Characterization of Halogen (Cl, Br, I) Emissions from Cooking Fuels in Nigerian Households Using Energy-Dispersive X-ray Fluorescence Spectrometry

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Abstract

Studies have shown that most of the fuels used in developing countries were generally from wood biomass. Residential emission from traditional biomass cookstoves is a major source of indoor and outdoor air pollution. However, the exact quantification of the contribution of biomass cookstove emissions to outdoor air is still lacking. To address this gap, we designed a study to estimate the halogens present indoors, from cookstove smoke using biomass fuel. A non-destructive analysis method for total bromine (Br), chlorine (Cl), and iodine (I) contents in $PM_{2.5}$ were established using an energy-dispersive X-ray fluorescence (EDXRF) spectrometry. The results (ng m^{-3}) were Not detectable (ND) to 0.39, 1.94 - 181, and ND - 233.40 for Br, Cl, and I respectively. Results depicted that fuels from Bamboo, palm, maize shafts, and *Spondias mombin* produced the highest emissions of halogens.

Keywords: bromine, halogens, iodine, *Tectona grandis*, *Gliricidia sepium,* biomass, polarizing EDXRF.

Introduction

There has been increasing evidence, that halogens (Cl, Br and I) play important roles in determining the composition of the troposphere (Sherwen *et al*., 2017), effects on regional and global species, and also focused on the chemistry of chlorine, iodine, and bromine (Allen *et al*., 2009; Fernandez *et al*., 2014; Simpson *et al*., 2015; Hossaini *et al*., 2016). Halogen has been confirmed to influence the formation of secondary air pollutants (Li *et al*., 2019). Interactions between the halogens and HOx, NOx, and volatile organic compounds (VOC) species leads to halogens having a pervasive influence throughout the tropospheric chemistry system (Schmidt *et al*., 2016, Sherwen *et al*., 2016). The chemistry of Br and I is thought to lead to reductions in O_3 and OH mixing ratios globally (Parrella *et al*., 2012, Saiz-Lopez et al., 2014, Schmidt *et al*., 2016, Sherwen *et al*., 2016) whereas the chemistry of Cl is thought to lead to both increases in O_3 due to more rapid oxidation of VOCs (Simon *et al*., 2009, Burkholder *et al*., 2015) and decreases due to halogen nitrate hydrolysis reducing O_3 production (via decreasing NOx) (Schmidt *et al*., 2016).

Air pollution in the atmosphere is due to natural and anthropogenic activities such as fossil fuel combustion, i.e., natural gas, coal, and oil, to power industrial processes and motor vehicles (Beguma *et al.*, 2009). CO_2, CO, NOx, SO_2, and aerosols get into the atmosphere through the combustion of materials, such as traditional biomass fuels which include, wood, cow dung, and crop wastes. It is on a note that the byproducts of produces constitute problems that affect the populace within the combustion and beyond (Smith *et al.*, 2004). Residents of the particular areas of biomass combustion are prone daily to harmful emissions and other health risks. In the affected areas of pollution, those individuals exposed to enhanced concentrations of pollutants are women and their children, who spend most of their time in the kitchen cooking.

Acute respiratory infection, lung cancer, and chronic obstructive pulmonary disease were linked to open fires used in the kitchens as household fuels in developing countries (Smith *et al.*, 2000; Chowdhury *et al.*, 2015). Generally, in these countries, fuels such as biomass, coal, dried woods, plastics, animal dung, paper, crop residues, and dried leaves are the common ones used. High morbidity and mortality rates were recorded in young children in developing countries, the symptoms of these were acute respiratory infections and primarily pneumonia. According to WHO (2010), indoor air pollution is the cause of death of over 1.5 million young children and moms who stayed most times at home and in the kitchen.

There are many types of household stoves for cooking and heating across the world. These stoves emissions are known to be hazardous to human health and impact climate, but in practice emissions measurements largely focus on a subset of these; those that are important markers for health endpoints (respirable particles, carbon monoxide, SO_2), and those that are important to estimate climate impacts (CO_2, CO, CH_4, non-methane hydrocarbons, N_2O, and the mixtures of elemental (black) and organic carbon in the fine particulate matter) (WHO 2016).

During recent years, there have been many studies conducted to evaluate indoor air pollution. These studies were based on the kitchen, living rooms, and other parts of the buildings (Lim *et al.*, 2012; Smith *et al.*, 2014; WHO, 2016; Khan *et al.*, 2017; (Ubuoh and Nwajiobi, 2018). Many studies showed that most of the fuels used in developing countries were generally from wood biomass. The biomass combustion consists of emissions due to the types and quality of fuel used, combustion technologies, and operating conditions (Tissari *et al.*, 2008). In Chandrasekaran *et al.*, (2012) report, it was stated that the quality and chemical composition depends upon the nature of the plant species, for example, the ash content varies with inorganic species present in the biomass, which ranges from 0.5 to 3% dry weight (dw), carbon (from 45 to 50% of the mass), oxygen (about 40−50%), hydrogen (about 6%), nitrogen (less than 1%), and elements such as Ca, K, Na, Mg, Mn, Fe, Al, Cd, Cr, Cu, Ni, Zn, As, Hg, and Pb. Iodine (I) is known to be useful in human nutrition for the synthesis of thyroid hormones, but its deficiency results in goiter. It was reported that over two billion people over the world were linked to the risk of I problem due to little intake (WHO 2004; de Benoist *et al.*, 2008). The action and effect of I in the environment should be elucidated, due to its significant effect on agricultural production and human health (Takeda *et al.*, 2011). According to Kabata-Pendias and Mukherjee (2007), Br (as methyl bromide and ethylene dibromide) is used in as fungicides, herbicides, and insecticides in agricultural productions. Br in excess in the human body is harmful. McLeod *et al.* (2015), reported the usefulness of the halides in solar cells. The usefulness was enumerated as light-absorbing materials and improves device performance. Also reported was that the halides' ratios are useful in tracing groundwater salinity (Alcalá, 2019).

Previous research dealt purposely on the Cl content on air quality over large spatial scales (Li *et al*., 2019). Little or no attention has been paid to the halogen contents on air quality due to household cooking energy. This paper aimed at assessing the concentrations of Br, I, and Cl in particulate matter ($PM_{2.5}$ μm) obtained from different fuels firewood, plastic, and the gas used by different homes in Akure. The report in this study is an overview of the results of the EDXRF analysis.

Materials and methods

The study location, Akure is the capital of Ondo State is one of the cities in Southwest Nigeria with an area of 991 km^2 and a population of approximately 484,798 million. It has an average temperature of 29°C, Wind W at 8 km/h, 73% Humidity. The measurement site was at Oba Ile (7°15'56.21'' N–5°15'18.16'' E), in the typical residential urban area (Figure 1). The measurement period was from July 24th July to August 1st, 2018. During the period, a three-stone (same height) cooking fire stove using ten different fuels (Teak, *Tectona grandis*), (Bamboo, *Bambusa valgaris*), (Mango, *Mangifera indica*), (Gliricidia, *Gliricidia sepium*), (Palm Kernel seeds, *Elaeis guineensis*), and (Hog Plum, *Spondias mombin,* Maize cob, *Zea mays*) were used for cooking of *Vigna unguiculata* in two different kitchens (Figure 2). The fuels used during the cooking periods were obtained within the vicinity of the study area and sun-dried until they were devoid of moisture. The cooking time for each period was one hour thirty minutes.

During sampling, one type of filter (nylon) was used (Table 1). All the samples were collected using Partisol™2025 samplers (Thermo Scientific, USA) placed on a stand. The filter sample was exposed for 5h. The flow rate was 16.7 L min^1. Flow rates were recorded before and after sampling. The filters were pre- and post-weighed using an XP2U Microbalance (Mettler Toledo, Columbus, OH). After sampling, the filter were placed in Petri dishes, and sealed in plastic bags until returned to the United States, there and then post-weighed. X-ray fluorescence measurement was performed on an EDXRF spectrometer (Takeda *et al*., 2011).

The data obtained in the study was compiled and analyzed using SPSS 12.0 software.

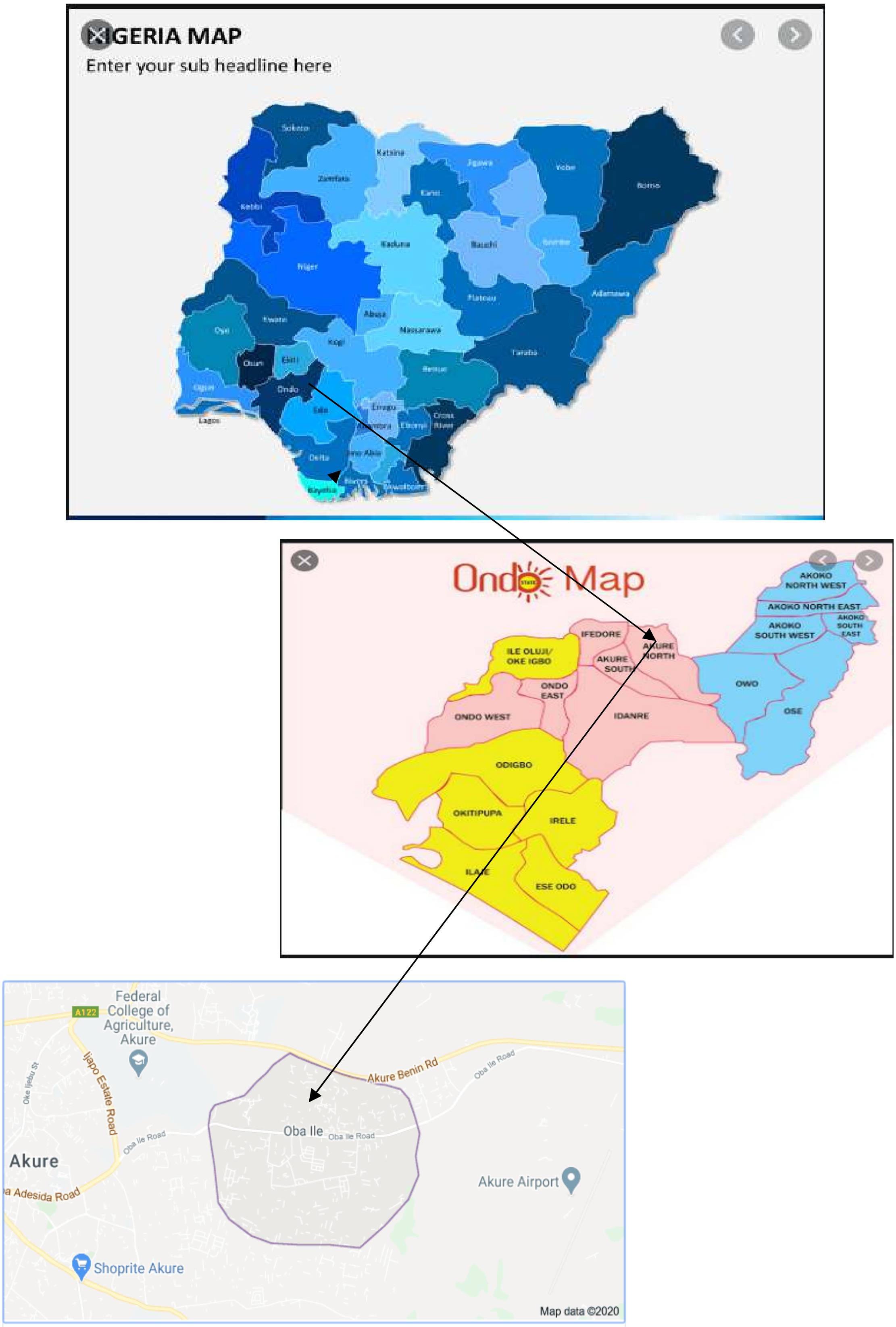

Figure 1. The map of Nigeria, State, and the location of sampling Oba Ile (7°15’56.21N–5°15’18.16’’E)

Results and Discussion

Concentrations of Br, Cl, and I in the samples measured by the EDXRF are shown in Table 2. The concentrations of Br ranged from ND to 0.39 ng m^{-3}, Cl ranged between ND to 181.20 ng m^{-3}, and those of I ranged from ND to 273.26 ng m^{-3}. Most of the Br, Cl, and I contents reported previously for particulate matter are within the concentration ranges in this study (Bettinelli *et al*., 2002; Flores *et al*., 2008; Peng *et al*., 2011), but lower than those reported by Eleanne *et al*. (2013).

The information about the kitchen characteristics, cookstove type, fuel composition, and other attributes related to cooking activity in the households used for this study has been presented in Table 1 with ventilation status classified according to Adhikari *et al*. (2020). From this study, it was revealed that most of the households in areas chosen are poorly ventilated. These tallies with the results of a study undertaken by Akagi *et al*. (2011) in Nepal a developing country, it was observed that over 70% and 85% of households in land and rural locations of Nepal are poorly ventilated.

Br, I, and Cl concentrations in the PM obtained from the kitchens (Figure 3) exhibited great variations and were much higher than those in the ambient urban atmosphere. The highest mean Cl concentration, 181.20 ng m^{-3}, was observed in the PM from household cooking with maize straw, followed by cooking fuel with *Spondias mombin* (147.63 ng m^{-3}). In contrast, the PM obtained from the cooking with gas supply had the lowest average PM_{10} concentration (1.94 ng m^{-3}). The Cl concentration ranged from 1.94 – 181.20 ng m^{-3} with a mean value of 70.38 at a 95% confidence interval. The variability of Cl concentrations of smoke among the households can be attributed to factors such as types of kitchen structures/size/volume, cooking style, exfiltration rate, air exchange rate between inside and outside the kitchen, combustion temperature, moisture content of the fuel, the carbon content of the fuel, and prevailing metrological conditions (Begum *et al*., 2009; Soneja *et al*., 2015; Stockwell *et al*., 2016; Adhikari *et al*., 2020). The large variation in particle concentrations among the household cookings was mainly attributed to the differences in charcoal fuel, food, cooking condition, surrounding buildings, and the wind direction and speed.

Conclusion

The results of the investigation revealed that smoke from the firewood, plastic, and gas, contained chlorine, while plastic and mango did not produce bromine and iodine. The use of firewood in cooking released more iodine. The exposure of women, children, and the atmosphere to halogen may have negative effects which may be short-term or long-term. Although the emission of the halogen content of firewood in this study may not be at an alarming concentration, the constant use of the fuels may result in indoor and outdoor pollution. To overcome the effect of halogen from cooking fuels, it is better to use alternatives (fossil fuels).

Figure 2. A typical representative of household kitchen used in the study area

Table 2: Concentrations of Br, Cl, and I in the samples (ng m^{-3})

Fuels	Chlorine	Bromine	Iodine
Teak (T*ectona grandis*)	7.94 - 11.40	ND - 0.06	ND - 181.53
Bamboo (Bambuseae)	67.38 - 137.59	ND - 0.23	ND
Mango (*Mangifera indica*)	47.28 - 77.80	ND	ND
Gliricidia (*Gliricidia sepium*)	47.28 97.06	ND	ND - 233.40
Palm *(Elaeis guineensis)*	67.38 - 137.59	0.11 - 0.20	ND
Spondias (*Spondias mombin)*	ND - 147.63	ND - 0.24	ND - 233.40
Maize (*Zea mays*)	ND - 181.20	ND - 0.39	ND

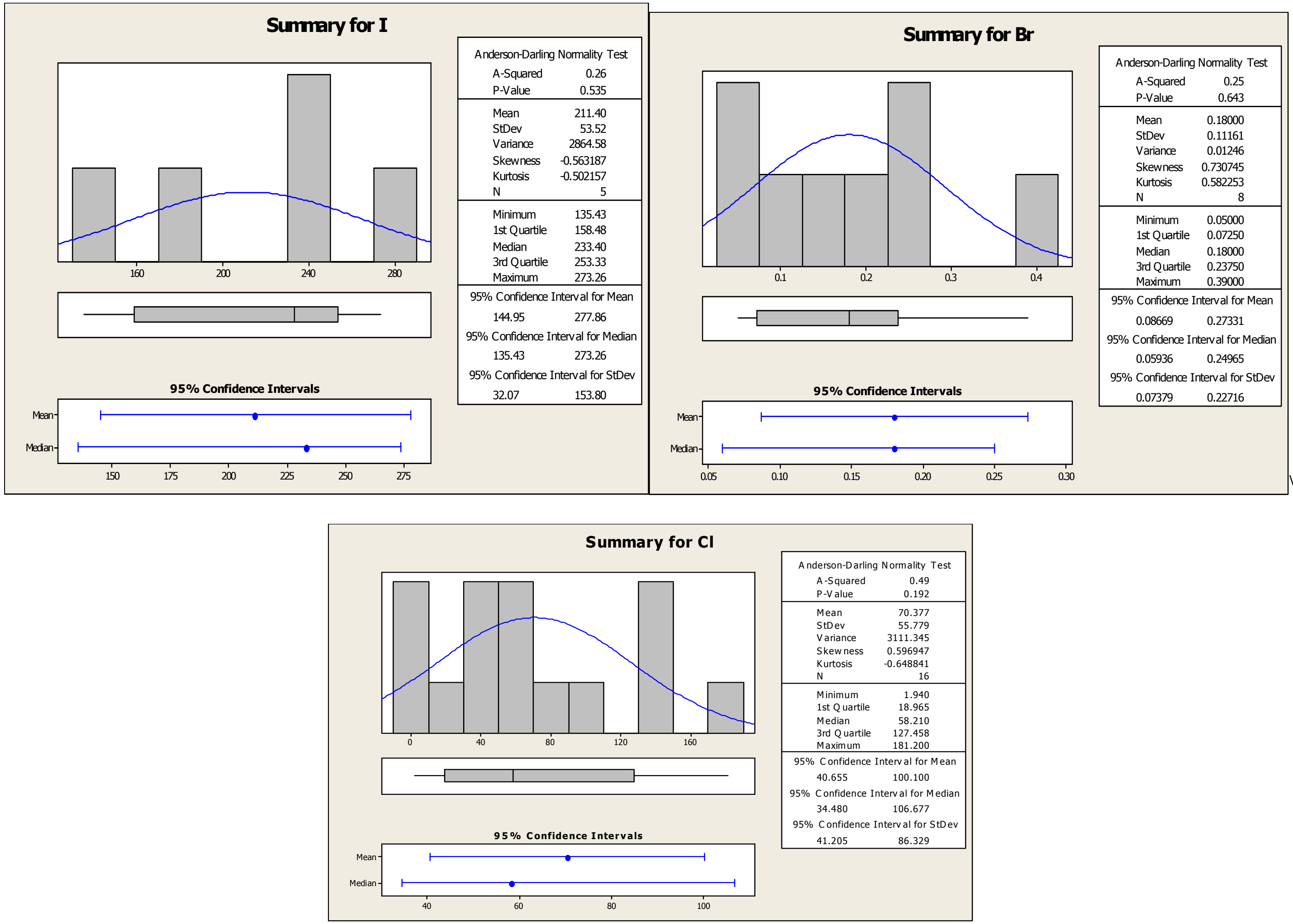

Figure 3. Graphical Summary Results of the Halogens in the Samples

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