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Panu Veikko Rantakokko, Tiina Kuningas, Katri Saastamoinen, Terttu Vartiainen

► **To cite this version:**

Panu Veikko Rantakokko, Tiina Kuningas, Katri Saastamoinen, Terttu Vartiainen. Market basket study on the dietary intake of organotin compounds in Finland. *Food Additives and Contaminants*, 2006, 23 (08), pp.749-756. 10.1080/02652030600779908 . hal-00577488

HAL Id: hal-00577488

<https://hal.science/hal-00577488>

Submitted on 17 Mar 2011

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Market basket study on the dietary intake of organotin compounds in Finland

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|-------------------------------|--|
| Journal: | <i>Food Additives and Contaminants</i> |
| Manuscript ID: | TFAC-2006-080.R1 |
| Manuscript Type: | Original Research Paper |
| Date Submitted by the Author: | 26-Apr-2006 |
| Complete List of Authors: | Rantakokko, Panu; National Public Health Institute, Department of Environmental Health Kuningas, Tiina; National Public Health Institute, Department of Environmental Health Saastamoinen, Katri; National Public Health Institute, Department of Environmental Health Vartiainen, Terttu; National Public Health Institute, Department of Environmental Health |
| Methods/Techniques: | Chromatography - GC/MS |
| Additives/Contaminants: | Environmental contaminants, Organic tin compounds |
| Food Types: | Fish and fish products, Fruit, Potatoes, Vegetables |
| | |

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4 **Market basket study to assess the dietary intake of organotin**
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7 **compounds in Finland**
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12 Panu Rantakokko^{a,*}, Tiina Kuningas^a, Katri Saastamoinen^a, Terttu Vartiainen^{a,b}
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18
19 ^aNational Public Health Institute, Department of Environmental Health, P.O. Box 95,
20
21 FI-70701 Kuopio, Finland
22

23
24 ^bUniversity of Kuopio, Department of Environmental Sciences, P.O.Box 1627, FI-
25
26 70211 Kuopio, Finland
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31
32
33 *Corresponding author
34

35
36 Panu.Rantakokko@ktl.fi
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Abstract

The objective of this study was to estimate the intake of organic tin compounds from foodstuffs in the Finnish market basket. The study was conducted by collecting thirteen market baskets from supermarkets and market places in the city of Kuopio, eastern Finland. Altogether 115 different food samples were bought. In each basket, foodstuffs were mixed in proportion to their consumption and analysed by GC/MS for seven organic tin compounds (mono-, di-, and tributyltin, mono-, di-, and triphenyltin, and dioctyltin). Organotin compounds were detected in only four baskets, with the fish basket containing the largest number of different organotins. The European Food Safety Authority has established a tolerable daily intake of 250 ng/kg body weight for the sum of dibutyltin, tributyltin, triphenyltin, and dioctyltin. According to this study, the daily intake of these compounds was 2.47 ng/kg body weight, of which 81% originated from the market basket for fish. This exposure is only 1% of the tolerable daily intake and thus poses a negligible risk to the average consumer. However, for high fish consumers using fish from contaminated areas, the intake may be much higher.

Keywords: Organotin compounds, tributyltin, triphenyltin, market basket, dietary intake

Introduction

Organotin compounds (OTCs) are a large class of compounds with widely varying properties and have been used for many different purposes. The mono-, di- and trisubstituted compounds are the most widely employed of the various OTCs. Mono- and disubstituted compounds (e.g. monomethyltin (MMT), monobutyltin (MBT), dimethyltin (DMT), dibutyltin (DBT), mono-n-octyltin (MOT) and di-n-octyltin (DOT)) are used extensively as heat and light stabilizers in the production of polyvinyl chloride (PVC) polymers and as catalysts in the manufacture of polyurethane and silicone elastomers. Therefore they are present in water pipes, food packaging materials, glass coatings, polyurethane foams and many other consumer products. With respect to the trisubstituted OTCs, tributyltin (TBT) and triphenyltin (TPT) compounds have acquired a wide range of uses mostly associated with their strong biocidal activity toward aquatic organisms such as bacteria, fungi, algae, molluscs and crustaceans. (Fromme et al. 2005; Hoch 2001). Most attention has been paid to TBT pollution in water, sediments, and aquatic biota resulting from its use in antifouling paints in boats and ships. TBT and TPT are extremely hazardous to some aquatic species. Several restrictions on the use of TBT have been imposed, but even after a total ban, TBT deposited in sediments will remain an important exposure source for marine biota for many years to come, because of its high sorption to suspended matter and sediment and its slow degradation to DBT, MBT, and inorganic tin under anoxic sediment conditions (European Union 2003; Hoch 2001).

The toxicity of OTCs has also been demonstrated in a variety of laboratory animals. They have effects on the immune system, reproductive and developmental effects at

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4 levels near to those that are maternally toxic. A European Food Safety Authority
5 (EFSA) scientific panel has assessed the health risks to consumers associated with
6 exposure to OTCs in foodstuffs. The critical toxicological endpoint for risk assessment
7 was considered to be immunotoxicity. The panel focused on the most toxic of the
8 OTCs: TBT, DBT and TPT primarily found in fish and fishery products. DOT was also
9 included in the study because all these tin compounds exert their immunotoxic effects
10 by similar modes of action and with equivalent potency. Because of their toxicological
11 similarities, the panel considered it reasonable to establish a group Tolerable Daily
12 Intake (TDI) for these OTCs. In the absence of specific studies on combined effects, it
13 seemed justified to consider the immunotoxic effects of these compounds as additive.
14 By applying a safety factor of 100, a group TDI of 250 ng/kg body weight for the sum
15 of TBT, DBT, TPT and DOT was established (European Food Safety Authority 2004).
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35 Fish and fishery products are generally considered to be the most important source for
36 human exposure to OTCs, and for this reason studies on health risks have mainly
37 focused on seafood. Two studies on the TBT health risks from market bought seafood
38 came to the conclusion that either the seafood was unlikely to pose any risk or else the
39 risk was negligible. In the first of these studies, seafood samples were collected solely
40 from US cities, and in the second study samples were collected from Asian, Australian,
41 European, and North American cities (Cardwell et al. 1999; Keithly et al. 1999). A
42 European study on sources, consumer exposure and risks of TBT contamination in
43 seafood also came to the conclusion that for a person to be at risk of exceeding the TDI
44 set by WHO (250 ng/kg body weight per day) for TBT as a result of seafood
45 consumption, the person has to be a high consumer of seafood and has to consume
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4 seafood with a higher-than-average concentration of TBT (Willemsen et al. 2004). On
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6 the other hand, in another intake study, a tool called the Tolerable Average Residue
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8 Level (TARL) was developed to assess TBT exposure (Belfroid et al. 2000). The TARL
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10 is defined as the level in seafood that is tolerable for the average consumer with an
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12 average body weight of 60 kg. TARLs were calculated using the WHO's TDI value for
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14 TBT and average daily seafood consumption in many countries. (CHECK) In 9 of the
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16 22 countries studied, where TBT levels in seafood were available, the TARL was
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18 exceeded in one or more samples..
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26 OTCs have also been measured in other foodstuffs, e.g. wines (Azenha and Vasconcelos
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28 2002) and drinking water (Sadiki and Williams 1999). Recently twelve types of food
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30 from four areas (south 1 and 2, north 1 and 2) in China were analysed for butyltins
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32 (MBT, DBT, and TBT). In both southern areas, seven food types contained detectable
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34 amounts of at least one butyltin, whereas in only one and three food types in the two
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36 northern areas was at least one butyltin was detected (Qunfang et al. 2004). However,
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38 research on the full dietary intake of OTCs is limited to two Japanese studies. In the
39
40 early 1990s, daily intakes of TBT and TPT from a market basket were on average 6.8
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42 $\mu\text{g}/\text{person}$, and 3.3 $\mu\text{g}/\text{person}$, respectively. Of the different food groups, TBT and TPT
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44 were detected in only two baskets, one of seafood and one of vegetables and seaweeds;
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46 however, the seafood accounted for more than 95% of the intake (Tsuda et al. 1995). In
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48 a later study conducted in 1998, daily intakes had decreased, and were 1.7 $\mu\text{g}/\text{person}$ for
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50 TBT and 0.09 $\mu\text{g}/\text{person}$ for TPT. In this study DBT was also measured at a daily intake
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52 of 0.45 $\mu\text{g}/\text{person}$. Of the 14 food groups assessed, only the fish and shellfish food
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54 group contributed to intakes of TBT and TPT (Toyoda et al. 2000).
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7 The aim of this study was to measure the daily intake of seven OTCs (MBT, DBT,
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9 TBT, MPT (monophenyltin), DPT (diphenyltin), TPT, and DOT) by the market basket
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11 method in Finland and to compare the intake of OTCs to the group TDI proposed by
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13 EFSA. This study can also serve as a model for the population from North Europe.
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16 17 18 **Materials and methods**

19 20 *Food consumption data and composition of the market baskets*

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22 The methodological principle of the study was to pool a well defined food group
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24 (market basket) into a single composite sample to be analysed. Each market basket
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26 contained a number of different items, such as wheat, rye, rice, oat and barley in the
27
28 market basket of cereals (see Table I). The division of food items into different market
29
30 baskets was adopted from the "Nutrition Report 2003" study of the Finnish National
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32 Public Health Institute (Lahti-Koski and Sirén 2004). A minimum of two packages/units
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34 of at least 100 g of each food item were purchased from different manufacturers. If
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36 possible and practical, packages/units of those domestic or foreign manufacturers were
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38 purchased, that have the largest market share in Finnish supermarkets. Fruits and berries
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40 and vegetables were an exception, as only one unit was purchased owing to the large
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42 number of items in the baskets. In some cases local producers were also used for these
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44 baskets. To keep the total number of purchased packages/units within reasonable limits
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46 and to simplify their collection, low-processed products that are frequently bought from
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48 supermarkets for daily cooking were selected. In many cases, this required some
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50 balancing, by buying for example cereal flours rather than whole grains (rice was an
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52 exception). Altogether 115 different food packages/units were bought for the thirteen
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4 baskets examined in this study. The food and food group consumption data over the
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6 years 2000 - 2002 used in the composition of the market baskets and in the intake
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8 calculations were taken from the report "Balance Sheet for Food Commodities 2001 and
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10 2002" (preliminary) (Finnish Ministry of Agriculture and Forestry 2003). The annual
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12 calculations in the Balance Sheets are based on the production of different foodstuffs,
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14 changes in stockpiles, export and import figures and domestic consumption. Sample
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16 collection was carried out during the period May – August 2005. Seasonal products
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18 were collected in the peak season. Samples were collected from local supermarkets and
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20 market places. Altogether, thirteen individual market baskets were created: (1) cereals;
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22 (2) potato; (3) vegetables; (4) peas and nuts; (5) fruits and berries; (6) meat; (7) eggs;
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24 (8) fish and crustaceans; (9) milk and sour milk; (10) milk products; (11) fats and oils;
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26 (12) sugar; (13) juices and soft drinks. Alcoholic beverages were omitted from the
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28 market baskets. Canned food was only bought for tuna and herring (two packages of
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30 both items), since these food items are typically bought as canned. Table I shows the
31
32 average daily consumption of the market baskets, and the main items within the baskets.
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34 If the Balance Sheets did not contain sufficient details of the consumption of different
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36 food items in the baskets, the relevant specialized national authority was consulted. This
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38 was especially pertinent with the very important market basket of fish and crustaceans,
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40 for which the most recent and accurate consumption figures from the years 2001 - 2003
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42 were obtained from the Finnish Game and Fisheries Research Institute.
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54 *Preparation of food samples for analysis of organotin compounds*

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56 Common household conditions were followed as far as possible in the sample
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58 preparation, e.g. fruits and vegetables were washed/peeled/sliced/grated, inedible parts
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4 of the fish were removed etc. High quality stainless steel kitchen tools were used
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6 throughout and washed after every sample. Next the edible parts of the package/unit
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8 from the same manufacturer were mixed (e.g. small fish, small vegetables etc), unless
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10 they were homogenous when bought (e.g. liquids, flours, fats etc). Subsequently,
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12 identical masses of separate food samples (e.g. apples) from different manufacturers for
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14 each food item (apple) were weighed and homogenized with a BÜCHI Mixer B-400.
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16 Finally, all separate food items inside the market basket were mixed and thoroughly
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18 homogenized in proportion to their consumption. The proportion of those minor items
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20 in a basket that were not bought or were classified as “others” in Balance Sheets, were
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22 distributed to the purchased items according to their share inside the collected basket.
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24 Baskets (1) – (8), and (10) were freeze-dried and stored at –20 °C before analysis.
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26 Baskets (9) and (11) – (13) were only frozen at –20 °C before analysis.
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35 *Analysis of organotin compounds by GC/MS*

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37 The compounds to be analysed were MBT, DBT, TBT, MPT, DPT, TPT, and DOT. All
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39 weights and concentrations of OTCs are expressed as organotin cations. Individual, pure
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41 model OT compounds were bought either from Dr. Ehrenstorfer or from Acros. The
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43 purity of model compounds was checked before use. Perdeuterated analogs of MBT,
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45 DBT, TBT, MPT, DPT, and TPT were used as internal standards for the respective
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47 native ¹H-compounds. These were purchased from the Swiss Federal Institute for
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49 Environmental Science and Technology, where they had been synthesized (Arnold et al.
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51 1998). Perdeuterated DPT was used as an internal standard for DOT. Sample analysis
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53 was performed according to the method developed by Ikonomidou et al. with slight
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55 modifications (Ikonomidou et al. 2002). Baskets (1) – (11) were analysed according to
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4 Ikonomou's procedure for tissue samples. The sample amount taken for the analysis
5 was 0.25 g of the freeze dried material for the baskets (1) – (8), and (10) (the amount of
6 fresh sample taken for analysis thus varies according to the moisture content). For
7 baskets (9) and (11) that were not freeze dried, the sample amount taken for analysis
8 was 2.0 g and 0.1 g of the fresh material respectively. Baskets (12) and (13) were
9 analysed according to Ikonomou's procedure for water samples, in which 1 g and 20 g
10 of sample materials were dissolved in/diluted to 200 ml with MQ-water, respectively.
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23 A few minor modifications were made to the Ikonomou procedures for tissue and water
24 samples. In the tissue method, NaCl (1 g) used to aid in the extraction was added in a
25 solid form rather than as 30% solution, and the 2 ml of 1 M sodium acetate acetic buffer
26 acid was not added, since the addition of 2 ml of glacial acetic acid undoes the effect of
27 buffer addition. In the water method, sugar/juice samples dissolved in/diluted to 200 ml
28 of MQ water were extracted only once overnight with 20 ml of hexane. In the water
29 method, the derivatization reagent, sodium tetraethylborate, was applied as 2% solution
30 instead of 1%. With both methods, only 3 cm of activated (200°C overnight, 90 min at
31 300°C, and 200 °C until use) basic alumina was loaded in the Pasteur pipette, instead of
32 6 cm. The samples were eluted with 10 ml of 4% diethylether in hexane instead of 20%.
33 Thus more dilute diethylether-hexane solution was sufficient to elute all of the
34 derivatized OTCs from the column and eluted fewer matrix impurities. Tetrabutyltin
35 was used as the syringe standard instead of tetrapentyltin.
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56 The limit of detection (LOD) and the limit of quantitation (LOQ) were calculated using
57 MassLynx software as the concentrations corresponding to 3 times and 8 times the
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4 baseline noise in the channels of the monitored ions, respectively. LODs and LOQs
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6 were calculated separately for each compound in each sample on a fresh weight basis.
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9 The LODs are recorded in Table III for each compound with a concentration below the
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11 LOD. If the concentration was between LOD and LOQ, then the LOQ is added for these
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13 compounds. If the concentration was above the LOQ, then the measured concentration
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15 is recorded in Table III. The LODs and the LOQs vary considerably between different
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17 market baskets mainly because of the different amounts of the fresh sample taken for
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19 analysis.
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26 The three level calibration for the tissue method was performed by spiking 0.25 g of
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28 freeze dried pike tissue with known amounts of OTCs and treating it in exactly the same
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30 way as the true samples. The spiked pike tissue had previously been confirmed to be
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32 free of OTCs. The three level calibration for the water method was performed by
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34 spiking 200 ml of ultrapure water with OTCs and treating it in the same way as the true
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36 samples.
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42 The GC/MS analysis was performed using a HP 6890 Gas Chromatograph connected to
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44 a Waters Autospec Ultima high resolution mass spectrometer operating in the selected
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46 ion monitoring mode. The two most intensive fragment ions of each ethylated OTC
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48 were monitored. Fragment ions are given in Table II. The column used was an HP-1
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50 capillary column (12 m, 0.20 mm I.D., 0.33 μm film).
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Quality control and assurance

Each sample was extracted in duplicate and the mean was reported. The relative standard deviation of the parallel market basket samples with concentrations over the LOQ had to be less than 20%. The laboratory reagent blank samples were treated and analysed using the same method as the actual samples, one blank for each series of samples. The blank result was subtracted from the sample measurements. All glassware in contact with samples was washed and soaked in 1 M HNO₃ overnight before use. In-house-made spiked and freeze dried control fish samples and spiked control water samples were analysed in the sample series for the respective method. The results of the in-house-made control sample had to be within the accepted limits (spiked value ± 2 * standard deviation of the results in the control chart) for the entire sample series to be acceptable. In the same series in which market basket samples were analysed using the tissue method, the certified reference material CRM 477, freeze dried mussel tissue, was also analysed for organic tin compound. CRM 477 is produced under the Standards, Measurement and Testing Programme of the European Commission, and has certified concentrations for MBT, DBT, and TBT, and indicative concentrations for MPT, DPT, and TPT, respectively (Pellegrino et al. 2000). For butyltins, the recoveries were 125%, 85%, and 108% of the certified values, and for phenyltins the recoveries were 151%, 94%, and 96% of the indicative values, respectively. To confirm the identity of the OTC peak, peak retention times had to match within $\pm 3s$ of those of calibration samples, and the area ratio of primary and secondary ions in the MS-chromatograms had to be within 20% of the theoretical value. The mean LODs varied from 2.9 pg/g fresh weight (fw) (juices and soft drinks) to 0.31 ng/g fw (fats and oils) and the mean LOQs varied from 7.8 pg/g fw (juices and soft drinks) to 0.82 ng/g fw (fats and oils). These values differ

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4 from compound to compound and matrices, and therefore LODs or LOQs are presented
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6 in Table III only for those results where the concentration was either less than the LOD
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8 or LOQ, respectively. The Chemistry Laboratory of the National Public Health Institute
9
10 of Finland is an accredited laboratory according to ISO17025 . The scope of
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12 accreditation includes organic tin compounds from tissue, sediment, and water samples.
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16 17 18 *Intake calculations*

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20 In the intake calculations, the average daily consumption of the food basket was
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22 multiplied by the corresponding concentration of OTCs. When the concentration of an
23
24 OTC in a basket was less than the limit of quantification, the result was reported as
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26 zero. Daily intakes (ng cation/day) for OTCs were calculated on a fresh weight basis as
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28 the sum of individual baskets. When calculating the daily intakes per kg body weight
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30 (ng cation/kg bw), the average weight (77 kg) of the adult population (25 – 74 years)
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32 obtained from national FINRISK 2002 study was used (Laatikainen et al. 2003).
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40 **Results and discussion**

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42 Table III presents the concentrations of OTCs in the different market baskets. Of the
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44 thirteen baskets, four contained OTCs at levels higher than the limit of quantitation. As
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46 in the Japanese intake studies, in this case, too, TBT and TPT were exclusively present
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48 in the fish basket (Toyoda et al. 2000; Tsuda et al. 1995). The fact that the number of
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50 individual fish and crustacean samples pooled to the fish basket was quite limited in this
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52 study, consisting of only 22 different packages/units, must be taken into consideration.
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54 The concentrations of TBT and TPT in the fish basket were low, in fact similar to those
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56 measured for TBT in US market bought seafood shortly after the peak of TBT usage in
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4 anti-fouling paints in the US (Cardwell et al. 1999). In the current study, there was a
5 large contribution of imported farmed salmon (from Norway), tuna and saithe in the fish
6 basket (see Table I). Imported Norwegian salmon bought in Sweden and France and
7 imported tuna bought in Germany were analysed in the European Commission research
8 project "Sources, consumer exposure and risks of organotin contamination in seafood"
9 (Willemsen et al. 2004). In salmon bought in Sweden and France, only TBT was found,
10 with the concentrations varying from less than the limit of quantification (4 ng/g fw) to
11 11 ng/g fw. The concentrations of TBT in tuna bought in Germany were also very low,
12 only a few ng/g fw. These low concentrations in imported salmon and tuna in the
13 European Commission project are in good agreement with the concentrations in the fish
14 basket measured in the current study. In another European Commission project, a report
15 on a Scientific Co-operation (SCOOP) task, eight EU Member States provided data
16 available at the national level on the occurrence of butyltins and phenyltins in different
17 seafood species. The spread of the concentrations in different species in the different
18 countries was large; in some countries, levels were on average an order of magnitude or
19 more higher than those measured in this Finnish seafood market basket (European
20 Commission 2003). Currently very little is known about the levels of OTCs in
21 individual seafood species originating from Finnish water areas. In particular, the OTC
22 concentrations in the Finnish background areas have still not been measured. In a study
23 carried out in the vicinity of twelve cities in Finland, the sum of OTCs (mostly tri-
24 substituted) in pooled pike muscle samples was 1 - 33 ng cation/g fw in inland fish and
25 8 - 141 ng cation/g fw in coastal fish (Mannio et al. 2005). However, in those Finnish
26 costal areas with a high density of shipping, sums of OTCs up to several hundred ng/g
27 fw in individual pike perch and burbot samples have been measured (Mannio et al.
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4 2005; Vatanen and Niinimäki 2005). A project intended to study the OTC
5 concentrations from the most commonly eaten domestic fish species from background
6 and contaminated areas is currently underway.
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14 In addition to fish, low concentrations of MBT and/or DBT were also detected in the
15 vegetable, potato, and fruit and berries baskets. These compounds have also been
16 observed in similar food types by other research groups. Low concentrations (1 – 2 ng
17 cation/g) of butyltins have been detected in French lettuces grown on OTC-
18 contaminated sludged soil (Marcic et al. 2005). Higher concentrations (10 – 200 ng
19 cation/g) of butyltins were detected in southern areas of China in beans, vegetables,
20 fruits, eggs, milk, sugar, meat, potatoes, and beverages. In the northern Chinese regions
21 these compounds were not detected, but this may be partly attributable to the higher
22 limits of detection, which were from 10 (MBT) – 17 (TBT) ng cation/g (Qunfang et al.
23 2004). There are a number of possible sources of MBT and DBT in these food
24 commodities. These include the use of sludge as fertilizer, some pesticides that may
25 contain OTCs, and butyltin stabilized plastic products which may have come into
26 contact with these food products. It has to be emphasized that the market baskets
27 collected in this study did not contain highly processed food, but mainly raw materials
28 intended for further cooking and processing. It is possible that more highly processed
29 foods come more into contact with plastics which may contain MBT and DBT.
30 However, to simplify the sample collection, such foods were omitted from this study.
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56 Table IV presents the daily intakes for OTCs (ng cation/person). Results less than the
57 limit of quantitation were taken as zero. This approach was adopted because only ten
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4 results between LOD and LOQ were found (see Table III), and many of those were only
5 marginally higher than the LOD. Of the total intake, 57% is attributable to MBT. This is
6 due to both the higher consumption of those baskets containing lower concentrations of
7 MBT (potato, vegetables, and fruits) and higher concentrations in the less consumed
8 fish, which contribute only 23% to the intake of MBT. The situation is similar for DBT,
9 for which vegetables and fruits dominate, while fish contributes only 21%. The intakes
10 of TBT, DPT and TPT originate solely from fish. For the sum of OTCs of health
11 interest (DBT, TBT, TPT, and DOT), fish contributes 81% to the intake, with the
12 remainder attributable to DBT in vegetables (9%) and fruits (10%). When compared to
13 a Japanese market basket study (Toyoda et al. 2000), the daily intakes in this study (in
14 ng/person) were 10% for DBT, 6% for TBT, and 49% for TPT of those in Japan.
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33 The total daily intake in ng cation/kg bw is presented in the bottom row of Table IV.
34 The sum of DBT, TBT, TPT, and DOT, is 2.47 ng cation/kg bw, which is only 1.0% of
35 the group TDI of 250 ng/kg body weight established by the EFSA (European Food
36 Safety Authority 2004). If in Table III the results <LOQ had been taken as LOQ and the
37 results <LOD as 0, the recalculated total daily intake in the bottom row of Table IV
38 would only have risen to 3.81 ng cation/kg bw. Furthermore, if also the results <LOD
39 had been taken as LOD, then the daily intake would still only amount to 7.69 ng
40 cation/kg bw. However, especially this latter result bears no quantitative accuracy, and
41 represents only a theoretical maximum intake. Furthermore, even these values are only
42 1.5% and 3.1% of the EFSA group TDI, respectively. These very low intakes,
43 irrespective of the way they were calculated, mean that the average Finnish consumer
44 need not be alarmed about the intake of organic tin compounds from typical raw
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4 materials in their daily meals. However, if more processed foods had been selected for
5
6 this study, intake of monobutyltin and dibutyltin might have increased slightly, since the
7
8 foods could have been in greater contact with plastics possibly containing these
9
10 compounds. More importantly, for those groups of the population who consume larger
11
12 than average amounts of fish from contaminated or background areas, the daily intakes
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14 could be significantly higher. The possible OTC intake from fish from contaminated
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16 and background areas of Finland is currently under investigation.
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Table 1. Market baskets, their average daily consumption in g/day (percentage of total daily consumption), and their main items (percentage in the composed basket, minor items not shown for every basket)

| Market basket | Consumption g/day (%) | Main items (%) |
|--------------------------|--------------------------|--|
| (1) Cereals | 207 (9.7) | Wheat (65) Rye (21) Rice (8) |
| (2) Potato | 174 (8.1) | Potato (100) |
| (3) Vegetables | 177 (8.2) | Tomato (24) Cucumber (17) Carrot (18) Onion (11) |
| (4) Peas and nuts | 5.2 (0.2) | Peas (63) Nuts (37) |
| (5) Fruits and berries | 244 (11.4) | Banana (28) Apple (28) Orange (16) Mandarin (13) Lingonberry (6) |
| (6) Meat | 190 (8.9) | Pork (50) Beef (28) Poultry (22) |
| (7) Eggs | 26.8 (1.25) | Eggs (100) |
| (8) Fish and crustaceans | 39.5 (1.8) | Salmon and rainbow trout (39) Tuna and saithe (20) |

| | | | |
|----|-----------------------------|------------|-----------------------------------|
| 1 | | | |
| 2 | | | Baltic herring (8) |
| 3 | | | |
| 4 | | | Herring (8) |
| 5 | | | |
| 6 | | | Vendace (6) |
| 7 | | | |
| 8 | | | Pike (6) |
| 9 | | | |
| 10 | | | Perch (5) |
| 11 | | | |
| 12 | | | Shrimp (5) |
| 13 | | | |
| 14 | | | Whitefish (3) |
| 15 | | | |
| 16 | (9) Milk and sour milk | 445 (20.7) | Low-fat milk (56) |
| 17 | | | |
| 18 | | | Fat-free milk (24) |
| 19 | | | |
| 20 | | | Whole milk (10) |
| 21 | | | |
| 22 | | | Sour milk (10) |
| 23 | | | |
| 24 | (10) Milk products | 163 (7.6) | Yoghurt (29) |
| 25 | | | |
| 26 | | | Cheese (28) |
| 27 | | | |
| 28 | | | Ice cream (22) |
| 29 | | | |
| 30 | | | Cream (11) |
| 31 | | | |
| 32 | | | ¹ Sour whole milk (10) |
| 33 | | | |
| 34 | (11) Fats and oils | 52.4 (2.4) | Margarines and butter-oil |
| 35 | | | |
| 36 | | | mixtures (56) |
| 37 | | | |
| 38 | | | Vegetable oils (26) |
| 39 | | | |
| 40 | | | Butter (18) |
| 41 | | | |
| 42 | (12) Sugar | 88.8 (4.1) | Sugar (100) |
| 43 | | | |
| 44 | (13) Juices and soft drinks | 334 (15.6) | Soft drinks (57) |
| 45 | | | |
| 46 | | | Juices (43) |
| 47 | | | |
| 48 | | | |
| 49 | | | |
| 50 | | | |
| 51 | | | |
| 52 | | | |
| 53 | | | |
| 54 | | | |
| 55 | | | |
| 56 | Total | 2146 (100) | |
| 57 | | | |
| 58 | | | |
| 59 | | | |
| 60 | | | |

¹ Sour whole milk or curdled milk is a typical Finnish semisolid milk product that is distinctive and different from ordinary liquid sour milk.

Table II. Ions monitored in the GC-HRMS analysis of the organic tin compounds. Perdeuterated analogs of organic tin compounds are depicted with “OTC-dx”, where x is the number of deuterium atoms in the internal standard molecule.

| Compound | Primary ion | Secondary ion | Compound | Primary ion | Secondary ion |
|----------|-------------|---------------|----------|-------------|---------------|
| MBT | 233.0504 | 235.0510 | MBT-d9 | 242.1069 | 244.1075 |
| DBT | 233.0504 | 235.0510 | DBT-d18 | 242.1069 | 244.1075 |
| TBT | 289.1131 | 291.1137 | TBT-d27 | 316.2826 | 318.2831 |
| MPT | 253.0192 | 255.0197 | MPT-d5 | 258.0505 | 260.0511 |
| DPT | 301.0193 | 303.0198 | DPT-d10 | 311.0820 | 313.0826 |
| TPT | 349.0193 | 351.0199 | TPT-d15 | 364.1135 | 366.1140 |
| DOT | 373.2072 | 375.2077 | TeBT | 289.1131 | 291.1137 |

Table 3. Concentrations (ng cation/g fresh weight) of organic tin compounds in different market baskets. Results less than the LOQ are depicted with “< x.x“, and results less than the LOD are depicted with nd (x.x), where x.x is either the LOQ or the LOD.

| Market basket | MBT | DBT | TBT | MPT | DPT | TPT | DOT |
|-----------------------------|-------------|-------------|-------------|------------|-------------|-------------|-------------|
| (1) Cereals | nd (0.053) | nd (0.086) | nd (0.16) | nd (0.55) | nd (0.086) | nd (0.032) | nd (0.16) |
| (2) Potato | 0.57 | < 0.054 | nd (0.031) | nd (0.11) | nd (0.012) | nd (0.008) | nd (0.042) |
| (3) Vegetables | 0.35 | 0.10 | < 0.030 | nd (0.031) | nd (0.005) | nd (0.002) | < 0.061 |
| (4) Peas and nuts | < 0.13 | < 0.19 | nd (0.20) | nd (0.22) | nd (0.049) | nd (0.022) | < 0.64 |
| (5) Fruits and berries | 0.17 | 0.080 | nd (0.024) | nd (0.049) | nd (0.005) | nd (0.007) | nd (0.019) |
| (6) Meat | nd (0.021) | nd (0.030) | nd (0.060) | nd (0.14) | nd (0.023) | nd (0.011) | nd (0.075) |
| (7) Eggs | nd (0.041) | nd (0.075) | nd (0.13) | nd (0.17) | nd (0.044) | nd (0.041) | nd (0.22) |
| (8) Fish and crustaceans | 1.52 | 0.25 | 2.53 | nd (0.076) | 0.14 | 1.11 | nd (0.091) |
| (9) Milk and sour milk | nd (0.011) | < 0.054 | nd (0.024) | nd (0.045) | nd (0.015) | nd (0.007) | nd (0.059) |
| (10) Milk products | < 0.059 | <0.10 | nd (0.052) | nd (0.10) | nd (0.014) | nd (0.010) | < 0.20 |
| (11) Fats and oils | nd (0.15) | nd (0.34) | nd (0.23) | nd (0.50) | nd (0.15) | nd (0.35) | nd (0.43) |
| (12) Sugar | nd (0.033) | nd (0.026) | nd (0.043) | nd (0.20) | nd (0.009) | nd (0.006) | nd (0.016) |
| (13) Juices and soft drinks | nd (0.0014) | nd (0.0014) | nd (0.0017) | nd (0.013) | nd (0.0011) | nd (0.0008) | nd (0.0010) |

Table 4. Daily intakes of organic tin compounds (ng cation/person) from different market baskets. Only those compounds that were detected in at least one basket, and only those baskets that contained at least one compound at a higher level than the LOQ, are tabulated.

| Market basket | MBT | DBT | TBT | DPT | TPT | Σ OTCs | Σ DBT, TBT, TPT, DOT |
|--|------|------|------|------|------|--------|----------------------|
| (2) Potato | 98.8 | | | | | 98.8 | |
| (3) Vegetables | 61.4 | 17.1 | | | | 78.5 | 17.1 |
| (5) Fruits and berries | 40.7 | 19.5 | | | | 60.2 | 19.5 |
| (8) Fish and crustaceans | 60.1 | 9.9 | 99.9 | 5.5 | 43.9 | 219 | 154 |
| Total intake | 261 | 46.6 | 99.9 | 5.5 | 43.9 | 457 | 190 |
| Total intake (ng cation/kg body weight) ^a | 3.39 | 0.61 | 1.30 | 0.07 | 0.57 | 5.93 | 2.47 |

^a Weight of the average person in the intake calculations is 77 kg.