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Emissions from open burning of used agricultural pesticide containers

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ABSTRACT

Emissions from simulated open burning of used agricultural pesticide containers were sampled for polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/PCDFs), polycyclic aromatic hydrocarbon compounds (PAHs), and particle matter (PM₁₀ and PM_{2.5}). Clean high density polyethylene (HDPE) containers, containers with trace pesticide, and triple-rinsed containers were burned separately in an open combustion facility and their emissions compared. Two common chlorinated pesticides were used: 2,4-dichlorophenoxyacetic acid (2,4-D) and 1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine (atrazine). PCDD/PCDF emission factors ranged from 0.1 to 24 ng toxic equivalents (TEQ)/kg C burned with a mean and median of 4.9 and 1.9 ng TEQ/kg C burned, respectively. In a limited number of trials, the trace 2,4-D in the HDPE container led to a statistically significant increase in PCDD/PCDF formation compare to all other conditions. Residual atrazine did not lead to more PCDD/PCDF than the unrinsed 2,4-D container. Total (16 compounds) PAH emission factors varied from 1.5 to 6.7 mg/kg C burned. These limited data suggest that rinsing the 2,4-D container prior to burning reduces both PCDD/PCDF and PAH emissions. Nine PM_{2.5} emission factors ranged from 9 to 35 mg/g C burned and ten PM₁₀ values ranged from 6 to 43 mg/g C burned. Neither pesticide appeared to have any effect on PM concentration.

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1. Introduction

In 2005 the U.S. EPA estimated that there were more than 218 million plastic nonrefillable (single use) containers for liquid pesticides in use [1], presenting a significant after-use challenge. After pesticide product containers are emptied, they are recycled, reconditioned for reuse, disposed of in a landfill, combusted in an incineration facility or burned in the open by the user. The U.S. agricultural pesticide industry has collected for recycling 50,000 Mg of plastic used in pesticide product containers from 1992 through 2010 [2]. Containers not collected for recycling are reutilized or left for disposal.

Pesticide labels include instructions on how the end user must clean the container by triple rinsing or pressure rinsing the containers [3]. These procedures are meant to remove residual pesticides so the containers can be recycled or disposed. Because the industry recycling program inspects pesticide containers before they are accepted, recycled containers are likely to be cleaner than containers that are disposed of in a landfill, burned, or dumped. The latter means of disposal incur environmental hazards that are poorly documented, if at all.

Open burning of used agricultural containers, typically made of high density polyethylene (HDPE), is banned in many U.S. states, but it is nevertheless believed to be a common practice. The published literature appears to lack any emission assessment from open burning of used agricultural containers so the hazards of improper disposal by burning are unclear. There are some emissions data available from laboratory and open combustion of low density polyethylene (LDPE) sheeting [4–6] and combustion of PE pellets in a laboratory reactor [7], but these are of uncertain relevance to open air combustion of HDPE pesticide containers.

There are concerns that burning residual chlorinated pesticides in agricultural containers can lead to the release of toxic polychlorinated dibenzodioxin and dibenzofurans (PCDD/PCDF) either through vaporization of trace pesticide byproducts or through formation from pesticides as precursors. The effect of following recommended rinsing procedures to abate this potential risk is also unknown. In order to aid an assessment of disposal practices for agricultural containers, this work conducted open burning of HDPE agricultural containers, examining the effect of pesticide residues and rinsing procedures for their impact on subsequent combustion emissions.

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Combustion testing was conducted in an open burn test facility (2.5 m $H \times 3.0$ m $W \times 2.7$ m D, volume = 21 m³) which consisted of an enclosed building with flow-through air (16 m³/min) to prevent oxygen depletion and to simulate natural mixing (a thorough description of this facility has been published elsewhere [8–11]). The fuels were placed on a platform in the middle of the facility and ignited with a hand-held propane torch. Combustion air was exhausted from the facility with an induced draft fan and treated in an air pollution control system before release to the atmosphere. Emissions were sampled using ambient air samplers within the facility or with extractive probes from the facility exhaust duct. The sampling was terminated when the CO₂ concentration returned to ambient levels.

The agricultural containers burned in this effort were common, high density polyethylene (HDPE), 10 L (2.5 gal) vessels with a screw cap, obtained from a commercial agricultural pesticide supplier. They have an average mass of 400 g. Between two and four containers were burned to obtain each sample. Clean, as-received containers were burned intact as a control. Two conditions relating to residual pesticide were tested using two pesticides, with each test condition duplicated. Residual pesticide amounts were determined by filling the container about 10% full of pesticide, lightly shaking the container, emptying the container with an anticipated pour procedure, and then inverting the container for 30 min to collect any residual pesticide. Trials resulted in an approximate residual pesticide volume of about 10 mL or about 0.1% of the container capacity. For the first test condition, 10 mL of residual pesticide was poured into a container, the container was shaken to disperse the pesticide, and then it was subjected to combustion testing. The other condition followed this same procedure but with the addition of a triple rinse step. During the rinse step, the HDPE containers with pesticide were filled three times (1/4) full of deionized water, shaken three times, and drained prior to combustion testing. Clean HDPE containers without pesticide were also tested in duplicate.

The two pesticides used in this work were selected for their commonness of use, their applicability to HDPE containers, and the presence of Cl in their composition. 2,4-Dichlorophenoxyacetic acid, commonly termed 2,4-D (CAS 94-75-7, $C_8H_6Cl_2O_3$), is a common pesticide used for broadleaf weed control. 1-Chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine, commonly termed atrazine (CAS 1912-24-9, $C_8H_{14}ClN_5$), is a pesticide used worldwide for control of weeds in agricultural applications. The 2,4-D and atrazine were obtained from local agricultural sources and had an active ingredient concentration of 46% and 41% by mass, respectively.

A total of 11 tests were conducted with HDPE containers in the burn facility plus a pre- and post-test facility blank. Table 1 contains the test matrix and resulting emission factors.

The burn facility was equipped with a continuous emission monitor (CEM) system for carbon monoxide (CO), carbon dioxide (CO₂), and oxygen (O₂). A heated (120 °C) Teflon tube with an inline, heated quartz filter, connected to the exhaust of a high volume sampler, was used to sample the gases. An in-line refrigerated gas dryer and silica desiccant is used prior to the CEMs. Three-point calibrations of the CEMs are accomplished by the use of compressed calibration gases, both before and after testing.

Ambient air sampling for PCDD/PCDF was performed according to U.S. EPA Method TO-9A [12]. The sampling train consisted of a quartz filter and polyurethane foam (PUF) sorbent cartridge in series. Combustion gases were drawn through the filter and sorbent cartridge using a high-volume ($\sim 1 \text{ m}^3/\text{min}$) sampling pump. Five tetra-octa PCDD/PCDF isotopically labeled pre-sampling standards were spiked onto the PUF as per EPA Method 23 [13]. For analysis the combined PUF and filter sample were spiked with ¹³C standards, extracted in toluene overnight, concentrated, filtered, and then further concentrated to 1 mL. Half of this sample was cleaned through acidic silica gel until clear. Subsequent processing through the standard EPA Method 23 [13] PCDD/PCDF sample cleanup used acidic, basic, and neutral silica gel, basic alumina, and a celite/carbon mixture. The remaining half of the sample was archived. The resultant solution was spiked, concentrated, and analyzed on a high resolution gas chromatography with high resolution mass spectrometry (HRGC/HRMS) for PCDD/PCDF. Calculation of toxic equivalencies (TEQs) used toxic equivalency factors from the World Health Organization [14].

Polycyclic aromatic hydrocarbons (PAHs) were extractively sampled in the exhaust duct using U.S. EPA Method 0010 [15] with a filter and XAD. Values of the 16 "EPA PAHs" were determined. The filters and XAD were Soxhlet extracted in methylene chloride overnight following EPA Method 3540 [16] and analyzed by EPA Method 8270 [17]. The extracts were concentrated, filtered, and then concentrated again to a final volume of 1 mL. A portion of the extracts were diluted 100-fold, spiked with internal standards, and analyzed via HRGC with a low resolution mass spectrometer (LRMS). Subsequently they were spiked at full strength and analyzed again in order to reduce the number of non-detects.

Particle matter (PM) was sampled using two automated PM samplers which pull air through a pre-weighed Teflon filter mounted in a size-selective impactor assembly. PM_{2.5} and PM₁₀ were determined from the filters gravimetrically.

The possibility of contamination of the 2,4-D pesticides with byproduct PCDD/PCDF, noted previously by others [18,19], was examined. Each pesticide (1 mL) was extracted with 0.5 mL of hexane and then analyzed via LRMS.

Emission factors were calculated in terms of mass of PCDD/PCDF per mass of combusted carbon sampled as CO_2 and CO gases. Other carbon sources, such as hydrocarbons, were comparatively minimal (<5%) and were not included in the calculations.

3. Results and discussion

The HDPE containers ignited relatively easily, slumping into a burning liquid pool. Typical combustion emissions of CO and CO₂ reached a peak about 25-30 min into the approximately 60 min burns. The 60-min mean CO and CO₂ levels are shown in Table 1 for each test condition. The CO₂ reached peak levels of about 1.5% or 15,000 ppm on the first two of three clean HDPE burns. These burns had four containers per burn but the PM filter was quickly overwhelmed, so subsequent burns were reduced to two containers. The use of four containers was also the likely cause for the elevated mean CO₂ (Table 1) of 2670 ppm; the third Clean HDPE burn with only two containers had a maximum CO₂ value of about 6500 ppm and a mean value of 1042 ppm, in line with the rest of the burns. Similar comparative results were observed for CO during the four- and two-container burns. An analysis of the carbonnormalized CO and CO₂ data (Fig. 1) shows that the two-container burn reached peak emission values about 5 min faster than the four-container burns during the 60 min test periods. This may have been due to less depletion of localized oxygen with only half of the combustible material. This is borne out by an analysis of the massnormalized carbon sampled-the mass of the two-container burn reached a maximum rate of carbon loss about 5 min faster than the four-container burn over the 60 min burns. The average modified combustion efficiency $(CO_2/(CO + CO_2))$ was greater than 99% for all of the test conditions.

The summarized PCDD/PCDF emission values are shown in Table 1 and graphed in Fig. 2. Individual values for the 11 tests (not shown) ranged from a low of 0.09 ng TEQ per kg C burned (ng

Test matrix and emission factors.

Pesticide/test condition	PCDD/PCDF (ng TEQ/kg C, ND = 0)	PCDD/PCDF $(ng/kgCND=0)$	Total 16 PAHs $(mg/kgC, ND = 0)$	CO (ppm)	CO ₂ (ppm)	PM _{2.5} (mg/g _C)	PM ₁₀ (mg/g _C)
	Mean (rsd/rpd, N)	Mean (rsd/rpd, N)	Mean (stdv or rpd, N)	60-min mean	60-min mean		
Clean HDPE	3.0 (0.68, 3)	720 (130, 3)	5.6 (0.2, 3 [*])	19	2670	19.1	17.1
2,4-D/unrinsed	17. (0.60, 2)	95,000 (12, 2)	4.6 (23,2)	10	1009	35.1	24.7
2,4-D/rinsed	4.2 (0.28, 2)	1,500 (10, 2)	2.1 (2.3,2)	9	1435	9.49	7.79
Atrazine/unrinsed	0.23 (0.88, 2)	380 (25,2)	1.75 (26, 2)	9	1484	10.6	8.46
Atrazine/rinsed	0.73 (0.16, 2)	1200 (8, 2)	2.95 (45,2)	8	1423	21.9	17.60
Pre-test blank	0.00 (NA, 1)	5 (NA, 1)	NM	NA	NA	NA	NA
Post-test blank	0.00 (NA, 1)	11 (NA, 1)	NM	NA	NA	NA	NA

NA = not applicable.

NM = not measured.

rsd = relative standard deviation, Stdev/Avg Conc, fraction.

rpd = relative percent difference.

Two PAH samples were taken during one of the three burns.



Fig. 1. Carbon $(CO+CO_2)$ sampling rate during Clean HDPE burns with four (Tests A, B) and two (Test C) containers. Test $C \times 2$ indicates the doubled mass rate of Test C for comparison with Tests A and B.

TEQ/kg C, at non-detects, ND = 0) to a high of 24.50 ng TEQ/kg C. The mean PCDD/PCDF emission factor was 4.5 ng TEQ/kg C, the SD 7.14, the standard error of the mean was 2.15, the upper 90% mean was 21.6 and the lower 90% was 0.15. The median value was 1.92 ng TEQ/kg C.

Recoveries of over 50 pre-sampling PCDD/PCDF surrogates showed only three deviations from recovery criteria. Less than 4% of the targeted TEF-weighted congeners were recorded as Estimated Maximum Potential Concentrations (values that achieve most but not all of the recovery criteria) but were considered valid based on their presence in other samples from this effort.

Both pre- and post-test burn facility blanks resulted in sample volumes of 140 m^3 and 341 m^3 , respectively, from 2 to 17 times the amount of test condition volumes sampled. Both blanks resulted in 0.00 ng TEQ/m³ for both ND = 0 and ND = DL, confirming the absence of background contributions.

Nine of the 11 samples had detectable levels of all 17 TEFweighted congeners. One sample had a single non-detect congener that had less than a 2% effect on the PCDD/PCDF TEQ value when its value was taken as ND=DL rather than ND=0. The other sample had 7 non-detect congeners and its PCDD/PCDF TEQ value almost doubled when using the DL value. This latter case was for atrazine/unrinsed, which had the lowest emissions value of the 11 samples. Henceforth, data are treated assuming the non-detect congeners=0. These PCDD/PCDF emission factors are within a



Fig. 2. PCDD/PCDF results from individual tests (triangles), averages (stars), and ±1 standard deviation (line and bars). TEQ values on left, total (tetra- to octa-) on right.



Fig. 3. Congener distributions (mass congener per mass of all 2,3,7,8-Cl-substituted congeners) for all 11 tests.

factor of three above the range of values for open biomass combustion reported elsewhere [20].

A Student's *t* test (α = 0.05, *t* = 2.4469) showed that the only significant difference between PCDD/PCDF TEQ values for the five conditions was between 2,4-D/unrinsed and the other four conditions. Similar results were found for PCDD/PCDF total. The distributions of the 2,3,7,8-Cl-substituted congeners were virtually unchanged throughout the tests (Fig. 3) and the dominant congeners were 2,3,7,8-TeCDD,2,3,7,8-TeCDF, and 2,3,4,7,8-PeCDF. The 2,4-D/unrinsed sample had a significantly higher average PCDD/PCDF TEQ value (17.2 ng TEQ/kgC) than all of the other test conditions (average of 2.1 ng TEQ/kgC). This suggests that without rinsing, the residual 2,4-D in the HDPE container had a higher propensity to form PCDD/PCDF TEQ, much more so than the atrazine pesticide.

The presence of PCDD/PCDF from the burn of the clean HDPE container suggests that perhaps trace Cl in the containers or in the combustion air itself might lead to PCDD/PCDF formation. XRF analysis of the HDPE container and lids showed 83 ppm of Cl, orders of magnitude more Cl than necessary to explain these PCDD/PCDF yields.

For the pesticide-exposed, unrinsed containers, the 10 mL of residual 2,4-D and atrazine pesticides contributed about 1.2 g and 0.7 g, respectively, of additional Cl to the system, much greater than that contributed by the HDPE container's 33 mg of Cl. The 2,4-D residual trials resulted in two to five times higher PCDD/PCDF TEQ yields and over 60 times higher than the PCDD/PCDF total yields (comprising all of the congeners in the tetra- to octa-homologues), than from the other nine tests, suggesting a role of 2,4-D in the formation of PCDD/PCDF other than that of Cl supply. The ring structure of 2,4-D (Fig. 4, left) is also more amenable to simple reactions to form PCDD/PCDF than is atrazine (Fig. 2, right) and, hence, is more likely to act as a reactant to form PCDD/PCDF.



Fig. 4. Structures of 2,4-dichlorophenoxyacetic acid (2,4-D, left) and 1-chloro-3ethylamino-5-isopropylamino-2,4,6-triazine (atrazine, right).



Fig. 5. Total 16 PAH concentrations from individual tests.

The 11-run average PCDD/PCDF total to TEQ ratio was about 2100 to 1, much higher than range of values found in other sources such as open biomass combustion (4–46 to 1) [8], municipal waste facilities (2–10 to 1) [21], and controlled combustion of mobile phone cases (19 to 1) [22]. This value, however, was significantly affected by the 2,4D-unrinsed total/TEQ values ranging between about 3000 and 10,000, with the TeCDF homolog contributing over 95% of the total mass.

The as-purchased 2,4-D pesticide was analyzed for PCDD/PCDF to determine if the elevated PCDD/PCDF total values were due to vaporization of potential contaminant byproducts in the commercial formulation. Analyses focused on TeCDF, as the most abundant homolog impurity in samples of 2,4-D with concentrations of 0.12-2.6 ng TeCDF/g [19] and 2.7 and 0.0093 ng TeCDF/g [18]. Our analyses showed results reasonably consistent with the literature at approximately 10 ng TeCDF/g. Based on our contaminant levels, use of 40 mL(20 g) of active ingredient 2,4-D would have resulted in 200 ng TeCDF in the emissions. We sample less than 5% of the combustion gas, resulting in a maximum possible value of 10 ng TeCDF in our sampling train. The two-run average TeCDF concentration was about 2,200 ng TeCDF/train suggesting that the TeCDF contaminant level from the original 2,4-D could explain less than 1% of the observed emissions. This shows that PCDD/PCDF are formed during combustion and are not simply due to volatilization of pesticideborne contaminants.

PAHs were similarly sampled and analyzed to determine emission factors (Table 1) and to compare the test conditions for their propensity to form PAHs. The 16 "EPA PAHs" were determined and their emission factors are reported in Table 2. Of the twelve samples, five registered non-detects on at least one of the 16 PAHs, such that their emission factors for ND = 0 differ from those at ND = DL. However, the average effect on these four emission factors is less than 1%, lending confidence to the values.

A Student's *t*-test on the PAHs (t = 2.4, $\alpha = 0.05$) showed that the clean HDPE (5.6 mg/kg C) was distinctively higher than all test conditions but the 2,4-D/unrinsed (Fig. 5). When the first two runs of the clean/HDPE are discounted (in which four containers were burned rather than two containers for all subsequent tests), no distinction is observed between the remaining clean HDPE burn and the other tests. As indicated earlier, it is possible that burning four containers in close proximity rather than two reduced local oxygen concentration, resulting in more PAH formation, but this



Fig. 6. PM_{2.5} and PM₁₀ concentrations from individual tests.

remains undetermined. Another consistent possibility is that the four containers produced a higher, localized temperatures, resulting in higher PAH emissions as observed by Wang et al. [23] with PE pellets. The two 2,4-D/rinsed tests and the two 2,4-D/unrinsed tests were distinctive in their PAH emission factors at the α = 0.05 level. No difference was observed for their atrazine counterparts of rinsed versus unrinsed.

A comparison of PAH emissions with 14 common compounds from laboratory combustion of polyethylene sheeting [4] shows minimum and maximum total emission factors of 0.32 and 64.9 mg/kg of plastic burned, which compares well with our result of 5.58 mg/kg C burned (clean HDPE). A similar comparison with PE agricultural film burns, in piles or with forced air, showed total PAH concentrations within a factor of five [5], albeit with quite different PAH distributions. Combustion of shredded PE trash bags (25 g sample size) in a laboratory furnace with a flowing atmosphere to simulate open combustion resulted in emission fac-

tors of about 750 mg/kg for the total of 12 PAHs [24]. Li et al. [25] found PAH concentrations (N=21) for HDPE combustion in a batch incinerator around 450 mg/kg-waste. Co-combustion of LDPE film with wood [6] showed the same dominance of naph-thalene and acenaphthylene as in Table 2, albeit with much higher concentrations of about 75–100 mg/kg C_b due to the wood itself.

 $PM_{2.5}$ emission factors (see Table 1) were similar to those of PM_{10} , indicating that most of the particle matter emitted was less than 2.5 µm in diameter. This conclusion appears consistent with test data [26] for PE powder burned in a laboratory apparatus. Similarly, their emission factor data for total soot yields (8–43 mg/g of PE [26]) are aligned with our PM values of about 8 to 25 mg/g Cb (Fig. 6). For PM_{2.5}, the 2,4-D unrinsed container was significantly different than its rinsed counterpart, but not the clean HDPE container. The PM₁₀ showed no statistical distinction between any of the conditions. These observations, however, are significantly tempered

Table 2

Concentrations of 16 PAHs.

РАН	Clean HDPE		2,4-D/unrinsed		2,4-D/rinsed		Atrazine/unrinsed		Atrazine/rinsed	
	Avg conc (mg/kgC)	rsd	Avg conc (mg/kg C)	rpd	Avg conc (mg/kg C)	rpd	Avg conc (mg/kgC)	rpd	Avg conc (mg/kg C)	rpd
Naphthalene	2.935	0.19	2.488	0.17	1.143	0.14	1.077	0.18	1.688	0.46
Acenaphthylene	1.104	0.30	0.993	0.16	0.354	0.08	0.320	0.05	0.623	0.26
Acenaphthene	0.020	0.34	0.015	0.00	0.012	0.00	0.012	0.00	0.013	0.00
Fluorene	0.236	0.16	0.170	0.05	0.078	0.00	0.063	0.01	0.120	0.04
Phenanthrene	0.594	0.28	0.473	0.18	0.298	0.11	0.162	0.05	0.246	0.05
Anthracene	0.036	0.98	0.033	0.01	0.019	0.01	0.006	0.00	0.016	0.01
Fluoranthene	0.093	0.16	0.067	0.03	0.066	0.04	0.027	0.01	0.052	0.02
Pyrene	0.097	0.19	0.067	0.02	0.054	0.03	0.015	0.01	0.049	0.01
Benzo(a)anthracene	0.054	0.32	0.026	0.01	0.012	0.00	0.006	0.00	0.013	0.01
Chrysene	0.051	0.36	0.023	0.01	0.012	0.00	0.006	0.00	0.010	0.01
Benzo(b)fluoranthene	0.074	0.32	0.056	0.02	0.015	0.00	0.009	0.00	0.023	0.02
Benzo(k)fluoranthene	0.028	0.35	0.019	0.01	0.006	0.00	0.006	0.00	0.010	0.01
Benzo(a)pyrene	0.074	0.32	0.052	0.03	0.015	0.00	0.009	0.00	0.023	0.02
Indeno(1,2,3-cd)pyrene	0.087	0.32	0.064	0.03	0.015	0.00	0.012	0.00	0.029	0.02
Dibenz(a,h)anthracene	0.007	0.08	0.005	0.00	0.000	0.00	0.000	0.00	0.002	0.00
Benzo(ghi)perylene	0.087	0.32	0.064	0.03	0.015	0.00	0.015	0.01	0.033	0.01

rsd = relative standard deviation, Stdev/Avg Conc, fraction.

rpd = relative percent difference.

by the limited number of trials; definitive conclusions regarding pesticide residual effects on PM should await further results.

4. Conclusions

A limited number of tests show that relatively low PCDD/PCDF are emitted from clean HDPE combustion (mean 4.9 ng TEQ/kgC burned, median 1.9 ng TEQ/kg C burned), within a factor of three above reported biomass values [20]. Residual 2,4-D in used agricultural pesticide containers produces more PCDD/PCDF (17 ng TEQ/kgC burned) than clean containers (4.9 ng TEQ/kgC burned) or triple rinsed 2,4-D containers (4.2 ng TEQ/kgC burned) when burned under conditions simulating open burning. This additional PCDD/PCDF is due to combustive formation and not trace contaminant byproducts within the pesticide formulations. While residual atrazine in containers contributed chlorine to the combustion mixture, emissions of PCDD/PCDF seemed unaffected (0.23 ng TEQ/kg C burned for the unrinsed and 0.73 ng TEQ/kg C burned for the rinsed). PM_{2.5} and PM₁₀ concentrations appeared indistinctive between the five test conditions indicating that virtually all of the PM is below 2.5 µm. Total PAHs were higher for clean HDPE, but this appears due to the use of a charge size twice that of the other tests. Other than a PM_{2.5} and PM₁₀ correlation, no relationship was observed between PAH levels, PM, and PCDD/PCDF in these 11 tests.

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References

- U.S. EPA, Economic Analysis of the Bulk Pesticide Container Design and Residue Removal Standards, 2006.
- [2] A.C.R. Council, Recycling Adds Up, Brochure, 2011, www.acrecycle.org, http://acrecycle.org/pdf/9-4041%20mariner%20proof.pdf.
- [3] CFR, Ch. 1 (7-1-07 Edition), 2007.
- [4] C. Wrobel, T. Reinhardt, Review of Potential Air Emissions from Burning Polyethylene Plastic Sheeting with Piled Forest Debris, USDA Forest Service, Pacific Northwest Research Station, Seattle, WA, 2003. http://www.odva.state.or.us/ODF/FIRE/docs/SMP/FinalPEReportOct2803.pdf.
- [5] W.P. Linak, J.V. Ryan, E. Perry, R.W. Williams, D.W. DeMarini, Chemical and biological characterization of products of incomplete combustion from the simulated field burning of agricultural plastic, J. Air Pollut. Control Assoc. 39 (1989) 836–846.
- [6] S.E. Hosseini, Q. Li, M. Sharivastava, D. Cocker, D. Weise, H. Jung, Influence of polyethylene cover of silviculture burn piles on emissions, 2009 Fall Technical Meeting, Western States Section of the Combustion Institute, Paper 09F-28, 2009.

- [7] M. Piao, S. Chu, M. Zheng, X. Xu, Characterization of the combustion products of polyethylene, Chemosphere 39 (1999) 1497–1512.
- [8] E. Grandesso, B. Gullett, A. Touati, D. Tabor, Effect of moisture, charge size, and chlorine concentration on PCDD/F emissions from simulated open burning of forest biomass, Environ. Sci. Technol. 45 (2011) 3887–3894.
- [9] B. Gullett, A. Touati, L. Oudejans, PCDD/F and aromatic emissions from simulated forest and grassland fires, Atmos. Environ. 42 (2008) 7997–8006.
- [10] B. Gullett, A. Touati, PCDD/F emissions from burning wheat and rice field residue, Atmos. Environ. 37 (2003) 4893–4899.
- [11] R.R. Black, C.P. Meyer, A. Touati, B.K. Gullett, H. Fiedler, J.F. Mueller, Emissions of PCDD and PCDF from combustion of forest fuels and sugarcane: a comparison between field measurements and simulations in a laboratory burn facility, Chemosphere 83 (2011) 1331–1338.
- [12] U.S. EPA, Determination of Polychlorinated, Polybrominated and Brominated/chlorinated Dibenzo-p-dioxins and Dibenzofurans in Ambient Air, 1999.
- [13] U.S. EPA, EPA Test Method 0023, SW-846 (NTIS PB88-239223), Office of Solid Waste and Emergency Response, U.S. EPA, Washington, DC, 1996.
- [14] M. Van den Berg, L.S. Birnbaum, M. Denison, M. De Vito, W. Farland, M. Feeley, H. Fiedler, H. Hakansson, A. Hanberg, L. Haws, M. Rose, S. Safe, D. Schrenk, C. Tohyama, A. Tritscher, J. Tuomisto, M. Tysklind, N. Walker, R.E. Peterson, The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds, Toxicol. Sci. 93 (2006) 223–241.
- [15] U.S. EPA, Method 0010, Modified Method 5 Sampling Train, September, 1986, http://www.epa.gov/wastes/hazard/testmethods/sw846/online/under.htm.
- [16] U.S. EPA, Method 3540C, Soxhlet Extraction, SW-846 (NTIS PB88-239223), Office of Solid Waste and Emergency Response, Ch 4.2.1.
- [17] Semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS), 2007.
- [18] S. Masunaga, T. Takasuga, J. Nakanishi, Dioxin and dioxin-like impurities PCB impurities in some Japanese agrochemical formulations, Chemosphere 44 (2001) 873–875.
- [19] E. Holt, R. Weber, G. Stevenson, C. Gaus, Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) impurities in pesticides: a neglected source of contemporary relevance, Environ. Sci. Technol. 44 (2010) 5409–5415.
- [20] R.R. Black, C.P. Meyer, A. Touati, B.K. Gullett, H. Fiedler, J.F. Mueller, Emission factors for PCDD/PCDF and dl-PCB from open burning of biomass, Environ. Int. 38 (2012) 62–66.
- [21] B. Wyrzykowska-Ceradini, B.K. Gullett, D. Tabor, A. Touati, PBDDs/Fs and PCDDs/Fs in the raw and clean flue gas during steady state and transient operation of a municipal waste combustor, Environ. Sci. Technol. 45 (2011) 5853–5860.
- [22] R. Font, J. Moltó, S. Egea, J.A. Conesa, Thermogravimetric kinetic analysis and pollutant evolution during the pyrolysis and combustion of mobile phone case, Chemosphere 85 (2011) 516–524.
- [23] Z. Wang, J. Wang, H. Richter, J.B. Howard, J. Carlson, Y.A. Levendis, Comparative study on polycyclic aromatic hydrocarbons, light hydrocarbons, carbon monoxide, and particulate emissions from the combustion of polyethylene, polystyrene, and poly(vinyl chloride), Energy Fuel 17 (2003) 999–1013.
- [24] A. Valavanidis, N. Iliopoulos, G. Gotsis, K. Fiotakis, Persistent free radicals, heavy metals and PAHs generated in particulate soot emissions and residue ash from controlled combustion of common types of plastic, J. Hazard. Mater. 156 (2008) 277–284.
- [25] C.-T. Li, H.-K. Zhuang, L.-T. Hsieh, W.-J. Lee, M.-C. Tsao, PAH emission from the incineration of three plastic wastes, Environ. Int. 27 (2001) 61–67.
- [26] B. Shemwell, Y. Levendis, Particulates generated from combustion of polymers (plastics), J. Air Waste Manage. Assoc 50 (2000) 94–102.