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# Occupational exposures to particulate matter and $PM_{2.5}$-associated polycyclic aromatic hydrocarbons at the Agbogbloshie waste recycling site in Ghana

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ABSTRACT

Electronic waste (e-waste) disposal and recycling activities such as burning and smelting can emit particulate matter (PM), polycyclic aromatic hydrocarbons (PAHs), and other pollutants that expose workers and nearby communities. At informal e-waste recycling facilities, both emission controls and protective measures for workers are absent. This study characterizes personal exposures (breathing zone) of PM and PAHs of e-waste workers at the large Agbogbloshie e-waste site in Accra, Ghana. We collected gravimetric and optical measurements of $PM_{2.5}$ and $PM_{10}$ using shift samples for workers and for an age- and gender-matched reference population. $PM_{2.5}$ filters were analyzed for 26 PAHs using gas chromatography/mass spectroscopy. Among e-waste workers, $PM_{2.5}$ and $PM_{10}$ concentrations were 99 ± 56 and 218 ± 158 $\mu g/m^3$ (median ± interquartile range, optical measurements), respectively; these levels were 78 and 57% higher, respectively, than levels measured at a fixed site that was centrally located at the waste site. In the reference community, breathing zone $PM_{2.5}$ and $PM_{10}$ levels were lower, 49 ± 20 and 131 ± 108 $\mu g/m^3$, respectively, and the fraction of coarse PM was larger. We detected all 26 target PAHs, of which naphthalene and phenanthrene were the most abundant. PAH concentrations were weakly correlated to PM levels, but PAH abundances, representing the fraction of PAH mass to the total $PM_{2.5}$ mass collected, were strongly and inversely correlated to PM levels, suggesting multiple and different sources of PAHs and PM that affected exposures. Both PM and PAH levels were elevated for workers performing burning and dismantling, and both exceeded standards or risk-based guidelines, e.g., lifetime excess cancer risks for several PAHs were in the $10^{-4}$ to $10^{-6}$ range, indicating the need to reduce emissions as well as provide respiratory protection. The study emphasizes the importance of using personal and shift samples to accurately characterize worker exposure.

## 1. Introduction

Waste recycling, including electronic waste (e-waste), involves scavenging and collection of e-waste, sorting, dismantling, and burning or smelting to recover metals. Technologies used for these tasks, as well as emission control and safety measures, vary widely (Bauer et al., 2019; Julander et al., 2014; Kwarteng et al., 2020; Makoni, 2020; Mukherjee and Agrawal, 2017), particularly in informal settings in low and middle income countries where crude methods, e.g., open burning, are used with few if any emission controls or worker protection (Baldé et al., 2017; Cayumil et al., 2016). Moreover, informal e-waste sites can be in the midst of urban areas, exposing the community to pollutant emissions. Typically, little information regarding pollutant emissions or concentrations is available at such sites, including the ambient and breathing zone concentrations needed to understand exposure and risk to workers and the community. The Agbogbloshie waste site in central

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Accra, Ghana is an example of such a site. This large site is adjacent to crowded markets, dense formal and informal housing, and extensive commercial activity. Two important classes of pollutants emitted at such sites are particulate matter (PM, e.g., $PM_{2.5}$ or PM below 2.5 μm equivalent aerodynamic diameter) and polycyclic aromatic hydrocarbons (PAHs). While PAHs and PAH metabolites at waste sites have been measured in soil and human specimens (urine, breastmilk) (Asamoah et al., 2019; Daso et al., 2016; Feldt et al., 2014; Moeckel et al., 2020; Tue et al., 2016), airborne measurements are lacking.

The health burden due to exposure to airborne PM is high in developing countries (Mannucci and Franchini, 2017; Slezakova et al., 2010; WHO, 2013). Given the limited monitoring networks, poor quality data, and limited access to monitored data, information on PM exposures tends to be scarce in Africa, although several recent studies have provided information on sources, concentrations and health risks (Bauer et al., 2019; Kwarteng et al., 2020; Makoni, 2020; Mukherjee and Agrawal, 2017). Exceedances of air quality guidelines(WHO, 2016) are widespread due to emissions from biomass combustion for agriculture and domestic energy needs, vehicles, power generation and industry (Bauer et al., 2019; Karagulian et al., 2015). Waste burning at roadsides, residential areas and dumpsites has been associated with high $PM_{2.5}$ levels in India and Mexico (Li et al., 2012; Vreeland et al., 2016), and waste site activities have been demonstrated to increase average $PM_{2.5}$ and $PM_{10}$ levels by 88 and 214 $\mu g/m^3$, respectively (Kwarteng et al., 2020). Information regarding PM levels in Africa is based mostly on measurements at fixed sites, but some recent personal measurements are now available, including some more recent personal exposure data in Ghana, e.g., $PM_{2.5}$ levels among 56 students in Accra averaged 56 $\mu g/m^3$ and reached 150 $\mu g/m^3$ (Arku et al., 2015), and $PM_{2.5}$ levels among e-waste workers at Agbogbloshie averaged 81 $\mu g/m^3$ and reached 1501 $\mu g/m^3$ (Laskaris et al., 2019).

Waste burning emits PAHs, and the poor and incomplete combustion conditions associated with typical burning practices may increase these emissions. However, PAH sources are ubiquitous and include tobacco smoke, wood smoke, fireplaces, cooking, many industrial processes, and vehicle exhaust. Globally, anthropogenic sources, specifically combustion of fossil and biomass fuels, are the major contributors of PAHs, which emit far more PAHs than natural sources (Dybing et al., 2010), but these emissions have been declining with the growing use of cleaner fuels and emission controls (Shen et al., 2013). PAHs are emitted as complex mixtures (Rengarajan et al., 2015), and the quantity and composition of emissions depend on many factors (Wielgosinski, 2012). PAHs with four or more rings, classified as high molecular weight (HMW) compounds, have low vapor pressures, high affinity for the solid phase, and may be of particular concern due to their persistence, bioaccumulation and chronic health effects, compared to low molecular weight (LMW) PAHs (Hussain et al., 2019). Airborne PAHs partition between vapor and particulate phases, especially smaller-sized PM like $PM_{2.5}$ (Andreou and Rapsomanikis, 2009; Javed et al., 2019; Mohanraj et al., 2012; Morakinyo et al., 2016).

Historically, environmental monitoring has focused on a subset of 16 PAHs (naphthalene, acenaphthylene, benzo[b]fluoranthene, acenaphthene, fluoranthene, fluorene, phenanthrene, anthracene, pyrene, benzo [a]anthracene, indeno[1,2,3-c,d]pyrene, chrysene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[g,h,i]perylene, dibenz[a,h]anthracene). PAHs include carcinogens, mutagens, and teratogens (Gearhart-Serna et al., 2018), and carcinogenic effects to the lungs, bladder and skin are considered the key risks at environmental levels (Honda and Suzuki, 2020). Benzo[a]pyrene (BaP) has been the most studied in terms of toxicity and exposure (Hussain et al., 2019); this is the only PAH known to be carcinogenic to humans and classified as a Group 1 compound (Dybing et al., 2010). In addition, benz[a]anthracene is classified as probable human carcinogens, and four PAHs (benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene and indeno[1,2,3-c,d] pyrene) are considered possible carcinogens (Driscoll, 2014). Risks of PAH mixtures have been evaluated using various toxicity, mutagenicity and relative potency factors (Jung et al., 2010; Samburova et al., 2017). The toxicity equivalent factor (TEF) approach is commonly used (Adeniji et al., 2018), which expresses the toxicity of a mixture as a BaP equivalent concentration.

This study was designed to characterize $PM_{2.5}$ and PAH exposure of workers at the informal Agbogbloshie e-waste site in Accra, Ghana. We obtain shift measurements of PM exposure for both workers at the site and for an age- and gender-matched reference population in the same city. A subset of PM samples is analyzed for 26 different PAHs. We estimate personal exposures for various site activities (e.g., waste burning), and the health risks to workers and the reference population. This work is part of the West Africa-Michigan Charter II for the GEOHealth study, which is investigating occupational exposures, worker health, and environmental risks at the Agbogbloshie site (Acquah et al., 2019; Kwarteng et al., 2020; Laskaris et al., 2019; Nti et al., 2020; Takyi et al., 2020).

## 2. Material and methods

### 2.1. Study design and study sites

We collected sociodemographic and air pollution exposure data for e-waste workers at Agbogbloshie and a reference population in four sampling rounds conducted from March 2017 through August 2018. Each round involved participant recruitment, consenting, administration of questionnaires, and personal air monitoring. Study procedures have been documented elsewhere (Kwarteng et al., 2020; Laskaris et al., 2019). The present study focuses on rounds 1–3.

The Agbogbloshie e-waste site is within 1 km of Accra's central business district. This informal dumping and recycling site accepts all types of e-waste from multiple destinations, and employs an estimated 4500–6000 individuals (Beecham and Montoya, 2016; Daum et al., 2017). The site is surrounded by informal housing, commercial offices, churches, mosques and markets. E-waste activities include direct metal recovery, burning, molding and casting; weighing and sorting, stripping of cables, dismantling, and trading and selling of recovered products (Nyamadi, 2015). These activities are usually done in the open with workers in sets of two or more, and activities are conducted year round except on religious holidays (Prakash et al., 2010). Most workers reside in densely populated areas adjacent to the site, about 100 m across the Odaw river (Srigboh et al., 2016). The Agbogbloshie food market, the largest market for foods and services in the Greater Accra (Amuzu, 2018), is adjacent and downwind of the site.

The reference site was in the La Nkwantanang-Madina Municipality, located ~10 km north-west of Agbogbloshie. This area ("Madina-Zongo") is densely populated with individuals who have migrated to Accra from northern Ghana for work opportunities, like most of the e-waste workers. Most (70%) of the Madina-Zongo population is 15 years and older, economically active, and most are involved in trading (Ghana Statistical Service, 2014). Activities frequently observed in Madina-Zongo include vehicular traffic, trading, commercial cooking, and children attending a large public school. The community is surrounded by other informal housing areas and the Madina market to the northeast, the second largest open market of Accra (Horowitz, 2018).

### 2.2. Participant recruitment

Study recruitment first involved obtaining the consent of worksite and community leaders, holding community parties ("durbars") (Laskaris et al., 2019), and on-site recruitment activities, which included setting up a registration desk, holding brief interviews, and consenting. Eligibility criteria for e-waste workers included being male, aged 18–55 years, being engaged in at least one e-waste activity (collecting, sorting, dismantling and burning), and willingness to provide consent. Workers provided their signature or thumbprint as evidence of written consent. At Madina, eligibility criteria were identical other than the occupation:

participants could not work in e-waste recycling. As incentives, participants completing initial questionnaires were provided a snack, and enrolled participants who wore backpacks for personal monitoring and completed surveys were given 30 Ghana Cedis (US $7) and a tee-shirt.

In round 1, 100 e-waste workers and 51 individuals from Madina-Zongo were recruited and enrolled. In follow-up rounds, we again held on-site recruitment activities and attempted to contact and recruit prior participants using telephone calls and the assistance of key e-waste workers and other community individuals. In round 2, we sampled 112 and 53 participants at Agbogbloshie and Madina-Zongo, respectively, which included 42 and 14 new participants at the two sites to replace individuals lost to follow-up. In round 3, we sampled 105 and 41 individuals at Agbogbloshie and Madina, respectively. Overall, we recruited 142 different participants at Agbogbloshie and 65 at Madina-Zongo.

Ethical approvals were obtained from the Ethical and Protocol Review Committee (EPRC) of the College of Health Sciences and the Institutional Review Board of the University of Michigan.

### 2.3. Sociodemographic and occupational data

A detailed (25 page) questionnaire was administered to participants during registration by trained translators fluent in English, Hausa, Twi and Dagbani. Questions addressed the current jobs (type of work, years working, days per week, hours per day, daily income), previous job (if held over 6 months), health status, cigarette smoking history, housing (e.g., location), cooking activities (e.g., fuel used), and sociodemographic characteristics (e.g., age, education and daily income). Each e-waste worker was assigned to one of the following job categories: “burner” (e.g., burning materials to recover copper), “dismantler” (disassembling electronic equipment or scrap), “sorter” (offloading, weighing, and/or consolidating e-waste and scrap brought to the site), “collector” (purchasing obsolete electronics and electrical products and scrap outside the yard), and “other” (buy/sell e-waste within the site). Although a worker may be engaged in several tasks, a job category based on the most frequent task they performed was assigned. The reference group was assigned a “non-e-waste worker” response. We also asked about tasks performed the day of sampling using pre- and post-shift surveys administered before backpack deployment and then after backpack retrieval.

Prior work has categorized activities of many of the same workers using survey data and time-lapse photographs from a camera mounted to the front shoulder strap of the participant’s sampling backpack (described later) into work activities (e.g., burning, dismantling, collecting or sorting), non-work activities (e.g., smoking, resting, eating, praying), and transport-related activities (e.g., walking, bicycling, driving); these photos were also used to note the presence of a “black plume” from burning, and proximity to the burning area (Laskaris et al., 2019). Three of five backpack systems used to measure personal concentrations were equipped with these cameras, and activity coding was completed for 171 shifts for rounds 1–3. These data were summarized to correspond to the integrated (shift-long) samples collected, and the final categorization used the image-based activity (including transport-related activities) with the longest duration if it lasted 30 min or longer. Of the 171 shifts with image data, 112 shifts could be classified. For the other shifts, survey questions were used that described activities during the past week, if available, or similar questions for a 1-month long recall period. This categorized activities for 83 additional shifts. Work activities could not be classified for 59 shifts (36%), either because no single task was performed for at least 30 min (based on the time-lapse photographic analysis) or because of insufficient survey data.

### 2.4. Air sampling

Integrated $PM_{2.5}$ and continuous 1-min PM measurements were obtained using personal sampling and backpack systems that contained a battery-operated 5-channel optical particle counter (OPC; Aerocet 831, Met One Instruments, Inc., Oregon, USA) and a sampling pump (SKC Leland Legacy, PA, USA) operating at 10 L/min connected to a size selective $PM_{2.5}$ inlet (Impact Sampler, SKC). Both the sampler and OPC inlets were placed on a front shoulder strap of the participant’s backpack (Fig. S1). Five such systems were used, allowing up to five participants to be studied on the same day. Sampling typically started from 9:30 to 10:19 am, and the sampling duration averaged 4.42 ± 0.80 hr (±standard deviation), excluding the “Harmattan period” (Jan. 12 through Feb. 22, 2018 in round 3) during which durations were reduced (averaging 2.94 ± 0.40 hr) due to concerns of Saharan Desert dusts that were observed to overload the samplers. Gravimetric and optical measurements are referred to as $PM_{2.5,GRAV}$ and $PM_{2.5,OPC}$, respectively.

As part of the GEOHEALTH II Study, we also obtained gravimetric and optimal PM measurements at three fixed sites: a fairly isolated upwind site, a site centrally located at the e-waste facility, and a downwind site near the Graphic Road in Accra (Kwarteng et al., 2020). These sites used the same type of OPC and $PM_{2.5}$ samplers and similar collection and analysis protocols as the backpack samplers, but collected 24-hour samples every 6th day (N = 20–38 depending on site).

Prior to deployment, the pump and OPC batteries (including an auxiliary battery in the backpack) were charged, a new pre-weighed filter (PTFE, 2 μm pore size) and an oiled impaction disc were installed in the Impact sampler, flow rates were set and confirmed using a flowmeter (VFB-67, Dwyer Instrument Inc, IN, USA) connected to a HEPA capsule filter (Pall Gelman Science, Ann Arbor, MI, USA), instrument clocks were synchronized, and OPC operation was confirmed via a “zero” test with a HEPA filter. After sampling, flow rates were rechecked, the filter was removed using clean forceps, folded in half with exposed side closed, and placed in small, labelled Ziploc bag. OPC data was downloaded to a laptop.

Filters were stored in a clean and sealed plastic box at room temperature until transferred to the University of Michigan (Ann Arbor, MI, USA) for gravimetric and PAH analyses. Filters were conditioned for 48-hr (25 ± 1 °C, RH = 33 ± 2), deionized for 30 min, and weighed to 1 μg precision. Each weighing was repeated and averaged if weights were within acceptance criterion (10 μg). Otherwise, filters were archived and later reweighed, and any filter with excessively high or low weights from the tare weight was not used.

### 2.5. PM analysis and calibration

We excluded gravimetric $PM_{2.5}$ measurements that collected over 600 μg of PM or if flows, totalizer or time values did not meet criteria, and optical measurements were exceeded if the (1-min) measurement exceeded 2000 $\mu g/m^3$ (Kwarteng et al., 2020). With the cleaned dataset, we compared optical and gravimetric measurements and evaluated differences that may have resulted from potential differences in calibration as well as losses in the inlet tubing. $PM_{2.5,OPT}$ measurements were adjusted to match $PM_{2.5,GRAV}$ using a correction factor equal to the ratio of the mean concentrations for pairs of optical and gravimetric measurements that had at least 80% overlap of the sampling period.

Since gravimetric $PM_{10}$ measurements were not obtained, only a partial adjustment could be made for $PM_{10,OPT}$. This used the sum of the corrected $PM_{2.5,OPT}$ and the corrected coarse fraction optical concentration ($PM_{2.5\text{-}10,OPT}$), determined as the difference between $PM_{10,OPT}$ and $PM_{2.5,OPT}$ for each measurement pair multiplied by an experimentally-determined correction for $PM_{2.5\text{-}10}$ losses in the inlet tubing. This correction was based on experiments that compared OPC measurements with and without the inlet and associated tubing in five consecutive 7-min phases using two new OPCs, designated “reference” and “test” instruments, respectively. In these tests, instruments were placed side-by-side and 1-min measurements of ambient air were obtained throughout the following phases. In “baseline” phases 1, 3, and 5, inlets of both instruments were connected to short (5 cm) tubes and conical aerodynamic inlets; in phases 2 and 4, the “test” sampler used inlet tubing comparable to that in the backpack. The 2-min of data between phases were excluded, and trend plots were checked to ensure that PM levels during each phase were approximately stationary. Baseline data were used in regressions to calibrate the two instruments for each size range, after which PM losses attributable to the inlet tubing, $L_D$ (%), were calculated as:

$$L_D = 100\%[1 - C_{TEST,D}/C_{REF,D}] \tag{1}$$

where $C_{TEST,D}$ and $C_{REF,D}$ are the average (calibrated) test and baseline concentrations for size range D (μm). These experiments were repeated twice. Uncertainties were estimated as standard deviations of the measurements and for $L_D$ using error propagation techniques.

Numerical experiments were conducted to better understand losses in the inlet and tubing. These simulated the penetration of particles from 0.1 to 10 μm diameter through the tubing and inlet configuration (tubing diameter, length, transitions, and orientation) using the Particle Loss Calculator (Max-Planck Institute for Chemistry, 2020), which accounts for diffusion, deposition, and sedimentation losses. The simulated system had four tube sections representing the vertical inlet, a vertical tube from the inlet to the shoulder, a horizontal tube over the shoulder, and finally a downward tube into the backpack. (The geometry of four sections were: 2 cm × 0.6 cm × 90° (length, diameter, inclination); 20 cm × 0.3175 cm × 90°; 15 cm × 0.3175 cm × 0°; and 20 cm × 0.3175 cm × 90°). For the inlet, we assumed an aspiration angle of 90° in a 3 m/s wind, and for particles, we assumed shape factor of 1.8 and density of 1300 kg/$m^3$. Finally, the size-specific PM losses were converted to $PM_{2.5}$ and $PM_{10}$ losses using procedures in ISO 16890-1 Annex B and the standard urban particle size distribution.

### 2.6. PAH analysis

For analysis of PAHs, 41 exposed $PM_{2.5}$ filters were selected from 31 e-waste workers and 10 participants from Madina. The selection was balanced among the participants in rounds 1 and 2, and selected workers by task as follows. Among e-waste workers, we identified “burners” who conducted waste burning, and “dismantlers,” “collectors” and “sorters” who performed these activities but who did not perform burning during the sampling period. Workers were excluded if a gravimetric filter measurement was missing, or if they or others nearby were observed smoking. All identified participants or the first ten (whichever came first) with the longest activity duration were chosen from each category. Among Madina-Zongo participants, individuals were selected randomly.

PAHs were extracted by liquid-liquid extraction. After their final weighing, filters were placed in pre-cleaned 15 mL glass centrifuge tubes (Kimble Conical-bottom, Fisher Scientific, Pittsburgh, PA, USA), spiked with 10 μL of deuterated (Perylene-$d_{12}$, 0.5 μg/mL in nonane) surrogate standard, 1 mL of 6 M HCl was added, and the tube was sonicated to disrupt any biological materials. Then, 6 mL methanol: isopropanol (1:1) was added and the mixture was sonicated for 20 min, followed by additions of 6 mL of hexane:methyl tert butyl ether (MTBE; 1:1), 2 mL of PAH-free water, and sonication for another 20 min. The contents were then centrifuged for 10 min at 4500 rpm. The organic layer was transferred to a new disposable 15 mL polypropylene centrifuge tube (Falcon, Fisher Sci., Pittsburgh, PA, USA). We added 3 mL of hexane:MTBE (1:1) to the bottom layer leftover in original glass tube, vortexed both tubes for 1 min, and then centrifuged for 10 min at 4500 rpm. The organic layers of the two tubes were combined into another 15 mL pre-cleaned glass conical tube and evaporated down to 1 mL under ultrapure nitrogen flow at 40 °C. We then added 3 mL of hexane and proceeded to clean-up the extract using a pre-cleaned fritted glass column with a Teflon stopcock containing 1 mL of activated silica/$H_2SO_4$ and 0.5 mL of activated silica. The column was conditioned with 9 mL hexane/dichloromethane (DCM; 1:1). The sample extract was introduced, eluted and further washed with 8 mL of hexane/DCM (1:1). The eluant was evaporated to 1 mL, 0.5 mL of n-nonane was added, and then re-evaporated to 1 mL. The final extract was spiked with internal standard (chrysene-$d_{12}$), transferred into a GC–MS vial, crimp capped, and refrigerated at 4 °C until analysis.

We quantified 26 PAHs, including the standard EPA list plus other abundant and potentially toxic compounds (Table S1) using gas chromatography/mass spectrometry (GC/MS). A 2 μL aliquot was injected into a splitless injector port maintained at 280 °C on the GC/MS (Agilent 6890 N/5973, Agilent Technologies, Santa Clara, CA) equipped with a 30 m × 0.25 mm i.d. × 0.25 μm thickness capillary column (Equity-5, Supelco, St. Louis, MO, USA). The MS was operated in electron impact (EI) mass-selective detection (SIM) mode using helium carrier gas (flow, pressure and average velocity of 0.7 mL/min, 5.43 psi and 31 cm/s, respectively). The GC temperature program started at 80 °C (held for 1 min), increased at 15 °C/min to 150 °C, then further increased at 5 °C/min to 200 °C, increased at 10 °C/min to 300 °C, and then held for 20 min (total run time of 46 min). PAHs were identified based on retention time and abundance of quantification/confirmation ions (Table S1). Quantification was performed using multipoint calibration curves spanning 0.2–100 ng/mL concentrations. Samples with concentrations exceeding this range were diluted and re-analyzed to obtain results in the reportable range. Calibrations used authentic standards (Cambridge Isotope Laboratories, Inc., Tewksbury, MA, USA). The method detection limit (MDL) estimated using a signal/noise (S/N) ratio of 3 varied from 0.2 to 5.9 ng/mL (Table S1); the MDL for air concentrations (ng/$m^3$) is obtained by dividing this value by 2.9 (the typical sampling volume in $m^3$).

### 2.7. Health risk calculations

Cancer and non-cancer risks attributable to PAH exposure were estimated for e-waste workers and the reference population following U. S. Environmental Protection Agency guidelines (US EPA, 2009). The cancer risk attributable to exposure to the $i^{th}$ PAH, $CR_i$, was estimated as:

$$CR_i = C_i \times IUR_i \times \frac{FR \times FA \times ET \times EF \times ED}{AT} \tag{2}$$

where $C_i$ = concentration (μg/$m^3$) of the $i^{th}$ PAH, $IUR_i$ = inhalation unit risk factor for the $i^{th}$ PAH, FR = retention factor (dimensionless), FA = absorption factor (dimensionless), ET = exposure time (hr/day), EF = exposure frequency (day/year of work), ED = exposure duration (upper bound time for occupational exposure time), and AT = average duration of exposure (hr). IURs are available for 12 PAHs (USEPA, 2017) and listed in Table S2. For the dosimetry factors, we assumed that FR = 1, FA = 1, ED = 40 years, and AT = 350,400 hr (40 years), and the worker survey averages were used for ET = 9.4 hr/day and EF = 307 day/years, which gave a result of 0.33, i.e., occupational exposure was assumed to occur 33% of the working life. This exceeds the 23% typically assumed in developed countries where ET = 8 hr/day and EF = 250 day/yr.

The likelihood of non-cancer risks was based on the ratio of the concentration of each PAH compound to its reference concentration ($RfC_i$, μg/$m^3$):

$$RQ_i = \frac{C_i}{RFC_i} \tag{3}$$

where RQ = risk quotient (unitless). The RfC is a concentration where continuous lifetime exposure is likely to be without an appreciable risk of deleterious effects. Adverse health impacts may occur as RQ approaches 1; sometimes a more conservative value of 0.1 is used. RfCs exist for only two of the 26 PAHs (BaP and naphthalene; Table S2).

### 2.8. Quality control and assurance

Quality control and assurance (QA/QC) included the use of standard log forms, blanks, check samples, and standard reference materials. Strict contamination control procedures were implemented, e.g., cleaning and purity checking of standards, solvents and apparatus, periodic spike and surrogate recovery tests, and sample replicates and blanks (field, laboratory and instrumentation). Field and laboratory blanks were analyzed together with the samples. Blanks were run with each sample batch. Each sample used internal standards and a labeled surrogate, and surrogate recovery ranged from 70 to 110%. Spike recoveries were within 20% of expected values. All PAHs had linearity plots with $R^2$ exceeding 0.997. Three field blanks showed trace and consistent levels of several PAHs, but only naphthalene, phenanthrene and fluoranthene exceeded MDLs, and blank levels were low relative to samples. Blank subtractions were performed. Demographic (questionnaire) and exposure data were double entered and stored in Microsoft Access.

### 2.9. Data analysis

For each PAH compound, we calculated detection frequencies, and replaced values below the MDL with one-half of this value. For each sample, we calculated the sum of the total PAH, denoted ΣPAH, the sum of low (2–4 ring compounds) and high molecular weight (5–6 ring) PAHs, and computed abundances for each compound (μg/g), i.e., the mass fraction of the corresponding $PM_{25}$ concentration. PM and PAH measurements were investigated using correlations, trend plots, scatterplots and other descriptive statistics. Differences in concentrations and risks between groups, work tasks, and other factors were evaluated using two-tailed t and Mann-Whitney (M-W) tests for two independent samples and a significance level of $P = 0.05$. Due to the right-hand skew of the data and potential outliers, we report results of the non-parametric tests, e.g., M-W tests.

## 3. Results

### 3.1. Socio-demographic, health, occupational and residential characteristics

Table 1 and S3 summarize sociodemographic and some occupational characteristics of study participants. There were several differences between e-waste workers and the reference group: e-waste workers were younger (mean age of 26.7 versus 31.3 years); more likely to be single as compared to married or living with a partner (41.5 versus 68.5%); and fewer had attained at least a middle/junior high school education (48.1 versus 81.6%). 48.5–60.0% of individuals in both groups reported that they were current smokers, although few said that they had smoked more than 100 cigarettes in their lifetime. Fewer e-waste workers rated their general health as good to excellent (67.5 versus 84.2%).

**Table 1**
Sociodemographic and health characteristics of study participants at Agbogbloshie and Madina. SD is standard deviation. N = number of respondents to the question.

| Variable | Agbogbloshie | | | Madina | | |
|---|---|---|---|---|---|---|
| | Ave / % | SD | N | Ave / % | SD | N |
| Age at recruitment (years) | 26.7 | (6.6) | 142 | 31.3 | (9.4) | 65 |
| Educational attainment: middle school or more (%) | 48.1 | – | 129 | 81.6 | – | 49 |
| Marital status (single/no partner) (%) | 41.5 | – | 130 | 68.5 | – | 54 |
| Years working at e-waste site (years) | 4.0 | (5.9) | 113 | – | – | – |
| Working at e-waste site over 1 year (%) | 86.2 | – | 130 | – | – | – |
| Working a second job (%) | 14.8 | – | 128 | – | – | – |
| Working second job for > 6 month (%) | 50.4 | – | 129 | 36.7 | – | 49 |
| Days per week worked | 5.9 | (1.1) | 130 | – | – | – |
| Daily income less than 40 Cedis (%) | 50.0 | – | 130 | 39.2 | – | 51 |
| Sleeping at e-waste site (%) | 31.4 | – | 229 | – | – | – |
| Indoor cooking at residence (%) | 16.6 | – | 229 | 48.7 | – | 113 |
| Health status: good to excellent (%) | 67.5 | – | 231 | 84.2 | – | 114 |
| Ever smoked over 100 cigarettes (%) | 30.8 | – | 172 | 9.7 | – | 113 |
| Current smoker (%) | 48.5 | – | 99 | 60.0 | – | 5 |

Among e-waste workers, participants reported working at the site an average of 4.0 years (range: 1–25 year), 5.9 days per week (range: 3–7 day/week), and 9.4 hr/day (range: 2–15 hr/day). Almost half (50%) of the workers had held another job for 6 months or more. E-waste workers and the reference group earned more than Ghana's minimum daily wage of 11.82 Cedis (Vinorkor, 2019), although 50% of e-waste workers and 39% of the reference group earned below 40 Cedis. Nearly half (48%) of e-waste workers lived off-site but within 1 km of Agbogbloshie, and 31.4% reported sleeping at Agbogbloshie. Fewer e-waste workers reported cooking in their residence (16.6%) compared to the reference group (48.7%). Overall, Agbogbloshie workers were slightly younger, less educated, and poorer than the reference group.

Using survey and time-lapse photography data, we analyzed work activities for 383 shifts. "Other" work was performed by 17.0% of workers (N = 65), followed by dismantling (16.4%, N = 63), and collecting (6.5%, N = 25). There were few e-waste traders (2.1%, N = 9) or transporters (2.1%, N = 8). More dismantlers (59%) lived in homes where cooking occurred indoors compared to other e-waste recyclers (41%). Burners were the youngest and reported the fewest years of work (7.8 years) compared to other e-waste workers, while collectors had the longest tenure (11.4 years).

Time allocations for 171 shifts derived using the time-lapse photography showed that workers performed their primary activity for about half of the sampling period, e.g., burners averaged 99 min (range: 34–191 min) burning, and dismantlers spent 130 min on this task (range: 32–285 min; Table S4). Nearly all workers moved around the site and performed non-work activities, especially walking and resting, for substantial portions of the sampling period. Several workers performed multiple tasks. Workers indicated that their activities varied from day-to-day, and we saw considerable movement across the site and frequent overlap in work categories.

### 3.2. OPC correction factors and comparability of gravimetric and optical measurements

Optical $PM_{2.5}$ measurements were corrected using a correction factor of 1.425, based on the 346 paired optical and gravimetric measurements. This factor did not vary significantly or consistently when data were stratified by site (Agbogbloshie and Madina-Zongo), round (1–3), or backpack system (1–5). For $PM_{10}$, experiments comparing optical measurements with and without the inlet tubing showed losses of 1, 19 and 23% for $PM_{2.5}$, $PM_{10}$ and $PM_{2.5\text{-}10}$, respectively (Fig. S2); uncertainties were higher for the larger particles due to relatively low concentrations during these tests. These results give a correction factor of 1.300 (derived as 1/[1–0.231]) for optical $PM_{2.5\text{-}10}$, which compensated for particle losses in the inlet and tubing. The final "hybrid" $PM_{10}$ correction factor uses the $PM_{2.5}$ correction factor (1.425) and the $PM_{2.5\text{-}10}$ correction factor (1.300), which are applied to the $PM_{2.5}$ and $PM_{2.5\text{-}10}$ fractions of each $PM_{10}$ measurement. For the average $PM_{10}$ measurement (N = 428), the adjusted $PM_{10}$ concentration was 35.4% higher than the unadjusted mean.

Inlet and tubing losses predicted using the Particle Loss Calculator (Fig. S3) were under 2% for 1 μm diameter and smaller particles, and 18 and 85% for 2.5 and 7 diameter μm particles, respectively. Applying the ASTM 1680-1 procedure gave losses of 12 and 36% for $PM_{2.5}$ and $PM_{10}$, respectively. Losses for larger particles mount quickly due to sedimentation in non-vertical sections of the tubing, deposition, and inlet losses at high wind velocities. This analysis suggests that inlet and tubing losses explain ~40% of the $PM_{2.5}$ adjustment factor. While higher than field experiments, predicted losses showed similar trends. Experimental losses may be affected by particle bounce, differences in aerosol characteristics (e.g., reflectivity, size distributions, density, shape factors), approximations in the geometric representation, uncorrected discrepancies between the two OPC instruments, modeling limitations, and other reasons. Predictions from the Particle Loss Calculator, while not used directly in these corrections, support this approach.

The gravimetric and optical $PM_{2.5}$ measurements had a correlation coefficient 0.74 (N = 346). Correlations were higher with higher coverage criteria (time overlap), e.g., 98% coverage increased correlations to 0.84, although the sample size decreased (N = 118; Fig. S4B). The most notable discrepancies in the scatterplot (Fig. 1) were several samples with high gravimetric concentrations but low optical concentrations. Possible reasons for these discrepancies were explored, e.g., a disconnected OPC sampling tube or contaminated filter, but none could be confirmed. Table 2 summarizes these data (listed under “simult”) and shows that the corrected optical measurements had the same mean concentration as gravimetric measurements (as intended), but slightly less dispersion (e.g., 10th to 90th percentile ranges for optical and gravimetric measurements were 40–133 and 35–147 μg/m$^3$, respectively). Overall, these results show good agreement between optical and gravimetric measurements.

### 3.3. $PM_{2.5}$ and $PM_{10}$ levels

The PM data are summarized in Table 2, and $PM_{2.5}$ and $PM_{10}$ trend plots are shown in Figs. 2 and 3, respectively. Across the study, $PM_{2.5}$ concentrations at Agbogbloshie (93 ± 56 and 99 ± 56 μg/m$^3$ for $PM_{2.5,GRAV}$ and $PM_{2.5,OPC}$, respectively, median ± interquartile range) were twice that measured for the Madina-Zongo reference group (43 ± 25 and 49 ± 20 μg/m$^3$; N = 114–138), and these groups differed significantly ($P < 0.001$). $PM_{10,OPT}$ levels were also significantly elevated at Agbogbloshie compared to Madina (medians of 218 ± 158 versus 131 ± 108 μg/m$^3$; $P < 0.001$; N = 138–290). Both optical and gravimetric measurements were right skewed with several potential outliers, especially $PM_{10,OPT}$, e.g., 1-min measurements reached 1600 μg/m$^3$ at Madina-Zongo in January 2018, which affected metrics like averages and standard deviations.

As noted, gravimetric and optical measurements of $PM_{2.5}$ were highly correlated (Fig. S4). $PM_{2.5,OPT}$ and $PM_{10,OPT}$ measurements also were highly correlated, however, the relationship varied between the two sites (Fig. S5). $PM_{2.5}$ represented 45 ± 17% (median and interquartile range, N = 281) of $PM_{10}$ at the e-waste site, but only 34 ± 16% (N = 118) at Madina-Zongo. This difference increased at higher concentrations, e.g., for the highest 10% of $PM_{2.5,OPT}$ measurements, the $PM_{2.5}$ fraction was 51 ± 8% (N = 28) at Agbogbloshie but only 29 ± 7% (N = 14) at Madina-Zongo. This suggests the significance of combustion-related PM at Agbogbloshie since most $PM_{2.5}$ is combustion-related, while coarse fraction PM ($PM_{2.5\text{-}10}$) is mostly mechanically-derived with a large crustal fraction. PM levels by task provide additional evidence of PM sources, as discussed next.

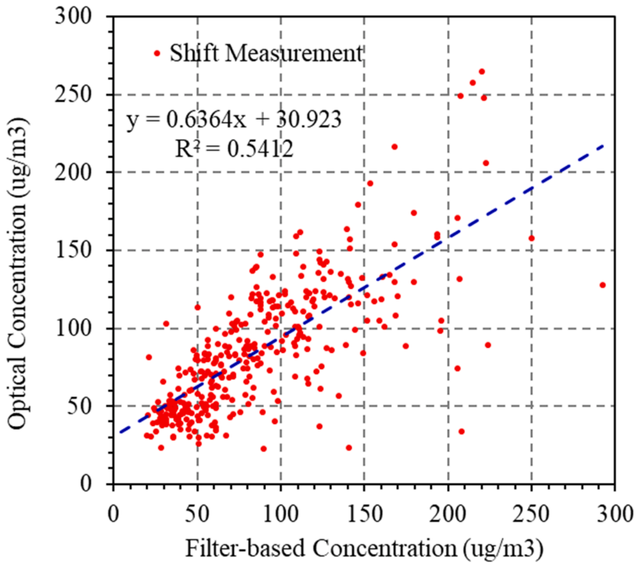

**Fig. 1.** Comparison of gravimetric and adjusted optical $PM_{2.5}$ concentrations for first three sampling rounds. (N = 346).

PM levels at the e-waste site differed by task. Based on worker classification (based on time lapse photo and survey data), $PM_{2.5}$ and $PM_{10}$ levels were highest for burners, intermediate for dismantlers, and lowest for sorters and collectors (Table 3). Based on activities determined by the time lapse photos, the differences were often large and statistically significant, e.g., burners had the highest $PM_{2.5,\ GRAV}$ (median concentrations of 124 versus 88 μg/m$^3$ for other workers, $P = 0.03$) and e-waste traders the lowest (56 versus 93 μg/m$^3$, $p < 0.004$, Table S7). Considering activities lasting at least 30 min, workers performing dismantling had higher $PM_{10,OPT}$ levels (277 versus 214 μg/m$^3$, $P = 0.02$); workers on a motorbike or in a car had lower $PM_{2.5,OPT}$ levels (78 versus 104; $P = 0.02$); and walking was associated with higher $PM_{2.5,OPT}$ (112 versus 93 μg/m$^3$; $P = 0.03$). A black smoke plume visible in the time lapse photos was associated with higher $PM_{2.5,OPT}$ (132 versus 98 μg/m$^3$, $p = 0.01$) and higher $PM_{10,OPC}$ (334 versus 220 μg/m$^3$, $P = 0.01$); and being in or near the fire pit was associated with higher $PM_{2.5,GRAV}$ levels (109 versus 91 μg/m$^3$, $P = 0.03$; Table S7).

At the fixed sites, $PM_{2.5,OPC}$ levels were 48 ± 49, 74 ± 58, and 55 ± 45 μg/m$^3$ at the upwind, central and downwind locations, respectively, and $PM_{10,OPT}$ levels were 157 ± 128, 182 ± 133, and 163 ± 125 μg/m$^3$ (median ± IQR). Hourly data showed a strong and consistent diurnal pattern with much higher levels in the evening and the lowest levels during the day. $PM_{2.5,OPT}$ levels for the 9 am to 3 pm period corresponding to the shift samples collected in the present study were 39 ± 31, 56 ± 36, and 40 ± 23 μg/m$^3$ at the three sites; $PM_{10,OPT}$ levels were 118 ± 114, 154 ± 101, and 139 ± 78 μg/m$^3$. Comparisons using the central site during the midday period are most relevant to the present study, and using medians reported above, breathing zone concentrations of workers were 78% higher for $PM_{2.5}$ and 57% higher for $PM_{10}$ compared to the fixed site levels. For the reference community, breathing zone $PM_{2.5}$ and $PM_{10}$ levels were 22 and 15% lower, respectively, than levels at Agbogbloshie, but comparable (within 9%) to downwind levels. Overall, PM in breathing zone air of workers is considerably elevated compared to the ambient monitoring data, expected given the many activities performed by workers that generate emissions at the e-waste site.

Measured $PM_{2.5}$ levels far exceeded WHO and other community standards (Chowdhury et al., 2019; Niaz et al., 2016; USEPA, 2019; WHO, 2006), although they do not exceed occupational exposure limits, e.g., the 8-hour time-weighted average (TWA) for total and respirable PM (5 and 10 mg/m$^3$, respectively (Occupational Safety and Health Administration, 2018). $PM_{2.5}$ and $PM_{10}$ levels at the e-waste site were approximately twice those at the reference site, and substantially elevated over fixed site monitoring at the site. $PM_{2.5}$ levels experienced by burners likely reflected fire-related emissions. $PM_{10}$ levels experienced by dismantlers likely resulted from hammering, machete cutting, and other mechanical activities that generated coarse fraction PM. The differences in PM levels by worker classification and activity were smaller than expected, probably since most hazardous activities were performed for short periods, workers were mobile and performed multiple tasks, and even while resting, workers often were near (~10 m) burning areas (Laskaris et al., 2019).

### 3.4. PAH concentrations, composition and abundances

Table 4 summarizes PAH concentrations among e-waste workers and the Madina-Zongo reference group using samples that met QA criteria

**Table 2**

Gravimetric and optical $PM_{2.5}$ and $PM_{10}$ concentrations (μg/$m^3$) for e-waste workers (AG) and reference sample (MD). NOBs is the number of observations. "Simult" is for periods when both gravimetric and optical measurements are available. Optical measurements adjusted as described in text.

| | Gravimetric PM2.5 | | | | Optical PM2.5 | | | | Optical PM10 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | All | Simult | AG | MD | All | Simult | AG | MD | All | AG | MD |
| NOBs | 361 | 347 | 247 | 114 | 428 | 347 | 290 | 138 | 428 | 290 | 138 |
| **Average** | **86** | **85** | **101** | **53** | **96** | **85** | **107** | **74** | **251** | **255** | **244** |
| St.Dev. | 47 | 47 | 44 | 38 | 70 | 41 | 66 | 73 | 221 | 158 | 317 |
| Min | 4 | 4 | 21 | 4 | 23 | 23 | 28 | 23 | 53 | 68 | 53 |
| 10th | 35 | 35 | 52 | 28 | 39 | 41 | 52 | 31 | 94 | 114 | 82 |
| 25th | 50 | 50 | 68 | 34 | 51 | 51 | 76 | 41 | 127 | 156 | 97 |
| **50th** | **76** | **76** | **93** | **43** | **83** | **81** | **99** | **49** | **188** | **218** | **131** |
| 75th | 112 | 111 | 124 | 59 | 118 | 113 | 122 | 61 | 290 | 314 | 205 |
| 90th | 149 | 147 | 161 | 80 | 157 | 133 | 155 | 178 | 419 | 408 | 599 |
| 95th | 179 | 178 | 184 | 115 | 206 | 153 | 180 | 268 | 680 | 483 | 1035 |
| Max | 292 | 292 | 292 | 221 | 631 | 265 | 631 | 337 | 1693 | 1228 | 1693 |

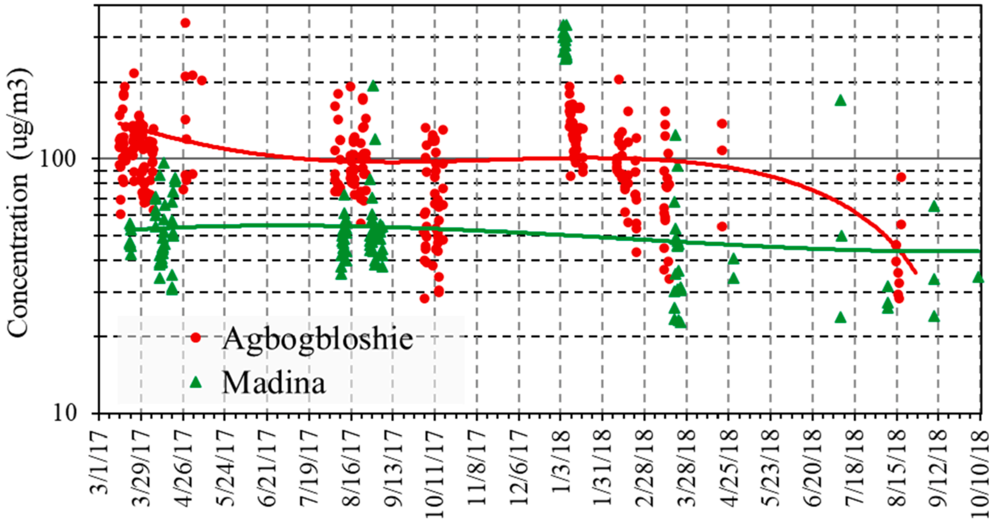

**Fig. 2.** Trends of personal $PM_{2.5}$ concentrations at Agbogbloshie and Madina over the entire study. Uses adjusted optical concentrations; points show individual measurements. Trend lines fitted with 3rd order polynomial.

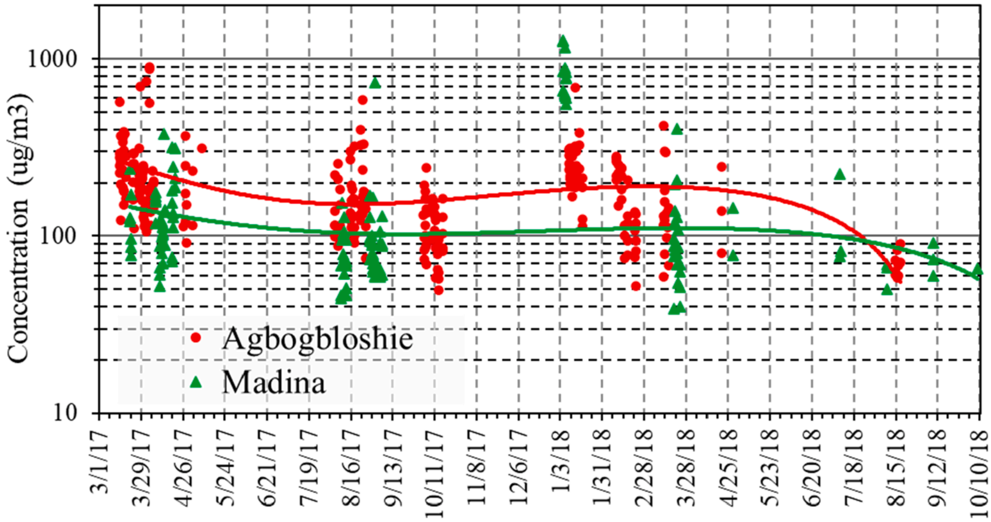

**Fig. 3.** Trends of personal $PM_{10}$ concentrations at Agbogbloshie and Madina. Otherwise as Fig. 2.

(N = 31). Most PAHs were detected in most samples above MDLs with the exception of several pyrene compounds that had high MDLs. PAH levels across the samples showed considerable variability, and several outliers were apparent. At the e-waste site, the median ΣPAH concentration was 88.4 ng/$m^3$ compared to 67.7 ng/$m^3$ at Madina. Fig. 4 displays concentrations of each PAH ranked by concentration. Naphthalene was the most abundant compound, reaching 82.83 and 72.53 ng/$m^3$ in individual measurements at the e-waste and reference

**Table 3**
$PM_{2.5}$ and $PM_{10}$ concentrations (μg/$m^3$) by work category. Optical concentrations are adjusted. Uses rounds 1 and 2. "Other" is non-e-waste jobs. NOBs is number of observations.

| Measurement Type | | Work Type | | | | |
|---|---|---|---|---|---|---|
| | | Burner | Dismantler | Sorter | Collector | Other |
| Gravimetric PM2.5 | NOBs | 44 | 91 | 10 | 22 | 89 |
| | **Average** | **112** | **86** | **64** | **73** | **43** |
| | St.Dev. | 43 | 33 | 21 | 30 | 17 |
| | Min | 39 | 34 | 39 | 21 | 4 |
| | 10th | 58 | 51 | 48 | 40 | 26 |
| | 25th | 85 | 61 | 51 | 52 | 32 |
| | **50th** | **108** | **79** | **59** | **74** | **39** |
| | 75th | 140 | 100 | 73 | 87 | 53 |
| | 90th | 164 | 125 | 80 | 96 | 67 |
| | 95th | 192 | 157 | 97 | 103 | 72 |
| | Max | 206 | 179 | 113 | 170 | 115 |
| Adjusted Optical PM2.5 | NOBs | 57 | 99 | 11 | 23 | 93 |
| | **Average** | **138** | **102** | **84** | **85** | **54** |
| | St.Dev. | 111 | 55 | 17 | 30 | 21 |
| | Min | 40 | 28 | 56 | 31 | 31 |
| | 10th | 72 | 57 | 63 | 45 | 39 |
| | 25th | 87 | 73 | 75 | 67 | 43 |
| | **50th** | **111** | **94** | **81** | **86** | **50** |
| | 75th | 134 | 119 | 97 | 105 | 56 |
| | 90th | 207 | 140 | 103 | 120 | 72 |
| | 95th | 366 | 181 | 107 | 122 | 84 |
| | Max | 631 | 500 | 111 | 147 | 195 |
| Adjusted Optical PM10 | NOBs | 57 | 99 | 11 | 23 | 93 |
| | **Average** | **300** | **244** | **236** | **210** | **159** |
| | St.Dev. | 222 | 153 | 110 | 94 | 115 |
| | Min | 112 | 68 | 144 | 77 | 61 |
| | 10th | 137 | 115 | 177 | 119 | 83 |
| | 25th | 167 | 153 | 182 | 146 | 98 |
| | **50th** | **239** | **211** | **194** | **180** | **131** |
| | 75th | 336 | 285 | 230 | 271 | 172 |
| | 90th | 455 | 392 | 343 | 331 | 234 |
| | 95th | 757 | 488 | 435 | 394 | 320 |
| | Max | 1228 | 1009 | 528 | 428 | 967 |

sites, respectively. This is the most volatile PAH, and most is expected to be in the vapor phase (ATSDR, 2005). While levels of individual PAHs at the e-waste site generally exceeded levels at the reference site (differences were statistically significant for several compounds), compositions at the two sites were similar.

PAH and $PM_{2.5}$ concentrations had low correlation (Fig. 5A). However, PAH abundances were inversely related to $PM_{2.5}$ concentration (Fig. 5B) and several compounds showed strong inverse relationships, e.g., dibenzo(a,i)pyrene and dibenzo(a,h)pyrene ($R > 0.8$, Fig. S6). PAH abundances differed significantly between the e-waste and reference sites ($p < 0.03$), and target PAH compounds comprised a median of 981 and 1834 μg/g of $PM_{2.5}$ mass at the e-waste site and the reference community, respectively. Both low and high molecular weight PAHs had similar trends. Thus, while $PM_{2.5}$ levels at the e-waste site were approximately twice that of the reference community, PAH abundances were only about half as much.

While larger differences between e-waste workers and the reference community were expected, these results have several explanations. First, the high PM concentrations at Agbogbloshie result from multiple sources, including entrained soil, dust, metals, and other organic-poor compounds, as well as combustion products containing PAHs. This is supported by the finding that many of the most elevated $PM_{2.5}$ measurements at Agbogbloshie also had high $PM_{10}$ levels, suggesting sizeable contributions from PAH-poor dusts and soils (Fig. S5). Further support is suggested by the 7 filters analyzed for PAHs but rejected due to filter overload (which alters the PM size cut) that showed relatively low PAH levels in coarse fraction PM. Finally, the reference community has PAH exposure due to vehicle exhaust and biomass fuel combustion (e.g., cooking), supported by the extensive traffic in Madina-Zongo and our survey data that showed more individuals cooking at home at Madina-Zongo.

### 3.5. Health risk estimates

Non-cancer and cancer risk estimates are listed in Table 5 for e-waste workers and the reference community. Hazard quotients (HQs) calculated for naphthalene and benzo(a)pyrene, the PAHs with reference concentrations, were below 1, which suggests minimal likelihood of an adverse non-cancer health effect. As mentioned, much of the naphthalene is likely to be in volatile phase, and thus is not reflected in the $PM_{2.5}$ measurements. For several PAHs, lifetime excess cancer risks exceeded the $10^{-6}$ criterion often used (USEPA, 2017). This occurred for upper bound concentrations of dibenz(a,h)anthracene and several pyrenes (benzo{[e] or [i]} aceanthrylene, dibenzo(a,l)pyrene, dibenzo(a,i)pyrene and dibenzo(a,h)pyrene. While some of the higher risk estimates occurred for dibenzo(a,i)pyrene, this compound had very low detection frequencies and thus these measurements are uncertain. Alternate exposure metrics, in particular the geometric mean, did not substantially alter these results. Table 5 also shows the cancer risk due to all PAHs, calculated as the sum of the risks, which ranged from $3.4 \times 10^{-6}$ for the median exposure to $1.5 \times 10^{-5}$ for the maximum exposure, did not exceed the $10^{-4}$ criteria (USEPA, 2017). These risk estimates reflect occupational exposure for 9.4 hr/day and 5.9 day/week; no exposure is assumed the remainder of the time, and only the 12 PAHs that have cancer slope factors are considered. The average total cancer risk for e-waste workers was 30% higher than for the reference group.

Cancer risks attributable to PAH inhalation have been reported at a number of e-waste sites in several countries. The highest risk level reported, $9.7 \times 10^{-3}$ at the Guiyu, China e-waste incineration field, included both gaseous and particulate PAHs (Zhang et al., 2011). Most

**Table 4**

PAH concentrations (ng/m$^3$) measured on PM$_{2.5}$ filters from personal sampling. Also shows detection frequency (%) and relative difference (%) based on medians. T-test and MW-test show P values for difference between sites; statistically significant ($P < 0.05$) and marginally significant ($P < 0.10$) results are highlighted. Sample size is 34 for All, 24 for Agbogbloshie, and 10 for Madina.

| | All | | | | | Agbogbloshie | | | Madina | | | Site Differences | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Detect Freq (%) | Average | Median | IQR | Maximum | **Median** | IQR | Maximum | **Median** | IQR | Maximum | Percentage | *t*-test | MW-test |
| Naphthalene | 100 | 34.97 | **29.90** | 38.65 | 82.83 | **30.81** | 37.71 | 82.83 | **25.79** | 19.85 | 72.53 | 18 | 0.48 | 0.52 |
| 2-methylnaphthalene | 100 | 3.26 | **2.95** | 2.12 | 6.65 | **2.95** | 2.17 | 6.65 | **3.09** | 2.09 | 5.80 | −5 | 0.95 | 0.91 |
| Acenaphthylene | 41 | 0.37 | **0.05** | 0.65 | 1.25 | **0.05** | 0.81 | 1.25 | **0.05** | 0.30 | 1.03 | 6 | 0.31 | 0.31 |
| Acenaphthene | 41 | 1.34 | **0.21** | 2.51 | 4.83 | **0.21** | 2.63 | 3.95 | **0.20** | 1.51 | 4.83 | 6 | 0.87 | 0.57 |
| Fluorene | 100 | 2.54 | **2.27** | 1.94 | 5.64 | **2.18** | 1.84 | 5.64 | **2.82** | 2.66 | 5.01 | −26 | 0.97 | 0.91 |
| Phenanthrene | 100 | 16.11 | **15.73** | 8.65 | 30.20 | **14.67** | 6.04 | 30.20 | **19.39** | 8.36 | 23.14 | −28 | 0.73 | 0.57 |
| Anthracene | 41 | 0.14 | **0.12** | 0.08 | 0.35 | **0.12** | 0.09 | 0.35 | **0.09** | 0.08 | 0.33 | 28 | 0.54 | 0.15 |
| Fluoranthene | 100 | 3.78 | **3.57** | 1.58 | 6.75 | **3.77** | 1.79 | 6.10 | **3.55** | 0.32 | 6.75 | 6 | 0.75 | 0.73 |
| Pyrene | 100 | 1.90 | **1.80** | 1.43 | 4.46 | **2.04** | 1.69 | 3.93 | **1.28** | 1.08 | 4.46 | 46 | 0.49 | 0.34 |
| Benzo[c]phenanthrene | 68 | 0.28 | **0.33** | 0.36 | 0.59 | **0.35** | 0.36 | 0.59 | **0.28** | 0.32 | 0.51 | 22 | 0.40 | 0.23 |
| Benzo(a)anthracene | 65 | 0.15 | **0.14** | 0.21 | 0.45 | **0.17** | 0.18 | 0.45 | **0.03** | 0.17 | 0.31 | 135 | 0.12 | **0.10** |
| Chrysene | 97 | 1.59 | **1.62** | 0.39 | 2.73 | **1.64** | 0.28 | 2.73 | **1.35** | 0.43 | 2.14 | 19 | **0.07** | **0.04** |
| 5-Methylchrysene | 3 | 0.05 | **0.04** | 0.01 | 0.51 | **0.04** | 0.01 | 0.51 | **0.04** | 0.00 | 0.04 | 6 | 0.26 | **0.04** |
| Benzo[b]fluoranthene | 97 | 1.29 | **1.13** | 0.88 | 3.85 | **1.23** | 0.85 | 3.85 | **0.84** | 1.01 | 1.90 | 38 | 0.13 | 0.29 |
| Benzo[k]fluoranthene | 88 | 0.61 | **0.46** | 0.63 | 2.33 | **0.39** | 0.45 | 2.33 | **0.52** | 0.60 | 1.34 | −28 | 0.87 | 0.68 |
| Benzo[j]aceanthrylene | 100 | 2.52 | **2.52** | 0.91 | 4.34 | **2.60** | 0.82 | 4.34 | **2.28** | 1.23 | 3.31 | 13 | 0.46 | 0.52 |
| Benzo[e]pyrene | 85 | 0.74 | **0.63** | 0.77 | 2.79 | **0.68** | 0.67 | 2.79 | **0.27** | 0.60 | 1.45 | 86 | **0.07** | **0.03** |
| Benzo[a]pyrene | 76 | 0.54 | **0.58** | 0.40 | 1.33 | **0.59** | 0.24 | 1.33 | **0.20** | 0.48 | 0.83 | 101 | **0.01** | **0.03** |
| Perylene | 35 | 0.51 | **0.07** | 0.61 | 4.24 | **0.07** | 0.65 | 4.02 | **0.06** | 0.00 | 4.24 | 12 | 0.90 | **0.04** |
| Indeno[1,2,3-cd]pyrene | 74 | 1.96 | **0.79** | 2.87 | 9.38 | **1.12** | 2.95 | 9.38 | **0.15** | 0.31 | 5.61 | 153 | **0.10** | **0.01** |
| Dibenz[a,h]anthracene | 100 | 3.09 | **2.55** | 3.92 | 8.42 | **2.19** | 3.50 | 8.42 | **3.75** | 4.93 | 8.39 | −52 | 0.35 | 0.50 |
| Benzo[g,h,i]perylene | 76 | 1.82 | **0.96** | 2.81 | 7.00 | **1.99** | 2.75 | 7.00 | **0.25** | 0.29 | 4.19 | 155 | **0.02** | **0.01** |
| Dibenzo[a,l]pyrene | 38 | 0.81 | **0.21** | 1.16 | 4.48 | **0.22** | 1.26 | 4.48 | **0.19** | 0.02 | 2.10 | 16 | **0.10** | **0.05** |
| Dibenzo[a,e]pyrene | 15 | 0.59 | **0.44** | 0.17 | 2.30 | **0.47** | 0.24 | 2.30 | **0.42** | 0.03 | 0.87 | 13 | **0.06** | **0.03** |
| Dibenzo[a,i]pyrene | 0 | 0.97 | **0.98** | 0.14 | 1.12 | **1.00** | 0.12 | 1.12 | **0.94** | 0.06 | 1.06 | 6 | **0.07** | **0.04** |
| Dibenzo[a,h]pyrene | 0 | 0.94 | **0.94** | 0.14 | 1.08 | **0.96** | 0.12 | 1.08 | **0.91** | 0.06 | 1.02 | 6 | **0.07** | **0.04** |
| Sum_PAH | – | 82.9 | **84.1** | 35.8 | 132.4 | **88.4** | 29.7 | 123.4 | **67.7** | 39.4 | 132.4 | 26 | 0.31 | 0.17 |
| Sum_PAH_LMW | – | 66.3 | **63.6** | 35.3 | 114.1 | **66.9** | 26.6 | 111.2 | **55.9** | 27.8 | 114.1 | 18 | 0.48 | 0.31 |
| Sum_PAH_HMW | – | 16.5 | **15.2** | 8.5 | 45.3 | **15.7** | 7.6 | 45.3 | **13.5** | 7.4 | 30.5 | 16 | 0.19 | 0.12 |

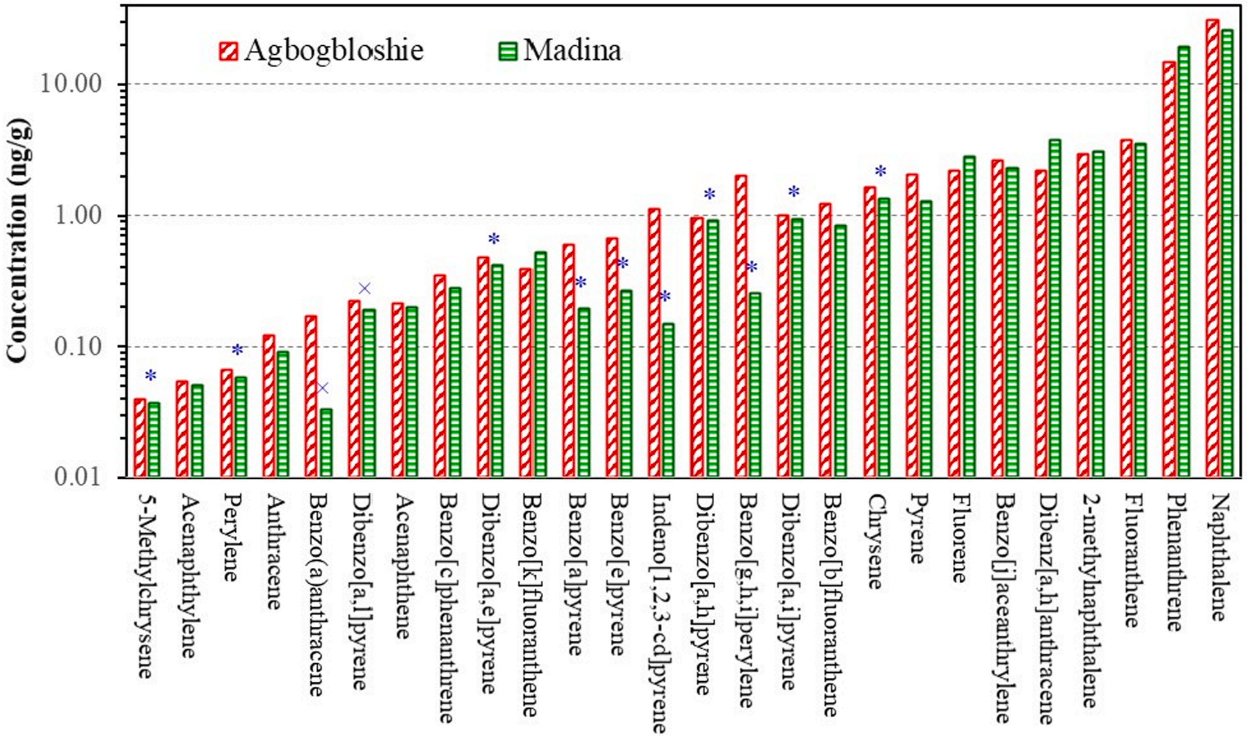

**Fig. 4.** Median PAH concentrations at Agbogbloshie (N = 24) and Madina (N = 10) ranked by concentration. Statistically significant differences shown by "*" and "x" at P = 0.05 and P = 0.10 levels, respectively.

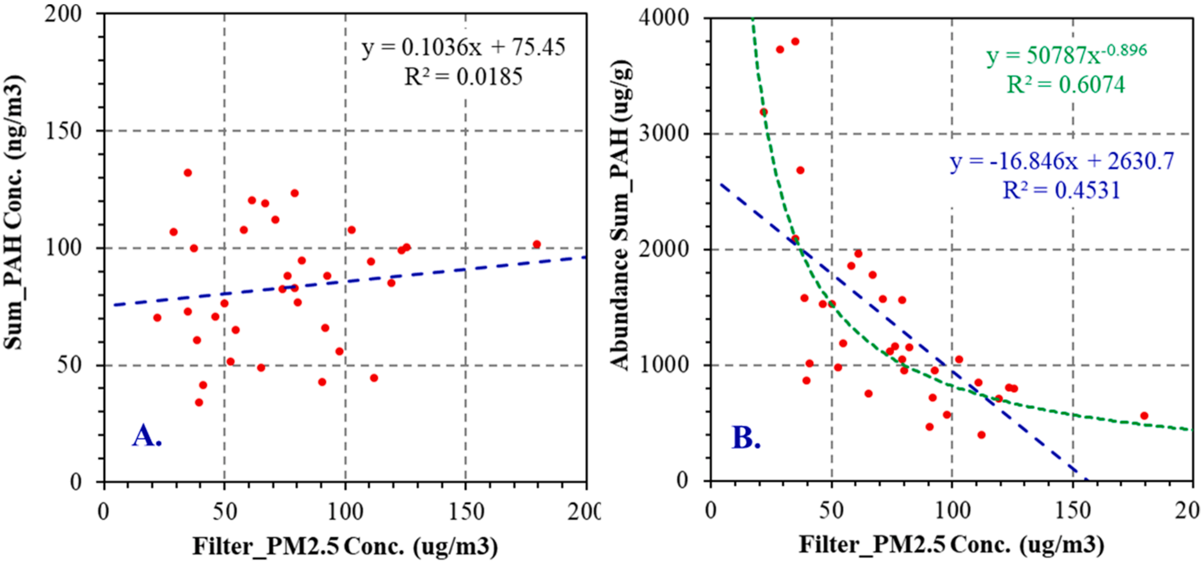

**Fig. 5.** A. ΣPAH concentrations versus $PM_{2.5}$ concentrations. B. ΣPAH abundance in $PM_{2.5}$ versus $PM_{2.5}$ concentrations. Dashed lines show linear and exponential model fits. N = 34.

studies, however, report risk levels in the $10^{-6}$ to $10^{-5}$ range. Cancer risk from PAH exposure at an e-waste site in Qingyuan, China was 1.5 × $10^{-5}$, about twice that at a nearby urban site, and much of the excess risk was attributed to 5 ring compounds (e.g., benzo(a)anthracene, benzo(b) fluoranthene, benzo(a)pyrene and dibenzo[a,i]pyrene) (Wang et al., 2012). Lower cancer risks, 1.0–1.9 × $10^{-6}$, were reported for e-waste and urban sites in Qingyuan and Guangzhou in southern China (Luo et al., 2015). At an e-waste dismantling area in southern China, median and high-end cancer risks were 0.5–3.0 × $10^{-6}$ and 1.2–7.8 × $10^{-6}$, respectively (Chen et al., 2019). In other industrial settings, risks associated with PAH have ranged widely, e.g., 4.7 × $10^{-5}$ in Changhua County, Tawian (S.J. Chen et al., 2016), 3.4 × $10^{-7}$ in Petaling Jaya, Malaysia (Jamhari et al., 2014), 3.6 × $10^{-4}$ in Guiyang, southwest China (Fan et al., 2018), and 6.0 × $10^{-4}$ in Guangzhou, in southeastern China (Liu et al., 2015). Comparable risk levels have been reported in several cities, e.g., 2.9–4.3 × $10^{-4}$ in Guiyang City, China (Fan et al., 2018), 4.7 × $10^{-5}$ in Changhua County, Taiwan (Y.C. Chen et al., 2016), and 0.7–2.3 × $10^{-6}$ in Beijing, China (Gao et al., 2016). Some of the urban risk may be attribution to the formation of secondary products (Liu et al., 2015).

**Table 5**
Estimated risks due to inhalation of particulate phase PAHs at the Agbogbloshie e-waste site and the Madina reference community. Based on analysis of personal sampling, $PM_{2.5}$ filters, and median and maximum concentrations.

| | Hazard Quotient | | | | Cancer Risk ($1 \times 10^{-6}$) | | | |
|---|---|---|---|---|---|---|---|---|
| | Agbogbloshie | | Madina | | Agbogbloshie | | Madina | |
| PAH | Median | Max | Median | Max | Median | Max | Median | Max |
| Naphthalene | 0.01 | 0.03 | 0.01 | 0.02 | 0.35 | 0.93 | 0.29 | 0.81 |
| Benzo(a)anthracene | – | – | – | – | 0.00 | 0.01 | 0.00 | 0.01 |
| Chrysene | – | – | – | – | 0.00 | 0.00 | 0.00 | 0.00 |
| 5-Methylchrysene | – | – | – | – | 0.01 | 0.10 | 0.01 | 0.01 |
| Benzo[b]fluoranthene | – | – | – | – | 0.02 | 0.08 | 0.02 | 0.04 |
| Benzo[k]fluoranthene | – | – | – | – | 0.00 | 0.00 | 0.00 | 0.00 |
| Benzo[a]pyrene | 0.30 | 0.66 | 0.10 | 0.41 | 0.12 | 0.26 | 0.04 | 0.16 |
| Indeno[1,2,3-cd]pyrene | – | – | – | – | 0.02 | 0.19 | 0.00 | 0.11 |
| Dibenz[a,h]anthracene | – | – | – | – | 0.43 | **1.67** | 0.74 | **1.66** |
| Dibenzo[a,l]pyrene | – | – | – | – | 0.44 | **8.88** | 0.38 | **4.16** |
| Dibenzo[a,e]pyrene | – | – | – | – | 0.09 | 0.46 | 0.08 | 0.17 |
| Dibenzo[a,i]pyrene | – | – | – | – | **1.98** | **2.23** | **1.87** | **2.10** |
| Sum | 0.31 | 0.69 | 0.11 | 0.44 | **3.47** | **14.80** | **3.43** | **9.25** |

## 4. Discussion

To our knowledge, this is the first study to estimate PAH exposures and risks at e-waste sites using personal air sampling, which provides the most accurate estimate of exposure. We found that $PM_{2.5}$ levels in personal air samples of workers were elevated compared to measurements at fixed sites at the informal Agbogbloshie e-waste site, and that worker exposure was approximately twice that of individuals in the reference community. Differences between PAH levels and risks, however, were smaller.

### *4.1. PM levels*

Personal monitoring in Accra area and the Brong Ahafo region of Ghana has shown that biomass burning is a major contributor to poor air quality (Arku et al., 2015; Van Vliet et al., 2013). Traffic also makes a significant contribution (Kwarteng et al., 2020). E-waste activities, including dismantling, sorting, shredding, and open burning of electrical wires/cables and e-waste waste, circuit boards and Styrofoam, as well as entrained dust and soil, further elevate PM levels at the e-waste site, demonstrated by both personal and fixed site monitoring.

Across all the e-waste workers, personal exposure measurements of $PM_{2.5}$ and $PM_{10}$ were substantially higher (78 and 57%, respectively) than the fixed site measurements, reflecting the localized activities occurring at Agbogbloshie to which workers are exposed. Waste burners had the highest PM exposures among the e-waste workers. Their exposure is influenced by the quantity and type of waste burnt, proximity to fire, frequency and time spent in the burning zone, and other factors (Bungadaeng et al., 2019). The prevailing wind speed and direction also influences worker exposure (Laskaris et al., 2019). Personal monitoring at e-waste sites has been limited. Our findings emphasize the need to account for worker tasks and activities, and to estimate exposure using personal measurements.

### *4.2. PAH sources and levels*

PAH sources at Agbogbloshie include the open burning of wastes such as printed circuit boards and plastic casings (Gu et al., 2019; Liu et al., 2020; Nishimura et al., 2017). Other PAH sources include traffic emissions, biomass burning, cooking, and resuspended dust (Awasthi et al., 2016; Bungadaeng et al., 2018; Fang et al., 2013; Gangwar et al., 2019; Gu et al., 2009a). PAH levels measured at Agbogbloshie and the reference community (median ΣPAH levels of 88 and 68 ng/$m^3$, respectively) can be compared to measurements at other e-waste and urban areas, however, PAH levels span an enormous range, e.g., 0.01–110,000 ng/$m^3$ in a review of 44 African studies (Munyeza et al., 2019). Comparisons among studies must account for measurement type (e.g., particulate versus gaseous phase; personal versus area sampling), setting (ambient, indoor, workplace), PAHs included (i.e., number and type of PAHs in ΣPAH), averaging times and statistics, and analytical approaches. Table S11 summarizes PAH levels reported in recent studies at e-waste recycling sites. These studies, which use fixed site monitoring at both on– and off-site locations, show average ΣPAH levels from 15 to 148 ng/$m^3$. An e-waste dismantling area in Taizhou, China showed site impacts and higher PAH levels (in $PM_{2.5}$) at night, and identified petroleum and biomass combustion as PAH sources (Gu et al., 2009b). At an e-waste site area in southern China, PAH levels were attributed to dismantling activities (Chen et al., 2019). At an e-waste site in a rural area in South China, PAH levels varied diurnally and seasonally, and both e-waste and non-e-waste emission sources were identified as contributors to PAH concentrations (Cayumil et al., 2016). The influence of wind speed and direction on PAH levels was noted in Guangzhou City, China (Liu et al., 2015).

Table S11 also summarizes ΣPAH levels reported in several urban studies, including cities in China and India where PAH emissions sources include poorly controlled biomass and coal combustion. Average ΣPAH levels in these studies ranged from 0.4 ng/$m^3$ in $PM_{10\text{-}2.5}$ to 263 ng/$m^3$ in $PM_{2.5}$. The most abundant PAHs were 4–6 ring PAHs (Andreou and Rapsomanikis, 2009; Liu et al., 2015; Mohanraj et al., 2012; Shi et al., 2010), and identified sources included vehicle emissions, petroleum, oil and coal combustion, domestic heating and biomass burning. These and other studies show that PAHs are mostly found in smaller PM, e.g., $PM_{2.5}$ (Shi et al., 2010; Zioła and Słaby, 2020).

In Ghana, airborne PAHs have been measured in four studies. As part of the MONET-Africa project (examining persistent organic pollutants in 15 African countries), monitoring at two residential locations in Accra showed median levels of 6–11 ng/$m^3$ at East Legon and 3–6 ng/$m^3$ at Kwabenya (based on assumed sampling volumes of 300–600 $m^3$), which exceeded estimated background levels by 2–3 times (Klánová et al., 2009). At Kwame Nkrumah University of Science and Technology campus and Kumasi city centre (~245 km northwest of Accra), median ΣPAH concentrations were 2.6 and 30 ng/$m^3$ respectively, and phenanthrene and benzo[g,h,i]perylene were the most abundant PAHs. Chemical mass balance apportionments identified diesel and gasoline combustion as PAH sources; estimated cancer risks were $1.2 \times 10^{-6}$ and $3.3 \times 10^{-6}$ for adults and children, respectively (Bortey-Sam et al., 2015). At the Accra-Tema highway tollbooth ~7 km east of Accra, sampling in November and December 2011 yielded ∑PAH concentrations of 810 ng/$m^3$, representing ~1% of the ambient $PM_{10}$ mass (89 ± 19 μg/$m^3$), and pyrene, anthanthrene, benzo(g,h,i)perylene and benz(a) anthracene were the most abundant PAHs (average concentrations of 171, 92, 74 and 71 ng/$m^3$, respectively). PAH levels were correlated with daily vehicular traffic (R = 0.7), and diesel and gasoline combustion were identified as PAH sources (Safo-Adu et al., 2014). At a semi-urban site in Abetifi, in eastern Ghana (~160 km from Accra), mean PAH levels reached 8.4 ng/m$^3$, gas phase PAHs exceeded particle-bound levels, and vehicle emissions and biomass combustion were identified as PAH sources using principal component analyses (Palm et al., 2019).

The e-waste and urban studies discussed above used fixed site monitoring. A review of PAH studies in Africa from 2000 to 2018 identified only one using personal monitoring (Munyeza et al., 2019). This review also noted that while 14 studies measured PAHs in both gaseous and particulate phases, 6 measured gaseous only, and 24 measured particulate only. The much higher levels found in personal samples at Agbogbloshie compared to fixed site sampling highlight the need for breathing zone samples, and the significance of both vapor and particulate phases indicates the need to sample both phases in future work.

### 4.3. PAH composition

PAH emissions arise from both petrogenic sources, e.g., spillage, pollution and transportation of oils and petroleum (Neff et al., 2005) and pyrogenic sources, e.g., incomplete combustion of coal, wood, petroleum, petroleum products and biomass (Balmer et al., 2019), which tend to produce different compositions. In urban settings, the dominance of 4–6 ring PAHs in particulate samples suggests that most of the PAH is emitted from pyrogenic sources and volatilization of 2–3 ring PAHs (S.J. Chen et al., 2016; Y.C. Chen et al., 2016). PAH composition also depends on phase partitioning, deposition, and atmospheric degradation (Cai et al., 2018; Liu et al., 2020; Zhang et al., 2011).

We found relatively high levels of 2 and 3-ring PAHs (particularly naphthalene and phenanthrene) on our particulate samples; other studies generally have shown larger contributions by 4 to 7 ring compounds. At lower temperatures, LMW PAHs may be found in the particulate phase (Chen et al., 2019; Luo et al., 2015; Zhang et al., 2011). Our results might be a consequence of high PM levels, which would enhance absorption of LMW compounds onto PM (Luo et al., 2015). In addition, our results may reflect “fresh” combustion and emission sources that differ somewhat from the literature studies, particularly since personal sampling would emphasize near-field activities of participants as compared to fixed sampling at locations that are relatively distant from sources that collect more “aged” aerosols.

### 4.4. Study limitations

Our results may not be representative or reflect worst-case conditions. In particular, we previously documented that the highest PM concentrations at the e-waste site and elsewhere in the community occur in the evening, a result of increasing atmospheric stability, continued burning, and other emissions (Kwarteng et al., 2020). This would increase breathing zone concentrations, moreover, burning and other recycling activities continue through the evening and night (Yu et al., 2016). We did not examine all PAHs (e.g., toxic nitrogenous PAHs, PAH metabolites), as well as other pollutants (e.g., metals), or other exposure routes, including ingestion and dermal contact that are relevant to PAH exposure (Obiri et al., 2013). While sampling included two seasons, we excluded the rainy season, and the sample sizes for PAHs were not always sufficient to contrast results. As in other risk assessments, the combined effect of exposures to multiple PAHs assumed additivity and does not account for possible synergetic and antagonistic effects (Gil et al., 2019). We did not measure gas-phase PAHs, which have been shown to be the dominant fraction in some studies. In addition, we did not measure PAH metabolites in urine, a technique used to assess occupational exposure at Agbogbloshie and elsewhere (Daso et al., 2016; Feldt et al., 2014; Tue et al., 2016), although this technique does not separate the inhalation pathway from other exposure pathways. Despite uncertainties, this study provides new findings on exposures and health risks associated with occupational exposure to $PM_{2.5}$ and PAHs among informal e-waste recyclers at Agbogbloshie e-waste site.

### 4.5. Study implications

Worker exposure to $PM_{2.5}$ and PAHs exceeded guidelines and risk based levels, and the gradient at the site shows the significance of emissions attributable to waste handling and recycling activities at the Agbogbloshie e-waste site. Chronic exposure to PM and PAHs can produce a number of adverse health effects. Among the PAHs, for example, naphthalene can cause chronic nasal inflammation, olfactory epithelial metaplasia, and respiratory epithelial adenoma (Table S2). Measures to reduce emissions and inhalational exposures are warranted, especially at the e-waste recycling site and among workers experiencing the greatest exposures. The contribution from non-industrial sources, including traffic and biomass combustion, is also significant and widespread and deserves attention. Implementation of effective workplace health and safety measures and an air quality management program are required to minimize exposures and reduce risks of adverse health effects. Future studies could help to establish the relationship between PAHs in ambient air and biological markers of exposure and health effects among e-waste workers.

## 5. Conclusion

This study characterized personal exposures of PAHs, $PM_{2.5}$ and $PM_{10}$ among e-waste workers at the Agbogbloshie e-waste site using personal measurements, shift samples, and gravimetric and optical sampling. Compared to an age- and gender-matched reference population, workers experienced approximately twice the PM exposure, with median $PM_{2.5}$ and $PM_{10}$ concentrations of 99 and 218 μg/m$^3$, respectively. PAH concentrations, determined for a subset of $PM_{2.5}$ samples, were elevated among workers by approximately 10–25%. Naphthalene and phenanthrene were the most abundant PAHs. Breathing zone measurements were significantly elevated compared to fixed site sampling at the e-waste site, showing the effect of worker activities and emphasizing the importance of using personal and shift samples to characterize worker and community exposure. Exposures were contributed by multiple sources, including vehicle exhaust and biomass burning, in addition to e-waste activities. Both PM and PAH levels exceeded standards and risk-based guidelines, indicating the need to reduce emissions and provide respiratory protection.

## 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 material

Supplementary data to this article can be found online at https://doi.

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