BIOMONITORING OF SELECTED HALOGENATED ORGANICS AND METALS IN VIETNAMESE WOMEN ELECTRONIC WASTE RECYCLERS

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Introduction:

Electronic waste (e-waste) has increased enormously in recent years. According to the *Solving the E-waste Problem* (StEP) Initiative worldwide estimates of total e-waste generation are on the order of 40 million tons annually and increasing 5 to 10 % each year.¹ For economic reasons, some e-waste is shipped to developing countries where it is less expensive to recycle. Vietnam is one of these developing countries experiencing a marked increase in e-waste from more developed countries as well as from domestic origin.

Primitive e-waste recycling and unsafe working conditions can lead to hazardous exposures from halogenated organics and metals from electronics.²⁻³ Many of these halogenated organics and metals have been associated with adverse health effects. For example, lead has been associated with neurotoxic effects on children and reproductive problems, ^{4, 5} while polybrominated diphenyl ethers (PBDEs) have been associated with neurological and reproductive toxicity, disruption of thyroid homeostasis, and cancer⁶. There are reports of workers, children, and residents living near e-waste sites who have elevated body burdens of organics and/or metals.⁷⁻⁹ Safe handling of e-waste has become an important and growing topic in the environmental justice arena. Improvement in worker safety protocols has been shown to reduce the body burden of some e-waste compounds, including PBDEs.¹⁰

This study involved biomonitoring of metals as well as halogenated organics found in e-waste to determine if there were elevated levels in rural northern Vietnamese women working as e-waste recyclers. Last year, we reported results from a cohort of 10 workers and 10 comparisons with no known exposure to toxic chemicals.² We found some elevated PBDE congeners and elevated dioxin CALUX levels in workers. This year we focus on a larger sample size of 40 e-waste recyclers and 20 comparisons. We also compare our data to the National Health and Nutrition Survey (NHANES) data, a large, representative sample of the US population. Our objective is to help improve worker safety among e-waste workers in a developing country and to identify locations for conducting future health studies to help understand health risks from e-waste exposure.

Materials and Methods:

This study was conducted in the rural, northern Vietnamese province of Hung Yen within the My Hao district. Ewaste recyclers were recruited primarily by word of mouth in Bui Dau village; comparisons were recruited by similar methods in the neighboring village of Cam. The comparisons had no known exposure to toxic chemicals according to their questionnaire records. Inclusion criteria included selection of healthy women only as well as women with similar age (e-waste workers median age: 39; comparison group median age: 37). Whole blood, serum and urine were collected in chemically cleaned containers supplied by the US Centers for Disease Control and Prevention (CDC). Informed consent was obtained before the health care worker began any data collection on the participant. Questionnaires were administered before specimen collection to gather demographic information. Specimens were handled according to the CDC protocol, frozen immediately at -20C and remained frozen and express shipped on dry ice to CDC where they were analyzed as previously described². Data analysis was performed at the University of Texas Southwestern Medical Center using IBM SPSS V21. Institutional Review Boards (IRBs) at both the University of Texas Health Science Center at Houston and at the Hanoi School of Public Health reviewed and approved the protocol for this study.

Results and Discussion

Commercial mixtures of brominated diphenyl ethers (BDEs), particularly OctaBDEs and DecaBDEs, appear to be a significant exposure risk to e-waste workers. Serum concentrations of BDE-153, a constituent of both the octaBDE and pentaBDE mixture, are significantly higher in the e-waste workers [median: 13 ng/g lipid weight (lw); range: 1.7 to 59.9 ng/g lw] than in the comparison group with a p value <0.0001 (median: 1.2 ng/g lw; range: 0.2 to 3.9 ng/g). Last year, we also noted a statistically significant difference (p < 0.04) between PBDE-153 serum concentration in e-waste workers and comparisons in our smaller cohort.² We also observed an elevated serum concentration of BDE-183 in the e-waste workers (median 7.3 ng/g lw; range: 1.3 to 38.9 ng/g lw) whereas serum concentrations in the comparison group were statistically lower, p value <0.0001 (median: 0.75 ng/g lw; range 0.2 to 3.5 ng/g lw). We also found a very high concentration of BDE-209, the major component of the decaBDE mixture, in the e-waste workers (73.3 ng/g lw; range: 5.4 to 1418.2 ng/g lw) with all 40 workers having a detectable amount of BDE-209; this is in contrast to the comparison group where it was only detected in 5 out of the 20 women. Most recyclers had measurable pentaBDE, as BDE-47 (median: 1.45 ng/g lw; range: 0.2 - 21.2 ng/g lw), BDE-99 (0.65 ng/g lw; range: 0.2 to 7.9 ng/g lw), and BDE-100 (median: 0.55 ng/g lw; 0.05 to 15.4 ng/g lw), while less than 50% of the comparison samples had detectable concentrations of these three congeners. **Table 1** and **Figure 1** provide summaries of our key findings so far.

Measure	Comparison (n=20)				E-Waste (n=40)				Mann- Whitney U Test
	Median	Interquartile Range			Median	Interquartile Range			p-value
PBDE153	1.20	0.93	-	1.70	13.00	6.63	-	20.23	<0.0001
PBDE183	0.75	0.26	-	1.20	7.30	4.28	-	12.25	<0.0001
PCB153	8.05	5.53	-	11.88	7.70	4.33	-	9.65	0.3309

Those with non-detectable levels were analyzed using LOD/2

Figure 1: PBDEs and a PCB congener in Vietnamese e-waste workers and comparison group (log scale)

Organohalogen Compounds



We also measured polychlorinated biphenyls (PCBs) in our cohort to see if there were any increased levels of this group of compounds formally used in the manufacturing of electronics. Of the 37 congeners measured, there were no statistically significant differences between the e-waste workers and comparisons.

Comparing metal concentrations between the e-waste workers and the comparisons, there are statistically significant differences with lead, total mercury, and methylmercury in whole blood as well as lead and total mercury in urine (p < 0.05). The lead differences were consistent across both matrices; the workers had elevated urine and whole blood median concentrations of $3.22 \,\mu\text{g/g}$ Cre and $4.82 \,\mu\text{g/dL}$, respectively; this is in contrast to the comparison group median urine of 2.31 μ g/g Cre and whole blood of 2.93 μ g/dL. Both groups' lead concentrations as compared to the median in the U.S. women's population from NHANES (http://www.cdc.gov/exposurereport/pdf/FourthReport UpdatedTables Sep2013.pdf) indicate statistically significant higher concentrations (p value < 0.001) in our study suggesting that lead exposure is a concern for these women. This observation was consistent with what we found in our first group of 10 workers and 10 matched controls where lead was elevated in both groups as compared to the NHANES data. There was a significant difference (p = 0.04) between urinary mercury in workers (median: 0.49 μ g/g Cre) as compared to the control group (median: $0.36 \mu g/g$ Cre); however, the comparison group had a statistically significant greater concentration (p= 0.03) of whole blood mercury (median: 3.46 μ g/L) than the e-waste workers (median: 2.49 μ g/L) as well as a greater concentration of methylmercury (median: 4.16 μ g/L) than what was measured in the e-waste workers (median = $2.76 \,\mu g/L$; p =0.0013). Arsenobetaine and total arsenic acid urinary concentrations are elevated in both Vietnamese groups as compared to NHANES. Our results suggest that both mercury and arsenic contamination could be attributed to dietary habits and water consumption. Previous publications have reported elevated arsenic concentrations in drinking water of the Red River Delta in northern Vietnam where our sampling was conducted.^{11,}

The high BDE209 in our Vietnamese recyclers poses a potential concern. Tue et al. (2010) reported elevated levels of breast milk PBDE, 4.1 ng/g lw in the Bui Dao e-waste recycling site compared to their comparison site in Hanoi.¹³ Our BDE209 median serum concentration of 73.3 ng/g lw in e-waste workers is in agreement with other PBDE studies where higher brominated congeners are reported in lower levels in breast milk than in serum.^{14, 15} Tue et al. (2010) also indicated PCB levels in e-waste workers were comparable to their reference sites¹³ consistent with the fact that PCBs have been phased out over the past 30 years in manufacturing.¹⁶ In our study, we found higher levels of congeners typically from in the Octa- and Deca- commercial mixtures as compared to congeners found in pentaBDE mixtures, which are much more commonly found in North America. Elevated levels consistent with exposure to Octa- and Deca mixtures has been reported in other studies.^{13, 17, 18} Cadmium, lead, total mercury, cobalt, cesium, molybdenum, antimony, total arsenic, thallium as well as metal species arsenobetaine and dimethylarsonic acid measured in our participants were elevated in either urine or blood compared to the U.S. NHANES data (p value <0.01 for all metals measured).

E-waste recycling in combination with other heavy metal processing industries can be possible contributors to the elevated exposure from environmental contamination. This study suggests extending the sampling to a larger and more representative population of e-waste workers as well as the general population in additional locations in Vietnam. Elevated lead and PBDE levels in women workers also emphasize the importance of monitoring these compounds in vulnerable populations such as infants and children near such facilities. This study suggests that there is a need to establish and enforce better industrial hygiene protocols as well as improve techniques that decrease e-waste exposure to the environment. Water filtration, use of deep wells, and washing rice and other vegetables may prove effective methods in reducing exposure of the general population as well as workers to some of the compounds studied.

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