Atmospheric Environment 42 (2008) 7997–8006

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

PCDD/F and aromatic emissions from simulated forest and grassland fires

B. Gullett [a,*], A. Touati [b], L. Oudejans [b]

[a] U.S. Environmental Protection Agency, Office of Research & Development, National Risk Management Research Laboratory, E305-01, Research Triangle Park, NC 27711, USA
[b] ARCADIS U.S., 4915 Prospectus Drive, Suite F, Durham, NC 17713, USA

ARTICLE INFO

Article history:
Received 7 March 2008
Received in revised form 19 June 2008
Accepted 20 June 2008

Keywords:
PCDD
PCDF
Fire
Biomass
Emissions
Pollution
Forest
Grass

ABSTRACT

Emissions of polychlorinated dibenzodioxin and polychlorinated dibenzofuran (PCDD/F) from simulated grassland and forest fires were quantitatively sampled to derive emission factors in support of PCDD/F inventory development. Grasses from Kentucky and Minnesota; forest shrubs from California and Florida; and pine forest biomass from the Piedmont region of North Carolina, western North Carolina, and coastal Oregon were collected and tested in a burn facility that mimicked a prescribed fire in the natural environment scenario. Ambient sampling methods for PCDD/F were variously accompanied by real-time measurements of major aromatic species, including benzene, toluene, naphthalene, and styrene. Emission factors in mass of toxic equivalent (TEQ) of PCDD/F per kg of carbon burned (kg_{Cb}) for the two grasses averaged 0.32 ng TEQ/kg_{Cb}. Burn tests ($n = 27$) on forest biomass from the five sources show PCDD/F emission factors ranging from 0.3 to 26.3 ng TEQ/kg_{Cb}, with a mean and median of 5.8 and 3.3 ng TEQ/kg_{Cb}, respectively. Variation of the forest green/brown needle content, sample size, burn scenario, and facility ventilation rate showed no consistent effects on PCDD/F emissions. For forest burns, 30–35% of the PCDD and 50-55% of the PCDF emissions occurred during the flaming period from 0 to 5 min, while the highest emission factors (per mass of carbon burned) were recorded during the smoldering period from 5 to 60 min. Emissions of PCDD/F exceeded those present in the raw biomass by a factor of four, confirming PCDD/F formation from combustion rather than from simple surface volatilization. The majority of the PCDD/F partitions to the emissions rather than the ash.

Published by Elsevier Ltd.

1. Introduction

Efforts to reduce anthropogenic sources of polychlorinated dibenzodioxin and polychlorinated dibenzofuran (PCDD/F) emissions over the last few decades have significantly reduced levels from major industrial sources, such as municipal waste combustors. For example, estimated PCDD/F releases to the air from U.S. municipal waste combustors have dropped from 7915 g I-TEQ_{DF} (international toxicity equivalents) in reference year 1987 to 79 g I-TEQ_{DF} in year 2000 (U.S. EPA, 2006). The total U.S. year 2000 inventory of sources for which reasonably quantifiable data were available was about 1500 g I-TEQ_{DF}. However, emissions from forest and brush fires, assigned a low confidence rating of D (based on extremely limited and likely non-representative data), are estimated to have exceed 4200 g I-TEQ_{DF} for reference year 2000 (U.S. EPA, 2006). Thus, the uncertain value for forest and brush fires may exceed the value for all known and compiled U.S. industrial sources. This uncertainty should be minimized in order to promote policies and regulations that will be effective at reducing emissions and, ultimately, minimizing human and environmental exposure.

PCDD/F emission factors for forest and brush fires are very limited in number. This is primarily due to a historical focus on industrial sources and an under-appreciation of

* Corresponding author. Tel.: +1 919 541 1534; fax: +1 919 541 0554.
E-mail address: gullett.brian@epa.gov (B. Gullett).

1352-2310/$ – see front matter Published by Elsevier Ltd.
doi:10.1016/j.atmosenv.2008.06.046

biomass sources, but also reflects the difficulty in obtaining accurate and representative values for emissions from large scale, open, uncontrolled burning. Indirect approaches estimate the amount of PCDD/F emitted by analyzing the residual ash but this method has considerable uncertainty due to unknown PCDD/F partitioning to the air and the ash. Direct air sampling methods in the field can be hampered by the difficulty of representatively sampling a large source with sufficient gas volume to exceed method detection limits. Further, variations in vegetation types and fire conditions will lead to different emissions, such that limited field measurements may not characterize the range of emission factors. Fire simulations, in which the fuel is brought to a testing chamber for contained combustion, can suffer from limitations of accurately simulating the field combustion scenario on a small scale (see for example, discussions in Supplementary Information in Gullett et al., 2006, and Meyer et al., 2004a,b).

Kim et al. (2003) applied an indirect approach by sampling forest soils and ash, showing elevated levels of PCDDs/Fs 1 month after a fire. The United Nations Dioxin and Furan Toolkit (UNEP Chemicals, 2001) uses a correlation between biomass ash and emissions of PCDD/F, citing emission factors of 4 and 5 ng TEQ/kg burned, respectively. However, few studies have been done to support this partitioning. Clement and Tashiro (1991) applied direct measurement using tower-mounted high volume samplers to find PCDD/F concentrations around 20 pg/m^3. Experimental studies (Martínez et al., 1999; Prange et al., 2003) have raised doubts as to whether forest fires were even a significant source of PCDD/F, suggesting that fires act only to redistribute the PCDD/F contamination. This conclusion contrasts to that demonstrated by Gullett and Touati (2003) whose forest burn simulations found a 10-fold increase in PCDD/F levels above that of as-received levels. Emission factors for two coniferous forest biomasses ranged from 1 to 56 ng TEQ/kg burned, with median values of 3.8 and 14.0 ng TEQ/kg burned. Recent data (Collet, 2004) from forest biomass burns in France from a burn chamber simulation showed an average and median emission factor of 34.0 and 26.2 ng/kg$_{Cb}$. Field burning samples using fixed towers in Florida (USA) and indirect correlations with measured pollutants found a range of PCDD/F values, ranging from 0.9 to 9.3 ng TEQ/kg fuel. Emission factors ranging from 0.1 to 2.9 ng TEQ/kg fuel for PCDDs/Fs and PCBs from diverse sources including prescribed fire, wildfires, and sugarcane fires have been found in Australia (Meyer et al., 2004b). More recent work by this group found about 0.5 ng TEQ/kg fuel (1 ± 0.5 ng TEQ/kg$_{carbon}$) for prescribed fires, wild fires, and savannah fires (Meyer et al., 2007).

The testing, sampling, and assumptions with these methods are certainly responsible in part for the large variation in emission factors. However, these apparent contradictions may also be attributed to variation in emissions due to likely species-specific differences, fire type differences (e.g., forest crown fires versus understory fires), and geographical differences (e.g., near-coastal versus inland). Differences in combustion conditions, such as moisture, have been noted (Yokelson et al., 1996) to affect emissions as well as the fuel's physical orientation. Carbon monoxide, methane, and formaldehyde emissions (for example) varied in studies simulating forest-floor, ground fires, crown fires, broadcast burns, and slash pile fires (Yokelson et al., 1996). Source-specific differences in PCDD/F emission factors ($10\times$) have been noted with sugarcane (genus *Saccharum*) types (Gullett et al., 2006).

These uncertainties limit confidence in our ability to sample or simulate open biomass fires and to determine a representative emission factor for these fuels. Questions regarding whether PCDD/F forms anew or simply volatilizes from biomass surfaces are critical toward understanding the role of biomass combustion in the global PCDD/F balance. This paper attempts to lessen these uncertainties by presenting PCDD/F emission results from multiple forest tree, forest shrub, and grass burn simulations. Different burn scenarios are simulated and different stages of combustion emissions are sampled in order to understand variables that affect emission factors.

2. Experimental

2.1. Biomass sources

Two grass sources and five forest sources from field sites throughout the USA were collected opportunistically from multiple research projects and tested over a several-year period in an "open" burn facility. The Central North Carolina (CNC) Piedmont region (Research Triangle Park, NC), about 250 km from the Atlantic Ocean coast, provided the majority of the forest biomass tested. The CNC forest green biomass and brown pine needle litter were both composed of loblolly pine (*Pinus taeda*) and were typically tested in equal mass amounts. The Oregon (OR) forest biomass consisted of lodgepole pine (*Pinus contorta*) and western white pine (*Pinus monticola*) and was collected at the coast near Seal Rock in a 200×250 m collection area. The OR green biomass was composed of pine needles (about 30% *Pinus contorta* and 70% *Pinus monticola*) and hemlock needles (100% *Tsuga heterophylla*), and the litter was about 20% pine needles and 80% hemlock needles. These first two forest locations correspond to source sampling sites reported earlier (Gullett and Touati, 2003). Green needles were cut from tree branches (live shoots, $55 \pm 9\%$ average moisture levels) and litter was gathered from the forest floor ($18 \pm 8\%$ average moisture). The WNC species were comprised of eastern white pine (*Pinus strobus*), native to eastern North America, and were gathered near Blue Ridge Parkway, Western North Carolina. The Florida (FL) forest samples (average of 8% moisture) were taken in Tate's Hell Swamp, 16 km east of Carrabelle, FL, along the southern tip of the Apalachicola National Forest. The biomass shrub samples were taken in conjunction with a field sampling program (Battelle, 2004a). The fuel loading in the sampled area was heavy and consisted of titi (*Cyrilla racemiflora* L.), pine straw, and gallberry (*Ilex glabra*) under a canopy of unburned tall pine timber. The California (CA) biomass was collected from the former Fort Ord site in northwestern Monterey County. The vegetation type was primarily uniform and dense stands of maritime chaparral species with minor acreage of grasslands (MACTEC, 2004). Minnesota (MN) grasses were taken from the site of a prescribed burn (Battelle, 2004b) in