HALOGENATED ORGANICS AND METALS IN VIETNAMESE FEMALE ELECTRONIC WASTE RECYCLERS AND A NON-EXPOSED COHORT

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Introduction

The amount of generated electronic waste (e-waste) has increased markedly in recent years, with rising global demand for electronic equipment. During e-waste recycling, exposure to organics and metals present in e-waste may lead to unsafe exposures. Recycling of the waste is frequently outsourced to developing countries including China and India for economic reasons. Recycling of e-waste has also been increasing rapidly in Vietnam where home based e-waste recycling is common. Although there are rules and regulations for workplaces, home based e-waste recycling typically has inadequate worker protection. We have used biomonitoring to study a population of healthy rural, northern Vietnamese female e-waste recyclers and a demographically similar comparison population with no known exposure to e-waste for at least the previous five years. Polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and persistent pesticides were measured in serum while metals were measured in whole blood, serum and/or urine. PCBs and persistent pesticides, not related to e-waste, were included due to potential health concern in Vietnam.

An earlier report from this study reported elevated CALUX dioxin like toxic equivalents in 10 other recyclers as compared to 10 non e-waste exposed comparisons. It also described dioxins, dibenzofurans and dioxin like PCB levels in recyclers and comparisons; some polychlorinated dibenzofurans and dioxin like PCBs were reported as statistically significantly higher in recyclers[1]

Materials and methods

We present biomonitoring data from 40 healthy e-waste female workers and 20 age matched females without recent exposure to e-waste. The women were all from rural northern Vietnam (Hung Yen province in the My Hao district) and were initially located by word of mouth. The workers each had at least 5 years continuous work with e-waste recycling and the comparisons had no exposure to e-waste for at least the previous 5 years. Specimens were collected in December 2013 and January 2014. The waste stream being processed included cell phones, tablets, computers, printers and television sets, among others, but not large items such as transformers or refrigerators. The source of the e-waste is believed to be importation from developed countries including Japan as well as originating from Vietnam.

The Persistent Organic Pollutants (POPs) and the Metals Laboratories at CDC, which analyze human blood and urine samples for NHANES, analyzed these Vietnamese specimens. Measurements included 16 elements and seven arsenic species in urine and five elements and three mercury species in blood. The organohalogens measured included PBDEs, PCBs, and persistent pesticides. The analytical procedures used have been published.[2,3] Data analysis was performed using SAS, v9.3 SAS Institute Inc. (Cary, NC, USA). All concentrations less than the limit of detection (LOD) were substituted with the LOD divided by the square root of two. We did not calculate a median concentration for any analyte with less than 60% detects. This was chosen to assure that the reported median would be based on detectable results.

Institutional Review Boards (IRBs) at the University of Texas Health Science Center at Houston and the Hanoi School of Public Health approved the protocol for this study. The Centers for Disease Control and Prevention (CDC) determined that the agency was not involved in human subjects' research since no personally identifiable

information was made available to the agency as documented in writing between the University of Texas Health Science Center at Houston and CDC.–

Results and discussion

This study included women only, who all reported they were non-smokers. There were no significant differences in age (39 [range: 19-50] and 37 years [range: 18-52] years), weight (50 [range: 40-72] and 50 kg [range: 44-70]) and body mass index (BMI) (20.8 [16.6-30.4] and 20.3 kg/m^2 [17.9-27.3]), between the e-waste workers and controls, respectively. All e-waste recyclers (n=40) reported "farmer" as their occupation while in the comparison group (n=20) 50% of the women reported farmer as their occupation; other occupations reported were tailor (n=6), nurse (n=2), student (n=1), and accountant (n=1).

PBDE congeners were measured at significantly higher concentration in the e-waste recyclers than in the comparison group (Table 1). The PBDE congener profile among the e-waste recyclers was dominated by PBDE congeners with 6 to 10 bromines characteristic of commercial octa- and decaBDE commercial mixtures. E-waste workers also had significantly higher and mostly detectable concentrations of PBDE congeners present in commercial PentaBDE than the comparison population (Table 1). Commercial PentaBDE has not been used in consumer electronics, to our knowledge, but was used in polyurethane foam, i.e., BDE-47, 99, 100, 153, and 154. Detection rates for the same congeners in the comparison group were less than 20% (except BDE-153 that are present in both commercial penta- and octaBDE mixtures and thus present in consumer electronics). A possible explanation for this finding is accumulation of indoor dust inside the electronic goods being recycled. Of the 37 PCB congeners measured, only 16 of the congeners (43%) had greater than or equal to 60% detection rate in both comparisons and e-waste recyclers. Total summed PCB levels were not significantly different between workers and comparisons; p,p'-DDE was observed at 28% higher lipid adjusted serum concentration in the comparison population relative to the e-waste workers (Table 1), while no statistically significant difference was observed for p,p'-DDT. None of the seventeen PCB congeners with detection rates over 60% were significantly different between the two groups.

There are statistically significant elevations of lead in whole blood and urine of e-waste workers vs. the comparisons (Table 1). Methyl mercury in blood on the other hand was measured at significantly higher concentrations in the comparison group than in the e-waste recyclers. Urinary total mercury was marginally higher in the comparison group. Lead and mercury measurements in both Vietnamese groups were apparently higher than the US NHANES concentration, which is of concern, especially regarding perinatal exposure. Our results are consistent with other studies that measured elevated lead in e-waste recyclers.

Urinary mercury includes primarily inorganic mercury, whereas whole blood total mercury includes both inorganic *and* organic forms, such as ethyl and methyl mercury. Methyl mercury, which biomagnifies up the aquatic food chain, was higher in the comparisons than in the e-waste recyclers. Arsenobetaine, another indicator of dietary exposure through consumption of shell-fish, was apparently higher in urine from e-waste recyclers and also comparisons in relation to the NHANES values. Urinary concentrations of total mercury suggest chronic exposure to inorganic mercury, which could explain why it was higher in the recyclers. Both Vietnamese populations have greater concentrations of blood methyl mercury, is likely due to fish consumption. Total urinary arsenic was apparently higher in the e-waste recyclers and also the comparison population relative to NHANES. Although seafood also contributes to total arsenic, arsenic speciation data indicated that both Vietnamese populations had apparently higher levels of arsenous acid, monmethlyarsonic acid and dimethylarsonic acid, when compared to the US NHANES.

A striking aspect of the data is that most metals, with the exception of lead which was significantly higher in the recyclers, measured in our study were found to have no significant difference between the recyclers and comparisons, while higher compared to the NHANES median concentrations. In addition, other metals - antimony, cesium, cobalt, molybdenum, and thallium- were also apparently higher in both study populations as compared to NHANES values in US women. This is particularly of concern for such metals as cadmium, a probable human carcinogen. The source of exposures in both groups of Vietnamese women in this study is unknown.

This study, as in other e-waste studies, suggests the need to conduct further health risk assessment and to study emissions to air, water, and the local environment. Improved worker safety or industrial health measures should reduce intake of some compounds found in e-waste as shown by others[5]. Elevated levels of compounds found in comparisons will require environmental measures.

Table 1. Median serum concentration (ng/g lipid) of polybrominated diphenyl ether (PBDE) congeners with a detection frequency over 60% in the e-waste recyclers and selected organochlorines and metals in urine (µg/g creatinine) and whole blood (µg/L). Limit of detection (LOD; ng/g lipid) and detection frequency is given as well as the p-value for the comparison of the two exposure groups. The United States National Health and Nutrition Examination Survey median estimate is given as a comparison for women 18-52 years of age.

Compound	LOD[a]	Comparison (n=20)		E-waste recyclers (n=40)		Median test[b]	NHANES[c]
		Median (95%CI)	PCT >LOD	Median (95%CI)	PCT >LOD	p-value	Median (95%CI)
Polybrominated Diphenyl Ethers (PBDEs)							
PBDE-47	***0.4***	***<LOD***	***15%***	***1.5 (1.1-2.4)***	***88%***	***<0.0001***	19.4 (15.0-23.8)
PBDE-99	***0.4***	***<LOD***	***0%***	***0.7 (0.4-0.9)***	***65%***	***<0.0001***	<LOD
PBDE-100	***0.4***	***<LOD***	***0%***	***0.55 (0.4-0.7)***	***60%***	***<0.001***	3.5 (3.0-4.3)
PBDE-153	***0.4***	***1.2 (1.0-1.7)***	***95%***	***13.0 (10.2-18.8)***	***100%***	***<0.0001***	4.2 (3.3-5.1)
PBDE-154	***0.4***	***<LOD***	***0%***	***0.5 (0.4-0.7)***	***60%***	***<0.0001***	<LOD
PBDE-183	***0.4***	***0.75 (0.4-1.2)***	***65%***	***7.3 (6.1-10.0)***	***100%***	***<0.0001***	<LOD
PBDE-209	***3.2***	***<LOD***	***25%***	***73.3 (32.4-138.2)***	***100%***	***<0.0001***	n/a
		<LOD	30%	82.4 (22.2-271.8)	100%	<0.01	n/a
		<LOD	20%	68.8 (19.8-138.2)	100%	<0.001	n/a
Polychlorinated Biphenyl (PCBs)							
PCB-138/158	***0.4***	***7.95 (5.4-9.9)***	***100%***	***7.7 (6.8-8.5)***	***100%***	***>0.5***	11.6 (9.9-14.2)
PCB-153	***0.4***	***8.1 (4.0-22.9)***	***100%***	***7.8 (2.4-18.9)***	***100%***	***>0.5***	15.5 (14.1-18.4)
Persistent Pesticides							
p,p'-DDE	***2.3***	***182.5 (139.3-258.7)***	***100%***	***132(108-187)***	***100%***	***<0.05***	163 (138-220)
p,p'-DDT	***1.6***	***26.1 (22.8-32.0)***	***100%***	***21.3 (19.0-25.7)***	***100%***	***0.3***	<LOD
Whole blood measurements (µg /L)							
Cadmium	***0.1***	***0.59 (0.41 – 0.78)***	***100%***	***0.59 (0.53 – 0.68)***	***100%***	***>0.5***	0.30 (0.28 - 0.32)
Lead	***0.07***	***2.93 (2.62 – 3.88)***	***100%***	***4.82 (4.52 – 5.96)***	***100%***	***<0.0001***	0.69 (0.63 - 0.75)
Methyl mercury	***0.12***	***4.16 (2.93 – 5.08)***	***100%***	***2.76 (2.30 – 3.22)***	***100%***	***<0.05***	0.50 (0.41 - 0.64)
Mercury, total	***0.28***	***3.46 (2.50 – 3.88)***	***100%***	***2.49 (2.08 – 2.90)***	***100%***	***0.055***	0.68 (0.59 - 0.81)
Urine measurements (µg /g Creatinine)							
Arsenic, total	***0.26***	***46.94 (38.56 – 65.70)***	***100%***	***42.35 (37.54 – 49.55)***	***100%***	***0.17***	6.84 (5.95 - 8.04)
Arsenobetaine	***1.16***	***7.62 (2.32 – 24.90)***	***100%***	***6.96 (5.37 – 10.29)***	***84%***	***>0.5***	2.15 (1.75 - 2.90)
Cadmium	***0.036***	***0.832 (0.484 – 1.070)***	***100%***	***0.998 (0.816 – 1.249)***	***100%***	***0.41***	0.192 (0.172 - 0.219)
Lead	***0.03***	***2.31 (1.73 – 2.68)***	***100%***	***3.22 (2.69 – 3.99)***	***100%***	***<0.05***	0.34 (0.31 - 0.40)
Mercury, total	***0.13***	***0.34 (0.23 – 0.71)***	***75%***	***0.52 (0.42 – 0.80)***	***90%***	***0.21***	0.41 (0.33 - 0.46)

Abbreviations: LOD, Limit of Detection; 95%CI, 95% confidence intervall; PCT >LOD, percentage of results above the limit of detection; PBDE-47, 2,2',4,4'-

[a] Limit of detection (LOD) is given as a median LOD since depended on available serum amount; [b] Median test for the comparison of comparison group and E-waste recyclers; [c] The US median population estimate for females from the National Health and Nutrition Examination Survey (NHANES) for the survey years 2003 and 04 (PBDEs, PCBs and Persistent pesticides) and 2011/12 (metals) [http://www.cdc.gov/exposurereport/]

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