



Influence of the Properties of Macromolecular Carbon on *de Novo* Synthesis of PCDDs, PCDFs, PCBs, and Chlorobenzenes

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ABSTRACT

We examined the influence of the properties of macromolecular carbon on thermochemical *de novo* synthesis of toxic chlorinated aromatic compounds (aromatic-Cl)s, such as polychlorinated dibenzo-*p*-dioxins (PCDDs), furans (PCDFs), biphenyls (PCBs), and chlorobenzenes (CBzs). Six types of macromolecular carbons were prepared. Some activated carbon samples were modified by chemical solvents, such as nitric acid, hydrogen peroxide, sulfuric acid, and urea solutions, to change the properties of the activated carbon. We characterized six macromolecular carbons by surface area (8.8–1540 m²/g), free radicals (N_s , not analyzed to $67.0 \times 10^{19} \text{ g}^{-1}$, $g = 2.0011\text{--}2.0098$), and functional groups (O–H, C–H, C=O, C=C, C–O, and C–OH). Concentrations of aromatic-Cl)s at 300–400°C, such as PCDDs, PCDFs, PCBs, and CBzs, were clearly influenced by the type of macromolecular carbon. Their distribution between the ash/gas phases implied that increasing the surface area mainly enhanced the adsorption capacity of macromolecular carbon, while increasing the number of free radicals mainly enhance the reaction activity of macromolecular carbon. The PCDD/PCDF ratio suggested that various modifications of macromolecular carbon contributed to the generation of PCDDs in addition to the catalytic behavior of copper. Under most conditions, the surface area of macromolecular carbon did not have a strong correlation with the generation of PCDDs, PCBs, and CBzs, but it did show have a correlation with the generation of PCDFs. One of the destructive effects of aromatic-Cl)s resulted from the free radicals in macromolecular carbon. The C=O bond (ca. 1720 cm⁻¹) functional group in macromolecular carbon had no strong correlation with the generation of aromatic-Cl)s, because free radicals had a destructive effect. The functionalities of ether (C–O) or phenolic OH (C–OH) in macromolecular carbon were causative factors in the generation of oxygen-containing aromatic-Cl)s, such as PCDDs and PCDFs.

Keywords: Functional group; Free radical; Surface area; Dioxins; Chlorobenzenes.

INTRODUCTION

Many anthropogenic thermal processes are sources of toxic chlorinated aromatic compounds (aromatic-Cl)s. Municipal solid waste incineration (MSWI) is a well-known source of aromatic-Cl)s, such as polychlorinated dibenzo-*p*-dioxins (PCDDs), furans (PCDFs), biphenyls (PCBs), and chlorobenzenes (CBzs) (Huang and Buekens, 1995; Olie *et al.*, 1977; Shin and Chang, 1999; Huang *et al.*, 2003). Aromatic-Cl)s have been reported to be heterogeneously generated in the postcombustion zone of a MSWI (Addink and Olie, 1995). The presence of chlorine in solid/gas phases is essential for the formation of aromatic-Cl)s generation. Oxygen is also incorporated into the structure of PCDD/Fs and its presence influences their formation. In addition, trace metal compounds (CuCl₂, FeCl₃, CuO, etc.) act as

catalyst-like promoters in the formation of aromatic-Cl)s (Fujimori *et al.*, 2009).

Several studies on the heterogeneous formation of aromatic-Cl)s have considered various carbon sources, and the term *de novo* synthesis is generally used to describe the heterogeneous formation of macromolecular carbon structures via oxidative breakdown (Addink *et al.*, 1995; Hell *et al.*, 2001). Native carbon, activated carbon, sugar coal, charcoal, soot, graphite, aliphatic aromatic, monocyclic aromatic, polycyclic aromatic hydrocarbons (PAHs), and amorphous ¹²C-/¹³C-labeled carbon have been selected as macromolecular carbon sources in various experiments of *de novo* synthesis (Stieglitz *et al.*, 1989a; Milligan and Altwicker, 1993; Addink *et al.*, 1995; Ino *et al.*, 1999; Hell *et al.*, 2001; Weber *et al.*, 2001; Wilhelm *et al.*, 2001). Different macromolecular carbon types can influence the formation of PCDD/Fs. The properties of various carbon types might be important factors controlling the potential formation of aromatic-Cl)s. Graphite with a low [aliphatic]/[aromatic] ratio and crystalline structure has a lower potential

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of PCDD/Fs formation than activated carbon (Stieglitz *et al.*, 1989a). Addink *et al.* (1995) reported the important role of functional groups in forming PCDD/Fs by using three anthraquinone derivatives. The –OH and –COOH groups had a particularly potential to form PCDD/Fs. The –OH group contributed to the selective formation of PCDDs. A study using ^{18}O -labeling of gaseous oxygen revealed that preexisting oxygen in carbon reactants such as PAHs was a major source of the ether group in PCDD/Fs (Wilhelm *et al.*, 2001). Carbon gasification results in a higher potential for the oxidation of various PAHs with the ether group (C–O) compared to the carbonyl group (C=O).

These previous studies focused on the functionalities of macromolecular carbon using simple aromatics with 1–3 aromatic rings. Native carbon in heterogeneous fly ash is believed to possess a more complex system. The large structure of macromolecular carbon is characterized by various indicators such as surface area, free radical, and functional groups (Hontoria-Lucas *et al.*, 1995; Manivannan *et al.*, 1999; Adib *et al.*, 2000; Takaoka *et al.*, 2007). These properties of the large structure of macromolecular carbon can be altered following the application of various chemical solutions including nitric acid (HNO_3), hydrogen peroxide (H_2O_2), sulfuric acid (H_2SO_4), and urea (Otake and Jenkins, 1993; Gomez-Serrano *et al.*, 1994; Gomez-Serrano *et al.*, 1997; Adib *et al.*, 2000; Takaoka *et al.*, 2007). To better understand the oxidative destruction of macromolecular carbon during *de novo* synthesis, developing a quantitative data set related to the properties of macromolecular carbon would be beneficial. To achieve this goal, the modification of “one” original carbon source is a useful method for assessing the influence of the properties of macromolecular carbon.

Oxidative destruction of macromolecular carbon could have the potential to generate various chlorinated compounds (Stieglitz *et al.*, 1989b). Although many studies have reported on the formation of PCDD/Fs and dioxin-like PCBs, other chlorinated compounds have not received such attention. CBzs are well-known precursors of PCDD/Fs (Addink *et al.*, 1995; Tuppurainen *et al.*, 1998). Moreover, highly chlorinated benzenes, such as hexa- and pentachlorobenzenes, are classed as persistent organic pollutants (POPs). In general, CBzs have a one-order higher concentration and a higher volatilization through *de novo* synthesis than PCDD/Fs (Stieglitz *et al.*, 1989b; Fujimori *et al.*, 2009; Fujimori *et al.*, 2010), indicating the atmospheric impact of CBzs from thermal MSWI process.

In this study, we examined the influence of the properties of macromolecular carbon on the *de novo* synthesis of PCDD/Fs, PCBs, and CBzs. Six types of macromolecular carbons were prepared. Some activated carbon samples were modified by chemical solvents such as HNO_3 , H_2O_2 , H_2SO_4 , and urea solutions to change the property of one original activated carbon. We measured surface area, free radicals, and the functional groups of six macromolecular carbons using the Brunauer–Emmett–Teller (BET) method, electron spin resonance (ESR), and Fourier-transformed infrared (FT-IR) spectroscopy, respectively. Concentrations of PCDD/Fs, PCBs, and CBzs after heating experiments were measured by gas chromatography/mass spectrometry.

METHODS

Macromolecular Carbon

Activated carbon made from palm shell (Takeda Pharmaceutical Co., Ltd.) was used in the experiments. We made five types of macromolecular carbon from one original activated carbon using the pretreatments described here. The trace chemical composition of the activated carbon was presented previously (Takaoka *et al.*, 2007). Any organic compounds in the activated carbon were removed by heating at 500°C for 2 hours under a stream of 100% nitrogen gas (50 mL/min). Following the treatment with nitrogen gas, the activated carbon was designated “ $\text{N}_2\text{-AC}$.”

The activated carbon was modified with 70% HNO_3 solution at 70°C for 24 hours and was designated “ $\text{HNO}_3\text{-AC}$.” The activated carbon was modified by using 30% H_2O_2 solution at 30°C for 24 hours and was designated “ $\text{H}_2\text{O}_2\text{-AC}$.” The details of the $\text{HNO}_3\text{-AC}$ and $\text{H}_2\text{O}_2\text{-AC}$ treatments are described elsewhere (Takaoka *et al.*, 2007).

In addition, we also prepared activated carbons modified by H_2SO_4 or urea solutions, which were not reported previously. The detailed procedure for this is described here by reference to previous similar treatments with solutions of H_2SO_4 (Gomez-Serrano *et al.*, 1997) or urea (Adib *et al.*, 2000). When H_2SO_4 was used, 30 g of $\text{N}_2\text{-AC}$ was mixed and heated in 800 mL of 48% H_2SO_4 at 70°C for 24 hours. After decanting the H_2SO_4 , the activated carbon was washed with ultrapure water until the pH became neutral. After verifying that the pH of the supernatant was neutral, the remaining water in the activated carbon was removed by a rotary evaporator, and the activated carbon was stored in a desiccator. The activated carbon treated by the above process was designated “ $\text{H}_2\text{SO}_4\text{-AC}$.” Similarly, activated carbon generated by the same procedure with urea solution (i.e., 400 g urea in 400 mL ultrapure water) at 70°C for 24 hours was designated “Urea-AC.”

Compared with the properties of the various activated carbons, we also purchased graphite powder (special grade). We used these six macromolecular carbons as carbon sources.

Characterization of Macromolecular Carbon

The six types of macromolecular carbon were characterized by the following methods before the quantitative experiment investigating the synthesis of aromatic-Cl_s was conducted. The BET surface areas were obtained from N_2 adsorption–desorption isotherms at 77 K with a vacuum volumetric sorption instrument (ASAP 2400; Micromeritics). Prior to the N_2 sorption analysis, ca. 0.15 g of the samples was preheated at 130°C for ca. 15 hours to remove physically sorbed material from narrow pores.

The ESR spectra of a sample were measured using a JES-TE200 (JEOL) to identify the types and amounts of radicals. The measured amount of sample was limited to 3 mg due to dielectric loss. All measurements were performed at a frequency of 9.443–9.453 GHz and a power of 0.61 mW at $16\text{--}17^\circ\text{C}$ under a nitrogen atmosphere as described in our previous study (Takaoka *et al.*, 2007). The number of spins in macromolecular carbon was calculated by measuring the peak area of the ESR spectrum standardized

by a Mn^{2+} digital marker (ES-DM1). The g value was calculated from the ESR spectrum.

To characterize the functional groups in the samples, infrared spectra were recorded on an FT-IR spectrometer (model 2000; Perkin-Elmer) in a $500\text{--}3700\text{ cm}^{-1}$ wave number range with 100 scans taken at a scan speed of 0.1 s and 4 cm^{-1} resolution. Disks were prepared by completely mixing the sample with potassium bromide (KBr) at a ratio of 1:100 in a mortar and then compressing the mixture under a vacuum using 10-tons oil press.

Model Fly Ash

Simplified model fly ashes were prepared from various macromolecular carbons to assess the potential formation of aromatic-Cl_s. The model fly ash was admixed with macromolecular carbon (5%), cupric chloride dehydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 5%) as a catalyst for the formation of aromatic-Cl_s (Stieglitz et al., 1989a) and silicon dioxide (SiO_2 , 90 wt%) as a base material by grinding in a mortar for ca. 10 min in the proportions determined in our previous research (Fujimori et al., 2009).

Quantification of PCDDs, PCDFs, PCBs, and CBzs

The concentration of PCDDs ($\text{Cl}_4\text{--Cl}_8$ homologs) and PCDFs ($\text{Cl}_4\text{--Cl}_8$) in model fly ashes was analyzed by high-resolution GC/high-resolution MS (HRGC/HRMS) as performed in our previous study (Takaoka et al., 2008). PCBs ($\text{Cl}_2\text{--Cl}_8$) and CBzs ($\text{Cl}_2\text{--Cl}_6$) were analyzed by HRGC/low-resolution MS (models: HP-6890/HP-5973; Hewlett-Packard). Sample pretreatment for the determination of chlorinated aromatic compounds was undertaken according to Japanese Industrial Standards (JIS) K 0311 and 0312.

We placed 5 g of model fly ash into a quartz boat contained within a quartz tube ($120 \times 4\text{ cm}$ internal diameter), which was then placed in a preheated electronic furnace at 300°C and 400°C for 30 min under a flow of 10% oxygen/90% nitrogen delivered at 50 mL/min , to simulate the postcombustion zone of a MSWI. After heating, the concentrations of chlorinated aromatic compounds in the model fly ash residue and in the gas phase, collected in an impinger containing 100 mL of toluene, were analyzed separately. Experimental details were reported in our previous study (Fujimori et al., 2009).

Statistical Analysis

By combining the properties of macromolecular carbon with the generation of aromatic-Cl_s, we assessed the causative factors by which macromolecular carbon generated aromatic-Cl_s. Because surface area, the common logarithm of N_s , and the g value are continuous values, we statistically calculated correlations between these properties of macromolecular carbon and the concentrations of aromatic-Cl_s. Our study involved six types of macromolecular carbons. Therefore, Pearson's correlation coefficient (r) was calculated from scatterplots of only six points (five points for the $\log N_s$) using IBM SPSS Statistics, ver. 21. Generally, $p = 0.05$ is the cutoff value for determining statistical significance. Here, we also decided to use $p = 0.25$ as a looser cutoff value to discuss the "possibility" of correlation with statistical significance because our data set had a small sample size ($n = 5$ or 6), although in future studies, we will undertake more rigorous correlations by using a larger sample size.

RESULTS AND DISCUSSION

Surface Area, Free Radical, and Functional Groups of Macromolecular Carbon

Various macromolecular carbons were characterized by their surface area, free radicals, and functional groups as shown in Table 1. Graphite had the lowest surface area ($8.8\text{ m}^2/\text{g}$), which was consistent with previous reports (Hontoria-Lucas et al., 1995). The graphite therefore had the lowest porosity of the macromolecular carbons. Activated carbon without treatment by a solution ($\text{N}_2\text{-AC}$) had the highest-level surface area of $1530\text{ m}^2/\text{g}$. Our previous study using the same activated carbon reported numerous pores of ca. $10\text{ }\mu\text{m}$ in diameter on the surface of the activated carbon (Takaoka et al., 2008). Compared with $\text{N}_2\text{-AC}$, the activated carbon modified by the HNO_3 solution ($\text{HNO}_3\text{-AC}$) had a smaller surface area ($918\text{ m}^2/\text{g}$). This feature of $\text{HNO}_3\text{-AC}$ might be derived from the destruction of meso- and micropores by oxidation (Takaoka et al., 2008). A similar decrease in surface area was noted following the H_2O_2 treatment ($\text{H}_2\text{O}_2\text{-AC}$). The oxidation effect on the surface area following H_2O_2 treatment was relatively smaller than that following the HNO_3 treatment. In contrast, the surface area of activated carbon did not change following modification with H_2SO_4 and urea solutions ($\text{H}_2\text{SO}_4\text{-AC}$ and Urea-AC). In general, SO_3 generated from H_2SO_4 heated to over 290°C had potential of oxidative breakdown.

Table 1. Surface area, number of spins (N_s), g value, and the functional group of various carbon treatments. "y" indicates that a functional group is present. "na" indicates not analyzed.

Properties	$\text{N}_2\text{-AC}$	$\text{HNO}_3\text{-AC}$	$\text{H}_2\text{O}_2\text{-AC}$	Urea-AC	$\text{H}_2\text{SO}_4\text{-AC}$	Graphite
Surface area (m^2/g)	1530	918	1250	1540	1500	8.8
$N_s (\times 10^{19}\text{ g}^{-1})$	0.00304	67.0	0.0781	0.0160	3.07	na
g value	2.0020	2.0098	2.0011	2.0019	2.0078	2.0084
O–H ($3000\text{--}3520\text{ cm}^{-1}$)		y	y			
C=O (1720 cm^{-1})		y			y	
C=C (1580 cm^{-1})	y	y	y	y	y	y
C–H or O–H (1390 cm^{-1})					y	y
C–O (1270 cm^{-1})				y	y	
C–O or C–OH (1200 cm^{-1})	y	y	y			

However, in this study, the H_2SO_4 solution with activated carbon was heated to 70°C . Therefore, H_2SO_4 -AC did not display a change in surface area. Urea solution also had no oxidation potential at 70°C , although modification by urea was expected to decrease the surface area at higher temperatures (e.g., over 450°C) as reported in Adib *et al.* (2000).

ESR activity was apparent in every macromolecular carbon. Although the number of spins (N_s) of graphite powder was difficult to analyze from the ESR spectrum, the g value was determined as 2.0084 (Table 1). Similar previous measurements reported 10^{19} – 10^{20} g^{-1} as N_s of graphite (Prasad *et al.*, 2000; Smith *et al.*, 2009). The g -value of graphite was determined to be 2.003 and was almost independent of the measured temperatures between 100 K and 300 K (Matsubara *et al.*, 1991). When graphite was milled to powder (10 μm average diameter), the g value was 2.002–2.010 (Matsubara *et al.*, 1996). Therefore, our graphite powder might have the normal properties of a free radical. N_2 -AC produced values of $N_s = 3.04 \times 10^{16} \text{ g}^{-1}$ and $g = 2.0020$. Three activated carbons with surface areas of 1000–2000 m^2/g were previously reported to have ESR activities of $N_s = 1.8 \times 10^{16}$ – $8.9 \times 10^{17} \text{ g}^{-1}$ and $g = 2.0028$ (Manivannan *et al.*, 1999). N_2 -AC with a surface area of 1530 m^2/g was considered to produce reasonable values of N_s and g . Because the g value of N_2 -AC was quite close to that of free electrons (2.0023), the unpaired electron was almost unyoked. HNO_3 -AC produced the highest number of spins ($6.70 \times 10^{20} \text{ g}^{-1}$) and g value (2.0098). This tendency was consistent with our previous results, and modification of activated carbon with HNO_3 solution was thought to contribute to the stable condition of the free radicals (Takaoka *et al.*, 2008). H_2O_2 -AC produced a value of N_s (7.81×10^{17}

g^{-1}) one-order higher than that of N_2 -AC. The g value of H_2O_2 -AC was close to that of N_2 -AC. According to Takaoka *et al.* (2008), free radicals in H_2O_2 -AC do not maintain a stable condition because they are affected by the surrounding gas. For example, the adsorption of oxygen scavenges the free radicals on the surface. Modification of activated carbon by urea solution (Urea-AC) did not produce a large change in the free radicals compared with N_2 -AC. Free radicals in activated carbon were only minimally influenced by the urea treatment. In contrast, for H_2SO_4 -AC, free radicals in the activated carbon dramatically increased. The N_s ($3.07 \times 10^{19} \text{ g}^{-1}$) and g value (2.0078) of H_2SO_4 -AC were higher than those of N_2 -AC.

Yabuta *et al.* (2008) suggested that the free radical content (i.e., N_s) was positively related to the amount of carboxyl ($-\text{COOH}$) functional groups following an analyses of various humic substances using ESR and solid-state ^{13}C nuclear magnetic resonance. HNO_3 -AC and H_2SO_4 -AC produced a stretching of the $\text{C}=\text{O}$ bond at ca. 1720 cm^{-1} , as shown in Fig. 1, which was mainly derived from the carboxyl group (Hontoria-Lucas *et al.*, 1995; Chen *et al.*, 2008; Keiluweit *et al.*, 2010). Therefore, an increase of free radicals in activated carbon might result from the addition of carboxyl groups to the macromolecular carbon matrix using HNO_3 or H_2SO_4 solutions.

Various macromolecular carbons were separately categorized by the characterization of various functional groups (Table 1). The measured FT-IR spectra are shown in Fig. 1. For graphite powder, a band was located at ca. 1580 cm^{-1} , which was assigned to stretching of the $\text{C}=\text{C}$ bond in aromatic components (Hontoria-Lucas *et al.*, 1995; Figueiredo *et al.*, 1999; Adib *et al.*, 2000; Keiluweit *et al.*, 2010). The $\text{C}=\text{C}$ stretching occurred in all macromolecular

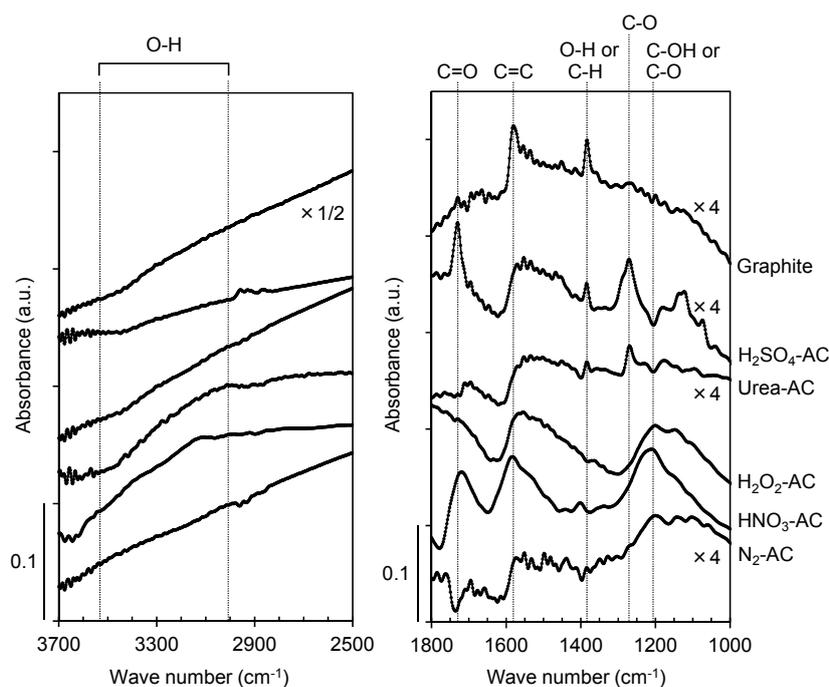


Fig. 1. FT-IR spectra of six macromolecular carbons (1000 – 1800 cm^{-1} and 2500 – 3700 cm^{-1}). Characteristic vibrations are noted.

carbons. Therefore, the aromatic ring, which is the basic structure of aromatic-Cl_s, was contained in each matrix of macromolecular carbon. The band located at ca. 1390 cm⁻¹ was assigned to vibrations of O–H or C–H groups (Gomez-Serrano *et al.*, 1994; Hontoria-Lucas *et al.*, 1995; Guo *et al.*, 2009). The graphite powder used in this study might contain O–H or C–H groups in its carbon matrix. This band at ca. 1390 cm⁻¹ was small or undetected by chemical modifications. The functional groups in (modified) activated carbons differed from graphite. N₂-AC displayed a band at ca. 1200 cm⁻¹ that was derived from stretching of the C–O bond in ether structures or stretching of the C–OH bond in phenolic OH (Fanning and Vannice, 1993; Gomez-Serrano *et al.*, 1994; Gomez-Serrano *et al.*, 1996; Figueiredo *et al.*, 1999; Szabo *et al.*, 2006; Keiluweit *et al.*, 2010). Oxidative modification of macromolecular carbon by HNO₃ and H₂O₂ increased the functionalities of ether (C–O) or C–OH as indicated by the growth of the band peak at ca. 1200 cm⁻¹. In addition, HNO₃-AC and H₂O₂-AC displayed a band at 3000–3520 cm⁻¹, which was assigned to the stretching of

intercalated water molecules in the carbon matrix (Hontoria-Lucas *et al.*, 1995; Guo *et al.*, 2009). A band at ca. 1270 cm⁻¹ was displayed in Urea-AC and H₂SO₄-AC. Although various ether groups are known to exist in the 1000–1300 cm⁻¹ region (Fanning and Vannice, 1993; Figueiredo *et al.*, 1999), the band at ca. 1270 cm⁻¹ was assigned to stretching of the C–O bond in the anhydride and an aryl ether linkage (Smith and Chughtai, 1995; Keiluweit *et al.*, 2010). Oxygen molecules were functionalized in the carbon matrix by various chemical solution techniques.

The Generation of PCDDs, PCDFs, PCBs, and CBzs

The total concentration of aromatic-Cl_s at 300–400°C was clearly influenced by the type of macromolecular carbons. Overall, graphite showed the least potential to form aromatic-Cl_s except for ΣPCBs at 400°C (Fig. 2). A previous study also identified a similar minimal potential of graphite to generate PCDD/Fs compared with activated carbon (Stieglitz *et al.*, 1989a). We also found that graphite had the least potential to generate PCDDs and PCDFs. Therefore, gaseous

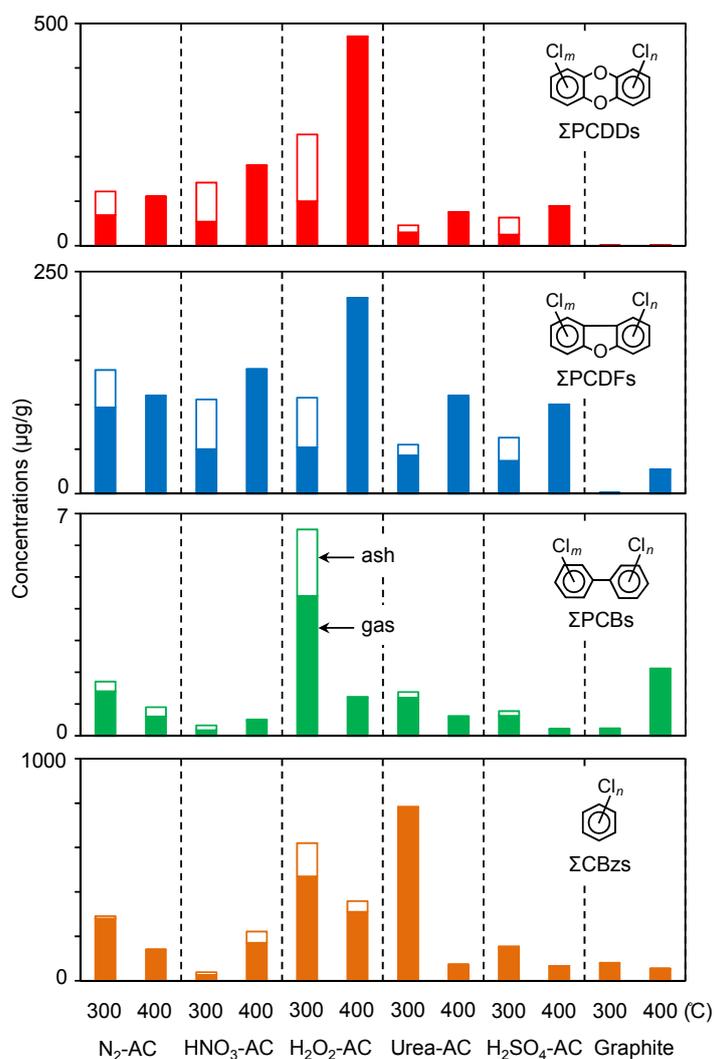


Fig. 2. Total concentrations of PCDDs (Cl₄–Cl₈ homologs), PCDFs (Cl₄–Cl₈ homologs), PCBs (Cl₂–Cl₈ homologs), and chlorobenzenes (CBzs, Cl₂–Cl₆ homologs) from model fly ashes using various macromolecular carbons after heating at 300°C and 400°C. ash, aromatic-Cl_s in residual solid sample by heating; gas, aromatic-Cl_s in toluene liquid in impinger.

oxygen was considered to have less potential for generating PCDDs and PCDFs than macromolecular carbon that contain oxygen within their structure, which is consistent with the results of a similar study by Wilhelm *et al.* (2001). In contrast, the concentrations of Σ CBzs and Σ PCBs generated from graphite were comparable to those from other macromolecular carbons. CBzs and PCBs do not contain oxygen in their structures. The generation of aromatic-Cl_s containing no oxygen was thought to be mainly influenced by the oxidative destruction of macromolecular carbon, which might be caused by gaseous oxygen and the catalytic role of cupric chloride (Takaoka *et al.*, 2005; Fujimori and Takaoka, 2009). Concentrations of Σ PCDFs and Σ PCBs from graphite at 400°C were 22 and 9 times higher, respectively, than that at 300°C. These increasing concentrations of Σ PCDFs and Σ PCBs were observed for all macromolecular carbons tested. It was possibly related with strong relationship between the biphenyl structure and PCDF formation (Wilhelm *et al.*, 2001). In addition, the conversion rate of macromolecular carbon to aromatic-Cl_s was comparable with the conversion rate of PAHs (Weber *et al.*, 2001). It implies possible formation path of chlorinated aromatics via PAHs fragments derived from thermal breakdown of macromolecular carbon.

The macromolecular carbons were distributed in the ash/gas phases of aromatic-Cl_s at 300°C (Fig. 2). The ash/gas ratios of 0.77–1.6 (Σ PCDDs), 0.28–1.1 (Σ PCDFs), and 0.15–0.83 (Σ PCBs) achieved from macromolecular carbons were larger than those of 0.16 (Σ PCDDs), 0.21 (Σ PCDFs), and 0.11 (Σ PCBs) achieved from graphite. PCDDs, PCDFs, and PCBs remained in the residual solid phase of macromolecular carbon after heating at 300°C. In contrast, the ash/gas ratio of CBzs from macromolecular carbons showed 0.0047–0.50 which included that from graphite (0.035). It might be caused from high volatilization of CBzs. HNO₃-AC displayed the highest ash/gas ratios of aromatic-Cl_s. HNO₃-AC had the smallest surface area and the highest number of free radicals (Table 1). H₂O₂-AC with a smaller surface area, and H₂SO₄ with a higher N_s , also produced higher ash/gas ratios. Therefore, aromatic-Cl_s might be held on macromolecular carbon based on their adsorption capacity and the reaction activity of macromolecular carbon as generated by modification of the surface area as well as by the number of free radicals.

Graphite produced the lowest PCDD/PCDF ratio as shown

in Fig. 3. The PCDD/PCDF ratio produced from graphite decreased from 300°C (0.29–0.37) to 400°C (0.027–0.056) by one order of magnitude. The influence of thermochemical interactions between oxygen in a gas stream and an unmodified macromolecular carbon (i.e., graphite-like carbon matrix) results in a more selective formation of PCDFs than PCDDs, which tendency was also shown in case of PAHs (Iino *et al.*, 1999; Weber *et al.*, 2001). So, oxygen in the starting carbon matrix might be a key to generate PCDDs. Previous studies have reported that the chemical form of cupric chloride changed to cupric oxide (CuO) at 400°C in model fly ash (Fujimori and Takaoka, 2009) and CuO catalyzed a dimerization of PCDFs via their precursors (Gullett *et al.*, 1990; Fujimori *et al.*, 2009). Therefore, the lowest PCDD/PCDF ratio at 400°C for graphite might result from the role of CuO as a catalyst. Although thermochemical changes in the chemical form of Cu were believed to occur in each macromolecular carbon, no clear selectiveness of PCDF formation was found in macromolecular carbons. The treatments with N₂-, HNO₃-, Urea-, and H₂SO₄-AC produced almost the same concentrations of Σ PCDDs and Σ PCDFs because the PCDD/PCDF ratios were between 0.57 and 1.6. H₂O₂-AC generated two to three times more PCDDs than PCDFs. The difference between macromolecular carbon and graphite might be derived from the modification of various physicochemical properties of this study (Table 1) and other possible properties. Various modifications of macromolecular carbon contributed to the generation of PCDDs in addition to the catalytic behavior of copper.

The homolog distributions of PCDDs and PCDFs indicated a dominance of highly chlorinated homologs (particularly Cl₈) in all samples (Fig. 4). So, total toxicity of PCDD/Fs was relatively small, compared with total concentration of them. Cupric chloride had a strong potential to promote highly chlorinated dioxins and furans in model fly ash (Fujimori *et al.*, 2009). Therefore, the characteristic distribution patterns of PCDDs and PCDFs were mainly derived from the high chlorination of carbon as promoted by cupric chloride. Although the type of macromolecular carbons, ash/gas phases, and the difference of temperature only minimally influenced the homolog distribution patterns of PCDDs and PCDFs, the concentrations of PCDDs and PCDFs were dependent on these factors (Fig. 2). The role of cupric chloride might be a key factor in determining the

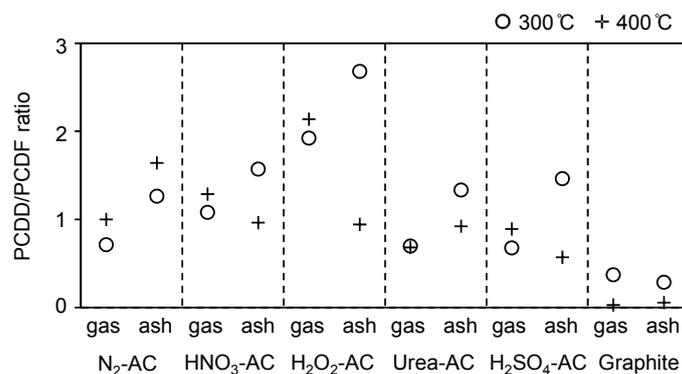


Fig. 3. PCDD/PCDF ratios of model samples using various macromolecular carbons after heating at 300°C and 400°C.

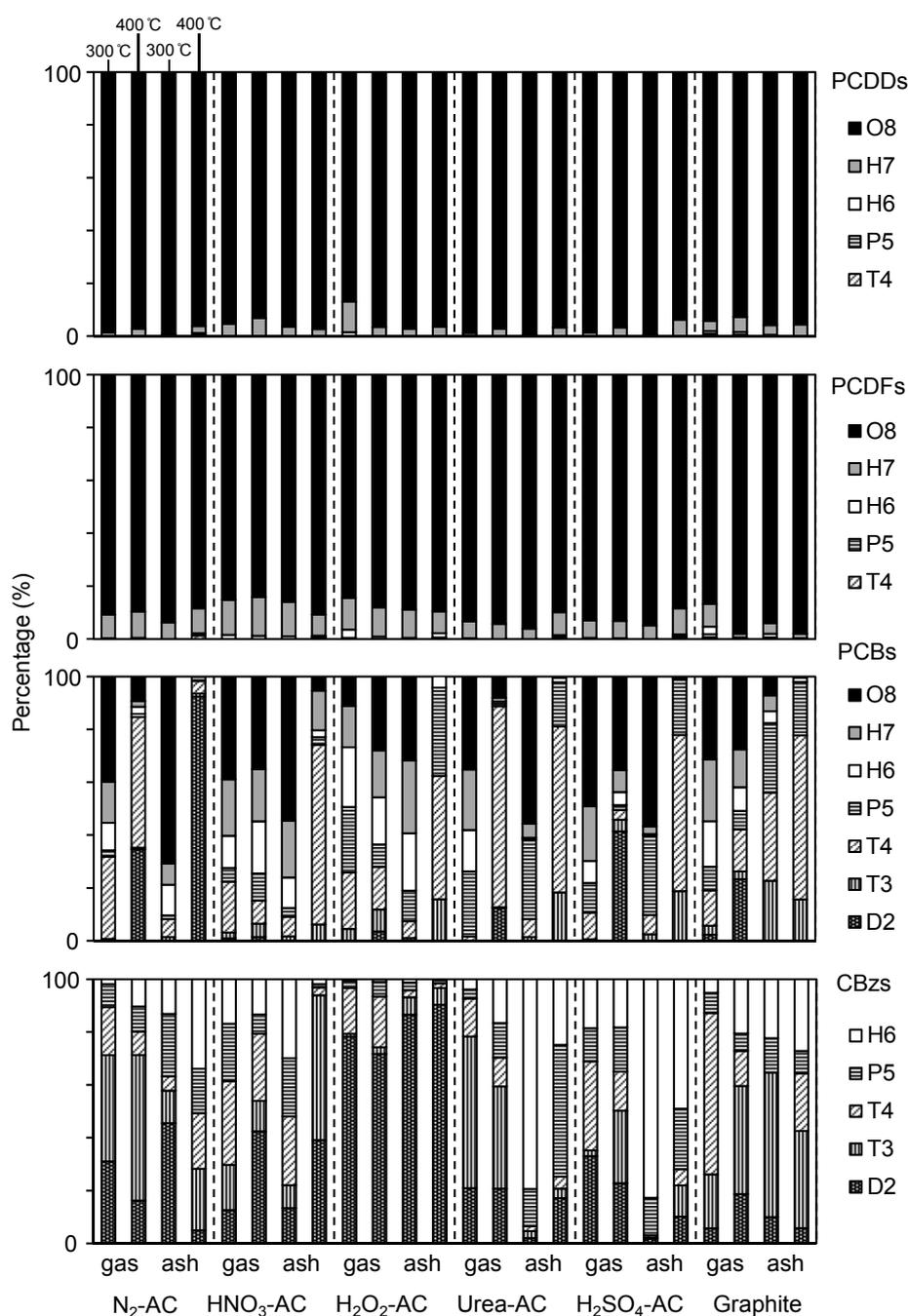


Fig. 4. The homolog distribution patterns of PCDDs, PCDFs, PCBs, and CBzs from model fly ashes using various macromolecular carbons after heating at 300°C and 400°C.

formation path of PCDDs and PCDFs, according to the similarity of their homolog distribution pattern. The properties of macromolecular carbon were considered to contribute to the thermochemical reaction activity between cupric chloride and the carbon matrix, distribution between the ash/gas phases, and the temperature dependence of PCDDs and PCDFs. In contrast, PCBs and CBzs had various homolog distributions for the different types of macromolecular carbons. Therefore, the formation paths of PCBs and CBzs might be derived from not only cupric chloride but also the properties of macromolecular carbon.

Influence of the Properties of Macromolecular Carbon

Few statistical and possible correlations were identified between the surface area and concentrations of aromatic-Cl_s (Table 2). Σ PCDFs in the ash phase at 400°C and Σ PCBs in the gas phase at 400°C displayed significant negative correlations with surface area ($r = -0.91$, $p = 0.01$ and $r = -0.84$, $p = 0.04$, respectively). Possible positive correlations with the surface area were identified in the Σ PCDDs of the ash phase at 400°C ($r = 0.60$, $p = 0.21$) and Σ PCDFs in the gas phase at 300°C ($r = 0.72$, $p = 0.11$). Considering the effect of the surface area of macromolecular

Table 2. Correlations between the properties of macromolecular carbon and concentrations of aromatic-Cl's. *, $p < 0.05$. #, $p < 0.25$.

	ΣPCDDs						ΣPCDFs						ΣPCBs						ΣCBZs						
	300°C		400°C		300°C		400°C		300°C		400°C		300°C		400°C		300°C		400°C		300°C		400°C		
	gas	ash	gas	ash	gas	ash	gas	ash	gas	ash	gas	ash	gas	ash	gas	ash	gas	ash	gas	ash	gas	ash	gas	ash	
Surface area	<i>r</i>	0.48	0.27	0.27	0.60#	0.72#	0.39	0.52	-0.91*	0.34	0.2	-0.84*	0.34	0.12	0.19	-0.05									
	<i>p</i>	0.33	0.61	0.61	0.21	0.11	0.44	0.29	0.01	0.51	0.71	0.04	0.52	0.82	0.72	0.92									
log N_s	<i>r</i>	-0.25	0.18	0.01	-0.68#	-0.57	0.33	0.03	-0.72#	-0.43	-0.21	-0.41	-0.58	-0.14	-0.02	0.54									
	<i>p</i>	0.68	0.78	0.98	0.21	0.31	0.59	0.97	0.17	0.47	0.73	0.5	0.3	0.83	0.98	0.35									
<i>g</i>	<i>r</i>	-0.59#	-0.3	-0.45	-0.61#	-0.54	-0.16	-0.49	0.38	-0.75#	-0.58#	0.06	-0.4	-0.5	-0.42	0.09									
	<i>p</i>	0.22	0.56	0.38	0.2	0.27	0.77	0.32	0.46	0.09	0.23	0.91	0.44	0.31	0.4	0.87									

carbon on the generation of aromatic-Cl's was difficult because we did not conclude whether the correlation was positive or negative. However, we suggest that under most conditions, the surface area of macromolecular carbon does not have a strong potential to generate PCDDs, PCBs, and CBZs, but a potential exists to generate PCDFs. This suggestion agrees with the results of Hinton and Lane (1991), who reported no correlation between the surface area of fly ash and the concentration of PCDDs.

We found a tendency for negative correlations between the properties of free radicals and the concentrations of aromatic-Cl's. ΣPCDDs, ΣPCDFs, ΣPCBs, and ΣCBZs were negatively correlated with log N_s and *g* values under at least one experimental condition. ΣPCDDs in the ash phase at 400°C and ΣCBZs in the gas phase at 300°C displayed significant or possible correlations with log N_s and *g* values (Table 2). A possible negative correlation with log N_s was identified for ΣPCDFs in the ash phase at 400°C ($r = -0.72$, $p = 0.17$); possible negative correlations with the *g* value were identified for ΣPCDDs in the gas phase at 300°C ($r = -0.59$, $p = 0.22$) and for ΣPCBs in the gas/ash phases at 300°C ($r = -0.75$, $p = 0.09$ in gas phase; $r = -0.58$, $p = 0.23$ in ash phase). Free radicals in the carbon matrix were reported to have the potential for dechlorination from penta- and hexachlorobenzenes (Takaoka *et al.*, 2007; Gao *et al.*, 2008). Brubaker and Hites (1998) mentioned the importance of the OH radical to remove PAHs, PCDDs, and PCDFs through PAH-OH and PCDD/H-OH reactions. Our results showing negative correlations between free radicals in macromolecular carbon and the concentration of aromatic-Cl's are consistent with these previous findings. Therefore, we concluded that one of the destructive effects of aromatic-Cl's resulted from the free radicals in the macromolecular carbon.

The influence of functional groups in the macromolecular carbon on the generation of aromatic-Cl's was assessed by a statistical t-test (without homoscedasticity) comparison of concentrations of aromatic-Cl's with and without functionalities. The stretching of the C=C bond at 1580 cm^{-1} could not be assessed because all macromolecular carbons had this functional group. Because sample sizes in the subgroup were $n = 2-4$ (Table 1), we also considered statistical results by two cutoff criteria: $p = 0.05$ (significant) and $p = 0.25$ (probable). The O-H bond at 3000–3520 cm^{-1} , C=O bond at ca. 1720 cm^{-1} , C-H or O-H at 1390 cm^{-1} , and C-O bond at ca. 1270 cm^{-1} did not show clear differences between two subgroups, with or without these functionalities in macromolecular carbon. The carboxyl (-COOH) functional group has been reported to have the potential to generate PCDD/Fs by using anthraquinone derivatives whose structure is composed of two aromatic rings (Addink *et al.*, 1995). Although the C=O bond (ca. 1720 cm^{-1}) was considered to be mainly derived from the carboxyl group, this functional group had no strong potential to generate aromatic-Cl's. Our statistical results contradict the results of Addink *et al.* (1995). HNO₃-AC and H₂SO₄-AC were macromolecular carbons with a C=O bond at ca. 1720 cm^{-1} and also had the highest amounts of free radicals (Table 1). Free radicals have a role in the destruction of aromatic-Cl's as noted above. If the carboxyl group promoted the generation of aromatic-

Cl_s, net concentrations of aromatic-Cl_s did not show a dramatic increase because of the destructive effect of free radicals. Macromolecular carbon in this study differed from the simple aromatic structure used in the previous study (Addink *et al.*, 1995). Macromolecular carbon might have more free electrons resulting from the defects in the carbon matrix than such simple aromatic structures.

The strong potential to selectively generate aromatic-Cl_s by C–O or C–OH functional groups at ca. 1200 cm⁻¹ was one of our most important findings. Fig. 5 shows that these functional groups significantly ($p < 0.05$) or probably ($p < 0.25$) contributed to the formation of oxygen-containing aromatics such as PCDDs and PCDFs in the gas/ash phases at each temperature, except for Σ PCDFs in ash at 400°C. In contrast, the generation of PCBs (no oxygen in its structure) was not influenced by these functional groups. Although the structure of CBzs also has no oxygen, concentrations of Σ CBzs at 400°C were probably influenced by these functional groups in the ash/gas phases. Overall, note that functionalities of ether (C–O) or phenolic OH (C–OH) in macromolecular carbon were causative factors in the generation of oxygen-containing aromatic-Cl_s. The

C–O bond at ca. 1270 cm⁻¹ was also derived from ether groups, but did not influence the formation of aromatic-Cl_s. Phenolic OH (C–OH) in macromolecular carbon might be a more important causative factor. However, a need exists to determine the differences between ether bonds at various wave numbers such as ca. 1200 and ca. 1270 cm⁻¹ of the FT-IR spectrum. 1,2-Ethers (i.e., epoxides) on the carbon matrix have been identified in graphite oxide, which might have a similar structure to the macromolecular carbon oxidized in this study (Szabo *et al.*, 2006; Dreyer *et al.*, 2010). So, similar ethers may form in our macromolecular carbon.

CONCLUSIONS

In this study, we examined various properties of macromolecular carbon and assessed the interrelations between these properties and the formation of aromatic-Cl_s. We characterized six macromolecular carbons by surface area, free radicals, and functional groups. Concentrations of aromatic-Cl_s at 300–400°C were clearly influenced by the type of macromolecular carbons. From the distribution

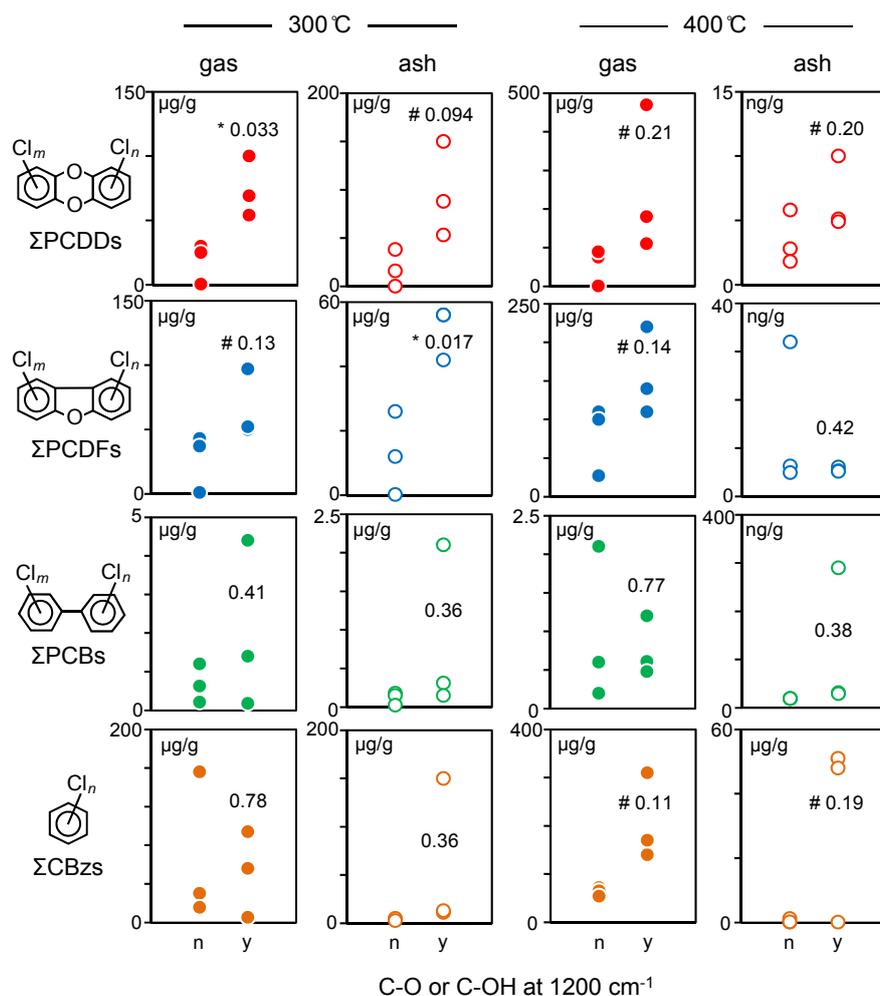


Fig. 5. Influence of C–O or C–OH functional groups at 1200 cm⁻¹ on the formation of PCDDs, PCDFs, PCBs, and CBzs. “n” indicates no C–O or C–OH functional groups; “y” indicates having the functional groups. Inside numbers of graph boxes are statistical p values (t-test without homoscedasticity). *, $p < 0.05$. #, $p < 0.25$.

between the ash/gas phases, increasing surface area might mainly cause adsorption capacity of macromolecular carbon and increasing number of free radicals might mainly cause the reaction activity of macromolecular carbon. The PCDD/PCDF ratio suggested that various modifications of macromolecular carbon contributed to the generation of PCDDs in addition to the catalytic behavior of copper. Under most conditions, the surface area of macromolecular carbon did not have a strong potential to generate PCDDs, PCBs, and CBzs, but a potential to generate PCDFs was noted. One of the destructive effects of aromatic-Cl_s resulted from the free radicals in macromolecular carbon. The C=O bond (ca. 1720 cm⁻¹) functional group in macromolecular carbon had no strong potential to generate aromatic-Cl_s because of the destructive effect of free radicals. The functionalities of ether (C–O) or phenolic OH (C–OH) in macromolecular carbon were a causative factor in the formation of oxygen-containing aromatic-Cl_s such as PCDDs and PCDFs. A need exists to determine more rigorous statistical relationships for the properties of macromolecular carbon by using larger sample sizes in future studies.

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