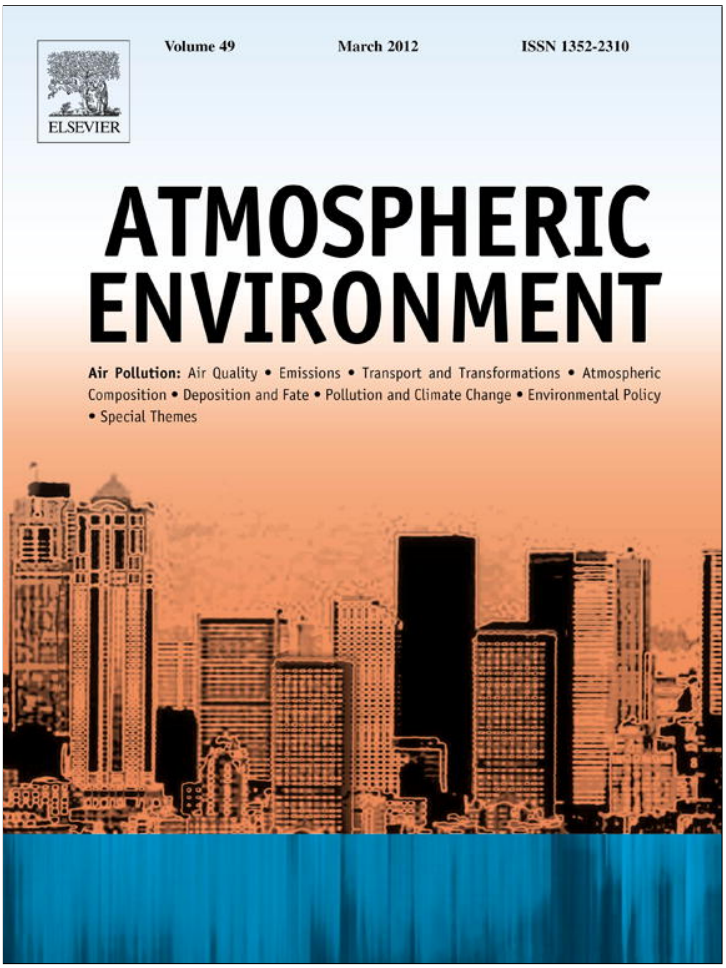

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Short communication

Dioxin inhalation doses from wood combustion in indoor cookfires

Amanda L. Northcross*, S. Katharine Hammond, Eduardo Canuz, Kirk R. Smith

Department of Environmental Health Sciences, School of Public Health, University of California Berkeley, 50 University Hall # 7360, Berkeley, CA 94720, USA

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ABSTRACT

Approximately 3 billion people worldwide rely on solid biomass fuels for household cooking and space heating, and approximately 50–60% use wood, often indoors in poorly ventilated situations. Daily exposures to high concentrations of smoke from cookstoves inside kitchens create large smoke exposures for women cooks and their small children. The smoke from burning the wood fuel contains hundred of toxic compounds, including dioxins and furans some of the most toxic compounds known to science. Health effects from exposure to dioxins include reproductive and developmental problems, damage the immune system, interference with hormones and also cause cancer. This study measured concentrations of dioxins and furans in a typical Guatemalan village home during open cookfires. Measured concentrations averaged 0.32 ± 0.07 ng m^{-3} over 31 fires. A Monte Carlo simulation was conducted using parameter estimates based on 8 years of research experience in the study area. The estimated total daily intake of 17 particle phase dioxin and furans for women, a 5-year-old child and a 6-month-old infant were 1.2 (S.D. = 0.4), 1.7 (S.D. = 0.7) and 2.0 (S.D. = 0.5) respectively. The 46% of babies have and estimated total daily intake (TDI) which exceed the WHO TDI guideline for dioxins and furans, 3% of women and 26% of 5-year-old children based solely inhalation of particle phase dioxins in woodsmoke from an open cooking fire. These values maybe underestimates, as they did not include gas phase concentrations or ingestion of dioxins and furans through food, which is the largest route of exposure in the developed world.

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1. Introduction

Dioxins – polychlorinated dibenzo-*p*-dioxins (PCCDs) and polychlorinated dibenzofurans (PCCFs) – refer to a class of compounds containing two aromatic rings and at least one chlorine molecule; the structures are shown in Fig. 1. For simplicity we refer to both dioxins and furans as dioxins in this paper. They have been identified to be among the most toxic anthropogenic compounds known. Once released into the environment, typically either through combustion processes or as industrial byproducts, dioxins/furans are dispersed, deposited and accumulated in both the local and regional areas. Dioxins are formed by processes such as municipal and medical waste incineration, domestic waste burning, forest fires, wood processing, and wood-burning fire places (Lemieux et al., 2000; Yasuhara et al., 2003; Lavric et al., 2004; Shibamoto et al., 2007; Committee on EPA's Exposure and Human Health…, 2006). In addition to being highly toxic, dioxins/furans are strongly persistent in the environment and bioaccumulate due to their long half life in the body; 7 years on average. In industrial countries the largest fraction and most common pathway of dioxin exposure is through ingestion of foods grown in contaminated soils or fish and animals living in contaminated environments.

A possibly larger and unmeasured exposure to dioxins of the world's poorest people who do not live in industrial countries may come from the use of wood and other biomass fuels used for cooking. Nearly half of the people in world cook on inefficient stoves such as open fires using solid fuels including biomass fuels like wood, crop residues and charcoal. Indoor air pollution from household solid fuel use accounts for almost 2 million premature deaths each year ("WHO|Global health risks," 2011). The concentrations of fine particles during cooking with biomass fuels can reach hundreds of mg m^{-3}.

The levels of dioxins and furans from wood combustion range from 0.02 to 1.8 ng TEQ Nm^{-3} and are lower than levels emitted from industrial waste incineration, 0.2–63 ng TEQ Nm^{-3} (Huang and Buekens, 1995). For example PCDD/PCDFs reached 0.02 ng m^{-3} in forest fire smoke while atmospheric levels before and after the fires were found to be negligible (Tashiro et al., 1990). In Australia, during a prescribed burn of a Eucalypt forest PCDD/PCDFs concentrations of 0.0215 ng m^{-3} compared to 0.0004 ng m^{-3} from the control period were measured (Prange et al., 2003). Another emission study simulated a fireplace by keeping the door open on a wood boiler;

* Corresponding author. Tel.: +1 510 643 0887.
E-mail address: amandaln@berkeley.edu (A.L. Northcross).

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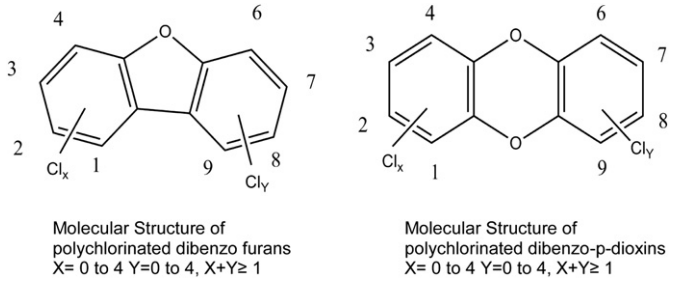

Fig. 1. Molecular structures of dioxins and furans.

dioxin concentrations in the combustion emissions of beechwood were 0.077 I-TEQ kg^{-1} dry wood (Schatowitz et al., 1994). Vikelsøe et al. (1994) measured 1.29 ng TEQ kg^{-1} fuel of dioxins in emissions of wood burning stoves used in Denmark. Although the fraction of dioxins in wood smoke emissions is small in comparison to the fraction present other emission sources, the high concentrations of smoke from cookstoves inside the kitchens may create non-negligible exposures to dioxins.

To explore what levels of dioxin exist in village kitchens using biomass fuel for cooking, we undertook a study in highland Guatemala of airborne particle-borne dioxin in households where woodfuel is used indoors for cooking with open fires. Plastic, which is often added to the fires by the local population, was collected from the area and added to the cookfires to determine the effect on dioxin production.

2. Materials and methods

2.1. Sampling

This study was conducted in the separate kitchen of a rented uninhabited house in La Calleberia, San Lorenzo San Marcos in the highlands of Guatemala. An open fire cookstove was used in this study. The people of this area are indigenous *Mam* speaking Mayans. The rented home was in a community where we have been studying the relationship between indoor air pollution from cookstoves and health for more than 8 years. Our extensive knowledge about the cooking practices of the people who live in this area and training by a village woman was useful in ensuring the conditions under which the cookfires were set were as authentic as possible. Based on our previous studies in the area (Smith et al., 2010) each fire used ~3.6 kg of wood weighed using Seca balance (Germany). Polyethylene soda bottles and potato chip bags were added to the fires in varying percentages compared to the mass of wood used, of 0, 3%, 7–13%, 15–19%, and 21–25%. Each group consisted of at least 4 replicates. Table 1 lists the conditions for each sampling period. Each sampling period was conducted for 100 min, the entire length of the burn cycle of the fire. The kitchen was vented after each burn cycle using a fan until particle concentrations returned to baseline conditions, typically at least 1 h.

Background concentrations of particulate matter with aerodynamic diameter less than 2.5 μg m^{-3} (PM2.5) was monitored before each exposure using a TSI Dust Trak model 8250 (Shoreview, MN) with PM2.5 impactor. The average background concentration was required to be less than 15 μg m^{-3} as measured with the Dust Trak, before setting the fire. All fuel was weighed, including logs, kindling, and plastic. The fire was set and observed throughout the burn. The kitchen was monitored with a protocol similar to that used in our previous work in the area (Northcross et al., 2010). All monitoring equipment was placed 1.5 m above the floor and 1.5 m horizontally from the center of the cookfire. A UCB/PATS particle monitor (Edwards et al., 2006; Chowdhury et al., 2007) was used to monitor PM2.5 concentrations continuously. The Dust Trak was used primarily for determining concentrations before and after each fire. Samples were collected on Teflon (Pallflex 2.0 μm pore) filters for PM2.5 mass concentrations and on 37 mm quartz fiber filters (Pall) for dioxin analysis at 1.5 Lpm (SKC model PCRX8) with a personal cyclone (BGI). Pumps were calibrated at the beginning and end of each day with Gilian Gilabrator flow calibrator. Filters were pre and post weighed using a Metler Toledo MT5 Microbalance (Columbus, OH), and used to correct the Dust Trak and UCB. Carbon monoxide was measured using a HOBO electrochemical CO monitor, which was compared to a 50 ± 0.1 ppm calibration gas on a weekly basis; sampled data was corrected.

Quartz fiber filters were pre-cleaned 18 h in a Soxhlet extractor using a 50:50 solution of dichloromethane (DCM) and toluene and contained in 37 mm solvent resistant polypropylene sample holders, which were cleaned with DCM and toluene. All filters were stored at 3 °C after sampling.

Table 1
Description of fuel mass for each exposure sample.

n	Plastic %	Wood mass (kg)	Plastic mass (kg)
4	0	3.0	0
6	3%	3.8	0.1
8	9%	3.5	0.3
7	16%	3.7	0.7
6	25%	3.6	1.2

2.2. Extraction

A DIONEX ASE200 automated solvent extractor (Sunnyvale, CA) was used to remove the organic fraction of the PM from the quartz filters. This method utilizes high temperature and pressure to reduce the time and volume of solvent required for extraction. Filters were spiked with 10 mL of recovery solution containing 1,2,3,4-tetrachlorodibenzo para dioxin (TCDD) ($^{13}C1_2$ 99%) and 1,2,3,7,8,9-hexachlorodibenzo para dioxin (HxCDD) ($^{13}C1_2$ 99%) and placed into cells, filled with diatomaceous earth. The extraction program heated to 100 °C at 1500 psi for 20 min with 150 ml of solvent twice. The extract was eluted through a chromatographic cleanup column of layers of $AgNO_3$, silica gel, 44% H_2SO_4 silica gel, 22% H_2SO_4 silica gel, and 2% KOH silica gel similar to EPA REF METHOD 23 to remove unwanted organics. The extract was then reduced in volume using a Turbo Vap II made by Caliper Life Sciences (Hopkinton, MA) followed by final blow down under pure nitrogen and spiked with 5 μL of 2,3,7,8-TCDD ($^{37}Cl_4$ 96%).

2.3. GC/MS analysis

Of the hundreds of dioxins and dioxin-related compounds, only 17 are considered toxic (US EPA National Center for Environmental Assessment and Audrey Hoffer, 2011) with 2,3,7,8 TCDD the most toxic and listed as a Group 1 carcinogen by the International Agency on Research for Cancer (IARC). Table 2 contains a listing of the toxic dioxin and furan congeners and their toxic equivalency factors (TEQ) in reference to TCCD that were analyzed in this study. A 5 point calibration curve was created to determine analyzed concentrations. Dioxins were analyzed on a Hewlett Packard 6890 Gas Chromatograph equipped with a mass selective detector (MS) and a DB-5MS 60 m, 0.25 mm, 0.25 μm capillary column with a heating program of 200 °C for 2 min, heating at 5 °C min^{-1} to 250 °C hold for 16 min, heat to 235 °C hold for 7 min and then to 310 °C for 10 min. The MS was operated in selective ion mode to increase sensitivity, with acceleration voltage of 5 kV, ion

Table 2
Listing of toxic dioxin and furan congeners and toxic equivalency factors. T = tetra, Pe = Penta, HX = hexa, Hp = hepta, and O = octa.

Dioxin congener	TEF	Furan congener	TEF
2,3,7,8-TCCD	1	2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDD	0.5	1,2,3,7,8-PeCDF	0.05
		2,3,4,7,8-PeCDF	0.5
1,2,3,4,7,8-HxCCD	0.1	1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCCD	0.1	1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCCD	0.1	1,2,3,7,8,9-HxCDF	0.1
		2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDD	0.01	1,2,3,4,6,7,8-HpCDF	0.01
		1,2,3,4,7,8,9-HpCDF	0.01
OCDD	0.001	OCDF	0.001

temperature of 240 °C and ionization energy of 48 eV. All chromatographs were integrated manually using. All standards were purchased from Cambridge isotopes, (Cambridge, MA).

2.4. Statistical analysis

SAS statistical software (SAS Institute Inc., Cary, NC) was used to conduct all statistical analysis. ANOVA was used to determine statistical differences between the groups of plastic mass $p = 0.05$. Confidence intervals for all averages were determined at a 95% confidence level as well. In addition a Monte Carlo simulation was conducted to estimate personal exposures to dioxins. This was conducted using Crystal Ball software (Oracle, Redwoodshores, CA).

3. Results

Fig. 2 presents the total mean PM2.5 and CO concentrations for the fires grouped by the percent plastic added to the fire for the 100 min exposures. There was no significant difference between the groups for the PM2.5 concentrations. Adding plastic to the fire increased the CO concentrations, although not linearly.

The total dioxin mass concentration of all the experiments was 0.32 ± 0.07 ng m^{-3}, and did not vary based on mass percentage of plastic added to fires. All confidence intervals have determined using $\alpha = 0.05$. The average TEQ (TEF in Table 2) for all experiments was 0.051 ± 0.02 TEQ ng m^{-3}. Fig. 3 shows the average mass concentration of each speciated dioxin measured. The average PM2.5 concentration in the kitchen as determined by gravimetric filters for all experiments was 5.5 ± 0.3 mg m^{-3}.

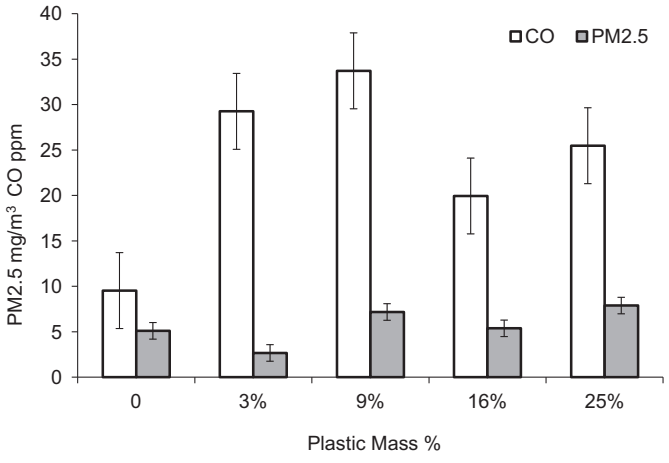

Fig. 2. Mean PM2.5 mg m^{-3} and CO (ppm) concentrations grouped by mass% of plastic for the cooking fires as listed in Table 1.

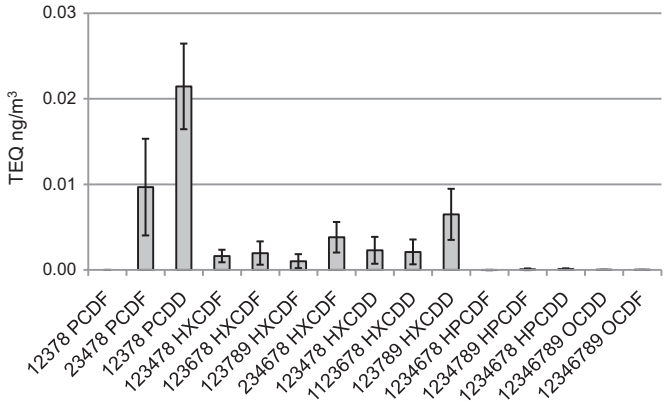

Fig. 3. Average 1 h dioxin TEQ (Table 2) kitchen concentration of the 17 particle phase dioxin analyzed.

4. Discussion

In the USA 90% of personal exposure to dioxins occurs through food consumption, not inhalation (Institute of Medicine). This estimate comes from studies that show the major fate pathways of dioxin air emissions are air-to-plant-to-animal-human and water-and-sediment-to-fish-to-human (Compounds and Toxicology, 2006). In industrialized nations this estimate holds because most of the exposed population is not in immediate proximity to emission sources. However in homes where biomass fuels are used for cooking, the emission sources operate near family members every day, sometimes several times. Thus, inhalation doses of dioxins in these settings may not be insignificant. Comparing the TEQ mass concentrations measured in this study to the values listed in the introduction, the measured concentrations in the kitchen are greater than vales measured during forest fires.

Based on the concentrations and the mean TEQ for the kitchen fires measured in this study, estimates of nominal inhalation doses of particle-phase dioxins in a kitchen were made for a woman, a 5 year old child, and a 6 month old baby in this setting (equation (1)).

$$\text{Daily Inhalation Dose}\left(\text{TEQ pg kg-day}^{-1}\right) = \text{TEQ}\left(\text{pg m}^{-3}\right)/\text{meal*BR*TV*\%time*}n_{\text{meal}}/\text{weight} \quad (1)$$

This equation uses breathing rate (BR), tidal volume (TV), percent of time a person would spend in the kitchen while the fire was lit (%time), the number of meals cooked per day (n_{meal}), and body weight (weight) to estimate the daily inhaled dose and subsequent exposure to dioxins from time in the kitchen only. The parameters in equation (1) each represent a range of values. A Monte Carlo simulation using 10,000 iterations was conducted with estimated triangular distributions for each range of the parameters. The estimated parameters were taken data collected as a part of our previous research studies conducted in the area (Northcross et al., 2010; Smith et al., 2010). The range and mean of the values used in the Monte Carlo analysis are given in Table 3. The TEQ as determined by this study were measured on a per fire basis that can be assumed to be representative of a single meal; most families cook 3 meals per day. A women's breathing rate may be slightly elevated as cooking is moderate work, but a conservative values were used. The percent time spent in the kitchen while a cooking fire was lit is assumed to be 60% for mother and baby who are commonly carried on the mother's back. The percentage of time was determined using previous collected data from the UCB time activity monitors (Allen-Piccolo et al., 2009), which measures the

Table 3
Estimated particle-dioxin doses for an adult woman, 5 year old child, and 6 month old infant from kitchen exposures using equation (1). Mean Dioxin TEQ values shown in pg kg-day^{-1} and standard deviation in parentheses. Mean values of parameters are shown, with range used in simulation in brackets.

	Mother	Child	Infant
Breath/min	14 [12–16]	23 [21–25]	40 [38–44]
Tidal volume L/br	0.5 [0.4–0.6]	0.2 [0.1–0.3]	0.05 [0.03–0.06]
% Time in kitchen	0.6 [0.4–0.8]	0.4 [0.3–0.5]	0.6 [0.5–0.7]
Body mass kg	45 [40–50]	17 [14–20]	9 [8–10]
Dioxin TEQ pg kg-day^{-1}	1.2 (0.4)	1.7 (0.7)	2.0 (0.5)

amount of time a person spends in a room. The 5-year-old child can walk and spends less time in the kitchen as they are no longer carried by their mother. These values are from unpublished time activity data from a previous study in the area.

The total daily intake (TDI) limits or guidelines for dioxin range from Japan 4 pg TEQs/kg-day, WHO 2.3 pg kg-day^{-1}, the United Kingdom 2 pg kg-d^{-1}, and the European Union 2 pg kg-day^{-1}. The United States does not have a TDI standard but does have a suggested reference dose of 0.7 pg kg-day^{-1}. The estimated inhalation doses for women and children are just below the TDIs, and the babies are at the recommended values. The probability distribution produced using a Monte Carlo analysis can also be used to estimate the probability of a household exceeding a TDI standard using the parameters in Table 3. A 3%, 26% and 40% chance of exceeding the WHO TDI of 2.0 pg kg-day^{-1} for mothers, children and babies respectively was determined. It is important to note that the estimated inhalation doses to particle phase dioxins per kg-day do not represent the today daily inhalation of particle-borne dioxins since they only represent doses in the kitchen. Also the total inhalation exposures of the gas phase dioxins were not measured. Also the ingestion of dioxins is neglected in this study, possibly making the actual larger.

5. Conclusion

Exposure to smoke from indoor cookstoves is a known and well-documented health hazard. Our estimated daily doses to particle phase dioxins and furans from inhalation of particles in wood smoke provide additional information on the chemical speciation of wood smoke exposures. In addition, this study highlights a previously undocumented exposure to one of the world's most toxic compounds.

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