

PCDD AND PCDF EMISSIONS FROM SIMULATED SUGARCANE FIELD BURNING

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ABSTRACT

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The emissions from simulated sugarcane (*Saccharum officinarum*) field burns were sampled and analyzed for polychlorinated dibenzodioxins and dibenzofurans (PCDDs and PCDFs). Sugarcane leaves from Hawaii and Florida were burned in a manner simulating the natural physical dimensions and biomass density found during the practice of pre-harvest field burning. Eight composite burn tests consisting of 3 to 33 kg of biomass were conducted, some with replicate samplers. Emission factor calculations using sampled concentration and measured mass loss compared well to rigorous carbon balance methods commonly used in field sampling. The two sources of sugarcane had distinctive emission levels, as did tests on separate seasonal gatherings of the Florida sugarcane. The average emission factor for two tests of Hawaii sugarcane was 253 ng toxic equivalent (TEQ) per kg carbon burned (ng TEQ/kg_{Cb}) (rsd = 16%) and for two gatherings of Florida sugarcane was 25 ng TEQ/kg_{Cb} (N=4, rsd = 50%) and 5 ng TEQ/kg_{Cb} (N = 2, rsd = 91%). The Hawaii sugarcane, as well as most of the Florida sugarcane tests, had emission values which are well above the value of 5 ng TEQ/kg_{Cb} commonly attributed to biomass combustion. Application of this emission factor range to the amount of U.S. sugarcane fields burned suggests that this practice may be a relatively minor source of PCDDs and

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5 PCDFs in the U.S. national inventory, but the limited sample size and range of results make this conclusion tenuous.

Introduction

Limited data (1, 2) suggest that field burning of agricultural crops can result in formation and emission of polychlorinated dibenzodioxins and dibenzofurans (PCDDs and PCDFs). In 2002, four U.S. states, Florida, Hawaii, Louisiana, and Texas, produced over 35 million tons of sugarcane, *Saccharum officinarum* (3). A common pre-harvest practice is to burn off the leaves, dry cane tops, and ground trash (4), aiding in the stalk harvest by minimizing unwanted biomass and reducing snake and insect hazards. Sugarcane residue burning is also applied to post-harvest fields, after the whole stalks (with leaves) have been laid onto heap rows or removed by a combine system.

Few references are available on air emissions from this practice. Particulate matter (PM), polycyclic aromatic hydrocarbons (PAHs), and elemental constituents of particles have been sampled during sugarcane field burning and laboratory combustion tests (5) and in wind tunnel combustion experiments (6). Emission data for PCDDs and PCDFs appear limited to recent reports from Australia (2, 7). These reports cite field sample values of 1.2 and 2.9 ng TEQ (kg fuel C)⁻¹, while noting significantly higher values from laboratory simulations: 3.7 to 20 ng TEQ (kg fuel C)⁻¹. The authors attribute the apparent discrepancy to inadequate laboratory simulations (extended gas/particle duration at elevated temperatures) of open field burning, while also mentioning a reactant role of prevalent octachlorodibenzodioxin (OCDD) found in the local soil samples. The apparent order of magnitude difference between field-sampled and laboratory-simulated emissions complicates accurate determination of emission factors for all biomass burning and, hence, global inventories required by the Stockholm convention on persistent organic pollutants or POPs (8).

In an effort to estimate emissions of PCDD and PCDF from sugarcane field burning and to reconcile discrepancies in published field sampling with laboratory simulations, testing on two U.S. sugarcane sources was undertaken. Emission factors were determined by direct mass measurement as

5 well as by carbon balance methods typically employed during field sampling. Simulation conditions, sampling methods, interlaboratory analyses, and PCDD/PCDF isomer and homologue results were examined and compared with literature references.

10 **Experimental Methods**

Test Facility. Sugarcane biomass from Hawaii and Florida was tested for its combustion emissions of PCDD and PCDF in an “open burn test facility.” This facility has been used previously (9, 10) to quantify PCDD/F emissions from uncontrolled burning of numerous fuel sources, including forest matter (11) and wheat and rice stubble (1). Measurements of the emissions exiting from the enclosed facility, coupled
15 with the dilution rate of incoming combustion air and a loss-in-weight combustion sample pan (1.1 m x 1.1 m x 15 cm), allow for calculation of emission factors in terms of pollutant mass per mass of biomass burned. The open burn test facility consists of a 3.0 x 2.8 x 2.4 m structure constructed with sheet metal walls that have been finished on the inside with sheetrock wallboard. The walls were lined with a certified (ASTM B-479) clean aluminum foil (Ultra High Vacuum) and changed between source types and
20 composite runs to prevent cross-contamination from previous biomass burns. Thermocouples (Type K) were placed atop the fuel pile in the sample pan, 2 m above the combustion pan, at two of the walls, and at the entrance to the transfer duct.

High volume air handlers provided metered dilution air into the test facility to help ensure that
25 open burn conditions (high ambient air dilution with minimal depletion of the oxygen concentration) were maintained within the facility during the tests. Other fans and flow deflectors within the test facility were positioned to enhance air circulation, while preventing the incoming air from directly blowing on the flames. For the Hawaii sugarcane tests, the air handlers resulted in approximately 1 volume change every 2 min. For the first gathering of Florida sugarcane (FLI), high-volume air handlers and an induced
30 draft fan (to account for the addition of a baghouse filter) resulted in a higher air exchange rate of about 1 volume change every 1 min. All of the dilution air and combustion emissions exited the test facility through a 20.3 cm diameter transfer duct. The second gathering of Florida sugarcane (FLII) was tested in

5 a new, larger burn facility with inner dimensions of 3.86 m x 3.86 m x 4.06 m high. The concrete block walls were lined with aluminum panels for ease of cleaning. The input fans resulted in an air exchange rate of about 1 volume change every 40 s.

Continuous emission monitors (CEMs) for carbon monoxide (CO), carbon dioxide (CO₂), oxygen
10 (O₂), and total hydrocarbons (THCs) received emissions from the transfer duct via a heated (120 °C) Teflon tube with an in-line heated (120 °C) quartz filter. The gases were dried with a refrigerated air drier and silica desiccant prior to measurement. The CEMs were calibrated using compressed gases before and after sampling, including range midpoints, as per published procedures (12). Potential bias due to losses in the sample transfer line was monitored by injecting the calibration gases both at the point of
15 sampling and at the inlet of the gas analyzers.

The effect of sugarcane leaf orientation was tested to assess potential difference in emissions from on-stalk burning versus on-ground litter burning. The sugarcane leaves were either set upright by supporting them within a grid comprised of three horizontal levels of rigid woven wire screen (1 m x 1 m
20 square, with 2.5 cm mesh size) or laying them in a pile (10 cm high) atop a layer of pre-cleaned sand, both fully supported by a metal combustion pan. The Hawaii sugarcane was burned upright using the grid. The Florida sugarcane was burned in a pile, except for a single run which was burned in the grid to check the effect of biomass orientation. In either orientation, the sugarcane leaf trash fuel load, about 10% of the whole plant mass, was about 1.5 kg/m² (15 ton/ha) similar to average loadings (1.9 kg/m² or
25 19 ton/ha) cited elsewhere (2).

The fire was started with a propane torch and sampling was initiated upon self-sustained combustion. Emissions were gathered from composite burns (about 1-2 kg/burn, totaling about 4 to 34 kg) in an effort to collect sufficient sample to avoid non-detects for the PCDD/F congeners. The nominal
30 flaming burn time was less than 2 min; sampling continued for approximately 20 min until visible smoldering was no longer observed.

5 **PCDD/PCDF Sampling, Analytical, and Quality Assurance.** Samples to characterize PCDD/F air emissions were taken both inside the burn hut and from the transfer duct. PCDD/F measurements were made inside the facility via a Graseby PS-1 sampler following EPA's ambient TO9A (13) 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
10 the PUF module cool. Multiple burns were sequentially run using a common filter and PUF sorbent to result in a single, composite sample of sufficient concentration to avoid non-detects on any of the 17 toxic equivalency factor (TEF)-weighted congeners (14). The initial test consisted of 39 composite burns. Results of early tests established sufficient concentrations to avoid non-detects, and the number of runs was eventually lowered until only four runs were combined to create a sample.

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The combined filter and PUF/XAD-2 module were analyzed using high-resolution gas chromatography and high resolution mass spectrometry (HRGC/HRMS) for PCDD/F (in this paper, all references to PCDD/F concentrations include tetra- to octa-homologues only). PCDDs/Fs were analyzed via SW846 Method 8290B (15). Redundant TO9A samples were collected during each test and
20 samples sent to two different analytical laboratories [Analytical Perspectives in Wilmington, NC (USA) and the US Department of Agriculture's ARS Biosciences Research Laboratory in Fargo, ND (USA)] as a check on the sampling and analytical methods. Both laboratories followed Method 8290B. Surrogate/internal recoveries were all within the specified limits of the respective methods (40 to 130% for the tetra- through hexa-chlorinated PCDD/F isomers, 25 to 130% for the hepta- and octa-chlorinated
25 PCDD/F isomers, and 70 to 130% for the surrogate standard recoveries).

Background blank tests (sampling without biomass burning) 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. Over 60 h of sampling within the burn facility resulted in a
30 background concentration of 0.3 pg TEQ/m³, a value based on detectable concentrations of all 17 TEF-weighted congeners. These results indicate that background levels of TEQ PCDD/F emissions, amounting to less than 0.2% of the average TEQ emissions for both the Hawaii and FLI burns,

5 respectively, were due to the ambient background. This indicates that inter-test bias due to facility contamination was insignificant.

10 Samples on one test (FL sugarcane) were also collected from the exhaust transfer duct by an extractive sampling procedure, sampling through a PUF cartridge, to assess the effect, if any, on elevated burn hut temperatures on potential degradation of the PUF in the TO9A head. As a check on the laboratory analyses, one of the Hawaii and all four of the Florida samples were sampled with parallel TO9A samplers and sent to different laboratories, Analytical Perspectives (Wilmington, NC, USA) and the U.S. Department of Agriculture laboratory in Fargo, NC, USA (USDA).

15 **Calculations.** Data were reported as both TEQ and Total values, where the latter are defined as the summed mass concentration of the tetra- to octa-chlorinated congeners. Toxic equivalency factors (TEFs) for the 2,3,7,8-chlorine-substituted congeners (often referred to as "TEQ-WHO₉₈") were used to derive the TEQ value (14). All non-detects (NDs) were set to zero. No non-detects were observed for the Hawaii sugarcane; the Florida sugarcane had less than 3% of its congeners as non-detects. PCDD and
20 PCDF values are normalized by the mass of burned sugarcane carbon, assuming that sugarcane is 46% by mass carbon, and reported as ng toxic equivalent per kg carbon burned (ng TEQ/kg_{Cb}).

Emission factors of PCDDs/Fs per unit mass burned were calculated using

$$EF = (C_{\text{sample}} Q t_{\text{run}}) / (m_{\text{burned}})$$

25 where EF is the emission factor in ng/kg burned, C_{sample} is the concentration of the pollutant in the sample in ng/m³, Q is the flow rate of dilution air into the burn facility in m³/min, t_{run} is the run time in min, and m_{burned} is the mass in kg of sugarcane burned over the run. These estimated emissions express a mass of analyte produced per mass of fuel consumed in the combustion process.

30 Emission factors were additionally calculated using a carbon (C) balance approach aptly described in Ref. (16). This method requires measurement of the C emissions and knowledge of the

5 fuel's C stoichiometry. C emissions are commonly calculated using CO₂ and CO measurements and, optionally, using measurements of other carbon species such as particulate carbon and total hydrocarbons. The ratio of the coincidentally-sampled target analyte mass with the C mass provides the emission factor in units of target mass per mass of fuel burned. In addition to emission factors, results were compared by assessing PCDD to PCDF ratios, relative homologue profiles (mass of homologue divided by total PCDD and PCDF), and distribution patterns of the TEF-weighted congeners (mass of the congener divided by the homologue mass).

The raw sugarcane was analyzed for levels of PCDD/PCDF by first shredding the sugarcane in a high-speed blender, spiking with 17 ¹³C₁₂-2,3,7,8-substituted PCDD/F standards, and then extracting with 15 toluene in a Dean-Stark apparatus for 17 h prior to analysis. The sugarcane ash was similarly analyzed, without the shredding step. Following extraction, the concentrated extracts were solvent-exchanged with hexane following procedures adapted from US EPA Methods 8290 (15). Isotopically-labeled cleanup standards and injection standards were added to the extracts prior to fractionation and prior to GC/MS analysis (60-m DB-5MS column; MicroMass Ultima AutoSpec), respectively.

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Biomass Tested. Sugarcane biomass was obtained from Hawaii and Florida (Table 1 presents a proximate and ultimate analysis of these sources). The Hawaii biomass was obtained from an anonymous source. No information was available regarding its exact source location, time of harvest, or 25 herbicide, insecticide, maturant, and fungicide treatments. Typical application in Hawaii involves soil-applied herbicide treatment for weeds at levels higher than the norm in the continental U.S. because tropical soils have larger iron oxide content and larger adsorptive surface area (17). However, these herbicides are chronologically separate from the burning periods; once the dense sugarcane canopy develops, weeds are usually not an issue. The Florida sugarcane was obtained from a USDA test field in 30 which pre- and post-emergent herbicides are used. Insecticides are seldom used. Leaf drying agents are not used in the USDA fields, although proximal commercial growers use them often with the early-harvest sugarcane. There was a substantial difference in the chlorine (Cl) concentration of the two

sources (Table 1); the mass concentrations for HI and FL were 1.20 % and 0.17 %, respectively. Two gatherings of the Florida sugarcane were made, separated by 13 months. The sugarcane was transported by ground and tested 1 to 6 weeks from cutting. The second gathering (FLII) and its burn tests examined emission variations across crops (seasons) and the emissions at different stages (flaming and smoldering) of the burn. In addition, the FLII tests used ~ 5 cm of the USDA field soil as a base below the sugarcane to further simulate the actual burn conditions.

Results and Discussion

Table 2 presents the test parameters measured during the sugarcane testing. The average mass loss (on a dry weight basis) for all of the sugarcane burns averaged 96%, leaving about 4% ash. Although slightly over 9% ash was found in the raw biomass via an ultimate analysis, the difference is likely due to particulate matter entrainment into the gases during the burns. No apparent difference was observed between the two sugarcane sources (HI and FL).

The sugarcane burned rapidly, with CO, CO₂, and THCs reaching peak levels within 2 min and returning to ambient levels within 15-20 min (an illustrative burn is shown in Supporting Information, Figure S1). Temperatures atop the fuel pile in the sample pan and above the flame typically reached 220-320 °C, but dropped below 100 °C by 5 min into the burn (Supporting Information, Figure S2). Temperatures on the interior walls within the burn facility ranged from 75-150 °C for no more than 3 min into the burn. The sampling location temperature never exceeded 75 °C.

The PCDD and PCDF results (Table 3; complete results are including in the Supporting Information) show relatively consistent intra-source values for TEQ and Total emissions. Considerable difference, however, exists between values from the two sources. The average TEQ emission factor for two tests of Hawaii sugarcane was 253 ng toxic equivalent per kg carbon burned (ng TEQ/kg_{Cb}) (rsd = 16%). Four tests of Florida sugarcane (FLI) were 25 ng TEQ/kg_{Cb} (N=4, rsd = 50%) while a second Florida sugarcane gathering (FLII) resulted in average test emissions of 5 ng TEQ/kg_{Cb} (N = 2, rsd = 91%).

The emission homologue distributions (Figure 1) for both sources are quite similar; the furans are dominated by the TCDFs and the dioxins by the TCDDs and PeCDDs. The PCDFs dominate the PCDDs by a factor of 3 to 5 (also see Table 3). Likewise, the 2,3,7,8-Cl-substituted isomers show similar patterns between sources (Figure 2). The most prevalent isomers are 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-
10 HpCDF. The PCDF contribution to the TEQ outweighs that of the PCDDs from about 1.5 to 4, depending on the biomass source (Table 3).

The as-received biomass contained minimal quantities of extractable PCDDs and PCDFs (Table 3, Raw Biomass Content). Compared to the emissions (Table 3), the raw PCDD and PCDF TEQ
15 concentration was less than 5% that of the emissions, with a median of <1%. The raw sugarcane biomass concentrations of the HpCDD, OCDD, HpCDF, and OCDF homologues from FLII exceeded the emissions in their respective homologues; notably this was not the case for FLI, although no explanation is apparent for this difference.

20 The homologue distributions (Figure 1) show considerable distinction between the analytes present on the raw biomass versus those in the emissions: the raw biomass is dominated by PCDDs, particularly OCDD, whereas the emissions are dominated by PCDFs, primarily PeCDFs. These observations suggests that the emissions are not simply a result of target analyte volatilization and dechlorination, but represent *in situ* formation. Typically over 99% of the observed total PCDDs and
25 PCDFs were found in the emissions versus the ash (Table 3). The ash reported a generally similar homologue distribution to that of the emissions (Figure 1). The isomer patterns for the raw sugarcane, ash, and emissions (Figure 4) are very similar whereas the raw sugarcane, ash, and emissions homologue distributions (Figure 3) show considerable variation.

30 The orientation of the sugarcane in the Florida tests (piled versus standing) had no obvious effect on the temperatures and emissions patterns. Comparisons of two runs (figures not shown) with standing sugarcane and two runs with piled sugarcane showed no remarkable differences in temporal

5 comparisons of stack temperature, mass loss, or stack CO₂ elevation.

Single-laboratory analyses (Analytical Perspectives, NC) were quite repeatable; the relative accuracy for TEQ and Total of PCDD and PCDF ranged from 7 to 12%. Samples that were analyzed in both laboratories showed greater differences in values, as expected. Two HI samples analyzed at
10 Analytical Perspectives had an average value of 218 ng TEQ/kg_{Cb} (rsd = 6%) as compared to the analysis at USDA of a single parallel sample at 174 ng TEQ/kg_{Cb}. Four runs of the FL sugarcane with parallel sampling resulted in average values of 19.7 and 21.2 (avg rsd = 40%) ng TEQ/kg_{Cb} from Analytical Perspectives and USDA, respectively, indicating little differences in results. The relative accuracy between the two laboratories with 14 common samples for TEQ and Total of PCDD and PCDF ranged
15 from 38 to 48% for TEQs and 54 to 75% for Totals. Part of the reason for the greater interlaboratory relative accuracy (RA, which is proportional to the difference between paired data and the standard deviation of the measurements and is defined in (18) is likely also attributable to different extraction and clean-up laboratories; the USDA samples were handled at the EPA, while the samples sent to Analytical Perspectives were completely done there.

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The samples extracted from the exhaust transfer duct via a probe into a PUF module compared reasonably well with the TO9A PUF sample from inside the facility: values of 28.8 and 11.5 ng TEQ/kg_{Cb} were obtained from the parallel, extractive samples and 10.4 ng TEQ/kg_{Cb} was obtained for the internal sample. These limited tests showed no apparent bias due to potential exposure to elevated temperatures
25 and, hence, increased PCDD and PCDF formation, for the PUF sample inside the facility.

Emissions. The TEQ and Total emission factor ranges for both the HI and FL sources are high compared to other published data for wheat and rice straw stubble (~1.0 ng TEQ/kg_{Cb} (1), yet the FL source data are within the range of median values from two forest biomass sources (4 to 30 ng TEQ/kg_{Cb} (11). The HI emission factors are much higher than any other known published biomass values. Sugarcane biomass is a comparatively “clean” fuel in terms of potential for PCDD/PCDF formation, however, still contains the metal catalyst and chloride content necessary for formation. Cu, the most
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5 active catalyst for PCDD/PCDF formation, is an essential element for sugarcane growth and has been found within the biomass matrix (4). Typical optimal growth levels found in sugarcane are on the order of 5 ppm (4). Cu levels in both the HI and FL sugarcane were near or below the detection limits (20 ppm) of the x-ray fluorescence (XRF) method. Fe is also noted as an active catalyst for formation. Levels of Fe were about four times higher (~550 ppm) in the FL biomass than the HI biomass (~150 ppm). Cl is
10 also essential for normal growth (19). The Hawaiian cane fields are swept by salt-laden (Cl) ocean winds and the growers use considerable KCl (4), at least at the time of the citation (1980), likely making Cl availability non-limiting for PCDD/PCDF formation. XRF (Table 1) showed that the HI sugarcane had total Cl levels about seven times that of the FL cane (~12,000 ppm versus 1,700 ppm).

15 Within each source gathering, the measured TEQ values are internally consistent, showing little variation. The same facility, personnel, testing procedures, and analytical methods were followed for both sources; measurements of temperature, CO, O₂, THC, and CO₂ showed no distinctive trends or values, suggesting that the variation in the emissions was due more to source-specific factors, rather than procedural or analytical variation. The difference in raw sugarcane Cl content (Table 1) may explain the
20 observed Hawaii and Florida TEQ and Total values but with such limited data, this remains speculative.

Emission factors were determined from direct mass loss measurements and carbon balance methods. Carbon balance methods use measurements of CO and an assumption that CO/CO₂ = 5% to calculate carbon loss or, alternatively, direct CO and CO₂ sampling (to measure mass of carbonaceous
25 material burned) to calculate emission factors. Results from thirteen runs show that differences in the TEQ and Total values between the methods can be significant. Use of CO measurements only and an assumed CO/CO₂ ratio of 5/100, resulted in relative accuracies of 268% and 259% for PCDD/F TEQ and Total, respectively, using the mass loss method as the reference. Use of CO, CO₂, and THC resulted in relative accuracies of 80% and 73% PCDD/F TEQ and Total, respectively. This suggests that emission
30 factors which rely solely on CO measurements may contain considerable inaccuracies (see also Supporting Information).

5 **Comparison with Published Data.** The average PCDD and PCDF TEQ results from the Hawaii and Florida sugarcane burns are compared with the Australian sugarcane data from laboratory and field tests (2) in Figure 3. The Hawaiian sugarcane data are high compared to the relatively similar Australian and Florida data. Given the variation observed between the Hawaii and Florida sugarcane that resulted from the same test facility procedures and same analytical laboratory, the laboratory results for the Australian
10 sugarcane are not exceptionally distinctive from that of the laboratory results reported here. Further comparisons are presented in Supplementary Information.

U.S. Emission Estimates. The impact of these emissions on the total U.S. PCDD/PCDF inventory must be assessed with the use of an activity factor which indicates the prevalence of sugarcane field burning.
15 Determination of the amount of sugarcane burned in the U.S. is somewhat problematic: estimates vary widely, data are likely only available on a local or state level, and most data are likely inaccessible to web-based searches. About 400,000 ha (~1,000,000 acres) were harvested in 2001 (20) in four states: Florida, Hawaii, Louisiana (LA), and Texas (TX). Of this harvest, estimates for burning range from 96% (21) to 3% (22). More confidence in this value can be obtained from state-specific data. County data on
20 crop harvests in Texas (23) cited in (24) determine that 64% of the harvested acreage in Texas was burned. Values of sugarcane burn harvesting in Louisiana from unreferenced estimates range from about 50% in 2000 (25) to about 30% in 2003 (26) to 75% (27). Given that considerable uncertainty exists in these emission factors, a four-state estimate of 50% of the harvest acres for burn practices seems reasonable and is unlikely to introduce significant additional uncertainty into the inventory calculation.
25 There is also some uncertainty regarding the actual mass amount of sugarcane trash burned per unit area. This uncertainty is likely due to the wide range of actual values, caused by considerable differences in harvest/burn practices, which vary by region, crop condition (e.g., standing versus lodged), and method of harvesting. An estimate for fuel load of 20 ton (dry)/ha is used, derived from (28). Finally, when the emission factor is based on an actual mass loss, a 90% mass combustion efficiency (the measure of raw
30 C burned into CO and CO₂) is estimated based on measurements in this work and literature (23).

5 Table 4 reports the four-state emission estimates. This table assumes that the FL emission factor data apply more appropriately to the LA and TX estimate than the HI data, due to geographic proximity. This estimate suggests about 38 g TEQ/a from sugarcane burning in the U.S. In contrast, application of the HI emission factor to the LA and TX sugarcane results in a total of almost 230 g TEQ/a. These values compare to a total estimated U.S. inventory from known sources of about 1,500 g TEQ in year 2000 (29).
10 These preliminary emission factors for sugarcane burning place these sources in perspective with the total U.S. inventory and are a first step in assessing exposure risk of this source.

Data Limitations. These estimates should be considered with a number of caveats. Emission factors are likely to be area-specific, potentially differing with growth/harvest practices (potential effects of
15 insecticides/herbicides) or environmental conditions (potential effects of sea salt exposure). Seasonal variations are also possible, as sugarcane gathered from the same region (Florida) a year apart showed somewhat different emission factors. These emission factors derived here were based on only two sources, laboratory simulations of field conditions, limited sample mass, and uncertain herbicide/pesticide history. Increased certainty in derivation and use of an emission factor for sugarcane burning will require
20 more testing, including field validation, multiple sources, and comprehensive sampling to understand those factors which effect the PCDD and PCDF emissions.

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SUPPORTING INFORMATION

5 The Supporting Information section provides typical results of gas concentrations and temperature conditions in the burn facility; full congener and homologue data values for emissions, raw sugarcane, and ash residues for all of the sugarcane sources; and further analysis of emission factors and method comparisons with published sugarcane emissions data.

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REFERENCES

(1) Gullett, B.K.; Touati A. PCDD/F emissions from burning wheat and rice field residue. *Atmos. Environ.* **2003**, 37, 4893-4899.

15 (2) Meyer, C.; Mueller, J.; Beer, T.; Marney, D.; Bradbury, G. Field and laboratory based emission factors for PCDD/PCDF/PCB from sugarcane fires. *Organohalogen Compd.* **2004**, 66, 913-919.

(3) Hawaii, Hawaii Agricultural Statistics Service, Hawaii Sugarcane, <http://www.nass.usda.gov/hi/speccrop/sugar.htm>, November 20, 2003.

20

(4) Clements, H.F. *Sugarcane Crop Logging and Crop Control, Principles and Practices*. The University of Hawaii Press: Honolulu, 1980.

(5) Dos Santos, C.Y.M.; Azevedo, D. A.; Neto, F.R.A. Selected organic compounds from biomass
25 burning found in the atmospheric particulate matter over sugarcane plantation areas. *Atmos. Environ.* **2002**, 36, 3009-3019.

(6) Turn, S.; Jenkins, B.; Chow, J.; Pritchett, L.; Campbell, D.; Cahill, T.; Whalen, S. Elemental
characterization of particulate matter emitted from biomass burning: Wind tunnel derived source profiles
30 for herbaceous and wood fuels; *J. Geophys. Res.* **1997**, 102 (D3), 3683-3699.

(7) Meyer, C.; Beer, T.; Mueller, J.; Gillett, R.; Weeks, I.; Powell, J.; Tolhurst, K.; McCaw, L.; Cook,
14

- 5 G.; Marney, D.; Symons, R. Dioxin Emissions from Bushfires in Australia; National Dioxins Program
Technical Report No. 1, Australian Government, Department of the Environment and Heritage, Canberra
2004.
- (8) UNEP, 2004. Interim Guidance For Developing A NIP For The Stockholm Convention. United
10 Nations Environment Programme, Geneva, Switzerland,
http://www.pops.int/documents/implementation/nips/guidance/guidances/docdirec_en.pdf.
- (9) Lemieux, P.; Gullett, B.; Lutes, C.; Winterrowd, C.; Winters, D. Variables affecting emissions of
PCDD/Fs from uncontrolled combustion of household waste in barrels. *J. Air Waste Manage. Assoc.*
15 **2003**, 53, 523-531.
- (10) Gullett, B.K.; Lemieux, P.M.; Lutes, C.C.; Winterrowd, C.K.; Winters, D.L. Emissions of PCDD/F
from uncontrolled, domestic waste burning. *Chemosphere* **2001**, 43, 721-725.
- 20 (11) Gullett, B.K.; Touati A. PCDD/F emissions from forest fire simulations. *Atmos. Environ.* **2003**, 37,
803-813.
- (12) U.S. EPA M-6C. Test Method 6C, Determination of sulfur dioxide emissions from stationary
sources (instrumental analyzer procedure). CFR Promulgated Test Methods 1990.
25 <http://www.epa.gov/ttn/emc/promgate/m-06c.pdf>, accessed September 2005.
- (13) U.S. EPA TO-9A. Compendium Method TO-9A – Determination of polychlorinated,
polybrominated and brominated/chlorinated dibenzo-p-dioxins and dibenzofurans in ambient air, in
Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, 2nd ed.
30 Office of Research and Development, EPA/625/R-96/010b, January 1999, in Air Toxic Methods,
<http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-9arr.pdf>, accessed September 2005.

- 5 (14) Van den Berg, M.; Birnbaum, L.; Bosveld, A.; Brunstrom, B.; Cook, P.; Feeley, M.; Giesey, J.; Hanberg, A.; Hasegawa, R.; Kennedy, S.; Kubiak, T.; Larsen, J.; van Leeuwen, F.; Liem, A.; Nolt, C.; Peterson, R.; Poelinger, L.; Safe, S.; Schrenk, D.; Tillit, D.; Tysklind, M.; Younes, M.; Warn, F.; Zacharewski, T. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environmental Health Perspectives* **1998**, *106*, 775-792.
- 10 (15) U.S. EPA M-8290. Test Method 8290 – Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) by high-resolution gas chromatography/high resolution mass spectroscopy (HRGC/HRMS). In EPA-SW-846 On-Line, 3rd ed., 1994.
<http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8290.pdf>, accessed February 2005.
- 15 (16) Andreae, M.O.; Merlet, P. Emission of trace gases and aerosols from biomass burning. *Global Biogeochemical Cycles*. **2001**, *15* (4), 955-966.
- (17) Santo, L.T.; Schenck, S.; Chen, H.; Osgood, R.V. Crop profile for sugarcane in Hawaii; Hawaii
20 Agriculture Research Center, Aiea, Hawaii,
<http://www.ipmcenters.org/cropprofiles/docs/hisugarcane.html>, accessed Feb. 2006), May 8, 2000.
- (18) U.S. EPA. Performance specification 2 -- specifications and test procedures for SO₂ and NO_x
continuous monitoring systems in stationary sources. 2000. 40 CFR Ch.1 Pt.60, App. B, Spec.2.
25 <http://www.epa.gov/ttn/emc/perfspec.html>, accessed March 2005.
- (19) Bowen, J.E. Essentiality of chlorine for optimum growth of sugarcane. Proc. 14th Congress, Int.
Soc. Sugar Cane Technol., New Orleans, **1972**, 1102-1112.
- 30 (20) USDA. Crop Production. National Agricultural Statistics Service (NASS), Agricultural Statistics Board, U.S. Department of Agriculture, February 8, 2002.
<http://usda.mannlib.cornell.edu/reports/nassr/field/pcp-bb/2002/crop0202.pdf>

(21) USDA. Air Quality Policy On Agricultural Burning. Recommendation from the Agricultural Air Quality Task Force. U.S. Department of Agriculture, November 10, 1999.
<http://aaqtf.tamu.edu/Archives/2000/Policy/Burning%20Policy.htm>

10 (22) USDA. U.S. Agriculture and Forestry Greenhouse Gas Inventory: 1990-2001. Global Change Program Office. Office of the Chief Economist, U.S. Department of Agriculture. Technical Bulletin No. 1907, March 2004.

(23) TASS. Crop Production Data; Texas Agricultural Statistics Service, 1999.
 15 <http://www.io.com/~tass>

(24) Dennis, A.; Fraser, M.; Anderson, S.; Allen, D. Air pollutant emissions associated with forest, grassland, and agricultural burning in Texas. *Atmos. Environ.* **2002**, 36, 3779-3792.

20 (25) LSUAC, Agricultural Burning Smoke Management Program Survey (Sorted by Question); Louisiana State University Cooperative Extension – Agriculture Center. LSU Agriculture Center, Baton Rouge, LA, March 30, 2001. http://www.wrapair.org/forums/fejf/documents/task2/ag_surv_xquest.pdf

(26) LSUAC, Louisiana State University Agricultural Center Annual Report, FY 2003, October 1, 2002-
 25 September 30, 2003; 2003.
<http://www.reeis.usda.gov/web/areera/Reports/2003/La/Combined.1862.LA.pdf>

(27) LSUAC, Louisiana State University Agricultural Center , email communication, Benjamin Legendre to B. Gullett, 1/22/2006.

(28) Lara, L.L.; Artaxo, P.; Martinelli, L.A.; Camargo, P.B.; Victoria R.L.; Ferraz, E.S.B. Properties of aerosols from sugar-cane burning emissions in Southeastern Brazil. *Atmos. Environ.* **2005**, 39, 4627-

5 4637.

(29) U.S. EPA. The inventory of sources and environmental releases of dioxin-like compounds in the United States: the year 2000 update. U.S. Environmental Protection Agency, Washington, DC; EPA/600/P-03/002A, National Technical Information Service, Springfield, VA, 2005, <http://epa.gov/ncea>,

10 accessed October 2005.

BRIEF

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Simulations of sugarcane field burning find widely variant emissions of chlorinated dioxins/furans, depending on the biomass source.

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Figure 2. Comparison of the 17 TEF-weighted congener patterns from the Hawaii and Florida sugarcane emissions. Units are moles of the congener per total moles of the homologue, tetra- to hepta-chlorinated.

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Figure 3. PCDD and PCDF TEQ results from Hawaii and Florida sugarcane burns compared with laboratory and field data of Ref. (7).

Table 1. Proximate and ultimate analysis of sugarcane leaf sources.

%	Hawaii	Florida I	Florida II
Carbon	45.22	44.51	46.43
Hydrogen	5.45	4.15	4.55
Nitrogen	0.80	0.89	0.66
Sulfur	0.21	0.10	0.13
Ash	9.03	10.16	10.50
Chloride (XRF)	1.20	0.17	NA
Moisture	7.29	8.94	6.50

NA = not analyzed

Table 4. U.S. emission estimates for PCDD and PCDF from sugarcane burning.

	Area harvested (ha) ¹	Area burned (%)	Residue burned (dry ton/ha)	Combustion efficiency (%)	EF (ng TEQ/kg _{cb})	Emissions (g TEQ/a)
FL	180,500	50	20	90	17.9	13.5
HI	8,700	50	20	90	252.6	8.7
LA	186,200	50	20	90	17.9	13.9
TX	18,400	50	20	90	17.9	1.4
SUM						37.5

¹Ref. 20.

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Table 2.

Biomass origin	Hawaii		Florida I				Florida II	
Test number	1	2	3	4	5	6	7	8
Number of runs per test	39	24	10	7	5	4	3	10
Cumulative run time (min)	781	480	135	90	75	60	60	200
Carbon burned per run (g)	430 ± 58	430 ± 36	360 ± 31	380 ± 14	370 ± 5	370 ± 5	580 ± 210	660 ± 140
CO _{average} (0-20 min) (ppm)	140 ± 25	180 ± 40	100 ± 72	91 ± 32	100 ± 31	86 ± 11	20 ± 5.8	25 ± 3.2
CO _{max} (ppm)	890 ± 150	980 ± 70	480 ± 60	410 ± 90	470 ± 60	590 ± 46	370 ± 130	140 ± 21
CO _{2 average} (0-20 min) (ppm)	0.52 ± 0.11	0.67 ± 0.10	0.41 ± 0.28	0.37 ± 0.06	0.44 ± 0.04	0.45 ± 0.04	0.08 ± 0.02	0.10 ± 0.01
CO _{2 max} (%)	2.57 ± 0.52	2.97 ± 0.22	4.59 ± 0.45	4.49 ± 0.36	4.67 ± 0.48	5.12 ± 0.0	1.71 ± 0.77	0.87 ± 0.15
THC _{average} (0-20 min) (ppm)	9.7 ± 5.4	9.6 ± 4.1	15 ± 15	8.9 ± 5.6	11 ± 8.9	6.5 ± 2.5	N/A	N/A
THC _{max} (ppm)	81 ± 36	80 ± 21	68 ± 27	44 ± 21	92 ± 44	53 ± 11	N/A	N/A
Flue gas temperature (°C)	88 ± 26	85 ± 6	141 ± 12	157 ± 9	153 ± 18	157 ± 18	32 ± 14	12 ± 2.8

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Table 3

PCDD/F Concentration	Emissions (ng/kg C _{burned})						Raw Biomass Content (ng/kg C _{initial})			Ash Content (ng/kg C _{initial})		
	Hawaii		Florida I		Florida II A	Florida II B	Hawaii	Florida I	Florida II	Hawaii	Florida I	Florida II
	Average	% RSD	Average	% RSD	with stalks	w/o stalks						
PCDD TEQ	79.3	50.8	5.6	67.9	3.7	0.5	0.32	0.02	0.44	0.40	0.000	0.004
PCDF TEQ	173.3	25.1	19.5	62.0	4.2	1.2	1.06	0.00	0.02	0.83	0.079	0.000
PCDD/F TEQ	252.6	15.9	25.1	49.8	7.9	1.7	1.38	0.02	0.46	1.22	0.079	0.004
PCDD Total	1303.1	18.4	186.6	41.0	109.4	7.3	107.14	17.39	414.77	5.40	1.597	3.034
PCDF Total	6905.4	32.3	724.9	50.3	177.4	80.7	191.38	5.12	25.12	40.63	7.246	4.770
PCDD/F Total	8208.5	26.5	911.6	47.5	286.8	88.0	298.51	22.51	439.89	46.03	8.843	7.804

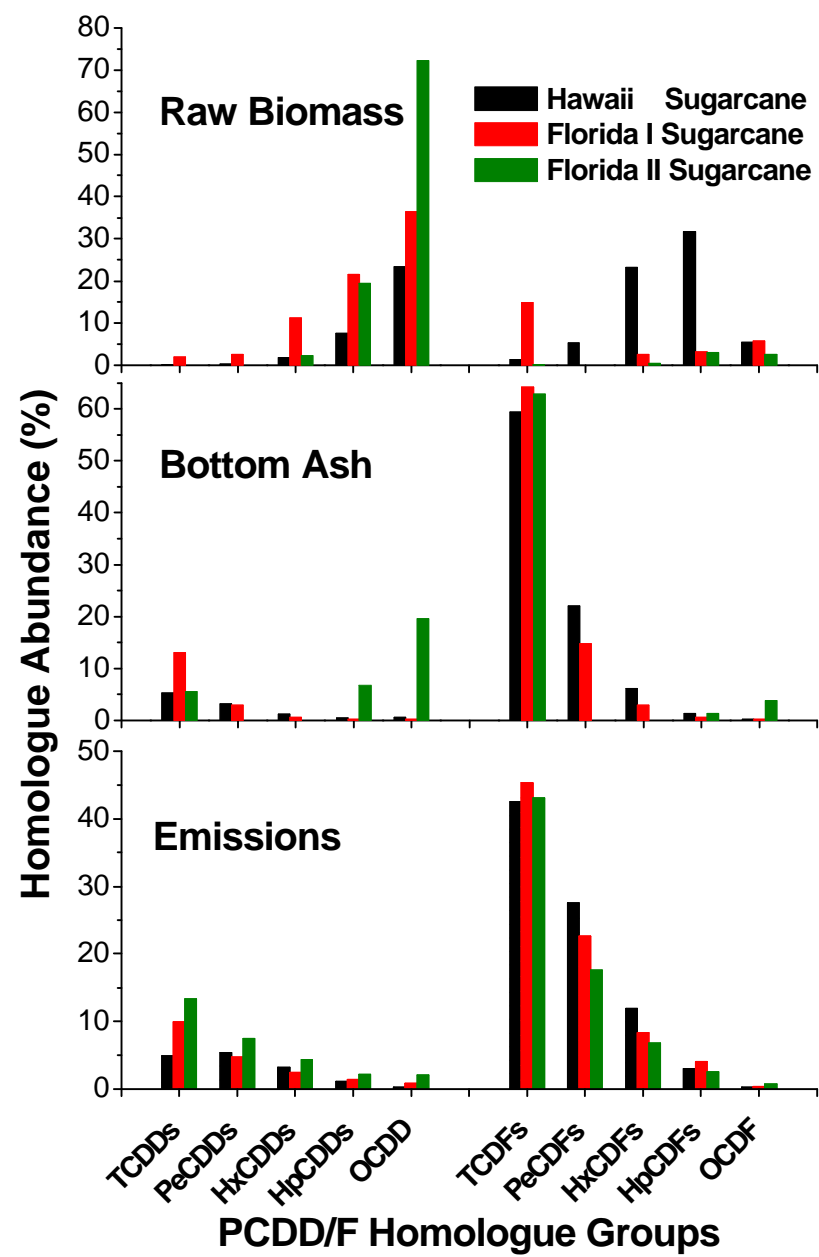


Fig. 1

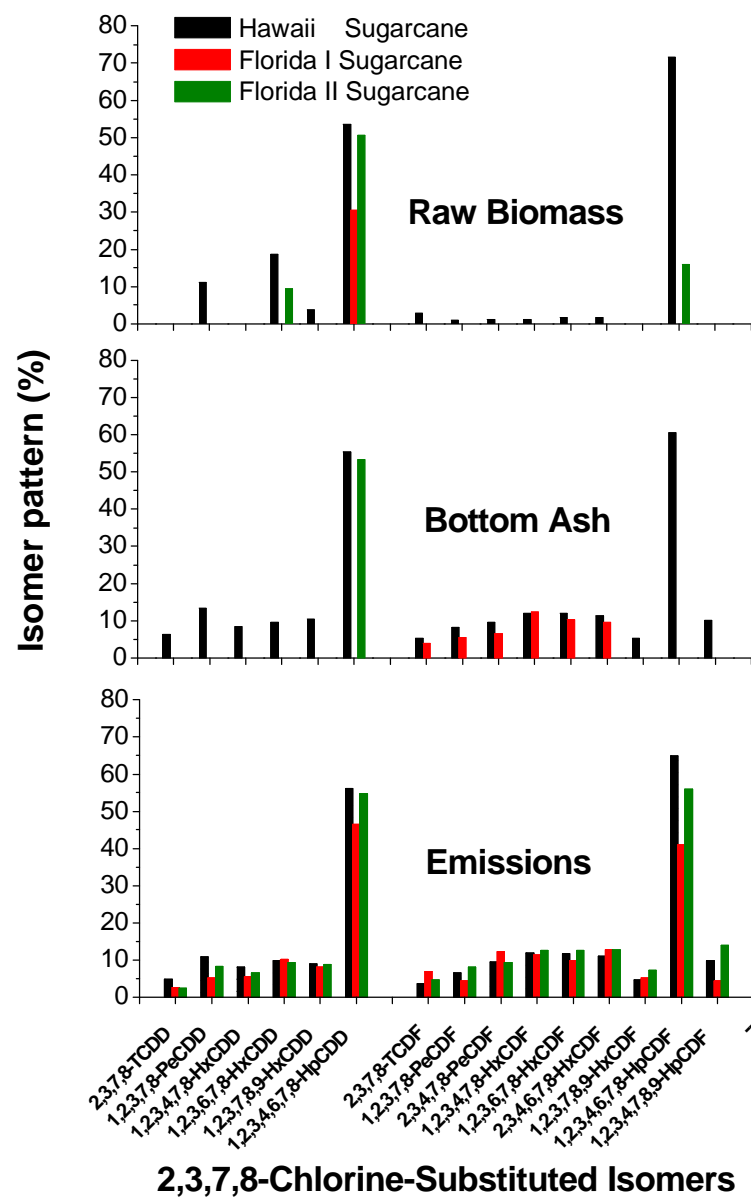


Fig. 2

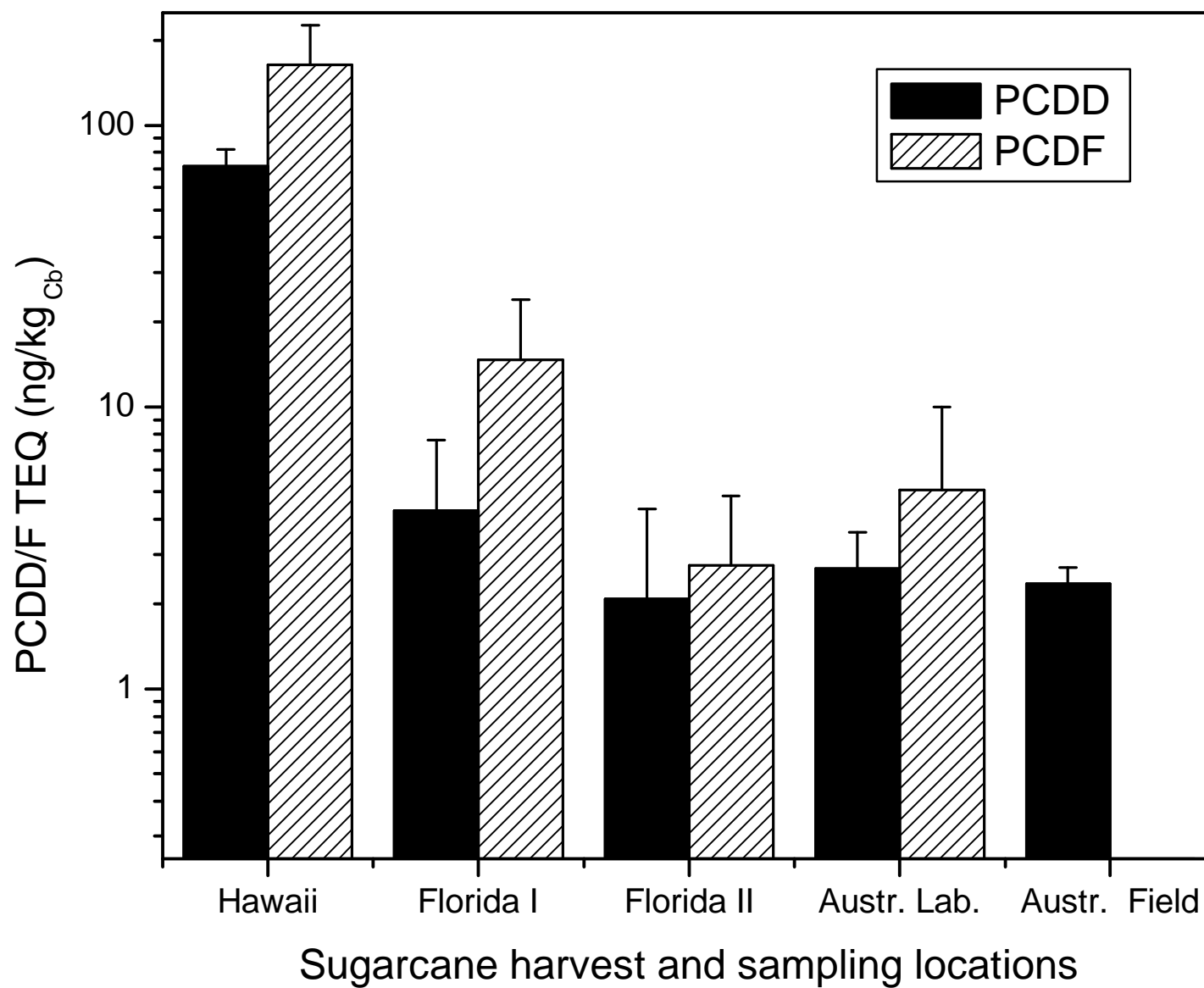


Fig. 3