

Determination of Dechlorane Plus in Serum from Electronics Dismantling Workers in South China

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Received June 8, 2009. Revised manuscript received October 11, 2009. Accepted October 29, 2009.

Previous studies have reported high serum concentrations of polybrominated diphenyl ethers in residents of an electronic waste (e-waste) dismantling site in Guiyu town, South China. In this study, serum levels of Dechlorane Plus (DP), a chlorinated flame retardant of growing concern, were measured in residents of this region, and compared to those of a matched cohort from a nearby region in Haojiang, where fishing is the dominant industry. DP was detected in all the serum samples, with concentrations ranging from 7.8 to 465 ng/g lipid (median: 42.6 ng/g) and 0.93 to 50.5 ng/g lipid (median: 13.7 ng/g) in Guiyu and Haojiang, respectively. The Pearson's correlation coefficient between DP and decabromodiphenyl ether showed a positive relationship in Guiyu ($r = 0.931$, $p < 0.01$), but no correlation in Haojiang ($r = 0.321$, $p = 0.34$). The average *anti*-DP fractional abundances (f_{anti} ratio) were 0.58 ± 0.11 and 0.64 ± 0.05 for Guiyu and Haojiang, respectively ($p < 0.01$). Tentatively identified dechlorination product ($[-Cl + H]$) was found in 19/40 serum samples (11/20 for Guiyu, 8/20 for Haojiang). These results suggest that the Guiyu and Haojiang cohorts experienced different dominant exposure routes. It is also possible that DP could bioaccumulate in a stereoselective manner, and undergo dechlorination metabolism. To the best of our knowledge, this is the first study to report DP levels in human serum. Further studies are needed to confirm the results of this study.

Introduction

During the past decade, many studies have indicated that some halogenated flame retardants (HFRs), especially polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls, persist in the environment and can bioaccumulate in biota, including in humans (1, 2). The European Union and the United States have therefore initiated regulations aimed at phasing out the production and usage of penta- and octa-BDE technical mixtures (3, 4). The Stockholm Convention also recently declared penta- and octa-BDE commercial mixtures and hexabromobiphenyl to be per-

sistent organic pollutants. However, the increasing demand for flame retardants means that other new or unregulated flame retardants could enter the marketplace as replacements (5, 6). It is necessary to consider the environmental fate and risk assessment of new emerging HFRs.

Dechlorane Plus (DP) is an unregulated chlorinated flame retardant, first introduced into the market in the 1960s to replace the toxic Dechlorane or Mirex. Commercial DP comprises two isomers (*syn*- and *anti*-), and is mainly used for coating electrical wires and cables, for connectors used in computers, and as a plastic roofing material (7). Although DP has been classified as a high production volume substance by the United States Environmental Protection Agency (8), it has received little attention until recently. DP has been detected in the air, in fish, in herring gull eggs, and in sediments from the Great Lakes region (9–12). Tomy et al. studied the different isomers of DP in food webs in Lake Winnipeg and Lake Ontario (13), and suggested that the isomers were bioavailable in the sediment and had different biomagnification potentials in different parts of the food web. They found clear differences in bioaccumulation potentials between *syn*- and *anti*-isomers in juvenile rainbow trout (14). Furthermore, Zhu et al. found that the levels of DP in residential indoor dust were several times higher than those in the Great Lakes sediments (15). Since some DP-containing products are primarily used indoors, this exposure route suggests a high potential for DP to enter the body through the ingestion of indoor dust.

Although DP is sold worldwide, information on the extent of environmental contamination of DP in biota is sparse and most of the published studies are from studies in North America (9, 10, 13, 14). Qiu and Hites recently found that DP concentrations in bark samples from Korea and China were relatively high, compared with those in North America (16), suggesting that the compound may also be manufactured or released in Asia. Levels of atmospheric DP in 97 Chinese urban and rural sites implied that open burning of e-waste could be a potential source of DP emission in some rural sites (17). This study is part of our ongoing research into organic contaminants at e-waste recycling sites in China. Our previous studies indicated that e-waste dismantling workers had much higher concentrations of PBDEs, especially decabromodiphenyl ether (BDE-209), than previously reported (18, 19). DP isomers have physicochemical properties similar to those of BDE-209 (7), and dismantling workers with high levels of BDE-209 could also accumulate DP isomers. The current study investigated serum DP levels in residents of an e-waste dismantling region (Guiyu, South China), where 80% of the families worked in e-waste recycling, and compared them with levels in a matched cohort from a nearby region, where fishing was the dominant industry (Haojiang). To our knowledge, no previous studies have reported DP concentrations in human serum.

Experimental Section

Serum Samples. Serum samples were collected from residents at two sites in 2005. A detailed description of the sampling areas has been given elsewhere (18). In brief, the first cohort consisted of 20 residents from an e-waste dismantling region, Guiyu town, Shantou City, Guangdong Province. Eighty percent of the families in Guiyu town were engaged in recycling work using primitive methods (including chipping and melting plastics without proper ventilation, burning coated wire to recover copper, removing electronic components from printed circuit boards, and burning unsalvageable materials in the open air). The second cohort

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TABLE 1. Concentrations of Dechlorane Plus(DP) and BDE-209 and Different f_{anti} Values in Serum Samples from an e-Waste Dismantling Region (Guiyu) and a Nearby Region (Haojiang)

compound	median		mean		minimum		maximum	
	Guiyu	Haojiang	Guiyu	Haojiang	Guiyu	Haojiang	Guiyu	Haojiang
<i>syn</i> -DP	17.1	5.1	16.2	4.3	2.7	0.35	236	17.6
<i>anti</i> -DP	21.2	8.6	22.5	7.5	5.1	0.54	229	32.9
f_{anti}^a	0.53	0.64	0.57	0.63	0.40	0.57	0.77	0.78
ΣDP^b	42.6	13.7	39.8	11.8	7.8	0.93	465	50.5
BDE-209 ^c	69.4	17.0	70.6	18.1	ND	ND	1255	245
BDE-209 ^d	83.5	18.5	NA	NA	ND	ND	3436	337
BDE-209 ^e	310	86	340	130	ND	ND	3100	370

^a *anti*-DP/*anti*-DP + *syn*-DP. ^b The sum of *syn*-DP and *anti*-DP. ^c This study. ^d From reference 19. ^e From reference 18; NA: Not Available; ND: Not Detected.

consisted of 20 residents of Haojiang district, Shantou City, Guangdong Province, about 50 km east of Guiyu, where fishing was the predominant industry.

Before sampling, all participants were informed of the procedure and provided signed consent. Blood samples were taken from each volunteer by medical professionals using BD Vacutainer serum tubes (with clotting agent and polymer separator). Samples were then centrifuged, immediately frozen, and kept at -20°C until analysis. The volunteers' ages ranged from 23 to 67 years, and 73% were male (27% female).

Chemicals and Materials. Individual solutions of the *syn*- and *anti*-isomers (50 $\mu\text{g/mL}$, in toluene, purity >95%) were purchased from Wellington Laboratories (Guelph, ON, Canada). BDE-209, decachlorodiphenyl ether (PCB-209), and the ^{13}C mass labeled PCB-208 were obtained from Cambridge Isotope Laboratories (Andover, MA). 4-HO-PCB-72 was obtained from AccuStandard Inc. (New Haven, CT). All calibration standards and spiking solutions were prepared by serial dilution in *n*-hexane using volumetric flasks. Solvents and other chemicals used in the analysis of human samples were: *n*-hexane (pesticide grade, Fluka; Germany); methyl *tert*-butyl ether (MTBE) and 2-propanol (HPLC grade; Sigma-Aldrich, Germany); silica gel (63–200 μm , Merck; Germany); sulfuric acid (99.9%; Sigma-Aldrich); hydrochloric acid (37%; Sigma-Aldrich). Sodium sulfate and potassium chloride (analytical grade, Xilong Chemical Factory of Guangdong) were stored in sealed containers after baking at 450°C .

Sample Cleanup and Analysis. The methods used for sample extraction and cleanup have been described in detail previously (18, 20, 21). Briefly, surrogate standards (PCB-209 and 4-HO-PCB-72) were first added to the sera (5 g) in a Teflon separating funnel and denatured using hydrochloric acid and propan-2-ol. The samples were then extracted three times with hexane/ MTBE (1:1). After combining the extracts, the phenolic and neutral compounds were separated using an aqueous solution of potassium hydroxide (0.5 M in 50% ethanol). The neutral fractions were treated with concentrated sulfuric acid, followed by a sulfuric acid-impregnated silica gel column (silica/sulfuric acid 2:1 w/w; 1 g). DP and BDE-209 were eluted with 8 mL of hexane followed by 10 mL of hexane/dichloromethane (1:1, vol/vol). The final extracts were concentrated to 20 μL under a gentle nitrogen stream, and a known amount of internal standard (^{13}C -PCB 208) was added before injection.

The phenolic fractions were derivatized with an excess of diazomethane solution at room temperature for one night, then further cleaned with sulfuric acid-impregnated silica gel (silica/sulfuric acid 2:1 w/w; 1 g) using 12 mL of hexane/dichloromethane (1:1, vol/vol) as the eluent. The final extracts were concentrated to 20 μL under a gentle nitrogen stream and a known amount of internal standard (^{13}C -PCB 208) was added before injection.

Samples were analyzed for the two DP isomers and BDE-209 using an Agilent 7890 series gas chromatograph coupled to an Agilent 5975C mass spectrometer (GC/MS) using negative chemical ionization (ECNI) in the selected ion monitoring (SIM) mode. Manual injection (1 μL) was made in the pulse splitless mode with a purge time of 2.0 min. The injection port and the GC to MS transfer line were held at 280 and 290°C , respectively. A 15-m DB-5-HT MS column (250 μm i.d., 0.25- μm film thickness; J&W Scientific, Folsom, CA) was used for DP analysis. The GC oven temperature program was as follows: held at 110°C for 5 min, $20^{\circ}\text{C}/\text{min}$ to 200°C , held for 4.5 min, and then $7.5^{\circ}\text{C}/\text{min}$ to 300°C , and held for 16 min. The following ions were monitored: m/z 475.7 and 473.7 for the internal standard (^{13}C -PCB 208), m/z 498 and 500 for PCB-209, m/z 653.7 and 651.7 for DP, m/z 619.7, 617.7, 583.7, and 585.7 for the dechlorination metabolites of DP, m/z 79, 81, 486.7, and 488.7 for BDE-209.

QA/QC. The peaks were identified and quantified only if the GC retention times matched those of the standard compounds to within 0.1 min, the signal-to-noise ratio was >5, and the isotope ratio between the two monitored ions was within 15% of the standard value. DP was analyzed using ^{13}C -PCB208 as an internal standard. Since there was no obvious difference in extraction efficiencies between DP and the lesser chlorinated PCB, we used recovery of the PCB surrogate as an indicator of DP recovery. The spiked PCB recoveries averaged 91–108%. Laboratory blanks, using fetal bovine serum, were treated and analyzed in the same way as the regular samples and constituted about 20% of the total samples analyzed. The DP concentrations in the blank samples were undetectable or <1% of the average value. Concentrations were not blank- or recovery-corrected.

Statistical Analysis. The concentrations of all target compounds were reported on a lipid weight basis. Statistical analysis was performed using SPSS 15.0 software. Statistical significance was defined as $p < 0.05$.

Results and Discussion

Levels of DP. Recent studies have indicated that DP can bioaccumulate in the biota, e.g., in lake food webs, fish, and herring gull eggs (9, 10, 13). These results raise concerns over the potential bioaccumulation of DP in humans. Using purified analytical solutions of individual isomers as standards, we determined the serum DP concentrations from residents of Guiyu and Haojiang. A pooled serum sample from the reference population from Guangzhou, a typical urban city in South China, was also included for DP screening analysis. DP isomers were detected in the pooled sample, but the concentration was below the limit of quantitation. Table 1 summarizes the serum levels of DP and BDE-209 in residents of Guiyu and Haojiang. DP was detected in all serum samples. The sum of the serum concentrations of the *anti*- and *syn*- isomers (ΣDP) ranged from 7.8–465 ng/g lipid

TABLE 2. Correlation Matrix for Serum Samples from an e-Waste Dismantling Region (Guiyu) and a Nearby Region (Haojiang), Determined Using Pearson's Simple Correlation Tests^a

variable	samples from Guiyu			variable	samples from Haojiang		
	<i>anti</i> -DP	ΣDP ^b	BDE209		<i>anti</i> -DP	ΣDP	BDE209
<i>syn</i> -DP	0.897** (<i>p</i> < 0.01)	0.971** (<i>p</i> < 0.01)	0.976** (<i>p</i> < 0.01)	<i>syn</i> -DP	0.984** (<i>p</i> < 0.01)	0.993** (<i>p</i> < 0.01)	0.241 (<i>p</i> = 0.32)
<i>anti</i> -DP		0.977** (<i>p</i> < 0.01)	0.845** (<i>p</i> < 0.01)	<i>anti</i> -DP		0.998** (<i>p</i> < 0.01)	0.224 (<i>p</i> = 0.36)
ΣDP			0.932** (<i>p</i> < 0.01)	ΣDP			0.231 (<i>p</i> = 0.34)

^a Correlations determined using individual samples. ^b The sum of *syn*-DP and *anti*-DP. ** Statistically significant (*p* < 0.01).

(median: 42.6 ng/g) and 0.93–50.5 ng/g lipid (median: 13.7 ng/g) for Guiyu and Haojiang, respectively. The median concentration of ΣDP was three times higher in Guiyu than in Haojiang, consistent with the expected elevated exposure due to dismantling of e-waste products. The maximum serum DP concentration in Guiyu was 465 ng/g lipid. This is the highest reported concentration so far reported from biota or human samples.

Serum ΣDP concentrations were not correlated with age in either the Guiyu or Haojiang samples. However, a previous study on serum PBDE levels in this region did find a positive correlation with age (significant at the 95% level) in Haojiang, though no correlation in Guiyu. According to the results of the questionnaire, most of the dismantling workers in Guiyu were temporary migrants from other parts of China and had worked there for various lengths of time. It is therefore possible that DP exposure was largely associated with the recent expansion of the e-waste industry in this region (over the past decade), and people of all ages will have been exposed for a similar period of time. The pattern was similar in Haojiang, and it is possible that the heavier DP was transported via air from Guiyu to Haojiang. It is important to point out that, since the number of participants in this study was relatively small, these associations must be interpreted with caution (18).

DP shows similarities with BDE-209, with a high molecular weight and high log_{K_{ow}} (9.3), and it is thus interesting to compare the environmental fates and behaviors of these two chemicals. Recent studies have demonstrated that both DP and BDE-209 were predominantly sorbed into the sediment or distributed in the particle phase (11, 12, 15, 17). To provide more information on the routes of human exposure in Guiyu and Haojiang, BDE-209 and DP concentrations were determined simultaneously (Table 1). Levels of BDE-209 in this study were comparable with those reported previously for this region (18, 19): the median values were 69.4 and 17.0 ng/g lipid for Guiyu and Haojiang, respectively, which were higher than the DP concentrations in the same samples. These discrepancies were likely to be the result of differences in the production and usage volumes between the two compounds. Correlations between BDE-209 and DP isomers in all the serum samples were analyzed using Pearson's correlation matrices (Table 2). The results showed that ΣDP and BDE-209 in Guiyu were positively correlated (*r* = 0.931, *p* < 0.01), suggesting that residents in Guiyu may be exposed to these via the same dominant routes. Food consumption is not thought to be the main route of human exposure in Guiyu, because most food is bought in from other regions. Thus, inhalation of DP from the air and from dust is likely to be more important. Our preliminary tests verified that the DP levels in the air and in indoor house dust in Guiyu were high. The correlation between ΣDP and BDE-209 in Haojiang, however, was poor (*r* = 0.321, *p* = 0.34). This lack of correlation may be due to the different sources (air pollution by long-range transport or agricultural application to food

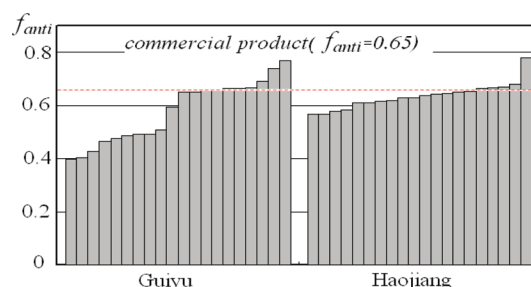


FIGURE 1. f_{anti} values for all serum samples from an e-waste dismantling region (Guiyu) and a nearby region (Haojiang). The red line indicates the f_{anti} value of the commercial product derived from the literature.

crops, fish, and poultry). It is possible that atmospheric transport of DP from Guiyu may contribute to inhalational exposure, but ingestion could be the main exposure route. Further studies are needed to qualify and quantify the exposure routes and the potential health risks to humans.

DP Isomer Profiles. Technical DP has two conformational isomers: *syn* (U-shaped) and *anti* (chair-shaped). The isomer ratios f_{anti} in the serum as determined in the environmental matrix can be defined as follows:

$$f_{anti} = [anti\text{-DP}] / ([anti\text{-DP}] + [syn\text{-DP}])$$

The individual isomer concentrations and f_{anti} values in the serum samples are shown in Table 1 and Figure 1. As shown in Table 1, the average f_{anti} values (mean ± one standard deviation) were 0.58 ± 0.11 and 0.64 ± 0.05 for Guiyu and Haojiang, respectively. The f_{anti} values in Haojiang ranged from 0.57 to 0.78, with relatively little variation (Figure 1). In contrast, the f_{anti} values in Guiyu varied greatly (0.40–0.77), with 8 of 20 serum samples having f_{anti} values lower than the minimum value found in Haojiang. Statistical analysis using independent-samples *t*-tests showed that the f_{anti} values differed significantly (*p* < 0.005) between samples from the two cohorts, suggesting that they may suffer from exposure to different sources. DP may have been subjected to stereoselection in the environment before entering the body via inhalation, ingestion, or dermal contact. Although the three industrial formulations of the technical DP product only differ in terms of particle size and not in composition, different f_{anti} values have been reported in the literature. Hoh et al. determined an f_{anti} value for the technical DP products of 0.75, whereas other studies have reported an f_{anti} value of 0.65 (16, 17). A study of airborne DP across 97 Chinese urban and rural areas found f_{anti} values of 0.68 and 0.66, respectively, which were close to those measured in the Haojiang serum samples in this study. The relatively low f_{anti} values in Guiyu might be associated with a low f_{anti} DP in the environmental matrix. In Guiyu, workers dismantle e-waste using primitive methods, including burning coated wire to recover copper

and burning unsalvageable materials in the open air. According to OxyChem's product information, DP will start to thermally decompose at temperatures above 285 °C. The burning process could lead to decomposition of DP technical mixtures at e-waste sites, resulting in changes in the f_{anti} values due to the different physical or chemical properties of the two isomers. Stereoselective photodegradation of DP could also occur; Sverko et al. performed a simple UV exposure study of individual DP and showed that *anti*-DP was degraded more readily than *syn*-DP (12).

Limited information has so far been available on the stereoselective biodegradation or biotransformation of DP in biota samples. Previous studies have produced conflicting results. Stereoselective enrichment of *syn*-DP (low f_{anti} value) might occur in Lake Ontario (whole body) smelt and alewife, and in Lake Erie fish (9, 13). Hoh et al. (9) further suggested that the chemical structure of the *anti*-DP isomer should be more susceptible to biological attack than the less sterically hindered *syn*-DP isomer. Other evidence for stereoselective enrichment of *syn*-DP came from *Diporeia* and sediment from Lake Ontario (13). *Diporeia* are benthic organisms, and contamination of sediments was thought to be their primary exposure route. The relatively low f_{anti} value (0.704) of *Diporeia* compared to those of sediment (0.860) implied that stereoselective accumulation may have occurred. However, Sverko et al. and Qiu et al. reported stereoselective enrichment of *anti*-DP in the surface sediment and in sediment cores from the lower Great Lakes (11, 12). Although we found significant differences between the f_{anti} values in serum samples from Guiyu and Haojiang, we were unable to draw any conclusions regarding the possible stereoselective biotransformation of DP in human body. Further in vivo and in vitro studies are needed to confirm the bioaccumulation trend of the two isomers in the biota and in human samples.

Possible DP Metabolites. We detected relatively high levels of DP in the electronics dismantling workers, and we therefore hypothesized that DP might produce metabolites in the serum. This is possible because (1) DP has physical and chemical properties similar to some halogenated organic contaminants such as PBDEs and PCBs, and many studies have verified that hydroxylated metabolites of PCBs and PBDEs can be detected in the biota and in serum/milk samples (23, 24); (2) several in vivo and in vitro studies using liver subcellular fractions have shown that reductive debromination of PBDEs can occur in fish, rats, and birds (20, 25–28). Before investigating the presence of DP metabolites in this study, we conducted two control experiments to see if the sample treatment procedures or instrumental analysis produced any metabolites, using individual *anti*- and *syn*-DP (1000 µg/L). The results showed that no dechlorinated compounds or hydroxy- or MeO-DP were produced as a result of the sample cleanup procedures. To determine if reductive dechlorination or hydroxylated metabolites of DP were formed in humans, several serum samples from electronics dismantling workers were isolated and screened using GC/ECNI-MS. We detected no hydroxylated metabolites in the phenolic extracts, suggesting that no metabolic oxidation occurred, or that any metabolites were below the detection limit. In the neutral fraction, the molecular weight of reductive dechlorinated DP was calculated and the corresponding m/z ion fragment clusters (619.7/617.7) and (585.7/583.7) related to $[-Cl + H]$ and $[-2Cl + 2H]$ species were monitored using SIM mode. Typical GC/ECNI-MS chromatograms are shown in Figure 2A and B; a new unidentified peak was found with retention times between those for *syn*- and *anti*-DP (Figure 2B). To further identify this unknown compound, full-scan mass spectra of this peak were obtained in ECNI mode. The characteristics of the peak were similar to those of DP, except that the molecular ion

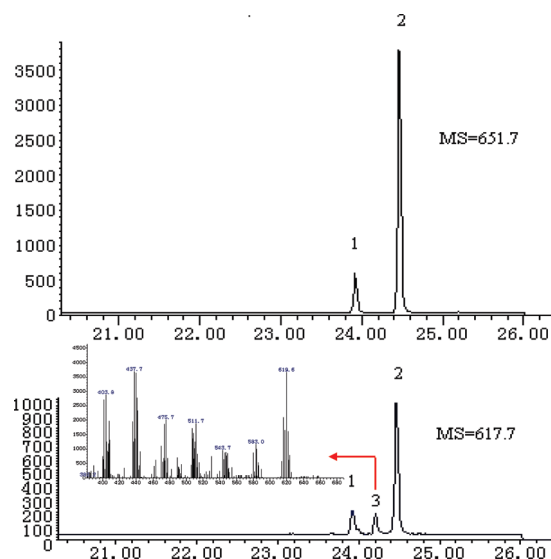


FIGURE 2. Representative selected ion mass (SIM) chromatogram for the worker samples. 1: *syn*-DP; 2: *anti*-DP; 3: signify $-1Cl$ dechlorination DP species. The inserted picture is the mass spectrum of the $-1Cl$ dechlorination DP species for pooled worker samples.

had a lower 34 amu, which could be due to the loss of a chlorine atom and the addition of a hydrogen atom. The same peak was also reported by Sverko et al. in sediment from the lower Great Lakes (12). After analysis using high resolution TOFMS, they tentatively identified this peak as a $-1 Cl$ dechlorination product of DP. If the unidentified compound in the pooled serum was the dechlorinated metabolite of *anti*-DP, it could partially explain the lower variation in f_{anti} values, compared with that in the DP commercial mixture. Another possible explanation for the unknown peak is that DP dechlorination could occur via photolytic or thermal decomposition in the environmental matrix, and then enter the body through ingestion, inhalation, or dermal exposure.

We detected DP in 40 serum samples, and the unidentified peak was present in 19 of the 40 samples (11 of 20 from Guiyu town and 8 of 20 from Haojiang town). Due to a lack of authentic standards, the peak could not be quantified. To our knowledge, this is the first report of the DP dechlorination compound in biota and human samples, but more studies are needed to confirm this result. Further attention should also be paid to this and other dechlorination products in environmental and biomonitoring research. Degradation will alter the physicochemical properties of DP; e.g., the K_{ow} will decrease as the molecular weight decreases. This will in turn affect the environmental fate and transport of DP, leading to changes in its bioaccumulation and toxicological effects.

Acknowledgments

This study was financially supported by the Chinese Academy of Sciences (KZCX2-YW-403), the National Basic Research Program of China (2008CB418205), the National Science Foundation of China (40590392, 40873075), the Earmarked Fund of the State Key Laboratory of Organic Geochemistry (SKLOG2008A03). This is contribution No. IS-1129 from GIGCAS.

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ES901672M