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ORIGINAL ARTICLE

ANALYSIS OF ACRYLAMIDE, 3-MONOCHLOROPROPANE-1,2-DIOL, ITS ESTERS AND GLYCIDYL ESTERS IN CARBOHYDRATE-RICH PRODUCTS AVAILABLE ON THE POLISH MARKET

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ABSTRACT

Background. Carbohydrate-rich foods, such as breakfast products, snacks and biscuits because of its nutritional or sensory qualities are an inherent part of human diet. However, their production might contribute to the formation of acrylamide, 3-monochloropropane-1,2-diol (3-MCPD) and its esters and glycidyl esters.

Objective. The aim of this work was to assess the levels of acrylamide, free and bound 3-MCPD and glycidyl esters in selected carbohydrate-rich, thermal processed products, present on the market in Poland in 2016-2017.

Material and Methods. The survey involved 60 samples of snacks, breakfast products and biscuits. Acrylamide and free 3-MCPD was determined using modified QuEChERS approach. Analysis of 3-MCPD and glycidyl esters was based on the acid-catalysed method of sample preparation, derivatisation with PBA and GC-MS analysis.

Results. Free 3-MCPD contents were within the values of 9.3-63.3 μg kg^{-1}, with the highest mean content for muesli (33.3 μg kg^{-1}), and the lowest for baby biscuits (11.7 μg kg^{-1}). The levels of bound 3-MCPD were higher (from 9.3 μg kg^{-1} to 1500 μg kg^{-1}). The highest average content was observed for sugar free biscuits (599 μg kg^{-1}), whereas the lowest for breakfast cereals (50.2 μg kg^{-1}). Glycidyl esters were detected only in four samples with the highest content at the level of 28.8 μg kg^{-1}. The acrylamide levels varied from 195 to 1352 μg kg^{-1}, with the highest content for organic biscuit samples (913 μg kg^{-1}), and the lowest for muesli (348 μg kg^{-1}).

Conclusions. Regular consumption of popular snacks such as potato chips, crackers and biscuits may result in risk to human health as the effect of high content of acrylamide or 3-MCPD. Due to a high level of these contaminants detected in some type of breakfast products, and products targeted for children, its consumption should be restricted, especially in younger population groups.

Key words: *thermal processing contaminants; acrylamide, 3-monochloropropane-1,2-diol; 3-MCPD; 3-MCPD esters; glycidyl esters*

STRESZCZENIE

Wprowadzenie. Produkty bogate w węglowodany, takie jak przekąski, produkty śniadaniowe i herbatniki ze względu na ich właściwości odżywcze lub sensoryczne, są nieodłączną częścią codziennej diety. Ze względu na fakt, że technologia ich produkcji wymaga zastosowania wysokich temperatur, co sprzyja tworzeniu niektórych zanieczyszczeń, mogą być one zanieczyszczone akrylamidem, 3-monochloropropano-1,2-diolem (3-MCPD) i jego estrami oraz estrami glicydolu.

Cel badań. Celem pracy była ocena występowania akrylamidu, wolnego i związanego 3-MCPD oraz estrów glicydolu w wybranych próbkach produktów bogatych w węglowodany, obecnych na rynku detalicznym w Polsce w latach 2016-2017.

Materiał i metody. Badania obejmowały 60 próbek przekąsek, produktów śniadaniowych i herbatników. Zawartość akrylamidu i wolnego 3-MCPD oznaczono za pomocą zmodyfikowanej metody QuEChERS. Estry 3-MCPD i estry glicydolu analizowano z wykorzystaniem hydrolizy kwasowej, derywatyzacji z użyciem PBA i końcowej detekcji techniką GC-MS.

Wyniki. Zawartość wolnego 3-MCPD mieściła się w granicach 9.3-63.3 μg kg^{-1}, z najwyższą średnią zawartości w musli (33.3 μg kg^{-1}), a najniższą w herbatnikach przeznaczonych dla dzieci (11.7 μg kg^{-1}). Zawartość związanego 3-MCPD była znacznie wyższa (od 9.3 μg kg^{-1} do 1500 μg kg^{-1}). Najwyższą średnią zawartość stwierdzono w herbatnikach bez dodatku cukru (599 μg kg^{-1}), natomiast najniższą w płatkach śniadaniowych (50.2 μg kg^{-1}). Estry glicydolu wykryto jedynie w czterech próbkach (najwyższa zawartość – 28.8 μg kg^{-1}). Zawartość akrylamidu wahała się w zakresie 195-1352 μg kg^{-1}, przy czym najwyższą ilość oznaczono w próbkach herbatników ekologicznych (913 μg kg^{-1}), a najniższą w musli (348 μg kg^{-1}).

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Wnioski. Regularne spożywanie popularnych przekąsek, takich jak chipsy ziemniaczane, krakersy i herbatniki, z uwagi na wysokie zawartości w nich akrylamidu i 3-MCPD może przyczynić się do narażenia zdrowia. Ze względu na znaczną ilość badanych zanieczyszczeń w niektórych popularnych produktach śniadaniowych oraz produktach przeznaczonych dla dzieci, ich spożywanie powinno być ograniczone, zwłaszcza w młodszych grupach wiekowych.

Słowa kluczowe*: zanieczyszczenia procesowe; akrylamid, 3-monochloropropano-1,2-diol; 3-MCPD; estry 3-MCPD; estry glicydolu*

INTRODUCTION

Carbohydrate-rich foods, especially cereal products, because of its nutritional and sensory qualities are an inherent part of human diet being therefore a significant segment of global confectionery market. Recently, ready-to-eat breakfast products, such as breakfast cereals, muesli or granola, which use facilitates breakfast preparation, are becoming increasingly popular. Apart from cereal products, a high content of carbohydrates can be found in various kinds of processed sweets, e.g. biscuits or in savoury snacks. Despite of its low nutritional value, consumption of these products has been on an increase as a result of urbanisation and lifestyle changes. For most people these products have become a regular part of the diet and nowadays the products are eaten at least a few times a week. Taking into account that all aforementioned products are produced during thermal processing, the question is whether – besides of its nutritional or sensory qualities – the products are still safe for consumers.

Generally, thermal treatment of food containing lipids, certain amino acids, and sugars processed at temperatures above 160 °C can lead to the formation of many toxic compounds such as e.g. acrylamide, chloropropanols, its esters and glycidyl esters. 3-monochloropropane-1,2-diol (3-MCPD), the most abundant chlororopropanol, is produced mainly by monoacyl- (MAG), diacyl- (DAG) and triacyl- (TAG) glycerol or free glycerol with chloride ions (present naturally or added) [17]. 3-MCPD occurs in foodstuffs not only as a free compound but also in the bound form with higher fatty acids. The formation of 3-MCPD esters (3-MCPDE, e.g. 1,2-bis-palmitoyl-3-chloropropanediol, 1,2-distearoyl-3-chloropropanediol, 1,2-dioleoyl-3-chloropropanediol) are associated mainly with the processes of oil refining, but they are also formed during thermal processing of food [21]. Glycidyl esters (GE) are generated mostly upon refining of oil [9, 15]. Hence, 3-MCPD in both forms might be found in dried savoury and sweet foods containing salt and fat, such as crisp bread, salty crackers, biscuits, but also in certain breakfast products [13, 38].

The second contaminant, acrylamide (AA), is a product of *Maillard* reaction with free asparagine and reducing sugars during heat treatment at temperatures higher than 120°C under low moisture conditions. In food with a high fat content, the alternative acrylamide formation is a pathway via acrolein, which is formed by the degradation of lipids, mainly oxidized fatty acids or glycerol. Acrolein might be then oxidized to acrylic acid, which could react with ammonia to form acrylamide [41]. Initial surveys have shown that relatively high concentrations of acrylamide are found in potato chips, French fries, pan-fried potato products, crisp bread, biscuits, crackers and coffee [14, 25].

Free 3-MCPD is a potential carcinogen (Group 2B), affects kidneys, male fertility and renal function [20]. Glycidol was classified by the International Agency for Research on Cancer (IARC) as probably carcinogenic (group 2A) [19]. In the case of esters of chloropropanols and glycidyl esters, they have been shown to undergo complete decomposition in human digestive tract to free chloropropanols or glycidol [21]. For this reason, in 2014, European Commission adopted Recommendation 2014/661/EU on the monitoring of the presence of 2 and 3-monochloropropane-1,2-diol (2 and 3-MCPD), 2- and 3-MCPD fatty acid esters and glycidyl fatty acid esters in food [8]. Recently, European Food Safety Authority decreased Tolerable Daily Intake (TDI) level for total 3-MCPD (sum of 3-MCPD content both in free and bound form) to 0.8 $\mu g\ kg^{-1}$ bodyweight [13].

In case of AA, neurotoxicity, adverse effects on male reproduction, developmental toxicity and carcinogenicity were identified as possible critical endpoints for AA toxicity from experimental animal studies [14]. International Agency for Research on Cancer has classified acrylamide as probably carcinogenic to humans (Group 2A) [18]. Having this in mind, the European Commission in 2013 adopted on Commission Recommendation 2013/647/EU on investigations into the levels of acrylamide in food. According to the document, member States should to carry out investigations in cases where the levels of acrylamide in a foodstuff, tested in the monitoring exercise, exceeds certain acrylamide indicative values, published in the Annex to this Recommendation [7].

Therefore, the aim of this work was to assess the levels of acrylamide, free and bound 3-MCPD and glycidyl esters in selected carbohydrate-rich, thermal processed products, present on detail market

in Poland in 2016-2017. The results were discussed and compared to tolerable daily intake established by EU (in case of 3-MCPD) or to certain indicative values (in case of acrylamide). The evaluation of dietary exposure in case of acrylamide with respects to different age groups has been also provided.

MATERIALS AND METHODS

Chemicals and reagents

Hexane and acetonitrile, HPLC grade for liquid chromatography LiChrosolv® were purchased from Merck KGaA, Germany. Methanol, tetrahydrofuran, acetone, sulphuric acid (98%), sodium hydrogen carbonate, sodium bromide, magnesium sulphate anhydrous, and sodium chloride were purchased from Chempur S.A., Poland. PSA (primary secondary amine), and C_{18} (octadecyl) SPE Bulk Sorbent derived from Agilent Technologies, USA. 3-MCPD, 3-monochloropropane-1,2-diol-d_5 (3-MCPD-d_5) (internal standard), 3-monobromochloropropane-1,2-diol (3-MBPD), phenylboronic acid (PBA) (derivatisation agent), acrylamide, acrylamide-d_3 (internal standard) and *N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) were obtained from Sigma-Aldrich, USA. 1,2-bis-palmitoyl-3-chloropropanediol-d_5 (PP-3-MCPD-d_5, internal standard) and glycidyl palmitate were obtained from LGC Standards (Teddington, United Kingdom) and Leco Dry (infusorial soil) was from Leco (USA). All reagents were at least of analytical purity.

Deionised water (18 MΩ) was produced by a Milli-Q system (Millipore; USA). A sodium chloride solution of 200 mg mL^{-1} (20%), saturated solution of sodium hydrogen carbonate and solution of sodium hydrogen carbonate (0.9%) were prepared in deionised water. Stock (1 mg mL^{-1}), intermediate (100 µg mL^{-1}) and working (2 µg mL^{-1}) standard solutions of each chloropropanol were prepared in 20% NaCl. Stock (1 mg mL^{-1}), intermediate (100 µg mL^{-1}) and working standard solutions of AA (1 µg mL^{-1}), and d_3-acrylamide (5 µg mL^{-1}) were prepared in acetonitrile. PP-3-MCPD-d_5 and glycidyl palmitate (both 5 µg mL^{-1}) were dissolved in ethyl acetate. PBA solution was prepared by dissolving 5 g PBA in 20 mL mixture of acetone and water (19:1, v/v).

Instrumentation

3-MCPD and AA analyses were performed using Varian IonTrap 4000 GC/MS (Varian, Inc., USA) with a CP-8410 auto-injector (Bruker, USA) and DB-5MS column (30 m x 0.25 mm x 0.25 µm; Agilent Technologies, USA). The injector temperature was set at 270 ºC for AA analysis and 180 ºC (3-MCPD determination), and an injection volume of 1.0 µL. Each injection was performed in triplicate. The GC oven was operated with the following temperature program: 3-MCPD analysis: 60 ºC (1.0 min) – 6 ºC min^{-1} – 190 ºC (1.0 min) – 30 ºC min^{-1} – 280 ºC (6.0 min); AA analysis: 50 ºC – 3 ºC min^{-1} – 100 ºC – 25 ºC min^{-1} – 250 ºC (5.0 min). The analyses were carried out with a solvent delay of 8.0 min. Helium 5.0 (Linde Gas, Poland) was used as the GC carrier gas at a flow rate of 1.0 mL min^{-1}. The emission current of the ionisation filament was set at 15 µA. The ion trap mass spectrometer was operated in the internal ionisation mode. The trap and the transfer line temperatures were set at 180 °C and 230 °C for both analyses. Analyses were conducted in the selected ion monitoring mode (SIM) based on the use of one quantitative ion of PBA derivatives of 3-MCPD and BSTFA derivatives of AA. Confirmation ions and retention times were also used to ensure the identification of the analytes (Table 1). Acquisition and processing data were performed using Varian Start Workstation software and NIST 2.0 library.

MS1 Minishaker (IKA, Germany) and MPW 350 R Centrifuge (MPW Med. Instruments, Poland) were used during sample preparation. Accublock™ (Lab-net, USA) with nitrogen 5.0 (Linde Gas, Poland) was accomplished to evaporate solvents and concentrate the extracts. Fat extraction was performed using TFE 2000 (LECO, USA).

Table 1. Parameters of GC-MS analysis of examined compounds

R_t [min]	Compound	Quantification ion	Confirmation ions
Chloropropanols*			
17.14	3-MCPD-d_5	150.1	93.0, 149.1, 201.0
17.23	3-MCPD	147.0	91.0, 146.1, 196.0
19.02	3-MBPD	147.0	91.0, 146.1, 241.9
Acrylamide**			
9.13	AA-d_3	132.1	132.2, 204.2, 220.1
9.17	AA	128.1	128.2, 129.2, 131.1

*analysed as PBA derivatives
**analysed as BSTFA derivatives
R_t – retention time; 3-MCPD-d_5 – 3-monochloropropane-1,2-diol-d_5; 3-MCPD – 3-monochloropropane-1,2-diol; 3-MBPD – 3-monobromopropane-1,2-diol; AA-d_3 – acrylamide-d_3, AA – acrylamide

Sample preparation

The samples analysed in this study involved 22 samples of snacks (potato chips, corn puffs, sticks, crackers, and peanuts), 13 samples of breakfast products (breakfast cereals, muesli and granola) and 25 samples of biscuits (sugar free, organic farming, gluten free, intended for children and classic). The selection of the products to analysis was based mostly on brand recognition among consumers, and the popularity of the products on Polish market.

Determination of AA and free 3-MCPD

The determination of free 3-MCPD and AA were conducted using modified QuEChERS approach [35, 37]. Briefly, 1 g of a thoroughly homogenized sample was weighted into a 50 mL polypropylene (PP) tube, spiked with 25 µL of 3-MCPD-d_5 and 40 µL of AA-d_3, then 5 mL of water and 10 mL of acetonitrile was added and the mixture was shaken vigorously for 1 min. Next, 1 g of NaCl and 4 g $MgSO_4$ were added; the sample was shaken vigorously for 1 min., and centrifuged for 15 min. at 9000 rpm. 8 mL of the supernatant was transferred into a 15 mL PP tube and the extracts were kept in freezer (-20 °C) for overnight to freeze out the fat. Thereafter the extract was immediately filtrated in a freezer by filter paper to remove precipitated co-extractives. 6 mL of filtrate were transferred to the 15 mL PP tube containing 0.15 g of PSA sorbent, 0.3 g of C_{18} sorbent and 0.9 g of $MgSO_4$. The tubes were shaken for 2 min. and centrifuged for 15 min at 10,000 rpm. Two portions of the extract (2 mL each) were transferred into a 4 mL screw cup vials and the extracts were evaporated under a stream of N_2 to dryness. Each sample was prepared in triplicate.

AA derivatisation: the residues were dissolved in 500 µL of acetonitrile and placed in a vial containing 50 µL of BSTFA. The mixture was heated for one hour at 65 °C. After cooling to ambient temperature, 200 µL of hexane were added and liquid-liquid extraction was performed for 1 min using a vortex. 100 µL of upper hexane layer were transferred to insert and 1 µL of extract was analyzed by GC-MS.

3-MCPD derivatisation: the residues were dissolved in 100 µL of 20% NaCl aqueous solution and 25 µL of PBA solution was added. The mixture was heated at 90 ºC for 20 min. After cooling 300 µL of hexane was added, the mixture was shaken vigorously and 200 µL of upper hexane layer was transferred into an insert in an autosampler vial. The extracts were then analysed by GC-MS.

Determination of 3-MCPDE and GE

3-MCPDE and GE were determined in fat extracted from the samples, which had been previously spiked with 270 µL of PP-3-MCPD-d_5. The extraction was performed using CO_2 in critical phase [33]. Extracted fat, collected in Eppendorf vials, was dissolved in two portions of tetrahydrofuran, 1 mL each, transferred to 7.5 mL glass tube, and 30 µL of NaBr solution in 5% H_2SO_4 was added to the sample, which was incubated at 50 ºC for 15 min. The reaction was stopped by adding 2 mL of a solution of sodium hydrogencarbonate 0.9%. Then, 2 mL of hexane were added to separate phases. After mixing the upper hexane phase was transferred to 4 mL glass vial and evaporated to dryness. The residue was diluted with 1 mL of tetrahydrofuran and 1.8 mL of sulphuric acid solution in methanol (1.8%, v/v) was added to the sample. The mixture was incubated at 40 ºC for 20 h. The reaction was stopped by addition of 0.5 mL saturated sodium hydrogen carbonate solution and the organic solvents were evaporated under a nitrogen stream. Fatty acid methyl esters were separated from the sample by addition of 2 mL of aqueous sodium chloride solution (20%, w/v) followed by liquid–liquid extraction with hexane (2 x 2 mL). The released 3-MCPD and 3-MBPD present in the extract were then derivatised as previously and analysed by GC-MS.

Standards preparation

A series of standard solutions in acetonitrile were prepared by dilution of the standard mixture solution within the range of 0.002 – 2 µg mL^{-1} (AA) and 0.004-1 µg mL^{-1} (3-MCPD and 3-MBPD) and derivatised according to the appropriate procedures. Each standard solution was prepared in triplicate.

Validation protocol

The results of method performance for the determination of free and esterified 3-MCPD in fat-rich cereal samples have been already published [33, 35], however, to confirm the usefulness of proposed procedures for glycidyl esters analysis as well as acrylamide determination in examined products, the method was in-house validated in terms of linearity, limit of detection (LOD), limit of quantification (LOQ), accuracy (recovery), and precision (repeatability and within-laboratory reproducibility). The parameters were evaluated by analysis of crackers (fat content equal to 19%) spiked with AA and AA-d_3 at the level of 200 and 1000 µg kg^{-1} in the case of AA analysis, and 100 µg kg^{-1} and 500 µg kg^{-1} in the case of GE (expressed as glycidol moiety, according to EFSA [13]). Six replicates were prepared for each concentration level. Each sample was subjected to whole analytical procedure including fat extraction and transesterification (in case of GE), clean-up and derivatisation steps.

For AA obtained results showed good linearity ($r^2 > 0.996$) in the range 2-2000 µg kg^{-1}. LOD and LOQ, calculated based on the standard deviation of the response (S_y) of the curve and the slope of the calibration curve (S), according to the formula: LOD = 3.3(S_y/S) and LOQ = 10(S_y/S), were 3 µg kg^{-1} and 9 µg kg^{-1} respectively. The results of analyte recoveries (86.4% and 90.5%) for each spiking level with the RSD (relative standard deviation) lower than 6.1% (repeatability) and below 9% (within-laboratory reproducibility) confirmed the possibility of the use of modified QuEChERS concept for the determination of AA in analysed products.

The results for GE validation showed the linearity ($r^2 > 0.998$) in the range 0.006-1.43 mg kg^{-1} expressed as

glycidol moiety. LOD and LOQ, calculated as for AA, were equal to 3.1 μg kg^{-1} and 9.4 μg kg^{-1}, respectively. Recovery ratios for both spiking levels were 79% and 82% with RSD not higher than 6.0 (repeatability) and 9.3% (within-laboratory reproducibility).

RESULTS AND DISCUSSION

3-MCPD CONTENT

The level of free and bound 3-MCPD

The results of the content of free 3-MCPD (Table 2) were within the values of 9.3-63.3 μg kg^{-1}. Among the group of analysed products, the highest mean content of free 3-MCPD was noted for muesli samples (33.3 μg kg^{-1}), while the lowest for baby biscuits (11.7 μg kg^{-1}). Analysing the results obtained for the individual products, the highest content of free 3-MCPD was observed in the sample 4C (gluten free salty sticks, 63.3 μg kg^{-1}). In the samples of 1C (breadsticks), 1E and 2E (peanuts), 3F (granola with fruits), 5H (rye flakes), 1K (gluten free biscuits), and 1M (baby biscuits) the level of free 3-MCPD was below the limit of quantification (9.3 μg kg^{-1}), while in the sample of classic corn puffs (3B), free 3-MCPD was not detected at all (the level below the limit of detection, 3.1 μg kg^{-1}).

The levels of bound 3-MCPD were substantially higher (from 9.3 μg kg^{-1} to 1500 μg kg^{-1}, expressed as free 3-MCPD, according to EFSA 2016). The highest average content of 3-MCPD esters in the analysed groups of products was observed for biscuits without sugar added (599 μg kg^{-1}), whereas the lowest for breakfast cereals (50.2 μg kg^{-1}). Taking into account the individual samples, the highest 3-MCPDE content was found in the sample 1I (biscuits with no sucrose added, 1500 μg kg^{-1}) and lowest for sample 5A (tortilla chips, below the limit of quantification, 9.3 μg kg^{-1}). The extremely high level of 3-MCPDE in the sample 1I can be explained by the presence of fructose, added as a sugar replacer. Reducing sugars upon heat treatment decompose with the generation of organic acids that lowers pH, which is a valuable factor contributing to formation of 3-MCPD [34].

The presence of glycidyl esters was reported only in four samples: 5A (tortilla chips), 2C (breadsticks for children), 2E (roasted and salted peanuts) and 2F (granola with nuts). The latter product contained the highest level of glycidyl esters (28.8 μg kg^{-1}, expressed as glycidol moiety).

The level of free and bound 3-MCPD in the examined products were also analysed regarding the content of fat, salt and sugar, present in the samples. No statistically significant correlation was found between the content of free 3-MCPD and the sample ingredients. In contrary, for 3-MCPD esters it has been revealed that their levels were correlated with the fat content (correlation coefficient equal to 0.62). With a view to this correlation, we also investigated the origin of the fat present in the samples. In the products contained palm oil the 3-MCPD ester level was higher than 400 μg kg^{-1}, even if the total fat content in the sample was not extremely high (below 18%; e.g. samples 1F, 3F, 3G, 5I, 3K, 4M, 2N). For comparison, in the samples with rapeseed oil only, the 3-MCPDE level was below 200 μg kg^{-1}, although the overall fat content was high (more than 20%; e.g. samples 1B, 2B, 3B). Additionally, products containing butter (1J, 4J, 2M) were characterised by significantly lower level of 3-MCPD esters (<88 μg kg^{-1}). This confirms that the presence of palm oil in food products is largely responsible for the 3-MCPD esters formation.

Comparison with other studies

The results received in this study were compared to the data obtained in other surveys. The results of free 3-MCPD level determined in the investigated samples are generally in a good agreement with those from other studies.

The content of free 3-MCPD in potato chips reported by *Chung* et al. [5] ranged from 6 μg kg^{-1} to 11 μg kg^{-1}, which was similar to the results obtained by *Gawarska* et al. [16] and *Svejkovska* et al. [39] (4.7-9.5 μg kg^{-1}, and 15.4 μg kg^{-1}, respectively). For corn puffs, the data were previously provided only by *Gawarska* et al. [16] who revealed the 3-MCPD level of 2.8-8.3 μg kg^{-1}. The 3-MCPD content in crackers was at a similar level in the work performed by *Arisseto* et al. [2] (20-30 μg kg^{-1}), *Chung* et al. [5] (17-22 μg kg^{-1}), *Crews* et al. [10] (14 μg kg^{-1}), *Starski* [36] (0-55 μg kg^{-1}), *Svejkovska* et al. [39] (10.7 μg kg^{-1}) and *Vicente* et al. [40] (14-32 μg kg^{-1}).

As far, breakfast cereals have been analyzed several times giving results much more diversified; *Arisseto* et al. [2], *Leon* et al. [23] and *Vicente* et al. [40] demonstrated the 3-MCPD content in the ranges 19-113 μg kg^{-1}, 0.22-143 μg kg^{-1}, 0-107 μg kg^{-1}, respectively, while in the report provided by *Chung* et al. [4] the content was significantly lower (9-23 μg kg^{-1}), but much more comparable to our results. Granola samples were investigated only in the study conducted by *Vicente* et al. [40], providing results noticeably higher (0-156 μg kg^{-1}) than the results presented in this work.

In case of biscuits, *Leon* et al. [23] reported free 3-MCPD at the ranges of 0.22–103 μg kg^{-1}, while the free 3-MCPD contents in the samples of biscuits from Polish market [16, 36] were lower and ranged from 13 to 58.8 μg kg^{-1}. In a study performed by *Kusters* et al. [22] the biscuits present in retail market reached the free 3-MCPD level in the range of 8.5-40.5 μg kg^{-1}. All these results are in good accordance with the data obtained in this research.

Table 2. The level of acrylamide, free 3-MCPD, 3-MCPD esters, and glycidyl esters detected in analysed samples (mean ± SD)

	Contaminants' content [μg kg^{-1}]				Sample ingredients			
	Acrylamide	Free 3-MCPD	3-MCPD esters[a]	Glycidyl esters[b]	Fat [%]	NaCl[c] [%]	Sugar[c] [%]	Fat origin
Potato chips (n=5)								
1A	465 ± 43	18.9 ± 0.9	436 ± 21	< 3.1	29.9 ± 1.1	1.7	2.1	palm oil, sunflower oil
2A	764 ± 62	14.4 ± 1.1	604 ± 16	< 3.1	32.6 ± 1.5	1.9	0.9	palm oil
3A	946 ± 23	11.2 ± 1.9	522 ± 23	< 3.1	29.5 ± 1.5	1.0	1.0	vegetable oil
4A	797 ± 37	18.8 ± 0.5	595 ± 11	< 3.1	20.1 ± 1.1	1.9	2.2	rapeseed oil
5A[d]	321 ± 15	12.2 ± 0.9	< 9.3	9.5 ± 0.5	23.1 ± 1.0	0.7	1.2	palm oil
Corn puffs (n=4)								
1B	227 ± 19	16.7 ± 0.8	261 ± 0	< 3.1	22.8 ± 0.5	1.8	4.3	rapeseed oil
2B	308 ± 20	11.3 ± 1.6	267 ± 6	< 3.1	20.2 ± 0.5	1.6	4.6	rapeseed oil
3B	< 3.1	24.0 ± 2.3	207 ± 8	< 3.1	20.7 ± 0.8	1.6	5.1	rapeseed oil
4B	884 ± 42	11.2 ± 0.6	45 ± 2	< 3.1	13.8 ± 0.8	2.0	2.0	sunflower oil
Sticks (n=5)								
1C	235 ± 29	< 9.3	163 ± 10	< 3.1	8.6 ± 0.1	2.0	2.6	olive oil
2C	681 ± 58	43.2 ± 0.6	257 ± 12	11.6 ± 0.6	4.9 ± 0.1	2.3	6.4	palm oil, coconut oil
3C	825 ± 55	16.6 ± 0.3	156 ± 7	< 3.1	9.5 ± 0.1	1.4	2.2	rapeseed oil
4C	998 ± 16	63.3 ± 2.6	25 ± 1	< 3.1	5.9 ± 0.1	3.3	0.2	rapeseed oil
5C	832 ± 52	31.4 ± 3.8	36 ± 1	< 3.1	1.5 ± 0.1	4.8	3.4	palm oil
Crackers (n=5)								
1D	345 ± 23	35.5 ± 2.2	592 ± 24	< 3.1	21.8 ± 1.0	2.3	5.7	palm oil, coconut oil
2D	538 ± 35	11.1 ± 1.8	748 ± 28	< 3.1	19.1 ± 0.9	1.5	8.5	palm oil, coconut oil
3D	887 ± 81	16.4 ± 2.1	434 ± 20	< 3.1	14.4 ± 0.7	1.4	7.6	palm oil, rapeseed oil
4D	789 ± 34	29.0 ± 3.5	112 ± 5	< 3.1	14.3 ± 0.7	5.0	5.9	palm oil
5D	853 ± 52	< 3.1	361 ± 16	< 3.1	14.9 ± 0.6	3.0	1.0	palm oil
Peanuts (n=3)								
1E	345 ± 22	< 9.3	251 ± 3	< 3.1	26.9 ± 0.5	3.3	5.2	palm oil, rapeseed oil
2E	290 ± 10	< 9.3	422 ± 13	< 9.4	44.9 ± 0.8	0.8	7.8	palm oil, sunflower oil
3E	577 ± 41	< 9.3	753 ± 31	< 3.1	29.5 ± 0.2	2.3	7.3	vegetable oil
Granola (n=3)								
1F	1003 ± 56	12.5 ± 0.6	406 ± 14	< 3.1	11.8 ± 0.6	0.3	22.0	palm oil
2F	950 ± 116	27.1 ± 1.4	206 ± 3	28.8 ± 1.5	17.3 ± 0.5	0.5	19.0	palm oil
3F	612 ± 30	< 9.3	513 ± 26	< 3.1	11.2 ± 0.5	0.5	18.0	palm oil
Muesli (n=3)								
1G	265 ± 24	46.6 ± 2.4	86 ± 5	< 3.1	8.9 ± 0.2	0.9	15.6	rapeseed oil, palm oil
2G	344 ± 33	19.6 ± 2.0	390 ± 25	< 3.1	16.1 ± 0.3	0.4	18.1	rapeseed oil, palm oil, cocoa fat, milk fat
3G	435 ± 50	33.7 ± 3.5	585 ± 30	< 3.1	15.8 ± 0.1	0.3	16.3	rapeseed oil, palm oil
Flakes (n=3)								
1H	370 ± 20	16.4 ± 0.8	74 ± 4	< 3.1	2.7 ± 0.1	0.7	22.6	
2H	477 ± 27	25.0 ± 0.5	39 ± 2	< 3.1	1.1 ± 0.1	1.0	15.0	
3H	512 ± 31	20.8 ± 0.6	55 ± 3	< 3.1	0.9 ± 0.1	2.1	6.8	
4H	269 ± 12	18.8 ± 3.1	78 ± 3	< 3.1	1.4 ± 0.1	1.2	4.8	
5H	816 ± 49	< 9.3	26 ± 1	< 3.1	1.3 ± 0.1	1.1	8.6	
6H	565 ± 65	13.3 ± 0.4	42 ± 3	< 3.1	1.1 ± 0.1	0.8	1.4	
7H	733 ± 22	26.8 ± 1.4	38 ± 3	< 3.1	0.5 ± 0.1	1.9	9.1	
Sugar free biscuits (n=5)								
1I	504 ± 32	33.1 ± 2.0	1501 ± 70	< 3.1	28.3 ± 0.1	0.1	17.6	palm oil
2I	685 ± 11	13.9 ± 0.9	133 ± 6	< 3.1	12.8 ± 0.4	0.8	2.5	sunflower oil
3I	1188 ± 60	38.1 ± 2.5	245 ± 13	< 3.1	22.3 ± 0.1	0.7	9.0	palm oil, rapeseed oil

	Contaminants' content [μg kg^{-1}]				Sample ingredients			
	Acrylamide	Free 3-MCPD	3-MCPD esters[a]	Glycidyl esters[b]	Fat [%]	NaCl[c] [%]	Sugar[c] [%]	Fat origin
4I	933 ± 47	9.8 ± 0.2	612 ± 21	< 3.1	22.4 ± 0.1	0.4	0.5	palm oil, rapeseed oil
5I	1151 ± 24	10.3 ± 0.1	505 ± 28	< 3.1	18.7 ± 0.1	0.5	0.5	palm oil
Organic farming biscuits (n=5)								
1J	1352 ± 3	15.0 ± 0.3	72 ± 2	< 3.1	14.3 ± 0.3	0.2	20.3	butter
2J	526 ± 21	13.3 ± 0.4	59 ± 2	< 3.1	11.8 ± 0.8	1.0	25.0	butter
3J	927 ± 23	17.0 ± 1.2	495 ± 15	< 3.1	12.2 ± 0.2	0.5	16.6	coconut oil
4J	914 ± 56	23.0 ± 1.1	78 ± 3	< 3.1	11.2 ± 0.3	1.0	25.0	butter
5J	847 ± 46	19.8 ± 1.1	481 ± 20	< 3.1	24.4 ± 0.4	0.1	19.0	palm oil
Gluten free biscuits (n=4)								
1K	427 ± 22	< 9.3	460 ± 21	< 3.1	16.3 ± 1.0	0.2	19.0	vegetable oil
2K	590 ± 45	11.3 ± 0.5	183 ± 9	< 3.1	14.2 ± 0.2	0.3	9.5	palm oil
3K	787 ± 12	11.7 ± 0.2	571 ± 21	< 3.1	12.6 ± 0.4	0.6	19.0	palm oil
4K	615 ± 38	20.2 ± 1.0	91 ± 3	< 3.1	11.6 ± 0.1	0.5	13.0	palm oil
Baby biscuits (n=6)								
1M	251 ± 22	< 9.3	363 ± 15	< 3.1	9.1 ± 0.6	0.6	24.6	palm oil
2M	437 ± 10	16.6 ± 1.3	88 ± 2	< 3.1	10.8 ± 0.1	0.4	23.2	butter
3M	858 ± 38	11.7 ± 0.4	424 ± 11	< 3.1	12.0 ± 0.2	0.1	22.6	palm oil, sunflower oil
4M	758 ± 14	10.1 ± 0.7	443 ± 20	< 3.1	10.6 ± 0.7	0.7	17.0	palm oil
5M	195 ± 20	10.1 ± 0.6	246 ± 18	< 3.1	10.8 ± 0.1	0.7	17.0	palm oil
6M	201 ± 56	14.8 ± 0.5	137 ± 4	< 3.1	10.7 ± 1.1	0.4	22.0	coconut oil
Classic biscuits (n=5)								
1N	454 ± 36	15.3 ± 0.7	380 ± 20	< 3.1	10.9 ± 0.2	0.9	18.0	palm oil
2N	273 ± 20	21.0 ± 1.0	588 ± 19	< 3.1	12.0 ± 0.1	1.1	19.0	palm oil
3N	443 ± 42	24.9 ± 1.2	363 ± 12	< 3.1	11.3 ± 0.5	1.5	20.0	palm oil
4N	373 ± 10	21.4 ± 1.0	749 ± 18	< 3.1	12.5 ± 0.2	0.7	22.6	palm oil, soybean oil, sunflower oil, cotton oil
5N	544 ± 41	18.1 ± 1.3	870 ± 14	< 3.1	20.7 ± 0.1	1.5	16.8	palm oil

[a]expressed as 3-free 3-MCPD; [b]expressed as glycidol moiety; [c]levels declared by manufacturers on the label;
[d]tortilla chips;
n – number of samplers
< 3.1 – below the limit of detection (LOD) for GE;
< 9.4 – below the limit of quantification (LOQ) for GE;
< 3.1 – below the limit of detection (LOD) for 3-MCPD;
< 9.3 – below the limit of quantification (LOQ) for 3-MCPD

For 3-MCPD esters, the results were comparable as well. In the studies reported by *Arisseto* et al. [1] and *Chung* et al. [4] the 3-MCPDE content in potato chips varied from 110 μg kg^{-1} to 810 μg kg^{-1} and 22-660 μg kg^{-1}, respectively, while the data presented by *Svejkovska* et al. [39] were extremely high – the mean content of 3-MCPD esters was equal to 6100 μg kg^{-1}. The ester content in crackers was found to be at the level of 200-850 μg kg^{-1} in the work carried out by *Chung* et al. [4], which is in line with our results. However, *Svejkovska* et al. [39] observed remarkably lower content of 3-MCPDE (140 μg kg^{-1}). The report presented by EFSA [13] revealed the 3-MCPDE content at the level of 123-137 μg kg^{-1} for snacks in general, and 210-223 μg kg^{-1} for potato chips. This is two times lower than the results obtained in this study.

For breakfast products, the level of bound 3-MCPD were examined only by *Chung* et al. [4], who reported considerably low values (11-43 μg kg^{-1}). Referring the obtained results to the data included in EFSA report [13] it has been observed the same level of magnitude only in the case of flakes (19-33 μg kg^{-1}) in contrary to the results for muesli, for which EFSA report demonstrated much lower values (88-102 μg kg^{-1}) than those provided by this study.

In case of biscuits, *Kusters* et al. [22] disclosed the 3-MCPDE level in the range of 330-1520 μg kg^{-1}. Results of a study conducted in Hong Kong [4] showed that the level of 3-MCPDE in biscuit samples varied from 100 to 1140 μg kg^{-1}. These values are similar to those from this work. On the contrary, data obtained from the surveys carried out in European countries in 2009-2015 [13] provided lower levels of these contaminants (194-206 μg kg^{-1} for total 3-MCPD), which is lower than the results received in this survey.

The data of GE occurrence in similar food commodities were presented only as far by EFSA [13], giving the GE levels in the range 12-59 μg kg^{-1} for snacks in general and 16-85 μg kg^{-1} for breakfast products. Regarding these values, our results are comparable in the case of samples of granola (2F) and slightly lower for sample 5A (tortilla chips).

Risk assessment

The risk assessment resulted from the exposure to total MCPD was calculated based on an average product consumption and the level of the compounds in the products. The assessment was performed for all population groups, up to 75 years old (infants, toddlers, other children, adolescents, adults, elderly, very elderly), using data available from the EFSA Comprehensive Food Consumption Database [12] and compared with Tolerable Daily Intake, established recently by EFSA at 0.8 μg kg^{-1} bodyweight [13].

The results (Table 3) showed that the highest average daily intake was found for biscuits in "other children" group, while the lowest for breakfast products ("elderly" and "very elderly"). In the group of toddlers TDI was exceeded mostly for the samples of snacks: potato chips (except of sample 5A), crackers (1D, 2D, 3D), peanuts (3E) but also for some biscuits (3K, 2N, 4N, 5N). Although most of these products are not usually consumed by toddlers, the problem is the occurrence of 3-MCPD esters in the sample 2D, which is intended for children, as it was declared by manufacturer. Within the group of other children, the exceedance of TDI was observed in the same snack samples as for toddlers, but additionally TDI was higher than 100% in case of the consumption of muesli (2G, 3G), and most of the biscuits samples (4I, 5I, 3J, 5J, 1K, 3M, 4M, and all classic biscuits). Particular attention should be paid to the fact, that the samples 3M and 4M, according to manufacturers, are produced and intended for children. For adolescents TDI was exceeded for two samples of potato chips (2A and 4A), crackers (1D, 2D), nuts (3E) and biscuits (1I, 4I 2N, 4N and 5N). For other population groups, TDI higher than 100 % could be observed only in the case of the consumption of the sample 1I, that showed the highest content of 3-MCPD esters.

Table 3. Daily intakes of total 3-MCPD and acrylamide in different population groups

Daily intake (μg kg^{-1} bodyweight)						
Food products	Toddlers (12-35 months); 13 kg*	Other children (1-9 years); 24 kg	Adolescents (10-17 years); 47 kg	Adults (18-64 years); 70 kg	Elderly (65-74 years); 73 kg	Very elderly (75 years and older); 66 kg
3-MCPD						
Snacks	0.05-1.63 (0.72)**	0.05-1.61 (0.68)	0.03-1.23 (0.44)	0.01-0.66 (0.22)	0-0.52 (0.16)	0-0.57 (0.14)
Breakfast products	0-0.24 (0.09)	0.04-1.31 (0.37)	0.03-0.56 (0.19)	0.02-0.37 (0.13)	0-0.06 (0.02)	0-0.05 (0.02)
Biscuits	0.11-2.36 (0.65)	0.15-3.21 (0.88)	0.10-2.09 (0.58)	0.05-1.08 (0.30)	0.05-1.07 (0.30)	0.05-1.15 (0.32)
Acrylamide						
Snacks	0-2.27 (1.13)	0-2.46 (1.10)	0-1.33 (0.66)	0-0.63 (0.34)	0-0.6 (0.27)	0-0.67 (0.26)
Breakfast products	0.53-2.06 (1.29)	0.29-1.49 (0.82)	0.20-0.91 (0.49)	0.15-0.61 (0.37)	0.16-0.52 (0.33)	0.14-0.41 (0.27)
Biscuits	0.3-2.08 (1.00)	0.41-2.83 (1.36)	0.27-1.84 (0.89)	0.14-0.95 (0.46)	0.14-0.95 (0.45)	0.15-1.02 (0.49)

* average body weight

** min-max (mean)

ACRYLAMIDE CONTENT

The level of AA in analysed samples

The content of acrylamide detected in analysed samples varied from 195 to 1352 μg kg^{-1}. The highest content was observed for the samples of organic biscuits (913 μg kg^{-1}), while the lowest content was found in muesli products (348 μg kg^{-1}). Considering the individual products, the highest AA content was observed in the sample 1J (organic biscuits, 1352 μg kg^{-1}), while in the sample 3B (classic corn puffs), the level of AA was below the limit of detection (3 μg kg^{-1}).

Comparison with other studies

Comparing the results obtained with the indicative data from EU Regulation [7] (Table 4), it was found

that the AA content was higher for one sample of corn puffs (4B), almost all sticks and crackers (except the sample 1C and 1D), one sample of peanuts (3E), all granola and flake samples, muesli (3G), all samples of sugar free biscuits and organic biscuits, most gluten free biscuits and baby biscuits samples (with the exception for 1K and 5M), and, finally, for only one sample of classic biscuits (5N).

Table 4. Indicative acrylamide values based on the EFSA data from 2007-2012 [7]

Foodstuffs	Indicative value [μg kg^{-1}]
Potato crisps from fresh potatoes and potato dough	1000
Breakfast cereals: bran products and whole grain cereals wheat and rye based products maize, oat, spelt, barley and rice based products	 400 300 200
Biscuits and wafers	500
Crackers with the exception of potato based crackers Products similar to the other products in this category	500 500
Biscuits and rusks for infants and young children	200

Number of studies providing results for AA in different food commodities have been published in the literature since AA was first detected in food. The data from these surveys showed that the level of acrylamide was significantly differentiated in each group of analysed products. For potato chips, the highest AA level (up to 3647 μg kg^{-1}) was observed by *Mojska* et al. [26], whereas the lowest in the work conducted by *Razia* et al. [31] (29 μg kg^{-1}). The level of AA in corn puffs was ranged from 59 μg kg^{-1} [28] to 3200 μg kg^{-1} [6]. Sticks, so far, were analysed by *Mojska* et al. [26, 27], and *Russo* et al. [32], showing the AA at the level of 62-879 μg kg^{-1} and 74-85 μg kg^{-1}, respectively. For crackers the AA levels ranged from 15 μg kg^{-1} [24] to 3200 μg kg^{-1} [30]. Among breakfast products, the AA highest content was detected in a work realised by *Pacetti* et al. [29] (up to 2288 μg kg^{-1}), and the lowest in the study carried out by *Mojska* et al. [26] (AA level starting from 11 μg kg^{-1}). For biscuits, the AA contents varied from 10 μg kg^{-1} [24, 28] to 3200 μg kg^{-1} [30]. Among them, baby biscuits were analysed in five studies, giving the results from 25 μg kg^{-1} [3, 11] to 1217 μg kg^{-1} [6]. In principle, our results are comparable to the data presented above and place in the AA content ranges reported by other authors.

Risk assessment

Since any level of exposure to a genotoxic substance could potentially damage DNA and lead to cancer, EFSA's scientists conclude that they cannot set a tolerable daily intake (TDI) of acrylamide in food [14]. However, to assess human exposure on acrylamide a daily intake of AA was calculated based on an average consumption of examined food products and the AA level in investigated samples. The calculation was performed for the same population groups as for 3-MCPD.

In general, dietary exposure decreased with age for all analysed groups of food commodities (Table 3). Toddlers and other children showed the highest level of exposure (1.13 μg kg^{-1} bw (body weight)/day for snacks, 1.27 μg kg^{-1} bw/day for breakfast cereals and 1.36 μg kg^{-1} bw/day for biscuits), which could be attributed mainly to low body weight of toddlers. On the contrary, the lowest average daily intake of acrylamide was noted for the very elderly group (0.26 μg kg^{-1} bw/day snacks, 0.27 μg kg^{-1} bw/day breakfast products and 0.45 μg kg^{-1} bw/day for biscuits). Comparing the results of daily intake within the food products, the highest acrylamide intake was found for breakfast products (toddlers, 1.29 μg kg^{-1} bw/day), while for the rest of population groups, the daily intake showed the highest level in the case of consumption of biscuits (0.45-1.36 μg kg^{-1} bw/day, from elderly to other children, respectively). The results are significantly higher (3-9 times) than the data obtained by *Zając* et al. [42], and mainly arise from the high level of AA observed in our survey.

CONCLUSIONS

1. Based on the presented findings, it can be concluded that the consumption of popular snacks such as potato chips, crackers and biscuits may result in risk to human health as the effect of a high content of acrylamide or 3-MCPD in the products.
2. Another important outcome is a high level of these contaminants detected in some type of breakfast products, such as muesli or granola. As far, these commodities have been associated with a healthy lifestyle, but, however, the results showed that regular consumption of these products also might contribute to harmful effects to human body.
3. Finally, it should be underlined that some of the products targeted for children (biscuits, sticks, and crackers) also contained high amount of acrylamide and 3-MCPD. Therefore, consumption of these products should be restricted, especially in younger population groups.

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Conflict of interest
The authors declare no conflict of interest.

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