In Situ Formed Soot Deposit as a Carbon Source for Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans

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The aim of this study was to investigate the role of in situ formed soot deposits generated during a combustion process for the formation of polychlorinated dibenzo-pdioxins and dibenzofurans (PCDDs/Fs). In situ formed soot deposits were generated in an entrained flow reactor by using a sooting methane (CH₄) flame (sooting phase), with or without chlorine doped into the flame, and fly ash added into the gas phase. The presence of fly ash in the soot deposit was found to be critical, as a catalyst for formation and/or a chlorinating agent. The presence of chlorinated aromatic structures in the soot matrix was not enough to promote de novo formation of PCDDs/Fs without the presence of fly ash. PCDFs were formed via direct release of the molecule backbone structure from the soot. PCDDs were formed via a similar mechanism as well as an equally important formation pathway of condensation reactions of C₆ compounds. The formation rate of the soot/ash deposit was still at half its original activity 34 h after the deposits were formed, suggesting a persistent de novo formation occurring for a long time after the sooting incidences (memory effect).

Introduction

Reaction studies with field-collected or artificial fly ash in microscale quartz reactors (1-5) have demonstrated formation de novo of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/Fs) from carbon, chlorine, and catalysts. Experiments under more realistic combustion conditions of time and temperature, in which fly ash and ashbound soot are formed in situ, are necessary to clarify the role of carbon sources and structures contributing to PCDD/F emissions.

Fly ash/soot formed during combustion contains a complex, macromolecular carbon matrix that can interact with the gas phase by adsorbing and desorbing volatile and semivolatile compounds, such as polyaromatic hydrocarbons (PAHs), during the continuous carbon oxidation reactions. Indeed, studies on individual PAHs, in the presence of cata-

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lysts, such as perylene, coronene, anthracene, and chloroanthracene have shown significant formation of PCDDs/Fs (mainly PCDFs) (3, 6-8). PCDD/F byproducts can be formed via carbon oxidation reactions, either from direct release (volatilization) of the C₁₂ backbone ring structure or via volatilization, condensation, and subsequent reaction of smaller carbon fragments. Past efforts to understand the origin of carbon in de novo PCDD/F formation using a mixture of ¹²C and ¹³C amorphous carbon added to an artificial fly ash showed no scrambled ¹²C and ¹³C PCDF within the benzenic structure (9), confirming that the three-ring carbon "backbone" of the PCDF molecule is derived from large ($\geq C_{12}$) carbon structures (e.g., PAHs) present in the matrix rather than from a composite product of smaller carbon structures. The PCDDs, however, resulted in both unmixed (all ¹²C₁₂ or all ¹³C₁₂ structures) and mixed (¹²C₆ plus ¹³C₆) structures, indicating an additional formation (9) pathway other than direct release of the PCDD backbone from the fly ash's carbon matrix. These results, however, are in apparent contradiction with others' results (10), although these other authors attributed this discrepancy to their inability to sufficiently mix the ¹²C and ¹³C reactants. Further experiments (9) suggested that the mixed ¹²C₆/¹³C₆ PCDD structures were the result of an additional formation pathway via a surface condensation of an aromatic ring structure, such as polychlorinated phenol (PCPh), followed by reaction with a fly ash-bound aromatic structure.

A link between soot formation and PCDD/F levels has been demonstrated through both laboratory experiments (*11*, *12*) and field measurements (*13*). This may provide a partial explanation for unpredictably high and temporally persistent PCDD/F yields in waste incinerators, sometimes referred to as a "memory effect" (*13–15*). The newly formed soot/fly ash matrix present on the walls of the incinerator, due to a poor combustion incident, could then act as an active carbon source for formation of PCDDs/Fs, even a long time after the incident has passed.

Significant questions remain regarding the importance of de novo reactions for the total PCDD/F emission in an incinerator. The focus of this paper is understanding the mechanistic aspects of de novo synthesis with in situ formed soot and fly ash mixtures, such as what carbon structures ($C_{6,} \geq C_{12}$, or $< C_{6}$) are involved in such formation and the role of gas-phase chlorine. The importance of de novo formation with respect to time for PCDD/F emissions is also addressed.

Materials and Methods

The total net output of PCDDs/Fs emitted (i.e., a function of formation, destruction, and desorption reactions occurring simultaneously) via de novo synthesis from solid carbon derived from both combustion-generated in situ formed soot and municipal waste combustor fly ash was studied in an entrained flow reactor (EFR). The EFR consists of a horizontal reactor (HR) equipped with a diffusion-type burner and a vertical reactor (VR). A constant temperature of 1000 °C was employed in the HR, while a quenched profile, 650–240 °C, was used in the VR to simulate postcombustion conditions. A detailed description of the EFR can be found elsewhere (*5*).

Prior to all de novo experiments, in situ formed soot deposits on the walls of the VR were generated by combustion of methane (CH₄) at an equivalence ratio (Φ) of 0.86 in the presence or absence of fly ash or gas-phase chorine (Cl₂) (termed the "sooting phase"). Thus, a soot deposit with or without preexisting organic chlorine (C–Cl) bonds and with or without catalytic activity (fly ash) was generated in the

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TABLE 1. Operating Conditions Used in the Sooting Phase and the de Novo Experiment^a

parameter	setting							
Sooting Phase								
CH ₄ flow	1.0 L/min							
O ₂ flow	2.3 L/min, burner O_2 ; 1.0 L/min, secondary O_2							
N ₂ flow	6.7 L/min							
Cl_2 flow (10% in N ₂)	0 or 25 mL/min (equal to 0 or 200 ppm Cl ₂ added)							
total flow	11 L/min							
burner equivalence ratio, Φ	0.86 ^b							
fly ash feeding	0 or 1 a/h							
combustion time	60 min							
temperature in HR/VR	1000 °C/550-240 °C, avenched							
gas-phase residence time, HR/VR	0.7 s/1.0 s							
D	De Novo Experiment							
O ₂ flow	0 or 3.3 L/min							
N ₂ flow	7.7 or 11 L/min							
Cl_{2} flow (10% in N ₂)	25 mL/min (equal to 200 ppm Cl ₂ added)							
total flow	11 L/min							
sampling time	120 min							
temperature in HR/VR	1000 °C/550-240 °C							
gas-phase residence time, HR/VR	0.7 s/1.0 s							

^a All units are presented at STP. ^b Due to the chemical properties of CH₄ and the burner constrution, a significant amount of soot is formed at a Φ of 0.86.

EFR depending on the conditions employed in the sooting phase. Combustion of CH₄ can result in an unstable diffusion flame and varying amounts of soot formation despite a rather low value of Φ (0.86) (16).

Isotopically labeled ¹³CH₄ (99% purity, Cambridge Isotope Laboratories, CAS No. 6532-48-5) and ³⁷Cl₂ gas (95% purity, Cambridge Isotope Laboratories, CAS No. 13981-73-2) were employed in selected experiments to study the importance of carbon and chlorine forms, respectively, for de novo formation of PCDDs/Fs. No yields are reported for experiments conducted with labeled ¹³CH₄ or ³⁷Cl₂; the levels are semiquantitative since only external standards could be employed and, thus, only valid for relative comparisons. Results are presented as relative homologue profiles, calculated as percentages of the homologue molar yields to the total PCDD and PCDF molar formation.

Table 1 lists the operating conditions used in the sooting phase and the experimental settings used for the de novo experiments. In all experiments except where noted, a toluene-extracted (EX) fly ash was fed into the VR simultaneously with the formation of the soot deposit, to provide a catalytic environment. The amount of chlorinated organics present in the EX ash was virtually negligible (less than 50 pmol/g of PCDDs/Fs). The toluene extraction reduced the total amount of carbon to 1.0 wt % as compared to the 1.2 wt % present in the as-received ash (a detailed description of the EX ash can be found in Wikström et al. (5)). Each de novo experiment was conducted for 120 min (unless otherwise indicated) in a N₂ or air environment with or without 200 ppm Cl₂ added into the gas environment (Table 1). It should be noted that low parts per million levels of oxygen could be present in the N₂ environment due to unavoidable small leaks in the experimental setup.

The samples from each de novo experiment consisted solely of the collected gases since no soot generation or fly ash feeding occurred during the actual experiments. In addition, the sampled values represent only emissions, and may not reflect the additional formation that remains within the deposits. The cleanup and analyses of the mono–octa-PCDD/F homologues were conducted according to a slightly modified version of U.S. EPA Method 0023a (*17*). A highresolution gas chromatograph (Hewlett-Packard 589)/lowresolution mass spectrometer (Agilent 5971) with a 60 m J&W DB dioxin column and single-ion monitoring (SIM) was used for the PCDD/F analysis. To ensure unambiguous results, the SIM ion windows were modified to include all possible PCDD/F ions, irrespective of isotopic distribution, for the experiments conducted with ${}^{37}Cl_2$ and ${}^{13}CH_4$.

Results and Discussion

Table 2 lists the amount of PCDDs and PCDFs sampled, expressed as picomoles per minute (pmol/min), formed in each experiment conducted, where the denominator represents the sampling time. The molar-based, average degree of chlorination ($\#Cl_{PCDD}$ and $\#Cl_{PCDF}$) is also listed to indicate the effect of changes in the experimental conditions on the homologue profile.

Origin of Chlorine for de Novo Formation of PCDDs/Fs. De novo formation of PCDDs/Fs in an air/200 ppm Cl₂ environment on a soot/ash matrix, formed with or without the presence of gas-phase Cl₂ during the sooting phase, results in about the same PCDD/F yields (experiment 1b vs experiment 5). Soot formation in the presence of Cl₂ results in a prechlorinated soot matrix (existing C-Cl bonds prior to the de novo experiment), while the soot/ash deposit generated without Cl₂ likely has significantly lower C-Cl amounts on the soot. This is supported by the reported percent level uptake of gas-phase chlorine by carbon (18), while carbon chlorination by chloride in fly ash alone results in only parts per million levels of organic chlorine (without the addition of gas-phase chlorine) (19). The similar PCDD/F yields irrespective of initial C-Cl amounts in the soot/ash deposits suggest that fast reactions between the solid matrix and the gas-phase chlorine (1 s gas-phase residence time in VR) occur during the de novo experiment. The importance of fast gasphase chlorine reactions for de novo formation of PCDDs/ Fs is thoroughly discussed in a related paper (20).

The initial chlorine content of the soot matrix (prechlorinated vs unchlorinated) was observed to affect the PCDD/F homologue distribution (but not the overall yields). Significantly higher yields of octachlorinated dibenzofuran (OCDF) and octachlorinated dibenzo-*p*-dioxin (OCDD) congeners were formed in experiments conducted with the prechlorinated soot compared to the unchlorinated soot, despite the fact that both experiments were conducted with supplementary Cl_2 (200 ppm) added into the air environment (Figure 1).

The participation of preexisting C–Cl bonds in the soot matrix versus chloride in the fly ash for PCDD/F formation

TABLE 2. Experimental Matrix and Measured Yields of PCDDs/Fs from de Novo Experiments on in Situ Formed Soot Deposits^a

	experimental matrix				measured yields				
expt no.	deposit	surface	[CI ₂] (ppm)	gas phase	soot amt ^b (mg)	PCDD amt (pmol/min)	PCDF amt (pmol/min)	#CI _{PCDD}	#CI _{PCDF}
1a	CI-soot	EX	200	air	413	9	92	7.7	7.5
1b	CI-soot	EX	200	air	203	10	43	6.5	5.6
1c	CI-soot	EX	200	air	44	2	9	7.5	7.4
1d	CI-soot	EX	200	air	99	8	38	7.2	7.1
1e	CI-soot	EX	200	air	291	20	107	7.2	6.7
1f	CI-soot	EX	200	air	83	18	63	7.0	6.5
2	CI-soot	EX	0	air	125	8.0	47	7.3	7.1
3	CI-soot	EX	200	N ₂	103	5.4	41	7.6	7.2
4	CI-soot	EX	0	N_2	88	1.1	7	7.3	6.7
5	soot	EX	200	air	166	9	31	6.8	5.8
6	CI-soot	none	0	N_2	NA	BDL	BDL	ND	ND

^a BDL = below the detection limit, ND = no data, and NA = not analyzed. The experiments were conducted in random run order to avoid systematical errors; thus, the experimental number is not equal to the run order. ^b Amount of soot detected in the M23 train during the sooting phase of the EFR prior to the de novo experiment.



FIGURE 1. Relative PCDD/F homologue profile formed de novo in an air/200 ppm Cl_2 environment with or without preexisting C-CI bonds in the soot matrix.

was further studied by generating a CH₄ flame soot doped with 100 ppm isotopically labeled ${}^{37}Cl_2$. EX ash was simultaneously fed into the VR as a catalyst and a native chloride (${}^{35}Cl$) source. De novo formation of PCDDs/Fs from the ${}^{37}Cl$ soot/ ${}^{35}Cl$ ash deposit was studied by exposing the soot/ash deposit to an air environment and sampling for 60 min. A homologue profile dominated by the tetrachlorinated and higher chlorinated homologues resulted, with consistently 1–2 Cl atoms in each congener originating from the fly ashbound chloride (i.e., ${}^{35}Cl$); this finding is in agreement with previous work (*12, 20*) designed to study the role of various chlorine species involved in PCDD/F formation. The majority of the chlorine was derived from the ${}^{37}Cl$ -chlorinated soot deposit, consistently nearly 78% and 85% of all chlorine in the tri- to octa-CDFs and tri- to octa-CDDs, respectively.

The consistent participation of the native and labeled chlorine within the PCDD/F products in these three experiments suggests that the same predominant chlorination pathway occurs despite the differences in experimental conditions. One possible pathway for ³⁷Cl in the PCDD/F molecule could be via formation of additional metal chloride (Me³⁷Cl) complexes in the soot/ash matrix, which have been shown in other studies to be very active and necessary for de novo formation of PCDDs/Fs and low-temperature carbon oxidation (*3*, *21–23*). Another probable pathway is that the labeled gas-phase chlorine directly forms new, chlorinated carbon (C⁻³⁷Cl) bonds in the soot/ash carbon matrix.

The amounts of DF and DD (i.e., unchlorinated dibenzofurans and dibenzo-*p*-dioxin structures) formed were analyzed in a select number of samples from the EFR. Levels below the detection limit were observed in all samples, consistent with the observed declining homologue pattern from tri- to monochlorinated DD/DF for all samples analyzed in this study (examples of two average profiles are presented in Figure 1). Thus, chlorination of the carbon macromolecular matrix appears to be critical for the release of the PCDD/F carbon backbone structure from the carbon matrix, a reaction step closely related with the definition of de novo formation. The highly chlorinated structures are sufficiently resistant to the oxidation process to be released from the carbon matrix intact.

Role of Fly Ash and in Situ Formed Soot for de Novo Formation of PCDDs/Fs. Two carbon sources were available for formation of PCDD/F when a fly ash/soot mixture was present in the VR (experiments 1–5). However, the amount present as fly ash carbon (1.0 wt %) was estimated as being between 20 and 100 times less than the amount of soot carbon. Consequently it was not a surprising result that more than 98% of the PCDDs/Fs detected were found to originate from the soot carbon in an experiment conducted with a labeled [¹³C]soot/native [¹²C]fly ash mixture. The relative contribution of each carbon source (soot and fly ash) to the total PCDD/F formation was determined by a direct comparison of the GC/MS ion signals corresponding to the characteristic peaks of each mono- to octacongener within each sample.

The role of fly ash was demonstrated by comparison of two experiments done with and without fly ash added during the sooting phase. Nondetectable levels of PCDDs/Fs were found in an experiment conducted on a matrix consisting of solely a Cl-laden soot deposit (no added fly ash) produced with a sooting CH₄ flame doped with 200 ppm Cl₂ during the preconditioning sooting phase (experiment 6). However, significant levels of PCDDs/Fs were detected in an identical experiment (experiment 4) performed with the presence of fly ash, showing the importance of fly ash as a catalyst for PCDD/F formation. Thus, in the absence of catalytic fly ash, the presence of chlorinated and/or nonchlorinated aromatic carbon structures in the soot deposit and the addition of gas-phase Cl₂ are not sufficient to form detectable amounts of PCDDs/Fs, a result in agreement with a previous study (11). It should be noted that a new vertical quartz reactor tube was used for the nonash experiment. Significant formation has been observed in a cleaned reactor (previously exposed to fly ash), without the subsequent addition of fly ash, due to catalytic residues on the quartz tube wall (12).

Importance of the Soot Structure for de Novo Formation of PCDDs/Fs. Table 2 presents six experiments (experiments 1a-1f) conducted at the same de novo condition (air/200 ppm Cl₂) but with a large variation in PCDD/F yields. The amount of soot formed during each of the six sooting phases varied widely between 100 and 400 mg due to the unstable sooting properties of the CH₄ flame (*16*). Thus, the amount



FIGURE 2. Relative PCDD/F homologue distributions detected from the different carbon sources present on the prechlorinated $[^{13}C]-[^{12}C]$ soot/ash deposit.

of carbon present for de novo formation of PCDDs/Fs in the VR differs significantly between each experiment. A linear relationship (not shown) between the amount of soot and the amount of PCDDs/Fs is observed, suggesting that the amount of carbon present is one important factor controlling the rate of de novo formation of PCDDs/Fs. This finding is supported by other work (*5*) showing PCDD/F formation proportional to fly ash carbon content.

Further de novo experiments were conducted on a sequential [13C]soot/ash, [12C]soot/ash deposit to investigate the relative importance of the two de novo pathways, namely, via direct release of the PCDD/F carbon backbone structure during catalyzed soot/carbon oxidation, and via condensation reactions of smaller carbon fragments ($< C_{12}$) also formed during the low-temperature carbon oxidation process. The deposit was generated by 10 min of ¹³CH₄/200 ppm Cl₂ sooting combustion ($\Phi = 0.86$) followed by 10 min of combustion with a sooting ${}^{12}CH_4/200$ ppm Cl₂ flame ($\Phi = 0.86$). EX ash was simultaneously fed into the VR during the combustion to promote catalyzed reactions. On the basis of previous results, the activity of the fly ash carbon to form PCDDs/Fs is assumed to be negligible compared to that of the soot carbon. De novo formation of PCDDs/Fs from the [13C]-[12C]soot/ash deposit was sampled in an air environment for 30 min to investigate the role of the two carbons. The entire experiment, i.e., the sooting phase and the following 30 min de novo experiment, was repeated, resulting in acceptable variation in terms of both homologue patterns and total formation. The two-run averages of the relative homologue profiles of the PCDF and PCDD are presented in Figure 2; the mono- to trichlorinated DD/DF homologues were excluded from the figure due to their relatively insignificant levels.

All PCDFs detected at the two conditions were either completely ${\rm ^{12}C_{12}}$ or completely ${\rm ^{13}C_{12}},$ which indicates that PCDFs are formed via direct release from larger carbon structures, such as PAHs present in the soot/ash matrix (Figure 2). The lack of mixed $[{}^{13}C_{x}{}^{12}C_{y}]PCDFs$ indicates that these compounds are not formed via condensation/recombination reactions of smaller carbon fragments. The PCDDs, on the other hand, were found to contain both ¹²C and ¹³C in equal proportions $({}^{13}C_{6}{}^{12}C_{6}$, Figure 2). Additionally, equivalent yields of ¹³C and ¹²C polychlorinated benzenes (PCBz's) and PCPh's were observed, with all compounds containing only a single isotope of carbon. The lack of PCDD congeners with mixed-carbon-isotope rings (e.g., ${}^{13}C_{3}{}^{12}C_{3}$) and the absence of mixed-isotope PCBz and PCPh structures indicate that the $[{}^{13}C_{6}{}^{12}C_{6}]PCDDs$ are formed via a combination of whole C_6 aromatic compounds, and not by a combination of smaller carbon fragments such as C₃. Due to the unlikelihood of homogeneous reactions under these low-temperature conditions, these C₆ aromatics are likely volatilized from the soot structure, only to adsorb and react on surfaces to form PCDDs.



FIGURE 3. Statistical distributions between the possible combinations of PCDDs formed by C_{12} and C_6 carbon structures.



FIGURE 4. Changes in de novo formation rate on a CI-soot/ash deposit with time.

The observed PCDD distribution is almost identical to the expected statistical distribution presented in Figure 3, demonstrating that C_6 structures are as important for the de novo formation of PCDDs as larger aromatic carbon structures ($\geq C_{12}$), such as PAHs, in the soot matrix. The approximately equivalent distribution among the [$^{12}C_{12}$]- and [$^{13}C_{12}$]PCDFs and the [$^{12}C_{12}$]-, [$^{12}C_6$]⁻ and [$^{13}C_{12}$]PCDDs observed in Figure 2 shows that the two carbon sources (^{13}C and ^{12}C) present in the soot deposit are equally active for de novo formation of PCDDs/Fs, consistent with others' findings (9). The equal ^{12}C and ^{13}C participation occurs despite the slight difference in relative age of the soot (i.e., the ^{13}C soot was 10 min older than the ^{12}C soot at the start of the sampling).

Change in PCDD/F de Novo Formation with Time. Experiments to study the change in de novo PCDD/F formation with time (memory effect) were conducted in the EFR over a period of 34 h. A ¹³CH₄/200 ppm Cl₂ sooting flame was operated for 10 min, simultaneously while feeding EX ash, to supply a [13C]soot/ash layer on the wall of the VR. The gas phase was changed to N2, and a 2 h sample was taken directly after the flame combustion was terminated. The soot deposit in the VR was further exposed to a constant flow of N₂ (11 L/min) over the next 24 h, after which four samples were taken: a 2 h sample in a N2 atmosphere, two samples for 4 h in air, and a 2 h sample during the operation of a nonsooting ¹²CH₄ flame ($\Phi = 0.67$). The relative yields for the five samples taken during the 34 h are shown in Figure 4. The levels declined only by about a factor of 2 after 26 h in N₂, and only a slight increase was noticed when the environment was changed to air. Even 34 h after sooting, the persistently high rate of formation suggests that the de novo PCDD/F formation pathway may remain significant in applied conditions beyond a day after sooting incidences. Moreover, de novo formation from the [13C]soot/ash matrix was not found to be affected by the presence of flame radicals in the gas phase since the PCDD/F yields detected with a native CH₄ lean flame present were in the same range as those of formation in the N₂ or air environments as shown in Figure 4. Furthermore, no detectable amounts of [12C]PCDDs/Fs were observed, showing that the pathway for PCDDs/Fs at this condition was via de novo synthesis involving the ¹³C soot and not the fuel lean CH4 flame products or the fly ash carbon.





The importance of PCDD/F formation via de novo synthesis compared to other formation pathways, such as formation via gas-phase carbon precursors, remains unknown. Figure 5 presents the PCDD/F homologue profiles detected at three experimental conditions: (1) de novo formation in air via a soot deposit, (2) during operation of a moderately sooting CH_4/Cl_2 flame ($\Phi = 0.86$), and (3) with CH_4/Cl_2 at a high-sooting, poor combustion condition ($\Phi = 1.03$). Ash was present in the VR in all three experiments to provide catalytic activity. A clear shift in the homologue profile toward the lower chlorinated DD/DF homologues was observed when a flame was present compared to the de novo formation experiments on the deposits alone, a shift even more pronounced during poor combustion conditions. The shift may be partially due to the reported dechlorination effect of water and the conversion of Cl₂ to HCl in the presence of the flame; however, this does not explain the significant difference observed between the two flame experiments at relatively equivalent water concentrations. The C:Cl ratio will be higher during poor combustion because of higher soot concentrations at constant Cl₂ addition. However, it may be likely that an additional or more prominent formation pathway occurs during flame combustion in the presence of soot, and especially during poor combustion, contributing to the formation of mono- and dichlorinated DDs/DFs. These results are consistent with others' findings during low combustion efficiency conditions in various solid fuel combustors (13, 24, 25).

The total PCDD/F yields during the moderately sooting flame (condition 2 above) and in the de novo experiment on the soot deposit (condition 1) were of the same magnitude (90 vs 60 pmol/min, respectively). At the higher sooting condition, the total formation increased significantly (500 pmol/min); as noted above, this increase was predominately due to the increase in mono- and dichlorinated DDs/DFs. These experiments suggest that de novo synthesis involving in situ formed solid carbon matrixes (soot) is an important formation pathway of PCDDs/Fs during sooting combustion processes. The emissions from the resulting carbon/ash deposits can persist with little diminution for more than 30 h. The potential for additional pathways leading to the significant increase in yield of the lower chlorinated congeners under different combustion conditions is discussed in further detail in a related research paper (12).

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