

Environmental and Human Health Risks

**Associated with the End-of-Life
Treatment of Electrical and
Electronic Equipment**



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PREFACE

This review was conducted as part of a research project which explores the feasibility and benefits of a regional information system on chemicals contained in electrical and electronic equipment carried out by IGES. The objective of the review was to gather available scientific knowledge on the hazards and risks associated with treatment of waste electrical and electronic equipment (WEEE) in order to substantiate the need for information sharing. When the review was being conducted, it became clear that the available information on the subject is scarce and fragmentary, and the authors concluded that it would be useful to compile the available data into a stand-alone publication. Therefore, it was decided to publish the review in its present form as an IGES report. The authors believe that this review would be of interest to the research community, environmental NGOs and others concerned with the environmental and health impacts of electrical and electronic equipment over its life-cycle.

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EXECUTIVE SUMMARY

This review aims to summarize the existing knowledge on the environmental and occupational health risks of waste electrical and electronic equipment (WEEE) recycling and other end-of-life options. Hazardous substances present in WEEE, including heavy metals (e.g., mercury, cadmium, lead, etc.), flame retardants (e.g., pentabromophenol, polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol-A (TBBPA), etc.) and other chemicals may pose significant human and environmental health risks, if improperly managed. The substances are found in complex combinations in numerous electrical and electronic devices.

Chapter I of the review describes the components commonly found in electrical and electronic equipment (EEE) that contain the highest amounts of the hazardous substances. These are:

- Mercury-containing components (gas discharge lamps, relays and switches);
- Batteries containing cadmium, lead, lithium, and mercury;
- Printed circuit boards (PCBs) containing lead (in solder), antimony (in solder), beryllium (in connectors), cadmium (in contacts and switches), brominated flame retardants (in plastics);
- Cathode ray tubes (CRTs) containing antimony (in CRT glass), lead (in CRT glass), barium (in getter of electron gun) and phosphors composed of cadmium, zinc and rare earth metals;
- Liquid crystal displays (LCDs) containing substances that make up liquid crystals;
- Plastics containing brominated flame retardants (BFRs, in various plastic parts) and plastics made of polyvinylchloride (PVC, in wire insulation).

Chapter II examines the existing WEEE management practices and associated environmental and human health hazards and risks in industrialized/developed countries. Typically, recycling of WEEE consists of manual disassembly (selective removal of hazardous and valuable components for further special treatment), followed by mechanical size reduction (shredding/grinding), mechanical separation (separation based on magnetic properties, electric conductivity, density, etc.) and metallurgical treatment (pyrometallurgical and/or hydrometallurgical treatment).

The major hazards in the recycling chain are associated with the size reduction and separation and pyrometallurgical treatment steps. Shredding, grinding or other size reduction processes lead to formation of dusts composed of plastics, metals, ceramic, and silica (glass and silicon dust). Several scientific studies have demonstrated the release of BFRs during mechanical treatment of WEEE. Pyrometallurgical treatment, namely smelting, has been shown to generate fumes of heavy metals (especially low melting point metals such as mercury, lead, cadmium, etc.). Besides, there are concerns that pyrometallurgical treatment may lead to the formation of mixed

halogenated dioxins and furans, if the feedstock contains PVC or other plastics flame retarded with BFRs.

There is a lack of information on occupational exposure during WEEE recycling in industrialized/developed countries, although exposure to substances of concern may occur throughout the WEEE processing cycle, primarily via inhalation or dermal exposure pathways. Data is only available for three groups of electronics dismantling workers whose blood samples were analyzed for BFRs. The results show that the electronics dismantling workers had been exposed to higher levels of BFRs than the general population as a result of processing BFR retarded plastics.

Other WEEE treatment options, incineration and landfilling, are also associated with potential risks. Concerns over the incineration of WEEE are similar to those raised over pyrometallurgical treatment of WEEE, i.e. the possible formation of halogenated dioxins and furans and emissions of metal fumes. The risks associated with landfilling of WEEE are due to leaching and evaporation of hazardous substances.

Chapter III describes the hazards associated with WEEE treatment in developing countries. WEEE recycling operations in developing countries are mostly unregulated and employ rudimentary techniques. WEEE recycling operations in several locations in China, India and Ghana have been particularly well investigated. The potentially hazardous recycling practices include manual disassembly of WEEE with little regard to its hazardous content, recovery of solder and chips from printed circuit boards (PCBs) by heating them, acid extraction of metals from complex mixtures, melting and extruding plastics, and burning of plastics to isolate metals.

A number of studies reviewed in the chapter have demonstrated that the crude recycling of WEEE practiced in developing countries leads to significant releases of various chemicals into the environment. High levels of various chemicals were observed in various media (dust, air, water, soil and sediments) in the workplace and ambient environment within WEEE recycling areas. The chemicals commonly detected at elevated levels in the environment were those incorporated into WEEE (e.g., metals, PBDEs) or generated through processing of WEEE (halogenated dioxins and furans).

Scientific studies on residents of Guiyu, a town in China that has become a prominent recycling hub for WEEE, reveal that exposure of the workers and general population in developing countries to WEEE-derived hazardous chemicals may be significant. Higher levels of PBDEs, polychlorinated dibenzo-*p*-dioxins and furans (PCDDs/Fs) and polychlorinated biphenyls were observed in WEEE recycling workers in Guiyu than in people living far away from the recycling site. The general population of Guiyu was also affected by the WEEE recycling activities. The levels of lead, cadmium and chromium in the blood of children in Guiyu were higher than those of children in control groups from other locations.

INTRODUCTION

Recycling of waste electrical and electronic equipment (WEEE) is an emerging industry that is at a critical point in its development, in terms of both growth and challenges. One of the challenges of recycling (and other WEEE treatment options) is the presence of various hazardous substances in WEEE, including heavy metals (e.g., mercury, cadmium, lead, etc.), flame retardants (e.g., pentabromophenol, polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol-A (TBBPA), etc.) and other hazardous chemical substances, which, if improperly managed, may pose significant human and environmental health risks.

Although WEEE is generally considered a hazardous waste, little is known about the hazards and risks associated with the end-of-life management of WEEE. Available information on the subject is scattered, and to our knowledge, so far there has been no overview publication covering the three major end-of-life WEEE management options, i.e. recycling, incineration and landfilling. This review aims to fill the gap and summarize the existing knowledge on the hazards, risks and actual adverse effects of recycling and other treatment options of end-of-life WEEE.

HAZARD vs. RISK

In the discussion about chemicals, the words “risk” and “hazard” are very often used as synonyms. However, there is a difference between these two expressions. Appreciation of which is fundamental to any informed debate on the safety of chemical products or processes.

A hazard is a built-in ability of an object (or substance) or situation to cause an adverse effect. **Risk**, on the other hand, is the chance that such effects will occur. The risk can be high or negligible. **For harm to occur – in other words, for there to be a risk – there must be a hazard and the exposure to that hazard; without both simultaneously, there is no risk. If expressed as an equation: Risk = Hazard + Exposure**

We can use an example of a dangerous animal. It can be seen as a “hazard”. When the animal is free, people in the surroundings are exposed to it. Consequently, there is a risk that these people might be attacked. However, when the animal is closed in a cage, it remains “hazardous” but there is no exposure and, therefore, no risk.

The hazard of a chemical means it has an intrinsic ability to cause an adverse effect for humans or environment. Risk is the chance that such effect will occur. Even if a chemical has hazardous properties, any risk to human health or environment is extremely low if the chemical is handled safely under controlled conditions. In order to assess risk, both hazard and exposure must be considered.

Source: CEFIC (The European Chemical Industry Council), 2003. Risk and hazard – how they differ. <http://www.cefic.be/Files/Publications/Risk%20&%20Hazard2.pdf>

An extensive survey of the available scientific literature was conducted in order to gather the hard data on workplace and environmental pollution, human exposure to chemicals and resulting adverse effects due to recycling, incineration and landfilling of WEEE. Based on the available data, the review attempts to examine the actual risks of the WEEE treatment options, not just the potential hazards. Thus, the review adheres to a risk based approach (consideration of the overall risks taking into account hazards and exposure) in characterizing the issues, in contrast to a solely hazard based approach. However, the data on the actual releases of WEEE-derived chemicals and human exposure to the chemicals are extremely scarce, making it difficult to assess the risks. Nevertheless, the authors made their best effort to provide as far as possible an objective overview of the risks associated with the end-of-life WEEE treatment options.

I. COMPONENTS AND HAZARDOUS SUBSTANCES IN WEEE

Electrical and electronic equipment (EEE) contains a wide range of substances. Some of the substances are valuable, some are toxic or otherwise hazardous and some are both. The following substances are commonly found in EEE (Hagelüken, 2006):

- Precious metals: Gold (Au), silver (Ag), palladium (Pd), and platinum (Pt);
- Base metals: Copper (Cu); aluminium (Al), nickel (Ni), tin (Sn), zinc (Zn), iron (Fe), etc.;
- Metals of concern: Mercury (Hg), beryllium (Be), indium (In), lead (Pb), cadmium (Cd), arsenic (As), antimony (Sb), etc.;
- Halogens: Bromine, fluorine, chlorine.

The substances are found in complex combinations in numerous EEE items. Although there is a huge diversity of EEE items, most of the items are made up of a relatively small number of component types. Thus, there are certain components/parts commonly found in EEE that contain the highest amounts of hazardous substances. The following sections describe the components and substances in EEE considered to be the most hazardous. The inventory is not exhaustive, only the most common and hazardous components were included. Lists of the substances of concern in the following sections were compiled from AEA (2004) and EPS Canada (2006).

Annex II of the WEEE Directive (2002/96/EC) requires that, as a minimum, the following substances, preparations and components must be removed from any separately collected WEEE:

- Capacitors containing polychlorinated biphenyls
- Mercury-containing components such as switches or backlighting lamps
- Batteries
- Printed circuit boards of mobile phones and of other devices if the surface area of the circuit board is greater than 10 cm²
- Toner cartridges
- Plastic containing brominated flame retardants
- Asbestos waste and components which contain asbestos
- Cathode Ray Tubes
- Chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) and hydrocarbons (HCs)
- Gas discharge lamps
- Liquid crystal displays, together with their casing where appropriate, of a surface area greater than 100 cm² and all those back lighted with gas discharge lamps
- External electrical cables
- Components containing refractory ceramic fibres
- Components containing radioactive substances above exemption thresholds
- Electrolyte capacitors containing substances of concern (height > 25 mm, diameter > 25 mm or proportionally similar volume).

However, some of the WEEE components listed above were not included and discussed in the review. Basically, the reason for their exclusion is that the substances of concern in the components are either not so hazardous or not used in the currently produced equipment. The following are the components not included in the review and the reasons for their exclusion:

- Capacitors containing polychlorinated biphenyls

Polychlorinated biphenyls were widely banned in the 1970s and were not used in the manufacture of new equipment since the 1980s. Thus, unless an appliance is more than 20 years old, the chances that it contains capacitors containing polychlorinated biphenyls are low.

- Toner cartridges

No information on substances of concern in toner cartridges and specific hazards related to recycling the cartridges was found.

- Asbestos waste and components which contain asbestos

Asbestos was used in older appliances such as electric coffee pots, toasters, irons and electric heaters. Modern appliances are not permitted to contain asbestos. Only appliances that are over 20 years old might contain asbestos.

- Chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) and hydrocarbons (HCs)

These substances were used in refrigeration and cooling systems, but actions taken by the Montreal Protocol have led to replacement of the ozone depleting substances. Although the substances may still be present in older appliances, they do not seem to be a major hazard anymore.

- Components containing refractory ceramic fibres

Used in furnace/heater/kiln linings. Although refractory ceramic fibres may be used in both domestic appliances and building heating appliances, the insulation material used in domestic electrical appliances is more likely to contain components based on mineral wool rather than refractory ceramic fibres.

- Components containing radioactive substances above exemption thresholds

Radioactive substances are found typically in some medical equipment, certain test instruments, and commonly in smoke detectors. Presence of the substances in the commonly used domestic or office appliances is unlikely.

- Electrolyte capacitors containing substances of concern (height > 25 mm, diameter > 25 mm or proportionally similar volume)

The WEEE Directive does not define the substances of concern in the electrolyte capacitors. However, the typical content of electrolyte capacitors (with glycol used as electrolyte) would not render the capacitors hazardous.

1.1. Mercury-containing components

As a result of the unique properties of mercury, including its uniform volumetric thermal expansion and good electric conductivity, it is used in a number of EEE. It is estimated that 22% of the yearly world consumption of mercury is used in EEE (AEA, 2004). However, its use has declined in recent years. The RoHS Directive of the European Union banned its use from 1st July 2006 (although certain uses are exempted).

Mercury is used in relays and switches (often soldered onto printed circuit boards (PCBs)), batteries, and gas discharge lamps. The following mercury-containing components seem to be widespread in EEE (NEWMOA, 2008):

- Switches used in a variety of consumer, commercial, and industrial products, including appliances, space heaters, ovens, air handling units, security systems, leveling devices, and pumps.
- Relays used in telecommunication circuit boards, commercial/industrial electric ranges, and other equipment.
- Cold-cathode lamps used for backlighting in liquid crystal displays (LCDs) on a wide range of electronic equipment, including computers, flat screen TVs, cameras, camcorders, cash registers, digital projectors, copiers, and fax machines.

1.2. Batteries

Batteries commonly contain the following substances of concern:

- Cadmium: Contained in nickel cadmium (Ni-Cd) batteries.
- Lead: Contained in sealed lead acid batteries.
- Lithium: Contained in coin cell and lithium ion batteries.
- Mercury: Contained in mercury batteries and in small amounts in several other types of batteries.

Batteries are produced in many shapes, sizes and types. From an environmental perspective, mercury-containing batteries and rechargeable batteries containing cadmium, lead and lithium are of concern. Mercury-containing batteries are banned in many countries due to concerns over their hazardous properties. Rechargeable batteries include rechargeable nickel cadmium (Ni-Cd), nickel metal hydride (NiMeH), lithium ion and lead acid batteries. About 80 % of rechargeable batteries are Ni-Cd batteries and the use of the batteries continues to grow. Rechargeable batteries are commonly used in portable (notebook/laptop) computers, mobile phones, video cameras, portable power tools, etc.

1.3. Printed circuit boards

Printed circuit boards (PCBs) are typically very complex from a chemical point of view and they can contain a number of substances of concern including:

- Antimony: Contained in some kinds of lead solder.
- Beryllium: Small amounts in the form of a copper-beryllium alloy (typically 98% copper, 2% beryllium) are used for connectors.
- Cadmium: Small amounts in plated contacts and switches.
- Chlorine and/or Bromine: Brominated and inorganic flame retardants may be present in the plastic in printed circuit boards.

- Lead: Contained in solder and some board components.

PCBs are ubiquitous in modern EEE. The glass fiber boards are coated with fire retardant epoxy plastic masses and interlaced with copper circuitry. The flame retardants used in PCBs are tetrabromobisphenol-A (TBBPA) and polybrominated diphenyl ethers (PBDEs). Semiconductor chips and other components (switches, resistors, capacitors etc) are mounted on these boards and connected to the copper circuitry by solder. The typical tin-lead solder content in scrap PCBs ranges between 4-6%, consequently lead represents 2-3% of the weight of the original board (AEA, 2004). Multi-pin connectors are also attached to the board. Copper beryllium alloys are used in the electronic connectors where a capability for repeated connection and disconnection is desired and, thus, where solder is not used to make a permanent joint. Such connectors are often gold plated to avoid oxidation of copper and, thus, the formation of a non-electrically conductive barrier of copper oxide between the two connectors.

Individual solid state devices may also be present in PCBs, i.e. attached to the boards. These are mercury relays and switches (described earlier in the section “Mercury-containing components”), capacitors and light emitting diodes (LEDs). The European WEEE Directive recommends removing such devices from PCBs prior to shredding and recovery. However, it has been suggested (AEA, 2004) that there is no need to remove capacitors as the content of the possible substance of concern, ethylene glycol, would not render the capacitors hazardous. Electrolyte capacitors usually contain electrolyte (a conductive salt, water and ethylene glycol), aluminum and copper. LEDs cause concern and may require removal because they contain gallium arsenide (GaAs). The toxicological properties of GaAs have not been thoroughly investigated, and it is unclear whether LEDs require special treatment.

Besides the hazardous substances, PCBs contain a substantial quantity of copper and valuable concentrations of gold, silver and palladium. The precious metals in the boards, mainly gold and/or platinum group metals, represent the major potential for recovery and recycling. These metals are usually recovered through copper smelting followed by metal-specific refining. In almost all respects, PCBs could serve as a substitute for primary copper concentrates from ore, because they contain not only high concentrations of copper, but also many other metals commonly found in copper ore, such as lead, cadmium, gold and silver.

1.4. Cathode ray tubes

Cathode ray tubes (CRTs) contain a number of substances of concern:

- Antimony: May be present in the screen and/or cone glass of CRTs.
- Barium Oxide: May be contained in the getter plate of the electron gun and

deposited on the interior surface.

- Lead: Contained in the CRT glass in the form of lead oxide (PbO).
- Phosphors: A phosphor coating, typically containing zinc sulfide and rare earth metals, is used on the interior panel glass of CRT screen. Cadmium sulfide has also been used in some older CRTs.

CRTs contain the greatest amount of all substances of concern in older desk top computers and TV sets. An older polychrome CRT can contain 2-3 kg of lead, while a new one typically contains no more than 1 kg of lead. The cone glass (or funnel glass) contains about 20-24% PbO, the neck glass about 28-30 % PbO and the glass frit about 80% PbO, whereas the screen glass (or panel glass) normally contains no lead (OECD, 2003). The lead is encapsulated in glass and, thus, immobilized unless and until the glass is broken. However, the glass must be broken into relatively small pieces before significant levels of lead would be available for release into the environment. The inside of CRT panel is coated with a fluorescent phosphor layer which presents an inhalation hazard if managed in a dry state. Wet processes are therefore often used to remove the phosphors. The electron gun of the CRT contains a small getter plate, weighing approximately 1-2 g including its frame and includes barium and barium compounds (OECD, 2003).

1.5. Liquid crystal displays

Liquid crystal displays (LCDs) contain one group of compounds of concern:

- Liquid crystals: Embedded between display glass and electrical control elements. Suspected to be hazardous.

LCDs are used in a wide variety of applications. Liquid crystals are embedded between thin layers of glass and electrical control elements. A cellular phone display can contain about 0.5 mg of liquid crystals, a notebook PC display about 0.5 g. Commercially available liquid crystals are mixtures of 10-20 substances, which belong to groups of substituted phenylcyclohexanes, allylbenzenes and cyclohexylbenzenes. About 250 substances are used for formulating more than a thousand marketed liquid crystals. The substances contain oxygen, fluorine, hydrogen and carbon. The liquid crystals are suspected to be hazardous, but studies on their toxicity are scarce. Studies conducted so far have not found carcinogenic potential and acute oral toxicity, although a few substances showed corrosive, irritant or sensitizing properties to the skin (AEA, 2004). The WEEE Directive seems to take a precautionary approach towards LCDs by including them among the most hazardous components and recommending a separate treatment.

It should be pointed out that LCDs are often back lighted with cold-cathode fluorescent lamps that contain mercury (see section “Mercury-containing components”).

1.6. Plastics

Plastics can be substances of concern in themselves or contain such substances as additives:

- Polyvinylchloride (PVC): Insulation on wires and cables.
- Brominated flame retardants (BFRs): Present in the plastic in plastic housings and circuit boards.
- Cadmium: Small amounts present in stabilizers for PVC.

Plastics make up a significant constituent of WEEE, about 30% by weight (Schlummer et al., 2007). PVC is one of the most widely used in EEE polymers, often as insulation coating on wires and cables. The reason for concern is the presence of chlorine in PVC and, thus, potential to yield polychlorinated dibenzo-*p*-dioxins and furans (PCDDs/Fs) during uncontrolled burning. Concerns have also been raised about the use of metals, particularly cadmium, as stabilizers and phthalates as plasticizers in PVC.

BFRs are another group of chemical additives used not only in PVC but also in other types of plastics. BFRs are used to reduce the flammability of commercial products and are found in printed circuit boards, cables, plastic covers of computers and TV sets, and other products (Birnbaum & Staskal, 2004). Two primary families of BFRs have been used in electrical and electronic equipment. The first family is polybrominated diphenyl ethers (PBDEs), which are mainly used in cabinets. The second family of BFRs is the phenolics, which includes tetrabromobisphenol A (TBBPA). TBBPA (also referred to as TBBA) is used primarily in printed circuit boards (AEA, 2004).

Table 1. Overview of the hazardous components and substances commonly found in WEEE.

| Components | Found in | Substances of concern |
|------------------------|--|--|
| Cathode ray tubes | Old TV sets, PC monitors, oscilloscopes | Pb in cone glass Ba in electron gun getter Cd in phosphors |
| Printed circuit boards | Ubiquitous, from beepers to PCs | Pb, Sb in solder Cd, Be in contacts Hg in switches BFRs in plastics |
| Batteries | Portable devices | Cd in Ni-Cd batteries Pb in lead acid batteries Hg in Hg batteries |
| Gas discharge lamps | Backlights of LCDs | Hg in phosphors |
| Plastics | Wire insulation, plastic housing, circuit boards | PVC BFRs |

II. HAZARDS AND RISKS ASSOCIATED WITH WEEE TREATMENT IN DEVELOPED COUNTRIES

The presence of hazardous substances in EEE inevitably links its end-of-life disposal with potential risks to human health and the environment. Landfilling and incineration of WEEE are options that do not allow recovery of valuable components and pose threat to the environment. In landfills, disposed WEEE may leach hazardous substances. The incineration of WEEE may result in airborne emissions. Recycling involving the removal of hazardous and recovery of valuable components represents an opportunity from both environmental and resource conservation perspectives. However, the recycling of WEEE is also associated with the potential hazards and risks of occupational exposure to hazardous substances and environmental pollution. This section examines the existing WEEE management practices and associated environmental and human health hazards and risks in developed countries.

2.1. Typical WEEE recycling methods

Recycling of WEEE consists of the following major steps: (a) disassembly: selective disassembly, targeting and singling out hazardous or valuable components for special treatment, is an indispensable process in WEEE recycling; (b) upgrading: using mechanical processing and/or metallurgical processing to upgrade the content of desirable materials, i.e. preparing materials for the refining process; (c) refining: in the last step, recovered materials are refined or purified using chemical (metallurgical) processing so as to be acceptable for their original use (Cui and Forsberg, 2003).

Disassembly is usually done manually and, at this stage, certain components (circuit boards, casings, external cables, batteries, etc.) are separated. A wide range of methods used in the upgrading and refining stages of the recycling chain can be divided into mechanical and metallurgical methods depending on the nature of the processes employed.

2.1.1. Mechanical processes

Mechanical processes are usually employed during the upgrading stage, when the various metals and materials contained in WEEE are liberated and separated. The very first and indispensable liberation process is manual dismantling, which allows the recovery of whole homogenous parts, i.e. metal, plastic or glass parts, and valuable and hazardous components that require further special treatment. Further liberation or size reduction is usually done by some kind of shredding or crushing process. After the size reduction, the materials are sorted into defined output fractions based on their specific physical characteristics, such as weight, size, shape, density, and electrical and magnetic characteristics. Typical sorting processes used are magnetic separation of

ferrous parts, eddy current separation (electric conductivity) of aluminium, and gravity separation (water or airflow tables, heavy media floating, sifting). Alternatively or in addition, manual sorting or new optical sorting techniques are also used. Intermediate screening processes and further size reduction steps might be used to support the mechanical sorting. Final output streams are usually components taken out as a whole, a magnetic fraction (going for further treatment to a steel plant), an aluminium fraction (to aluminium smelters), a copper fraction (to copper smelter), sometimes clean plastic fraction(s), and waste. The latter comprises mixed plastic fractions, glass, wood, rubber, etc, often in the form of a “shredder light fraction”, which is sent for further processing, incineration or landfilling (Cui and Forsberg, 2003).

2.1.2. Metallurgical processes

Metallurgical processes are used in the upgrading and refining stages of the recycling chain. In metallurgical processes, metals are melted (pyrometallurgical processes) or dissolved (hydrometallurgical processes) and further sorted by making use of their chemical/metallurgical properties.

Pyrometallurgical processing, notably smelting, has become the dominant method to recover metals from WEEE in the last two decades (Cui & Zhang, 2008). The majority of secondary copper and a main part of the electronic scrap is processed pyrometallurgically in a copper smelter, which includes steps such as reduction and smelting of the material, blister or raw copper production in the converter, fire refining, electrolytic refining and processing of the anode mud. In a modern secondary copper smelter, many different kinds of copper containing materials are recycled. Besides copper, these materials contain nickel, lead, tin, zinc, iron, arsenic, antimony and precious metals amongst many others (Antrekowitsch et al., 2006).

In hydrometallurgical treatment, the main process is acid or caustic leaching of solid material. This process normally requires a small grain size to increase the metal yield. Leaching solvents are mainly H_2SO_4 and H_2O_2 , *aqua regia*, thiourea, cyanide leach solutions, HNO_3 , NaOH, HCl, etc. From the solutions, the metals of interest are then isolated and concentrated via such processes as solvent extraction, precipitation, cementation, ion exchange, filtration and distillation (Antrekowitsch et al., 2006). Very little information is available on the current use of hydrometallurgical technologies for the recovery of metals from WEEE. From the available literature, it appears that hydrometallurgical processes are usually used in combination with pyrometallurgical operations, for example in so called “integrated” smelters (please see the next section).

2.1.3. Recycling processes in practice

Overall, there are two types of facilities engaged in the recycling chain according to the nature of the methods involved. The first group is the facilities that are principally engaged in the dismantling and mechanical processing of WEEE for the recovery of raw materials. The second group is the facilities employing metallurgical processes to recover metals.

The facilities in the first group vary in throughput (from relatively small to quite large operations) and degree of automation (manual labor based to highly automated operations). Figures 1 & 2 show the processes employed for the separation of materials at the WEEE treatment plant IMMARK in Switzerland (Morf et al., 2005) and a Japanese recycling facility (Matsuto et al., 2004). Both the facilities use manual disassembly and various mechanical methods for the recovery of valuables. The recyclable output fractions include various metallic fractions that are sent to smelters for further processing. The combination of the recovery methods in the Japanese recycling facility shown in Fig. 2 is representative of a group of such facilities that were constructed after the introduction of Electrical Household Appliance Recycling Law in Japan and were designed to process the four types of products regulated by the law, i.e. TV sets, refrigerators, washing machines, and air conditioners (Matsuto et al., 2004).

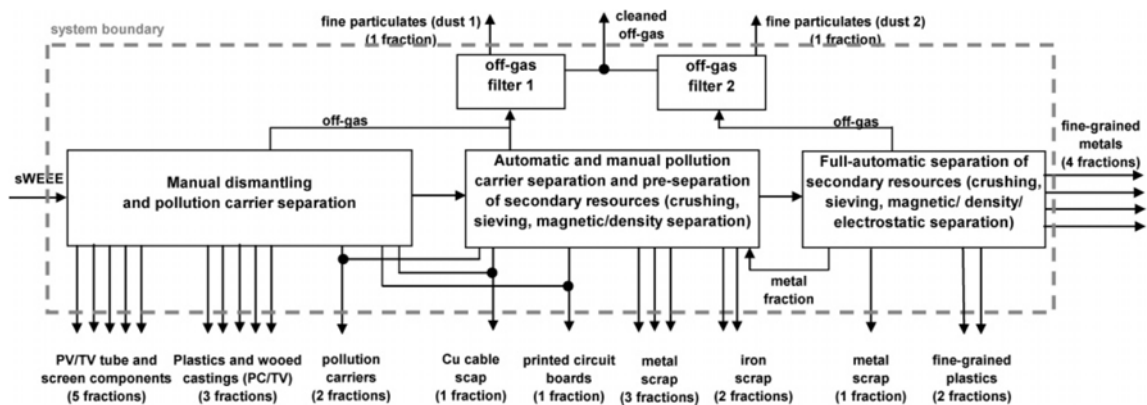


Fig. 1. Process flow in WEEE treatment plant IMMARK, Switzerland. Reprinted from Morf et al. (2005) with permission from Elsevier.

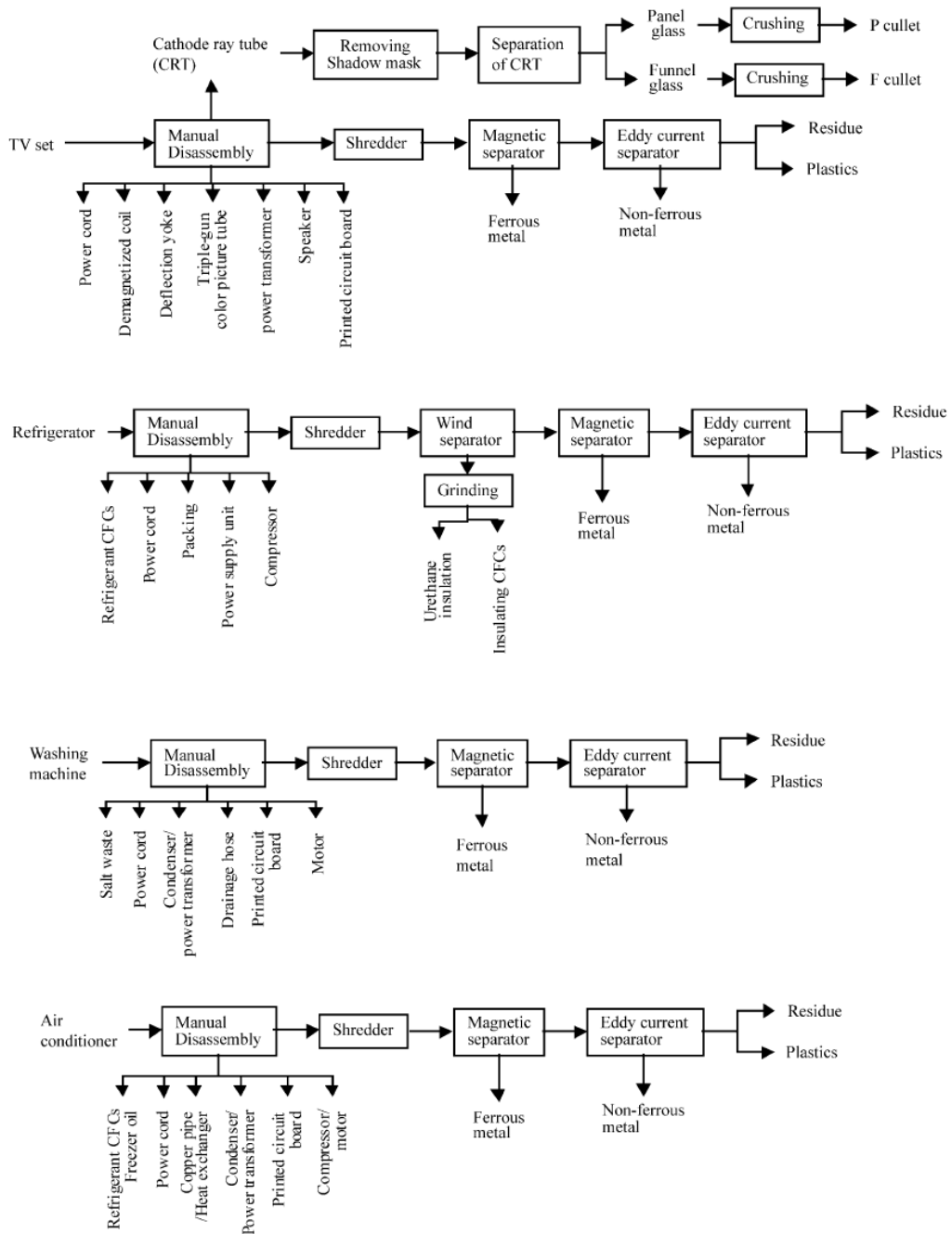


Fig. 2. Process flow in a Japanese recycling facility. Reprinted from Matsuto et al. (2004) with permission from Elsevier.

Facilities that are involved in the metallurgical recovery of metals represent an established industry, these are facilities designed to extract metals from ores, and electronic scrap is often only a small part of the feedstock. There are few large metallurgical operations which are dealing with a lot of WEEE. These so called “integrated” smelters include Boliden in Sweden, Umicore in Belgium, Noranda in

Canada, Norddeutsche Affinerie AG in Germany (Allsopp et al., 2006), and Dowa Eco-System in Japan. The term “integrated” is used to define the smelters because they represent a sophisticated combination of several metallurgical and chemical units that are closely interlinked and designed to work together.

For example, Umicore plant in Belgium, shown in Fig. 3, includes an ISAsmelt furnace, a blast furnace, a copper leaching and electrowinning plant, a precious metal concentration, a lead refinery and at the end a special metals refinery and a precious metals refinery (Hagelüken, 2005). Thus, pyrometallurgical and hydrometallurgical processes are used in a combination where pyrometallurgy comes first, and further upgrading of the output streams is done using hydrometallurgy.

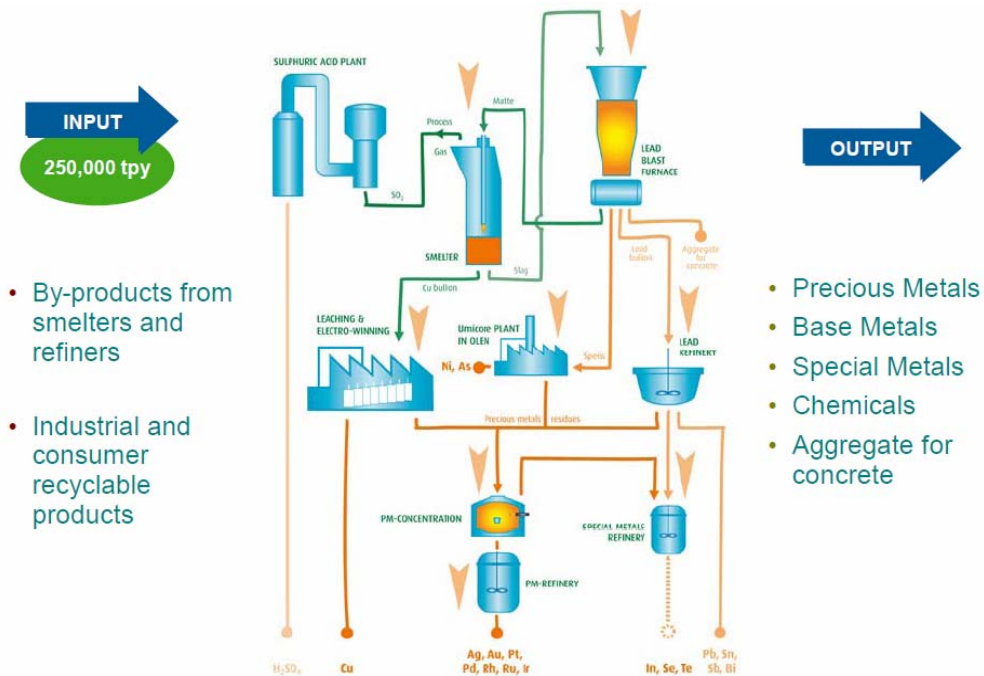


Fig. 3. Flowchart for Umicore’s integrated metals smelter and refinery. Reprinted from Hagelüken (2005) with permission from the author.

2.2. Hazards and risks associated with WEEE recycling

Our review of the literature indicates that there is very little data available on the release of substances from current WEEE processing practices in developed countries. The following sections discuss the various steps involved in WEEE processing and the occupational health and environmental pollution concerns that arise from each of the steps.

The degree of risk posed to workers and the environment varies greatly depending on the specifics of the individual facility operation (for example, Davis & Smith, 2003). Some manual disassembly operations pose few health or environmental issues, while others that involve the breaking of CRTs or the use of shredders present a range of more serious concerns.

2.2.1. Disassembly

Disassembly with the removal of hazardous and recovery of valuable components is an indispensable step prior to further treatment of WEEE. The hazard involved in this step is the possibility of accidental releases and spillages of hazardous substances. The step is also important for the later stages, i.e. the complete removal of hazardous components should be ensured, otherwise there is a risk of downstream pollution.

Mercury-containing components

Mercury found within light sources (fluorescent tubes in scanners, photocopiers, etc.) as well as switches could be released into the air of a recycling facility upon breakage of the shell. A study carried out in the United States found that between 17 and 40 % of the mercury in broken low-mercury fluorescent bulbs is slowly released to the air over a two-week period following breakage (Aucott et al., 2003). The experiment was designed to mimic a typical solid waste disposal scenario, in which a discarded bulb was broken during handling and then stored in an uncovered container for a period of time before final disposal. Almost one-third is lost in the first 8 hours after breakage. Depending on the incoming waste supply, persistently elevated airborne levels of mercury are likely to exist in the vicinity of broken bulbs. Depending on the number of bulbs, it is conceivable that air-borne mercury concentrations could exceed occupational exposure limits for inhalation.

All mercury-containing components are generally recommended to be sent to a specialized mercury recovery facility or environmentally sound and appropriately authorized hazardous waste incinerator with modern flue gas cleaning systems including iodated activated carbon filters or equivalent measures guaranteeing separation or immobilization of mercury (OECD, 2003).

Batteries

Batteries should also be removed in the initial dismantling process. All battery cells present a risk of inadvertent external short circuits and should be properly handled to avoid such risks. Large inventories of batteries should be avoided and batteries should be sent for metal reclamation or final disposal.

Ni-Cd batteries are classified as hazardous waste in many countries. The International Precious Metals Institute (IPMI, 2003) recommends recycling Ni-Cd batteries through

metal recovery to avoid final disposal, particularly by incineration. The recovery of nickel and cadmium from such batteries is achieved through heating in a furnace, where the cadmium is evaporated at a relatively low temperature, sometimes under vacuum, is removed in the furnace exhaust stream, and is then condensed in a concentrated form. The separated cadmium and nickel are then purified in additional refining steps to market grades. This operation requires a pollution control system that will capture metal fumes and particulate, particularly the cadmium and cadmium oxide that is being intentionally driven into a volatile state in the furnace exhaust.

NiMH and Li-ion batteries are considered suitable in some countries for land disposal in municipal waste, and such disposal may be appropriate if there is no economically feasible metal recovery process. But nickel can be recovered from NiMH batteries, and cobalt can be recovered from Li-ion batteries, through metal-specific smelting. There are no current economically feasible technologies for the recovery of the Li-ion polymer itself, as a separate substance, but new technologies may be developed (IPMI, 2003).

Cathode ray tubes

During the dismantling stage, CRTs stripped of their casings should be handled carefully as there is a risk of implosion due to the vacuum inside the tubes. Thus, aeration (release of the vacuum) by drilling into the CRT is required prior to its further treatment. The next steps in the CRT recycling chain, cutting the CRT and separation of its components, pose inhalation hazards to workers. First of all, the phosphor coating on the inner side of the CRT glass would be dispersed and inhaled if managed in a dry state. Wet processes are therefore often used to remove the phosphors. Second, removal of the electron gun getter may be required prior to any mechanical processing (shredding) in order to avoid the release of harmful barium oxide dusts. Furthermore, shredding/crushing the glass for the subsequent recovery of glass or lead would lead to the formation of fine glass particles. Therefore, workers should be protected from inhalation of dust that may contain phosphors, lead or barium oxide as a result of CRT breaking.

There are two major options for environmentally sound management of the leaded glass in a CRT (OECD, 2003; Kang & Schoenung, 2005). The cleaned, leaded glass fractions, with assayed lead concentrations, can be used as a feedstock in the manufacture of new leaded glass components in the CRT manufacturing industry. This process seems to be used in the U.S. in industrial scale CRT recycling (Kang & Schoenung, 2005). Another option is to recover the lead in CRTs through lead smelting. The glass would serve as a silicate flux in the lead smelting process, and is a substitute for silicate which the smelter would otherwise acquire and use (Kang & Schoenung, 2005; HCSC, 2008).

Other applications for the recovered CRT glass are limited because of its high lead content. Particularly it was noted that the smelted waste glass should not be used in

applications such as food and drink containers where there are limits on lead, barium and strontium oxide levels (ICER, 2003).

Liquid crystal displays

The WEEE Directive demands the removal and special treatment of LCDs. Although there is limited knowledge about the hazards of LCDs themselves, the main concern is over gas discharge lamps containing mercury that are used as backlights for LCDs. Like other mercury-containing components, the backlights should be removed and subject to special treatment. In its guidelines for recycling PCs (OECD, 2003), OECD suggests LCDs to be either sent for recovery operations (recently glass recovery involving the catalytic destruction of liquid crystal substances has started) or thermal treatment at an environmentally sound and appropriately authorized incinerator with modern flue gas cleaning systems.

Printed circuit boards

As mentioned earlier, PCBs typically represent the highest economic value of all EEE components but they also contain a number of substances that make their end-of-life treatment hazardous (Hagelüken, 2006). The reason is the content and intense interlinkage of different metals with flame retarded plastics and ceramic materials in PCBs. Some PCBs also have mercury switches, LED lights and electrolyte capacitors attached to them. The WEEE directive requires the dismantling and separate treatment of PCBs. The most common practice seems to be to send dismantled PCBs to smelters for the recovery of metals (Aizawa et al., 2008; Hagelüken, 2006). Mechanical preprocessing by the shredding and grinding of PCBs prior to smelting would give rise to dust containing substances of concern. The burning of circuit boards, whether before or during smelting, gives rise to concern due to the release of metals in furnace exhaust emissions, as well as the release of other products of combustion. Facilities that shred and/or burn PCBs and smelters need to pay attention to these hazards and take appropriate risk prevention measures. The hazards associated with the shredding and smelting/burning of WEEE will be further discussed in the following sections.

Plastics

Plastics make up a significant part of electronic and electric devices, and the WEEE Directive requires plastic parts to be removed and treated separately. Moreover, the high recycling and recovery targets set by the Directive can be only achieved if plastics are recycled.

Dismantling large visible plastic parts of WEEE does not pose significant risks to workers or the environment. However, if disassembly (or further treatment) involves shredding or heating, it can generate hazardous dusts or fumes. When hard plastic components containing BFRs are shredded, workers can be exposed to dust containing these chemicals. Thus, workers in shredding areas should be protected through

adaptations in shredder design, air flow controls, personal protective devices or a combination of these measures. Recycling options involving thermal treatment of plastics are associated with the risk of the formation of halogenated dioxins and furans (PXDDs/Fs), if BFRs and/or PVC are present in the plastic fraction of WEEE. The recycling facilities where thermal treatment of plastics is conducted should be equipped with modern flue gas cleaning systems.

Hazards associated with the shredding and thermal treatment of plastics are further discussed in detail below, in the sections “Mechanical processes” and “Metallurgical processes”.

Plastics are the one major category of WEEE components for which recycling opportunities are limited. The large number of polymers used in EEE is one of the obstacles, as material recycling is possible only for plastics with defined polymer composition (Kang & Schoenung, 2005; Schlummer et al., 2007). Thermal recycling of plastics, for example, as fuel and a reducing agent in smelting or as refuse derived fuel, also has limitations due to the presence of chlorine and bromine compounds. Thus, not only the particular polymer types of the various parts, but also the types of additives that are present in the plastics should be considered in the choice of an environmentally sound recycling option.

The best recycling option is the closed loop recycling, i.e. when waste plastics are recycled into new high grade plastics that could be used in the manufacture of EEE. Some manufactures in Japan have established such closed loop recycling (Aizawa et al., 2008 and references therein). In 2007, Japan has also introduced an industrial standard for identifying plastic parts to promote the closed-loop recycling systematically.

2.2.2. Mechanical processes

The primary hazards of mechanical treatment methods are associated with the size reduction and separation steps. Shredding, grinding or other size reduction processes generate dusts of the components being shredded in the facility. The composition of the dusts formed during this process includes plastics, metals, ceramic, and silica (glass and silicon dust) (MJC, 2004). Separation processes are associated with the same hazard of dust as during the step in which shredded particles are handled. The dusts may pose risk of inhalation and dermal exposure to workers as well as risk of environmental contamination.

As a minimum, inhalation of dusts may lead to aggravation of respiratory difficulties (e.g., a person pre-disposed with emphysema, chronic obstructive pulmonary disease, etc.). The actual toxicity of these particles is dependent on their composition. Particles that are metallic in nature are a cause for greater concern. For example, particles containing

metals such as cadmium, lead, copper, beryllium, and mercury have the potential to cause a variety of adverse health effects ranging from neurotoxicity (lead) to lung cancer (cadmium). Metals such as thallium (used to make optical lenses, semiconductors, and switching devices) and cadmium (used in nickel-cadmium rechargeable batteries as well as semiconductors) also have very long half-lives (decades) of elimination from the body and accumulate in various organs (primarily kidneys) resulting in toxicity (MJC, 2004).

There is scientific evidence that hazardous substances are released during shredding. In a U.S. based electronics recycling facility, assessment of air quality in the vicinity of electronic waste shredders has shown cadmium and lead levels as high as 0.27 and 1.4 $\mu\text{g}/\text{m}^3$, respectively (Peters-Michaud et al., 2003). Although the facility in which the measurements were taken was a well-run facility, the findings indicated that there was workplace contamination and a possibility of continuous exposure of workers to the toxic metals.

As it was mentioned above, shredding of plastics flame retarded with BFRs may lead to the release of the chemicals into the ambient environment. There is a relatively large body of information regarding the fate of the chemicals during recycling processes.

Brominated flame retardants, particularly PBDEs, were detected in the grams per kilogram concentration range in the fine dust fraction recovered in the off-gas purification system of a Swiss recycling plant engaged in mechanical treatment of WEEE (Morf et al., 2005). This emphasizes the high potential for BFR emissions during the mechanical processing of WEEE.

Takigami et al. (2006) measured concentrations of BFRs, i.e. PBDEs, TBBPA and hexabromocyclododecanes (HBCDs), and polybrominated dibenzo-*p*-dioxins /dibenzofurans (PBDDs/Fs) in the air of a TV recycling facility. All the chemicals were detected at concentrations higher than background levels. During the shredding process of TV housing cabinets, concentrations of the investigated brominated compounds were one to two orders of magnitude higher compared to the levels in the dismantling hall air.

Sjödín et al. (2001) reported concentrations of brominated and organophosphate flame retardants in the air at an electronics recycling facility and other environments (a factory assembling printed circuit boards, a computer repair facility, offices equipped with computers, and outdoor air). The highest concentrations of all compounds were detected in air from the recycling plant, with average concentrations of BDE-209, TBBPA and triphenyl phosphate (TPP) in air of the dismantling hall of the recycling plant equivalent to 38, 55 and 58 pmol/m^3 , respectively (Fig. 4). Significantly higher levels of these additives were present in air in the vicinity of a shredder at the dismantling plant.

The lowest concentrations within the recycling plant were detected in a storage area, furthest away from the shredder.

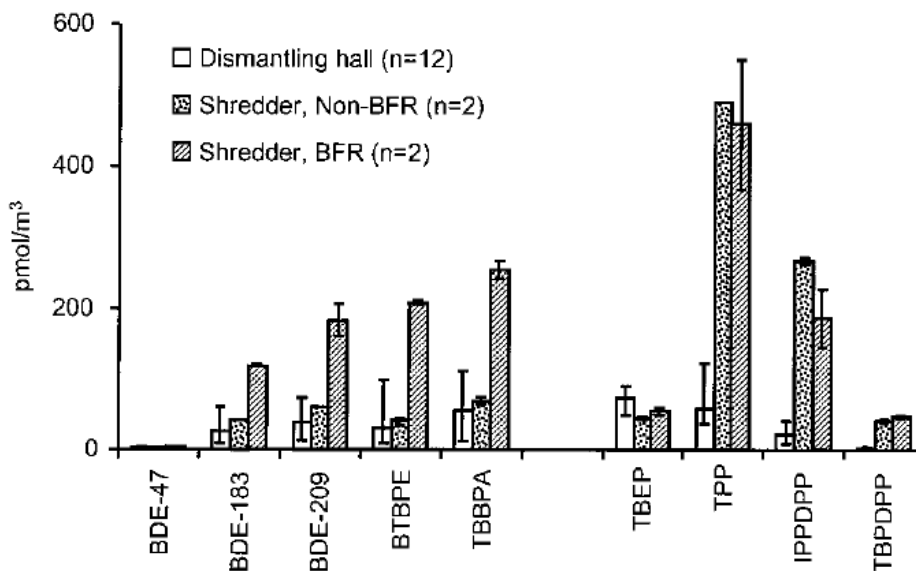


Fig. 4. Average concentrations of selected brominated and organophosphate flame retardants in air from the dismantling hall and close to the shredder, during processing of plastics containing BFRs (BFRs) or lacking such additives (non-BFR). Reprinted from Sjödin et al. (2001) with permission from American Chemical Society.

The same research group assessed exposure of workers at the above recycling plant to PBDEs (Sjödin et al., 1999). Serum samples from 19 workers were analyzed for PBDEs and the results were compared with the serum PBDE levels of clerks working full-time at computer screens and hospital cleaners (control group). The total median PBDE concentrations in the serum from workers at the electronics-dismantling plant, clerks, and cleaners were 37, 7.3, and 5.4 pmol/g lw, respectively (Fig. 5). The results show that PBDEs are bioavailable and that occupational exposure to PBDEs occurs at the electronics dismantling plant.

When the results from air measurements at the electronics recycling plant (Sjödin et al., 2001) and serum concentrations of PBDEs in the workers (Sjödin et al., 1999) were reported, the company took measures in order to reduce the exposure of the dismantlers. Structural changes of the plant were performed and the main contamination source, the shredder, was moved outside the dismantling hall. A process ventilation system was installed and cleaning routines were upgraded. These structural changes are shown in Fig. 6. In the year of 2000, the electronics recycling plant was again revisited to evaluate if the changes had had any effect on the exposure situation (Thuresson et al., 2006).

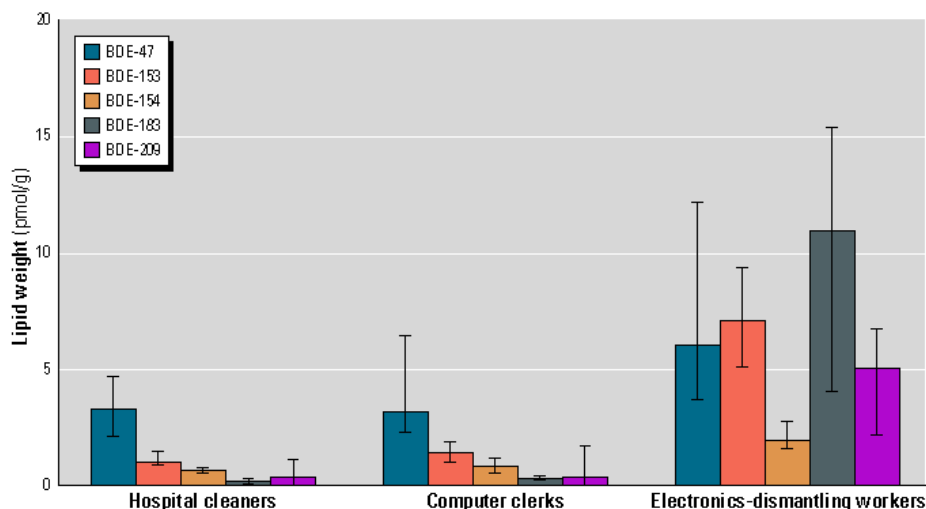


Fig. 5. Median concentrations (pmol/g lipid weight) of five polybrominated diphenyl ether congeners in the study groups. Reprinted from Sjödin et al. (1999) with permission from Environmental Health Perspectives.

A follow-up study (Thureson et al., 2006) revealed that the industrial hygiene improvements clearly reduced occupational exposure to BDE-183 and BDE-209 at the plant. Even though the amount of processed goods had doubled in 2000 as compared to 1997, there was a significant decrease in the serum levels of BDE-183 and BDE-209. In contrast to the decrease of higher brominated diphenyl ethers, the concentrations of BDE-47 and BDE-153 did not significantly change. The study showed that occupational exposure to BFRs can be reduced by proper industrial hygiene measures.

A research group from Norway (Thomsen et al., 2001) also investigated how exposure to BFRs is related to specific occupations, using plasma samples from three occupational groups: workers at an electronics dismantling facility, workers engaged in the production of printed circuit boards and laboratory personnel. The work of the electronics recycling facility workers was the manual dismantling of all kinds of electronic wastes, such as television sets and personal computers. Dust protection masks were occasionally used on a voluntary basis. The subjects working at the electronics dismantling plant had significantly higher plasma levels of TBBPA and BDE-153 compared to the other groups, and the heptabrominated congener BDE-183 was only detected in plasma from this group (Fig. 7).

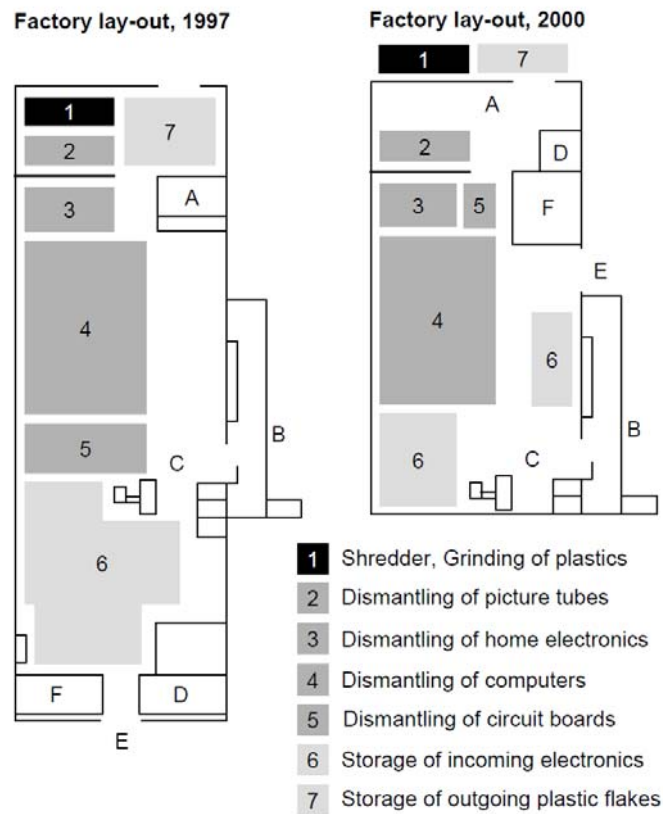


Fig. 6. Schematic plan of the electronics recycling plant in 1997 and 2000, showing the structural changes made within the plant between the years. Reprinted from Thuresson et al. (2006) with permission from Elsevier.

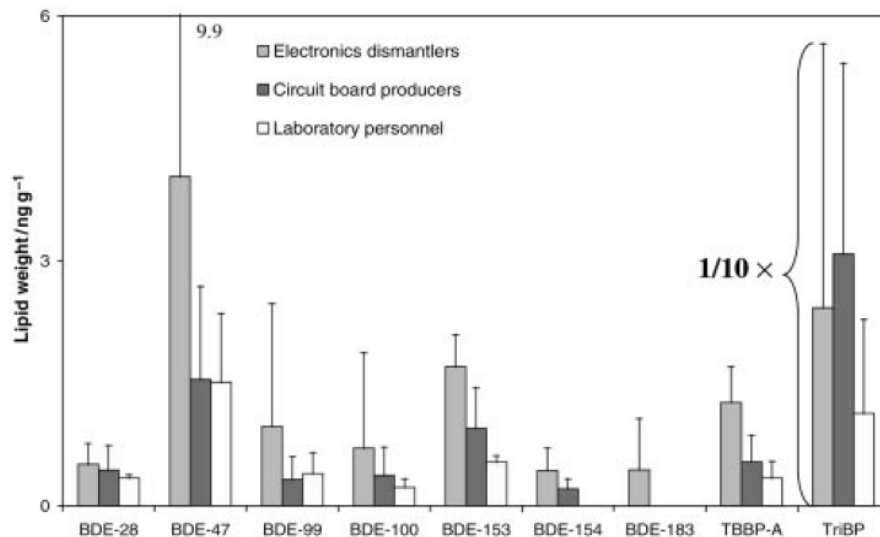


Fig. 7. The mean plasma concentrations in ng/g lipid weight of BFRs in the three occupational groups. Reproduced from Thomsen et al. (2001) by permission of The Royal Society of Chemistry.

Thus, the above studies demonstrate that chemicals could be released during mechanical treatment of WEEE. Personnel of the recycling facilities might be exposed to e-waste derived chemicals primarily through inhalation and dust ingestion. Thus, installations, such as bag houses, to capture fugitive emissions from shredding are necessary. Besides, as in any industry, WEEE recycling workers should use personal protective clothing, i.e. inhalation masks, gloves and other gear.

No scientific reports are available on outdoor environmental pollution caused by WEEE recycling facilities engaged in mechanical processing. Although hypothetically the dust and pollution generated during mechanical treatment may be released outdoors through the ventilation system, doors, windows and floor drains.

2.2.3. Metallurgical processes

Hydrometallurgy and pyrometallurgy utilize different technological approaches for the recovery of metals. With regard to pollution from these methods, pyrometallurgical processes generate atmospheric pollution, while hydrometallurgical processes produce large volumes of waste water.

Pyrometallurgical processes, particularly smelting, seem to be a widely practiced method of metal recovery from WEEE. Hazards associated with the pyrometallurgical processes are possible emissions of fumes of metals, particularly the low melting point metals like copper, cadmium, lead, etc.

Two studies that investigated emissions of metals from smelting were found in the scientific literature. Both studies assessed metal emissions from a copper smelter of Noranda Inc. in Quebec, Canada (Telmer et al., 2004; Zdanowicz et al., 2006). The smelter was processing metal scrap from WEEE as one of its feedstocks. Telmer et al. (2004) monitored the levels of 35 different elements in snow up to a radius of 50 km around the smelter in 1998. Results showed that many of the elements (Cu, Ag, In, Sb, Pb, As, Tl, Mo, Zn, Cd, Co, Be, Ni, Na, Ba, Fe, Cr, V, Ti, Y, Al, U, Ce, Li, S, La, and Sr) were emitted from the smelter. The concentrations of many of the metals remained higher than the regional background levels even at a distance of 50 km from the smelter. Concentrations of Cu, Pb, and Zn near the smelter were 525, 353, and 149 $\mu\text{g}/\text{L}_{\text{meltwater}}$, respectively, and dropped to 2.1, 3.5, and 3.1 $\mu\text{g}/\text{L}$ by 45 km distance. Regional background concentrations estimated for more distant sites were 1.1, 1.7, and 1.6 $\mu\text{g}/\text{L}_{\text{meltwater}}$ for Cu, Pb, and Zn, respectively.

Zdanowicz et al. (2006) analyzed the elemental composition of particulate matter in air and snow near the Noranda's copper smelter. Around 58 % of particles in the smelter plume were metal-bearing particles, while in ambient air or snow around 15 % were such particles. The dominant metal-bearing particle type in snow was Fe-S-Cu but Zn-S,

Fe-S, and Cu-S were also common. Pb was dominant in air-filtered particles, even those collected far (>60 km) from the smelter.

Pyrometallurgical treatment of WEEE also raises concerns which differ from those most commonly associated with metal ores. The presence of halogens in plastics (e.g., chlorine in PVC and bromine in BFR treated plastics) in the electronics scrap feedstock may lead to the formation of brominated and chlorinated dibenzofurans and -dioxins in burning processes, unless special installations and measures are present.

Numerous scientific studies have shown that thermal treatment of bromine and chlorine containing substances may lead to the formation of chlorinated, brominated and mixed brominated-chlorinated dibenzodioxins and -furans (PCDDs/Fs, PBDDs/Fs and PXDDs/Fs) (see review by Weber & Kuch, 2003). The total amount of PBDDs/Fs (and PXDDs/Fs) formed during thermal processes was shown to depend largely on the quality of precursor compounds and thermal conditions. High dioxin and furan formation potential was shown for insufficient combustion (e.g. accidental fires, uncontrolled burning) and pyrolysis (350-800^oC) conditions in the presence of potent precursors (polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs) and polybrominated phenols (PBPs), high amounts of PBDDs/Fs can be formed via the precursor pathways. In contrast, under controlled combustion conditions (high temperature incinerators), there is a low potential for the formation of PBDDs/Fs as BFRs can be destroyed with high efficiency and may then not serve as precursors for PBDDs/Fs formation.

Although the formation of chlorinated, brominated and mixed chlorinated-brominated dioxins was observed in a number of studies on actual incineration and laboratory tests, there are no scientific data on emissions of these substances specifically from pyrometallurgical treatment of WEEE. Some data are only available from personal communication of Allsopp et al. (2006) with staff of the integrated smelters in Belgium (Umicore) and Sweden (Boliden) who were dealing with the smelting of WEEE. The informants from Umicore explained that chlorinated dioxin emissions were low (below the regulatory standards) due to destruction by high temperatures (1200 to 1300 ^oC), rapid cooling of the gasses and a gas cleaning system. However, only one measurement of brominated dioxins and furans had been made. The test was carried out on electrical/electronic waste in which the BFR fraction was described as “rather modest”. Six polybrominated dioxins and nine polybrominated furans were analyzed but none was above the detection limit. Thus, the data was not enough to confirm whether brominated or mixed brominated-chlorinated dioxins and furans were produced. At the time of the survey (ca. 2006), brominated dioxins and furans were not routinely measured at Umicore and Boliden. Therefore, Allsopp et al. (2006) suggested that it was likely that other smelters processing WEEE were not monitoring the chemicals either.

Although it seems possible to control dioxin emissions through the design of the technological process (high temperature, off-gas treatment, etc.), Hagelüken (2006) raised concerns that not every smelter can currently process WEEE in an environmentally sound manner. According to Hagelüken (2006), state-of-the-art integrated metal smelters designed for the treatment of electronic scrap have the necessary off-gas treatment systems and can safely prevent dioxin emissions; however standard copper smelters, designed for the treatment of mining concentrates or simple copper scrap, usually are lacking such installations. Thus, on a global scale only a handful of integrated smelters have the capability to treat electronic scrap in an environmental sound way.

From the above information it is possible to assume that occupational exposure to metals and brominated and chlorinated dioxins may occur at smelting facilities processing WEEE. However, there appears to be no scientific studies specifically on exposure from pyrometallurgical treatment of WEEE.

Hydrometallurgical processes are usually used to further upgrade and refine metals recovered by pyrometallurgical methods. Hydrometallurgical processes, such as electrowinning and electrorefining, use an acidic solution (typically concentrated sulfuric acid and peroxide at elevated temperatures, and also hydrogen cyanide in some cases) to dissolve metal shreds and electric current to remove the metals from the solution. Such treatment will result in higher levels of exposure to acid fumes, acid in its liquid form, as well as cleaning solvents which may be used to prepare the shreds for acid etching. Acid fumes are hazardous to human health as they are generally irritating to the upper respiratory system. Furthermore, the fumes can reach the lungs and result in direct damage to the pulmonary tissue (MJC, 2004). In addition to the volatile emissions, the hydrometallurgical processes generate large volumes of acidic and often corrosive effluent. Disposal of the effluent is a major concern associated with the use of hydrometallurgy. For example, several accident cases at gold mines resulting in severe environmental pollution have raised concerns about the use of cyanide as a leaching reagent. Currently, research on the development of metallurgical methods is focused on the search of less hazardous reagents (Cui & Zhang, 2008).

2.3. Hazards and risks associated with incineration of WEEE

One strategy for dealing with WEEE is to incinerate the combustible fraction of the waste, either to reduce its volume prior to landfilling or to concentrate valuable metals in the residual ash so they can be reclaimed in a subsequent operation. Concerns over such treatment option are similar to those raised for pyrometallurgical treatment of WEEE, i.e. the possible formation of polyhalogenated dioxins and furans and emissions of metal fumes. These issues have received considerable attention in scientific studies.

Stewart & Lemieux (2003) conducted WEEE incineration experiments using a pilot-scale rotary kiln incinerator. A mixture of personal computer motherboards, keyboards, and cases were burnt over a range of temperatures to investigate the potential toxic emissions from the incineration of WEEE. The flue gas was analyzed for metals, halogens, volatile and semi-volatile organic products of incomplete combustion, including polychlorinated dibenzo-*p*-dioxins and -furans (PCDDs/Fs). Ash residues were analyzed by toxicity characteristic leaching procedure. Measured metal emissions were significant, and consisted primarily of copper, lead, and antimony. Although brominated dioxins and furans (PBDDs/Fs) were not measured, the emission of bromine in its diatomic and ionic forms was detected. Emissions of chlorinated dioxins and furans (PCDDs/Fs) were well below regulatory limits. Based on the results, Stewart & Lemieux (2003) suggested that incineration may be a viable option for electronics waste disposal, provided an appropriate particulate control device is used to control metal emissions. However, the drawback of the study is that brominated dioxins and furans were not measured.

The monitoring of halogenated dioxins and furans (PXDDs/Fs) from controlled combustion of BFRs containing waste was done in several other studies (Vehlow et al., 2000; Sakai et al., 2001; Söderström & Marklund, 2002; Watanabe et al., 2008).

Söderström & Marklund (2002) combusted municipal solid waste pellets treated with three brominated flame retardants, decabromodiphenylether (DecaBDE), hexabromocyclododecane (HBCD), and tetrabromobisphenol-A (TBPPA). All of the bromine-chlorine containing fuels formed PXDDs/Fs as well as PCDDs/Fs and PBDDs/Fs when burned in a reactor. No original brominated flame retardants were found in the flue gas, indicating that they were destroyed in the combustion zone and that new brominated organic compounds were formed in the cooling zone.

However, the association between content of BFRs in real WEEE and formation and/or release of dioxins and furans from its controlled combustion is less clear. Some studies indicate formation of dioxins and furans from combustion of WEEE and importance of bromine content in the feedstock (Funcke & Hemminghaus, 1997; Watanabe et al., 2008), others, to the contrary, show thermal destruction of the dioxins and furans and little effect of bromine/chlorine content on the final amounts of dioxins and furans (Vehlow et al., 2000; Sakai et al., 2001; Tange & Drohmann, 2005).

One study (Funcke & Hemminghaus, 1997) did observe the formation of PBDDs/Fs and PXDDs/Fs as a result of combustion of BFR containing WEEE. The experiment involved combustion of municipal waste and co-combustion of municipal waste with WEEE. When BFR containing WEEE was added, the quantity of PBDDs/Fs and PXDDs/Fs in the flue gas increased.

Watanabe et al. (2008) also observed the formation of PBDDs/Fs, PCDDs/Fs, and PXDDs/Fs during combustion of waste printed circuit boards (PCBs) in a pilot-scale incinerator, but most of the formed brominated and chlorinated compounds were decomposed and/or removed during the flue gas treatment and, as a result, were not detected in flue gas at the final exit. From the material balance perspective, formation of PBDDs/Fs, PCDDs/Fs, and PXDDs/Fs took place as their amounts after primary combustion were several orders of magnitude higher than the input amounts. Along with the formation of dioxins and furans, decomposition of BFRs, notably like PBDEs, TBBPA and decabromodiphenylethane (DBDPE), was observed. The decomposition rates of these compounds were 30-99.999 %.

Sakai et al. (2001) combusted used TV casings and waste printed circuit boards under controlled conditions in a test incinerator equipped with a flue gas treatment system. The experiments demonstrated a high destruction efficiency of BFRs, PBDEs were destroyed by more than 99.9% at a residence time of 2 s. In these tests, PBDDs/Fs present in the input materials were decomposed during the incineration process, and when PBDDs/Fs, PCDDs/Fs and PXDDs/Fs were considered as a total, the total output amount was less than the total input amount. The overall destruction rate in all runs was more than 90%.

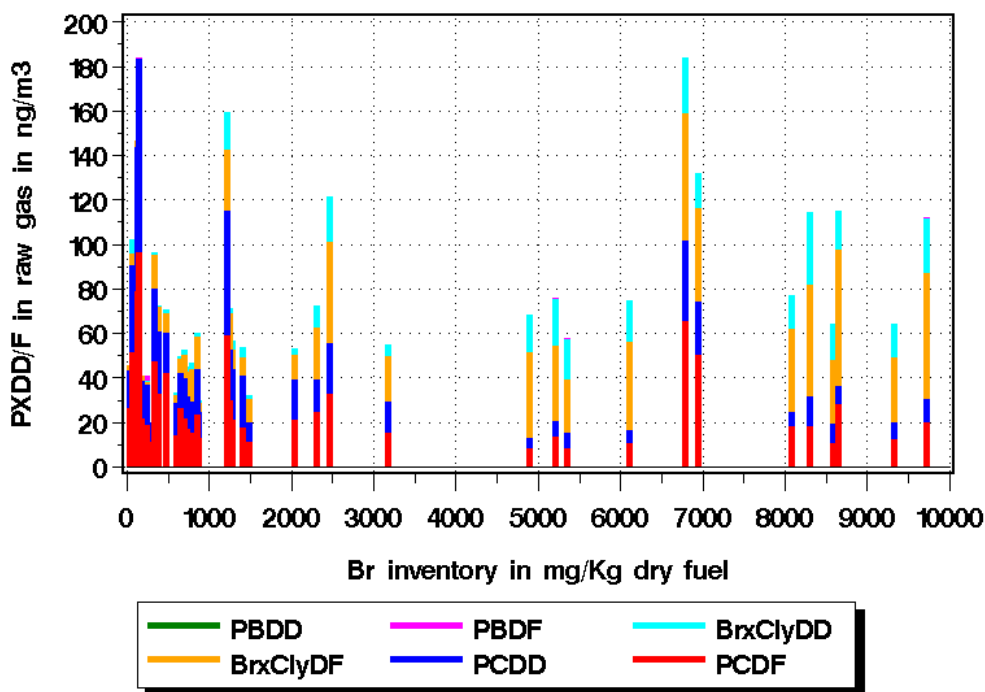


Fig. 8. Total concentration of PXDDs/Fs in flue gas versus bromine inventory in fuel. Reprinted from Tange and Drohmann (2005) with permission from Elsevier.

In a series of incineration experiments (Vehlow et al., 2000; Tange & Drohmann, 2005), municipal solid waste containing up to 20 % wt. of different types of WEEE plastics was combusted in a test incinerator. Although the elevated bromine concentrations resulted in increased proportion of mixed brominated-chlorinated PXDDs/Fs, the total levels of PXDDs/Fs were not altered significantly by the co-combustion of materials containing BFRs (Fig. 8). Similar to the results of Sakai et al. (2001), more than 90% of PBDDs/Fs present in the input materials were destroyed in these combustion tests (Tange and Drohmann, 2005).

Regardless of their results, all of the studies did emphasize the importance of adequate flue gas treatment. For example, in the study by Watanabe et al. (2008) levels of dioxins and furans in flue gas dropped significantly after flue gas treatment (a difference in the levels in kiln exit gas and final exit gas was up to two orders of magnitude). This indicates that BFRs and the formed PXDDs/Fs could be decomposed/removed under controlled combustion conditions with efficient flue gas treatment system. Furthermore, Tange & Drohmann (2003) argued that plastics containing brominated flame retardants can be safely handled in modern incinerators.

However, incineration is no longer an available disposal option in EU, where WEEE Directive set high recycling and recovery quotas for WEEE. The quotas ranging from 50 to 75% for recycling and 70 to 80% for recovery could not be achieved without including plastics into the recovery or recycling systems. Thus, material recycling of plastics is important to achieve the targets. Incineration with energy recovery could be the best second option. Similarly, Fisher et al. (2005) suggested that thermal treatment with energy and material recovery should be considered as a complement to mechanical recycling of plastics.

2.4. Hazards and risks associated with landfilling of WEEE and waste residues from WEEE recycling

The hazards associated with placing WEEE in landfills are due to the variety of substances they contain. The main problem in this context is the leaching and evaporation of hazardous substances. There is no guarantee that controlled landfills with liners and leachate collection systems completely eliminate risks of pollution, and potential environmental impacts are considerably higher when WEEE is put in uncontrolled landfills. In the case of uncontrolled landfills contaminated leachate goes directly to the soil, groundwater and surface water.

It is difficult to assess the environmental consequences of WEEE in landfills due to the extreme complexity and long time span of the processes in landfills. This may be the reason for a very limited number of scientific studies available on the fate of WEEE in landfills. The studies that were located applied Toxic Characteristic Leaching Procedure

(TCLP) to WEEE to assess leachability of certain WEEE components. TCLP is a method developed by the US EPA to determine toxicity of waste in landfill by simulating the leaching that waste will undergo if disposed in a sanitary landfill.

A group led by Professor Townsend at the University of Florida conducted several experimental studies on the leachability of WEEE using the standard TCLP or modified versions of it. In one of the studies (Townsend et al., 1999), 36 CRTs were processed and analyzed with the TCLP test. CRT samples produced an average concentration of 18.5 mg/L lead. This exceeded the 5.0 mg/L Toxicity Characteristic (TC) level. In initial testing, twenty-one of the thirty color CRTs exceeded the 5 mg/l of lead regulatory limit for characterization as a hazardous waste. None of the six monochrome CRTs exceeded this limit. The largest concentration of leachable lead came from the funnel portion of the CRTs at an average lead concentration of 75.3 mg/L. Based on the results, the authors called for inclusion of CRTs into regulatory programs targeting hazardous chemicals.

In another study, Townsend et al. (2004) tested 12 different types of electronic devices (CPUs, computer monitors, laptops, TV sets, printers, VCRs, cellular phones, remote controls, etc.). In many cases, lead concentrations in the leachates exceeded the regulatory limit of 5 mg/L and every device type leached lead above this level in at least one test. The authors concluded that the results provided sufficient evidence that discarded electronic devices that contain a color CRT or printer wiring boards with lead-bearing solder have a potential to be hazardous wastes for lead.

The same group also analyzed leachate samples from Florida landfills for BFRs and heavy metals (Townsend et al. 2003). Concentrations of all measured heavy metals in the leachate were far below the TCLP limits, but unexpectedly high levels of unknown organo-bromine compounds (possibly, BFRs, BFR breakdown products or other organo-bromine compounds) were detected. Authors suggested a possibility of transformation of BFRs into other chemicals and propensity for BFRs to migrate from landfills through leaching.

The low levels of heavy metals in landfill leachates in the above study of Townsend's group were explained in their other study (Townsend and Chang, 2003). They showed that TCLP, designed to simulate worst-case leaching in a laboratory setting, might be too "aggressive" and might not accurately reflect the concentrations observed under typical landfill conditions. In the study, two lead-containing components found in electronic devices (computer PCBs and CRTs) were leached using the TCLP and leachates from 11 Florida landfills. The results indicated that the extractions using landfill leachates resulted in lower lead concentrations than those by the TCLP.

Osako et al. (2004) have also showed the presence of BFRs in leachate from landfills in

Japan. Higher concentrations of BFRs (PBDEs and TBBPA) were detected in the landfills that had crushed WEEE.

Besides the leaching of substances in landfills, there is also a risk of vaporization of volatile hazardous substances. For example, for mercury, both the leaching of mercury and the vaporization of metallic mercury and methylated mercury are of concern. Once buried, some of the inorganic mercury in the landfill is converted by bacteria living there into more toxic organic mercury forms. Organic mercury can be released into the atmosphere from landfills in the same way as inorganic mercury is released. Dimethyl mercury, an organic form of mercury, was detected in landfill gas at levels 1,000 times higher than what has been measured in open air (Lindberg, 2001).

Overall, scientific studies suggest that WEEE leach various substances in landfills. In view of the complex material mixture in WEEE and unpredictability of landfill processes, it is not possible to exclude environmental (long-term) risks even in controlled landfills.

III. HAZARDS AND RISKS ASSOCIATED WITH WEEE TREATMENT IN DEVELOPING COUNTRIES

The WEEE recycling sector in developing countries is largely unregulated and WEEE is often processed to recover valuable materials in small workshops using rudimentary recycling methods. In addition to domestically generated WEEE, developing countries with lax environmental legislation and cheap labor are often the destinations for WEEE generated abroad. China, India and Pakistan have been identified as common destinations for WEEE in Asia (BAN & SVTC, 2002; Brigden et al., 2005). Recently, there has been an increase in WEEE recycling activities in other regions, particularly in some African countries, including Ghana (Brigden et al., 2008). It is noteworthy that only the informal recycling sector was surveyed in these four countries.

WEEE recycling operations in several locations in China, India and Ghana have been particularly well investigated. The locations in India, Pakistan and Ghana are New Delhi, Karachi and Accra, respectively (BAN & SVTC, 2002; Brigden et al., 2005, 2008). The most prominent areas for the informal processing of WEEE in China are in southern Guangdong Province and around the city of Taizhou, in eastern Zhejiang Province (Hicks et al., 2005). The town of Guiyu, in Guangdong Province, has attracted a lot of attention from NGOs and scientists (BAN & SVTC, 2002; Brigden et al., 2005; and a number of publications reviewed below). It is, in a sense, an established WEEE recycling center with the recycling activities being a fundamental part of Guiyu's economy (Hicks et al., 2005).

3.1. Methods employed for recovery of valuable materials

In developing countries, WEEE is often processed in small workshops, where there is no real control over the materials processed, the processes used, or the emissions and discharges from these facilities (BAN & SVTC, 2002; Brigden et al., 2005; Brigden et al., 2008). The primary goal of such recycling operations is the recovery of valuable materials, and the goal is pursued with little regard for the environment or human health.

Figure 9 shows recycling processes typically used in India and China for processing WEEE. According to BAN & SVTC (2002) and Brigden et al. (2005), similar recycling activities occur in both countries. Most of the operations employ rudimentary techniques and are conducted by workers without protective clothing. The potentially hazardous recycling practices included manual disassembly of WEEE with little regard to its hazardous content, recovery of solder and chips from printed circuit boards (PCBs), acid extraction of metals from complex mixtures, melting and extruding plastics, and burning of plastics to isolate metals.

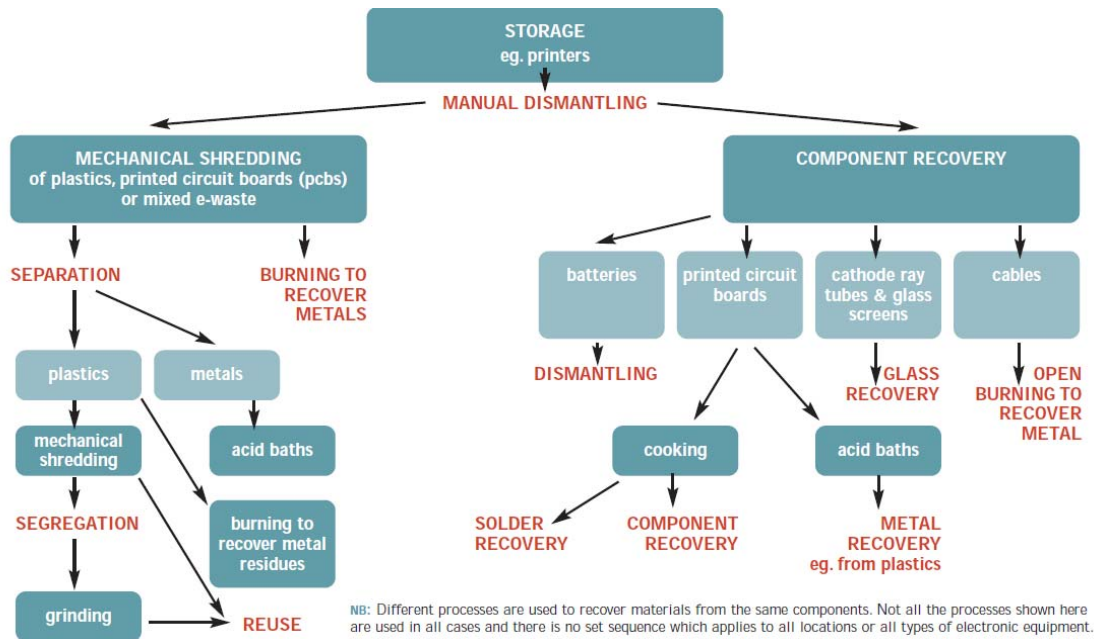


Fig. 9. WEEE recycling processes in India and China. Reprinted from Brigden et al. (2005) with permission from Greenpeace International.

In Ghana, the primary activities were the manual disassembly of WEEE to isolate metals (mainly copper and aluminium) and the open burning of certain components to isolate copper from plastics in which they are encased, particularly from plastic coated wires and cables (Brigden et al., 2008). More complex processes, like solder recovery, plastic shredding, and the use of acid leaching, used in China and India are not known to be used in Ghana.

Manual disassembly and recovery of valuables

All the recycling processes start with the manual disassembly of WEEE. According to a report by BAN & SVTC (2002), in Guiyu, the following components are separated for further recycling: materials containing copper (including motors, wires and cables, CRT yokes), steel (including internal computer frames, power supply housings, printer parts, etc.), plastics (including housings of computers, printers, faxes, phones, monitors, keyboards, etc.), aluminium (printer parts, etc), printer toners and printed circuit boards (PCBs). At this stage, manual disassembly and recovery of valuable components from CRTs and PCBs are of particular concern.

In the manual disassembly process, CRTs are broken to remove copper yokes that are further used for copper recovery. This exposes the worker to the phosphor powder covering the inner surface of the front panel that contains heavy metals. Environmental pollution is also a likely outcome of the breaking and further handling of CRTs. In Guiyu, broken CRTs were dumped on open land after removal of the yokes (BAN & SVTC,

2002). In India, CRTs were reportedly smelted for recovery of glass, but prior to the treatment they were stored in an open area (Brigden et al., 2005). The open air storage and dumping of CRTs raise concerns regarding the possibility of lead contained in the CRT glass leaching out into the environment.

The common method to recover valuables and solder from PCBs is by heating PCBs until the connecting solder is melted. Heating is done using coal grills, propane torches, kerosene burners, or other simple devices. Melted solder is then collected and individual components attached to PCBs are manually removed. Valuable chips are sold or subject to acid digestion for precious metal extraction. Waste boards stripped of chips are further burnt or acid digested in order to recover the remaining metals. Heating of PCBs for de-soldering and removal of chips undoubtedly exposes the worker to fumes of metals, particularly those in solder (often lead and tin), and other hazardous substances that can be potentially released during such treatment.

Acid extraction of metals

In both China and India, primitive hydrometallurgical processes are used to recover metals from WEEE (BAN & SVTC, 2002; Brigden et al, 2005). Metals are dissolved in strong acid solutions and subsequently recovered from the solutions. According to Brigden et al. (2005) in Guiyu, China, the workshops were situated in the open on the banks of rivers, while in Delhi, India, this type of activity took place in small, enclosed workshops. *Aqua regia* (a mixture of 25% concentrated nitric acid and 75% concentrated hydrochloric acid) was apparently used in Guiyu for extraction of gold (BAN & SVTC, 2002). Concentrated nitric acid and hydrochloric acids were also reportedly used for the extraction of copper in similar operations in Delhi (Brigden et al., 2005). The reports have noted that workers employed in the operations had nothing to protect them from inhaling toxic acid fumes. Various volatile compounds of nitrogen and chlorine are known to be emitted during such processes. The wastes generated along the process, i.e. waste acid solutions and sludges, were poured out and dumped onto open ground or into water streams.

Melting and extruding plastics

Plastics are processed in a similar way in both China and India (Brigden et al., 2005). It is manually removed from WEEE and mechanically shredded. The next treatment step may be some kind of separation (e.g., by color or density) and/or further grinding. Plastics melting and extruding operations were reported to be taking place in Guiyu. The operations were carried out in rooms with little ventilation and no respiratory protection (Brigden et al., 2005; BAN & SVTC, 2002).

Burning of plastics

At workshops in both China and India, some WEEE parts are burned on open fires to recover metals from plastics in which they are encased; this includes plastic coated wires as well as other complex components (Brigden et al., 2005). The burning of plastics, mainly plastic coated wires and cables, to separate metals is also common in Ghana (Brigden et al., 2008). Open burning of unwanted scrap and wastes is also a common practice everywhere. It is extremely likely that due to the presence of PVC or brominated flame retardants in plastics, the emissions and ashes from such burning will contain high levels of mixed brominated and chlorinated dioxins and furans (PXDDs/Fs).

Indeed, the formation of dioxins and furans was observed in an experimental study on simulating open burning of wires and printed circuit boards (PCBs) (Gullet et al., 2007). In the study, combustion of PCBs and wires was performed in an open burn simulation facility to provide a preliminary characterization of emissions, including PCDDs/Fs, PBDDs/Fs, fly ash particulate matter (PM) and metals, and residual ash, from rudimentary recycling operations. Fly ash from both types of waste contained considerable amounts of several metallic elements and halogens. In the case of PCBs, PM emissions were composed of bromine, lead, tin, copper, antimony, and arsenic. Lead emissions exceeded US municipal waste combustor limits by over 200 times. PM emissions from insulated wire were composed of chlorine and lead, with smaller amounts of antimony and bromine. Exceptionally high emissions of PCDDs/Fs were observed during open burning of insulated wire (around 12000 ng TEQ/kg of wire), likely due to the uncontrolled nature of the fire as well as to the high chlorine content. Emissions of PCDDs/Fs from PCBs (around 100 ng TEQ/kg of PCBs) were also relatively high compared to other sources, such as residential waste and biomass burning. PBDD/F emissions were measured only in PCB burning tests and were also high. Leaching tests of the residual bottom ash showed that lead concentrations exceeded US EPA landfill limits.

Very similar amounts of PCDDs/Fs emissions were observed by Leung et al. (2006) during experimental burning of PCBs and wires in an open burning test facility. Emission of PCDDs/Fs in two separate PCB burning tests were 31 ng TEQ/kg waste input and 155 ng TEQ/kg waste input, whereas two separate wire tests showed extremely high PCDDs/Fs (12419 ng TEQ/kg waste input and 15610 ng TEQ/kg). The wire results were about three orders of magnitude higher than those for the open burning of household waste.

3.2. Workplace and environmental contamination

Rudimentary recycling techniques coupled with the amounts of WEEE processed have already resulted in adverse environmental and human health impacts in China, India

and Ghana (Brigden et al. (2005) and a number of publications reviewed below). The impacts have been particularly well documented for Guiyu in China, while there is less information for India and Ghana (except for the reports by Brigden et al. (2005, 2008)). Therefore, the data reviewed in the following sections are mainly for Guiyu. The town is made up of several villages located in the Chaozhou region of Guangdong Province, 250 km northeast of Hong Kong. Since 1995, the traditionally rice-growing community has become a recycling center for WEEE arriving from overseas.

Dust

Brigden et al. (2006) screened dust samples from the workshops in China and India involved in de-soldering and PCB disassembly. With the exception of one sample of dust, all other dust samples from the workshops in both China and India contained extremely high concentrations of lead and tin. For all dusts collected from the workshops in China, the concentrations of lead (31300-76000 mg/kg) were hundreds of times higher than typical levels in indoor dusts. The levels of lead in Indian workshop dusts (2360-10900 mg/kg) were elevated by approximately 5-20 times background levels. Tin concentrations in the same samples were in the range 25100-293000 mg/kg and 3140-17400 mg/kg for China and India, respectively. For all samples from both countries, high lead concentrations were associated with high tin concentrations, indicating a common source. Other metals found at elevated concentrations in the dust samples from the workshops in both China and India were antimony, cadmium, copper, nickel, silver and zinc.

Leung et al. (2008) evaluated the extent of heavy metals (Cd, Co, Cr, Cu, Ni, Pb, Zn) contamination from PCB recycling in Guiyu using surface dust samples collected from recycling workshops, adjacent roads, a schoolyard, and an outdoor food market. As expected, elevated concentrations of lead, copper, zinc and nickel were detected in workshop dust (with mean values of 110000, 8360, 4420, and 1500 mg/kg, respectively) and in dust from adjacent roads (22600, 6170, 2370, and 304 mg/kg, respectively). In road dust, lead and copper levels were 330 and 106 mg/kg, which were 371 and 155 times higher, respectively, than in non e-waste areas located 8 and 30 km away. Levels at the schoolyard and food market showed that public places were adversely affected.

Air

Elevated concentrations of metals were also observed in ambient air in Guiyu (Deng et al., 2006). Cd, Cr, Cu, Ni, Pb, Zn, Mn and As were monitored in 29 air samples of total suspended particles (TSP, particles less than 30-60 μm and 30 samples of particles with aerodynamic diameter smaller than 2.5 μm ($\text{PM}_{2.5}$). In both the TSP and $\text{PM}_{2.5}$ fractions, the most enriched metals were chromium (with mean levels of 1161 and 1152 ng/m^3 , respectively), zinc (1038 and 924 ng/m^3), lead (444 and 392 ng/m^3), manganese (60.6 and 25.42 ng/m^3) and copper (483 and 126 ng/m^3). Concentrations of most of the

metals in the ambient air in Guiyu were much higher than those observed for other sites in Asia. Concentrations of chromium, copper and zinc in PM_{2.5} were 4-33 times higher than in the Asian metropolitan cities such as Tokyo, Shanghai, Ho Chi Minh, Taichung and Seoul. The same ambient air samples were also screened in this study for 16 US EPA priority polycyclic aromatic hydrocarbons (PAHs). Elevated concentrations of benzo(a)pyrene (BaP), a well known carcinogen, were of concern. The average concentration of BaP was 2-6 times higher than in other Asian cities.

In another study, the same research group (Deng et al., 2007) monitored PBDE concentrations in TSP and PM_{2.5} fractions of ambient air in Guiyu. In addition, air samples from three urban sites in Hong Kong and two urban sites in Guangzhou were also examined. The monthly concentrations of the sum of 22 BDE congeners contained in TSP and PM_{2.5} at Guiyu were 21.5 and 16.6 ng/m³, up to 58-691 times higher than the levels for other urban sites and more than 100 times higher than concentrations reported for other locations (Table 2).

Table 2. Comparison of PBDE concentrations in air particles in Guiyu and other sites. Reprinted from Deng et al. (2007) with permission from Elsevier.

| Sites | Description | PBDEs conc. (pg m ⁻³) | References |
|---|---|-----------------------------------|---------------------------|
| <i>e-waste sites</i> | | | |
| Outside area in Guiyu, China | 22 congeners (particulate) | 21,474±7241 | This study |
| Inside an e-waste recycling factory in Örebro, Sweden | 24 congeners (dust respirable particles) | 6200±800 | Julander et al. (2005) |
| | 24 congeners (dust total particles) | 33,500±3400 | |
| <i>Urban and rural sites</i> | | | |
| Guangzhou | 22 congeners (particulate) | 204–372 | This study |
| Hong Kong | 22 congeners (particulate) | 33.8–358 | This study |
| Ontario, Canada | 21 congeners (particulate) | Below determine limit-34 | Gouin et al. (2005) |
| | 21 congeners (gaseous+particulate) | 6–85 | |
| Great Lakes, USA | 7 congeners (gaseous + particulate) | 5.5–15 | Strandberg et al. (2001) |
| Chicago, USA | 7 congeners (gaseous + particulate) | 52 | Strandberg et al. (2001) |
| Island Gotska Sandö, Sweden | 10 congeners (gaseous + particulate) | 8.6 | Ter Schure et al. (2004) |
| Urban ambient UK air | 6 congeners, excluding BDE209 (particulate) | 1.3–6.7 | Harrod and Hunter, (2004) |
| Over the continent of Europe | | 250 | Wurl et al. (2006) |
| Over the continent of Asia | | 340 | Wurl et al. (2006) |
| <i>Background sites</i> | | | |
| Over the Indian Ocean | 8 congeners (gaseous) | 2.5 | Wurl et al. (2006) |
| Mace Head, Ireland, European background site | 8 congeners (gaseous + particulate) | 2.6 | Lee et al. (2004) |
| Canadian Arctic and Siberia, Russia | BDE-47 and-99 (gaseous + particulate) | 1–7 | Alaee et al. (2001) |

Similar to metals, PAHs, and PBDEs, chlorinated and brominated dibenzo-*p*-dioxins and furans (PCDD/Fs and PBDD/Fs) were also detected at high concentrations in ambient air in Guiyu (Li et al., 2007). Atmospheric PCDD/F (tetra to octa) concentrations and toxic equivalent (TEQ) values were 64.9-2365 pg/m³ and 0.909-48.9 pg of W-TEQ/m³, respectively; the highest documented levels of these compounds in ambient air in the world. PBDD/Fs (eight 2,3,7,8-substituted congeners) were also found at high levels (concentrations of 8.124-61 pg/m³ and 1.6-2104 pg of I-TEQ /m³). Profiles of the 2,3,7,8-PCDD/F homologues in the air of Guiyu differed from typical urban air patterns reported in the literature, and the concentration of homologues increased with the

chlorination degree of 2,3,7,8-PCDDs/Fs except for OCDF. The severe dioxin pollution present in Guiyu was found to spread to the adjacent area of Chendian, where atmospheric PCDD/F and 2,3,7,8-PBDD/F levels were higher than those commonly observed in urban areas of the world. Inhalation risk assessment showed that residents in Guiyu are at a high risk of exposure to dioxins. The total PCDD/F intake doses far exceeded the WHO 1998 tolerable daily intake limit of 1-4 pg of W-TEQ/kg/day.

Freshwater

Freshwater ecosystems in Guiyu have also been affected by the intensive recycling activities taking place there. Freshwater analysis of dissolved metals showed that the metal concentrations were higher in water of Lianjiang and Nanyang rivers within Guiyu than in a reservoir outside of Guiyu (Wong et al., 2007a). Lianjiang was enriched with dissolved As, Cr, Li, Mo, Sb and Se, while Nanyang river had elevated dissolved Ag, Be, Cd, Co, Cu, Ni, Pb and Zn. Excessive levels of the metals were attributed by the authors to acid leaching operations taking place along the rivers. Concentrations of metals varied during daytime (8 samples were collected during a day) suggesting recent discharges of metals. Concentrations of dissolved Ag, Cd, Cu and Ni (0.344 ± 0.014 , 0.547 ± 0.074 , 87.6 ± 3.0 and 93.0 ± 1.4 mg/L, respectively) exhibited increasing trends. Analysis of Pb isotopic composition confirmed that there was input of non-indigenous Pb isotopes into the rivers.

Soil and Sediments

Leung et al. (2007) assessed levels of PBDEs and PCDDs/Fs in surface soils in Guiyu. Along with soil samples, combusted residue samples were also analyzed. Total PBDE concentrations were highest in combusted residue of plastic chips and cables collected from a residential area (33000-97400 ng/g, dry weight), in soils from an acid leaching site (2720-4250 ng/g, dry weight) and a printer roller dump site (593-2890 ng/g, dry weight). BDE-209 was the most dominant congener (35-82%) among the study sites indicating the prevalence of commercial Deca-BDE, however signature congeners from commercial Penta- and Octa-BDE were also found. PCDD/F concentrations were also highest in soil from the acid leaching site (12500-89800 pg/g, 203-1100 pg WHO-TEQ/g, dry weight) and in combusted residue (13500-25300 pg/g, 84.3-174 pg WHO-TEQ/g, dry weight) and were comparable to PCDD/F levels reported for some open dumping sites in Asian developing countries. Of the e-waste activities, acid leaching and open burning apparently emitted the highest concentrations of PBDEs and PCDD/Fs.

Yu et al. (2006) studied concentration, distribution, profile and possible sources of polycyclic aromatic hydrocarbons (PAHs) in soil in Guiyu. For the sixteen US EPA priority PAHs measured in 49 soil samples (0-10 cm layer), total concentrations ranged from 44.8 to 3206 $\mu\text{g}/\text{kg}$ (dry weight basis) and were the highest in soil from open burning sites (2065 $\mu\text{g}/\text{kg}$), followed by areas near burning sites (851 $\mu\text{g}/\text{kg}$), rice fields

(354 µg/kg) and reservoir areas (125 µg/kg). The dominant PAHs were naphthalene, phenanthrene and fluoranthene, which are mainly derived from incomplete combustion of WEEE (e.g. wire insulations and PVC materials), and partly from coal combustion and motorcycle exhausts.

Leung et al. (2006) have analyzed polybrominated diphenyl ethers (PBDEs) and metals in just three samples, but the samples were collected from places that were likely to be highly contaminated. Two soil samples were collected from a burnt plastic dump site and from a printer roller dump site, and a sediment sample was collected from Lianjiang River where WEEE was dumped. The total mono- to hepta-brominated substituted PBDE concentrations in the soils were 1140 and 1169 µg/kg dry wt., and were higher than the concentration in the sediment sample (32.3 µg/kg). The PBDE concentrations in soils from dumping sites were approximately 10-60 times those reported for other PBDE contaminated locations in the world.

Among the metals analyzed, Cu, Pb, and Zn were the most abundant in the samples. Cu concentration in the soil from the printer roller dump site (712 mg/kg) and the burnt plastic dump site (496 mg/kg), and sediments from Lianjiang River (528 mg/kg) exceeded the new Dutch list action value of 190 mg/kg (the Dutch guidelines were used for comparison since no such guidelines exist in China). No other metals exceeded the Dutch action level, however, Cd, Cu, Ni, Pb, and Zn concentrations in the three samples exceeded so called optimum values set by the same Dutch guidelines. In general, Cu, Pb, and Ni concentrations in the sediment sample of the Lianjiang River were higher than those measured in river and coastal sediments in Guangzhou, Deep Bay, Shenzhen, and Hong Kong.

Sediments of Linjiang and Nanyang rivers flowing through Guiyu were tested for metals by Wong et al. (2007b). Elevated concentrations of Cd (n.d.-10.3 mg/kg), Cu (17.0-4540 mg/kg), Ni (12.4-543 mg/kg), Pb (28.6-590 mg/kg), and Zn (51.3-324 mg/kg) were observed. The magnitude of contamination was higher in sediments of Lianjiang River than Nanyang River. The distribution of Cu, Pb and Zn concentrations of the Lianjiang sediments indicated that these metals were possibly discharged into the river at various points and that these metals might be discharged simultaneously. Pb isotopic composition in sediments indicated input of non-indigenous Pb isotopes into the rivers, higher in the case of Lianjiang.

Thus, the crude recycling of WEEE practiced in developing countries lead to significant releases of various chemicals into the environment. This is supported by the high levels of various chemicals observed in the workplace and ambient environment in WEEE recycling areas, as well as by the fact that the chemicals commonly detected at elevated levels in the environment were those incorporated into WEEE (e.g., metals, PBDEs) or generated through the processing of WEEE (PXDDs/Fs).

3.3. Human exposure and health effects

As revealed by the studies reviewed in the previous section, unregulated recycling activities generate workplace and environmental contamination by a wide range of chemicals. As a result, the workers and local residents are exposed to the chemicals through inhalation, dust ingestion, dermal exposure, and dietary intake.

Inhalation and dust ingestion were suggested as particularly important routes of human exposure. Leung et al. (2008) conducted an assessment of risk from ingestion of contaminated dust, based on metal concentrations in dust from recycling workshops and adjacent environments. The assessment revealed that ingestion of lead and copper contaminated dust may pose serious health risks to workers and local residents of Guiyu. For a printed circuit board recycling worker, the estimated oral average daily dose (ADD) of lead exceeded the “safe” oral reference dose for lead by 50 times, indicating a high risk of adverse health effects. The inhalation risk assessment conducted by Li et al. (2007) based on PCDD/F concentrations in ambient air showed that residents in Guiyu are at a high risk of exposure to dioxins. The total PCDD/F intake doses far exceeded the WHO 1998 tolerable daily intake limit of 1-4 pg of W-TEQ/kg/day.

3.3.1. Occupational exposure

High exposure to polybrominated diphenyl ethers (PBDEs) in Guiyu residents engaged in WEEE recycling was demonstrated by Bi et al. (2007). Concentrations of PBDEs, polychlorinated biphenyls, and organochlorine pesticides (OCPs) were measured in serum from residents of Guiyu ($n=26$) and compared to a matching cohort ($n=21$) from a nearby region where the fishing industry dominates (Haojiang). Serum concentrations of PBDEs and OCPs, but not polychlorinated biphenyls, were significantly different in the two regions: the median PBDE concentration was 3 times higher in Guiyu than Haojiang, whereas the opposite was true for pesticide dichlorodiphenyltrichloroethane (DDT). PBDEs typically accounted for 46% of the total organohalogen chemicals in samples from Guiyu, but 8.7% in Haojiang. The median BDE-209 concentration in Guiyu was 50-200 times higher than those previously reported in occupationally exposed populations. The highest BDE-209 concentration was 3100 ng/g lipid, the highest ever reported in humans. Serum PBDE concentrations did not correlate with polychlorinated biphenyls or OCPs, whereas polychlorinated biphenyls and OCPs showed positive correlations, suggesting that sources of PBDEs to humans are different from polychlorinated biphenyls and OCPs.

In another study, Yuan et al. (2008) revealed that occupational exposure to PBDEs may have an effect on the levels of thyroid-stimulating hormone (TSH) and cause genotoxic damage in WEEE recycling workers. In the study, 23 subjects were recruited among the

workers of the WEEE recycling site (exposed group) and 26 subjects were selected from a community located 50 km away from the recycling site (control group). Serum levels of PBDEs (median, 382 ng/g lipid weight; range, 77-8452 ng/g lipid weight) and TSH (median, 1.79 μ U/mL; range, 0.38–9.03 μ U/mL) and frequencies of micronucleated binucleated cells (MNed BNC; median, 5‰; range, 0-96‰) were significantly higher in the exposed group than in the control group (158 ng/g, range of 18-436 ng/g, and $p < 0.05$; 1.15 μ U/mL, range of 0.48-2.09, and $p < 0.01$; and 0‰, range of 0-5‰, and $p < 0.01$, respectively). History of working with WEEE was significantly associated with increased MNed BNC frequencies (odds ratio, 38.85; 95% confidence interval (CI) = 1 - 1358.71, $p = 0.044$), independent of years of local residence, a perceived risk factor. However, there was no association between PBDEs exposure and indicators of oxidative DNA damage such as malondialdehyde (MDA), superoxide dismutase (SOD), and glutathione (GSH) in serum samples as well as urinary 8-hydroxy-2'-deoxyguanosine (8-OHdG) in the exposed group.

Oxidative stress indicated by the elevated urinary 8-OHdG levels was demonstrated in another group of exposed workers by Wen et al. (2008). The study evaluated levels of polychlorinated PCDDs/Fs, PBDEs, and polychlorinated biphenyls in hair samples from male workers ($n=64$) and assessed levels of 8-OHdG in their pre- and postworkshift urines (64 of each). The concentrations of PCDD/Fs, PBDEs and polychlorinated biphenyls were the highest so far reported, e.g. PCDDs/Fs levels in the study were about 20 times higher than the upper limit of the concentration in healthy subjects in Japan, and polychlorinated biphenyls levels were nearly 2 orders of magnitude greater than those in hair samples from Japan and Belgium. The 8-OHdG levels significantly increased from 6.40 ± 1.64 μ mol/mol creatinine in preworkshift urine to 24.55 ± 5.96 μ mol/mol creatinine in postworkshift urine ($p < 0.05$). The authors concluded that there was a high cancer risk due to oxidative stress indicated by the elevated 8-OHdG levels in WEEE recycling workers exposed to high concentrations of PCDD/Fs, PBDEs, and polychlorinated biphenyls.

3.3.2. General population exposure

General population exposure to WEEE-derived chemicals is best studied in Guiyu, and this section summarizes the findings of some scientific papers on this aspect. The intensive WEEE recycling activities and associated ubiquitous workplace and environmental contamination affect the general population of the town. Residents of Guiyu have reported their children suffering from medical problems such as breathing ailments, skin infections, and stomach diseases. There has also been a surge in cases of leukemia (Leung et al., 2006). Drinking water has been contaminated and is transported from a town located 30 km away (BAN & SVTC, 2002).

The primitive WEEE recycling activities were apparently contributing to the elevated

blood levels of lead and cadmium in children living in Guiyu (Hue et al., 2007, Zheng et al., 2008).

Huo et al. (2007) found that blood lead levels in 165 children of Guiyu ranged from 4.40 to 32.67 µg/dL with a mean of 15.3 µg/dL, whereas blood lead levels in 61 children of neighboring town Chendian (control site) were from 4.09 to 23.10 µg/dL with a mean of 9.94 µg/dL. Of children in Guiyu, 81.8% (135 of 165) had blood lead levels > 10 µg/dL, compared with 37.7% of children (23 of 61) in Chendian ($p < 0.01$). In addition, a significant increasing trend in blood lead levels was observed with increasing age in Guiyu ($p < 0.01$). However, no significant difference in hemoglobin level or physical indexes (height, weight, head circumference and chest circumference) was found between the two towns.

In a similar epidemiological survey (Zheng et al., 2008), 278 children under 8 years old from Guiyu and Chendian were tested for lead and cadmium in their blood. Similar to the previous survey, children living in Guiyu had significantly higher blood levels of lead and cadmium as compared with those living in Chendian ($p < 0.01$). In Guiyu, 70.8% of children (109/154) had blood lead levels < 10 µg/dL, and 20.1% of children (31/154) had blood cadmium levels > 2 µg/L, compared with 38.7% (48/124) and 7.3% of children (9/124), respectively, with such levels in Chendian ($p < 0.01$). A significant increasing trend in blood lead levels with increasing age was also observed in Guiyu ($p < 0.01$). Mean height of children in Guiyu was significantly lower than that in Chendian ($p < 0.01$). The risk factors related to children's blood levels of lead and cadmium mainly included father's engagement in the work related to e-waste, children's residence in Guiyu and the amount of time that children played everyday outside.

In another epidemiological study involving neonates in Guiyu (in 2006, $n=100$; in 2007, $n=100$) and a control group of neonates from a fishing town of Chaonan (in 2006, $n=52$; in 2007, $n=50$), chromium levels of umbilical cord blood (UCB) were measured and DNA damage of cord blood lymphocyte was assessed (Li et al., 2008). The mean chromium levels in UCB of neonates in the Guiyu group in 2006 and 2007 were 303.38 µg/L and 99.90 µg/L (median, 93.89 µg/L and 70.60 µg/L), respectively, and were significantly higher than the results for the control group ($p < 0.01$) (Table 3). Higher levels of chromium in neonates were found to correlate with their mothers' exposure to WEEE recycling. There were significant differences in terms of DNA damage between the Guiyu group and the control group ($p < 0.05$). The authors attributed the DNA damage to high chromium levels in UCB, based on the fact that there was a correlation between the two parameters ($p < 0.05$). However, the observed DNA damage might be due to different factors or a combination of factors. Nevertheless, the high chromium levels in UCB of neonates are of concern and, probably, reflect the general environmental situation in Guiyu.

Table 3. Chromium levels in umbilical cord blood ($\mu\text{g/L}$) of newborn children in Guiyu compared with control group. Reprinted from Li et al. (2008) with permission from Elsevier.

| Year | Group | N | Range | $\bar{X} \pm s$ | median |
|------|---------|-----|--------------|---------------------|-----------------|
| 2006 | Guiyu | 100 | 0.45–6029.92 | 306.20 ± 845.78 | $93.87^{1) 3)}$ |
| | Control | 52 | 1.66–56.54 | 19.95 ± 8.37 | 18.10 |
| 2007 | Guiyu | 100 | 20.16–630.00 | 99.90 ± 96.77 | $70.60^{2)}$ |
| | Control | 50 | 8.62–197.18 | 32.48 ± 32.74 | 24.00 |

Notes: compare with control group in the same year: 1) $Z = -8.44$, $P < 0.01$; 2) $Z = -8.08$, $P < 0.01$; compare between the year of 2006 and 2007 in Guiyu group: 3) $Z = -0.999$, $P > 0.05$.

IV. CONCLUSIONS

The reviewed studies collectively reveal that WEEE contains a number of hazardous substances. Heavy metals and halogenated compounds in WEEE are of particular concern. Hazardous substances are often concentrated in certain WEEE components/parts. Thus, improper handling and management of WEEE during recycling and other end-of-life treatment options may pose potentially significant risks to both human health and the environment.

Although there are various methods of WEEE recycling, the following processes seem to be commonly used in recycling facilities in industrialized/developed countries: manual disassembly (selective removal of hazardous and valuable components for further special treatment), followed by mechanical size reduction (shredding/ grinding), mechanical separation (e.g., magnetic separation of ferrous metals, Eddy current separation of Al and non-ferrous metals) and metallurgical treatment (e.g., smelting and electrowinning). Scientific evidence suggests that the major hazards in the recycling chain are associated with the size reduction and separation and pyrometallurgical treatment steps. Shredding leads to the formation of dust composed of plastics, metals, ceramic, and silica (glass and silicon dust). Additive chemicals like brominated flame retardants (BFRs) which are embedded in WEEE are also released during shredding. Pyrometallurgical treatment generates fumes of heavy metals (especially low melting point metals such as Hg, Pb, Cd, etc.). Besides, if the feedstock contained PVC or other plastics flame retarded with BFRs (PBDEs, TBBPA, PBBs, HBCDs, etc.), pyrometallurgical treatment may lead to the formation of mixed halogenated dioxins and furans (PXDD/Fs, where X=Cl, Br).

Exposure to substances of concern can occur throughout the WEEE processing cycle via inhalation or dermal exposure pathways. However, there is a lack of information on occupational exposure during WEEE recycling in industrialized/developed countries. The data are only available for three groups of electronics dismantling workers whose blood samples were analyzed for BFRs. The results demonstrated that the electronics dismantling workers had been exposed to higher levels of BFRs than general population as a result of processing BFR treated plastics.

One strategy for dealing with WEEE is to incinerate the combustible fraction of the waste, either to reduce its volume prior to landfilling or to concentrate valuable metals in the residual ash so they can be reclaimed in a subsequent operation. Concerns over such treatment options are similar to those raised for pyrometallurgical treatment of WEEE, i.e. the possible formation of polyhalogenated dioxins and furans and emissions of metal fumes.

Landfilling is often the final disposal option for WEEE or by-products of WEEE treatment. Scientific studies suggest that WEEE leach various hazardous substances in landfills.

Another concern over landfilling of WEEE is the evaporation of volatile hazardous substances (notably mercury and its organic forms).

The above described hazards arising from various WEEE treatment options can be mitigated by the use of state-of-the-art installations, such as dust containment systems (in shredding facilities), flue gas, fly and bottom ash capture and treatment systems (in smelters and incinerators), lining and leachate and gas collection systems (in landfills).

In terms of the occupational hazards present, the WEEE recycling/processing industry is no different from the other industrial sectors. Thus, the basic safety rules should also be applied to the workers in WEEE treatment facilities. These include appropriate personal protection clothing, i.e. masks, protective glasses, gloves, overalls and other gear.

WEEE recycling operations in developing countries are mostly unregulated and employ rudimentary techniques. The potentially hazardous recycling practices include manual disassembly of WEEE with little regard to its hazardous content, recovery of solder and chips from printed circuit boards (PCBs) by heating them, acid extraction of metals from complex mixtures, melting and extruding plastics, and burning of plastics to isolate metals.

The crude recycling of WEEE practiced in developing countries leads to significant releases of various chemicals into the environment. This is substantiated by the high levels of various chemicals observed in the workplace and ambient environment in WEEE recycling areas. The chemicals commonly detected at elevated levels in the environment were those incorporated into WEEE (e.g., metals, PBDEs) or generated through processing of WEEE (PXDDs/Fs).

Scientific studies indicate that, in developing countries, the exposure of workers and the general population to WEEE-derived hazardous chemicals may be significant. Higher levels of various chemicals were observed in WEEE recycling workers and people residing close to the recycling sites than in control groups of people living far away from such sites. The high levels of some chemicals were associated with changes in clinical parameters in exposed groups, indicating induction of toxic effects.

Overall, there is a paucity of empirical data on which to base the assessment of environmental and human health risks of various WEEE treatment options. While potential hazards of WEEE itself, i.e. its hazardous content, are relatively well known, there are only fragmentary data concerning actual releases of hazardous chemicals and human health effects due to WEEE treatment processes. The lack of data greatly limits objective assessment and management of the existing risks. Given the paucity of scientific evidence, further research should be done to ascertain the potential risks.

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