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Burn to kill: Wood ash a silent killer in Africa

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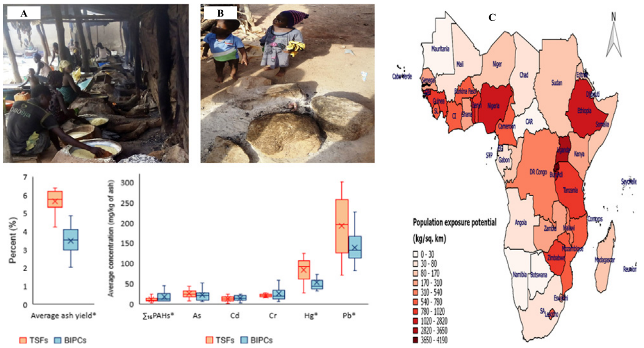
HIGHLIGHTS

- Wood ash from the traditional cook-stoves contains toxic levels of metals and PAHs.
- TSFs generate higher levels of ash or metals, but lesser PAHs, than BIPCs
- The high end dose of Pb or PAH surpass the limit recognized as safe for children.
- The potential for exposure in Africa is: Rwanda>Burundi>Uganda>Nigeria> elsewhere

GRAPHICAL ABSTRACT



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ABSTRACT

Aside the emissions, burning of wood in traditional cookstoves (TCs) also generates substantial amount of ash containing hazardous pollutants such as polycyclic aromatic hydrocarbons (PAHs) and toxic metals. But, their concentrations in the ash, particularly in Africa where over 70% of the population utilize TCs, remain unknown. Here, we determined concentrations of sixteen PAHs and eleven heavy metals in ashes from twelve different African TCs, comprising six three-stone fires (TSFs) and six built-in-place cookstoves (BIPCs), burning common African wood species under real world situation. For each TC, ash samples were collected for six consecutive days (Monday–Saturday), and a total of seventy-two daily samples were collected from January–June 2019. Ash yields were measured gravimetrically, and concentrations of the pollutants were determined following standard analytical protocols. The results were used alongside secondary data (annual fuelwood consumption, African fuelwood densities, population proportion using fuelwood and surface human population density) to estimate annual tonnage, exposure potential and risk to health in Africa, using Monte Carlo simulation technique. The ash yields from all TCs studied exceeded 1% on dry weight basis, indicating that ash is a major waste by-product of wood combustion in TCs. TSFs produced more ash ($5.7 \pm 0.7\%$) than BIPCs ($3.4 \pm 1.0\%$). Concentrations of As, Cd, Hg and Pb in ashes were significantly higher ($\alpha = 0.05$) for TSFs than BIPCs. In contrast, concentrations of PAHs were higher in ashes from BIPCs than TSFs. Assuming ash consumption rates range from 250 to

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500 mg/day for young children weighing 10 to 30 kg, the upper dose (μg/kg-day) of Pb (0.2–3.9) or Σ_{16}PAHs (0.02–0.34), for instance, surpasses the 0.3 μg/kg-day of Pb or PAH recognized as causing adverse effects in children, indicating a concern. The top five countries with the highest annual tonnage or exposure potential to toxic pollutants are Nigeria>Ethiopia>DR-Congo>Tanzania>Uganda, or Rwanda>Burundi>Uganda>Nigeria>Guinea-Bissau, respectively.

1. Introduction

Globally, about 2.6 billion people burn wood (firewood or charcoal) in inefficient traditional cookstoves (Bonjour et al., 2013; UNDP/WHO, 2009), releasing emissions that affect human health and global climate (Champion et al., 2020; Etchie et al., 2018a; Kar et al., 2012; Kaur-Sidhua et al., 2020; Lea-Langton et al., 2019; Smith et al., 2014; Zhang et al., 2014). However, besides the emissions, substantial amount of ash is also produced. Wood ash may contain highly variable concentrations of hazardous constituents, depending on the combustion technology, the operating conditions and wood composition. For example, the reported concentrations of arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb) and sum of sixteen polycyclic aromatic hydrocarbons (Σ_{16}PAHs) in wood ashes from different controlled combustion studies (using ovens, furnaces, incinerators or thermal power plants) ranged from 0.2–60 mg/kg, <0.02–203 mg/kg, 2.6–1040 mg/kg, 0.02–1.7 mg/kg, 0.03–13,700 mg/kg and 0.02–193 mg/kg respectively; greatly exceeded regulatory thresholds in most cases (Dahl et al., 2010; Maschowski et al., 2016; Masto et al., 2015; Pitman, 2006; Reimann et al., 2008; Vassilev et al., 2013). To our knowledge, very limited information of this kind is available for traditional cookstoves, globally (Li et al., 2017; Li et al., 2018), and none so far for Africa. Yet, over 70% of the population in sub-Saharan Africa (hereinafter, Africa), burn wood for cooking using traditional cookstoves (UNDP/WHO, 2009). Therefore, it is still unknown what level of risk to health is associated with exposure to wood ash from African traditional cookstoves.

Apart from the depletion of forest floras due to high reliance on wood for cooking in Africa, the methods of disposing the generated ash give cause for concern. The ash is often discarded on surface soil close to where people live, without processing, or dumped on farmlands where crops are grown. Such poor management of biomass ash was also reported in China (Li et al., 2017). Hazardous components in the ash may be re-suspended into air, concentrate, polluting residential and arable soils, leach into drinking water resources and bioaccumulate along the food chain leading to humans (Adewuyi et al., 2014; Etchie et al., 2012; Li et al., 2017; Mathee et al., 2018; Nieuwoudt et al., 2011).

Children who crawl, play, eat and sleep on bare floor laden with ash may be disproportionately affected. They are additionally exposed through dermal contact with the polluted soil and incidental ingestion of the soil (Plumlee et al., 2013). Furthermore, with limited access to running water in Africa and due to low literacy level, children often eat food using unwashed hands. Nriagu (1992) reported that African children ingest at least 250 mg of soil per day. For extremely dusty African localities, the soil ingestion rate may reach 500 mg per day (Plumlee et al., 2013). Such levels of consumption of soil may lead to very high systemic doses of toxic metals and PAHs in children, with the potential for serious health effects. For example, a study that assessed blood lead levels (BLLs) of children in semi-urban areas in South Africa found significantly higher BLLs among young children 3–5 years old (range 6.9–35.8 μg/dL) compared with their older siblings or neighbors that were aged 8–10 years (range 4.3–11.6 μg/dL) (Nriagu et al., 1997). The observed difference in BLLs between the two age categories was attributed to younger children playing dirty on polluted soils. A more recent study revealed BLLs and blood Hg concentrations ranging from 37 to 445 μg/dL and 0.3 to 6.6 μg/L, respectively, for eighty-six under five Nigerian children (Dooyema et al., 2012), indicating high intake of the metals. Documented adverse health effects linked to high doses of toxic metals or PAHs in children include childhood mortality, permanent cognitive and systemic disability, and reduced longevity (Etchie et al., 2013, 2014; Greig et al., 2014; Horiguchi et al., 2010; Lo et al., 2012; Tellez-Plaza et al., 2013; USEPA, 2017).

In this study, we determined, for the very first time, the concentrations of toxic metals and priority PAHs in wood ashes from different African traditional cookstoves, operated under real world situation, and estimated the potential for exposure and risk to human health in Africa.

2. Materials and methods

2.1. Description of the cookstoves and fuelwoods

African traditional cookstoves burning wood as fuel consist of two major designs: the three-stone fires (TSFs) and the built-in-place cookstoves (BIPCs). TSFs are used typically by households for small-scale cooking, while BIPCs are primarily used for commercial or large-scale cooking (Fig. 1). Kshirsagar and Kalamkar (2014) described the BIPC as a semi-permanent mud structure that encloses fire from at least three directions other than the ground itself, and typically has one opening for addition of fuelwood. BIPCs may however have some modifications in size or construction material e.g. may be metallic, cement, ceramic or hybrid. In Africa, BIPCs are popularly called *mogogo*, *jiko*, *kilakala* or *aro amo*, whereas in India (specifically in north India), they are known as *chullah*, *angithi* or *haroo*. Detailed description of both traditional cookstove types has been documented (Johnson and Bryden, 2012; Kshirsagar and Kalamkar, 2014).

Here, we studied twelve traditional cookstoves comprising six each for TSF or BIPC, in households and factories selected randomly in a rural locality in Omu-Aran, Central Nigeria. All six BIPCs were constructed with mud materials, while the TSFs were made of cement and sand. Both cookstove types burn mixed fuelwoods for cooking. BIPCs usually burn woody stems of trees sourced from the forest, while TSFs burn branches, twigs and barks of the trees, as well as locally grown shrubs and cut sizes of waste woods from construction and demolition sites as fuels. Common tree species used as fuelwoods in this locality include: *Hymenocardia acida*, *Pseudocedrela kotschyi*, *Terminalia glaucescens*, *Parkia biglobosa*, *Funtumia Africana*, *Citrus paradise*, *Daniellia oliveri*, *Vitellaria Paradoxa*, *Anogeissus leiocarpa*, *Trichilia emetic*, *Pterocarpus erinaceus*, *Gmelina arborea*, and *Khaya ivorensis*.

2.2. Assessment of wood ash constituents from African traditional cookstoves

We measured the quantity (in kg) of wood burnt in the twelve cookstoves per day, and the amount (in kg) of ash generated, noting the type or part of wood used. Prior to use, the cookstoves were properly cleaned to remove debris of wood, ash or dirt from the previous day's cooking. At the end of the day's cooking, the bottom residues were collected and allowed to cool to ambient temperature. Any leftover wood after cooking was subtracted from the initial amount apportioned for that day by the household or factory. Reusable residue (i.e. charcoal) was removed and ash was weighed onsite. We considered ash to be the non-reusable bottom residue that is discarded as waste. It consists of the

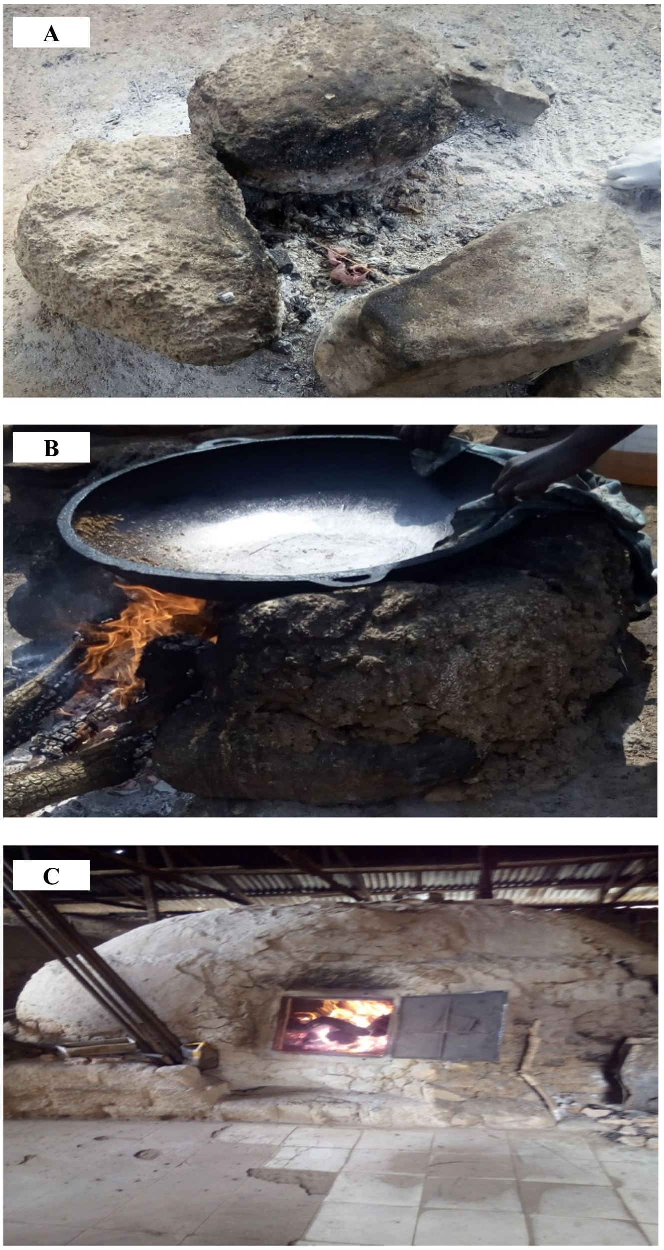

Fig. 1. African traditional woodstove designs: three-stone design for residential cooking (A); mud-type designs for commercial cooking (B) and bakery (C).

white powdery residue and tiny black particles of charcoal left after burning of wood. The measurements were performed for six consecutive days (Monday to Saturday), and a total of seventy-two daily measurements were taken between January and June 2019. To adjust for the wood dry weight, daily wood samples (20 g) from each cookstove were collected in ziploc bags and transported immediately to the laboratory. In the laboratory, the samples were crushed and homogenized, and approximately 10 g of the homogenized samples were oven dried at 105 °C for 6 h, or to a constant weight. The oven-dried samples were allowed to cool in desiccators and reweighed. Two field blank experiments were conducted for each cookstove to account for external contamination. Detailed information is presented in the Supplemental materials.

Wood ash samples collected for PAHs determination were wrapped in methanol pre-cleaned aluminum foil, while those for heavy metals were collected in pre-cleaned polythene bags. The samples were labeled and placed in an ice chest at temperature below 4 °C and transported to the laboratory. As soon the samples got to the laboratory, they were immediately placed in a freezer while awaiting analysis.

The concentrations of sixteen PAHs (naphthalene, acenapthylene, acenapthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(*c*)anthracene, chrysene, benzo(*a*)anthracene, benzo(*e*) pyrene, benzo(*k*)fluoranthene, benzo(*j*)fluoranthene, benzo(*a*)pyrene and dibenz(*a*,*h*)anthracene) were determined by an external calibration based on method 610 (USEPA, 1984) and cleanup method 3630C (U.S.E.P.A., United States Environmental Protection Agency, 1996a), using gas chromatography, flame ionization detector (GC-FID, Agilent 7890B). Details of the extraction, cleanup and recovery procedures are available in the Supplemental materials.

The concentrations of ten heavy metals (As, Cd, Cr, Pb, aluminum (Al), cobalt (Co), copper (Cu), iron (Fe), nickel (Ni) and zinc (Zn)) were determined using microwave plasma atomic emission spectrometry (Agilent MP-AES 4200) after samples digestion according to method 3050B (U.S.E.P.A., United States Environmental Protection Agency, 1996b). Hg concentrations were determined directly in the ash samples according to method 7473 (USEPA, 2007) using direct Hg analyzer (DMA-80 Milestone Inc.). Details of the heavy metals analyses are available in the Supplemental materials.

2.3. Statistical tests

We used one-way multivariate analysis of variance (MANOVA, $\alpha = 0.05$) to examine whether there is a significant difference in the percent ash yield and concentrations of PAHs and heavy metals between TSFs and BIPCs, using IBM SPSS 20. The multivariate tests used were Pillai's Trace, Wilk's Lambda, Hotelling's Trace and Roy's Largest Root. We used linearly independent pairwise comparisons to compare the mean concentration of individual constituent between TSFs and BIPCs.

2.4. Estimating the potential for exposure across Africa

The potential for exposure (E_i) to toxic pollutants in wood ash was estimated as:

$$E_i = Q_p \times P_d \times P_p \tag{1}$$

where: Q_p is per capita annual production of wood ash from traditional cookstoves in a country; P_d is surface gridded (version 4) human population density (persons/km^2) in the country for year 2020 (CIESIN, 2020); P_p is proportion of people cooking with wood in the country.

Q_p and P_p were calculated for each country using the following algorithms:

$$Q_p = \frac{A \times Q_w}{100 \times P} \tag{2}$$

$$P_p = F_S \times 0.69 \tag{3}$$

where: A is Monte Carlo simulated percent ash yield of wood from the traditional cookstoves; Q_w is simulated annual quantity of wood consumed by households in the country; P is total population of people in the country in 2020 (UNDESA, 2019); F_S is fraction of the population in the country using solid fuel (WHO, 2015); 0.69 is fraction of the population in sub-Saharan African region cooking with wood (UNDP/WHO, 2009).

For each country the value of Q_w (measured in kg) was calculated from three-year (2014, 2015 and 2016) moving average value of the volume of wood consumed for cooking in that country (V_w) using Eq. (4).

$$Q_w = V_w \times D_w \tag{4}$$

where: D_w is Monte Carlo simulated densities of African tree species. The average, minimum and maximum values of D_w used for the simulations were obtained from the United Nations Food and Agricultural

Organization (FAO, 1997). Details of the estimation, including the uncertainty and variability analyses are documented in the Supplemental materials.

2.5. Assessing the risk to health of PAHs and heavy metals from wood ash ingestion

We assessed the risk to human health of PAHs and toxic metals (Pb, Hg and As), particularly of young children who suffer the most immediate and severe consequence of wood ash. We calculated Pb, Hg, As and PAHs uptake levels over the range of concentrations detected in the wood ashes. The following algorithms (Drexler and Brattin, 2007; Plumlee et al., 2013) were used for the estimation:

$$B = 0.5 \times [(0.878 \times G) - 0.028] \quad (5)$$

$$D_m = B \times D_s \times {}^{1}/_{1000} \quad (6)$$

where: B is bioavailability of metal or PAH (mg/kg); G is maximum gastric bioaccessible metal concentration (mg/kg); D_m is daily uptake of metal or PAH (μg/day); D_s is daily wood ash consumption rates of 250 and 500 mg/day (Nriagu, 1992; Plumlee et al., 2013): a range typical for children residing in unpaved and extremely dusty environments in Africa.

The maximum percentage of gastric bioaccessibility of Pb, Hg and As is 66%, 0.9% and 2.1%, respectively (Plumlee et al., 2013). For PAHs, we converted individual PAH concentrations into benzo[*a*]pyrene equivalence (B[*a*]P_{eq}) using relative potency factor for carcinogenicity (Etchie et al., 2019; USEPA, 2010), and assumed 100% gastrointestinal absorption of PAH (MDH, 2016).

3. Results and discussion

3.1. Ash yield of woods burnt in African traditional cookstoves

The percent ash yields of woods burnt in TSFs and BIPCs under real world situation are shown in Table 1. For comparison, we also included literature information on ash content of woods combusted under controlled conditions in Table 1. The field blank experiments revealed that the mean particle deposition on the ashes from external sources was 0.02 ± 0.04% and 0.16 ± 0.06%, on dry weight basis, for the BIPCs and TSFs, respectively.

The ash yields from all traditional cookstoves studied exceeded 1% on dry weight basis. This suggests that ash is a major waste by-product of wood combustion in African traditional cookstoves. However, the average ash yield for TSFs (5.66 ± 0.73%) is substantially greater compared with BIPCs (3.41 ± 0.99%). The hazardous components (Σ_{16}PAHs and toxic metals) in the ash samples also varied according to the cookstove-type (Fig. 2). Multivariate tests (Pillai's Trace, Wilk's Lambda, Hotelling's Trace and Roy's Largest) revealed a significant difference ($\alpha = 0.05$) in both the ash yields and ash components between TSFs and BIPCs (see Supplemental material, Table S1). Linearly independent pairwise comparisons showed a significant difference ($\alpha = 0.05$) in ash yields between the cookstove types (see Supplemental material, Table S2), indicating that BIPCs burn more efficiently, producing significantly lesser ash compared with TSFs.

The studied BIPCs and TSFs typically burned different types/parts of wood, over different daily burning time. The BIPCs were fed mostly with stems of woody trees sourced from the forest, whereas the TSFs burned cut pieces of branches, twigs and barks of the trees, as well as locally grown shrubs and waste woods from construction/demolition sites. The average daily burning time for the BIPCs ranged between 6 and 10 h, whereas that of TSFs ranged between 4 and 5 h. The difference in operating conditions, specifically the burning time and burning temperature, may be key factors responsible for the observed difference in ash yield between the two types of cookstove. Indeed, longer length of cooking results in longer residence time of the ash in the flame leading to smaller amount of unburn residues or ash. Also, BIPCs have just one opening by the side for addition of fuelwood, thus conserve more heat leading to higher burn temperature than TSF, which has three of such openings and loses heat more rapidly. Pitman (2006) reported that by increasing the burn temperature from 650 °C to 1300 °C, ash yields of different wood species reduced by 23–48%. Similarly, Vassilev et al. (2013) found up to 70% reduction in ash yield moving from low to high burn temperatures.

The type/part of wood burn by the BIPCs and TSFs may be an additional reason for the difference in ash yield. Waste woods are known to produce more ash compared with forest woods due to increased contamination of the former (Cuiping et al., 2004; Vassilev et al., 2010). Wood bark, leaves and twigs were reported to generate up to 10 times more ashes than woody stems (Meszaros et al., 2004; Obernberger et al., 2006; Werkelin et al., 2005).

The average wood ash yield from the African BIPCs of 3.41 ± 0.99% is comparable to firewood-walnut ash yield from Chinese BIPCs, which was 3.43 ± 0.36% (Li et al., 2017). However, the average ash yield from TSFs, but not BIPCs, exceeded the range of values reported for controlled wood combustion in the literature (Table 1). But, lower than the 7.9% ash yield reported for wheat straw combusted at 575 °C in Turkey (Bakisgan et al., 2009).

3.2. Concentrations of metals and PAHs in wood ashes from African traditional cookstoves

The concentrations of eleven heavy metals and sixteen PAHs (Σ_{16}PAHs) in wood ashes from the traditional cookstoves are shown in Table 2 and Fig. 2, respectively. The average concentrations of

Table 1
The range (mean ± standard deviation) of ash yield (%) of biomass fuels (dry weight basis) burnt in African traditional woodstoves and laboratory controlled conditions.

Ash yield (%)	Number of fuel species investigated	Combustion technology	Reference
3.39–6.40 (5.66 ± 0.73)	Not differentiated – mixed species/parts of wood	African traditional cookstoves: TSFs	Present study
2.04–4.85 (3.41 ± 0.99)	Not differentiated – mixed species/parts of wood	African traditional cookstoves: BIPCs	Present study
3.43 ± 0.36–13.6 ± 1.9	7 biomass types (firewood-walnut and crop straws: millet, sorghum, sesame, corn, cotton and soybean)	Chinese traditional cookstoves: BIPCs (Zaotai)	Li et al. (2017)
0.1–54	532 varieties of biomass type	Not specified	Vassilev et al. (2017)
0.75–3.78	8 African wood species	Not specified	Johnson and Bryden (2012)
1.72–5.49	15 African wood species	Furnace (at 600 °C, 45 min)	Abbot et al. (1997)
0.07–4.54	28 African wood species	Not specified	Torelli et al. (2003)
0.34–2.79	5 African wood species	Furnace (at 575 °C, 3 h)	Munalula and Meincken (2009)
0.61–5.04	6 African wood species	Furnace (at 600 °C, 4 h)	Mitchual et al. (2014)
0.80–1.31	European beechwood chips*	Electric oven (500 °C – 1300 °C, 1–2 h)	Vassilev et al. (2013)
0.3–5	Different parts of coniferous and deciduous wood and short coppice willow	Furnace (at 550 °C)	Obernberger et al. (2006)

TSFs: three-stone fires; BIPCs: built-in-place cookstoves.

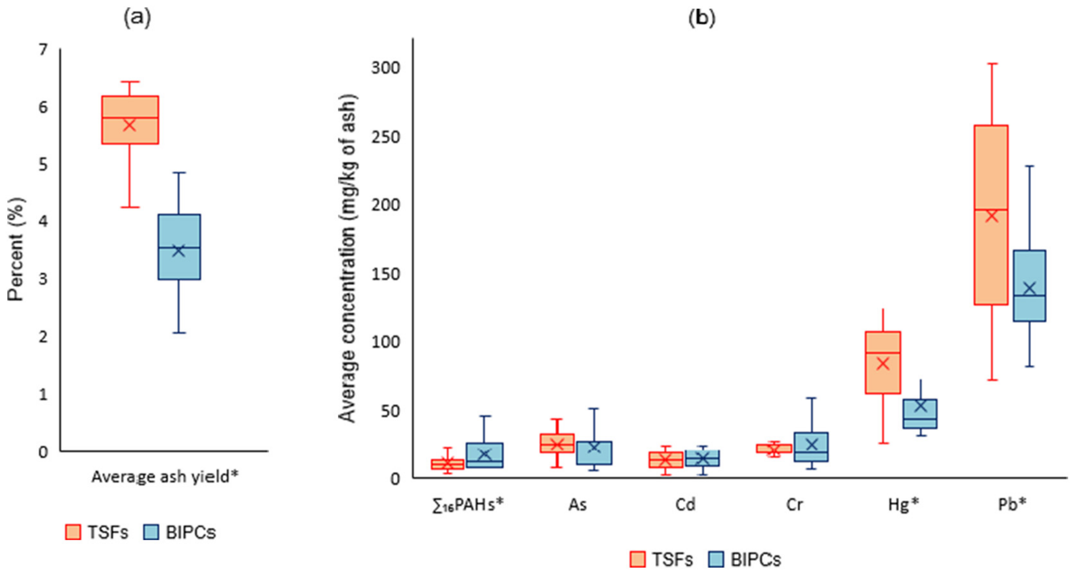

Fig. 2. Percent ash yield (a) and ash components, in mg/kg of ash (b), from three stone fires (TSFs) and built-in-place cookstoves (BIPCs). *Statistically significant difference at $p < 0.05$; the box indicates the upper and lower quartile, while the whiskers show variability outside the quartiles; 'x' indicates mean value while the line drawn across each box shows the median.

individual PAHs are available in the Supplemental material (Table S3). For comparison, we also included literature information on biomass ashes from controlled combustion systems in Table 2 and Supplemental material Table S4. Among the constituents investigated, Al and Fe were the major components (>1%) in the ashes from both types of cookstoves. The other constituents (As, Cd, Cr, Co, Cu, Hg, Ni, Pb, Zn and Σ_{16}PAHs) were all at trace level (<0.1%) (see Supplemental material Table S5).

The average concentrations of the components in the ashes follow this order of decreasing magnitude: Al > Fe > Pb > Zn > Hg > Cu > As > Cr > Co > Cd > Σ_{16}PAHs > Ni for TSFs, and Al > Fe > Pb > Zn > Hg > Cu > Cr > As > Co > Σ_{16}PAHs > Cd > Ni for BIPCs. Both cookstove-types have similar distribution of metals in their ashes, suggesting that the soils where the trees were grown have similar metal profile. The concentration of a metal in ash would ultimately depend on its level in the soil where the wood was grown and the wood species (Pastircakova, 2004). Surprisingly, the average concentration of Pb exceeded that of Zn or Cu in ashes from both cookstove-type. The average Hg concentration also exceeded that of Cu or Cr.

Our patterns of metal distribution in wood ashes from the traditional cookstoves contrast those of previous studies, which have consistently found lower concentrations of Pb or Hg compared with Zn or Cu in wood ashes from controlled combustion systems (Table 2). For example, Masto et al. (2015) found Fe > Cu > Zn > Ni > Cr > Cd > Co > Σ_{16}PAHs > Pb > As in ashes of four thermal power plants burning biomass at 850 °C in India. Bakisgan et al. (2009) reported Fe > Zn > Cu > Ni > Cr > Pb > Co in ashes of Turkish wheat straw, olive bagasse and hazelnut shells, burnt at 575 °C. Maschowski et al. (2016) reported Zn > Cu > Ni > Pb > As > Cd for ashes of eight African wood species burnt in open fireplace. A few other studies that included Al in their investigations reported this order of metal concentrations in wood or mustard stalk ashes: Al > Fe > Zn > Cu > Pb > As ≥ Hg (Freire et al., 2015; Demeyer et al., 2001; Obernberger et al., 2006; Singh et al., 2011). In all these studies, the concentrations of Pb in the ashes were consistently lower than those of Zn or Cu. However, a study in Norway reported a higher average concentration of Pb compared with Cu in wood ashes (Reimann et al., 2008). The order of metal concentration was Fe > Zn > Pb > Cu > Cr > Cd > Ni > As > Hg.

It appears that African soils have high baseline levels of Pb. A systematic review of toxic metal pollution in Africa, conducted as far back as 1991, found Pb concentration in African soils and dusts ranging from 50 to 300 mg/kg (Nriagu, 1992). The reported range of soil Pb levels in 1991 is comparable with our wood ash values for TSFs or BIPCs, which ranged from 89–269 mg/kg or 97–210 mg/kg, respectively (Table 2). Furthermore, top soils from farmlands, uncultivated lands, village square, and ore mining and processing sites in five villages in Northern Nigeria had Pb concentrations that ranged from 17 to 4150 mg/kg (Uriah et al., 2013). Hg concentrations in the soils ranged from 3 to 13 mg/kg (Uriah et al., 2013). The average metal concentration in the top soils in the villages followed this pattern: Pb > Zn > As > Hg > Cd (Uriah et al., 2013). Furthermore, even though Pb pollution is not commonly associated with gold mining (Lo et al., 2012), surface soils of 116 residential compounds in two artisanal gold mining villages in Nigeria had Pb and Hg concentrations reaching 100,000 mg/kg and 4600 mg/kg, respectively (Dooyema et al., 2012; Plumlee et al., 2013). The concentrations of Pb in samples of ore collected from the two villages ranged from 330 to 175,000 mg/kg (Dooyema et al., 2012), suggesting high background Pb concentrations in Nigerian soils.

Pb uptake levels by plants depend primarily on the bioavailable Pb concentration in the soil as well as the specific plant species. Some plant species can accumulate Pb from contaminated soil (Tangahu et al., 2011). Likewise, some specific plant species hyper-accumulates other toxic metals such as Hg, As and Cd. Such plant species have been suggested for phytoremediation of contaminated soils (Mertens et al., 2006). Thus, when such woods are burnt as fuels they tend to produce ash with very high concentrations of toxic metals. For instance, Pb concentration in Norwegian wood ash samples reached 13,700 mg/kg (Reimann et al., 2008), which is by far greater than the highest Pb concentration of 269 mg/kg we observed in this study. Similarly, our highest Pb value is substantially lower than the medium Pb level of 311 mg/kg reported for spruce bark ashes collected from a background site in Canada (Dunn et al., 1992). Because we were more interested in studying wood ash yield and the concentrations of toxic components under real world combustion in African traditional cookstoves, we could not assess specific wood species because all studied households and factories burn mixed species of fuelwood, rather than single tree species as, fuel.

Linearly independent pairwise comparisons showed that concentrations of Pb or Hg, but not As, Cd or Cr, were significantly higher ($\alpha = 0.05$) in wood ashes from TSFs compared with BIPCs (see Supplemental material Table S2). This suggests that locally grown brushwood, twigs, bark and waste woods, used in TSFs, contain higher concentrations of

Table 2
Range (mean ± standard deviation) of metals concentration, in mg/kg of wood ash.

Al	As	Cd	Co	Cr	Cu	Fe	Hg	Ni	Pb	Zn	Explanation	Reference
6250–23,800 (13,000 ± 6300)	12.0–35.8 (24.1 ± 8.7)	1.50–23.9 (16.1 ± 8.2)	1.30–52.8 (18.0 ± 19.2)	16.9–25.5 (21.2 ± 3.6)	14.4–38.2 (27.7 ± 9.2)	6380–16,300 (11,600 ± 3700)	38.0–120 (85.4 ± 31.1)	5.38–9.12 (7.03 ± 1.50)	89.3–269 (186 ± 69)	57.7–357 (137 ± 112)	Traditional cookstoves: TSFs Mixed wood-type: locally grown brushwood, bark, twigs, wood chips or construction/demolition wood.	Present study
5320–31,400 (14,600 ± 9300)	4.90–53.7 (19.2 ± 19.7)	3.70–17.1 (8.84 ± 4.44)	6.23–32.9 (18.0 ± 12.4)	10.4–47.9 (24.4 ± 17.5)	16.1–74.9 (37.2 ± 20.9)	4480–26,400 (11,600 ± 8300)	35.4–194 (76.0 ± 63.0)	3.20–13.5 (8.12 ± 3.48)	97.2–210 (144 ± 40)	77.4–185 (123 ± 48)	Traditional cookstoves: BIPCs Log of woody stem from forest.	Present study
ND	ND	4.9	ND	24	98	ND	ND	36	ND	213	European beechwood chips burnt in electric oven (500 °C, 2 h)	Vassilev et al. (2013)
ND	0.2–3	0.4–0.7	0–7	>60	15–300	ND	<0.4	40–250	15–60	15–103	Bottom ash of wood boilers	Pitman (2006)
ND	1–60	6–40	2–300	40–250	~200	ND	0–1	20–100	40–1000	40–700	Fly ash of wood boilers	
ND	1.97–5.19	0.84–1.21	ND	2.56–4.58	29.3–43.0	ND	0.06–0.11	ND	28.4–35.0	ND	Beech and trunk wood ash	Demirbas (2001)
ND	1.8–2.9	17–23	5.2–12.1	15–51	236–481	ND	ND	50–79	2–8	51–400	Fly ash of animal and plant mix, burnt in thermal power plants at 850 °C with 40–50% excess air.	Masto et al. (2015)
ND	<0.5–1.4	13–20	4.1–6.2	11–45	295–478	ND	ND	71–186	<1–2	10–51	Bottom ash of animal and plant mix, burnt in thermal power plants at 850 °C, with 40–50% excess air.	
13,000–23,650	ND	3–21	4	14–86	78–145	3300–19,500	ND	12–47	66–130	700	Ashes of wood and bark in the US	Demeyer et al. (2001)
12,500–82,100	ND	<1–2	14	75–1036	67–151	6260–14,300	ND	16–65	32–72	183–423	Ashes of paper and pulp in the US	
20–800	<0.1–1	0.1–2	ND	1–5	2–5	25–500	0.02–0.05	0.5–10	0.1–5	10–100	Coniferous and deciduous woods and short coppice willow in Europe	Obernberger et al. (2006)
ND	0.79–2.31	<0.02–0.85	ND	ND	64.6–230	ND	ND	19.3–34.9	0.03–21.1	58.1–810	Eight African tree species: open fire burn	Maschowski et al. (2016)
ND	4	0.4	ND	39	28	ND	<0.04	20	7	620	Bottom ash of a large-size (246 MW) wood-fired power plant	Dahl et al. (2010)
ND	2–52	4–203	1–98	147–508	138–860	1400–3060*	0.1–1.7	14–156	8–13,700	2630–43,500	Norwegian birch and spruce wood ashes	Reimann et al. (2008)
NA	30	30	NA	100	400	NA	3	70	300	7000	Recommended maximum limit of metals in ashes intended for spreading in forest land	SNBF, 2002
NA	30	17.5	NA	300	700	NA	1	150	150	4500	Maximum allowable metal level of Finnish legislation for ash used as forest fertilizer	Dahl et al. (2010)
77,000	0.68	71	23	120000* 0.3**	3100	55,000	11	840	400	23,000	Residential soil screening level	USEPA (2016)

*Median values; TSFs: three-stone fires; BIPCs: built-in-place cookstoves; ND: not determined; NA: not applicable; *Cr(III); **Cr(VI).

Pb or Hg compared with woody stems from forest, used by BIPCs. This observation corroborates most previous reports. For example, Demeyer et al. (2001) reported that waste woods such as construction or demolition woods produce more metals than forest woods. Obernberger et al. (2006) found substantially higher concentrations of metals in ashes of wood bark compared with wood without bark. Vassilev et al. (2013) reported that ash content, and indeed metal concentration, decreases in the following order: foliage leaves or needles ≥ bark > branches or twigs > wood stems/stumps. Heavy metals concentrations have been shown to vary significantly with ash content (Nitsche et al., 2017). Metal volatilization during wood combustion may significantly affect the level in bottom ash (Nitsche et al., 2017). Previous studies have reported higher concentrations of some heavy metals in fly ashes of combusted biomass or coal compared with bottom ashes (Masto et al., 2015; Nitsche et al., 2017; Pitman, 2006; Verma et al., 2015). A review found that Pb or Cd concentrations in the fly ashes of combusted biomass were about 9–15 times greater than their respective concentrations in bottom ash (Singh et al., 2011). The potential for metal volatilization during biomass combustion was found to be: Hg > Cd > Cr > Pb > Zn > As (Vassilev et al., 2013).

The average concentration of individual PAH in wood ashes from BIPCs ranged from 0.149 ± 0.293 mg/kg (for naphthalene) to 2.56 ± 1.54 mg/kg for (benzo(*j*)fluoranthene) (see Supplemental material, Table S3). The order of the top five PAH concentration in ashes from BIPCs was benzo(*j*)fluoranthene > benzo(*a*)anthracene > anthracene > benzo(*k*)fluoranthene. Nitsche et al. (2017) reported that fluoranthene and benzo(*b*)fluoranthene dominated ashes of leaf litter from urban street trees in Germany (Nitsche et al., 2017). In contrast, anthracene (a 3-ring PAH) was the most abundant PAH we found in the ashes from TSFs. The average concentration of PAH in wood ashes from TSFs ranged from 0.035 ± 0.042 mg/kg (for naphthalene) to 2.93 ± 4.35 mg/kg (for anthracene). Anthracene comprised 27% of the Σ_{16}PAHs concentrations in ashes from TSFs. Other dominant PAHs in the ashes from TSF were benzo(*k*)fluoranthene > benzo(*j*)fluoranthene > benzo(*e*)pyrene. The 3-ring PAHs also dominated bottom ashes of biomass-fired thermal power plants in India, operating at 850 °C with 40–50% excess air (Masto et al., 2015). Similar observation was reported for coal-fired power plants ashes (Ruwei et al., 2013; Sahu et al., 2009; Verma et al., 2015).

We found higher proportion of heavier carcinogenic (≥4 rings) PAHs in the wood ashes from BIPCs compared with TSFs: 79% and 66%, respectively (see Supplemental materials, Table S4). It is believed that PAH formation during pyrolysis of wood is by pyrosynthesis i.e. free radicals undergo a series of bimolecular reaction with native unsaturated aliphatic or monocyclic aromatic precursors to form larger ring structures (Etchie et al., 2018b). Thus, heavier PAHs must be formed from lighter PAHs with higher burn temperatures and longer residence time of ash in the flame (Etchie et al., 2018b). The residence time of ash in the hot combustion zone of BIPCs or TSFs ranged from 6–10 h or 4–5 h, respectively, per day.

The average concentrations of Σ_{16}PAHs in wood ashes from BIPCs or TSFs, which is 17.6 ± 12.2 mg/kg or 10.9 ± 7.2 mg/kg, respectively, greatly exceeded the average Σ_{18}PAHs concentration range of 0.065 ± 0.011 to 1.31 ± 0.13 mg/kg in different biomass ashes from Chinese traditional BIPCs (Zaotai) (Li et al., 2018), or for bottom ashes of some biomass, combusted under controlled conditions in furnace or thermal power plants (Freire et al., 2015; Masto et al., 2015; Straka and Havelcová, 2012) (see Supplemental materials, Table S4). They are however within the range of concentrations reported for waste ashes. For example, Johansson and van Bavel (2003) reported a range of Σ_{16}PAHs concentrations of 0.1–77 mg/kg for biomass and municipal solid waste ashes. Similarly, Zhao et al. (2008) reported that concentration of Σ_{16}PAHs or total carcinogenic PAHs in waste ashes varied from 4 to 199 mg/kg or 0.7–97 mg/kg, respectively.

We found significantly higher ($\alpha = 0.05$) concentrations of PAHs in wood ashes from BIPCs compared with those from TSFs (Fig. 2). This result indicates that cookstove-type plays an important role in the formation and yield of PAHs. In contrast to metals, wood characteristics may play far lesser role in the formation of PAH than the operation conditions, which are the stove ventilation rate, burn temperature and residence time of the ash in flame (Bignal et al., 2008; Freire et al., 2015; Masto et al., 2015; Straka and Havelcová, 2012). Compared with TSFs, BIPCs have relatively poorer ventilation rate, higher burn temperature and longer residence time, all of which favor formation and yield of PAHs.

We compared the concentrations of toxic metals and PAHs in the ashes with maximum limits for ashes intended for use as forest fertilizers. The concentrations of Hg in the ashes from all traditional cookstoves studied exceeded both the Finnish and the Swedish allowable limit for Hg in ashes intended for use as forest fertilizers, which is 1 mg/kg and 3 mg/kg, respectively (Dahl et al., 2010; SNBF, 2002). Similarly, the average concentration of Pb in the ashes from TSFs, but not BIPCs, exceeded the Finnish allowable limit of 150 mg/kg for ashes intended for spreading in forest land (Dahl et al., 2010). Furthermore, the concentrations of Σ_{16}PAHs in ashes from all traditional cookstoves investigated exceeded the Swedish limit of 2 mg/kg for ashes intended for spreading on forest land (SNBF, 2002), or the Czech limit of 6 mg/kg for ashes intended for use in agricultural soils (Straka and Havelcová, 2012). These results suggest that the ashes are not suitable for direct use as forest fertilizers.

The United States Environmental Protection Agency (USEPA) has developed residential soil screening level (RSSL) for toxic metals and some PAHs (see Supplemental materials, Table S3). The concentrations of As or Hg, but not Pb, in all ash samples greatly exceeded the RSSL. The average concentration of most of the heavier PAHs e.g. benzo(*a*)pyrene, benzo(*a*)anthracene, benzo(*j*)fluoranthene and dibenz(*a*,*h*)anthracene, but not the lighter PAHs, exceeded the RSSL. Similarly, the Swedish EPA has set guidelines for total carcinogenic PAHs in soils. For sensitive land use, the regulated limit is 0.3 mg/kg, whereas, for less sensitive land use with groundwater protection, the limit is relaxed to 7 mg/kg (Johansson and van Bavel, 2003; Straka and Havelcová, 2012). The average concentration of total carcinogenic PAHs in the wood ashes from both TSFs and BIPCs exceeded these limits, suggesting that disposal of the ashes on residential soils pose substantial risk to health and environment.

3.3. The risk of exposure to hazardous components in ash across Africa

The share of ash production and the potential for population exposure to hazardous ash constituents from residential and commercial burning of wood in traditional cookstoves across Africa is shown in Fig. 3. The national surveys used in our estimations had complete information for 46 out of the 50 countries making up the sub-Saharan African region. Therefore one or the two estimates (Fig. 3) were not performed for the 4 countries with incomplete national surveys (Liberia, Mayotte, Reunion and Saint Helena). Nigeria, Ethiopia, DR Congo, Tanzania and Uganda are the top five producers of wood ash in Africa, with estimated annual average (2.5th and 97.5th percentile**s**) production rate of 4.9 (2.0, 8.9), 2.3 (0.95, 4.2),1.8 (0.74, 3.3), 1.3 (0.53, 2.3) and 1.1 (0.44, 1.9) megatonnes, respectively. The percentile estimates reflect the magnitude of the uncertainties or variations in wood composition, cookstove designs, burn temperature and cooking duration across the country. We estimate that Nigeria alone, or the top five countries combined, accounts for about 27% or 62%, respectively of the total wood ash production in Africa. The proportion of people utilizing wood for cooking in these five countries ranged from 52 to 66%.

In general, residential and commercial burning of woods in traditional cookstoves in Africa generates, on the average, 19 (8, 33) megatonnes of ash per year. This translates into an annual average production of 380 t of As, 230 of Cd, 430 of Cr, 1500 of Hg, 3000 of Pb and 10 t of benzo(*a*)pyrene in Africa (Table 3). Individual country

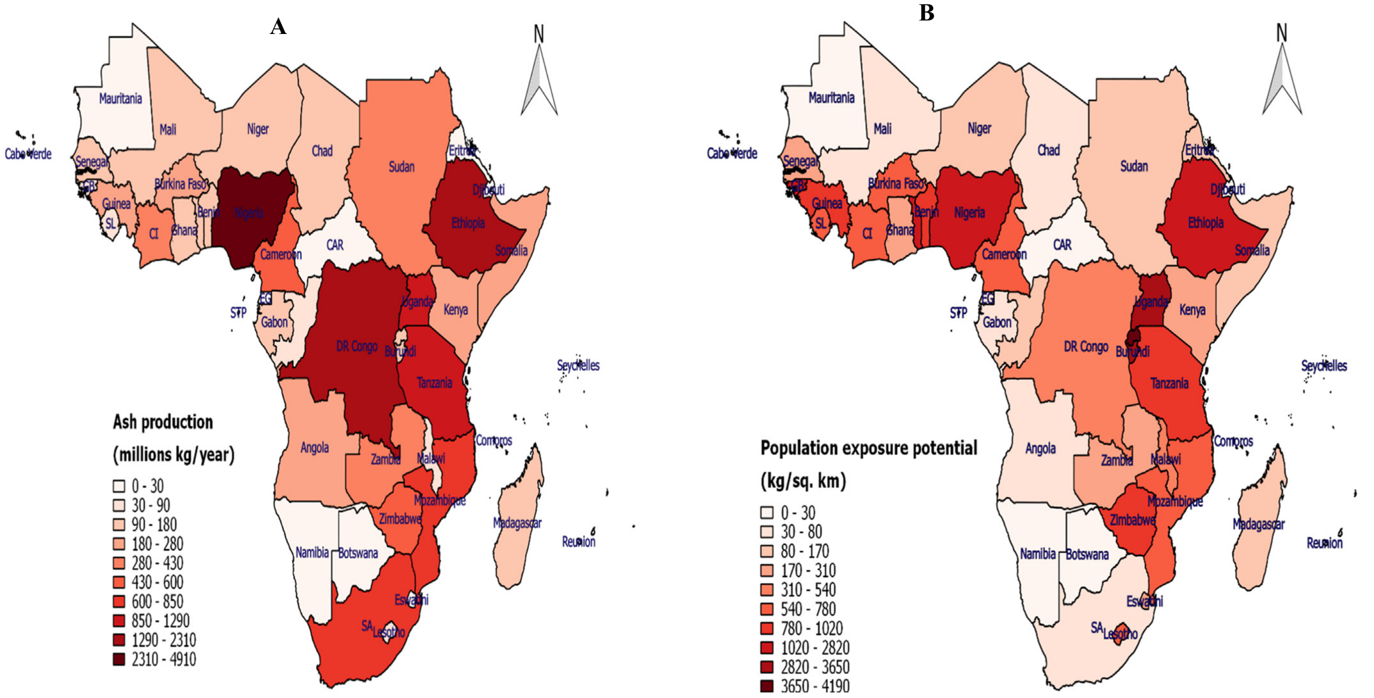

Fig. 3. Annual ash production (A) and population exposure potential to hazardous constituents of ash (B) from residential and commercial burning of wood in traditional cookstoves across Africa. The classification is based on the Jenks natural breaks. CAR: Central African Republic; CI: Cote d'Ivoire; DR Congo: Democratic Republic of the Congo; EG: Equatorial Guinea-Bissau; SL: Sierra Leone; SA: South Africa; STP: Sao Tome and Principe.

estimates are available in the Supplemental materials (Table S6). Our estimates do not include emission of toxic metals or PAH in the form of fly ash, particulate matter or gases during burning of wood in traditional cookstoves in Africa. Nriagu (1992) estimated the amount of toxic metals emitted during burning of wood in African households, forests and savannas in 1991 (Table 3). Also, Shen et al. (2013) gave estimates of PAHs emission from residential and commercial, or open-field burning of biomass (agricultural wastes, deforestation and wildfire) in Africa in 2007 (Table 3). Our values are comparable or greater than the estimates for toxic metals emissions, but substantially lower than PAH emissions in 2007. This suggests that wood burning in African traditional cookstoves produces more toxic metals, but lesser PAHs, as ash residues compared with emissions. If the routes of exposure is taken into cognizance, the risk to health from direct exposure to metal or PAH emissions may very likely surpass the intake via ash ingestion or resuspension, even in Africa.

We ranked the countries in Africa based on their potential for exposure to wood ash constituents using the per capita ash production in each country adjusted by the human population density and proportion of households in the country burning woods for cooking (Fig. 3). We found that the top eight countries with the greatest potential for exposure to hazardous constituents in wood ash, in a decreasing order of magnitude, are Rwanda, Burundi, Uganda, Nigeria, Guinea-Bissau, Ethiopia, Togo and Tanzania. The estimated potential for human exposure in these countries ranged from 1020 to 4190 kg of wood ash deposited per squared kilometers per annum. In contrast, Botswana, Seychelles, Namibia, Mauritius, Mauritania and Djibouti are countries with the lowest potential for human exposure to ash constituents, with estimates ranging between 3 and 11 kg of wood ash deposited per squared kilometers per annum.

Table 3
Average (2.5th and 97.5th percentiles) production of toxic chemicals from wood burning in Africa.

Toxic chemical	African traditional cookstoves[a]		African forests and savannas fires[b] (annual tonnage)	African households[b] (annual tonnage)
	mg per kg of wood burnt	Annual tonnage		
As	1.0 (0.19, 2.0)	380 (60, 1200)	300	69
Cd	0.6 (0.1, 1.3)	230 (20, 630)	200	46
Cr	1.0 (0.4, 1.6)	430 (100, 1200)	–	–
Hg	3.7 (1.3, 6.8)	1500 (290, 4400)	300	69
Pb	7.7 (3.5, 14)	3000 (980, 6700)	3500	805
B[*a*]P	0.02 (0.003, 0.04)	10 (3, 26)	–	–
TPAHs	0.6 (0.3, 1.4)	270 (50, 890)	20654[c]	94772[d]

[a] Bottom ash (present study).
[b] Emissions in 1991 (Nriagu, 1992).
[c] Emissions from open-field burning of agricultural waste, deforestation and wildfire in Africa in 2007 (Shen et al., 2013).
[d] Emissions from residential and commercial biomass burning in Africa in 2007 (Shen et al., 2013); B[*a*]P: benzo[*a*]pyrene, TPAHs: total of 16 PAHs.

Table 4
Comparison of range of Pb intake via wood ash in Africa and the WHO (2011) estimates of national average dietary Pb intake.

Country/region	Children age	Exposure (μg/kg bw per day)
Africa[a]	<1–6 years	0.2–3.9
Australia	2 years	0.03–0.93
Canada	2–4 years	0.19–0.26
Chile	Not specified	6–9
China	2–7 years	3.1 (8.2 = 97.5th percentile)
Europe	1–3 years	1.1–3.1
India	Not specified	0.9–1.3
New Zealand	<1–3 years	0.31–0.34
USA	<1–2 years	0.11–0.13
		0.3[b]

[a] Present estimates of Pb intake for young children in Africa via inadvertent ingestion of wood ash.
[b] Exposure level associated with impaired neurodevelopment (population reduction in intelligent quotient by 0.5 point) in young children (WHO, 2011); bw: body weight.

3.4. Risk to health from the wood ash ingestion in Africa

Because of poor solid waste management in most African countries, wood ashes are often discarded on surface soil close to where people reside. Therefore, to gain a better insight into the relevance of our result to human health, particularly young children who suffer the most immediate and severe consequence of wood ash exposure, we calculated and compared daily doses of Pb, Hg, As and PAHs through this particular route for young children. We estimate that the daily dose of Pb, Hg, As and $B[a]P_{eq}$ acquired through wood ash ingestion is between 6.5–39, 0.03–0.38, 0.01–0.24 and 0.58–3.43 μg, respectively. For young children below 5 years of age weighing between 10 and 30 kg, the daily intake of Pb, Hg, As and $B[a]P_{eq}$ through this particular medium is estimated to be between 0.2–3.9, 0.001–0.04, 0.0003–0.02 and 0.02–0.34 μg/kg of body weight (bw), respectively.

The daily intake of Pb is estimated to be, by far, greater than that of Hg, As or PAH through inadvertent consumption of wood ash, due to a combination of high Pb concentrations in the ashes and high metal bioavailability. The higher end of the dose range for Pb of 3.9 μg/kg bw per day is by far greater than the intake of 0.3 μg/kg bw per day that the World Health Organization (WHO, 2011) recognizes as causing neurodevelopmental impairment in young children. The upper end dose is also substantially greater than the intake level of 1.9 μg/kg bw per day associated with a population decrease in intelligent quotient by 3 points (WHO, 2011), indicating a concern. Furthermore, the WHO (2011) gave estimates of national average dietary Pb intake for young children in eight countries/regions (Table 4). The top value of our range of Pb intakes is substantially greater than the national average dietary Pb intakes in all the countries/regions, except in Chile. The average dietary Pb intake for young children in Chile ranged from 6 to 9 μg/kg of bw per day (WHO, 2011).

Our estimates of Pb dose are considerably lower than the Pb uptakes from soil and house dusts that resulted into deaths of about 400 young children aged below 5 years, with over 2000 children permanently impaired, in artisanal gold mining villages in Northern Nigeria (Dooyema et al., 2012; Greig et al., 2014; Lo et al., 2012; Plumlee et al., 2013; Thurtle et al., 2014; von Lindern et al., 2011). Furthermore, the USEPA (2017) gave chronic reference doses (RfDs) of benzo(*a*)pyrene that may not result into an appreciable risk of neurodevelopmental impairment, reproductive abnormality or immunological effect as 0.3, 0.4 or 2.0 μg/kg bw per day, respectively. Our highest value for $B[a]P_{eq}$ of 0.34 μg/kg bw per day surpass the RfD value for impaired neurodevelopment in children, but lower than the values for reproductive effect or immunological impairment. Considerably high levels of dioxins and furans have also been detected in wood ash samples (Freire et al., 2015).

It is important to state here that our assessment of the risk to health from wood ash did not consider the synergistic toxic effects of multiple chemical mixtures in human, which is well documented (Heys et al., 2016; Karri et al., 2016; Li et al., 2019; Singh et al., 2017). We also did not account for the additional, plausibly lesser, exposure to the harmful chemicals through inhalation of the wood ash dust or consumption of contaminated water and food, which can increase the estimated exposure. Nonetheless, our results show that the concentrations of hazardous constituents in wood ash may pose substantial risk of adverse effect, particularly to young children in Africa, because of their unique pattern of exposure. Also, because children who are exposed to wood ash in Africa are also exposed to multiple pollution sources including emissions from households and traffic (Etchie et al., 2017), our estimates, if added to existing exposures, can silently push the overall exposure of children, especially those at borderline exposures, to levels that may cause mortality or severe disability. Lastly, assuming similar pattern of exposure to wood ash across Africa, we estimate that the associated risk to health of children would be greatest in Rwanda, followed in a decreasing order by Burundi, Uganda, Nigeria and Guinea-Bissau, than elsewhere in the region.

We note some limitations in this study. First, we did not conduct leachability or in vitro bioaccessibility tests for toxic pollutants in the wood ashes. Thus, we could not ascertain the availability of pollutants from ashes to ground/surface water, plants uptake or gastrointestinal uptake in humans. Our estimates of daily uptake of the pollutants were based on the maximum percentage gastric bioaccessiblity reported for house dusts and residential soils in a locality in Nigeria (Plumlee et al., 2013), but not for wood ashes from the traditional cookstoves. Secondly, because we focused on real world conditions, we could not assess the levels of toxic pollutants in specific plant species without influencing the households and factories using the cookstoves. All studied cookstoves burned mixed species of woods per cooking event, rather than a single tree species. Therefore, future studies may consider examining the levels of toxic pollutants in ashes of specific wood species combusted in traditional cookstoves, and their corresponding soil levels.

4. Conclusion

Previous studies revealed that controlled burning of wood in more efficient combustion systems such as ovens, furnaces, incinerators and thermal power plants, produce substantial amount of ash containing considerable, but highly variable, concentrations of toxic metals and PAHs. However, such information was limited hitherto for traditional cookstoves even though a large proportion of the world's population burn wood using such combustion systems. For the very first time, we have shown that burning of wood in traditional cookstoves in Africa produces more ash, containing greater concentrations of toxic metals and PAHs, than the levels typically found in controlled combustion systems. Although the high concentrations of metals owe mostly to their levels in the fuelwoods, the PAHs concentrations can be linked closely to the operating conditions of the stoves and presence of metals like Cu and Fe acting as catalysts (Nitsche et al., 2017).

Therefore, from the results of this study, we reach the following conclusion:

- Burning of wood in African traditional cookstoves generates substantial amount of ash containing toxic levels of metals and PAHs.
- The concentrations of toxic metals and PAHs in wood ash from traditional cookstoves, though variable, surpass the levels typically found in controlled combustion systems.
- The detected levels of toxic metals and PAHs in wood ash from traditional cookstoves, alone, can cause permanent cognitive disability in young children, but when taken in concert with exposures from other pollution sources may result in more severe heath consequences, including mortality.
- In order to cut-off the additional or synergistic health effects associated with wood ash exposure in Africa, effective solid waste management is required.

CRediT authorship contribution statement

Ayotunde Titilayo Etchie: Conceptualization, Methodology, Validation, Formal analysis, Data curation, Writing - original draft. **Tunde Ogbemi Etchie:** Conceptualization, Methodology, Validation, Investigation, Resources, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Olugbenga Oluseun Elemile:** Investigation, Resources, Visualization, Supervision, Project administration. **Oluwatobi Boladale:** Investigation, Resources. **Timileyin Oni:** Investigation, Resources. **Ifeanyi Akanno:** Investigation, Resources. **Deborah Temitope Bankole:** Investigation, Resources. **Olanrewaju Obasanjo Ibitoye:** Investigation, Resources. **Ajay Pillarisetti:** Writing - review & editing, Visualization. **Saravanadevi Sivanesan:** Writing - review & editing, Visualization.**Tokunbo Yemisi Afolabi:** Investigation, Resources. **Kannan Krishnamurthi:** Writing - review & editing, Visualization, Supervision. **Nedunchezhian Swaminathan:** Conceptualization, Writing - review & editing, Visualization, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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