Polychlorinated naphthalene concentrations and profiles in cheese and butter, and comparisons with polychlorinated dibenzo-\(p\)-dioxin, polychlorinated dibenzofuran and polychlorinated biphenyl concentrations

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Polychlorinated naphthalenes (PCNs) are candidates for inclusion in the Stockholm Convention on persistent organic pollutants. PCNs are structurally and toxicologically similar to 2,3,7,8-tetrachlorodibenzo-\(p\)-dioxin (2,3,7,8-TCDD) and its analogues. Intake in food is considered to be an important human exposure pathway for PCNs. In this preliminary study, cheese and butter samples were analysed for PCNs, polychlorinated dibenzo-\(p\)-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) using an isotope dilution gas chromatography high-resolution mass spectrometry method. The aim of this study was to evaluate the PCN concentrations in the cheese and butter samples and to compare them with the PCDD, PCDF and PCB concentrations. The PCN concentrations were 5.6–103 pg g\(^{-1}\) of wet weight in the seven cheese samples tested and 5.0–199 pg g\(^{-1}\) of wet weight in the seven butter samples tested. The mass concentrations of lower chlorinated congeners were greater than those of the higher chlorinated congeners. Congeners of CN45/36, CN27/30 and CN33/34/37 were much more abundant than other congeners found in tetrachlorinated PCNs. Congeners of CN51, CN66/67 and CN73 were determined to be the predominant congeners in penta-, hexa- and heptachlorinated homologs, respectively. The PCNs contributed around 5% of the total PCN, PCDD, PCDF and PCB toxic equivalence (TEQ) values. CN73 was found to be the dominant PCN congener and contributed more than 40% to the PCN TEQ value. Congeners CN66/67, CN69 and CN63 were also found at relatively high levels. The PCB congener CB118 was the predominant congener (by mass-based concentration) of the 12 dioxin-like PCBs (dl-PCBs). The PCBs contributed 53.8% of the total TEQ, and congener CB126 contributed more than any other compound that was analysed to the total TEQ. The PCDDs and PCDFs contributed 11.6% and 29.7% of the total TEQ values, respectively.

**Keywords:** polychlorinated naphthalenes; persistent organic pollutants; dairy products; congener profiles

1. Introduction

Polychlorinated naphthalenes (PCNs) are a group of chemicals based on the naphthalene ring system with chlorine substitutions. PCNs were mass-produced industrial chemicals until the 1980s, and they were commonly used in electrical equipment [1]. PCNs, like their brominated and brominated/chlorinated counterparts (PBNs, PB/CNs) as well as brominated and mixed brominated/chlorinated dioxins, furans and biphenyls, could also be unintentionally formed and released from industrial activities such as waste incinerations and metal smelting, and are widely

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found in the environment [2–6]. PCNs are toxic to and persistent in biota, and are bioaccumulative [7]. PCNs have been detected in air, water, soil, sediment and biota (including human tissues) from many locations [8–10]. Pan et al. [11] found total PCN concentrations of 122.8 and 224.1 pg g⁻¹ lipid weight in yak muscle and fatty tissue, respectively. PCNs have also been found in human serum [12], adipose tissue [13] and milk [14]. Furthermore, an increasing number of studies show that PCNs are widespread persistent organic pollutants (POPs) found globally, including in polar areas [9]. PCN congeners can have dioxin-like toxic effects because they have similar planar configurations to polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs and PCDFs, respectively, together called PCDD/Fs) and some polychlorinated biphenyls (PCBs) [15]. The toxicities of individual PCN congeners relative to 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), called relative potency factors (RPFs), have been evaluated [15,16]. The RPFs for PCNs have recently been re-evaluated and updated [17]. Park et al. [12] found that PCNs contributed 26.8% of the total PCDD, PCDF, PCB and PCN toxic equivalence (TEQ) values (relative to 2,3,7,8-TCDD) in human serum samples from Korea. PCNs have, therefore, recently been attracting increasing amounts of attention.

The 12 POPs that were initially covered by the Stockholm Convention included the PCDDs, PCDFs and PCBs. The primary route of human exposure to PCDDs, PCDFs, PCBs, PCNs and related brominated and mixed brominated/chlorinated analogues is the consumption of food [10]. Cheese and butter are typical dairy products. PCDD, PCDF and PCB concentrations in foodstuffs have been determined in many studies [18]. However, data about PCN concentrations in food and human samples are simply inadequate [7,10]. In the preliminary study described here, we performed congener-specific PCN analyses on cheese and butter samples using isotope dilution high-resolution gas chromatography high-resolution mass spectrometry (HRGC/HRMS). The levels of PCNs were reported and compared with that of PCDDs, PCDFs and PCBs, which are helpful to understand the relative importance of these four POPs in cheese and butter samples.

2. Experimental

2.1 Chemicals and reagents

Pesticide grade hexane, acetone and dichloromethane were purchased from J.T. Baker (Phillipsburg, NJ, USA). Anhydrous Na₂SO₄ (Tianjin Jinke Institute of Fine Chemicals, Tianjin, China) and alkaline Al₂O₃ (100–200 mesh; Sinopharm Chemical Reagent, Shanghai, China) were activated at 660°C for 6.5 h before use. Silica gel (100–200 mesh; Qingdao Haiyang Chemical Company, Qingdao, China) was cleaned with anhydrous methanol and dichloromethane, dried at 35°C for 12 h, then activated at 550°C for 6.5 h before use. Sulphuric acid, NaOH and AgNO₃ were purchased from Sinopharm Chemical Reagent (Shanghai, China) and used to prepare the absorption column. ¹³C-labelled PCN standards (ECN-5102 (containing the ¹³C₁₀-labelled tetra–octa PCN congeners CN27, 42, 52, 67, 73 and 75) and ECN-5260 (containing CN64)) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA) and ¹³C-labelled PCDD and PCDF standards (EPA-1613LCS and EPA-1613IS) and PCB standards (68B-LCS and 68B-IS) were purchased from Wellington Laboratories (Guelph, ON, Canada). The standard solutions were diluted to 100 ng mL⁻¹ or 200 ng mL⁻¹ in nonane before use.

2.2 Sample extraction and clean-up

Fourteen cheese and butter samples (each of different brands) were purchased from supermarkets in 2013, and subsequently stored at 4°C until they were analysed. Information on the
samples is presented in Table 1. A 10 g cheese sample was dried using anhydrous sodium sulphate and ground into a dry free-flowing powder. Each homogenised sample was mixed with diatomaceous earth and spiked with 10 µL of 100 ng mL\(^{-1}\) \(^{13}\)C\(^{12}\)-labelled PCDD/F internal standards (EPA-1613LCS), 10 µL of 100 ng mL\(^{-1}\) \(^{13}\)C\(^{12}\)-labelled PCB internal standards (68B-LCS) and 10 µL of 100 ng mL\(^{-1}\) \(^{13}\)C\(^{10}\)-labelled PCN internal standards (ECN-5102). Each sample was then transferred to a stainless steel vessel and extracted with a 1:1 (v:v) mixture of acetone and hexane in an accelerated solvent extraction system (ASE 350; Thermo Fisher Scientific, Waltham, MA, USA). The extraction cells were filled with solvent, pressurised to 1500 psi and then heated to 125°C for 6 min. The extraction cells were then held at this pressure and temperature for 10 min. The extraction, rinse and purge steps were performed three times for each sample, and the extracts were combined. Each butter sample was heated to 60°C and filtered through glass wool, then 10 g of the filtered sample was dissolved in hexane and spiked with internal standards as described for the cheese samples.

Each sample extract was subjected to a series of purification steps, including purification through a sulphuric acid-treated silica bed, a sulphuric acid-treated silica column, a multilayer silica column and a basic alumina column. Sulphuric acid-treated silica (44%, w/w) and hexane were added to the extract, and the resulting mixture was stirred, then filtered through anhydrous sodium sulphate and rinsed with hexane. These steps were repeated until the solution became colourless and transparent. The filtrate was then collected and concentrated under vacuum on a rotary evaporator. The sulphuric acid-treated silica column was packed from bottom to top with 1 g of activated silica gel, 8 g of acidic silica gel (22%, w/w), 1 g of activated silica gel and 2 cm of anhydrous sodium sulphate. The column was preconditioned with 70 mL of hexane, and the concentrated extract was then loaded onto the top of the column and eluted with 90 mL of hexane. The multilayer silica column was packed from bottom to top with 1 g of activated silica gel, 1.5 g of AgNO\(_3\) silica gel (10%, w/w), 1 g of activated silica gel, 3 g of basic silica gel (33%, w/w), 1 g of activated silica gel, 8 g of acidic silica gel (44%, w/w), 1 g of activated silica gel and 2 cm of anhydrous sodium sulphate. The column was preconditioned with 70 mL of hexane and eluted with 90 mL of hexane. The basic alumina column was used to separate the PCDD/Fs from the PCBs and PCNs. The sample was applied to the basic alumina column, which consisted of 8 g of basic alumina topped with 2 cm of anhydrous sodium sulphate, and eluted with 100 mL of a 95:5 (v/v) mixture of hexane and dichloromethane to elute the PCBs and PCNs. The column was subsequently eluted with 50 mL of a 1:1 (v/v) mixture of hexane

| Samples | Region of production    | Type of sample          | Fat content (%) |
|---------|-------------------------|-------------------------|-----------------|
| C1      | Inner Mongolia, China   | Cheese                  | 8.00            |
| C2      | Tibet, China            | Zangnaiguo              | 25.7            |
| C3      | America                 | Mozzarella cheese (soft cheese) | 21.0 |
| C4      | France                  | Brie cheese (soft cheese) | 22.5 |
| C5      | New Zealand             | Gouda cheese (semi-hard cheese) | 30.0 |
| C6      | Ireland                 | Mild cheddar cheese (hard cheese) | 32.0 |
| C7      | Australia               | Cheddar cheese (hard cheese) | 33.7 |
| B1      | Inner Mongolia, China   | Butter                  | 99.8            |
| B2      | Tibet, China            | Butter                  | 99.8            |
| B3      | America                 | Unsalted butter         | 82.3            |
| B4      | France                  | Unsalted butter         | 82.0            |
| B5      | New Zealand             | Unsalted butter         | 83.2            |
| B6      | Ireland                 | Softer butter           | 80.0            |
| B7      | Australia               | Butter                  | 81.0            |
and dichloromethane to elute the PCDD/Fs. Both fractions were concentrated to about 20 µL. Prior to instrumental analysis, 5 µL of a 200 ng mL\(^{-1}\) \(^{13}\)C-labelled PCDD/F injection standard (EPA-1613IS) was added to the PCDD/F fraction and 5 µL of a 200 ng mL\(^{-1}\) \(^{13}\)C-labelled PCB injection standard (68B-IS) and 5 µL of a 200 ng mL\(^{-1}\) \(^{13}\)C-labelled PCN injection standard (ECN-5260) were added to the PCB and PCN fraction. The injection standards were later used for quantification of recovery.

2.3 Instrumental analysis and quality assurance/quality control

The cleaned extracts were analysed for PCNs using a GC instrument coupled to a DFS HRMS instrument (Thermo Fisher Scientific, Waltham, MA, USA). A J&W DB-5 capillary column (60 m × 0.25 mm i.d., 0.25 µm; Agilent Technologies, Santa Clara, CA, USA) was used to separate the PCN congeners. The GC temperature programme started at 80°C, which was held for 2 min, then increased at 20°C min\(^{-1}\) to 180°C, which was held for 1 min, then increased at 2.5°C min\(^{-1}\) to 280°C, and then increased at 10°C min\(^{-1}\) to 290°C, which was held for 5 min. The HRMS used an electron-impact ionisation source and was operated at a resolution of approximately 10,000 in selected ion-monitoring mode. The monitored traces for analysis of these compounds are shown in Table 2. The cleaned extracts were analysed for PCDD/Fs and PCBs using a 6890N GC instrument (Agilent Technologies, Santa Clara, CA, USA) coupled to an AutoSpec Ultima HRMS instrument (Waters Micromass, Manchester, UK). The oven temperature programme used for the PCDD/F analyses started at 160°C, which was held for 2 min, increased at 7.5°C min\(^{-1}\) to 220°C, which was held for 16 min, increased at 5°C min\(^{-1}\) to 235°C, which was held for 7 min, and then increased at 5°C min\(^{-1}\) to 330°C, which was held for 1 min. The oven temperature programme used for the PCB analyses started at 120°C, which was held for 1 min, increased at 30°C min\(^{-1}\) to 150°C, then increased at 2.5°C min\(^{-1}\) to 300°C, which was held for 1 min. The HRMS instrument used an electron-impact ionisation source and was operated in selected ion-monitoring mode at a resolution higher than 10,000. Further details of the analytical methods have been described elsewhere [19,20].

Each target compound was identified using three criteria to ensure that the quality control requirements were met. The GC retention time had to match the appropriate \(^{13}\)C\(_{12}\)-labelled standard compound, the signal-to-noise ratio had to be >3 and the isotopic ratio between the quantification and confirmation ions had to be within ±15% of the theoretical value. The compounds of interest were quantified using an isotope dilution method. The recoveries of the \(^{13}\)C\(_{10}\)-labelled PCN standards (CN27, 42, 52, 67, 73 and 75) were 35–125%, except for two samples, where the \(^{13}\)C\(_{10}\)-labelled CN75 recoveries were 30%. The recoveries of the \(^{13}\)C\(_{12}\)-labelled PCDD/F standards were 21–100%, and the recoveries of the \(^{13}\)C\(_{12}\)-labelled PCB standards were 23–125%. The limit of detection (LOD) values were in the range of 0.01–0.57 pg g\(^{-1}\) for the PCNs (Table S1), 0.04–1.3 pg g\(^{-1}\) for the PCDD/Fs and 0.03–0.45 pg g\(^{-1}\) for the dl-PCBs. The total TEQ values were calculated in two forms, one with each concentration lower than the LOD replaced with a concentration of zero and one with each concentration lower than the LOD replaced with a concentration of half of the LOD.

3. Results and discussion

3.1 PCN, PCB and PCDD/F concentrations in the cheese and butter samples

The PCN, dl-PCB and 2,3,7,8-chlorinated PCDD/F concentrations found in the commercial cheese and butter samples that were analysed are shown in Figure 1. The concentrations are expressed in picograms per gram of wet weight material and picograms TEQ per gram wet.
Table 2. Molar masses (g/mol) and monitored traces for the PCDD and PCDFs, dioxin-like PCBs (dl-PCBs), PCNs and $^{13}$C-labelled compounds.

| Congener | PCDD/Fs | | | dl-PCBs | | | PCNs | | | Homologue/ | | | Congener | Molar mass | Trace 1 | Trace 2 | Molar mass | Trace 1 | Trace 2 | Molar mass | Trace 1 | Trace 2 |
|----------|---------|---|---|---------|---|---|---------|---|---|---------|---|---|---------|---|---|---------|---|---|---------|---|---|
| 2,3,7,8-TeCDF | 303.9016 | 303.9016 | 305.9087 | 2,3,7,8-PeCDF | 337.8627 | 339.8597 | 341.8567 | CB77 | 289.9224 | 289.9224 | 291.9194 | MonoCN | 162.0236 | 162.0236 | 164.0207 |
| 1,2,3,7,8-PeCDF | 337.8627 | 339.8597 | 341.8567 | CB81 | 289.9224 | 289.9224 | 291.9194 | DiCN | 195.9847 | 195.9847 | 197.9817 |
| 2,3,4,7,8-HxCDF | 371.8237 | 373.8208 | 375.8178 | CB105 | 323.8834 | 325.8804 | 327.8775 | TriCN | 229.9457 | 229.9457 | 231.9427 |
| 1,2,3,6,7,8-HxCDF | 383.8639 | 385.8610 | 387.8581 | CB114 | 323.8834 | 325.8804 | 327.8775 | TetraCN | 263.9067 | 265.9038 | 267.9008 |
| 2,3,4,6,7,8-HxCDF | 383.8639 | 385.8610 | 387.8581 | CB118 | 323.8834 | 325.8804 | 327.8775 | PentaCN | 297.8677 | 299.8648 | 301.8618 |
| 1,2,3,7,8,9-HxCDF | 383.8639 | 385.8610 | 387.8581 | CB123 | 323.8834 | 325.8804 | 327.8775 | HexaCN | 331.8288 | 333.8258 | 335.8229 |
| 1,2,3,4,6,7,8-HpCDF | 405.7847 | 407.7818 | 409.7789 | CB156 | 357.8444 | 359.8415 | 361.8385 | HeptaCN | 365.7898 | 367.7868 | 369.7839 |
| 13C-labelled compounds | | | | 13C-2,3,7,8-TeCDF | 315.9419 | 315.9419 | 317.9389 | CB157 | 357.8444 | 359.8415 | 361.8385 | OctaCN | 399.7508 | 401.7479 | 403.7449 |
| 13C-1,2,3,7,8-PeCDF | 349.9029 | 351.9000 | 353.8970 | CB167 | 357.8444 | 359.8415 | 361.8385 | | | | |
| 13C-2,3,4,7,8-PeCDF | 349.9029 | 351.9000 | 353.8970 | CB169 | 357.8444 | 359.8415 | 361.8385 | | | | |
| 13C-1,2,3,7,8,9-HxCDF | 383.8639 | 385.8610 | 387.8581 | CB189 | 391.8054 | 393.8025 | 395.7995 | | | | |
weight. Concentrations of zero were used in the summed concentration calculations for congeners that were found at concentrations below their LODs. In general, the concentrations of each of the four groups of POPs that were analysed were higher in the butter samples than in the cheese samples, which might have been because the fat contents were higher in the butter samples than in the cheese samples.

3.1.1 Mass-based concentrations of PCNs, PCBs and PCDD/Fs in the cheese and butter samples

The mass-based PCN concentrations (i.e., the sums of CN4, 5/7, 10, 24/14, 48/35, 38/40, 50, 54, 57, 56, 66/67, 64/68, 69, 71/72, 63, 65/70 and 73) in the cheese and butter samples (which were from seven different regions around the world) are shown in Table 3. The PCN concentrations in the seven cheese samples were 5.6–103 pg g\(^{-1}\), and both the mean and median were 43 pg g\(^{-1}\). The PCN concentrations in the butter samples were 5.0–199 pg g\(^{-1}\), and the mean and median were 82 and 75 pg g\(^{-1}\), respectively. PCN concentrations in dairy products have been determined in several previous studies [21–24]. The PCN concentrations in the 14 butter
Table 3. Concentrations of the analytes in the cheese and butter samples, and the contributions of the congeners to the total TEQ concentrations.

| Congener                  | WHO-TEF/RPF | Percentage of total TEQ | Cheese |          |          | Range       | Butter |          |          | Range       |
|---------------------------|-------------|-------------------------|--------|----------|----------|-------------|--------|----------|----------|-------------|
|                           |             |                        | Mean   | Median   | <LOD     | –           | Mean   | Median   | <LOD     | –           |
| 2,3,7,8-TeCDF             | 0.1         | 2.5                     | 0.004  | –        | <LOD     | –           | 0.047  | –        | <LOD     | –           |
| 1,2,3,7,8-TeCDF           | 0.03        | 0.4                     | –      | –        | <LOD     | –           | 0.026  | –        | <LOD     | –           |
| 2,3,4,7,8-TeCDF           | 0.3         | 7.8                     | –      | –        | <LOD     | –           | 0.053  | –        | <LOD     | –           |
| 1,2,3,4,7,8-HxCDF         | 0.1         | 3.6                     | –      | –        | <LOD     | –           | 0.073  | –        | <LOD     | –           |
| 1,2,3,6,7,8-HxCDF         | 0.1         | 3.5                     | –      | –        | <LOD     | –           | 0.071  | –        | <LOD     | –           |
| 2,3,4,6,7,8-HxCDF         | 0.1         | 2.5                     | –      | –        | <LOD     | –           | 0.051  | –        | <LOD     | –           |
| 1,2,3,7,8,9-HxCDF         | 0.1         | –                       | –      | –        | <LOD     | –           | –      | –        | <LOD     | –           |
| 1,2,3,4,6,7,8-HpCDF       | 0.01        | 6.8                     | 0.43   | 0.47     | 0.15–0.67| 0.94         | 0.95   | 0.14–1.7 | <LOD     | –           |
| 1,2,3,4,7,8,9-HpCDF       | 0.01        | 0.1                     | –      | –        | <LOD     | –           | 0.024  | –        | <LOD     | –           |
| OCDF                      | 0.0003      | 2.3                     | 5.3    | 3.0      | 0.29–20  | 10           | 6.5    | 2.0–42   |          |             |
| ∑2,3,7,8-PCDFs            |             | 29.7                    | 5.7    | 3.3      | 0.76–20  | 12           | 7.7    | 3.0–44   |          |             |
| 2,3,7,8-TeCDD             | 1           | –                       | –      | –        | <LOD     | –           | –      | –        | <LOD     | –           |
| 1,2,3,7,8-TeCDD           | 1           | –                       | –      | –        | <LOD     | –           | –      | –        | <LOD     | –           |
| 1,2,3,4,7,8-HxCDD         | 0.1         | 2.8                     | –      | –        | <LOD     | –           | 0.057  | –        | <LOD     | –           |
| 1,2,3,6,7,8-HxCDD         | 0.1         | 6.2                     | 0.029  | –        | <LOD     | –           | 0.10   | 0.14     | <LOD     | –           |
| 1,2,3,7,8,9-HxCDD         | 0.1         | –                       | –      | –        | <LOD     | –           | –      | –        | <LOD     | –           |
| 1,2,3,4,6,7,8-HpCDD       | 0.01        | 1.8                     | 0.083  | –        | <LOD     | –           | 0.27   | 0.15     | <LOD     | –           |
| OCDD                      | 0.0003      | 0.8                     | 1.8    | 1.4      | 0.59–4.5 | 3.7           | 0.78   | 0.14–17  |          |             |
| ∑2,3,7,8-PCDDs            |             | 11.6                    | 1.9    | 1.4      | 0.59–4.5 | 4.1           | 1.1    | 0.31–18  |          |             |
| CB77                      | 0.0001      | 0.03                    | 0.22   | 0.060    | <LOD     | 0.81         | 0.41   | 0.22     | 0.11–1.3 |             |
| CB81                      | 0.0003      | 0.08                    | 0.12   | 0.090    | <LOD     | 0.33         | 0.40   | 0.32     | 0.18–1.0 |             |
| CB105                     | 0.00003     | 0.3                     | 2.4    | 1.4      | <LOD     | 9.7          | 15     | 6.8      | 2.1–48   |             |
| CB114                     | 0.00003     | 0.02                    | 0.25   | 0.12     | 0.020–0.86| 0.86        | 1.3    | 1.1      | 0.21–3.1 |             |
| CB118                     | 0.00003     | 1.2                     | 12     | 6.4      | 0.18–50  | 67           | 29     | 6.0–223  |          |             |
| CB123                     | 0.00003     | 0.03                    | 0.28   | 0.16     | 0.010–0.85| 0.85        | 1.6    | 1.3      | 0.21–4.3 |             |
| CB126                     | 0.1         | 46                      | 0.18   | 0.15     | <LOD     | 0.50         | 0.76   | 0.69     | 0.22–1.8 |             |
| CB156                     | 0.00003     | 0.1                     | 1.3    | 0.53     | <LOD     | 5.8          | 7.6    | 3.1      | 1.2–28   |             |
| CB157                     | 0.00003     | 0.03                    | 0.28   | 0.13     | <LOD     | 1.2          | 1.7    | 1.1      | 0.31–5.9 |             |
| CB167                     | 0.00003     | 0.05                    | 0.55   | 0.23     | 0.040–2.2 | 2.2         | 3.1    | 1.6      | 0.16–12  |             |
| CB169                     | 0.03        | 5.9                      | 0.046  | 0.050    | <LOD     | 0.90         | 0.35   | 0.32     | <LOD     | 0.79       |
| CB189                     | 0.00003     | 0.02                    | 0.21   | 0.18     | 0.050–0.66| 0.88         | 0.68   | 0.12–2.8 |          |             |

(continued)
Table 3. Continued.

| Congener      | WHO-TEF/RPF | Percentage of total TEQ | Cheese |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|---------------|-------------|-------------------------|--------|--------|--------|-------|--------|-------|--------|--------|-------|--------|-------|--------|-------|--------|-------|--------|-------|--------|-------|--------|-------|--------|-------|--------|-------|--------|-------|--------|-------|
|               |             |                         | Mean   | Median | Range  | Mean  | Median | Range  | Mean  | Median | Range  | Mean  | Median | Range  | Mean  | Median | Range  | Mean  | Median | Range  | Mean  | Median | Range  |
| Σdl-PCBs      |             |                         | 53.8   | 18     | 10     | 0.62–72 | 100    | 46     | 12–331 | 3.3   | 2.2    | 0.90–9.5 | 47    | 49     | 3.1–106 | 0.11  | –      | <LOD-0.53 | 27    | 20     | <LOD-81 | 0.011–0.22 |
| CN4           | 0.00000002  | 0.00007                 | 3.8    | 3.5    | <LOD-11 | 3.3   | 2.2    | 0.90–9.5 | 47    | 49     | 3.1–106 | 0.11  | –      | <LOD-0.53 | 27    | 20     | <LOD-81 | 0.011–0.22 |
| CN5/7         | 0.000000018 | 0.0006                  | 21     | 16     | 1.8–67  | 47    | 49     | 3.1–106 | 0.11  | –      | <LOD-0.53 | 27    | 20     | <LOD-81 | 0.011–0.22 |
| CN10          | 0.000027    | 0.02                    | 1.5    | 1.4    | 0.021–3.8 | 0.11  | –      | <LOD-0.53 | 27    | 20     | <LOD-81 | 0.011–0.22 |
| CN24/14       | 0.000001    | 0.02                    | 16     | 17     | <LOD-34 | 0.11  | –      | <LOD-0.53 | 27    | 20     | <LOD-81 | 0.011–0.22 |
| CN48/35       | 0.000021    | 0.0009                  | 0.059  | 0.016  | <LOD-0.20 | 0.028 | –      | <LOD-0.14 | 0.13  | 0.005  | <LOD-0.87 | 0.25  | 0.12   | <LOD-0.96 | 0.011–0.22 |
| CN38/40       | 0.000008    | 0.002                   | 0.12   | 0.067  | <LOD-0.52 | 0.37  | 0.041  | <LOD-2.2  | 0.13  | 0.005  | <LOD-0.87 | 0.25  | 0.12   | <LOD-0.96 | 0.011–0.22 |
| CN50          | 0.000068    | 0.007                   | 0.065  | 0.021  | <LOD-0.20 | 0.13  | 0.005  | <LOD-0.87 | 0.25  | 0.12   | <LOD-0.96 | 0.011–0.22 |
| CN54          | 0.00017     | 0.02                    | 0.045  | 0.044  | 0.004–0.13 | 0.25  | 0.12   | <LOD-0.96 | 0.011–0.22 |
| CN57          | 0.0000016   | 0.0004                  | 0.13   | 0.055  | <LOD-0.47 | 0.36  | 0.10   | <LOD-1.4  | 0.10  | 0.10   | 0.011–0.22 |
| CN56          | 0.000046    | 0.003                   | 0.050  | 0.033  | 0.002–0.14 | 0.10  | 0.10   | 0.011–0.22 |
| CN66/67       | 0.0025      | 1.2                     | 0.17   | 0.064  | 0.005–0.60 | 0.78  | 0.26   | <LOD-2.4  | 0.40  | 0.073  | <LOD-1.2  | 0.011–0.22 |
| CN64/68       | 0.001       | 0.2                     | 0.10   | 0.022  | 0.008–0.37 | 0.51  | 0.20   | 0.003–1.6  | 0.38  | 0.18   | <LOD-1.5  | 0.38  | 0.068  | <LOD-2.1  | 0.011–0.22 |
| CN69          | 0.002       | 0.6                     | 0.067  | 0.044  | 0.002–0.22 | 0.51  | 0.20   | 0.003–1.6  | 0.38  | 0.18   | <LOD-1.5  | 0.38  | 0.068  | <LOD-2.1  | 0.011–0.22 |
| CN71/72       | 0.0000035   | 0.0008                  | 0.10   | 0.063  | 0.033–0.17 | 0.38  | 0.18   | <LOD-1.5  | 0.38  | 0.068  | <LOD-2.1  | 0.011–0.22 |
| CN63          | 0.002       | 0.5                     | 0.13   | 0.045  | <LOD-0.37 | 0.38  | 0.068  | <LOD-2.1  | 0.011–0.22 |
| CN65/70       | 0.0011      | 0.2                     | 0.10   | 0.059  | 0.024–0.25 | 0.21  | 0.19   | <LOD-0.58 | 0.38  | 0.068  | <LOD-2.1  | 0.011–0.22 |
| CN73          | 0.003       | 2.2                     | 0.34   | 0.14   | <LOD-1.0  | 1.1   | 0.18   | <LOD-2.8  | 1.1   | 0.18   | <LOD-2.8  | 1.1   | 0.18   | <LOD-2.8  | 1.1   | 0.18   | <LOD-2.8  |
| ΣSelected PCNs|             |                         | 4.9    | 43     | 5.6–103 | 82    | 75     | 5.0–199 |

Notes: For congeners with concentrations below their LOD, the mean and median concentrations have been shown as ‘–’. Concentrations below the LOD were assigned zero values.
and cheese samples (one sample of each from seven regions around the world) that were analysed were comparable with the PCN concentrations reported in these previous surveys, as shown in Table 4. The PCN concentrations varied markedly between the samples, which most likely reflected the relative proximities of the source regions of the samples to centres of population and industrial activity. Further research will be needed to investigate the regional variability in PCN concentrations in the different dairy samples.

The sums of the concentrations of the 12 dl-PCBs that were analysed in the cheese samples were 0.62–72 pg g\(^{-1}\), and the mean and median were 18 and 10 pg g\(^{-1}\), respectively. The sums of dl-PCB concentrations in the butter samples were 12–331 pg g\(^{-1}\), and the mean and median were 100 and 46 pg g\(^{-1}\), respectively. The dl-PCB concentrations in the cheese and butter samples were much higher than the 2,3,7,8-PCDD/F concentrations, which was similar to the results of a previously published study concerning butter from Spain [25]. The dl-PCB concentrations were different in the cheese and butter samples from different regions, and the lowest concentrations were found in both the cheese and butter samples from Tibet. The highest concentrations were found in both the cheese and butter samples from France, and relatively high concentrations were found in the other cheese and butter samples from Europe. In a previous study, the highest PCB concentrations were found in butter from Europe and North America, whereas the lowest concentrations were found in butter from the southern hemisphere (i.e., Australia and New Zealand) [26].

The sums of the 2,3,7,8-PCDF concentrations in the cheese samples were in the range of 0.76–20 pg g\(^{-1}\), and the mean and median were 5.7 and 3.3 pg g\(^{-1}\), respectively. The sums of 2,3,7,8-PCDF concentrations in the butter samples were found to be in the range of 3.0–44 pg g\(^{-1}\), and the mean and median were 12 and 7.7 pg g\(^{-1}\), respectively. The sums of the 2,3,7,8-PCDD concentrations in the cheese samples were in the range of 0.59–4.5 pg g\(^{-1}\), and the mean and median were 1.9 and 1.4 pg g\(^{-1}\), respectively. The sums of the 2,3,7,8-PCDD concentrations in the butter samples were in the range of 0.31–18 pg g\(^{-1}\), and the mean and median were determined to be 4.1 and 1.1 pg g\(^{-1}\), respectively. Only a few 2,3,7,8-PCDD/F congeners were found at concentrations above their LOD values, so the concentrations of several congeners were assigned values of zero when the summed concentrations were calculated. Bordajandi et al. [25] reported an upper-bound concentration (replacing each congener

| Type of sample         | Origin            | Sampling year | Sum of PCNs | PCN TEQ     | Reference     |
|------------------------|-------------------|---------------|-------------|-------------|---------------|
| Irish unsalted butter  | Ireland           | 2007–2008     | 1.9\(^a\)   | 0.0039\(^b\) | [21]          |
| English unsalted butter| UK                | 2007          | 6.1\(^a\)   | 0.010\(^b\)  | [22]          |
| Butter                 | Spain             | 2006          | 22\(^c\)    | –\(^f\)      | [23]          |
| Butter                 | Chinese market    | 2013          | 5.0–199\(^d\) | 0.00020–0.018\(^e\) | This study |
| Red cheddar            | Ireland           | 2007–2008     | 0.68\(^a\)  | 0.0015\(^b\) | [21]          |
| Welsh medium cheddar   | UK                | 2007          | 1.1\(^a\)   | 0.0020\(^b\) | [22]          |
| Cheese                 | Spain             | 2006          | 23\(^c\)    | –\(^f\)      | [23]          |
| Cheese                 | Chinese market    | 2013          | 5.6–103\(^d\) | 0.00030–0.0050\(^e\) | This study |

Notes: \(^a\)Sum of 12 PCNs (CN52/60, 53, 66/67, 68, 69, 71/72, 73, 74 and 75) in ng kg\(^{-1}\) whole weight.
\(^b\)The PCN TEQ was calculated using the toxic equivalence factor values published by Behnisch et al. [29], Blankenship et al. [16], Hanberg et al. [30] and Villeneuve et al. [15].
\(^c\)The sum of the tetra- to octa-chloronaphthalenes, in ng kg\(^{-1}\) wet weight.
\(^d\)The sum of selected PCNs (CN4, 5/7, 10, 24/14, 48/35, 38/40, 50, 54, 57, 56, 66/67, 64/68, 69, 71/72, 63, 65/70 and 73), in pg g\(^{-1}\) wet weight.
\(^e\)The RPF values used were published by Behnisch et al. [29], Blankenship et al. [16], Falandysz et al. [2], Hanberg et al. [30], Kannan et al. [31], Noma et al. [28] and Villeneuve et al. [15].

Not reported.
concentration below the LOD with the LOD) of 4.95 pg g\(^{-1}\) for the 17 toxic 2,3,7,8-PCDD/Fs found in butter samples from Spain.

3.1.2 TEQ concentrations of PCNs, PCBs and PCDD/Fs in the cheese and butter samples

The World Health Organisation (WHO) toxic equivalence factors (TEFs) developed by Van den Berg et al. [27] were used to calculate the TEQ for the PCDDs, PCDFs and dl-PCBs. The PCN TEQ values were calculated using RPFs that were derived from other publications [2,15,16,28–31]. The TEFs and RPFs that were used are presented in Table 3.

The PCN TEQ concentrations in the cheese samples were 0.0003–0.005 pg TEQ g\(^{-1}\), and the mean and median were 0.002 and 0.001 pg TEQ g\(^{-1}\), respectively. The PCN TEQ concentrations in the butter samples were 0.0002–0.018 pg TEQ g\(^{-1}\), and the mean and median were 0.008 and 0.003 pg TEQ g\(^{-1}\), respectively. In a previous study, the upper-bound concentrations of selected PCNs were 0.0039 pg TEQ g\(^{-1}\) of the whole weight in Irish unsalted butter and 0.0015 pg TEQ g\(^{-1}\) of the whole weight in red cheddar [21].

The dl-PCB WHO-TEQ concentrations in the cheese samples were 0.0004–0.054 pg TEQ g\(^{-1}\), and the mean and median were determined to be 0.020 and 0.018 pg TEQ g\(^{-1}\), respectively. The dl-PCB WHO-TEQ concentrations in the butter samples were 0.040–0.20 pg TEQ g\(^{-1}\), and the mean and median were 0.089 and 0.073 pg TEQ g\(^{-1}\), respectively. In a previous study, dl-PCB WHO-TEQ concentrations of 4.94 and 1.55–3.68 pg WHO-TEQ g\(^{-1}\) wet weight were found in cheese and butter samples, respectively, from Egypt [32].

The PCDF TEQ values in the cheese samples were 0.003–0.013 pg TEQ g\(^{-1}\), and the mean and median were 0.006 and 0.005 pg TEQ g\(^{-1}\), respectively. The PCDF TEQ values in the butter samples were in the range of 0.007–0.14 pg TEQ g\(^{-1}\), and the mean and median were 0.054 and 0.030 pg TEQ g\(^{-1}\), respectively. The PCDD TEQ concentrations in the cheese samples were 0.0002–0.013 pg TEQ g\(^{-1}\), and the mean and median were found to be 0.004 and 0.001 pg TEQ g\(^{-1}\), respectively. The PCDD TEQ values in the butter samples were 0.0002–0.041 pg TEQ g\(^{-1}\), and the mean and median were 0.019 and 0.015 pg TEQ g\(^{-1}\), respectively. In a previous study, PCDD/F WHO-TEQ concentrations of 9.06 pg g\(^{-1}\) wet weight and 2.94–3.74 pg g\(^{-1}\) wet weight were found in cheese and butter, respectively [32]. Jensen et al. previously found mean TEQ concentrations of 0.068 pg g\(^{-1}\) wet weight in cheese and 0.061 pg g\(^{-1}\) wet weight in butter [33]. PCDD/F TEQ values of 0.107 pg TEQ g\(^{-1}\) fresh weight and 0.334 pg TEQ g\(^{-1}\) fresh weight have been found in cheese and butter samples, respectively, from Spain [34].

3.1.3 Contributions of the PCNs, PCBs and PCDD/Fs to the total TEQ

The average contributions of the PCNs, PCBs, PCDDs and PCDFs to the total TEQ are shown in Figure 2. When concentrations below the LODs were replaced with values of zero, the PCBs made the greatest contribution (53.8%) to the total TEQ, with the PCDDs and PCDFs contributing only 11.6 and 29.7%, respectively. The PCNs contributed around 4.9% of the total TEQ. However, when concentrations below the LODs were replaced with 1/2LOD, the contributions made by the PCDDs and PCDFs to the total TEQ increased significantly to about 63.7 and 23.1%, respectively. This increase occurred because the concentrations of many of the 2,3,7,8-PCDD/F congeners, especially those with higher TEFs (including 2,3,7,8-TCDD), were below the LOD values. Using a value of 1/2LOD for these congeners significantly increased the total TEQ.
3.2 PCN, PCB and PCDD/F congener profiles

The PCDD/F concentration profiles were dominated by octachlorodibenzofuran, octachlorodibenzo-p-dioxin and 1,2,3,4,6,7,8-heptachlorodibenzofuran. The main contributors to the PCDD/F TEQ were 2,3,4,7,8-pentachlorodibenzofuran, 1,2,3,4,6,7,8-heptachlorodibenzofuran and 1,2,3,6,7,8-hexachlorodibenzo-p-dioxin.

Of the 12 dl-PCB congeners, CB118 was the predominant congener, accounting for more than 66.9% of the total dl-PCB concentrations, followed by CB105 and CB156. Similar dl-PCB patterns were found in buffalo milk and mozzarella cheese by Santelli et al. [35]. CB126 was the dominant contributor (accounting for 85.7%) to the total PCB WHO-TEQ.

The PCN patterns were dominated by the less-chlorinated homologues, with the dichlorinated and trichlorinated PCNs being the most important contributors. The contributions of these homologues were comparable, and they together accounted for 68.8% of the total PCN concentrations. CN5/7 and CN24/14 were the dominant congeners, accounting for 31.5% and 20.0% of the total PCN concentrations, respectively. Congeners of CN45/36, CN27/30 and CN33/34/37 were found to be the major contributors to the mass-based concentrations of tetrachlorinated homolog. The higher chlorinated congeners of PCNs were dominant with CN51 in the pentachlorinated homolog, CN66/67 in the hexachlorinated homolog and CN73 in the heptachlorinated homolog. CN73 made the largest contribution (44.2%) to the total PCN TEQ, and congeners CN66/67, CN69 and CN63 also made relatively large contributions of 23.8, 11.7 and 10.2%, respectively (Figure 3). This was because those congeners were found at relatively high concentrations and also have relatively high RPFs.

Similar trends in the contributions of PCNs to the total PCN concentrations have been found in soil and yak fatty tissue samples from the Wolong Mountains in western China [11]. Wang et al. [36] found that the trichlorinated PCNs were the dominant homologue group in soil samples and that CN24 was the most abundant congener. A similar pattern was found in sewage sludge from China by Guo et al. [37]. Meijer et al. [38] analysed sewage sludge and sludge-amended soil and also found that the PCN profiles were dominated by the less-chlorinated homologues.

Figure 2. Contributions of the selected PCNs, PCDD and PCDFs and dioxin-like PCBs (dl-PCBs) to the total toxic equivalences (TEQs) in the samples. (a) A value of zero was used in the TEQ calculations for congeners that were found below their LODs. (b) A value of ½ LOD was used in the TEQ calculations for congeners found below their LODs.
4. Conclusions

The PCN concentrations and profiles of the 14 cheese and butter samples (a sample of each from seven different regions) were determined and compared with the PCB, PCDD and PCDF concentrations and profiles. The concentrations of all four types of POPs were generally higher in the butter samples than in the cheese samples. PCNs contributed around 5% to the total PCN, PCB and PCDD/F TEQ values. PCBs was the major contributor to the total TEQ. Most of the 2,3,7,8-chlorinated PCDD/F congeners were found at concentrations below their LODs. The results of the current study could be used as reference data for PCN concentrations and profiles and the relative contributions of PCNs, PCBs, PCDDs and PCDFs to the total TEQ values of cheese and butter samples. Further research is needed to investigate regional variations in the PCN concentrations of different dairy samples.

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Supplemental data

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References

[1] J. Falandysz, K. Nose, Y. Ishikawa, E. Łukaszewicz, N. Yamashita and Y. Noma, J. Environ. Sci. Heal. A. 41, 2237 (2006). doi:10.1080/10934520600872748
[2] J. Falandysz, A. Fernandes, E. Gregoraszczuk and M. Rose, J. Environ. Sci. Heal. C. 32, 239 (2014). doi:10.1080/10590501.2014.938945
[3] M. Van Den Berg, M.S. Denison, L.S. Birnbaum, M.J. DeVito, H. Fiedler, J. Falandysz, M. Rose, D. Schrenk, S. Safe, C. Tohyama, A. Tritscher, M. Tysklind and R.E. Peterson, Toxicol. Sci. 133, 197 (2013). doi:10.1093/toxsci/kft070
[4] J. Falandysz, M. Rose and A.R. Fernandes, Environ. Int. 44, 118 (2012). doi:10.1016/j.envint.2012.03.006
[5] G. Liu, Z. Cai and M. Zheng, Chemosphere. 94, 1 (2014). doi:10.1016/j.chemosphere.2013.09.021
[6] G. Liu, M. Zheng, P. Lv, W. Liu, C. Wang, B. Zhang and K. Xiao, Environ. Sci. Technol. 44, 8156 (2010). doi:10.1021/es102474w
[7] J. Falandysz, Food Addit. Contam. 20, 995 (2003). doi:10.1080/02652030310001615195
[8] K. Kannan, T. Imagawa, A.L. Blankenship and J.P. Giesy, Environ. Sci. Technol. 32, 2507 (1998). doi:10.1021/es980167g
[9] T.F. Bidleman, P.A. Helm, B.M. Braune and G.W. Gabrielsen, Sci. Total Environ. 408, 2919 (2010). doi:10.1016/j.scitotenv.2009.12.039
[10] J.L. Domingo, J. Chromatogr. A. 1054, 327 (2004). doi:10.1016/j.chroma.2004.03.072
[11] J. Pan, Y. Yang, X. Zhu, L.W.Y. Yeung, S. Taniyasu, Y. Miyake, J. Falandysz and N. Yamashita, Sci. Total Environ. 444, 102 (2013). doi:10.1016/j.scitotenv.2012.11.013
[12] H. Park, J.-H. Kang, S.-Y. Baek and Y.-S. Chang, Environ. Pollut. 158, 1420 (2010). doi:10.1016/j.envpol.2009.12.039
[13] T. Kunisue, B. Johnson-Restrepo, D.R. Hilker, K.M. Aldous and K. Kannan, Environ. Pollut. 157, 910 (2009). doi:10.1016/j.envpol.2008.11.012
[14] J. Falandysz, A. Fernandes, E. Gregoraszczuk and M. Rose, Organohalogen Compd. 75, 336 (2013).
[15] Y. Noma, T. Yamamoto and S.-I. Sakai, Environ. Sci. Technol. 38, 1675 (2004). doi:10.1021/es035101m
[16] P.A. Behnisch, K. Hosoe and S. Sakai, Environ. Int. 29, 861 (2003). doi:10.1016/S0160-4120(03)00105-3
[17] A.R. Fernandes, C. Tlustos, M. Rose, F. Smith, M. Carr and S. Panton, Chemosphere. 85, 322 (2011). doi:10.1016/j.chemosphere.2011.06.093
[18] A. Hanberg, D. Mortimer, M. Gem, F. Smith, M. Rose, S. Panton and M. Carr, Environ. Sci. Technol. 44, 3533 (2010). doi:10.1021/es903502g
[19] J.L. Domingo, J.M. Llobet, V. Castell and J.L. Domingo, Environ. Sci. Technol. 42, 4195 (2008). doi:10.1021/es800064p
[20] J.L. Domingo, G. Falcó, J.M. Llobet, C. Casas, A. Teixidó and L. Müller, Environ. Sci. Technol. 37, 2332 (2003). doi:10.1021/es030099b
[21] L.R. Bordajandi, G. Gómez, E. Abad, J. Rivera, M.D. Fernandez-Baston, J. Blasco and M.J. Gonzalez, J. Agric. Food Chem. 52, 992 (2004). doi:10.1021/jf030453y
[22] D. Santillo, A. Fernandes, R. Stringer, R. Alcock, M. Rose, S. White, K. Jones and P. Johnston, Food Addit. Contam. 20, 281 (2003). doi:10.1080/02652030321000057494
[23] M. Van Den Berg, L.S. Birnbaum, M. Denison, M. De Vito, W. Farland, M. Feeley, H. Fiedler, H. Hakansson, A. Hanberg, L. Haws, M. Rose, S. Safe, D. Schrenk, C. Tohyama, A. Tritzsch, J. Tuomisto, M. Tysklind, N. Walker and R.E. Peterson, Toxicol. Sci. 93, 223 (2006). doi:10.1093/toxsci/kf055
[24] Y. Noma, T. Yamamoto and S.-I. Sakai, Environ. Sci. Technol. 38, 1675 (2004). doi:10.1021/es035101m
[25] A.R. Fernandes, C. Tlustos, M. Rose, F. Smith, M. Carr and S. Panton, Chemosphere. 85, 322 (2011). doi:10.1016/j.chemosphere.2011.06.093
[26] A. Fernandes, D. Mortimer, M. Gem, F. Smith, M. Rose, S. Panton and M. Carr, Environ. Sci. Technol. 44, 3533 (2010). doi:10.1021/es903502g
[27] R. Marti-Cid, J.M. Llobet, V. Castell and J.L. Domingo, Environ. Sci. Technol. 42, 4195 (2008). doi:10.1021/es800064p
[28] J.L. Domingo, G. Falcó, J.M. Llobet, C. Casas, A. Teixidó and L. Müller, Environ. Sci. Technol. 37, 2332 (2003). doi:10.1021/es030099b
[29] L.R. Bordajandi, G. Gómez, E. Abad, J. Rivera, M.D. Fernandez-Baston, J. Blasco and M.J. Gonzalez, J. Agric. Food Chem. 52, 992 (2004). doi:10.1021/jf030453y
[30] D. Santillo, A. Fernandes, R. Stringer, R. Alcock, M. Rose, S. White, K. Jones and P. Johnston, Food Addit. Contam. 20, 281 (2003). doi:10.1080/02652030321000057494
[31] M. Van Den Berg, L.S. Birnbaum, M. Denison, M. De Vito, W. Farland, M. Feeley, H. Fiedler, H. Hakansson, A. Hanberg, L. Haws, M. Rose, S. Safe, D. Schrenk, C. Tohyama, A. Tritzsch, J. Tuomisto, M. Tysklind, N. Walker and R.E. Peterson, Toxicol. Sci. 93, 223 (2006). doi:10.1093/toxsci/kf055
[32] Y. Noma, T. Yamamoto and S.-I. Sakai, Environ. Sci. Technol. 38, 1675 (2004). doi:10.1021/es035101m
[29] P.A. Behnisch, K. Hosoe and S. Sakai, Environ. Int. 29, 861 (2003). doi:10.1016/S0160-4120(03)00105-3
[30] A. Hanberg, F. Waern, L. Asplund, E. Haglund and S. Safe, Chemosphere. 20, 1161 (1990). doi:10.1016/0045-6535(90)90238-O
[31] K. Kannan, N. Yamashita, T. Imagawa, W. Decoen, J.S. Khim, R.M. Day, C.L. Summer and J.P. Giesy, Environ. Sci. Technol. 34, 566 (2000). doi:10.1021/es990966e
[32] N. Loufyy, M. Fuerhacker, P. Tundo, S. Raccanelli, A.G. El Dien and M.T. Ahmed, Sci. Total Environ. 370, 1 (2006). doi:10.1016/j.scitotenv.2006.05.012
[33] E. Jensen and M. Bolger, Food Addit. Contam. 18, 395 (2001). doi:10.1080/02652030119893
[34] J.M. Llobet, R. Marti-Cid, V. Castell and J.L. Domingo, Toxicol. Lett. 178, 117 (2008). doi:10.1016/j.toxlet.2008.02.012
[35] F. Santelli, F. Boscaino, D. Cautela, D. Castaldo and A. Malorni, Eur. Food Res. Technol. 223, 51 (2006). doi:10.1007/s00217-005-0112-0
[36] Y. Wang, Z. Cheng, J. Li, C. Luo, Y. Xu, Q. Li, X. Liu and G. Zhang, Environ. Pollut. 170, 1 (2012). doi:10.1016/j.envpol.2012.06.008
[37] L. Guo, B. Zhang, K. Xiao, Q. Zhang and M. Zheng, Chinese Sci. Bull. 53, 508 (2008). doi:10.1007/s11434-008-0129-4
[38] S.N. Meijer, T. Harner, P.A. Helm, C.J. Halsall, A.E. Johnston and K.C. Jones, Environ. Sci. Technol. 35, 4205 (2001). doi:10.1021/es010071d