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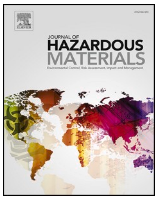

Airborne volatile organic compounds at an e-waste site in Ghana: Source apportionment, exposure and health risks

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ABSTRACT

Informal e-waste recycling processes emit various air pollutants. While there are a number of pollutants of concern, little information exists on volatile organic compounds (VOCs) releases at e-waste sites. To assess occupational exposures and estimate health risks, we measured VOC levels at the Agbogbloshie e-waste site in Ghana, the largest e-waste site in Africa, by collecting both fixed-site and personal samples for analyzing a wide range of VOCs. A total of 54 VOCs were detected, dominated by aliphatic and aromatic compounds. Mean and median concentrations of the total target VOCs were 46 and 37 $\mu g/m^3$ at the fixed sites, and 485 and 162 $\mu g/m^3$ for the personal samples. Mean and median hazard ratios were 2.1 and 1.4, respectively, and cancer risks were 4.6×10^{-4} and 1.5×10^{-4}. These risks were predominantly driven by naphthalene and benzene; chloroform and formaldehyde were also high in some samples. Based on the VOC composition, the major sources were industry, fuel evaporation and combustion. The concentration gradient across sites and the similarity of VOC profiles indicated that the e-waste site emissions reached neighboring communities. Our results suggest the need to protect e-waste workers from VOC exposure, and to limit emissions that can expose nearby populations.

1. Introduction

Electrical and electronic equipment (EEE) is indispensable and ubiquitous in modern societies. Globally, EEE production reached 53.6 million tons in 2019, or 7.3 kg/year per capita, and is estimated to increase by 2.5 million tons/year and reach 74.7 million tons by 2030 (Forti et al., 2020). This massive production has generated a parallel stream of EEE waste or e-waste. In the relatively small West African country of Ghana, e-waste recycling has become an important revenue source in the informal economy (Asibey et al., 2020). While Ghana has enacted e-waste legislation and is trying to adopt the Basel Convention that would restrict e-waste imports, as well as establish funds to support related facilities and support research and public education addressing recycling (Daum et al., 2017), e-waste imports have grown from about 149,000 tons in 2009 to an estimated 300,000–840,000 tons in 2020 (Amoyaw-Osei et al., 2011). Described as Africa's largest electronic waste dumpsite, Agbogbloshie in central Accra, the capital of Ghana, has attracted international attention. Approximately 4500–6000 workers and another 1600 indirectly work at this well-organized scrapyard (Grant and Oteng-Ababio, 2012), where e-waste is processed using rudimentary methods, e.g., manual stripping to remove electronic boards for resale, open burning of wires to recover metals (copper, aluminum, iron), and open dumping of bulk components such as cathode-ray tubes (CRTs) (Ackah, 2017). Enforcement of environmental and workplace health and safety regulations is largely absent.

EEE itself can contain hazardous substances, including toxic metals (e.g., mercury, cadmium, lead) and persistent organic pollutants (polychlorinated biphenyls or PCBs, flame retardants). Open burning at e-waste sites can emit these chemicals, as well as polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs) and particulate matter (PM) (An et al., 2014; Tue et al., 2017; Wang et al., 2020). Chemicals found at e-waste sites have been associated with DNA damage, tissue damage, increased glucose levels, reproductive and genital disorders, and carcinogenicity (Ji et al., 2010; Li et al., 2019; McDonald, 2002; Zani et al., 2013). Attention to pollutant exposure and health impacts associated with e-waste recycling has increased (Asante et al.,

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2012; Bruce-Vanderpuije et al., 2019; Feldt et al., 2014; Moeckel et al., 2020), and stress, body aches, shortness of breath, chest pain, cough and dizziness have been reported among e-waste workers and in neighboring communities (Amphalop et al., 2020; Burns et al., 2016; Li et al., 2008; Ma et al., 2013; Yu et al., 2017).

While PM and metals measurements have been reported at e-waste sites in Ghana and elsewhere (Ackah, 2019; Kwarteng et al., 2020; Laskaris et al., 2019), information on VOCs is scarce. VOCs include a diverse set of chemicals, e.g., formaldehyde, benzene, chloroform, toluene, and ethylbenzene, and they include many known or suspected toxicants that cause irritation to eyes, skin and nose, damage to the respiratory system, liver and kidney; reproductive effects, and cancer (Anderson et al., 2007; Wolkoff et al., 2000, 2006). Several e-waste recycling processes, especially heating and burning, have been reported to produce extremely high concentrations of VOCs, especially aromatic hydrocarbons (An et al., 2014).

This study focuses on VOC exposures at e-waste sites with the overall objective of characterizing levels and exposures to a wide set of VOCs at the Agbogbloshie e-waste site. We used both fixed-site and personal measurements at the e-waste site, as well as measurements at up- and down-wind sites, to identify background levels and evaluate possible effects on neighboring communities. We examined the distributions of VOC concentrations, identified possible sources, and assessed exposure and health risks.

2. Material and methods

2.1. Sampling sites and subject recruitment

The Agbogbloshie e-waste site and scrap yard is about 1 km from central Accra (Ghana's capital, 2.5 million inhabitants), and it forms part of the city's South Industrial Area. The site is adjacent to densely populated residential and commercial areas, and ~144,000 residents live in the 16 km^2 Asiedu Keteke sub-metropolitan area, a commercial hub. Another light industrial area is located north of Accra, and a heavy industrial area is ~41 km to the east. More details are provided elsewhere (Kwarteng et al., 2020; Laskaris et al., 2019).

We utilized fixed site sampling at three sites. At the e-waste site (site 2), sampling equipment was placed near the ceiling (~2 m height) of a 2-wall metal shed that served as a meeting area for the e-waste leaders. This shed was ~300 m from two areas used for burning waste. The immediate area contained a number of sheds and small structures used for weighing, dismantling and storing e-waste, as well as a mosque. We observed individuals cooking, eating, resting, sleeping and selling/buying food, beverages and medicine in this and adjacent sheds. The e-waste site (site 2) was 50 m from the busy 2-lane Abossey-Okai Road. The upwind site (site 1) was located near the banks of the Korle Lagoon, 1.35 km to the southeast (Fig. 1). Sampling equipment was placed on a concrete shelf in an open structure, part of an unused pumping station, 6.5 m above ground level. While this area is mostly vacant, a teaching hospital and mortuary is 400 m west (where occasional open burning of waste was observed), a dense residential area was to the east, the 4-lane Ring Road West was to the south, and fields 100–300 m to the northwest were used to transfer rubbish to trucks for disposal elsewhere, occasional open burning of waste, and a football pitch. In late 2017, the lagoon and adjoining Odaw River were dredged, and spoils and municipal waste were placed in windrows 3–5 m high near the site 2. These materials sometimes burned and smoldered. The downwind site (site 3) was 0.48 km northeast of the e-waste site. Sampling equipment was mounted at ~6 m height on the balcony of a 3-story building used for pharmaceutical production (first two floors) and apartments (third floor). Activities in this area included a brewery, warehouses, car and truck repair facilities, a rail crossing, and the busy 4-lane Graphic Road. We also observed construction activities, e-waste sorting, and occasional fires on the nearby Odaw River's west bank.

For personal sampling, we recruited on-duty e-waste workers at Agbogbloshie who performed e-waste recycling activities (e.g., burning, dismantling, sorting, loading, buying, weighing, transporting, repairing, and smelting), were at least 18 years of age, and able to provide verbal and written consent. A detailed questionnaire was administered to each participant during registration by trained translators fluent in English and local languages Hausa, Twi and Dagbani asking about their current job (type of work, years working, days per week, hours per day, daily income), previous job, health status, cigarette smoking history, housing, cooking activities, and sociodemographic characteristics. We obtained written informed consent from all participants, and the study protocols, consent forms, and other study aspects were approved by the University of Michigan's IRB and Ethical and Protocol Review Committee (EPRC) of the College of Health Sciences, University of Ghana. Samples were collected from March 2017 to February 2018.

2.2. Sampling methods

Both fixed site and personal monitoring utilized passive (diffusion) sampling using 10 cm long stainless tubes packed with 60/80 mesh Tenax-GR (Scientific Instrument Services, Inc., Palmer, Massachusetts, USA) with a 0.5 cm diffusion gap. At the fixed sites, sampling tubes were mounted on stands in open metal "cages" that were locked for safety and security (Kwarteng et al., 2020). For personal sampling, the tubes were secured to backpacks worn by participants during a typical working day. Formaldehyde was monitored at the three sites every 30-min using a colorimetric/photoelectric sensor (FM-801, GrayWolf Sensing Solutions, Shelton, Connecticut, USA) from November 2016 to March 2017. This instrument has a limit of detection (LOD) of 6 μg/m^3. Non-detects were set to 0 and shown as "ND".

The sampling duration was 24 hr at fixed sites and 4–6 hr for personal samples; actual times were recorded. Excluding samples with sampling and delivery issues, we collected 102 valid samples: 11 personal samples from different workers, 24 samples from upwind site (including 3 duplicates), 31 samples from e-waste site (including 3 duplicates), 30 samples from downwind (including 3 duplicates), and 6 field blanks. We also obtained continuous measurements (1-min) of temperature and relatively humidity (RH) using integrated loggers (UX100–003 data logger; Onset Corporation, Bourne, MA, USA) at each fixed site.

2.3. VOCs analysis, calibration and quality control

After sampling, VOC tubes were shipped back to the laboratory at the University of Michigan, refrigerated, and analyzed within 30 days of sampling. Tubes were injected with internal standards (fluorobenzene, *p*-bromofluorobenzene, and 1,2-dichlorobenzene-d$_4$), then loaded into a short-path automated thermal desorption system (Scientific Instrument Services, Inc., Ringoes, New Jersey, USA). The system was coupled to a gas chromatography - mass spectrometer (GC-MS, Model 6890/5973, Agilent Technologies, Santa Clara, California, USA) equipped with a cryotrap/focuser (−140 °C to focus, 250 °C to inject) (Zhong et al., 2017). Chromatographic separation was achieved using a DB-VRX capillary column (60 m × 0.25 mm, 1.4 μm film thickness) and a 5-stage temperature program (Lin et al., 2021). The MS detector, transfer line, ion source, and quadrupole temperatures were 250, 300, 230 and 150 °C, respectively. The MS was operated in scan mode from 27 to 270 atomic mass unit (AMU). Peak areas were extracted using a ChemStation macro program (G1701BA Version B.01.00, Agilent, Santa Clara, California, USA) and adjusted for internal standards. Analyte masses (ng) were converted to concentrations (μg/m^3) by dividing by the calculated sampling volume (m^3, determined as the diffusion coefficient of the chemical × porosity of diffusion medium × tortuosity of diffusion medium × diffusion area × sampling time / diffusion distance) (Batterman et al., 2012; Chin et al., 2014; Jia et al., 2012; Lin et al., 2021). Sampling protocols, including tube preparation, transport, storage and analysis, are detailed elsewhere (Batterman et al., 2006; Du

Fig. 1. Area map showing three sampling sites (upwind, e-waste and downwind sites) in this study (Kwarteng et al., 2020).

et al., 2012; Jia et al., 2012).

Samples were analyzed for 99 target VOCs. Standards were purchased from MilliporeSigma (Burlington, Massachusetts, USA) as mixtures (four mixtures for 61 target VOCs and one mixture for three internal standards) or as neat compounds (28 target VOCs). Stock solutions (2000 μg/mL and 200 μg/mL) were prepared in methanol; standard solutions for calibrations (0.5, 1.5, 5, 15, 50 μg/mL) were prepared in pentane, except for the four ketones which used methanol. Multipoint calibrations (1, 3, 10, 30, and 100 ng) were performed. Recovery rates for most compounds ranged between 80% and 120%. Method detection limits (MDLs), determined as the standard deviation of seven replicate low concentration injections multiplied by 3.14 (Ohio EPA, 1996), ranged from 0.02 to 3.5 μg/m^3 for the sampling conditions (e.g., 24 h sampling period). The target VOCs were divided into eight chemical groups: 6 aldehydes, 12 alkanes, 19 aromatics, 40 halohydrocarbons, 2 terpenes, 4 ketones, 7 esters, and 9 others. Table S1 lists the target VOCs, internal standards, chemical groups, MDLs and detection frequencies (DFs). Results below MDL were set to 0 and shown as "ND". The total target VOC (TTVOC) concentration was determined as the sum of target VOC concentrations excluding formaldehyde.

Field blanks and duplicates, representing 8% and 12% of samples, respectively, were utilized during sampling campaign. True duplicates showed a coefficient of variation (COV) that averaged 43% across all detected analytes above 1 μg/m^3; this is higher than the 20% usually obtained as most samples contained low concentrations of individual VOCs that had high uncertainties. A freshly loaded tube injected with 10 ng of standards was analyzed daily, and differences between the daily checks and calibration results were under 30%. Trace level contamination (<7 μg/m^3) was detected in blanks for five compounds (hexane, chloroform, benzene, toluene, and n-nonane), and methylene chloride was found up to 30 μg/m^3 in blanks. Blank-corrected results were used for these compounds.

2.4. *Exposure and health risk*

Exposures were calculated for a reasonable upper level exposure scenario that assumed e-waste workers working for 9.4 hr/day × 307 day/year (based on worker survey data) and living in one of the three sites after work. For formaldehyde, we assumed continuous exposure (24 hr/day, 365 day/year). The non-cancer hazard ratio (HR) and lifetime cancer risk (CR) for VOCs other than formaldehyde were estimated as:

$$HRi = \frac{C_{ip} \times \frac{9.4\times307\text{hr/year}}{24\times365\text{hr/year}} + C_{if} \times \frac{(24\times365-9.4\times307)\text{hr/year}}{24\times365\text{hr/year}}}{\text{RfC}_i} \tag{1}$$

$$CRi = \left(C_{ip} \times \frac{9.4 \times 307 \text{ hr/year}}{24 \times 365 \text{ hr/year}} + C_{if} \times \frac{(24 \times 365 - 9.4 \times 307) \text{ hr/year}}{24 \times 365 \text{ hr/year}}\right) \times \text{URi} \tag{2}$$

where C$_{ip}$ = concentration (μg/m^3) for the ith VOC in personal samples; C$_{if}$ = concentration (μg/m^3) for the ith VOC in fixed-site samples; RfC = reference concentration (μg/m^3); and UR = unit risk (m^3/μg). The RfC and UR values (Table S2) were obtained from the US Environmental Protection Agency (U.S. EPA, 2020c) and the Michigan Department of Environment, Great Lakes and Energy (EGLE, 2020). Since personal measurements of formaldehyde were not obtained, we assumed that the fixed site formaldehyde values applied across the day and the weighting in Eqs. (1) and (2) were not used.

2.5. *Data analysis*

Descriptive statistics were calculated for each sample type (e.g., fixed and personal). Differences by sample type and location were evaluated using two-sided Mann-Whitney *U* tests for two samples and Kruskal−Wallis H tests for multiple comparisons and a significance level of $p = 0.05$. A principal component analysis (PCA) was performed to identify potential VOC sources. Data were analyzed using SPSS (SPSS, Inc., Chicago, Illinois, USA) and R version 3.5.2 (R Core Team (2019). https://www.R-project.org/).

3. Results

3.1. *VOC levels in samples*

A total of 54 VOCs was detected (Table S1). The mean ± standard deviation (sd) and median TTVOC levels were 102 ± 289 and 43 μg/m^3 respectively, suggesting a right-skewed distribution. Detection frequencies (DF) exceeded 50% for 18 VOCs, including alkanes and aromatics (n-hexane, benzene, n-heptane, toluene, ethylbenzene, *p- and m*-xylene, n-nonane, styrene, *o*-xylene, 1,3,5-trimethylbenzene, n-decane, 1,2,4-trimethylbenzene, n-undecane, naphthalene, n-tridecane, and n-tetradecane), as well as methylene chloride and limonene (a halohydrocarbon and terpene). Alkanes comprised 31% (mean and median) of TTVOC concentration, and aromatics averaged 39% (Fig. 2). The BTEX compounds (benzene, toluene, ethylbenzene, xylenes), an indicator of combustion emissions, were found in most samples and comprised 31% of TTVOC (range to 69%). The median and mean BTEX concentrations were 10 and 25 μg/m^3, respectively; the highest level, 580 μg/m^3, was found in a personal sample (sample id: PS7). The DF of formaldehyde was 13%, with a mean and median level of 10.2 μg/m^3 and ND; the highest level, 848 μg/m^3 for a 30-min sample and 187 μg/m^3 for that 24-hr period, was found at the downwind site.

A number of VOCs that are known or suspected toxicants were detected. Chloroform, a likely human carcinogen (U.S. EPA, 2020b), was found in 16% of samples, and the highest concentrations (222 and 214 μg/m^3) were detected in a personal sample (PS1) and at a fixed site (DS2). A probable human carcinogen, 2-nitropropane (U.S. EPA, 2020c), was detected in 2 samples with a maximum concentration of 4.0 μg/m^3. Trichloroethylene, an identified carcinogen (U.S. EPA, 2020c), was found in 6 samples (4 at the e-waste site and 2 at the downwind site), with a maximum level of 1.5 μg/m^3. 1,1,2,2-Tetrachloroethane, classified as a likely human carcinogen (U.S. EPA, 2020c), was found in an e-waste site sample at 3.3 μg/m^3. Isopropylbenzene was detected in 31% of samples at levels up to 4.6 μg/m^3 (PS7). Lastly, nitrobenzene, a suspected carcinogen (U.S. EPA, 2020c), was found in an e-waste site sample at 1 μg/m^3.

3.2. *Differences by sample and site type*

VOC concentrations for the personal, upwind, on-site, and downwind samples are summarized in Table 1 and Fig. S1, and the composition is shown in Fig. 2. The mean and median TTVOC levels were 46 and 37 μg/m^3, respectively in fixed-site samples; while 485 and 162 μg/m^3 for personal samples. Personal samples had the highest levels of most VOCs (except for methylene chloride, styrene, and chloroform) and generally the highest DFs, and the median concentrations (and proportions) of aromatics and alkanes were 55 μg/m^3 (37%) and 66 μg/m^3 (43%), respectively (Means were 158 ± 234 and 257 ± 420 μg/m^3).

At fixed sites, the upwind site (Site 1) had the lowest levels of most VOCs (except for methylene chloride, n-heptane, styrene, and chloroform), a high proportion (48%) of aromatics, and a relatively low proportion (27%) of alkanes. The e-waste site (Site 2) had the highest levels of most VOCs (including formaldehyde), with the exceptions of methylene chloride, chloroform and trichloroethylene. Aromatics and alkanes had similar proportions (means of 36% and 37%). The downwind usually had intermediate VOC levels, a high fraction of aromatics compounds (like the upwind site), and fairly high proportions of halogenated VOCs (median proportion of 13%). Site differences for most of these VOCs were significant (Table 1).

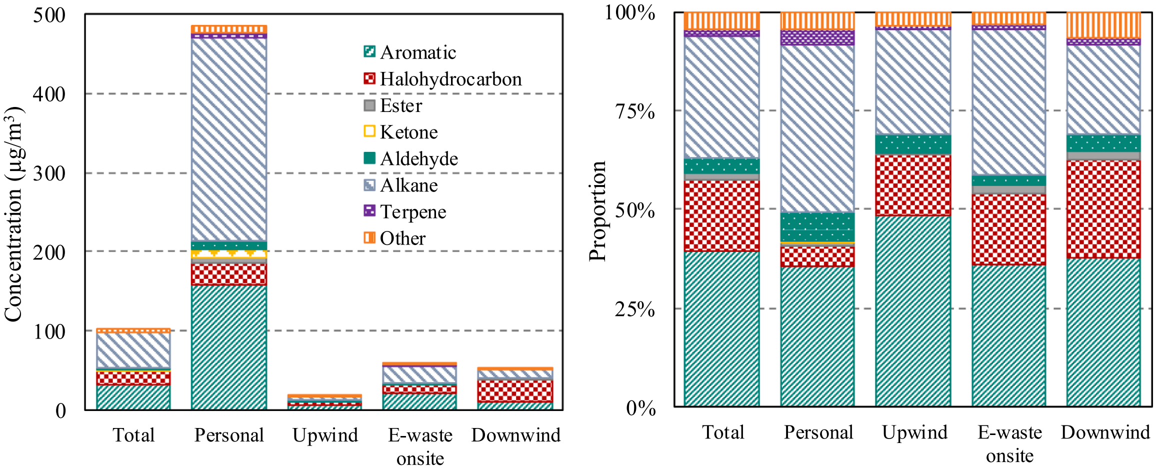

Fig. 2. Concentrations and proportions of VOC groups in personal and fixed-site samples.

3.3. Health risks

Table 2 lists hazard ratios (HRs) and cancer risks (CRs) for e-waste workers. HRs and CRs for formaldehyde at the fixed sites are broken out separately in the table. For VOCs other than formaldehyde, the HR averaged 2.1 and ranged to 8.6, and was mostly attributable to naphthalene (41%) and benzene (15%). The CR for VOCs other than formaldehyde averaged 4.6×10^{-4}, ranged to 5.2×10^{-3}, and was mostly attributable to naphthalene (41%) and benzene (30%). The mean HR and CR for formaldehyde were 1.0 and 1.3×10^{-4}, respectively. Most HRs of formaldehyde exposure were below 1, although the maximum reached 87 (downwind site). CRs derived from formaldehyde occasionally reached very high levels (1.1×10^{-2} at the downwind site; assuming continuous exposure).

These health risks were mostly driven by work exposure, although the average work shift was only 9.4 hr (mentioned in Section 2.4). Each of the personal samples collected during work shifts exceeded reference levels (HR = 1, CR =1×10^{-6}), e.g., sample PS7 (as noted in Section 3.1) had a HR of 6.8, largely due to naphthalene and benzene, while sample PS1 had a CR of 1.9×10^{-3}, largely due to chloroform (222 μg/m^3). While VOC exposures at the fixed sites provided only a limited contribution to the health risk to e-waste workers, risks were increased by occasional high chloroform levels at the downwind site (reaching 214 μg/m^3) and by formaldehyde at all fixed sites (up to 639, 673, and 848 μg/m^3 at Site 1, 2, and 3, respectively). Chloroform may arise from cleaning and disinfectant agents or by-products in water used to mop the area. While health risks and especially the CRs should be estimated using long-term averages, our results suggest the potential of high exposures and the need to obtain additional measurements of formaldehyde using both fixed and personal monitoring.

4. Discussion

4.1. Comparison to VOCs levels in literature

Relatively few studies have utilized personal monitoring of VOCs in community settings, and no such monitoring was identified for e-waste workers globally. Table S3 summarizes studies in several countries utilizing personal monitoring. BTEX exposures averaged 34–43 μg/m^3 among women in Cape Town, South Africa (Everson et al., 2019), much lower than in this study. In contrast, street cooks in Nigeria using biomass fuels experienced much higher levels of benzene and toluene than in the present study, and Σ_{23}VOC averaged up to 2400 μg/m^3 (Awopeju et al., 2017). Personal monitoring in most other countries (e.g., China and UK) shows lower exposures than among e-waste workers in this study, although a study in Seoul, South Korea in 2001 reported extremely high personal VOC levels (Son et al., 2003).

VOC levels at the fixed sites were somewhat higher than that reported in developed countries (Jia et al., 2008; Seo et al., 2014; Xiong et al., 2020), but generally lower than levels reported elsewhere in Africa and in other developing countries (Table S3). For example, Σ_{15}VOC concentration ranged from 6.3 to 72 μg/m^3 at urban sites in Côte d'Ivoire in 2016, (Dominutti et al., 2019). In an earlier study at selected urban sites in Nigeria in 2009–2011, benzene levels ranged from 0.2 to 10 μg/m^3 (Olajire and Azeez, 2014; Olumayede and Okuo, 2012), compared to averages of 1.4, 5.4, and 2.7 μg/m^3 at upwind, e-waste site, and downwind site respectively at Agbogbloshie. In the same study in Nigeria, toluene levels ranged from 0.7 to 12 μg/m^3 compared to 2.1–6.2 μg/m^3 at Agbogbloshie. Also, xylene was found as high as 400 μg/m^3 at traffic sites (Olajire and Azeez, 2014) compared to only 0.2–1.1 μg/m^3 at Agbogbloshie. While benzene and xylene levels are comparable, the *o*-xylene levels far exceeded our measurements at Agbogbloshie. In northern China and in a polluted area in southern China, BTEX levels were 12.6–36.8 μg/m^3, slightly higher than levels in this study (Guo et al., 2006; Liu et al., 2016; Yang et al., 2019).

TTVOCs (Σ_{99}VOCs) among e-waste workers in Agbogbloshie averaged 485 μg/m^3, greatly exceeding levels at the fixed sites, which ranged from 18 to 60 μg/m^3. Levels at the fixed sites followed our expectations, i.e., lowest at the upwind site, highest at the e-waste site, and intermediate at the downwind site. None of these sites were extremely close to e-waste burning sites, e.g., the e-waste fixed sampling site, which was the closest among the three, was ~300 m away from the nearest burn pit. In contrast, personal samplers were carried by workers who may have been near or performed VOC emitting activities such as burning, smelting, dismantling, and transport of waste. Workers spend varying amount of time on such activities, as well as resting, walking or biking. Based on photographic records of worker activities, some of the highest TTVOCs levels (1856 and 1979 μg/m^3) were found for a worker (PS1) who dismantled e-waste for 100 min and another worker (PS7) who rode a motorbike or drove a car for 90 min; the other nine workers who spent less time on work activities had much lower VOC levels (ranging from 86 to 344 μg/m^3).

4.2. Sources and factors influencing VOC levels

PCA results for all samples (Fig. 3) identified three major factors: Factor 1 (accounting for 35% of the variance) included a variety of chemicals used as fuels, paints, coatings, solvents and degreasers, e.g., methyl cyclohexane, ethylbenzene, *p*- and *m*-xylene, *o*-xylene, isopropylbenzene, n-propylbenzene, 4-chlorotoluene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, naphthalene, benzene, and tetrachloroethane (ECHA, 2020; U.S. EPA, 2020a). This factor also

Table 1

Concentrations (μg/m^3) of selected VOCs for personal and fixed site samples. Results of Mann-Whitney (p-values) for differences between sample types.

	Personal samples (N = 11)					Site 1 - Upwind (N = 21)					Site 2 - Onsite (N = 28)					Site 3 - Downwind (N = 27)					Mann-Whitney *U* test			
	mean	sd*	median	min	max	mean	sd*	median	min	max	mean	sd*	median	min	max	mean	sd*	median	min	max	Personal vs Fixed-sites	Site 1 vs 2&3	Site 2 vs 1&3	Site 1 vs 3
TTVOC	485	712	162	86.1	1979	18.1	20.0	11.2	1.6	79.5	59.6	23.2	55.3	24.2	133	53.7	91.9	26.7	6.2	380	**< 0.001**	**< 0.001**	**< 0.001**	**0.01**
BTEX	128	190	45.5	17.7	580	4.5	4.4	3.7	0.9	21.2	15.6	7.1	16.7	0.5	27.0	7.2	4.5	6.3	1.1	19.3	**< 0.001**	**< 0.001**	**< 0.001**	**0.01**
Methylene chloride	6.9	15.2	ND	ND	38.2	5.1	15.3	ND	ND	43.9	10.2	16.7	2.1	ND	59.5	19.6	77.9	1.3	ND	309	0.67	0.13	0.34	0.26
Hexane	118	205	17.6	8.9	612	3.0	6.2	1.4	ND	27.0	9.1	9.2	5.1	1.4	34.6	8.5	24.7	2.9	ND	125	**< 0.001**	**0.001**	**< 0.001**	0.06
Benzene	22.9	33.4	10.0	4.0	114	1.4	1.3	1.1	ND	5.5	5.4	3.3	5.4	ND	12.9	2.7	1.8	2.0	ND	7.7	**< 0.001**	**< 0.001**	**< 0.001**	**0.01**
n-Heptane	16.5	30.4	5.8	ND	88.0	0.6	1.0	ND	ND	3.4	1.5	1.0	1.3	ND	4.3	0.3	0.3	ND	ND	1.5	**0.001**	0.14	**< 0.001**	0.61
Toluene	60.4	90.4	23.0	4.1	259	2.1	3.0	1.2	0.3	14.4	6.2	3.6	5.8	0.2	14.2	2.8	2.5	2.4	ND	11.5	**< 0.001**	**< 0.001**	**< 0.001**	**0.02**
Ethylbenzene	11.3	16.7	4.4	1.2	55.2	0.3	0.3	0.3	ND	1.3	1.5	0.9	1.6	ND	3.4	0.6	0.5	0.5	ND	2.3	**< 0.001**	**0.001**	**< 0.001**	0.18
p-,*m*-Xylene	20.6	33.5	8.1	1.3	108	0.3	0.4	0.3	ND	1.8	1.3	0.9	1.2	ND	3.7	0.6	0.6	0.5	ND	2.6	**< 0.001**	**0.001**	**< 0.001**	0.06
n-Nonane	2.7	4.3	1.8	ND	14.9	0.3	0.3	ND	ND	1.0	0.7	0.9	0.6	ND	3.6	0.2	0.2	0.2	ND	0.8	**0.001**	**0.05**	**0.001**	0.48
Styrene	2.1	4.2	0.2	ND	11.9	0.6	1.4	0.1	ND	4.5	1.3	1.3	0.9	ND	5.2	0.5	1.2	0.2	ND	4.7	0.61	0.26	**0.007**	0.95
o-Xylene	13.2	23.3	5.7	1.1	81.6	0.2	0.3	0.2	ND	1.1	1.1	0.7	1.0	ND	3.0	0.4	0.4	0.4	ND	1.6	**< 0.001**	**< 0.001**	**< 0.001**	**0.01**
1,3,5-Trimethylbenzene	4.3	8.8	1.8	ND	28.7	0.03	0.06	ND	ND	0.2	0.5	0.2	0.5	ND	1.2	0.2	0.1	0.1	ND	0.4	**< 0.001**	**< 0.001**	**< 0.001**	**< 0.001**
n-Decane	2.2	2.4	2.0	ND	8.6	0.04	0.2	ND	ND	0.4	0.8	0.6	0.7	ND	3.5	0.2	0.2	0.2	ND	0.8	**< 0.001**	**< 0.001**	**< 0.001**	**0.01**
1,2,4-Trimethylbenzene	14.2	27.3	6.2	1.0	95.8	0.1	0.2	ND	ND	0.7	1.2	0.6	1.4	ND	3.1	0.4	0.3	0.4	ND	1.1	**< 0.001**	**< 0.001**	**< 0.001**	**< 0.001**
Limonene (R)-(+)	5.4	9.2	1.3	ND	21.3	0.1	0.3	ND	ND	0.9	0.6	0.4	0.6	ND	2.0	0.4	0.6	0.3	ND	2.6	**< 0.001**	**0.001**	**< 0.001**	**0.01**
n-Undecane	3.1	1.8	3.2	ND	7.4	0.2	0.1	0.2	ND	0.4	0.9	0.4	0.9	ND	1.8	0.4	0.3	0.4	ND	1.1	**< 0.001**	**< 0.001**	**< 0.001**	**< 0.001**
Naphthalene	5.4	7.2	2.6	1.2	26.0	0.4	0.2	0.4	ND	1.0	1.4	0.9	1.1	ND	3.7	1.1	0.8	1.0	ND	3.0	**< 0.001**	**< 0.001**	**0.001**	**0.01**
n-Tridecane	2.8	3.0	2.3	ND	10.6	0.07	0.06	ND	ND	0.3	0.9	0.6	0.8	ND	2.3	0.2	0.2	0.2	ND	0.9	**< 0.001**	**< 0.001**	**< 0.001**	**0.03**
n-Tetradecane	2.7	3.6	1.6	ND	11.8	0.04	0.1	ND	ND	0.3	1.1	0.7	1.0	ND	2.6	0.2	0.2	0.02	ND	0.8	**< 0.001**	**< 0.001**	**< 0.001**	**0.01**
Chloroform	20.7	154	ND	ND	222	0.02	0.1	ND	ND	0.5	0.1	0.4	ND	ND	1.2	8.8	93.6	ND	ND	214	0.69	0.10	0.36	0.14
2-Nitropropane	0.4	1.2	ND	ND	4.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.1	0.4	ND	ND	2.2	0.10	0.54	0.45	0.38
Trichloroethylene	0.2	0.6	ND	ND	1.5	ND	ND	ND	ND	ND	0.01	0.04	ND	ND	0.2	0.01	0.06	ND	ND	0.2	**0.003**	0.28	0.92	0.21
Hexanal	1.5	0.8	1.5	ND	3.4	0.4	0.8	ND	ND	2.5	0.1	0.3	ND	ND	0.8	0.04	0.6	ND	ND	1.0	**< 0.001**	**0.006**	0.78	**0.004**
1,1,2,2-Tetrachloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.1	0.6	ND	ND	3.3	ND	ND	ND	ND	ND	0.70	0.54	0.19	1.00
Isopropylbenzene	0.8	1.8	ND	ND	4.6	ND	ND	ND	ND	ND	0.2	0.2	0.2	ND	0.9	0.04	0.1	ND	ND	0.4	**< 0.001**	**0.001**	**< 0.001**	0.07
n-Propylbenzene	2.0	8.9	ND	ND	18.7	ND	ND	ND	ND	ND	0.07	0.1	ND	ND	0.5	0.01	0.05	ND	ND	0.3	**0.006**	0.09	**0.005**	0.38
Formaldehyde	–	–	–	–	–	8.0	37.1	ND	ND	639	9.7	37.2	ND	ND	673	12.2	52.1	ND	ND	848	–	**0.001**	**0.001**	**0.03**
Aromatics	158	234	55.4	22.4	765	5.6	4.6	5.0	1.2	23.3	20.4	9.0	20.9	0.5	33.1	9.3	6.3	8.1	1.7	24.4	**<0.001**	**<0.001**	**<0.001**	0.02
Halohydrocarbons	28.5	65.6	3.1	ND	222	5.1	11.4	ND	ND	43.9	11.0	15.6	3.3	ND	62.8	28.5	73.7	2.9	ND	330	0.63	**0.02**	0.16	**0.06**
Esters	5.6	16.1	ND	ND	53.9	0.2	1.0	ND	ND	4.8	1.0	4.1	ND	ND	21.3	1.3	2.2	ND	ND	7.5	0.25	**0.04**	0.13	**0.004**
Ketones	10.4	34.4	ND	ND	114	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**0.009**	1.00	1.00	1.00
Aldehydes	11.5	7.9	13.0	ND	24.5	0.9	1.6	ND	ND	4.9	1.4	2.1	0.6	ND	8.9	0.8	2.9	ND	ND	15.0	**< 0.001**	0.78	**< 0.05**	0.13
Alkanes	257	420	65.8	19.1	1180	4.4	6.4	2.5	ND	28.3	22.2	13.4	21.3	1.9	53.1	10.9	23.6	4.3	1.2	125	**< 0.001**	**< 0.001**	**< 0.001**	**0.02**
Terpenes	5.4	8.3	1.3	ND	21.3	0.1	0.3	ND	ND	0.9	0.6	0.5	0.6	ND	2.0	0.4	0.5	0.3	ND	2.6	**0.02**	**0.001**	**< 0.001**	**0.01**
Others	9.2	14.2	4.0	ND	47.5	1.8	5.6	ND	ND	24.9	2.9	6.9	ND	ND	24.8	2.4	7.2	ND	ND	30.9	**0.007**	0.59	0.59	0.74

[*] sd: standard deviation.

Table 2
Hazard ratios and cancer risks for e-waste workers for different scenarios, and health risks derived from formaldehyde in fixed-sites.

	Mean	Standard deviation	Median	Min	Max
TTVOC (excluding formaldehyde)					
Total e-waste workers					
Hazard ratio	2.1	1.8	1.4	0.5	8.6
Cancer risk	4.6×10^{-4}	6.6×10^{-4}	1.5×10^{-4}	4.8×10^{-5}	5.2×10^{-3}
If workers lived in upwind					
Hazard ratio	1.9	1.8	1.2	0.5	7.9
Cancer risk	3.8×10^{-4}	5.4×10^{-4}	1.1×10^{-4}	4.8×10^{-5}	1.9×10^{-3}
If workers lived in e-waste onsite					
Hazard ratio	2.2	1.8	1.6	0.5	8.1
Cancer risk	4.3×10^{-4}	5.4×10^{-4}	1.7×10^{-4}	5.1×10^{-5}	2.0×10^{-3}
If workers lived in downwind					
Hazard ratio	2.1	1.8	1.4	0.5	8.6
Cancer risk	5.7×10^{-4}	8.3×10^{-4}	1.5×10^{-4}	4.9×10^{-5}	5.2×10^{-3}
Formaldehyde					
Total fixed sites (N = 8620)					
Hazard ratio	1.0	4.4	0	0	87
Cancer risk	1.3×10^{-4}	5.6×10^{-4}	0	0	1.1×10^{-2}
Upwind (N = 2029)					
Hazard ratio	0.8	3.8	0	0	65
Cancer risk	1.0×10^{-4}	4.8×10^{-4}	0	0	8.3×10^{-3}
E-waste onsite (N = 3529)					
Hazard ratio	1.0	3.8	0	0	69
Cancer risk	1.3×10^{-4}	4.8×10^{-4}	0	0	8.7×10^{-3}
Downwind (N = 3062)					
Hazard ratio	1.2	5.3	0	0	87
Cancer risk	1.6×10^{-4}	6.8×10^{-4}	0	0	1.1×10^{-2}

included alkanes commonly found in fuels, e.g., n-heptane, n-octane, and n-nonane, and the toluene/benzene ratio of personal samples, which averaged 2.8 ± 1.7 (mean ± standard deviation; median ratio was 2.7) suggested fresh vehicle emissions (Barletta et al., 2005; Lee et al., 2002; Liu et al., 2009). Factors 2 and 3 accounted for relatively low variance (14% and 10%, respectively) and had few highly abundant loadings (e.g., >80%), although n-tridecane, n-tetradecane and n-pentadecane reached 68%, 67% and 65% in factor 2; and n-hexadecane, n-pentadecane, n-tetradecane were 72%, 71%, and 67% in factor 3. These alkanes, as well as chlorinated and aromatic hydrocarbons, are abundant during plastic recycling, which is an important process in the e-waste dismantling industry (He et al., 2015). Other factors accounted for less than 5% of the variance and are not shown in Fig. 3. The profiles of personal and e-waste onsite samples were very similar, suggesting similar sources and the contribution of e-waste site activities.

The higher concentrations at the e-waste site compared to levels at up- and down-wind sites, the similarity of the PCA profiles and the VOC compositions, and site observations all suggest that e-waste site activities are the primary source of VOCs at the e-waste site and neighboring communities. Site activities likely to emit VOCs include solvent use (vehicle repair, metal working, painting), fuel combustion (vehicle emissions, waste burning, cooking), industrial and commercial activities, and evaporation from fuel, oil and solvent spillage.

We examined daily and seasonal patterns to understand influences and help identify sources. Wind patterns in Accra are quite consistent through the year and mostly from the southwest (some rotation occurs on most days between west and south) (Kwarteng et al., 2020), however, one notable weather pattern is the arrival of the Harmattan season, typically in the November to February period. This period is often associated with warmer, less humid, and dustier conditions (Table S4). We did not see consistent and statistically significant seasonal differences in VOC concentrations ($p > 0.05$; Fig. S2), although concentrations in several chemical groups appeared elevated during Harmattan season, e.g., alkanes and aromatics at the upwind site. However, these higher concentrations may have been sampling artifacts since very high humidity, which is very common in the region, can diminish the absorption efficiency and capacity of the sampling media as it absorbs atmospheric water (Biagini et al., 2019); for this reason, we utilized a small sample volume to avoid excessive uptake of water.

Diurnal patterns of VOC concentrations are driven by variation in emission sources and dispersion. E-waste activities start in the morning and, in most cases, can run through the evening, e.g., waste burning has been observed at night. Traffic throughout Accra shows typical morning and afternoon commuting peaks, while commercial traffic at the site and in the market is fairly constant through the daytime. Cooking in the market is carried out through the day. Generally, rapid dispersion during the daytime would lower levels associated with local sources, compared to evening and night, when increasing atmospheric stability would lower dispersion rates and tend to increase concentrations from local sources. Thus, emissions and dispersion are countervailing factors that may reduce the diurnal variation in VOC levels. Since we used integrated VOC sampling (~24 h at fixed sites, ~4 h for personal samples), we have limited information on temporal variation. Continuous monitoring of $PM_{2.5}$ at Agbogbloshie showed some of the highest levels in the evening, and personal $PM_{2.5}$ levels were approximately twice those of the fixed site samples (Kwarteng et al., 2020); we saw yet larger (proportional) increases for the personal samples of VOCs. While portable instrumentation for continuous VOC monitoring is available, these provide a measure of total VOCs, not the compound-specific information needed to understand sources and health risks. While we were unable to describe diurnal patterns, it is likely that we have not captured the maximum VOC concentrations due to temporal (and spatial) variability; this may particularly affect personal sampling results since these samples were collected only during daytime.

4.3. Health risks

Health risks were evaluated using a reasonable upper exposure scenario, which assumed workers lived at the e-waste site or in a nearby community. This scenario does not apply to other residents of these communities. We used personal exposure data to represent occupational exposures, and fixed-site data for residential (non-working) exposures. As noted earlier, much of the risk was attributable to naphthalene and benzene. Acute inhalational exposure to naphthalene, which is classified as a possible carcinogen, is associated with hemolytic anemia, damage to the liver, and neurological damage (U.S. EPA, 1999; U.S. EPA, 2000);

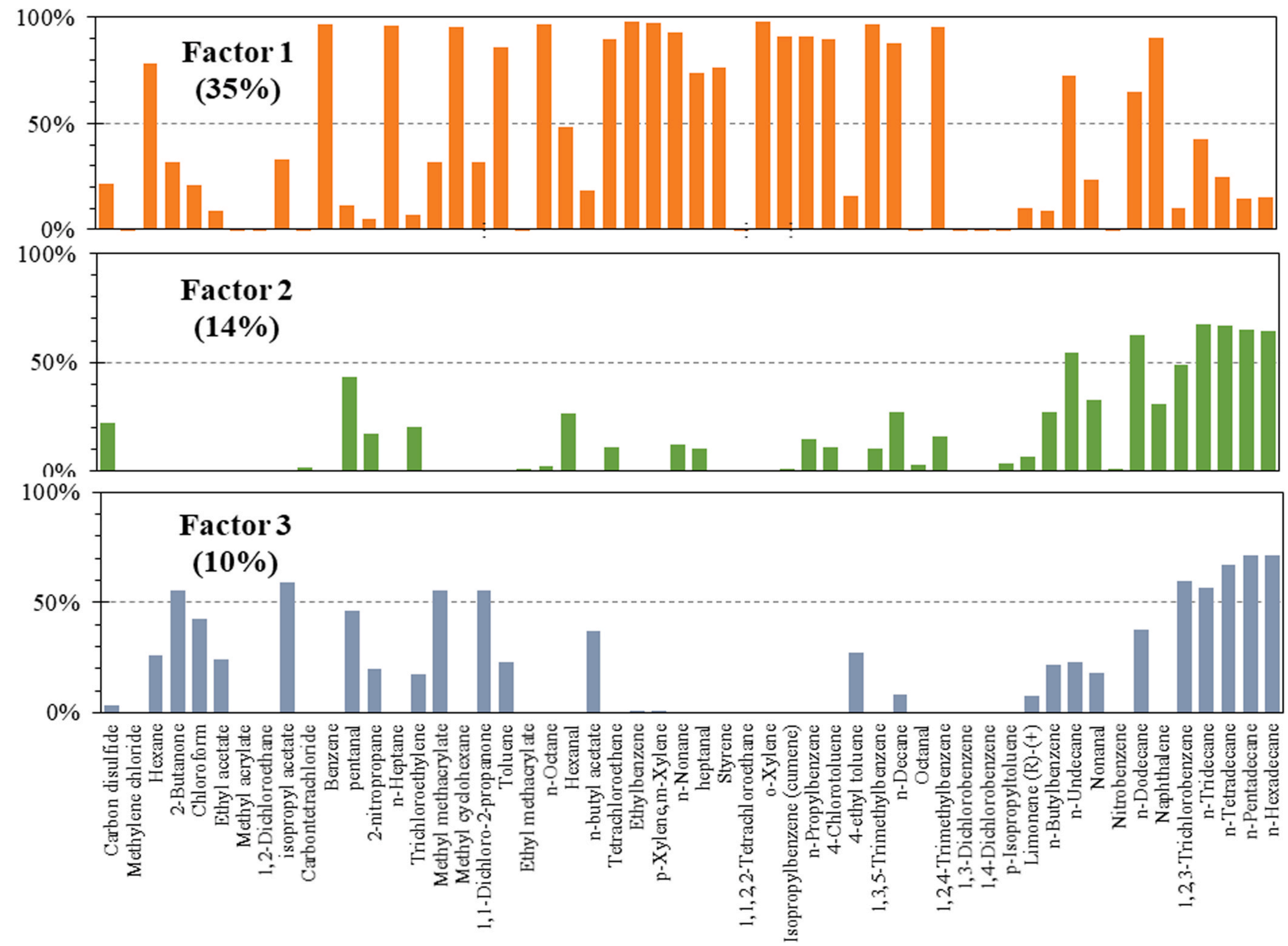

Fig. 3. Factor loadings (source profiles) from PCA for all samples.

chronic exposure can cause cataracts, retinal damage, anemia and hepatic injury (Molloy et al., 2004; Orzalesi et al., 1994; Sahni et al., 2019). Acute exposure to benzene may cause drowsiness, dizziness, headaches, as well as eye, skin, and respiratory tract irritation and, at high levels, unconsciousness (ILO, 2019); chronic exposure can cause blood disorders, reproductive effects, and leukemia (Green et al., 1978; ILO, 2019; Snyder et al., 1993). Benzene is classified as a known human carcinogen (IARC, 2018; U.S. EPA, 2012).

While generally not the largest contributor, chloroform induced the highest cancer risk (DS2). At high exposures, chloroform can cause central nervous system effects, respiratory depression, delayed hepatotoxicity kidney and liver damage, and reproductive effects (Lionte, 2010; Williams et al., 2018; Yamamoto et al., 2002). Chloroform is classified as a likely human carcinogen that is associated with kidney, liver and bladder tumors (Golden et al., 1997; IARC, 1999; U.S. EPA, 2001). Formaldehyde also exceeded guideline levels and some measurements yielded extremely high health risks (HR = 87, CR = 1.1 × 10^{-2}). Formaldehyde is considered a probable or known carcinogen (Cogliano et al., 2005; Muir, 1996), and this VOC is associated with nasopharynx, sinonasal and leukemia cancers (Golden, 2011).

A number of measures can be used to reduce pollutant exposures to e-waste workers and to limit off-site transport and exposure to neighboring communities. Measures might include, for example, the use of enclosed workshops equipped with appropriate removal technologies, e.g. filters or electrostatic precipitators for particles, and carbon adsorbents or oxidation or photocatalytic reactors for VOCs (Chen et al., 2016a, 2016b). Such systems should target aromatic and halogenated hydrocarbons, the VOCs driving the health risks, as found in our and earlier studies (Liu et al., 2019).

4.4. Study strengths and limitations

This study has several strengths. To our knowledge, it is the first study to provide temporal and spatial measurements using both personal sampling and ambient VOC measurements at an e-waste site. We collected both fixed-site samples and personal samples, which helped to confirm the significance of e-waste activities as well as indicate occupational exposures, used several fixed sampling sites to show up- and down-wind impacts, and included a wide range of VOCs, including many toxic VOCs. Our analyses identified several factors and likely emission sources, and we used reasonable assumptions to estimate health risks for e-waste workers.

Our study has several limitations. The sample size was small for personal samples (N = 11). Risks were estimated for only target VOCs and were not assessed for non-target VOCs as well as PAHs, PBDEs, and metals. Health risks due to formaldehyde were estimated separately from the other VOCs due to the use of different measurement methods. Uncertainties in the RfCs and URs may be large. We also assumed that the measurements reflected chronic exposure. Despite these limitations, the study reveals the potential for significant VOC exposure among e-waste workers and the need for more comprehensive follow-up studies.

5. Conclusion

Informal e-waste recycling activities emit VOCs that expose workers and nearby communities. We detected a total of 54 VOCs in personal and fixed-site samples collected at the Agbogbloshie waste site in Ghana. VOC levels in personal samples from e-waste workers considerably exceeded levels at the fixed sites and resulted in risks that far exceeded reference levels, especially for cancer, largely due to naphthalene and benzene, and occasionally from chloroform and formaldehyde. The dominant VOC sources likely include solvent use, traffic and fuel combustion, industrial and commercial activities, and fuel, oil and solvent spillage. Our results suggest the need for restrictions on VOC emitting activities, and the use of personal protective equipment and other control measures for e-waste workers.

CRediT authorship contribution statement

Nan Lin: Software, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Lawrencia Kwarteng:** Software, Investigation, Data curation, Writing - review & editing. **Christopher Godwin:** Methodology, Investigation, Writing - review & editing. **Sydni Warner:** Writing - original draft, Writing - review & editing. **Thomas Robins:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition. **John Arko-Mensah:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Julius N. Fobil:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Stuart Batterman:** Conceptualization, Methodology, Validation, Formal analysis, Resources, Data curation, Writing - original draft, Writing - review & editing, Supervision, Project administration, Funding acquisition.

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. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.126353.

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