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PCDD/F emissions from forest fire simulations

Brian K. Gullett[a,*], Abderrahmane Touati[b]

[a] US Environmental Protection Agency (E305-01), Air Pollution Prev. and Control Division, Office of Research and Development, National Risk Management Research Laboratory, Research Triangle Park, NC 27711, USA

[b] ARCADIS Geraghty & Miller, Inc., P.O. Box 13109, Research Triangle Park, NC 27709, USA

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Abstract

Polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran (PCDD/F) emissions from combustion of forest biomass were sampled to obtain an estimated emission factor for forest fires. An equal composition of live shoot and litter biomass from Oregon and North Carolina was burned in an enclosed monitored facility, and emissions were sampled with a modified ambient air sampling method. Seven tests resulted in an average PCDD/F toxic equivalency (TEQ) emission of 19 ng/kg burned, a value close to previous indirect estimates. Emissions from the Oregon biomass averaged 25 ng TEQ/kg burned (range: 14–47) and those from the North Carolina biomass averaged 15 ng TEQ/kg burned (range: 1–56). Source-specific distinctions in isomer patterns and homologue profiles, however, suggest that the type of biomass has a significant effect on the composition of the resulting PCDD/F emissions. The mass-specific emissions are about 20 times higher than the concentration of the extracted biomass, suggesting that PCDD/F emissions are not simply a result of vaporization of cuticle-bound PCDD/F but are formed predominantly during the biomass combustion.

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1. Introduction

The year 2000 draft United States inventory of polychlorinated dibenzodioxin and polychlorinated dibenzofuran (PCDD/F) sources indicates that about 6% of the estimated total annual emissions come from forest fires (US EPA, 2001). Considerable uncertainty is associated with this estimation, primarily due to the difficulty in sampling forest fires for PCDD/F emissions and secondarily due to the challenge of quantifying the amount of biomass burning. Further, there are likely different emissions from different types of forest fires (such as crown fires versus understory and duff fires), from different species, and from different locations (e.g., near-coastal versus inland). Different combustion conditions, such as wind speed conditions and fuel moisture, may also result in variation of emissions. Same-fuel fires are likely to have distinct emissions depending on the fuel's physical orientation and combustion condition. Studies simulating forest-floor ground fires, crown fires, broadcast burns, and slash pile fires had significantly different emissions (Yokelson et al., 1996) of, for example, carbon monoxide, methane, and formaldehyde. These uncertainties limit confidence in our ability to simulate and determine a representative emission factor for forest fires.

A number of approaches have been made to determine forest fire emissions, from direct air sampling to post-fire soil sampling. Direct measurements of total PCDDs/Fs from forest fires via elevated, fixed collectors and aircraft averaged about 20 pg/m^3 (Clement and Tashiro, 1991). Buckland et al. (1994) compared soil concentrations both before and after brush fires using 2 cm surface cores, concluding that little PCDD/F

*Corresponding author. Tel.: +1-919-541-1534; fax: +1-919-541-0554.

E-mail address: gullett.brian@epa.gov (B.K. Gullett).

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increase was found and that over 94% of the PCDD/F content was octachlorodibenzodioxin (OCDD). A similar conclusion was reached with a straw burning study (Walsh et al., 1994), although OCDD concentrations increased as a result of the fire. Likewise, post-fire soil and ash samples did not yield detectable PCDD/F levels (Van Oostdam and Ward, 1995). Soil analyses from 1 to 9 months after forest fires in Korea (Kim et al., 2001) showed only slightly elevated (2×) PCDD/F levels compared to unburned soils. More evidence for a PCDD/F impact was demonstrated by the large shift in homologue profiles: the unburned control soils were dominated by the OCDD congener (60% of the total PCDD/F), while the 1-month post-burn samples show a more equal homologue distribution with only 20% due to OCDD. With time, the PCDD/F levels declined, likely due to degradation/volatilization processes.

Due to the lack of direct forest fire measurements for PCDDs/Fs and the uncertain relevance of the post-fire soil measurements, estimates of emissions have been inferred from wood-derived chimney soot PCDD/F concentrations. This inference used the assumption that all flueborne particle matter (PM) had the same PCDD/F concentration as the soot. With soot measurements by Bacher et al. (1992) and national PM estimates by Ward et al. (1993), EPA estimated (US EPA, 2001) 54 and 18 ng TEQ_{DF}/kg[1] of biomass burned in wildfires and prescribed burns, respectively. An alternative method used PCDD/F emission factors from residential wood-fired stoves (US EPA, 2001), resulting in 2 ng TEQ_{DF}/kg burned. None of the inferential methods or soil sampling methods lends great confidence to estimates of PCDD/F emissions from forest fires. Greater confidence can be obtained if actual forest fire emissions exhibit similar characteristics, such as isomer pattern distributions, to the inferential samples.

It is further unclear whether PCDD/F emissions result from combustion of the biomass itself, or whether observed levels are simply due to volatilization of compounds on the biomass surface that had previously been "scrubbed" from the atmosphere. Elevated levels of chlorinated semivolatile organics on leaf surfaces have been associated with industrial point sources (Riss et al., 1990; Sinkkonen et al., 1995, 1996) or regional emission trends (Tremolada et al., 1996), and the ability of the waxy cuticle layer on pine needles to adsorb lipophilic compounds from the atmosphere has been demonstrated (for example, Strachan et al., 1994; Horstmann and McLachlan, 1996). Comparisons of vegetation and soil after a fire with nearby unburned material show a decrease in PCDD/F after the fire, although the tetra-CDD/F homologues increased relative to the other homologues (Martinez-Cored et al., 1999). The ability to discern between PCDD/F formation anew versus simple volatilization is important in developing global balances of sources and sinks of PCDD/F.

Efforts to characterize forest fire emissions will require determination of whether emissions are affected by biomass source, fire type, geographic location, and combustion conditions. If emissions are relatively unaffected by different fire conditions, then quantification of representative PCDD/F emission factors from forest fires will be simplified.

In an initial effort to minimize some of the uncertainty regarding forest fire emission factors, forest biomass was gathered for testing in a controlled-burn facility that allowed for quantification of PCDD/F emissions. Biomass from two sites was tested to provide an initial estimate of composition-related variability in PCDD/F emissions. One additional test examined influences of fuel configuration on emissions, and another test compared a new mobile sampling method with conventional sampling results. Analyses of polychlorinated biphenyl (PCB) emissions were completed for one test.

2. Experimental

Four forest biomass samples each from the western and eastern continental US were tested for PCDD/F emissions in an "open burn facility". This facility has been used previously (see Lemieux, 1997; Gullett et al., 2001) to quantify PCDD/F emissions from uncontrolled burning (in barrels) of residential waste. Measurements of the exiting emissions from the enclosed facility, coupled with the dilution rate of the incoming combustion air and the loss-in-weight combustion platform, allow for calculation of emission factors in terms of pollutant mass/mass of biomass burned. High-volume air handlers provided metered dilution air into the burn hut, resulting in 2.5 volume changes per minute. This ensured that oxygen concentrations were not depleted and that open burn combustion conditions were maintained. Additional fans were set up inside the burn hut to enhance recirculation. PCDD/F measurements were made via a Graseby™ PS-1 sampler by EPA's ambient TO-9 (Winberry et al., 1988) method which consists of an open-faced filter holder followed by polyurethane foam (PUF) surrounding an XAD-2 sorbent. A copper cooling coil was fabricated to enclose the exterior of the PUF module, thereby keeping the PUF module cool. For two tests, parallel sampling was conducted with a prototype portable sampler ("Nomad", denoted as "N" in figures) meant for mobile, in-field sampling. The Nomad consists of a TO-9 head and

[1] TEQ_{DF} is toxic equivalency for PCDD/F. Values cited in the Introduction are based on the International toxic equivalency factor assignments (US EPA, 1989), while this work used more recent factor assignment based on Van den Berg et al., 1998.

PUF/XAD/PUF cartridge coupled to a high-volume sampler. In these tests, the Nomad was stationary, with its probe inserted into the burn hut. In both sampling cases, the combined filter and PUF/XAD-2 module was analyzed using high-resolution gas chromatography and mass spectrometry (HRGC/HRMS) for PCDD/F (in this paper, all references to PCDD/F concentrations include tetra- to octa-homologues only). PCDDs/Fs and PCBs were analyzed via SW846 Method 23/8290 (US EPA, 1995) and Modified EPA Method 1668A (US EPA, 1999), respectively. Surrogate/internal recoveries were all within the specified calibration limits of the respective methods (40–130% for the tetra- to hexa-chlorinated PCDD/F isomers and PCB isomers, 25–130% for the hepta- and octa-chlorinated PCDD/F isomers, and 70–130% for the surrogate standard recoveries). Background blank tests (sampling without waste combustion) were conducted to ensure that the sampling and analysis methods, potential facility contamination, and ambient feed air PCDD/F concentrations were not biasing the tests.

Estimated emissions of PCDD/Fs per unit mass burned were calculated using

$$E = (C_{\text{sample}} Q_{\text{hut}} t_{\text{run}})/(m_{\text{burned}}),$$

where E is the estimated emissions in ng/kg burned, C_{sample} is the concentration of the pollutant in the sample in ng/m^3, Q_{hut} is the flow rate of dilution air into the burn hut in m^3/min, t_{run} is the run time in min, and m_{burned} is the mass in kg of biomass burned over the run. These estimated emissions express a mass of analyte produced per mass of fuel consumed in the combustion process. TEQ factors for the 2,3,7,8-chlorine-substituted congeners (Van den Berg et al., 1998; often referred to as "TEQ-WHO$_{98}$") were used to derive the TEQ value. All non-detects (NDs) were set to zero. Isomer peaks that did not meet the ion ratio criteria, but whose presence was confirmed in other replicate experiments, were set to the estimated maximum potential concentration (EMPC, defined from the integrated peak area as if the ion ratio criterion was satisfied). This had only a 4% effect on the average TEQ value. Background levels sampled through the controlled burn facility resulted only in consistently detectable isomers 2,3,7,8-TeCDF, 1,2,3,4,7,8-HxCDF, and OCDD. The average sample run/background ratios for these isomers were highest for the NC samples at > 2, 2, and 6, respectively. However, since the TEQ factors for these isomers are $\leqslant 0.1$, the calculated TEQ value was affected <4% by the exclusion of these isomers. This suggests that the emission samples were of sufficient concentration to minimize concerns of background effects. Besides emission factors, variable effects were also assessed by comparing PCDD-to-PCDF ratios, relative homologue profiles, and TEQ isomer patterns. Profiles and patterns were compared visually and by multivariate correlation analyses.

Forest biomass was gathered from two locations: the Oregon (OR) coast near Seal Rock (44°29′N and 124°4′W) in a 200×250 m^2 collection area and the North Carolina (NC) Piedmont region (35°52′N, 78°47′W, about 200 km from the Atlantic Ocean coast) from a similarly sized area. In both locations, biomass was obtained by cutting needles from tree branches (live shoots, 49–58% moisture) and gathering the needle litter from the forest floor (6–20% moisture). The OR live shoots were composed of pine needles (about 30% *Pinus contorta* and 70% *Pinus monticola*) and hemlock needles (100% *Tsuga heterophylla*), and the needle litter was about 20% pine needles and 80% hemlock needles (Table 1). An as-received OR live shoot and litter sample (ORas-rec) was extracted to determine the PCDD/F concentration in the waxy cuticle. In general, equal proportions of live shoots and needle litter composed the combusted test samples. The NC live shoots and needle litter were both composed of loblolly pine (*Pinus taeda*) and, again, were generally tested in equal amounts. The needle litter layer had a much lower Cl concentration than that of the green needles. This may be due to environmental weathering processes such as biological

Table 1
Composition and chlorine content of the forest biomass

Biomass location	Biomass type	Composition	Species/composition	Mass (%)	Cl (mg/kg)	Composite Cl (mg/kg)
Oregon (OR)	Live shoots	Pine needles	*P. contorta*	30	3400	
			P. monticola	70		
		Hemlock needles	*T. heterophylla*	100	1800	1600
	Needle litter	Plant litter	Pine needles	20	650	
			Hemlock needles	80		
North Carolina (NC)	Live shoots	Pine needles	*P. taeda*	100	380	300
	Needle litter	Plant litter	*P. taeda*	100	220	

decay and rain-induced leaching (McKenzie et al., 1996).

All but one test used a simple, low-lying (10 cm high) pile of biomass on top of an open, flat combustion platform (in one test, OR2B, the biomass was filled into a metal barrel with air holes cut in the bottom to determine the effect of fuel configuration on PCDD/F emissions). Fuel loadings varied from about 10 to 40 kg. The fire was started with a propane torch, and sampling was initiated upon sustained combustion. The biomass burned varied from 7 to 32 kg during sampling times ranging from 60 to 210 min, with a typical burn rate of 0.10 to 0.15 kg/min. At all times, sampling continued until smoldering was no longer observed.

3. Results and discussion

PCDD, PCDF, and total PCDD + PCDF TEQ emission factors for the two forest biomasses are shown in Fig. 1. The average total emission factor for the four NC biomass runs (NC1, 2, 3, and 4) is 15 ng TEQ/kg burned (range: 1–56), but this value is strongly influenced by one run (NC2). The average total emission factor for the three repeat OR biomass runs (OR1, 3, and 4) is 25 ng TEQ/kg burned (range: 14–47). These emission factors compare with an average of 0.60 ng TEQ/kg from industrial wood combustors in the US (US EPA, 2001). While the NC and OR biomasses have similar total TEQ values, these values are derived inconsistently from the PCDD and PCDF fractions. Most of the NC TEQ value is derived from the PCDD congeners; whereas, for the OR emissions, most of it comes from the PCDF congeners (see Fig. 1). Comparison of the PCDD/F emission concentrations and ratios of PCDD to PCDF concentrations (Fig. 1) highlights distinctions between the biomass emissions. The PCDD to PCDF concentrations for the NC biomass were significantly higher than those of the OR, resulting in a PCDD/PCDF ratio always greater than 1. The OR biomass emissions had a PCDD/PCDF ratio of around 1 or less. This may be due to an effect of the Cl content on PCDD/PDF ratio. Earlier work (Ryan, 2001) pointed out that PCDD/PCDF ratios dropped with increasing Cl concentration, consistent with results observed here, but the data reported here are insufficient to make conclusions.

Considerable intra-biomass-source TEQ variation (a factor of > 50 for NC biomass, caused by one run, and a factor of about 4 for OR biomass) is observed. This relatively high variation is consistent with previous results for domestic waste burns (Gullett et al., 2001) and likely reflects the impact of random variation in fuel orientation on PCDD/F formation. Run NC2 has a distinctively high PCDD TEQ value when compared to the other NC runs. This run was sampled after replacing the Tedlar® lining of the burn facility (necessitated by a previous run in which high temperatures had melted the Tedlar), but this is unlikely to have affected the results. Comparison of NC2's 2,3,7,8-Cl-substituted PCDD isomer pattern (Fig. 2A) and its PCDD homologue profile (shown later in Fig. 4A) shows similarities with the other NC biomass runs [large distinctions are noted with NC2's PCDF profile (Fig. 4A), but the PCDF component of the TEQ value is minor]. These comparisons suggest that NC2's TEQ value, while appearing exceptionally high, did not result from some significant mechanistic shifts or sampling/analytical errors but,

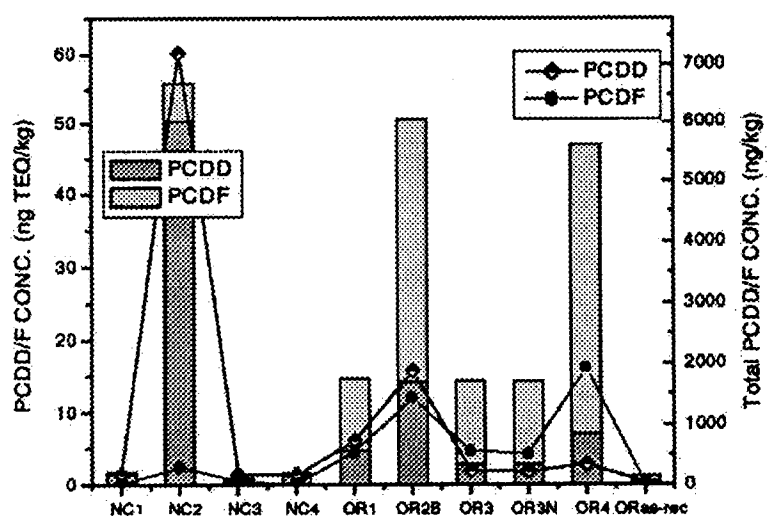

Fig. 1. Total and TEQ PCDD and PCDF emissions from forest biomass tests. OR = Oregon biomass, NC = North Carolina biomass. ORas-rec is the raw, as-received, extracted OR biomass. Numbers indicate test identification, B = barrel test, N = nomad sampler. Bars, left axis; symbols and lines, right axis. Solid circle = PCDF, diamond = PCDD.

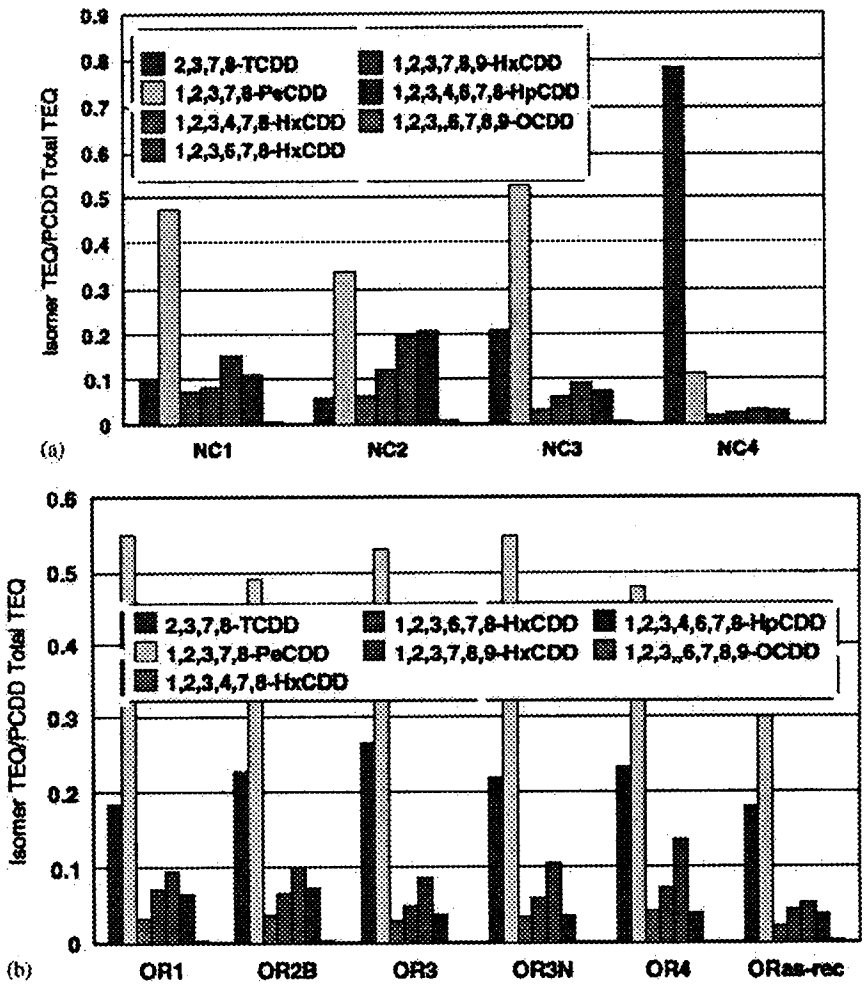

Fig. 2. (A) Distribution of PCDD TEQ isomers, NC biomass emissions. (B) Distribution of PCDD TEQ isomers, OR biomass emissions and ORas-rec.

rather, is reflective of the vagaries of combustion condition effects on emissions. More rigorous monitoring of combustion conditions would be expected to clarify the cause of the large variation in emission values.

Figs. 2A and B compare the contribution of the 2,3,7,8-Cl-substituted PCDD congeners relative to the total PCDD TEQ value for the NC and OR sources, respectively. With one exception (NC4), the 1,2,3,7,8-PeCDD contributed about 50% of the TEQ value for both biomass sources. The NC4 2,3,7,8-Cl-substituted PCDD pattern closely resembles that obtained from wood chimney soot (Bacher et al., 1992), from which the US EPA has based its forest fire PCDD/F emission factor (US EPA, 2001). The TEQ fraction distributions are relatively consistent within and between sources, with the possible exception of a consistently higher contribution of 2,3,7,8-TCDD from the OR biomass (Fig. 2B). The cause of the strong contribution of 2,3,7,8-TCDD limited to NC4 (Fig. 2A) is unknown.

Figs. 3A and B illustrate the relative contribution of the 2,3,7,8-Cl-substituted PCDF congeners to their total TEQ values for the NC and OR sources, respectively. These patterns consistently show that the largest contribution to the PCDF TEQ value comes from the 2,3,4,7,8-PeCDF. As with the PCDD patterns, there is only slight variation of the PCDF patterns both within and between biomass sources.

Figs. 4A and B show that there is general consistency of homologue profiles within a source (compared on a mass fraction basis), although there is a surprising difference between the two biomass sources. The NC profiles (from Fig. 4A) are dominated by the OCDD and TCDF homologues whereas the OR profiles (from Fig. 4B) are dominated by the TCDD and TCDF homologues. While homologue profiles have been

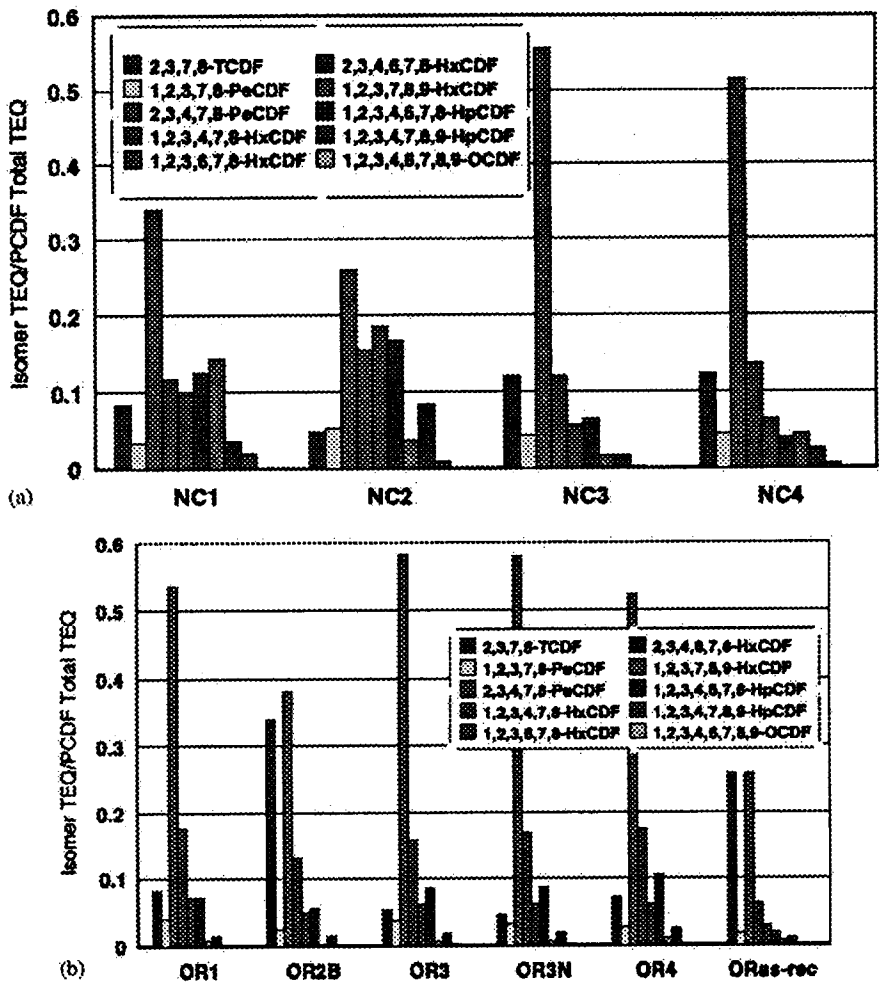

Fig. 3. (A) Distribution of PCDF TEQ isomers, NC biomass emissions. (B) Distribution of PCDF TEQ isomers, OR biomass emissions and ORas-rec (2,3,7,8-TeCDF value is a co-eluting contaminant: actual value is less than that plotted).

observed to shift with combustion conditions (Gullett et al., 1998, Wikström et al., 1999), the repetitive procedures of the experiments suggest that this is an insufficient explanation. More likely the cause of the profile distinctions is in the fuel composition itself.

The toxic equivalency factor (TEF)-weighted isomer patterns and homologue profiles (Figs. 2–4) were further analyzed via principal components analysis (PCA) to discern similarities and distinctions between the runs. The score plot in Fig. 5A shows the relationships among the observations, and the loading plot in Fig. 5B does the same for the variables. The first two principal components, plotted in Figs. 5A and B, account for 66% of the variation. The OR observations are grouped together (Fig. 5A), reflecting the similarity of their patterns and profiles. Little distinction is observed with the ORas-rec sample. The NC samples show more scatter and are distinctive from the OR results. NC2 and NC4 show more divergence from the other runs. The load plot (Fig. 5B) indicates that the variation of NC2 is due to low fractions of TeCDD and high concentrations of the HpCDD/HxCDD isomers, and that of NC4 is due to the high concentration of 2,3,7,8-TeCDD (noted earlier). This analysis provides preliminary evidence for substantial biomass source-specific variation in PCDD/F emission characteristics.

Comparison of these forest emission homologue profiles with average homologue profiles for multiple industrial wood combustion facilities (US EPA, 2001) shows interesting distinctions. The wood combustion has maximum homologue peak concentrations for OCDD and TCDF-PeCDF (not shown) consistent with the NC profiles but not with the high TCDD peak of the OR biomass. However, the total PCDD/PCDF ratio from these facilities, 0.75, is more consistent with the OR runs than the NC runs (see Fig. 1). This appears also

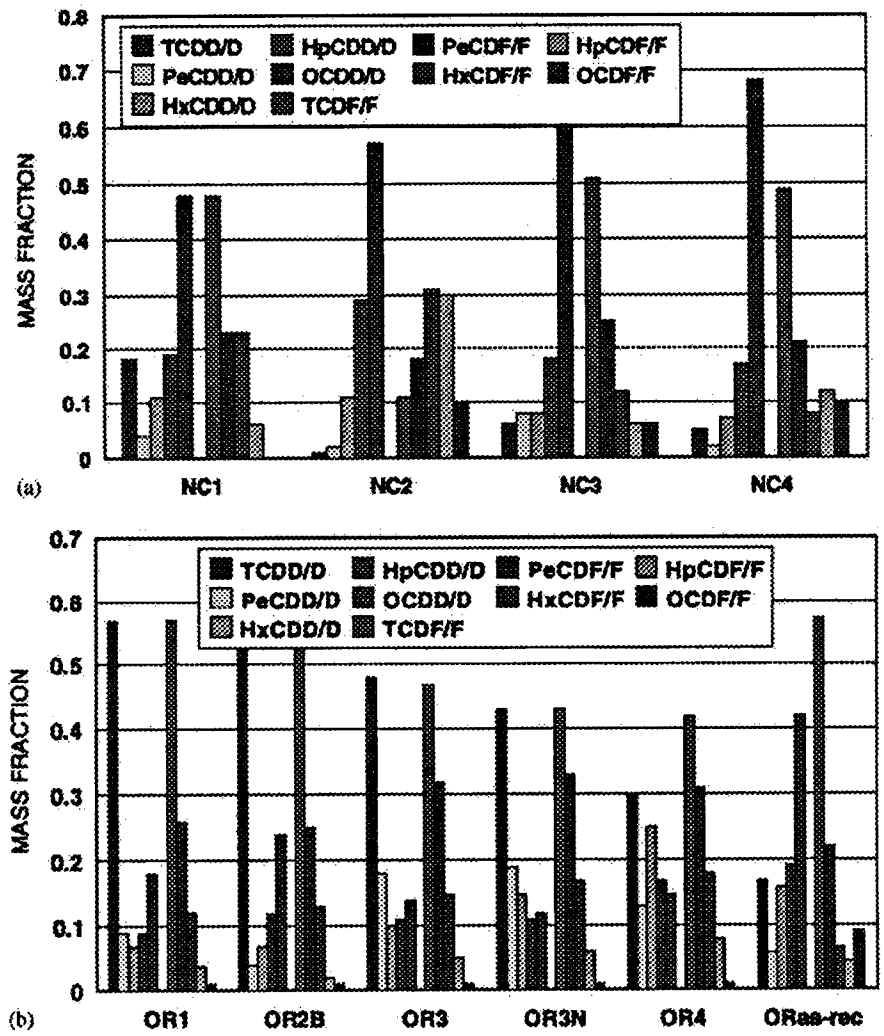

Fig. 4. (A) Distribution of PCDD and PCDF homologues, NC biomass emissions. (B) Distribution of PCDD and PCDF homologues, OR biomass emissions.

true for the PCDD/PCDF TEQ ratio (not shown), although a high degree of scatter tempers this conclusion.

While too few replicate samples were run to declare these emission factors to be statistically distinct, the slightly higher values for the OR biomass burns may have been due to the higher Cl content of the OR biomass (1615 versus 300 ppm for the NC biomass—see Table 1). Chlorine concentration varies with proximity to large sources of chloride ions, and coastal vegetation has particularly high concentrations relative to inland vegetation (McKenzie et al., 1996). This may be responsible for the generally higher PCDD/F TEQ and total values observed with OR biomass but, since the experiments were not specifically designed to answer this question, this conclusion remains tentative. Likely, other combustion-related factors are more critical toward determining distinctions in emissions than Cl (Gullett et al., 2001).

The run with biomass combusted in the barrel (OR2B) has the highest total TEQ emission value (47 ng TEQ/kg burned) for the OR samples. However, this is not inconsistent with the value obtained with run OR4 (46 ng TEQ/kg burned) during the typical open platform burn (see Fig. 1). This suggests that, while combustion conditions may significantly vary PCDD/F emissions, any differences induced by the barrel burning (with this single test) are within the range of variation observed in the open burning conditions. The third OR biomass run included both a TO-9 sample (OR3) and a Nomad sample (OR3N). Both of these samples show very similar PCDD/F TEQ values (Fig. 1). PCDD/F

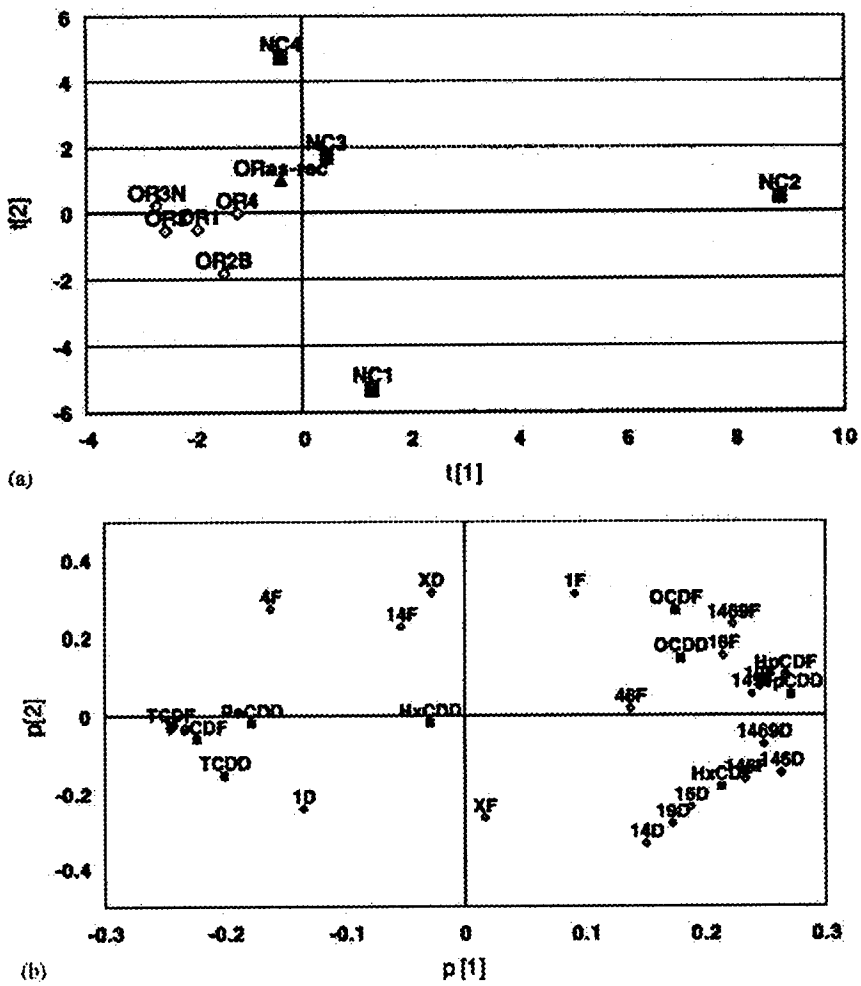

Fig. 5. (A) PCA score plot of first two principal components of isomer pattern and homologue profile fractions, showing each experiment. (B) PCA loading plot of first two principal components of isomer pattern and homologue profile fractions (isomers are indicated by the chlorine positions in addition to 2,3,7,8; e.g. "14F" = 1,2,3,4,7,8-hexachlorodibenzofuran, "XD" = 2,3,7,8-tetrachlorodibenzodioxin).

total (Fig. 1), PCDD/PCDF ratio values (Fig. 1), homologue profiles (Fig. 4B), and isomer patterns (Figs. 2B and 3B).

A multivariate correlation analysis of the non-TEF-weighted, 2,3,7,8-Cl-substituted, isomer fraction patterns and homologue fraction profiles for all of the OR runs showed remarkable similarity. Pearson product moment correlations, R, were greater than 0.86 and 0.84 for the isomer patterns and homologue profiles, respectively, suggesting that the barrel method of combustion (OR2B) and the use of the Nomad sampler (OR3N) are indistinguishable from the baseline OR1, 3, and 4 tests. These results suggest that any potential differences in combustion conditions for these specific tests had minimal impact on the emissions and that the two sampling methods employed are consistent. These results are preliminary, due to the limited run numbers, but they do suggest that emissions are not a function of biomass depth (open pile versus stacked pile in the barrel) and that the Nomad sampling method has promise as a method of near-fire mobile sampling.

The ability of needle cuticle layers to "scrub" halogenated contaminants from the air (Froese et al., 1998, 1999) raises a question as to whether the observed emissions are due to simple vaporization of existing PCDDs/Fs or formation anew. The raw, as-received OR biomass was extracted and analyzed for PCDDs/Fs to compare with the emissions. The PCDD/F concentration measured 1.3 ng TEQ/kg, considerably lower than the measured OR emissions which ranged from 14 to 47 ng TEQ/kg (the denominator value of 'as-received mass' for the former, versus 'mass burned' for the latter, makes little difference, as virtually all of the mass is lost during combustion). Comparison of the 2,3,7,8-Cl-substituted PCDD (Fig. 2B) isomer fraction pattern for the emissions with that of the raw needles (ORas-rec)

shows no discernible distinction. The same comparison for the PCDF isomers (Fig. 3B) indicates overall pattern similarity (the elevated level of 2,3,7,8-TeCDF on ORas-rec is a co-eluting contaminant so its real value is less than the plotted bar indicates). Since these are only single samples, conclusions from these samples would be premature. Nonetheless, the overall similarity between the on-needle concentrations (ORas-rec) and the multi-run OR emissions is worth noting; correlations, R, are > 0.81. Previous studies have indicated that pine needle concentrations were indicators of ambient air concentrations [for example, Ok et al., 2002; Tremolada et al., 1996 (for polychlorinated biphenyls)]. This work preliminarily suggests that, if pine needles adsorb emissions primarily from proximal pine forest fires, the needles appear to do so without isomer preference, preserving the emission isomer pattern. The ORas-rec homologue profile shows significant distinctions over those of the OR emissions (Fig. 4B), averaging only $R = 0.50$.

PCB emissions for one run (OR4) were 0.7 pg TEQ/kg for ND = 0 and 1.5 pg TEQ/kg for ND = instrument detection limit (DL). The PCBs represent a fairly minor (<2%) fraction of the total PCDD/F TEQ value. The 18 coplanar PCB isomers were 5.24% of the total PCB mass (390 ng/kg, at ND = 0), which compares well with 5.58% found in totally burned, post-forest-fire soil samples (Gabos et al., 2001). The sum of the mono- to tri-chlorinated biphenyls, 206 ng/kg, is much greater than that reported earlier for industrial wood combustion, 37 ng/kg (CARB, 1990a, b). The sampled PCB levels were over 100 times the concentration of the background blank, lending confidence to their values.

4. Conclusions

The greater than 10-fold increase in the PCDD/F TEQ emission factor (ng TEQ/kg) for the emissions over that of the extracted ORas-rec biomass offers preliminary evidence that forest fire emissions are not solely due to vaporization of cuticle-bound PCDD/F. PCDD/F is formed anew during forest fires and may be adsorbed by the waxy cuticle in such a manner that the isomer pattern (and less so the homologue pattern) is reflective of the ambient concentrations.

The results of high OCDD emissions are contrary to the common combustion homologue profile (as shown in Baker and Hites, 2000). The discrepancy between environmental sink profiles from soils and sediments (with high OCDD levels) and this assumed combustion profile has been explained by photoreactive degradation of less chlorinated congeners (Brubaker and Hites, 1997), atmospheric reactions of pentachlorophenol into OCDD (Baker and Hites, 2000), degradation or volatilization of less chlorinated congeners (Gaus et al., 2001), and dechlorination (Gaus et al., 2001). However, given the prevalence of OCDD observed in our work from forest biomass fires, an alternative, if only partial, explanation is that the "common combustion profile" is more typical of industrial, rather than biomass, sources, reflecting predominant sampling efforts from anthropogenic sources.

Annual US forest fire emissions of PCDD/F can be estimated based on annual wildfire consumption data. Between 1991 and 2000, a yearly average of about 1.7 million ha were consumed by forest fires in the US (NIFC, 2001) with an estimated consumption of 23,000 (Ward et al., 1976) to 38,000 kg/ha (Yamate, 1973). Using an average emission factor from this work of 20 ng TEQ/kg burned results in an annual emission of about 800–1300 g TEQ, among the largest from any single source category in the US (US EPA, 2001). However, this estimate is only preliminary until additional work can further understand the potential for emission factor differences due to species type, location, and type of fire.

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