ASSESSMENT OF FORMATION OF MIXED CHLORINATED / BROMINATED DIPHENYL ETHERS AND BROMINATED DIOXINS / FURANS DURING FOOD PROCESSING.

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The aim of this study was to evaluate effects of heat treatment on degradation of PBDEs and possible formation of chlorinated diphenyl ethers or brominated dioxins/furans. PBDEs heated in the presence of chlorine (from either organic or inorganic sources) formed mixed chlorinated (PCDE) / brominated diphenyl ethers. However, no PCDEs were formed in the presence of lipids. Grilling processes of meat increased concentrations (calculated on the fresh product basis) of the studied compounds by 4–8/22–34% for electric/coal grill, respectively. Depending on the congener and on the applied heat treatment, PBDE mass in pork meat after grilling dropped by 26–53%. No detectable quantities of either brominated dioxins or furans were formed during thermal processing of food containing typical levels of PBDEs.

Key Words – **brominated dioxins, chlorinated diphenyl ethers, food processing,**

I. INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are chemical contaminants of industrial origin widely spread in the environment. Due to their chemical inertness, lipophilic characteristics, and bio-accumulative potency PBDEs are classified as Persistent Organic Pollutants (POP). Some reports suggest that under heat treatment or exposition to UV irradiation they may undergo transformations into such analogue forms as debrominated compounds, hydroxylated compounds, chlorinated diphenyl ethers, or brominated dioxins/furans. Majority of published results concern relatively high levels of the compounds, well beyond typical environmental backgrounds. Levels of PBDEs/other POPs found in food/environmental samples have been reported in numerous papers. Majority of authors involved in studies of food contamination have investigated unprocessed products, information on influence of processing on levels of contamination is rather limited. Rawn et al. [1] have noticed that the available data on impact of cooking on POP levels in food are inconsistent. Some authors have reported drop of the contamination, while others have reported increased concentrations [2–5]. Bayen et al.[3] have reported that limited papers point out that correlation between POP losses and lipid change during cooking of food products exists. Also, there are no reports whether the degradation/ transformation reactions of PBDEs observed in the model studies or the environmental samples may occur in food products during processing. Polychlorinated and / or mixed chlorinated / brominated diphenyl ethers have been identified in thermally treated samples containing PBDEs. If a chlorine source was present, low temperature processing was sufficient [6]. Some recent study reported elevated levels of those compounds in fried/grilled fish [7]. Some literature data suggest that PBDE thermolysis may produce various debromination products [8], while pyrolysis - brominated dioxins and furans [9,10]. Weber et al. [11] and Ortuno et al. [12] reported PBDD/Fs produced when plastic materials containing PBDEs were heated to relatively low temperatures. Hanari et al. [13] reported significant quantities of PBDD/Fs in technical mixtures of PBDEs. However, earlier papers [14,15] did not give any indication of PBDD/Fs or PCDD/Fs in such technical mixtures. There are also no literature data on possible formation of those compounds from thermally treated PBDEs at background levels typical for the environment.

The aim of this study was to investigate: (i) influence of heat treatment on degradation kinetics of PBDEs at concentrations typical for environmental / food samples;

(ii) kinetics of formation of chlorinated diphenyl ethers from corresponding BDEs using various chlorine sources; (iii) effects of food processing on BDE concentrations and possible formation of PBDE degradation products (including brominated analogues of dioxins/furans).

II. MATERIALS AND METHODS

Eight studied BDE congeners included ## 28, 47, 99, 100, 153, 154, 183, 209. The chemicals were dissolved in n-hexane to final concentration of 50 mg mL^{-1}. Pure BDEs and vegetable oil samples spiked with BDEs were placed in 10 mL glass ampoules, flame-sealed without evacuation of air, and heated using laboratory muffle furnace or ordinary heating blocks. Minced pork meat mixed with small amount of rapeseed oil spiked with known amount of BDEs (to assure their homogeneity) was grilled using an electric grill operated at 180 °C or a charcoal-fired grill. The meat samples were directly placed above the heat source and processed until temperature of about 80 °C was obtained in the sample center. Pure BDE samples were directly transferred into amber chromatographic vials and analyzed. Pork samples were freeze-dried before further analysis. Both pork and vegetable oil samples were extracted and/or cleaned-up using gel permeation chromatography / solid phase extraction before analysis. All experiments were performed in triplicates. Determination of the studied compounds was performed using gas chromatography - mass spectrometry, as reported previously [16].

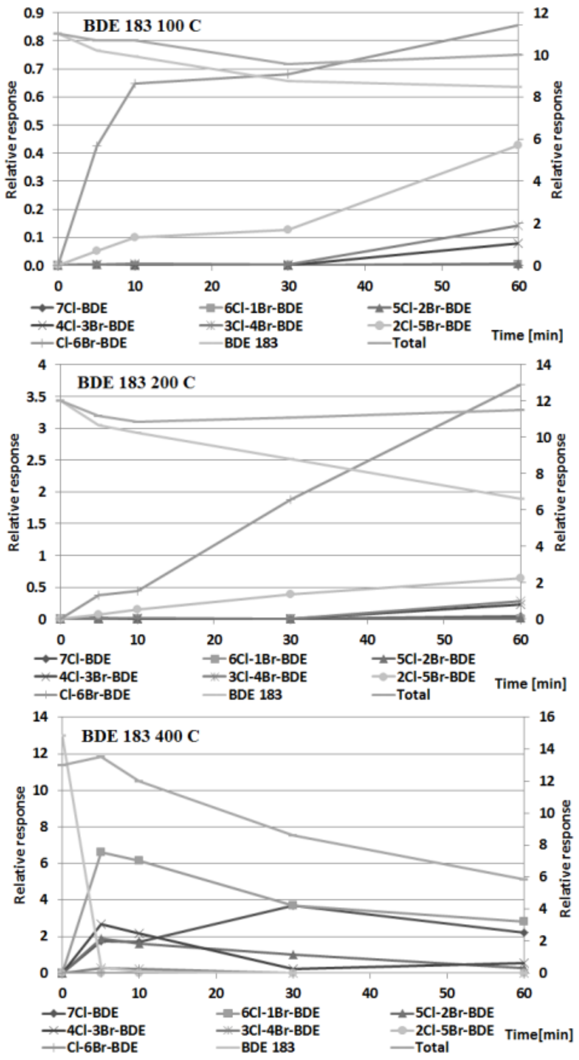
III. RESULTS AND DISCUSSION

Experiments conducted with pure standards showed degradation of BDEs with time of heating. However, no debromination products at levels above LOQs were identified in any of the tested reaction mixtures. Various studied compounds degraded differently at various temperatures. Thermal stability of the studied BDE congeners was inversely proportional to the number of bromine atoms per molecule. None of the investigated samples contained any detectable amounts of brominated dibenzo-p-dioxins or dibenzofurans. No such compounds have also been found in samples heated under nitrogen. However, Ortuno et al. [12] reported PBDD/Fs found in PBDE technical mixtures heated to low temperatures and in products of combustion of plastic materials containing relatively large quantities of PBDEs. This discrepancy may suggest that PBDD/F formation strongly depends on initial mass of precursors or on some other compounds in the reaction mixture. Watanabe et al. [17] indicated that formation of dioxins from native BDEs might be a complex process involving some intermediate degradation products. Peng et al. [18] found no debromination of BDE 209 in technical mixtures heated up to 250 °C, but 17 different BDE congeners were identified in mixtures heated up to 300 °C. No congeners containing less than five bromine atoms per molecule were observed. Moreover, it was suggested the commonly reported co-occurring congeners are the contaminants of the technical mixtures of this compound. Formation of mixed chlorinated/ brominated DEs during heating of PBDEs was previously reported by Rupp et al. [6] and Weber et al. [19] have also indicated on possible formation of mixed chlorinated/brominated dioxins under similar conditions. PBDEs heated in our experiments in the presence of some chlorine source formed mixed chlorinated/ brominated DEs or even molecules, in which bromine atoms were completely substituted by chlorine ones. Such reactions were observed in the presence of both organic and inorganic sources of chlorine. Dichloromethane or aqueous hydrochloric acid at concentration corresponding to 250 mM of chlorine were used. The reactions were run in flame-sealed glass ampules containing 500 ng of the studied compound. Chlorinated DEs were produced in samples heated at relatively low temperatures. Chlorinated analogues were identified in reaction mixtures of all tested congeners heated at 100 °C.

Substitution of a single Br atom was observed mostly at low temperatures, while heating to higher temperatures gave rise to full Br/Cl substitution. Change in concentration of chlorinated DEs with time of heating of BDE 183 reaction mixtures is shown in Figure 1.

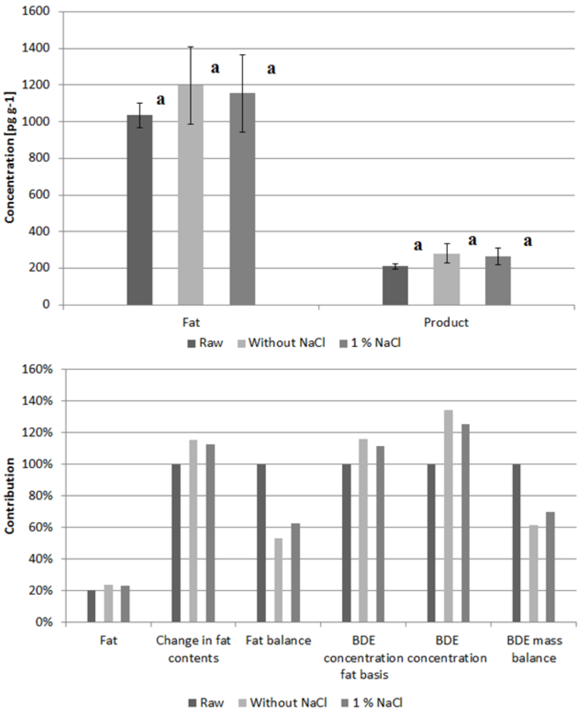
Pork meat samples spiked with known amount of selected BDEs (99, 183 and 209) were grilled in electric or charcoal- fired grill (without any membrane). To evaluate possibility of formation of chlorinated DEs, the oil samples were also heated in the presence of chlorine sources. As can be seen in Figures 2 and 3, mass of lipids in the grilled pork dropped (by 32–47% for coal-fired grill and by 31–51% for electric grill) in result of grilling, but fat contribution relative to dry matter increased (by 8–15% for coal-fired grill and by 7–10% for electric grill). Concentrations of BDE 99 and BDE 183 determined in grilled pork were higher than in raw meat. On the other hand, smaller amounts of BDE 209 were found in grilled pork than in raw meat (probably because of relatively smaller thermal stability of the latter congener).

Figure 1. Time evolution of concentration of BDE 183 (right axis) and of their identified chlorinated analogues (left axis) during heating of reaction mixtures with dichloromethane. Temperature: 100^{O}C, 200^{O}C and 400^{O}C.



However, the found differences in mean concentrations were not statistically significant. BDE 99 and 183 concentrations found after the grilling process normalized to the fresh meat basis were also higher by 4–8% (electric grill) and 22–34% (coal-fired grill). The differences observed for BDE 183 were statistically significant. The observed change of concentration reflected increase of lipid concentration, dry matter contents, and congener concentration in lipids (the latter might be caused by thermal degradation of lipids resulting in drop of their mass). No statistically significant influence of sodium chloride added to the processed meat on the observed concentrations was noticed. Neither any evidence of debromination/formation of lower-brominated BDE congeners nor detectable quantities of brominated dioxins/furans were found after the grilling process. Such observations are in line with results of experiments performed using pure BDE standards. No detectable quantities of brominated dioxins/furans were also found in air/smoke exiting the coal-fired grill during meat processing.

Figure 2. Concentrations of BDE 99 in raw pork and meat grilled on a coal-fired grill (not salted meat and meat with 1% NaCl added).

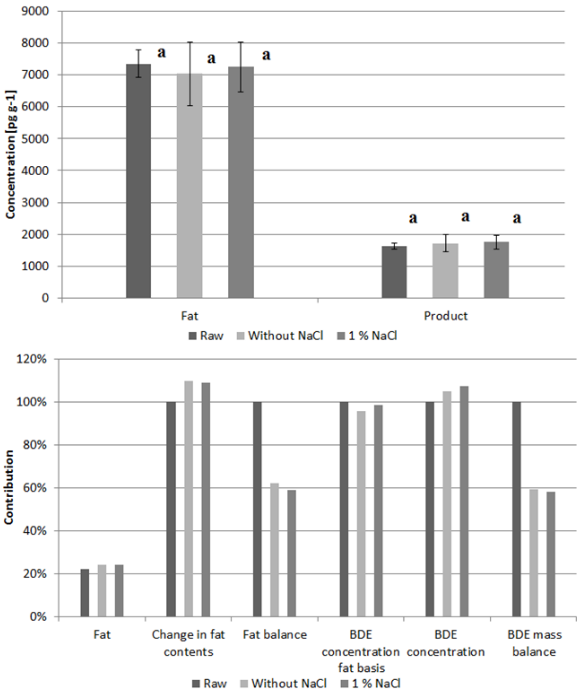


No statistically significant change in concentration of the investigated BDEs was noticed for tested vegetable oil samples heated up to temperatures 60–180 °C during the applied heating times up to 120 min. Some concentration drop observed in samples heated to 300 °C was statistically insignificant, too. The results are in line with those reported for thermally-treated pure BDEs. However, contrary to the latter results we have not detected any PCDEs in any of the investigated cases.

IV. CONCLUSION

Heat treatment of food products may change PBDEs concentration and burden level. However, the observed differences reflect only changes in water/lipids contents and their masses. Model studies have revealed that PCDEs may be formed at high yield from native BDEs heated to even low temperatures. However, no detectable amounts of chlorinated compounds were identified in our food samples exposed to heat in the presence of chlorine. Food processing at actually observed PBDE background levels in food is not likely to be responsible for formation of detectable quantities of either brominated dioxins or furans.

Figure 3. Concentrations of BDE 99 in raw pork and meat grilled on a electric grill (not salted meat and meat with 1% NaCl added).



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