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Estimating acute and chronic exposure of children and adults to chlorpyrifos in fruit and vegetables based on the new, lower toxicology data

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ABSTRACT

This paper presents, for the first time, results for chlorpyrifos (CHLP) in Polish fruits and vegetables over the course of a long period of research, 2007–2016, with toxicological aspects. The challenge of this study was to re–evaluate the impact of chlorpyrifos residues in fruit and vegetables on health risk assessed via acute and chronic exposure based on old and new, lower, established values of: Average Daily Intakes (ADIs)/Acute Reference Doses (ARfDs) and Maximum Residue Levels (MRLs). A total of 3 530 samples were collected, and CHLP in the range of 0.005–1.514 mg/kg was present in 10.2% of all samples. The MRL was exceeded in 0.7% of all samples (MRL established in 2009–2015), and recalculation yielded a much greater number of violations for the new MRL (2016), which exceeded 2.9% of all samples. Acute exposure to CHLP calculated according to the old, higher toxicological data (0.10 mg/kg bw/day), does not exceed 14% of its respective ARfDs for adults and both groups of children, but when calculated for incidental cases according to the current value (ARfD 0.005 mg/kg bw) for infants and toddlers, was above 100% of its respective ARfDs in: white cabbage (263.65% and 108.24%), broccoli (216.80% and 194.72%) and apples (153.20% and 167.70%). The chronic exposure calculated for both newly established ADI values (0.001 mg/kg bw/day and 0.100 mg/kg bw/day) appears to be relatively low for adults and children.

1. Introduction

The presence of pesticide residues in food commodities has always been a matter of serious concern (Hossain et al., 2015). The problem is especially serious when these commodities are consumed raw or semi–processed, and consequently, it is expected that they contain higher pesticide residue levels than other food groups (Claeys et al., 2011). According to the World Health Organization (WHO), food consumption consists, on average, of 30% of fruits and vegetables (FAO, 2001), and it is well known that fruits and vegetables are more contaminated by pesticides than products of animal origin (Boada et al., 2014).

Organophosphates (OPs) are routinely applied to fruits and vegetables for broad–spectrum insect and disease control (Quijano et al., 2016). However, the use of these pesticides raises serious food safety and environmental issues, as residues may translocate, accumulate or deposit into fruit and vegetable tissues (Jeong et al., 2012). Over the past decade, chlorpyrifos (O,O–Diethyl–O–(3,5,6–trichloro–2–pyridyl) phosphorothioate) has been one of the most commonly used broad–-spectrum OPs (Yuan et al., 2014). The US Environmental Protection Agency (EPA) banned chlorpyrifos as a residential (controlling termiticide) and field pesticide (controlling agricultural insects) due to its harmful effects on human health (EPA, 2000). Chlorpyrifos is moderately toxic to humans and can affect the central nervous system, cardiovascular system and respiratory system (Hulse et al., 2014).

Exposure to high doses of chlorpyrifos can lead to acute poisoning by covalently inhibiting acetylcholinesterase (AChE), which overstimulates the nervous system, causing neuromuscular symptoms and at very high exposures, initiating seizures, respiratory paralysis and death. In addition, there are human epidemiological studies demonstrating that long–term, low–level exposure to chlorpyrifos can lead to chronic neurotoxicity in the absence of cholinesterase inhibition, including deficits in cognition, memory, emotional state and syntactic reasoning (Yang et al., 2017). Therefore, chlorpyrifos should be controlled at the optimum level due to its relative toxicity to the environment and human health.

To protect the population from the negative effects of the use of pesticides, the European Union (EU) establishes limits on all pesticides for foods to be consumed fresh, and there are national and European surveillance programs to ensure that these are complied with. Analysis of pesticide residues in food is a key tool for monitoring the levels of human exposure to pesticide residues (Boobis et al., 2008). Pesticide

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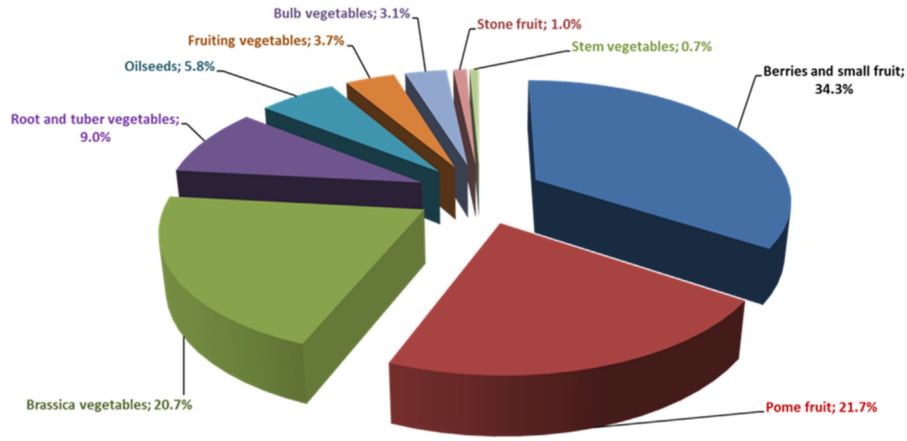

Fig. 1. Group of tested fruit and vegetables.

residues in food are usually monitored with reference to Maximum Residue Levels (MRLs), Average Daily Intakes (ADIs) and Acute Reference Dose (ARfD) (Chen et al., 2012).

The MRL is an index that represents the highest concentration (expressed in mg/kg) of pesticide residue that is legally permitted or accepted in a food or animal feed after the use of pesticides (Darko and Akoto, 2008). The ADI is the estimated amount of a chemical in food (mg/kg body weight/day) that can be ingested daily over a life time without appreciable health risk to the consumer. The ARfD means the amount of pesticide in food, expressed on a body weight basis, that can be ingested over a short period of time, usually during one day, without appreciable risk to the consumer on the basis of the data produced by appropriate studies and taking into account sensitive groups within the population (e.g. children and infants) (Lozowicka et al., 2016a).

Chlorpyrifos has been subject to a preliminary human health risk assessment based on new toxicological studies which led to the establishment of new toxicological reference values (EFSA, 2014). The values established by the Joint Meeting of FAO/WHO on Pesticide Residues (JMPR) (ADI 0.01 mg/kg bw/day and ARfD 0.1 mg/kg bw) have been in force since 2004. The European Union has established a comprehensive legislative framework for approving the chemicals used in pesticides, and for setting levels of pesticide residues that are acceptable in food. The newly available toxicological data led to the decrease of reference values for chlorpyrifos which were established by the European Food Safety Authority (EFSA) (2014: ADI 0.001 mg/kg bw/day and ARfD of 0.005 mg/kg bw). According to European Commission Regulation (EU) No. 2016/60, MRL values were also decreased from 0.05 to 0.01 mg/kg for many commodities: from 0.05 to 0.01 mg/kg in apples, pears, blackberries and from 0.1 to 0.01 mg/kg in carrots, from 1.00 to 0.01 mg/kg in gooseberries and blackcurrants, and from 0.05 to 0.03 mg/kg in chokeberries.

The risk associated with the residues of chlorpyrifos was studied in a variety of cultivations: on rice and in cabbage (Chen et al., 2012), in celery (Fang et al., 2015), in apples, lettuce and cucumber (Quijano et. al, 2016) and in crops (rice, maze, soybean) (Li et al., 2015), but none of these studies have identified such a long study period and included changes in ADI and ARfD values.

In this study, the impact of chlorpyrifos residues present in fruit and vegetables on human health was re-evaluated via long and short term intake for the first time. Therefore, based on Polish pesticide residue monitoring data over the last ten years (2007–2016) and the consumption data of adults and children, the acute and chronic exposures to chlorpyrifos residues were recalculated (current and previous toxicological values established by JMPR and EFSA) using a deterministic model in the 97.5th percentile.

2. Material and methods

The analytical chlorpyrifos (98.5% purity) standard [O,O–diethyl O–(3,5,6–trichloro–2–pyridinyl)–phosphorothioate] was kindly supplied by Sigma Aldrich (Steinheim, Germany). Acetonitrile of analytical grade was provided by J.T. Baker (Deventer, Netherlands). Florisil (60–100 mesh) was supplied by POCH (Gliwice, Poland). Anhydrous sodium sulfate was purchased from Fluka (Seelze–Hannover, Germany). Silica gel (230–400 mesh), sodium sulfide nonahydrate, formic acid and ammonium formate were obtained from Merck (Darmstadt, Germany). LC–grade water (18 MV cm) was obtained from a Milli–Q water purification system (Millipore Ltd., Bedford, MA, USA). QuEChERS sorbent kits (PSA, bulk Carbograph) and salt pouches: magnesium sulfate, sodium chloride, sodium citrate and citric acid disodium salt, were purchased from Agilent Technologies (Santa Clara, CA, USA). Standard stock solutions of various concentrations were prepared in acetone and stored in dark glass bottles at temperature below 4 °C. Standard working solutions were prepared by dissolving the appropriate amounts of stock solution of individual pesticides with a mixture of n–hexane/acetone (9:1) for GC − ECD/NPD and GC − MS/MS analysis.

2.1. Samples

Samples of fresh fruits and vegetables were obtained under the official control of plant protection product residues conducted in 2007–2016 by the Ministry of Agriculture and Rural Development from north–eastern and central Poland.

This study included 3530 samples of commonly consumed raw fruits and vegetables (at least 1 kg) (Fig. 1): berries and small fruits − 34.3% (mainly blackcurrants, raspberries and strawberries), pome fruit − 21.7% (mainly apples) and *Brassica* vegetables − 20.8% (mainly broccoli, cauliflower and white cabbage). All samples were manually cut into small pieces, homogenized and kept frozen (−15 °C) until analysis.

2.2. Sample preparation

The fruit and vegetable samples were analysed by two accredited (ISO, 2005) multi–residue methods (MRM): Matrix Solid Phase Dispersion (MSPD) and Quick Easy Cheap Effective Rugged and Safe (QuEChERS) (Fig. 2). The details of sample preparation were described in a previous publication (Lozowicka et al., 2016b).

The MSPD method is based on solid phase dispersion on the fruit and vegetable matrix. Two grams of sample was manually blended with 4 g of solid phase: 5% silica gel (strawberries, peaches and raspberries), and others with Florisil, in a mortar, to produce a homogeneous mixture. This mixture was then transferred to a glass column packed with