

Chemical contamination at e-waste recycling and disposal sites in Accra and Korforidua, Ghana

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Executive summary

The global market for electrical and electronic equipment continues to expand, while the lifespan of many products becomes shorter. Consequently, the waste stream of obsolete electrical and electronic products, commonly called "e-waste", is also vast and growing, with estimates of 20-50 million tonnes per year being generated world-wide. Many of the products contain numerous hazardous chemicals and materials, and therefore the recycling and disposal of e-waste poses a threat to the environment and to human health.

In some countries and regions regulations have been introduced with the aim of restricting the use of hazardous substances in these products, and the management of e-waste at the products end of life. However, no such regulations exist in many of the countries in which where products are manufactured, used and disposed of. Furthermore, even where they apply, regulations do not control all hazardous chemicals and materials that are used in newly manufactured products, nor fully address the management of e-waste. Even in the EU, where some of the more stringent regulations apply, as much as 75% of generated e-waste is unaccounted for.

There is evidence that e-waste is transported internationally from many countries to destinations where informal recycling and disposal take place, often in small workshops with little or no regulation. As a result, impacts have already been reported in many countries, particularly in Asia. Recently there has been a growth in these types of activities in other regions, particularly in some African countries, including Ghana.

This study, the first to investigate workplace contamination in areas in Ghana where e-waste recycling and disposal is carried out, focussed on the main centre for this type of work, at the Agbogbloshie scrap market in Ghana's capital, Accra. One of the numerous similar, though far smaller, operations that take place throughout Ghana was also investigated, at the location of a scrap dealer in Korforidua, a smaller city to the north of Accra. At these workshops, e-waste is recycled in a crude way, primarily involving manual disassembly and open burning to isolate copper from plastics. Much of the work is carried out by children, commonly using only rudimentary tools and with no protective equipment.

Severe chemical contamination was found in ash contaminated soil samples from open burning sites at both Agbogbloshie and Korforidua, as well as in sediment from a shallow lagoon at the Agbogbloshie site. Most samples contained numerous toxic and persistent organic chemical pollutants, as well as very high levels of many toxic metals, the majority of which are either known to be used in electronic devices, or are likely to be formed during the open-burning of materials used in such devices. The nature and extent of chemical contamination found at these sites in Ghana were similar to those previously reported for e-waste open burning sites in China, India and Russia.

At the open burning sites, some metals were present at concentrations over one hundred times typical background levels for soils, including lead, a highly toxic metal. High levels of other toxic metals, including cadmium and antimony, were also present. Numerous classes of organic chemicals were also present in one or more of the samples, including many halogenated (chlorinated or brominated) chemicals. Many of the compounds identified are intentionally used in electronic devices. These included phthalates, widely used as plasticisers in flexible plastics such as PVC, polybrominated diphenyl ethers (PBDEs) and triphenyl phosphate (TPP) both used as flame retardants, and polychlorinated biphenyls (PCBs), long banned from manufacture and use but a persistent legacy in some older electrical goods. Others compounds found are known to be formed when hazardous materials in e-waste, such as PVC, are burned. Overall, a wide range of the chemical contaminants present in the samples are toxic, persistent in the environment and, in some cases, able to bioaccumulate (build up in the body).

Two samples were also analysed for polychlorinated dioxins and furans (PCDD/Fs), a class of chemical that can be formed during the combustion of materials present in e-waste. Soil from an open burning site was moderately contaminated, while sediment from the Agbogbloshie lagoon contained a very high level of these highly toxic, highly persistent and bioaccumulative chemicals, at a level just below the threshold defined as being indicative of serious contamination for sediments in the Netherlands.

Though this study did not attempt to quantify damage caused to the environment or human health, the results do indicate that the exposure of workers and bystanders to hazardous chemicals may be substantial. In areas in other countries where e-waste recycling takes place, increased exposure to toxic chemicals has been reported for workers and/or local residents, including for chlorinated dioxins and furans (PCDD/Fs), certain PBDEs, and the toxic metal lead.

This study demonstrates the urgent need for action to address the problems posed by the crude recycling and disposal of hazardous e-waste in Ghana, as well as in other places in which similar activities take place. In part, this requires tighter controls on the transboundary movement of e-waste, including where obsolete equipment is shipped under the guise of 'used goods', and also more effective controls on the manner in which they are recycled.

Impacts arising from the recycling and disposal of hazardous e-waste can, however, only be fully addressed by eliminating the use of all hazardous chemicals and materials during manufacture of new products coming on to the market and eventually entering the waste stream themselves. Where legislation currently exists to regulate the use of certain hazardous substances in electrical and electronic equipment, such as the RoHS Directive in the EU, the scope needs to be extended to cover all hazardous substances and materials used in their manufacture. Notable examples not currently regulated by RoHS include PVC and phthalates (plasticisers widely used in flexible forms of this plastic). Furthermore, similar regulation is required in countries that currently have no strict controls.

Until such regulations are in force, the producers of electrical and electronic equipment must:-

- lead the way by voluntarily phasing out all hazardous chemicals and materials from their products
- take responsibility for the entire life cycle of their products, which includes responsibility at the products' end of life, such as through effective take back and recycling schemes that are offered free of charge and globally
- take the necessary steps to individualise their financial responsibility and internalize their own products end-of-life costs and
- encourage the introduction, in all countries, of adequately stringent regulation for both the manufacture of electrical and electronic equipment and the end of life waste management.

The ultimately goal must be to ensure that the quantities of e-waste generated are minimized and that those e-wastes which do arise are recycled and disposed of in the best achievable manner to minimize impacts on human health and the environment. This can be achieved in part through the design of products with greater life-spans, that are safer and easier to repair, upgrade and recycle, and which, as far as possible, avoid the use of hazardous chemicals.

Introduction

The manufacture of electrical and electronic equipment is a major and fast growing global sector. As a consequence, the waste stream of obsolete electrical and electronic products, commonly called “e-waste”, is also vast and growing, with estimates of 20-50 million tonnes per year being generated world-wide (UNEP 2005). The recycling and disposal of e-waste poses significant problems, largely because many of the products contain numerous hazardous chemicals and materials (including heavy metals such as lead and cadmium, and organic compounds of chlorine and bromine) which can pose a threat to the environment and to human health. Impacts resulting from the recycling and disposal of e-waste have been reported in many countries, particularly in Asia (e.g. Brigden *et al.* 2005, Wong *et al.* 2007, Leung *et al.* 2007).

In some countries and regions, laws have been introduced to regulate the use of hazardous substances in electrical and electronic equipment. The most well known of these is the EU Restriction of the use of certain Hazardous Substances in electrical and electronic equipment (RoHS) Directive (EU 2002a) which prohibits the use, above strict limits, of the heavy metals cadmium, lead, hexavalent chromium (VI) and mercury, as well as certain brominated flame retardants (BFRs). The RoHS legislation, however, only currently addresses a very limited number of hazardous chemicals and materials commonly used in electronics and, even for those substances that are regulated, numerous exemptions allow their use for specific applications. Similar legislation has been recently introduced in China and other countries. The related EU Waste Electrical and Electronic Equipment (WEEE) Directive requires that producers set up systems and finance for the collection and treatment of electrical and electronic wastes. Even with such regulation, however, it is estimated that only 25% of the e-waste generated within the EU is currently collected and treated, with as much as 75% being unaccounted for (Huisman *et al.* 2007). In the US this figure is around 80%. In both regions, some of the e waste that is unaccounted for is exported to non-OECD countries. This practice is illegal from the EU, however, in the US such exports are routinely classified by the US EPA as legitimate recycling (Cobbing 2008).

There is evidence that hazardous e-waste is transported internationally to various destinations where recycling and disposal take place, often in largely unregulated small workshops with little or no concern for potential impacts on human health or the environment. Recently there has been a growth in the recycling and disposal of e-waste in regions beyond those in Asia, in which it has historically taken place, particularly in some African countries, including Ghana. As part of this investigation, evidence was obtained that obsolete electrical and electronic equipment being exported to Ghana is originating from the European Union and the United States, some being transported under the guise of second hand goods in order to overcome restrictions on the exporting of hazardous waste from the EU.

E-waste recycling within Ghana

In Ghana, the main centre for the recovery of materials from e-wastes is within the Agbogbloshie Scrap Market in Accra, the capital city of Ghana. This is the only place where this type of work is known to be taking place on a large scale. There are reports of numerous similar, though far smaller, operations at other places throughout Ghana. The primary activities at these sites are the manual disassembly of obsolete electrical equipment to isolate metals (mainly copper and aluminium), and the open burning of certain components to isolate copper from plastics in which they are encased, particularly from plastic coated wires and cables. Much of this work is carried out by children, most using only rudimentary tools and with no protective equipment. There are anecdotal reports that plastic casings and printed circuit boards are separated and collected for sale to traders, mainly from Asian countries, who export these materials out of Ghana, presumably for the recovery of materials in other countries. According to recycling workers, copper is sold at 22 US cents (0.22 USD) per half kilo, and collected plastic is sold at 1 US cent (0.01 USD) per kilo. In some other countries, particularly China and India, the recycling of e-waste makes use of a wider range of activities which includes manual dismantling and open burning, but also somewhat more technical processes such as solder recovery, plastic shredding, and the use of acid leaching. These type of more complex processes are not known to be used in Ghana.

At the Agbogbloshie Market, the main electronic wastes being processed are obsolete computers, monitors and televisions. These are manually dismantled at numerous small workshops within the market. Certain materials, mainly plastic coated wires and cables, are subsequently taken to sites on the edge of the market where they are burned to enable the separation of metals from plastic materials. These wires and cable are commonly attached to fragments of other types of materials, including printed circuit boards, which consequently are also burned. Materials of no value are disposed of in a large area on the edge of the market that is also used for the disposal of a wide range of other types of wastes. Scattered fires are set within this area and used to burn e-wastes. Similar burning also takes place in a second area approximately 100m from the disposal area; no other processing or disposal of wastes is carried out in this second area.

Two shallow lagoons are situated on the edge of the market, close to the general disposal area. The larger lagoon is situated along one side of this area, the smaller lagoon is situated on the opposite side, close to areas used for the open burning of e-waste.

Within the open burning areas, numerous temporary fires are used to burn plastics and other combustible materials from individual batches of materials. These small fires are repeatedly set on the sites of previous fires, leading to an accumulation of ash and partially burned materials. Insulating foam from obsolete refrigerators, primarily polyurethane, is the main fuel used to sustain the fires, and this is likely to contribute in itself to acute chemical hazards and longer-term contamination at the burning sites. In addition, chlorofluorocarbons (CFCs) were routinely used as blowing agents for polyurethane foam until the early 1990's (UNEP 2003). The burning of foam containing CFCs can result in releases of these ozone-depleting substances into the atmosphere.

The Agbogbloshie market is situated on flat ground alongside the Densu River. During periods of heavy rainfall much of the site becomes flooded and, during these times, it is likely that surface dusts and soils, along with any chemical contaminant that may contain, are carried into the adjacent, lower-lying lagoons and the Densu river which ultimately flows into the ocean.

In addition to this major site in Accra itself, smaller e-waste recycling and disposal operations can be found in other cities. For example, a scrap yard in Korforidua, a smaller city to the north of Accra, is thought to be typical of these numerous small e-waste recycling operations within Ghana, engaged in similar activities to those at Agbogbloshie but on a far smaller scale.

Sampling program

In order to explore the extent of contamination of wastes and of surrounding soils and sediments which can arise from the types of e-waste recycling and disposal operations conducted in Ghana, samples were collected from the above mentioned locations in both Accra and Korforidua. Full details of the samples collected are given in Table 1.

Sample no.	Type	Location
GH08001	Soil/ash	Burning area adjacent to scrap dealer, Korforidua
GH08002	Soil/ash	Burning site (no disposal), Agbogbloshie Market
GH08003	Soil/ash	Burning site (no disposal), Agbogbloshie Market
GH08004	Soil/ash	Burning site within disposal area, Agbogbloshie Market
GH08005	Soil	Below broken CRT glass within disposal area, Agbogbloshie Market
GH08006	Sediment	Lagoon adjacent to disposal and burning areas, Agbogbloshie Market

Table 1. Description of samples collected from e-waste open burning and disposal sites in Accra and Korforidua, Ghana, 2008

Five samples were collected from e-waste processing areas within the Agbogbloshie Market. Three samples of soil/ash were collected from areas where open burning of separated components takes place. Two of these were from separate parts of the area used exclusively for open burning, approximately 100m from the main disposal area (GH08002, GH08003). The third sample (GH08004) was collected from a burning site within the general waste disposal area in which fires are more scattered compared to the area used exclusively for open burning at the market. One further sample of soil (GH08005) was collected from a part of the main disposal area where glass from cathode ray tubes (CRTs), from both televisions and computer monitors, had been broken to enable recovery of plastic casings and other materials. Following this crude separation, the broken glass and other unwanted materials are simply left at the site. In addition, a sample of sediment (GH08006) was collected from the smaller of the two lagoons, that which is situated adjacent to the open burning areas.

At the smaller workshop in Korforidua, one sample of soil/ash (GH08001) was collected from a small area adjacent to the scrap yard that is regularly used for the open burning of components from e-wastes, primarily plastic coated wires and cables and some transformers.

Methodology

All samples were collected and stored in pre-cleaned 100 ml glass bottles that had been rinsed thoroughly with nitric acid and analytical grade pentane in order to remove all heavy metal and organic residues. Following collection, all samples were returned to the Greenpeace Research Laboratories in the UK for analysis.

Extractable organic compounds were isolated from each sample and identified as far as possible using gas chromatography and mass spectrometry (GC/MS), including the use of Selective Ion Monitoring (SIM) for certain groups of organic chemicals. A wide range of metals and metalloids were quantified in all samples, based on their known use in electronic devices & previous reports of contamination at e-waste recycling yards (Brigden *et al.* 2005). Additional information on sample preparation and analytical procedures are presented in Appendix 1. Two of the samples collected at Agbogbloshie, an ash-contaminated soil and a sediment from a lagoon, were also analysed quantitatively for 2,3,7,8-substituted polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) at an external laboratory.

Results and discussion

The results of the metals quantification (Table 2), and the screening for organic chemicals (Table 3) for all samples are presented and discussed below, along with the quantification of PCDD/Fs in two of the samples (Table 4).

Open burning sites

The samples of soil/ash from open burning sites generally contained high levels of many metals that are known to be present in electronic devices, some of which have toxic properties. Numerous organic chemical pollutants were also identified. Again, many of these are known to be used in electronic devices, or likely to be formed during the combustion of materials used in such devices. Similarities were found between the samples from the different open burning sites, with regard to those metals present at high levels and the range of organic chemicals present.

	GHO8001	GHO8002	GHO8003	GHO8004	GHO8005	GHO8006
	Soil/ash	Soil/ash	Soil/ash	Soil/ash	Soil	Sediment
Metal	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw
Antimony	159	286	592	16	8	256
Arsenic	<20	<20	<20	<20	<20	<20
Barium	270	1190	1260	107	114	400
Beryllium	<0.2	0.6	<0.2	0.3	0.4	0.6
Bismuth	<20	<20	<20	<20	<20	<20
Cadmium	3	10	10	<1	<1	6
Chromium	47	45	33	27	34	34
Cobalt	10	68	129	135	7	19
Copper	14300	7240	9730	119	85	2260
Gallium	<20	<20	<20	<20	<20	<20
Germanium	<30	<30	<30	<30	<30	<30
Indium	<20	<20	<20	<20	<20	<20
Lead	3530	4160	5510	110	190	1685
Manganese	297	317	272	150	171	183
Mercury	0.6	<0.5	<0.5	<0.5	<0.5	<0.5
Molybdenum	<4	<4	<4	<4	<4	31
Nickel	9	28	33	14	21	24
Selenium	<30	<30	<30	<30	<30	<30
Silver	<2	7	7	<2	<2	2
Tin	123	1290	1175	7	16	220
Vanadium	27	38	11	23	31	26
Yttrium	2	8	2	4	33	9
Zinc	382	6920	18900	31300	274	2425

Table 2. Concentrations of metals and metalloids (in mg/kg dry weight) in samples collected from e-waste open burning and disposal sites in Accra and Korforidua, Ghana, 2008

Similar profiles of metal contamination were found in two samples from an open burning area within the Agbogbloshie Market (GH08002-03) and in the sample from the open burning site in Korforidua (GH08001). Many of the same groups of organic chemicals were also identified in each of these three samples. These data suggest that similar materials had been burned at these different sites. However, one sample from a burning site within the disposal area at the Agbogbloshie Market (GH08004) contained only a fraction of the organic chemicals found in the other samples, and had generally lower levels of metals, other than zinc. This difference may be due to the more scattered setting of fires in the disposal area, as well the presence of large amounts of other type of wastes in this area, which could lead to the dilution of contaminants arising from the e-wastes.

For the two more highly contaminated samples from the Agbogbloshie Market (GH08002 03), numerous metals were present at concentrations far exceeding those typically seen in uncontaminated soils. Copper, lead, tin and zinc concentrations were over one hundred times typical background levels. Concentrations of antimony and cadmium in these samples, while lower, are still indicative of contamination of the site, exceeded typical background soil levels by around fifty times for antimony and five times for cadmium (a metal usually found in the environmental at only very low levels). In addition, barium concentrations in these samples were higher than those found in the other soil samples, though within the broad range of levels found in uncontaminated soils (Alloway 1990, Salomons & Forstner 1984).

The sample from an open-burning site in Korforidua (GH08001) had a similar profile of high metal concentrations. Copper and lead concentrations were of similar orders of magnitude. Levels of antimony, tin and zinc in this sample were lower than those found in the samples from the Agbogbloshie Market, but all still approximately ten times higher than general background soil levels (Alloway 1990, Salomons & Forstner 1984).

The concentration profiles (relative concentrations) of metals in these samples were similar to those reported for samples collected from electronic waste open burning sites in China and India (Brigden *et al.* 2005, Wong *et al.* 2007) and also more recently in Russia (Labunska *et al.* 2008). Absolute concentration ranges of most metals were also similar to those reported in these other studies, though levels of some, especially cadmium, were lower in the samples Ghana.

All the metals found at high levels have known uses in electronic devices and therefore could be expected in e-waste. For example, a major potential source of lead from e-waste is electrical solders, which until recently have largely been comprised of a mixture of lead and tin (Geibig & Socolof 2005). The presence of elevated levels of both these metals in some samples indicates that leaded solder is a major source of lead at these sites. Unlike lead, exposure to inorganic tin does not usually cause toxic effects in humans or animals, unless ingested in very large amounts (ATSDR 2005). Another major use of lead in materials found in e-waste has been the use of lead compounds as stabilisers in polyvinyl chloride (PVC), a chlorinated plastic widely used as a coating on wires and cables. Chemicals used as PVC stabilisers also include compounds of other metals found at high levels in these samples, including barium, cadmium and zinc (Matthews 1996). Compounds of antimony have also been widely used as additives in polymers, principally in flame retardant formulations incorporated into the materials (Lau *et al.* 2003). The high levels of copper are likely to be due to the presence of fragments of metallic copper wire.

The elevated levels of lead and cadmium reported here are of particular concern, as both are highly toxic and can build up in the body following repeated exposures. The use of both cadmium and lead in electronic devices sold within the EU is now regulated, and largely prohibited, under the RoHS Directive (EU 2002a), though these and other toxic metals will inevitably persist in components of older electrical and electronic equipment and will therefore continue to enter the waste stream for years, if not decades, to come. Antimony compounds also have known toxic properties, though these chemicals are not regulated by RoHS. Additional information on the uses and toxicity of these metals is given in Box 1.

Box 1: Metals

Lead has many uses in electronics products. Metallic lead has been used in electrical solder, commonly as an alloy with tin. Lead oxide is used in the glass of cathode ray tubes (CRTs) (OECD 2003), and 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 (Alloway 1990, Salomons & Forstner 1984). Under landfill conditions lead can leach from CRT glass (Musson *et al.* 2000). Incineration and burning 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 2007). Following exposure humans can accumulate lead, as can many plants and animals (Sauve *et al.* 1997, ATSDR 2007). Where soils and dusts are contaminated with lead, children can be particularly exposed through hand-to-mouth transfer (Malcoe *et al.* 2002). Children living in an area in China where electronic wastes are recycled and disposed of have been found to have elevated blood lead levels compared to children in a neighboring area (Huo *et al.* 2007).

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 2007, 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. It is currently thought that there may be no level of blood-lead that does not produce a toxic effect, particularly in the developing central nervous system (ATSDR 2007, Canfield *et al.* 2003). Similar toxic effects are seen in animals, and lead is also toxic to all aquatic life (WHO 1989, Sadiq 1992).

A number of regional controls exist on the use of lead in electrical and electronic equipment. EU legislation restricting the use of certain hazardous substances in electrical and electronic equipment (RoHS), 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 certain exemptions. 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).

Cadmium and its compounds are used in a number of applications within electrical and electronic products (OECD 2003). Cadmium metal is used in some contacts, switches and solder joints. Many devices 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 (Matthews 1996). Cadmium sulphide has been also used in cathode ray tubes (CRTs) as a phosphor on the interior surface of the screen to produce light (Burstall 1997). Cadmium is a rare metal, found naturally in the environment at very low concentrations, typically below 2 mg/kg in soils and sediments (Alloway 1990, Salomons & Forstner 1984). When released to aquatic environments cadmium is more mobile than most other metals (ATSDR 1999). Cadmium is highly toxic to plants, animals and humans, having no known biochemical or nutritional function (ATSDR 1999, 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 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 1999, Elinder & Jarup 1996, WHO 1992). Furthermore, cadmium and its compounds are known to be human carcinogens, primarily for lung cancer following inhalation (DHSS 2005).

There are a number of regional controls on the use of cadmium in products. EU legislation restricting the use of certain hazardous substances in electrical and electronic equipment (RoHS) 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).

Antimony and its compounds have a number of industrial uses. For example, antimony compounds are used in semiconductor manufacture (antimony trihydride) and in flame retardant formulations in plastics (antimony trioxide), normally in combination with brominated flame retardants, especially PBDEs (Lau *et al.* 2003), though there are also reports of use in combination with phosphorus based flame retardants. Antimony is also used in the manufacture of lead acid starter batteries (Kentner *et al.* 1995) and can occur as a component of electrical 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 and antimony trisulfide have been 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 (IARC 1989). 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).

The three soil/ash samples with high metal levels also contained numerous classes of organic chemicals, including many halogenated (chlorinated or brominated) chemicals (see Table 3). For example, all three samples contained chlorinated benzenes and polybrominated diphenyl ethers (PBDEs), though some only at trace levels. PBDEs have been widely used as flame retardants in electronic devices, though once again this use is now regulated within new products manufactured or sold in the EU as a result of environmental and human health concerns (EU 2002a). One of the samples from the Agbogbloshie Market (GH08003) also contained polychlorinated biphenyls (PCBs) and other chlorinated chemicals (chlorinated alkyl benzenes and a chlorinated alkane). Phthalates were also present in two of the samples. The sample from Korforidua (GH08001) contained triphenyl phosphate (TPP), an organophosphate compound that has been used as a flame retardant (IPCS 1991). Other types of compounds were also abundant in these samples, many of which can be emitted during the open burning of plastic coated wires and cables, or other plastic containing electronic wastes, including polycyclic aromatic hydrocarbons (PAHs), alkyl benzenes, nitrile compounds and numerous alkanes/alkenes (Andersson 2004, Watanabe *et al.* 2007). The one sample that had far lower levels of metals (GH08004) also contained far fewer organic contaminants.

Just as for the metals, the majority of organic chemical groups identified in the samples from Ghana have been previously reported in samples from e-waste open burning sites in China, India and Russia (Brigden *et al.* 2005, Labunska *et al.* 2008), including chlorinated compounds (chlorinated benzenes, PCBs), brominated compounds (PBDEs), and phthalates.

Where present in the soil/ash samples (i.e. GH08001 & GH08003), the phthalate ester DEHP was the most abundant of all organic chemicals isolated. One of the samples (GH08001) also contained three other phthalates commonly used as plasticizers (softeners) in flexible PVC, namely DBP, DiBP and DiNP. All phthalates identified have known toxic properties, and two, DEHP and DBP, have been classified in Europe as toxic to reproduction, due to their ability to interfere with sexual development in mammals, especially in males (Langezaal 2002). Phthalate-plasticized PVC is commonly used for the flexible coatings of both internal and external wires and cables used for electrical and electronic devices. These were the predominant materials being burned at the time that the samples were collected, and it is likely that they are largely responsible for the presence of phthalates in these samples.

In addition to the release of chemical additives, including heavy metals and phthalates, the burning of PVC itself can generate many of the organic chemicals identified in some of the samples, including chlorinated benzenes from monochlorobenzene through to hexachlorobenzene (Grimes *et al.* 2006) and, in the case of sample GH08003, chlorinated alkyl benzenes (Andersson 2004), as well as certain polychlorinated biphenyls, or PCBs (Hedman *et al.* 2005). It is also possible, however, that the presence of PCBs in sample GH08003 could have arisen from the disposal of obsolete transformer components or capacitors in which these compounds were formerly used as electrical insulants and heat transfer fluids (de Voogt & Brinkman 1989), sometimes in conjunction with chlorinated benzenes, mainly tri- and tetrachlorobenzenes (Swami *et al.* 1992, de Voogt and Brinkman 1989).

Chlorinated benzenes and PCBs are groups of compounds that, once emitted, will persist (resist breakdown) in the environment and can bioaccumulate (build up in the body), especially the PCBs. A wide range of toxic effects have been reported for chlorinated benzenes (particularly the more highly chlorinated compounds) and for PCBs, in the latter case even at relatively low doses. PCBs are regulated as persistent organic pollutants, or POPs, under the 2001 Stockholm Convention. For more information on these compounds see Text Box 2. No information could be found on the potential impacts of the chlorinated alkyl benzenes identified (cis- and trans-beta-chlorostyrene), though these compounds are unlikely to persist in the environment following release. In addition to the compounds identified, the burning of chlorinated plastics such as PVC also releases large quantities of hydrogen chloride, a corrosive gas that can be acutely toxic through inhalation.

One of the soil/ash samples collected (GH08003) was also analysed quantitatively for polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), highly persistent toxic chemicals that can be produced during the combustion of chlorinated organic materials, including PVC. This sample contained a moderately high level of PCDD/Fs. The results of the PCDD/F analysis of this sample, along with those of the lagoon sediment (GH08006) are discussed in a separate section below.

	GH08001	GH08002	GH08003	GH08004	GH08005	GH08006
No. of organic compounds isolated	139	144	184	162	64	158
No. reliably identified (% of total)	66 (47%)	54 (38%)	98 (53%)	30(19%)	16 (25%)	57 (36%)
CHLORINATED AND BROMINATED CHEMICALS						
chlorinated benzenes:						
di-penta chlorinated	2 + (8)	6 + (3)	8 + (1)	-	-	4 +(4)
hexa chlorinated	(1)	(1)	1	-	-	(1)
polychlorinated biphenyls (PCBs)	-	-	(7)	-	-	-
chlorinated alkyl benzenes	-	-	2	-	-	-
chlorinated alkanes	-	-	1	-	-	-
PBDEs:						
Tri-hepta brominated	(9)	(8)	(9)	-	(4)	(11)
octa brominated	(1)	-	-	-	-	(1)
OTHER ORGANIC CHEMICALS						
triphenyl phosphate (TPP)	1	-	-	-	-	-
phthalate esters:						
DEHP	1	-	1	-	1	1
DBP, DiBP, DiNP	3	-	-	-	-	-
Nitrogen compounds:						
alkyl & alkyl benzene nitriles	2	-	2	-	-	1
nitro derivatives	-	-	-	2	-	-
oxygenated benzene derivatives						
phenyl ketones	1	1	3	-	-	2
phenol & derivatives	1	-	-	-	-	5
benzoic acid ester	-	-	-	-	-	1
Hydrocarbons & others						
PAHs and derivates	6	2	15	3	5	7
biphenyl and derivatives	1	3	8	-	-	3
alkyl benzenes	2	14	18	7	2	7
alkanes and alkenes	26	14	22	18	3	9
steroids & hopanoids	1	2	-	-	-	-

Table 3 Organic chemicals identified in samples collected from e-waste open burning and disposal sites in Accra and Korforidua in Ghana, 2008. The numbers represent the numbers of compounds reliably identified for each group; (#) signifies compounds identified at trace levels using a selective SIM method; (-) not detected.

Box 2: Phthalates

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 coated wires and 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. Within the EU alone, this amounts to thousands of tonnes per year (CSTEE 2001). 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). It was also found that DBP can not only be taken up by crops and enter the food chain, but also affects the physiology and the morphology of some crops during growth (Liao 2006). 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. Of the controls which do exist, however, probably the best known is the EU-wide ban on the use of six phthalates in children’s toys and childcare articles, first agreed as an emergency measure in 1999 and finally made permanent in 2005 (EC 2005). While this addresses one important exposure route, exposures through other consumer products remain unaddressed, including electrical and electronic equipment.

Box 3: Chlorinated compounds

Polychlorinated biphenyls (PCBs) Polychlorinated biphenyls (PCBs) are a group of 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, capacitor dielectrics, hydraulic fluids, plasticisers, 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). At least one third of the PCBs that have been produced are now estimated to have entered the environment (Swedish EPA 1999). The other two thirds remain in old electrical equipment and in waste dumps, from which they continue to leach into the environment, including when obsolete equipment is dismantled, recycled and/or disposed of. PCBs can also be produced during the combustion of chlorinated organic materials, including PVC (Hedman *et al.* 2005, Wikstrom & Marklund 2001).

Once released to the environment from whatever source, PCBs are highly persistent. Furthermore, PCBs that are taken up by organisms accumulate in them, for aquatic organisms and fish levels can reach many thousands of times higher than levels in surrounding water (ATSDR 2000, Jones *et al.* 1988). PCBs can also 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 a 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 also affect many endocrine systems (Brouwer *et al.* 1999). Although it is difficult to assess the impact on animal 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 populations of the Netherlands and the Arctic and families of Swedish fishermen suggested that even relatively low levels of exposure to PCBs can result in impacts on the immune system growth retardation and neurological effects (Allsopp *et al.* 1999, Allsopp *et al.* 2001a, Weisglas-Kuperus *et al.* 2004).

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.

Chlorinated Benzenes

Chlorinated benzenes, or chlorobenzenes, are 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 (Budavari *et al.* 2000, ATSDR 2002). Today only mono- and dichlorobenzenes continue to be manufactured in substantial quantities. In addition, chlorinated benzenes can be emitted during the combustion of the chlorinated plastic PVC (Grimes *et al.* 2006).

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 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 plants, 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), and 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).

Box 4. Flame retardants

Polybrominated diphenyl ethers (PBDEs) Polybrominated diphenyl ethers (PBDEs) 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 positioning 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 (Santillo *et al.* 2003 a & b). They also occur in almost every part of the environment, including sediments (Allchin & Morris 2002), freshwater and marine fish (Asplund *et al.* 1999a, b), birds eggs (Hites 2004) and even whales from the deep oceans and the Arctic (Ikononou *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 (Sjödén *et al.* 2001, Sjödén *et al.* 2003). Similarly, elevated levels have been reported in the blood of workers (Qu *et al.* 2007) and local residents (Bi *et al.* 2007) at an e-waste recycling area in China. For the general population, exposure to PBDEs probably occurs through a combination of food contamination and direct exposure to 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 (hormone) 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/furans (IPCS 1998) or mixed bromochloro dioxins/furans (Söderström & Marklund 2002), which appear to be of equivalent or even greater toxicity to chlorinated dioxins (Olsman *et al.* 2007).

Because of these environmental and human health concerns, controls are increasingly being placed on the use of PBDEs (along with some other brominated flame retardants) in some regions. Penta-BDE is included as a “priority hazardous substance” under the EU Water Framework Directive (EU 2001) and remains under consideration for inclusion as a POP (persistent organic pollutant) under the 2001 global Stockholm Convention (Peltola & Ylä-Mononen 2001, UNEP 2006a). Both “penta” and “octa” are now banned from use in Europe (EU 2003), and specifically within the electronics sector the use of all PBDEs, including “deca”, is prohibited under the Restrictions on Hazardous Substances in electrical and electronic equipment Directive (RoHS) (EU 2002a).

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 (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 some computer 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 & 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).

Cathode ray tube (CRT) dismantling site

In addition to samples from the open burning sites, soil from an area in which CRT glass was disposed of (GH08005) contained some metals at levels above those typically found in uncontaminated soils, including copper, lead, yttrium and zinc, though at levels far lower than those recorded in some of the open burning site samples.

This was, however, the only sample with a level of yttrium above typical background soil levels of this metal (Tyler 2004). Compounds of yttrium have been used in CRTs as 'phosphor' coatings, materials on the inside surface of the glass screen that produce light when the CRT is in operation (Burstall 1997). While there is little evidence to suggest that yttrium is toxic, the elevated level of this metal further demonstrates the potential for chemicals within e-waste to become distributed into the environment through disposal. Copper, lead and zinc have also been used with CRTs, including the use of lead in electrical solder (Geibig & Socolof 2005) and within the glass as lead oxide (ICER 2003), and the use of zinc compounds in 'phosphor' coatings (Burstall 1997). Under landfill conditions, metals including lead and zinc are able to leach in appreciable amounts from CRTs and other electronic devices (Musson *et al.* 2006). Elevated soil levels of yttrium, lead and zinc have been previously reported at CRT recycling sites in India (Brigden *et al.* 2005).

This soil also contained some of the organic pollutants identified in the samples from the burning sites, including DEHP and traces of PBDEs, though fewer compounds overall were present in this sample.

The chemical contamination at this location may be due to releases from CRT monitors as well as dispersal of these pollutants from other more contaminated sections of the market, particularly during periods of flooding. Such dispersion was also indicated by the results for the sediment sample from the nearby lagoon (GH08006).

Lagoon sediment

The sample of sediment (GH08006) collected from a shallow lagoon located near to e-waste disposal and open burning areas within the Agbogbloshie Market contained a very similar profile of metal concentrations to those in the more contaminated soil/ash samples described above. The concentrations of these metals were all somewhat lower in the sediment than the soil/ash samples, but were still significantly higher than levels typically found in the environment.

Furthermore, the sediment also contained most classes of organic chemicals that were found in the soil/ash samples, including the phthalate DEHP, a wide range of chlorinated benzenes (some at trace levels), traces of PBDEs and numerous hydrocarbons which can be generated as residues of incomplete combustion.

The similarities in the range of chemicals present in the lagoon sediment to those found in the more contaminated burning site samples suggests the migration of pollutants away from the burning sites into surface waters, probably as a result of heavy rainfall and flooding.

Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs)

The combustion of chlorinated organic materials, including PVC coated wires, can produce polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) (Andersson 2004, Gullet *et al.* 2007, Hedman *et al.* 2005), compounds that are toxic, highly persistent in the environment and able to bioaccumulate, and are also classified as human carcinogens (ATSDR 1998, IARC 1997).

As noted above, two of the samples collected in the current study were subjected to quantitative analysis for a range of the more toxic PCDD/Fs (2,3,7,8-substituted congeners); ash-contaminated soil from the open-burning site at the Agbogbloshie Market at which the widest range of chlorinated compounds had been identified (GH08003), and sediment from the adjacent shallow lagoon (GH08006). Levels of PCDD/Fs are commonly reported as toxicity equivalent value (TEQs, i.e. concentration equivalents to the most toxic congener, 2,3,7,8-tetrachlorodibenzo-p-dioxin, or TCDD)) as well as concentrations by mass, to take into account the different toxicities of individual congeners. The TEQ levels for the two samples are summarized in Table 4, with detailed data presented in Appendix 1.

Congeners	PCDD/Fs (pg/g TEQ)	
	GH08003	GH08006
2378-PCDDs	10	359
2378-PCDFs	21	629
TOTAL 2378-PCDD/Fs	31	988

Table 4 Levels of 2,3,7,8-substituted polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) in GH08003 & GH08006, expressed as toxicity equivalent value (TEQs) in pg/g.

The level of PCDD/Fs in the soil/ash (GH08003) was 31 pg/g TEQ. This value is considerably lower than some very high levels that have been reported for soils and combustion residues from e-waste open burning sites in China, where levels as high as 9265 TEQ pg/g have been reported (Wong *et al.* 2007). Other studies have reported concentrations in e-waste combustion residues ranging from 84-174 pg/g TEQ (Leung *et al.* 2007) up to 675 pg/g TEQ (Brigden *et al.* 2005).

Nonetheless, the TEQ value for sample GH08003 does indicate moderate contamination of this location with PCDD/Fs. Although background levels of PCDD/Fs in soils and sediments have not been reported for Ghana, the level in GH08003 is higher than soil concentrations reported for unpolluted areas in other countries, which are commonly below 1 pg/g TEQ and rarely above 10 pg/g TEQ, including lightly polluted urban and industrial soils (Zhu *et al.* 2008).

A far higher PCDD/F level was found in the lagoon sediment (988 pg/g TEQ). Unlike many of the other contaminants identified, PCDD/Fs are not released as components of the materials being burned, but rather are formed as products of incomplete combustion in the presence of sources of carbon and chlorine (e.g. PVC), with the reaction being catalysed by the presence of metals such as copper. This process can disperse fine ashes containing PCDD/Fs to areas surrounding burning sites, leading to contamination of surface soils and dusts. The far higher level in the lagoon sediment is perhaps the result of the deposition of ashes formed during open-burning directly to the lagoon as well as run-off of contaminated dusts and soils from surrounding areas, as well as the open burning sites themselves, during times of heavy rain and flooding.

Though data on dioxin distribution are not available for Ghana, levels of PCDD/Fs in surface sediments from lakes and rivers in other countries are generally below 20 pg/g TEQ, even in moderately polluted locations (Lui *et al.* 2007, El-Kady *et al.* 2007). The lagoon sediment level is very close to the 1000 pg/g TEQ threshold level defined as being indicative of serious contamination for soil and sediment in the Netherlands (NMHSPE 2000), and also the level in soil used to assess the need for clean up of a site in the United States (USEPA 1998).

The profile of congeners (individual PCDD/F compounds) for the two samples (GH08003 & GH08006) were very similar. These were also similar to the profiles reported for PCDD/Fs produced during the combustion of PVC coated wires under open burning conditions (Gullet *et al.* 2007) and also for combustion residues collected from e-waste open burning sites in China (Brigden *et al.* 2005, Leung *et al.* 2007). These similarities indicate that the open burning of e-wastes may be a primary source of PCDD/Fs at this site.

Conclusions

This study is the first to investigate environmental contamination resulting from the crude recycling of e-waste in Ghana, and highlights the nature of health and environmental concerns arising from these activities.

The recovery of materials at the recycling yards is carried out with little regard for the health and safety of the workers, and with no regard for the environment. These practices have resulted in severe contamination of the workplaces with a range of toxic metals as well as persistent and toxic organic contaminants. Many of the chemical pollutants identified are either intentionally incorporated into electronic products, or are known to be generated during crude recovery processes from materials in the e-wastes, particularly through the widespread practice of open burning commonly employed to separate metals from plastics. Many of the chemicals identified may be associated with the presence of PVC formulations within e-waste being recycled. This chlorinated plastic, which generally requires the use of chemical additives, is widely used in coated wires and cables, one of the main materials burned at the sites investigated.

The extent of workplace contamination found in Ghana was similar to that reported for locations in other countries where manual dismantling and open burning of e-waste is carried out, though some additional activities known to take place at e-waste recycling workshops in other countries were not observed at either of the sites investigated in Ghana. Contamination of the wider environment surrounding e-waste recycling yards with many of the same chemicals has also been demonstrated in other countries, including within the homes of recycling workers (Brigden *et al.* 2005, Leung *et al.* 2008).

The investigation in Ghana focused exclusively on chemical contamination in and around the workplaces and did not attempt to quantify the damage likely to be caused to human health from these activities. Nevertheless, the results do indicate that the exposure of workers and bystanders to hazardous chemicals may be substantial as a result of the hazardous chemicals and materials contained within electrical and electronic equipment, and the crude processes used to recycle and dispose of them. Increased exposure to toxic chemicals associated with e-waste recycling has been demonstrated in other countries, for both workers and local residents. In an e-waste recycling area in China, for example, children have been found to have significantly higher levels of the toxic metal lead in their blood compared to children in a neighboring area (Huo *et al.* 2007). Other studies indicate that people living in areas where e-waste recycling takes place carry higher tissue levels of chlorinated dioxins and furans (Chan *et al.* 2007). Furthermore, recycling workers may commonly carry significantly higher concentrations of certain PBDEs in their blood compared to the general population (Qu *et al.* 2007).

This study extends current knowledge on the consequences of poor management of the large and ever-growing waste stream of obsolete electrical and electronic goods, particularly through crude recycling operations. It was conducted against the backdrop of an apparent recent increase in the prevalence of e-waste recycling in countries such as Ghana, beyond those countries more commonly associated with such activities, especially China and India.

The data demonstrate the urgent need for action to address the management of hazardous e-waste, both the need for tighter controls on the transboundary movement of such wastes, and also on the manner in which they are recycled. Furthermore, this study highlights the need for the redesign of new electronic goods to avoid the use of hazardous chemical components during their manufacture, not least to facilitate safer and more effective dismantling and component separation at the products end of life.

Within Europe, the Waste Electrical and Electronic Equipment (WEEE) and the related Restrictions on Hazardous Substances (RoHS) Directives go some way towards addressing the problems. However, these legislation apply only within the EU and, even then, cover only a fraction of the hazardous substances used in electronics manufacturing. To offer the necessary protection to human health and the environment, the EU RoHS Directive and similar regulations in other countries need to be extended to cover the far wider range of hazardous substances and materials used by this sector, including chemicals specifically identified in this study, for example phthalates, PVC and antimony. Until such regulations are in force, the producers of electrical and electronic equipment need to lead the way by voluntarily phasing out all hazardous chemicals and materials from their products. These chemicals will, of course, remain as a problem for some time to come as older equipment becomes obsolete and enters the waste stream, but ultimately it is only through stricter controls applied at the manufacturing stage that we will stop adding to this toxic legacy of poor design.

In addition to the analytical results presented in this report, evidence is available that e-waste from other countries, some imported under the guise of 'used goods', provides much of the material being recycled within Ghana. These include materials from the EU, from where the export of working used goods is permitted though the export of hazardous e-waste to non-OECD countries is illegal (Houben *et al.* 2008). Proper control of this transboundary movement, at both the export and import stages, could, therefore, reduce the scale of e-waste recycling and the resulting impacts. A requirement to test used goods prior to export, in order to ensure that they are not obsolete devices, would offer greater protection against improper, and in some cases illegal, shipments. Decision trees have been developed for evaluating whether equipment is obsolete and therefore the suitability of transboundary movement for re-use, including for example within the Basel Convention (UNEP 2006b).

National guidelines are currently being developed in Ghana to regulate the importation of used electronic goods into the country (Good Electronics 2008), but other controls are also needed. The transboundary shipment of hazardous waste, including e-waste, from within the EU is already regulated, with export to developing countries such as Ghana supposedly being prohibited (EU 2006). Furthermore, the UN Basel Convention is a global agreement that addresses the international transport of hazardous waste, including e-waste. The Ban Amendment of the Basel Convention which prohibits the shipment of e-waste and other hazardous waste to non-OECD countries (including Ghana) from OECD countries is still awaiting its entry into force. There is clearly an urgent need for the ratification of the Basel Convention Ban Amendment, and stricter enforcement of all laws regulating the transboundary movement of e-waste. Furthermore there is a need for greater regulation of informal e-waste recycling in all countries where it takes place, to improve conditions and to formalise this sector.

Ultimately, however, the manufacturers of electronic products must take responsibility for the entire life cycle of their products, even before it is a global legal requirement. This includes responsibility at the products' end of life, such as through take back and recycling schemes offered free of charge and globally (wherever their products are sold). To achieve the necessary goals these schemes must be highly publicised and accessible, of a high quality, and, where necessary, offer adequate financial compensation to support collection and recycling in order to minimise the transfer of e-waste to the informal recycling and disposal sector. Increased levels of scrutiny of the take-back (collection) chain as well as improvements in product identifiability will help to better identify 'leaks' from the formal to informal channels. Greater individualization of a producers responsibility for its own branded products will drive efforts to verify the producers own take-back rates and more readily enable identification of its own products at the end of their lives, thereby offering greater opportunities for closer scrutiny of the take-back chain.

Furthermore, manufacturers have a responsibility to encourage the strengthening of existing legislation and, where lacking, the development new legislation regulating electrical and electronic equipment, including control of the use of hazardous substances during their manufacture, and also the financial responsibility for end of life management of products, in part through ensuring that funds are available to set up and operate the necessary high quality collection and treatment infrastructures.

The combination of improved regulation and greater responsibility on the part of producers can not only enable verification that e-wastes are recycled and disposed of in the best achievable manner to minimize impacts on human health and the environment, but can also provide producers with financial and other incentives that will encourage the design of products with greater life-spans, that are safer and easier to repair, upgrade and recycle, and which avoid the use of hazardous chemicals during their manufacture.

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Appendix 1. Results from the quantification of 2,3,7,8-substituted polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) in samples GH08003 and GH08006

Congener	GH08003 (soil/ash)		GH08006 (lagoon sediment)	
	Conc (pg/g)	TEQ (pg/g)	Conc (pg/g)	TEQ (pg/g)
2378-TCDF	15.2	1.5	298	29.8
12378-PCDF	15.1	0.8	406.6	20.3
23478-PCDF	19	9.5	702.5	351.3
123478-HxCDF	26.6	2.7	673.9	67.4
123678-HxCDF	19	1.9	602	60.2
234678-HxCDF	30.3	3.0	613.6	61.4
123789-HxCDF	6.9	0.7	185.8	18.6
1234678-HpCDF	84.2	0.8	1774.9	17.7
1234789-HpCDF	10.1	0.1	194	1.9
OCDF	51	0.1	665.7	0.7
2378-TCDD	2	2.0	48.8	48.8
12378-PCDD	2.4	1.2	242.4	121.2
123478-HxCDD	12.1	1.2	234.1	23.4
123678-HxCDD	21.9	2.2	573.1	57.3
123789-HxCDD	12.5	1.2	474.2	47.4
1234678-HpCDD	167.5	1.7	5222.1	52.2
OCDD	351.7	0.4	8272.1	8.3
TOTAL		30.9		988

Table A1. Results of the quantification of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-p-furans (PCDFs) in GH08003 and GH08006, expressed as concentrations and toxicity equivalent values (TEQs), both in pg/g.

Appendix 2. Analytical methodology

On arrival at the lab, two sub-samples were taken from each original sample. One of the sub-samples was subjected to qualitative organic analysis and the other was analysed for metals content. Details of the methods for sample preparation, organic chemicals screening analysis and metals analysis are given below.

Analysis for extractable organic compounds

20 µg of deuterated naphthalene was added as an Internal Standard (IS) to each sub-sample. For sediment samples, approximately 30 g of each sample was extracted twice using 15ml pentane and 5ml acetone at 69°C with sonication for 2h, once at the original pH and once following acidification to pH 2 with nitric acid (10% v/v). The extracts underwent clean-up prior to analysis. The two extracts obtained were combined, concentrated to 3ml, shaken with 3ml isopropyl alcohol and 3ml TBA-reagent (mixture of 3% tetrabutylammonium hydrogen sulphate and 20% sodium sulphite in deionised water) and left for separation. The pentane phase was collected and eluted through a Florisil column using a 95:5 pentane:toluene mixed eluent, and then concentrated to 2ml. 20 µg of bromonaphthalene was added as an IS to each extract prior to GC/MS analysis.

Sample extracts were analysed using an Agilent 6890 Series gas chromatograph with a Restek Rtx-XLB column (30m, 0.25mm ID, 0.25 µm film thickness) linked to an Agilent 5973 Inert MSD operated in EI mode and interfaced with an Agilent Enhanced Chem Station data system. GC oven temperature program was: 35°C, raised to 260°C at 100°C/min, then to 295°C at 50°C/min (held for 5min), then to 325°C at 50°C/min (held for 12min), and then to 330°C at 50°C/min (held for 4min). Carrier gas was helium at 2ml/min. Identification of compounds was carried out by matching spectra against Agilent Wiley7N and Pesticides Libraries. Additionally, spectra and retention time of compounds isolated from the samples were matched against those obtained during GC/MS analysis of standard mixtures containing a range of chlorinated benzenes, phenols and pesticides, polychlorinated biphenyls (PCBs), phthalates, polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons.

Extraction efficiency was evaluated using the response of IS deuterated naphthalene spike.

Analysis for metals

Sediment and soil samples were air dried to constant weight, sieved through a 2mm mesh and then powdered using a pestle and mortar. Approximately 0.5g of each sample was digested by the addition of 7.5ml concentrated hydrochloric acid, 2.5 ml concentrated nitric acid and 10 ml deionised water, firstly overnight at room temperature, then for 4 hours under reflux at 130°C. Digests were filtered and made up to 50ml with deionised water.

Two samples were prepared in duplicate and analysed to verify method reproducibility, along with an identically prepared blank. To check the method efficiency certified reference material (CRM) samples were prepared in an identical manner (GBW07406, yellow-red soil, certified by the China National Analysis Centre for Iron and Steel, Beijing, China and LGC6180, Pulverised Fuel Ash certified by the Laboratory of the Government Chemist, UK)

Prepared samples were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using a Varian MPX Simultaneous Spectrometer. Multi-element standards at concentrations of 1 mg/l and 10 mg/l, and matrix matched for the samples, were used for instrument calibration. Calibration of the ICP-AES was validated by the use of quality control standards at 8 mg/l prepared from different reagent stocks to the instrument calibration standards. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

In addition, for each sample, mercury (Hg) was also determined using cold vapour generation ICP-AES. Ionic mercury, Hg (II), was reduced to elemental mercury, Hg (0), through reaction of the sample with sodium borohydride (0.6% w/v), sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar). The elemental mercury vapour was carried in a stream of argon into the spectrometer. Two calibration standards were prepared, at 10 µg/l and 100 µg/l, matrix matched to the samples. The calibration was validated using a quality control standard (80 µg/l), prepared internally from different reagent stock.

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