Corso di Laurea in Ingegneria per l'Ambiente e il Territorio

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INVESTIGATION OF THE RECOVERY OF SECONDARY RAW MATERIALS FROM DESKTOP PERSONAL COMPUTERS

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Summary

The European directives about the management of Waste electrical and electronic equipments (WEEE) have aimed to enforce the development of a circular economy in the last decade. Nevertheless, efforts have also been made by the governments of many Asian developing countries, in order to monitor and manage volumes of e-waste. The Italian current regulation, despite some still controversial definitions of the WEEE categories (R1 to R5), is putting into act an effective collection system based on the extended producer-responsibility principle (EPR). As a consequence, the WEEE collection rate has increased in recent years reaching 4.67 Kg in 2016 which, however, is still below the rate of many European countries.

In these view, desktop personal computers are one of the most interesting and large share in the *small household appliances* category. Hence, the recovery of raw materials from these devices is key to the development of urban mining, in particular for the printed circuit boards embedded in the mainframe.

The process of manual sorting on a flow of discarded desktop PCs at industrial extent, was analysed, describing features and destinations of every sorted fraction. This step is crucial for the optimization of further treatments.

The aim of this work is to find out the mainframe's components which have the highest economical revenue, to characterize the mass composition of waste PCs, and to assess the feasibility of their manual dismantling in a circular recycling scheme. In particular CPUs, despite their very small weight share in the whole mainframe, turned out to be the second most profitable fraction in one single unit, after the large PCBs applied as motherboards or graphic-boards. Additionally, chemical analysis by X-ray fluorescence spectrometer were conducted in order to investigate the elemental composition of specific components. Beside high quantities of Cu (17.58 % by mass percentage of the motherboard's PCB), significant content of Ag (51.8 mg/Kg), Rd (47.6 mg/Kg) and Pd (14.9 mg/Kg) were measured. Since it was also found a large application of elements marked as Critical Raw Materials by the European Commission, the environmental advantages of proper recycling of waste PC are crucial, keeping into consideration not only the resources saving, but also the avoided volumes of WEEE which may be stocked in dumps, or sent to informal and harmful recycling treatments.

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Chapter 1

Introduction

Domestic and industrial waste has undergone many changes in composition (material), as well as quantity (volume and mass) all over the world, in the last two decades. These modifications are even more evident for electric and electronic equipment (EEE or e-product). One of the most rapidly growing kind of refuse is made by the waste electric and electronic equipments (WEEEs). This is a result, not only of the huge demand of new products coming from consumers, but especially of the shortening of EEEs lifespan. Electronic products market is still unsaturated, especially for devices such as mobile phones and laptops which are getting obsolete at an increasing rate, due to rapid advancement in technology and functionality. The total e-waste produced all over the world was 41.8 million tons in 2014, it raised to 44.7 in 2017 and it is expected to overcome 52 million tons by 2021, which accounts approximately for more 6.8 kg/year per person [Baldé *et al.*][2017]. The composition of e-products is very complicated, making their separation and treatment more difficult. Since several critical metals are usually required in the production of electronic goods, their high demand may lead to problems of scarcity of metals, and to the depletion of other resources. Moreover, many hazardous substances are present in electronic components, which could indirectly lead to an increase in the human toxicity and cancerogenicity risk, when they are unproperly managed. According to Heacock *et al.* [2016], in 2015, only 15% of the global e-waste was fully recycled.

On the other hand, e-waste can be seen as a secondary source of raw materials. Materials with high market price make their recovery profitable; usually precious metals and significant amount of copper are found in the printed circuit boards, used as component in mobile phones, laptop and many other e-devices.

It is crucial to analyse WEEE-related issues on a global scale, from a political, environmental, and economical points of view. An overview on the most used methods and recently developed technologies for WEEE recycling is helpful to understand how the current situation is going to evolve in the recycling development area. Literature provides many analysis concerning the technical perspectives for WEEE treatment and recycling. However a detailed analysis focused on desktop and laptop PCs recycling, carried out on a significant number of devices, is still missing. Thus, the main purpose of this study is to assess the actual material recovery from waste desktop

PCs, through an industrial test performed on 100 devices in a WEEE treatment plant located near Turin and managed by AMIAT SpA, belonging to IREN Group.

The industrial test included a phase of introduction to the working system, followed by the collection of data required for the goal of this study, which include: quantification of the amount of treated products, measurements directly taken on the products, technical parameters of the employed technologies and so on. Thus, the potential recycling achievement was estimated according to the collected data, and the consequent economic revenue of the outflow secondary raw materials was assessed, together with the economical viability and the environmental aspects, the effectiveness of the treatment and its potential improvements. Moreover, some related aspects such as public awareness, strategic management and legislation directives, were discussed.

I would like to thank AMIAT SpA, and particularly eng. Alessandro Ronco, my co-supervisor, for the opportunity to perform my Master thesis in a real industrial environment. This experience was fundamental for my personal and professional growth.

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Chapter 2

The WEEE management

2.1 WEEE's quality and quantity features

WEEE (waste electric and electronic equipment) or e-waste consists of a wide group of devices. As some of them are commonly found in the waste coming from households since many years such as refrigerators, washing machines and TVs, some other have just become common in recent years, such as laptop and desktop PCs, mobile phones and LCD monitors. Electronic industry is recently providing a more and more wide set of e-products, ranging from top quality to medium-low quality grade with very competitive costs. Therefore nowadays an increasing number of people can easily afford the purchase of electronic goods, and many of these ones, especially laptops and mobile phones, are actually becoming basic needs. As a result, the volume of e-waste is considerably growing, carrying with it a variety of different materials. If the total waste produced around the world was properly recycled , it was estimated that the achievable amount of money, deriving from the recovery of secondary raw materials, could be 55 billion € [Baldé *et al.*][2017].

From a global point of view, it is reported "in 2012 an average of 7 kg of electronic waste for each of the worlds 7 billion people was generated" [Fan *et al.*, 2016].In 2016 the average WEEE generation was 6.1 kg [Baldé *et al.*][2017]. Figure 2.1 provides and overview on the global generation of WEEE in the recent years and the predictions in short-term future. The life expectancy of electronic equipment is becoming shorter and shorter, especially for the small electronic devices such as cell phones, tablets, and small laptops. As a results close to 1 billion devices will be discarded within 45 years [Kumar *et al.*, 2017]. According to the estimation made by Cucchiella *et al.* [2015] "in 2014 smart phones and cell phones were the waste streams with the highest generation rate (in volumes); while considering the mass, the highest quantity of wastes are related to the CRT technology (TVs and monitors)".

The e-waste growth has become considerable in every country which has earned a wealthy life standards. Nowadays, e-waste is concentrated in the regions where economic development is the greatest. United States and China have significantly higher than any other country Gross Domestic Product ($17419 billion and $103601 billion) and the high amounts of e-waste generated (7072 and 6033 kt) can be regarded as a consequence of their strong economic development and larger

Figure 2.1. Global e-waste generation (2014 - 2017, forecast to 2021). Source: Baldé *et al.*

population. Statistics suggest that the amount of electronic waste generated by every inhabitant increases together with the increase in their individual wealth hence purchasing power. Moreover, a country with higher GDP is more likely to have a high e-waste generation. On the other hand, "a country with larger population does not necessarily produce significantly larger amount of e-waste if the purchasing power and GDP is lower". [Kumar *et al.*, 2017] Therefore, all over the world, the biggest WEEE generator countries are USA and China, followed by Japan, Germany and India [Zhang *et al.*, 2017]. The data reported in Table 2.1 are imported from the report made by Baldé *et al.*[2017], and they represent the average WEEE generation for each continent.

In Europe quantities of WEEE generated vary considerably between wealthy countries and less prosperous ones. In many extra-European developing countries, generated amounts are comparatively lower, but in the last years they are not stable and they are expected to increase in an unpredictable way. In his work, Ikhlayel [2016] made an estimation of the WEEE generation considering as a case study Jordan, which is a developing country, where many categories of electronic products are still in unsaturated market conditions. The per capita rate in this country, varies between 3 and 4.8 kg/person/year.

In Iran, the magnitude of e-waste generation in the country was 20 million wasted computers until 2016 and 39 million waste mobile phones until 2014 [Rahmani *et al.*, 2014]. In the same study, the forecast by logistic equation indicates that by the year 2040, in Iran there will be 50 million units of obsolete computers. According to the same model, also 90 million mobile phones will be obsolete by 2035.

The cell phone equipment rate in the city of Beijing is considerably higher (2.1-2.3 per house) than in Vienna (1.0 per house), and the same occurs for TV sets [Salhofer *et al.*, 2016]. A characterization of the e-waste generation and management within the European boundaries would not be effective, in order to understand the current situation, since very high quantities are transboundary traded in extra-european countries. Accordingly, a special interest for the generation in Asian countries must be taken into consideration, also because, in addition to their own local production, many of their end-of-life products come from other developed countries. These traded goods are hard to control and to estimate.

Some of the most populated countries only in the last few years have developed basic recycling principles. For instance, in US producers have not been required so far to contribute to the environmental and social costs of the WEEE disposal issue; just in 2015 approximately half of the federal states regulated producer responsibility, but in an heterogeneous way, without fixing some common standards. In India even if the regulation named Hazardous Material Laws and Rules has been published, there is still no separate system and WEEE is treated as municipal waste [Ildar *et al.*, 2017].

Table 2.1. Total e-waste generation, estimated per continent in 2017. Source: Baldé *et al.*

Continents	Amount (in million tonnes)	Amount (kg/inh.)
Africa	2.2	1.9
Americas (North & South)	11.3	11.6
Asia	18.2	4.2
Europe	12.3	16.6
Oceania (Australia)	0.7	17.3

A great amount (almost 50%) of current WEEEs yearly generated by developed countries continues to be illegally transferred in developing countries disguised as humanitarian aids or general used products. The precise amount of these informal volumes remains, even nowadays, unknown [Cucchiella *et al.*, 2015]. A decade ago, the WEEE traffic routes were towards Asia, particularly China. The introduction of a more stringent legislation urged the emergence of new WEEE transport destinations, such as Ghana, Nigeria, South Africa, Vietnam, India and the Philippines [Ildar *et al.*, 2017]. The main trans-boundary destinations for WEEEs are currently China, India, Mexico, Brazil, Malaysia, Philippines, Vietnam, Thailand, Pakistan and Nigeria. Local policy in Southeast Asia is still unable to control the potential WEEE import and export since most of the traded quantities are unmonitored by the local administrative associations [Song *et al.*, 2017]. In their recent work, Song *et al.* [2017] showed that "in the Chinese region of Macau, regarding the PCs, laptop, mainframe and tablet, import and export is very very small or absent; on the contrary, there is a considerable trade of CRT monitors (used and even higher for waste), characterized by a decreasing trend since 2000. Regarding Tvs, similar results have been found out, however import and export volumes are larger and they have assumed a decreasing trend starting in 7-8 years later".

The obsolete products that people keep saving in their houses represent a certain portion of electronic devices, which is hard to quantify. In fact these idle products, are in their end of life so that they are doomed to be waste. "There clearly is a huge gap between the quantities of used computer equipment being recycled and obsolete, suggesting that a large quantity is stored in-house, creating a greater risk of ending up with improper recycling/treatment/disposal" [Fan *et al.*, 2016]. This condition concerns especially the small equipment like cell phones and other household appliances, which many people do not discard immediately since they are not bulky. More efforts should encourage people to find the proper collection points.

Table 2.2. International e-waste generation ranking in 2013. Source: Ildar *et al.* [2017]

Country	Annual estimated WEEE in 2013 (10^6 tons)	WEEE per inhabitant (kg/person)	Increase between 2013 and 2020
United States	9359	29.3	7%
China	6033	4.4	98%
Japan	3022	23.8	5%
India	2751	2.2	145%
Germany	1696	21.9	16%
Russia	1556	10.9	28%
Brazil	1530	7.1	20%
France	1224	21.6	32%
Italy	**1154**	**19.3**	**16%**
Korea	961.3	19.2	9%
Turkey	661	8.8	21%
Romania	394	23.3	6%

2.2 WEEE as a source of secondary raw materials

In order to save resources from mining of raw materials and to alleviate the environmental impacts, policies and directives are making efforts to enhance the WEEE recycling systems. As a support, many scientific studies have been done about the LCA (Life-cycle assessment) of the e-products. The goal is to highlight the economic feasibility and the environmental damage which can be a avoided in a full recycling scenario, in a so called scheme of Circular Economy. In this context comprehensive definition of Circular Economy is provided by the Ellen McArthur foundation: "an industrial economy that is restorative or regenerative by intention and design. The benefits that could be earned from an environmental point of view are mainly about: climate change (CO2 emissions), Ozone depletion, human toxicity, freshwater eco-toxicity, particulate matter formation, water eutrophication, fossil fuels and metals depletion. As an example of over-mined resources, the production of indium (which is mainly used in the production of transparent conductive films in LCDs due to its adequate electrical conductivity and optical transparency) increased from 149 to 819 tons in twenty years. China controls about half of the global indium mining, making this material critical and creating geopolitical constraints [Zhang *et al.*, 2017]. According to this, the latest directives aim to organize a recycling scheme together with the WEEE producers by extending their responsibility of the products they release on the market.

This attitude is spreading in UE countries, USA, Japan, Canada, and also policy efforts have been made in developing countries such as China and Mexico. Fan *et al.* [2016] investigated the computer recycling in Taiwan: an increasing trend was observed since 1999. It gradually flattened out between 2005 and 2006. After 2007, the recycling amount remained relatively constant at an average of 12.7 million kg. In the same study they also categorized the main computer users into four groups: government, community, private sector and academic. Private sector and community resulted to be the largest contributions of recycled PCs and the future recycling forecast suggests approximately an increasing rate of computer recycling.

Another contribution to the development of a circular economy comes from the reuse of discarded devices. Reuse schemes mainly take place in developing countries where often there are second-hand markets which gather the discarded devices coming from households, by door-to-door private traders. High amount of obsolete devices are transferred from the Europe to other developing countries with a re-use purpose; the same thing occurs from USA, Canada and Japan to south-east Asian countries. Thus, second-hand market mainly takes place through "unofficial" ways. Since consumers' attitude is mainly driven by advanced technological requirements, the market of resold goods is limited. Rarely some companies in Europe have promoted re-use schemes of their own end-of-life products including a proper re-manufacturing, or a preparation for a second life cycle. Moreover, European commission currently does not see the re-use schemes as a good option for the mitigation of environmental impacts and the resource savings. A resistance by the European Commission to set up some specific re-use targets is probably due to a lack of assessments about the feasibility and the benefits of re-use schemes. Regarding the re-use, a study conducted by Gonzalez *et al.* [2017] deemed that "in 2011, 2.9 million computers were replaced in Spain, representing a replacement rate of 15.5% relative to the total stock. However their second useful life is estimated to last not more than 2 years".

Together with the technological development, also the level of complexity in the manufacture of electronic components has grown and many different materials are employed. As a very general result, the overall output from a WEEE treatment plant which includes all the kind of electronic devices is made by: 38.1% ferrous metals, 16.5% non-ferrous metals, 26.5% plastic, and 18.9% others [Ildar *et al.*, 2017]. Keeping into consideration the potential economical benefits of material recovery, the most valuable materials found in the e-products are:

- Precious metals
- Copper
- Rare earth metals (REEs)

Obviously, these materials can vary their amount widely and according to the type of e-device. They can be totally absent or present in negligible quantities compared with some other, less valuable and interesting from a recycling point of view, such as plastic materials, steel, iron, glass and aluminium. In the REEs group, many metals classified as hazardous are present. "The printed circuit board represents the most valuable part of e-waste, accounting for over 40% of the total e-waste metal value" (Golev et al., 2016) [Kumar *et al.*, 2017]. These components are integrated in every laptop, desktop PC and other kind of Information Technology Equipment, in mobile phones, LCD and in Cathod Ray Tube TVs.

The main applications of precious metals in electronics are multilayer ceramic capacitors and hybridized integrated circuits. Mobile phones and desktop computers amounted to almost 40%, secondly laptops and DVD player amounted to 29% among the manufacturing application of precious metals. Main uses for each metal are: gold as connectors, switch and relay contacts, soldered joints; palladium for multilayer ceramic capacitors (MLCCs); platinum and rhutenium for hard disks drives. In general, the usage of precious metals in the production has recently decreased, because of substitutions with other non-precious metals [Zhang *et al.*, 2017]. Nevertheless the data about material consumption report that, in 2014, only electronics industry holds 12% of the total gold demand [Ildar *et al.*, 2017]. Therefore it is clear the potential benefit that could be achieved if these valuable materials are recovered from the discarded devices, by undertaking a proper treatment. This strategy can be defined as Urban Mining, and actually it will lead to obtain secondary raw metals, with high percentage of purity, resalable on the international market. For instance, it has been observed that "certain types of WEEE items contain gold in concentrations 200 times greater than in typical gold ores" [Charles *et al.*, 2017].

"Notebooks and tablets together with desktops and servers, are the most valuable WEEE category, given their extremely high content of key metals in some of their main sub-systems. Especially Tablets have an higher content of valuable materials than notebooks from both screen and PCB components. However, because of their extreme compactness and complicated assembling the recycling is still hard to manage" [Cucchiella *et al.*, 2015].

Cucchiella *et al.* [2015] provided a basic idea of the money revenue that can be achieved by different WEEEs: CRT monitors and CRT TVs value 25 €/product unit and 18 €/product unit, respectively. Cell phones and smartphones value 25 €/kg of product and 19 €/kg of product, respectively. Copper and precious metals make up to 90 to 100% of the total value of mobile phones and laptops [Duygan and Meylan, 2015]. Figure 2.2 illustrates for both critical and non-critical raw materials the current recycling rates in Europe deriving from the treatment of discarded devices [European Commission Commission [2018]].

According to a survey made by Cao *et al.* [2016] in Zhejiang Province, China, "many inhabitants (83.8% of respondents in the survey) have no idea about how to find formal WEEE collecting enterprises. As a result, most people prefer private traders to formal classified recovery enterprises".

2.3 Current international and national regulations

By the end of 2014," approximately 4 billion people were covered by the national e-waste legislation" [Zhang *et al.*, 2017]. Baldé *et al.*[2017] reports that from 2014 to 2017 the world's population covered by e-waste legislation increased by 22%, reaching a total of 67 countries which have established a regulation. Figure 2.3 summarize the information. Despite this, laws are not always effectively enforced.

In Europe the legislation state specific targets and regulation of the recycling schemes. As a consequence of these regulations, it is possible to monitor the WEEE management. However still a considerable portion of the traded products is suspected to avoid standard controls. Many more efforts are needed and more strict rules should be established in order to monitor the transboundary movement of WEEE. Avoiding the illegal transfer of considerable amount is still a challenge in Europe, Japan and South Korea. In Japan, the enforcement of the "Home Appliance Recycling

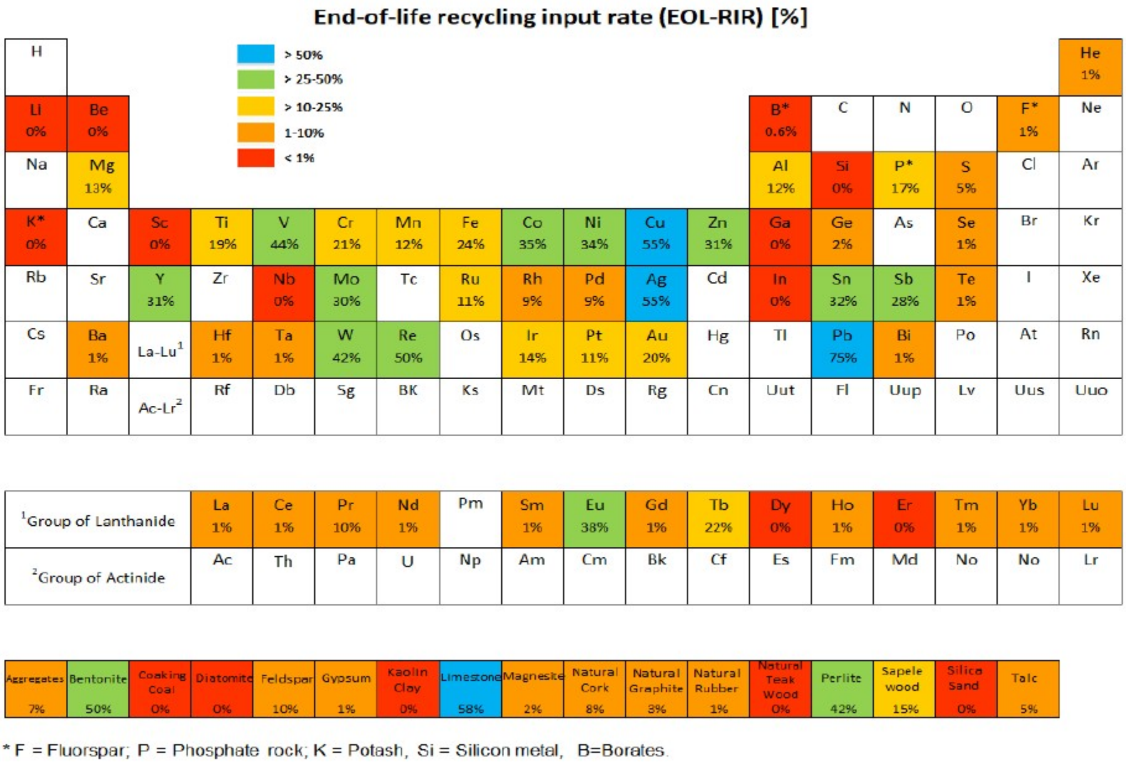


Figure 2.2. Recycling rates from end of-life products. Source: European Commission Commission [2018].

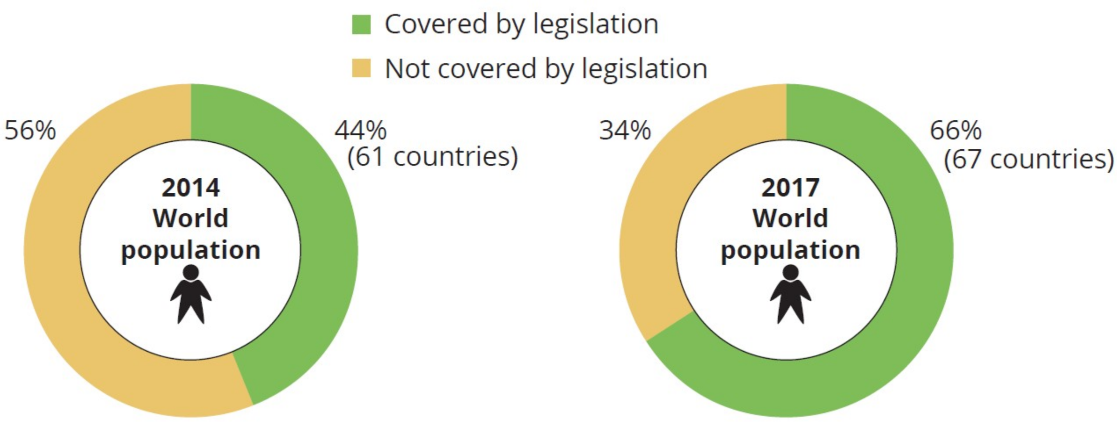


Figure 2.3.

Population covered by e-waste legislation. Source: Baldé *et al.*

Act", in 2001, made the recycling rates of target products vary from 50% to 70% . After 2012 recycling rates of many specific categories reached even 85-90 %. "In Africa few countries have enforced national WEEE related legislation, but they are mostly recycled through backyard recycling or substandard methods which moreover lead to serious environmental pollution". [Zhang *et al.*, 2017].

All over the world there are several categorization systems for the electronic devices. A very detailed EEEs classification is provided from the United Nation University [Balde *et al.*, 2015], the so called UNU-KEYS. A total of 54 categories are listed in UNU-KEYS, which is mainly intended for a statistical purpose about the market sales. By the way the 54 categories can be grouped into 10 primary categories, which can be directly matched with the current EU WEEEs categories. In Europe, to manage all kind of wastes in the administration, the List of Wastes (LoW) has been made. In this classification each waste type is characterised by a six-digit code. There are 13 LoW codes that refer to e-waste. They are subdivided into hazardous and non-hazardous waste. The problem is that this classification is not directly correlated with the last recasted directive. In fact, in July 2012, EU recasted the WEEE Directive (Directive 2012/19/EC). It specified the minimum recovery targets for each category till 2019. As indicated in the regulation: "The purpose of this Directive is to contribute to sustainable production and consumption by, as a first priority, the prevention of WEEE and, in addition, by the re-use, recycling and other forms of recovery of such wastes so as to reduce the disposal of waste and to contribute to the efficient use of resources and the retrieval of valuable secondary raw materials...[]. In particular, different national applications of the producer responsibility principle may lead to substantial disparities in the financial burden on economic operators...[].For that reason, the essential criteria should be laid down at the level of the Union and minimum standards for the treatment of WEEE should be developed". This directive is set according to the "Extended producer responsibility" (EPR) principle: "In order to give maximum effect to the concept of producer responsibility, each producer should be responsible for financing the management of the waste from his own products. The producer should be able to choose to fulfil this obligation either individually or by joining a collective scheme. Each producer should, when placing a product on the market, provide a financial guarantee to prevent costs for the management of WEEE from orphan products from falling on society or the remaining producers. The responsibility for the financing of the management of historical waste should be shared by all existing producers through collective financing schemes to which all producers that exist on the market when the costs occur contribute proportionately" - Directive 2012/19/EC [Parliament and the Council of the European Union., 2012].

This idea is being followed not only in Europe, but also by many other governments all over te world. For instance, the Administrative Measure on Tax Levy and Use for WEEE Recycling was issued from Chinese government in July 2012, as an attempt to put into effect the EPR idea [Cao *et al.*, 2016].

All the e-products covered by this directive are divided into 10 categories, then for each category a list of the included devices is provided:

1. Large household appliances;

2. Small household appliances;

3. IT and telecommunications equipment;

4. Consumer equipment and photovoltaic panels;

5. Lighting equipment;

6. Electrical and electronic tools (with the exception of large-scale stationary industrial tools);

7. Toys, leisure and sports equipment;

8. Medical devices (with the exception of all implanted and infected products);

9. Monitoring and control instruments;

10. Automatic dispensers.

This classification is supposed to be employed officially until the 14 August 2018. The minimum recovery targets are specified for almost every category, during the "transitional period", which is till August 2018. After that, starting from August 2018, the targets are specified for every category.

Focusing on the purpose of this study, Laptop ad Desktop PCs, are part of the group no.3 of the classification made in the directive (Annex II): IT AND TELECOMMUNICATIONS EQUIPMENT. Starting from 15 August 2018 all the EEEs shall be classified within the categories set out in Annex III of the Eu Directive, which are the following: (1) Temperature exchange equipment; (2) Screens, monitors, and equipment containing screens having a surface greater than 100 cm 2; (3) Lamps; (4) Large equipment; (5) Small equipment; (6) Small IT and telecommunication equipment (no external dimension more than 50 cm). In the future adoption classification, PCs are listed among the products falling into the category number 6 (Small IT and telecommunication equipment). However not all the kind of PCs can be included, since in the annex IV, Laptops and Notebooks are defined as part of the group number 2 (Screens, monitors, and equipment containing screens having a surface greater than 100 cm^2). It should be noticed that the Directive includes under the definition "PC" not only the mainframe and the screen, but also the mouse and the keyboard. According to the Directive, during the transitional period (until August 2018), as a minimum target, 85 % of the PCs shall be recovered, and 80 % shall be prepared for re-use and recycled. Then in the subsequent period (starting from August 2018), 80 % of the PCs shall be recycled.

Art. 11 of the directive, about Recovery targets, states: "The achievement of the targets shall be calculated, for each category, by dividing the weight of the WEEE that enters the recovery or recycling/preparing for re-use facility, after proper treatment in accordance with Article 8(2) with regard to recovery or recycling, by the weight of all separately collected WEEE for each category, expressed as a percentage" - Directive 2012/19/EC [Parliament and the Council of the European Union., 2012]. Therefore, the percentages of the targets are related to the total weight of the collected devices per category. Some other targets regarding the collection itself, are required. About this, starting in 2016, the collection targets defined by EU commission are no longer counted as a fixed amount per inhabitant (previously 4 kg/cap), but as at least 45% of the average amount of EEE placed on the market (PoM) in the three preceding years. From 2019 onwards, this amount should increase to at least 65% of the average amount of EEE PoM or alternatively 85 % of WEEE generated on the territory of that Member State [Eygen *et al.*, 2016] The European Waste Shipment Regulation has set the regulation for WEEE exports in the future; inspections will be applied and in case of export for reuse, evidence of the functional capability is required [Salhofer *et al.*, 2016]

The European categorization of WEEE is nowadays discussed, since many member countries have quite different classifications (generally less categories are employed), that often are hard to correlate with the categorization from the EU directive. The adopted classification in Italy is established as reported below:

- R1 - Cooling appliances: refrigerators, air conditioners, freezers.
- R2 - Large white devices: washing machines, ovens, dishwashers.
- R3 - Video equipments: Tvs, monitors.
- R4 - Household appliances and electricity-powered appliances: PCs, phones, vacuum cleaners, small household appliances.
- R5 - Light equipments: neon, low energy consumption light bulbs, gas light.bulbs by mercury, sodium, iodium.

This classification was issued in the act DLgs 151/July2005 (so called ”Decreto RAEE”, Ministro per le politiche comunitarie e Ministro dell'ambiente e della tutela del territorio [2005]) and enriched with additional specifications by the DM 185/September 2007 about the establishment of working modes of the national registry for the financing of WEEE's management, creation and validation of an administration unit for the optimization of the activities regarding collection systems. These acts are focused on the WEEE's sector and they came in addition to the main Italian regulation about waste. In fact the standards for the waste management, collection, treatment and administration are basically defined in the act D.Lgs. 152/2006 ”Norme in materia ambientale”. Some especial components usually embedded in the electronic waste (such as batteries and capacitors) are out of the application area of the DLgs 151/2005, and, due to their content of hazardous substances, their smelting is regulated in the D.Lgs. 152/2006. More recently, most of the detailed rules have been properly indicated in the act D.Lgs 49/March 2014 which is actually the transposition of the Directive 2012/19/UE about WEEEs. Nevertheless, the traditional classification from DM 185/2007 is the one officially adopted, at least by the administrators of collection. Therefore laptop and desktop PCs fall in the category R-4 ”Household appliances and electricity-powered appliances”. The main change brought by the Dlgs 151/05 is the fact that WEEE's processes of collection, transportation and treatment must economically depend on the EEE's producers through their participation at adequate collective systems, applying the principle of extended producer responsibility. Accordingly the only activity that now is still on charge of the local authorities is the management of the collection points. Municipalities must warrant the availability and conformity of domestic WEEE, and they also must bear the costs for the preparation of collection points, so that the final users should be able to send their devices free of charge. The EEE's producer for each new device available for domestic users put on the market must warrant the free-of-charge retirement of the equivalent discarded device. Hence, the collective systems are the subjects, for example no-profit associations, settled and money funded by the EEE producers to carry out their duty related to the WEEE's retirement.

The National Registry for the financing of WEEE's management has been established with the task of monitoring how the WEEE's system works and establishing the market shares, according to which the obligations related to the WEEE management are shared among the producers. The EEEs producers and the Collective systems must be subscribed at the National Registry for the financing of WEEE's management [Dlgs 151/2005].

The legislation provides the definition of ECR ("Eco contributo RAEE" - Eco-contribution for WEEE), which is an amount intended for covering the costs for domestic WEEEs treatment and smelting. This sum is decided by the collective systems. The regulation states also that, when selling a product, it is forbidden for the producer to separately communicate the costs of collection, treatment and smelting to the purchaser.

It is very important, when weighting an electronic discarded device, to take into consideration the entire body of the product including every material or component which is part of it. Therefore it is a mistake to measure only the weight of the electronic components [Dlgs 151/2005].

2.4 WEEE collection systems

2.4.1 Europe

EPR in the European Union has resulted in two forms of product take-back, (1) collective and (2) individual. Municipalities, which collect qualifying products that are discarded by consumers, usually carry out collective product take-back, and then the government charges the manufacturers of these products by fees associated with collection, and additional processing. Under individual product take-back, each manufacturer is responsible for collecting its own product discarded by consumers at end-of-life, and the manufacturer absorbs all costs, but also maintains complete control of its product. Under collective take-back schemes, products are typically routed to recycling operations. Under individual take-back, each individual manufacturer can decide its profit maximizing strategy, such as re-manufacturing, or salvaging key materials for use in its own production [Ildar *et al.*, 2017]. In Europe, collection quantities range between 4 and 17 kg/cap/yr, depending on the development stage of the collection schemes. On average the collection rate in EU member states was 36% in 2014. The most successful collections are performed in Sweden (about 20 kg/cap/yr)[Salhofer *et al.*, 2016]. Beside conventional take-back at municipal collection sites, the following collection routes can be found as current systems in some countries:

- collection at multi-family dwellings: it is a convenient option for residents of densely populated areas, with an expected collection rate for small WEEE of 0.4 to 1.1 kg/cap/yr, as found out in Vienna;
- container collection in public places: it has an expected collection rate for small WEEE of 0.04 to 0.84 kg/cap/yr, as found out in Germany;
- intensified collection of small WEEE at retail outlets: its application in Germany and Sweden showed low recovery rate.

In Switzerland separated collection of WEEEs has been carried out since 1992 by producer responsibility organizations (PROs) through financing and ensuring safe operation in collection, transportation and recycling processes. This system was able to achieve, over all the devices put on the market, an amount of 35% of laptops and 37% of mobile phones returned to collection points and retailers [Duygan and Meylan, 2015]. According to the market analysis the local company Recupel collected only 11% of the waste laptops generated in 2013 in Belgium. The majority of the materials are recycled in the EU, which keeps these resources within the European market [Eygen *et al.*, 2016]. However, unfortunately, the involvement of local authorities and retail in collection is not uniform across members of the European Union.

To achieve significant recycling benefits, huge quantities of e-waste need to be sent to the recycling facility; many times they can be shipped from all over the country, and this is why the transportation distance have to be considered and optimized. A logistical modeling of the collection system is very important for the recycling feasibility. For example, geospatial modeling software has been used to help plan the optimal placement of collection facilities for end-of-life photovoltaics in New York state [Gaustad *et al.*, 2017].

One of the reason which make the collection ineffective, is often the unawareness of the consumer about the proper sorting of the devices. For instance, Parajuly and Wenzel [2017] conducted a study, analyzing a WEEE stream of 1115 end-of-life devices from households, which was collected at civic amenity sites, around the city of Odense, in Denmark. The products were sorted into the categories defined by the WEEE Directive. Even though most of the items were found to be deposited correctly in the designated cages, a few cases of mis-sorting were found, especially in the small appliances. Most of the problems came from the separation of batteries as hazardous-waste. The most common products that were found with portable batteries inside them were remote controls, wireless phones, keyboards/mice. Also, some other small products and special hazardous items, which were supposed to be collected in their own adequate cages, were found in the sampled cages mixed with devices, which weighed 2% of the total.

2.4.2 Italy

In Italy, the unit that manages the WEEE collection is the "Centro di Coordinamento RAEE" (WEEE coordination centre - CdC RAEE). The collection is carried out by different kind of facilities, supposed to receive the waste, which are identified as *Waste collection points (WFCS)*, *grouping points (GPS)*, *household waste collection facilities (HWCFS)*, *TSC and sales outlets* and *large-scale users (LSU)*. The *collection points* are managed by the municipalities or by local authorized companies, where all the citizens can discard their electronic appliances for free. WFCS can also manage a WEEE retirement service from urban areas and receive the WEEEs coming from the distribution system. The*private collection points* work in the same manner, except for the fact that they are intended for the waste coming from voluntary collection schemes and from non-household users. The *grouping sites* are the destination of the carriers of WEEEs coming from door to door collection at households. Here the incoming WEEEs are grouped. They must be registered at the CdC RAEE. In the *shops and technical assistance points*, it is possible to have the free retirement of domestic appliances which were sold by the shop's company, after their use phase. The shop then delivers the WEEEs to the proper treatment plant. Finally the *big users* are those public or private facilities (such as hospitals, airports, factories, etc.) which generate a large amount of WEEEs (category R4 and R5), and they are allowed to ask for an in-site retirement [WEEE annual report CDCRAEE [2016]].

The facilities mentioned above have been counted, and their number is shown in Table 2.3. The last results highlights the fact that the highest increase in collected waste have been observed in the southern regions, which are rapidly reducing the gap in per capita collected waste which there was towards the northern regions. However, still southern regions suffer the scarcity of waste collection facilities, still undersized in respect to the population density.

When weighting an electronic discarded device, it is very important to take into consideration the entire body of the product including every material or component which is part of it. Therefore it is a mistake to measure only the weight of the electronic components.

In the last report made by CdC RAEE, related to the year 2016, results show that around 283 million Kg of WEEE were collected, which correspond to a national waste collection of 4.67 Kg per person. During 2016 there was an increase of 13.57% in WEEE collection, managed by Collective Systems, compared with 2015, which is a significant result. This improvement came along an increase in the number of waste collection facilities over the whole national territory. The collection quantities per category are reported in Figure 2.4. By considering only the collection related to the category R4 (which includes desktop and laptop PCs), the increase rate in relation to 2015 is even slightly higher, accounting for 17.14%. All the collective systems are associated with the coordination centre (CdC RAEE) and are differentiated by the type of WEEE processed, legal form and the market share they represent. Each Collective System must manage a quantity of WEEE that is proportional to the amount of Electric and Electronic Equipment placed on the market every year by the Producers belonging to the same Collective System, therefore the quantities of WEEE they each manage can be very different. For the same reason, certain Collective Systems are required to treat all types of WEEE, while others are just specialised in the treatment of certain types. The legislation provides also the definition of ECR (Eco contributo RAEE - Eco-contribution for WEEE), which is an amount intended for covering the costs for domestic WEEEs treatment and smelting. This sum is decided by the Collective Systems.

Table 2.3. Accounted WEEE collection facilities in 2016. Source: WEEE annual report CDC RAEE [2016]

WCFs	Grouping points	Large- scale users	HWCFs	TSCS and sales outlets	Treatment facilities
4107	202	6	19	2363	1108

2.4.3 Piedmont

Piedmont has a per capita average WEEE collection equal to 4.92 Kg per inhabitant, slightly higher than the national average. In recent years an increasing trend in collected quantities has been observed, and over the regional territory are currently located nearly 300 waste collection facilities,

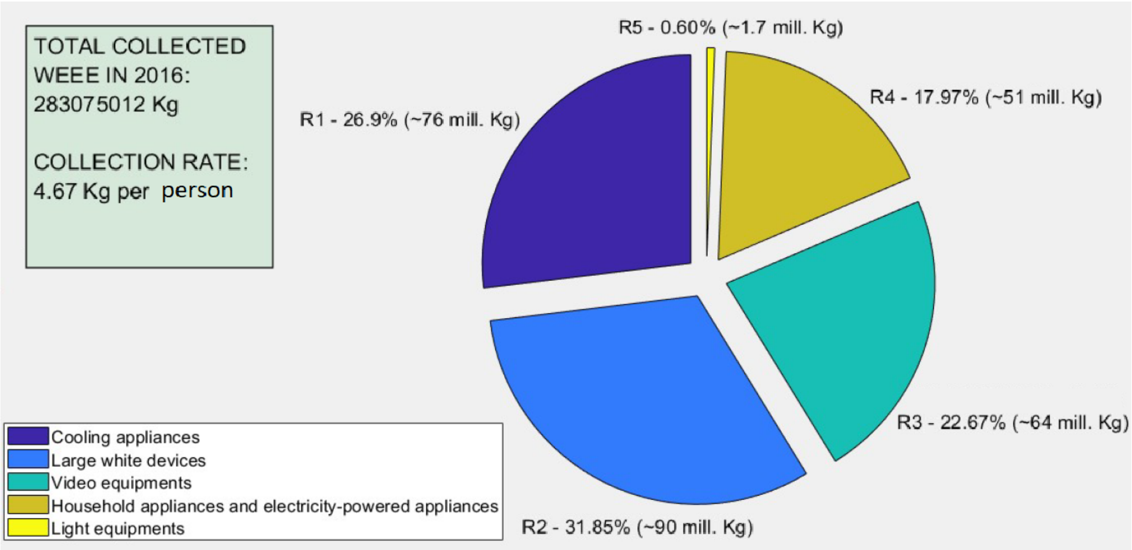


Figure 2.4.

Collection quantities in Italy per WEEE category, in 2016. Source: WEEE annual report CDC RAEE [2016]

and an estimated number of disposal facilities per 100000 inhabitants equal to 7. Though, the most interesting data about Piedmont, from the RAEE report, is that a total of 21673066 kg of WEEE was collected in 2016 which is the best result in the country. Furthermore, Turin is the leading Province, with 8895210 kg of WEEE (among these 1054240 consisting of household appliances) and an increase of 15.30% in respect to 2015. Although this encouraging data, it should be noted that in Turin province the collection rate is only 3.9 Kg/inhabitant which is not only lower than the regional average, but even than the national average.

2.5 WEEE treatment processes

Although many different solutions for a proper waste treatment of end-of-life electronic devices are employed, and many technologies have been deemed to be effective, there are some common steps that have to be performed in every WEEE treatment plant. The path that the materials have to follow, since the discharging of the electronic device till the preparation of a secondary raw material, is:

- 1. Collection and delivery to the recycling station
- 2. Manual sorting and separation
- 3. Size reduction/ Comminution
- 4. Separation in main components (i.e. metals, plastics, hazardous fractions, etc.)

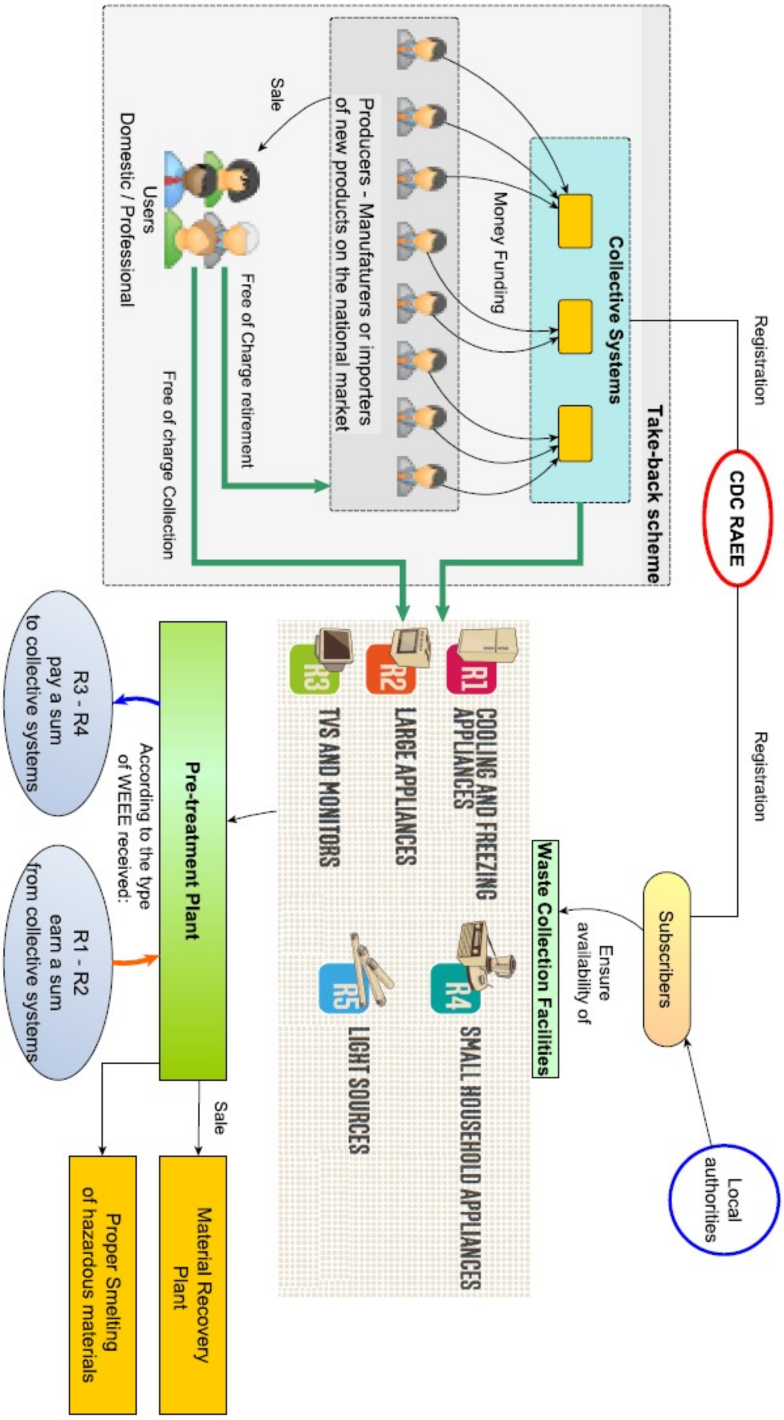


Figure 2.5.

Scheme of the Italian WEEE's management system.
The green arrows highlight the material's transfers granted free of charge.

- 5. Treatment and refining for metal recovery
- 6. Treatment for energy recovery of plastic components

After collection, which has been described in section 2.3, WEEE is sent from the collection points, which can be several around an urban or metropolitan area, to the pre-treatment facilities.

First of all, the collected devices should be disassembled until manual separation with mechanical simple tools such as screwdrivers, air drivers, hammer, tongs and conveyor, is no longer possible. The goal is to separate the materials and components into different categories, with particular accuracy towards the parts containing hazrdous substances. "Batteries attached to motherboards should be removed prior to shipping and recycling to avoid firing and explosion" [Razi, 2016]. Due to high costs of manual labour, dismantling in Europe is mainly performed with mechanical processing. In China, unlike this, since the cost of the labour is much lower, the dismantling process is undertaken manually, typically with the aid of conveyor belts, working stations with tools and boxes or shafts for the output materials from dismantling.

"Volume reduction includes those techniques that remove the hazardous portion of waste from a non-hazardous portion. These techniques are usually to reduce the volume, and thus the cost of disposing of a waste material. They split into 2 categories: source segregation and waste concentration" [Rahmani *et al.*, 2014].

The following part of the pre-processing phase is the size reduction which usually consists of a crushing, shredding (giving output particles smaller than 5 mm) , or pulverization (output particles smaller than 0.05 mm) performed with milling machines (ball-milling machine or disc milling machine) or using a shearing machine and a hammer grinder equipped with a bottom sieve. Ball-milling machine is preferable than disc-milling machine due to its uniform pulverization although the time requires to ball-mill is longer than disc-mill [Hanafi *et al.*, 2012]. In most developed countries, PCBs are recycled in the mechanical-physical processes: crushed directly without dismantling, and sometimes, they previously undergo a thermal treatment, so that some of the inner components can be liberated from their external shell by heating. The subsequent step is a sieving process, with a line of sieves characterized by a mesh width from 0.1 mm up to 15-20 mm.

Then, one or more of the following methods on a raw makes the automatic sorting: magnet separator, corona-electrostatic separation, eddy-current separation, gravity separation. The magnetic separation is typically performed after the comminution. This process is able to separate the iron and nickel fractions in most of the cases. "In a corona separator, particles pass over a high-speed drum equipped with a high energy permanent magnet drum to separate plastic particles, non-ferrous metals and ferrous metals according to their electrical conductivity difference. Eddy-current based electrostatic separators operate based on a similar principle of the conductivity difference, its separation efficiency depends on the different trajectories of particle movement due to eddy current, induced in the non-ferrous particles,and the external magnetic field which deflects the particles respective to their conductivity" [Ildar *et al.*, 2017]. Gravity separation is performed in order to separate heavy fraction of metals from plastics. Since the efficiency of this method decreases with size of the material, this process usually can achieve good separation when performed on large size particles. Generally it is non-effective in separating crushed material smaller below

0.5 mm size.

Treatment and refining of WEEE can be carried out in a range of alternative ways, more or less suitable according to which component is required to be recovered: thermal treatment (incineration, pyrolysis and gasification), electrochemical metal recovery, hydro-metallurgical treatment, bio-leaching. Everyone of these methods has its own advantages and disadvantages; therefore it is recommend employing the best solution keeping into consideration the efficiency towards the target material to recover, and the impacts. Nowadays thermal treatments are still the most applied for recovery, despite of their high energy requirements and pollution releases (material is heated in a bed reactor at more than 600°C). Bio-leaching is one of the last developing technologies, still not applied in large recycling plants, but is seen as the best option for future recycling, given its environmental friendliness. Hydrometallurgy generally is performed by oxidizing the milled material using an acid solution as medium. It's actually the best option to recover precious metals and copper [Ildar *et al.*, 2017].

The application of many of these processes can cause considerable environmental impacts. In fact, thermal treatments are high-energy consumption, and low selectivity towards individual metals, and most importantly, they are significant sources of SO2, toxic heavy metals, dioxins and some more hazardous products located in the chars or in the ashes. Likewise, the hydro-metallurgical treatment, although it has very low energy requirements, it can release dangerous effluent residues and solid waste, due to the use of large amounts of toxic, corrosive and flammable reagents [Ildar *et al.*, 2017].

Concerning the treatments for energy recovery, they are mostly related to the plastic fraction which has great potential as an energy source. The pyrolysis output material can be refined as a fuel oil. The pyro-oils have high gross calorific values (about 30 MJ/kg), mainly with aromatic and with oxygenated compounds. Then, the recovered energy from of WEEE plastic components can be used in cement kilns or in the steel industry. However pre-treatments for recovering or reducing the metal content before incineration are required [Kumar *et al.*, 2017]. Non-material recovery processes take place as well: for example, "the base metals in form of impurities transferred to the slag, can be used as cement; organic impurities in smelters act as an additional reducing agent and fuel; mineral fractions are used as a construction material, replacing gravel from mines" [Eygen *et al.*, 2016].

The flow-chart reported in figure 2.6 shows the steps and applied technologies for WEEE recycling, grouped into two phases: the physical pre-processing and the processing phase. This chart should not be intended as a sequence of mandatory steps, but as an overview on alternative ways of both pre-processing and processing, where the best option should be chosen based on the different cases. The main treatment technologies have been introduced concerning the recycling of the general WEEEs, including all the kind of devices. A more detailed argumentation will be carried out in the next chapter, by setting the focus on laptop and desktop PCs and their specific components as a secondary source of raw materials.

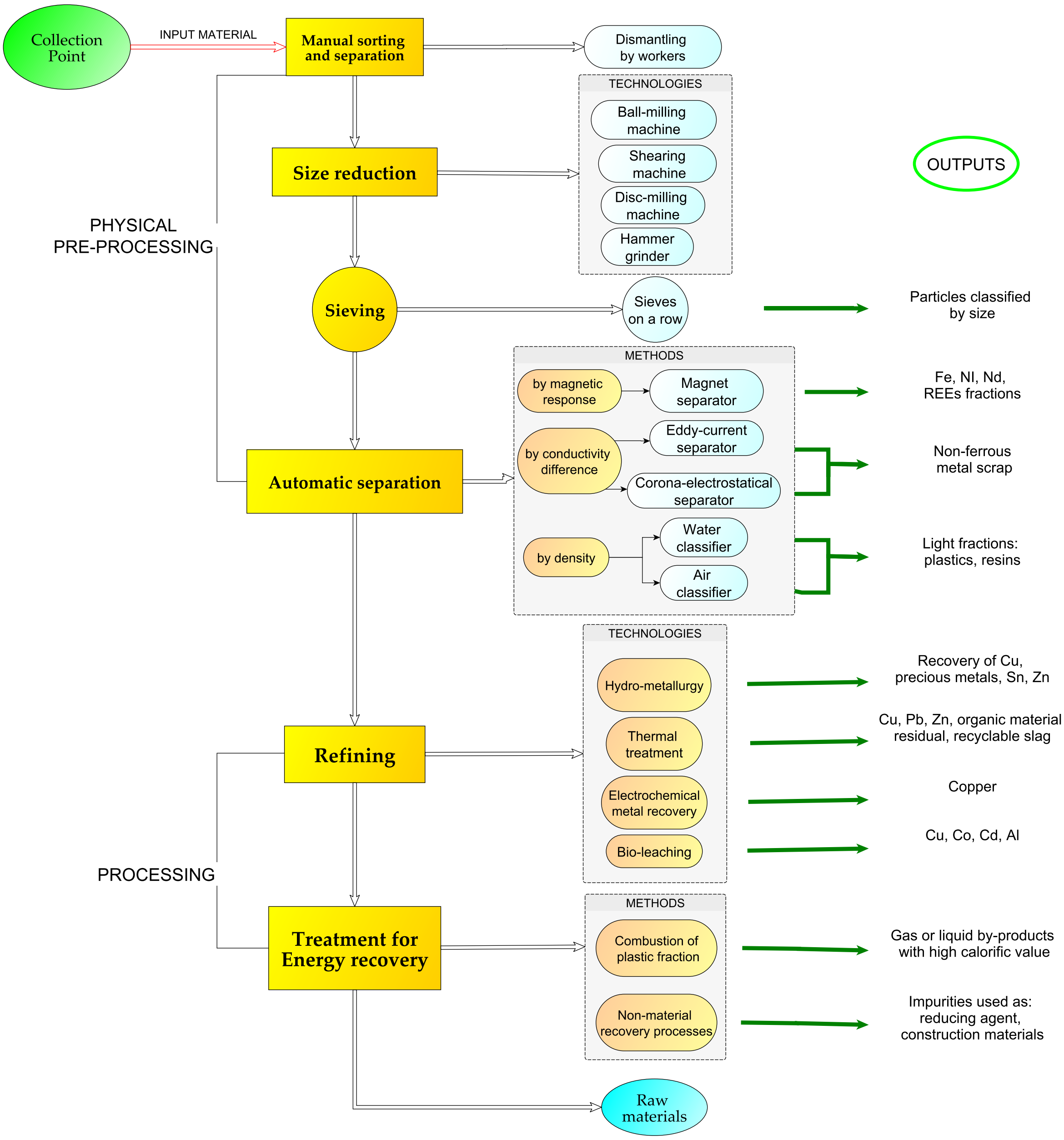


Figure 2.6. WEEE treatment system for resources recovery.

2.6 Environmental issues related with the WEEE management

Electronic waste together with the recoverable materials mentioned above, carries a lot of hazardous elements. When an item is discarded, then this one can follow 2 destinations: disposal, with the related costs for the adequate storing of waste volumes, or recycling. Therefore, there are environmental risks concerned with both these ways. One of the most direct risks for landfilled WEEEs is the leaching of both heavy metals and organic micropollutants into the groundwater from the dump and stockpiles. According to Ildar *et al.* [2017] "WEEE sites are 100 times more contaminated by PBDE, heavy metals, and polycyclic aromatic hydrocarbons (PAHs) than residential areas".

Even though thermal disposal methods such as incineration, are able to hold some toxic elements (Pb and other heavy metals), many other are released in the form of dioxins. Moreover, due to the high releases of CO_2, thermal smelting processes has a significant carbon footprint, which must be considered, because of its global warming potential. The collection phase also generates some environmental loads due to the related transport activities, however its magnitude is very small in comparison with use and production phase.

A lot of Life cycle assessments have recently been conducted, which evaluate the impacts originated during the production, use and recycling phases of an electronic device . By considering a desktop PC, it has been deemed that "during its life-cycle, the most of the energy consumption is required during the use phase, clearly higher than the energy required for the device production" Subramanian and Yung [2017]. The main impact categories which are indirectly affected by a PC production/use/disposal are: human toxicity, climate change, metal and fossil fuel depletion, freshwater ecotoxicity, freshwater eutrophication, ionising radiation. In the smelting phase by incineration, for instance, an energy reduction in the use of fuels from oil in the smelter would reduce the concentrations of polluting substances in emissions, as well as the efficient use of furnaces. Consequently, impacts on health, environment and climate change would be reduced. Currently the most dangerous compounds found in the emissions from thermal treatment are due to the presence of brominated flame-retardants, which are very common materials contained especially in the PCBs.Other important risks include the presence of chlorinated dioxins PCDD/Fs and PBDD/Fs for uncontrolled burning of plastics. "Among the smelting processes, the one required for the steel has the greatest impacts. In the pre-processing phase the sorting has also considerable impacts, when performed by automatic systems" Alcantara-Concepcion *et al.* [2016]. In fact machinery has significant electricity requirements, therefore it is recommended in an environmental view the manual dismantling, performed by workers, which not only saves resources, but it's more effective in the material separation. Unfortunately, most of the developed countries are following the path of the mechanical and automatic separation, as mentioned previously, due to high costs of labour. Likewise, LCA can be seen as a useful tool to quantify the avoided environmental damages and their monetary valuation. In their work Gonzalez *et al.* [2017] found through the LCA, that "promoting re-use against recycling saves 45.20 € in avoided environmental costs per functional unit (PC). Specifically, the particulate matter formation is the category with the highest savings in social terms (16.9 € per PC)".

Hydrometallurgy as a recycling process definitely has small environmental burdens than thermal treatments. The recycling of precious metals (indium and tin) from LCD glass will be economically viable. The employing of chloride metallurgy seems to be more safe with regard to the release of hazardous substances, in comparison with acid leaching [Wang and Xu, 2014].

In the analysis made by Wang and Xu [2014], the recycling of non metallic fractions has been evaluated by the LCA of different recycling and disposal processes. Three disposal processes were compared, landfilling, incineration and pyrolisis. The landfilling was the less-impact method on short-term climate change, but requires large amounts of space. Incineration was the most effective method of reducing carbon deposits, but produced the most greenhouse gases. Compared with the former two processes, pyrolysis saved most resources without emissions of a large amount of greenhouse gas or requirement of much space. As recycling solutions in the same study they found that comparatively speaking, SCF (Super Critical Fluid) and gasification technology might have a potentially smaller environmental impact than pyrolysis process due to the high debromination efficiency, but higher energy consumption than pyrolysis process. Often it's not simple to find out the less-impact solution, in the WEEE management, since its feasibility depends on the economical and political background.

Especially "informal substandard WEEE processing activities include acid stripping and open burning, heating circuit boards for dismantling, melting of plastics which release the hazardous chemicals contained in WEEE as secondary pollutants" [Zhang *et al.*, 2017] Adequate measures need also to be taken in relation to the worker's safety. In fact, nowadays, in many treatment facilities located in both China and India, "a large number of e- waste dismantling workers suffer physical injuries while breaking and dismantling end-of-life products. Dioxins and furans can cause neurological and reproductive problems, and cancer. Dust is a transporting medium" [Kumar *et al.*, 2017]. An analysis of the PCs recycling performances in Belgium showed that, by comparing with a no-recycling situation, recycling of the desktops saves 80% of natural resources, while for laptops this is 87% [Eygen *et al.*, 2016].

Finally below are listed only the most dangerous elements which can come from the electronic waste:

- Lead: it is contained in the batteries and in the device's welds. It causes damages to the neural systems, and causes vascular problems and genetic problem to DNA. It is carcinogenic.
- Cadmium: it is contained in devices components, semiconductors, old cathode ray tube. It causes growth problems, irreversible damages to kidneys and bones. It is carcinogenic.
- Mercurium: it is contained in medical appliances, thermostats, communication technologies and cellphones. It is to be assimilated by organisms. It causes damages to the brain.
- Polichlorobihenyls: they are cooling compounds employed in many electronic devices.
- Chromium VI: It is used as an anti-corrosive agent for metallic surfaces. It is carcinogenic.

Chapter 3

The management of end-of-life Desktop and Laptop PCs

3.1 Components and materials

Plenty of studies and researches have been carried out in the last years in order to characterize the electronic waste from domestic users. Undoubtedly, desktop and laptop PCs are one of the most interesting segments of the electronic waste. It is deemed that they can contain up to 60 elements in various mixtures of metals [Ildar *et al.*, 2017]. Therefore it is important to provide the most relevant results from the literature.

As a first step, the average composition of a desktop and laptop PC should be described. As a general indication, Fan *et al.* [2016] reported that a personal computer comprises 23% plastic, 32% metallic material and 18% non-metallic material. Furthermore, 12% precious and specific metals, but it is not specified if this is referred to a desktop pc or a laptop/notebook. Table 3.2 lists the main functional components of a laptop and a desktop PC taken from the investigation made by Puca *et al.* [2017]. Laptops are smaller and more compact, resulting in a larger concentration of valuable resources, in comparison with desktop PCs. Eygen *et al.* [2016] in their work found out the compositions reported in Table 3.1, based on the waste collected at the Galloo plant in Belgium in 2013 (consisting of about 40 tonnes of desktops and 20 tonnes of laptops). A very accurate investigation was made by Cucchiella *et al.* [2015] who listed all the materials which can be found in different items from e-waste by collecting data from previous literature. Liquid Crystal Diode (LCD) and Light Emitting Diode (LED) Notebooks resulted to be the items with the highest number of embedded precious metals (4, respectively listed per higher concentration: Silver, Gold, Palladium, Platinum) among all the e-waste items, and especially in LCD Notebooks was found the maximum number of critical materials embedded (14). LED screens are the upgraded product of LCD screens and are expected to replace LCD in the short to medium term. Thus, a trend of discarded LCD can be expected in the coming years.

Batteries in laptops contains mostly lithium and cobalt. Particularly there is a rapidly increasing rate of lithium batteries, accounted for around 40 million tons/year [Kumar *et al.*, 2017].

Generally the outer body of the computer case is made of iron, steel or plastic so that it makes the scrap computer less profitable to recycle, considering that mass and volume of the case drive up the shipping cost. This is especially relevant for the desktops. Hence its disassembling is a very important and recommended step. The inner body of the PC includes the most profitable components which are the printed circuit boards. Nevertheless, by considering the economical revenue, nowadays just copper and precious metals make up more 90% of the total recycling value of laptops.

	Mass %	
	Desktop PC	Laptop PC
Fe	37.16	14.23
Al	4.61	8.44
Cu	4.32	6.85
PMs	0.01	0.03
NFe	0.64	10.9
Plastics	18.78	40.58
Other organics	0.09	0.09
Minerals	30.04	12.56
Others	4.36	6.32

Table 3.1. Comparison between Laptop and Desktop material composition. Source: Eygen *et al.* [2016]

Inventory	Desktop PC (g)	Laptop PC (g)
Blu-ray/DVD/CD Players	8.62E+02	1.71E+02
Keyboard	7.37E+02	1.02E+02
Screws and bolts	4.33E+01	5.50E+01
Motherboard	8.22E+02	2.54E+02
Battery	n.a.	3.30E+02
Motherboard Speaker	3.30E+01	1.49E+01
HDD	3.86E+02	9.70E+01
Case	5.01E+03	5.14E+02
Monitor	4.30E+03	8.51E+02
Power Supply	8.43E+02	357E+02
Cable	3.99E+02	2.05E+02
Mouse	9.25E+01	n.a.
Total weight (g)	1.35E+04	2.95E+03

n.a.= not applicable.

Table 3.2. Inventory of components for a laptop and a desktop PC. Taken from Puca *et al.* [2017]

3.1.1 The printed circuit boards

"A typical PCB consists of more than twenty different types of metal, besides ceramic compounds and plastics" [Cucchiella *et al.*, 2015]. "The value of the each scrap PCB is different and it depends on the size and number of integrated circuit chips, small capacitors, gold pins, gold plated connectors, area of gold plates" [Razi, 2016]. Currently the products on the market with the most interesting features in PCBs are the smartphones, while PCBs from PC have a value slightly minor, if related to the total mass of the device. According to Ildar *et al.* [2017], "the weight fraction of a PCB varies from 2% for large electronic devices to 11% for laptop computers and up to 22% for mobile phones of the total device weight".

A common classification in literature distinguishes among: high grade PCBs (e.g. embedded in mainframes and smart phones), medium grade PCBs (e.g. embedded in PCs, laptops or desktop computers) and low grade PCBs (e.g. embedded in TVs, monitors printers and cordless phones) [Cucchiella *et al.*, 2015]. PCBs are basically located in the hard drive, the CPU and the motherboard. Important constructive features for PCBs are their number of layers: (a) single layer, (b) double layer board, in which circuits with two layers of copper are linked by metallized holes, and (c) multilayered boards, in which the circuits are placed in multiple layers on a single board. This distinction allows figuring out the amount of contained copper.

As PC components, hard drives and CPUs have the most valuable circuit boards, with abundance of precious and rare earth, metals. Motherboards have a slightly minor value, because even if they have the largest circuits, these are not densely packed [Razi, 2016]. Figure 3.1 illustrates a sample motherboard together with description of the components which are commonly attached to it. One ton of PWB can contain between 80 and 1500 g of gold and between 160 and 210 kg of copper, which actually represents 40 to 800 times the amount found in gold ores, and 30 to 40 times the concentration of copper typical of the copper ores exploited in the United States [Alcantara-Concepcion *et al.*, 2016] Kumar *et al.* [2017] conducted a cost-benefits analysis, taking as input the data about e-waste provided by the United Nations report (E-waste statistics. Guidelines on classification, reporting and indicators, 2015, Balde et al.). According to this study, the potential revenue from the printed circuit boards is $21200/t and the incidence of Gold accounts for 72%.

3.1.2 Screens

The most important material that can be extracted (even if in limited amounts) by LCD screens is Indium. This is typically present as Indium tin oxide (ITO) films, which act as the electrode in LCD, and account for more than 70% of In used worldwide [Ildar *et al.*, 2016]. However, many studies showed that also in Printed Circuit Boards (PCBs) coming from LCD monitors and displays there are interesting contents in other valuable materials [Cucchiella *et al.*, 2015]. Anyway, it should be noticed that most of the mass of LCDs embedded in PC monitors, laptops and tablets, is made of glass, which accounts on average for 85%. As a re-use option, LCD glass could be employed as a construction material, but the environmental assessment needs to be carried out first [Wang and Xu, 2014]. In fact LCD glass contains several hazardous materials. "Although minor in weight, the constituents of the liquid crystals are complex: from 10 to 25 potentially harmful to the ecosystem and human health compounds" [Razi, 2016]. Despite this, recycling of critical metals (indium and tin) from LCD glass could be economically viable.

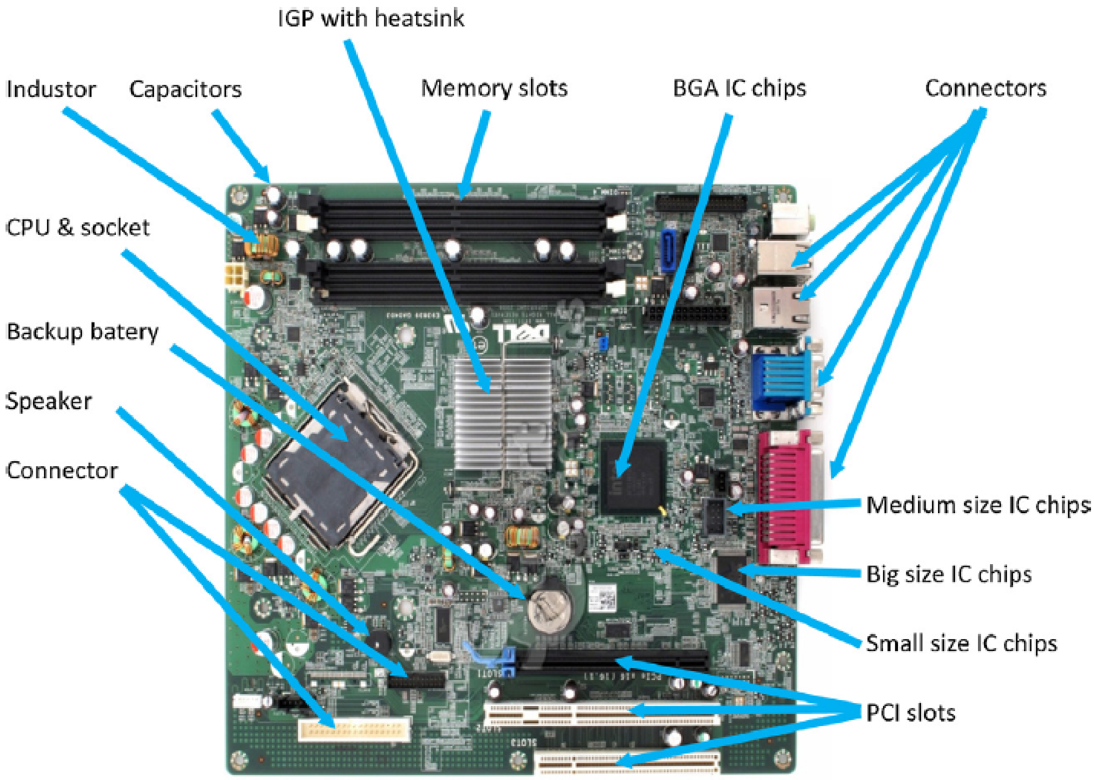


Figure 3.1.   Motherboard of a scrap PC. Source: Razi [2016]

3.1.3 Hard Disk Drives and Solid State Drives

Besides their embedded PCBs, Hard disk drives (HDD) could be an important secondary source of rare earth elements (REE) since a significant amount of these are used for their magnetic properties in various complex alloys. The most used alloy in HDD manifacture is a mixture of neodymium, iron and boron, with the acronym NdFeB. "In 2008, six hundred million HDD were manufactured, each containing approximately 20 g of NdFeB" [Ildar *et al.*, 2017].

Typically, a desktop PC HDD weights around 542 g. Unlike printed circuit boards, the weight fraction of HDD of PC and laptops is comparable, as a HDD occupies 3.6% of the total weight. Unfortunately the recover of material from hard disk drives is nowadays not a common practice, and there is not a developed state of art for this purpose [Ildar *et al.*, 2017]. HDDs present some difficulties in their recycling because of their constructive philosophy, having lots of little parts matched together. The compact design makes the separation of permanent magnets, which are strongly attached to other components, very hard. In addition to the low recovery of metals, HDDs are now turning obsolete and substituted by Solid State Drives, which are less interesting than HDDs in recycling terms, due to the absence of magnetic compounds [Cucchiella *et al.*, 2015].

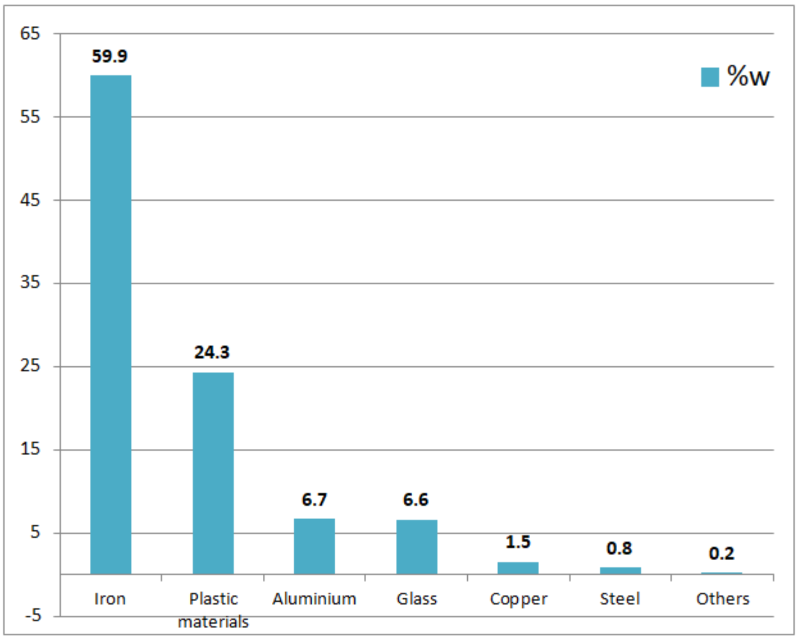


Figure 3.2. Weight composition of a Desktop PC. Taken from Puca *et al.* [2017]

Table 3.3. Weight of dismantled components. Taken from Kida *et al.* [2011]

Name of the components		Weight (g)	Weight (%)
No 1	Metal (Outer frames)	6571	49.8%
No 2	Plastic	306	2.3%
No 3	Screws	44	0.3%
No 4	Mother boadr 1	564	4.3%
No 5	Mother boadr 2	253	1.9%
No 6	Graphics card	109	0.8%
No 7	Memory Module (2pieces)	2595	19.7%
No 8	CPU	251	1.9%
No 9	CD drive	338	2.6%
No 10	Floppy drive	463	3.5%
No 11	Hard drive	461	3.5%
No 12	Wires	104	0.8%
No 13	Power boards	1146	8.7%
Total		13205	100.0%

3.2 Occurrence of precious metals in PCs and laptops

Gold

In order to have a general idea of the amount of gold present in PCs, the material flow analysis made by Duygan and Meylan [2015] for instance, showed that out of 956 tonnes of collected laptops, gold content is estimated to be 36 Kg. Charles *et al.* [2017] reported in his study the gold amounts found in a list of selected PCBs from RAM modules employed by the main companies from early 90's till 2011. Their concentrations ranged from 251 up to 1319 ppm.

DRAM modules, where "D" stands for Dynamic, are exchangeable components connected to the motherboard, which can be added or removed in order to set the random access memory. On average, a concentration of 1022 ppm was extracted from all the considered PCBs. However, since a clear decreasing trend has been observed regarding the use of gold in PCBs, this data doesn't represent correctly the current composition in modern production. There are two reasons which drive the continuous variation in gold content of PCBs. On one hand, because of the higher performances required by modern PCs, the average RAM has increased, and, as a result of that, modules with higher memory are used in PCs, usually not less than 2 Gb, at least in European market. An increase in the memory requires an enlargement in the integrated circuits of the RAM modules, which corresponds in higher amounts of gold employed. On the other hand, the advancement in technology is moving the production to the reduction of precious metals employed, through the substitution with less expensive metals, such as tin, and through the miniaturization of all the PC's components, including the integrated circuits. By considering only the RAM modules with a memory higher than 1 Gb, among the set analyzed by Charles *et al.* [2017], the average composition results to be 999 ppm. However, CPU's PCBs are the components on which Au is mainly accumulated, these units may contain up to 1900 ppm Au (Birloaga et al., 2013). This amount is contained in a contact layer, which throught the years has reasonably decreased its thickness from 12.5 m in the 1980s to a 300600 nm in modern appliances. Several studies aimed to assess the recycling efficiency have deemed that a significant amount of gold get lost in the ferrous scrap, namely in the output material from the magnetic separator. Gold, like many other precious metals, is subject to dispersion and contamination with other materials during the automatic physical sorting.

Concerning the purity features, it is estimated that in PCBs gold plates are made by 18-carat pure gold [Razi, 2016].

Copper

Copper is the most employed metal in circuits and chips. Its concentrations in printed circuit boards are between 15% and 35% by weight [Ildar *et al.*, 2017]. It positively correlates with the number of PCB's layers and the capacity of the conductor current. Generally, as it can be noted in 3.1, the laptops contain a copper's weight percentage a few points higher than the desktop PCs Duygan and Meylan [2015]; out of 956 tonnes of collected laptops copper content is estimated to be about 67 tonnes.

Copper is one of the elements with the highest recovery rate, quite higher than the precious metals, due to a better efficiency of WEEE pre-treatments. It is clear that this metal offers the highest economic incentive for recycling, for its high demand in industry. According to Charles *et al.* [2017] who analysed RAM modules from early 90's to 2010 production, an increase in copper amount has been observed through the years. Most of the copper, in the modern recycling plants, can be separated manually before mechanical processing (basically by the dis-attachment of cables and connectors), but 20% still ended in the sorting residues after automatic separators [Ueberschaar *et al.*, 2017a].

Other precious metals

Platinum group metals are also embedded in PCBs. Main application in electronics are multilayer ceramic capacitors and hybridized integrated circuits, especially the specific uses are: palladium for multilayer ceramic capacitors (MLCCs); platinum and rhutenium for hard disks drives. In general, the usage of precious metals has recently decreased per product, due to substitutions with other non-precious metals.

Indium

Indium's usage as transparent conductive films in LCDs has raised its mining and led to an increase in the production from 149 tons to 819 tons in twenty years. It has been estimated that recovering one tonne of Indium requires the collection of 3.85 million units of LCD TVs or 30 billion LED lights [Gaustad *et al.*, 2017]. Indium is found in a concentration range between 100 and 400 ppm in display units. Recovery of In from discarded LCD is currently immature, and there is not yet a commercial application, so that globally only 1% of total In is recycled [Ildar *et al.*, 2016]. For the recovery of Indium the manual sorting is a particularly important step, otherwise all the Indium embedded in the computers will be dispersed together with the other fractions, during the automatic sorting. .

Gallium

PCBs and Printed Wiring Boards represent the major carriers of gallium. In fact, in the EEE sector,"almost 68% of the applied gallium is used for integrated circuits (ICs), which are required for high frequency wireless communication with the current mobile radio standards like 2G, 3G, 4G or WLAN, so in cellphones and tablets. The remaining material is mostly used for opto-electronic components such as LEDs or laser diodes. In each IC chip, at least one fraction holds a gallium mass share between 25 and 34% [Ueberschaar *et al.*, 2017b].. Mobile phones clearly account the major share with 43% of the total gallium collected with WEEE, followed by desktop PCs (14%)". Therefore, its demand is rapidly increasing, due to the growing market of general wireless communication and also by higher sales of light emitting diodes (LEDs) used as background lighting and in lighting industry in general [Ueberschaar *et al.*, 2017b].

"Since Gallium is contained in very small amounts, the usual recycling processes of PCBs and LEDs determine a dilution of this material with the other ones and subsequently lost. Due to this, gallium is classified as not recyclable. Currently, a recovery is carried out only for material streams with high gallium mass fractions. Furthermore, Used pyro-metallurgical processes are not optimized for gallium recovery". However Ueberschaar *et al.* [2017a] deemed in their study that a recovery would be feasible if gallium rich components are separated prior to any mechanical processing with other material. This material "must be treated subsequently for a selective isolation of gallium from the copper, gold matrix" [Ueberschaar *et al.*, 2017b].

3.3 Treatment technologies

In relation to the scheme represented in Figure 2.6, this section will go through the most suitable techniques for each treatment step, which have been developed by the state of art through the years. First of all, regarding the most valuable components to treat, the recommended flow of pre-processing, suggested by Razi [2016], for higher grade PCBs is:

1)shredding; 2)thermal treatment; 3)pulverization; 4) chemical leaching; 5) precious metal and base metal recovery.

Thermal decomposition of lower grade PCBs under an air flow may give negative commercial yield. As a result, the thermal treatment process might be appropriate only for higher grade PCBs. Chemical leaching can be partly or totally replaced by the bio-leaching, which is more modern and environmentally sustainable. By the way, nowadays the vast majority of the industrial metal recovery processes from WEEE use physical pretreatment and pyro-metallurgical processes, and to a smaller extent hydro-metallurgical processes [Ildar *et al.*, 2017]. A recommended modal treatment, which involves different technologies according to the recovery's target materials [Ildar *et al.*, 2017]. Hydro-metallurgical processes and bio-leaching will be analysed in the following sections.

3.3.1 Pre-processing and separation

Firstly, it is recommended to remove the aluminium capacitors, copper inductors, heat sinks (aluminium or copper), metal or plastic frames from the PCBs to improve its scrap value prior to transferring the PCBs for a further recovery process of precious metals. This operation is fundamental for every kind of laptop/desktop component. If waste PCBs are dismantled at high temperature, resins and adhesives may produce toxic products. Both PBDD/Fs (Polybrominated dibenzo-p-dioxins and dibenzofurans) and PCDD/Fs (Polychlorinated dibenzo-p-dioxins and dibenzofurans) has been found to form, indicating a rapid increase as the temperature rose, in amounts much higher than in unheated PCBs [Sun *et al.*, 2016]. Comparatively low temperature is preferred in use. Though, sometimes the pre-heating step is absolutely recommended since no manual or mechanical treatment is possible in order to disassemble containing materials and components, especially for laptops which are characterized by a complex design. For instance, Ueberschaar *et al.*, 2017b in their work considered as standard treatment for a mixed set of laptops, mobile phones and tablets, a heating at 250°C for 110 min and again at 550°C for 360 min in a muffle furnace. With this procedure, the plastics casings were burned and the inboard components were set free. Recently, ionic liquid is applied to dismantling [Sun *et al.*, 2016].

Results of the material flow analysis made by Ueberschaar *et al.* [2017a] in a conventional sorting processes, and size separation by sieving, are useful to estimate the expected efficiencies of every material's recycling. Accordingly, PCB pieces were dispersed amongst almost all plant output fractions. PMs, REEs, indium and cobalt were relatively higher in smaller grain sizes. Towards copper recovery the manual separation is generally effective, being able to obtain most of its fraction before the mechanical processing. For precious metals, almost 25% of them are lost after collection, by using mechanical systems such as magnetic separation, as well as lost in the dust during the shredding process. Hence, to avoid the loss integrated recycling plants by pyro-metallurgical method should be preferred to the conventional disposal methods. Ueberschaar *et al.* [2017a] demonstrated that an actual gold mass fraction of 0.9 ppm was found in the output from magnetic separator, together with ferrous scrap, after a conventional automatic sorting. Also noticeable was the high transfer of PMs as well as copper (20%) and aluminium (15%)to the sorting residues, which consisted mostly of mixed plastics.

In China PCBs treatment takes place mainly by means of density based separation or dry mechanical processing. With mechanical treatment only the copper content can be recovered from PCBs, while precious metals are lost. He and Xu (2014) noted a recovery metal rate of 6070% in density separation (crushing and water separation), while the rest is lost. Definitely, European technology has been established earlier, so it is more advanced and able to recover metals, including precious metals at high recycling rates, and removing the hazardous material, especially from plastics, such as brominated flame retardants. Many plants, mostly located in developing countries still skip this step.

3.3.2 Hydro-metallurgy

Hydro-metallurgical processes are usually performed on powdered samples from treated devices through the addition of specific solutions. There are many different ways to perform this, according to the type of chemicals employed and the metal to be recovered [Ildar *et al.*, 2017]:

- *Oxidative acid leaching*: "In oxidative acid leaching, the important parameters are temperature, concentration and contact time, with the former being the most important. The oxidative media can be hydrochloric acid, sulfuric acid, nitric acid , thiosulfate, and with a lower efficiency, sodium hypochlorite, thiourea and halides" [Ildar *et al.*, 2017]. This method is essential when extracting valuable materials from PCB, indium from ITO glass and neodymium from HDD. Since aqua regia can dissolve most of the precipitates of sulfate ions and nitrate ions as well as ferrous metals, it was demonstrated that 99.99% leaching efficiency of Au, Ag, Pd and Cu was obtained from a waste PCB by adding this to sulfuric acid leaching [Razi, 2016].

- *Cyanide leaching of precious metals*: "it is the industrial norm for the leaching of precious metals from their primary ores, so that many Au and Ag mines still use cyanide as a lixiviant. Au is bound by cyanide in a reaction named the Elsners equation. It is very cost-effective, especially when employed in selective or multiple step leaching of metals of interest (it is recommended to avoid competition when both Cu and precious metals are present)" [Ildar *et al.*, 2017]. Its main problem is the release of effluent rich of cyanide which are lethal to forms of life.

- *Thiosulfate leaching of gold*: Au leaching with thiosulfate is a non-toxic alternative to cyanidation for primary and secondary ores. It also has advantages related to a faster leaching rate, a lower interference from other cations and its cost. As a modern technology, this is not yet widely implemented in treatment plants.

- *Halide leaching of gold*: "the halides iodine(I_2) and chlorine (Cl_2) can act as redox, complexing and precipitating agents under certain conditions. This property gives them an advantage to achieve selective recovery of PGM from waste materials. Several approaches including leaching of metals using electro-generated chlorine have shown leaching efficiencies of up to 71% Cu along with 98% Zn, 96% Sn and 96% Pb, respectively.very high rates of reagent consumption and reagent costs are the main obstacles of this process for practical applications" [Ildar *et al.*, 2017].

3.3.3 Bioleaching

The bio-processing treatments are attracting interest for metal recovery from waste materials due to their environmental-friendly and cost-effective nature. These processes require a bio-leaching medium containing active growing cultures of bacteria. "A wide range of chemolithotrophic, heterotrophic, and thermophilic bacteria as well as fungi have recently been tested in order to find the best solution" [Ildar *et al.*, 2017]. Although the biological processes have environmental advantages related to avoiding large use of acid chemicals and pollutants, their disadvantage is related to slower kinetics, when compared with the conventional hydro-metallurgy methods. In bio-leaching systems, the bacterial activity can be monitored by measuring pH and ORP. The metal recovery can be single or multi-step. Metal removal efficiencies reportedly decrease significantly with increasing pulp density, good removal efficiencies are obtained with leaching periods exceeding 7 days. In their study, Ildar *et al.* [2016] tested the performance gained by bio-leaching of copper and gold from discarded PCB, coming from laptop and desktop PCs." Components of the boards such as connectors, capacitors, and integrated chips were removed using a thermal gun. Then the material underwent a washing in distilled water, crushing and sieving at a smaller than 500 m size, and heating at 95°C. The mixture of crushed material and 100 ml bio-leaching medium should stay in an orbital shaker for 480 h (20 days) at 150 rpm speed. In their experiment they tested a two step bio-leaching, so that a successive application of bacteria to mobilize metals was carried out. The dried filtered residue of the first leaching was added to cultures of cyanogenic bacteria at the point of maximal cyanide generation, at operating conditions of temperature, agitation rate, and leaching period set to 30°C, 150 rpm, and 120 h, respectively". Copper bio-leaching showed a logarithmic increase trend followed by a decrease in the concentration curve, typical for bio-leaching systems. Metal ions leached from the waste material could be the reason of the microbial inhibition; otherwise, previous studies reported that the inhibitory effect may also originate from the organic fraction of the PCB. "Base metals, e.g. copper, nickel, iron, and zinc form stable complexes with cyanide. Their presence at a high concentration would interfere with gold cyanidation. Instead, if referred to the standard electrode potential gold is less reactive than other metals such as nickel and copper. The obtained pH and ORP profiles showed that microorganisms thrived well at a pulp density of 1% and below. Gold leaching using biogenic cyanide at 0.5% pulp density by P. putida strains achieved the highest gold recovery of 44%" [Ildar *et al.*, 2016]. After bioleaching, the surfaces of the material had eroded, and removal of metallic particles was visually observable by microscope. Latest researches showed that pure cultures of A. ferrivorans, A. thiooxidans, are able to mobilize copper with an efficiency equal to about 90% and even higher (a maximum of

98%) when a mixture of both is employed. Besides copper and gold, bio-leaching methods can be employed to recover: cobalt (Co), nickel (Ni), zinc (Zn), arsenic (As), molybdenum (Mo), cadmium (Cd), and uranium (U).

3.3.4 Thermal treatment

E-waste can also be smelted by thermal treatments, which are one of the most developed technology. The disadvantages of smelting are high-energy consumption, detrimental environmental effects, and low selectivity towards individual metals. The pyrolisis process target is the recovery of organic fractions in WEEE. Pyrolisis of PCB samples can be performed in a tube type oven under nitrogen atmosphere, at temperature ranging from 300 to 900°C. The main decomposition of PCBs occurs theoretically between 250°C and 370°C in pyrolytic conditions within half an hour and the solders of IC chips and electronic components can be peeled off from PCB by means of external forcesor vibrations. Pyrolysis of discarded PCB, carried out at elevated temperatures up to 900°C in the presence of inert gases, generates 23% oil, 5% gases and 70% metal-rich residue. Some strategies have been developed in order to control the emission of hazardous elements. During pyrolysis process total PBDD/F content in the bottom ash and the flue gas decrease as the pyrolisis temperature increases. Moreover, the addition of CaO is effective in adsorbing HBr and results in the inhibition of PBDD/F synthesis by more than 90% and further prevents the acid gases. Appropriate temperature attributes to the inhibition of PBDD/F and gas scrubbing apparatus should be equipped for pyrolysis monitoring and filtration; further separation is essential for the mixture of pyrolysis residues and metals. Generally, the perfect thermal decomposition of the non-metallic part of PCB and electronic parts with a sufficient supply of air produces fly ashes, which cannot be recycled anymore and need to be dumped in landfill [Sun *et al.*, 2016].

3.3.5 Recovery of specific elements

Indium

Certain operations during the dismantling phase can optimize the recovery of indium from laptop and desktop's screens. In fact TFT panels (Thin film transistor) from LCD monitors must be manually separated from other waste flows to allow for indium recovery and to avoid the potential contamination to other recyclable fractions [Razi, 2016]. Presently, the direct smelting of LCD materials is performed mainly in integrated smelters, in which around 85% of the glass would end up in the slag. This method means a disproportionally high energy input to recover a very small amount of indium, which is not economically advantageous. Simple acid leaching or hot immersion techniques are economical processes from waste ITO targets. If the polymer film attached to the LCD screen is removed before the processing, the concentration of available Indium can be raised dramatically. Moreover, experimental works by [Ildar *et al.*, 2017] deemed that Indium leaching shows a positive correlation with temperature and acid concentration.

Lithium

The existing methods for recycling spent Li-batteries are mainly pyro-metallurgy and hydro-metallurgy processes [Zhang *et al.*, 2017]. Some companies have started to recycle batteries, such as Umicore in Belgium, Jinmen GEM High-tech Co., Ltd. in China. In Umicore, by combining a unique pyro-metallurgical treatment and a hydro-metallurgical process, all kinds of rechargeable batteries found in portable electronic devices can be recovered.

Rare earth elements

Even though there are some PC's components particularly rich of rare earth elements (such as the hard drive), on the other hand none of them can be considered poor of REEs. In recent years, some recycling processes have been developed, such as electrochemical processing, acid leaching, ionic liquid extraction and also recovering from scrap NdFeB magnets via membrane assisted solvent extraction [Zhang *et al.*, 2017]. Precisely, more than 90% of neodymium, dysprosium and praseodymium were recovered through the membrane extraction system. Anyway, according to the current process standard there is not yet a specific technical strategy aimed to the recovery of REEs, which are typically found in the output fraction from separators together with other elements present in PCBs. For instance, Ueberschaar *et al.* [2017a] after performing a batch test, taking as input 40 Mg of mixed small and medium size household devices, and considering a common dust extraction system similar to 2.6, found out that REE and cobalt represented the highest share of the selected critical raw materials. Most of it was concentrated in the pre-sorting step (REE 38%, Co 46%) due to battery removal. In the same study, a high share of the tantalum (over 40%) was accounted for pre-sorted PCBs, probably derived from alloys and tantalum capacitors contained. The estimated loads are nearly 1400 ppm, was accounted for pre-sorted PCBs. Laptop and desktop PCs, as complete devices, retain tantalum in lower concentrations due to their higher total weight. Over 30% of Co and about 60% of REE was enriched in the ferrous metals scrap from the magnetic separation. Estimations indicate that the total potential recycled REEs ranges between 1935% of REEs waste in 2020.

Plastics and glass

The conversion of WEEE, especially mobile phone and printed wire-boards plastics into either fuel or gas by feedstock recycling outcomes in a high yield of energy and by-products. Especial chemical recycling methods intended for plastic recovery are pyrolysis, Super-Critical-Fluid (SCF) de-polymerization and gasification. More recently Catalytic De-polymerization Process Technology (CDPT) is being developed in China as the most advanced option, showing promise for the generation of energy from synthetic materials. The exploitable energy from the plastic in e-waste is connected with a high heating potential value which makes it economically feasible and a good candidate for the transition from conventional fossil-fuel energy sources and minimizing gaseous emissions. Heating potential of gaseous and liquid products from plastics is estimated to be between 12.3 and 48.6 MJ m^3 and 26.5 44.8 MJ kg^1, respectively [Kumar *et al.*, 2017].

According to the work made by Wang and Xu [2014] "the plastic waste is pyrolyzed in the fixed bed reactor which is heated to 600°C at a heating rate of 10°C min^{-1}". They collected data from the pyrolysis experiments, the results showed that around 70 wt% of the mixed plastic can be converted to potential fuel. The pyrolysis products consist mainly of oil followed in quantity by char and gas. "SCF has unique properties which confer good solvent ability for oxidation, gasification, liquefaction, solvolysis and other organic reactions". Its preparation requires the use of a solvent. Isopropanol is one of the most suitable for its mild temperature and pressure requirements, and it is able to recover oil from BFR containing plastic with excellent debromination effectiveness (95.7%). However because "the removed bromine mostly existed in the oil after evaporating isopropanol, also an addition of KOH is required in order to fix 94% of bromine in the solid residue. The products of reactions in the SCF included gas, oils and solid residues. The oils contained various benzene derivatives, meanwhile with respect to the gases both plastics produced hydrogen and hydrocarbon gases as the predominant products. Up to 99 wt% of the bromine atoms in the plastics was removed into the aqueous phase, and nearly the entire antimony in the plastics was found in the solid residues" [Wang and Xu, 2014]. Comparatively speaking, SCF and gasification technology might have a potentially smaller environmental impact than pyrolysis process due to the high debromination efficiency, but higher energy consumption than pyrolysis process.

Besides plastics, the other main material containing hazardous substances is the monitor's glass. Not only LCD screens should be considered as a source of glass, since still a considerable number of CRT monitors are nowadays found in the electronic waste. Razi [2016] in his work investigated the material composition of CRT monitors through the separation process. After a first step of manual disassembling, a separation of lead-bearing glass from pure "clean" glass is performed (together with the removing of the electron-gun), then funnel and panel glasses are shredded in small particles. The pyrovacuum process is performed in order to recycle the funnel glass of waste CRT monitors: "funnel glass powder are homogeneously mixed with 09% carbon powder, which is used as the reductant. Using the pyrovacuum process lead is successfully removed from CRT funnel glass by a maximum removal of 98.6%, requiring conditions of 1000°C, 1000 Pa for 4h long, with a carbon added amount of 9%" [Razi, 2016]. Furthermore, "a novel process for lead nano-powder synthesis from the funnel glass by combining vacuum carbon-thermal reduction and inert gas consolidation procedures was developed; results showed that lead leaching from the residue glass met the US EPA threshold" [Wang and Xu, 2014].

3.4 Eco-Friendly management strategies adopted by producers

Nowadays still most of the countries do not have a sufficient number of proper treatment plants able to recycle all the waste computers income. For instance, a study conducted about Mexico, revealed that there is a great potential to increase installed capacity and treatment technologies within the country, in fact currently there are some issues related to the management of end-of-life computers: most printed wiring boards are sent abroad for processing and refining of precious metals. For the CRT (cathode ray tube) computer monitors there is only one treatment plant, located in the north of the country whereas metallic materials are usually sent to foundries in the

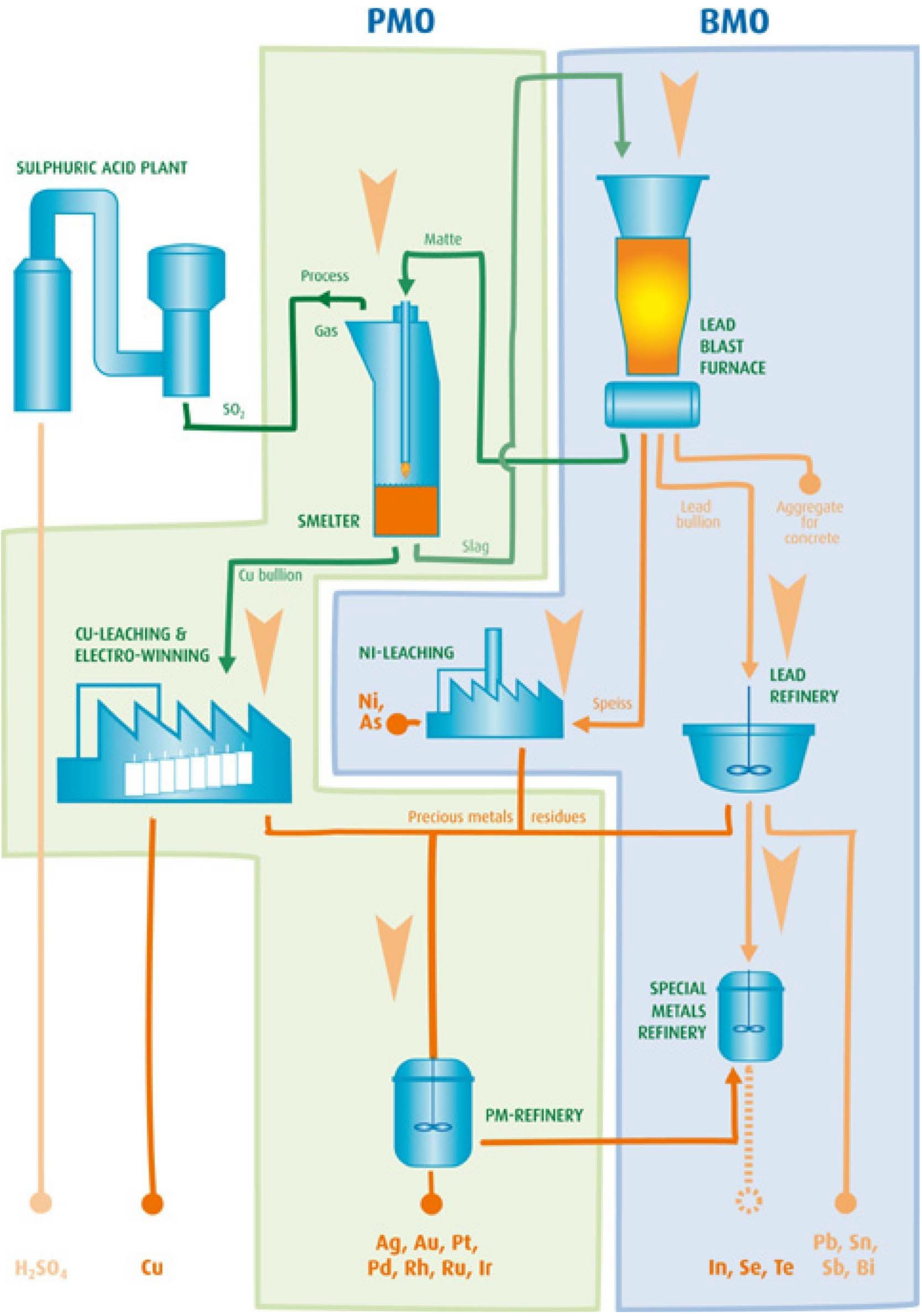


Figure 3.3.

Material recovery related to thermal treatments. Source, Ildar *et al.* [2017]

northeast of country [Alcantara-Concepcion *et al.*, 2016].

To assess the efficiency of the WEEE management in Europe Eygen *et al.* [2016] made a detailed analysis of system and performances in Belgium, considering as case the recycling of laptop and desktop PCs, carried out in 2013. The main output destinations for desktops are the steel smelters and the minerals recyclers. In the case of laptops, the percentage of material is more evenly distributed among the various recycling destinations. Recovery of ferrous metals from desktops and laptops already achieves high rates so that its potential improvements are limited, and the same goes for aluminum. On the other hand, recycling of precious metals could be better managed because a large portion of them is still lost in dust fractions which are landfilled. The indicators related to the material weight recycling Eygen *et al.* [2016] show that 49% of the materials in desktops and 39% of the materials in laptops are effectively recycled to form secondary raw materials. These low values are caused partly by the low recycling rates for plastics, especially in the case of laptops where still a large fraction of the plastics is landfilled. In the same study it was finally deemed that the end-processing step has by far the biggest impact, compared to the ones deriving from the collection and primary treatment steps. As expected, for desktops they are caused mostly by the production of secondary steel, for laptops the impacts are more evenly distributed, with the main share coming from the secondary production of aluminum. In Europe the most important plants that apply different smelting processes are Aurubis, Boliden, Umicore, followed by other steps such as hydrometallurgy.

An optimal recovery of raw materials could be generally achieved by three different circular economy strategies: re-manufacturing, optimal product design, refunding policy for companies that develop take-back scheme. According to Zlamparet *et al.* [2017] re-manufacturing ”is a process of bringing used or worn-out products to a ”like-new” functional condition, offering an equal functional warranty like a new product and reducing the environmental impacts, and the levels of raw materials used in production”.

Nowadays in Europe some firms apply re-manufacturing policy only in the automotive and aerospace sector, for the vehicles components, but also for the medical devices and copy machines. Lately re-manufacture is slightly spreading in the electronic sector at a small extent. Though, due to the device and the high performance standards for the new products, the application of re-manufacturing scheme to PCs seems an unlikely scenario to achieve. An evaluation of predicted benefits in an hypothetical scenario of PC re-use scheme in Spain was made by Gonzalez *et al.* [2017] framed within the so-called *ecoRaee* project. They compared the achievable benefits and avoided environmental damages by performing a LCA for the PC's recycling and re-manufacturing scenario. In the latter scenario they assumed that a preparation for re-use process was performed in Spain with the principle of proximity (local or regional scale). The selected desktop PC for this analysis consisted of Intel Pentium IV, 2 GHz, 40 GB HDD, CD-ROM unit, 512 MB RAM, screen (CRT or LCD), with keyboard, and optical mouse, and it was assumed to be initially manufactured in Asia and intended for a first useful life of 5 years. The time period for the second useful life (2 years) of re-used PCs was set according to the feedback from meetings with different stakeholders and partners of the ecoRaee project. Their analysis showed that clear benefits would be achieved (45.20 in avoided environmental costs per single PC)if re-use is promoted against recycling. However, to achieve a significant result the percentage of replaced PCs out of the total selling should be higher than the rate observed in Spain which ranged between 15 and 24% from 2008 to 2011. Furthermore, this re-use rate keeps in account the replacement by every kind of used PC, without considering whether their first useful life is longer or shorter than 5 years. Besides that, the main assumption of their model is that the PCs compared in the second useful life are perfectly substitutable goods so that they report the same utility to the consumer.

Many other studies have clearly deemed that for a better saving of resources and energy re-manufacturing must be preferred rather than material recycling. Undoubtedly, also great results concerning the avoided impacts would come from a re-use scheme managed by producers themselves, but in Europe the adoption of this system is still far to develop, regarding the personal computer. This is due to the fact the companies which carry out a preparation for re-use ought to offer in their new re-manufactured products the last upgrading, which means new interface and software, hardware, guarantee, and efficiency. This is a big issue, since the the design of upgrade has a short life-cycle. Therefore in the case of laptop the high construction complexity determines lower possibility of re-manufacturing [Zlamparet *et al.*, 2017].

The feasibility of a preparation for re-use is strictly related to design of the devices. Arguably, for this purpose it is fundamental to design standard and easily removable components, connected each other in a not too high level of complexity. For example, Xerox utilized a modular design approach for its multifunction office machine products (copy machines, scanner, fax), which allowed customers to add a module to a base machine in order to gain additional functionality. Xerox designers also standardized components as much as possible across modules and product families in order to optimize the opportunities for component reuse [Gaustad *et al.*, 2017].

In China, where about 6 million tons of e-waste is approximately accounted [Kumar *et al.*, 2017], re-manufacturing companies are insignificant being only five in the whole country. This is mainly due to a lack of knowledge about these not promoted solutions, which affects the customer's orientation [Zlamparet *et al.*, 2017]. Funding of WEEE recycling is organised by state authorities. There is no obligation for producers to fund WEEE collection, they are only indirectly involved by being taxed for products brought onto domestic market [Salhofer *et al.*, 2016].

Cucchiella *et al.* [2015], in their work, highlighted the importance of multi-WEEE recycling centres able to treat different waste streams together. In fact even though the settlement of aimed recycling plants to particular waste stream or product would allow maximum exploitation of the critical resource embedded in the waste, this would not permit to reach an economic advantage for all of the valuable materials from WEEE. Therefore, designing flexible plants, able to treat a mix of different cores, is the recommended alternative.

Adequate measures need also to be employed in relation to the worker's safety. In most developed countries, PCBs are recycled in the mechanical-physical processes: crushed directly without dismantling, noise is generated by each facility in the workshop, especially from crushing machines like shredder and harmer grinder, which overcomes the Occupational Safety and Health Standards (OSHS). Nowadays in country such as China large numbers of e-waste dismantling workers suffer physical injuries while breaking and dismantling end-of-life products. "Also, when applying thermal treatments, dioxins and furans can cause neurological and reproductive problems, and cancer. Dust is a transporting medium"[Sun *et al.*, 2016]. Mianqing Xue (Xue, Yang, Ruan, & Xu, 2012) has evaluated, on average, the noise and heavy metals (Cr, Cu, Cd, and Pb) in the Chinese formal plants. ”The mass concentrations of TSP and PM10 in the ambience of the production line are 282.6 and 202.0 g/m3 respectively which is safe in relation to the Chinese grade III guideline. The concentrations of Cu, Pb, Cr, and Cd in PM10 are 0.88, 0.56, 0.12, and 0.88g/m3, respectively, with Cr and Pb being mostly released in crush and separation processes” [Sun *et al.*, 2016].

Chapter 4

Experimental activity

4.1 The plant Amiat TBD in Volpiano (TO)

TBD (Trattamento Beni Durevoli) plant is located in Volpiano, few km from Turin, and it is managed by AMIAT (Azienda Multiservizi Igiene Ambientale Torino) SpA, which belongs to IREN Group (www.gruppoiren.it). Amiat SpA is in charge of the collection and management of municipal solid waste in the city of Turin (900,000 inhabitants). TBD plant hosts four different treatment lines for R1, R2, R3 and R4 WEEE categories on a 7000 m2 covered area plus 5000 m2 outdoor.

According to the documentation of financial statements (Bilancio d'Esercizio Amiat) from the previous years (2014 and 2015), the waste totally processed was around 9500 ton/y in the last years; R4 quantity, has ranged between 1850 and 2100 ton/y from 2014 onwards.

As reported in the compositional data of the WEEE mass, made by CDC RAEE, in Italy the PCs make up 61.84% of the total R4 weight, obviously taking into account only the mainframe, since mouse, keyboard, and monitor are treated separately (as small household appliances, or, concerning the monitors, as R3).

4.1.1 Inflows

The origin of the electronic waste entering TBD plant is represented by both domestic WEEE (including not only the waste generated by households, but also from industrial and commercial activities when it is characterized by the same composition and quantities [Dlgs 151/2005, Ministro per le politiche comunitarie e Ministro dell'ambiente e della tutela del territorio [2005]) and large scale users (from professional activities, schools, offices, etc).

AMIAT S.p.a. is the second biggest subscriber per quantity, managing 9 Waste Collection facilities in Torino's province, and handling 14.15% of the waste from the provincial area (table 4.1). This percentage corresponds to 1259 tons totally coming from every WEEE category, collected in the year 2016 - "Subscribers are those who have completed their registration at the WEEE Coordination Centre and who ensure the availability of their Waste Collection Facilities to Citizens, Distributors, Technicians and Technical Assistance Centres" [WEEE annual report CDC RAEE [2016].

Besides the quantity coming from its own collection facilities, Amiat TBD receives WEEE (R1 to R4) from other associated consortia operating in Torino's district ("Città metropolitana"), and the nearby provinces, and regions (Lombardia and Emilia Romagna), due to the agreements with collective systems located in those areas. According to the report made by di Torino *et al.* [2016] 2.977 t of WEEE collected by the other subscribers within the provincial area, are sent to this plant annually. Therefore, by comparing these amounts with the total weight of treated WEEEs per year, it can be stated that 13% of the incoming material comes from AMIAT's own waste collection facilities and 31% from the consortia operating all over the province. The rest (approximately 56%) comes from other sources located in the nearby provinces and regions.

As stated by the related regulation, the collective systems are allowed to sell batches of their WEEE to the treatment facilities, paying a fee calculated by the cost per unit of weight related to each category. This is valid for R3 and R4, whereas for the retirement of R1 and R2, is paid by the collective systems to the receiving plant.

Amiat S.P.A has made agreement with many different authorized collective systems. On average the cost for the R4 WEEE material income ranges between 120 and 150 €/ton.

Table 4.1. Provincial Collection Ranking. Source, RAEE [2016]

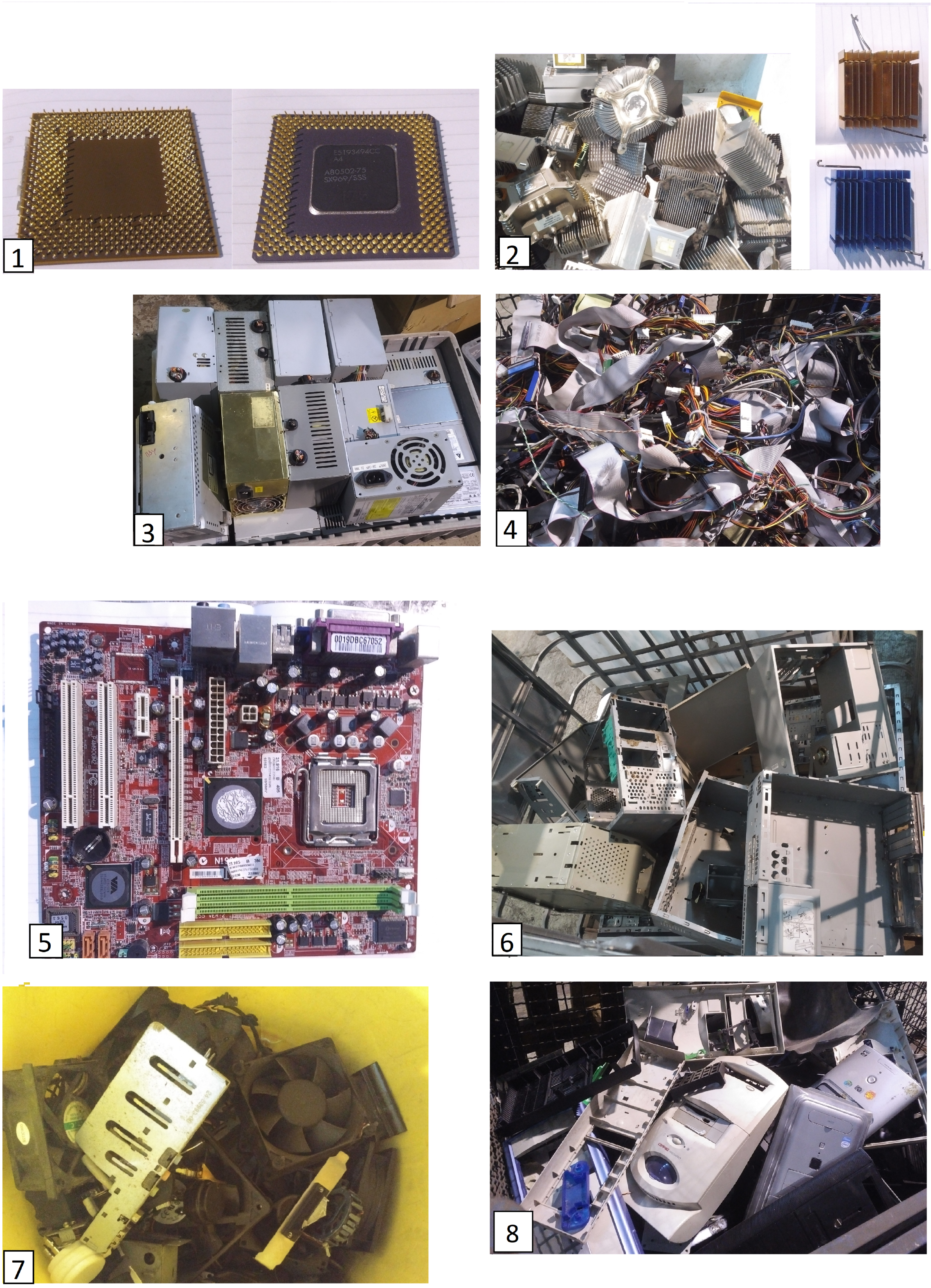
Province of Torino [43 subscribers]				
Top 5 Subscribers	N sites	Type of site	Kg	%
Elettroimpianti SAS	1	GP	1991350	22.39%
AMIAT S.p.A.	**9**	**WCF**	**1258830**	**14.15%**
Società Canavesana S.p.A.	6	WCF	561743	6.32%
Coop. lavoratori ausiliari del traffico L.A.T.	7	WCF	530512	5.96%
ACEA Pinerolese industriale S.p.A.	18	WCF	438621	4.93%
TOTAL	41		4781056	53.75%
TOTAL PROVINCE	130		8895210	

In the following sections the adopted methods for 4 different investigations are reported, respectively about:

- the characterization of the disassembling process;
- Mass Balance of the PC batch;
- Economical evaluation of costs and benefits.
- Elemental chemical analysis on a motherboard PCB

4.2 Desktop PCs treatment at regimen

At TBD plant, desktop PCs are manually disassembled by two workers within a 6-hours shift per day. Figure 4.1 illustrates the 13 categories adopted for sorting the treated material.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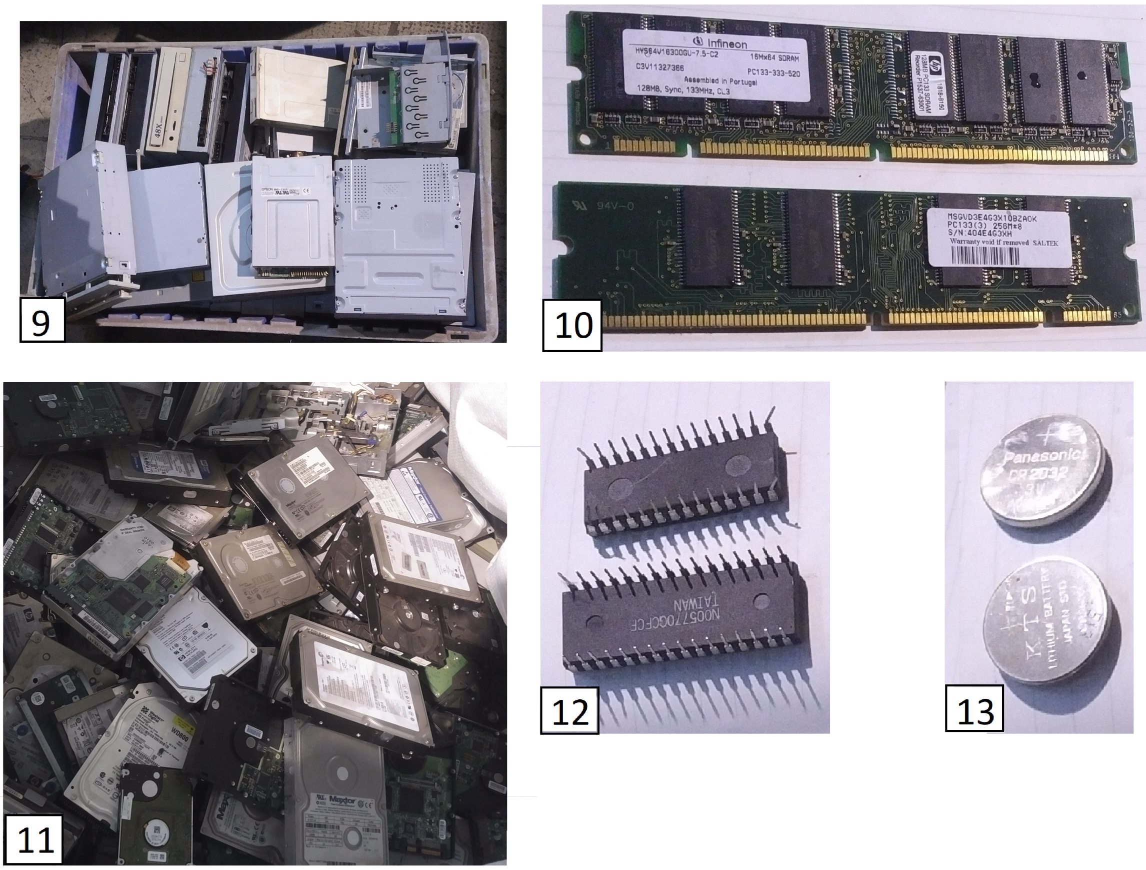

Figure 4.1. .

Categorization of the sorted material:
1. Plastic CPU (on the left) and ceramic CPU (on the right); 2. Aluminium - heating sinks; 3. Power supplies; 4. Cables; 5. Motherboards; 6. Iron scraps; 7. PED R4 and fans; 8. Plastics; 9. Drivers (CD/floppy); 10. RAM Modules; 11. Hard Disks; 12. Integrated circuits; 13. Batteries.

The manually-sorted output fractions are sold to the best purchaser among the national and international recycling companies. Average market values in February 2018 of the sorted fractions are listed in table 4.2 for every fraction leaving the plant. After the manual sorting, each output is sent to a certain destination according to the recoverable material: Iron and Aluminium stays within the northern part of Italy reaching specific recovery stations. The same goes for most of the plastic fraction, although a minor portion exits the European boundaries, being sold to Chinese buyers. The remaining outputs, such as power suppliers, hard disks, motherboards, RAM modules and CPUs are sent to recovery stations managed by big international recycling companies, mostly located in the northern Europe. Clearly, these ones are the outputs requiring the most advanced technology due to their wide variety of embedded elements and complexity. The separated PCBs which are expected to be found in the waste computers, according to the categorization explained in section 3.1.1, are medium-high grade PCBs. In fact, their content is less valuable than smartphone's and tablet's PCBs, which also are treated in this plant.

Table 4.2. Sale prices of sorted fractions.

	Price €/ton
Hard Disks	1500
Drivers	300
Gold RAM modules	25000
Silver RAM modules	11000
Cables	1200
1st Quality PCBs	3000
2nd Quality PCBs	2500
Ceramic CPU	100000
Plastic CPU	25000
Fans	180
Mixed Plastics	130
Iron	200
Aluminium	600
Power Supplier (without cables)	500

4.2.1 The disassembling procedure

The regular activity performed by dismantling workers goes through the following steps: firstly, by using an electric conveyor, the external case of the mainframe is separated, generally taking out both a plastic and an iron part. After this, the power supplier, which is one of the bulkiest and heaviest components in the inner body, is removed. Since it is tightly fixed on the main body, this also requires the use of an electric conveyor. Several cables are connected with the power supplier, they are cut out using a nipper. Also the connector from the opposite end of the cable is removed and sorted separately from the cable itself. Furthermore, the stored power suppliers, need to be checked for the presence of cylindrical capacitors embedded in, and must be sorted separately when their size exceeds a fixed standard, due to their content of hazardous substances.

Independently by the constructive model, those mentioned above usually are the initial manual sorting steps. Then the worker goes on with the separation of several important components attached to the main body, which consists of a large printed circuit board stuck on a ceramic wafer. Metallized pins and connections are densely jointed on this board (4.2, number 5), that is the reason why this kind of PCB is characterized by an heterogeneous material composition making them so hard to treat.

Compact components such as the drivers and hard disks are dis-attached, requiring the use of a conveyor. The disassembling of RAM and motherboard PCBs is made either using a simple screwdriver or just manually without any tool. One more precautionary operation processed by the workers is the separation of small batteries connected to the motherboard, although these ones are not present in some mainframe models. Instead, an usual operation is separating the heat sink and the fan. Both these components are properly located next to the CPU, in order to efficiently allow its cooling. The fans are then stored in a box, together with the removed cable connectors, while the heat sinks are saved separately. Due to this, the CPU turns out to be one of the most complicated component to separate, keeping into consideration that several components need to be removed first, in order to do that, requiring a considerable time lapse.

Motherboards, RAM modules and CPUs are respectively collected in their own containers since their PCBs have different features, materials and values.

To figure out the speed of dismantling process a few workers were observed in operative conditions. The supposed target for this plant is to get dismantled of 6 to 8 mainframes in one hour. This theoretical speed was actually found out; Table 4.3 reports these data, which confirm the minimum recommendations for the performed activity.

Table 4.3. Dismantling time.

	Time (min)	Rate (PC/h)
Average observed	9.7	6.2
Theoretical time	7.5 - 10	6 - 8

4.3 The mass balance

First of all, a quantitative evaluation of the incoming components from discarded PCs, was performed through a mass flow analysis. This was conducted on two levels, considering respectively the operative conditions and the experimental test.

The mass balance in operative conditions, refers to a batch, consisting totally of 210 Kg of PCs, which suitably represents the average composition treated in the plant. Therefore, a typical balance of the sorting fractions related to the standard working condition, is provided and it will be compared with the results of the industrial test. Obtained weights and percentages are listed in Table 4.4. It should be noted that the third line of the table, which considers the weight of circuits boards (motherboards, and eventually graphic boards, audio-boards etc.) does not split the categorization into 1st and 2nd quality, since all the PCBs found can be categorized as 1st quality, characterized by the presence of gold.

4.4 The industrial test

The sample selected for the industrial test is a batch of 100 mainframe units, accounting for a total weight of 1020 Kg. The disassembling process was observed at the workplace and lasted for three working days. After that, the cages containing each of the sorting outputs were weighted. The results are shown in Table 4.5. The output category ”Integrated circuits” is not reported because less then 100 grams were sorted out of 1020 Kg. Therefore, since its share of the total weight is negligible, it was reasonable to consider it null in the depicted by Table 4.4. Though, the weighting

Table 4.4. Mass balance related to the operative conditions sample.

	Weight [Kg]	%
Power supplier	22.38	10.66
RAM	0.8	0.38
Circuit boards	12.93	6.16
Batteries	0.05	0.02
Driver	30.62	14.58
Hard Disk	11.07	5.27
Cables	6.075	2.89
Iron	103	49.05
Aluminium	4.165	1.98
PED R4	1.66	0.79
CPU	0.255	0.12
Plastics	17	8.10
Total	210.05	100

operations carried out for the industrial test highlighted more details due to a higher accuracy and to the larger amount of processed material.

By calculating the mean mass of the mainframe over 100 units weighted, it was also determined an average value of 10.2 Kg for each unit. For the average weight of the single components, an estimate made by dividing the total weight of the selected fraction for the number of 100 units it would be pointless for many components, due to their absence from many mainframes. In fact, there is evidence that, in a considerable number of mainframes entering the plant, several components are missing. This is especially true for RAM modules, drivers, hard disks and fans. Nevertheless, some more reliable weights of components which can always be found in the PCs, are respectively:

- Power supply: 1.42 Kg
- Iron external case: 5.24 Kg
- CPU: 18.4 g

Furthermore, by observing the stock of sorted CPUs, it was found out that ceramic boards while one-third by plastic boards make two thirds of these.

4.5 Economic sssessment

The calculations related to the economic analysis are shown in this section. This analysis has been conducted on the entire annual weight of treated material, considering the revenue gained by AMIAT TBD through the sales of each fraction. It was assumed as average weight composition the one which was found in the sample batch made of 100 PCs. Beside the calculation of money revenue per year, results will be expressed as value per unit of weight (ton).

Taking into consideration the amounts reported in the plant's documentation from the last few years and mentioned above in section 4.1, it is reasonable to assume 1950 ton/y as m_{R4} - total

Table 4.5. Mass balance related to the experimental test sample.

	Weight [Kg]	%
Power supplier	142	13.92
RAM	2.52	0.25
Circuit boards	80	7.84
Batteries	0.3	0.03
Driver	120	11.77
Hard Disk	31.8	3.12
Cables	28.35	2.78
Iron	524	51.38
Aluminium	29.4	2.88
PED R4	14.52	1.42
CPU	1.84	0.18
Plastics	45	4.41
Integrated circuits	0.098	0.01
Total	1019.828	100

R4 weight processed per year - and the composition data from CDC RAEE to figure out the PCs mass.

Table 4.6. mass data

m_{R4} (ton)	R4/PC ($\%_w$)	m (ton)	m_h (ton)
1950	61.84	1205.86	-

The positive money incomes derived from the sorted fractions sold to external facilities are represented by R.

$$R = (\sum_i f_i \cdot v_i) \cdot m \tag{4.1}$$

- f_i [%] stands for the percentages by weight of the i fractions (see Table 4.5).
- v_i [€/ton] are the sale prices of i fractions (see Table 4.2).
- m [ton/y] is the average weight of desktop PCs totally processed per year.

The revenue deriving from the CPUs was calculated according to the quantity-rate of ceramic and plastic CPUs which was found out (respectively 67% and 33 %). In fact, since their prices are quite different (100000 €/ton the former and 25000 €/ton the latter), the CPUs mass share f_i was multiplied for an average sale price weighted by the fractions of these two different types. The same goes for the RAM modules, since their price is 25000 €/ton for the ones containing gold and 11000 €/ton for the ones containing silver. In this case instead, the quantity-rate at which they split is the same, so that a 50-50% composition for the two types was considered, multiplying the RAM mass share for the mean of the two prices.

In Table 5.1 the column r_u reports the revenues of each separated fraction calculated per single PC unit by knowing the average mass of a mainframe. The negative values are represented by the costs coming from: the wages and machinery C_{lm}, the purchase of input material from collective systems C_{im}, and waste management costs C_{wm}(this term is related to the fee paid for the proper smelting of hazardous fractions). C_{im} and C_{wm} include the costs for transportation of waste.

$$C_t = C_{lm} + C_{im} + C_{wm} = c_{lm} \cdot m + c_{im} \cdot m + c_{wm} \cdot m_{ha} \tag{4.2}$$

- c_{lm} [€/ton] is the cost of the labour and machinery per weight unit of treated material.
- c_{im} [€/ton] is the cost of the purchased material.
- c_{wm} [€/ton] is the waste management costs.
- m_h [ton y] is the mass of hazardous components separated in one year.
- m [ton/y] is the same as above.

Table 4.7. Cost-evaluation data.

Specific costs (€/ton)	
c_{lm}	180
c_{im}	135
c_{wm}	1800

The costs mentioned above are reported in table 4.7.

The input material cost was set as 135 €/ton, as an average value of the market cost which ranged between 120 and 150 €/ton, in February 2018.

In this analysis the term related to waste management will have a null value since no extra costs are required for smelting both the hazardous components, namely batteries and capacitors. In fact the batteries are assumed to be sent to smelting facilities belonging to the CDC-RAEE system, which ensure the free of charge retirement. As stated by Dlgs 151/2005, Ministro [per le politiche comunitarie e Ministro dell'ambiente e della tutela del territorio, 2005], the capacitors must be separately removed from the WEEE components sent to material recovery if their size exceeds 25 mm by diameter and 25 mm by height. Given that all the capacitors found in the mainframes of the sample batch were smaller than 20 mm, there is no need to separately remove them prior to sending the waste mass to the material recovery stations. Nevertheless, if they had overcome these sizes, the average cost for their treatment would be 1800 €per ton of capacitors. Their mass in a single PC unit is very small, about the same of the batteries.

The final gain from the activity conducted at the plant takes into account only the flow of PCs entering and exiting the plant. The default operational cost, taxes and administration service were excluded by the evaluation. Therefore the equation for the gain is simply expressed as:

$$G = R - C_t \tag{4.3}$$

whereas the specific gain per weight unit is:

$$g = r_u - (c_{im} + c_{lm} + c_{wm}) \tag{4.4}$$

The results from equation 4.3 should not be intended as a net gain of the plant since many other operational costs related to the work activity are not taken into account. Instead, they will highlight how worth, in economic terms, is the manual disassembling, and which portion of the achievable feedback from the whole WEEE's recycling chain, is held by this process. Moreover the purpose of equation 4.4 is to find out the most profitable fractions for which a manual disassembling would be recommended, outweighing the costs of work, in an urban mining view.

4.6 Elemental analysis

To precisely assess the presence and amount of chemical elements contained in the treated material, a piece of scrap motherboard was analysed using XRF technology through a AMETEK XEPOS D spectrometer. The selected material was cut from a motherboard's PCB, covering a rectangular area from which all the connectors, metallic pins and integrated circuits were removed. Therefore the surface was manually "cleaned" by the attached components so far as possible, so that only the PCB itself was analysed. This operation required a high accuracy for the separation of every single metal pins, and is not something usually performed in the industrial manual disassembling. The separated motherboards are left as illustrated in 4.2. As recommended preparation of the sample, the material was pulverized to optimize the detection of mass by the spectrometric instrumentation.

At industrial scale it is much more effective the milling of PCBs followed by a magnetic separation than the manual separation of such miniaturized components, which are tightly attached, at least for the isolation of ceramic and plastic parts.

The motherboard's model is a SATA 3 SLAVE, made in Taiwan, and the sampled piece has a weight of 10 g, which took an areal extension of 22.5 cm^2 framed within the PCB.

Chapter 5

Results and discussion

5.1 Quantification and composition of the treated waste - mass balnce findings

5.1.1 Significant and critical fractions

Firstly, the results obtained by the mass balance will help to assess how far the selected batch for the experimental test is representative of the actual default composition of the regular activity of TBD plant. Secondly, to better figure out the composition found in the investigated set of waste PCs, it is due to compare it with the data from literature. One of the most reliable analysis of the mainframe's composition, which easily suits the classification of sorting fractions in our case of study, was made by Kida *et al.* [2011] (see table 3.3). Some adjustments were done since some of the detailed categories in table 3.3 can be grouped into more general categories of tables 4.2 and 4.1. Since their analysis was made on a mainstream brand desktop PC about 9 years ago, this comparison will also help to notice the changes in composition of Desktop PCs in the last decade. Figure 5.1.1 illustrates this comparison. In addition to this, the weight of some single components can be compared to the data in the table 3.1 from [Puca *et al.*, 2017].

Before comparing the mass balance results, it should be basically noticed that the determined average weight of a mainframe unit is significantly different from the results provided by literature. In fact the average weight of the selected PC according to Kida *et al.* [2011] is 13.2 kg, whereas in this experimental analysis, the averaged result on the 100-PCs-batch, is 10.2 Kg, making them 3 kg lighter. This relevant gap clearly depends on the evolution in industrial manufacture, which has moved to the application of lighter materials and smaller components in the last ten years.

By observing Figure 5.1.1, it is clearly notable that the heaviest fractions from all the three data's sources, have quite close to each other values. The Iron percentage makes up about 50% of the mainframe weight in each bar, dominating the weight distribution of the device. All the ferrous material is actually located in the external laminated boards of the case, which constitute the mainframe's shell, except for a few internal framework's parts, working as a support for the allocation of hard disk and the drivers. Therefore, it can be concluded that the majority of the

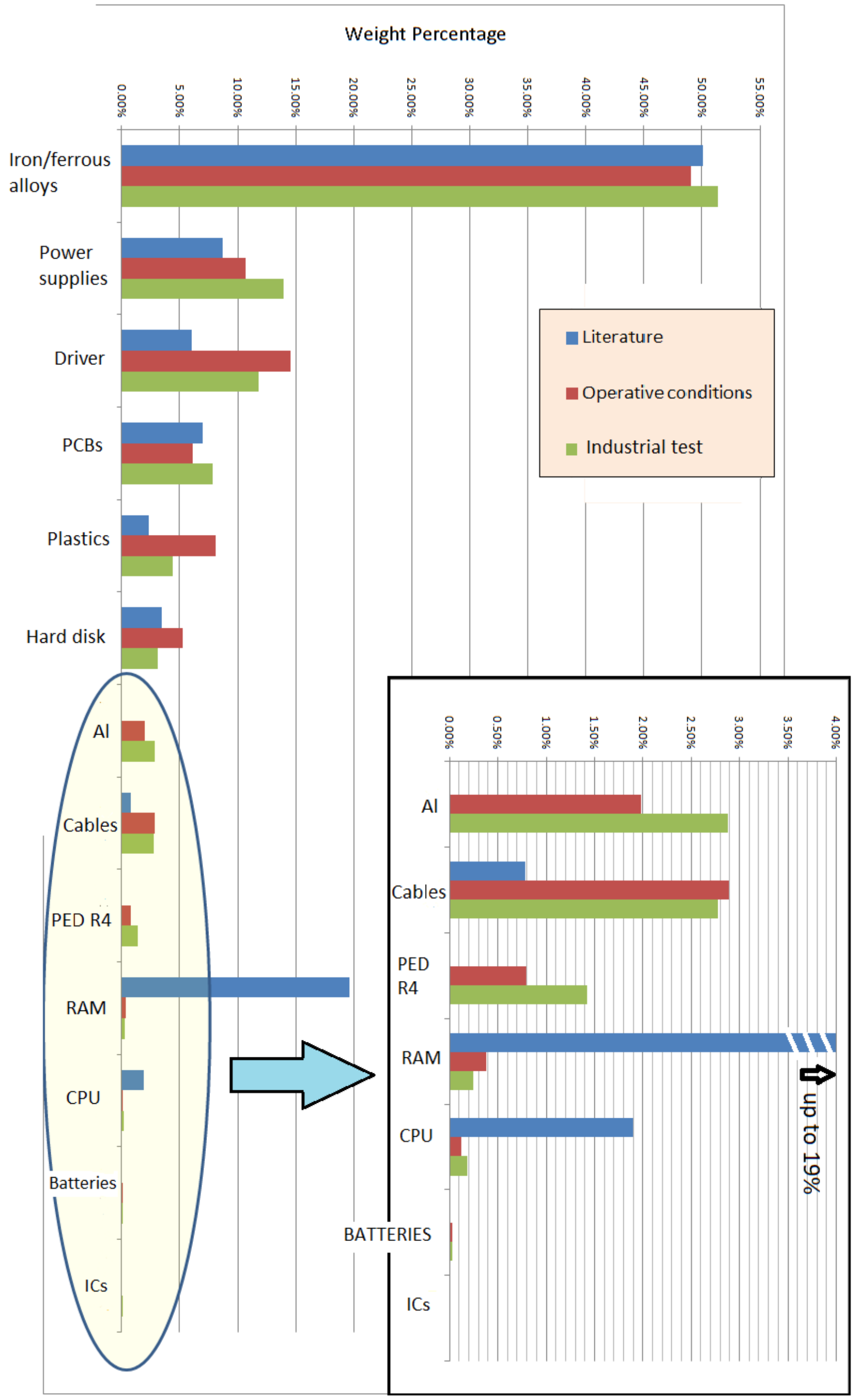

Figure 5.1. Mass balance of the industrial test (green) compared to TBD plant operative conditions (red) and literature data (blue). Data are expressed as %wt.

device's mass is made only by the external case.

Power supplies, by observing the green bars in the chart (related to the conducted experiment), represent the second most heavy fraction of the mainframe, followed by the CD/floppy drivers and the PCBs of motherboards and graphic boards. Then, accounting for less than 5% in the mass balance, there are all the remaining fractions, namely plastics, hard disks, aluminum, cables, PED R4 (fans) and with less than 1% RAM, CPUs, batteries and Integrated circuits. Most of the mainframes contained both a CD and floppy drive so that they make 11.77% of the device's weight which is nearly 6% higher than the percentage found in Kida *et al.* [2011]'s work.

A strong discrepancy from the literature data Kida *et al.* [2011] is clearly observable for the RAM percentage by weight, containing PCBs. This is mainly due to the fact that in the analysed batch for this case of study, a considerable majority of the mainframes reaches the plant without the RAM modules, which were removed in the upstream path of the e-waste. In fact those components are easily removable, also designed for a re-use purpose. So most probably, end-users hold many modules, and this large difference in weight composition can be seen as a consequence of the common habit to retain them before sending the waste PCs to treatment. Moreover, a secondary reason may well be the miniaturization of components, and the application of lighter materials by manufacturing companies, which has made this component less relevant as weight share in compared to the literature data [Kida *et al.*, 2011] from one decade ago. Similarly the CPU's weight share in our experimental batch is much smaller than the percentage indicated in literature. This fact can be seen as a loss in economic terms given that motherboards and CPUs contain precious metals in high concentrations.

The only category that has a considerable difference when comparing the experimental test to the default weight composition in operative conditions, is the Plastics fraction, which resulted to be nearly a half of that, 4% lower. Since the fans are stored separately, this fraction basically consists only of the frontal part of the outer case.

Table 5.1. Revenues from each sorting output.

Sorted fraction	composition ($\%_w$)	r (€/ton)	R (€/year)	r_u (€/PC unit)
PCBs	7.84	235.33	283780	2.40
CPU	0.18	135.77	163717	1.38
Iron/ ferrous alloys	51.38	102.76	123917	1.05
Power supplies	13.92	69.62	83952	0.71
Hard Disks	3.12	46.77	56401	0.48
RAM	0.25	44.48	53634	0.45
Drivers	11.77	35.30	42567	0.36
Cables	2.78	33.36	40226	0.34
Aluminium	2.88	17.30	20858	0.18
Plastics	4.41	5.74	6917	0.06
PED R4/ fans	1.42	2.56	3090	0.03
Integrated circuits	0.01	1.06	1275	0.01
Batteries	0.03	-	-	-
Total	100	**729**	**1421529**	**7.44**

Table 5.2. Cost benefits analysis - summary.

	€/ton	€/y
Revenue	729	879059
Cost (material)	-135	-162791
Cost (wages)	-180	-217055
Gain	414	517301

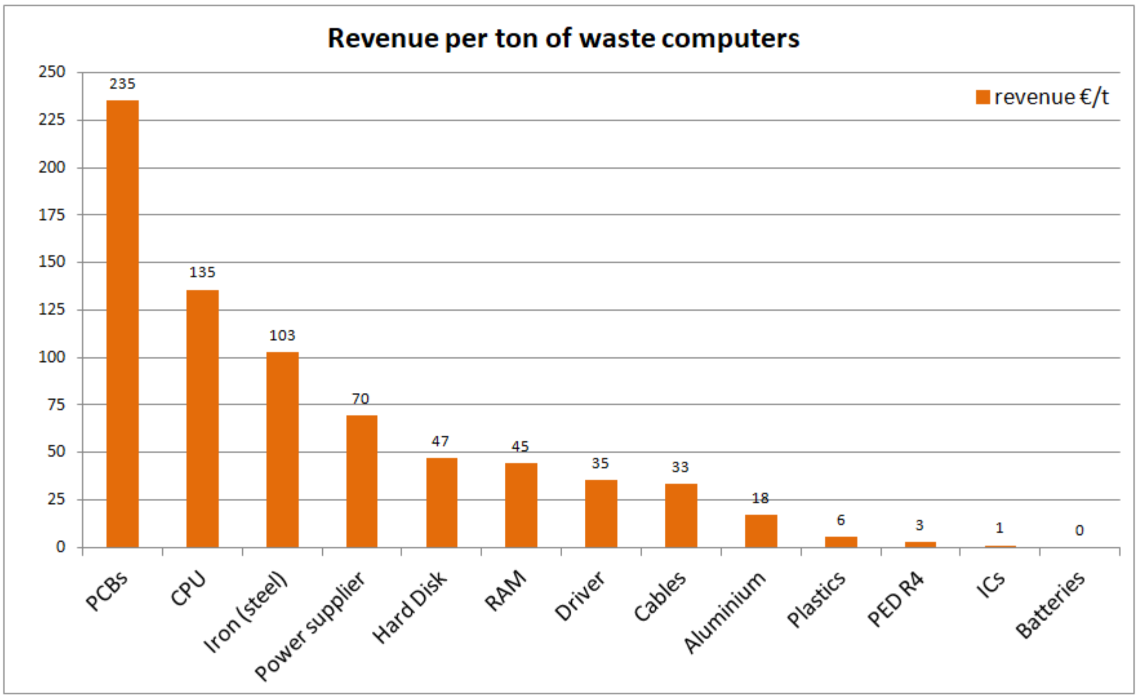

Figure 5.2. Ranking of the sorted fractions by economical value.

5.2 Costs and benefits outcomes

The figure 5.2 shows that PCBs from Motherboards and graphic boards have a quite higher recoverable value than any other component, namely 2.40 €/PC unit (235.33 €/ton), which only by itself is almost one third of the total revenue from a PC's mainframe. It is interesting to note that, even though CPUs have an extremely small weight percentage (0.18%), they are the second most valuable component among all the sorted materials since only their presence makes a revenue of 135.77 € out of one ton of waste PCs (1.38 € per PC unit).

The economical revenue achievable by completely disassembling a PC desktop mainframe resulted to be 7.44 €. This value when compared to the average cost of a mainstream brand PC for domestic use put on the market, makes up the 1.14% of its value as a new product. In fact the vast majority of the PC mainframes nowadays are sold on the Italian market with prices homogeneously distributed from 500 to 800 €, averagely 650 €.

At its end of life a PC still keeps a portion of its original value. That very small percentage found above (1.14%) is only the value recovered by the plant's company through the pre-treatment process. The remaining part is shared among the other processes and destinations which the waste PC is intended for. Therefore, other phases should be considered as money feedbacks, such as the recovery of raw materials, the avoided environmental damages (accountable as economical value), eventually the re-manufacturing of components, the social benefits (availability of job places), etc.

Table 5.2 shows the potential gain related to the annual treated amounts of personal computers, excluding administrative costs of the company. It was also assumed that all the sorted materials were sold at the prices listed in table 4.2, not affected by drops on the market. Therefore the theoretical gain would be 414 €/ton and about half a million euro per year.

5.3 Chemical analysis findings

5.3.1 Results overview

In accordance with the calculated economical revenue, the elemental analysis was conducted on the most profitable fraction in the mainframe, namely the motherboard.

The chemical measurements have found out the elemental concentrations reported in Table 5.4. This table reports the concentrations measured on the powder sample. The underlined lines highlight the elements currently recognized as CRMs according to the last Report on Critical Raw Materials and the Circular Economy by European Commission [2018]. According to the XRF measurements more than 80 elements were detected in the sample. Totally 98.98 % of the mass was detected.

The main content is represented by metal oxides and copper. The first ones, consisting of Silicon oxide (43.26 %), Calcium oxide (12.22 %), Aluminum oxide (13.05 %), Iron oxide (2.06 %) as most concentrated elements, makes up a considerable part of the total mass. The SiO_2, also known as Silica resulted to be the most applied material, which must be taken into consideration since it is marked as CRM. In nature this is present as quartz, which is largely mined and processed for the production of silica. The copper was also found in a high concentration 178300 μg/g, making the further recycling treatments of this component undoubtedly profitable for a money revenue from the only copper fraction.

5.3.2 Presence of precious metals and hazardous compounds

Quite relevant was also the content of different hazardous elements. Among these, bromine, which is well-known for its application under the form of flame-retardant compounds, has the highest concentration (6293 μg/g), followed respectively by lead, chromium, arsenic and antimony.

The content of precious metals consists in Silver, and Palladium. Gold was also detected, but in a concentration below 0.5 μg/g. Comparatively, silver is characterized by a concentration of 52 μg/g, which is much more significant aiming to its potential recovery. Also important is the

Table 5.3. Measured concentrations on powder sample by XRF.

Powder sample PCB		
	Concentration	Standard dev.
SiO_2	**43.26 %**	0.05
Cu	17.58 %	100
Al_2O_3	13.05 %	0.08
CaO	12.22 %	0.01
Fe_2O_3	2.06 %	0.004
SO_3	1.20 %	0.004
Ti	8430 mg/Kg	12
Br	6293 mg/Kg	20
Ni	5326 mg/Kg	12
Ba	**3727 mg/Kg**	6
Pb	3425 mg/Kg	10
Sn	3294 mg/Kg	7
Zn	2320 mg/Kg	8
P_2O_5	1887 mg/Kg	0.0029
K_2O	0.1417 %	0.0011
Cl	0.1051 %	4
Sr	712.7 mg/Kg	2
MnO	0.0527 %	1.3
W	**231 mg/Kg**	10
As	189.6 mg/Kg	7.3
Cr	156.2	1.2
Ag	51.8 mg/Kg	0.9
Rd	**47.6 mg/Kg**	0.4
Pd	**14.9 mg/Kg**	0.9
V	**12.3 mg/kg**	4.2
Sb	**12 mg/Kg**	0.9
Ga	**< 5.8 mg/Kg**	-
Ge	4.7 mg/kg	1.6
Y	**3.6 mg/kg**	1.1
Cd	1.7 mg/kg	-
Hf	**1.0 mg/kg**	-
Hg	< 0.7 mg/kg	-
Ta	< 0.6 mg/kg	-
Te	< 0.6 mg/kg	-
Au	< 0.5 mg/kg	-
U	0.5 mg/kg	-
Th	< 0.4 mg/kg	-
Tl	< 0.4 mg/kg	-
Mo	< 0.2 mg/kg	-
Ru	**< 0.2 mg/kg**	-
In	**< 0.2 mg/kg**	-
Co	**< 0.1 mg/kg**	-

Table 5.4. Measured concentrations on powder sample by XRF.

	Concentration	Standard dev.
Se	< 0.1 mg/kg	-
Rb	< 0.1 mg/kg	-
Nb	< 0.1 mg/kg	-
I	< 0.1 mg/kg	-
Cs	< 0.1 mg/kg	-
La	**< 0.1 mg/kg**	-
Ce	**< 0.1 mg/kg**	-
Bi	**< 0.1 mg/kg**	-
Sum of concentration	98.98%	-

presence in a concentration about 50 μg/g of Rhodium, belonging to the Platinum Group Metals (PGMs) which are marked by EU Commission as CRMs.

For the confrontation with literature some comparable data were found in the work by Razi [2016], based on the investigation made by Kida *et al.* [2011] who conducted their analysis using ICP-OES. A strong decrease in the content of gold is evident while the silver's and the palladium's decrease was slightly less remarkable. On the other hand the content of copper has more than duplicated showing a value over 100000 μg/g higher than the one reported in literature. Also the content in Nickel and Zinc have significantly higher concentrations.

In accordance with many recent studies this comparison between the current material composition in waste PCBs and the late 2000s waste PCBs confirms the decreasing trend in PMs content and the increase in copper applied in the electronic components production.

p

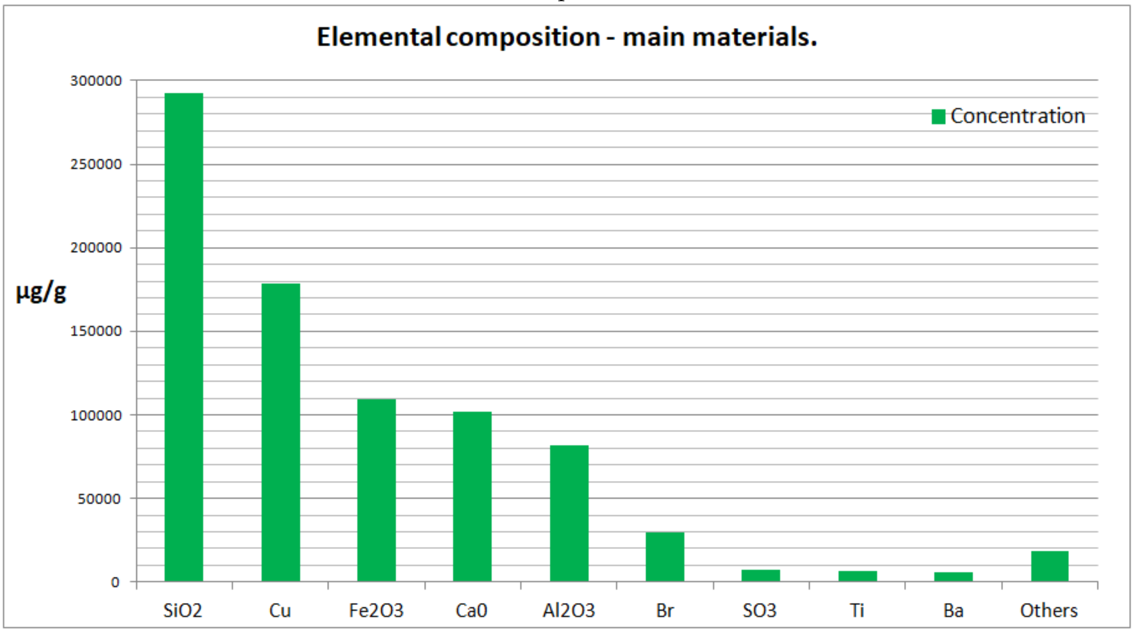

Figure 5.3. Top ten detected materials by concentration in the analysed motherboard.

Table 5.5. Elemental composition of motherboard PCB compared to literature data.

	Literature Razi [2016], Kida *et al.* [2011], Li & Xu [2015], JX[2010] mg/Kg	Literature Ildar *et al.* [2016] mg/Kg	This work mg/Kg
Au	13 - 823	2	< 0.5
Ag	73 - 790	-	52
Pd	10 - 89	-	15
Ni	140 - 6400	2600 ± 600	5326
Cu	20400 - 120000	163600 ± 13000	178300
Zn	100 - 10000	2900 ± 300	2320

Chapter 6

Conclusions

This work has brought up the fact that the PC waste stream ic connected with several issues for each phase it goes through. The discussed outcomes can be summarized as below:

- The framework of the administrative and financial system for the waste PCs management is fundamental. The current Italian system has a complex organization, which gives priority to granting the free of charge retirement of e-waste from domestic users. Beside the fact that recovery stations for most of the valuable materials are still missing on the national territory, the best option for a company performing the manual sorting of this waste is to send their output materials to foreign large companies. The collection and take-back system also allows the plant receiving the e-waste to afford the PCs manual dismantling costs by financing the retirement of specified appliances (namely categories R1 and R2 in the Italian organization).

- The PCs mainframes, as found in the composition of the treated waste by CdC RAEE, make up the majority of the mass within the R4 category. A half of this is related to the Iron components, which constitute also the highest volumes.

- Except for the hazardous components, all the fractions exiting the pre-treatment plant are doomed to be sold. Among these PCBs attached to the main body of the mainframe are the most interesting ones giving back a revenue of 2.40 €PC unit, but also the CPUs, despite their very small weight share, turned out to be significantly profitable with a revenue of 1.38 €PC unit. The total revenue from the sorting process of a PC mainframe is 7.44 € or referred to the mass, 729 €/ton.

- The choice of manual sorting as a first step rather than the direct application of automatic treatments, has its disadvantages, but also the crucial advantages related to the subsequent processes should be considered. In fact this would improve capacity and efficiency of automatic downstream treatments, dealing with a more uniform material fractions.

- The actual composition of discarded mainframes, in most of the cases, is poorer, in economic terms, compared to the theoretical. In fact the most valuable parts (Hard Disks and

RAM modules) are missing when PCs enter the sorting pre-treatment. So the lack of these components should be taken into account when considering the composition of this waste.

- The elemental analysis demonstrated how complex is the material composition for a motherboard PCB, and highlighted the importance of repeating several measurements when using the XRF technology, to clearly detect the presence of some precious or hazardous compounds in minor concentrations. Moreover most of the detected elements, even if not toxic or carcinogenic in the form occurring in the PCB, may turn into more hazardous substances when managed in an non-proper way. For instance, barium itself as a metal is not so particularly harmful (although toxic anyway), but if exposed to external air it rapidly oxidizes, forming soluble compounds, which are extremely toxic.

- Also, it is relevant to notice how rich in CRMs this kind of products are, since most of the analysed mass consisted of these ones. Together with copper, found in a motherboard in a concentration of 178300 μg/g, elements such as SiO_2, Barium, Tungsten, Rhodium are some of the most interesting resources recoverable from urban mining, given their large application in industry which makes European producers dependent on the few countries which own almost the total extractive capacity at global scale, first among these, China.

- Subsequently, if for the recovery of copper the technology is already well-developed, for some other CRMs there are no specific treatments and larger research should be made in order to avoid their loss.

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