Journal of Exposure Science and Environmental Epidemiology (2013), 1–8
© 2013 Nature America, Inc. All rights reserved 1559-0631/13
www.nature.com/jes

ORIGINAL ARTICLE

Impact of biogas digesters on cookhouse volatile organic compound exposure for rural Kenyan farmwomen

Carolyn Dohoo[1], Judith Read Guernsey[1,2], Mark D. Gibson[3] and John VanLeeuwen[1,2]

Women living on rural Kenyan smallholder dairy farms burn wood as biofuel in family cookhouses. Unventilated biofuel combustion produces harmful levels of respirable particles and volatile organic compound (VOC) emissions in indoor environments. Biogas digesters, which can generate high methane-content biogas from livestock manure composting were recently installed on 31 farms. The study objectives were to compare VOC exposure profiles for women cooking on farms with and without biogas digesters, and to compare seasonal variations in VOC exposures for those women cooking with biogas. Participants ($n = 31$ biogas farms, $n = 31$ referent farms) wore passive thermal desorption VOC sampling tubes and recorded cookhouse fuel use on time activity sheets for 7 days. Women using biogas spent significantly less time (mean = 509 min/week) exposed to cookhouse wood smoke compared with the referent group (mean = 1122 min/week) ($P < 0.01$). Total VOC exposure did not differ between farm groups ($P = 0.14$), though concentrations of trans-1,3-dichloropropene, bromoform, and 1,4-dichlorobenzene in biogas cookhouses were significantly lower than in referent cookhouses, even after Bonferroni correction. The composition of VOC species was also significantly different, reflecting the different fuel sources. Biogas digester technologies have great potential for reducing exposure to wood smoke VOCs in low-income countries.

Journal of Exposure Science and Environmental Epidemiology advance online publication, 31 July 2013; doi:10.1038/jes.2013.42

Keywords: wood smoke; volatile organic compounds; indoor air quality; global health; biogas digester; renewable energy

INTRODUCTION

The burning of solid biomass (e.g. wood) during cooking in unventilated indoor environments produces harmful emissions of respirable particulate matter and volatile organic compounds (VOCs) well in excess of national and international exposure standards.[1] Negative health outcomes have been associated with exposure to wood smoke, such as pneumonia, cardiovascular disease, lung cancer, chronic obstructive pulmonary disease, acute respiratory infections, and cataracts.[2–4]

Fifty percent of the world's population relies on the combustion of solid biomass fuels for domestic energy needs, such as cooking, light, and warmth, whereas up to 90% of all rural households in developing countries use solid biomass fuels for domestic energy production.[5] Women living on smallholder dairy farms in rural Kenya follow this trend, burning primarily wood for cooking. The cookhouses in which they work are separate from the main house structure and are poorly ventilated. Consequently, women, and children in their care, are probably exposed to elevated concentrations of particulate matter, nitrogen oxides,[3] carbon monoxide,[6] and VOCs[7] in these buildings.

Reducing exposure to wood smoke has been shown to decrease observed negative health outcomes in women and children.[8–12] Biogas digesters represent an alternative renewable energy technology that has been identified as one of the most energy-efficient and environmentally beneficial technologies for bioenergy production.[13] Biogas digesters anaerobically decompose organic material, such as livestock waste, to produce high methane (CH_4)-content combustible gas that burns cleanly and at high temperatures, which can be used for cooking. Biogas provides a sustainable and cleaner burning alternative to wood as a fuel source.[14] Biogas digesters provide the additional advantage of using locally available compost materials.

There have been relatively few studies that have characterized VOC exposure in cookhouses using biomass in developing countries.[15] Wang et al.[15] collected VOC samples from inside cookhouses that used five types of biofuels (brushwood, maize straw, wheat straw, rice straw, sorghum stalk) and two different stove types in order to determine VOC species profiles from biomass combustion in rural China. Benzene was found to be the most dominant of the >90 VOC species analyzed, followed by propylene, acetone and toluene, but the emission characteristics depended significantly on the biofuel and stove combinations. Though Ezzati et al.[6] did not examine VOCs in their investigation of rural Kenyan cookhouses, they observed an 87% reduction in overall particulate emissions when the fuel source was switched from wood to charcoal; reductions were also observed when using an improved wood burning stove. There have been no reported comparisons of personal exposure to VOC species in cookhouses fueled by a biogas digester to those using traditional biomass sources in rural Kenya.

The objectives of this study were: (1) to quantify and compare the indoor exposure concentrations of VOCs present in the cookhouses of Kenyan dairy farms fitted with biogas digesters *versus* the cookhouses on farms employing traditional cooking

[1]Department of Community Health and Epidemiology, Faculty of Medicine, Dalhousie University, Halifax, Canada; [2]Centre for Veterinary Epidemiological Research, Department of Health Management, Atlantic Veterinary College, University of Prince Edward Island, Charlottetown, Canada and [3]Department of Process Engineering and Applied Science, Faculty of Engineering, Dalhousie University, Halifax, Canada. Correspondence: Dr John VanLeeuwen, Centre for Veterinary Epidemiological Research, Department of Health Management, Atlantic Veterinary College, University of Prince Edward Island, 550 University Avenue, Charlottetown PE C1A 4P3, Canada.
Tel.: +902 566-0457. Fax: +902 620-5053.
E-mail: jvanleeuwen@upei.ca
Received 25 January 2013; revised 15 May 2013; accepted 22 May 2013

technologies; (2) to quantify and compare the personal wood smoke exposure profiles of women who work in the biogas cookhouses compared with the cookhouses on referent farms; (3) to compare winter and summer seasonal differences in VOC exposure in cookhouses on Kenyan dairy farms with biogas digesters; and (4) to compare indoor cookhouse VOC exposure to outdoor ambient concentrations.

METHODS

Study Population

All participants included in the study lived on member dairy farms of Wakulima Dairy Limited, located in the Mukurwe-ini area of central Kenya. Thirty-one farms were identified to have had biogas digesters installed recently (with the assistance from a Canadian based non-governmental organization called Farmers Helping Farmers).[16] Thirty-one additional Wakulima Dairy Limited member farms, without biogas digesters (referent farms), were selected from a list created using a chain referral sampling method.[17,18] The referent farms were matched to the biogas farms based on age of the participant, family size, and number of cows. These methods are described in greater detail in Dohoo et al.[9]

Exposure Data Collection

Data collection took place in February 2010 (biogas farms only) and again in June and July 2010 (biogas and referent farms). The repeat measures for the biogas farms were taken to investigate variation in VOC exposure and cooking time with biogas or wood due to seasonal changes in biogas production.

At each phase of data collection, measures of cookhouse size (m^3), cookhouse ventilation aspects (whether the cookhouse had a chimney, windows, etc.), and time spent cooking with biogas or wood (per day; recorded on time activity sheets by the participants) were collected for each participant. Indoor (cookhouse) VOC concentrations were sampled for each participant farm using methods described below. In order to measure background ambient outdoor VOC concentrations in the local environment, two passive samplers were placed in trees at a height of 2 m, and at locations far from anthropogenic sources of VOCs. Outdoor VOC concentrations were measured over 24- and 72-hour periods of continuous sampling.

The time activity sheets used by the participants to record cooking activity and fuel use were set up so that the participants were only required to fill in the times during which they were cooking with a specific fuel type. Times could be recorded in either traditional 24-hour time or according to the Kikuyu (local language) method of tracking time. For cases where the latter method was used, times were converted to traditional 24-hour time with the help of a translator.

VOC Sampling

Perkin-Elmer (Perkin-Elmer, Waltham, Massachusetts, USA) stainless steel 1/4″ OD × 3.5″ thermal desorption tubes (TDT), packed with Tenax TA 60/80 mesh, were used to sample VOC species personal exposure species over a 7-day period, according to the standard passive sampling protocols described by BSI and ISEA: BS EN 13528-2:2002, ISO 16107:2007 and ANSI/ISEA104.[19–21]

Women wore the TDTs every day, while cooking, for one week. Participants recorded the total amount of time spent cooking with either biogas or wood on a time record sheet each day. Training on how to use the TDTs and how to record cooking activity on the record sheets was provided for each participant by the research staff, with the help of a translator. During times when women were not cooking, and consequently not being exposed to cookhouse smoke, the participants removed the TDTs and stored them in two sealed Ziploc bags (one inside the other) to prevent ingress of non-sample air. This sealing method was adopted as it was deemed more practical for the participants to achieve rather than using the standard brass Swagelok nut and ferrule seals. The TDTs were also fitted with stainless steel wire gauze end caps over the entire week to prevent dirt and debris contaminating the inside of the tube. Ten percent of the VOC TDTs that traveled to Kenya were used as sampling blanks, remaining in a sealed bag and traveling to participant farms, during the entire data collection period. In order to ensure that the Ziploc method of sealing the TDTs was effective against the ingress of non-sample air sampling, blanks were treated with the same method and transported on farm visits with the research staff. These blank TDTs were used for blank correcting the sample TDTs.

The samplers were transported back to the Dalhousie University Atlantic RURAL Centre Research Laboratory in Halifax, Nova Scotia, Canada, for analysis. The TDTs were analyzed using a Perkin-Elmer TurboMatrix automatic thermal desorption system coupled to a Perkin-Elmer Clarus 500 gas chromatograph, equipped with a Restek Rtx-1 60 m, 0.53 mm ID, 3-μm-diameter film capillary column with electron capture and flame ionization detectors. The capillary column flow rate was 3.67 ml/min, whereas the automatic thermal desorption pre-trap split and the exit trap split were set to zero. Prior to the primary desorption procedure, moisture was removed from the TDTs by purging with helium carrier gas (50 ml/min) at room temperature for 1 min. During primary desorption (again using a helium carrier at 50 ml/min; split-less), the TDTs were heated to 300 °C for 10 min, with the liberated VOCs collected and focused on a cold trap (Perkin-Elmer, M041-3628) set to 15 °C. After primary desorption, the trap was heated to 330 °C for 5 min to initiate the transfer of the VOCs to the gas chromatograph column for measurement.

We used a seven-point calibration for each VOC species. The mixed VOC standards were contained in sealed amber ampoules of purge and trap grade methanol obtained from Perkin-Elmer. They were kept at 4 °C until required. A Markes International (Gwaun Elai Medi Science Campus, Llantrisant, UK) calibration solution loading rig was used to load TDTs with a known amount of mixed VOC standard. The calibration solution loading rig resembles a gas chromatograph injector. A stream of hydrocarbon-free ultrapure helium swept injected aliquots of mixed calibration standards onto the TDTs located downstream of the injector and at a flow rate of 50 ml/min. The TDT was left in the stream of helium for 5 min to purge the methanol diluent. Once the TDTs were loaded with the VOC mixed standard, they were analyzed in the same way as the TDT samples.

The final VOC species concentration was calculated using the TDT exposure time obtained from the time activity sheet and the known VOC uptake rates[22,23], according to methods described in Brown et al.[24,25]

The limit of detection, given in nanograms for each VOC species, was calculated as three times the SD of the blank VOC species.[26]

Data Analysis

A comparison of sociodemographic characteristics and time-activity exposure profiles to fuel sources between groups during the June/July sampling, and time activity profiles between time points from February to June/July within the biogas group, were performed using basic descriptive statistics. Graphical evaluation and the Shapiro–Wilk test were conducted to assess variables for normal distribution, and square-root transformations for normality were applied to the data, as needed. Standard paired *t*-tests (between time points among biogas farms) and unpaired *t*-tests (between biogas and referent farms) were used to compare normally distributed continuous variables by dichotomous variables, and two dichotomous variables were compared using χ^2-tests. For non-normally distributed continuous variables (that could not be transformed to create a normal distribution),

© 2013 Nature America, Inc.

Mann–Whitney rank sum tests were used to compare exposure levels of individual VOCs between the biogas and referent groups. The Wilcoxon sign rank test was used for comparisons between February and June/July for the biogas group. In cases with multiple comparisons (e.g. for individual VOCs), the Bonferroni correction was used.

Significant differences in the VOC species profiles (i.e. the order of the most predominant VOCs) in the cookhouses of the biogas group and the referent group (June/July data) were assessed using a multivariate analysis of variance on ranked VOC data—VOC concentrations were ranked for each cookhouse. The overall difference in exposure levels of all VOCs (total exposure concentration, regardless of individual compounds) between the two groups was assessed using a multivariate two-sample nonparametric comparison test.[27] All participant and VOC data were analyzed using Stata/IC 11.1 for Mac (StataCorp, College Station, Texas, USA).

The study was conducted according to the ethical guidelines established by the Canadian Tri-Council Guidelines for Involvement of Human Subjects in Research published by the National Sciences and Engineering Research Council, the Social Sciences and Humanities Research Council and the Canadian Institute for Health Research. The Office of Research Ethics of Dalhousie University in Canada reviewed this research project.

RESULTS

Population Characteristics

Table 1 summarizes the sociodemographic characteristics for each participant group. There were no statistically significant differences in age, family size, or number of cows between the biogas digester and referent participants, confirming that the matching procedure used in the selection of the referent group was successful. Moreover, no statistically significant differences in education level, employment, smoking status, cookhouse size, or aspects of the cookhouse ventilation systems (chimney, window) were observed. As expected, the referent group relied completely on wood as their principal fuel source, whereas biogas was the principal (but not sole) fuel source for most of the biogas group.

Comparison of Exposure Times in Cookhouse Environments

A comparison of the biogas and referent groups in June/July showed that there was no significant difference between the two groups with respect to the total amount of time that the women were spending in the cookhouses (Table 2). However, the times exposed to wood smoke by the women on farms without biogas digesters (Figure 1) were, on average, 2.2 times higher than the biogas group (1122 min/week *versus* 509 min/week, respectively; $P < 0.01$).

A comparison of exposure time between February and June/July data (Table 2), for the biogas group, shows that the women were spending, on average, more time in the cookhouse in June/July compared to in February, although the difference was not significant (1037 min/week *versus* 810 min/week; $P = 0.08$). The relative time spent exposed to biogas combustion products while cooking (Figure 2) increased, on average, from 20% in February to 39% ($P < 0.01$) in June/July, whereas the amount of time exposed to wood smoke remained essentially the same between the two seasons.

Table 1. Sociodemographic characteristics of participants living on farms with biogas digesters compared with participants living on referent farms with traditional wood burning stoves, June/July 2010.

Variable	*Participants on biogas farms* n = *31*				*Participants on referent farms* n = *31*		
	Mean (SD)	*Median*	*Range*	P *value*	*Mean (SD)*	*Median*	*Range*
Age[a]	45 (10)	45	22, 63	0.65	44 (11)	44	24, 72
Number of cows [b]	3.7 (0.24)	3	2, 12	0.49	3.4 (0.25)	3	1, 10
Family size[a]	3.5 (1.7)	3	1, 7	0.46	3.9 (1.7)	3	1, 8
Cookhouse size[a] (m^3)	20 (6.8)	21	6.5, 32	0.63	19 (7.5)	18	8.4, 37
	Percent (number) n = *31*					*Percent (number)* n = *31*	
Education[c]				0.54			
None	6 (2)			—		10 (3)	
Standard 4	13 (4)			—		6 (2)	
Standard 8	48 (15)			—		61 (19)	
Form 4	19 (6)			—		19 (6)	
Technical college	13 (4)			—		3 (1)	
Employed[c]	39 (12)			0.79		35 (11)	
Married[c]	74 (23)			0.35		84 (26)	
Husband employed[c]	74 (17)[d]			0.09		50 (13)[e]	
Smoker[c]	3 (1)			0.31		0 (0)	
Principal fuel source[c]				<0.01			
Biogas	77 (24)			—		0 (0)	
Wood	23 (7)			—		100 (31)	
Cookhouse ventilation[c]				—			
Chimney	35 (11)			0.16		19 (6)	
Windows	87 (27)			0.39		94 (29)	

Abbreviation: SD, standard deviation.
[a]Parametric test performed on raw (normally distributed) data.
[b]Parametric test performed on square-root transformed data; means and standard deviations presented were back-transformed for the table.
[c]Categorical test performed on raw data.
[d]$n = 23$.
[e]$n = 26$.

© 2013 Nature America, Inc.

Table 2. Comparison of personal exposure times (min/week) between participants in biogas and referent groups (June/July) and between seasons (February and June/July) for the biogas group participants in Kenya in 2010.

Exposure time (min/week)	*Participants on biogas farms (June/July)* n = *31*			*Participants on referent farms (June/July)* n = *31*			P *value*
	Mean (SD)	*Median*	*Range*	*Mean (SD)*	*Median*	*Range*	
BG exposure	404 (125)	518	0, 1502	—	—	—	—
WS exposure	509 (65)	500	95, 1703	1122 (52)	1050	455, 2925	<0.01
Total exposure	1022 (77)	1009	310, 2807	1122 (52)	1050	455, 2925	0.46

	Participants on biogas farms (June/July) n = *29*[a]			*Participants on biogas farms (February)* n = *29*[a]			P *value*
	Mean (SD)	*Median*	*Range*	*Mean (SD)*	*Median*	*Range*	
BG exposure	400 (133)	518	0, 1502	162 (86)	165	0, 1024	0.01
WS exposure	526 (64)	500	95, 1703	568 (71)	452	170, 2345	0.68
Total exposure	1037 (82)	1047	310, 2807	810 (74)	806	170, 2607	0.11

Abbreviations: BG, biogas; SD, standard deviation; WS, wood smoke.
Parametric tests were performed on square-root transformed data for all variables; means, medians and standard deviations presented were back-transformed.
[a]Two February biogas participants declined to participate in the June phase; data are presented only for subjects for whom data from both seasons are complete.

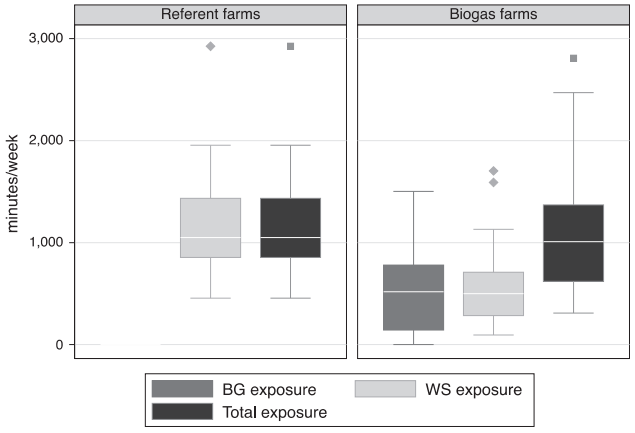

Figure 1. Boxplots of median biogas (BG), wood smoke (WS), and total exposure times, with 25th and 75th percentiles and outliers, for study participants on referent and biogas farms, in Kenya in June/July 2010.

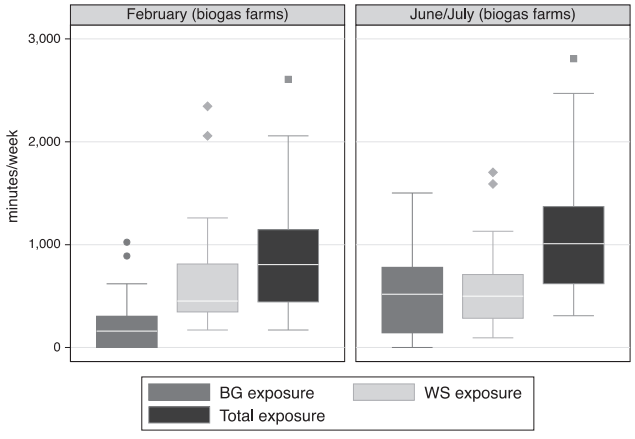

Figure 2. Boxplots of median biogas (BG), wood smoke (WS), and total exposure times, with 25th and 75th percentiles and outliers, for study participants on biogas farms, in Kenya in February and June/July 2010.

Comparison of Cookhouse VOC Concentrations

During checks on the reliability of the Ziploc method of sealing the TDTs between sampling, only some VOC species were detected from the sampling blanks at very low concentrations relative to the TDTs used for sampling, indicating that this method was sufficient for preventing continued sampling at all points during the study, including during transportation between farms as well as while at the participant farms.

The number and percent of VOC species above the limit of detection for the biogas and referent groups in June/July are contained in Table 3 and individual VOC concentrations for February and June/July are presented in Table 4. Ten of the forty-one individual VOCs (Table 4) were significantly different ($P<0.05$) between the biogas and referent groups. After applying the Bonferroni correction for multiple comparisons (α/n, where $\alpha=0.05$ and $n=41$; consequently $P=0.001$), *trans*-1,3-dichloropropene, bromoform, and 1,4-dichlorobenzene were the only VOCs that remained significantly different between the two groups (as shown in bold in Table 4), although nearly all of the VOCs were numerically lower in the biogas group compared with the referent group.

To test the hypothesis that the mixtures of the individual VOCs present in the cookhouses of the two groups were different, we used a ranked multivariate analysis of variance. Ranks (for each cookhouse) of the individual VOC concentrations were compared between the June/July biogas and referent groups, and revealed that there was a significant difference in the composite mixture of the VOCs between the cookhouses of each group ($P=0.01$). We also used a multivariate two-sample non-parametric comparison test to assess the overall difference in the total VOC concentrations between the biogas and referent groups. According to this test, there was no significant difference in the overall concentrations between the two groups (U-statistic = 49.5; $P=0.14$).

Among the biogas group, 29 of 38 individual VOCs tested (Table 4) were significantly different between the two seasons (Feb and June/July; $P<0.05$). Correction for multiple comparisons (α/n, where $\alpha=0.05$ and $n=38$; consequently $P=0.001$) left approximately 45% of the individual VOC exposure levels (17/38) significantly different between the two seasons, as shown in bold in Table 4. Sixteen of the 17 VOCs were higher in February than June/July, with the exception being 1,3-dichlorobenzene.

© 2013 Nature America, Inc.

Table 3. VOC list and percentage of samples above the sample limit of detection.

	LOD (ng)	*Samples above LOD (%)*
Halogenated aliphatic VOCs		
1,1-Dichloropropene	0.05	84.0
1,1,1-Trichloroethane	4.09	63.0
1,1,2-Trichloroethane	0.18	62.0
1,1,2,2-Tetrachloroethane	0.13	54.0
1,2-Dichloroethane	0.03	85.0
Dibromomethane + 1,2-dichloropropane	0.01	85.0
cis-1,3-Dichloropropene	0.18	66.0
1,2-dibromoethane + 1,3-dichloropropane	0.18	74.0
trans-1,3-Dichloropropene	0.18	61.0
Dibromochloromethane	0.19	41.0
1,2-Dibromo-3-chloropropane	0.15	54.0
1,2,3-Trichloropropane	0.18	56.0
Trichlorofluromethane	0.41	79.0
Tetrachloroethene	0.18	59.0
Carbon tetrachloride	0.05	83.0
Chloroform + bromochloromethane	29.9	10.0
Bromoform	0.13	45.0
Bromodichloromethane + trichloroethene	0.04	76.0
Hexachlorobutadiene	0.66	23.0
Aromatic and halo-aromatic VOC		
Benzene	3.23	87.1
Ethylbenzene	0.18	70.0
Isopropylbenzene	0.62	64.0
n-Propylbenzene	0.18	64.0
1,3,5-Trimethylbenzene	0.48	72.0
Sec-butylbenzene	13.7	71.0
Tert-butylbenzene	0.18	74.0
n-Butylbenzene	1.88	62.0
Bromobenzene	24.3	56.0
Chlorobenzene + *1,1,2,2*-tetrachloroethane (aliphatic)	5.43	24.0
1,3-Dichlorobenzene	0.74	80.0
1,4-Dichlorobenzene	2.2	77.0
1,2-Dichlorobenzene	0.67	78.0
1,2,4-Trichlorobenzene	11.1	10.0
1,2,3-Trichlorobenzene	2.79	21.0
p-Xylene	0.69	76.0
o-Xylene	2.44	63.0
Styrene	3.25	65.0
Toluene	0.99	97.6
4-chlorotoluene	0.18	70.0
p-Isopropyltoluene	0.18	78.0
Naphthalene	0.37	77.0

Abbreviations: LOD, limit of detection; VOC, volatile organic compound.

Outdoor VOC Concentrations

As the number of outdoor samples ($n = 2$) was much lower than indoor samples ($n = 62$), statistical tests between the indoor and outdoor VOC concentrations were not possible. However, with the exception of benzene, indoor cookhouse concentrations were numerically much higher than the ambient concentrations present in the outdoor surroundings of farms (Table 5).

DISCUSSION

This study, despite its small sample size, illustrates aspects of the importance that the application of biogas digester technology may have towards improving indoor air quality in cookhouses throughout the developing world. A dramatic reduction in exposure time to elevated concentrations of wood smoke, plus reduced VOC exposures to certain agents, were observed in this investigation of cookhouse environments using biogas in rural Kenya. This study also provides insight into VOC species concentrations associated with biogas and wood fuel used in rural Kenyan cookhouses, where women have traditionally relied upon wood fuel for cooking. To our knowledge, there have been few studies reporting VOC species concentrations in rural cookhouses globally. The passive sampling methods described in this study could be readily applied to VOC exposure studies of a similar nature.

There were a number of individual VOCs that were present in significantly higher concentrations in referent cookhouses compared with cookhouses on farms with biogas digesters (Table 4), and the mixture of VOCs was significantly different between groups using the ranked multivariate analysis of variance. However, when comparing the overall difference in VOC exposure levels between groups, the multivariate two-sample non-parametric test showed no significant difference between the two groups ($P = 0.14$), and there were fewer significant differences in VOC concentrations between the two groups than there were between February and June/July sampling within the biogas group (Table 4). There are a number of possible reasons for these inconsistent results between groups. (1) It is likely that the sample size was insufficient to detect overall changes in concentrations of all the 41 VOCs using the non-parametric test, especially because only a few of the VOCs had significant differences at the individual level, especially after the Bonferroni correction. (2) During the study, we noted that cookhouses were also used as storage areas for other household items, usually items that were undesirable to store in the house, such as pesticides. We did not collect information on what was stored in the cookhouses because this was only noticed partway through the data collection period in June/July. It is possible that these circumstances led to the sampling of VOCs that were not emitted solely from the combustion of wood or methane as fuel. (3) Biogas was still supplemented with wood fuel use, meaning that wood smoke exposure was not eliminated on the biogas farms, reducing the differences between groups. (4) Many of the women had biogas burners located in cookhouses that were charred from years of exposure to large amounts of wood smoke, and it is possible that these structures continue to off-gas VOCs even if cooking with wood is significantly reduced or eliminated. The ventilation mechanisms present in the cookhouses and the size of the cookhouses were similar among both groups, and therefore these variables were unlikely to be confounders of any relationship, or lack thereof, between biogas farm status and cookhouse VOC concentration or wood smoke exposure times. The biogas combustion VOCs among biogas farms was likely the main reason for the mixtures of VOCs being significantly different with the ranked multivariate analysis of variance test.

The women in the two groups participating in the week-long study spent similar total amounts of time cooking in their cookhouses (Figure 1). However, the women on farms with biogas digesters had spent a 50% shorter amount of time cooking with wood compared with the referent group, and consequently had a shorter amount of time exposed to wood smoke. These women spent, on average, more than 6.5 h cooking with biogas per week, thus reducing the reliance on cooking with wood fuel. This large number of hours cooking with biogas was expected because a related study showed that two cows fueling a digester reduced wood consumption for a family of four by approximately 44%.[9]

When comparing the seasonal variation in time spent cooking with wood (Figure 2), the women spent similar amounts of total time cooking with wood, however, cooking with biogas increased by about 147% from February to June/July. There are at least two possible reasons for this increase in biogas cooking time. During the February 2010 data collection, it was found that many of the digesters were not functioning optimally. Consequently, farmer training sessions on biogas digester maintenance, as well as servicing for non-functioning digesters, were provided by Farmers

© 2013 Nature America, Inc.

Table 4. Total VOC exposure concentrations ($\mu g/m^3$) for the biogas and referent groups (June/July 2010) as well as for February for the biogas group in Kenya.

	CAS number	*February biogas farms*	*June/July biogas farms*	*June/July referent farms*	P[a]*-value (seasonal comparison)*	P[b]*-value (fuel comparison)*
		Median (range)	*Median (range)*	*Median (range)*		
Halogenated aliphatic VOCs						
1,1-Dichloropropene	563-58-6	21 (6.6, 86)	30 (0, 169)	30 (0, 1185)	0.04	0.58
1,1,1-Trichloroethane	71-55-6	0.52 (0.20, 3.0)	0.28 (0, 0.96)	0.23 (0.08, 5.8)	<**0.01**	0.44
1,1,2-TRichloroethane	79-00-5	0.98 (0, 3.3)	0 (0, 3.1)	0 (0, 5.7)	<0.01	0.11
1,1,2,2-Tetrachloroethane	79-34-5	—	0.47 (0, 1.4)	0.80 (0, 3.5)	—	0.08
1,2-Dichloroethane	107-06-2	69 (11, 635)	82 (8.4, 443)	96 (0, 692)	0.72	0.62
Dibromomethane + 1,2-dichloropropane	74-95-3 + 78-87-5	0.12 (0.03. 1.0)	0.04 (0, 0.34)	0.03 (0, 3.9)	<**0.01**	0.81
cis-1,3-Dichloropropene	10061-01-5	6.7 (1.1, 70)	2.6 (0.30, 21)	5.1 (0, 20)	<**0.01**	0.02
1,2-Dibromoethane + 1,3-dichloropropane	106-93-4 + 78-87-5	0.49 (0.05, 3.0)	0.17 (0, 1.5)	0.18 (0.03, 1.5)	<0.01	0.34
trans-1,3-Dichloropropene	10061-02-6	0.78 (0, 19)	0.20 (0, 6.8)	2.0 (0, 18)	0.10	<**0.01**
Dibromochloromethane	124-48-1	0.05 (0, 0.34)	0 (0, 0.17)	0 (0, 0.30)	<0.01	0.53
1,2-Dibromo-3-chloropropane	96-12-8	0.21 (0.03, 8.0)	0.10 (0, 0.93)	0.13 (0.02, 21)	0.01	0.25
1,2,3-Trichloropropane	96-18-4	8.9 (2.2, 90)	2.0 (0, 15)	4.1 (0.34, 37)	<**0.01**	<0.01
Trichlorofluromethane	75-69-4	—	2.3 (0.69, 8.7)	2.0 (0, 11)	—	0.57
Tetrachloroethene	127-18-4	0.45 (0.11, 2.5)	0.21 (0.04, 16)	0.19 (0.03, 0.37)	<**0.01**	0.34
Carbon tetrachloride	56-23-5	1.6 (0.56, 7.4)	2.8 (0.68, 31)	2.3 (0.77, 13)	0.02	0.46
Chloroform + bromochloromethane	67-66-3 + 74-97-5	0.85 (0.25, 44)	0.07 (0, 53)	0 (0, 11)	<**0.01**	0.12
Bromoform	75-25-2	0.85 (0.15, 6.1)	0.05 (0, 0.72)	0.15 (0.01, 0.77)	<**0.01**	<**0.01**
Bromodichloromethane + trichloroethene	75-27-4 + 79-01-6	0.26 (0.07, 1.3)	0.04 (0, 0.33)	0.08 (0, 1.4)	<**0.01**	0.04
Hexachlorobutadiene	87-68-3	0.11 (0, 0.87)	0 (0, 0.69)	0 (0, 3.0)	0.33	0.10
Aromatic and halo-aromatic VOCs						
Benzene	71-43-2	36 (7.7, 4984)	28 (0, 467)	34 (0, 232)	<0.01	0.18
Ethylbenzene	100-41-4	38 (2.6, 7198)	15 (1.6, 997)	18 (1.0, 1198)	<**0.01**	0.83
Isopropylbenzene	98-82-8	0 (0, 843)	7.6 (0, 375)	11 (1.5, 108)	0.24	0.36
n-Propylbenzene	103-65-1	9.8 (0.67, 1000)	8.8 (0.11, 247)	12 (0.23, 216)	0.05	0.99
1,3,5-Trimethylbenzene	108-67-8	46 (1.1, 3208)	17 (0.31, 813)	21 (2.5, 611)	<0.01	0.50
Sec-butylbenzene	135-98-8	70 (6.7, 911)	23 (0, 446)	20 (0.45, 100)	<**0.01**	0.69
Tert-butylbenzene	98-06-6	103 (19, 6936)	52 (4.0, 2221)	63 (9.8, 1037)	<0.01	0.50
n-Butylbenzene	104-51-8	60 (0, 829)	25 (0.57, 459)	22 (0.12, 201)	<**0.01**	0.30
Bromobenzene	108-86-1	132 (38, 3045)	27 (0, 837)	95 (3.2, 1180)	<0.01	<0.01
Chlorobenzene + 1,1,2,2-tetrachloroethane (aliphatic)	108-90-7 + 79-34-5	0.06 (0.01, 2.7)	0.05 (0, 1.1)	0.04 (0, 0.38)	0.14	0.71
1,3-Dichlorobenzene	541-73-1	3.7 (0, 18)	6.4 (0.41, 76)	17 (0, 83)	<**0.01**	<0.01
1,4-Dichlorobenzene	106-46-7	—	2.9 (0, 15)	8.1 (0.93, 43)	—	<**0.01**
1,2-Dichlorobenzene	95-50-1	6.9 (0, 119)	1.7 (0, 26)	6.7 (0, 21)	0.01	<0.01
1,2,4-Trichlorobenzene	120-82-1	2.8 (0, 14)	0 (0, 15)	0 (0, 0)	<**0.01**	0.32
1,2,3-Trichlorobenzene	87-61-6	1.7 (0, 22)	0 (0, 3.6)	0 (0, 2.5)	<**0.01**	0.13
p-Xylene	106-42-3	64 (15, 12445)	28 (0.30, 1372)	33 (6.4, 2240)	<0.01	0.32
o-Xylene	95-47-6	33 (4.8, 6655)	27 (1.3, 1960)	40.9 (9.4, 1472)	0.28	0.10
Styrene	100-42-5	36 (4.0, 620)	22 (3.6, 516)	30 (6.7, 118)	0.06	0.40
Toluene	108-88-3	107 (23, 20842)	46 (2.3, 2286)	26 (3.6, 2477)	<**0.01**	0.01
4-Chlorotoluene	106-43-4	72 (6.2, 12167)	55 (0, 2923)	46 (0, 1909)	0.06	0.98
p-Isopropyltoluene	99-87-6	108 (28, 2361)	45 (5.4, 587)	39 (5.8, 436)	<**0.01**	0.34
Naphthalene	91-20-3	66 (0,1379)	5.1 (0, 723)	18 (0, 201)	<**0.01**	0.12

Abbreviation: CAS, Chemical Abstract Services Registry Number.
Non-parametric tests were performed on raw (non-normally distributed) data for all variables.
[a]Comparison between February and June/July data (biogas group).
[b]Comparison between biogas and referent groups (June/July data).
Bold indicates significant difference between the two seasons.

Helping Farmers. During the June/July 2010 data collection, the farmers reported that nearly all the digesters were functioning optimally, potentially causing women to increase the amount of time spent cooking with biogas. Another possibility is that there may have been a decrease in anaerobic decomposition during the colder period of June/July that resulted in decreased biogas

© 2013 Nature America, Inc.

Table 5. Total VOC exposure concentrations ($\mu g/m^3$) for the 24 and 72 h continuous outdoor sampling (June/July 2010).

	CAS number	*June/July outdoor samples*	
		24 h	*72 h*
Halogenated aliphatic VOCs			
1,1-Dichloropropene	563-58-6	5.9	2.2
1,1,1-Trichloroethane	71-55-6	0.1	<0.1
1,1,2-Trichloroethane	79-00-5	0.1	<0.1
1,1,2,2-Tetrachloroethane	79-34-5	0	<0.1
1,2-Dichloroethane	107-06-2	0.2	7.5
Dibromomethane + 1,2-dichloropropane	74-95-3 + 78-87-5	<0.1	<0.1
cis-1,3-Dichloropropene	10061-01-5	0.1	<0.1
1,2-Dibromoethane + 1,3-dichloropropane	106-93-4 + 78-87-5	0.3	0.1
trans-1,3-Dichloropropene	10061-02-6	<0.1	0
Dibromochloromethane	124-48-1	<0.1	0
1,2-Dibromo-3-chloropropane	96-12-8	<0.1	<0.1
1,2,3-Trichloropropane	96-18-4	0	0.4
Trichlorofluromethane	75-69-4	0.5	0.4
Tetrachloroethene	127-18-4	<0.1	<0.1
Carbon tetrachloride	56-23-5	0.3	0.3
Chloroform + bromochloromethane	67-66-3 + 74-97-5	0.1	<0.1
Bromoform	75-25-2	0	<0.1
Bromodichloromethane + trichloroethene	75-27-4 + 79-01-6	<0.1	<0.1
Hexachlorobutadiene	87-68-3	0	0
Aromatic and halo-aromatic VOCs			
Benzene	71-43-2	64.6	21.2
Ethylbenzene	100-41-4	0	0
Isopropylbenzene	98-82-8	0	0
n-Propylbenzene	103-65-1	0	0
1,3,5-Trimethylbenzene	108-67-8	12.5	0
Sec-butylbenzene	135-98-8	0	0
Tert-butylbenzene	98-06-6	0	0.3
n-Butylbenzene	104-51-8	3.7	5.3
Bromobenzene	108-86-1	3.5	16.9
Chlorobenzene + 1,1,2,2-tetrachloroethane (aliphatic)	108-90-7 + 79-34-5	0	<0.1
1,3-Dichlorobenzene	541-73-1	0.4	0.4
1,4-Dichlorobenzene	106-46-7	0	0.2
1,2-Dichlorobenzene	95-50-1	<0.1	<0.1
1,2,4-Trichlorobenzene	120-82-1	0	0
1,2,3-Trichlorobenzene	87-61-6	0	0
p-Xylene	106-42-3	0.6	0.4
o-Xylene	95-47-6	0	0
Styrene	100-42-5	1.7	0.8
Toluene	108-88-3	2.2	1.2
4-Chlorotoluene	106-43-4	0	0
p-Isopropyltoluene	99-87-6	1.0	4.6
Naphthalene	91-20-3	0.5	0.6

Abbreviation: CAS: Chemical Abstract Services Registry Number.

production (not measured), and consequently, lower pressure in the biogas digester, causing longer cooking times over reduced heat. Average maximum temperature in Embu in February was 30 °C, whereas in June/July it was 26 °C.[28]

When comparing the exposure levels of individual VOCs between the two seasons, 16 of the 38 VOCs tested decreased significantly in concentration in June/July compared to February, after adjustment for multiple comparisons (Table 4). Wood smoke exposure times were similar between the two seasons, so it is difficult to determine why there was a reduction in VOC concentrations for some VOCs in June/July, particularly when the time of exposure to biogas smoke was higher in June/July than in February. It could be possible that the cookhouse internal surfaces were off-gassing more during the hotter month of February, causing higher levels of VOC exposure, despite the fact that time spent cooking with wood remained the same, on average.

As expected, the individual VOC concentrations were much higher in the cookhouses than in the outdoor ambient air, with the exception of benzene, which was equally high in both the indoor and outdoor samples. Air quality is generally good in this area of Kenya, which is located far from large anthropogenic sources of industrial air pollutants. However, automobile exhaust is a major source of atmospheric benzene emissions, so it is possible that the higher concentrations of ambient benzene seen in the outdoor samples could be due to automobile traffic in the area.[29]

In conclusion, this study was small but it has provided valuable information to the establishment of VOC species profiles in rural Kenyan cookhouses, where women rely primarily on wood for cooking fuel. Women on farms with biogas digesters spent significantly less time cooking over a wood fire compared with women in the referent group. Individual VOC exposure was significantly lower on biogas farms than referent farms, and on average, the mixture of VOCs was lower in cookhouses on farms using biogas digesters than on farms without biogas digesters. By reducing time spent cooking over a wood fire, women using biogas digesters are being exposed to reduced amounts of wood smoke and are almost certainly experiencing reductions in VOC exposure.

© 2013 Nature America, Inc.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ACKNOWLEDGEMENTS

We thank R. Wanjiru, A. Wambura, G. Kariuki, T. Mellish, K. Mellish, and Farmers Helping Farmers for their guidance and assistance. We appreciate the assistance and cooperation of the participants, the respiratory clinic hosts, the Wakulima Dairy staff, and all those involved in the fieldwork. Dr. Neil Brewster and Klara Chrzanowski produced the laboratory analytical chemistry results. This project was primarily funded with Pilot Study funding from the Atlantic RURAL Centre, enabled through Canadian Institutes of Health Research Grant number CDA-66534. Additional support was provided by the University of Prince Edward Island, Dalhousie University, Veterinarians without Borders-Canada, the Killam Graduate Fellowship Awards, and the NSERC Graduate Fellowships.

REFERENCES

1 WHO Regional Publications European Series. *Air quality guidelines for Europe*, 2nd edn. WHO Regional Publications, European Series. World Health Organization: Copenhagen, Denmark, 2000, pp 1–273.
2 Emmelin A, Wall S. Indoor air pollution: a poverty-related cause of mortality among the children of the world. *Chest* 2007; **132**: 1615–1623.
3 Naeher LP, Brauer M, Lipsett M, Zelikoff JT, Simpson CD, Koenig JQ *et al*. Woodsmoke health effects: a review. *Inhal Toxicol* 2007; **19**: 67–106.
4 Smith KR. Wood: the fuel that warms you thrice. In: Colfer CJP (eds). *Human Health and Forests: A Global Overview of Issues, Practice, and Policy*. Earthscan: London, UK, 2008, pp 97–111.
5 Bruce N, Perez-Padilla R, Albalak R. The health effects of indoor air pollution exposure in developing countries. *Protection of the Human Environment*. World Health Organization: Geneva, Switzerland, 2002.
6 Ezzati M, Mbinda BM, Kammen DM. Comparison of emissions and residential exposure from traditional and improved cookstoves in Kenya. *Environ Sci Technol* 2000; **34**: 578–583.
7 Jeong C-H, Evans GJ, Dann T, Graham M, Herod D, Dabek-Zlotorzynska E *et al*. Influence of biomass burning on wintertime fine particulate matter: source contribution at a valley site in rural British Columbia. *Atmos Environ* 2008; **42**: 3684–3699.
8 Dohoo C, Guernsey J, Critchley K, VanLeeuwen J. Pilot study on the impact of biogas as a fuel source on respiratory health of women on rural Kenyan smallholder dairy farms. *J Environ Public Health* 2012; **2012**: 636298.
9 Dohoo C, VanLeeuwen J, Guernsey JR, Critchley K, Gibson M. Impact of biogas digesters on wood utilisation and self-reported back pain for women living on rural Kenyan smallholder dairy farms. *Glob Public Health* 2013; **8**: 221–235.
10 Díaz E, Smith-Sivertsen T, Pope D, Lie RT, Díaz A, McCracken J *et al*. Eye discomfort, headache and back pain among Mayan Guatemalan women taking part in a randomised stove intervention trial. *J Epidemiol Commun Health* 2007; **61**: 74–79.
11 McCracken JP, Smith KR, Díaz A, Mittleman M, Schwartz J. Chimney stove intervention to reduce long-term wood smoke exposure lowers blood pressure among Guatemalan women. *Environ Health Perspect* 2007; **115**: 996–1001.
12 Smith-Sivertsen T, Díaz E, Pope D, Lie RT, Díaz A, McCracken J *et al*. Effect of reducing indoor air pollution on women's respiratory symptoms and lung function: The RESPIRE randomized trial, Guatemala. *Am J Epidemiol* 2009; **170**: 211–220.
13 Weiland P. Biogas production: current state and perspectives. *Applied Microbiol Biotechnol* 2010; **85**: 849–860.
14 Karanja GM, Kiruiro EM. Biogas Production. KARI Technical Note Series. Embu Kenya, Embu: KARI 2003, (10).
15 Wang S, Wei W, Du L, Li G, Hao J. Characteristics of gaseous pollutants from biofuel-stoves in rural China. *Atmos Environ* 2009; **43**: 4148–4154.
16 Farmers Helping Farmers [Internet]. Available from http://www.farmershelpingfarmers.ca.
17 Biernacki P, Waldorf D. Snowball sampling: Problems and techniques of chain referral sampling. *Sociological Methods Res* 1981; **10**: 141–163.
18 Penrod J, Preston DB, Cain RE, Starks MT. A discussion of chain referral as a method of sampling hard-to-reach populations. *J Transcult Nurs* 2003; **14**: 100–107.
19 International Safety Equipment Association. *American National Standard for Air Sampling Devices - Diffusive Type for Gases and Vapors in Working Environments*. Virginia: Arlington, Texas, USA, 1998, pp 1–104.
20 British Standards Institution. *Ambient Air Quality: Diffusive Samplers for the Determination of Concentrations of Gases and Vapours—Requirements and Test Methods* London, UK, 2002, pp 1–30.
21 International Organization for Standardization. *Workplace Atmospheres - Protocol for Evaluating the Performance of Diffusive Samplers* Geneva, Switzerland, 2007, pp 1–17.
22 Plant N, Keen C. Application of thermal desorption to occupational exposure monitoring. Perkin-Elmer Gas Chromatography Application Note 007367_05 2007 1–12.
23 H.a.S.E.C. Committee Working Group 5. *Diffusive Uptake Rates on Perkin Elmer Sorbent Tubes* Sheffield, UK, 2001.
24 Brown VM, Crump DR, Gardiner D. Measurement of volatile organic compounds in indoor air by a passive technique. *Environ Technol* 1992; **13**: 367–375.
25 International Organization for Standardization. *Workplace Air Quality—Sampling and Analysis of Volatile Organic Compounds in Ambient Air, Indoor Air and Workplace Air by Sorbent Desorption/Capillary Gas Chromatography—Part 2: Diffusive Sampling* Geneva, Switzerland, 2008, pp 1–35.
26 Armbruster DA, Tillman MD, Hubbs LM. Limit of detection (LOD)/limit of quantitation (LOQ): comparison of the empirical and the statistical methods exemplified with GC–MS assays of abused drugs. *Clin Chem* 1994; **40**: 1233–1238.
27 Leach C. Nonparametric methods for complex data sets. In: Lovie P, Lovie AD (eds). *New Developments in Statistics for Psychology and the Social Sciences*, 2nd edn. (British Psychological Society and Routledge: London, 1991.
28 World Meteorological Organization. World weather information service - Kenya. [Internet]. Available from http://worldweather.wmo.int.
29 Wallace L. Major sources of benzene exposure. *Environ Health Perspect* 1989; **82**: 165–169.

© 2013 Nature America, Inc.