

# FORMATION MECHANISMS OF UNINTENTIONAL PERSISTENT ORGANIC POLLUTANTS MEDIATED BY ORGANIC FREE RADICALS DURING THERMAL-RELATED PROCESSES

Liu Xiaoyun<sup>1,2</sup>, Yang Lili<sup>1</sup>, Liu Guorui<sup>1,2,3</sup>, Zheng Minghui<sup>1,2,3</sup>

<sup>1</sup> Center for Eco-Environmental Science, Chinese Academy of Sciences, Beijing, China, 100085, [xyliu9966@163.com](mailto:xyliu9966@163.com); <sup>2</sup> College of Resource and Environment, University of Chinese Academy of Sciences, Beijing, China, 100049; <sup>3</sup> Hangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, Hangzhou, China, 310000

## Introduction

Unintentional persistent organic pollutants (UPOPs) are known as notorious contaminants for their highly toxic, bioaccumulative, long-distance migration and environmental stable properties. They are found ubiquitous in the environment. Industrial thermal processes include waste incineration, metal smelting, cement kilns co-processing solid waste, etc. are found to be important UPOPs sources. It is worthy to clarify UPOPs formation mechanisms for theoretical support to UPOPs formation control and emission reduction from those sources. Homogeneous reactions at high temperatures (400–800 °C) and heterogeneous reactions at relatively low temperatures (200–400 °C) were widely recognized formation mechanisms of polychlorinated dibenzo-p-dioxins and dibenzo furans (PCDD/Fs), which is a group of typical UPOPs. The heterogeneous reaction mechanism involves *de novo* formation and precursors formation mechanisms. Chlorophenols have been verified to be important precursors of UPOPs formation, especially with transition metals as catalysts. With the detection of environmentally persistent free radicals (EPFRs) during thermochemical processes, UPOPs formation mechanism with EPFRs involved have received more and more attention.

As typical EPFRs, phenoxy radicals, semiquinone radicals, and cyclopentadiene radicals can be stable for a long time, with its half-life measured in hours, days or even months. The relatively strong stability of EPFRs compared to common radicals can be attributed to the stable conjugated structure. Existence of transition metals is proposed to be benefit for EPFRs stability further for the formation of organic free radical–metal ion particle stabilized resonance structures<sup>1</sup>. Toxicities and formation mechanisms of EPFRs are focused currently. The important roles EPFRs play in toxic UPOPs formation during thermal processes are still in its early stage.

Organic free radicals are intermediates in the formation of both EPFRs and UPOPs. As a group of stable products which can be detected during and after thermochemical processes, EPFRs are supposed to be vital intermediates for or competitors to UPOPs formation. UPOPs and EPFRs can both be formed during thermal-related processes. Different types of EPFRs preferentially form different UPOPs. Temperature, existence of transition metals and proportion of oxygen are all vital factors influencing both concentration and distribution of EPFRs and UPOPs<sup>2</sup>. Some of the UPOPs formation mechanism mediated by EPFRs have been proposed. For example, low chlorinated PCDFs could be formed by Langmuir–Hinshelwood mechanism starting with radical–radical reactions, and low chlorinated PCDDs formation through the Eley–Rideal mechanism starting with radical–molecule reactions<sup>3</sup>. Parent and low chlorinated PCNs and PCDFs formation mechanisms from coupling of two chlorinated phenoxy radicals were proposed based on the several detected PCNs and PCDFs distribution<sup>4</sup>. Some of the proposed mechanisms were also verified by theoretical calculation<sup>5,6</sup>. However, experimental identification of intermediate structure of these mechanisms were missing. Other UPOPs formation mediated by EPFRs were still remained to be clarified.

In this research, a simple system was designed in a laboratory scale to simulate the industrial thermal processes with SiO<sub>2</sub> as matrix, 2-chlorophenol (2-CP) as precursor and CuO as catalyst. UPOPs formation mechanism will be focused in this system.

## Materials and methods

In situ thermochemical experiments were conducted on a Bruker EMX-plus X-band electron paramagnetic resonance spectrometer (EPR) to obtain spectrum and concentration of free radicals. The heating experiments of the same CP-SiO<sub>2</sub>-CuO system were conducted in a Tube Furnace to obtain the reaction products. Products outflowed with the airflow were captured by toluene during the whole period. Other formed compounds in the solid residue were extracted by Soxhlet extraction after cooling with toluene as extraction solvent for more than 20 h.

Isotopic dilution high-resolution gas chromatography coupled with high-resolution mass spectrometry (HRGC/HRMS) was used to detect chlorinated polycyclic aromatic hydrocarbons (Cl-PAHs) and UPOPs including PCDD/Fs, polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) formed in the thermal reactions in selective ion monitoring mode.

The collected gas phase products and solid residue products were spiked with clean-up standards (EPA 1613 LCS for PCDD/Fs, EPA 1668 C LCS for PCBs, ECN 5102 for PCNs, mixture of <sup>13</sup>C<sub>6</sub>-9-chlorophenanthrene, <sup>13</sup>C<sub>6</sub>-

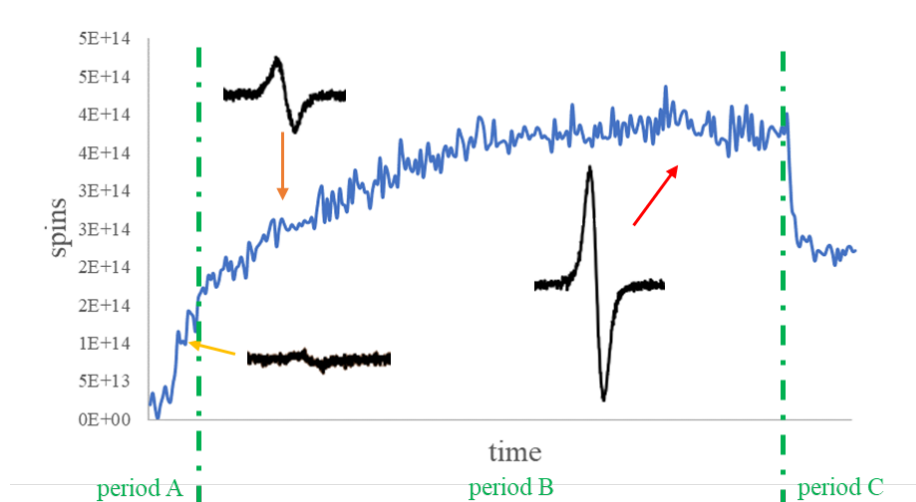
2-chloroanthracene,  $^{13}\text{C}_6$ -1-chloropyrene,  $^{13}\text{C}_6$ -7-chlorobenz[a]anthracene,  $^{13}\text{C}_6$ -7-bromobenz[a]-anthracene, and  $d_9$ -9-bromophenanthrene for Cl-PAHs) before purification.

An acid silica gel followed by a multi-layer silica gel column and an activated carbon column was used for purification of PCDD/Fs, PCBs and PCNs purification. An activated silica gel was used for Cl-PAHs purification. The samples were concentrated to about 20-50  $\mu\text{L}$  on rotating evaporator and nitrogen blower. Internal standards were spiked in the samples before detection (EPA 1613 IS for PCDD/Fs, EPA 1668 C IS for PCBs, ECN 5260 for PCNs,  $^{13}\text{C}_6$ -7,12-chlorobenz[a]-anthracene for Cl-PAHs).

Unknown compounds in the two types of products were also screened on a high resolution GC/Q-TOF MS in the full scan mode. Screened compounds were identified by mass spectrum comparison with the NIST library.

## Results and discussion

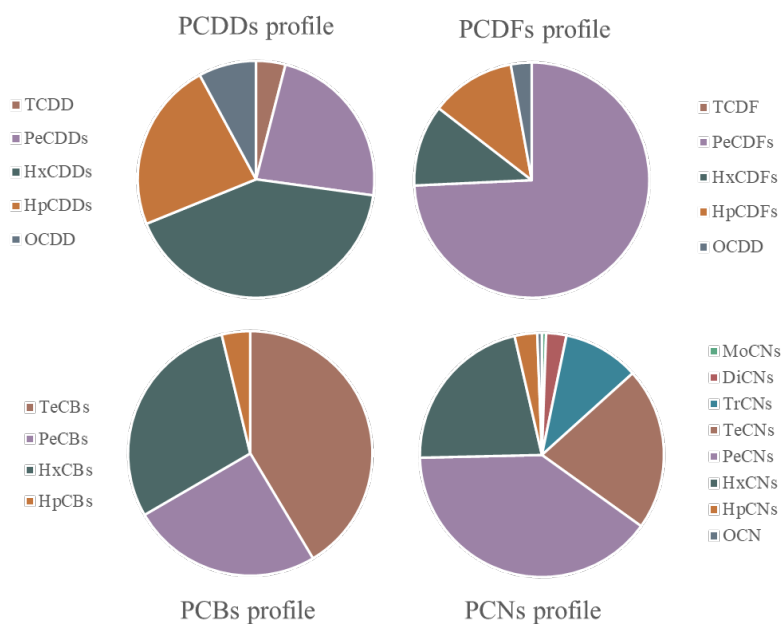
EPFRs were detected during and after cooling of the in situ experiments on EPR. Variation of radical spins with time and temperature was shown in figure 1. The concentration of EPFRs increased significantly with the temperature increased in the heating period (period A). Formed radicals were detected with a slight intensity in this period. When the temperature was maintained at 600K (period B), concentration of EPFRs increased slowly and then maintained. The radical signal got stronger and stronger until it reached a certain level and stayed. Considering the negligible change of peak width, the stronger intensity reflected the higher concentration of free radicals, which was consistent with the variation of radical concentration obtained by the semi-quantitative method. EPFRs were mostly formed in the heating period. During the cooling period (period C), EPFRs concentration first decreased significantly and then maintained at a certain level with the temperature decreased. Cooling led to partial free radical quenching. The remaining final free radicals were more stable in this condition.



**Figure 1.** Change of spins and EPR spectrums of formed free radicals with time and different heating period. Temperature increased from 298 K to 600 K in period A. Temperature maintained at 600 K in period B. Temperature decreased from 600 K to 298 K in period C.

In the same system and condition that EPFRs can be easily formed, Cl-PAHs and many kinds of UPOPs including PCDD/Fs, PCBs and PCNs were also detected. EPFRs and these toxic compounds can be formed simultaneously in the designed chlorophenol-SiO<sub>2</sub>-CuO system under thermochemical conditions. High concentrations of Cl-PAHs, PCDD/Fs, PCBs and PCNs were detected in the collected gas phase product and these chlorinated compounds were hardly detected in the solid residue. Profiles of UPOPs were shown in figure 2.

Total concentration of 18 toxic PCDD/Fs was 1.84  $\mu\text{g/g}$ . 1,2,3,4,7,8-HxCDD was the dominant PCDDs congener and 1,3,4,6,8-PeCDF was the dominant PCDFs congener. The concentration ratio of PCDDs to PCDFs was greater than 1, which was agree with the results of precursor formation mechanism. Total concentration of 75 PCNs was 0.11  $\mu\text{g/g}$ . PeCN were the dominant homolog, followed by HxCN and TeCN. 1,2,3,7,8-PeCN was the dominant PCNs congener. The proportion of low chlorinated and high chlorinated naphthalenes were lower than that of middle chlorinated naphthalenes. The total concentration of 12 dioxin like PCBs (dl-PCBs) was 0.03  $\mu\text{g/g}$ . 3,4,4',5-TeCB was the dominant congener followed by 3,3',4,4',5,5'-HxCB and 2,3,4,4',5-PeCB. Pentachlorinated, hexachlorinated and heptachlorinated were dominant homolog of 7 PCDDs and 11 PCDFs while tetrachlorinated, pentachlorinated and hexachlorinated were the dominant homolog of 12 dl-PCBs and 75 PCNs.



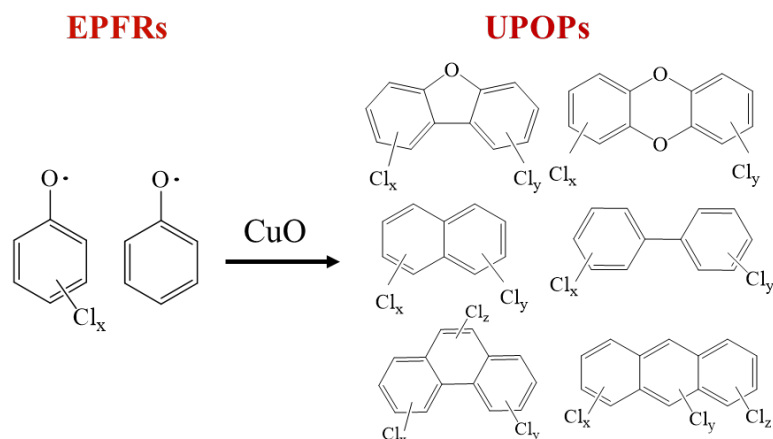
**Figure 2.** Profiles of different chlorinated PCDDs, PCDFs, PCBs and PCNs in the gas phase products.

The 18 common Cl-PAHs were also detected in the gas phase product. The total concentration was 7.61 ng/g, which was lower than that of PCDD/Fs, PCBs and PCNs. Cl-Phe, Cl-Ant, Cl-Flu were important congeners. 9,10-Cl<sub>2</sub>-Phe was the dominant congener followed by 3,8-Cl<sub>2</sub>-Flu. Concentration of dichlorinated Ant, Phe and Flu were higher than the monochlorinated Ant, Phe and Flu, respectively. The dichlorinated congeners in the gas phase products can be formed by two chlorinated benzene ring compounds, or further chlorination of the corresponding monochlorinated congeners.

To obtain more information about the thermochemical reaction, gas phase and solid residue samples with no purification treatment were analyzed on the GC/Q-TOFMS with high resolution. The screened compounds were identified by mass spectrum comparison with the standard spectrum in the NIST library. Benzaldehyde and benzyl alcohol were both identified in gas phase and solid residue samples. In addition to these two compounds, many kinds of methyl biphenyls and other PAHs with alkyl chain, ether bond or carbonyl were also identified in the solid residue sample. The existence of alkyl chains in many compounds indicated the easily occurrence of ring-opening and alkyl chain fracture reactions under the experimental conditions. Contrary to the gas phase sample, nearly no chlorinated compounds was found in the solid residue sample, which was consistent with the results of Cl-PAHs and UPOPs concentration on the HRGC/HRMS.

In the gas phase sample, besides the benzaldehyde and benzyl alcohol, 4 kinds of ortho- and para- substituted phenols were identified with 2-CP was the adopted precursor. 2-CP was the only source of Cl in the simulated system. Formation of higher chlorinated phenols indicated occurrence of both dechlorination and chlorination reactions and potential existence of Cl<sup>•</sup> in the gas phase. Based on this inference, phenoxy radical and chlorinated phenoxy radicals were supposed to be formed in the thermochemical process. Besides high chlorinated PCDD/Fs, DD and low chlorinated PCDDs and PCDFs were also identified. The roughly concentration ratio of PCDDs to PCDFs was also greater than 1, which was matching the results of HRGC/HRMS and accordance with the precursor formation mechanism. Several chloride, hydroxyl biphenyl were also identified in the gas phase sample.

UPOPs and Cl-PAHs formation mediated by EPFRs in the simulated thermochemical process was overviewed in figure 4. The detected EPFRs during the in situ EPR experiments were speculated to be phenoxy and chlorinated phenoxy radicals. Semiquinone radicals were also considered to be exist from resonance of phenoxy radicals. EPFRs were mostly formed in the heating period and UPOPs were more formed in the cooling zone. The obviously decrease of EPFRs concentration in the cooling period was inferred to the participation of EPFRs for UPOPs and other final molecular products formation.



**Figure 4.** UPOPs formation mediated by EPFRs in the simulated thermochemical process.

In this research, EPFRs were verified to be formed during thermochemical conditions, under which many kinds of UPOPs including PCDD/Fs, PCBs and PCNs were easily formed simultaneously. EPFRs were more formed during the heating period. Cooling will lead to partial free radical quenching, which is speculated to participate in UPOPs and Cl-PAHs formation. Dechlorination and chlorination reactions happened commonly in the simulated system. PCDDs were easier to be formed than PCDFs, PCBs, PCNs and Cl-PAHs under the experimental condition. Clarification of the full and detailed UPOPs formation mechanism mediated by EPFRs in this system under thermochemical conditions still need further analysis and validation.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China (grant nos. 21936007).

#### References

1. Dellinger B, Lominicki S, Khachatryan L, et al. (2000) *Proc. Combust. Inst.* 31: 521-528.
2. Liu X, Yang L, Liu G, et al. (2021) *Environ Sci Technol.* 55(10): 6529-6541.
3. Evans C, Dellinger B (2005) *Environ Sci Technol.* 39(13): 4857-4863.
4. Kim D, Mulholland J, Ryu J (2005) *Proc. Combust. Inst.* 30: 1245-1253.
5. Yang L, Liu G, Zheng M, et al. (2017) *Environ Sci Technol.* 51(9): 4999-5007.
6. Xu F, Yu W, Gao R, et al. (2010) *Environ Sci Technol.* 44(17): 6745-6751.