

1 Article

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Risk assessment of BTEX concentration from 3 combustion of coal in a controlled laboratory 4 environment

5 **Daniel Masekameni^{1,3*}, Raeesa Moolla², Mary Gulumian^{4,5} and Derk Brouwer¹**6 ¹ Occupational Health Division, School of Public Health: University of the Witwatersrand, Parktown, 2193.7 Derk.brouwer@wits.ac.za8 ² School of Geography, Archaeology and Environmental Studies, University of the Witwatersrand, Private
9 Bag X3, WITS, 2050. Raeesa.molla@wits.ac.za10 ³ Department of Geography, Environmental Management and Energy Studies, University of Johannesburg,
11 Johannesburg, South Africa.12 ⁴ National Institute for Occupational Health, National Health Laboratory Services, Braamfontein,
13 Johannesburg, South Africa. mary.gulumian@nioh.nhls.ac.za14 ⁵ Haematology and Molecular Medicine, School of Pathology, University of the Witwatersrand University of
15 the Witwatersrand, Parktown, Johannesburg, 219316 * Corresponding author: danielmasekameni@gmail.com, +27 11- 717 235517 **Abstract:** A D-grade type coal was burned under simulated domestic practices in a controlled
18 laboratory set-up, in order to characterize emissions of volatile organic compounds (VOCs); viz.
19 benzene, toluene, ethylbenzene and xylenes (BTEX). Near-field concentrations were collected in a
20 shack-like structure constructed using corrugated iron, simulating a traditional house found in
21 informal settlements in South Africa. Measurements were carried out using the Synspec Spectras
22 GC955 real-time monitor over a three-hour burn cycle. The 3-hour average concentrations (in $\mu\text{g}/\text{m}^3$)
23 of benzene, toluene, ethylbenzene, p-xylene and o-xylene were 919 ± 44 , 2051 ± 91 , 3838 ± 19 , 4245 ± 41
24 and 3576 ± 49 , respectively. The cancer risk for adult males and females in a typical SA household
25 exposure scenario, was found to be 1.1 -1.2 and 110-120 folds higher than the US EPA designated
26 risk severity indicator (1E^{-6}), respectively. All four TEX compounds recorded the Hazard Quotient
27 (HQ) of less than 1, indicating a low risk of developing related non-carcinogenic health effects. The
28 HQ for TEX ranged from 0.001–0.05, with toluene concentrations being the lowest and ethylbenzene
29 the highest. This study has demonstrated that domestic coal burning may be a significant source of
30 BTEX emission exposure.31 **Keywords:** Coal, BTEX, Hazardous air pollutants, domestic fuel burning32

33

1. Introduction

34 The introduction of several chemicals in the atmosphere has been widely associated with
35 increased health risks (1,2). Anthropogenic sources of higher exposure to air pollutants is suggested
36 to be attributed to industrial activities (3,4). Several studies have been conducted globally,
37 investigating the emissions of larger industrial activities such as power generation on the external
38 environment (5,6). The mechanisms as to how pollutants are emitted and distributed are well
39 understood, especially on larger stationary sources in developed countries and parts of developing
40 Asia.41 There is a growing concern globally, regarding pollutant inventories in order to understand
42 major sources of emissions and their impacts (7). There is an emerging body of knowledge which
43 suggests that indoor household burning presents a major threat to public health (8,9) arising from
44 lack of access to clean energy sources, which has been identified as a major contributor to local indoor

45 air pollution(10,11). Majority of households, especially in developing countries, rely on multiple
46 energy sources combusted daily using inefficient devices in poorly ventilated environments (12,13).

47 Emission of volatile organic compounds (VOCs) under these conditions may present an
48 important class of pollutants as it has been associated with several health and environmental impacts
49 (14–16). It is reported that VOCs, even at low concentrations, can produce several health effects
50 including nausea, eye and throat irritation, induction of asthma attacks, fatigue, dizziness and mental
51 confusion (17–21). VOCs in general are quite numerous however; emphasis is given to mono-
52 aromatic volatile organic compounds termed BTEX (benzene, toluene, ethyl benzene and xylenes).
53 This group of VOCs are often considered carcinogenic (22,23). Particularly, benzene and
54 ethylbenzene exposure is linked with increased risk of leukemia and hematopoietic cancers (24–26).
55 Toluene and xylene are non-carcinogenic but may produce reproductive adverse effects; especially
56 when exposures are chronic at low to high concentrations (27).

57 Efforts to create an exposure inventory for BTEX is mainly done in occupational environments,
58 while less information is available at non-occupational settings (28–34). The sources of BTEX in
59 residential areas are diverse including domestic care products; life style related chemicals such
60 cigarette smoke; and combustion energy-related sources (35). It has also been suggested that the
61 risk of exposure is higher in indoor environments relative to outdoor environments (36–41).

62 Exposure to airborne pollutants is influenced by many factors such as emission rate at the source,
63 air exchange rate, pollutant concentration and time spent indoors and meteorological conditions
64 (32,35,38,42). Children and the elderly are the most vulnerable groups as they spend most of their
65 time indoors and also due to weaker immune system (42). Moya, Bearer and Etzel (2004), have
66 emphasized that infants and children are at greater risk than adults due to their high metabolic and
67 resting rate compared to adults (32,35). It was further found that children spend most of their time
68 indoor next to their mothers and are thus exposed to elevated concentrations of combustion
69 pollutants, during cooking and heating conditions (20).

70 In regulating exposure to toxic compounds on human health, many countries use risk
71 assessments as a tool to determine the relative risk and develop action plans based on the emissions
72 or concentration. However, risk assessment considers various factors in estimating a possibility of a
73 biological response. Factors such as hazard source identification, exposed group, exposure pathway,
74 concentration of the contaminant, target organ and potential biological response dose which might
75 trigger a response are investigated (32,42). Hematotoxicity and immunotoxicity have been widely
76 used as indicators for non-carcinogenic effects of benzene exposure (44–46). Chronic exposure to
77 benzene have been reported in several studies and reviews indicating the risk of anemia, bone
78 marrow hyperplasia, aplastic anemia, leukopenia, lymphocytopenia, thrombocytopenia and
79 pancytopenia has been shown (24,46,47).

80 Exposure to high concentrations of BTEX have been widely associated with several adverse
81 health effect in countries such as USA, India and China (46–50). Despite several human health effects
82 reported elsewhere regarding exposure to BTEX, in South Africa very few studies have been
83 conducted to quantify indoor and environmental exposure to BTEX, especially from domestic
84 activities where coal burning has been consistently linked to severe health effects (51,52). The present
85 study aims to quantify concentrations of BTEX from domestic coal burning process and evaluate
86 potential health risk in respect of cancer and non-cancer effects. The study uses experimental data on
87 BTEX emission were used as proxies for near field concentration to estimate exposure mimicking
88 indoor use of coal in a brazier applicable in the South African informal settlements. The study is

89 hoped to assist in contributing knowledge on domestic solid fuel burning technologies and might aid
90 in supporting future epidemiological and other studies in South Africa and in other low to medium
91 income countries with domestic coal burning activities.

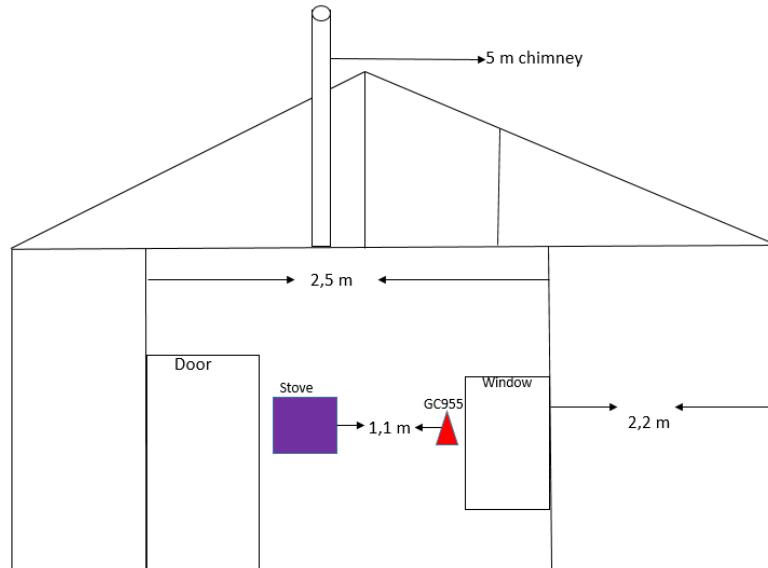
92 **2. Materials and Methods**

93 **2.1. BTEX sampling condition**

94 BTEX were sampled under the laboratory conditions simulating community based activities.
95 The combustion laboratory was constructed using corrugated iron and combustion materials
96 included coal, wood kindling and paper. The selection of the stove, known as brazier (*imbaula*), to
97 fuel combination (Top-Lit Updraft (TLUD) and High ventilated stove), was based on the government
98 project roll-out program of TLUD ignition method as an interim air pollution reduction strategy
99 initiative and the selection of high ventilated stoves was based on local studies which proven that the
100 use of high ventilated stove lit with TLUD leads to the reduction of emissions (13,53). Tests were
101 performed over a period of three hours and further details on the burn sequences are provided in
102 (13,54). Stove was lit up using the (TLUD) method in a high ventilated brazier, using D-grade
103 bituminous coal. Further, details on the stove and fuel combination can be obtained in published
104 literature as contained in the references (13,16,55,56).

105 The study was carried out at the University of Johannesburg's Sustainable Energy and Research
106 Centre in South Africa. The stove was placed at the center of the combustion lab. The combustion
107 laboratory is built simulating a typical informal house colloquially known as a shack, constructed
108 using corrugated irons, with a small window (300 mm x 400 mm) and a standard door (840 mm x 1.8
109 m) as shown in Figure 1.

110



111

112 Figure 1: Schematic diagram of a traditional corrugated iron house in a typical South African
113 informal settlement. (Not drawn to scale)

114 **2.2. Domestic combustion scenario in South African low income settlement**

115 Prior to stove ignition, all openings leading to the outside of the shack were closed/ sealed
116 mimicking field based practices. Nevertheless, it must be noted that air leaks could occur since the

117 sealing of openings were not comprehensive enough to contain all emitted pollutants, which might
118 be similar to a typical shack. The stove was placed at the center of the combustion lab and
119 measurements were taken at 1 m above the floor and 1.2 m away from the stove as shown in Figure
120 1. Domestic coal fire is generally associated with high heat generation, simultaneously increasing the
121 indoor temperature significantly. Due to the sensitivity of the monitoring equipment care was given
122 to separate the experimental and data capturing rooms. The detection device was placed in the
123 analysis room next to the combustion laboratory. The sampling probe of 1.9 m in length was used to
124 draw in sample to the detection device/ gas analyzer. The isolation or removal of the detection device
125 from the hot environment was to avoid similar challenges experienced during field monitoring in
126 Moolla *et al.* (2014), where higher temperature led to instrumentation malfunctioning and loss of data.

127 Samples were taken and averaged for each distinct time aggregate (15 minutes, 45 minutes and
128 2 hours, to coincide with burn cycles). The first sample was taken from the time the fuel is lit until
129 the establishment of the flame i.e. the first 15 minutes of the combustion where the condition is
130 smoldering (i.e. burning slowly with visible smoke but without flames) with insufficient air supply
131 and low fuel bed temperature, the next stage is when a flame is well established and the combustion
132 process is at the mixing stage and takes about 45 minutes, the last stage where there is no visible
133 flame and only coke/ fixed carbon burns and char formation often takes place (~120 minutes). The
134 laboratory experiments were done three times per each combustion time interval, where the average
135 concentrations over three experiments was used in the study.

136 2.3. BTEX sampling instruments

137 In the present study, five VOCs were monitored using the Synspec Spectras gas chromatography
138 (GC955, series 600). This instrument is widely used to monitor BTEX and has been approved as per
139 service specification EN 14662-3. The samples were drawn in through the inlet feeder operated at a
140 flowrate of 5 ml/min connected at the back of the instrument. A 37 mm filter was connected between
141 the monitoring instrument and the inlet probe to isolate or exclude foreign particles. Drawn in
142 hydrocarbons are firstly pre-concentrated in the Tenax GR, where they were pre-heated and
143 desorbed, and thereafter separated according to columns. The instrument is coupled with a photo
144 ionizer detector (PID) which assists in increasing sensitivity for benzene and other aromatic
145 hydrocarbons. The running cycle can be from 15 minutes upwards, which can be adjusted and operates
146 at a temperature of <70 °C. Helium was used as a carrier gas set at a pressure of 350 kPa, connected
147 using Teflon tubing at a distance of 1.8 m (from the gas cylinder to the GC).

148 2.4. Risk assessment

149 BTEX emissions were monitored at near field (inside the room at 1.2 m away from the emitting source)
150 and were then used as room concentrations. In a typical coal burning house in South Africa, coal stoves
151 are often used indoors during the winter season between 18h00 pm to 21h00 pm. This is due to the
152 inherent heat production of the technology while in summer it is unlikely that the stove will be used
153 indoors for either cooking or space heating. The winter period in South Africa is from June to August
154 (equivalent to 92 days). During winter, all outlets leading to the external environment are closed with
155 the intention to contain all produced or radiated heat from the device. Due to the hazardous nature of
156 coal and associated carbon monoxide poisoning, households often extinguish the fire and remove the

157 stove from the indoor spaces before going to bed. We therefore, used this scenario to estimate the
 158 exposure duration.

159 In general, we have conducted risk assessment to estimate the potential exposure to BTEX from domestic
 160 coal burning and similar to other studies, used the data to assess the risk to human health (48,57,58). Risk
 161 assessment is a comprehensive process which includes hazard source identification, evaluation,
 162 characterisation and control, aiming at prevention of possible health outcomes. Thus, this research has
 163 aimed at assessing both carcinogenic and non-carcinogenic potential risk by estimating exposure to
 164 BTEX.

165 a) Hazard identification

166 During data collection, BTEX concentrations from the coal burning device was monitored. The focus of
 167 the monitoring was limited to BTEX emissions due to their inherent carcinogenic and non-carcinogenic
 168 health impacts on exposed groups. As mentioned earlier, benzene is classified as a Group A human
 169 carcinogenic according to US Environmental Protection Agency (EPA) (59,60). Using the approach
 170 similar to the one described below, a lifetime exposure duration of 30 years was assumed for residential
 171 dwellers as a default value based on the USEPA (61). Common occupants in South African informal
 172 settlements are often unemployed individuals or those who falls in the low income brackets. In the study
 173 conducted by (62,63), it was found that majority of household live on average income of R3 500.
 174 Predominately, adult males and females resides in informal settlements while just a small number of
 175 school going children (64). Informal settlements are often built closer to employment sites or in industrial
 176 zones (63,65). The average age of dwellers was estimated to be 35 years, while majority of shack owners
 177 are males at 61% relative to females (64). A small proportion of children below 18 years were recorded
 178 during census 2010 at 1% of the total dwellers in the informal sector(65).

179 b) Exposure assessment

180 For the exposure assessment we have considered the estimated dose expressed as chronic daily intake
 181 (mg/kg/day). Due to inadequate available methodologies to determine the internal dose we used near
 182 field breathing zone concentration for the exposure assessment. We assumed that the breathing zone
 183 concentration is equal to the near field concentration or emission zone (61). The driving factors in dose
 184 estimation were exposure pathway (air) including route of entry (inhalation), frequency to which one is
 185 expected to be exposed, duration of exposure and population age group (Adults male and females).
 186 Since, this was a laboratory based study simulating the experience of residents, where population index
 187 is not present, the study adopted some of the parameters for the exposure scenario from the US EPA's
 188 risk assessment guidelines and South African Statistics as in Table 1(61,64).

189 Table 1: Summary of exposure scenario factors and values used in this study

Parameter	Description	Value	Unit
C	Room concentration	-	mg/m ³
IR	Inhalation rate	20	m ³ /day
BW	Body weight	70 males/ 60 kg females	Kg

ED	Exposure days	92 (3 hr per day)	Days/ year
YE	Years of exposure	30 (Residential)	Years
AT	Years in lifetime	60 male/67 female	Years

190 ¹The default inhalation rate, body weight and residential exposure where from USEPA (61) while the male and female years in life
 191 were adopted from (64).

192 Dose response relationship was used to estimate potential biological response for each pollutant. Similar
 193 to (66,67), average concentration for the entire burn cycle was used to calculate the chronic intake
 194 concentration. Chronic daily intake (CDI) (equation 1) for both carcinogenic and non-carcinogenic
 195 pollutants was calculated using values as shown in Table 1. The average CDI_{year} provides estimated daily
 196 intake corresponding to an annual dose.

$$197 \quad CDI(\text{averaged daily intake}) = \frac{C \times CF \times IR \times ED}{BW \times AT} \quad \text{Equation 1}$$

198 The chronic daily intake (CDI) determination was used as a basis for risk assessment calculation
 199 similar to current risk assessment studies (66,68–70) where:

200 CDI is the Chronic (averaged) daily intake over a year (mg/kg/day);

201 C is the breathing zone concentration of a BTEX in (µg/m³) derived from three identical
 202 experiments taken over 3-hour burn cycle;

203 CF is the concentration conversion (mg/ µg= 0.001 or 1 µg) factor;

204 IR is the inhalation rate (default adults 20 m³/day);

205 ED is the exposure duration as in equation 2 (11.5 days);

206 BW is the average body weight (70 kg, 60 kg for male and female adult respectively);

207 AT is the number of days per year.

208 However, default values as contained in Table 1, assume a daily intake of pollutant over a 24-hour
 209 period, is often constant and can be extrapolated over a year. In our study, there was a variation on
 210 exposure duration due to the nature on how households use the technology.

211 In equation 2, we determined a procedure used to estimate exposure duration in a typical winter period
 212 in South Africa. The limitation of this method is that the exposure duration seeks to be confined to coal
 213 combustion period (3 hours), without taking into account exposure resulting from accumulated
 214 concentrations which might take time to vent out from indoor to outdoor. Since, this was a laboratory
 215 study the authors intentionally left out other variables in an ordinary house in informal settlements. Such
 216 variables may include ventilation rate or the building envelope which influences the air ratio taking into
 217 account the exchange from inside to outside. The exposure duration obtained in equation 2 indicates a
 218 daily average exposure, given that exposure involves a 3-hour duration over 92-day period in a year
 219 from this source (to allow for a full season).

$$220 \quad ED = \frac{\text{Actual exposure duration}}{24 \text{ hours}} \times 92 \text{ days}$$

221 Equation 2

222 Where:
223 ED is the exposure duration (days/year);
224 Actual exposure duration is the 3-hour combustion period;
225 24 hours is the total hours in a day; and
226 92 days is the number of exposure days in a year.
227 In equation 1, an average annual chronic daily intake was determined. However, for risk assessment, a
228 cumulative lifetime exposure concentration intake needs to be completed. In equation 3 the average 30
229 years chronic dose (CDI_{30 year}) is calculated using the 30 year residential exposure duration as obtained
230 from USEPA default value

$$231 \text{ CDI(30 years dose)} = \frac{\sum \text{CDI} \times 365 \times \text{YE}}{60/67} \quad \text{Equation 3}$$

232 Where:
233 CDI is the cumulative average 30-year dose (mg/kg/day);
234 CDI is the chronic daily intake (mg/kg);
235 YE is estimated lifetime residential exposure duration which is equivalent to 30 years;
236 365 is the total number of days in a year;
237 60 is the male life expectancy and 67 is the female life expectancy in South Africa.
238

239 Therefore, for risk assessment calculation we need the adjusted lifetime chronic daily intake (CDI_{adj.}),
240 taking in to account the life expectancy for a female and male South African adult resident. In equation
241 4, we calculated the average CDI_{adj.} assuming a lifetime daily dose intake.
242

$$243 \text{ CDI}_{\text{adj.}} = \frac{\text{CDI (30 years average dose)}}{\text{life expectancy in days}} \quad \text{Equation 4}$$

244 We assume that the average chronic daily adjusted dose over a lifetime amongst female and male adults
245 will better simplify risk assessment calculation as in equation 4.
246

247 c) Toxicity assessment and risk characterisation

248 Risk characterisation is the last step in risk assessment which provides information on the hazard status
249 of a contaminant or pollutant (71). For both carcinogenic and non-carcinogenic effects, the use of
250 inhalation Reference Concentration (RfC) assists in determining the health risk associated in exposed
251 population. For carcinogenic pollutants (such as benzene) the use of the slope factor can be used to
252 estimate the relative risk. Furthermore, the use of the inhalation reference concentration was based on
253 toxicological/ occupational epidemiology studies focusing on several health outcomes such as cellular
254 necrosis. In summary, inhalation Reference Concentration (RfC) is an estimated daily human inhalation
255 exposure which is suggested not to cause a health effect in a lifetime. (46,47,72).

256 A lifetime inhalation dose of BTEX was determined based on the absolute lymphocyte count (ALC) at
257 the benchmark concentration adjusted (BMCL) of 8.2 mg/m³. The inhalation benzene lifetime exposure
258 was therefore calculated using the benchmark dose modelling and was found to be 0.03 mg/m³. The 0.03
259 mg/m³ was therefore, described as the RfC for benzene (72). The non-carcinogenic effects of TEX
260 inhalation reference concentration for each pollutant was used to calculate the hazard quotient as in
261 Table 2 (73–75).

262 Since benzene is the only confirmed human carcinogenic (category A) pollutant amongst the BTEX
 263 pollutants, the slope factor was used to calculate the cancer risk. We have adopted the methodology for
 264 calculating the cancer risk using the slope factor from previous similar studies (44–46,72,76). It must be
 265 noted that there is no threshold for carcinogenic compounds. Therefore, the use of reference levels is
 266 used as a guide to probably support a decision. In our study we used both designated cancer severity
 267 indicator of 1 case /10⁴ (1E⁻⁴) and 1/10⁶ (1E⁻⁶) (59,77).

268 Table 2: Benzene slope factor and TEX inhalation reference values

Chemical	Inhalation Reference concentration (RfC)	Inhalation Slope Factor (SF) (mg/kg/day)-1
	(mg/m ³)	
Benzene	0.03	0.0273
Toluene	5	N/A
Ethylbenze ne	1	N/A
O-xylene	0.1	N/A
P-xylene	0.1	N/A

269 For carcinogenic pollutants, it must be noted that there is no safe threshold, therefore risk
 270 characterisation followed was similar to the method described by the US EPA's Risk
 271 Assessment Guidance for Superfund (61); We thus calculated the risk of cancer by using
 272 equation 5 (72).

273 $CR = CDI_{adj} \times SF$ Equation 5

274 Where:

275 SF is the slope factor for carcinogenic pollutant (0.0273);
 276 CR is the carcinogenic risk; and
 277 CDI_{adj} is the cumulative lifetime adjusted dose (equation 4) over an estimated exposure in a lifetime
 278 of 60 or 67 years for male and female adult, respectively.

279 Therefore, Cancer risk > 1E⁻⁶ and 1E⁻⁴ means carcinogenic effects of concern while the cancer risk < 1E⁻⁶
 280 and <1E⁻⁴ means a designated cancer severity indicator.

281 For non-carcinogenic pollutants a hazard quotient (HQ) was used to estimate the potential health risk of
 282 dwellers. Where a HQ value is greater than one, it is regarded as a hazardous exposure; while HQ value
 283 of less than one means there is a low probability of developing associated health effects. In equation 6,
 284 the procedure for calculating HQ is shown.

285 $HQ = CDI_{adj} \cdot ((mg/kg)/day) / (RfC(mg/m^3) \times 20m^3 / (70 kg))$ Equation 6

286 Where:

287 HQ is the hazard quotient;
 288 CDI_{adj} is the cumulative intake dose;
 289 RfC is the reference;
 290 20 m³ is the default value for average adult daily air volume; and

291 70 kg is the average body weight for a male adult while 60 kg will be used for female adult.

292 2.5. *Quality control*

293 All monitoring instruments were maintained and operated, according to the manufacturer's
294 instructions, and returned to the suppliers for factory calibration at prescribed intervals. Before each
295 test, the gas probes were cleaned by means of compressed air, to remove any residue from prior tests,
296 which might negatively affect the next results. All monitoring instruments were zero checked,
297 according to the manufacturer's instructions, before monitoring/ sample collection

298 The GC955 instrument was been tested in with accordance the EMC directive 89/336/EMC, test
299 specification EN 50081-1:1991 and EN 50082-2: 1994. The monitoring instruments were calibrated
300 before use (calibration was done in the range of 0 to 10 ppb). Quality control checks were conducted
301 during and after the monitoring campaign and a correction factor of 2 ppb and 4 ppb for benzene
302 and toluene, respectively were used, to counter systematic under-sampling of the instrument.

303 Background concentrations were accounted for as BTEX from outside the testing facility could
304 possibly infiltrate the testing laboratory and contribute to the final concentration readings. The
305 instrument was run for 30 minutes before the three-hour testing duration and the background
306 concentrations were calculated using equation 7.

307
$$C_{\text{combustion}} = C_{\text{activity}} - C_{\text{without}}$$

308 Equation 7

309 Where:

310 the $C_{\text{combustion}}$ is the final concentration;

311 C_{activity} is the actual sample collected during the BTEX generating activity was taking place +
312 background concentration;

313 C_{without} is the concentration of BTEX obtained in the absence of the activity under investigation.

314
315 In experimental studies the use of equipment which are accurately calibrated is an important quality
316 control feature and it assist in reducing the uncertainty of data set. Trial runs before the actual tests
317 might help in the identification of instruments malfunctioning and detection signal faults.

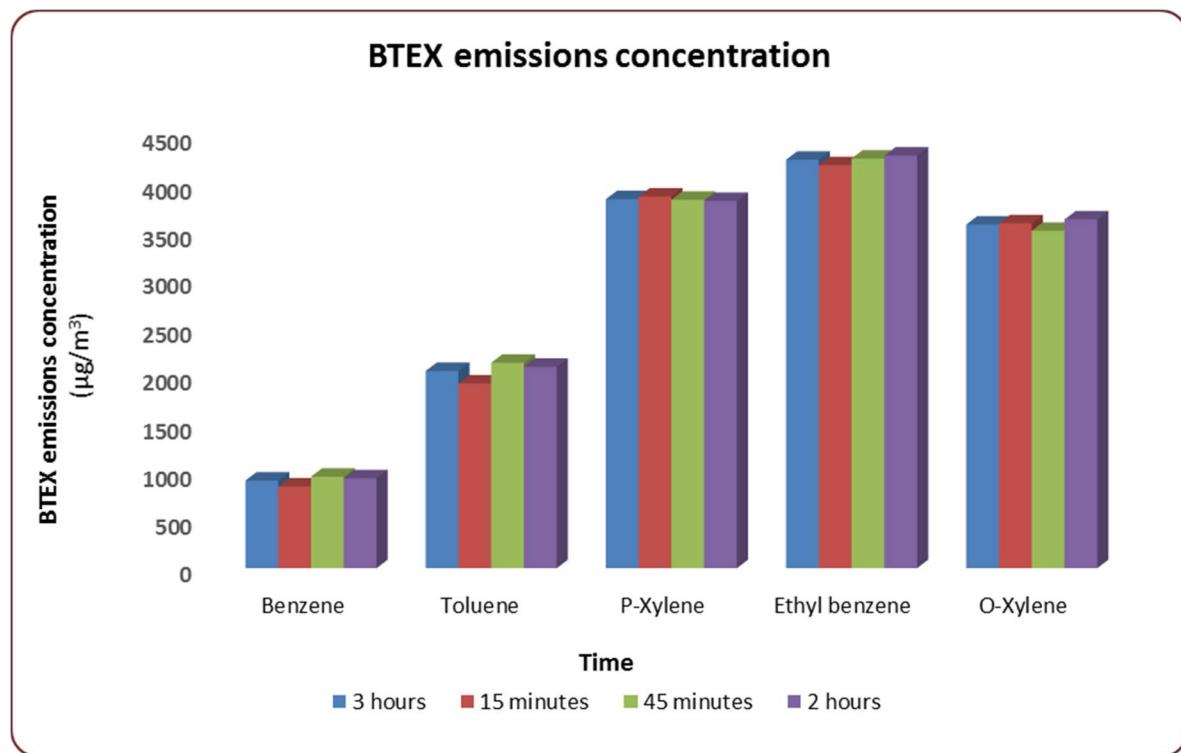
318 3 Results and Discussion

319 3.1. BTEX concentration under laboratory conditions

320 The results from the coal combustion *brazier*; under a laboratory controlled environment are
321 presented herein. In Figure 2, time aggregates concentration for each BTEX compound is presented
322 as an average concentration for the specified time (15, 45 and 120 minutes). Using a 3-hour average
323 concentration Benzene is the lowest emitted VOC, while ethyl benzene was found to be the most
324 emitted pollutant throughout the combustion cycle. From the results, it is shown that the
325 concentration of BTEX are consistent throughout the entire burn cycle of the three-hour period.

326 Benzene and ethyl benzene concentration steadily increases as the combustion process
327 progresses. The minimum concentration as can be depicted from Figure 2, is associated with the first
328 15 minutes of the combustion. Contrary, to benzene and ethyl benzene the concentration of toluene
329 and xylene were highest in the 45 minutes and 120 minutes respectively. The observed BTEX profile
330 reported in our study is similar to the one presented in the study by (29). However, the observed
331 differences may require additional statistical analysis to provide more details on concentration

332 variation at different time intervals. Unfortunately, the differences on BTEX concentration at different
 333 time aggregates was not within the scope of the current project. The implication of this finding
 334 indicates for the first time in South African domestic sector the determination of domestic coal
 335 combustion as might be an important source of BTEX in indoor air spaces.



336

337

Figure 2: Time series BTEX concentration for a 3-hour combustion cycle

338

339

In table 3, BTEX near field room concentrations are presented for replicates three experiments
 340 as averages over a 3-hour burn cycle. Benzene concentration ranged from 857 – 942 µg/m³ with the
 341 mean of 919 µg/m³ over a three-hour burn cycle. The benzene concentration observed in our study
 342 varied from those conducted in India where the concentrations have ranged from 44 – 167 µg/m³ (50).
 343 However, in the latter study, the emissions of benzene were associated with kerosene burning which
 344 is different from our present study. Lower values of indoor benzene concentrations were also
 345 reported in several other studies where the concentration ranged from 0.7 – 7.2 µg/m³ (78–80). In
 346 Hong Kong Special Administrative Region of China similar low benzene indoor level were reported
 347 which was mainly associated with vehicular emissions at 0.5 – 4.4 µg/m³ (30,81). However, studies
 348 conducted in petrol refineries reported concentrations for benzene varied between 12 – 17 000 µg/m³,
 349 with the highest exposure concentrations being mainly from refinery workers working in indoor
 350 environment (82–84).

351

352

Toluene, ethylbenzene and xylenes (TEX) results are comparable with several studies conducted
 353 elsewhere; however, most of this studies were conducted in occupational settings (34,58,69). The
 354 ethylbenzene concentration measured in our study was 2 folds higher than the concentration
 355 reported by (80). Toluene, ethyl benzene and xylenes also present several health effects even at lower
 356 concentrations (85–87).

357

Table 3: Time weighted average BTEX room concentrations

Duration	Benzene	Toluene	P-Xylene	Ethyl benzene	O-Xylene
	($\mu\text{g}/\text{m}^3$)				
	n=3	n=3	n=3	n=3	n=3
15 minutes	857 ± 32.40	1922 ± 127.5	3864 ± 48.33	4189 ± 87.11	3589 ± 48.74
45 minutes	958 ± 5.73	2137 ± 27.04	3831 ± 15.12	4257 ± 31.26	3510 ± 13.66
2 hours	942 ± 13.36	2095 ± 36.59	3819 ± 9.60	4288 ± 91.51	3628 ± 9.42
Average conc.	919 ± 44	2051 ± 93	3838 ± 19.04	4245 ± 41.13	3576 ± 49

358

359 In table 4 we investigated a percentage contribution of individual BTEX compound. From the
 360 total BTEX indoor air concentration benzene was found to have contributed less at 6% while ethyl
 361 benzene was the highest at 29%. Fairly, comparable percentage contribution between P- xylene and
 362 O-xylene were observed at 26 and 25, respectively. However, despite benzene being the least
 363 quantified VOC it is worrying given its hazardous nature to human health. Toluene was found to be
 364 the lowest contributed VOC amongst the TEX at 14%.

365 Table 4: Percentage contribution of each BTEX pollutant averaged over a 3-hour burn cycle

Pollutant	Ignition	Conc.	Contr.
	Stove vent.	($\mu\text{g}/\text{m}^3$) n=3	%
Benzene	TLUD	919 ± 44	6
	HIGH		
Toluene	TLUD	2051 ± 93	14
	HIGH		
P-Xylene	TLUD	3838 ± 19.04	26
	HIGH		
Ethyl benzene	TLUD	4245 ± 41.13	29
	HIGH		
O-Xylene	TLUD	3576 ± 49	25

366

367 3.2. *Potential Health Risk Analysis of BTEX*

368 Results presented in tables 5 and 6 depict carcinogenic and non-carcinogenic risks of BTEX
 369 exposure from domestic coal burning for adult female and males, respectively. The determination of
 370 risk associated with BTEX were achieved using the cancer risk for the carcinogenic compound
 371 (benzene), while non-carcinogenic effects of TEX were determined by calculating the hazard quotient
 372 as shown in equation 5 and equation 6, respectively. The cancer risk for adult female and male were

373 determined 1.2×10^{-4} and 1.1×10^{-4} respectively. The cancer risk for woman was found to be higher than
374 that of males. This finding suggest that women will be more vulnerable than men even though the
375 exposure concentration is the same. As shown in table 5, the cancer risk for women suggest that 120
376 people will be at risk of cancer per 10^6 of the exposed population. Furthermore, in table 6, results
377 show that 110 men per million exposed will be at risk of carcinogenic health effects. In both exposure
378 scenarios (male and female) the cancer risk was found to be higher than the acceptable risk levels of
379 10^{-6} and 10^{-4} .
380



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Table 5: Carcinogenic and non-carcinogenic risk for adult female

Pollutant	Average concentration		CDI _{year}	CDI _{30 year}	CDI _{adj.}	CR	HQ	CR/ 1E ⁶	CR/ 1E ⁴
	μg/m ³	mg/kg/day							
Benzene	919	0,0097	1,06E+02	4,32E-03	1,2E-04	N/A	120	1	
Toluene	2051	0,0215	2,36E+02	9,64E-03	N/A	0,001	n/a	n/a	
P-Xylene	3838	0,0403	4,41E+02	1,73E-02	N/A	0,050	n/a	n/a	
Ethyl benzene	4245	0,0446	4,88E+02	2,00E-02	N/A	0,006	n/a	n/a	
O-Xylene	3576	0,0376	4,11E+02	1,68E-02	N/A	0,049	n/a	n/a	

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Table 6: Carcinogenic and non-carcinogenic risk for adult male

Pollutant	Average concentration		CDI _{year}	CDI _{30 year}	CDI _{adj.}	CR	HQ	CR/ 1E ⁶	CR/ 1E ⁴
	μg/m ³	mg/kg/day							
Benzene	919	0,0083	9,06E+01	3,70E-03	1,1E-04	N/A	110	1	
Toluene	2051	0,0185	2,02E+02	8,27E-03	N/A	<0,001	n/a	n/a	
P-Xylene	3838	0,0345	3,78E+02	1,55E-02	N/A	0,045	n/a	n/a	
Ethyl benzene	4245	0,0382	4,18E+02	1,71E-02	N/A	0,005	n/a	n/a	
O-Xylene	3576	0,0322	3,52E+02	1,44E-02	N/A	0,042	n/a	n/a	

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387 We presented the cancer risk for adult females and males where reference was given to the
388 female/ male body weight (default value from US EPA, 2010) and life expectancy (64) as in table 1.
389 The cancer risk in adult female and male were found to be 120 and 110 folds higher than the
390 designated cancer severity indicator of $1E^{-6}$, respectively. These findings confirm those reported by
391 WHO (WHO.int: Media Centre fact sheets Internet Geneva, Switzerland: World Health Organization;
392 updated 8 May 2018; cited 9 November 2018. Available from:
393 <http://www.who.int/mediacentre/factsheets/fs292/en/>) and the World Bank (Household Cookstoves,
394 Environment, Health, and Climate Change THE WORLD BANK A NEW LOOK AT AN OLD
395 PROBLEM (2011) and the International Bank for
396 Reconstruction and Development. <http://documents.worldbank.org/curated/en/732691468177236006/pdf/632170WP0House00Box0361508B0PUBLIC0.pdf>) where 17% of premature lung cancer deaths
397 in adults were found to be attributable to exposure to carcinogens from household air pollution
398 caused by cooking with kerosene or solid fuels such as wood, charcoal or coal and the risk for women
399 was higher, due to their role in food preparation.
400

401
402 For non-carcinogenic health effects, we used the hazard quotient to determine the risk. A hazard
403 quotient of greater than 1, was used as a reference value; whereby, a value greater than one indicated
404 higher probability of contracting a related health effect. For both adult male and female, the hazard
405 quotient was found to be below 1 for the TEX's. Toluene indicated the lowest hazard quotient, whilst
406 ethylbenzene was found to potentially shown to have the highest hazard quotient, at a value of 0.05.
407 The results presented in our study indicate that there is a lower probability of non-carcinogenic health
408 effects as a result of exposure to domestic coal combustion technology as described in this study.
409

410 Despite, the non-carcinogenic effects rated hazard quotient of less than one, this might change
411 significantly especially in households were coal burning devices are used indoors for longer
412 durations. This includes overstretched winter periods and prolonged exposure durations based on
413 activity. For instance, in some households especially during winter this type of technology can be
414 used to warm for the entire day time (06:00 am to 18:00 pm) and some part of the night period (18:00
415 pm and 21:00 pm). This implies that exposure to TEX from this combustion activity may significantly
416 vary from one household to the other depending on the use case scenarios.

417 4 Study limitations

418 In the absence of field exposure data, results presented herein had several limitations.

419 Individual information used for risk assessment are average person default values. As known
420 that there is no an average person in the world, this might significantly affect the accuracy of risk
421 determination. Individual varies based on the biological make-up which might affect parameters
422 such as breathing rate and moreover the exposure scenario. Furthermore, using average values
423 overlook the issue of individual susceptibility which might affect the risk score. In addition, we have
424 used a room concentration to assess the risk, assuming that a three-hour exposure at near field
425 breathing zone is the average exposure duration. The influence of pollutants leakages also was not
426 addressed, where there might be loss due to leakages. The BTEX concentration reported in this study
427 was obtained from a laboratory environment which might vary from field concentrations.

428 Despite, these limitations this study has shown that exposure to domestic coal combustion
429 pollutants may lead to risk of carcinogenic effect while the non-carcinogenic effects were found to be
430 unlikely. However, it must be noted that the results presented herein was based on laboratory
431 experiment study where several variables which might influence stove to fuel performance were
432 controlled. Such performance determinants includes stove operational method, fire ignition method,
433 coal particle size, moisture content and coal grade (13,53,88–90)

434 **5 Conclusion**

435 The study attempted to quantify BTEX concentration from domestic coal combustion in a
436 brazier, simulating its use in the South African informal settlements. Based on the results presented
437 in this study, it can be concluded that domestic coal burning might be significant source of BTEX in
438 indoor spaces. The results showed a constant concentration of BTEX throughout the combustion cycle
439 of 3-hours.

440 The study further, attempted to utilise breathing zone near field BTEX concentration as averaged
441 over a 3- hour burning cycle in adult female and male to estimate carcinogenic and non-carcinogenic
442 health effects, simulating practices in informal settlements. The cancer risks were found to be 110 to
443 120 folds higher than the designated cancer severity indicator of $1E^{-6}$.

444

445 The health risk assessment of TEX, through calculating the hazard quotient, was below the
446 reference value of 1; indicating potentially low exposure to these pollutants and possibly a reduced
447 risk of associated health effects. Lessons drawn from this laboratory experimental study indicate the
448 need for further studies in this field in order to have a better understanding on exposure scenarios
449 and better inform risk characterisation from this source. The study presented the first risk assessment
450 arising from domestic coal burning activities in a laboratory environment while mimicking field
451 practices relevant to South African situation.

452

453 Notably, risk assessment is a comprehensive and iterative process to assess the relative risk for
454 several exposure scenarios. It must be understood that risk assessment has several uncertainties, the
455 accuracy of the results depends on the correct risk identification and use of accurate exposure
456 information. Despite all uncertainties, in our studies we attempted to ensure that exposure scenarios
457 are accurately defined which might be used in future for future studies.

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