, transportation and production facilities. Similar to farm products, dairy foods such as, butter and cheese did not contain butyltin residues.

Among meat products, chicken muscle and liver collected in Bombay, India, contained detectable levels of butyltins (3.5-14 ng/g wet wt). MBT was the predominant compound followed by TBT and DBT. Chicken feed (such as, fish meal) and water supplied through PVC pipes and containers may be the source of butyltins in chicken. Wu et al. (1989) reported extraction (leaching) of organotins from commercial PVC pipes into the flowing water. Presence of high concentrations of DBT in the liver of chicken (when it was administered as an anthelmintic) was reported earlier (Epstein et al. 1991). Although, butyltin concentrations in liver were noticeable, it is unlikely that, given lower consumption rates of liver than

Table 1. Concentrations of butyltin residues (ng/g wet wt) in certain foodstuffs

Food item	Location	MBT	DBT	TBT	ΣBT
Farm products					
Rice	Atherton (A)	<3.0	<1.0	<1.0	<3.5
Sunflower oil	Sydney (A)	<3.0	<1.0	<1.0	<3.5
Peanut oil	Sydney (A)	<3.0	<1.0	<1.0	<3.5
Dairy products					
Butter	Sydney (A)	<3.0	<1.0	<1.0	<3.5
Cheese	Sydney (A)	<3.0	<1.0	<1.0	<3.5
Meat Products					
Chicken meat	Bombay (I)	<3.0	1.0	1.0	3.5
Chicken liver	Bombay (I)	6.1	3.3	4.4	14
Goat liver	Bombay (I)	<3.0	<1.0	<1.0	<3.5
Duck liver	Ho Chi Minh (V)	<3.0	<1.0	<1.0	<3.5
Pork meat	Magadan (R)	<3.0	1.5	<1.0	3.5
Pork liver	Magadan (R)	<3.0	<1.0	5.0	7.0
Fish					
Rubberlip morwong					
muscle	Sydney (A)	5.0	1.0	1.0	7.0
liver	Sydney (A)	54	9.0	2.0	65
Shovelnose ray					
muscle	Sydney (A)	13	1.0	6.2	20
liver	Sydney (A)	180	1.2	1.5	183
Blue groper					
muscle	Sydney (A)	42	2.2	3.2	47
liver	Sydney (A)	310	8.1	23	341
Greenspotted kingfish					
muscle	Honiara (S)	4.3	<1.0	1.0	5.3
liver	Honiara (S)	180	22	20	222

(A) - Australia; (I) - India; (V) - Vietnam; (R) - Russia; (S) - the Solomon Islands.

Concentrations below the detection limit were assigned half of its value to calculate mean muscle meat, butyltin burdens in chicken will pose serious health risks to humans. Pork meat and liver from Magadan, Russia, contained low, but detectable concentrations of butyltins. Duck and goat livers had no butyltin residues, implying less exposure and or rapid metabolism of butyltins in these animals following exposure. We analyzed more liver samples than muscle tissues (although muscle is more important from the human consumption point of view), because earlier studies have shown preferential accumulation butyltins in liver, which could be a suitable organ to indicate butyltin contamination in various animal origin foods (Short and Thrower 1986; Kannan et al. 1994).

Among various food items analyzed, fish muscle and liver contained the highest concentration of butyltins. Monobutyltin was the predominant species followed by TBT and DBT. Fish liver had an order of magnitude higher concentration than in muscle. The predominance of butyltins in marine products clearly indicates contamination from commercial usage of TBT as an antifoulant in boats. Noticeable levels of TBT have been found (69-170 ng/g) previously in aquacultured salmonids (Short 1987) exposed to TBT treated sea pens. Ishizaka et al. (1989) and Suzuki et al. (1992) detected considerable concentrations of butyltins in marine food products purchased from local markets. Therefore, consumption of seafood may be one of the major sources of human exposure to butyltins. Although, the liver of fish contained high residues, its significance in view of human exposure may be less.

In general, human dietary exposure of butyltins *via* foods may be regarded as follows: Marine foods > animal-origin foods > farm products. Although the significance of butyltins towards human health is not clear, it was shown that human red blood cells are extremely sensitive to TBT, even low concentrations inducing membrane breakdown.

In addition to antifoulant sources of TBT, disposal of sewage sludge treatment plant effluents containing butyltins (Fent and Müller 1991), can be another source of contamination in fish, particularly in countries where sewage is disposed directly into water bodies. Butyltin contamination in animal and farm origin foods arising from packing materials (wrappage), PVC containers and plastics may be minimum, unless foodstuffs contain extracting components such as alcohol, acids, etc. Therefore, food commodities like alcoholic beverages, fruit juices, vinegar etc. may worth be examined for butyltin contamination. Irradiation of plastic food packaging materials resulted in the degradation of butyltins to inorganic tin (Buchalla et al. 1993). However, cooking methods were ineffective in eliminating butyltins from fish tissues (Short and Thrower 1986). These results indicate that seafood rather than agricultural and animal origin foodstuffs is the major source of butyltin exposure in humans.

Acknowledgments. The authors would like to thank Mr. Robert J. Williams (Fisheries Research Institute, Cronulla, Australia), Dr. Alexander Andreyev (Research Center, Eastern Palearctic Wetlands, Magadan, Russia) and Dr. A.N. Subramanian (Centre of Advanced Study in Marine Biology, Porto-Novo, India) for their assistance during sampling. This research was supported by grants from the Sumitomo Foundation (93-104-141) and the Global Environmental Research Program of the Environment Agency, Japan.

REFERENCES

Ainsworth SJ (1992) Plastic additives. C & EN 70: 34-52.

Alzieu C, Sanjuan J, Michel P, Borel M, Dreno JP (1989) Monitoring and assessment of butyltins in Atlantic coastal waters. Mar Pollut Bull 20: 22-26.

Batley GE, Scammell MS, Brockbank CI (1992) The impact of banning of tributyltin-based antifouling paints on the Sydney rock oyster, *Saccostrea commercialis*. Sci Total Environ 122: 301-314.

Buchalla R, Schüttler C, Bögl KW (1993) Effects of ionizing radiation on plastic food packaging materials: a review. Part 2. Global migration, sensory changes and the fate of additives. J Food Protect 56: 998-1005.

Cullen WR, Eigendorf GK, Nwata BU, Takatsu A (1990) The quantitation of butyltin and cyclohexyltin compounds in the marine environment of British Columbia. Appl Organomet Chem 4: 581-590.

Crowe AJ (1987) Organotin compounds in agriculture since 1980. Part 1. Fungicidal, bactericidal and herbicidal properties. Appl Organomet Chem 1: 143-155.

Davies IM, McKie JC (1987) Accumulation of total tin and tributyltin in muscle tissue of farmed Atlantic salmon. Mar Pollut Bull 18: 405-407.

Epstein RL, Phillippo ET, Harr R, Koscinski W, Vasco G (1991) Organotin residue determination in poultry and turkey sample survey in the United States. J Agric Food Chem 39: 917-921.

Evans CJ, Karpel S (eds) (1985) Organotin Compounds in Modern Technology. Journal of Organometallic Chemistry Library, 16, Elsevier Science Publishers, Amsterdam, p 279.

Fent K, Müller MD (1991) Occurrence of organotins in municipal wastewater and sewage sludge and behavior in a treatment plant. Environ Sci Technol 25: 489-493.

Forsyth DS, Cléroux C (1991) The determination of butyltin, methyltin and tetraalkyltin in marine food products using gas chromatography-atomic absorption spectrometry. Talanta 38: 951-957.

Forsyth DS, Weber D, Cléroux C (1992a) Determination of butyltin, cyclohexyltin and phenyltin compounds in beers and wines. Food Addit Contam 9: 161-169.

Forsyth DS, Weber D, Daglish K (1992b). Survey of butyltin, cyclohexyltin and phenyltin compounds in Canadian wines. J Assoc Off Anal Chem. 75: 964-973.

Forsyth DS, Weber D, Barlow L (1992c) The determination of organotin compounds in fruit juices using gas chromatography-atomic absorption spectrometry. Appl Organomet Chem 6: 579-585.

Ishizaka T, Nemoto S, Sasaki K, Susuki T, Saito Y (1989) Simultaneous determinations of tri-*n*-butyltin, di-*n*-butyltin and triphenyltin in marine products. J Agric Food Chem 37: 1523-1527.

Kannan K, Yasunaga Y, Iwata H, Ichihashi H, Tanabe S, Tatsukawa R (1994) Concentrations of heavy metals, organochlorines and organotins in horseshoe crab, *Tachypleus tridentatus* from Japanese coastal waters. Arch Environ Contam Toxicol (in press).

Maguire RJ (1987) Environmental aspects of tributyltin. Appl Organomet Chem 1: 475-498.

Maguire RJ (1991) Aquatic environmental aspects of non-pesticidal organotin compounds. Water Poll Res J Canada 26: 243-360.

Nakashima H, Hori S, Nakazawa H (1990) Determination of dibutyltin and dioctyltin compounds in PVC food containers, wrappage and clothes by reversed phase HPLC with column switching. Eisei Kagaku 36: 15-20. (in Japanese).

Penninks AH (1993). The evaluation of data-derived safety factors for bis(tri-*n*-butyltin)oxide. Food Addit Contam 10: 351-361.

Short JW (1987) Measuring tri-*n*-butyltin in salmon by atomic absorption: analysis with and without gas chromatography. Bull Environ Contam Toxicol 39: 412-416.

Short JW, Thrower FP (1986) Accumulation of butyltins in muscle tissue of chinook salmon reared in sea pens treated with tri-*n*-butyltin. Mar Pollut Bull 17: 542-545.

Snoeij NJ, Penninks AH, Seinen W (1988) Dibutyltin and tributyltin compounds induce thymic atrophy in rats due to a selective action on thymic lymphoblasts. Intern J Immunopharmacol 10: 891-899.

Suzuki T, Matsuda R, Saito Y (1992) Molecular species of tri-*n*-butyltin compounds in marine products. J Agric Food Chem 40: 1437-1443.

Wu W, Roberts RS, Chung Y-C, Ernst WR, Havlicek SC (1989) The extraction of organotin compounds from polyvinyl chloride pipe. Arch Environ Contam Toxicol 18: 839-843.

Yamada S, Fujii Y, Mikami E, Kawamura N, Hayakawa J, Aoki K, Fukaya M, Terao C (1993) Small-scale survey of organotin compounds in household commodities. J Assoc Off Anal Chem 76: 436-441.