NOMAD Sub-Committee on Open Burning - Recommendations

**Land Clearing Debris:** Recommend EPA update the activity data.

The 2011 EPA calculations used BELD2 to identify acres of hardwoods, softwoods, and grasses in each county. This proposal would be to update the BELD2 data with whatever is going to be used for the 2014 Event data calculations. This would then be used for weighted average county-level loading factors by the percentage contribution of each type of vegetation class for each county (as described in the 2011 EPA documentation). Then the total county-level acres disturbed would then be multiplied by the weighted average loading factor to derive tons of land cleaning debris. EPA could then share the weighted average loading factors by county with the states for their calculations. The updated weighted average loading factors would be used for all open burning categories where applicable. (Lynn, KS)

Another alternative to BELD2 is The 2011 National Land Cover Database. This can be found at: <http://www.mrlc.gov/index.php>. . (Lynn, KS)

The fuel loading factors should also be looked at to see if there are updated factors for various fuel types. It was also noted that there is not a fuel loading factor for mixed forest type (hardwood/evergreen), which is a very common forest type. (Lynn, KS)

Burning large piles could require multiple burning periods to complete. Multiple burns on the same pile may result in more smoldering and less flaming than a single burn. If this is the case, does that affect the emissions factors? Or has EPA already accounted for this? (Chun Yi, MN)

Is there a factor to account for not all land clearing debris being burned? If a state has data on this indicating chipping or other disposal methods, can EPA’s calculations be adjusted accordingly? (Chun Yi, MN)

**Yard Waste – Leaf/Brush:** Recommend EPA update the activity data. One thing to note is the 55-65 percent of the total waste attributed to residential waste is not in the more current EPA reports, although it could be assumed that this would not likely have changed that much in just a few years…

**Household Waste:** Recommend EPA update the activity data. Same note as above on the percentage of residential waste to the total waste reported….

We do have a recommendation from Chris (OR) on household waste burning and plastics. We recommend that EPA look at the study he has shared (attached) and see if there is enough data to justify adjusting the current emissions factors. EPA’s calculations seem to have already taken this into account according to this link: <http://www.ecy.wa.gov/programs/air/outdoor_woodsmoke/PDFs/EPAbarlbrn1.pdf>. But OR does have statewide survey estimates on newspaper and plastic open-burned for households if EPA is interested.

Some states do have bans on the burning of household waste but might not have 100% compliance. EPA should provide a way for those states to give a compliance rate so emissions can be calculated accordingly. (Denise, ME)

**General Comments:** We also have a general recommendation from Denise on allocation tables used by EPA to fill various activity data. Denise suggests that when EPA generates these that they share them with the states in case they want to use them as well. This is a good idea if it can be done.

Recommend that any links used to reference data be more specific where possible. There are a lot of generic links that don’t always help much when comparing state data to EPA data.

**QUANTITATIVE ANALYSIS OF TOXIC COMPOUNDS FORMED FROM COMBUSTION OF SOME PLASTIC MATERIALS AND NEWSPAPER**

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**Introduction**

Our earlier investigations demonstrated that formation of hydrocarbons such as polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), polycyclic aromatic hydrocarbons (PAHs),

popychlorophenols (PCPhs) and polychlorobenzenes (PCBzs) and their toxic equivalent quantity

(TEQ) with dioxin-free flyash and unburnt hydrocarbon with varied temperatures as well as different hydrochloric acid (HCl) concentrations. The results highlighted that minimum

concentration of all the chlorinated aromatics with presence of paraffin powder and absence of

dioxin-free fly ash. Furthermore depending upon the temperature and HCl concentration, the formation chemistry varied at considerable manner1,2. There are several reports documented the formation of toxic substances when burning the plastic materials. However, the studies are scarce about formation of HCl, HCN, PCDD/DFs, co-planar PCBs their TEQ, BTX, parent compounds of dibenzodioxin, dibenzofuran, biphenyl and PAHs from various plastic materials. Besides, so far studies reports only the basic theory of formation chemistry, which lacks the formation of non- chlorine compounds.

In this study we conducted formation of PCDDs, PCDFs, coplanar PCBs, benzene, toluene, xylene (BTX), 16- polycyclic aromatic hydrocarbons (PAHs), HCN, parent compounds of biphenyls, dibenzodioxins and dibenzofurans and carbonmonoxide (CO) from polyethylene (PE), polyethyleneterephthalate (PET), nylon, newspaper, polypropylene (PP), acrylonitrile butadiene styrene (ABS) and polyvinyl chloride (PVC) plastic particles with our incinerator apparatus that was developed in Shimadzu Techno Research Inc., as shown in Figure 1. Based on the formation of PCDD/DFs and co-planar PCBs, we calculated the toxic equivalent quantity (TEQ) using WHO-TEF values in each sample analyzed in present investigation and discussed.

**Materials and Methods**

**Apparatus.** As shown in Figure 1, the experimental apparatus were developed with O2=20.9%/N2 balance meter that further connected with flow meter and quartz tube. The diameter of quartz tube is 25 mm with 1000-mm length that mainly travels inside the double furnace (600-mm) with the furnace temperature of 900oC. The samples for the formation test were placed in the sample tray located in the quartz tube in furnace 1.

**Sampling Unit**. For the dioxins and PAHs, the sampling unit can be classified as ice-bath with 3 impinger and XAD. The impinger 1 contains 100-mL toluene with 200 mL H2O. The impinger 2 and 3 respectively contains 150-mL toluene and 150 mL diethylene glycol. This impinger was

connected with XAD-1 and 2 and the sampling was mainly done in 3 impinger and 2 XADs. For HCN, the ice-batch contains 2 impinger in that both contain 30 mL of 0.1 mol/L NaOH solution. For BTX analysis, it was fixed with 10 L Flek-sampler bag. The impinger and XAD of dioxins and PAHs and HCN impinger unit was finally connected with flow meter with pump and CO, O2, CO2 monitoring meter. After the completion of experiment, the back end of quartz tube, impinger of dioxins, PAHs and HCN was rinsed with H2O, acetone and toluene for analysis.

DXN,PAHs

CO,O2 monitor

Furnace(900oC)

Furnace(900oC)

Flow meter

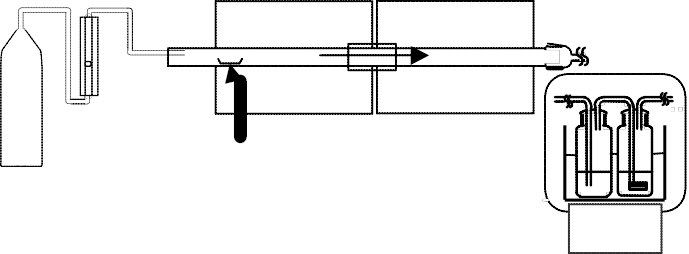
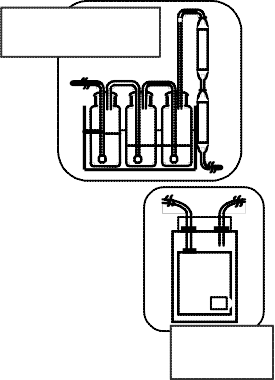
O2=20.9%

/N2-Balance

Sample

HCN BTX

Flow meter



& Pump

meter

**Figure 1.** The experimental apparatus employed in this study.

**Samples**. The PE, PET, nylon, newspaper, PP, ABS and PVC were either cut into tiny pieces or powdered. The sampling speed and gas flow was set as 2.0 L/min trapping time. Each interval 20

Pg of sample was burned at 900oC at the double furnace as shown in Figure 1 with regular intervals (until completion of CO, CO2, O2 monitor cycles in each and every 20 mg sample

burning). For dioxin and PAHs analysis 1 g sample were used with 100 cycles, whereas 200 and

100 Pg samples were used for HCN and BTX analysis with 20 and 10 cycles respectively. For each sample matrix, the CO, O2, CO2were monitored and recorded (Figure 2).

**Analysis**. The identification and quantification of PCDD/DFs, co-planar PCBs, PAHs were performed using Micromass Autospec Ultima high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) at a resolution of > 10, 000 along with 13C-internal standards as a reference. For the HCN analysis, the JISK0102 method was adopted. For BTX sampler bag, GC-FID was used and then scanning test confirmation was done with GC-MS quadrapule. The concentrations of BTX, HCN, parent compounds of biphenyl, dibenzofuran, dibenzodioxins, and PAHs were expressed as ng/g-sample basis while TEQ, chlorinated -PCDDs, -PCDFs and -co- planar PCBs represents pg/g-sample basis and CO was expressed on ppm basis.

**Results and Discussion**

The concentrations of HCl, HCN, Dioxin [PCDFs, PCDDs, co- planar PCBs their TEQ], BTX, parent structure viz., [biphenyl, dibenzodioxins, dibenzofuran] and 16 polycyclic aromatic

hydrocarbons (PAHs) were shown in Table 1. In addition to the samples described, the blank run was also conducted and the results were shown in Table 1. In the blank samples, dioxins, furans,

co-planar PCBs and few PAH compounds were noticed. This study was conducted without flyash

and thus the results were considered to be a theoretical formation of thermo-chemical process.

**Table 1.** Concentrations of toxic compounds (ng/g-sample) in various sample matrix and blank in the incinerator apparatus.

Detection Limit: HCN<3000, PCDD/DF (4-5Cl)<0.001, (6-7Cl,co-PCBs)<0.002, (8Cl)<0.005, BTX<3000, PAHs<10 on ng/g-sample

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample | Blank | PEa | PETb | Nylon | Newspaper | PPc | ABSd | PVCe |
| HCl |  |  |  |  |  |  |  | 584,000,000 |
| HCN | LRLg |  | LRLg | 12,000,000 |  | 73,000 | 1,000,000 | LRLg |
| CO (ppm) | 13 | 310 | 20 | 730 | 790 | 400 | 49 | 170 |
| % CO2 (v/v) | <0.2 | 1.4 | 1.5 | 0.9 | 0.8 | 1.1 | 1.0 | 0.4 |
| % O2 (v/v) | 20.9 | 18.8 | 19.4 | 19.6 | 20.0 | 19.1 | 19.6 | 20.4 |
| Sum PCDFs | 0.021 | 0.043 | 0.14 | 0.014 | 0.23 | 0.065 | 0.005 | 12 |
| Sum PCDDs | 0.031 | 0.032 | 0.17 | 0.06 | 0.15 | 0.047 | 0.058 | 3.4 |
| Sum Coplanar PCBs | 0.074 | 0.16 | 0.12 | 0.077 | 0.15 | 0.18 | 0.08 | 0.19 |
| Sum PCDD/DFs + PCBs | 0.13 | 0.24 | 0.43 | 0.15 | 0.53 | 0.29 | 0.14 | 16 |
| hTEQf | 0.58 | 1.2 | 4.3 | 0.072 | 5.4 | 0.95 | 0.59 | 130 |
| Biphenyl | 300 | 120,000 | 170 | 130,000 | 50,000 | 370,000 | 650 | 450 |
| Dibenzofuran | 27 | 8,400 | 17 | 13,000 | 39,000 | 14,000 | 360 | 28 |
| Dibenzodioxin | LRLg | LRLg | LRLg | LRLg | LRLg | LRLg | LRLg | LRLg |
| Benzene | LRLg | 26,000,000 | LRLg | 12,000,000 | 2,800,000 | 730,000 | 2,300,000 | LRLg |
| Toluene | LRLg | 33,000 | LRLg | 200,000 | 170,000 | 38,000 | 75,000 | 60,000 |
| Xylene | LRLg | LRLg | LRLg | LRLg | LRLg | LRLg | LRLg | LRLg |
| Naphthalene | 10,000 | 1,200,000 | 7,600 | 2,200,000 | 780,000 | 2,600,000 | 6,400 | 4,300 |
| Acenaphthylene | LRLg | 1,300,000 | LRLg | 1,500,000 | 270,000 | 1,400,000 | 360 | 26 |
| Acenaphthene | LRLg | 6,800 | LRLg | 11,000 | 3,900 | 13,000 | 62 | 100 |
| 9H-Fluorene | 590 | 130,000 | 260 | 170,000 | 44,000 | 220,000 | 580 | 1,300 |
| Phenanthrene | 500 | 670,000 | 410 | 760,000 | 250,000 | 940,000 | 860 | 410 |
| Anthrathene | 360 | 140,000 | 260 | 190,000 | 49,000 | 240,000 | 280 | 280 |
| Fluoranthene | 60 | 490,000 | 61 | 560,000 | 180,000 | 520,000 | 360 | 51 |
| Pyrene | 130 | 380,000 | 120 | 500,000 | 160,000 | 620,000 | 200 | 94 |
| Benzo[a]anthrathene | LRLg | 85,000 | LRLg | 89,000 | 29,000 | 120,000 | 58 | 37 |
| Crysene\*1 | LRLg | 95,000 | LRLg | 100,000 | 38,000 | 130,000 | 68 | 20 |
| Benzo[b]fluoranthene | 50 | 140,000 | 37 | 150,000 | 48,000 | 180,000 | 100 | 40 |
| Benzo[k]fluoranthene\*2 | LRLg | 45,000 | LRLg | 42,000 | 14,000 | 58,000 | 22 | LRLg |
| Benzo[a]pyrene | LRLg | 140,000 | LRLg | 160,000 | 38,000 | 170,000 | 22 | LRLg |
| Indeno[1,2,3-cd]pyrene | LRLg | 86,000 | LRLg | 110,000 | 28,000 | 140,000 | 18 | LRLg |
| Benzo[g,h,i]perylene | LRLg | 120,000 | LRLg | 140,000 | 33,000 | 130,000 | 11 | LRLg |
| Dibenzo[a,h]anthrathene\*3 | LRLg | 9,300 | LRLg | 9,000 | 3,700 | 14,000 | LRLg | LRLg |
| Total 16 PAHs | 12,000 | 5,000,000 | 8,700 | 6,700,000 | 2,000,000 | 7,500,000 | 9,400 | 6,700 |

apolyethylene,bpolyethyleneterephthalate,cpolypropylene,dAcrylonitrile butadiene styrene,epolyvinylchloride,

fpgTEQ/g-sample basis,gLess than reportable limit;hToxic Equivalent Quantity

\*1Triphenylene, \*2Benzo[j]fluoranthene, \*3Dibenzo[a,c]anthracene, respectively. The values rounded to two singificant digits

The HCN formation was explained to be nitrogen containing compounds such as ABS and nylon. The HCN concentration levels were reasonable however, levels in PP likely to be formation from additive hindered amine anti-oxidant (Table 1). The study of Mingjim Piao’s pyrolysis experiment3 showed that PAHs were formed at the incinerator temperature of 900oC due to the aliphatic hydrocarbons was converted as PAHs with benzene ring. These results were compared with our study and results implied that PE, PP, nylon, newspaper formed elevated levels of BTX and PAHs, particularly, benzene, naphthalene, acenaphthalene found to be mg/g levels, the Benzo[a]pyrene with Pg/g. The lower levels were found for PET, ABS and PVC with 1/4000-fold

less levels. It is probable that presence of oxygen in PET might impacted the low formation of PAHs. The O2, CO, CO2 monitored in PP and PET has been shown in Figure 2. The PAHs were predominantly found in PE, nylon, newspaper and PP. As for an example, in Figure 2, highlights that formation of O2 reduced burning and reductions of dioxins while PP seemed to form elevated

CO due to incomplete burning. This also leads to greater formation of toxic PAHs in PP at 900oC

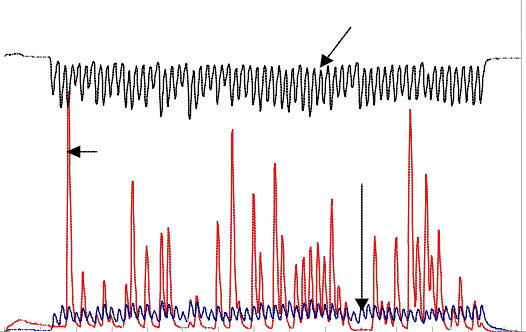
(Figure 2).

In terms of the TEQ and homologues of PCDD/DFs and co-planar PCBs, nylon, ABS levels were similar to blank levels and negligible. The, PE, PP, PET levels were slightly higher but considered to be equal to blank due to the background levels. The elevated levels of TEQ in PVC were

considered to the influence of Cl contents which is 57% of parent compound and thus 1 to 100- million of chlorinated aromatics occur to form and nevertheless, these values are several magnitude lesser when compare to the parent Cl contents.

(p p m )

50 00



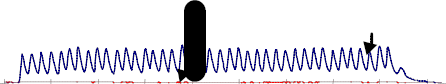
PP 90 0 o C

O2 (% )

PE T

90 0 o C (% )

25



O2 (% )

40 00 20

30 00

20 00

CO (p p m )

15

CO 2 (% )

10

10 00

CO (p p m )

CO 2 (% ) 5

0

16 :1 3 1 6:4 3 17 :1 3

Tim e

0

10 :3 4 1 1:04

Tim e

**Figure 2.** Percentage evolution of CO2 and O2 and concentration (ppm) of CO in popypropylene and polyethyleneterephthalate samples.

We also determined the parent compounds of biphenyls, dibenzofurans and dibenzodioxins in order to understand the formation mechanism of above-said compounds. It should be worth indicating that biphenyl and dibenzofuran was detected in all the samples while dibenzodioxin were less than 10 ng/g. It is assumed that chlorinated dioxins might have formed during the reaction of chlorophenol dimerization effect1,2. This results indicated that the formation mechanism of PCBs and PCDFs were different from PCDDs that formed with entirely different manner. The formation of PCB and PCDF could be explained as pyrolysis effect and the formation of chlorine from the carbon skeleton might be a suitable explanation.

**Literature Cited**

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