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2005

RECYCLING OF ELECTRONIC WASTES IN CHINA & INDIA: WORKPLACE & ENVIRONMENTAL CONTAMINATION

REPORT

GREENPEACE

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GUIYU, CHINA - 8 MARCH 2005 - A MIGRANT WORKER STRIPS WIRES FROM E-TRASH IN A JUNK YARD IN GUIYU IN GUANGZHOU PROVINCE.

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authors K. Brigden, I. Labunska, D. Santillo, & M. Allsopp, *Greenpeace Research Laboratories, Department of Biological Sciences, University of Exeter, Exeter EX4 4PS, UK*
design & layout Tania Dunster, kÏ design, Sweden
contact persons
communications mdunlop@diala.greenpeace.org
campaign zeina.alhajj@int.greenpeace.org


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DELHI, INDIA - 11 AUGUST 2005 - YOUNG WORKERS AT AN E-WASTE RECYCLING YARD IN DELHI.

executive summary

introduction Expansion of the global market for electrical and electronic products continues to accelerate, while the lifespan of the products is dropping, resulting in a corresponding explosion in electronic scrap. As noted by UNEP (2005):

> ***"Every year, 20 to 50 million tonnes of electrical and electronic equipment waste ("e-waste") are generated world-wide, which could bring serious risks to human health and the environment. While 4 million PCs are discarded per year in China alone."***

This rapidly growing "e-waste" stream presents additional difficulties because a wide range of hazardous chemicals are, or have in the past been, used in components of electrical and electronic devices, and these subsequently create substantial problems with regard to handling, recycling and disposal of obsolete products.

The European Union (EU), Japan, South Korea, Taiwan and several states of the USA have introduced legislation making producers responsible for their end-of-life products. The EU has banned the use of certain hazardous substances in electrical and electronic products from July 2006, to facilitate safer recycling.

For the present, however, the "e-waste" recycling sector in many parts of Asia remains largely unregulated. It is also poorly studied with regard to its impacts on the environment and on the health of recycling workers and surrounding communities.

design of the study This study was designed to provide a snapshot of workplace and environmental contamination from a selection of industrial units and dump sites associated with the electronic waste-recycling sector in China and India. A total of more than 70 samples were collected during March 2005 from sites located in the vicinity of Guiyu Town, Guangdong Province in southern China and in the suburbs of New Delhi, India. Samples included industrial wastes, indoor dusts, soils, river sediments and groundwater from typical sites representing all major stages routinely employed in the dismantling, recycling and final disposal of electrical and electronic wastes (i.e. storage, component separation, plastic shredding, acid processing/leaching, open burning and residue dumping) in both countries.

summary of key findings Results confirm that all stages in the processing of electrical and electronic wastes have the potential to release substantial quantities of toxic heavy metals and organic compounds to the workplace environment and, at least to the extent studied, also to surrounding soils and water courses. Among the toxic heavy metals most commonly found in elevated levels in wastes from the industry, as well as in indoor dusts and river sediments, were those known to have extensive use in the electronics sector, i.e.

- lead and tin, most probably arising in large part from solder and, in the case of lead, batteries
- copper, for example from wires and cables
- cadmium, from a variety of uses including batteries and solder joints
- antimony, most probably from use of antimony trioxide as a flame retardant additive in plastics and resins as well from use in electrical solders

Many other metals associated with the electronics industry were also relatively abundant in many samples, including barium, chromium, cobalt, gold, mercury, nickel, silver and zinc.

The range of organic contaminants identified in waste and sediment samples also reflected current or historical use in electrical and/or electronic goods, including brominated, chlorinated and phosphorus-based flame retardants, phthalate esters and esters of long-chain organic acids. Polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) were particularly in evidence, as well as many other organic chemicals, some containing chlorine or bromine, which could not be reliably identified. Given the crude methods employed in much of the recycling sector investigated, it is likely that some of these chemicals arose as products of incomplete combustion or of chemical reactions occurring in complex mixed wastes.

Key results according to the different activities and processes employed in the "e-waste" recycling sector in both China and India, as well as brief information on the hazards of some of the chemical groups investigated, are summarised below.

component separation and solder recovery Samples of dust collected from the floors of three solder recovery workshops in Beilin, Region of Guiyu (China) contained high levels of a variety of metals compared to background levels, particularly lead and tin, as well as copper, antimony and, in some cases, cadmium and mercury. One such sample comprised 29.3% by weight tin, 7.6% lead and 1.1% copper. For all dusts collected from the workshops in China, the concentrations of lead were hundreds of times higher than typical levels recorded for indoor dusts in other parts of the world.

lead (Pb) is widely used in electronic goods, as a major component of solders (as an alloy with tin) and as lead oxide in the glass of cathode ray tubes (televisions and monitors), as well as in lead-acid batteries. Its compounds have also been used as stabilisers in some PVC cables and other products. Lead is highly toxic to humans, as well as to animals and plants. It can build up in the body through repeated exposure and have irreversible effects on the nervous system, particularly the developing nervous system in children.

A similar picture was apparent in the component separation workshops sampled in India. Dusts from general separation workshops contained the same metals at levels which, though somewhat lower than those recorded in China, were nevertheless still greatly elevated (5-20 times) over background levels. Dust samples from battery dismantling workshops in Mayapuri and Buradi districts were particularly heavily contaminated, the former containing 8.8% by weight lead and the latter 20% cadmium. This last figure is around 40 thousand times higher than levels typical for indoor dust samples.

cadmium (Cd) occurs in electronics both as cadmium metal, in some switches and solder joints, and as cadmium compounds in rechargeable batteries, UV stabilisers in older PVC cables and "phosphor" coatings in older cathode ray tubes. Like lead, cadmium can accumulate in the body over time, with long-term exposure causing damage to the kidneys and bone structure. Cadmium and its compounds are known human carcinogens, primarily through inhalation of contaminated fumes and dusts.

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Of the dust samples from the Indian workshops analysed for organic contaminants, all contained the persistent organic pollutants PCBs (more than 35 individual congeners in each case), chemicals once widely used in electrical and electronic applications (among others), though now banned from new uses throughout the world. One of these three samples, namely that from a workshop in Shashtri Park, also contained two congeners of the brominated flame-retardants PBDEs, still in use over much of the globe. In all three cases, a substantial proportion (52-69%) of all organic chemicals isolated from the dust samples could not be identified. A single sample of dust collected from a Shashtri Park workshop in the previous year also showed the presence of PCBs among a complex mix of other organic contaminants.

Until the late 1970s, PCBs (polychlorinated biphenyls) were widely used in insulating fluids for electrical transformers and capacitors, as well as flame-retardant plasticisers in PVC and other polymer applications. They are highly persistent and bioaccumulative chemicals, rapidly becoming widespread through the environment and building up several thousand-fold in body tissues of wildlife. PCBs exhibit a wide range of toxic effects including suppression of the immune system, liver damage, cancer promotion, damage to the nervous system, behavioural changes and damage to both male and female reproductive systems.

A preliminary study in Beilin (China), in which dust samples were collected from the houses of two solder-recovery workers and from one household having no connection with the industry, indicated the potential for the home environment to become contaminated with chemicals from the workplace (e.g. as a result of contamination of work clothing). Even though the houses were remote from the solder recovery works themselves, levels of copper, lead, tin, antimony and, to a lesser degree, cadmium were higher in the dusts from the two solder-workers' houses than in the single control house sampled. This indicative result illustrates the need for further research into contaminant exposure in the homes of workers in this sector.

Contamination of the environment beyond the workplace was also indicated by the results of analysis of street dusts from several locations around the recycling district of Shashtri Park in Delhi, compared to those of two other, more residential areas. Although results for heavy metals were somewhat less conclusive, three of the four road dusts collected in the Shashtri Park area contained traces of PCBs, chemicals which were not detectable in road dust from either Kailashnagar or Safourjung districts.

mechanical shredding Sediments accumulating in discharge channels arising from mechanical shredding facilities in the Guiyu town of China contained variable but generally very high levels of heavy metals as well as complex mixtures of organic contaminants. Discharge channel sediments from one such facility close to the Guiyu to Nanyang road, and from two similar facilities close to the Chendiandian to Guiyu road contained elevated levels of copper (between 9500 and 45900 mg/kg), lead (4500-44300 mg/kg) and tin (4600-33000 mg/kg) as well as antimony (1390-2150 mg/kg), nickel (150-2060 mg/kg) and cadmium (13-85 mg/kg). For copper, lead, tin, nickel and cadmium, these levels are between 400 and 600 times higher than would be expected for uncontaminated river sediments. For antimony, the levels are around 200 times higher than background. Wastewater collected from one of the two Chendiandian to Guiyu road facilities, consisting of a thick slurry of particulates suspended in water, was also found to contain high concentrations of these and other heavy metals.

Common organic contaminants in these wastes included the brominated flame retardant compounds PBDEs. A total of 43 PBDE congeners, from tribrominated to hexabrominated, were isolated from the sediment sample taken from the wastewater ditch of the facility close to the Guiyu to Nanyang road. A similar range of PBDEs was found in two samples of sediment collected from the waste channel serving one of the two facilities close to the Chendian to Guiyu road. Traces of PBDEs were also detectable in the wastewater/slurry flowing from this facility to the channel at the time of sampling.

PBDEs (polybrominated diphenyl ethers) one of several classes of brominated flame retardants used to prevent the spread of fire in a wide variety of materials, including casings and components of many electronic goods. They are environmentally persistent chemicals, some of which are highly bioaccumulative and capable of interfering with normal brain development in animals. Several PBDEs are suspected endocrine disruptors, demonstrating an ability to interfere with hormones involved in growth and sexual development. Effects on the immune system have also been reported.

Both sediment samples from this channel also contained the hormone-disrupting chemical nonylphenol (in one case, as an isomeric mixture). Furthermore, one of these samples (that collected closer to the facility itself) contained a diversity of phthalate esters, chemicals used as plasticisers in a range of polymers (especially PVC), including the known reproductive toxins dibutyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP). This sample also contained residues of the hazardous organophosphorus flame retardant triphenyl phosphate (TPP), as well as two closely related chemicals which may be contaminants in, or primary degradation products of, TPP preparations.

It was not possible to collect wastewater from the channel serving the other shredding facility on the Chendian to Guiyu road. Nevertheless, a sample of sediment from this channel revealed the presence of a diverse array of chlorinated and mixed chlorinated/brominated benzenes and chlorinated naphthalenes. The presence of the chlorinated naphthalenes may well arise from their former use as flame retardant additives in plastics and rubbers, though they have had a diversity of other uses.

nonylphenol (NP) is a chemical most widely known as a breakdown product of nonylphenol ethoxylate (NPE) detergents, though it has reportedly also been used as an antioxidant in some plastics. It is a strong endocrine disruptor, capable of causing intersex (individuals with both male and female characteristics) in fish. Nonylphenol can also build up through the food chain and may be capable of causing damage to DNA and even sperm function in humans.

DELHI, INDIA - 11 AUGUST 2005 - A WORKER IN AN ELECTRONICS WASTE RECYCLING YARD IN DELHI.

DELHI, INDIA - 11 AUGUST 2005 - SPARKS FLY FROM A GRINDING MACHINE, WHILE OUNGSTERS SITTING A FEW METRES AWAY SORT DISCARDED COMPUTER PARTS IN PREPARATION FOR THE RECYCLING PROCESS.

Although no similar facilities were identified and sampled in India, a single sample of shredded plastic waste collected from a workshop in Zarfarabad did contain PBDEs and the organophosphate flame retardant TPP, as well as traces of nonylphenol. Whereas concentrations of most metals were relatively low in this sample, antimony was present at a significant level (124 mg/kg), probably reflecting the presence of antimony trioxide in the plastic components being shredded (thought to be mainly keyboards and monitor housings).

antimony (Sb) is a metal with a variety of industrial uses, including as a flame retardant (as antimony trioxide) and as a trace component of metal solders. In some forms, antimony shows many chemical similarities to arsenic, including in its toxicity. Exposure to high levels in the workplace, as dusts or fumes, can lead to severe skin problems and other health effects. Antimony trioxide is recognised as a possible human carcinogen.

acid processing/leaching Several samples of acidic solid waste collected from open pits within two facilities located in Longmen village (China) and engaged in acid processing/leaching of electronic waste contained expected high levels of several heavy metals. These included lead (350-5400 mg/kg), tin (640-3600 mg/kg), copper (230-6600 mg/kg), antimony (360-1590 mg/kg) and nickel (27-940 mg/kg). These levels of copper, lead and tin are more than 100 times higher than typical background values for uncontaminated soils and sediments. Three of these four solid waste samples were found to contain traces of a number of chlorinated benzenes, while two also contained significant residues of PCBs and PBDEs.

Phthalate esters were also in evidence, along with, in one of the four acid waste samples (collected from an open pool within one of the two facilities), a brominated nitrophenol of unknown origin. Highly acidic wastewater collected from the same open pool contained five different phthalate esters, an oxygenated derivative of triphenyl phosphate (TPP) and a chlorinated nitrophenol, again of unknown origin. Concentrations of metals were again expectedly high, including 31.8 mg/l antimony, 12.2 mg/l cadmium, 774 mg/l copper, 153 mg/l nickel and 85.5 mg/l tin.

triphenyl phosphate (TPP) is one of several organophosphorus flame-retardants used in electronic equipment, for example in the casings of computer monitors. TPP is acutely toxic to aquatic life and a strong inhibitor of a key enzyme system in human blood. It is also known to cause contact dermatitis in some individuals and is a possible endocrine disruptor.

Comparison of a sample of sediment collected from the river upstream from the acid works with a similar sample collected downstream gives a clear indication of the nature and extent of contamination resulting from the activities taking place within these facilities. Concentrations in the downstream sample, as compared to the upstream sample, were more than 20 times higher for antimony, mercury and nickel, around 10 times higher for cadmium and copper and between 3 and 6 times higher for lead, tin and zinc. Moreover, whereas the upstream sample (pH 6) contained only 15 extractable organic compounds, dominated by non-halogenated hydrocarbons, the downstream sample (pH 4, i.e more acidic) contained more than 70 compounds, including the phthalate DEHP and 24 separate PBDE congeners. The acidification of the water and sediments, as well as making toxic metals more mobile and, therefore, more likely to have toxic effects, may in itself be expected to have substantial impacts on aquatic life.

Phthalate esters and PBDEs were also among the organic contaminants detected in river sediments adjacent to two other acid working facilities, located close to the Guiyu to Nanyang road. Acidic solid wastes collected from the “overflow” area adjacent to the larger of these two facilities contained high levels of copper, lead, tin and antimony, as expected, as well as elevated levels if nickel and silver. These wastes also contained PBDEs, PCBs and chlorinated benzenes, as well as a chlorinated and a propylated naphthalene derivative and, in one of the two samples, the phthalate ester DEHP. The adjacent river sediments were highly acidic and contained a similar range of metal contaminants along with the phthalate esters and PBDEs. A control sample collected from the same river some distance from the facility contained little in the way of organic contamination. Concentrations of many metals in this control sample were also tens to hundreds of times lower.

polychlorinated naphthalenes (PCNs) were the precursors to the PCBs, once used extensively in capacitors and as insulating compounds in wiring (among many other uses). They also share many properties with the PCBs, including environmental persistence and toxicity to wildlife and possibly humans. Impacts on the skin, liver, nervous system and reproductive system have been reported in animals.

Samples collected at an acid processing/leaching facility in New Delhi, located in a small workshop in the Mandoli Industrial Area, focused on materials and wastes at different stages in the leaching process. As expected, heavy metals detectable in the original ground plastic waste appear to be concentrated to very high levels in the final spent acid wastes (e.g. 68 mg/l antimony, 240 mg/l copper, 20 mg/l lead, 478 mg/l nickel, 340 mg/l tin and 2710 mg/l zinc). Residues of phthalate esters and chlorophenols were also detectable in these acid wastes.

Additionally, several samples collected in association with the acid processing facilities contained a number of so-far unidentified compounds showing fragmentation patterns characteristic for polyhalogented (probably polybrominated) organic compounds. Further research would be necessary in order to identify these.

Aside from the obvious health and safety concerns which arise from the handling of concentrated acid solutions in these workshops, indications from workers that the contaminated spent acid wastes are simply disposed of to land also raises substantial environmental concerns.

open burning Analysis of several (five) samples of ashes and partially burned electronic wastes collected from a dumpsite in the Longgang village of Guiyu (China) revealed both the extent and degree of variability of contamination of such wastes. Levels of each specific contaminant in these wastes almost certainly depend on the precise nature of the components burned as well as the techniques used. Cadmium, copper, lead and zinc were abundant in most samples. Levels of antimony were notably high, with concentrations in four of the five samples at or above 1000 mg/kg and in one of these reaching 15200 mg/kg.

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This latter sample also contained the greatest number and diversity of hazardous organic contaminants, including a range of chlorinated and mixed chlorinated/brominated benzenes, 2-bromophenol, tetrabromodiphenyl ether (a PBDE), 3,4-dibromostyrene, 1,3-dibromobutane and three isomers of tribromotoluene. Some or all of these may arise from their specific use as flame retardant additives in certain plastics though the possibility that some have been formed as products of incomplete combustion of electronic goods cannot be ruled out. Among the many other organic compounds identified were numerous polycyclic aromatic hydrocarbons (PAHs, typical products of incomplete combustion) and chlorinated biphenyls (PCBs), as well as more than 10 additional compounds suspected to be halogenated but which could not be identified to any degree of reliability. A possible positive result for the most toxic dioxin congener, namely 2,3,7,8-tetrachlorodibenzo-p--dioxin (TCDD) was subsequently confirmed by an external laboratory accredited for dioxin analysis. It was not possible to analyse the other samples for presence of chlorinated dioxins, nor any of the samples for brominated dioxins (though their presence may well be anticipated).

High levels of cadmium, copper, lead and zinc were also characteristic of ashes collected from two waste burning operations in New Delhi (India), at Ibrahimpur and Shashtri Park. PCBs, chlorinated benzenes and PAHs were also in evidence here.

mercury (Hg) is still used in some batteries and lighting components for flat screen electronic displays, and was formerly used also in switches and relays. Mercury and its compounds are highly toxic, causing damage to the central nervous system and kidneys. Once in the environment, mercury can be converted to its organic methylated form by bacterial activity, a form, which is highly bioaccumulative, as well as being toxic.

storage of wastes for processing Soil and dust samples collected from two locations in New Delhi (Kantinagar and Brijgang) used to store cathode ray tubes (CRTs), from televisions or computer monitors, demonstrated the potential for contamination of these materials with heavy metals from the tubes. Cadmium, zinc and yttrium sulphides have been used in the “phosphor” coatings inside CRTs while lead oxide occurs in the glass itself. Levels of all these metals were elevated in the dusts and soils collected in the CRT storage areas.

MUYU, CHINA - 13 FEBRUARY 2004 - A MIGRANT WORKER REMOVING COPPER FROM AN AIR-CONDITIONING UNIT, THEN RECYCLING THE REMAINING ALUMINIUM IN MUYU, TAIZHOU CITY, ZHEJIANG PROVINCE.


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MUYU, CHINA - 13 FEBRUARY 2004 - A MIGRANT WORKER POURING LIQUID ALUMINIUM INTO MOULDS IN MUYU, TAIZHOU CITY, ZHEJIANG PROVINCE.

conclusions Although clearly not an exhaustive study of “e-waste” recycling facilities in either country, the results summarised above do provide an illustration of the breadth and scale of health and environmental concerns arising from this industrial sector. Both wastes and hazardous chemicals used in the processing are commonly handled with little regard for the health and safety of the workforce or surrounding communities and with no regard for the environment. Overall, the result is severe contamination of the workplace and adjacent environment with a range of toxic metals and persistent organic contaminants.

Clearly, it is not possible from the results of this study to evaluate the damage likely to be caused to human health from these widespread practices. Nor was it possible to conduct a comprehensive survey of the full extent of environmental impacts arising from each facility, or from the sector as a whole, in either country. Nevertheless, the results do indicate that exposure to hazardous chemicals arising from the waste-stream can be locally severe. Further research would be necessary in order to identify and quantify the full impact of this industrial sector, including studies on the health of workers and of residents in adjacent communities.

In the mean time, however, the data available do provide a compelling case for immediate action in both countries to address workplace health and safety and waste management.

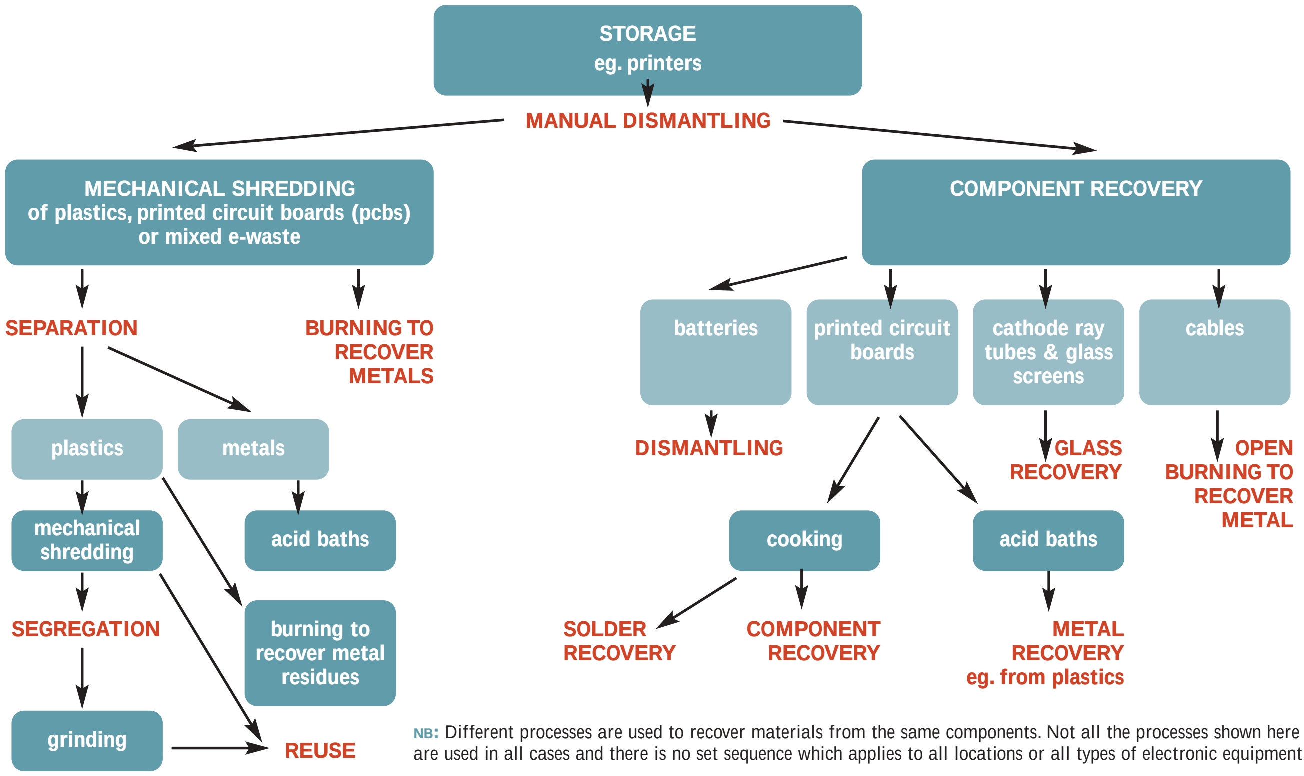
The problems identified are greatly exacerbated by the poor working practices and lack of responsible waste management in the areas sampled in this study. However, the fact that wastes generated by every stage of the recycling process are contaminated with a range of toxic heavy metals and persistent organic pollutants is a direct result of the use of these hazardous materials in electronic goods at the manufacturing stage. Therefore, as well as bringing to light some of the many unseen impacts of the vast and growing electronics waste stream, and the need for much tighter controls both on the transboundary movement of such wastes and the manner in which they are recycled, this study also adds weight to the need to redesign and reformulate all new electronic goods in order:-

- to facilitate proper dismantling and component separation and
- to avoid the use of hazardous chemical components at source.

The European Directive on Waste Electrical and Electronic Equipment (WEEE) and the related Restrictions on Hazardous Substances (RoHS) go some way towards addressing the problem, though applying only regionally and covering only a fraction of all the hazardous substances used in electronics manufacturing.

In short, this study provides a further illustration of the urgent need for manufacturers of electronic goods to take responsibility for their products from production through to the end of their lives. As a major contribution towards addressing these problems, manufacturers must develop and design clean products with longer life-spans, that are safe and easy to repair, upgrade and recycle and will not expose workers and the environment to hazardous chemicals.

DIAGRAM 1: DIFFERENT STAGES OF E-WASTE RECYCLING PROCESSES SAMPLED IN INDIA AND CHINA



NB: Different processes are used to recover materials from the same components. Not all the processes shown here are used in all cases and there is no set sequence which applies to all locations or all types of electronic equipment.

I INTRODUCTION

The production of electrical and electronic equipment is increasing worldwide (Cui and Forssberg 2003) and the lifespan of some of the equipment is very short. For example, computers in the early 1980s were used on average for about ten years but their lifespan has since reduced to an average of about three years. This is due to the rapid and continual improvements in technology, which quickly outdate older models. Mobile phones too become outdated and are replaced on average after about two years (Boghe 2001). As a consequence of the increasing market expansion in electrical and electronic goods and their short lifespan, the waste stream of these products, commonly called “e-waste”, is fast growing.

This is a significant problem because some of the products, including computers and mobile phones, contain heavy metals and other chemicals, which are hazardous, and are consequently a threat to the environment and to human health. Much of this electronic waste (“e-waste”) goes into the normal municipal waste stream to be landfilled or incinerated. Indeed, electrical and electronic waste has been identified as one of the largest sources of heavy metals and organic pollutants in municipal waste (Boghe 2001), and is identified as the fastest growing waste stream (Betram *et al.* 2002).

As noted by UNEP (2005): ***“Every year, 20 to 50 million tonnes of electrical and electronic equipment waste (“e-waste”) are generated world-wide, which could bring serious risks to human health and the environment. While 4 million PCs are discarded per year in China alone.”***

In an attempt to overcome the waste disposal problems, recycling schemes are now being set up to recover some of the metals and plastics in the waste. In the 1990s, governments in the European Union, Japan and in some states of the USA set up “e-waste” recycling schemes. For example, in Germany (Zhang and Forssberg 1998), Switzerland (Künzler Bossart & Partner GmbH 2001) and Taiwan (Shih 2001), legislation has been implemented which requires that manufacturers take back domestic electrical/electronic goods at the end of their lifespan.

Within the European Community, two directives have been adopted, namely the directive of the European Parliament and the European Council on Waste Electrical and Electronic Equipment (WEEE) and the directive on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS). These directives necessitate, among other requirements, that Member States are responsible for ensuring that the producers set up systems for treatment and recovery of electrical and electronic waste (Feszty *et al.* 2003), as well as placing prohibitions on the use of certain hazardous substances in the manufacture of electrical/electronic goods at the outset.

It remains the case, however, that many countries do not have the capacity to deal with the sheer quantity of “e-waste” they generate or with its content of hazardous chemical constituents. For this reason, these countries began exporting the problem to Asian countries in which legislation to ensure take-back and safe and environmentally sustainable recycling and disposal practices is lacking. Here the products are dismantled, with some materials recovered for reuse and the remainder disposed of to land or water courses.

In many parts of Asia, few controls are in place and dismantling and recycling of electronic wastes is frequently carried out in small workshops and industrial units with little in the way of exposure or emission controls for hazardous constituents of the waste stream.

The United Nations Environment Program (UNEP) has recently proposed establishing a network of policy makers and experts to help deal with the problem of electrical/electronic waste in Asia and the Pacific (UNEP 2004). For the present, however, the electronic waste (“e-waste”) recycling sector in many parts of Asia remains largely unregulated. It is also poorly studied with regard to its impacts on the environment and on the health of recycling workers and surrounding communities.

As noted above, many of the components that make up electrical/electronic products are hazardous, and therefore both the disposal and recycling of “e-wastes” is of concern. Hazardous chemicals may be released from the “e-wastes” through disposal or recycling processes, with the potential to expose workers as well as input these chemicals into the environment.

In China and India, many facilities where “e-wastes” are processed and materials recovered for recycling are often small independent workshops. There is often little or no real controls over the materials processed, the processes used, or the emissions and discharges from these facilities.

This study was undertaken to investigate the types of activities being carried out in this sector, and provide a snap-shot of contamination of the workplaces and surrounding environments with hazardous chemicals from the wastes being processed. In both China and India, the recycling of “e-wastes” is known to occur in many locations. This study focuses on workshops in just one area for each country; New Delhi in India and around Guiyu in China, a town close to Shantou City in Guangdong Province.

II SAMPLING PROGRAM

In March 2005 Greenpeace visited recycling facilities for electrical and electronic wastes (“ ”e-wastes” ”) at locations in China and India. In China, facilities were visited in and around the town of Guiyu, close to Shan Tou City, Guangdong Province in southern China. In India, the investigation was centred on workshops in New Delhi, mainly in the East Delhi area. In both countries recycling operations were generally taking place in small backstreet workshops, and in some instances in the open air. At the workshops visited, the materials being recycled were primarily computers and their peripheral equipment (monitors, keyboards, printers) with the aim of recovering components and raw materials (e.g. plastics, copper).

Samples were collected from a range of recycling activities. The sectors were common to both countries, though in some cases the actual techniques employed differed between workshops in China and India. The recycling sectors included;

- Separation, processing and recycling of plastics
- Manual separation of products
- Removal and collection of solder using heating
- Acidic extraction of metals from complex mixtures
- Burning of wastes to remove combustible plastics and isolate metals
- Glass recovery from cathode ray tubes (CRTs)

Samples included a range of wastes produced by the recycling activities as well as environmental samples from locations around the workshops to demonstrate the wider impacts of the various recycling activities.

All samples were collected and stored in pre-cleaned glass bottles that had been rinsed thoroughly with nitric acid and analytical grade pentane in order to remove all heavy metal and organic residues. Wastewater samples were collected in a 1 litre screw-cap bottle. Solid samples (recycling waste, ash, soil, sediment & dusts) were collected in 100ml bottles. All samples were kept cool and returned to the Greenpeace Research Laboratories for analysis. Detailed description of sample preparation and analytical procedures are presented in Appendix 1.

i plastic recycling

At the workshops in both India and China, plastic removed from waste electrical and electronic equipment is processed and recycled in a similar way. The plastic materials that can be manually separated from waste electronic products are mechanically shredded to produce small fragments. In some cases the plastic fragments are then crudely segregated, typically by mixing with water to separate those plastics that float from those that do not. Plastic fragments are reused directly, or processed further by mechanically grinding to produce fine powders prior to reuse.

Workers in China and India reported that the plastics being recycled included ABS (acrylonitrile-butadiene-styrene), high-density polystyrene, HDPE (high-density polyethylene) and PVC (polyvinyl chloride).

TABLE 2.1: DESCRIPTION OF SAMPLES ASSOCIATED WITH PLASTIC RECYCLING ACTIVITIES IN GUIYU, CHINA AND NEW DELHI, INDIA, 2005

SAMPLE #	SAMPLE TYPE	AREA	SAMPLE LOCATION
		CHINA	
CH05001	dust	Longgang	floor of plastic shredding & heat-extruding workshop (A)
CH05002	dust	Longgang	floor of plastic shredding & heat-extruding workshop (A), around the mechanical plastic shredded
CH05003	dust	Longgang	plastic shredding & heat-extruding workshop (B)
CH05004	dust/soil	Longgang	street between shredding workshops A & B
		INDIA	
IT05012	plastic fragments	Zarfarabad	shredded plastic from electronics goods
IT05014	plastic powder	Gaziabad	mechanically ground plastic fragments
IT05015	dust	Gaziabad	floor of workshop where plastic is mechanically ground

In China, two workshops were visited in the Longgang area of Guiyu. At both facilities, plastic waste was mechanically shredded, and new products produced by heated extrusion of shredded plastic material. Two samples of dusts were collected from the floor of one workshop (A), one composite sample (CH05001) from the floor of the whole workshop, and a second sample (CH05002) from the floor in the area around the shredder unit. At a second workshop (B), approximately 100m away from workshop (A), another sample of dust (CH05003) was collected from the workshop floor. A sample of street dust/soil (CH05004) was also collected from the road on which both workshops were situated, approximately half way between the two workshops.

Samples were also collected from plastic recycling workshops in New Delhi, India. One sample of shredded plastic fragments (IT05012) was collected from a workshop in Zarfarabad. Two samples were collected from a separate workshop in Gaziabad where plastic fragments are ground to a fine powder for reuse; a sample of the finely ground plastic powder (IT05014), and dust (IT05015) from the floor of the workshop.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DELHI, INDIA - 11 AUGUST 2005 -
CHILDREN EXTRACT COPPER FROM DISCARDED COMPTER PARTS

ii manual printed circuit board separation & solder recovery

At workshops in both China and India, the primary activity in this recycling sector is the manual separation of components from printed circuit boards and the manual separation of some of the larger components into individual parts. Metallic solder used to link components to each other and to circuit boards is also recovered during these processes.

TABLE 2.2: DESCRIPTION OF SAMPLES ASSOCIATED WITH THE MANUAL SEPARATION OF COMPONENTS AND RECOVERY OF SOLDER AT RECYCLING WORKSHOPS IN GUIYU, CHINA AND NEW DELHI, INDIA, 2005. § SIGNIFIES ANALYSIS OF 63µM SIEVED FRACTION

SAMPLE #	SAMPLE TYPE	AREA	SAMPLE LOCATION
		CHINA	
CH05012	dust §	Beilin	floor of separation & solder recovery workshop (A)
CH05013	dust §	Beilin	floor sweepings, separation & solder recovery workshop (A)
CH05014	dust §	Beilin	floor of separation & solder recovery workshop (B), using open flame heating
CH05026a	dust §	Beilin	floor of separation & solder recovery workshop (C)
CH05011	solder	Beilin	from heated plate, solder recovery workshop (A)
CH05026b	solder	Beilin	floor of solder separation & recovery workshop (C)
CH05018	house dust §	Guiyu Town	home of solder recovery worker
CH05019	house dust §	Guiyu Town	home of solder recovery worker
CH05035	house dust §	Guiyu Town	home of neighbour NOT employed in e-waste recycling
		INDIA	
IT04001	dust §	Zarfarabad	floor of circuit board & component separation workshop
IT05007	dust §	Shashtri Park	floor of circuit board & component separation workshop
IT05008	dust §	Shashtri Park	floor of open-air rooftop workshop; circuit board heated on kerosene burners to recover solder
IT05011	dust §	Zarfarabad	floor of circuit board & component separation workshop
IT05018	dust §	Mayapuri	floor of battery separation workshop, mainly lead batteries
IT05029	dust §	Buradi	floor of battery separation workshop, range of batteries
IT04002	solder	Zarfarabad	recovered from circuit board (location as IT04001)
IT05009	solder	Shashtri Park	recovered from circuit board (location as IT05008)
IT05022	dust/soil	Shashtri park	narrow street; area of recycling workshops
IT05023	dust/soil	Shashtri park	narrow street; area of recycling workshops
IT05024	dust/soil	Shashtri park	narrow street; area of recycling workshops
IT05025	dust/soil	Shashtri park	narrow street; area of recycling workshops
IT05027	dust/soil	Kailashnagar	narrow street; no known recycling activities in area
IT05028	dust/soil	Safourjung, South Delhi	street in residential area; no known industrial or recycling activities in area

Prior to analysis all workshop dust samples described above were sieved through a 63µm mesh to isolate the fine dust fraction from small pieces of solder and other small materials/components.

workshops in China

At the workshops visited in China, printed circuit boards were placed onto a metal plate heated over a burner in order to melt the connecting solder. The heated metal plates held a pool of molten solder to aid the melting of solder from the circuit board. Solder melted from the circuit board became part of the molten pool on the hotplate. After the solder was melted, individual electrical components on the circuit boards were manually separated.

In the Beilin area of Guiyu, a sample of molten solder (CH05011) was collected from one of the heated metal plates in a small backstreet workshop (A). A sample of dust (CH05012) was collected from the floor of this workshop. A second sample of dust (CH05013) was collected from a container used to store dust sweepings from the workshop floor. A sample of dust (CH05014) was collected from the floor of a neighbouring workshop (B) where circuit board solder was being melted by heating over an open flame rather than using a hotplate. This method resulted in greater burning of the circuit board base. In a different part of Bei Lin, approximately _ km from workshops (A) & (B), a sample of dust (CH05026a) was collected from a third workshop (C) where heated metal plates were used to melt circuit board solder. A sample of recovered solder (CH05026b) was also colleted from this workshop.

As a preliminary investigation into whether workers involved in this type of solder recovery were transporting materials from the workshops back to their homes, two samples of house dust (CH050018 & CH05019) were collected from separate homes of two workers employed in this sector. For comparison, a sample of dust (CH05035) was also collected from a neighbouring house where none of the residents are employed in any form of work involving electronic wastes.

workshops in India

At workshops in India, a wide range of “e-wastes” are separated into their individual components by hand. Components are typically separated from printed circuit boards using a hammer and chisel. Following separation, some larger components are further separated into smaller parts in a similar way, primarily to recover metals. After removal of the recyclable materials, primarily copper and other metals, the residues are usually taken to acid processing workshops where metals are chemically recovered from the residues (see Section 2.4.4).

A number of small backstreet workshops were visited where this work was taking place. Samples of dust were collected from the floor of workshops in the Shashtri Park (IT05007) and Zarfarabad (IT0511) areas of East Delhi. In November 2004, a sample of floor dust had already been collected from a neighbouring workshop in the Zarfarabad area (IT04001) along with a sample of solder that had been recovered from circuit boards (IT04002).

At workshops in the same area, solder is recovered from printed circuit boards by heating them over an open-flame kerosene burner. Use of heated metal plates as observed in China was not seen at the workshops in New Delhi. A sample of dust (IT05008) was collected from the floor of an open-air rooftop workshop in Shashtri Park where this activity was taking place. A sample of solder recovered from circuit boards was also collected (IT05009). Many more similar rooftop workshops were observed in the neighbourhood.

Batteries isolated from “e-wastes” are separated into their individual components in small workshops dedicated to this work. A sample of dust (IT05018) was collected from the floor of such a workshops in the Mayapuri area of New Delhi where primarily lead acid batteries are recycled, including lead acid computer batteries. A second dust sample (IT05029) was collected from the floor of a workshop in the Buradi area of South Delhi where a wider range of batteries are recycled.

In one area of Shashtri Park, East Delhi, many small workshops were observed within a small neighbourhood. A number of samples of dust/soil (IT05022-IT05025) were collected from the narrow backstreets in this neighbourhood to investigate impacts on the local environment from these activities. The narrow backstreets had little motorised traffic and all samples were collected at least 100m from major roads. For comparison a sample of dust/soil (IT05027) was collected from a narrow backstreet in the Kailashnagar area of East Delhi, a similar neighbourhood to that of Shashtri Park but with no known electronic waste recycling activities in the area. A further sample (IT05028) was collected from a backstreet in a residential area of Safourjung, South Delhi with no known industrial or recycling activities. Again, both samples were collected at least 100m from major roads.

iii separation and mechanical shredding

In addition to the separation of components from printed circuit boards described above, other components of waste electronic products are separated and materials recovered from them for reuse.

TABLE 2.3: DESCRIPTION OF SAMPLES ASSOCIATED WITH THE SEPARATION AND MECHANICAL OF MATERIALS AT RECYCLING WORKSHOPS IN GUIYU, CHINA, 2005

SAMPLE #	SAMPLE TYPE	AREA	SAMPLE LOCATION
CH05015	sediment	Guiyu-Nanyang Road Lianjiang bridge	shredder workshop; wastewater discharge gully
CH05032	shredded components	Guiyu-Nanyang Road Lianjiang bridge	shredder workshop; dumped adjacent to workshop
CH05033	groundwater	Guiyu-Nanyang Road Lianjiang bridge	shredder workshop; adjacent hand pump
CH05036	sediment	Chendian-Guiyu Road, near Fucaodu Bridge	shredder workshop A wastewater discharge channel, as it enters the Lianjiang (see CH05038)
CH05037	sediment	Chendian-Guiyu Road, near Fucaodu Bridge	shredder workshop A wastewater discharge channel, at the point of discharge (see CH05038)
CH05038	wastewater	Chendian-Guiyu Road, near Fucaodu Bridge	shredder workshop A discharge pipe to channel . workshop 750m from Chendian-Guiyu Road
CH05039	sediment	Chendian-Guiyu Road, near Fucaodu Bridge	shredder workshop B wastewater discharge channel, at point of discharge. 500m from Chendian-Guiyu Road
CH05020	dust	Nanyang	floor of printers dismantling workshop
CH05021	soil/sediment	Nanyang	shallow pool, in yard outside printer dismantling workshop
CH05022	groundwater	Nanyang	hand pump, in yard outside printer dismantling workshop


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CHINA - 2005 - ELECTRONIC WASTE, ALSO KNOWN AS E-WASTE WITH NEC LOGO IN A SCRAP YARD ONE OF THE MANY PROMINENT BRAND NAMES OF IMPORTED JUNK, GUIYU, CHINA. MUCH OF MODERN ELECTRONIC EQUIPMENT CONTAINS TOXIC INGREDIENTS. VAST AMOUNTS ARE ROUTINELY AND OFTEN ILLEGALLY SHIPPED AS WASTE FROM EUROPE, USA AND JAPAN TO COUNTRIES IN ASIA AS IT IS EASIER AND CHEAPER TO DUMP THE PROBLEM ON POORER COUNTRIES WITH LOWER ENVIRONMENTAL STANDARDS. THIS PRACTISE EXPOSES THE WORKERS AND COMMUNITIES INVOLVED IN DISMANTLING E-WASTE TO SERIOUS, ENVIRONMENTAL PROBLEMS, DANGER AND HEALTH HAZARDS. GREENPEACE IS STRONGLY URGING MAJOR MANUFACTURES TO EXCLUDE TOXIC MATERIALS FROM THEIR PRODUCTS

mixed e-waste shredding and separating facilities

The shredding of electronic wastes was observed at a number of workshops in Guiyu, China. This is a separate sector to the shredding of plastics separated from e-waste as described in Section 2.1. By far the main material being shredded was printed circuit boards from which individual components had been removed. The shredded material was shaken on large vibrating platforms that were continually washed with water in order to separate heavier materials such as metals from lighter materials, including plastics.

The main material being recovered by this process appeared to be metals, including solder. At one facility, where sediment sample CH05039 was collected, crude solder recovered from circuit boards is purified by melting in open vessels over a fire, and the liquid solder decanted off. Any plastic in the crude solder is simply burnt off.

Water used in the vibrating platform separation process is not reused, and large quantities of wastewater are discharged, typically containing very high levels of suspended solids. These facilities were situated on, or close to, the banks of rivers that supply water for the processing and received the wastewaters produced. No form of treatment was observed prior to the discharge of wastewaters.

One workshop is located close to where the Guiyu-Nanyang Road crosses the main river Lianjiang, in an open shed on the banks of a river (approximately 200m from a large acid working area described in Section 2.4.3). This river runs parallel to the main Lianjiang, but is separated from it by a raised dyke. It was not possible to collect any wastewater discharged by this workshop, but a sample of sediment (CH05015) was collected the wastewater gully through which wastewaters are discharged to the river. None of the waterways around the workshop were found to contain acidic water, and there was no other evidence of the use of acid at this facility.

Large quantities of shredded material had been dumped immediately behind the shredding and separating workshop. A sample of this material (CH05032) was collected for analysis. A sample of ground water (CH05033) was also collected from a hand pump adjacent to the workshop. This samples was primarily collected to investigate impacts of the ground water from the nearby acid working area (see Section 2.4.2).

Two similar workshops are located along a path that runs from Chendian-Guiyu Road where it crosses Fucaodu Bridge, on the border of Guiyu and Chendian Dian. At each workshop, wastewaters are discharged via a pipe into a separate shallow channel that carries them to the Lianjiang. At both facilities the wastewaters contained very high levels of suspended solids, but neither discharge was acidic. It was not possible to access the Lianjiang in this area to collect samples of river sediment.

At the workshop situated furthest (750m) from Chendian-Guiyu Road, a sample of wastewater (CH05038) was collected at its point of discharge from a pipe into a shallow channel. A sample of sediment (CH05037) was collected from the channel at this point. A second sample of sediment (CH05036) was collected from the channel immediately before it entered the Lianjiang, 150m down from the pipe discharge. At the workshop closer to Chendian-Guiyu Road, a sample of sediment (CH0539) was collected from a separate discharge channel, at the point where wastewaters were discharged to it via a pipe.

In India the shredding and grinding of printed circuit boards and other components was only observed as part of the recovery of copper from mixed wastes by leaching with acids. Two samples from this activity (IT05001 & IT05002) are described in Section 2.4.4.

printer storage and dismantling workshop

In a number of workshops in Guiyu, China, other computer periphery equipment is dismantled and materials recovered. At a small workshop in the Nanyang area printers and some of their individual components are dismantled and materials recovered. A sample of dust (CH05020) was collected from the floor of the workshop. This material contained a high proportion of fine black powder, believed to be printer ink.

Prior to dismantling, printers are stored in a yard immediately outside the workshop. Workers reported that, after finishing dismantling work, they washed in a shallow pool of water in the yard. A sample of soil/sediment (CH05021) was collected from this pool. A sample of ground water (CH05022) was also collected from a hand pump in the same yard. This ground water is not used for drinking as when used to make tea this water produces a dark black solution with fine black precipitate, rather than a clear pale yellow solution produced with water from outside the area. The owner of the workshop reported other sources of groundwater in the area gave the same effect and that historically this had not occurred. At a separate workshop in Huamei village, approximately 1.5 km from this hand pump, acidic wastes are disposed into the environment, and may be affecting the groundwater in the area (see Section 2.4.2).

iv acid processing of wastes

Electronic wastes contain a wide range of metals. These are present in many forms, as pure metals, as mixtures (alloys) of different metals, and as metal compounds. Many of these materials will dissolve in strong acids, and can therefore be chemically separated from other materials that will not (e.g. plastics). Metals can subsequently be recovered from the acidic solutions. In Guiyu, China, the workshops using acids to extract materials from electronic wastes are sited in the open on the banks of rivers. In New Delhi, India this type of activity takes place in small, enclosed workshops.

China; Longmen village

Three open-air workshops using acid to extract materials from “e-wastes” are located in Longmen village, an area approximately 1 km from central Guiyu town. The workshops are situated on the banks of a very slow flowing river; it was not possible to ascertain the name of the river (Figure 1).

At the upstream working area, a shallow drainage pit is located adjacent to the working area, approximately 20m from the river. This pit was dry, but contained black waste residues and appeared to have previously received large quantities of wastewaters. A smaller pool containing water and black residues is situated between the dry pit and the river. This smaller pool is directly connected to the river, but not directly connected to the shallow pit. However, wastewaters had visibly leached from the dry pit into this pool in the recent past.

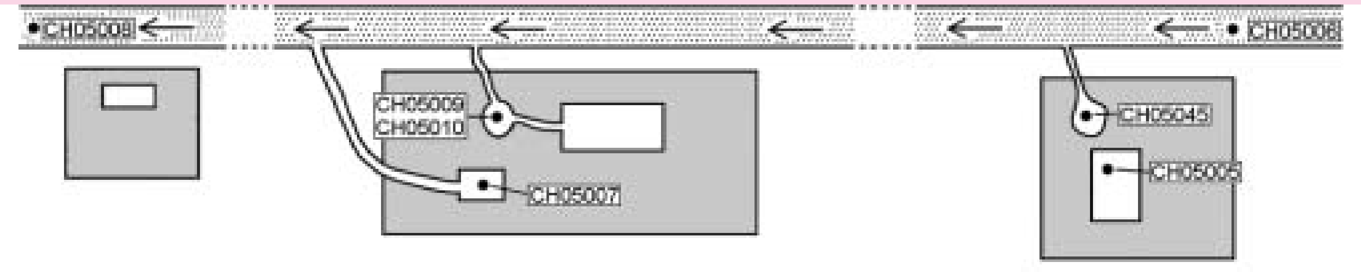
TABLE 2.4: DESCRIPTION OF SAMPLES ASSOCIATED WITH THE ACID PROCESSING OF WASTES IN GUIYU, CHINA AND NEW DELHI, INDIA, 2005

SAMPLE #	SAMPLE TYPE	AREA	SAMPLE LOCATION
		CHINA	
CH05005	soil & acid residues	Longmen	dry shallow pit, upstream working area
CH05006	sediment	Longmen	river, upstream of all working areas
CH05007	soil & acid residues	Longmen	smaller sump furthest from the river, central working area
CH05008	sediment	Longmen	river, downstream of all working areas
CH05009	sediment	Longmen	pool in channel between main sump and river, central working area
CH05010	wastewater	Longmen	pool in channel between main sump and river, central working area
CH05045	soil & acid residues	Longmen	small pool, upstream working area
CH05023	sediment	Huamei	stream, opposite corner of working area to CH05024
CH05024	sediment	Huamei	stream, adjacent to wastewater directly entering from the channel
CH05025	wastewater	Huamei	one of the four wastewater sumps
CH05016	soil & solid residues	Guiyu-Nanyang Road crossing	larger working area, middle of overflow area
CH05017	soil & solid residues	Guiyu-Nanyang Road crossing	larger working area, channel between overflow area and the river
CH05030	sediment	Guiyu-Nanyang Road crossing	river by larger working area, adjacent to the edge of the overflow area, furthest from the working area
CH05031	sediment	Guiyu-Nanyang Road crossing	river by larger working area, adjacent to the channel from the overflow area
CH05027	sediment	Guiyu-Nanyang Road crossing	Lianjiang, by smaller working area. Furthest from wastewater discharge channel (CH05028)
CH05028	soil & acid residues	Guiyu-Nanyang Road crossing	smaller working area by Lianjiang; dry unlined discharge channel between the working area and the river
CH05029	sediment	Guiyu-Nanyang Road crossing	Lianjiang, by smaller working area, adjacent to wastewater discharge channel (CH05028)
CH05034	sediment	Guiyu-Nanyang Road crossing	smaller river, 0.5 km from larger acid working area, in a duck breading area
		INDIA	
IT05001	powdered components	Mandoli	ground components removed from circuit boards
IT05002	slurry	Mandoli	slurry of water & ground circuit boards components
IT05003	process water	Mandoli	acid extracting solution
IT05004	wastewater	Mandoli	acid extraction solution prior to disposal
IT05005	burned fragments	Mandoli	fragments from burned circuit boards
IT05006	ash	Mandoli	ash from burned circuit boards
IT05021	copper metal	Mandoli	recovered from acid extraction solution

DELHI, INDIA - 11 AUGUST 2005 -
ACID-SOAKED RAGS ARE USED TO CLEAN OUT CATHODE RAY TUBES BEFORE THEY ARE REPROCESSED IN THIS WORKSHOP IN DELHI.

Two samples were collected from this upstream working area; mixed soil and solid waste residues from the dry drainage pit (CH05005) and from the smaller water filled pool (CH05045). A sample of sediment was also collected from the river (CH05006) upstream of this, and all other, working areas.

FIGURE 1: SKETCH MAP OF THE THREE ACID WORKING AREA ON THE BANKS OF A RIVER, LONGMEN VILLAGE NEAR GUIYU TOWN, CHINA MAP IS NOT TO SCALE



The central and main working area, located approximately 200m downstream, contained two large wastewater sumps that had been excavated in the ground and lined with a thin layer of natural clay. Wastewater was clearly permeating through the narrow ground between the sumps and the river. The main sump, that closer to the river, is connected to the river by a narrow channel that flows via a smaller pool. The sump, the connecting channel and the smaller pool all contained highly acidic water. Samples of water (CH05010) and bottom sediment (CH05009) were collected from the smaller pool connecting the main sump and the river.

A smaller separate sump, somewhat further from the river, is connected to a narrow channel that appeared to connect to the river downstream of the working area. This sump also contained highly acidic water over 1m deep. A sample of mixed solid waste/soil (CH05007) was collected from the bottom of this sump, close to its outlet channel to the river.

The third working area was located approximately 100m downstream of the central, main working area. This third area appeared to have been recently constructed and there was little evidence of e-waste processing here. However, the one water sump in this area did contain highly acidic water. There was no outflow channel connecting this sump to the river. No samples were collected from within this working area, but a sample of sediment (CH05008) was collected from the river immediately downstream of this, and all other acid working areas.

China; Huamei

A large open-air acid working area was visited in Huamei. At this location, four large sumps had been excavated in the ground to a depth of approximately 1m and lined with natural clay approximately 50cm thick. All sumps contained highly acidic waters (pH=0). Sealed containers that were reported by locals to contain hydrochloric and nitric acids were stored in an open area adjacent to the four sumps. This area appeared to have been used for treating wastes with acid.

A shallow channel had been created around the perimeter of the four sumps, this channel also contained highly acidic wastewater (pH=0) that appeared to be leaching from the sumps. Wastewater had broken through the walls of this perimeter channel and was flowing into an adjacent stream running along one edge of the working area. In addition, wastewaters were clearly leaching through the ground between the perimeter channel and the stream. The water in the stream, which did not appear to be flowing at the time of sampling, was also acidic, with a pH of 2.

A sample of wastewater was collected from one of the four sumps (CH050025). Samples of sediment were collected from the stream, one (CH05024) adjacent to where wastewaters were entering directly from the channel around the sumps, and a second (CH05023) from the opposite corner of the working area. A sample of ground water (CH05022) was also collected approximately 1.5 km from this acid working facility, see Section 2.3.2.

China; Guiyu-Nanyang road crossing of Lianjiang

The Guiyu-Nanyang Road crosses the main Lianjiang, which runs perpendicular to the road. Close to this crossing, a raised dyke separates the Lianjiang from a separate smaller river that runs parallel to it. It was not possible to determine if these two rivers are connected elsewhere via the complex network of interconnecting waterways in this low-lying area. At the time of sampling there was no visible flow in either river. In this area the Lianjiang was highly sedimented and its surface covered in thick vegetation.

Two open-air acid working areas are located in this area. The largest workshop is located on the banks of the smaller river, approximately 0.9 km from Guiyu-Nanyang Road. The smaller working area is situated on the banks of the main Lianjiang, approximately 1.3 km from Guiyu-Nanyang Road. The smaller river (not the main Lianjiang) on which the larger acid workings is situated, is the same as that which receives wastewaters from a workshop where circuit boards are mechanically shredded, approximately 200m along the river (see Section 2.3.1).

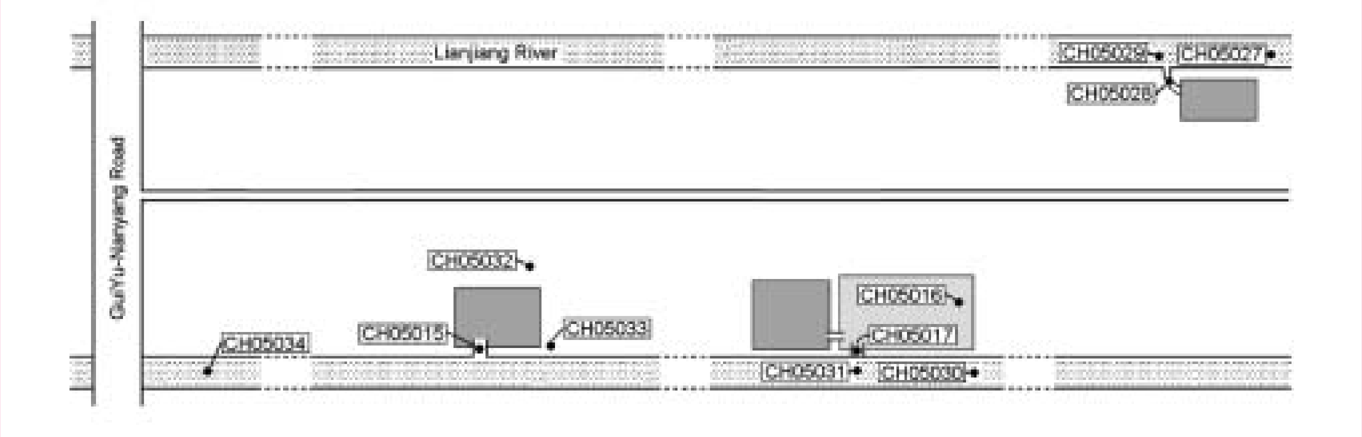
At the larger acid working area, that closest to the Guiyu-Nanyang Road, wastewaters from the fenced working area flow onto a large adjoining area of waste ground, which is covered with many shallow pools of black wastewaters. Black solid wastes have also been dumped on this waste ground. This area is separated from the river by a narrow path less than 1m wide. Near the working area, a narrow channel crosses the path, connecting the overflow waste ground area and the river. Acidic water also appeared to be leaching from the waste ground into the river. At this workshop, access was only possible to the area outside the fenced working area.

One sample of mixed soil and solid acidic waste residues (CH05016) was collected from the middle of the waste ground area, and another from the narrow channel between this area and the river (CH05017). Two samples of sediment were collected from the river, one adjacent to the narrow channel connecting the overflow waste ground area and the river (CH05031), and one by the edge of the overflow waste ground area furthest from the enclosed working area (CH05030). At both locations the river was highly acidic (pH=1).

A third sample of river sediment (CH05034) was collected approximately 500 m from the acid working area to determine the nature of the river sediment when not immediately impacted by acidic discharges. This part of the river is used for duck breeding. The river water in the area from where this sediment sample was collected was not acidic (pH=7).

A sample of ground water (CH05033) was also collected from a hand pump adjacent to a shredding and separating workshop situated approximately 200m along the river (see Section 2.3.1). The release of highly acidic wastewaters from the acid-processing workshop may have impacted the groundwater at this hand pump. There was no evidence of the use of acids at the shredding and separating workshop.

FIGURE 2: SKETCH MAP OF THE TWO ACID WORKING AREAS, AND THE SHREDDER WORKSHOP NEAR THE GUIYU-NANYANG ROAD CROSSING OF LIANJIANG, NEAR GUIYU TOWN, CHINA. MAP IS NOT TO SCALE



A smaller acid working area is situated on the banks of the main Lianjiang, approximately 1.3 km from Guiyu-Nanyang Road. At this workshop, a wastewater discharge channel flows from one side of the enclosed working area into the Lianjiang. At the time of sample collection, this channel was dry but contained acidic black residues demonstrating discharges at other times. A sample of mixed soil and waste residue (CH05028) was collected from this channel. Two samples of sediment were also collected from the Lianjiang in the vicinity of the working area, one close to the entry point of the discharge channel (CH05029), and one by the edge of the working area furthest from the discharge channel (CH05027).

India; Mandoli industrial area

From the reports of workers involved in the processing of electronic wastes with acids in India, the aim of this activity is solely to extract copper from mixed wastes. There is often some physical separation of complex wastes prior to extraction with acids, and some materials are burned on open fires to remove plastics prior to extraction.

A small back street workshop was visited in the Mandoli Industrial Area of East Delhi where the various stages in this processes were observed. Components, including those previously removed from printed circuit boards (see Section 2.2.2), are brought to this workshop where they are mechanically ground to a fine powder, which is then sieved to remove larger metal fragments. The powder is mixed with water to produce a slurry which is then treated with acidic solutions to extract metals. Workers reported that a mixture of concentrated hydrochloric acid and nitric acid are used in this process. Open barrels containing fuming acids were observed in the workshop. Workers reported that materials are first extracted with concentrated acid, and subsequently with weaker acid solutions. None of the workers using the acid solutions had any form of protective equipment to prevent damage to their skin and eyes from acid splashes and spills, or to protect against breathing acidic vapours.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CHINA - 2005 - THE REMAINS OF A COMPAQ COMPUTER IN A SCRAP YARD ONE OF THE MANY PROMINENT BRAND NAMES OF IMPORTED JUNK, GUIYU, CHINA.

Printed circuit boards from which individual components have been removed are also extracted with acid. Whole circuit boards are extracted with concentrated acid, the board is then removed and burned on an open fire adjacent to the workshop. Burned circuit board fragments are separated from the ash by sieving and then further extracted with acid. The ash created by the open burning is simply left of the ground at the site of the fire.

A sample of ground component powder (IT05001) and of the slurry made with the powder from a separate batch of components (IT05002) was collected from this workshop. Samples of burned circuit board fragments (IT05005), and of the ash produced by the burning of circuit board were also collected (IT05006).

Following the extraction of metals from the various wastes, the acidic solution is separated from insoluble material and then iron sheeting is placed into the acid solution to recover metallic copper. Over time, a chemical reaction occurs causing the dissolved copper compounds in the acid solution to become deposited as copper metal on the surface of the iron sheeting, while the metallic iron becomes dissolved iron compounds. It is possible, however, that other metals extracted from the wastes into the acidic solution may also deposit with the copper, producing an alloy of copper and other metals. A sample of deposited copper metal was collected from one of the iron sheets (IT05021). Workers reported that when no further copper can be recovered from the acidic solution it is disposed of by pouring onto open waste ground.

A sample of acid solution that had been used to extract electronic wastes (IT05003) was collected to determine the range and quantities of metals and other chemicals extracted from the wastes. A sample of acid wastewater ready for disposal, from which copper had been recovered, was also collected (IT05004).

v burning of wastes

At workshops in both China and India, some "e-wastes" 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.

In China, ashes and solid wastes from this type of recovery operation were found to have been discarded at an unofficial open dumpsite on the edge of the Longgang area of Guiyu. This dumpsite contained wastes derived from electronic goods as well a wide range of other wastes. Some waste electronics are burned at the dumpsite on open fires and metals recovered. A sample of mixed ash and soil (CH05040) was collected from an area where such burning had just been completed.

Other wastes appeared to have been burned elsewhere and the residue dumped at this site. Three samples of such residues were collected from separate locations within the dumpsite. All three samples consisted of mixtures of ash, partially burned small electronic components and partially burned plastic fragments. Two samples (CH05041 & CH05042) were collected from large uncontained piles of material dumped on the ground, and a third sample (CH05043) was collected from material dumped in sacks.

A similar sample was collected from an open dumpsite in Longmen village, an area approximately 1km from central Guiyu town. This dumpsite is close to the acid processing workshops in this area (Section 2.4.1). At the dumpsite, site small electronic components and plastic fragments had been spread onto the ground and then burned. A sample of ash and partially burned components/plastic fragments (CH05044) was collected from a pile that was still burning.

TABLE 2.5: DESCRIPTION OF SAMPLES ASSOCIATED WITH THE BURNING OF WASTES TO RECOVER METALS IN GUIYU, CHINA AND NEW DELHI, INDIA, 2005

SAMPLE #	SAMPLE TYPE	AREA	SAMPLE LOCATION
		CHINA	
CH05040	ash & soil	Longgang	waste dumpsite; material burned on a open fire on site
CH05041	ash & burned components	Longgang	waste dumpsite; burned material dumped at site
CH05042	ash & burned components	Longgang	waste dumpsite; burned material dumped at site
CH05043	ash & burned components	Longgang	waste dumpsite; burned material dumped at site in sacks
CH05044	ash & burned components	Longmen	waste dumpsite; burned material dumped at site in sacks
		INDIA	
IT05013	ash	Ibrahimpur	open burning of electronic waste to remove plastics and recover metals, open-air storage yard
IT05026	ash	Shashtri Park	open burning of plastic coated copper wire

The burning of composite electronic wastes to remove plastics and recover metals was also observed at a two sites in India. A sample of ash (IT05013) was collected from the remains of such a fire at an open-air yard in the Ibrahimpur area of New Delhi that is primarily used to store "e-wastes". Workers reported that food was often cooked on this fire over burning electronic wastes. At an open-air roof top workshop in the Shashtri Park area, plastic coated copper wires are burned to recover the copper. A sample of ash (IT05026) was collected from this burning. The wire burning was only on a small scale, but was reported to be representative of the many sites at which small amounts of plastic coated wire are burned

In addition to these samples, some materials are burned on open fires as part of the processes involved in the recovery of copper from electronic wastes by extracting with acids. Two samples from this activity (IT05005 & IT05006) are described in Section 2.4.4.

vi cathode ray tube (CRT) storage

TABLE 2.6: DESCRIPTION OF SAMPLES ASSOCIATED WITH THE STORAGE OF CATHODE RAY TUBES PRIOR TO RECYCLING OF THE GLASS; NEW DELHI, INDIA, 2005

SAMPLE #	SAMPLE TYPE	AREA	SAMPLE LOCATION
IT05016	surface coating powder	Kantinagar	eroded surface coating from inside broken cathode ray tubes
IT05017	soil	Kantinagar	ground on which CRTs stored
IT05019	dust	Brijgang	CRT storage shed
IT05020	Dust/soil	Brijgang	open ground by storage shed, under broken CRT glass

The glass portion of TVs and conventional, non-flat screen, computer monitor are known as cathode ray tubes (CRTs). In India, CRTs are collected and stored in various locations before being taken to facilities where the glass is smelted for use in new products.

In the Kantinagar area of East Delhi, CRTs are stored in an open area within an area used as a food market; many of the CRTs were found to be broken into smaller glass pieces. The glass of CRTs contain lead oxide, and the inside surface of the glass screens are coated with material (phosphor) that produces the light when the CRT is in use. A range of different chemicals have are used as phosphors in CRTs. For many of the broken CRTs at this storage area, the coating material was found to be eroding from the glass surface and fine powder was present inside the broken glass tubes, and potentially spreading to the immediate environment. Locals reported that this area had been used to store CRTs for 8-10 years. A composite sample of powder (IT05016) was collected from inside many broken CRTs, as well as a sample of soil (IT05017) from the ground on which the CRTs were stored.

Samples were also collected from a CRT storage shed in the Brijgang area of East Delhi. A sample of dust (IT05019) was collected from within the shed, which was open to the street. A sample of street dust/soil (IT05020) was also collected from an area adjacent to the shed where broken CRT glass is stored in the open. It was not possible to visit any facilities where the CRT glass is smelted.

DELHI, INDIA - 11 AUGUST 2005 - OLD CATHODE RAY TUBES ARE GIVEN A NEW LEASEOF LIFE AS THIS WORKER INSERTS NEW FILAMENTS, SEALING IT OFF WITH A RUDIMENTARY BLOW TORCH.

DELHI, INDIA - 11 AUGUST 2005 -
NEWLY REPROCESSED CRTS PILED UP HIGH.

III RESULTS AND DISCUSSION

The results of the qualitative organic screen and quantitative heavy metals analyses are presented below. For each recycling sector, Tables 3.1-3.6 provide the data on the heavy metal concentrations, the number of organic compounds isolated from each sample, and a breakdown of the groups of organic compounds reliably identified using a GC/MS screening method, as described in Appendix 1.

In Tables 3.1-3.6, metal concentrations are given in mg/kg dry weight for solid samples and mg/l for liquid samples. For the groups of organic compounds reliably identified, the number of compounds identified using general GC/MS screening method is presented for each group; ( ) signifies those additional compounds identified at trace levels using a selective ion monitoring (SIM) method. The concentrations of the organic compounds identified using this method were not determined. A full list of all organic compounds both reliably and tentatively identified in all samples is provided in Appendix 2.

All samples were analysed for a wide range of metals that are used in electrical and electronic equipment (OECD 2003). Some of these metals are toxic and their release from materials during recycling processes pose a risk from exposure of workers as well as the surrounding environment and its inhabitants. Other, including precious metals such as silver and gold, were analysed to give further insight into how materials used in such equipment are distributed during recycling processes.

A number of the metals analysed for were not found at levels above method detection limits in any of the samples. These metals and the detection limits for different types of samples are presented in Table 3. Data on these metals are not presented in the main sample results Tables 3.1-3.6

TABLE 3: METALS ANALYSED IN SAMPLES, BUT NOT PRESENT IN ANY SAMPLES ABOVE METHOD DETECTION LIMITS. CONCENTRATIONS ARE GIVEN IN MG/KG DRY WEIGHT FOR SOLID SAMPLES AND MG/L FOR LIQUID SAMPLES.

METAL	SOLID SAMPLES MG/KG DW	SOLDERS & COPPER MG/KG DW	ACID WATERS (CH05003, 4) MG/L	ACID WATERS (CH05010, 25) & UNFILTERED WASTEWATER (CH05038B), MG/L	GROUNDWATER (CH05022, 33) & FILTERED WASTEWATER (CH05038A), MG/L
Gallium	<20	<200	<0.4	<0.2	<0.02
Germanium	<30	<300	<0.6	<0.3	<0.03
Indium	<20	<20	<0.4	<0.4	<0.02
Palladium	<10	<100	<0.4	<0.2	<0.02
Platinum	<10	<10	<0.2	<0.1	<0.01
Selenium	<30	<300	<0.6	<0.6	<0.03
Tantalum	<10	<100	<0.4	<0.2	<0.01

i plastic recycling

Relatively similar numbers of organic compounds were isolated from three out of four dust samples collected from the plastic recycling facilities in Longgang area of Guiyu, China (CH05001, CH05003 and CH05004), dominated by aliphatic hydrocarbons (see Table 3.1). It was not possible to isolate any of the compounds from the dust sample CH05002 collected near the shredder unit of the workshop A. The chromatogram of this sample showed a high abundance of unresolved complex material (UCM), that contained long chain hydrocarbons that were not possible to separate by the method applied. These UCM “hills” are particularly evident when samples containing biodegraded petroleum or certain refined fractions such as lubricating oils are examined using gas chromatography (Gough & Rowland 1990). One sample of street dust/soil from this area (CH05004) also showed the presence of hexachlorobenzene (HCB) at trace levels. The origin of HCB in this sample is not known.

TABLE 3.1: ORGANIC CHEMICALS AND HEAVY METALS IDENTIFIED IN SAMPLES ASSOCIATED WITH PLASTIC RECYCLING ACTIVITIES IN GUIYU, CHINA AND NEW DELHI, INDIA, 2005. THE NUMBER IN PARENTHESES ( ) SIGNIFIES COMPOUNDS IDENTIFIED AT TRACE LEVELS USING A SELECTIVE ION MONITORING (SIM) METHOD.

Country	CHINA				INDIA		
Sample number	CH05001	CH05002	CH05003	CH05004	IT05012	IT05014	IT05015
Sample type	floor dust	floor dust	floor dust	dust/soil	plastic fragments	plastic powder	floor dust
Location	workshop A Longgang	workshop A Longgang	workshop B Longgang	street between workshops	workshop, Zarfarabad	workshop, Gaziabad	workshop, Gaziabad
metals	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw
Antimony	80	481	231	30	124	11	278
Arsenic	<20	<20	<20	<20	<20	<20	<20
Barium	98	386	124	166	2	64	310
Beryllium	<0.2	<0.2	<0.2	0.3	<0.2	<0.2	<0.2
Bismuth	<20	<20	<20	<20	<20	<20	<20
Cadmium	2.2	30.7	1.8	1.6	<0.5	8.0	11.4
Chromium	6	30	11	31	<2	5	20
Cobalt	3	28	<2	5	<2	<2	<2
Copper	106	3010	188	777	58	39	149
Gold	<10	<10	<10	<10	<10	<10	<10
Lead	47	404	89	163	17	32	100
Manganese	35	185	50	321	1	11	49
Mercury	1.8	2.2	0.6	0.7	<0.2	0.2	<0.2
Molybdenum	<2	3	<2	3	<2	<2	<2
Nickel	54	147	71	118	16	8	17
Silver	5	28	<2	6	3	<2	<2
Tin	<30	128	14	98	<30	<30	<30
Vanadium	<2	6	<2	9	<2	<2	3
Yttrium	<1	3	<1	10	<1	<1	<1
Zinc	167	822	199	443	7	396	549
No. of organic compounds isolated	78	0	94	81	64	60	108
No. reliably identified (% of total)	24 (31%)	0	30 (32%)	20 (25%)	38 (59%)	33 (55%)	27 (25%)
chlorinated compounds							
Chlorinated benzenes	0	0	0	(1)	(4)	0	0
brominated compounds							
PBDEs	0	0	0	0	5(5)	0	0
Other organobromines	0	0	0	0	1	0	0
non-halogentated compounds							
Aliphatic hydrocarbons	21	0	28	16	7	22	15
Aromatic hydrocarbons	1	0	2	2	5	9	12
Organosilicon compounds	1	0	0	0	0	1	0
Organophosphate compounds	0	0	0	0	2	0	0
Alkylphenols	0	0	0	0	1	0	0
Others	1	0	0	1	8	1	0

GUIYU, CHINA - 8 MARCH 2005 - A MIGRANT CHILD FROM HENAN PROVINCE HOLDS UP A PIECE OF E-TRASH, ONCE A COMPUTER SCREEN BEARING A "NOKIA" LOGO IN A JUNK YARD IN GUIYU IN GUANGZHOU PROVINCE.

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GUIYU, CHINA - 9 MARCH 2005 - A STACK OF OLD KEYBOARDS AND OTHER E-WASTE IN NANYANG, CHINA.

It is important to note that organic analysis of samples CH05001, CH05002 and CH05003 was limited by the small quantities of material available. These dusts might therefore contain other organic compounds that were at concentrations below the detection limit of the equipment used in this study.

In India, three samples were collected from the two separate plastic recycling workshops. Among those, a single sample of shredded plastic waste (IT05012) collected from a workshop in Zarfarabad was the only one that showed the presence of chlorinated and brominated compounds. This sample contained a range of common organic contaminants including polybrominated and organophosphate flame retardants such as polybrominated diphenyl ethers (PBDEs) and triphenylphosphoric acid (TPP). Traces of several chlorinated benzenes and a number of phenolic compounds, including nonylphenol and tribromophenol were also identified. PBDEs are use as additives to plastics, textiles, packaging and insulating materials to prevent combustion and/or retard the spread of flames (Lassen *et al.* 1999). Health and environmental concerns relating to the PBDEs are summarised in Box 1. TPP, a compound known to inhibit a human blood enzyme and a possible endocrine disruptor, was one of the most abundant organic compounds in this sample. Further information on this compound is provided in Box 2

Two samples that were collected from the workshop in Gaziabad (plastic powder IT05014 and dust from the floor IT05015) contained a range of aliphatic and aromatic hydrocarbons. One of the representatives of volatile methylsiloxane compounds, decamethylcyclopentasiloxane, was identified in the sample IT05014. Organosilicon compounds including decamethylcyclopentasiloxane are used in microelectronics industry to prepare silicon dioxide films (Zajickova *et al.* 1999). Methylated siloxanes are also widely used in personal skin and hair care products, cosmetics, antiperspirant, and deodorants (Latimer *et al.* 1998). Some have been found to be hepatotoxic to female Fisher rats (McKim *et al.* 1998).

For the samples collected at workshops in Guiyu, China, the dust sample (CH05002) collected from workshop A, in the area around the shredder unit, contained the highest concentrations for most metals analysed. This sample contained antimony (481 mg/kg), cadmium (30.7 mg/kg) and copper (3010 mg/kg) at elevated concentrations relative to background levels. The concentration of lead was not significantly higher than levels previously reported in house dusts (Butte & Heinzow 2002, Culbard *et al.* 1988).

Background levels of antimony in environmental samples such as soils and sediments are typically below 10 mg/kg (Salomons & Forstner 1984). Slightly higher levels, up to 15 mg/kg, have been found in indoor dusts and in road dusts (Butte & Heinzow 2002). Cadmium and copper are typically below 2 mg/kg and 30 mg/kg respectively in uncontaminated soils (Alloway 1990). Somewhat higher levels have been found in indoor dust samples in urban environments remote from major pollution sources; typically below 5mg/kg for cadmium and below 200 mg/kg for copper (Butte & Heinzow 2002, Kim & Fergusson 1993, Tong & Lam 2000). Similar levels to these have been found in urban road dusts (Culbard *et al.* 1988, Li *et al.* 2001, Rasmussen *et al.* 2001).

BOX 1: POLYBROMINATED DIPHENYL ETHERS (PBDEs)

Polybrominated diphenyl ethers are one of several classes of brominated compound in widespread use as flame retardant additives in plastics and foams, including plastic casings of electronic equipment (OECD 2003). There are many different chemicals (congeners) included in this group, differing in the numbers and positionings of bromine atoms in the molecules. Those in common commercial use are "penta" (i.e. a mixture rich in pentabrominated congeners), "octa", (rich in octabrominated congeners) and "deca" (almost exclusively the decabrominated congener).

PBDEs are environmentally persistent chemicals. Some, especially the lower brominated congeners (e.g. "penta-BDE"), are also highly bioaccumulative. Their manufacture and use as additives in plastics and other polymers, in which they are not tightly bound to the polymer matrix, has led to their widespread presence in the environment. PBDEs can be detected in indoor air and dusts in the workplace and in the home. They also occur in almost every part of the environment, including sediments (Allchin *et al.* 1999), freshwater and marine fish (Asplund *et al.* 1999a, b), birds eggs (Hites 2004) and even whales from the deep oceans and the Arctic (de Boer *et al.* 1998, Ikonomou *et al.* 2002).

PBDEs have also been reported as common contaminants in humans, including reports from Sweden, Spain, Finland and North America (Lindstrom *et al.* 1997, Meneses *et al.* 1999, Strandman *et al.* 1999, She *et al.* 2000). Concentrations of lower brominated PBDEs have shown increasing levels in both blood and breast milk in recent decades, particularly in regions in which "penta" remains in commercial use (Alaee *et al.* 2003, Meironyte *et al.* 1999, Thomsen *et al.* 2002). Workers in electronics recycling facilities in Europe have been found to have higher blood levels of PBDEs than other workers, probably as a result of inhalation of contaminated dust (Sjödin *et al.* 2001, Sjödin *et al.* 2003). For the general population, exposure to PBDEs probably occurs through a combination of food contamination and direct exposure the chemicals from consumer products and/or contaminated dusts (Harrad *et al.* 2004).

While their acute toxicity is considered low, chronic exposure to certain PBDEs (especially in the womb) has been associated with abnormal brain development in animals (Eriksson *et al.* 2002), with possible long-term impacts on memory, learning and behaviour (Darnerud 2003, Eriksson *et al.* 2001, 2002, Viberg *et al.* 2004). There are concerns that similar effects may be of relevance in humans (Branchi *et al.* 2003). PBDEs also exhibit endocrine disrupting properties, interacting with both oestrogen and thyroid hormone systems either as the parent compound or as metabolites (Meerts *et al.* 1998, 2001, Legler & Brouwer 2003). Effects on the immune system have also been reported (Birnbaum & Staskal 2004, Darnerud 2003). Furthermore, when plastics containing PBDEs are burned, either in an incinerator or by open burning, the potential exists for formation of brominated dioxins (IPCS 1998), which may be of equivalent toxicity to chlorinated dioxins.

Because of these environmental and human health concerns, controls are increasingly being placed on the use of PBDEs (along with some other brominated fame retardants) in some regions. Penta-BDE is included as a "priority hazardous substance" under the EU Water Framework Directive (EU 2001) and has been proposed for inclusion as a POP (persistent organic pollutant) under the 2001 global Stockholm Convention (Peltola & Yla-Mononen 2001). Both "penta" and "octa" are now banned from use in Europe (EU 2003a). Within the electronics sector, use of all PBDEs, including "deca" will be prohibited from July 2006 under the Directive on Restrictions on Hazardous Substances (RoHS), associated with the WEEE Directive (EU 2002a, b). Nevertheless, even when such controls take full effect, a substantial legacy of PBDEs will remain in obsolete electrical and electronic equipment.

The concentrations of antimony, cadmium and copper in this dust (CH05002) were higher than background levels by between five and thirty times. However, far higher concentrations of these metals were found in samples collected from other recycling processes, as discussed in the following sections.

Compared to the dust collected by the shredder unit, the composite dust sample from the whole floor of workshop A (CH05001), and the floor dust sample collected from a separate nearby workshop (CH05003) contained lower levels of these metals. These data indicate that the shredding of plastic is the major source of the metals found in elevated levels in the most contaminated sample (CH05002).

BOX 2: TRIPHENYL PHOSPHATE (TPP)

Triphenyl phosphate, one of a number of so-called triaryl phosphates, has long been used as flame retardant, primarily in phenolic and phenylene oxide-based resins (IPCS 1991). Other applications include use as a plasticiser in photographic films and as a component of hydraulic fluids and oils.

Loss of TPP to the environment as a result of leaching from polymers in which it is incorporated has long been recognised. Carlsson *et al.* (1997) reported the presence of TPP, among other organophosphorus flame retardants, as a contaminant of indoor air in buildings with different uses in Sweden. Although a relatively minor component compared to other flame retardants in air samples from three schools, a day care centre and an office, much higher levels were found in close proximity to computer monitors (video display units, or VDUs) when in normal use (Carlsson *et al.* 2000). Further investigations revealed that TPP was present at levels up to 10% by weight of the plastic in the outer covers of the monitors. Combustion of polymers containing TPP may also be a major source to the environment (IPCS 1991).

TPP is the most acutely toxic to aquatic life of all the triaryl phosphates in common use (IPCS 1991). It has been reported as a contaminant in human blood (Jonsson *et al.* 2001) and is a strong inhibitor of a key enzyme (monocyte carboxyl esterase) in human blood cells (Amini and Crescenzi 2003). Recent research has also indicated an ability to inhibit human androgen hormone reception in vitro (Honkakoski *et al.* 2004).

Contact dermatitis following exposure to TPP has been reported by several authors, with some cases dating back to the 1960s (Carlsson *et al.* 1997 and Sanchez *et al.* 2003).

BOX 3: NONYLPHENOL

Nonylphenol (NP) is a non-halogenated chemical, commonly found as an isomeric mixture, manufactured almost exclusively to produce nonylphenol ethoxylates (NPEs), a group of non-ionic surfactants. Once released to the environment, NPEs can degrade back to nonylphenol, which is persistent, bioaccumulative and toxic to aquatic life. NPEs have been used as surfactants, emulsifiers, dispersants and/or wetting agents in a variety of industrial and consumer applications (OSPAR 2001). Nonylphenol derivatives are reportedly also used as antioxidants in some plastics (Guenther *et al.* 2002).

As a result of their widespread use, nonylphenol and its derivatives have become widely distributed in fresh and marine waters, accumulating in particular in sediments. Research into levels in wildlife remains very limited, although there have been reports of significant levels in fish and aquatic birds downstream from sites of manufacture and/or use of NPEs. Nonylphenol is known to accumulate in the tissues of fish and other organisms, and to biomagnify through the food chain (OSPAR 2001). Nonylphenol residues have recently been reported in house dust and indoor air (Butte and Heinzow 2002, Rudel *et al.* 2003, Saito *et al.* 2004), possibly relating to use in consumer products. NP has also been detected in samples of human umbilical cord blood (Tan and Mohd 2003).

The main hazards associated with NPEs result from their partial degradation to shorter-chain ethoxylates and to the parent nonylphenol, both of which are toxic to aquatic organisms and to higher organisms through secondary poisoning (i.e. resulting from the accumulation through the food chain). The most widely recognised effects are undoubtedly oestrogenic activity, i.e. the ability of nonyphenol to mimic natural oestrogen hormones, leading to altered sexual development in some organisms, most notably the feminisation of fish (Jobling *et al.* 1995, 1996, 2002). Hazards to human health remain unclear, although recent studies have highlighted concerns directly relevant to humans. For example, Chitra *et al.* (2002) and Adeoya-Osiguwa *et al.* (2003) describe effects on mammalian sperm function, while DNA damage in human lymphocytes has also recently been documented (Harreus *et al.* 2002).

Nonylphenol has been included as a “priority hazardous substance” under the EU Water Framework Directive, such that action to prevent releases to water within 20 years will be required throughout Europe (EU 2001). Moreover, according to Directive 2003/53/EC, as of January 2005 products containing greater than 0.1% NP or NPEs may no longer be placed on the market within Europe, with some minor exceptions principally for “closed-loop” industrial systems (EU 2003b).

In the sample of street dust/soil (CH05004) collected from the road between the two plastic shredding workshops, only copper was present at a significantly elevated concentration. The street dust/soil did not contain antimony, cadmium or lead at concentrations significantly higher than typical background road dust concentrations (Culbard *et al.* 1988, Rasmussen *et al.* 2001).

The dust sample (IT05015) collected from the plastic shredder workshops in New Delhi, India also contained cadmium (11.4 mg/kg), at somewhat lower than the level in the most contaminated dust sample from the plastic recycling workshops in China, and approximately twice typical levels for indoor dusts. This dust sample (IT05015) did not contain other metals at concentrations greater than expected urban indoor dusts (Butte & Heinzow 2002, Tong & Lam 2000).

DELHI, INDIA - 11 AUGUST 2005 - PILES OF DISCARDED COMPUTER PARTS IN A GODOWN IN DELHI. THESE PARTS ARE SORTED, BROKEN APART AND SENT TO VARIOUS 'RECYCLING' WORKSHOPS.

The finely ground plastic powder (IT05014) collected from this same workshop contained cadmium at a concentration of 8.0 mg/kg, indicating that the plastics being recycled are a potential source of cadmium to the workshop environment. Other metals were also identified in this material also at trace levels, including antimony, copper, lead and zinc. Lower levels of metals were found in the sample of shredded plastic fragments (IT05012) collected from a separate workshop, indicating that this material is a different type to that used to produce the plastic powder (IT05014).

BOX 4: ANTIMONY

Antimony (Sb) is a naturally occurring element with a number of industrial uses. For example, antimony compounds are used as lubricants in vehicle brake linings (antimony sulphide, Sb2S3, von Uexkull *et al.* 2005), in semiconductors (antimony trihydride or stibine, Sb2H3) and as a flame retardant in plastics and other polymers (antimony trioxide, Sb2O3, Jenkins *et al.* 2000), normally in combination with brominated flame retardants, especially PBDEs. Antimony is also used in the manufacture of lead acid starter batteries (both Sb2H3 and Sb2O3, Kentner *et al.* 1995) and occurs as a component of solders. Although occurring naturally in soils and sediments, concentrations are commonly rather low.

Antimony shows many chemical similarities to arsenic (Andrewes *et al.* 2004). Like arsenic, it can undergo methylation as a result of microbiological activity (i.e. to form its trimethyl derivative, often called trimethylstibine), albeit at slower rates than for arsenic (Jenkins *et al.* 2000, Patterson *et al.* 2003). It also shows some similarities in its toxic effects, especially to skin cells (Patterson *et al.* 2003). However, unlike arsenic, there are relatively few studies concerning the toxicity and ecotoxicity of antimony and its compounds.

Those studies which are available indicate that the toxicity of antimony depends greatly on its particular form (i.e. its oxidation state). Trivalent antimony, such as is present in antimony trihydride and antimony trioxide, is the most toxic state whereas its pentavalent form is far less toxic (Flynn *et al.* 2003, Patterson *et al.* 2003). Some organic antimony compounds (including trimethylstibine) are very toxic (Andrewes *et al.* 2004). Antimony compounds have been associated with dermatitis and irritation of respiratory tract, as well as interfering with normal function of the immune system (Kim *et al.* 1999).

Antimony trioxide is listed by the International Agency for Research on Cancer (IARC) as "possibly carcinogenic to humans", with inhalation of dusts and vapours the critical route of exposure. Although this compound can be lost in vapour form from items such as PVC mattress covers during normal use (Jenkins *et al.* 2000), it is in occupational settings in which the greatest exposures and concerns arise. For example, several workers exposed to high levels of antimony dust and antimony trioxide fumes at a metal brazing plant developed severe skin problems, even at levels previously thought to be safe (White *et al.* 1993). Some studies suggest that antimony trioxide is a chromosomal mutagen, capable of preventing the mechanisms which normally repair damaged DNA (Schaumloffel and Gebel 1998, Cavallo *et al.* 2002), though its genotoxicity has been challenged by other authors (Leonard and Gerger 1996, Elliott *et al.* 1998).

Metabolism of antimony compounds in humans is similarly poorly studied. There is some evidence that inorganic antimony compounds, if ingested, can be converted to organic compounds and reduced to the more toxic trivalent forms in the body (Andrewes *et al.* 2004). Antimony compounds can be detected in human urine samples from both occupationally and non-occupationally exposed individuals, with levels in blood and urine correlating with levels in workplace air for those occupationally exposed (Kentner *et al.* 1995, Krachler and Emons 2001).

These data suggest that the recycling of plastics involving mechanical shredding & grinding can release metals or metal compounds bound within them to the work environment.

Compounds of cadmium have been used as stabilisers and pigments in plastics including PVC (ATSDR 1999a, Matthews 1996). Cadmium is a highly toxic metal, and exposure can occur through the ingestion or inhalation of contaminated dusts. For an overview of the hazards of cadmium, see text Box 11. Antinomy trioxide is used as a flame retardant additive in some plastic formulations (van Velzen *et al.* 1998). Antimony is also one of the trace metals used in metallic solders present in mixed "e-wastes". However, these solders also contain tin, and often lead, at far higher concentrations. At other locations, dusts contaminated with antimony from solder also contained lead and tin at far higher concentrations, see Section 3.2. This pattern was not found in the samples from this sector, suggesting that solder does not significantly contribute to the levels of antinomy in these dust samples. Antimony, in certain forms, is a toxic metal, with some similarities to arsenic. Further information on antimony is given in Box 4.

Copper compounds are not widely used in plastics, though the elevated dust levels of copper may result from the shredding of some plastics still containing fragments of copper wire or contact.

ii manual printed circuit board separation & solder recovery

The samples of solder collected in China and India in 2005 and that collected in India in 2004 had very similar compositions. These solders are primarily alloys of lead (36.2-38.5%) and tin (46.3-49.8%), but also contained trace amounts of other elements, primarily antimony, bismuth, copper, silver and zinc in varying amounts (all below 1% of the total material).

At the separation/solder recovery workshops in the Beilin area of Guiyu in China, only the removal of components from circuit boards and the recovery of metal solder was observed and so the samples collected from three separate workshops were only analysed for their metals content (Table 3.2.1). At the workshops in India, additional processes were carried out including the separation of some individual components. The samples collected from the workshops in India were therefore analysed for both metals and organic chemicals. The samples collected from the battery separation workshops in India are discussed below (Section 3.2.2)

With the exception of the sample of dust collected from a workshop in India in 2004 (IT04001), all other dust samples from the workshops in both China and India contained high concentrations of lead and tin as well as a range of other metals at concentrations above typical background levels; namely antimony, cadmium, copper, nickel, silver and zinc. For all these metals, the concentrations in the dusts from the workshops in China were higher than in dusts collected from the workshops in India. Samples from China, though not those from India, also contained bismuth at concentrations above typical background levels. High concentrations of barium and mercury were also found in some individual samples.

The concentration of lead and tin in the dust samples from the Chinese workshops were extremely high. The concentrations of lead were reasonably similar in all samples, in the range 31300-76000 mg/kg (3.12-7.60 %), while there was greater variation in tin concentrations; 25100-293000 mg/kg (2.51-29.3 %). The dusts from the Indian workshops had somewhat lower concentrations, with lead in the range 2360-10900 mg/kg (0.236-1.09%), and tin in the range 3140-17400 mg/kg (0.314-1.74%). For all samples from both countries, high lead concentrations were associated with high tin concentrations. The dust from workshop C in China (CH05026a) contained the highest concentrations of both lead and tin, constituting over 7% and 29% of the total dust, respectively.

Environmental samples typically contain low concentrations of lead and tin. These metals are usually below 30 mg/kg and 10mg/kg receptively in uncontaminated soils (Alloway 1990, Salomons & Forstner 1984). Levels of metals in indoor dusts are generally higher than in soils (Culbard *et al.* 1988, Rasmussen *et al.* 2001). Levels of lead between 100 and 500 mg/kg have been reported for indoor dusts, while levels of tin are generally below 200 mg/kg (Butte & Heinzow 2002, Culbard *et al.* 1988, Tong & Lam 2000).

GUIYU, CHINA - 8 MARCH 2005 - A WORKER USES A LIGHTER TO CHECK PLASTIC AS IT IS SORTED IN A JUNK-YARD FULL OF E-WASTE IN GUIYU IN GUANGZHOU PROVINCE.

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TONGSHAN VILLAGE, CHINA - 14 FEBRUARY 2004 - A PILE OF CIRCUIT-BOARD WASTE LAYING INFRONT OF A LOCAL RESIDENT'S HOUSE WAITING TO BE STRIPPED FOR METAL IN TONGSHAN VILLAGE, WENLIN CITY, ZHEJIANG PROVINCE.

TABLE 3.2.1: METALS IDENTIFIED IN SAMPLES ASSOCIATED WITH THE SEPARATION OF COMPONENTS AND RECOVERY OF SOLDER AT RECYCLING WORKSHOPS IN GUIYU, CHINA, 2005. § SIGNIFIES ANALYSIS OF 63µM SIEVED FRACTION.

Sample number	CH05011	CH05026b	CH05012	CH05013	CH05014	CH05026a	CH05018	CH05019	CH05035
Sample type	solder	solder	floor dust §	floor dust §	floor dust §	floor dust §	dust §	dust §	dust §
Description	heated plate workshopA	floor workshopC	workshopA	stored dust workshopA	workshopB	workshopC	solder worker	solder worker	not ewaste worker
Location	solder recovery workshops, Beilin						houses, Guiyu Town		
metals	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw
Antimony	446	795	382	1330	379	514	50	51	<10
Arsenic	<200	<200	36	<20	32	32	<20	<20	24
Barium	<5	<5	457	421	7200	863	236	355	151
Beryllium	<2	<2	1.5	2.3	1.0	1.0	<1.0	<2.0	1.8
Bismuth	145	134	114	296	35	68	<100	<200	<20
Cadmium	<5	<5	104	97	11.0	50.8	4.0	4.3	1.9
Chromium	<20	<20	83	41	146	96	50	65	33
Cobalt	<20	<20	21	10	25	18	8	7	13
Copper	8950	7290	4100	14000	25400	10700	585	579	176
Gold	<100	<100	20	36	30	<10	<40	<80	<10
Lead	375000	385000	51000	66350	31300	76000	719	4110	182
Manganese	<2	<2	491	261	1170	552	610	636	349
Mercury	<10	<10	5.9	2.1	<0.2	<0.2	<2	<2	0.6
Molybdenum	<20	<20	15	13	6	18	<10	<10	4
Nickel	40	21	292	507	1020	504	64	139	54
Silver	434	806	152	1170	268	527	9	36	4
Tin	485000	498000	61300	239000	25100	293000	908	5800	134
Vanadium	<2	<2	23	6	19	14	19	20	47
Yttrium	<1	<1	16	5	26	7	19	16	27
Zinc	<10	241	3770	9345	2340	9130	772	1160	1580

TABLE 3.2.2: ORGANIC CHEMICALS AND METALS IDENTIFIED IN SAMPLES ASSOCIATED WITH MANUAL SEPARATION OF CIRCUIT BOARDS & SOLDER RECOVERY AT WORKSHOPS
THE NUMBER IN PARENTHESES ( ) SIGNIFIES COMPOUNDS IDENTIFIED AT TRACE LEVELS USING A SELECTIVE ION MONITORING (SIM) METHOD

Sample number	IT04002	IT05009	IT04001	IT05011	IT05007	IT05008
Sample type	solder	solder	floor dust §	floor dust §	floor dust §	floor dust §
Description	from circuit boards	from circuit boards	separation workshop	separation workshop	separation workshop	solder workshop
Location	Zarfarabad	Shashtri Pk	Zarfarabad	Zarfarabad	Shashtri Park	Shashtri Park
metals	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw
Antimony	1580	1790	<10	137	70	139
Arsenic	<200	<200	<20	<20	<20	<20
Barium	8	<5	320	1425	532	766
Beryllium	<2	<2	0.6	1.0	0.5	0.3
Bismuth	175	363	<20	<20	<20	<20
Cadmium	<5	<5	1.1	97	14.1	15.5
Chromium	<20	<20	44	158	78	64
Cobalt	<20	<20	12	21	19	12
Copper	2070	2670	168	6805	2800	2140
Gold	573	<100	<10	107	<10	<10
Lead	362000	375000	150	8815	2360	10900
Manganese	<2	<2	336	640	834	446
Mercury	<10	<10	1.4	460	2.1	0.5
Molybdenum	<20	<20	<2	12	7	4
Nickel	163	14	28	541	239	163
Silver	2800	163	<2	343	97	134
Tin	463000	498000	73	13950	3140	17400
Vanadium	<2	<2	29	29	28	21
Yttrium	<1	<1	7	8	10	8
Zinc	<10	21	330	4440	2200	1410
No. organic compounds isolated	n/a	n/a	60	149	219	138
No. reliably identified (% of total)	n/a	n/a	44 (73%)	70 (47%)	68 (31%)	76 (55%)
chlorinated compounds						
Chlorinated benzenes	n/a	n/a	0	1(7)	0	0
PCBs	n/a	n/a	(23)	28(9)	13(25)	2(34)
Other organochlorines	n/a	n/a	3	0	0	7
brominated compounds						
PBDEs	n/a	n/a	0	0	(2)	2(3)
non-halogenated compounds						
Phthalate esters	n/a	n/a	0	0	0	0
Aliphatic hydrocarbons	n/a	n/a	15	17	26	18
Aromatic hydrocarbons	n/a	n/a	3	6	15	6
Organosilicon compounds	n/a	n/a	0	2	2	2
Others	n/a	n/a	0	0	0	1

DELHI, INDIA - 11 AUGUST 2005 - A WORKER IN AN ELECTRONICS WASTE RECYCLING YARD IN DELHI.

IN NEW DELHI, INDIA, 2005. § SIGNIFIES ANALYSIS OF 63UM SIEVED FRACTION.

IT05018	IT05029	IT05022	IT05023	IT05024	IT05025	IT05027	IT05028
floor dust §	floor dust §	street dust	street dust	street dust	street dust	street dust	street dust
battery workshop	battery workshop	workshop area	workshop area	workshop area	workshop area	no work-shops in area	residential area
Mayapuri	Buradi	Shashtri Park	Shashtri Park	Shashtri Park	Shashtri Park	Kailashnagar	Safourjung
mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw
574	46	<10	<10	<10	<10	<10	<10
<20	<20	<20	<20	<20	<20	<20	<20
1300	1130	126	141	178	144	305	208
0.4	0.4	0.3	0.3	0.5	0.5	0.3	0.4
<20	24	<20	<20	<20	<20	<20	<20
42.6	200000	<0.5	<0.5	1.4	<0.5	<0.5	<0.5
103	61	38	24	30	31	25	25
20	631	11	5	8	9	6	6
1730	1610	152	187	230	60	414	21
<10	41	<10	<10	<10	<10	<10	<10
88100	13300	1300	37	48	31	100	20
17700	362	604	250	628	367	295	258
3.5	48.2	0.3	<0.2	<0.2	<0.2	0.6	0.5
7	91	3	<2	<2	<2	<2	<2
154	47900	38	25	35	27	21	15
51	133	4	9	<2	2	8	<2
76	9610	2020	<30	<30	<30	<30	<30
27	14	19	15	25	27	18	29
6	5	4	4	6	6	5	6
4920	1240	359	263	710	297	414	83
93	n/a	140	44	59	66	102	45
45 (48%)	n/a	53 (38%)	24 (54%)	42 (71%)	48 (73%)	22 (22%)	20 (44%)
0	n/a	0	(2)	0	0	0	(3)
24(16)	n/a	14(20)	0	(25)	(29)	0	0
0	n/a	0	3	3	5	3	0
0	n/a	0	0	0	0	0	0
0	n/a	0	0	2	0	0	0
2	n/a	14	14	6	10	9	12
3	n/a	3	2	4	2	4	3
0	n/a	1	0	0	2	0	2
0	n/a	1	3	1	0	6	0

BOX 5: LEAD (PB)

Lead has two main uses in electronics products. Metallic lead is used in electrical solder, primarily on printed circuit boards (commonly as an alloy with tin). Lead oxide is used in the glass of cathode ray tubes (CRTs), which contain approximately 2-3kg of lead in older models and 1 kg in newer models (OECD 2003). In addition, lead compounds have been used as stabilisers in PVC formulations (Matthews 1996).

Concentrations of lead in the environment are generally low. Soils and freshwater sediments typically contain less than 30 mg/kg, while levels of between 100 and 500 mg/kg have been reported for indoor dusts (Alloway 1990, Butte & Heinzow 2002, Salomons & Forstner 1984). Under landfill conditions lead can leach from CRT glass (Musson *et al.* 2000). Incineration can also result in release of lead to the air as in the ash produced (Allsopp *et al.* 2001). Releases of lead oxide dust or lead fumes may also occur during glass crushing or high temperature processing, including smelting (OECD 2003). Following release to the environment lead has low mobility compared to most metals.

Workers involved in high temperature processes, such as at lead smelters, can be significantly exposed to lead fumes (Schutz *et al.* 2005). Workers using lead based solders may also be exposed to lead-bearing dusts and fumes (ATSDR 1999b). Following exposure humans can accumulate lead, as can many plants and animals (Sauve *et al.* 1997, ATSDR 1999b). Where soils and dusts are contaminated with lead, children can be particularly exposed through hand-to-mouth transfer (Malcoe *et al.* 2002).

Lead is highly toxic to humans as well as many animals and plants. Lead exposure is cumulative; the effects of exposure are the same whether through ingestion or inhalation, and some appear to be irreversible (ATSDR 1999b, Bellinger & Dietrich 1994, Goyer 1996). In humans, lead has a wide range of effects including damage to the nervous system and blood system, impacts on the kidneys and on reproduction. Of particular concern is the effect of low-level exposure on brain development in children, which can result in intellectual impairment (Canfield *et al.* 2003, Goyer 1993). Similar toxic effects are seen in animals, and lead is also toxic to all aquatic life (WHO 1989a, Sadiq 1992).

A number of regional controls exist on the use of lead in products. EU legislation restricting the use of certain hazardous substances (ROHS) in electrical and electronic equipment, prohibits the use of lead in new equipment put on the market from 1 July 2006 (EU 2002a), with a maximum allowable concentration of 0.1% lead by weight in homogeneous materials, with some exemptions including use in CRT glass. EU legislation addressing waste electrical and electronic equipment (WEEE) specifies that batteries containing more than 0.4% lead by weight must be separated from wastestreams and recycled where appropriate (EU 2002b). In addition, the European PVC industry has a voluntary agreement to phase out lead stabilisers in PVC by 2015 (ENDS 2002).

For all dusts collected from the workshops in China, the concentrations of lead were hundreds of times higher than typical levels in indoor dusts. The levels in the Indian workshop dusts were elevated by approximately 5-20 times background levels. Environmental concentrations of tin are generally lower than those of lead. In these dust samples, however, the tin concentrations were higher than those of lead in all but one sample (CH05014). In the most contaminated sample from China (CH05026a), the tin concentration was almost four times higher than the lead concentration, and almost 1500 times higher than typical tin levels in indoor dusts. The highest concentration of tin found in the Indian workshop dusts (CH05008) was 17400 mg/kg, approximately 90 times typical levels in indoor dusts. Lead is a highly toxic metal with accumulative effects, see text box 5.

Unlike lead, exposure to inorganic tin does not usually cause toxic effects in humans or animals, unless ingested in very large amounts (ATSDR 2003). The high concentrations of both tin and lead in these samples, however, demonstrates that lead-tin solders are the source of the lead contamination at these workshops.

Other metals identified in the solder samples were also found at elevated concentrations in dust samples collected from various workshops, namely antimony, bismuth, copper, silver and zinc. Previous studies have reported the concentrations of these metals in indoor dusts typically below 15 mg/kg, 10 mg/kg, 200 mg/kg, 6 mg/kg and 1500 mg/kg respectively (Butte & Heinzow 2002, Tong & Lam 2000). For each of these metals, concentrations varied significantly between the samples. Antinomy, copper and silver were present at the most elevated concentrations, ranging from 20 to between 100 and 200 times typical indoor dust concentrations in the workshop dust samples from China. Somewhat lower levels were found in the dusts from the Indian workshops, with elevation above background levels of 5-9 times (antimony), 10-34 times (copper) and 16-57 times (silver).

DELHI, INDIA - 11 AUGUST 2005 - COMPUTER MOTHERBOARDS BEING MELTED OVER OPEN FIRES IN A ELECTRONICS WASTE RECYCLING YARD IN DELHI.


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DELHI, INDIA - 11 AUGUST 2005 - A MAN TAKES A BREAK IN THIS WORKSHOP-LIVING QUARTERS, SURROUNDED BY HEAPS OF ELECTRONIC SCRAP.

BOX 6: BERYLLIUM

Beryllium is a metal with unique properties; it is lighter than aluminium and stronger than steel, as well as being a very good conductor of heat and electricity. In electrical equipment it is used in springs, relays and connections; typically in the form of a copper-beryllium alloy containing 2% beryllium (OECD 2003, Taylor *et al.* 2003).

During the refining and processing of beryllium and its compounds, fumes and dusts of beryllium and beryllium oxide can be produced; their inhalation is the main route of beryllium exposure for workers in these industries (Field 2001). Recent studies have shown that people working with beryllium-copper alloys also have a significant risk of exposure to beryllium can suffer health impacts including developing CBD (Balkissoon & Newman 1999, Schuler *et al.* 2005). While most reported cases of beryllium exposure are related to workers involved in processing and manufacturing activities, exposure may also occur during the recycling of electrical and electronic equipment containing beryllium-copper alloys. Beryllium dusts may be generated during shredding and grinding, or during high temperature processes such as those used at metal refineries (Basel 2004, OECD 2003), which can lead to beryllium sensitivity and CBD in workers (Cullen *et al.* 1987, Infante & Newman 2004).

Exposure to beryllium, even at very low levels and for short periods of time, can lead to beryllium sensitisation. Some individuals will go on to develop CBD, a debilitating disease with symptoms including emphysema and fibrosis of the lungs that can sometimes be fatal. Although symptoms can be suppressed with steroids, CBD is currently incurable (Field 2001). CBD can develop soon after exposure begins or be delayed for long periods, up to many years after initial exposure (Newman *et al.* 1996). The length of time and amount of exposure that results in sensitisation and subsequent development of CBD is highly variable between individuals and not all individuals who become sensitised will go on to develop CBD. Some people can develop berylliosis following seeming very low levels of exposure, and health effects have been reported following exposure to levels 20-100 times lower than widely used workplace exposure limits (Kelleher *et al.* 2001). In many cases CBD in workers is either undiagnosed or misdiagnosed (Infante & Newman 2004, Newman 1995). Skin contact can also produce dermatitis, and may cause beryllium sensitization, a precursor to CBD development (Tinkle *et al.* 2003). Furthermore, beryllium and beryllium compounds have been classified as known human carcinogens by the International Agency for Research on Cancer, based upon the increased rates of lung cancer in beryllium production workers (IARC 1993)

In some countries controls exist to address beryllium exposure in the workplace, with maximum allowable air concentrations. Many countries have adopted workplace exposure limits of 1-2 _g/m3 (WHO 1990). For example, in the USA a maximum average permissible exposure limit (PEL) is set at 2 _g/m3 over 8 hours, with a limit of 5 _g/m3 for any 30 minute period and a peak maximum of 25 _g/m3 (USCFR 1999).

Zinc is typically found at higher background concentrations in environmental samples than many other metals, and although the concentrations of zinc in the dusts was high, the levels were not as elevated above background levels. Zinc levels in the dusts from the Chinese workshops were 2-6 times background levels, while those from the Indian workshop were 1-3 times background levels. Bismuth contamination was only found in the dusts from the workshops in China, with concentrations ranging from 3-30 times background levels.

The concentrations of beryllium in the workshop dusts were up to 2.3 mg/kg from the Chinese workshop (CH05013) and up to 1.0 mg/kg from the Indian workshops (IT05011). In the only study found to report beryllium concentrations in indoor dusts, all levels were below 1 mg/kg, with an average concentration of 0.53 mg/kg (Rasmussen *et al.* 2001). Levels reported in workplaces are reported as total air concentrations (mg/m3) rather than dust concentrations, and so comparison is not possible (Filed 2001)

Beryllium is used in electrical equipment, typically as an alloy with copper containing 2% beryllium (OECD 2003). Beryllium does occur naturally at very low concentrations, and as the workshop dusts are not highly elevated, it is not possible to know the extent to which “e-wastes” processed in these workshops contribute to the dust concentrations. However, exposure to beryllium dusts, even at very low levels and for short periods of time, can cause beryllium sensitisation that can lead to chronic beryllium disease (CBD), a debilitating lung disease which is often misdiagnosed (Field 2001, Newman 1995). It is not clear if current beryllium levels in the workshops could cause health effects in the worker, but the ongoing processing of electronics containing beryllium will only increase the potential.

Clearly the manual separation of e-waste components and the recovery of solders at these workshops results in the release of the metals into the work environment, leading to highly elevated concentrations of many metals in workshop dusts. There is a high risk of exposure to these metals through the inhalation and possible ingestion of these dusts, which is of particular concern where toxic metals such as lead are included in the mixture of metals that make up the solders

Additional metals, which do not form part of solder mixtures, were also found at elevated concentrations in these workplace dusts; namely cadmium, gold and nickel. Again, the level of these metals varied significantly between the samples. The dusts from workshops in China contained cadmium in the range 11-104 mg/kg (2-20 times levels background levels) and nickel in the range 292-1020 mg/kg (3-10 times levels background levels). The dusts from workshops in India contained very similar concentration of cadmium (14-97 mg/kg), though somewhat lower concentrations of nickel (163-541 mg/kg, 2-5 times background levels) (Butte & Heinzow 2002, Culbard *et al.* 1988, Tong & Lam 2000).

Studies reporting the concentrations of metals in dusts do not generally report levels for gold, but environmental levels level are usually very low, with soils typically contain only 0.001-0.02 mg/kg of gold (Alloway 1990). One dust from India contained gold at 107 mg/kg, while three from China had gold in the range 20-36 mg/kg, far higher than typical background levels in environmental samples. These additional metals are employed for a number of uses in electrical and electronic equipment. For example, both cadmium and gold are used electrical contacts (OECD 2003). Their presence in components that are separated from circuit boards at these workshops may contribute to the elevated workplace dusts concentrations

Individual dust samples contained other metals at relatively high levels, though the dusts collected from the workshops were generally not contaminated with these metals above typical background levels. Dust from workshop B in China (CH05014) contained barium at 7200 mg/kg, significantly higher than levels in dusts from all other workshops. Dust from one workshop in India (IT05011) also contained mercury at a concentrations of 460 mg/kg, the highest in all samples from this study. Again these metals are known to be used in electrical and electronic equipment (OECD 2003).

BOX 7: CHLORINATED BENZENES

Chlorinated benzenes, or chlorobenzenes, are simple chlorinated derivatives of benzene, possessing between one and six chlorine atoms (i.e. mono- to hexachlorobenzene). Chlorobenzenes, especially mono-, di-, tri- and hexachlorinated forms, have had a variety of uses, including as solvents (e.g. in commercial PCB formulations) and intermediates in the manufacture of other chemicals such as antioxidants, dyes and pigments, pharmaceuticals and agricultural chemicals. Hexachlorobenzene was ued extensively as a pesticide, primarily as a wood preservative and fungicidal preparation for seeds (Budavari *et al.* 2000, ATSDR 2002). Today only mono- and dichlorobenzenes continue to be manufactured in substantial quantities.

Chlorobenzenes are relatively persistent in the environment and can bioaccumulate in both terrestrial and aquatic systems. Both acute and chronic effects have been reported in a wide range of aquatic organisms and in mammals. Effects of exposure vary depending on the chlorobenzene in question, though common impacts include those on the liver, thyroid and central nervous system (CNS). In general terms, toxicity tends to increase with increasing degree of chlorination (WHO 2004).

For example, human exposure to monochlorobenzene causes CNS depression and respiratory tract irritation, while animal studies have reported liver necrosis, renal toxicity and effects on the pancreas, blood and lymph and adrenal glands (Ware 1988a, Meek *et al.* 1994). Effects reported for dichlorobenzenes in humans include anaemia, skin lesions, vomiting, headaches and eye and respiratory tract irritation (Ware 1988b). For tri- and tetrachlorobenzenes, impacts on liver, kidney and thyroid are among the most commonly reported in mammals (Giddings *et al.* 1994a, b). Some evidence for fetal and developmental toxicity has been reported for both tetra- and pentachlorobenzenes (Giddings *et al.* 1994c).

Hexachlorobenzene (HCB) is toxic to aquatic life, land plants, land animals, and humans. It is listed by the IARC as a Group 2B carcinogen, i.e. possible carcinogen to humans and also appears to be a tumour promoter. Hexachlorobenzene may damage the developing foetus, liver, immune system, thyroid, kidneys and CNS, with the liver and nervous system the most sensitive to its effects. (Newhook & Meek 1994, van Birgelen 1998, ATSDR 2002). HCB has been shown to be an endocrine disruptor in laboratory animal studies (Ralph *et al.* 2003). Furthermore, research suggests that HCB has dioxin-like toxicity (van Birgelen 1998) and that it could therefore make a substantial contribution to overall dioxin-type toxic effects in humans and wildlife (Pohl *et al.* 2001).

Hexachlorobenzene is the most regulated chemical among all chlorinated benzenes, and is included as one of twelve priority POPs covered by the 2001 Stockholm Convention on persistent organic pollutants (POPs). Pentachlorobenzene is one of the priority substances under the EU Water Framework Directive (EU 2001). Recently pentachlorobenzene was proposed as a candidate for inclusion in the UNECE Protocol on POPs (under the LRTAP Convention), based on its potential for long-range atmospheric transport, persistence (in water, sediment and soil), bioaccumulation and (eco)toxicity (van de Plassche *et al.* 2002).

Some of the metals found in elevated concentrations in the samples of dusts are toxic. Of particular concern in these samples is the high concentrations of lead, which is highly toxic, to humans as well as many animals, whether it is ingested or inhaled in the form of fumes or dusts. In humans, exposure to lead can lead to accumulation and can result in a range of toxic effects many of which are irreversible, including damage to the nervous system, particularly during its development in children, which can result in intellectual impairment even at low levels of exposure (Bellinger & Dietrich 1994, Canfield *et al.* 2003, Goyer 1993). Further details are provided in Box 5.

The samples of dusts collected from workshops in India were also analysed for the presence of organic chemicals. The two samples collected from neighbouring facilities of the Zarfarabad area of New Delhi in 2004 (IT04001) and in 2005 (IT05011) had similar patterns of organic contaminants. Both samples contained a range of PCBs (23 and 37 congeners in IT04001 and IT05011 respectively). PCBs are toxic, persistent and bioaccumulative industrial chemicals, once used as dielectric fluids and even as plasticisers and flame retardants, now banned from use because of their hazardous properties. Further background information is provided in Box 10.

BOX 8: MERCURY (HG)

Mercury is used in lighting device that illuminate some flat screen displays. It has also been used in switches and relays, particularly for older mainframe computers, and older computer may also include batteries containing mercury (OECD 2003).

Releases of mercury can occur during the dismantling of equipment. Incineration or landfilling can also result in releases of mercury to the environment (Allsopp *et al.* 2001b, OECD 2003). For a metal, mercury is highly volatile and upon released to the atmosphere metallic mercury can travel globally and impact far from the source of its release (UNEP 2002). Following release to the environment, mercury can enter water bodies (either directly or following deposition) where it can become transformed into methyl mercury, a highly toxic form that can bioaccumulate and biomagnify (progressively concentrate) to high levels in food chains, particularly in fish. This is the major route of exposure for the general public (WHO 1989b, UNEP 2002). Workers may also be exposed to mercury through inhalation of mercury vapour or dust.

Mercury and its compounds are highly toxic and this metal that has no biochemical or nutritional value (WHO 1989b). Inhalation of high levels of mercury vapour may cause a range of effects including impact to the central nervous system (CNS) (ATSDR 1999c, Goyer 1996). Long-term exposure to lower levels of mercury vapour can also cause effects on the CNS and damage to the kidneys (Ratcliffe *et al.* 1996, Goyer 1996). These effects have also been reported in animal (ATSDR 1999c).

For the general population the primary route of exposure to mercury is through diet in the form of methyl-mercury (UNEP 2002). This form of mercury can accumulate in the body and its main impact is damage to the nervous system. Methyl-mercury can readily pass through the placental barrier and the blood-brain barrier, and can have adverse effects on the developing brain and central nervous system in foetuses and children, even at levels to which many people are currently exposed (Mahaffey *et al.* 2004, UNEP 2002). Recent research also indicates that exposure can increase cardiovascular and heart disease (Virtanen *et al.* 2005).

A number of regional controls exist on the use of mercury in products. EU legislation restricting the use of certain hazardous substances (ROHS) in electrical and electronic equipment, prohibits the use of mercury in new equipment put on the market from 1 July 2006 with a maximum concentration of 0.1% by weight in specific materials and components, with certain exceptions for the use of mercury in fluorescent lamps (EU 2002a). Under legislation addressing waste electrical and electronic equipment (WEEE), mercury containing components must be removed from any separately collected WEEE, and mercury must be removed from gas discharge lamps (EU 2002b). The use of mercury in products is further addressed under EU legislation, including the prohibition of batteries and accumulators containing more than 0.0005% of mercury, other than for button cells with a maximum allowable content of 2% (EU 1998).

Both dust samples also contained additional organochlorines: traces of DDT metabolites and beta-HCH in sample IT04001; and traces of chlorinated benzenes from di- to pentachlorinated in the sample IT05011. In the past, PCBs were widely used in electrical and electronic applications, though are now banned from new uses throughout the world. The presence of beta-HCH and metabolites of DDT is most likely due to the ongoing use of these chemicals as insecticides, and not connected to the workshops activities. Additionally, several aliphatic and aromatic hydrocarbons were identified in these samples, such as long chain linear hydrocarbons and polycyclic aromatic hydrocarbons (PAHs).

The two samples of dusts collected from workshops in the Shashtri Park area of New Delhi (IT05007 and IT05008) also where contaminated with the PCBs and contained up to 38 PCB congeners identified in the sample IT05007. Both samples contained a range of aromatic and aliphatic hydrocarbons, representatives of the metylated siloxanes (decamethylcyclopentasiloxane and octamethylcyclotetrasiloxane), and several PBDEs, though some of them only at trace levels. Additionally, sample IT05008 contained seven congeners of polychlorinated naphthalenes (PCNs) from tri- to pentachlorinated. In the past, PCNs had a similar application to the PCBs and were used as a flame retardants, dielectrics in capacitors, as additives in engine oils, electroplating stop-off compounds and as preservatives in wire insulation. PCNs exhibit some similarity in their toxic effects to those of PCBs, see Box 9.

GUIYU, CHINA - 9 MARCH 2005 - CHINESE WORKERS DISMANTLE MOTHERBOARDS IN AN E-WASTE WORKSHOP IN GUIYU, CHINA.

GUIYU, CHINA - 9 MARCH 2005 - A CHINESE WORKER DISMANTLES MOTHERBOARDS IN AN E-WASTE WORKSHOP IN GUIYU, CHINA.

BOX 9: POLYCHLORINATED NAPHTHALENES (PCNs)

The chlorinated naphthalenes (PCNs) show many similarities with PCBs and chlorinated dioxins and furans, but have been far less extensively researched. Theoretically, there are 75 possible PCN congeners, but not all are likely to form in practice. 60 or more are thought to be present in commercial preparations (e.g. “Halowax”) and environmental samples, although analysis is limited by the lack of availability of pure standards (Hayward 1998).

PCNs were predecessors to the PCBs, being used inter alia as dielectrics in capacitors, insulation in detonators, cutting oils, additives in engine oils, in electroplating and die casting, as insulating compounds in wiring and as preservatives for wood, paper and fabrics (Hayward 1998, Kimbrough & Grandjean 1989, Falandysz 1998). PCNs also appear as contaminants in PCB preparations as well as being generated as unintentional byproducts of thermal processes involving chlorine. Although they were largely removed from use in the 1960s and 1970s, PCNs remain in numerous long-lived items of household, industrial and laboratory equipment. An episode of laboratory contamination in Sweden in the early 1990s was found to be caused by PCNs volatilising from the capacitors and wire coatings of old electronic equipment (Weistrand *et al.* 1992).

The environmental persistence of PCNs increases with increasing degree of chlorination. The more highly chlorinated PCNs (penta - octa) do not appear to be metabolised (Safe 1989). Others may be partially metabolised to hydroxylated PCNs or methyl sulphone derivatives (Falandysz 1998). Though relatively little studied in comparison with PCBs and other persistent organochlorines, bioaccumulation in wildlife has been reported (e.g. Falandysz and Rappe 1997). Similarly there are few measurements of PCNs in human tissues, principally because of the difficulties in quantification, though some have been detected in breast milk in North America and Northern Europe (Mes *et al.* 1993, Hayward *et al.* 1989).

Occupational exposure to PCNs has produced numerous symptoms that are also typical of PCBs, PCDD/Fs and technical chlorophenol mixtures, including effects on the skin, liver, digestive tract and peripheral nervous system (Hayward 1998, Kimbrough & Grandjean 1989). In the cable industry, where PCNs were used for insulation, chloracne was reported among both cable manufacturers and subsequent handlers, especially those working with PCNs or PCN treated materials at high temperatures.

PCNs can cause adverse effects on the reproductive system, including low egg hatchability in birds and reduction in semen production and quality in mammals (Morrissey & Schwetz 1989). On the basis of their ability to induce certain key enzyme systems in mammals, some PCN congeners are also recognised to have dioxin-like toxicity (Hanberg *et al.* 1990, Kannan *et al.* 1998).

Clearly the recycling of “e-wastes” at these workshops using manual separation techniques results in the distribution of many organic chemicals and metals that are present in “e-wastes” into the workshop environment.

GUIYU, CHINA - 8 MARCH 2005 - WORKERS UNPACK A TRUCK-LOAD OF E-WASTE WHICH HAS JUST ARRIVED FOR PROCESSING IN GUIYU IN GUANGZHOU PROVINCE.

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BOX 10: POLYCHLORINATED BIPHENYLS (PCBS)

Polychlorinated biphenyls (PCBs) are a group of synthetic organic chemicals that contain 209 individual compounds (known as congeners) with varying patterns of chlorine substitution. PCBs have been used in a wide variety of applications, including transformer oils, hydraulic fluids, plasticisers and carbonless copy papers. They were also used in capacitor dielectrics, heat transfer fluids, lubricating and cutting oils, and in paints and printing inks (ATSDR 2000). Use in transformer oils (frequently with tri- and tetrachlorobenzenes as solvents, Swami *et al.* 1992) and capacitors accounted for the greatest tonnages (de Voogt & Brinkman 1989). Production of PCBs was banned in 1977 when their ability to accumulate in the environment and to cause harmful effects became apparent (ATSDR 2000).

PCBs enter the environment as mixtures containing a variety of individual components and impurities. At least one third of the PCBs that have been produced are now estimated to have entered the environment (Swedish EPA 1998). The other two thirds remain in old electrical equipment and in waste dumps, from which they continue to leach into the environment (for example, when obsolete equipment is dismantled, recycled and/or disposed of).

Once released to the environment from whatever source, PCBs are highly persistent. Furthermore, PCBs that are taken up by aquatic organisms and fish accumulate in them, reaching levels that may be thousands of times higher than in water (ATSDR 2000). PCBs are bioconcentrated to a factor of 6000 for fish and 47 000 for invertebrates (Jones *et al.* 1988). Train (1979) reports bioconcentration factors of between 2500 and 100 000.

PCBs can be absorbed through the skin as well as through ingestion and inhalation. For the general population today, food is undoubtedly the primary route of exposure to PCBs (see e.g. review by Allsopp *et al.* 2000), although dermal exposure may be dominant amongst those directly handling PCBs or PCB-contaminated materials (Lees *et al.* 1987).

PCBs exhibit wide range of toxic effects in animals, including immunosuppression, liver damage, tumour promotion, neurotoxicity, behavioural changes and damage to both male and female reproductive systems (Seegal and Shain 1992, Safe 1993, Rice 1999). PCBs may affect not only the oestrogen system, but also the androgen system, the thyroid hormone system, the retinoid system, the corticosteroid system and several other endocrine pathways (Brouwer *et al.* 1999). Although it is difficult to assess the impact of contaminants on populations in the wild, not least because they are exposed to complex mixtures of chemical contaminants, some immunological and reproductive disorders in marine mammals have nevertheless been linked to elevated levels of persistent organochlorines, in particular the PCBs (see reviews by Allsopp *et al.* 1999, 2001a, Haave *et al.* 2003).

In humans, the greatest body of research on the toxic effects of PCBs has come from two incidents in Japan and Taiwan where people consumed cooking oil that was contaminated with PCBs and other organochlorines.. A recent review of data for children born to mothers exposed to PCBs and PCDFs in the Taiwan incident notes higher incidences of retarded growth, delayed cognitive development and behavioural problems than in children of unexposed mothers (Guo *et al.* 2004). In young men with prenatal exposure there was also significantly increased abnormal morphology of sperm. Studies on the general population of the Netherlands and the Arctic and families of Swedish fishermen (reviewed by Allsopp *et al.* 2001a, Allsopp *et al.* 1999) suggested that even relatively low levels of exposure to PCBs can result in impacts on the immune system (see also Weisglas-Kuperus *et al.* 2004) growth retardation and neurological effects.

The control of PCBs is addressed under many international legal instruments relating to environmental pollution (inter alia, the Barcelona, Helsinki, Basel, Bamako, Rotterdam, OSPAR and LRTAP Conventions and the International Joint Commission on the Great Lakes). In addition, PCBs are targeted for global production ban under the 2001 Stockholm Convention on persistent organic pollutants (POPs), an instrument which also requires proper controls on destruction of stockpiles and the handling of wastes.

battery dismantling workshops, India

Samples of dust collected from two separate batteries dismantling workshops in New Delhi, India were heavily contaminated with toxic metals. The dust from a workshop in Mayapuri where batteries (primarily lead acid batteries) are recycled (IT05018) contained 8.8% lead (88100 mg/kg), about 200 times higher than typical indoor dust levels and the highest concentrations found all samples from both India and China (other than for pure metal solders). This dust also contained higher levels than typically found in indoor dusts for antimony (40 times), cadmium and copper (9 times) and zinc (3 times) (Butte & Heinzow 2002, Culbard *et al.* 1988).

BOX 11: CADMIUM (CD)

Cadmium and its compounds are used in a number of applications within electronics products. Cadmium metal is used in some contacts, switches and solder joints. Many laptop computers contain rechargeable nickel-cadmium (Ni-Cd) batteries which contain cadmium oxide. Cadmium compounds have also been used as stabilisers within PVC formulations, including those used as wire insulation. Cadmium sulphide has been also used in older cathode ray tubes (CRTs) as a phosphor coating, a material used on the interior surface of the screen to produce light (Li *et al.* 2004, OECD 2003).

Cadmium is a rare metal, found naturally in the environment as very low concentrations, typically below 2 mg/kg in soils and sediments, below 5 mg/kg in indoor dusts (Alloway 1990, Butte & Heinzow 2002, Salomons & Forstner 1984). When released to aquatic environments cadmium is more mobile than most other metals (ATSDR 1999A). Cadmium is highly toxic to plants, animals and humans, having no known biochemical or nutritional function (ATSDR 1999A, WHO 1992). Exposure can result in bioaccumulation of cadmium in humans. Many animals and plants, including those consumed by humans, can also accumulate cadmium, providing an additional route of dietary exposure for humans (Elinder & Jarup 1996, Olsson *et al.* 2005).

Cadmium exposure can occur occupationally through inhalation (breathing in) of fumes or dusts containing cadmium and its compounds, or through environmental exposures, primarily diet. Cadmium is a cumulative toxicant and long-term exposure can result in damage to the kidneys and bone toxicity. For the general population and for animals, cadmium exposure through diet primarily affects the kidneys (Elinder & Jarup 1996, WHO 1992). Recent studies have demonstrated kidney damage in humans at lower levels of exposure than previously anticipated (Hellstrom *et al.* 2001). Other health effects from cadmium exposure include disruption to calcium mechanisms causing bone effects, as well as the development of hypertension (high blood pressure) and heart disease. In the short term, inhalation of cadmium oxide fumes or dusts can also affect the respiratory system (ATSDR 1999A, Elinder & Jarup 1996, WHO 1992). Furthermore, cadmium and its compounds are known to be human carcinogens, primarily for lung cancer following inhalation (DHSS 2002).

There are a number of regional controls on the use of cadmium in products. EU legislation restricting the use of certain hazardous substances (ROHS) in electrical and electronic equipment prohibits the use of cadmium in new equipment put on the market from 1 July 2006 (EU 2002a), with a maximum allowable concentration of 0.01% cadmium by weight in homogeneous materials. There are exemptions to this for the use of cadmium in certain plating applications. Under legislation addressing waste electrical and electronic equipment (WEEE), batteries containing more than 0.025% cadmium by weight must be separated from wastestreams and recycled where appropriate (EU 2002b). The use of cadmium in products is further addressed under other EU legislation, including restrictions on its use as a colouring agent or stabiliser in a wide range of products (including PVC) where the cadmium content exceeds 0.01 %, with some exceptions for safety reasons (EU 1991).

In addition, 40 PCB congeners were identified in this dust sample, as well as two metylated siloxane compounds, and several PAHs and aliphatic hydrocarbons. No PBDEs were detected in this sample.

Dust from a workshop in the Buradi area of South Delhi (IT05029) where a wider range of batteries are recycled, including nickel-cadmium (Ni-Cd) batteries, was also highly contaminated with heavy metals. This dust contained very high levels of cadmium (20%), nickel (4.8%) and lead (1.3%). The concentrations of cadmium and nickel in this sample

were the highest concentrations found in this study. The levels are 40000 times higher than typical indoor dust levels for cadmium, and about 500 times higher for nickel.

Cobalt, copper, mercury and tin were also present at elevated concentrations, but less so; between 5 and 50 times typical indoor dust levels (Butte & Heinzow 2002, Culbard *et al.* 1988). Although the concentration of mercury in this sample was low compared to other metals (48 mg/kg), this metal is generally found at very low concentrations in uncontaminated samples. Studies of metal levels in indoor dusts seldom report mercury concentrations, though levels of <1-10mg/kg have been found in house dusts (Butte & Heinzow 2002). Some batteries, particularly button-cell types, incorporate mercury; their dismantling is a likely source of mercury at this location.

environmental around the separation and solder recovery workshops

In China, the two samples of house dust collected from the homes of solder-recovery workers (CH05018 & CH05019) contained higher levels of antimony, cadmium, copper, lead and tin than in dust from a house where none of the residents are employed in any form of work involving electronic wastes (CH05035). In one of the workers homes' dust samples (CH05019), the levels of lead and tin, the main metal identified in the metallic solder, were 23 and 43 times higher than levels found in the single control home (CH05035). The levels of lead and tin in the other workers homes' dust sample (CH05018), and of antimony, cadmium, copper in both workers homes' dust samples, were higher than levels in the single control home dust (CH05035) by between 2 and 7 times. As for the workshop dust samples, the high concentrations of both tin and lead in the dust from the workers homes demonstrates that lead-tin solders are the source of the lead contamination in these homes.

These data provide a preliminary indication that metals used in solders can be carried back to the homes of people working in this sector, presumably through contamination of work clothing, therefore increasing the potential of exposure to these metals for themselves and other members of the household. This is of particular concern where operations involve solders that contain lead, a highly toxic metal. Lead exposure is can lead to accumulative, and some resulting toxic effects on the nervous system appear to be irreversible. Increased exposure, which can occur through the inhalation or ingestion of contaminated dusts, has been linked to intellectual impairment in children as a result of effects on brain and nervous system development (Canfield *et al.* 2003, Lanphear *et al.* 2005).

In India, street dust samples were collected in the Shashtri Park area of East Delhi, in the vicinity of recycling workshops. One of the samples of street dust (IT05022) contained high concentrations of lead (1300 mg/kg) and tin (2020 mg/kg). These are major components of electronic solder and were also found in high concentrations in both samples of dust collected from workshops in this area (IT05007 & IT05008). Street dusts from other areas in New Delhi contained far lower concentrations of lead and tin; dust from a similar street in the Kailash area of East Delhi (IT05027) where e-waste recycling is not believed to take place contained only 100 mg/kg lead and <30 mg/kg tin. Dusts from a street in the Safourjung residential area of South Delhi (CH05028) contained even lower lead, at only 20 mg/kg.

All street dusts from Shashtri Park also contained copper and zinc at higher concentrations than those found in the sample from the Safourjung area (CH05028), though not higher than the street dust from the Kailash area. One sample from Shashtri Park (IT05024) also contained cadmium at 1.4 mg/kg, higher than in all other street dust samples though not significantly higher than typical levels reported for urban street dusts and uncontaminated soils (Alloway 1990, Culbard *et al.* 1988, Li *et al.* 2001, Rasmussen *et al.* 2001).

In addition three out of four Shashtri Park street dusts samples, with the exception of the sample IT05023, also contained PCBs – chemicals also identified in both samples of dust collected from workshops in the area (IT05007 & IT05008). The highest number of PCB congeners were identified in sample IT05022, that which also contained the highest lead and tin concentrations. One of the street dusts (IT05024) also contained two phthalate esters, namely diethylhexyl phthalate (DEHP) and dibutyl phthalate (DBP), which could also indicate the impact from the local workshops, though other sources cannot be ruled out. In contrast, the two control samples (IT05027 and IT05028) collected from streets with no known e-waste recycling activities did not contain any representatives of PCBs, PBDEs or phthalate esters.

BOX 12: PHTHALATES (PHTHALATE ESTERS)

Phthalates (or, more accurately, phthalate diesters) are non-halogenated chemicals with a diversity of uses, dominated by use as plasticizers (or softeners) in plastics, especially PVC (e.g. in cables and other flexible components). Other applications included uses as components of inks, adhesives, sealants, surface coatings and personal care products. Some phthalates are discrete chemicals, such as the well known di(2-ethylhexyl) phthalate (DEHP), while others are complex mixtures of isomers, such as diisononyl phthalate (DINP).

All uses of phthalates, especially the major use as PVC plasticisers, result in large-scale losses to the environment (both indoors and outdoors) during the lifetime of products, and again following disposal. Just within the European Union (EU) this amounts to thousands of tonnes per year (CSTEE 2001a). As a result, phthalates are among the most ubiquitous man-made chemicals found in the environment. They are widely found in the indoor environment, including in air and dust (Otake *et al.* 2001, Butte & Heinzow 2002, Fromme *et al.* 2004).. Phthalates are commonly found in human tissues, including in blood and, as metabolites, in urine (Colon *et al.* 2000, Blount *et al.* 2000, Silva *et al.* 2004). In humans and other animals they are relatively rapidly metabolised to their monoester forms, but these are frequently more toxic than the parent compound (Dalgaard *et al.* 2001).

Substantial concerns exist with regard to the toxicity of phthalates to wildlife and humans. For example, DEHP, one of the most widely used to date, is a known reproductive toxin, capable (in its monoester form MEHP) of interfering with development of the testes in early life. In addition, adverse impacts on female reproductive success in adult rats and on development of the young have been reported following exposure to this chemical (Lovekamp-Swan & Davis 2003). Butylbenzyl phthalate (BBP) and dibutyl phthalate (DBP) have also been reported to exert reproductive toxicity (Ema & Miyawaki 2002, Mylchreest *et al.* 2002). Both DEHP and DBP are classified as "toxic to reproduction" within Europe. Recent research has revealed a correlation between phthalate exposure during pregnancy and decreased ano-genital index (distance from the anus to the genitals) in male children (Swan *et al.* 2005). Decreased AGI correlated with concentrations of four phthalate metabolites, namely monoethyl phthalate (MEP), mono-n-butyl phthalate (MBP), monobenzyl phthalate (MBzP), and monoisobutyl phthalate (MiBP). Other commonly used phthalates, including the isomeric forms DINP and DIDP (diisodecyl phthalate), are of concern because of observed effects on the liver and kidney, albeit at higher doses.

At present, there are few controls on the marketing and use of phthalates, despite their toxicity, the volumes used and their propensity to leach out of products throughout their lifetime. DEHP is also proposed as a "priority hazardous substance" under the EU Water Framework Directive (EU 2001), such that action to prevent releases to water within 20 years will be required throughout Europe. Of the controls which do exist, however, probably the best known is the EU-wide emergency ban on the use of six phthalates in children's toys designed to be chewed (first agreed in 1999 and then repeatedly renewed, EC 2004). This is expected very soon to be replaced by a permanent ban. While this will address one important exposure route, exposures through other consumer products remain unaddressed.

Three of the street dust samples from Shastri Park (IT05023, IT05024 and IT05025), as well as the control sample from Kailashnagar (IT05027) also contained DDT and its metabolites. The source of these chemicals is presumably from use as a mosquito vector control, and not connected to the workshops activities.

These data indicate that the local environment around e-waste recycling facilities is significantly affected by the activities of these facilities.

iii separation and mechanical shredding

Sediments collected from the discharge channels of mechanical shredder workshops in China contained highly elevated concentrations of many heavy metals, indicating the accumulation of these metals from wastewaters discharged by facilities.

TABLE 3.3: ORGANIC CHEMICALS AND METALS IDENTIFIED IN SAMPLES ASSOCIATED WITH THE SEPARATION AND MECHANICAL SHREDDING OF MATERIALS AT RECYCLING THE NUMBER IN PARENTHESES ( ) SIGNIFIES COMPOUNDS IDENTIFIED AT TRACE LEVELS USING A SELECTIVE ION MONITORING (SIM) METHOD.

Sample number	CH05015	CH05032	CH05033	CH05036	CH05037	CH05038
Sample type	sediment	shredder waste	ground water	sediment	sediment	waste water
Description	discharge gully	adjacent dumpsite	hand pump	discharge channel; End	discharge channel; Start	discharge pipe (filtered)
Location	Guiyu-Nanyang Road shredder workshop	Guiyu-Nanyang Road shredder workshop	Guiyu-Nanyang Road shredder workshop	Chendian-Guiyu Road shredder workshop A	Chendian-Guiyu Road shredder workshop A	Chendian-Guiyu Road shredder workshop A
metals	mg/kg dw	mg/kg dw	mg/l	mg/kg dw	mg/kg dw	mg/l
Antimony	1750	1440	<0.05	1390	2150	0.21
Arsenic	<20	<20	<0.02	70	58	<0.02
Barium	2770	357	0.151	1890	1670	0.178
Beryllium	<0.2	<0.2	<0.002	1.1	<0.2	<0.002
Bismuth	126	13	<0.2	71	24	<0.2
Cadmium	13.5	62.9	<0.005	31.0	19.5	0.008
Chromium	92	53	<0.02	53	32	<0.02
Cobalt	38	22	<0.02	39	15	0.204
Copper	30100	2450	<0.02	9980	9520	0.15
Gold	<10	<10	<0.1	<10	<10	<0.1
Lead	12000	1580	0.063	10000	4505	0.041
Manganese	4440	1580	0.199	3860	1780	5.70
Mercury	2.0	7.5	<0.002	18.1	7.1	<0.02
Molybdenum	28	4	<0.02	22	7	0.026
Nickel	850	281	<0.004	349	149	0.017
Silver	258	112	<0.02	312	115	<0.02
Tin	5310	1600	<0.4	9830	4560	<0.4
Vanadium	10	15	<0.002	23	16	<0.002
Yttrium	3	3	<0.001	31	6	<0.001
Zinc	5250	2640	0.035	3710	2005	0.451
No. organic compounds isolated	113	132	10	124	143	n/a
No. reliably identified (% of total)	78 (69%)	37 (28%)	5 (50%)	81 (65%)	53 (37%)	n/a
chlorinated compounds						
Chlorinated benzenes	0	0	0	0	0	n/a
PCBs	0	0	0	0	0	n/a
Other organochlorines	1	1	0	1	1	n/a
brominated compounds						
PBDEs	30(13)	9(1)	0	27(15)	12(15)	n/a
Other organobromines	0	0	0	1	0	n/a
non-halogenated compounds						
Phthalate esters	0	0	2	0	6	n/a
Aliphatic hydrocarbons	29	22	0	19	2	n/a
Aromatic hydrocarbons	2	4	3	14	4	n/a
Organophosphate compounds	0	0	0	0	4	n/a
Alkylphenols	0	0	0	1	4	n/a
Others	2	0	0	3	5	n/a

Discharge channel sediment from a facility near the Lianjiang Bridge on the Guiyu-Nanyang Road (CH05015) contained copper, lead and tin at very high concentrations, (between 400 and 600 times typical background levels of these metals in soils and sediments) as well as antimony at nearly 200 times background levels. A wide range of other metals were also present at elevated concentrations, though to a lesser degree, including silver and zinc (at between 50 and 60 times typical background levels) as well as barium, bismuth, cadmium and nickel at between 5 and 20 times typical background levels (ATSDR 2000, Alloway 1990, Salomons & Forstner 1984).

For the two facilities located close to the Chendian to GyiYu road, two sediments were analysed from the discharge channel of the facility closest to the road (CH05036-37). A sample of discharged wastewater was also collected from this facility, the analysis of which is discussed below. For the channel sediments, the concentrations of metals found at elevated levels were of a similar magnitude in both samples, though the sediment from the end of the channel (CH05037), immediately before it entered the Lianjiang, contained a number of metals at concentrations up to 2 times higher than in the sediment collected at the start of the discharge channel (CH05036), where wastewaters are discharged from the workshop via a pipe.

WORKSHOPS IN GUIYU, CHINA, 2005.

CH05038	CH05039	CH05020	CH05020	CH05020
waste water	sediment	dust	dust	dust
discharge pipe (unfiltered)	discharge channel; Start	workshop floor	workshop floor	workshop floor
Chendian-Guiyu Road shredder workshop A	workshop B	Nanyang printer workshop	Nanyang printer workshop	Nanyang printer workshop
mg/l	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw
7.00	1800	97	97	97
1.515	42	<20	<20	<20
41.75	4460	93	93	93
0.003	0.4	<0.2	<0.2	<0.2
<0.2	250	<20	<20	<20
0.644	85.2	4.5	4.5	4.5
0.548	189	159	159	159
0.462	95	35	35	35
91.0	45900	19200	19200	19200
<0.1	<10	<10	<10	<10
46.9	44300	284	284	284
57.45	8750	1940	1940	1940
0.655	41.9	7.8	7.8	7.8
0.055	126	22	22	22
2.15	2060	398	398	398
0.949	739	12	12	12
62.7	33000	116	116	116
0.303	21	8	8	8
0.275	7	8	8	8
47.90	13700	8950	8950	8950
213	135	148	148	148
74 (35%)	83 (61%)	52 (35%)	52 (35%)	52 (35%)
1(1)	(5)	0	0	0
0	0	24(11)	24(11)	24(11)
1	4	0	0	0
4(9)	30(10)	0	0	0
0	5	0	0	0
0	0	0	0	0
36	16	9	9	9
17	5	6	6	6
0	0	0	0	0
0	1	0	0	0
5	7	2	2	2

With a few exceptions, the levels of metals present at elevated concentrations in these two sediment samples were generally similar (from 0.5 to 2 times) to the concentrations found in the discharge channel sediment collected from the facility near the Lianjiang Bridge on the Guiyu-Nanyang Road (CH05015), as described above.

The levels of bismuth, lead and nickel in sample CH05037, and of copper in both sediments (CH05036 & 37) from the facility close to the Chendian to GyiYu road were between 3 and 5 times lower than those at the Guiyu-Nanyang Road facility (CH05015). Conversely, concentrations of mercury were higher in samples CH05036 & CH05037. Although the concentrations of mercury in these samples were far lower than other metals, they still represent a significant elevation above background mercury concentrations, which are typically below 0.5 mg/kg (Alloway 1990, Salomons & Forstner 1984).

Organic contaminants that were identified in these two sediment samples (CH05036 & CH05037) included a range of PBDEs with up to 42 congeners in sample CH05036, a range of phenolic compounds including hormone-disrupting chemical nonylphenol (in one case, as an isomeric mixture), and the chlorinated compound Mirex. Although perhaps most widely known for its use to control fire ants, mirex also received extensive use as a flame retardant in plastics, rubber, paint, paper, and electrical goods from 1959 to 1972 (ATSDR 1995). Mirex is a highly persistent and bioaccumulative chemical which binds tightly to soils and sediments and can build up in fish or other organisms that live in contaminated water or that eat other contaminated animals. Further information is given in Box 13.

Furthermore, the sample CH05037 contained a diversity of phthalate esters, chemicals used as plasticisers in a range of polymers (especially PVC), including the known reproductive toxins dibutyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP). Box 12 provides additional information on uses and hazards of phthalates esters.

BOX 13: MIREX

Although probably better known for its use as an insecticide, mirex was also used extensively as a flame retardant (under the trade name "Dechlorane") in thermoplastic and thermosetting resins, rubber, paint, paper and electrical products (ATSDR 1995). Large-scale production continued until 1976, though manufacture as a flame retardant is thought to have ceased in 1972. Some use as an insecticide may continue in certain countries, though this is hard to verify. Similarly, the extent of its presence in obsolete electrical and electronic equipment around the world is not known.

Mirex is strongly bioaccumulative and is among the most persistent of all the chlorinated pesticides, remaining for extended periods in lipid tissue. Though it may be partially broken down over time to form photomirex or chlordecone, both these breakdown products are also toxic and persistent.

Mirex primarily affects the central nervous system (CNS) and behavioural effects have been reported in exposed animals. On the basis of evidence from animal studies, it is reasonably anticipated to be a human carcinogen (DHHS 1998) and was classified as group 2B (possibly carcinogenic to humans) by the IARC in 1987. The liver is the primary site of carcinogenesis in most animal models, though the kidney is also susceptible to damage. Chronic exposure to mirex, or its primary degradation product photomirex, can also disrupt thyroid hormones, depressing levels and altering the structure of the gland (Smith 1991). Reproductive effects include impairment of ovulation and testicular damage in rats, as well as formation of cataracts in both newborn mice and rats (ATSDR 1995).

Mirex is one of the chemicals targeted for elimination under the 2001 Stockholm Convention on persistent organic pollutants (POPs).

This sample also contained residues of the hazardous organophosphorus flame retardant triphenyl phosphate (TPP), as well as two closely related chemicals, which may be contaminants, or primary degradation products of TPP preparations. Traces of PBDEs and dichlorinated benzens, as well as mirex, were also detectable in the wastewater/slurry sample CH05038 flowing from this facility to the channel at the time of sampling. The latter sample had as many as 213 organic compounds isolated, the highest number among the samples collected in association with the physical separation/fragmentation/deconstruction of materials at recycling workshops in Guiyu, China. Additionally to the organic pollutants mentioned above, this sample contained PAHs and a wide range of aromatic and aliphatic hydrocarbons. Altogether, however, only 35% of all organic compounds isolated from this sample could be reliably identified.

Moreover, it was impossible to specify the identity of two organic compounds that were isolated from the sediment sample CH05036 which show GC/MS fragmentation patterns characteristic for polyhalogenated (probably polybrominated) organic compounds. This provides an additional indication of the diversity and complexity of the organic contaminants arising from such activities.

It was not possible to collect wastewater from the channel serving the other shredding facility on the Chendian to GyiYu road. Nevertheless, a sample of sediment CH05039 from this channel revealed the presence of a diverse array of chlorinated and mixed chlorinated/brominated benzenes and chlorinated naphthalenes, additional to contaminants that were found in sediments of the neighbouring facility such as PBDEs, Mirex, and nonylphenol. The presence of the chlorinated naphthalenes may well arise from their former use as flame retardant additives in plastics and rubbers, though they have had a diversity of other uses.

The discharge channel sediment from the facility located a little further from the Chendian to GyiYu road (CH05039) contained a similar pattern of metals at elevated concentrations. For all these metals, the concentrations in this sample were higher than, but of a similar order of magnitude to, those in the discharge channel sediments from the two facilities described above. Concentrations were generally only 2-3 times higher than those in the discharge channel sediment at the Guiyu-Nanyang Road facility (CH05015).

Of the three shredder workshops, it was only possible to collect discharged wastewater from the facility nearest to the Chendian to GyiYu road, where discharge channel sediments CH05036 & CH05037 were also collected. The wastewater (CH05038) contained very high levels of suspended particles. The concentrations of dissolved metals in a filtered portion of this sample, as well as the total concentrations of metals in the whole sample were separately determined.

The wastewater did not contain significantly elevated concentrations of dissolved metals. For most metals, concentrations in natural surface waters can vary over a large range depending on local conditions. Where dissolved metals in the filtered wastewater sample were present above method detection limits, their concentrations were within the background ranges reported for surface waters (ATSDR 2000, Salomons & Forstner 1984, WHO 1992).

Total metal concentrations in the unfiltered sample, however, were far higher for all metals. This wastewater contained barium, copper, lead, manganese, tin and zinc at total concentrations of between 42 and 91 mg/l, as well as antimony and nickel at between 2 and 7 mg/l. As the metals in this sample were primarily present in the form of waste particles suspended in the water, it is not possible to draw direct comparisons with equivalent data for typical background water concentrations. However, the discharge of wastewaters containing suspended particles with such a wide range of metals at these high concentrations will place a large and accumulating burden on receiving water bodies, as seen in the very high metal concentrations in the discharge channel sediments.

Other samples were collected in the vicinity of the shredder workshop located near to the Guiyu-Nanyang Road.

A sample of shredded material that had been dumped in the open behind the workshop (CH05032) contained a very similar pattern of metal contamination to that in the discharge channel sediment from this workshop (CH05015). For most metals, the concentrations in the sediment were somewhat higher than in this solid waste, by 2 to 10 times. Mercury and cadmium were both approximately 4 times higher in the solid waste (CH05032).

Organic contaminants that were detected in these two samples (sediment IT05015 and shredded material CH05032) were also of similar pattern and included the brominated flame retardant compounds PBDEs, the chlorinated insecticide or flame retardant Mirex and a range of aliphatic and aromatic hydrocarbons. A total of 43 PBDE congeners, from tribrominated to hexabrominated, were isolated from the sediment sample IT05015 taken from the wastewater ditch of the facility close to the GyiYu to Nanyang road. Additionally, sample IT05015 contained two representatives of fatty acid esters.

Clearly metals and organic contaminants contained within the "e-wastes" being processed at this facility are being released into the wider environment by a number of different routes.

A sample of groundwater (CH05033) was also collected from a hand pump located adjacent to the shredder workshop. This water did not contain any of the metals analysed for at levels significantly elevated above typical background concentrations. However, during organic analysis several compounds were reliably identified in this sample including two phthalate esters (DnBP and DiBP), benzothiazole and it's derivative, and also one phenolic compound. The origin of these contaminants cannot be discerned from these data, though clearly the recycling of plastic wastes is one possability.

printer storage and dismantling workshop

The sample of dust (CH05020) collected from the printer-dismantling workshop contained a high concentration of copper (approximately 100 times typical indoor dust levels) as well as antimony, nickel and zinc at less elevated concentrations (between 4 and 6 times typical background dust levels) (Butte & Heinzow 2002, Culbard *et al.* 1988).

A similar pattern of contamination was found in the mixed soil/sediment sample (CH05021) collected from a shallow pool immediately outside, demonstrating the spread of chemicals out of the workshop. This samples was highly contaminated with copper (at over 500 times typical background levels), as well as lead (80 times) and antimony, tin and zinc (at between 30 and 40 times background levels). This soil/sediment also contained both mercury and cadmium at approximately 30 mg/kg. While lower than the concentrations of other metals, these levels are still significantly elevated above typically very low background concentrations of these metals, by approximately 20 times for cadmium and 60 times for mercury (Alloway 1990, ATSDR 1999a&c, Salomons & Forstner 1984).

Both samples collected in association with the printer storage and dismantling workshop contained a range of PCBs identified to a high degree of reliability - from 35 to 53 congeners identified in the floor dust sample CH05020 and in the soil/sediment sample from pool outside workshop CH05021 respectively. In fact, the latter soil/sediment sample had the widest range of PCB congeners (from mono- to heptachlorinated) and the highest abundance of PCBs among all the samples considered in this study. It has been reported that some older, large printers included PCB containing capacitors (OECD 2003).

Taking into account that this shallow pool is used by workshop workers for washing after finishing dismantling work, this could represent a direct route of exposure to hazardous chemicals arising from the processing of printers. Although it is not possible from the results of this study to evaluate the extent of damage to health and the environment from these widespread practices, these results do underline the urgent need for such studies to be undertaken.

Despite the reports by locals of recent changes in the quality of the groundwater in the area, the groundwater collected from a hand pump in the yard adjacent to the workshop (CH05022) did not contain any metals at elevated concentrations. There were also few organic compounds present in this sample, as revealed by the organic analysis. Among five organic compounds that were isolated from this sample just two were reliably identified, namely phthalate esters DnBP and DiBP. The presence of traces of these compounds is unlikely to account for the unusual properties of the water from this pump previously described.

Note that very high concentrations of metals were found in samples collected from an acid working area, about 1.5 km away in Huamei (Section 3.4.2). However, the groundwater collected at the printer workshop (CH05022) does not appear to have been contaminated by the activities of at the Huamei acid working area.

GUIYU, CHINA - 8 MARCH 2005 - A MIGRANT WORKER STRIPS WIRES FROM E-TRASH IN A JUNK YARD IN GUIYU IN GUANGZHOU PROVINCE.

iv acid processing of wastes

China; Longmen village

At Longmen, both samples of soil/acid residues CH05005 and CH05045 that were collected from working areas within the upstream acid processing workshop contained a diverse range of organohalogen compounds including chlorinated benzenes, PCBs and brominated flame retardants (PBDEs), Mirex was detected in the sample CH05005 only. 34 and 36 PCB congeners and 11 and 9 PBDE congeners were identified in the samples CH05005 and CH05045 respectively, though some of them at trace levels. Also, both samples had a variety of aliphatic and aromatic hydrocarbons reliably identified.

In contrast, no PCBs and PBDEs were identified in the three samples of soil/acid residue CH05007, sediment CH05009 and the wastewater CH05010 that were collected from the main acid processing workshop in this area, approximately 200m downstream. Nevertheless, these samples have shown the presence of other organic contaminants such as phthalate esters, particularly in the wastewater sample with five representatives from this class of organic compounds including DEHP, DnBP, DiBP, DEP and BiBP (butyl isobutyl phthalate). Both sediment and wastewater samples collected from the pool between the main sump and the river contained halogenated phenolic compounds such as 2,6-dibromo-4-nitrophenol (sediment CH05009) and 4-chloro-2-nitrophenol (wastewater sample CH05010). The wastewater sample contained three more metylated nitrophenols. One of the samples from this workshop area, the sediment CH06009, also contained the chlorinated insecticide/flame retardant Mirex.

Two samples from this area, CH05005 and CH05007, contained several compounds which were impossible to identify. However, these compounds have shown GC/MS fragmentation characteristic for polyhalogenated organic compounds, such that their identity warrants further investigation.

All the soil/acid residue and sediment samples collected from the pools and discharge channels in both the upstream working area (CH05005 & CH05045) and the main working area (CH05007 & CH05010) contained a similar range of elevated metal concentrations, with antimony, copper, lead and tin generally at the highest concentrations.

TABLE 3.4.1: ORGANIC CHEMICALS AND METALS IDENTIFIED IN SAMPLES ASSOCIATED WITH THE ACID PROCESSING OF
THE NUMBER IN PARENTHESES ( ) SIGNIFIES COMPOUNDS IDENTIFIED AT TRACE LEVELS USING A SELECTIVE ION

Sample number	CH05005	CH05045	CH05007
Sample type	soil/acid residues	soil/acid residue	soil/acid residue
Description	shallow dry pit	small pool	smaller sump
Location	Longmen upstream area		Longmen Central area
metals	mg/kg dw	mg/kg dw	mg/kg dw
Antimony	1590	839	1245
Arsenic	<20	<20	<20
Barium	513	407	142
Beryllium	0.5	1.5	1.3
Bismuth	33	<20	99
Cadmium	<0.5	3.2	20
Chromium	11	66	11
Cobalt	3	9	8
Copper	229	6640	3295
Gold	<10	<10	36
Lead	2560	3600	5395
Manganese	81	239	226
Mercury	1.2	1.4	0.7
Molybdenum	8	<2	<2
Nickel	27	241	316
Silver	631	82	1920
Tin	3590	2720	1690
Vanadium	8	21	9
Yttrium	4	14	33
Zinc	39	648	241
No. of organic compounds isolated	110	120	53
No. reliably identified (% of total)	56(51%)	80 (67%)	25(47%)
chlorinated compounds			
Chlorinated benzenes	(9)	1(10)	(4)
PCBs	8(26)	22(14)	0
Other organochlorines	1	0	1
brominated compounds			
PBDEs	1(10)	4(5)	0
Other organobromines	0	0	0
non-halogenated compounds			
Phthalate esters	0	0	2
Aliphatic hydrocarbons	17	17	16
Aromatic hydrocarbons	1	6	1
Organophosphate compounds	0	0	0
Others	1	1	1

GUIYU, CHINA - 9 MARCH 2005 - A CHINESE WORKER “BAKES” MOTHERBOARDS IN AN E-WASTE WORKSHOP.

WASTES IN LONGMEN & HUAMEI, GUIYU, CHINA, 2005.
MONITORING (SIM) METHOD.

CH05009	CH05010	CH05006	CH05008	CH05023	CH05024	CH05025
sediment	wastewater	river sediment	river sediment	sediment	sediment	wastewater
pool between sump & river	pool between sump & river	upstream of all areas	downstream of all areas	stream; away input channel	stream; by input channel	1 of 4 water filled sumps
		Longmen		Huamei		
mg/kg dw	mg/l	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/l
356	31.8	14	346	21	26	0.215
25	<0.04	<20	24	<20	<20	<0.04
141	0.054	107	139	76	95	0.043
3.8	0.093	2.8	3.8	3.8	8.3	1.21
<20	2.29	<20	<20	<20	<20	<0.5
12.3	12.2	0.9	12.3	<0.5	<0.5	0.138
43	1.19	19	43	29	56	0.649
83	1.05	11	82	21	58	13.2
5080	774.5	474	4570	9530	1850	252.5
<10	<0.2	<10	<10	<10	<10	<0.2
350	3.66	130	362	2690	632	3.195
284	4.365	537	280	83	187	9.05
8.2	<0.02	0.2	6.1	8.0	20.1	0.676
10	0.056	<2	10	171	238	1.36
940	153.5	29	929	138	320	88.5
27	1.06	<2	27	26	60	<0.04
639	85.5	104	672	780	1480	2.03
27	0.075	27	27	23	40	0.03
49	0.103	46	48	5	22	0.451
839	48.75	187	832	2470	2120	583.5
33	57	15	76	132	27	27
6(18%)	17 (30%)	4 (27%)	45(59%)	65(49%)	15(56%)	6(22%)
0	0	0	0	0	0	0
0	0	0	0	29(12)	0	0
0	1	0	0	1	0	0
0	0	0	12(12)	0	0	0
1	0	0	0	0	0	0
1	5	0	1	0	0	4
3	2	2	15	20	13	0
0	4	0	0	2	0	1
0	1	0	0	0	0	0
1	4	2	5	1	2	1

TABLE 3.4.2: ORGANIC CHEMICALS AND METALS IDENTIFIED IN SAMPLES ASSOCIATED WITH ACID PROCESSING OF WASTES AT FACILITIES NEAR THE GUIYU-NANYANG ROAD
THE NUMBER IN PARENTHESES ( ) SIGNIFIES COMPOUNDS IDENTIFIED AT TRACE LEVELS USING A SELECTIVE ION MONITORING (SIM) METHOD

COUNTRY	CHINA						
Sample number	CH05016	CH05017	CH05030	CH05031	CH05034	CH05028	CH05029
Sample type	soil/acid residues	soil/acid residues	river sediment	river sediment	river sediment	soil/acid residues	river sediment
Description	overflow area middle	channel to river	away from channel	adjacent to channel	control; 0.5km away	discharge channel	Lianjiang; by channel
Location	Guiyu-Nanyang Road crossing; larger working area					Guiyu-N Rd; smaller working area	
metals	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw
Antimony	1300	1280	1290	190	<10	1670	1100
Arsenic	<20	<20	<20	<20	<20	<20	<20
Barium	62	118	129	99	83	61	141
Beryllium	0.4	0.5	1.4	1.0	2.0	0.7	1.1
Bismuth	108	49	71	12	<20	43	48
Cadmium	3.5	2.8	2.8	0.9	<0.5	<0.5	<0.5
Chromium	15	20	39	37	29	12	18
Cobalt	23	12	20	19	8	3	5
Copper	15200	2770	3210	1520	28	613	149
Gold	<10	<10	<10	<10	<10	<10	<10
Lead	3710	2540	83	161	44	246	137
Manganese	72	107	132	116	193	104	101
Mercury	0.8	3.0	3.8	1.3	0.5	4.7	2.1
Molybdenum	6	8	24	6	<2	<2	3
Nickel	707	469	829	388	13	44	21
Silver	945	577	79	13	<2	153	130
Tin	1280	1750	2350	237	34	716	1560
Vanadium	3	8	24	28	38	12	18
Yttrium	1	2	5	5	31	7	6
Zinc	230	237	204	138	62	31	49
Organic compounds isolated	175	137	93	56	34	48	88
Reliably identified (% of total)	84 (48%)	80 (58%)	28 (30%)	29 (52%)	14 (41%)	30 (63%)	40 (45%)
chlorinated compounds							
Chlorinated benzenes	8(2)	(9)	0	0	0	0	0
Chlorinated phenols	0	0	0	0	0	0	0
PCBs	19(27)	20(24)	0	0	0	0	0
Other organochlorines	2	2	0	0	0	0	1
brominated compounds							
PBDEs	2(6)	1(8)	0	(12)	0	8(8)	15(8)
Other organobromines	0	0	0	0	0	0	0
non-halogenated compounds							
Phthalate esters	1	0	1	1	0	0	0
Aliphatic hydrocarbons	1	18	12	10	12	11	13
Aromatic hydrocarbons	13	6	1	0	0	2	0
Organosilicon compounds	0	0	0	0	0	0	0
Organophosphate compounds	0	0	0	0	0	0	0
Others	3	1	14	6	2	1	3

DELHI, INDIA - 11 AUGUST 2005 -
WORKSHOP-LIVING QUARTERS FILLED WITH HEAPS OF ELECTRONIC SCRAP.

CROSSING OF THE LIANJIANG, GUIYU, CHINA AND IN MANDOL INDUSTRIAL AREA, NEW DELHI, INDIA, 2005.

	INDIA						
CH05027	IT05001	IT05002	IT05003	IT05004	IT05005	IT05006	IT05021
river sediment	powdered components	component slurry	process water	wastewater	burned fragments	ash	copper metal
Lianjiang; away chnl	ground component	slurry of powder	extraction solution	waste acid solution	burned e-wastes	ash from burning	recovered copper
	acid workshop, Mandoli Industrial Area						
mg/kg dw	mg/kg dw	mg/kg dw	mg/l	mg/l	mg/kg dw	mg/kg dw	mg/kg dw
105	7780	9830	18.2	68.6	900	5995	427
<20	<20	<20	<0.04	<0.04	<20	<20	<400
146	12	76	0.010	0.969	4610	1030	7
7.3	<0.2	1.1	0.151	0.108	1.4	0.9	<4
<20	66	202	<0.5	<0.5	95	<20	<400
<0.5	<0.5	1.5	0.500	0.339	11.2	6.7	<10
49	5	32	15.0	16.5	192	103	22
14	16	48	16.4	19.6	18	33	<40
1690	195000	147500	22000	241	136000	18200	565000
<10	194	100	<0.2	<0.4	<10	<10	<200
195	5460	9165	3.4	20.4	20500	3505	490
240	24	65	125	220	469	295	191
3.1	0.5	<0.2	<0.02	<0.02	<0.2	62.7	<20
4	<2	4	0.73	1.80	16	32	<40
436	2550	2255	457	478	203	121	316
35	588	708	<0.04	0.51	211	27	<20
295	1170	939	17.9	340	15500	1860	937
34	<2	3	1.53	0.941	56	29	<40
48	<1	<1	0.102	0.088	3	3	<2
225	323	595	3060	2710	6400	2615	2240
62	25	20	29	12	82	79	n/a
28 (45%)	5 (20%)	16 (80%)	16 (55%)	9 (75%)	32 (39%)	55 (70%)	n/a
0	0	(10)	1(1)	0	(5)	(11)	n/a
0	0	0	2	1	0	0	n/a
0	0	0	0	0	0	0	n/a
0	0	0	1	0	0	0	n/a
6(6)	0	0	0	0	9(8)	(23)	n/a
0	0	0	0	0	0	1	n/a
0	0	0	3	3	0	0	n/a
12	2	5	1	0	3	8	n/a
3	3	1	3	4	5	11	n/a
0	0	0	0	0	2	1	n/a
0	0	0	1	1	0	0	n/a
1	0	0	3	0	0	0	n/a

At the upstream working area, the sample from a wastewater pool (CH05045) that is connected to the river contained generally higher concentrations than that from the shallow drainage pit (CH05005). Copper, lead and tin concentrations in this sample were the most elevated, at more than 100 times typical background soil concentrations (Alloway 1990, Salomons & Forstner 1984). This sample was quite acidic, with a pH 4.5, and contained a high concentration of antimony. The mobility of metals is generally increased under acidic conditions. Being directly connected to the river, there is nothing to prevent to movement of metals from this pool into the aquatic environment. Copper and lead are highly toxic to aquatic life, particularly under acidic conditions, which increases the mobility and toxicity of these metals (Gerhardt 1993). Additional information on the aquatic toxicity of copper is given in Box 14.

The sample from the dry drainage pit (CH05005) was highly acidic, with a pH of 1, demonstrating the use and disposal of strong acids at this working area. For samples from this area, the highest concentrations of antimony (1590 mg/kg) and silver (631 mg/kg) were found in this sample.

In the main acid working area in Longmen, the highest concentrations of metals were generally found in the soil sample collected from the smaller sump (CH05007), with levels of antimony, copper, lead and tin between 100 and 200 times typical background concentrations. Other toxic metals (cadmium and nickel) were also present at concentrations up to 10 times background levels;. Relatively high concentrations of silver and gold were also found in this sample.

The sediment sample from a pool connecting the main sump and the river (CH05009) contained most metals at somewhat lower concentrations. Nevertheless, concentrations were still markedly above background, with cadmium, lead, mercury, nickel and zinc at between 10 and 20 times background levels; antimony and tin at between 30 and 50 times background levels, and the highest concentration of copper in this area at over 100 times background levels.

The water samples collected in these two parts of this working area (the pool connecting the main sump to the river, and in the smaller sump) were highly acidic, both at pH 0. Both areas where samples were collected were directly connected to the river.

As would be expected from the high sediment metal concentrations and the high level of acidity, the water sample (CH05010) collected from the pool connecting the main sump and the river contained very high concentrations of dissolved metals, particularly for antimony, copper, lead, nickel, tin and zinc. Dissolved metal concentrations in natural surface waters can vary significantly depending on local conditions. However, the concentrations of antimony, cadmium, copper and tin in this sample were ten of thousands of times higher than average background concentrations. Many other metals were also present at concentrations tens to hundreds of times average background concentrations for surface waters, including beryllium, bismuth, chromium, cobalt, lead, manganese, silver, yttrium and zinc (ATSDR 2000, Filella *et al.* 2002, Mance *et al.* 1984, Neal & Robson 2000, WHO 1992). The use of acid solutions at this Longmen sites clearly mobilizes a wide range of metals from the “e-wastes” being processed.

River sediment samples CH05006 and CH05008 collected upstream and downstream of the acid processing workshops discussed above clearly show the impact of these facilities on the surrounding environment e.g. the river, where wastewaters were discharged. While no organic contaminants of note were detected in the upstream sediment sample (CH05006), the downstream sediment sample (CH05008) contained contaminants identified in both acid processing areas including brominated flame retardants (PBDEs) and the phthalate ester DEHP. The concentrations of all metals were also higher in the downstream sample compared to those in the upstream sample, particularly for antimony, cadmium, copper, mercury and nickel, which were between 10 and 30 times higher in the downstream sample. The concentration of copper in this sample was almost 100 times higher than background sediment levels (Salomons & Forstner 1984). Furthermore, the downstream sediment was far more acidic (pH of 4.5) than the upstream sample (pH of 6.0). In addition to impacts from toxic metals to the river, the discharge of highly acidic wastewaters into rivers is likely in itself to have serious impacts. Acidification of rivers is harmful to a wide range fish and other aquatic organisms (Mason 1996).

The data for samples from the working areas and the adjacent river clearly demonstrate that where “e-wastes” containing metals are processed with acids, most if not all of these metals will become mobilised. Not all metals found at elevated concentrations in these samples are highly toxic to aquatic environments. Nevertheless, where “e-wastes” include toxic metals such as cadmium, copper and lead there will be clearly be impacts on the immediate environment.

BOX 14: COPPER (Cu)

Copper is widely used within electronics products due to its high electrical conductivity, primarily as a pure metal, or as part of mixture (alloys) with other metal, including beryllium (ATSDR 2004, OECD 2003).

Levels of copper in the environment are typically usually quite low, with soils containing less than 30 mg/kg, and only slightly higher in freshwater sediments; less than 50 mg/kg (Alloway 1990 Salomons & Forstner 1984). Levels up to 200 mg/kg have been reported in indoor dusts (Butte & Heinzow 2002).

Exposure to copper in metallic form does not generally result in toxic effects, though inhalation of very high levels of dust and vapours can cause effects including irritation of the nose, mouth and eyes as well headaches, dizziness and nausea (ATSDR 2004). Releases of soluble copper compounds to aquatic environments, however, can have significant impacts. Copper in soluble forms is highly mobile in the aquatic environment, particularly at high acidity (low pH). In these forms, copper is far more bioavailable and is toxic to a wide range of aquatic plants and animals (ATSDR 2004, Gerhardt 1993, Mance *et al.* 1984). Effects include reductions in growth and fertility rates as well as increases mortality (Bryan & Langston 1992, UNEP 1993). Although dependent of many others factors, the majority of aquatic organisms cannot tolerate or survive in copper concentrations above 1 mg/l, and impacts can occur at concentrations as low as 0.05 mg/l (50 ug/l) for some sensitive organisms (Nor 1987, Salomons & Forstner 1984).

China; Huamei

Three further samples were collected from another acid processing facility in the area of Huamei: a wastewater sample CH050025 from one of four large sumps surrounded by a ditch, and two sediments from an adjacent stream, one (CH05024) close to where a channel flows between the ditch and the stream, and second (CH05023) by the working area but away from the channel connecting the ditch and the stream.

The wastewater sample (CH05025) was highly acidic (pH=0) and contained high concentrations of a wide range of metals, as was found for the wastewater sample collected from the Longmen area (CH05010) described above. Copper and zinc were present in particularly high concentrations (over 100mg/l), while beryllium, cobalt, lead, manganese, mercury, molybdenum, nickel, tin and yttrium were also present at high concentrations. The wastewater contained four phthalate esters including DnBP, DiBP, DEP and BiBP, though none of these were detected in either stream sediment sample from this area. No halogenated compounds were identified in the wastewater sample.

The sediment (CH05023) collected from the adjacent stream, at the corner of the site opposite to where a channel flows between the working area and the stream, contained 41 congeners of PBDEs reliably identified as well as Mirex. It is unclear what was the source of these organohalogen contaminants in the latter sediment sample. This indicates the need for further investigation in the area. The other stream sediment sample (CH05024) did not containe any halogenated compounds.

The pattern of metal concentrations in the wastewater was different to that in the wastewater sample collected from equivalent workshops at Longmen. Beryllium, mercury and zinc were present at far higher concentrations at Huamei (CH05025), while concentrations of cadmium, silver and tin far higher in the wastewater collected at Longmen (CH05010). These data suggest that different e-waste materials are processed at the Huamei and Longmen sites, but that in both cases metals in the wastes are made highly water soluble and therefore mobile though the processes employed. In case of organic contaminants, both sites showed presence of phthalate esters, though organohalogen compounds were more diverse at Longmen area.

Both stream sediments contained copper, lead, mercury, tin and zinc highly elevated above typical background levels, ranging from 20-25 times for zinc in both samples and up to 150-200 times for copper in CH05023 and for lead in CH05024. There is no clear pattern to the metal concentrations in the stream sediments, possibly due to the very slow flow of water along the stream. Of the metals found at elevated concentrations, some were present at higher levels in the sample (CH05024) collected adjacent to a channel flowing from the working area into the stream, while other metals were at higher levels in the sample collected from the same stream as it flowed passed the opposite corner of the acid working area (CH05023).

The data indicates inputs to the stream of additional metals. The stream sediment collected by the discharge channel (CH05024) contained beryllium, cobalt, manganese, nickel and yttrium at concentrations more than two times higher than levels found in the other stream sediment (CH05023), colleted nearby but away from the discharge channel. These metals were all present at high concentrations in the wastewater sample (CH05025). The concentrations in both stream sediment samples, however, were not higher than the typical ranges of background concentrations reported for these metals. Furthermore, the stream was highly acidic (pH=2) in this area.

Groundwater (CH05022) collected approximately 1.5 km from this site did not contain elevated concentrations of metals (see Section 3.2.2).

China; Guiyu-Nanyang road crossing of Lianjiang

Two separate open air acid reprocessing areas are located near the crossing of the road between Guiyu and Nanyang and the Lianjiang. The two working areas are on the banks of separate, but parallel rivers that flow either side of a path along the top of a raised dyke. The largest working are is located on the banks of the smaller river, approximately 0.9 km from Guiyu-Nanyang Road. The smaller working area is on the banks of the main Lianjiang, approximately 1.3 km from Guiyu-Nanyang Road

At the larger working area, both samples of mixed soil/waste samples collected from waste ground/overflow area adjacent to the working area (CH05016) and from the channel between this area and the river (CH05017) were highly acidic (pH=0). Both contained high concentrations of antimony, copper, lead and tin, as well as bismuth, nickel and silver. Other than for bismuth and nickel, the concentrations in both samples were more than 100 times background soil concentrations. Sample CH05016 contained 1.5% copper, more than 500 times background levels (ATSDR 2004, Alloway 1990, Salomons & Forstner 1984). Both samples were also heavily contaminated with organohalogen compounds including chlorinated benzenes, PCBs, PBDEs, Mirex and one congener of trichloronaphthalenes. Additionally, sample CH05016 contained DEHP among those compounds reliably identified.

The river adjacent to the working area and overflow area is clearly impacted by the activities at this site. The river was highly acidic (pH=1) at both sediment sampling locations. All metals found at high concentrations in the samples from the waste ground/overflow area (CH05016-17) were also present in both river sediments (CH05030-31) at high concentrations, compared both to levels in the control river sediment (CH05034) collected away from this acid working area and typical background levels in river sediments. Levels of cadmium and mercury in samples by the working area (CH05030-31) were significantly higher than those in the control river sediment (CH05034). For all but lead, the river sediment collected near to the channel between the waste ground/overflow area and the river (CH05031) contained higher concentrations than in the sediment collected further from the working area (CH05030). Concentrations of antimony, copper and tin were the most elevated, all at more than 100 times background sediment concentrations, with nickel and silver at nearly 20 times, and lead at up to 5 times background sediment concentrations (ATSDR 1999b & 2000, Filella *et al.* 2002, Mance *et al.* 1984). Several PBDE congeners and DEHP were also detected in this sample (CH05031). In comparison, the control river sediment sample CH05034 contained little in the way of organic contamination. Furthermore this control sample was not acidic (pH=7).

Chemicals associated with "e-wastes" were also found in the discharge channel and river sediments at the smaller acid workshop in this area, located approximately 1.3 km from Guiyu-Nanyang Road on the banks of the main Lianjiang, on the other side of the raised dyke to the area described above.

The sample of soil/acid residues (CH05028) collected from the discharge channel between the working area and the Lianjiang was highly acidic (pH=0). It contained 16 congeners of PBDEs and range of aromatic and aliphatic hydrocarbons. This sample also had elevated concentrations of antimony and tin, as well as bismuth, copper, lead, mercury and silver. Other than for antimony, metal concentrations were lower than for similar samples associated with the larger working area described above.

Both river sediments contained elevated metal concentrations and organic pollutants indicating the direct impact of the acid reprocessing activities on the environment. Both contained PBDEs, with the larger number of these contaminants detected in the sample collected by the discharge channel (CH05029). This sample was highly acidic (pH=1) and also showed a very similar pattern to that found in the discharge channel, with antimony and tin in the highest concentrations, as well as elevated levels of bismuth, copper, lead, mercury and silver. However, the sediment collected by the edge of the working area furthest from the discharge channel (CH05027) contained even higher concentrations of beryllium, copper, lead and nickel, though was far less acidic (pH=6). The reason for the higher metal concentrations in sample CH05027 is not clear.

India; Mandoli industrial area

The workshop in the Mandoli Industrial Area of East Delhi, India was somewhat different to those located in the Guiyu area of China which were situated in the open on the banks of rivers. The processing of wastes at the workshop in India was being carried out in a small enclosed building far from any rivers. Workers reported that acidic wastewaters are disposed of simply by pouring onto waste ground in the vicinity of the workshop. The sole aim of the acid processing of "e-wastes" at this workshop was the recovery of copper.

Two samples of materials prior to processing were analysed to determine the range of chemicals they contained in addition to copper.

The sample of powdered e-waste components (IT05001) contained few organic compounds that could be reliably identified. Those which were identified included methylated nitrophenol, two aromatic and two aliphatic hydrocarbons. Nitrophenolic compounds are toxic chemicals that have been frequently detected in the wastes resulting from various industrial processes, including electric/electronic components production. These chemicals are commonly used as intermediates for the production of dyestuffs, pigments, and rubber chemicals (ATSDR 2000). Analysis of the second sample (IT05002), that consisted of the slurry made with the powdered components (but from a different batch to sample IT05001) showed the presence of chlorinated benzenes (from di- to hexachlorinated), though at trace levels. As it was mentioned in Section 2.4.4, some materials are burned on site on open fires to remove plastics prior to extraction. The presence of chlorinated benzenes, which could be formed during burning of PVC (Ruokojarvi *et al.* 2000), might indicate that the composition of the sample included such plastics. However, other possible sources cannot be ruled out.

Both samples (IT05001 & IT05002) contained very similar concentrations of metals, with copper being by far the most abundant metal at 19.5% and 14.8% of the total material respectively. Other metals included antimony (0.78-0.98%), lead (0.55-0.92%), nickel (0.22-0.26%) and tin (0.09-0.12%), as well as lesser amount of precious metals including silver (0.06-0.07%) and gold (0.01-0.02%).

Other materials, primarily printed circuit boards, are burned prior to extraction with acidic solutions, including printed circuit boards from which components have been removed. The sample of fragments from such burned waste (IT05005) contained a similar pattern of metals at high concentrations to the powdered components analysed (IT05001 & IT05002), primarily copper (13.6%), lead (2.05%) and tin (1.55%), as well as antimony, barium, zinc. Organic contaminants detected in this sample included PAHs (well known as the products of incomplete combustion), PBDEs, traces of chlorinated benzenes, and methylated cyclosiloxane derivatives, as well as aliphatic and aromatic hydrocarbons.

The ash produced by the burning of circuit boards is left of open ground at the burning site. The metal and organic chemical composition of a sample of this ash (IT05006) was very similar to that of the burned fragments (IT05005). Of the metals quantified, copper, lead and tin, as well as antimony, barium and zinc were at the highest concentrations in this sample. With the exception of antimony, all were between three and eight times lower levels than those found in the burned fragments (IT05005). Mercury, which was not detected in the burned fragments, was nevertheless present in the ash at 62.7 mg/kg. While this is far lower than the levels of many other metals, mercury is a highly toxic metal typically found in the environment at very low concentrations. The level in the ash is approximately 100 times higher than general background levels in environmental samples such as sediments and soils (Alloway 1990, Salomons & Forstner 1984). As for sample IT05005, organic contaminants detected in the ash (IT05006) included PAHs, PBDEs, traces of chlorinated benzenes, methylated cyclosiloxane derivatives, aliphatic and aromatic hydrocarbons, as well as tribromobenzene (in sample IT05006 only).

The processing of the powdered materials (IT05001-02) and burned materials (IT05005) solely for the copper they contain not only fails to recover useful and, in some cases, expensive metals, but is also likely to produce a waste stream contaminated with the remaining metals and organic chemicals.

The processes using acids at this workshop are clearly effective at extracting a wide range of metals and other chemicals from the wastes. As expected, the sample of acidic solution being used to extract copper from the wastes (IT05003) contained a very high concentration of copper (22000mg/l, 22g per litre). In addition, this solution contained zinc at over 3000 mg/l, manganese at over 100 mg/l as well as antimony, chromium, cobalt, tin at over 10 mg/l. The majority of the other metals quantified were also present at significant concentrations, including beryllium, cadmium, lead, molybdenum, vanadium and yttrium. All these metals are used in the manufacture of computers and other electronics (OECD 2003).

The process sample IT05003 had a wider range of organic compounds that those detected in samples IT05001 and IT05002. Additionally to chlorinated benzenes, these included chlorinated and non-chlorinated derivatives of phenol, three phthalate esters (DEHP, DiBP and DnBP) aw well as the phosphorus-containing flame retardant TPP. A possible source of some of these chemicals, the chlorinated benzenes, is the processing of burned materials (IT05005) at this facility, in which they were also identified.

After the acid solution has been used for extracting copper and (unintentionally) other chemicals from a number of batches of powdered e-waste, dissolved copper is recovered from the solution as copper metal as described in Section 2.4.4. When no more copper can be recovered the acidic solution is disposed of on to waste ground.

The sample of wastewater ready to be disposed of (IT05004) was moderately acidic (pH=5) and contained a similar range of metals at high concentrations to those in the process solution (IT05003) as well as some of the organic chemicals identified. As may be expected, the wastewater (IT05004) contained copper at a far lower concentration to the process solution (IT05003). All other metals, however, were present at similar or higher concentrations in the wastewater sample. Antimony, barium, lead, silver and tin were all found at much higher levels in the wastewater than the process solution.

Fewer organic compounds were isolated from the wastewater sample IT05004 than from the process sample IT05003. However, the majority of the main organic contaminants (phthalate esters, chlorophenol and TPP) were still present in the wastewater sample IT05004 that was supposedly ready for disposal.

The higher levels of metals in the wastewater compared to those in the process water is presumably due to their accumulation in the acidic process solutions as they are used to extract successive batches of “e-wastes”. It is not clear why some of the organic chemicals present in the process waters were not found in the wastewater sample. The accumulation of copper in the solutions is intentional, ultimately allowing the commercial recovery of this metal. The additional metals as well as the organic chemicals in the acidic wastes, however, are not recovered and are disposed of into the environment when the wastewaters are disposed of. The ongoing disposal of wastewaters from this and other, similar, facilities constitutes a significant source of hazardous chemicals into the environment.

In the wastewater being disposed to the environment without any form of treatment, the presence of a wide range of metals in water soluble forms, many at high concentrations, is of particular concern. Metals in these forms are generally far more mobile in the environment, they tend to be more bioavailable and therefore more toxic. Some of the metals in the wastewater, including cadmium & lead, are highly toxic even in very low amounts to humans as well as a wide range of animals and plants.

The sample of copper deposited on iron sheeting during the copper recovery process (IT05021) was analysed to determine whether other metals were co-recovered from the extraction solutions. This sample (IT05021) was primarily copper (57%), but also contained trace levels of other metals, primarily antimony, lead, tin and zinc at 427-2240 mg/kg (0.04-0.22%). This sample also contained large amounts of iron (11%), from the sheeting on which the copper is deposited.

This recovered copper is believed by the recyclers to be pure copper. The future uses of this material are not known, but the presence of the additional trace metals in this material may make it unsuitable for some purposes for which it is used.

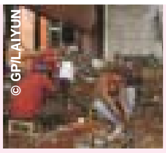
DELHI, INDIA - 11 AUGUST 2005 - A MAN WORKS IN A CATHODE RAY TUBE (CRT) 'RECYCLING' YARD.

v burning of wastes

The samples associated with the burning of the electronic waste that were collected from a dumpsite on the edge of the Loggang area of Guiyu consisted of one sample of ash/soil (CH05040) from an open fire at the site, and three separate samples of mixed ash/burned components (CH05041-43) that had been dumped there.

TABLE 3.5: ORGANIC CHEMICALS AND METALS IDENTIFIED IN SAMPLES ASSOCIATED WITH THE BURNING OF WASTES TO RECOVER METALS IN GUIYU, CHINA AND NEW DELHI, INDIA, 2005. THE NUMBER IN PARENTHESES ( ) SIGNIFIES COMPOUNDS IDENTIFIED AT TRACE LEVELS USING A SELECTIVE ION MONITORING (SIM) METHOD.

Country	CHINA					INDIA	
Sample number	CH05040	CH05041	CH05042	CH05043	CH05044	IT05013	IT05026
Sample type	ash & soil	ash/burned components	ash/burned components	ash/burned components	ash/burned components	ash	ash
Location	waste dumpsite, Longgang				dumpsite, Longmen	open burn Ibrahimpur	wire burning Shashtri Park
metals	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw
Antimony	979	15200	3900	94	2240	41	845
Arsenic	<20	<20	<20	<20	32	<20	<20
Barium	1845	441	1290	855	1020	1010	648
Beryllium	0.2	<0.2	<0.2	<0.2	<0.2	0.6	<0.2
Bismuth	<20	<20	<20	<20	<20	<20	<20
Cadmium	70.4	12.3	43.5	5.8	67.7	66.6	259
Chromium	429	54	32	228	42	293	54
Cobalt	20	21	10	13	17	18	<2
Copper	17550	738	260	4750	12000	13500	11000
Gold	<10	<10	<10	<10	24	<10	<10
Lead	1593	96	2000	875	3810	3560	6450
Manganese	349	154	42	600	1940	544	12
Mercury	<0.2	0.2	<0.2	0.5	3.4	0.3	<0.2
Molybdenum	24	6	<2	8	45	15	2
Nickel	931	141	54	298	286	118	54
Silver	26	2	4	19	226	15	6
Tin	320	<30	<30	<30	1360	2210	<30
Vanadium	30	10	11	11	7	31	<2
Yttrium	3	3	2	3	22	5	<1
Zinc	3055	2540	542	3380	3980	31700	897
Organic compounds isolated	177	231	130	167	50	27	159
Reliably identified (% of total)	40 (23%)	90 (39%)	45 (35%)	53 (32%)	18 (36%)	27 (100%)	30 (19%)
chlorinated compounds							
Chlorinated benzenes	(11)	9	(9)	0	0	(11)	0
Chlorinated phenols	0	0	0	0	0	0	0
PCBs	0	2	0	0	0	(15)	0
Other organochlorines	0	2	0	0	0	0	0
brominated compounds							
PBDEs	0	1	5(9)	0	(5)	0	0
Other organobromines	0	14	0	0	0	0	0
non-halogenated compounds							
Phthalate esters	0	0	0	3	4	0	0
Aliphatic hydrocarbons	22	20	10	18	5	0	2
Aromatic hydrocarbons	1	37	12	26	1	1	26
Organosilicon compounds	0	1	0	0	0	0	0
Organophosphate compounds	0	0	0	0	1	0	0
Others	6	4	1	6	2	0	2



FENG JIANG, CHINA - 13 FEBRUARY 2004 -
MIRGANT WORKERS IN FENG JIANG, TAIZHOU, ZHEJIANG PROVINCE.

Each sample contained a very complex mixture of organic compounds. The number of organic compounds isolated from these samples ranged from 130 (sample CH05042) to 231 (sample CH05041). The latter sample contained the most diverse composition of organic compounds, including a range of organochlorine and organobromine compounds (see Table. 3.5 for groups of compounds and Appendix 2 for complete list of identified compounds). In total, 27 organohalogen compounds that belong to various classes were reliably identified in this sample including the most toxic dioxin congener, namely 2,3,7,8-tetrachlorodibenzo-p--dioxin (TCDD). A sub-sample of CH05041 was sent to an external laboratory accredited for dioxin analysis. The results of this analysis showed that the sample contained a range of polychlorinated dioxins and polychlorinated furans from tetra- to octachlorinated congeners, and confirmed the presence of TCDD in this sample. For full results for dioxins/furans analysis in the sample CH05041 see the Appendix 3. The presence of PCBs, polychlorinated dioxins and furans in this sample may well indicate that plastics made of PVC were part of this sample components because such contaminants are produced during burning of PVC containing materials (Ruokojarvi *et al.* 2000, Wikstrom & Marklund 2001). Furthermore, this sample contained a range of brominated compounds, including one congener of brominated flame retardant tetrabromodiphenyl ether (a PBDE), brominated toluenes and styrene, bromochlorobenzenes, bromophenol and dibromobutane. Combustion of such chemicals may lead to a formation of brominated dioxins and furans (Desmet *et al.* 2005), although it was not possible in this study to confirm the presence of such compound. Additionally, a further twelve compounds that were isolated from the sample CH05041 show GC/MS fragmentation patterns characteristic for polyhalogenated (probably polybrominated) organic compounds. Unfortunately, it was impossible to specify the identity of these organic compounds. In total, of the 321 compounds isoltaed from this sample, fewer than 40% could be reliably identified.

Samples CH05040 and CH05042 also contained halogenated compounds, though not as diverse and abundant as those identified in the sample CH05041. Chlorinated benzenes at trace levels were detected in the samples CH05040 and CH05042, PBDEs were found in sample CH05042. Sample CH05043 did not contain any halogenated compounds. However, this sample contained, among other 53 reliably identified organic compounds, a range of PAHs and their derivatives, three phthalate esters and dehydroabietic acid. The latter compound is known as one of the major components of the colophony (or rosin), a natural product which comes from the pinesap. Rosin, which is used for solder flux in the electrical and electronics industry (Smith *et al.* 1996), is a well known irritant and sensitiser and is a major cause of occupational asthma (Health and Safety Executive 1997, Owens 1991).

The concentrations of metals varied greatly between these samples as may be expected. Antimony, copper, lead and zinc were abundant in most samples. Some very high levels were found; most notably the sample of ash/soil (IT05040) contained a very high concentration of copper (1.8%) and the sample of mixed ash/burned components most contaminated with organic chemicals (CH05041) contained a very high concentration of antimony (1.5%). These metal levels are more than 500 times background levels in the environment (soils). Concentrations of antimony and copper near or above 1000 mg/kg were also found in two of the other three samples. Other metals were present in two or more of the samples at concentrations far higher than levels generally found in the in the environment, including cadmium, lead, nickel, tin and zinc. The highest concentrations of these metals in the samples were between thirty and seventy times typical background levels (Alloway 1990, ATSDR 2000, Salomons & Forstner 1984).

The sample of mixed ash and burned components collected from a different dumpsite in Longmen (CH05044) had a similar metals composition to the ash/soil sample collected at Longgang (CH05040), containing 1.2% copper and concentrations of antimony, lead, tin and zinc between about 1000 and 4000 mg/kg (as well as cadmium at an elevated concentration). The pattern of organic chemicals in this sample also shows some similarities to those determined in the samples collected from the Longgang waste dumpsite. The sample CH05044, as well as sample CH05043, did not contain any chlorinated compounds but contained a range of phthalate esters, and a derivative of dehydroabietic acid (see above). At the same time, sample CH05044 contained several PBDEs at trace levels, which were also detectable in the sample CH05042. Additionally, sample CH05044 contained the flame retardant TPP, which wasn't found in the samples from the Longgang waste dumpsite.

High concentrations of copper (1.1-1.4%) and lead (0.36-0.65%) were also characteristic of the two samples of ashes collected from e-waste burning operations in New Delhi, India; from the burning of mixed waste at Ibrahimpur (IT05013) and of plastic coated copper wire at a workshop in Shastri Park (IT05026). Both ash samples also contained cadmium at concentrations far higher than typically found in the environment.

The pattern of organic contaminants found in these two samples, however, was quite different to that in the ashes collected in China. 27 compounds were isolated from the sample IT05013 and all of them but one (naphthalene) were represented by two classes of chlorinated organic compounds, namely chlorinated benzenes (from di- to hexachlorinated isomers) and PCBs (from tetra- to heptachlorinated congeners). Both were detected at only trace levels, however.

As many as 159 organic compounds were isolated from the sample IT05026, of which it was possible to identify only 30 due to the highly complex matrix of this sample. Those reliably identified were dominated by products of incomplete combustion such as polycyclic aromatic hydrocarbons (PAHs) and their derivatives.

In summary, different samples of e-waste burning residues collected in China and India contained a large diversity of organic chemicals and high concentrations of heavy metal. Many of these chemicals are persistent in the environment, bioaccumulative and toxic. These data indicate that a wide range of different materials are being burned, resulting in diverse inputs of hazardous chemicals into the environment from these activities.

In addition to impacts from the ongoing inputs to the environment that results from the open burning of "e-wastes", workers reported that food was often cooked over burning electronic wastes at the site in Ibrahimpur, New Delhi, India. There is clearly potential for food to become contaminated with many of the hazardous chemicals identified in the ash from this site. Many of the organic chemicals (e.g. chlorinated dioxins/furans, chloro- and bromobenzenes, PCBs, phthalates esters) and heavy metals such as cadmium and lead in the ash are highly toxic to humans, and some will bioaccumulate through ongoing exposure.

vi cathode ray tube (CRT) storage

Of the samples collected at a cathode ray tubes (CRTs) storage site in the Kantinagar area of East Delhi, India, the sample of eroded surface coating powder (IT05016) collected from the insides of broken (CRTs) contained very high concentrations of zinc (27%) and cadmium (1.7%), as well as barium (0.4%).

Elevated levels of zinc and cadmium, though not barium, were also found in the soil (IT05017) collected from the storage area. Background soil concentrations of zinc and cadmium are typically below 100 mg/kg and 2 mg/kg respectively. This soil sample also contained lead at a concentration of 1580 mg/kg, more than 50 times background soil concentrations (which are typically below 30 mg/kg) (Alloway 1990, ATSDR 1999b, Salomons & Forstner 1984).

TABLE 3.6: ORGANIC CHEMICALS AND METALS IDENTIFIED IN SAMPLES ASSOCIATED WITH THE STORAGE OF CATHODE RAY TUBES (CRTS) PRIOR TO RECYCLING OF THE GLASS; NEW DELHI, INDIA, 2005. THE NUMBER IN PARENTHESES ( ) SIGNIFIES COMPOUNDS IDENTIFIED AT TRACE LEVELS USING A SELECTIVE ION MONITORING (SIM) METHOD.

Sample number	IT05016	IT05017	IT05019	IT05020
Sample type	powder in CRTs	soil	dust	dust/soil
Description	Inside broken CRTs Kantinagar	ground under CRTs Kantinagar	CRT storage shed Brijgang	ground by storage shed Brijgang
metals	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw
Antimony	<10	<10	22	<10
Arsenic	<20	<20	47	<20
Barium	3850	277	2810	193
Beryllium	<0.2	0.3	<0.2	<0.2
Bismuth	<20	<20	<20	<20
Cadmium	16800	54.5	310	16.4
Chromium	11	20	86	21
Cobalt	<2	6	12	4
Copper	74	61	439	82
Gold	<10	<10	<10	<10
Lead	494	1580	14600	1370
Manganese	50	240	298	204
Mercury	<0.2	0.3	0.5	<0.2
Molybdenum	<2	<2	<2	<2
Nickel	121	47	3900	157
Silver	52	<2	10	155
Tin	<30	<30	<30	<30
Vanadium	<2	18	17	13
Yttrium	<1	171	10500	67
Zinc	273000	964	21100	506
No. of organic compounds isolated	37	16	88	82
No. reliably identified (% of total)	24 (65%)	6 (38%)	20 (23%)	16 (20%)
non-halogenated compounds				
Phthalate esters	1	0	0	0
Aliphatic hydrocarbons	18	6	20	16
Aromatic hydrocarbons	3	0	0	0
Organosilicon compounds	2	0	0	0

A similar range of chemicals was found in the samples collected from another CRT storage site in the Brijgang area of East Delhi.

Dust from a storage shed (IT05019) contained high concentrations of zinc, yttrium and lead, each between 1% and 2% of the total mass of dust. The levels of zinc and lead are between 20 and 30 times higher than background levels for dusts. Equivalent data are not available for levels of yttrium in dusts, but background concentrations of this metal in environmental samples like soils are typically below 20 mg/kg, more than 500 times lower than in this dust sample (Tyler 2004). The dust sample contained lower concentrations of cadmium and nickel, though these are still elevated above background levels for these metals in dust, by between 40 and 60 times (Butte & Heinzow 2002, Culbard *et al.* 1988).

The sample of street dust and soil (IT05020) collected from an open air CRT storage area adjacent to the shed contained far lower concentrations of metals, with only cadmium and lead at elevated concentrations, both approximately 3 times higher than typical background levels (Butte & Heinzow 2002, Culbard *et al.* 1988, Rasmussen *et al.* 2001)

Organic compounds detected in all four samples associated with CRT storage had a very similar pattern. Only one class of organic compounds - long chain linear aliphatic hydrocarbons or alkanes - was identified in three out of four samples (IT05017, IT05019 and IT05020). The sample IT05016 also contained a range of the compounds from this class. Alkanes are refined petroleum products (Overton 1994) and could arise in the environmental samples as a result the spillage of such products. Additionally, the latter sample had one phthalate ester DEHP, several PAHs, and two organosilicon compounds.

Many of the heavy metals identified in the samples from these two CRT storage locations are used in the production of CRTs. On the interior of a CRT screen, a fluorescent ‘phosphor’ coating is used to create light when the CRT is in operation (OECD 2003). For colour screens, three different types of coloured phosphors are used, typically based on cadmium sulphide (green), zinc sulphide (blue) and yttrium oxysulphide (red) (Burstall 1997). The use of these chemicals is clearly a major source of the very high concentrations of these three metals to various samples from these two sites.

Exposure through inhalation or ingestion of contaminated dusts is of particular concern for cadmium, a bioaccumulative and highly toxic metal with a range of effects, including kidney damage even at relatively low levels of exposure (Elinder & Jarup 1996, Hellstrom *et al.* 2001).

There is little evidence to suggest that yttrium is toxic. However, the presence of yttrium in these samples at moderate to very high concentrations does demonstrate the potential for the chemicals that from part of the e-waste to become distributed into the environment during the storage of the wastes.

The need to separately manage CRT fluorescent ‘phosphor’ coating is recognised under legislation within the European Union that addresses waste electrical and electronic equipment (WEEE), which specifies that this coating must be removed prior to waste treatment (EU 2002b). Such controls are not in operation in many other regions, however.

In addition to the chemicals used as phosphors used in CRTs, the glass also incorporates high concentrations of lead and barium. Different types of glass are used in different parts of a CRT; glass containing 25-40% lead oxide at is used in the CRT funnel, while glass containing similar concentrations of barium oxide is used for the front plate (ICER 2003).

The storage of CRTs at the two locations is clearly having an impact of the immediate environment, with elevated levels of heavy metals in soil and street dusts from the sites. It has been previously reported that when CRTs are disposed of in landfill sites, lead can leach from the glass and contaminate ground water (see ICER 2003).

DELHI, INDIA - 11 AUGUST 2005 - CHILDREN EXTRACT COPPER FROM DISCARDED COMPTER PARTS. NEW DELHI.

RECYCLING OF ELECTRONIC WASTES IN CHINA & INDIA: WORKPLACE & ENVIRONMENTAL CONTAMINATION

REPORT

conclusions

Although clearly not an exhaustive study of “e-waste” recycling facilities in either country, the results summarised above do provide an illustration of the breadth and scale of health and environmental concerns arising from this industrial sector. Both wastes and hazardous chemicals used in the processing are commonly handled with little regard for the health and safety of the workforce or surrounding communities and with no regard for the environment. Overall, the result is severe contamination of the workplace and adjacent environment with a range of toxic metals and persistent organic contaminants.

Clearly it is not possible from the results of this study to evaluate the damage likely to be caused to human health from these widespread practices. Nor was it possible to conduct a comprehensive survey of the full extent of environmental impacts arising from each facility, or from the sector as a whole, in either country. Nevertheless, the results do indicate that exposure to hazardous chemicals arising from the waste-stream can be locally severe. Further research would be necessary in order to identify and quantify the full impact of this industrial sector, including studies on the health of workers and of residents in adjacent communities.

In the mean time, however, the data available do provide a compelling case for immediate action in both countries to address workplace health and safety and waste management.

The problems identified are greatly exacerbated by the poor working practices and lack of responsible waste management in the areas sampled in this study. However, the fact that wastes generated by every stage of the recycling process are contaminated with a range of toxic heavy metals and persistent organic pollutants is a direct result of the use of these hazardous materials in electronic goods at the manufacturing stage. Therefore, as well as bringing to light some of the many unseen impacts of the vast and growing electronics waste stream, and the need for much tighter controls both on the transboundary movement of such wastes and the manner in which they are recycled, this study also adds weight to the need to redesign and reformulate all new electronic goods in order:-

- to facilitate proper dismantling and component separation and
- to avoid the use of hazardous chemical components at source.

The European Directive on Waste Electrical and Electronic Equipment (WEEE) and the related Restrictions on Hazardous Substances (RoHS) go some way towards addressing the problem, though applying only regionally andcovering only a fraction of all the hazardous substances used in electronics manufacturing

In short, this study provides a further illustration of the urgent need for manufacturers of electronic goods to take responsibility for their products from production through to the end of their lives. As a major contribution towards addressing these problems, manufacturers must develop and design clean products with longer life-spans, that are safe and easy to repair, upgrade and recycle and will not expose workers and the environment to hazardous chemicals.

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greenpeace international
Ottho Heldringstraat 5, 1066 AZ Amsterdam, Netherlands
t +31 20 718 2000 f +31 20 514 8151
www.greenpeace.org