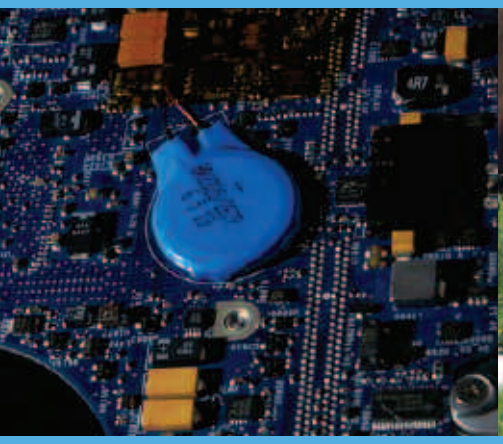

CUTTING EDGE CONTAMINATION

A STUDY OF ENVIRONMENTAL POLLUTION DURING THE MANUFACTURE OF ELECTRONIC PRODUCTS

GREENPEACE

A boy stands on the riverbed contaminated by the outflow of the Compeq factory in the Guangdong Province, China. October 2006

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COVER PHOTOS

Right: Treated wastewater being discharged to public canal from a combined wastewater treatment plant of Navanakorn Industrial Estate. Pathumthani, Thailand

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Left: Image shows the inside of a laptop and the components produced and assembled in the factories that are highlighted in this report.

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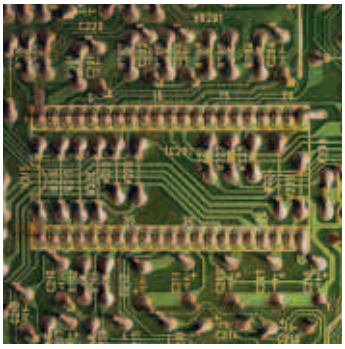
EXECUTIVE SUMMARY

THE USE OF ELECTRONIC EQUIPMENT IS WIDESPREAD WITHIN SOCIETY. CONSUMER GOODS, FROM MOBILE PHONES TO DESKTOP AND LAPTOP COMPUTERS, ARE PART OF DAILY LIFE FOR MANY PEOPLE. THESE PRODUCTS HAVE A VERY CLEAN IMAGE COMPARED WITH MANY OTHER CONSUMER GOODS. THE REALITY, HOWEVER, CAN BE SOMEWHAT DIFFERENT.

As the sun sets the farmer waters his plants near the Compeq Factory in the Guangdong Province, China. October 2006

An inside look into the printing wiring board (PWB)



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In recent years, concerns have grown over the use of hazardous chemicals and materials in these products. Attention has tended to focus on the impacts on human health and the environment due to such chemicals, through the use and ultimate disposal or recycling of these products. Less consideration has been paid to the potential environmental impacts that result from their manufacture. This industry has high resource intensity, in terms of chemicals, energy and water demands. This is especially the case for printed wiring board (PWBs) and semiconductor chip manufacture. Processes used in both sectors are highly complex and chemically intensive; many of the chemicals employed do not form part of the final product (e.g. solvents). Substantial concerns exist for many chemicals used in this industry, both for potential exposure in the workplace and the possible environmental consequences of their release in waste streams.

Electronic devices such as computers are incredibly complex constructions, consisting of a wide range of diverse components. The manufacture of an individual product can be a truly global process, with individual components manufactured at numerous specialised facilities in many different countries, before assembly into the final product.

This study was undertaken to highlight environmental contamination resulting from the manufacture of electronic equipment such as computers. It is not intended to be an exhaustive investigation of the electronics manufacturing industry, but rather an attempt to gain understanding of chemical wastes released to the environment by certain sectors of this industry, by providing some 'snap-shot' case studies in three major sectors of this industry. For each sector, many manufacturing facilities and Industrial Estates housing such facilities were investigated in four countries, as given in the table below

table 1.1 :: Facilities/Sites and Industrial Estates (IEs) investigated, the country in which they are based and the manufacturing sector to which they belong.

COUNTRIES	FACILITIES	MANUFACTURING SECTOR
China	Compeq	PWB manufacture
China	Fortune	PWB manufacture
Thailand	Elec & Eltek (EETH)	PWB manufacture
Thailand	Navanakorn IE	PWB manufacture
Thailand	Bangpa-in IE; CKL Electronics	PWB manufacture
Thailand	Hi-Tech IE; KCE	PWB manufacture
Thailand	Rojana IE; PCTT	PWB manufacture
Philippines	Gateway Business Park (mixed activity IE)	Semiconductor chip manufacture
Philippines	On Semicon (Also known as 'On Semiconductor')	Semiconductor chip manufacture
Philippines	Cavite Export Processing Zone, CEPZA; mixed activity IE	Semiconductor chip manufacture
Mexico	Kemet	Semiconductor chip manufacture
Mexico	Sanyo Video, Tijuana	Assembly (TV & LCD)
Mexico	Sony, Tijuana	Assembly (TV & LCD)
Mexico	Parque Integral (Flextronics), Guadalajara	Component assembly
Mexico	Jabil, Guadalajara	Component assembly
Mexico	Solectron, Guadalajara	Component assembly
Mexico	Sanmina-SCI plant 3, Guadalajara	Component assembly
Mexico	HP, Guadalajara	Assembly (PC & other components)
Mexico	IBM Site, Guadalajara	Assembly (PC & other components)

The use of electronic equipment is widespread within society. Consumer goods, from mobile phones to desktop and laptop computers, are part of daily life for many people. These products have a very clean image compared with many other consumer goods. The reality, however, can be somewhat different.

A number of different types of samples were analysed from the various sites, though it was not possible to collect all types of sample for each of the facilities. Discharged wastewaters and sediments from discharge pipes/channels were analysed for some locations, mainly from PWB facilities, though also from one component assembly facility. At some industrial estates, wastewaters are sent from many individual facilities to a common wastewater treatment plant (WWTP). Where possible, treated wastewaters and treatment sludges/sediments from these WWTPs were also collected and analysed. Groundwater samples from many sites were analysed to investigate impacts on local groundwater aquifers. In some cases, such as semiconductor manufacturing facilities, it was not possible to collect wastewater samples and the investigations therefore focussed entirely on groundwater samples collected from sources in the vicinity of the plants.

Though this study has certain limitations due to its overall scope and limited access to some types of samples at some sites, it does provide substantial information on the environmental contamination of these parts of the industry where little has previously been available. This study demonstrates the nature of environmental contamination due to the manufacture of some components used in electrical/electronic equipment at multiple sites in many countries.

Evidence of environmental contamination by a diverse range of chemicals, many with known uses in this industry, was found for each of the three sectors investigated. This included both chemicals incorporated into the products as well as chemicals used in manufacturing processes, many with known toxicity to humans and other potential environmental impacts. Some chemicals were found in wastestreams from more than one sector, including some toxic and environmentally persistent groups of chemicals;

- polybrominated diphenyl ethers (PBDEs); widely used as brominated flame-retardants
- phthalates; widely used as plasticizers (softeners) in plastics
- certain chlorinated solvents
- high levels of some heavy metals.

Of these chemicals, many that are incorporated into electronic products have also been identified within and around e-waste recycling yards in China and India in a recent Greenpeace investigation (Brigden et al. 2005), including certain heavy metals, phthalates and the brominated flame-retardants PDBEs. Laptop computers purchased in Europe within the last year have also been found to contain mixtures of PBDEs (Brigden et al. 2006), though the compositions were different from those found at the manufacturing sites.

Other chemicals found in wastestreams and groundwater samples were specific to each of the manufacturing sectors, for example the brominated flame-retardant TBBPA and photoinitiator-related chemicals at PWB manufacturing sites. These differences reflect the different processes employed within each sector, though this may also be due in part to the types of samples that it was possible to collect from facilities in each sector (e.g. no wastewaters samples were analysed from semiconductor chip manufacturers as no such wastestreams could be identified at the plants visited).

Phthalates

Phthalates are widely used as plasticizers (softeners) in plastics, especially PVC (e.g. in cables and other flexible components), though many other industrial uses exist. Many phthalates are toxic to wildlife and humans, often through their metabolites (chemicals to which they breakdown in the body). DEHP, a widely used phthalate, is a known reproductive toxin capable of causing changes to both male and female reproductive systems in mammals (e.g. development of the testes in early life). Other phthalates (e.g. DBP and BBP) also exert reproductive toxicity. Both DEHP and DBP are classified as "toxic to reproduction" within the EU. Certain other phthalates (DINP and DIDP) can affect the liver and kidneys, albeit at higher doses.

A farmer picking peanuts from a field near the Compeq Factory, in the Guangdong Province, China. October 2006

Flame Retardants

Flame-retardants are chemicals added to a wide variety of materials, including casings and components of many electronic goods, to prevent the spread of fire. Two widely used groups of chemicals are brominated flame retardants (including PBDEs and TBBPA) and phosphorus based compounds (including TPP).

- **PBDEs (Polybrominated diphenyl ethers)** 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.

- **TBBPA (Tetrabromobisphenol-A)** There is evidence that TBBPA may interfere with thyroid hormones, with the potential for effects on growth and development, and other in vitro studies (not within a living organism) indicate the potential for effects on other hormone systems, the immune system, liver and kidneys. Recently concerns have been raised over chemicals formed during the degradation of TBBPA in the environment.

- **TPP (Triphenylphosphate)** is acutely toxic to aquatic life and is a strong inhibitor of a key enzyme system in human blood. It can also cause contact dermatitis in some individuals and is a possible endocrine disruptor.

A large proportion of the compounds isolated from discharged wastewaters and associated samples could not be identified, and therefore their properties and potential impacts remain unknown. For some chemicals identified in wastestreams (e.g. photo-initiator related chemicals used in PWB manufacture), very little information is available on their toxicity and environmental properties, presumably largely as a result of rapidly changing manufacturing processes and the chemicals employed within certain sectors. The possible impacts on human health and the environment due to the use and release of these chemicals, therefore, remain largely unknown.

The ineffective treatment of wastewaters by the WWTPs to which they are discharged has been demonstrated at some industrial estates in Thailand where PWBs are manufactured. As is the case for many industrial estates where common WWTPs receive mixed wastes from many facilities, although treatment processes may be able to degrade certain chemicals they are not effective at dealing with persistent organic chemicals and heavy metals in wastewaters. As this study has found, this can mean that such chemicals are still present in treated wastewaters discharged to the environment. Furthermore, their accumulation in WWTP sludges creates an additional wastestream contaminated with heavy metals and persistent organic chemicals. For certain chemicals used in PWB manufacture (e.g. photoinitiator-related compounds) the results suggest that they are degraded by the treatment processes employed at some sites. However, such wastewater treatment is not universally carried out, and these chemicals were found in wastewaters being directly discharged to the environment from other PWB manufacturing facilities (both Fortune and Compeq in China). Due to the limited information available on these compounds the impacts of such discharges remains unknown.

In addition to the chemicals identified in wastewater networks, contamination of groundwater aquifers with chlorinated chemicals and some heavy metals (e.g. nickel) was evident at some sites. Many of these chemicals have known uses in the facilities located at the sites where they were found. Groundwater contamination is of particular concern as local communities use this resource for drinking water in many places.

Trihalomethanes (THMs) were also found in some groundwater samples from sites in all sectors. These chemicals are generally formed as by-products of chlorine based water disinfection, which is common practice for many groundwater sources including open wells, and this is their most likely source in these samples.

Despite the overall complexity of the sample set available and the result obtained, some distinct patterns of contamination could be attributed to each of the different sectors investigated

PWB manufacturing

For the PWB manufacturing facilities investigated, wastewaters and sediments from discharge pipes/channels contained many chemicals of environmental concern. Some groups of chemicals were found throughout wastewater distribution networks and WWTPs, as well as in wastewaters discharged directly to the wider environment, either by WWTPs or individual facilities. These included some persistent and toxic chemicals; PBDEs (brominated flame-retardants) and phthalates, as well as high levels of some heavy metals. Other types of flame-retardant were found in wastewaters from facilities in China; TBBPA (commonly incorporated into PWBs) and TPP; see flame-retardants box.

PBDEs were widely distributed, being found in wastewaters and/or sediments at all sites, including wastewaters released directly to environment. Though present in many samples, there were substantial differences in the number of PBDEs and their relative amounts in samples from different locations. Distribution patterns indicate that the facilities are significant point sources of these chemicals.

Other chemicals specific to the PWB sector were found in discharged wastewater networks at most sites, including photoinitiator-related compounds and very high levels of heavy metals, including copper, nickel and zinc.

This farmer is on his break, drinking water. His field is near the Compeq factory in the Guangdong Province, China. October 2006

Photoinitiators and related compounds

Photoinitiators and related compounds. Photoinitiators use UV light to induce polymerisation and are extensively used in the manufacture of PWBs. Benzophenone and acetophenone based chemicals have traditionally been used though new compounds have been recently introduced, including thioxanthones. There is very little information on the potential human health and environmental impacts of many of these compounds, especially those more recently introduced.

- **Benzophenones;** From animal experiments, the parent compound benzophenone can have toxic effects on the liver and kidneys. Benzophenone and some of its derivatives may effect the estrogenic hormone system.
- **Acetophenones;** Though in use for many years, little information exists on their toxicity. Acetophenone itself is a toxic chemical; exposure can cause sedative effects in humans as well as effects on the blood; vapours can cause skin irritation. Effects on lungs, kidneys, and liver have also been reported in animals.
- **Thioxanthones;** Thioxanthones are used in PWB photoresist processes. Little information is available on these compounds, though some derivatives of thioxanthone are known to be of high aquatic hazard and capable of causing long-term effects in aquatic organisms at low concentrations.

Copper and nickel are widely used in PWB manufacture. In some cases, manufacturing processes use other chemicals which can impede the recovery of metals from wastewaters. Releases of copper to aquatic environments can have significant impacts. At the EETH facility in Thailand, wastewater contained the highest level of copper of the sites at a concentration almost two times the maximum permitted level for industrial effluents in Thailand.

Metals

Some metals are used in the manufacture of PWBs and other electrical components; particularly copper but also nickel and other metals.

Copper is widely used due to its high electrical conductivity; some PWB manufacturing processes use water soluble copper compounds. Many aquatic organisms are extremely sensitive to copper, particularly in soluble forms, and releases to aquatic environments can have significant impacts. Effects can occur at very low levels, including reductions in growth and fertility rates as well as increased mortality.

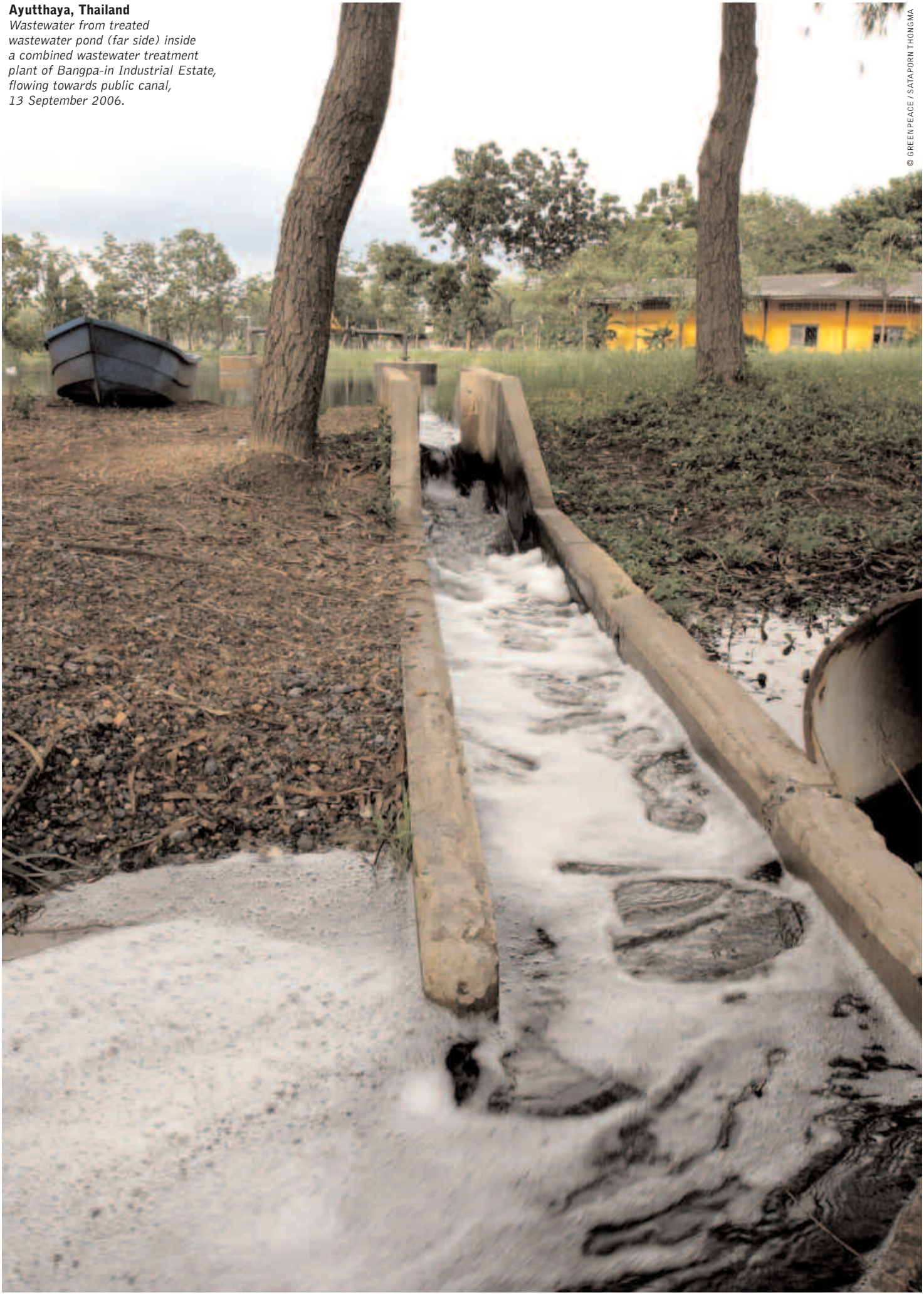
Nickel is also used in the manufacture of PWBs, including nickel electroplating involving water-soluble nickel compounds. Ingestion of some nickel compounds can cause toxic effects in humans and animals; gastrointestinal effects and even cardiac effects. 2-5% of the population are nickel sensitive and can suffer effects at far lower doses. Some nickel compounds are carcinogenic to humans, and possibly some animals.

Groundwater samples collected from PWB manufacturing sites were generally not impacted with the chemicals found in other samples. Although high levels of some metals were commonly present in wastestreams, their levels in groundwaters were generally not high. However, one sample from the Hi-Tech IE in Thailand did contain nickel at a level above the World Health Organisation (WHO) drinking water guideline value and nearly 5 times the Thai groundwater quality level for this metal.

Semiconductor chip manufacture

Volatile organic chemicals (VOCs) were found in samples from each of the sites where semiconductor chips are manufactured. The VOCs identified included chlorinated chemicals, commonly used as industrial solvents or degreasing agents, many with known toxic effects of the central nervous system, liver, and kidneys.

Ayutthaya, Thailand
Wastewater from treated wastewater pond (far side) inside a combined wastewater treatment plant of Bangpa-in Industrial Estate, flowing towards public canal, 13 September 2006.



Chlorinated volatile organic chemicals (VOCs)

Chlorinated methanes, ethanes and ethenes, many of which are or have been widely used as solvents in industrial processes, including surface cleaning in the manufacture of electrical equipment (PWBs & semiconductor chips); especially 1,1,1-trichloroethane, trichloroethene and tetrachloroethene. Many of these chemicals are potentially carcinogenic to humans. Most can affect the central nervous system (CNS), liver, and kidneys and are irritating to the skin, eyes, and mucous membranes. Some can be absorbed directly through the skin. The widespread use and storage of chlorinated solvents has led to releases of these chemicals into the environment, including groundwater aquifers.

The most extensive contamination was seen at the Cavite Export Processing Zone (CEPZA) industrial estate in the Philippines, where chlorinated VOCs (ethenes & ethanes) were found in 5 groundwater samples, all collected close to the centre of the industrial estate. The distribution of these chemicals in the groundwater indicates localised industrial inputs within the CEPZA IE. In three samples, the level of one or more chlorinated ethene exceeded maximum recommended levels for drinking water set by the World Heath Organisation (WHO) and/or US Environmental Protection Agency (EPA). For one of these the level of tetrachloroethene was 9 times the WHO guidance value and 70 times the USEPA maximum contaminant level.

The situation was less clear at the other sites. Chlorinated VOCs were found in only one sample at the Gateway IE (Philippines). In the case of the On Semicon site (Philippines), the greatest groundwater contamination was detected to the south of the facility, indicating that another so far unidentified source may be responsible.

Some samples associated with this sector contained high levels of metals, primarily zinc, though current levels would not be expected to pose a risk to health in drinking water. In many cases the likely sources were unclear, though high levels do appear to be centred around the On Semicon site.

Nonylphenol (NP)

Nonylphenol (NP) is a chemical most widely known as a breakdown product of nonylphenol ethoxylate (NPE) surfactants (detergents), though it has reportedly also been used as an antioxidant in some plastics. It is a strong endocrine (hormone system) 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.

The data give a snap-shot of groundwater contamination at each site. It was not the intention of this study to conduct a full comprehensive survey of the aquifers, nor was there the ability to do so due to the limited number of groundwater access points at each site. There is clearly a need for further detailed investigations of chlorinated VOCs in groundwater at the semiconductor chip manufacturing sites to find the full extent of the contamination of the aquifers, particularly at the CEPZA IE in the Philippines. As no samples of production wastes (such as wastewaters) could be collected from the facilities in this sector, the nature and extent of chemicals in these waste streams are unknown.

Component assembly

At the investigated sites in Mexico where component assembly takes place, high levels of some metals were found in about half the groundwater samples collected, principally nickel and zinc. The levels of nickel in 3 samples [1 from a well adjacent to the Sanyo Video facility in Tijuana, and 2 collected close to the Flextronics IE in Guadalajara] were above the WHO maximum guideline value for nickel in drinking water, the highest being over double the WHO value. No contamination with chlorinated VOCs was found in these groundwaters.

Samples of wastewater were only accessible at one site, that belonging to IBM in Guadalajara. A number of chemicals of environmental concern were found in these wastewaters, including nonyl phenols, a phthalate, and also trace levels of 2 PBDEs, flame-retardant chemicals discussed above. Nonyl phenols (NP) are persistent chemicals that are toxic to aquatic life, and can bioaccumulate. NPs are commonly formed as degradation products of nonylphenol ethoxylates (NPEs), a group of chemicals used as surfactants (detergents). One NPE was also found in the same wastewater, along with a phthalate (DEHP).

Collecting water samples from a well near the Sanyo plant in Tijuana. June 2006.

Overall, the results from this study clearly demonstrate that the current use of hazardous chemicals and practices in the manufacture of electronic equipment is resulting in contamination of the environment with many hazardous chemicals, some of which are persistent and able to bioaccumulate. Commonly used wastewater treatment processes are unable to deal with many of the chemicals used, including certain brominated flame-retardants and heavy metals.

At those sites where groundwater contamination has been highlighted it is imperative that any further inputs to the groundwaters aquifers are immediately prevented and full site investigations carried out to find the extent of the contamination and enable remediation. Where contaminated groundwater sources are used for drinking water, clean drinking water from other sustainable sources needs to be supplied in the interim.

Despite its high demand for resources, including a diverse array of hazardous chemicals, the electronics industry at a global level appears to remain relatively free from specific environmental regulation. This may, in part, be a consequence of the very rapid evolution and development of the sector, such that the rate of introduction of new industrial processes outpaces the development of regulatory controls.

When it comes to worker and environmental protection, there are some signs of change within the electronics industry. The EU Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment, or the RoHS Directive, has had a substantial impact on the industry well beyond Europe and, in the case of some companies at least, well before its official entry into force on July 1st 2006. This Directive prevents the use of the heavy metals lead, mercury, cadmium and hexavalent chrome and of certain brominated flame-retardants, namely PBBs and PBDEs (with exceptions for deca-BDE and some designated uses of metals). It does not control the use of all potentially hazardous chemicals, including other brominated flame-retardants such as TBBPA. Furthermore, it addresses only a very small part of the problem, with a heavy focus on avoiding the presence of only certain hazardous chemicals in the final products put on the market in the EU. Aside from the upstream changes these specific prohibitions require, RoHS alone is likely to have little impact on the use of the majority of the hazardous chemicals used in the manufacturing processes themselves, nor on the overall efficiency and resource intensity of those processes.

What is urgently required is a much more fundamental shift in thinking and emphasis by those companies engaged in electronics manufacture to ensure that concerns regarding chemical and other raw material use, workplace exposure and waste management become a routine part of company planning, research and development cycles, without waiting for legislative measures to catch up and without pursuing derogations from existing law. In technological terms, electronics manufacturing remains at the cutting edge and has a strong economic future. There is no reason why it should not also be at the cutting edge when it comes to clean designs and technologies, substitution of hazardous chemicals, increased resource efficiencies, greater worker health protection and the prevention of environmental pollution at source. In short, it is vital that, in the inevitable race for technological advances, the electronics manufacturing industry does not remain blind to the parallel need for pollution prevention and sustainability.

1 :: INTRODUCTION

THERE HAS BEEN GROWING CONCERN IN RECENT YEARS OVER THE PRESENCE OF HAZARDOUS CHEMICALS AND MATERIALS WITHIN ELECTRICAL AND ELECTRONIC EQUIPMENT. INTEREST HAS CENTRED IN PARTICULAR ON COMPUTERS AND THEIR PERIPHERAL EQUIPMENT, DUE LARGELY TO RAPIDLY INCREASING PRODUCTION OF SUCH GOODS GLOBALLY.

One of the residents near the Compeq factory in the Guangdong Province, China preparing her stove to make bread. October 2006

Examples include lead, a highly toxic metal that has traditionally been used in electrical solders and other materials used in the manufacture of such products, and certain toxic brominated compounds, such as polybrominated diphenyl ethers (PBDEs), the use of which as flame retardants has resulted in releases of these chemicals to the environment.

Studies investigating the use of hazardous chemicals in this sector have tended to focus on impacts on human health and the environment resulting from the recycling and disposal of old electrical/electronic equipment, an already large and rapidly increasing wastestream. Greenpeace recently conducted a study demonstrating workplace and environmental contamination due to recycling activities in China and India (Brigden et al. 2005). However, the use of hazardous chemicals in this type of product is not restricted to older, now obsolete models. Greenpeace recently reported the presence of certain hazardous chemicals in five laptop computers purchased in Europe in March 2006 (Brigden & Santillo 2006). Although legislation in some countries and regions has prohibited or imposed greater controls on the use of certain hazardous chemicals (e.g. the European RoHS Directive, EC 2003), and despite moves by some companies to replace hazardous substances with safer alternatives (Cobbing 2006), even very recently manufactured models of computers and related equipment may still contain some toxic heavy metals and other hazardous chemicals.

A topic that has received less public attention to date is the potential for environmental impacts during the manufacture of electrical/electronic equipment, from both chemicals incorporated into the products as well as other chemicals used in their manufacture but that do not form part of the final product, such as solvents and surfactants (Walters et al. 2006). This study was undertaken to investigate such impacts from certain sectors within this industry.

A typical computer is an incredibly complex construction consisting of a wide range of diverse components, from the visible external keyboard, casing and screen to the internal circuitry and wiring including printed wiring boards (PWBs), semiconductors, hard drives, interface sockets, cables, etc. many of which are themselves composed of numerous individual parts. The manufacture of this type of equipment is a truly global industry. A typical computer may have been assembled using thousands of components manufactured at numerous specialised facilities, which may be located in a number of different countries. There are many diverse manufacturing sectors within this industry.

This study is not, therefore, intended to be a comprehensive investigation into all aspects of the whole manufacture process of computers and peripheral equipment, but rather to provide some 'snap-shot' case studies into environmental contamination from the use of hazardous chemicals in three major sectors of this industry;-

- Printed wiring board (PWB) manufacture
- Semiconductor chip manufacture
- Component assembly

The assembly of individual component into discrete devices and the final product can make use of surfactants and chemical solvents as well as flux chemicals and metals in electrical solders. Historically solders were lead based alloys and, although lead-free alternatives are now widely used (Lau et al. 2003), numerous derogations permitting continued use of leaded solders have recently been agreed under the EU's RoHS Directive (EC 2005). The manufacture of PWBs and semiconductor chips are highly complex and chemically intensive processes using a wide range of chemicals, many of which do not form part of the final product. These processes, described in more detail by Walters et al. (2006) are outlined briefly below in order to put the current study into context.

Printed Wiring Board (PWB) manufacture

Printed wiring boards (PWB) are also known as printed circuit boards (PCB). In this report the term PWB is used to avoid confusion with another common use of PCB to refer to the chemicals polychlorinated biphenyls.

PWBs are essentially complex copper circuitry embedded within an electrically insulating baseboard. Baseboards are generally made from glass fibre-epoxy resin based composites to which flame retardant chemicals are commonly added. Tetrabromobisphenol-A (TBBPA), a brominated flame retardant (BFR), is widely used in epoxy resin boards. This compound becomes largely chemically bound into the polymer, though traces of unreacted TBBPA do remain unbound in the finished board (Sellstrom & Jansson 1995) and the harsh chemical environments used during PWB production may be expected to cause some leaching of unreacted monomer. The initial stage of baseboard manufacture is not further covered in this report.

The manufacture of a PWB involves producing complex copper circuitry on thin layers of insulating material (baseboard). The layers are then laminated together and holes drilled to allow electrical communication between layers. Additional circuitry may be laid down on the outer surface and a range of the surface finishing chemicals applied to clean, strengthen and protect the board. For each layer, the copper circuitry is produced by firstly coating the base material with copper. The circuit pattern is temporarily protected from the subsequent stripping (etching) stage by a template or 'mask' laid on top of the copper in the shape of the desired circuit (using the photochemical techniques described below), and then unwanted copper is selectively stripped back off from everywhere except where the circuit is required. Multiple processes and chemicals that can generate a mix of hazardous wastes are used in PWB manufacture; specific techniques applied vary between manufacturers.

The process of creating circuits utilises complex photochemistry, i.e. exploiting chemical changes through exposure to ultraviolet (UV) light. The (cleaned) copper surface is first coated with a photoresist mixture (of monomers, crosslinking agents and photocatalysts) that changes its solubility upon exposure to UV light. A diverse range of organic chemicals are used in photoresists. A mask (map) of the circuitry is applied and UV light shone on the board. Many processes are used, but in that most commonly used the photoresist mixture polymerise on exposure to UV light and becomes insoluble while unexposed areas remain soluble. The latter are then washed away using a suitable solvent, which can still include chlorinated solvents, though water based systems are increasingly available (Lau et al. 2003, Shaw et al. 1997). Spent developing solution containing dissolved photoresist mixtures is one of the largest liquid wastestreams generated by PWB manufacturing (USEPA 1995). Exposed copper is then etched from the surface, and the protective photoresist is subsequently removed using other chemicals ('film stripping') to leave the finished copper circuit. These processes create complex wastestreams that include soluble copper, photoreactive chemicals and solvents.

Individual layers are joined together using epoxy resins under heat and pressure. Holes, or 'vias', are drilled through the PWB to allow the attachment of components, or provide electrical connection between layers by copper coating the insides of the holes. Hole coating has traditionally been carried out using the 'electroless copper process' followed by electroplating. The electroless copper process uses dissolved copper compounds, formaldehyde and chelating chemicals (that can impede recovery of metals from wastewaters), as well as other hazardous chemicals. This process is therefore associated with significant environmental concerns, though some manufactures now use alternative processes which are less chemical intensive and environmentally impacting (Chang 1995, Hui et al. 2003). Outer layer circuitry is then laid down in a similar manner to that used for inner layers, and then surface finishes are applied primarily to prevent copper oxidation and give physical protection. These are usually based on metallic solders (either lead-tin or lead free alloys) and/or other metals including nickel and gold, which can involve the use of water-soluble nickel compounds.

The processes used, including numerous rinse cycles, result in significant loss of metals and process chemicals into wastewaters. Though some chemical recovery does take place at many facilities, wastewaters can represent a significant source of environmental pollution (USEPA 1995).

Semiconductor chip manufacture

Semiconductor chips, or 'microchips' consist of a complex array of microscopic components based on semiconducting material within an extremely small area. These circuits respond much more quickly and use less electricity than conventional circuitry. The manufacture of semiconductor chips involves many chemical processes that require vast quantities of process chemicals and water (Walters et al. 2006); over 30 kg of materials (including water) are required for the manufacture of a single 2 g memory chip (Williams et al. 2002). Due to the dynamic nature of this industry, technologies used and the chemicals and processes employed are rapidly changing (Dietrich 2004).

Semiconductor chips are constructed from ultra pure materials in a multiple step-wise process, essentially involving three basic elements: the layering of insulating, semiconducting or conducting material, the doping of semiconducting layers with an array of chemicals to tune their electrical properties and the surface patterning using masking and etching processes analogous to PWB construction. In this way multiple layers of circuitry are built up.

The processes are intolerant of even trace impurities, requiring the use of very high purity chemicals (gases and solvents), many in high volumes. Some recycling/reclamation of spent chemicals does occur, though recovered solvents and gases can contain impurities that may make clean-up to the necessary high purity impracticable, and so waste solvents may often be incinerated (Timms 1999). The processing of solvent waste is often out-sourced to separate companies. Use of chlorinated solvents by this industry has resulted in groundwater contamination at a number of locations (Williams 2003). Large volumes of wastewaters are generated, mainly from surface rinsing that follows etching and cleaning stages. These contain a wide range of chemicals including solvents, acids and metals, particularly dissolved copper.

Processes used in semiconductor manufacture also generate gaseous wastestreams containing a wide range of hazardous air pollutants. These can include heavy metals, perfluorinated compounds, inorganic acids and volatile organic chemicals (VOCs), some of which are potent greenhouse gases. Though abatement of chemicals in gaseous wastestreams commonly take place, significant chemical emissions to air have nevertheless been reported (Chein & Chen 2003).

The use of hazardous chemicals in this industry has raised concerns over workers health, particularly the potential impacts from long-term, low level exposure to a wide and frequently changing range of chemicals. Epidemiological studies have highlighted increased incidences of reproductive effects and certain cancers (Chen et al. 2002, Clapp 2006, Hsieh et al. 2005, Schenker et al. 1995), though establishing cause-effect relationships to chemical exposure is extremely difficult in such circumstances (Fowler 1999).

This study was not intended to be an exhaustive investigation of the electronics manufacturing industry, rather an attempt to gain understanding of the chemical wastes released to the environment by certain sectors of this industry in a number of different countries. It was not possible to investigate, and therefore compare, the same manufacturing sector in each of the different countries included in this study, nor to collect the same range of samples for each of the individual facilities investigated. This study does, however, provide substantial information on the environmental contamination of these parts of the industry where little has previously been available. The individual manufacturing facilities or Industrial Estates in each of the four countries, and the manufacturing activities carried out at each is presented in Table 1.1.

August 2006
Image shows the inside of a laptop and the type of component produced and assembled in the factories that are highlighted in this report.

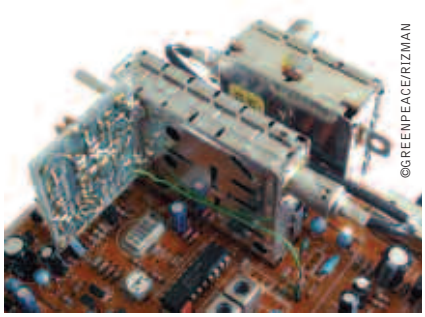


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table 1.1: Facilities/Sites and Industrial Estates (IEs) investigated, the country in which they are based and the manufacturing sector to which they belong.

COUNTRIES	FACILITIES	MANUFACTURING SECTOR
China	Compeq	PWB manufacture
China	Fortune	PWB manufacture
Thailand	Elec & Eltek (EETH)	PWB manufacture
Thailand	Navanakorn IE	PWB manufacture
Thailand	Bangpa-in IE; CKL Electronics	PWB manufacture
Thailand	Hi-Tech IE; KCE	PWB manufacture
Thailand	Rojana IE; PCTT	PWB manufacture
Philippines	Gateway Business Park (mixed activity IE)	Semiconductor chip manufacture
Philippines	On Semicon (Also known as 'On Semiconductor')	Semiconductor chip manufacture
Philippines	Cavite Export Processing Zone, CEPZA; mixed activity IE	Semiconductor chip manufacture
Mexico	Kemet	Semiconductor chip manufacture
Mexico	Sanyo Video, Tijuana	Assembly (TV & LCD)
Mexico	Sony, Tijuana	Assembly (TV & LCD)
Mexico	Parque Integral (Flextronics), Guadalajara	Component assembly
Mexico	Jabil, Guadalajara	Component assembly
Mexico	Solectron, Guadalajara	Component assembly
Mexico	Sanmina-SCI plant 3, Guadalajara	Component assembly
Mexico	HP, Guadalajara	Assembly (PC & other components)
Mexico	IBM Site, Guadalajara	Assembly (PC & other components)

2 :: SAMPLING PROGRAM

FOR EACH OF THE THREE MANUFACTURING SECTORS INVESTIGATED IN THIS STUDY, SEVERAL SEPARATE FACILITIES INVOLVED IN SIMILAR ACTIVITIES WERE VISITED AND A RANGE OF DIFFERENT TYPES OF SAMPLES COLLECTED FROM EACH, DEPENDING ON SAMPLE AVAILABILITY AND SUITABILITY AT THE SITE.

Greenpeace collecting samples from a wastewater channel on the IBM site in Guadalajara, Mexico. June 2006.

The types of samples collected include groundwaters, wastewaters (both treated and untreated), sediments from discharge channels and water bodies that receive discharged wastewaters, treatment facility sludges, and soil samples.

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. For those samples analysed for volatile organic chemicals, a sample was collected in a separate 125 ml amber bottle with a ground-glass stopper. Sediment and soil samples 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 the Appendix.

2.1 :: PRINTED WIRING BOARD (PWB) MANUFACTURE; CHINA & THAILAND

A number of facilities involved in the manufacture of printed wiring boards (PWB) were visited both in China and Thailand. A range of samples were collected including wastewaters, sediments from discharge channels and rivers, sludges from wastewater treatment plants (WWTP), soil and groundwater.

2.1.1 :: China

This study investigated two facilities involved in the manufacture of PWB in China; Fortune and Compeq. These two separate facilities are both located in Boluo County, Guang Dong, China, the location of which is shown in Figure 2.1. Both are stand-alone facilities, not situated within an Industrial Estate. Fortune is located in agricultural land at Bu Shang Village, near to the Bushang River while the Compeq facility is situated on the banks of the XianGang River, Hu Zhen Village.

Figure 2.1 :: Map of China showing the location of Boluo County in which the Fortune and Compeq manufacturing facilities were located.

At the Fortune facility, wastewaters are discharged via an underground channel which flows into an open ditch that in turn flows into the Bushang River. Wastewaters discharged via this route are not continuous but released in batches. At the time of sample collection wastewater discharge was not taking place. The underground channel and open ditch flow through farmland neighbouring the Fortune facility.

The Compeq facility, located on the banks of the XianGang River, has four outfalls that discharge wastewaters to the river. From the most upstream to the most downstream, these discharges are hereinafter referred to as;-

1. Open discharge channel #2
2. Pipe #2
3. Pipe #1
4. Open discharge channel #1, from wastewater treatment plant

Samples of discharged wastewaters were collected from both facilities, as well as sediments from discharge channels and the creeks / rivers into which they flow. Soil and groundwater samples were also collected from the vicinity of the Fortune facility. For both facilities, samples were collected on two separate occasions, firstly in November 2005 (MI05049-51) and a second set in January 2006 (MI06001-MI06010). Details and locations of the individual samples are given in Table 2.1 and in Figure 2.2 (Fortune) and Figure 2.3 (Compeq).

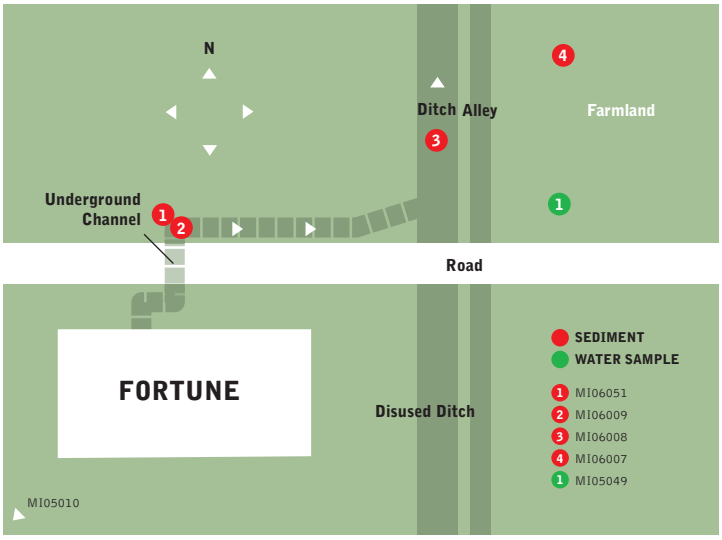

Figure 2.2 :: Sketch map of the locations from which samples were collected in the vicinity of the Fortune PWB manufacturing facility, China

table 2.1 :: description of wastewater, sediment, soil and groundwater samples associated with the Fortune and Compeq PWB manufacturing facilities, China

SAMPLE#	TYPE	DATE	SAMPLE LOCATION
			Fortune
MI05049	groundwater	19.11.05	well, located at the outfall of underground channel into the open ditch
MI05051	wastewater	18.11.05	underground channel; to an open ditch leading to the BuShang River
MI06009	sediment	19.01.06	underground discharge channel
MI06008	sediment	19.01.06	open ditch, leading to the Bushang River
MI06007	soil	19.01.06	field close to the Fortune facility, adjacent to the open ditch
MI06010	soil	19.01.06	field 500m from the Fortune facility; unaffected by wastewater discharges
			Compeq
MI06003	sediment	17.01.06	XianGang River; 500 m upstream of discharge pipes
MI05050	wastewater	19.11.05	discharge channel #2; furthest upstream outfall
MI06006	sediment	18.01.06	discharge channel #2; furthest upstream outfall
MI06002	sediment	17.01.06	discharge pipe #2; new outfall 0.3m upstream of old outfall (MI06001)
MI06001	sediment	17.01.06	discharge pipe #2, old (now unused) outfall
MI06004	wastewater	18.01.06	discharge pipe #1
MI06005	wastewater	18.01.06	discharge channel #1, furthest downstream outfall

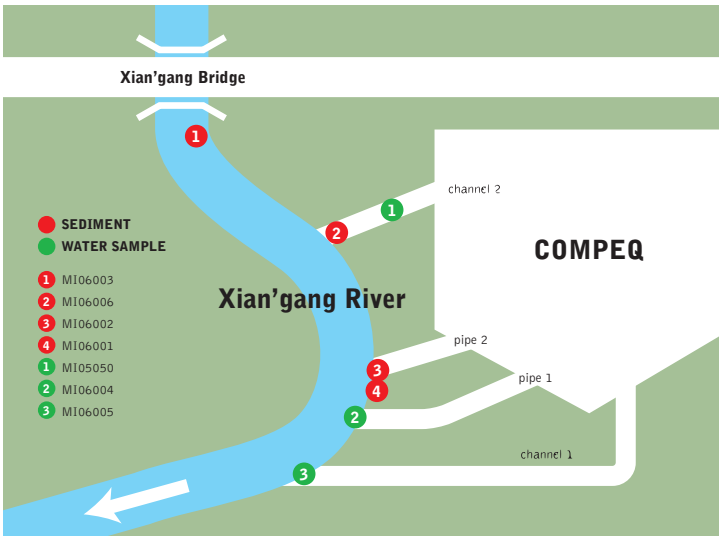

Figure 2.3 :: Sketch map of the locations from which samples were collected in the vicinity of the Compeq PWB manufacturing facility, China

2.1.2 :: Thailand

Five separate locations were investigated in Thailand, in each case where facilities are involved in the manufacture of PWBs. One location is a stand-alone facility (EETH), while the reminder are situated within Industrial Estates (IEs). Each of the Industrial Estates contains many individual facilities, some involved in the manufacture of PWBs, and many others involved in a range of industrial activities, though primarily centred on the manufacture of electronic devices. The five locations (and the individual PWB manufacturing facilities investigated within each Industrial Estate), as shown in Figure 2.4, are:-

- Elec & Eltek (EETH), Pathumthani Province
- Bangpa-in IE, Ayutthaya Province (CKL Electronics)
- Hi-Tech IE, Ayutthaya Province (KCE)
- Rojana IE, Ayutthaya Province (PCTT)
- Navanakorn IE, Pathumthani Province

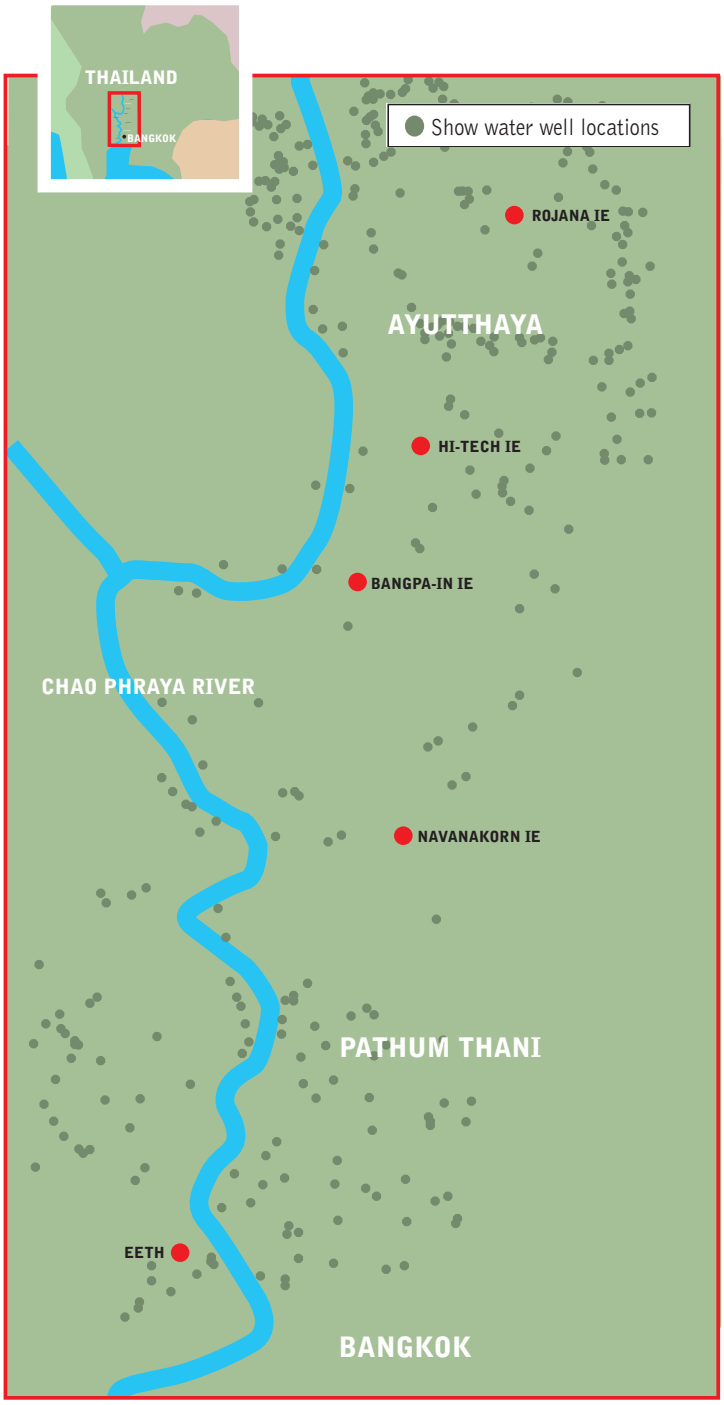

Figure 2.4 :: Map of the sites investigated in Thailand where facilities are involved in the manufacture of PWBs. Map derived from maps obtained from the Thailand Department of Groundwater Resources (www.dgr.go.th)

Detailed information on the exact processes employed is not available for all facilities. However, from information on some company websites it is known that the electroless copper process is used at the EETH and possibly other facilities. This process utilises water soluble copper compounds, hazardous chemicals such as formaldehyde, and chelating chemicals such as EDTA that impede the recovery of metals from wastewaters. In addition to copper, the use of nickel and other metals in the PWB manufacturing processes is widely reported, though detail on solvents, surfactants and other processes chemicals is not generally available (EETH 2006, CKL 2007, KCE 2007, PCTT 2006).

In May 2006, samples of groundwater were collected from the immediate vicinity of each of the five sites. In addition wastewaters, sediments and treatment plant sludges were collected from some of the sites. For each of the Industrial Estates there is at least one combined wastewater treatment plant (WWTP) that received wastewaters from many facilities within the estate. In some instances it was possible to collect wastewaters from individual PWB manufacturers prior to their treatment by WWTPs. In these instances, samples of treated wastewater were also collected from the WWTP, along with sludge and sediment samples where possible. Details of all samples are presented below and in Table 2.2.

At Elec & Eltek (EETH), a channel flows from west to east at the rear of the facility. There are no continuous direct discharges from EETH to the canal, but many small open pipes are visible on the banks of the channel below the EETH facility. Any liquids flowing through these pipes would be discharged into the channel. A sample of water and one of sediment were collected from this channel near the middle of the factory perimeter. A second sediment sample was collected from the channel at the upstream (western) edge of the factory perimeter. Two groundwater samples were collected to the north and southeast of EETH.

At the Navanakorn IE it was not possible to collect samples of wastewaters from PWB manufacturing facilities that operate within this industrial estate; PCTT. Four groundwater samples were collected; two to the northeast and one to the west of the estate as well as one from a residential property within the estate.

For the Bangpa-in, Hi-Tech and Rojana estates, wastewaters from individual facilities are carried via underground pipes to combined WWTPs. Manholes in front of individual facilities give access to individual wastewater inputs to the pipe network. At each estate, wastewater was collected from one of the PWB manufacturers as well as treated wastewater from the combined WWTP.

CKL, one of the two known PWB manufacturing facilities within the Bangpa-in IE was specifically sampled as collection of wastewaters from this facility was possible prior to their reaching the WWTP. It was not possible to collect wastewater samples form the other facility, Mectec. Wastewater was collected at its point of discharge from CKL via a manhole. Sediment was also collected from a separate manhole in which no water was flowing. Three samples were collected from the Bangpa-in WWTP that receives wastewaters from CKL and other facilities; one sample of treated wastewater at the point of discharge from the WWTP, and two samples of sludge from the many wastewater treatment tanks. Four groundwater samples were also collected from close to the Bangpa-in IE; one to the north, one to the south and one to the west of the estate as well as one from a drinking water tank within the CKL facility.

Ayutthaya, Thailand
Liquid dripping from a pipe above wastewater treatment tank inside a combined wastewater treatment plant of Bangpa-in Industrial Estate. 13 September 2006.

©GREENPEACE/SATAPORN THONGMA

table 2.2 :: description of wastewater, sediment, sludge and groundwater samples collected in from five separate sites in which facilities are involved in the manufacture of PWBs, Thailand

SAMPLE#	TYPE	DATE	SAMPLE LOCATION
			Elec & Eltek (EETH)
MI06024	wastewater	16.05.06	canal behind EETH; near the middle of factory perimeter
MI06025	Sediment	16.05.06	canal behind EETH; near the middle of factory perimeter, as MI06024
MI06026	Sediment	16.05.06	canal behind EETH; upstream (western) edge of the factory
MI06027	groundwater	16.05.06	groundwater tank; village 0.3 Km north (N) of EETH (G1185)
MI06028	groundwater	16.05.06	groundwater tank; village 1 Km southeast (SE) of EETH (MN0258)
			Navanakorn IE
MI06032	groundwater	16.05.06	groundwater tank; temple 1 Km northeast (NE) of estate (JICB0005)
MI06033	groundwater	16.05.06	groundwater tank; village 1 Km northeast (NE) of the estate (NB0052)
MI06034	groundwater	16.05.06	groundwater tank; temple 1 Km west (W) of the estate (MQ0546)
MI06059	groundwater	16.05.06	groundwater from a residential property within the estate
			Bangpa - in IE
MI06036	wastewater	26.05.06	CKL; manhole in front of facility containing flowing wastewater
MI06037	Sediment	16.05.06	CKL; manhole in front of facility; dry, no flowing water
MI06038	wastewater	26.05.06	combined WWTP; discharge treated wastewater
MI06039	Sludge	16.05.06	combined WWTP; one of many treatment tanks (dry tank)
MI06040	Sludge	16.05.06	combined WWTP; one of many treatment tanks (wet tank)
MI06035	groundwater	16.05.06	filtered drinking water; tank within the CKL facility
MI06041	groundwater	16.05.06	groundwater tank; school 3 Km north (N) of Bangpa-in IE (Q0859)
MI06043	groundwater	16.05.06	groundwater tank; school 1.5 Km south (S) of Bangpa-in IE (MQ0519)
MI06044	groundwater	16.05.06	groundwater tank; village 2 Km west (W) of Bangpa-in IE (G1223)
			Hi-Tech IE
MI06045	wastewater	17.05.06	KCE; manhole in front of facility
MI06046	wastewater	26.05.06	communal WWTP; treated wastewater pond, awaiting discharge to canal
MI06047	Sediment	17.05.06	communal WWTP; treated wastewater pond, as MI06046
MI06048	groundwater	17.05.06	groundwater tank; village 2 Km west (W) of estate (MQ0923)
MI06049	groundwater	17.05.06	groundwater tank; village 1.5 Km east (E) of Hi-Tech IE (MQ0521)
MI06050	groundwater	17.05.06	groundwater tank; school 2 Km northeast (NE) of Hi-Tech IE (G1344)
MI06051	groundwater	17.05.06	groundwater tank; village 2 Km southeast (SE) of Hi-Tech IE (14444)
			Rojana IE
MI06052	wastewater	26.05.06	PCTT; manhole in front of facility, pipe leading to WWTP (Phase 1)
MI06053	wastewater	17.05.06	WWTP (Phase 1); treated wastewater being discharged to a canal
MI06054	groundwater	17.05.06	groundwater tank; village 1.5 Km west (W) of estate (MQ0738)
MI06055	groundwater	17.05.06	groundwater tank; village 1 Km northwest (NW) of estate (MQ0629)
MI06056	groundwater	17.05.06	groundwater tank; village 1 Km southwest (SW) of estate (02578)
MI06057	groundwater	17.05.06	groundwater tank; temple 1.5 Km southeast (SE) of estate
MI06058	groundwater	17.05.06	groundwater tank; via an apartment, 1.5 Km east (E) of estate (17496)

Within the Hi-Tech IE, a sample of wastewater from the KCE facility was collected via a manhole. It was not possible to collected samples of wastewater from other PWB manufacturers known to operate within this estate. At the WWTP, treated wastewater is stored in a large pond prior to discharge to a public canal system. A sample of wastewater and sediment were collected from this pond. Four groundwater samples were also collected from close to the Hi-Tech IE; one to the west, one to the east, one to the northeast, and one to the southeast of the estate.

At the Rojana IE, wastewater was collected from the PCTT facility at its point of discharge to the underground pipe network leading to the Phase 1 WWTP. A sample of treated wastewater was collected from this WWTP as it was being discharged to an open canal system. Five groundwater samples were also collected from close to the Rojana IE; one to the west, one to the northwest, one to the southwest, one to the southeast and one to the east of the estate.

2.2 :: SEMICONDUCTOR CHIP MANUFACTURE; PHILIPPINES AND MEXICO

Facilities involved in the manufacture of semiconductor chips were investigated at three sites in the Philippines and one site in Mexico. The individual sites were;

- Philippines; Gateway Business Park Industrial Estate (IE), General Trias, Cavite
- Philippines; On Semicon, stand alone facility, Biñan, Laguna
- Philippines; Cavite Export Processing Zone (CEPZA) IE, Rosario, Cavite
- Mexico; Kemet, stand alone facility, Monterrey

The locations of the three sites in the Philippines are shown in Figure 2.5. The location of the Kemet facility in Monterrey, Mexico is shown on a map in Figure 2.6, in Section 2.3.

Figure 2.5 :: Map of the Philippines showing the location of three sites investigated with relation to the manufacture of semiconductor chips

It was not possible to collect wastewater from any of the facilities. To investigate impacts on the groundwater aquifers within the area of each site, samples of groundwater were collected from the vicinity of each site. A total of 20 samples were collected from the three sites in the Philippines in June 2006 and 1 sample was collected from within the Kemet facility in Mexico in February 2006. A summary of the samples collected is given in Table 2.3.

The Gateway Business Park IE in the Philippines is a mixed estate with facilities mostly engaged in the manufacture of electronic products. Located within this IE are Intel Philippines, a manufacturing and testing facility for Semiconductors and microprocessors, and Luzon Electronics, a subsidiary of Hitachi that is involved in the manufacture of hard drives. Four samples of groundwater were collected from locations within the estate.

table 2.3 :: description of groundwater samples collected from sites in the Philippines and Mexico where facilities are involved in the manufacture of semiconductor chips

SAMPLE#	TYPE	SITE	SAMPLE LOCATION
			Philippines
MI06060	06.06.06	Gateway IE	water tank; middle of Gateway IE
MI06061	06.06.06	Gateway IE	tap (groundwater) near Intel Philippines, northern part of Gateway IE
MI06062	06.06.06	Gateway IE	tap (groundwater) near the WWTP within Gateway IE
			(between MI06060 & MI06061)
MI06063	06.06.06	Gateway IE	tap (groundwater) near Luzon Electronics, southern part of Gateway IE
MI06064	06.06.06	On Semicon	handpump 200m to the northeast (NE) of On Semicon
MI06065	06.06.06	On Semicon	handpump 100m to the north (N) of On Semicon
MI06066	06.06.06	On Semicon	handpump 100m to the north (N) of On Semicon, 20m from MI06065
MI06067	06.06.06	On Semicon	handpump 500m to southwest (SW) of On Semicon; Barangay Maduya
MI06068	06.06.06	On Semicon	handpump 1 km to southwest (SW) of On Semicon; Barangay Maduya
MI06069	06.06.06	On Semicon	tap 750m to southwest (SW) of On Semicon; Health centre, B. Maduya
MI06070	06.06.06	CEPZA IE	tap; residential community 1 km north (N) of IE
MI06071	06.06.06	CEPZA IE	tap; residential community 1 km north (N) of IE, 150m east of MI07070
MI06072	06.06.06	CEPZA IE	water pump; residential community approx 2 km northeast (NE) of IE
MI06073	06.06.06	CEPZA IE	water tank within the IE; east side of IE
MI06074	06.06.06	CEPZA IE	water tank within the IE; east side of IE 250m south of MI07073
MI06075	06.06.06	CEPZA IE	tap within the IE; west side
MI06076	06.06.06	CEPZA IE	within IE, near the Danam facility; southeast side of IE
MI06077	06.06.06	CEPZA IE	within IE, near the MA Technology facility; southeast side of IE
MI06078	06.06.06	CEPZA IE	within IE, near the Keyrin Electronics facility; north side of IE
MI06079	06.06.06	CEPZA IE	within IE near Dae Duck facility; west side of IE 500m west of MI06075
			Mexico
MI06013	22.02.06	Kemet	Bathroom tap within the Kemet facility

On Semicon is a stand-alone facility that manufactures and tests semiconductor chips. The facility is located next to a small river, and a residential community is based to the northeast on the opposite side of the river downstream of On Semicon. Six samples of groundwater were collected in the vicinity of the facility; three from the residential community close to the northeast perimeter of the facility, and three from locations 0.5-1 km to the southwest in Barangay Maduya. Two of the groundwater samples by the northeast perimeter (MI06065 & MI06066) were collected from sources used by the community for drinking water.

The CEPZA IE is a large mixed use estate with over 250 facilities involved in a wide range of activities, including the manufacture of semiconductor chips and other electronic devices (PEZA 2007). A common WWTP is located within the Industrial Estate. A total of 10 samples of ground water were collected within and around this estate.

In Mexico, the Kemet facility in Monterrey is involved in the manufacture of capacitors and tantalum based chips. One sample of water was collected from a tap within a bathroom of the Kemet facility that is believed to be a source of groundwater, it is not known if this water had undergone purification treatment. Due to the location from which this sample was taken, it was not possible to collect the sample directly into a ground-glass stopper amber bottle, as described above. Instead the sample was collected in a clean, transparent PET water bottle.

Figure 2.6 :: Map of Mexico showing the locations of Tijuana and Guadalajara where sites involved in assembly were investigated, and also Monterrey, the site of the Kemet facility involved in semiconductor chip manufacture

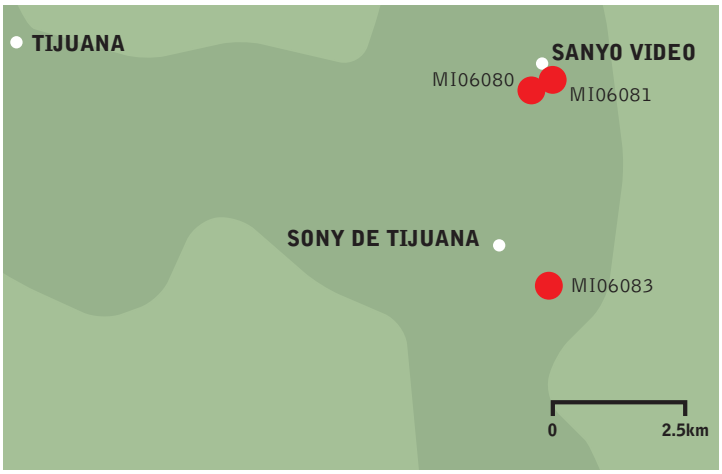

Figure 2.7 :: Map of the Tijuana area in Mexico showing the locations of component assembly facilities and some of the groundwater samples collected in their vicinities

2.3 :: COMPONENT ASSEMBLY, MEXICO

A number of locations were investigated in two areas of Mexico, Tijuana and Guadalajara, where facilities are involved in the assembly of computers and other electrical devices. The individual facilities and a brief description of their activities are given below;

Tijuana

- Sanyo Video; assemble televisions with liquid crystal displays (LCDs) or plasma screens
- Sony (stand alone facility); assemble televisions with LCDs or plasma screens

Guadalajara

- Parque Integral (Flextronics); an estate housing separate divisions of Flextronics that assemble PWBs, computer parts other electronic devices, plus facilities of their suppliers
- Jabil; assemble PWBs, PCs and other electronic devices
- Solectron; assemble PWBs, LCDs and other electronics devices
- Sanmina-SCI plant 3; assemble computer components
- HP; assembled personal computers (PCs) and other electronic devices
- IBM Site; assembled PCs, and hard disk components at the time of sampling. This site also houses Hitachi (assemble CD drives) and Sanmina SCI (assemble servers)

The locations of the Tijuana and Guadalajara sites in Mexico are shown in Figure 2.6. The sites of individual facilities and Industrial Estate located within the Tijuana and Guadalajara areas are shown in Figures 2.7 and 2.8 respectively.

Within each area, samples of groundwater were collected in the vicinity of the assembly facilities. Discharged wastewaters were also collected from one facility in Guadalajara as access to such samples was not possible for the other facilities investigated. A total of 13 samples of groundwater were collected from all sites; 4 samples from Tijuana in June 2006, and 9 samples from Guadalajara - 2 in February 2006 and 7 in June 2006. In addition, 2 samples of discharged wastewaters were collected from the IBM site, Guadalajara in June 2006. Details of the individual samples are given in Table 2.4.

In Tijuana, Sanyo Video is situated adjacent to two other facilities; one manufacturing electronic devices and the other, plastic products. Other facilities also involved in the manufacture of electronic products are sited a few kilometres to the north of Sanyo Video. Three samples of groundwater were collected from wells immediately to the south of the Sanyo Video facility. The second location in Tijuana was Sony, a stand-alone facility located approximately 5 km to the south of Sanyo Video. One groundwater sample was collected from a pumping station to the southeast of Sony.

The entrance of the Sanmina plant in Guadalajara, Mexico. June 2006.

table 2.4 :: description of groundwater and wastewater samples collected from facilities involved in the assembly of PWB, PC and other electronic devices, Mexico

SAMPLE#	DATE	SITE	SAMPLE LOCATION
			Groundwater
MI06080	09.06.06	Tijuana	Sanyo Video; covered well 400 m south (S) of Sanyo Video
MI06081	09.06.06	Tijuana	Sanyo Video; open well 250 m south (S) of Sanyo Video
MI06082	09.06.06	Tijuana	Sanyo Video; "new hope" well, close to Sanyo Video
MI06083	09.06.06	Tijuana	Sony; pumping station 1.5 km southeast (SE) of Sony (CESPT 41909)
MI06011	02.02.06	Guadalajara	Sanmina-SCI plant 3; well at rear of the facility
MI06012	15.02.06	Guadalajara	Flextronics; bathroom tap within the facility
MI06084	11.06.06	Guadalajara	Flextronics IE; 300 m north (N) of estate, from a dripping pipe
MI06085	11.06.06	Guadalajara	Flextronics IE; pumping station Well 61, adjacent to the estate entrance
MI06086	11.06.06	Guadalajara	Flextronics IE; 500 m northeast (NE) of estate, from a dripping pipe
MI06087	11.06.06	Guadalajara	Flextronics IE; groundwater tank 2 km northeast (NE) of estate
MI06088	11.06.06	Guadalajara	Jabil; groundwater tank 400 m northeast (NE) of the facility
MI06089	11.06.06	Guadalajara	Solectron; pipeline 2 km to the east (E) of the facility
MI06090	11.06.06	Guadalajara	HP; Well "San Sebastianito" immediately behind the facility
			Wastewater
MI06091	11.06.06	Guadalajara	IBM site; open channel #1, from storm water
MI06092	11.06.06	Guadalajara	IBM site; open channel #2 flowing from within the site

Six separate locations were investigated in the Guadalajara area. The Parque Integral is a large Industrial Estate owned by Flextronics. The estate houses a number of divisions of Flextronics that are involved in separate activities including the assembly of PWBs, other computer parts and other electronic devices. Some suppliers to Flextronics also have facilities within the estate. Five samples of groundwater were collected from the vicinity of the Flextronics facilities within this estate. One was collected in February 2006 from a bathroom tap within the Flextronics facility. The remainder were collected in June 2006; one from a pumping station adjacent to the estate entrance, two from pipes located very close to the estate, to the north and to the northeast, and one from a groundwater tank 2 km to the northeast.

For four other stand-alone facilities, one sample of groundwater was collected from locations near to each of the facilities. One sample was collected in February 2006 from a well located at the rear of Sanmina-SCI plant 3. The remainder were collected in June 2006; one sample from the "San Sebastianito" well located immediately behind the Hewlett Packard (HP) facility, one sample from a groundwater tank to the northeast of the Jabil stand-alone facility, and one sample from a groundwater pipe 2 km to the east of the Solectron facility. In the vicinity of the Solectron facility, groundwater is known to flow to the northeast.

Two samples of discharged wastewater were collected from the large IBM site in Guadalajara, Mexico, which has been producing electronic products since 1982. Within this large site, IBM assembled PCs and computers at the time of sampling. Two other facilities are also located within the IBM site; Hitachi (assemble hard drives and CD drives) and Sanmina SCI (assemble servers). The samples of wastewater were collected from separate open channels flowing from the IBM site. One channel (MI06091) carries combined wastewaters from two individual channels that join upstream of the sampling point; one of these is the discharged wastewater from within the site. The source of the other, and the relative contributions to overall wastewater flow and contaminant inputs to the combined channel, are not known. Similarly the exact source of the wastewater in the other channel that was sampled (MI06092) is not known, other than it originated within the IBM site.

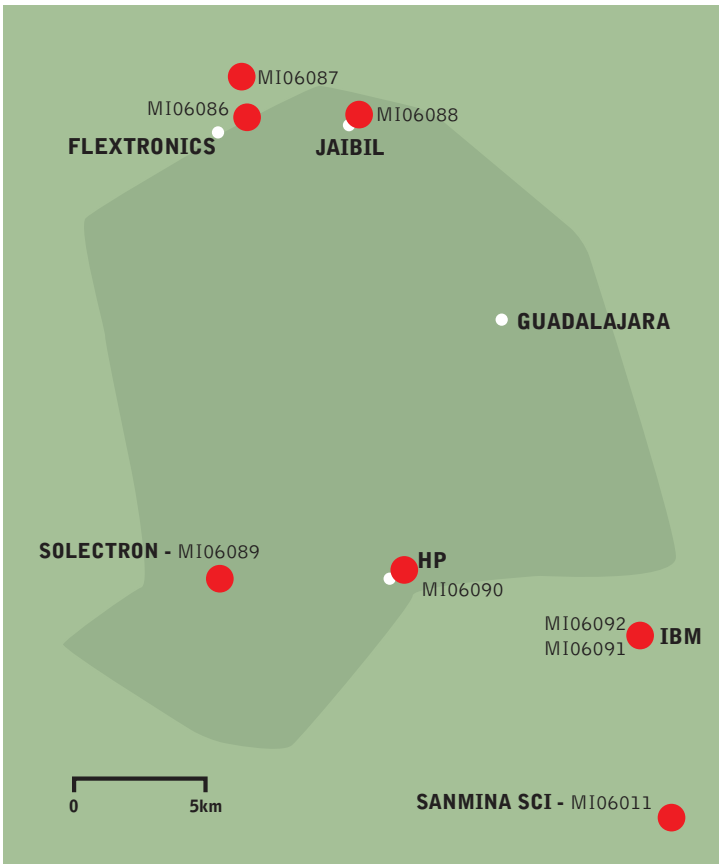

Figure 2.8 :: Map of the Guadalajara area in Mexico showing the locations of component assembly facilities and certain samples associated with them

3 :: METHODOLOGY

A RANGE OF DIFFERENT ANALYSES WAS CARRIED OUT ON THE VARIOUS SAMPLES COLLECTED DEPENDING ON THE SAMPLE TYPE. A SUMMARY OF THE TYPE OF ANALYSES FOR EACH GROUP OF SAMPLES IS GIVEN BELOW

	TYPE OF ANALYSIS		
SAMPLE TYPE	Metals (quantitative)	Extractable organic compounds (qualitative)	Volatile organic compounds (qualitative & quantitative)
Groundwater	√	-	√
Wastewater	√	√	√
Sediment	√	√	-
Sludge	√	√	-
Soil	√	√	-

Heavy metal concentrations were determined by ICP atomic emission spectrometry (AES), following acid digestion and using appropriate certified reference materials in addition to intra-laboratory standards. A wide range of metals and metalloids were quantified in all samples, the list being based on their known use in this sector & presence in e-waste recycling yards (Brigden et al. 2005). A full list of all elements quantified, and the method detection limits for different samples types is given in the Appendix.

Extractable organic compounds were isolated from each sample and identified as far as possible using gas chromatography and mass spectrometry (GC/MS), following liquid:solid extraction into a mixture of pentane and acetone for solid samples or liquid:liquid extraction with pentane only for wastewater samples. Volatile organic chemicals (VOCs) were identified and quantified in groundwater samples as received (with no pre-treatment) using GC/MS with HeadSpace sample introduction technique.

A full list of all VOCs that were used as a standards for Selective Ion Monitoring (SIM) GC/MS organic analysis, and for quantification of VOCs detected in water samples, is provided in the Appendix.

4 :: RESULTS AND DISCUSSION

FOR EACH MANUFACTURING SECTOR (PWB MANUFACTURING, SEMICONDUCTOR CHIP MANUFACTURE, ASSEMBLY) THE RESULTS FROM THE ANALYSES OF SAMPLES ARE PRESENTED AND DISCUSSED IN SEPARATE SECTIONS (4.1-4.3) AND THE DATA SUMMARISED IN TABLES 4.1-4.21.

For each sector, the data for individual sites are separately outlined. These data are collectively discussed for the sector as a whole towards the end of each section. Information on certain key pollutants detected during this study is presented in Text Boxes A-G.

Of the full range of metals and metalloids quantified in this study, a number were not present above method detection limits in any sample (arsenic, gallium, germanium, indium, mercury, selenium, thallium). For clarity these are not included in the individual results tables, but the detection limits for each is given in The Appendix.

It should be noted that all elements (metals and metalloids) quantified in this study are naturally found at some level in uncontaminated environmental samples such as soils, sediments, surface waters and groundwaters, though generally at low concentrations. Inputs from point sources such as industrial discharge can, however, result in levels that far exceed natural background concentrations. The following sections focus on those metals found at levels in the various samples that indicate levels above background due to inputs from industrial or other anthropogenic sources. In the case of organic contaminants, some of which may also have natural origins, the focus of discussions is on those compounds more likely to have arisen exclusively from man-made sources.

In the following sections the data from the analyses of the samples collected are presented and discussed separately for each of the three manufacturing sectors investigated in this study; printed wiring board (PWB) manufacture (Section 4.1), Semiconductor chip manufacture (Section 4.2), and component assembly (Section 4.3).

4.1 :: PRINTED WIRING BOARD (PWB) MANUFACTURE; CHINA & THAILAND

4.1.1 Facilities in China

A total of 13 samples were collected from the vicinity of two separate PWB manufacturing facilities in China. These included 4 wastewater samples, 6 sediment samples, 2 soil samples and 1 sample of groundwater. The results from these samples are presented in the tables below. Organic chemicals identified in all samples are presented in Tables 4.1, and 4.2 for the Compeq and Fortune facilities respectively. The metal quantification data for each facility are presented in Tables 4.3 and 4.4 respectively. VOCs were not quantified in the water samples associated with the Compeq and Fortune facilities.

Compeq

For the Compeq facility, sampling was carried out in November 2005 and January 2006. A single wastewater sample MI05050 was collected in 2005 from the most upstream discharge channel. In 2006, two more wastewater samples (MI06004 & MI06005) were collected from other discharges, as well as four sediment samples from discharge channels (MI06001, 02, 06) and the XianGang River (MI06003). The wastewater sample MI05050 contained the brominated flame retardant Tetrabromobisphenol A (TBBPA). Also present were diphenylmethone (benzophenone) and two derivatives of diphenylethone, and as well as a benzothiazole derivative. The two wastewater samples that were collected from other outfalls (MI06004 & MI06005) contained two PBDEs at trace levels: BDE-47 and BDE-99. One of these (MI06004) also contained an additional 7 brominated compounds that it was not possible to identify. Besides, all wastewater samples contained high concentrations of copper. The highest level was found in the sample collected from the most upstream outfall (MI05050) with copper at 811 µg/l. MI06004 contained about half this level (389 µg/l), while the level in MI06005 was far lower.

All sediment samples contained the same two PBDEs found in the wastewaters at trace levels, including that from the river upstream of Compeq, suggesting significant contributions from other sources. The outfall of pipe#2 had been recently moved. Sediment from the old outfall of pipe#2, MI06001, contained another PBDE (BDE-153) and one PCB congener (PCB-153). Both sediments from the old and the current outfall locations of pipe #2 contained a number of additional brominated compounds that could not be fully identified; 24 in the sediment from the old outfall (MI06001) and 7 from the new outfall location (MI06002).

Furthermore, all three sediments (MI06001, MI06002 and MI06006) collected close to wastewater outfalls contained copper and tin at very high levels. By far the highest concentrations were found in the sample from the most upstream outfall (MI06006), with copper at 21900 mg/kg (2.19%) and tin at 10800 mg/kg (1.08%). This sample also contained nickel and zinc at high concentrations, though to a lesser degree. The two sediments collected adjacent to pipe #2, located further downstream, (MI06001, MI06002) contained lower, but still elevated levels of copper (979-1460 mg/kg) and tin (194-355 mg/kg). For pipe #2, the higher levels were found at the current discharge point (MI06002), situated immediately upstream of the old and now unused discharge point (MI06001). In contrast, river sediment collected upstream of all wastewater discharges (MI06003) did not contain high metal concentrations indicating the high levels found were much more likely a direct result of discharges by Compeq.

table 4.1 :: organic chemicals identified in wastewater (WW) and sediment (Sed) samples from the Compeq PWB manufacturing facility, China. From left to right, samples are presented from upstream to downstreamlocations. The number of compounds reliably identified is presented for each group; (#) - signifies compounds identified at trace levels using a selective SIM method; (-) – not detected.

LOCATION	COMPEQ						
SAMPLE#	MI05050	MI06004	MI06005	MI06003	MI06006	MI06002	MI06001
SAMPLE TYPE	WW	WW	WW	Sed	Sed	Sed	Sed
No. of organic compounds isolated	27	19	6	18	33	17	43
No. reliably identified (% of total)	7 (26%)	2(11%)	2(33%)	6(33%)	12(36%)	2(12%)	5(12%)
PBDEs	-	(2)	(2)	(2)	(2)	(2)	(3)
PCBs	-	-	-	-	-	-	(1)
Tetrabromobisphenol A	(1)	-	-	-	-	-	-
Diphenylmethanone (benzophenone)	1	-	-	-	-	-	-
Benzoic esters and aldehyde	1	-	-	-	-	-	1
Diphenylethanone & derivatives	2	-	-	-	-		-
Sulphur or nitrogen compounds	2	-	-	-	-	-	-
Terpenoids	-	-	-	-	3	-	-
Aliphatic hydrocarbons	-	-	-	4	7	-	-

table 4.2.: organic chemicals identified in groundwater (GW), wastewater (WW), sediment (Sed) and soil samples from the Fortune PWB manufacturing facility, China. The number of compounds reliably identified is presented for each group; (#) - signifies compounds identified at trace levels using a selective SIM method; (-) – not detected.

LOCATION	FORTUNE					
SAMPLE#	MI05049	MI05051	MI06008	MI06009	MI06007	MI06010
SAMPLE TYPE	GW	WW	Sed	Sed	soil	soil
No. of organic compounds isolated	17	107	49	104	23	18
No. reliably identified (% of total)	2(12%)	25(23%)	17(35%)	45(43%)	3(13%)	4(22%)
PBDEs	-	(3)	(3)	7(12)	(3)	(2)
Tetrabromobisphenol A	-	(1)	-	-	-	-
Chlorinated benzene	(1)	-	-	-	-	-
Phthalates	1	3	-	-	-	-
Diphenylmethanone (benzophenone) and derivatives	-	2	-	1	-	-
Diphenylethanone derivative	-	1	-	-	-	-
Quantacure ITX	-	1	-	1	-	-
Cyclohexanone derivatives	-	2	-	-	-	-
Alkyl benzenes	-	5	-	19	-	-
Triphenyl phosphate (TPP)	-	1	-	-	-	-
Sterol derivatives	-	3	-	-	-	-
Other aromatic hydrocarbons	-	1	1	3	-	-
Fatty acids	-	2	-	-	-	-
Cyclic siloxane derivatives	-	-	-	-	-	1
Resin acid derivatives	-	-	-	1	-	-
Aliphatic hydrocarbons	-	1	13	1	-	1

table 4.3 :: metals quantified in groundwater (GW), wastewater (WW), sediment (Sed) and soil samples from the Compeq PWB manufacturing facilities, China. From left to right, samples are presented from up stream to downstream locations. Concentrations are given in mg/kg dry weight for sediment and soil samples, and µg/l for water samples. (-) - not detected.

LOCATION	COMPEQ						
SAMPLE#	MI05050	MI06004	MI06005	MI06001	MI06002	MI06003	MI06006
SAMPLE TYPE	WW	WW	WW	Sed	Sed	Sed	Sed
METAL	µg/l	µg/l	µg/l	mg/kg	mg/kg	mg/kg	mg/kg
Antimony	-	-	-	-	-	-	-
Barium	42	22	31	114	129	137	226
Beryllium	-	-	-	1.7	1.8	2.0	0.8
Bismuth	-	-	-	-	-	-	-
Cadmium	-	-	-	-	-	-	-
Chromium	-	-	-	14	15	15	22
Cobalt	-	-	-	35	48	73	49
Copper	811	389	60	979	1460	40	21900
Lead	-	-	-	42	48	46	40
Manganese	2315	130	32	521	440	389	1360
Molybdenum	-	-	-	-	-	-	-
Nickel	62	50	-	40	43	21	171
Tin	-	-	-	194	355	7	10800
Vanadium	-	-	-	49	54	57	15
Zinc	21	36	24	100	113	117	447

Image shows the inside of a laptop and the type of component produced and assembled in the factories that are highlighted in this report. 21 August 2006.

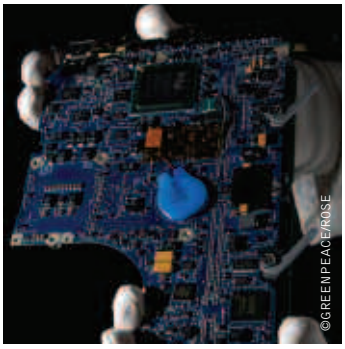

table 4.4 :: metals quantified in groundwater (GW), wastewater (WW), Sediment (Sed) and soil samples from the Fortune PWB manufacturing facility, China. Concentrations are given in mg/kg dry weight for sediment and soil samples, and µg/l for water samples. (-) - not detected.

LOCATION	COMPEQ						
SAMPLE#	MI05049	MI05051	MI05051	MI06008	MI06009	MI06007	MI06010
SAMPLE TYPE	GW	WW filtered	WW unfiltered	Sed	Sed	soil	soil
METAL	µg/l	µg/l	µg/l	mg/kg	mg/kg	mg/kg	mg/kg
Antimony	-	-	-	-	-	-	-
Barium	260	80	8200	127	217	113	62
Beryllium	-	-	8	2.4	1.8	2.3	1.1
Bismuth	-	-	-	-	-	-	-
Cadmium	-	-	-	<0.5	<0.5	<0.5	<0.5
Chromium	-	-	217	13	11	15	9
Cobalt	-	-	-	34	75	36	19
Copper	5	944	83900	143	23500	35	11
Lead	-	-	794	44	139	46	24
Manganese	220	137	568	263	260	301	372
Molybdenum	-	-	-	-	2	-	-
Nickel	-	314	4500	53	2690	21	9
Tin	-	-	1040	21	5610	-	-
Vanadium	-	-	35	52	36	57	28
Zinc	349	-	893	90	332	82	51

Fortune

Two sets of samples were collected from the Fortune facility: a groundwater (MI05049) and wastewater (MI05051) in November 2005 as well as four further samples in January 2006 including two sediment samples (MI06008 & MI06009) and two soil samples (MI06007 & MI06010).

Wastewater collected from the underground discharge channel from Fortune (MI05051) contained a large number of organic chemicals. These included;

- brominated chemicals: three PBDEs (BDE-47, BDE-99 and BDE-153), TBBPA and 18 additional brominated compounds that could not be fully identified.
- a phosphorus based flame retardant: triphenyl phosphate (TPP)
- photoinitiators and related compounds: derivatives of diphenylmethanone (benzophenone), diphenylethanone and a thioxanthen-9-one derivative known as "Quantacure ITX")
- three phthalate esters, dibutylphthalate (DBP), diisobutylphthalate (DiBP) and diethylhexyl phthalate (DEHP).
- other compounds including alkyl benzenes, aliphatic hydrocarbons, sterols derivatives and fatty acids

Discharge of wastewater was not occurring at the time of sampling. Wastewater in the underground channel was from a previous recent discharge, and contained a very high level of suspended solids which may have been due to resuspension of sediment that had accumulated in the channel over time from previous discharges. Therefore both total and dissolved (after filtration) metal concentrations were separately determined for this sample. Concentrations of dissolved copper (944 µg/l) and nickel (314 µg/l) were particularly high. Total metal levels (which includes the amounts in suspended solids) were far higher still, particularly for copper at 83900 µg/l. Other metals were also present at high levels in suspended material, particularly lead (794 µg/l), tin (1040 µg/l) and zinc (893 µg/l). The total metal levels indicate that the majority of each metal in the wastewater is mainly present in the suspended solids. This may be due to resuspension of sediment in the channel, sediment that has accumulated high levels of metals from discharged wastewaters over a longer period of time. Though possible, it is unlikely that the total levels of metals reflect the levels in wastewater as discharged.

Sediment samples from the underground channel and the ditch that it discharges into both contained PBDEs, including the tetrabrominated form BDE-47, the pentabrominated form BDE-99 and the hexabrominated form BDE-153 (which together are generally among the most abundant PBDEs found in environmental samples). The sediment from the underground wastewater channel (MI06009) contained by far the most PDBEs (19), many at well above trace levels. Both sediments contained at least 25 additional brominated compounds that could not be fully identified. The channel sediment (MI06009) also contained the photo-initiator related chemicals diphenylmethanone (benzophenone) and the thioxanthen-9-one derivative "Quantacure ITX", as well as a resin acid derivative and a range of alkyl benzenes. Metal concentrations in the channel sediment reflect the high levels in the discharged wastewater, with exceptionally high concentrations of copper (23500 mg/kg, 2.35%), tin (5610 mg/kg, 0.56%) and nickel (2690 mg/kg, 0.27%), and to a far lesser degree lead and zinc. Concentrations in the open ditch were far lower; only copper exceeded background levels at 143 mg/kg, nearly 200 times lower than in the channel.

Both soil samples also contained PBDEs and other brominated compounds that could not be fully identified; 18 in the soil collected adjacent to the open wastewater receiving ditch (MI06007), and 7 in the soil collected 0.5 km from the Fortune facility (MI06010). Metal concentrations in the soil sample MI06007 were moderately higher than in the soil collected 0.5 km from the Fortune facility (MI06010), though this was a consistent difference for all metals, i.e. there was no specific signature of contamination from those metals prevalent in the wastewater channel (copper, tin, nickel).

The one sample of groundwater (MI06049) contained a trace level of 1,4-dichlorobenzene and the phthalate ester dibutylphthalate (DBP). No brominated compounds were identified in this sample. Other than for zinc (349 µg/l), metal concentrations were not elevated in this groundwater.

4.1.2 :: Facilities in Thailand

32 samples associated with PWB manufacture in Thailand were collected in 5 separate locations, including 19 groundwater samples, 7 wastewater samples, 4 sediments and 2 sludge samples. The results of the organic analysis for wastewater, sediment and sludge samples are presented in Tables 4.5 & 4.7. VOCs were detected in only 5 water samples, which further underwent quantitative analysis (see Table 4.9 for results). The metal quantification data for wastewater and solid samples are presented in Tables 4.6 & 4.8; data for groundwater samples are presented in Tables 4.10-4.11.

Elec & Eltek (EETH)

5 samples were collected from the site of the EETH facility; one wastewater sample MI06024, two sediment samples MI06025 & MI06026 from the wastewater carrying canal, and two groundwater samples MI06027 & MI06028. The wastewater sample contained a high concentration of copper (3710 µg/l), and a range of chlorinated VOCs, though at trace levels, including chlorinated solvents (tetrachloromethane; di-, tri- and tetra-chlorinated ethenes and trichloroethane), hexachlorobutadiene, as well as trihalomethanes (THMs). THMs are chlorinated and brominated chemicals that are formed as by-products of chlorine based water disinfection. Other organic compounds detected in this sample were dichlorobenzene, camphor and two phthalate esters - diethyl phthalate (DEP) and diethylhexyl phthalate (DEHP).

Canal sediment from the same location (MI06025) contained a very high copper level (22650 mg/kg), i.e. with copper comprising over 2% of the sediment by weight. Other metals (beryllium, lead, nickel, tin and zinc) were also present at above background levels, though to a lesser degree. Levels of copper and tin were also high in canal sediment from the upstream edge of the factory (MI06026), though less than in MI06025. Both canal sediment samples contained dichlorobenzene and PBDEs at trace levels.

No elevated metal concentrations and no VOCs were detected in either of the two groundwater samples.

table 4.5 :: organic chemicals identified in wastewater (WW), sediment (Sed) and sludge samples from sites involved in the manufacture of PWBs; EETH and Hi-Tech IE, Thailand. The number of compounds reliably identified is presented for each group; (#) - signifies compounds identified at trace levels using a selective SIM method; (-) – not detected.

LOCATION	EETH			HI-TECH IE		
SAMPLE#	MI06024	MI06025	MI06026	MI06045	MI06046	MI06047
SAMPLE TYPE	WW	Sed	Sed	WW	WW	Sed
No. of organic compounds isolated	41	14	13	25	17	17
No. reliably identified (% of total)	15(36%)	4 (29%)	3 (23%)	12 (48%)	3 (18%)	2 (12%)
PBDEs	-	(3)	(2)	-	-	(2)
Chlorinated benzene	1	(1)	(1)	-	(1)	-
Trihalomethanes	(4)	-	-	(1)	-	-
Di- or tetrachloromethanes	(1)	-	-	(1)	-	-
Chlorinated ethanes/ethenes	(5)	-	-	-	-	-
Hexachlorobutadiene	(1)	-	-	-	-	-
Benzophenone, chlorophenyl	-	-	-	2	-	-
Benzophenone and its derivatives	-	-	-	3	-	-
Diphenylethanone derivatives	-	-	-	2	-	-
Xanthen-9-one derivative	-	-	-	1	-	-
Phthalates	2	-	-	1	1	-
Stigmast-5-en-3-ol	-	-	-	-	1	-
Benzoic acid and derivatives	-	-	-	1	-	-
Other aromatic hydrocarbons	1	-	-	-	-	-

table 4.6 :: metals quantified in wastewater (WW) and sediment (Sed) samples from sites involved in PWB manufacture; EETH & Hi-Tech IE, Thailand. Concentrations are given in mg/kg dry weight for sediment and sludge samples and µg/l for water samples. (-) - not detected.

LOCATION	EETH			HI-TECH IE		
SAMPLE#	MI06024	MI06025	MI06026	MI06045	MI06046	MI06047
SAMPLE TYPE	WW	Sed	Sed	WW	WW	Sed
METAL	µg/l	mg/kg	mg/kg	µg/l	µg/l	mg/kg
Antimony	-	-	-	-	-	-
Barium	33	153	147	30	15	125
Beryllium	-	5.8	1.1	-	-	1.7
Bismuth	-	-	-	-	-	-
Cadmium	-	-	-	-	-	-
Chromium	-	61	49	-	-	57
Cobalt	-	19	9	-	-	9
Copper	3710	22650	4260	1010	432	134
Lead	-	151	39	-	-	22
Manganese	732	224	116	2240	411	132
Molybdenum	-	-	-	-	-	7
Nickel	21	107	27	56	251	26
Tin	-	463	93	90	-	75
Vanadium	-	30	38	-	-	72
Zinc	65	190	70	77	295	77

Hi-Tech IE

Within the Hi-Tech IE, 7 samples were collected including two wastewater samples MI06045 (untreated KCE wastewater) & MI06046 (treated wastewater from WWTP), a single sediment sample MI06047 from the WWTP, and four groundwater samples MI06048-MI06051. The untreated wastewater from KCE (MI06045) contained the phthalate ester diisobutyl phthalate (DiBP) and a number of aromatic ketones (photoinitiators and related compounds); diphenyl-methanone (benzophenone) and two chlorinated diphenyl-methanone derivatives, two diphenyl-ethanone derivatives and a xanthen-9-one derivative chemically similar to "Quantacure ITX". Also present was a benzoic ester and two volatile chlorinated compounds; dichloromethane and chloroform at concentration of 1.1 µg/l and 1.9 µg/l respectively. The treated wastewater (MI06046) also contained a phthalate ester, diethylhexyl phthalate (DEHP), as well as traces of dichlorobenzene. Both wastewaters also contained high levels of copper and nickel. The wastewater from KCE (MI06045) contained the higher copper level (1010 µg/l), while nickel was higher (251 µg/l) in the treated wastewater (MI06046), which also had a somewhat elevated zinc level.

The sediment (MI06047) collected from the same WWTP pond as the treated wastewater sample (MI06046) contained copper and tin at somewhat high levels. The only organic compounds that could be identified in this sample were two PBDEs, both present at trace levels. Of the four groundwater samples, one (MI06049) contained two metals at above-background levels, namely zinc and nickel (the latter at 96 µg/l, or about 10 times background levels). To a lesser extent the level of zinc in two other groundwater samples (MI06048, MI06050) was also elevated. Neither the groundwater samples nor the treated wastewater sample collected from the WWTP contained any detectable VOCs.

Bangpa-in IE

Nine samples were collected from the Bangpa-in IE: two wastewater samples MI06036 (untreated KCL wastewater) & MI06038 (treated wastewater from WWTP), one sediment from a CKL manhole (MI06037), two WWTP sludge samples (MI06039-40), and four groundwater samples MI06035, MI06041, MI06043-44. The location of one of these samples (MI06041) is 3 km to the southwest of the Hi-Tech IE.

table 4.7 :: organic chemicals identified in wastewater (WW), sediment (Sed) and sludge samples from sites involved in the manufacture of PWBs; Bangpa-in IE and Rojana IE, Thailand. The number of compounds reliably identified is presented for each group; (#) - signifies compounds identified at trace levels using a selective SIM method; (-) – not detected.

LOCATION	BANGPA-IN IE					ROJANA IE	
SAMPLE#	MI06036	MI06038	MI06037	MI06039	MI06040	MI06052	MI06053
SAMPLE TYPE	WW	WW	Sed	Sludge	Sludge	WW	WW
No. of organic compounds isolated	63	39	14	32	14	29	32
No. reliably identified (% of total)	9(14%)	5(13%)	3(21%)	12(38%)	2(14%)	8 (28%)	8(25%)
PBDEs	-	(2)	(2)	(2)	(2)	(3)	-
Chlorinated benzene	-	-	(1)	-	-	(1)	-
Trihalomethanes THMs	-	-	-	-	-	(1)	(2)
Di- or tetrachloromethanes	-	-	-	-	-	(1)	-
Benzophenone, chlorophenyl	1	-	-	-	-	-	-
Other benzophenone derivatives	2	-	-	-	-	-	-
Diphenylethanone derivatives	2	-	-	-	-	-	-
Phthalate esters	-	1	-	-	-	1	3
Carbamodithioic acid, dimethyl-, methyl ester	-	-	-	-	-	-	1
l-Limonene	-	-	-	-	-	1	-
Benzoic acid and its derivatives	4	-	-	-	-	-	-
Cyclotetrasiloxanes	-	-	-	1	-	-	-
Other aromatic hydrocarbons	-	1	-	2	-	-	-
Aliphatic hydrocarbons	-	1	-	7	-	-	2

Both wastewaters contained high concentrations of copper, with the higher level (1780 µg/l) in the wastewater from KCL, while the treated wastewater contained 570 µg/l. Both wastewaters also contained nickel (59-114 µg/l) and zinc (134-153 µg/l) at notable levels. The two wastewater samples had different profiles of extractable organic compounds. Sample MI06036 from the CKL underground discharge pipe, contained a characteristic range of photoinitiators and related compounds; diphenylmethanone (benzophenone) derivatives including a chlorinated derivatives, two diphenylethanone derivatives, and a range of benzoic acid esters. Sample MI06038, treated wastewater from the WWTP where CKL and other facilities sends their wastewaters, contained dibutyl phthalate (DBP), two PBDEs (BDE-47 and BDE-99) at trace levels, and a terthiophene derivative, but none of the photoinitiator-related compounds were found in CKL's discharge.

The sediment sample MI06037, from a separate underground pipe of CKL (with no water flow at the sampling time), contained extremely high levels of copper (7.6% by weight) and tin (6.3%), as well as lead, nickel and zinc at elevated levels. This sample also contained the same two PBDEs found in the treated wastewater and dichlorobenzene, though all at trace levels.

Similarly, both sludge samples from the WWTP (MI06039 & MI06040) contained extremely high levels of those metals present in the wastewaters, namely copper (8.4-8.9%), tin (0.33-0.63%) and zinc (0.48-0.58%), as well as antimony, bismuth, nickel and lead at levels above background levels for uncontaminated environmental materials such as soils and sediments. The sludges also contained the same two PBDEs found in the treated wastewater. One of the sludge samples, MI06039, additionally contained a range of aliphatic hydrocarbons, a derivative of a cyclic siloxane, and diphenyl ether.

No VOCs were detected in any of the groundwater samples. Copper in MI06035 and zinc in MI06044 were present at levels slightly elevated above typical background levels for groundwater.

table 4.8 :: metals quantified in wastewater (WW), sediment (Sed) and sludge samples from sites involved in PWB manufacture; Bangpa-in IE & Rojana IE, Thailand. Concentrations are given in mg/kg dry weight for sediment and sludge samples and µg/l for water samples. (-) - not detected.

LOCATION	BANGPA-IN IE					ROJANA IE	
SAMPLE#	MI06036	MI06038	MI06037	MI06039	MI06040	MI06052	MI06053
SAMPLE TYPE	WW	WW	Sed	Sludge	Sludge	WW	WW
METAL	µg/l	µg/l	mg/kg	mg/kg	mg/kg	µg/l	µg/l
Antimony	-	-	-	70	49	-	-
Barium	95	36	792	286	327	37	33
Beryllium	-	-	0.4	0.4	0.3	-	-
Bismuth	-	-	-	79	106	-	-
Cadmium	-	-	-	-	-	-	-
Chromium	-	-	91	110	133	-	203
Cobalt	-	-	3	30	22	-	-
Copper	1780	570	75900	89000	84400	73	106
Lead	-	-	323	112	91	-	-
Manganese	479	311	603	1360	2500	26	73
Molybdenum	-	-	4	9	4	-	-
Nickel	59	114	114	1410	598	17	153
Tin	-	-	62600	3350	6290	-	81
Vanadium	-	-	19	15	8	-	-
Zinc	153	134	164	5790	4780	94	1470

Rojana IE

Among the 7 samples collected from the Rojana IE were two wastewater samples, MI06052 (untreated wastewater from PCTT) & MI06053 (treated wastewater from WWTP), and five groundwater samples, MI06054-MI06058. Both wastewater samples contained phthalate esters – diethylhexyl phthalate (DEHP) in PCTT wastewater and, in the treated wastewater (MI06053), a combination of diethylhexyl phthalate (DEHP), dibutyl phthalate (DBP) and diisobutyl phthalate (DiBP). The PCTT wastewater (MI06052) also contained chlorinated and brominated compounds (three PBDEs, dichloromethane, chloroform and dichlorobenzene). Dichloromethane and chloroform were present in this sample at concentration of 2.2 µg/l and 35.5 µg/l respectively. In addition to the phthalate esters listed above, the treated wastewater (MI06053) contained a derivative of carbamodithioic acid, two aliphatic hydrocarbons, chloroform (0.9 µg/l) and traces of bromodichloromethane. This treated wastewater also contained some metals above background levels for surface waters, including chromium, copper, nickel, tin and zinc. In the PCTT wastewater sample, only copper was present at the slightly elevated level of 73 µg/l.

Two groundwater samples collected near to the Rojana IE (MI06054 & MI06058) contained zinc at slightly elevated concentrations above background levels. No groundwaters contained any chlorinated VOCs, though two samples (MI06055 & MI06056) contained traces of the toxic compound phenol.

table 4.9 :: volatile organic chemicals (VOCs) quantified in groundwater (GW) and wastewater (WW) samples from sites involved in the manufacture of PWBs, Thailand. (-) - not detected.

SAMPLE#		MI06024	MI06045	MI06059	MI06052	MI06053
SAMPLE TYPE		WW	WW	GW	WW	WW
LOCATION		EETH	Hi-Tech IE	Navanakorn IE	Rojana IE	Rojana IE
COMPOUNDS		CONCENTRATION, µg/l				
THMS	Bromoform	<0.5	-	-	-	-
	Chloroform	<0.5	1.9	1.2	35.5	0.9
	Methane, bromodichloro-	<0.5	-	1.2	-	<0.5
	Methane, dibromochloro-	<0.5	-	-	-	-
CHLORINATED METHANES, ETHANES & ETHENES	Methane, dichloro-	-	1.1	-	2.2	-
	Methane, tetrachloro-	<0.1	-	-	-	-
	Ethane, 1,1,1-trichloro-	<0.5	-	-	-	-
	Ethene, 1,1-dichloro-	<0.1	-	-	-	-
	Ethene, 1,2-dichloro-, cis-	<0.5	-	-	-	-
	Ethene, trichloro-	<0.5	-	-	-	-
	Ethene, tetrachloro-	<0.1	-	-	-	-
	Hexachlorobutadiene	<0.5	-	-	-	-

Navankorn IE

Only groundwater samples were collected from the Navarkorn IE: MI06032-MI0634 and MI06059. No elevated metal concentrations were found in any sample. VOCs were detected only in MI06059; the compounds chloroform and bromodichloromethane. These THMs were both present at trace levels (1.2 µg/l).

table 4.10 :: metals quantified in groundwater (GW) samples from sites involved in PWB manufacture; Bangpa-in IE & Rojana IE, Thailand. (-) - not detected.

LOCATION	BANGPA-IN IE				ROJANA IE					
SAMPLE#	MI06035	MI06041	MI06043	MI06044	MI06054	MI06055	MI06056	MI06057	MI06058	MI06059
SAMPLE TYPE	GW	GW	GW	GW	GW	GW	GW	GW	GW	GW
METAL	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
Antimony	-	-	-	-	-	-	-	-	-	-
Barium	-	41	139	147	29	47	43	56	55	74
Beryllium	-	-	-	-	-	-	-	-	-	-
Bismuth	-	-	-	-	-	-	-	-	-	-
Cadmium	-	-	-	-	-	-	-	-	-	-
Chromium	-	-	-	-	-	-	-	-	-	-
Cobalt	-	-	-	-	-	-	-	-	-	-
Copper	49	-	-	-	-	-	-	-	-	-
Lead	-	-	-	-	-	-	-	-	-	-
Manganese	-	-	210	127	-	-	65	17	75	25
Molybdenum	-	-	-	-	-	-	-	-	-	-
Nickel	-	-	-	-	-	-	-	-	-	-
Tin	-	-	-	-	-	-	-	-	-	-
Vanadium	-	-	-	-	-	-	-	-	-	-
Zinc	-	-	20	50	71	-	-	-	67	-

table 4.11 :: metals quantified in in groundwater (GW) samples from sites involved in PWB manufacture; EETH, Navanakorn IE &- Tech IE, Thailand. (-) - not detected.

LOCATION	EETH		NAVANAKORN IE			HI-TECH IE			
SAMPLE#	MI06027	MI06028	MI06032	MI06033	MI06034	MI06048	MI06049	MI06050	MI06051
SAMPLE TYPE	GW	GW	GW	GW	GW	GW	GW	GW	GW
METAL	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
Antimony	-	-	-	-	-	-	-	-	-
Barium	118	125	93	47	198	57	14	27	66
Beryllium	-	-	-	-	-	-	-	-	-
Bismuth	-	-	-	-	-	-	-	-	-
Cadmium	-	-	-	-	-	-	-	-	-
Chromium	-	-	-	-	-	-	-	-	-
Cobalt	-	-	-	-	-	-	-	-	-
Copper	-	-	-	-	-	-	-	-	-
Lead	-	-	-	-	-	-	-	-	-
Manganese	97	110	144	-	-	119	29	24	213
Molybdenum	-	-	-	-	-	-	-	-	-
Nickel	-	-	-	-	-	-	96	-	-
Tin	-	-	-	-	-	-	-	-	-
Vanadium	-	-	-	-	-	-	-	-	-
Zinc	12	-	-	-	-	55	179	71	20

4.1.3 :: Discussion

Many similarities were seen in the chemicals identified in the wastewaters and other samples associated with the individual PWB manufacturing facilities located in China and Thailand. Similar patterns were seen in the distribution of certain groups of organic chemicals, and in those metals present at high concentrations, including;

- brominated flame-retardants, primarily polybrominated diphenyl ethers (PBDEs)
- phthalate esters
- chemicals used as photoinitiators, and related compounds
- chlorinated solvents
- benzoic acid esters
- heavy metals; primarily copper, nickel and zinc

Some groups of chemicals were found only in the wastewaters from PWB manufacturing facilities, while others were also present at other points, in wastewater pipes and channels, within communal WWTPs, and even in treated wastewaters discharged from WWTPs (although in this last case it is not possible to ascribe the presence of these chemicals to any individual chemical plant as many contribute wastewater to the treatment plant). In some cases accumulation was found in sediment and sludge samples collected from wastewater pipes and channels and communal WWTPs. Some heavy metals were found to have accumulated to very high levels in some of these samples.

Analysis of the organic chemicals in samples collected from the sites in China and Thailand has shown the complexity of the contaminants that arise from PWB manufacture. This was particularly obvious in case of the samples collected from China. The majority of the organic compounds that have been isolated during GC/MS screening analysis could not be reliably identified, partially due to the lack of the current databases on spectral characteristics of some industrial chemicals that have not been on the market for a long time, or which have not previously been recognised as significant environmental contaminants. Those chemicals include a range of brominated organic substances which it was possible to identify only as "polybrominated compounds" by Selective Ion Monitoring (SIM) GC/MS analysis (see Appendix for details of the analyses). It was found that 8 samples out of a total of 13 that were collected from the facilities in China contained unspecified brominated compounds which deserve further investigation. The number of such compounds ranged from 7 in samples MI06002, MI06004 and MI06010 to as many as 27 in sample MI06008. Both samples MI06007 and MI05051 contained 18 unspecified brominated organic compounds, samples MI06001 and MI06009 contained 24 and 25 compounds respectively. At the same time, other than groundwater, all samples from China were found to contain brominated organic compounds which were reliably identified, including congeners of PBDEs (in 9 samples) and TBBPA (in 2 samples) as discussed below. It is necessary to mention that samples containing brominated compounds were represented by wastewaters (MI05051 & MI06004), sediments (MI06001-MI06002 & MI06008-MI06009) and soil samples (MI06007 & MI06010). Therefore, the presence of these compounds in the environmental samples could have resulted from discharges or fugitive losses from the industrial sector in the investigated area.

Of all organic chemicals identified, the widest distribution was found for PBDEs, a group of polybrominated chemicals widely used as flame-retardants. Many PBDEs are environmentally persistent chemicals, and some are also toxic and highly bioaccumulative. More information on PDBEs is given in Text Box A.

PDBEs were identified in at least one sample collected from every site sampled, whether in wastewater or in sediments from wastewater channels and ponds. In almost all cases, the PDBE congeners identified at all sites were BDE-47, BDE-99 and BDE-153. All such samples contained two or three of these PDBE congeners, with the exception of one sample from the Fortune facility in China that contained these three along with many additional PBDEs.

PBDEs were found in discharged wastewaters from three facilities; Fortune and Compeq in China, and PCTT within the Rojana IE in Thailand. The wastewater from Fortune, and one of the wastewaters from Compeq also contained another brominated flame retardant, TBBPA, which is widely used in the manufacture of PWBs (in which it is generally polymerised, Lassen et al. 1999). The Fortune wastewater also contained a different type of flame retardant, TPP. This toxic chemical is an aryl phosphate, a phosphorus based chemical, different to the brominated compounds mentioned above. TPP was not found in any other sample. Additional information on TBBPA and TPP is given in Text Box A.

The river behind the Compeq factory in the Guangdong Province, China is slowly drying up. October 2006.

BOX A :: FLAME RETARDANTS

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 (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 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 (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 remains under consideration for inclusion as a POP (persistent organic pollutant) under the 2001 global Stockholm Convention (Peltola & Yla-Mononen 2001, UNEP 2006). Both "penta" and "octa" are now banned from use in Europe (EU 2003a). Within the electronics sector, use of PBDEs other than "deca" was prohibited from July 2006 under the Directive on Restrictions on Hazardous Substances (RoHS), associated with the WEEE Directive (EU 2002a, b).

Tetrabromobisphenol A (TBBPA), another form of brominated flame retardant, is used widely in various industrial and consumer products including electrical and electronic appliances (Lassen et al. 1999). This chemical is most frequently used in polymeric form, i.e. bound to the polymers in which it is incorporated, though a small percentage of total use is in additive uses (i.e. in a similar manner to the common additive flame retardants PBDEs and HBCD). Despite its primary use in reactive, polymeric forms, TBBPA has been found in the indoor environment, including in office dust samples (Leonards et al. 2001). It has been reported that TBBPA may interfere with the binding of thyroid hormones (Meerts et al. 1998, 2001), raising the potential for diverse effects on growth and development. Concerns have also been raised that TBBPA can induce oestrogen-like properties (Meerts et al. 2001, Samuelsen et al. 2001, Olsen et al. 2003), neurotoxicity (Mariussen & Fonnum 2003), immunotoxicity (Pullen et al. 2003), nephrotoxicity (Fukuda et al. 2004) or hepatotoxicity (Ronisz et al. 2004, Tada et al. 2006). However, most of the studies are in vitro studies and these are not used for the purpose of risk assessment.

A risk assessment report published by European Commission in 2006 (EC 2006) has concluded that "No health effects of concern have been identified for TBBP-A". This study has been prepared by the United Kingdom on behalf of the European Union and was based on the scientific publications up to 2004. But very recently the UK revised the environmental risk assessment to take into account new test data and exposure information provided by Industry (DEFRA 2006). "The exposure section was updated with site-specific monitoring data. Initial results of studies of degradation in anaerobic sewage sludge and anaerobic sediment were added. These show de-bromination of TBBPA to form bisphenol A, another substance being assessed under the Existing Substances Regulation. Other recent studies in the published literature also found evidence for debromination of TBBPA in the environment. TC NES agreed that this source of Bisphenol A to the environment should be considered further in an update to the Bisphenol A risk assessment". Finalisation of this revised environmental risk assessment, expected to identify some significant risks to the environment, is expected shortly.

Triphenyl phosphate (TPP), one of a number of so-called triaryl phosphates, has long been used as a flame retardant for polymers such as poly(butylene terephthalate) (PBT), an important polymeric material for the electrical and electronic industries and automotive production (Xiao et al. 2006) and in phenolic and phenylene oxide-based resins (IPCS 1991). This compound is not chemically bound to plastic material and therefore may be released into environment through leaching from polymers in which it is incorporated. As a result, phosphoric triesters have been detected in various environmental compartments such as air (Marklund et al. 2003, Hartmann et al. 2004, Carlsson et al. 1997), wastewater, surface and groundwater (Fries & Puttmann 2003), including location where electronic wastes are recycled (Brigden et al. 2005). 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).

Accumulation of PBDEs in sediments was also evident at some locations. At the Fortune and Compeq sites in China, the same PBDEs found in wastewater samples were also found in sediment samples collected from wastewater channels and the waterways into which they discharge. At the Compeq site, these PBDEs were also found in the XianGang River upstream of the wastewater discharge points and so there may be other inputs to the river upstream of Compeq.

The sediment sample (MI06009) from the Fortune wastewater channel contained by far the most PBDEs of all samples, many at well above trace levels. This sample, as well as the sediment from the open ditch to which wastewater is discharged, and the wastewater itself, also contained many additional polybrominated chemicals that could not be fully identified. It is possible that some of these were other PBDEs, a hypothesis which requires further investigation.

For two of the other PWB manufacturers, CKL within the Bangpa-in IE and the EETH facility (both in Thailand), PBDEs could not be detected in the wastewater from either facility, but were found in sediment samples from the wastewater discharge channels. This suggests previous discharge of wastewaters containing PBDEs, which generally have low water solubility and a high affinity for binding to sediment particulates.

The results demonstrate the distribution of PBDEs throughout wastewater discharge networks and treatment facilities, and in some cases the inability of the wastewater treatment processes to deal effectively with the presence of these chemicals in wastewaters. At three sites in Thailand where facilities are located within Industrial Estates (IEs), samples were collected from both an individual PWB manufacturing facility and a communal WWTP that receives wastewater from many different facilities. At one of these sites, the CKL facility within the Bangpa-in IE, the same PBDEs found in sediment collected from the CKL discharge pipe were also found in two samples of sludge from the WWTP as well as treated wastewater being discharged by the WWTP. PBDEs were also found in sediment from the treated wastewater pond of the WWTP at the Hi-Tech IE, presumably from wastewaters discharge to it from one or more facilities, though these were not found in the wastewater from the KCE facility at the time of sampling. It was not possible to collect sediment from the KCE discharge to see whether PBDEs had been previously discharged from this facility. At the Rojana IE, PBDEs were found in the wastewater from the PCTT facility though not in treated wastewater from the WWTP. It was not possible to collect sediment or sludge samples from this WWTP, which may have contained PBDEs accumulated from wastewaters discharged to it, found at the other sites. In all cases, the WWTPs receive wastewater from many facilities within the Industrial Estate, and therefore additional sources of PBDEs to the WWTP, from facilities other than the specific PWB manufacturers investigated, cannot be ruled out.

In addition to the distribution throughout the various wastewater networks, general background contamination with PBDEs was found in the vicinity of the two facilities in China. The XianGang River receives wastewater discharges from the Compeq facility. River sediment collected upstream of all discharge points contained two PDBEs that were also found in sediments collected by Compeq wastewater outfalls. However, many additional polybrominated compounds were found at the outfalls locations that were not present in the upstream river sediment. At the Fortune facility, two soil samples from the area showed traces of PDBE contamination. The soil collected adjacent to the wastewater ditch contained more PBDEs and other polybrominated compounds than the soil collected 500m from the Fortune site. It is not possible to distinguish the contribution to such general background contamination arising specifically from the PWB manufacturing facility from the contribution arising from other point and diffuse sources in the area.

Another class of chemicals found in wastewaters from individual facilities were phthalate esters, particularly DEHP, but also DiBP and DBP. Of these, DEHP was present in the wastewater from three facilities; PCTT (Rojana IE) and EETH, Thailand, as well as the Fortune facility in China. The latter also contained DiBP and DBP, while at the Hi-Tech IE (Thailand), DiBP was found in the wastewater from the KCE facility.

At one site, a phthalate ester discharged by an individual PWB manufacturer to a WWTP was also found in the treated wastewater discharged by the WWTP into the wider environment, though it is clearly not possible to state conclusively that the contamination had a common origin in both cases. The treated wastewater at the Rojana IE contained DEHP (also found in the PCTT wastewater), as well as DiBP and DBP which were not present in the PCTT wastewater. At the Hi-Tech IE and Bangpa-in IE, treated wastewaters from WWTPs also contained phthalates that were not found in the wastewaters from the PWB manufacturer investigated at each Industrial Estate. At some locations, there appear to be additional sources of phthalates to the communal WWTP.

Phthalates (phthalates esters) are predominantly used as plasticizers to soften plastics (especially PVC) and have undergone large-scale and ongoing releases to the environment (CSTEE 2001). They have been detected in various environmental compartments, including in the tissues of wildlife and in the human body (Otake et al. 2001, Butte & Heinzow 2002, Fromme et al. 2004, Colon et al. 2000, Blount et al. 2000, Silva et al. 2004). Phthalates are relatively persistent in the environment. Among the greatest concerns relate to the toxicity of some phthalates, including DEHP and DiBP, to the developing reproductive system in mammals (Ema & Miyawaki 2002, Mylchreest et al. 2002). More information on phthalates is presented in Box B.

Lao Zhao, one of the farmers who lives near the Compeq factory, preparing his meal by blowing through a bamboo tube to stoke the fire. Guangdong Province, China. October 2006.

BOX B :: PLASTICISERS - 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. Within the European Union (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 proteome formation as well as 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.

In addition to the widely distributed organic chemicals discussed above, some heavy metals were found at high concentrations either in discharged wastewaters or through the wastewater networks, including in samples from WWTPs.

Most significant among the contaminants found was copper, present at high concentrations in the wastewaters from all facilities (ranging from 60 µg/l to 3710 µg/l). For comparison, background concentrations of copper in uncontaminated surface waters can vary significantly but average levels are typically below 10 µg/l (ATSDR 2004, Salomons & Forstner 1984). Wastewater discharged by EETH had the highest copper concentration, over 300 times average background levels, and almost two times the maximum permitted level for industrial effluents in Thailand (2000 µg/l or 2.0 mg/l, PCD 2004). EETH is known to use the electroless copper process (EETH 2006), which uses soluble copper compounds and chelating chemicals that impede the recovery of metals from wastewaters (Walters et al. 2006). Some of the other facilities may also use this widely used process, though this cannot be confirmed without additional information.

Two other facilities sampled in Thailand (KCE and CKL) send wastewaters to WWTPs. Samples of these wastewaters also contained high copper concentrations (1010-1780 µg/l). At both sites, the treated wastewaters discharged from the WWTPs had somewhat lower levels (432-570 µg/l), and although these levels are below Thai discharge standards, they are still approximately 50 times average background copper concentrations. Similar copper levels were found in wastewaters discharged to waterways from the two facilities in China, Compeq and Fortune, which contained dissolved copper at 811 and 944 µg/l respectively, just below the maximum allowable national effluent standard for China of 1.0 mg/l (SEPA 1996).

Soluble copper compounds are widely used in PWB manufacture (Walters et al. 2006). In very high doses, copper can cause toxic effects in humans, though of greater concern is the impact of such discharges on aquatic organisms, may of which are highly sensitive to soluble copper even at very low doses. More information on the uses and effects of copper is given in Box C.

Treated wastewaters discharged by the WWTPs at the Bangpa-in, Hi-Tech and Rojana IEs in Thailand also contained elevated levels of nickel (114-251 µg/l) and zinc (134-1470 µg/l) and, in the case of the Rojana IE, tin (81 µg/l). These metals are generally present at far lower levels in uncontaminated fresh surface waters; nickel below 20 µg/l (ATSDR 2005b), zinc below 50 µg/l (ATSDR 2005c) and tin below 2 µg/l (ATSDR 2005d). High concentrations were not found in the individual wastewaters from the PWB manufacturers at the time of sampling, which suggests other facilities are the primary sources of nickel, zinc and tin to these WWTPs. However, wastewater from one facility, Fortune in China, did contain high levels of nickel and zinc as well as tin, though primarily in suspended rather than soluble forms, which may reflect accumulation of these metals in sediment within the channel from discharged wastewaters over some time

Nickel is widely used in the manufacture of PWBs, whereas the specific use of zinc is not well documented. Some processes employ water-soluble nickel compounds that have the potential to leach to groundwaters following release to the environment (Walters et al. 2006). Exposure to high concentrations of nickel can results in toxic effects, and some nickel compounds are carcinogenic to humans and animals (ATSDR 2005b, IARC 1990). More information on the uses and effects of nickel and zinc is given in Box C.

Tin is extensively used in PWB manufacture, in layering and etching processes as well as a component of electrical solder (Walters et al. 2006). Exposure to inorganic tin does not usually cause toxic effects in humans or animals, unless ingested in extremely large amounts (ATSDR 2003). However, the high concentrations of tin in some samples, together with other more toxic metals, demonstrate poor waste treatment and disposal practices.

Metals discharged in wastewater tend to bind to sediment particles and accumulate in bottom sediments. At all locations, the discharge of wastewaters containing high levels of heavy metals over considerable time has resulted in the accumulation of these metals (primarily copper, nickel, zinc and tin) to very high levels in discharge channel sediments as well as in sediments and sludges within WWTPs. Reflecting the levels in the wastewaters, copper was the most prevalent metal, with extremely high levels at some locations. At the Bangpa-in IE and EETH facility, Thailand, and at both facilities in China, for example where copper levels in sediments from discharge channels ranged from 22650-75900 mg/kg (2.3-7.6%). These levels are many hundreds of times higher than copper levels in uncontaminated sediments (ATSDR 2004, Salomons & Forstner 1984). The highest level found was in the CKL discharge channel at the Bangpa-in IE, over 1500 times typical background concentrations.

BOX C :: METALS

Copper is widely used within electronics products due to its high electrical conductivity, primarily as a pure metal, or as part of mixtures (alloys) with other metals, including beryllium (ATSDR 2004, OECD 2003). Levels of copper in the environment are typically quite low, with soils containing less than 30 mg/kg, and only slightly higher levels (less than 50 mg/kg) in freshwater sediments (Alloway 1990, ATSDR 2004, Salomons & Forstner 1984). Background concentration of soluble copper in uncontaminated surface waters can vary significantly, but average levels are typically below 10 µg/l (ATSDR 2004, Salomons & Forstner 1984).

Copper is an important element for humans and animals in low doses, though exposure to high levels of bioavailable copper can lead to bioaccumulation and toxic effects (ATSDR 2004). However, many aquatic organisms are extremely sensitive to copper, particularly in soluble forms, and releases of soluble copper compounds to aquatic environments can have significant impacts. Copper in soluble forms is highly mobile in the aquatic environment, particularly at higher acidity. 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 can occur at very low levels, including reductions in growth and fertility rates as well as increased mortality (Bryan & Langston 1992, UNEP 1993). Although dependent on many others factors, the majority of aquatic organisms cannot tolerate or survive at copper concentrations above 1 mg/l (1000 µg/l), and impacts can occur at concentrations as low as 0.05 mg/l (50 µg/l) for some sensitive organisms (Nor 1987, Salomons & Forstner 1984). The World Health Organisation (WHO) set a drinking water guideline value for copper of 2000 µg/l (WHO 2006).

Nickel is used in the manufacture of PWBs, primarily in the formation of metal surface finishes through electroplating, as well as in layering and etching processes used to produce the copper circuitry of the PWB (USEPA 1998). Nickel electroplating involves the use of water-soluble nickel compounds (USEPA 2001). Levels of nickel in the environment are typically quite low, with soils and freshwater sediments generally containing nickel below 60 mg/kg (Alloway 1990, ATSDR 2005b). Although nickel is generally persistent in soils, water-soluble nickel compounds can be quite mobile and have the potential to leach through soil and subsequently enter groundwater. Concentrations of nickel in uncontaminated surface waters are typically below 20 µg/l, while groundwater levels are generally below 10 µg/l (ATSDR 2005b, Salomons & Forstner 1984).

Very small amounts of nickel are essential for normal growth and reproduction in some animals and plants, and most likely also for humans (ATSDR 2005b, Alloway 1990). However, toxic and carcinogenic effects can result from exposure to higher concentrations for a wide range of life forms (ATSDR 2005b). Reported effects in humans include nausea, abdominal cramps, diarrhoea and vomiting, as well as cardiac effects following very high doses (ATSDR 2005b). A significant proportion of the population (2-5%) are nickel sensitive and effects can occur in sensitised individuals at far lower concentrations (ATSDR 2005b). Oral exposure to high nickel concentrations can also result in a range of toxic effects in many animals, predominantly gastrointestinal and cardiac effects, and nickel sensitisation has also been reported in some animals (ATSDR 2005b). Furthermore, some nickel compounds have been classified as carcinogenic to humans, and there is also evidence of carcinogenicity in animals (DHHS 2005, IARC 1990). The WHO set a nickel drinking water guideline value of 70 µg/l (WHO 2006), and in Thailand the groundwater quality level is 20 µg/l (SEPA 1996, PCD 2000).

Zinc

Reports on the manufacture of PWBs do not specifically list the use of zinc in the manufacturing processes employed (Walters et al. 2006). Elevated levels found in this study may be due to other manufacturing facilities within the industrial estates, though it remains a possibility that the PWB facilities may be contributing to the total load on the environment. Levels of zinc are generally quite low in the environment; in uncontaminated soils and sediments levels are typically below 100 mg/kg, while in uncontaminated fresh surface waters and groundwater levels are typically below 50 µg/l (ATSDR 2005c, Salomons & Forstner 1984).

Zinc is an essential nutrient for humans and animals, though exposure to high concentrations of bioavailable zinc can result in significant bioaccumulation with possible toxic effects (ATSDR 2005c). High doses of zinc in humans can induce a range of symptoms, including pancreatic damage, anaemia, gastrointestinal distress and diarrhoea. Similar effects are also seen in animals (ATSDR 2005c, Goyer 1996). The WHO does not set a drinking water guideline value for zinc, but levels up to 3 mg/l (3000 µg/l) are not considered unacceptable (WHO 2006).

Nickel and zinc were also present at elevated levels in sediments at these four sites, at levels (generally 2-4 times background levels), though to a far lesser extent than for copper (ATSDR 2005b, ATSDR 2005c, Salomons & Forstner 1984). Though not generally considered as a toxic metal, tin was also present at very high levels, ranging from 463-62600 mg/kg, the highest (over 6000 times background levels) again being found in the sediment from the CKL discharge channel (ATSDR 2003).

The impact of discharging heavy metals to WWTPs was clearly demonstrated at the Bangpa in IE. As seen for some organic chemicals (e.g. PDBEs), these facilities tend to concentrate metals into sludges, producing an additional contaminated wastestream. One of the sludge samples from this WWTP contained the highest levels of copper (89000 mg/kg, or 8.9% by weight), nickel (1410 mg/kg) and zinc (5790 mg/kg) of all samples.

Some groups of organic chemicals were found in samples from wastewater discharge pipes and channels from many of the individual PWB manufacturers, but were not present in any other samples from these sites. These included photoinitiator-related chemicals, benzoic acid esters, chlorinated solvents and trihalomethanes (THMs).

Photoinitiators are catalysts used in the photolithography processes, which is employed to print designs onto PWBs using UV light. More information is given on these compounds in Text Box D. Three similar groups of photoinitiator-related chemicals were commonly identified; diphenyl-methanone (also known as benzophenone) and its derivatives, diphenylethanone derivatives, and xanthen-9-one derivatives.

Photoinitiator-related chemicals were found in wastewaters collected from individual PWB manufacturers at four separate sites, in both Thailand (CKL in the Bangpa-in IE, KCE in the Hi-Tech IE) and China (Compeq and Fortune). A similar pattern of chemicals was found in the wastewaters from each of these facilities. Wastewater from all of the four facilities contained diphenylmethanone and the same diphenylethanone derivative (2,2-dimethoxy-diphenylethanone), while the related compound, diphenylethanedione was found in all but the Fortune wastewater.

There is little information available on the toxicity of the diphenylmethanone-related compounds. However, diphenylmethanone (or benzophenone) itself have been found to have toxic effects to liver and kidneys in animals (US DHHS 2000) and displayed potential hormone disrupting properties in several tests (Matsumoto et al. 2005, Kawamura et al. 2003). More information is given on these compounds in Text Box D.

Two other closely related chemicals, derivatives of diphenylmethanone, were also found in wastewaters from both the CKL and KCE facilities in Thailand; 2-chloro- and 2-hydroxy-diphenylmethanone. 2-Chlorodiphenylmethanone, also known as o-chlorobenzophenone, is known to be used as a photopolymerisation initiator for coating plastic mouldings (Adachi et al. 2005). Additional photoinitiator-related chemicals were also identified in wastewater samples, though each was only present in samples from one facility. These included three different derivatives of diphenylmethanone, and two xanthen-9-one derivatives. One of the latter, a thioxanthen-9-one derivate commonly known as Quantacure ITX, was present in the wastewater and underlying sediment in the discharge channel from the Fortune facility.

Quantacure ITX usually consists of several isomers of thioxanthone isopropyl derivatives. It has been widely used as a photoinitiator in inks in the flexographic printing industry (USEPA 2000). There is little information available on the properties of these chemicals, though it has been shown that thioxanthone-based compounds, including isomers of isopropylthioxanthone, can cause long-term effects in aquatic organisms at relatively low concentrations (USEPA 2000). Some additional information on thioxanthone-based photoinitiators is presented in Box D.

The Hi-Tech wastewater contained a related chemical, xanthen-9-one derivate. It was not possible to find any information about the toxicity of this compound. It is difficult to evaluate what effects on the environment and, consequently, wild life and human health, could be caused by such photoinitiator-related chemicals as their toxic properties have not been fully investigated.

BOX D :: PHOTOINITIATORS AND RELATED COMPOUNDS

Photoinitiators are additives that use ultraviolet (UV) or visible light to induce polymerisation, or to cure materials, as in the case of coatings and inks. Photoinitiators have extensive applications in the manufacture of printed circuits, encapsulation of electronic components, decorative coating, surface coating, etc. The main advantage of polymerization started by photoinitiators is temperature-independence and easy control. It can be conducted at very low temperatures and can be stopped simply by removing the light source.

Photoinitiators sold under various trade names including Quantacure, Irgacure, Darocure, Photocure, Vicure and others. Many photoinitiators that have been traditionally used by the industry in the past and those that remain in use are based on benzophenone (Allen et al. 1988, 1990, 1997, Eustis et al. 2006) and acetophenone (Torbiero et al. 2006, Umarji et al. 2005, Mijangos et al. 2006). Industrial developments during last two decades promoted fast growing research and synthesis of new chemicals that are used in the fields of photopolymerisation and photoimaging science and technology (Corrales et al. 2003, Yilmaz et al. 2004). As a result, new polymers bearing thioxanthone (Jiang et al. 2006), anthraquinone, camphorquinone or benzyl moieties (Seidl et al. 2006) have been synthesised. Information on these photoinitiators are mainly in the form of numerous patents. However, there is very little information on the toxicity of these new compounds. This is a major concern because it is unknown what effects they could cause on human health and the environment through use in, and release from, manufacturing processes.

Benzophenone based photoinitiators

Benzophenone itself and its derivatives are used as photoinitiators during production of UV-cured resins, inks and coatings (Eustis et al. 2006). Apart from this application, benzophenone has many other uses, including as a fragrance enhancer, and, occasionally, as a flavor ingredient. It is also used in the manufacture of insecticides, agricultural chemicals and pharmaceuticals and is an additive for plastics and adhesives (US DHHS 2000). In animals the liver is the primary target organ of benzophenone toxicity in rats and mice, based on increases in liver weights, hepatocellular hypertrophy, clinical chemistry changes, and induction of liver microsomal cytochrome P450 2B isomer. The kidney was also identified as a target organ of benzophenone toxicity in rats only, based on exposure concentration-related increases in kidney weights and microscopic changes (US DHHS 2000). Benzophenone and some of its derivatives displayed estrogenic activity in the MCF-7 cell proliferation assay (Matsumoto et al. 2005) and in the yeast two-hybrid assay (Kawamura et al. 2003).

Acetophenone based photoinitiators

One of the most widely used acetophenone-based photoinitiator is 2,2-dimethoxy-1,2-diphenylethanone, also known as 2,2-Dimethoxy-2-phenylacetophenone (DMPA) or "Photocure 51". DMPA is a photoinitiator which is added to polysiloxanes to produce photosensitive polymers that are widely used in silicon microelectronics (Torbiero et al. 2006, Umarji et al. 2005). Diphenylethanedione (also known simply as benzyl) is a raw material for production of DMPA. Another acetophenone-based photoinitiator, 2,2-diethoxyacetophenone, is used in the synthesis of telechelic polyurethane methacrylates which have widespread use in the coatings industry (Asha et al. 2005).

Despite the fact that acetophenone-based photoinitiators have been in use for over two decades, little information exists in the public domain concerning their toxicity. Acetophenone itself is a toxic chemical. Acute exposure of humans to acetophenone vapor may produce skin irritation and transient corneal injury. Acute oral exposure has been observed to cause hypnotic or sedative effects, hematological effects and a weakened pulse in humans. Congestion of the lungs, kidneys, and liver were reported in rats acutely exposed to high levels of acetophenone via inhalation (USEPA 2000). DMPA has been found to be toxic to HepG2 cells, a human hepatoma cell line, in dose-dependent manner during photopolymerisation experiments in tissue engineering (Liu & Bhatia 2002).

Thioxanthone based photoinitiators

Thioxanthones are widely used bimolecular photoinitiators in vinyl polymerisations. They have been employed in processes such as UV-cured printing inks, surface coating, microelectronics, and photoresists (Coralles et al. 2003). The thioxanthones were also often used in conjunction with other photoinitiators to design cost effective synergistic photoinitiator blends (Cho et al. 2003, Segurola et al. 1999, Andersen et al. 1996). Recently thioxanthone-based photoinitiators have received a revitalized interest because of their absorption characteristics at near UV range (Temel et al. 2006).

Isopropyl derivatives of thioxanthone are used as photoinitiators under the trade name Quantacure ITX in many applications, including production of UV-cured inks that comprise a comparatively new ink technology in the flexographic printing industry (USEPA 2000). Little information is available on these compounds, though derivatives of thioxanthone including isomers of isopropylthioxanthone are known to be of high aquatic hazard and capable of causing long-term effects in aquatic organisms even at concentrations of less than 0.1 mg/l (USEPA 2000).

Public and regulatory concerns arose around the proprietary product Quantacure ITX in September 2005, when a laboratory in Italy found that traces of this photoinitiator had been found in some milk products for babies. Quantacure ITX, which was used as a curing agent for ink on Tetra Pak's packaging, had migrated through packaging into the milk. Following this discovery, millions of litres of the baby milk were recalled or confiscated by government authorities.

Chlorinated chemicals, many commonly used as solvents, were found in wastewater at the EETH facility, and to a lesser extent at the PCTT facility on the Rojana IE, both in Thailand. Though present at only trace levels, the wastewater at EETH contained a range of these volatile chlorinated chemicals, while the PCTT wastewater contained only one, a chlorinated methane. Due to the volatile nature of these chlorinated chemicals, they can evaporate rapidly from waters and this may have contributed to the low levels found in these wastewater samples. It is possible that discharged wastewaters initially contained far higher levels. Wastewaters at some sites contained additional volatile chlorinated chemicals known as trihalomethanes (THMs). These chemicals are generally present due to use of chlorine based water disinfection rather than their intentional use in industrial processes.

Chlorinated solvents and THMs were also identified in many of the samples of groundwater collected in the vicinity of semiconductor chip manufacturing facilities investigated in this study, and these chemicals are further discussed under that section of the report (Section 4.2) with additional information provided in Boxes E & F.

Esters of benzoic acid were found in wastewater samples from the CKL and KCE facilities in Thailand and the Compeq facility in China. These chemicals are not of particular environmental concern as they can occur as natural components of plants (Dudareva et al. 2000), though their presence in the wastewaters at these three locations suggests their industrial application and provides further indications that similar processes are employed at the separate facilities.

The distribution of discharged chemicals through wastewater networks and treatment facilities was investigated at three sites where samples could be collected from WWTPs. A similar pattern was observed at these sites for some brominated flame-retardants (PBDEs), phthalates, and a number of metals. In many cases, representatives of these chemical groups were identified in the wastewaters from individual manufacturers and also in treated wastewater from the WWTP, as well as sludge and sediment samples from the WWTPs. These patterns of distribution suggest movement of the chemicals from individual facilities, through the wastewater network within the Industrial Estate and, in some cases, ultimately discharged from the WWTP into the wider environment. The accumulation of these chemicals in WWTP sludge and sediment samples further demonstrates the failure of the wastewater treatment processes employed to treat these chemicals effectively. Disposal of solid wastes such as WWTP sludge containing these chemicals, whether to landfill, poorly controlled dumps or incinerators, can provide additional routes of entry into the wider environment.

Some chemicals found in wastewaters from the CKL and KCE manufacturing facilities (photoinitiator-related chemicals, benzoic acid esters) were not found in treated wastewaters or solid samples from WWTPs. This pattern suggests that the WWTPs may be able to degrade these chemicals in wastewaters, at least to concentrations below the detection limits of the methods employed in this study. However, if this is the case, such treatment processes are not universally applied or effective as these, and other chemicals, were also found in wastewaters from the Fortune and Compeq facilities being discharged directly into the environment.

Impacts on groundwater

Although high levels of metals, particularly copper, were present in wastestreams from all sites, very high levels were not generally found in groundwater samples from the vicinity of these facilities. Only one groundwater sample contained copper at a detectable level, 49 µg/l in sample MI06035 collected from a water tank within the CKL facility. Though higher than in all other samples, which had copper levels below 20 µg/l, the level at this location is still within the range typically found in groundwater (ATSDR 2004). The only groundwater sample collected in China, adjacent to the Fortune facility, contained a high zinc level, though this groundwater did not contain high levels of copper and other metals that were present in discharged wastewaters. In Thailand, one sample collected to the east of the Hi-Tech IE (MI06049) contained somewhat higher levels of nickel (96 µg/l) and zinc (179 µg/l) than found in the majority of other groundwater samples. Levels of nickel and zinc in groundwater are typically below 10 µg/l and 50 µg/l respectively (ATSDR 2005b, ATSDR 2005c). One other sample collected close to the Hi-Tech IE also contained a slightly elevated level of zinc (71 µg/l), as did two of the five samples collected close to Rojana IE (67-71 µg/l). However, none of these samples contained high levels of copper, the most prevalent metal in the wastewaters at these sites. It is therefore not possible on the basis of the results from the current study to draw links between metal concentrations in groundwater and discharges from the PWB manufacturing sector.

table 4.12 :: volatile organic chemicals (VOCs) identified in groundwater (GW) samples from sites involved in the manufacture of semiconductor chips, Philippines and Mexico.

SAMPLE#	MI06060	MI06062	MI06068	MI06069	MI06073	MI06074	MI06075	MI06076	MI06077	MI06078	MI06079	MI06013
SAMPLE TYPE	GW	GW	GW	GW	GW	GW	GW	GW	GW	GW	GW	GW
LOCATION	GATEWAY IE PHILIPPINES		ON SEMICON PHILIPPINES		CAVITE PROCESSING ZONE IE PHILIPPINES							KEMET MEXICO
NO. OF VOC'S ISOLATED & RELIABLY IDENTIFIED	4	5	5	1	5	5	4	4	4	4	8	4
Trihalomethanes	(4)	(1)	-	-	-	-	(1)	(4)	(4)	-	(4)	(3)
Chlorinated methanes	-	(2)	-	-	-	-	-	-	-	-	-	-
Chlorinated ethanes	-	(2)	(1)	-	(1)	(1)	(1)	-	-	-	-	-
Chlorinated ethenes	-	-	(3)	(1)	(4)	(4)	(2)	-	-	(4)	(4)	(1)
Bis(chlorophenyl)sylfone	-	-	1	-	-	-	-	-	-	-	-	-

The somewhat elevated levels in these samples may be due in part to the activities at the nearby Industrial Estates, though other sources, including local geology cannot be discounted. Also the use of zinc and copper in water distribution piping can cause levels of these magnitudes. In all cases, the levels of copper and zinc found would not be expected to pose a risk to health in drinking water (WHO 2006) and do not exceed Chinese and Thai national groundwater quality levels. However, the one groundwater sample with elevated nickel, MI06049 collected to the east of the Hi-Tech IE, contained a level (96 µg/l) that exceeds both the Thai groundwater quality level of 20 µg/l and the World Health Organisation (WHO) drinking water guideline value of 70 µg/l (SEPA 1996, PCD 2000, WHO 2006). This potential contamination deserves further investigation.

All groundwater samples collected from these sites were generally free of organic chemicals. No chlorinated organic chemicals were found in any of the samples, other than two THMs in one sample, most likely as a result of chlorine based water disinfection. Other than chlorinated solvents, the organic chemicals highlighted in the wastewaters from the PWB manufacturing facilities, such as PBDEs, tend to have very low mobility in soils and would not be expected to be seen in groundwaters.

4.2 Semiconductor chip manufacture; Philippines & Mexico

Twenty-one groundwater samples associated with semiconductor chip manufacture were analysed for metals and VOCs. Twenty of these samples were collected from three sites in the Philippines: Gateway Business Park IE, On Semicon, and Cavite Processing Zone IE (CEPZA IE).

A single groundwater sample was collected from within the Kemet manufacturing facility in Monterrey, Mexico. VOCs were detected in 12 of the 21 samples (11 of the 20 from the Philippines and in the single sample from Mexico). Quantitative analysis was carried out on 11 of these samples (the sample from Mexico was not quantified due to the method of collection). A summary of the VOCs identified in the samples is presented in Table 4.12 and the levels of individual VOCs is presented in Table 4.13. The metals data for these samples are presented in Tables 4.14-4.15.

4.2.1 Facilities in Philippines

Gateway Business Park IE

Of the four samples that were collected from the Gateway Business Park IE, two (MI06060 & MI06062) contained low levels of VOCs, none of which were identified in the other two samples (MI06061 & MI06063). All four trihalomethanes (THMs) were detected in sample MI06060; bromoform and dibromochloromethane at concentrations 1.4 µg/l and 0.7 µg/l respectively; chloroform and bromodichloromethane at below the level of quantification (0.5 µg/l for each). Sample MI06062, which contained one THM (chloroform) at trace level, also contained other chlorinated compounds including chloromethane and chloroethane at concentrations of 0.8 µg/l and 5 µg/l respectively; dichloromethane and 1,1-dichloroethane were present, though at trace level. MI06062 was collected from a location between those of MI06060 & MI06061.

table 4.13 :: volatile organic chemicals (VOCs) quantified in groundwater samples from sites involved in the manufacture of semiconductor chips; Gateway Business Park IE and Cavite Processing Zone IE, Philippines. (-) - not detected.

SAMPLE#	MI06060	MI06062	MI06068	MI06069	MI06073	MI06074
LOCATION	GATEWAY IE PHILIPPINES		ON SEMICON PHILIPPINES			
COMPOUND					CONCENTRATION,µg/l	
					TRIHALOMETHANES (THMS)	
Bromoform	1.4	-	-	-	-	-
Chloroform	<0.5	<0.5	-	-	-	-
Methane, bromodichloro-	<0.5	-	-	-	-	-
Methane, dibromochloro-	0.7	-	-	-	-	-
					CHLORINATED METHANES	
Methane, chloro-	-	0.8	-	-	-	-
Methane, dichloro-	-	<0.5	-	-	-	-
					CHLORINATED ETHANES	
Ethane, chloro-	-	5.0	-	-	-	-
Ethane, 1,1-dichloro-	-	<0.5	<0.5	-	0.8	<0.5
Ethane, 1,1,1-trichloro-	-	-	-	-	-	-
					CHLORINATED ETHANES	
Ethene, 1,1-dichloro-	-	-	-	-	1.9	0.3
Ethene,1,2-dichloro-, cis-	-	-	21.3	1.4	28.9	20.0
Ethene,1,2-dichloro-, trans-	-	-	0.3	-	-	-
Ethene, trichloro-	-	-	1.6	-	12.8	6.4
Ethene, tetrachloro-	-	-	-	-	0.5	0.3

MI06075	MI06076	MI06077	MI06078	MI06079
CAVITE PROCESSING ZONE IE PHILIPPINES				
15.4	1.4	5.0	-	0.8
-	<0.5	1.6	-	0.5
-	0.8	4.0	-	<0.5
-	1.8	7.7	-	0.9
-	-	-	-	-
-	-	-	-	-
-	-	-	-	-
<0.5	-	-	-	-
-	-	-	-	-
-	-	-	19.0	0.2
-	-	-	31.9	2.8
-	-	-	-	-
3.3	-	-	14.5	<0.5
2.7	-	-	350	0.1

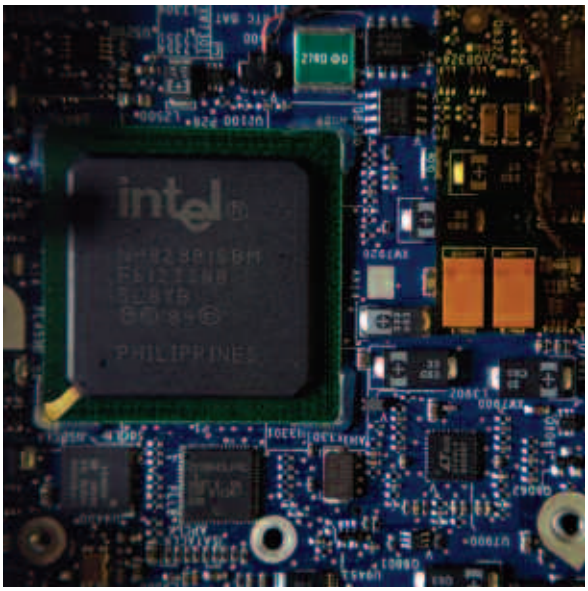

Image shows a chip produced by INTEL in the Philippines. Water samples were taken from the underground wells near the INTEL industrial complex highlighted in this report. 21 August 2006.

The sample collected in the northern part of the IE near Intel Philippines (MI06061) contained levels of copper (233 µg/l) and zinc (246 µg/l) higher than typical groundwater levels. All other samples contained copper below 20 µg/l. Somewhat less elevated levels of zinc (138-144 µg/l) were also present in MI06062 and MI06063, though not in sample MI06060 collected from a location between those of MI06062 and MI06063. Levels of zinc in groundwater are typically below 50 µg/l (ATSDR 2005c). In addition, all four samples contained very similar levels of vanadium (65-68 µg/l), above typical background levels for groundwater.

On Semicon (also know as 'On Semiconductor')

Of the six samples (MI06064 – MI06069) collected close to the On Semicon facility, all but one sample contained elevated levels of zinc, though levels of other metals may be considered normal for uncontaminated waters. The highest zinc levels were found in samples collected closest to the facility. To the southwest, MI06067 collected 500m from the facility contained 631 µg/l, with levels dropping to normal background levels for the sample furthest from the facility (MI06068). To the north, a sample collected 100m from the facility (MI06065) contained the highest level of all samples (852 µg/l), though a sample collected only 20m from this location had a somewhat lower level, 201 µg/l. Levels of zinc in groundwater are typically below 50 µg/l (ATSDR 2005c).

table 4.14 :: metals quantified in groundwater samples from sites involved in the manufacture of semiconductor chips; Gateway Business Park IE, On Semicon (Philippines) and Kemet (Mexico). (-) - not detected

LOCATION	GATEWAY BUSINESS PARK IE, PHILIPPINES	
SAMPLE#	MI06060	MI06061
METAL	µg/l	µg/l
Antimony	-	-
Barium	-	7
Beryllium	-	-
Bismuth	-	-
Cadmium	-	-
Chromium	-	-
Cobalt	-	-
Copper	-	233
Lead	-	-
Manganese	44	23
Molybdenum	-	-
Nickel	-	-
Tin	-	-
Vanadium	65	68
Zinc	-	246

table 4.15 :: metals quantified in groundwater samples from sites involved in the manufacture of semiconductor chips; CEPZA IE, Philippines (-) - not detected.

LOCATION		
SAMPLE#	MI06070	MI06071
METAL	µg/l	µg/l
Antimony	-	-
Barium	34	52
Beryllium	-	-
Bismuth	-	-
Cadmium	-	-
Chromium	-	-
Cobalt	-	-
Copper	-	-
Lead	-	-
Manganese	239	183
Molybdenum	-	-
Nickel	-	-
Tin	-	-
Vanadium	-	-
Zinc	255	20

GATEWAY BUSINESS PARK IE, PHILIPPINES				ON SEMICON, PHILIPPINES				KEMET, MEXICO
MI06062	MI06063	MI06064	MI06065	MI06066	MI06067	MI06068	MI06069	MI06013
µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
-	-	-	-	-	-	-	-	-
-	6	22	15	-	40	68	24	71
-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-
24	-	383	398	305	206	2410	364	-
-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-
66	67	-	-	-	-	-	-	-
138	144	128	201	852	631	23	469	-

CEPZA IE, PHILIPPINES							
MI06072	MI06073	MI06074	MI06075	MI06076	MI06077	MI06078	MI06079
µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
-	-	-	-	-	-	-	-
-	41	45	34	71	71	52	24
-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-
-	-	-	-	26	-	27	-
-	-	-	-	-	-	-	-
23	66	63	-	73	29	16	-
-	-	-	-	-	-	-	40
-	-	-	-	46	20	28	54
-	-	-	-	-	-	-	-
-	-	-	39	-	-	-	-
1770	-	-	48	236	-	-	-

No VOCs were found in any of the three samples collected to the north of On Semicon (MI06064-MI06066), nor in the sample collected to the southwest, closest to the facility (MI06067). Unexpectedly, the most contaminated sample was that collected furthest from On Semicon (MI06068), which contained five volatile organic chemicals, namely 1,1-dichloroethane, cis- and trans-isomers of 1,2-dichloroethene, trichloroethene, and bis(chlorophenyl)sulfone. This suggests significant groundwater contamination, but arising from a different facility. A further sample (MI06069), collected closer to the facility than MI06068, contained only one of these compounds, the trans-isomer of 1,2-dichloroethene, and at a far lower level that in MI06068.

Cavite Processing Zone IE

Of the 10 groundwater samples from CEPZA IE, 7 contained VOCs. In contrast, three samples collected outside the Industrial Estate, to the north and northeast (MI06070-72), did not contain any VOCs. Two samples (MI06076 & MI06077) collected on the southeast edge of Industrial Estate contained only THMs, chemicals formed as by-products of chlorine based water disinfection.

Of the THMs identified in all samples, bromoform was detected in four samples in the range from 0.8 µg/l (MI06079) to 15.4 µg/l (MI06075). Chloroform, bromodichloromethane and dibromochloromethane were detected in three samples (MI06076, MI06077 and MI06079), the highest concentrations being found in sample MI06077, at levels of 1.6 µg/l, 4 µg/l and 7.7 µg/l respectively.

In addition to the THMs, other chlorinated VOCs were found in five samples, all collected within the Industrial Estate, closest to its centre. The most contaminated samples were those collected in the northern (MI06078) and eastern (MI06073 & MI06074) side of the Industrial Estate. These samples contained a range of chlorinated ethenes (isomers of dichloroethene, trichloroethene and tetrachloroethene) and a chlorinated ethane (1,1-dichloroethane), suggestive of localised industrial inputs, perhaps from spills or leaks from storage tanks or transfer operations. Two samples collected in the western edge of the Industrial Estate (MI06075 & MI06079) also contained chlorinated ethenes, though fewer chemicals were found in these samples, and in lower concentrations.

The sample from the northern part of the Industrial Estate (MI06078) contained the highest concentrations of all the chlorinated ethenes identified, namely: 1,1-dichloroethene (19 µg/l), cis-1,2-dichloroethene (31.9 µg/l), trichloroethene (14.4 µg/l) and tetrachloroethene (350 µg/l). The two eastern samples (MI06073 & MI06074) contained similar but slightly lower levels of dichloroethene and trichloroethene, but far lower levels of tetrachloroethene (0.3-0.5 µg/l) and 1,1-dichloroethene (0.3-1.9 µg/l). Of these two samples, that collected closest to the centre of the Industrial Estate (MI06073) contained the higher levels of all chlorinated ethenes. In addition, both samples from the eastern part also contained 1,1-dichloroethane, though at trace levels in both samples. The distribution pattern of VOCs at this site, and implications from the use of groundwater as drinking water, are discussed in Section 4.2.3 below, for all sites.

In addition to the VOCs, a number of samples contained one or more metals at elevated concentrations. In general, the samples containing high levels of metals were different to the samples containing chlorinated ethanes and ethenes. High levels of zinc were found in 3 samples; two from locations outside the Industrial Estate to the north and northeast (MI06070 & MI06072), and one from the southeast edge of the Industrial Estate furthest from its centre (MI06076). These samples were free of VOCs, other than the THMs in sample MI06076. By far the highest zinc level was found in MI06072 (1770 µg/l), far higher than background levels in groundwater, which are typically below 50 µg/l (ATSDR 2005c). The most western sample (MI06079), which did contain VOCs (THMs and chlorinated ethenes), also contained nickel (54 µg/l) and molybdenum (40 µg/l) at levels slightly above typical groundwater background levels.

4.2.2 :: Facilities in Mexico; Kemet

A single sample of groundwater MI06013 was collected within the Kemet facility in Monterrey, Mexico. This sample contained 1,2-dichloroethene and three THMs (chloroform, bromodichloromethane and dibromochloromethane). All were detected at trace levels, though the precise levels were not quantified due to the method of collection for this sample. No metals were present above typical background levels.

Due to the method of collection and storage of this sample, it is possible that some VOCs may have been lost from the water sample by evaporation prior to analysis. It is possible that the water at source contains those VOCs identified above trace levels, including 1,2-dichloroethene, and may have contained additional VOCs to those identified.

4.2.3 :: Discussion

Of the four sites investigated in this sector, VOCs were found in one or more sample collected from each site. At all sites the VOCs identified including chlorinated chemicals commonly used as industrial solvents or degreasing agents, in addition to THMs which are commonly found as by-products of chlorine based water disinfection.

However, only the samples from the CEPZA IE site gave a clear indication of groundwater contamination arising from site under investigation. The data for the CEPZA IE in the Philippines clearly demonstrates contamination of the groundwater with chlorinated VOCs, with the highest degree of contamination centred within the IE. The distribution pattern of VOCs in the samples indicates that one or more facilities within the estate, probably in the northern/eastern part, are a source of chlorinated ethenes and ethanes to the groundwater aquifer.

At the On Semicon site, the distribution pattern of VOCs indicates that this facility is not the source of the VOCs in the groundwater in the area; rather another so far unidentified source is likely to exist to the south of the On Semicon facility.

For two other sites, the situation is less clear again; the Gateway IE (Philippines) and the Kemet facility (Mexico). VOCs were found in only one of the four samples from the Gateway IE and all at relatively low levels. While there is no clear pattern of groundwater contamination, there may be a source of chlorinated VOCs in the vicinity of the WWTP from where sample MI06062 was collected. At the Kemet facility, 1,2-dichloroethene was found in the one sample collected, though it was not possible to quantify the level of this chemical, nor to speculate on its origins. As mentioned above, due to the method of collection it is possible that some VOCs may have been lost from the water sample by evaporation prior to analysis.

BOX E :: DISINFECTION PRODUCTS - TRIHALOMETHANES (THMS)

THMs (trichloromethane or chloroform, tribromomethane or bromoform, bromodichloromethane and dibromochloromethane) are formed in drinking water primarily as a result of chlorination of organic matter present naturally in raw water supplies during disinfection. The rate and degree of THM formation increase as a function of the chlorine and humic acid concentration, temperature, pH and bromide ion concentration. Chloroform is the most common THM and the principal disinfection by-product in chlorinated drinking water. In the presence of bromides, brominated THMs are formed preferentially and chloroform concentrations decrease proportionally. THMs are not expected to be found in raw water (unless near a pollution source) but are usually present in finished chlorinated water. Although the THMs identified in groundwater samples in the current investigation are unlikely to be linked directly to industrial activities at the electronics manufacturing plants under study, the following background information is provided as their presence is nevertheless of some toxicological and environmental significance.

Two THMs, chloroform and bromodichloromethane, are established animal carcinogens (IARC 1999). There are numerous studies on the effects of the THMs on human health. Several studies (Cantor 1997, Koivusalo & Vartiainen 1997, Boorman 1999) have suggested that long-term consumption of chlorinated drinking water may increase the risk of bladder cancer and other site-specific neoplasms. A study (Vinceti et al. 2004) analysing cancer mortality in a residential cohort from an Italian municipality, where drinking water had high trihalomethanes content over a 22-year period, reported associations between chlorinated drinking water and cancer risk. The levels of chloroform and total THMs ranged from 33.1 g/l to 51.7g/l and from 39.7g/l to 70.0g/l respectively, depending on the time of the measurement after initial chlorination (just after treatment and after 24 hours). The study concluded that, despite the fact that the increased rates of some site-specific cancers could be due to life-style confounding factors, particularly to smoking, the higher death rates from prostate, breast and ovarian cancer and for melanoma may well have been related to long-term exposure to THMs in the drinking water. A recent publication (Tardiff et al. 2006) reviewing last findings concerning association between adverse reproductive and developmental effects and exposure to disinfection by-products found no impact of chlorination by-products on the highly controversial outcome of spontaneous abortion. However, as in the previously published review on the same subject (Graves et al. 2001), the updated weight of evidence suggested a positive association with disinfection by-products exposure and some measures of growth retardation such as intrauterine growth retardation, small for gestational age, term low birth weight, and small body length or head circumference. At the same time, in the last update on Guidelines for Drinking-Water Quality by the WHO (2006), it is stated that exposure to one of the THMs (bromodichloromethane) has been linked to a possible increase in reproductive effects (increased risk for spontaneous abortion or stillbirth).

Chloroform

IARC has classified chloroform as possibly carcinogenic to humans (Group 2B) (IARC 1999). The most universally observed toxic effect of chloroform is damage to the centrilobular region of the liver. The severity of these effects per unit dose administered depends on the species and pathway by which the chloroform enters the body (WHO 2006). Toxic effects in human following ingestion or inhalation of substantial doses include hallucinations and distorted perceptions, nausea, vomiting, and other unspecified gastrointestinal effects (Lewis 2004). Apart from being the principal THM in drinking water, chloroform has also been used in a range of industrial applications, including as a solvent, a heat transfer medium in fire extinguishers and an intermediate in the preparation of dyes and pesticides. The current extent of any of these recorded uses is unclear.

Bromoform

In an NTP bioassay, bromoform induced a small increase in relatively rare tumours of the large intestine in rats of both sexes, but did not induce tumours in mice. Data from a variety of assays on the genotoxicity of bromoform are equivocal. IARC has classified bromoform in Group 3 (not classifiable as to its carcinogenicity to humans). Studies in animals, combined with limited observations in humans, indicate that the principal adverse health effects associated with inhalation or oral exposure to bromoform are central nervous system depression and liver and kidney damage (ATSDR 2005a).

Dibromochloromethane (DBCM)

IARC has classified DBCM in Group 3 (not classifiable as to its carcinogenicity to humans). In an NTP bioassay, DBCM induced hepatic tumours in female and possibly in male mice (WHO 2006). Studies in animals, combined with limited observations in humans, indicate that the principal adverse health effects associated with inhalation or oral exposure to dibromochloromethane are central nervous system depression and liver and kidney damage (ATSDR 2005a)

Bromodichloromethane (BDCM)

IARC has classified BDCM in Group 2B (possibly carcinogenic to humans). BDCM gave both positive and negative results in a variety of in vitro and in vivo genotoxicity assays. In an NTP bioassay, BDCM induced renal adenomas and adenocarcinomas in both sexes of rats and male mice, rare tumours of the large intestine (adenomatous polyps and adenocarcinomas) in both sexes of rats and hepatocellular adenomas and adenocarcinomas in female mice. Exposure to BDCM has also been linked to a possible increase in reproductive effects (increased risk for spontaneous abortion or stillbirth) (WHO 2006).

Chlorinated ethenes and ethanes are known to have been used as solvents in the manufacture of semiconductor chips. Contamination of groundwater with these chemicals has previously been reported in the vicinity of facilities that used them as solvents, including those involved in the manufacture of materials for semiconductor chips, in a number of countries (Williams 2004). Previous investigations of contamination at two semiconductor chip manufacturing sites, in Japan and Thailand, reported high levels of two of the chemicals found in this study; trichloroethene (also known as trichloroethylene) and 1,2-dichloroethene (ERTC 2001, Williams 2004). At the site in northern Thailand, within the Northern Region Industrial Estate in Lamphun Province, groundwater was found to contain very high levels of both trichloroethene and 1,2-dichloroethene within a factory perimeter, both at far higher levels than those found in this study, over 100 mg/l (1mg/l = 1000 µg/l). The levels in the groundwater were found to vary greatly with depth and over short distances from the source of contamination (ERTC 2001). This previous report suggests that far higher levels of those VOCs identified at the CEPZA IE site may be present in the groundwater aquifer closer to the source or sources of these chemicals, though this could not be confirmed as it was not possible to collect samples within the perimeters of factories at the CEPZA IE.

There is clearly a need for further detailed investigations of chlorinated VOCs in groundwater at the chip manufacturing sites to find the full extent of the contamination of the aquifers, particularly at the CEPZA IE site.

BOX F :: CHLORINATED SOLVENTS AND OTHER CHLORINATED HYDROCARBONS

The widespread use and storage of chlorinated solvents has led to releases of these chemicals into the environment, including to groundwaters used as sources of drinking water. The main applications of chlorinated solvents include dry cleaning operations, manufacture of fluorocarbons, use as solvents for fats, oils, waxes and resins, as a degreasing agents, in organic synthesis, during cleaning of printed circuit boards, in polymer manufacture and in paint removers, as well as many others. Many of these chemicals are considered to be potentially carcinogenic to humans. Most can affect the central nervous system, liver, and kidneys and, following high exposures, can de-fat the skin (possibly causing dermatitis) and are irritating to the eyes and mucous membranes. Some can be absorbed through intact skin, and several can cause rapid and erratic heartbeats.

Dichloromethane is widely used as a solvent. It is listed by the International Agency for Research of Cancer (IARC) in Group 2B (possibly carcinogenic to humans). It causes central nervous system (CNS) depression, liver and kidney damage, and can cause elevated blood carboxyhemoglobin (also caused by exposure to carbon monoxide). Contact of the liquid with skin or eyes causes painful irritation and possible burns. Dichloromethane has been found in surface water samples at concentrations ranging from 0.1 to 743 µg/l. Levels are usually higher in groundwater because volatilization is restricted; concentrations as high as 3600 µg/l have been reported in some contaminated aquifers. Mean concentrations in drinking water are generally below 1 µg/l (WHO 2006).

Trichloromethane (Chloroform) has been used in industrial processes (e.g. as a solvent), although its presence in drinking water is usually due to chlorine-based disinfection (see THMs box).

Tetrachloromethane (carbon tetrachloride) is a confirmed carcinogen with experimental carcinogenic, neoplastigenic, and tumorigenic data (listed in Group 2B by IARC). It is toxic to humans by ingestion, subcutaneous and intravenous routes, and is mildly toxic by inhalation. Experimental data showed that carbon tetrachloride has teratogenic and reproductive effects, and can damage the liver, kidney and lungs (Lewis 2004). Because of its harmful and ozone depleting effects, many uses are now banned and it is only used in some industrial applications. Historically it was used in the production of chlorofluorocarbon (CFC) refrigerants (Budavari et al. 1986, WHO 2006) but this use of carbon tetrachloride was stopped in 1996 when CFC-11 and CFC-12 were themselves banned (UNEP 1997). Concentrations of tetrachloromethane found in drinking water are generally less than 5 µg/l (WHO).

1,1 - Dichloroethane is a highly flammable chemical. There are limited data showing that it can be present at concentrations of up to 10µg/l in drinking water (WHO 2006). However, because of the widespread use and disposal of this chemical, its occurrence in groundwater may still be on the increase in some regions. It is not listed as a suspect carcinogen. It is a CNS depressant, but seems to be less likely than other chlorinated solvents to cause liver or kidney damage.

1,2 - Dichloroethene exists in a cis- and a trans- forms. The cis- form is more frequently found as a water contaminant. Both cis- and trans-isomers are CNS depressants, and can irritate skin, eyes, or mucous membranes. The presence of these two isomers, which are metabolites of other unsaturated halogenated hydrocarbons in wastewater and anaerobic groundwater, may indicate the simultaneous presence of more toxic organochlorine chemicals, such as vinyl chloride. Accordingly, their presence indicates that more intensive monitoring should be conducted (WHO 2006). These chemicals have been found in drinking water supplies derived from groundwater at levels up to 120 µg/l.

1,1 - Dichloroethene is a central nervous system depressant and may cause liver and kidney toxicity in occupationally exposed humans. It causes liver and kidney damage in laboratory animals. 1,1-Dichloroethene has been detected in finished drinking water taken from groundwater sources at median concentrations of 0.28–1.2 µg/l and in public drinking water supplies at concentrations ranging from 0.2 to 0.5 µg/l (WHO 2006).

1,1,1 - Trichloroethane is widely used as a cleaning solvent for electrical equipment, and as a solvent for adhesives and coatings. Exposure to high concentrations can lead to hepatic steatosis (fatty liver) in both humans and laboratory animals. Toxic effects in laboratory animals included reduced liver weight and changes in the kidney consistent with hyaline droplet neuropathy. This solvent has been found in only a small proportion of surface waters and groundwaters, usually at concentrations of less than 20 µg/l; higher concentrations (up to 150 µg/l) have been observed in a few instances (WHO 2006).

Trichloroethene is used primarily in metal degreasing. IARC classified trichloroethene as Group 2A (probably carcinogenic to humans) based on sufficient weight of evidence of carcinogenicity in animals with supporting human data. It can cause CNS depression, can affect kidneys, liver, and lungs, and can cause rapid and irregular heartbeat, leading to death in extreme cases. Exposure can cause skin, eye, and mucous membrane irritation. Poor handling, as well as improper disposal of trichloroethene in landfills, have been the main causes of groundwater contamination. It is expected that exposure to trichloroethene from air will be greater than that from food or drinking water, unless the drinking water contains trichloroethene at levels above about 10 µg/l (WHO 2006).

Tetrachloroethene is widespread in the environment and is found in trace amounts in water, aquatic organisms, air, foodstuffs and human tissue. The highest environmental levels of tetrachloroethene are found in the commercial dry cleaning and metal degreasing industries. Emissions can sometimes lead to high concentrations in groundwater. Tetrachloroethene in anaerobic groundwater may degrade to more toxic compounds, including vinyl chloride. It is not classified as a carcinogen. It can cause depression of the CNS, and cause irritation of the skin, eyes, and upper respiratory tract. Very high exposure can cause death. Concentrations in drinking water are generally below 3 µg/l, although much higher concentrations have been detected in well water (23 mg/l) and in contaminated groundwater (1 mg/l) (WHO 2006).

The WHO and USEPA guidance values for THMs and maximum contaminant levels for chlorinated VOCs in drinking water are presented in Tables 4.16 and 4.17 respectively. None of the THMs detected in the samples from this study exceeded WHO and USEPA levels for drinking water, though the USEPA does set a contaminant level goal for bromoform and bromodichloromethane as zero (WHO 2006, USEPA 2006).

table 4.16 :: guidance values and maximum contaminant levels for THMs in drinking water (WHO 2006, USEPA 2006)

THM	WHO GUIDANCE VALUE, µg/l	USEPA MAXIMUM CONTAMINANT LEVEL, µg/l	USEPA MAXIMUM CONTAMINANT LEVEL GOAL, µg/l
Chloroform	300	n/a	n/a
Bromoform	100	n/a	0
Dibromochloromethane	100	n/a	60
Bromodichloromethane	60	n/a	0
Total THMs (TTHMs)	n/a	80	n/a

In contrast, several chlorinated ethenes that were found in the samples collected from CEPZA IE site exceeded WHO and/or USEPA levels (WHO 2006, USEPA 2006). Concentrations of trichloroethene were above USEPA levels in three samples MI06073 (2.5 times higher), MI06074 (about 1.3 times higher) and MI06078 (2.9 times higher). The concentration of 1,1-dichloroethene exceeded the USEPA level by 2.5 times in one sample (MI06078). However, the most significant contamination was detected for tetrachloroethene in this same sample, which exceeded both the WHO guidance value by almost 9 times, and USEPA maximum contaminant level by 70 times.

table 4.17 :: guidance values and maximum contaminant levels for chlorinated VOCs in drinking water (WHO 2006, USEPA 2006)

VOC	WHO GUIDANCE VALUE, µg/l	USEPA MAXIMUM CONTAMINANT LEVEL, µg/l
1,1-Dichloroethane	30	n/a
1,1-Dichloroethene	30	7
cis-1,2-Dichloroethene	50	70
trans-1,2-Dichloroethene	50	100
Dichloromethane	20	5
Tetrachloroethene	40	5
Trichloroethene	20	5

Greenpeace labelling a water sample from a well near the Sanyo plant in Tijuana. June 2006.

Many of the compounds that were detected in the samples of groundwater can affect the central nervous system, liver, and kidneys. A number of health studies of workers involved in the manufacture of electronics, including semiconductor materials and chips, have highlighted elevated incidence of certain diseases amongst workers (Zhu 1998, Brumfiel 2004, LaDou 2006), particularly some forms of cancers including cancer of the brain, central nervous system and kidney, melanoma of the skin, pancreatic cancer, and cancer of lymphatic and hematopoietic tissue (Clapp 2006). Due to certain limitations in the data available, some studies were not able to draw direct links between those diseases with elevated incidences and specific work activities or exposure to specific chemicals. However, the study conducted in China among workers of electronics and metal sectors of the industry with previous excellent health has clearly linked allergic skin diseases and hepatitis with occupational exposure to the chlorinated solvent trichloroethene (Zhu 1998). More information on THMs and chlorinated solvents is presented in Box E and Box F respectively.

In addition to VOC contamination, elevated levels of metals were found at all of the sites in the Philippines, primarily zinc. No elevated metal levels were found in the sample from Kemet, Mexico. At the On Semicon site, the distribution of high zinc levels suggest that On Semicon is contributing to elevated levels of zinc in the groundwater at this site. A sample collected 100m to the north of the facility (MI06065) contained the highest level of all samples (852 µg/l), more than ten times typical background levels of less than 50 µg/l (ATSDR 2005c).

High levels of zinc and other metals were also present in some sample associated with the Gateway IE and CEPZA IE sites, though the distribution patterns do not suggest impacts from facilities within these Industrial Estates on groundwater metal levels. At the CEPZA IE site, all samples that contained elevated concentrations were those collected outside, or on the edges of the Industrial Estate. No elevated levels of metals were found in any of the samples collected within the centre of the Industrial Estate, i.e. those samples which did show significant VOC contamination, as discussed above. At the Gateway IE site, the zinc levels were lower and there was no clear distribution pattern. One sample contained an elevated copper level, the highest level for all samples in this sector (233 µg/l), but this could be a result of the use of plumbing materials containing copper, which are able to cause such water levels (WHO 2006). The almost identical levels of vanadium in all four samples from this site suggests that the higher than normal background levels of vanadium in these samples is due to an elevated background level of vanadium in this area.

For all sites, the elevated levels of metals found were below levels generally accepted to be a risk to human health (WHO 2006), though collectively they do indicate inputs to the groundwater aquifers sampled. Any ongoing inputs are likely to result in increasing levels over time.

4.3 :: COMPONENT ASSEMBLY; MEXICO

4.3.1 :: Facilities in Mexico

A total of 15 samples associated with component assembly were collected from two areas in Mexico, Tijuana and Guadalajara. Samples included 13 groundwater samples and 2 wastewater samples. VOCs were detected in 3 of the 13 groundwater samples collected and in both wastewater samples. A list of organic compounds identified in the wastewater samples, and the quantitative results for VOCs analysis are presented in Tables 4.18 and 4.19 respectively. Results for metal analysis of these samples are presented in Tables 4.20 and 4.21.

Tijuana

VOCs were detected in two of the four groundwater samples collected from the two sites in Tijuana, though in both cases only THMs, rather than chlorinated industrial solvents, were found. Sample MI06081, collected from an open well near the Sanyo Video facility, contained only chloroform and then only at trace level. This groundwater was the only sample with any elevated metal levels for groundwater, containing a nickel concentration of 150 µg/l. Sample MI06083 from a pumping station near the Sony facility contained four THMs – bromoform, chloroform, bromodichloromethane and dibromochloromethane – at concentrations in the range 0.6-1.3 µg/l.

Guadalajara

9 groundwater samples and 2 wastewater samples were collected around the Guadalajara area. Among these, VOCs were detected only in one groundwater sample, MI06087, collected 2 km northeast of the Flextronics IE. Once again, this sample contained only THMs – chloroform, bromodichloromethane, and dibromochloromethane at concentrations 6.3 µg/l, 2.9 µg/l and 1.5 µg/l respectively. Bromoform was present at trace level only.

Groundwater (MI06012) colleted from a tap within the Flextronics facility contained copper at a concentration (226 µg/l) above typical background level. Elevated metal concentrations were also found in two samples collected to the northeast of the Flextronics IE. One sample (MI06086) collected 0.5 km from the estate contained high concentrations of zinc (492 µg/l) and nickel (129 µg/l). A second sample (MI06087) collected slightly further away (2 km to the northeast) contained only nickel, at a slightly lower level (106 µg/l). In contrast, high metal levels were not found in two further groundwater samples collected at the entrance of the estate (MI06085), and 300 m north of the estate (MI06084).

At a different site, a groundwater sample collected 2 km east of the Solectron facility (MI06089) contained a similarly elevated level of zinc (579 µg/l), as well as somewhat higher lead level than found in all other samples (59 µg/l). No VOCs were detected in this sample. No other groundwater samples were collected within the vicinity of this site.

table 4.18 :: organic chemicals identified in wastewater (WW) samples from the IBM Site, Guadalajara, Mexico. The number of compounds reliably identified is presented for each group; (#) - signifies compounds identified at trace levels using a selective SIM method; (-) – not detected

LOCATION	IBM SITE, GUADALAJARA	
SAMPLE#	MI06091	MI06092
SAMPLE TYPE	WW	WW
No. of organic compounds isolated	68	32
No. reliably identified (% of total)	14 (21%)	9 (28%)
PBDEs	-	(2)
Benzene, 1,4-dichloro-	(1)	1
Trihalomethanes	(1)	(1)
DEHP	1	-
Phenol	1	-
Phenol, nonyl-, mix isomers	1	-
Phenoxyethanol, nonyl-	1	-
Diphenyl ether	-	1
Alcohols	2	-
Fatty acids	5	-
Aliphatic hydrocarbons	1	4

table 4.19 :: Volatile organic chemicals (VOCs) quantified in groundwater (GW) samples from Tijuana and wastewater (WW) samples from Guadalajara, Mexico. (-) - not detected.

LOCATION		TIJUANA		GUADALAJARA		
SAMPLE#		MI06081	MI06083	MI06087	MI06091	MI06092
SAMPLE TYPE		GW	GW	GW	WW	WW
COMPOUNDS		CONCENTRATION, µg/l				
THMS	Bromoform	-	0.6	<0.5	-	-
	Chloroform	<0.5	1.3	6.3	<0.5	<0.5
	Methane, bromodichloro-	-	0.8	2.9	-	-
	Methane, dibromochloro-	-	0.9	1.5	-	-

Water sample collected from a wastewater channel on the IBM site in Guadalajara, Mexico. June 2006.

Both wastewater samples from the IBM site (MI06091 & MI06092) contained only one VOC, the THM chloroform, and even then at only trace levels. However, a range of extractable organic compounds was also detected in both samples. The wastewater that included discharge from the wastewater treatment plant (MI06091) contained diethylhexyl phthalate (DEHP), phenol, a mixture of nonylphenol (NP) isomers, nonylphenoxyethanol, octanol and decanol, several fatty acids, and a trace amount of dichlorobenzene. The second wastewater sample from the IBM site, MI06092, contained (other than dichlorobenzene) different organic compounds to those detected in sample MI06091, namely two PBDEs at trace levels (BDE-47 and BDE-99), diphenyl ether and several aliphatic hydrocarbons. Neither wastewater contained high metal concentrations.

table 4.20 :: metals quantified in groundwater (GW) samples from sites in Guadalajara, Mexico. (-) - not detected.

AREA	**GUADALAJARA**								
LOCATION	Sanmina	Flextronics	Flextronics IE	Flextronics IE	Flextronics IE	Flextronics IE	Jabil	Solectron	HP
SAMPLE#	MI06011	MI06012	MI06084	MI06085	MI06086	MI06087	MI06088	MI06089	MI06090
SAMPLE TYPE	GW	GW	GW	GW	GW	GW	GW	GW	GW
METAL	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
Antimony	-	-	-	-	-	-	-	-	-
Barium	132	9	-	-	-	18	21	13	40
Beryllium	-	-	-	-	-	-	-	-	-
Bismuth	-	-	-	-	-	-	-	-	-
Cadmium	-	-	-	-	-	-	-	-	-
Chromium	-	-	-	-	-	-	-	-	-
Cobalt	-	-	-	-	-	-	-	-	-
Copper	-	226	-	-	-	-	29	38	-
Lead	-	-	-	-	-	-	-	59	-
Manganese	362	-	-	-	-	-	-	-	36
Molybdenum	-	-	-	-	-	-	-	-	-
Nickel	42	28	-	-	129	106	-	-	30
Tin	-	-	-	-	-	-	-	-	-
Vanadium	-	-	-	-	-	-	-	-	-
Zinc	-	-	35	-	492	-	66	579	-

table 4.21 :: metals quantified in groundwater (GW) samples from Tijuana and wastewater (WW) samples from Guadalajara, Mexico. (-) - not detected.

AREA	TIJUANA					GUADALAJARA	
LOCATION	Sanyo	Sanyo	Sanyo	Sony	Sony	IBM Site	IBM Site
SAMPLE#	MI06080	MI06081	MI06082	MI06083	MI06083	MI06091	MI06092
SAMPLE TYPE	GW	GW	GW	GW	GW	WW	WW
METAL	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
Antimony	-	-	-	-	-	-	-
Barium	183	153	221	59	59	53	77
Beryllium	-	-	-	-	-	-	-
Bismuth	-	-	-	-	-	-	-
Cadmium	-	-	-	-	-	-	-
Chromium	-	-	-	-	-	-	-
Cobalt	-	-	-	-	-	-	-
Copper	-	-	-	-	-	15	17
Lead	-	-	-	-	-	-	-
Manganese	963	128	1125	-	-	50	962
Molybdenum	-	-	-	-	-	-	-
Nickel	41	150	21	-	-	31	35
Tin	-	-	-	-	-	-	-
Vanadium	-	-	-	-	-	-	-
Zinc	-	17	32	-	-	96	119

4.3.2 :: Discussion

The majority of groundwater samples that were collected close to the assembly facilities in both Tijuana and Guadalajara did not show any significant level of contamination with VOCs, containing only THMs at trace levels. Just under half of the samples, 5 out of 13, did contain high levels of some metals, principally nickel and zinc.

In Tijuana, water from one well (MI06081) adjacent to the Sanyo Video facility contained nickel at a level of concern as the water from this well is used for drinking. The concentration of nickel in this sample was 150 µg/l, the highest value among all groundwater samples from all sites in all countries considered in this study and more than two times higher than the WHO guideline value of 70 µg/l for nickel in drinking water. For comparison, concentrations of nickel in groundwater are normally less than 10 µg/l (ATSDR 2005b, WHO 2006).

Three samples associated with the Flextronics IE contained high metal concentrations. One sample collected from a tap within the Flextronics IE contained a high copper level (226 µg/l), though this level of copper does not pose a risk to health. Elevated levels of nickel, both above the WHO guideline value, were also detected in two more groundwater samples collected close to the Flextronics IE (MI06086 & MI06087), both collected to the northeast of the estate (129 and 106 µg/l). The sample with the highest nickel level (MI06086) also contained zinc at a level (492 µg/l) almost ten times levels typically found in groundwater, which are generally below 50 µg/l (ATSDR 2005c). A similar level of zinc was also present in groundwater close to the Solectron facility (MI06089, 579 µg/l).

Of these levels, the samples with elevated nickel levels are of greatest concern. Exposure to high concentrations of nickel can results in toxic effects, and some nickel compounds are carcinogenic (ATSDR 2005b, IARC 1990). More information on the uses and effects of nickel and zinc is given in Box C. Nickel and zinc, in water soluble forms, can be reasonably mobile in the environment and have the potential to leach into groundwater. It is not possible to pinpoint the exact sources of nickel and zinc to the groundwater samples that contain elevated levels, but their proximity to the assembly facilities suggest that releases from

these facilities may be contributing to the elevated levels found. Additional sources cannot be discounted, however, including the use of plumbing materials that can contain copper, nickel of zinc, which are able to cause elevated drinking water levels (WHO 2006). It was not possible to ascertain whether such materials were present at these locations.

The THMs detected in some groundwater samples from both Tijuana and Guadalajara sites are most certainly be due to the use of chlorine-based disinfectant materials. It was known from the local people that such materials are applied directly to some wells in the Guadalajara area investigated. The concentrations of THMs in all samples were below WHO guideline values.

In addition to the groundwater samples, two wastewater samples (MI06091 & MI06092) were collected from one site in Guadalajara, Mexico where IBM was involved in the assembly of PCs and computers at the time of sampling. The levels of metals in these samples in general were not elevated, though they did contain several classes of organic compounds of environmental concern.

Among the compounds reliably identified in the sample of treated wastewater MI06091 collected from an open channel within the IBM site was nonylphenoxyethanol, a member of a group of chemicals known as nonylphenol ethoxylates (NPEs). Also identified were a mixture of nonylphenol isomers, known degradation products of NPEs. NPs are persistent, bioaccumulative and toxic to aquatic life (OSPAR 2001). Phenol, a parent compound, was also detected in this sample. It is difficult to specify the precise source of these chemicals in this treated wastewater sample as NPEs have been used in various industrial and consumer applications (OSPAR 2001), though their principle uses are as surfactants and emulsifiers. The use of nonylphenol derivatives as antioxidants in some plastics has also been reported (Guenther et al. 2002). Numerous studies (Jobling et al. 1995, 1996, 2002, Thomas & Dong 2006, Razia et al. 2006) confirm that degradation products of NPEs, including nonylphenol, possess the ability to mimic natural hormones by interacting with the estrogen receptors. Toxic effects of nonylphenol to human health have also been reported (Chitra et al. 2002, Adeoya-Osiguwa et al. 2003, Harreus et al. 2002). More information on NPEs, NPs and related compounds is presented in Box G.

The wastewater sample MI06091 also contained a phthalate ester, diethylhexyl phthalate (DEHP), one of the most frequently detected environmental pollutants (Peijnenburg & Struijs 2006) and for which toxic effects to reproductive development in mammals, have been confirmed (Swan et al. 2005). The main use of DEHP is as a plasticizer in various plastics including PVC. Plasticizers are not chemically bound to plastics and able to leach (Loff et al. 2000). Therefore, waste streams containing DEHP are frequently reported and, if discharged into natural watercourses with industrial or sewage effluents, may exert a deleterious impact on aquatic life (Forget-Leray et al. 2005). See more information on DEHP and other plasticizers in Box B.

The second wastewater sample MI06092 was also collected within the IBM site but from a different open channel to that from which sample MI06091 was taken. It is unknown if this wastewater had been treated within the site. Two congeners of brominated flame-retardants PBDEs were detected in this sample. As was discussed in previous sections of the report (see 4.1.3 and Box A) PBDEs are toxic, persistent and bioaccumulative chemicals. Diphenyl ether, also reliably identified in this sample, is the parent molecule of PBDEs. It has various industrial uses such as a high boiling solvent to purify pharmaceuticals, as a starting material for the preparation of heat transfer fluid, speciality surfactants, and blowing agents.

BOX G :: SURFACTANTS AND RELATED COMPOUNDS

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). It is still included into Annex 2 List of Chemicals for Priority Action of the OSPAR Strategy with regard to Hazardous Substances (OSPAR 2006). 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).

Additionally, both wastewater samples contained trace amounts of chloroform and 1,4-dichlorobenzene. It is unknown if these wastewaters originally contained any other volatile organic compounds (VOCs) as they flow through the open channels within the site and any VOCs, if present, might quickly evaporate.

In general, the wastewater from a channel originating from the IBM Site in Guadalajara is a source of contamination by persistent organic compounds such as PBDEs, nonylphenols (NPs), and phthalates which could be linked to the electronics manufacture at this site. This would appear to contradict the 'Supplier Conduct Principles Guidelines' of IBM that states that suppliers should operate in a manner that is protective of the environment. (IBM 2004). Though groundwater samples collected around the Tijuana and Guadalajara sites did not show any significant contamination by organic compounds that could be linked to the assembly of PCs and other electronic devices, high concentrations of some metals (principally nickel and zinc) in groundwater sources close to a number of facilities suggest that their activities may be impacting groundwater aquifers. For those groundwater sources that contain levels of nickel above acceptable safe drinking water levels, the consumption of the water from these wells for drinking purposes should be discontinued.

A farmer sitting by the well from which the local communities pump water for their homes. Their homes are near the Compeq Factory, one of the electronics facilities in the Guangdong Province, China. October 2006.

5 :: Conclusions

Although this study is not an exhaustive investigation into environmental impacts resulting from the manufacture of computers and their peripheral equipment (and was not intended to be), the results nonetheless highlight releases of hazardous chemicals within each of the three sectors investigated; printed wiring board (PWB) manufacture, semiconductor chip manufacture and component assembly.

For many of the locations investigated this study demonstrates discharges to and/or contamination of the immediate environments around manufacturing facilities with a range of hazardous chemicals used to form the product or in the manufacturing processes employed. Within each sector, some similar patterns of contamination were seen at the sites of different facilities. It was not possible to collect samples from all waste streams generated by each facility and therefore additional chemical releases to the environment may be occurring undetected, either intentionally or as fugitive releases. Further research would be necessary to identify and quantify the full environmental impact of each sector, with the full cooperation of the manufacturing facilities.

Where wastewaters and associated samples could be collected, from PWB manufacturers and one assembly site, analysis showed a wide range of chemicals being discharged, many with known toxic characteristics and some of which are environmentally persistent. For some of the chemicals identified, such as the photoinitiators-related chemicals used in PWB manufacture, very little information is available on their possible impacts on human health and the environment, presumably largely as a result of rapidly changing manufacturing processes and the chemicals employed. Furthermore, a large proportion of the compounds isolated from these samples simply could not be identified and therefore their properties and potential impacts remain unknown. It was not possible to collect samples of wastewaters from the semiconductor facilities and therefore no conclusions can be drawn on potential impacts from such wastestreams from the facilities at the sites investigated. However, contamination of groundwater aquifers with toxic chlorinated chemicals, many of which have known uses as industrial solvents, was detected at some of the sites.

Some chemicals incorporated into electrical and electronic devices during manufacture were common to samples collected from many sites. Most noteworthy were PBDEs, a group of brominated chemicals widely used as flame retardants, and phthalate esters (phthalates), chemicals used in a wide range processes and materials though most commonly as plasticisers (softeners) in plastics. These two chemical groups both contain chemicals that are known to be toxic, and some are also persistent in the environment; certain PBDEs are also known to bioaccumulate (build up in animals and humans). PBDEs were particularly widespread, being present in wastewaters and other samples from the majority of sites investigated. Discharged wastewater from one PWB manufacturing facility (EETH, Thailand) also contained chlorinated VOCs, a group of chemicals widely used as solvents and more commonly reported as contaminants in groundwater samples collected near semiconductor chip manufacturing facilities.

Wastewaters from PWB facilities also commonly contained high levels of metals, particularly copper, nickel and zinc. Soluble copper compounds are widely used in PWB manufacture, particularly where the electroless copper process is used. From information available at the time of writing, this still appears to be the case at the EETH facility in Thailand, where the highest concentrations of copper in all sampled wastewaters was found, exceeding the maximum allowed level for industrial effluents in Thailand. The presence of soluble copper in wastewaters can have serious environmental impacts, as many aquatic organisms are highly sensitive to soluble copper even at very low doses. High levels were also found in wastewaters discharged to waterways from both facilities in China.

Where wastewaters undergo treatment prior to discharge to the wider environment, the processes typically employed are simply unable to deal with many of the hazardous chemicals identified in the wastewaters, such as the persistent brominated flame-retardants and toxic metals. At best these treatment processes simply scavenge such chemicals from wastewaters only to generate an additional contaminated wastestream in the form of sludges, as this study has demonstrated for some PWB manufacturers where it was possible to collect samples throughout wastewater disposal networks.

Wastewater discharged from the IBM site in Guadalajara, Mexico contained other hazardous compounds not found at other sites. Of particular concern is the presence of a nonylphenol ethoxylate (NPE) and a range nonylphenols (NPs), degradation products NPE. NPs are persistent, bioaccumulative and toxic chemicals that are commonly used as surfactants. These chemicals are prohibited from marketing and use throughout Europe because of the health and environmental concerns they present.

Contamination of groundwater aquifers with toxic chlorinated volatile organic chemicals (VOCs) and toxic metals including nickel was identified at a number of sites, particularly in the vicinity of semiconductor manufacturers. Contamination of groundwater is of particular concern as in many places local communities use this resource for drinking water. At one Industrial Estate in the Philippines (CEPZA IE) housing a number of semiconductor chips manufacturing facilities, safe drinking water levels set by the WHO and/or USEPA levels were exceeded for chlorinated VOCs, a group of chemicals some of which have been reported to be used as solvents in the manufacture of semiconductor chips. One sample from this site contained three VOCs at levels above one or more of these limits, with tetrachloroethene at a level 9 times the WHO guidance value and 70 times the USEPA maximum contaminant level. The limited scope of this study inevitably means that hotspots of higher contamination levels, such as may exist in regions of aquifers directly beneath storage tanks or other industrial facilities, may have gone undetected.

High levels of metals, particularly copper, nickel and zinc were also found in some groundwaters. At two sites, one involved in PWB manufacture (Hi-Tech, Thailand) and one in component assembly (Sanyo Video, Mexico), levels of nickel were above the WHO drinking water guideline value, and that from Thailand exceeded the Thai groundwater quality level.

Although it is not possible to pinpoint the exact source or sources of the contaminants found in groundwater in the vicinity of these facilities, it seem likely that the use of these chemicals in the manufacturing processes is contributing to chemical inputs to the aquifers either by intentional or fugitive releases.

The data from this study provide a compelling case for the substitution of hazardous chemicals in the products manufactured and the processes used by the sectors investigated, either by direct replacement with non-hazardous alternatives or through the altering the processes to eliminate the need for such chemicals.

Agricultural fields near electronics factories in the Guangdong Province, China. October 2006.

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