



Factors that affect polychlorinated naphthalenes formation and distribution during the heating of sucralose

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1. Introduction

Both the structures and toxicities of polychlorinated naphthalenes (PCNs) are similar to those of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), which are persistent, bioaccumulative chemical compounds. PCNs were also listed as persistent organic pollutants (POPs) under Annexes A and C of the Stockholm Convention in 2015 (POPRC, 2017), and are no longer produced commercially. However, these compounds can still be generated along with PCDD/Fs as undesired byproducts during various high-temperature processes (Liu, Cai, & Zheng, 2014; Weidemann & Lundin, 2015; Zhao et al., 2017).

There have been several studies of the mechanisms by which PCNs are formed during high-temperature combustion. One possibility is *de novo* synthesis from polycyclic aromatic hydrocarbons (PAHs) in the presence of copper compounds such as CuCl, CuCl₂ or Cu(OH)₂ (which act as catalysts) at temperatures such as 300 °C (Weber et al., 2001) or 400 °C (Iino, Imagawa, Takeuchi, & Sadakata, 1999). Kim et al. also reported the formation of PCNs via the ortho-ortho carbon coupling of phenoxy radicals during chlorophenol combustion at 550–750 °C, and demonstrated that the degree of chlorination of naphthalene declines with increasing temperature (Kim & Mulholland, 2005). PCNs can also be produced under relatively mild conditions. As an example, the chlorination reaction that is considered an important step in the formation of PCNs can take place at 200 °C (Jansson, Fick, & Marklund, 2008). The β-positions of naphthalene are more likely to be substituted by chlorine than the α-positions, possibly because of the relatively high stability of PCN congeners with β-position chlorines (Jansson, et al., 2008; Liu, Lv, Jiang, Nie, & Zheng, 2014; Zhai & Wang, 2005). However, Ryu et al. found that α-positions were favored over β-positions in PCNs produced by the CuCl₂-catalyzed chlorination of naphthalene, suggesting that naphthalene chlorination is not the primary pathway for PCN formation during combustion (Ryu, Kim, & Jang, 2013).

PCNs may also result from the application of high temperatures during cooking. A previous study by our group demonstrated the emission of PCNs from cooking oil containing sucralose at 245 °C (Dong, Liu, Zhang, Gao, & Zheng, 2013). Sucralose is an artificial

sweetener widely used as a food additive, and dry sucralose has been found to be unstable at high temperatures because it can undergo chlorination reactions, generating potentially toxic compounds. The degradation of sucralose can proceed under relatively mild conditions (such as at 119 °C) in conjunction with the loss of both H₂O and HCl (Bannach, Almeida, Lacerda, Schnitzler, & Ionashiro, 2009). The thermal decomposition of sucralose was also studied by Rahn et al., who reported levoglucosenone as the major product upon heating at 250 °C (Rahn & Yaylayan, 2010). Sucralose can also serve as a chlorine source for the formation of chloropropanols. A combination of analytical methods was recently used to study the thermal degradation of sucralose and both decomposition and the formation of chlorinated derivatives were observed after melting (Oliveira, Menezes, & Catharino, 2015). Polychlorinated aromatic hydrocarbons have been observed to form under mild conditions (Oliveira et al., 2015), while PCDD/Fs were found to be produced when sucralose was heated at high temperatures in the presence of a metal catalyst (Dong, Liu, Hu, & Zheng, 2013). Thus, decomposition, chlorination, cyclization and oxidation can all occur during the heating of sucralose. The formation of PCNs accompanied by PCDD/Fs has also been shown to result from high-temperature combustion, based on similar formation mechanisms (Iino et al., 1999; Weber et al., 2001), thus we considered that PCNs might also be produced during the heating of sucralose under certain conditions.

In the present study, the effects of temperature, container type and the presence of rust (metal oxides) on the formation and distribution of PCNs during the heating of sucralose were investigated. Both residues resulting from the heating of sucralose and the smoke collected during this process were analyzed for the presence of PCNs, using isotope dilution high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS). The distributions and patterns of PCNs in these materials were determined. In addition, to identify the potential PCN formation mechanisms associated with the heating of sucralose, PAHs in the smoke samples were also monitored, using gas chromatography-mass spectrometry (GC/MS).

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2. Materials and methods

2.1. Sampling

The sampling system used in the present study has been described previously (Dong, Wu, Liu, Zhang, & Zheng, 2011; Wu, Dong, Liu, Zhang, & Zheng, 2011) and the reagents and experimental procedures have also been provided in detail elsewhere (Dong et al., 2013; Dong et al., 2013). In each experiment, the sucralose (as solid) was heated for 15 min and an air pump was operating during this time span and for an additional 10 min during the cooling phase to trap the resulting smoke. The amounts of PCNs formed during the heating process were quantified by using a relatively large amount of sucralose (approx. 5 g) in each trial. Four types of experimental trials were conducted: (1) sucralose (5 g) heated in stainless steel containers (a commonly used cookware) at 200, 250, 300, 350 or 400 °C; (2) sucralose (5 g) heated in quartz, aluminum or copper containers having similar sizes (with the inner wall of the metal containers polished to ensure the absence of rust) at 400 °C; (3) sucralose (5 g) mixed with 1 g of Al₂O₃, Fe₂O₃ or CuO and heated at 400 °C; and (4) sucralose (5 g) mixed with 0.01, 0.1 or 1 g CuO and heated at 400 °C. Additional experiments were conducted by 5 g of sucralose with 1 g of CuO and heating at 300 °C. Each trial was repeated at least twice.

2.2. Sample extraction and analysis

The cleanup procedures and instrumental analysis methods for tetra- to octa-CN_s in the residues and smoke were based on HRGC/HRMS, employing previously established procedures (Dong et al., 2013; Dong et al., 2013). ¹³C-labelled PCNs were added to the samples as internal standards before pretreatment. The residues from each heating experiment were combined with 1.0 mol/L HCl (20.0 mL) and left overnight. Prior to freeze-drying, the residues were washed with deionized water until the wash water had a pH of approximately 7, after which they were Soxhlet extracted. The resins on which the smoke samples were absorbed were directly Soxhlet extracted without being subjected to the pretreatment applied to the residues. The Soxhlet extracts were cleaned using gel permeation, acidic silica gel, multilayer silica gel and basic alumina columns in succession. Tetra- to octa-CN_s in the samples were determined using a gas chromatograph coupled with a DFS mass spectrometer (Thermo Fisher Scientific, Hudson, NH, USA) having a resolution of $\geq 10,000$, using an electron ionization source and employing the selected ion monitoring mode. The details regarding the sample preparation and instrumental analysis of the sixteen PAHs in the smoke samples have been provided elsewhere (Dong et al., 2013). Detailed information on the materials and PCN analytical procedures is given in the [Supplementary Material](#).

2.3. Quality control and quality assurance

The relative percentage differences in the target compound concentrations between duplicate experiments were found to be less than 40%. The concentrations of the PCNs and PAHs in the residues and smoke were calculated based on the original mass of sucralose (5 g) used in the experiments. The recoveries of the ¹³C-labelled PCNs and d-PAHs were 40.2–109.7% and 67.9–92.4%, respectively. The limits of detection (LOD, equivalent to a signal-to-noise ratio of 3) of the PCNs and PAHs in the present study were determined to be 0.01–0.6 pg/g and 0.004–0.03 ng/g, respectively, and PCN congener concentrations in samples below these LODs are reported as zero. Concentrations of all the target compounds in the blanks and the unheated sucralose were near or below the LODs. Thus, there was no blank correction in this study.

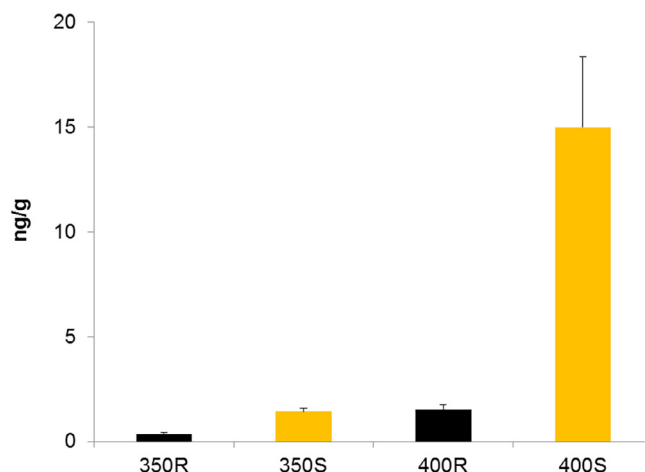


Fig. 1. PCN concentrations in the residues (R) and smoke (S) produced during the heating of 5 g of sucralose in stainless steel containers at 350 or 400 °C.

3. Results and discussion

3.1. Effect of temperature on PCN formation

No PCN congeners were detected either in the residues or smoke when the sucralose was heated in stainless steel containers at 200 or 250 °C. Although PCNs were not found in the residue following heating at 300 °C, certain PCN congeners were identified in the smoke, albeit at low levels. When the sucralose was heated at 350 °C, PCNs were detected both in the residues and the smoke (Fig. 1) and even greater amounts were identified following treatment at 400 °C. The total concentrations of the tetra- to octa-CN_s produced at 350 and 400 °C were 1.8 and 16.4 ng/g, respectively. In addition, the PCN concentrations in the residues were lower than those in the smoke. The relative proportion of PCNs in the smoke was found to be higher at 400 °C, possibly due to the increased evaporation of these compounds at the higher temperature. The concentrations of PCNs were higher than the PCDD/F (tetra- to octa-CDD/F) concentrations when the sucralose was heated at 350 °C (1.2 ng/g), but lower than the levels obtained at 400 °C (31 ng/g). (Dong et al., 2013)

The homologue and congener profiles of the PCNs in the residues and smoke were similar following heating at 350 and 400 °C (Fig. 2), suggesting that temperature did not affect the mechanism by which the PCNs were produced. Tetra-CN_s were the primary PCNs in all these samples, accounting for more than 40% of the total mass. The

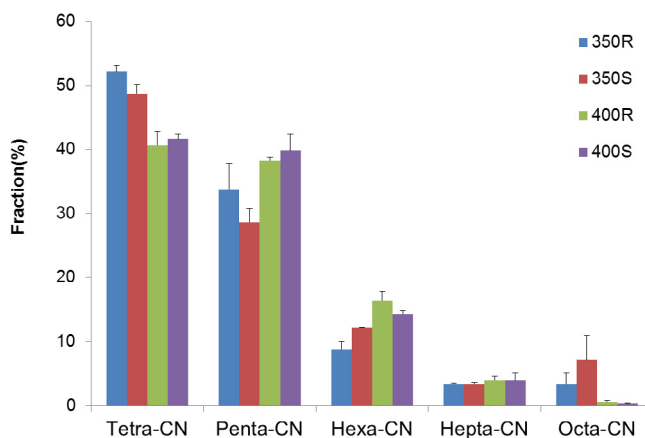


Fig. 2. Homologue profiles of PCNs in the residues (R) and smoke (S) produced during the heating of 5 g of sucralose in stainless steel containers at 350 or 400 °C.

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