Environmental impacts of a hydrometallurgical process for electronic waste treatment: a life cycle assessment case study

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Abstract

The recovery of precious metals through hydrometallurgical techniques is one of the most active research areas on recovery of metals from electronic scraps. In this perspective, a pilot plant was designed for the treatment of small WEEE (Waste Electrical and Electronic Equipment) via hydrometallurgy. The process is based on two different leaching steps, in nitric acid and in aqua regia, followed by electrodeposition processes, to mainly recover copper, silver and gold. Two adsorption steps were also carried out to recover nickel and tin.

The goal of the present study is to assess the environmental impacts associated with the designed hydrometallurgical treatment of the small WEEE through Life Cycle Assessment (LCA) methodology. The approach considered is cradle-to-gate, i.e., from the collected WEEE entering the collection centre to the secondary metals obtained from the hydrometallurgical treatment.

Results obtained by SimaPro software and CML-IA method show that the nitric acid leaching contributes mostly to the impacts of the hydrometallurgical process (from 40% to 80%), followed by the adsorption steps. From an environmental perspective, the latter can still be improved at the design phase by increasing the lifetime of the sorbents.

Keywords: Waste Electrical and Electronic Equipment; mobile phones; hydrometallurgy; recovery; Life Cycle Assessment

1. Introduction

Management of Waste Electrical and Electronic Equipment (WEEE) has been documented as the world's rapidly growing waste stream which has the growth rate of 3-5% per year and potentially the biggest challenge to sustainability (Menikpura et al., 2014). Electronic waste has been indeed generated two to three times faster than other waste streams, due both to rapid increase in consumer electronic devices, and to their ever wider distribution (Ilyas et al., 2014). Only in Europe, each citizen produces about 17 kg of WEEE per year and, according to European Union estimates, this value is expected to rise to 24 kg by 2020 (EU, 2012). These solid wastes are usually dumped at landfills (Ilyas et al., 2014) even if they are rich in precious and strategic metals and, in many cases, are characterized by higher valuable metals contents than those of natural minerals. From this context a new approach/ perspective has emerged: it is known as "urban mining", and bases on the development of best practices for collection, transportation, recycling and recovery of valuable metals from WEEE, so as to transform the waste into an economic valuable product and to minimize the consumption of resources. For these reasons, the study of a targeted and efficient recovery from WEEE can only lead to undeniable both socio-economic and environmental benefits (Iannicelli-Zubiani et al., 2012).

From a technological point of view, recycling of WEEE and recovering of metals therein contained can be divided into three major steps (Cui and Forssberg, 2003):

1. disassembly: operating a selective disassembly to single out hazardous or valuable components for special treatment;
2. upgrading: using mechanical and/or metallurgical processing to upgrade wanted materials content;
3. refining: recovered materials retreating or purifying by chemical processing so as to be acceptable for their original using. This final step can be realized by different metallurgical techniques: pyrometallurgical, biometallurgical, and hydrometallurgical.

Pyrometallurgical processing has become a traditional method to recover non-ferrous metals as well as precious metals from electronic waste in the past two decades. In the process, the crushed scraps are burned in a furnace or in a molten bath to remove plastics. However, most methods involving pyrometallurgical processing of electronic waste give rise to the following limits (Cui and Forssberg, 2003):

(1) integrated smelters cannot recover aluminium and iron as metals;

(2) the presence of halogenated flame retardants (HFR) in the smelter feed can lead to the formation of dioxins unless special installations and measures are present;

(3) ceramic components and glass in the e-waste increase the amount of slag from blast furnaces, which thereby increases the loss of precious metals and base metals from the scrap;
(4) energy recovery and utilizing of organic constituents as reducing agents are only on its beginning;
(5) only partial separation of metals can be achieved using pyrometallurgy, resulting in a limited upgrading of the metal value. Furthermore, hydrometallurgical techniques and/or electrochemical processing are subsequently necessary.

Regarding biometallurgical processing, recovery of metals by this method has been one of the most promising technologies and the understanding of the biochemical processes involved in the treatments of metals has been subjected to growing investigations in the last decade. At present, research and development are in progress for a number of rare earths, copper, nickel, cobalt, zinc, gold and silver. However, the advances obtained from the activity of leaching bacteria for recovery of gold and silver from ores are not those anticipated, due to the presence of elements toxic to the bacteria (Komnitsas and Pooley, 1991).

Anyway, the most active research area on recovery of metals from electronic scraps is recovering precious metals by hydrometallurgical techniques. Hydrometallurgical method has been indeed reported to be one of the most interesting, being generally applicable to very different compositions (Iannicelli-Zubiani et al., 2012). Furthermore, hydrometallurgical processes offer a promisingly eco-friendly and selective separation of the metals from the non-metallic parts (Fogarasi et al., 2013).

In this perspective, a pilot plant was designed for the treatment of small WEEE via hydrometallurgy. The process bases on two different leaching steps, in nitric acid and in aqua regia, followed by electrodeposition processes, to mainly obtain the recovery of copper and gold.

Since in some hydrometallurgical processes the use of high volumes of leaching solutions leads to the formation of large quantities of wastewater, it is important to assess the environmental impacts of the process and to exploit this information in scaling-up from the design phase to the realization of the pilot plant. For these reasons, it is necessary to make an environmental impact assessment of the designed processes before they can be applied at pilot or industrial scale. So the goal of the present study is to assess the environmental impacts by life cycle assessment (LCA) methodology associated with the hydrometallurgical treatment of WEEE, aimed at recovering precious metals. Furthermore, the present study is motivated by a lack in the LCA literature of a similar process.

This methodology has been applied to the management of electronic waste, by assessing the potential environmental impacts derived from different treatments processes (Bigum et al., 2012; Hischier et al., 2005; Menikpura et al., 2014; Tan et al., 2015) and scenarios (Hischier, 2014). Only

few studies have focused on hydrometallurgy (Rocchetti and Beolchini, 2014; Rocchetti et al., 2013; Rubin et al., 2014) even if more generic scraps are treated (i.e. fluorescent lamps, cathode ray tubes, Li-ion accumulators and PCBs) and different leaching agents are used (i.e. sulphuric acid and aqua regia).

2. Hydrometallurgical processes

The main steps in hydrometallurgical processing consist of a series of acid or caustic leaching steps of solid material. The solutions are then subjected to separation and purification procedures (such as precipitation of impurities, solvent extraction, adsorption, ion-exchange, electrorefining, chemical reduction or crystallization) to isolate and concentrate the metals of interest.

Among others, hydrometallurgy has been reported to be one of the most interesting being characterized, with respect to pyrometallurgy, by the following advantages:

(1) reduced risk of highly toxic and polluting emissions, in particular the ones caused by the presence of halogenated flame retardants (HFR), which can lead to the formation of dioxins and furans;

(2) efficient separation of metals avoiding purification steps (Cui and Zhang, 2008);

(3) low energy requirement by the plants, where it is not necessary a source of organic fuel;

(4) no combustion residue currently sent to final disposal (landfill);

(5) no dust emission that can pose a risk to both the environment and the human health (Tuncuk et al., 2012).

On the other hand, some disadvantages of this process are:

(1) the need of many process steps;

(2) the consumption of large amounts of chemicals;

(3) the generation of large amounts of waste water.

The separation and recovery of precious metals can be realized by means of different unitary operations. In the various analysed studies, the recovery of gold, coming both from computer printed circuit boards (PCBs) and from mobile phones, is accomplished through: ion exchange resins, carbon adsorption, solvent extraction, electrolytic deposition, precipitation and cementation. Silver is generally recovered with ion exchange resins, with solvent extraction or with electrorefining. Regarding the copper, instead, the most common techniques for separation are crystallization, solvent extraction, precipitation and cementation.

Ion exchange resins are composed by a polymeric matrix in which ions are entrapped or encapsulated: these ions are available for ion exchange (Sabot and Maestro, 2000). The resins can be cationic (capable of exchanging cations) or anionic (capable of exchanging anions). There are

numerous resins for ion exchange, most of which are polystyrene-based, typically crosslinked with divinylbenzene, to which are then added functional groups capable of capturing or releasing ions. Recently, the use of adsorption onto solid sorbents is obtaining more and more attention because of its advantages of high recovery, short extraction time, high enrichment factor, low cost and low consumption of organic solvents over liquid-liquid extraction (Li et al., 2011). In particular, adsorption has become one of the alternative treatments (Rao et al., 2008), being a simple and potentially low cost process. Indeed, technical applicability and cost-effectiveness are the key factors in the selection of the treatment technology (Nurchi and Villaescusa, 2012). The most used sorbent material is activated carbon. It is characterized by a highly porous structure and by a high specific surface area. Thanks to these properties, the activated carbon is able to hold inside many molecules of other substances, being able to accommodate these molecules on its extended internal surface area. In other words, the activated carbon is a material that exhibits high adsorbing capacity.
Another common separation technique is liquid-liquid extraction: the passage of a solute from a solvent to another different solvent. Two types of solvents with different polarity and different miscibility are therefore used: when the two liquids are placed into the separating funnel, thanks to agitation, they are divided into two phases (an aqueous phase and an organic phase containing the extracted substance) and they reach an equilibrium between the concentration of the solute in the first solvent and the concentration of the solute in the second solvent (Iannicelli-Zubiani et al., 2012).
Copper and gold are often recovered by electrochemistry, electrolytic refining (or electrorefining). Under the action of a potential difference supplied from outside the metal passes into the electrolytic solution in the form of ions: the metal ions are deposited at the cathode, while the impurities precipitate in form of "anode mud" (in case they have a higher nobility of the metal to be refined) or remain in solution (in case they have a lesser nobility of the metal to be refined).
Precipitation is the phenomenon of separation of a solid substance from a solution (Sabot and Maestro, 2000). This separation can take place as result of chemical reactions or as consequence of a variation of the physical conditions of the solution, for example temperature.
Cementation is a heterogeneous process in which ions are reduced to zero-valent metal at solid interface. The process is often used to refine leached solutions. A common example is the cementation of copper: copper ions in solution are precipitated in presence of metallic iron. The iron oxidizes and copper ions are reduced through the transfer of electrons. Nowadays it is also used in recycling processes from electronic scraps, in the particular case in which the initial mixtures are not as complicated as the ones coming from ore digestion (Innocenzi et al., 2013; Pietrelli et al., 2002).

Crystallization is a unit operation during which a chemical substance dissolved in a solvent precipitates in form of crystals in a controlled way, so as to be separable from the same solvent (for example by evaporation of the solvent). The crystallization is a particular case of precipitation but differs from this one from the moment that it is obtained by varying the solubility conditions and not by chemical reaction. In fractional crystallization, one or more metals in a mixture are precipitated by changing the salt concentrations in solution through evaporation or temperature control.

3. Materials and methods

3.1. WEEE characterization

Mobile phone PCBs were selected as the scraps to be treated in the pilot plant because of their rich metal content, high production volume and short life time (Arshadi and Mousavi, 2015; Palmieri et al., 2014).

The main metal composition of this kind of scrap is reported in Table 1. It is evident that copper is by far the most concentrated element and that nickel and tin are present in high amounts. Traces of precious metals are present while iron, chromium, zinc and rare earths (not reported) are present in very small percentages, confirming that they are negligible if compared to the other mentioned elements, since their concentrations differ by three of four orders of magnitude.

Table 1 - Main metal composition of mobile phone scraps.

Sn (kg /t)	Cu (kg /t)	Ni (kg /t)	Ag (kg /t)	Au (kg /t)
5.38	789.67	38.33	0.11	0.16

3.2. LCA methodology

The life cycle assessment methodology observes and analyses a product over its entire life cycle aiming to evaluate its environmental impacts (ISO, 2006a, b).

The stages included in a LCA study are the following:

- Definition of the scope of the study according to the aspired goals;
- Quantification of inputs and outputs flows of materials, energy and emission for each step of the analysed processes (Life Cycle Inventory, LCI);
- Assessment of determined inputs and outputs according to the selected environmental indicators chosen (Life Cycle Impact Assessment, LCIA);
- Discussion and interpretation of results, and process iteration, if needed.

3.2.1. Goal and scope definition

The goal of the present study is to assess the environmental impacts associated with the hydrometallurgical treatment of WEEE, aimed at recovering precious metals contained in the electronics boards of mobile phones.

The analysis follows the methodology defined by ISO 14040 and 14044 and it is performed using SimaPro 8 software adopting a cradle-to-gate perspective.

3.2.2. Functional unit and system boundaries

In a LCA study, the functional unit (FU) is a measure of the analysed product system and it is a reference to which all inputs and outputs are related. The FU adopted in the analysis is 100 kg of electronic boards of mobile phones entering the hydrometallurgical plant. The adopted approach is "cradle-to-gate", i.e. from the collected WEEE entering the collection centre to the secondary metals obtained from the hydrometallurgical treatment. The zero-burden hypothesis was assumed meaning that waste does not carry any environmental burdens when delivered to the gate of the collection centre: this choice is in line with the approach usually used in LCA of waste treatment (Ekvall et al., 2007).

The system boundaries and all the involved unit processes are showed in Figure 1. The core process of this study is the hydrometallurgical plant. Treatments of air emissions, neutralization and the processes required for a preliminary wastewater treatment are included in the core process.

The so called upstream processes (EPD International, 2015) comprehend the collection centre, the pre-treatment plant and all the auxiliary processes of energy and material production required by the core process. In the system boundaries, also the downstream processes (EPD International, 2015) like municipal wastewater treatment and solid waste disposal are considered. The final solid waste (e.g., plastics and ceramics) is assumed to be disposed in a sanitary landfill in order to not underestimate the end-of-life impacts even if different end-of-life scenarios are proposed in literature (Dangtungee et al., 2012; Guo et al., 2009; Yang et al., 2015).

In the present case study, the impacts concerning the infrastructure of the plants are not considered.

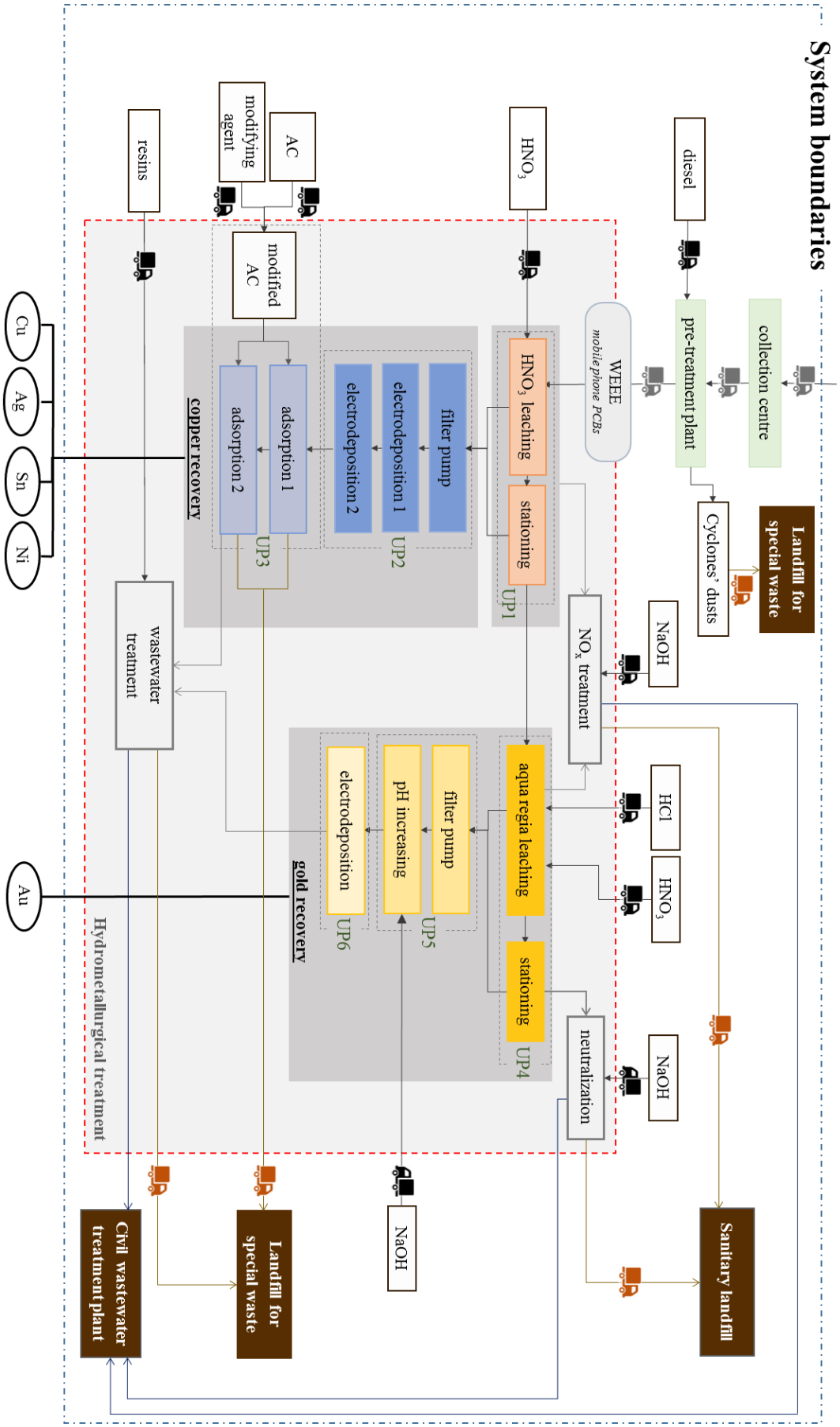

Figure 1 - Process scheme: the *core* process is the hydrometallurgical treatment (highlighted in the red box). In the system boundaries also the *upstream* and *downstream* processes are considered.

3.2.3. Data source, quality and allocation

In the present study, all the data regarding the core process are primary data obtained from Tecnochimica S.r.l., resulting from the project phase carried out in the pilot plant. Data about the pre-treatment phase are directly provided by Immark Italia S.r.l. Other primary data are those regarding the modification of the activated carbon.

For the transport of collected WEEE to the collection centre and the pre-treatment plant, average distances were assumed (Biganzoli et al., 2015).

The upstream processes of energy generation, materials production and transports are taken from Ecoinvent 3.1 database. In detail, for electricity used at the pre-treatment plant and the hydrometallurgical plant the Italian mix is selected, while European conditions are considered for transports and production of fuels. Also downstream processes are described through secondary data, while the transports of these phases are derived from average distances for Lombardia Region (ARPA Lombardia, 2014).

Since different metals are recovered through the hydrometallurgical treatment, the environmental impacts due to the various steps of the hydrometallurgical process have to be allocated to the different outputs. The allocation is performed adopting a mass allocation criterion. In addition, a preliminary economic allocation is considered in order to evaluate potential variations in the results obtained for the different recovered metals.

3.2.4. Impact assessment method

Impact assessment is a fundamental step in LCA because it translates inventory data in potential environmental impacts. The impact assessment method selected in this work is the CML-IA baseline 3.01, that is the problem-oriented methodology of the Institute of Environmental Sciences of Leiden University, The Netherlands (Guinée, 2002). This method is the most used in LCA studies regarding treatment of WEEE (Hischier et al., 2005; Rocchetti and Beolchini, 2014; Rocchetti et al., 2013; Tan et al., 2015). The CML method includes the following categories: abiotic depletion, global warming, ozone layer depletion, human toxicity, freshwater aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity, photochemical oxidation, acidification and eutrophication. Normalization was not performed in this study since it results in introducing additional uncertainties in the study, moreover this step is not mandatory according to ISO standards (ISO, 2006a, b).

4. Life cycle inventory

The Life Cycle Inventory phase (LCI) was developed in order to quantify input and output flows involved in the system under study. In particular, the use of resources and materials, the

consumption of energy, as well as the involved transports associated with the treatment of electronic boards of mobile phones are considered. The results of the LCI are presented in the next paragraphs following the upstream-, core- and downstream- division.

4.1. Collection centre

The first phase considered is the transport of waste from the domestic households to the collection centre. These data refer to the category of small house appliances R4 (Biganzoli et al., 2015). The waste can be either collected on-demand by the public service or delivered by the citizens to the collection platform, whose location is not specified. Table 2 summarizes the information regarding the two types of collection in Lombardia Region. The column reporting average transports is obtained multiplying the percentage of collected WEEE and the average mileage. For both collection systems, the use of small vans is assumed. No transfer of the collected WEEE within the centre is assumed in the study.

Table 2 - Transport data to the collection centre for 1 t of R4 category (Biganzoli et al., 2015).

Collection type	Percentage of WEEE collected (%)	Average mileage (km)	Average transport (t*km)	Mode of transportation
On demand collection by the public service	15.40	20.00	3.08	Small vans
Delivery by the citizens to the collection platform	84.60	4.20	3.55	Small vans

4.2. Pre-treatment phase

Once collected, the electronic wastes are transported to the pre-treatment plant located in Cornaredo (MI). Since the location of the collection centre is not specified in the present study, an average distance from the collection centre to the pre-treatment plant is assumed equal to 58.7 km (Biganzoli et al., 2015). The use of freight lorry (3.5-7.5 metric ton) is assumed, both Euro3 (70%) and Euro4 (30%).

The pre-treatment mainly consists of a preliminary separation unit able to select the PCBs and the valuable components of the R4 wastes. The PCBs compose the input flow of the hydrometallurgical plant while the remaining R4 components are further treated to separate the main components, as ferrous materials, copper and plastics. The pre-treatment data (Table 3) are referred to the entire process and are then allocated to the PCBs fraction, equal to around 3%.

Among the output, the amount of particulate matter generated is below the Italian emission limits thanks to the use of cyclones and bag filters. The cyclones' dusts are sent to a landfill for special waste (Paragraph 4.4) while bag filters are not considered in the study due to their long lasting use.

Table 3 - LCI data for 1 t of R4 category in the pre-treatment phase.

Input	Flow	Value	Unit
Energy	Electricity from the grid	93.70	kWh
Material/fuel	R4 waste	1.00	t
	Diesel	3.38	l
Transport	Diesel	28.10	kg·km
Output	**Flow**	**Value**	**Unit**
Material	Pre-treated R4 waste	1.00	t
	Cyclones' dust	0.06	t
Emission to air	Particulates	0.67	g

4.3. Hydrometallurgical plant

Data about the hydrometallurgical treatment of WEEE were supplied by Tecnochimica S.r.l, derived from the pilot plant located in San Giuliano M.se (MI).

For the sake of simplicity, the following paragraphs have been structured according to the different unit processes (UPs) and treatments shown in Figure 1.

4.3.1. Unit process 1: nitric acid leaching and stationing

The ground mobile phone PCBs are transferred from the pre-treatment plant to the hydrometallurgical one by freight lorry (3.5-7.5 metric ton, 70% of Euro3 and 30% Euro4) and the assumed travelled distance is 33.8 km.

The first unit process (UP 1, Figure 2) is composed of a step of nitric acid leaching and a stationing step of the not dissolved solid (required for improving the liquid percolation). During the leaching, nitric acid 16 % w/w is added to the ground PCBs to dissolve the metals therein contained. A solution of nitric acid 65% w/w is purchased from a company located 95.2 km far from the hydrometallurgical plant. Freight lorry (16-32 metric ton) Euro3 is assumed as means of transport for all the solutions used in the following process steps (i.e., hydrochloric acid and sodium hydroxide). The purchased solution is then diluted with distilled water to obtain the solution 16% w/w required by the process.

Concerning the input data (Table 4), the amount of acid is referred to a 100% pure acid, as available in Ecoinvent database. The heat from natural gas is used to increase the kinetics of the leaching process, set up at a temperature of 60°C.

From UP1, a solution containing the different dissolved metals and a residual solid are obtained as output. These flows will be further treated (UP2 and UP4, respectively). In addition, the generation

of NO_x occurs, and these emissions will be treated through NaOH-based neutralization located in-situ.

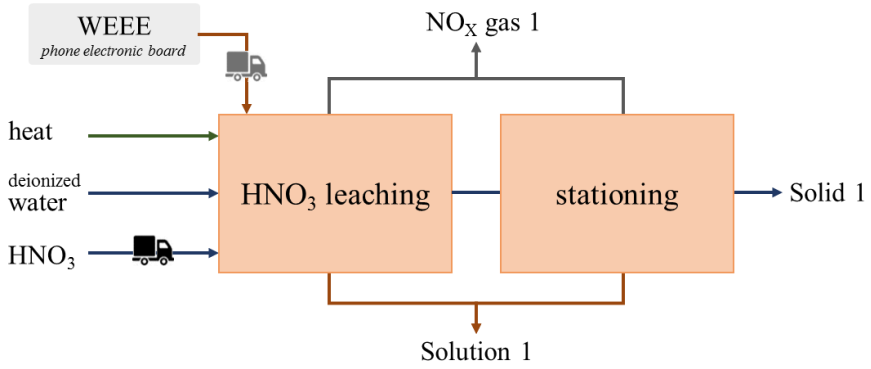

Figure 2 - Unit process 1: nitric acid leaching and stationing.

Table 4 - LCI data for FU in UP 1.

Input	Flow	Value	Unit
Energy	Heat from natural gas	121.00	MJ
Material	WEEE	100.00	kg
	HNO_3 (100% w/w)	136.64	kg
	Deionized water	643.79	kg
Transport	HNO_3 (65% w/w)	20.01	t·km
	WEEE	3.38	t·km
Output	**Flow**	**Value**	**Unit**
Material	Solution 1 (water, HNO_3, Cu, Ag, Sn, Ni)	822.70 (88.9%, 0.9%, 9.6%, 0.02%, 0.09%, 0.5%)	kg
	NO_x gas 1	12.63	kg
	Solid 1	16.04	kg

4.3.2. Unit process 2: electrodeposition

The outflowing solution generated in the UP1 is pumped up to two electrodeposition steps through a filter pump (Figure 3), whose consumption is 2 kWh (referring to the functional unit).

In Table 5, all the LCI data regarding this UP are reported. In particular, the electricity value includes the requirements of both the filter pump and the electrodeposition. The latter allows recovering copper and silver with efficiencies of 97.8% and 99%, respectively, for each electrodeposition step. The output solution generated by this step is poor in copper and silver but still rich in nickel and tin, and for this reason, further treatments are needed.

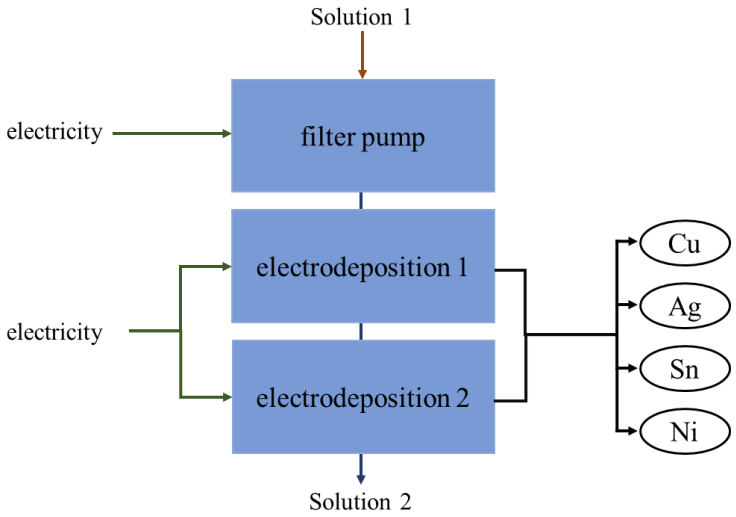

Figure 3 - Unit process 2: electrodeposition.

Table 5 - LCI data for FU in UP 2.

Input	Flow	Value	Unit
Energy	Electricity from the grid	26.00	kWh
Material	Solution 1 (water, HNO_3, Cu, Ag, Sn, Ni)	822.70 (88.9%, 0.9%, 9.6%, 0.02%, 0.09%, 0.5%)	kg
Output	**Flow**	**Value**	**Unit**
Material	Solution 2 (water, HNO_3, Cu, Ag, Sn, Ni)	743.64 (98.3%, 1.0%, 5.4E-03%, 2.6E-06%, 0.1%, 0.6%)	kg
	Recovered copper	78.93	kg
	Recovered silver	0.13	kg

4.3.3. Unit process 3: production of modified activated carbon and adsorption

In order to treat the remaining solution rich in nickel and tin, innovative materials based on modified activated carbon are used. UP3 thus includes both the production of the modified activated carbon (AC) and the adsorption steps (Figure 4).

The needed inputs for the synthesis of the modified AC are reported in Table 6.

The use of freight lorry (16-32 metric ton) and a distance of 95.2 km are assumed for transport of the activated carbon, while for the modifying agent, average transport conditions from Ecoinvent database are assumed.

The amount of modified AC reported in Table 7 refers to one treatment cycle (i.e., the treatment of 100 kg of WEEE, which is the FU). Once exhausted, the modified AC is sent to a landfill of special wastes (see Section 4.4).

During adsorption, the solution is contacted with the solid sorbent under stirring, therefore 10 kWh of electricity are necessary. Copper, tin and nickel are recovered with efficiencies of 53, 99 and 65%, respectively.

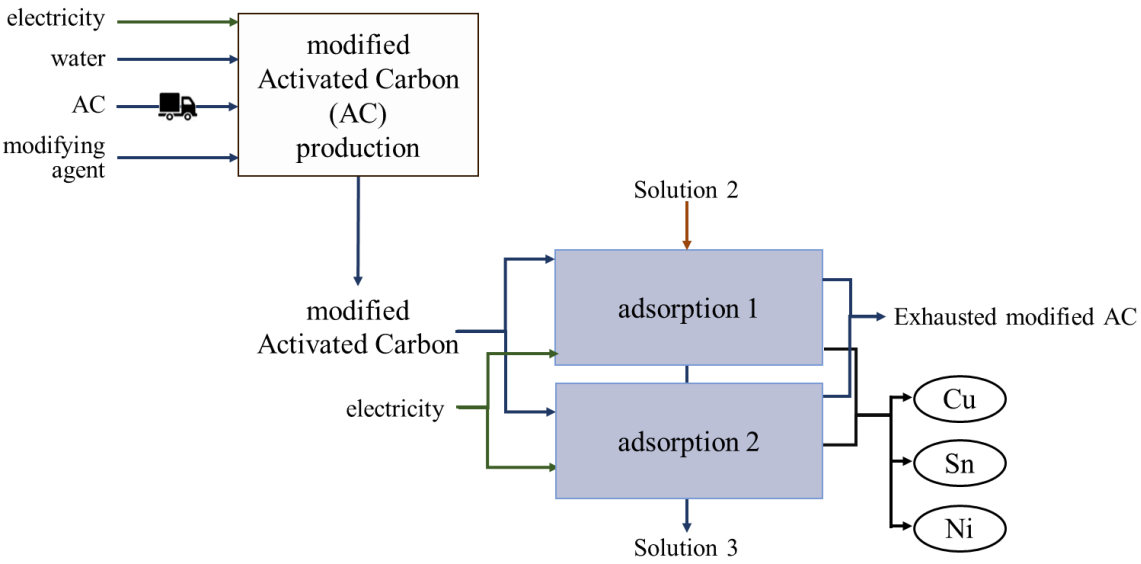

Figure 4 - Unit process 3: production of modified activated carbons and adsorption.

Table 6 - LCI data for the production of 6.4 kg of modified carbon.

Input	Flow	Value	Unit
Energy	Electricity from the grid	8.40	kWh
Material	Activated carbon	8.00	kg
	Modifying agent	6.68	kg
	Deionized water	160.00	kg
Transport	Activated carbon	0.76	t·km

Table 7 - LCI data for FU in the two adsorption phases.

Input	Flow	Value	Unit
Energy	Electricity from the grid	10.00	kWh
Material	Modified carbon	6.40	kg
	Solution 2 (water, HNO_3, Cu, Ag, Sn, Ni)	743.64 (98.3%, 1.0%, 5.4E-03%, 2.6E-06%, 0.1%, 0.6%)	kg
Output	**Flow**	**Value**	**Unit**
Material	Solution 3 (water, HNO_3, Cu, Ag, Sn, Ni)	739.24 (98.9%, 1.0%, 1.1E-3%, 2.6E-6%, 1.1E-5%, 0.1%)	kg
	Exhausted modified AC	6.40	kg
	Recovered copper	0.03	kg
	Recovered tin	0.78	kg
	Recovered nickel	3.59	kg

4.3.4. Unit process 4: aqua regia leaching and stationing

The solid output obtained from UP1 is sent to an aqua regia leaching treatment and the further stationing phase: these two steps constitute the UP4 (Figure 5).

This treatment is the best available for dissolving gold. The stationing step is needed to completely separate the liquid from the solid phase.

Concerning the inputs, aqua regia is synthesized starting from a solution of 65% nitric acid and 37% hydrochloric acid (1/3 v/v).

Besides the solution containing gold, other outputs of the UP4 are a small fraction of NO_x (that will be treated within the plant) and a solid waste sent to neutralization before the final disposal. All the data used for describing UP4 are summarized in Table 8.

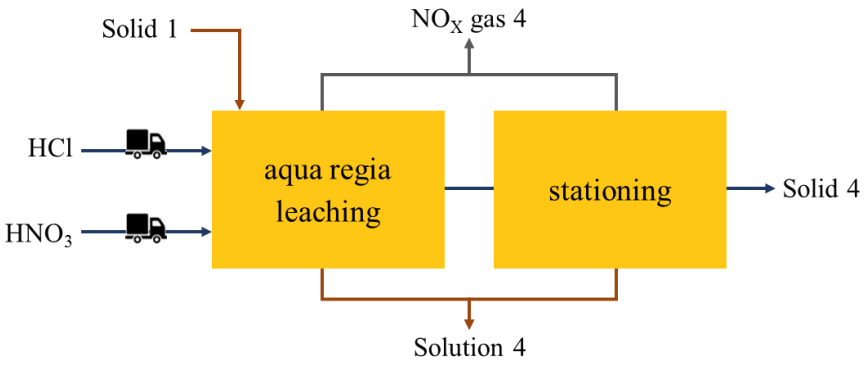

Figure 5 - Unit process 4: aqua regia leaching and stationing.

Table 8 - LCI data for aqua regia leaching.

Input	Flow	Value	Unit
Material	Solid 1	16.04	kg
	HNO_3 (65% w/w)	0.15	kg
	HCl (37% w/w)	0.20	kg
Transport	HCl (37% w/w)	0.02	t·km
	HNO_3 (65% w/w)	0.01	t·km
Output	**Flow**	**Value**	**Unit**
Material	Solution 4 (water, gold)	0.30 (70%, 30%)	kg
	NO_x gas 4	0.04	kg
	Solid 4	15.95	kg

4.3.5. Unit process 5: pH increasing

The output solution of UP4 is sent to a step aimed at increasing pH (Figure 6). This treatment, together with a filter pump (requiring 2 kWh/FU), represents UP5 and provides the increase of pH up to 4 by adding NaOH to the solution and generating some dissolved salts (i.e., NaCl and $NaNO_3$). This pH is necessary to obtain a good performance in gold recovery through the further electrodeposition step. Data about this UP are presented in Table 9.

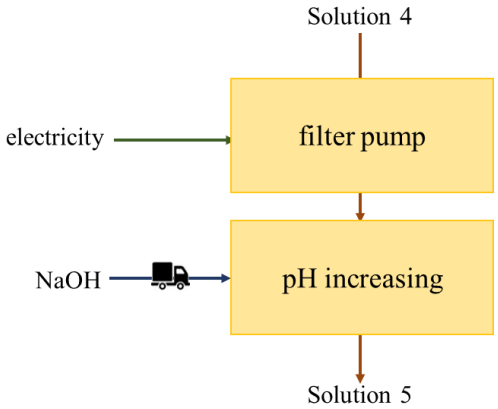

Figure 6 - Unit process 5: pH increasing.

Table 9 - LCI data for FU in pH increasing.

Input	Flow	Value	Unit
Energy	Electricity from the grid	2.00	kWh
Material	Solution 4 (water, gold)	0.30 (70%, 30%)	kg
	NaOH (30% w/w)	0.44	kg
Transport	NaOH (30% w/w)	0.04	t·km
Output	**Flow**	**Value**	**Unit**
Material	Solution 5 (water, gold, NaCl, $NaNO_3$)	0.74 (15%, 12%, 30%, 43%)	kg

4.3.6. Unit process 6: electrodeposition

The solution containing gold is thus ready for the electrodeposition (UP6) shown in Figure 7. The required electricity amounts to 12 kWh and the gold recovery efficiency reaches 95%. The generated solution contains a small amount of residual gold and the dissolved salts (Table 10).

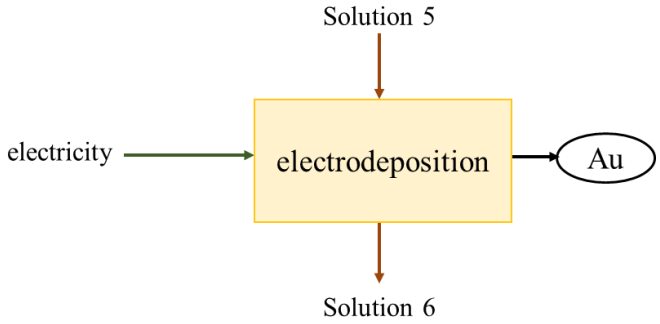

Figure 7 - Unit process 6: electrodeposition for the gold recovery.

Table 10 - LCI data for FU in electrodeposition.

Input	Flow	Value	Unit
Energy	Electricity from the grid	12.00	kWh
Material	Solution 5	0.74	kg
Output	**Flow**	**Value**	**Unit**
Material	Solution 6 (water, gold, NaCl, $NaNO_3$)	0.65 (11.3%, 0.7%, 34%, 54%)	kg
	Recovered gold	8.8E-02	kg

4.3.7. Treatment

The hydrometallurgical plant has three in-situ treatment processes: a wastewater treatment based on ionic resins for the outflowing solution from UP3 and UP6, a neutralization process for the solid waste (output of UP4) and a treatment of NO_x emitted by UP1 and UP4.

The first treatment aims at the abatement of the metal ions in the solutions outflowing from both the copper and gold recovery lines (LCI data reported in Table 11). The installed resins are efficient towards copper and nickel (by 99%) and the required amount is about 1 g of resin for each litre of treated wastewater (Hamdaoui, 2009; Stefan and Meghea, 2014). Since the specific producer is unknown to the authors, data about cationic resin production and transportation were provided by Ecoinvent 3.1 database. Once exhausted, they are sent to a landfill for special waste.

On the other hand, the generated wastewater will be sent to a civil waste water treatment plant since the metal contents are below the Italian legislative limits (Italian regulation D.Lgs 152/06, 2006).

Table 11 - LCI data for FU in the waste water treatment by ionic resins.

Input	Flow	Value	Unit
Material	Resins	8.8E-4	kg
	Solution 3 (water, HNO_3, Cu, Ag, Sn, Ni)	739.24 (98.9%, 1.0%, 1.1E-3%, 2.6E-6%, 1.1E-5%, 0.1%)	kg
	Solution 6 (water, gold, NaCl, $NaNO_3$)	0.65 (11.3%, 0.7%, 34%, 54%)	kg
Output	**Flow**	**Value**	**Unit**
Materials	Waste water	739.89	kg
	Exhausted resins	6.1E-3	kg
Transport	Exhausted resins	0.66	kg·km

The second treatment process concerns the solid waste. Even if it contains only plastics and ceramics, it requires a step of NaOH-based neutralization since it was subjected to highly acidic treatments. The amount of NaOH used is reported in Table 12.

After neutralization the solid is disposed in sanitary landfill, while the exhausted solution is sent to a civil waste water plant.

Table 12 - LCI data for FU in the neutralization.

Input	Flow	Value	Unit
Material	Solid 4	15.95	kg
	NaOH (30% w/w)	4.38	kg
Transport	NaOH (30% w/w)	0.42	t·km
Output	**Flow**	**Value**	**Unit**
Material	Solid waste	15.95	kg
	Solution from neutralization	4.38	kg

The last treatment is the NO_x abatement. It is composed by two towers performing wet abatement using NaOH already existing in Tecnochimica S.r.l. plant. The incoming flows come from the nitric acid and the aqua regia leaching phases (UP1 and UP4). In addition to the NaOH amount (see Table 13), electricity due to four pumps is required.

The generated wastewater is sent to the civil wastewater treatment plant, while the separated salts (from abatement reaction) are disposed in landfill.

Table 13 - LCI data for FU in the NO_x treatment.

Input	Flow	Value	Unit
Energy	Electricity from the grid	0.90	kWh
Materials	NaOH (30%)	62.00	kg
	NO_x gas 1+4	12.67	kg
Transports	NaOH (30%)	5.90	t·km
Output	**Flow**	**Value**	**Unit**
Material	Waste water (water, NaOH)	49.35 (97%, 3%)	kg
	$NaNO_3$	17.97	kg
	$NaNO_2$	14.59	kg

4.4. Downstream processes

The downstream processes considered in this study are the civil wastewater treatment plant, the sanitary landfill, and the landfill for special waste. These processes mainly concern the final destination of the residual waste coming from the treatments described in section 4.3.7, but also other exhausted materials used in the whole process.

In particular, the solids from neutralization and NO_x treatment are sent to the sanitary landfill. An average distance of 75.55 km and the use of freight lorry (16-32 metric ton) are assumed. The cyclones' dusts of the pre-treatment, exhausted modified activated carbon and exhausted resins are sent to the landfill for special waste. In this case, an average of 108.5 km and freight lorry (16-32 metric ton) are assumed. The average distances are calculated from the localization of the landfill in Lombardia Region (ARPA Lombardia, 2014).

The process concerning landfill of municipal solid waste is used for both the solids disposals, even if different distances are considered in the two cases. This is done because the modelling of landfill for special waste is not presented in Ecoinvent 3.1, reason that municipal sanitary landfill treats both the solids waste described above.

5. Results and discussion

5.1. Global process

The impacts caused by the overall process calculated through the CML methodology are reported in Table 14, where also the contributions of upstream, core and downstream phases are pointed out. The impacts of the core process range from 76 to 99% of the total impacts for all the considered categories, except for *"Fresh water aquatic ecotoxicity"*. In this impact category, indeed, the downstream processes show the highest contribution (i.e., 58% of the total value). The cause is the sanitary landfill: it was completely modelled by Ecoinvent and the related air and water emissions have a relevant contribution in terms of *"Fresh water aquatic ecotoxicity"* and *"Marine aquatic ecotoxicity"*. Furthermore, this process could be avoided, since different end-of-life scenarios can be adopted for the mentioned waste. Non-metals components could effectively be reused in thermosetting resin matrix composites, thermoplastic matrix composites, concrete and viscoelastic materials (Guo et al., 2009), and therefore the impacts could be reduced.

On the other hand, the upstream processes have negligible impacts with respect to the whole process.

Given the overall predominant contribution of the core process, and given the current design phase of the plant, the results hereinafter presented focus on the hydrometallurgical process.

Table 14 - Total impacts associated to the process from cradle-to-gate.

Impact category	Value	Unit	Upstream processes (%)	Core process (%)	Downstream processes (%)
Abiotic depletion	1.32E-03	kg Sb eq	0.62	98.97	0.41
Abiotic depletion (fossil fuels)	4.83E+03	MJ	2.47	96.90	0.63
Global warming (GWP100a)	7.02E+02	kg CO_2 eq	1.49	94.44	4.07
Ozone layer depletion (ODP)	6.64E-05	kg CFC-11 eq	1.84	97.63	0.54
Human toxicity	1.56E+02	kg 1,4-DB eq	1.72	90.97	7.31
Fresh water aquatic ecotox.	1.86E+02	kg 1,4-DB eq	6.93	35.50	57.58
Marine aquatic ecotoxicity	2.58E+05	kg 1,4-DB eq	3.71	76.00	20.30
Terrestrial ecotoxicity	6.50E-01	kg 1,4-DB eq	3.17	83.89	12.95
Photochemical oxidation	8.56E-02	kg C_2H_4 eq	3.04	88.02	8.94
Acidification	2.51E+00	kg SO_2 eq	1.34	98.12	0.53
Eutrophication	9.93E-01	kg PO_4^{3-} eq	2.17	82.58	15.25

5.2. Core process

Results reported in Figure 8 highlight the role of UP1 (i.e., nitric acid leaching and required stationing step) to the overall impact: its contribution ranges from 41 to 77% of the core process impacts. The main cause is the use of nitric acid, whose production is based on NH_3. The second highest contribution is due to the use of modified activated carbon in the adsorption phase: it ranges from 15 to 37% of the core process impacts. This is mainly due to the production of activated carbon in the categories *"Global warming"* and *"Abiotic depletion (fossil fuels)"*, while the production of the modifying agent is the main cause in the remaining categories.

The last "important" contribution in terms of environmental impacts is caused by the NO_x treatment (from 3 to 23%) due to the production of sodium hydroxide.

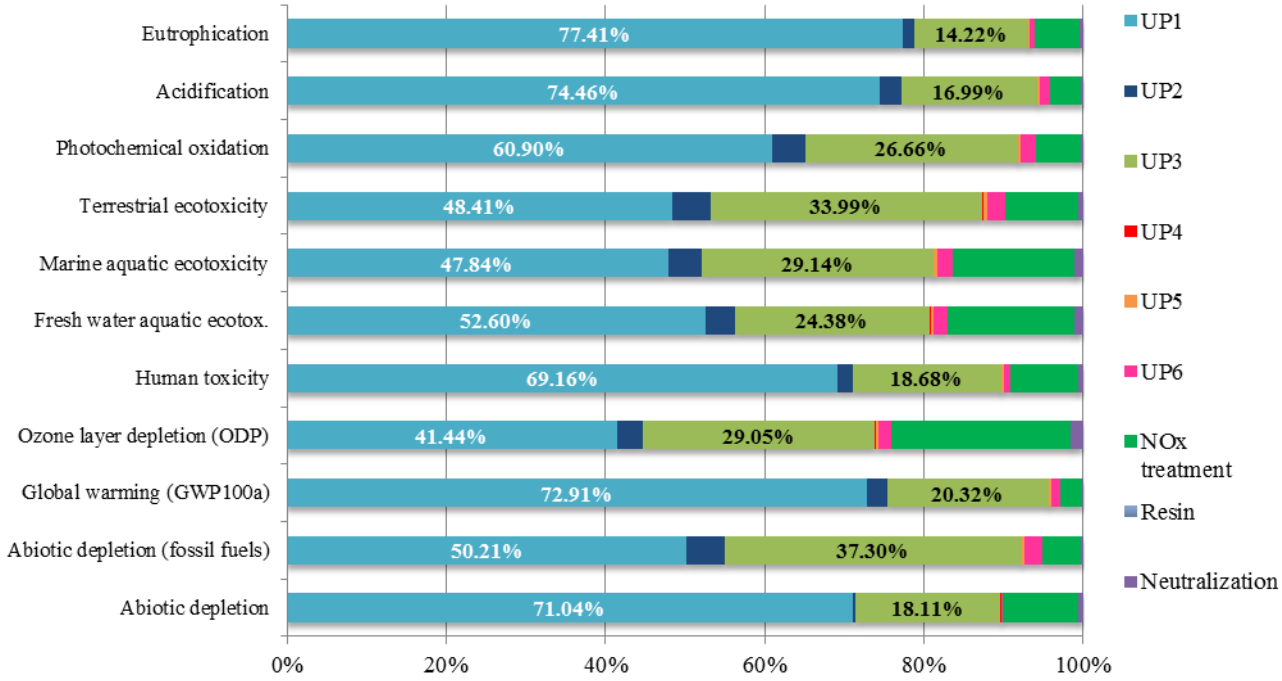

Figure 8 - Impacts percentages related to the core process.

In order to decrease the impacts, intervention on the nitric acid leaching phase would be required, but nitric acid guarantees high efficiency that other chemicals cannot ensure (Bas et al., 2014; Choubey et al., 2015; Naseri Joda and Rashchi, 2012). Furthermore, it is used in a very diluted way (16% w/w), that is already a trade-off between efficiency and NO_x emissions. For this reason, increasing in the dilution would reflect in both too low leaching efficiencies and too high reaction time.

On the other hand, interventions on the adsorption step (UP3), both using other sources and increasing the number of adsorption cycles, could positively affect the environmental performance. In the first case, AC obtained from industrial and agricultural by-products (Grace et al., 2015; Komnitsas et al., 2016; Nguyen et al., 2013) could reduce impacts of the raw material production as well as the economic costs, even if the uptake efficiencies towards the present metals should be first deeply studied.

The second proposal would, instead, correspond to lower amount of modified AC to be produced. The stages that are affected by this intervention would be adsorption and special landfill. Figure 9 shows the reduction of impacts concerning the UP3 when different scenarios are considered. Passing from the previously considered cycles (i.e., 10) to 20 or 50 cycles, the environmental impacts would be reduced. These improvements could be achieved also in the case of special

landfill. The latter are not reported in this section since they are lower than 3% of the total except for *"Fresh water aquatic ecotoxicity"* that decreases from 6.7% to 1.5% of the total impacts. Despite these advantages, the number of cycles should be tested in the pilot plant.

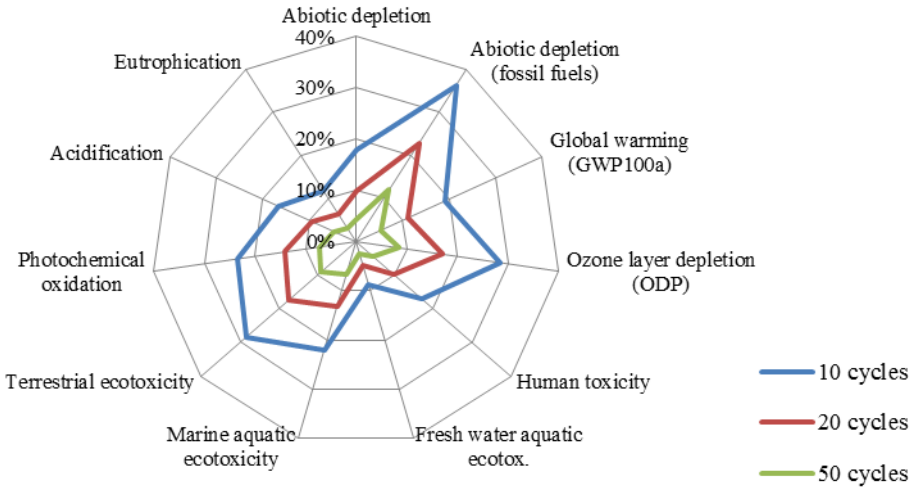

Figure 9 - Impacts percentages of UP3 in the three different scenarios (10, 20, 50 cycles of AC use).

5.3. Allocations

Since the hydrometallurgical treatment is designed for recovering metals, in the following analysis the assessed environmental impacts are referred to the recovered metals. Given the importance of economic profitability and its variability among the considered metals, besides the mass allocation (based on the amount of single metals outgoing every process step), the economic allocation factors have been estimated and applied. They are generally calculated from the economic value of products but the output materials of the considered pilot plant are secondary raw materials rich in metals even if still waste. So the economic values of metals does not correspond to the value of the output materials of this process and for this reason an assumption has been carried out: the ratios of metals prices are the same for primary metals with high purity and secondary metals recovered from the plant. These ratios were estimated comparing the average metals prices in the last three years (Table 15) and then used in the following Equation 1 as δ_i :

$$\lambda_i = \frac{\delta_i \cdot m_i}{\sum_i \delta_i \cdot m_i} \qquad \text{(Equation 1)}$$

where λ_i is the allocation factor of the i-metal and m_i is the recovered amount of the i-metal. This calculation has been performed for every process step.

Table 15 - Economic allocation factors.

	Unit	Copper[a]	Tin[a]	Nickel[a]	Silver[b]	Gold[b]
2013-2015 average prices	USD/kg	6.62	20.26	14.76	691.20	41,345.14
δ_i	-	0.02	0.05	0.04	1.67	100

[a] http://www.westmetall.com

[b] http://www.kitco.com

The obtained results show consistent differences between the two considered allocation procedures. The case of copper and gold are the most significant in these terms (see Figure 10). When mass allocation is applied, copper is characterized by higher impacts due to its large recovered amount. In contrast, when economic allocation is applied, the impacts related to recovered copper strongly decrease while gold shows an opposite behavior due to its higher economic value.

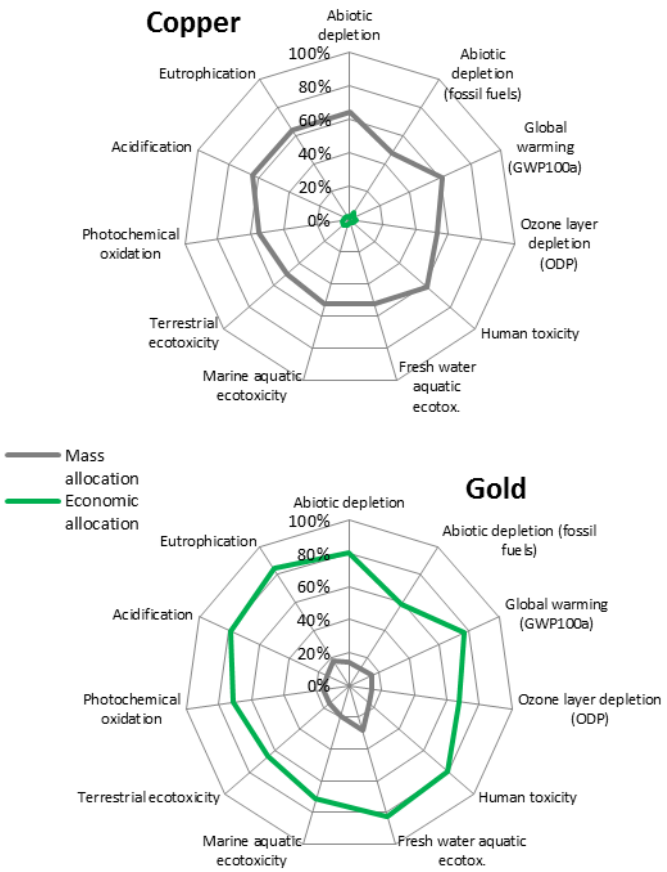

Figure 10 - Impacts percentages due to the recovered copper and gold, according to different allocations (mass and economic).

The results are then presented divided in the two main recovery lines of the core process: copper and gold (Figure 11). In this comparison, also the contributions of the related input materials (production and transport) and of the related downstream treatments are considered. Figure 11

reports the so obtained impacts as percentages for both the allocation methods. In the case of mass allocation (Figure 11 a) the gold recovery line has always lower impacts than copper line, ranging from 10 to 20% of the total. Applying economic allocation (Figure 11 b), the gold recovery line is characterized by a wider range of impact percentages, even if they are always higher than 40% of the total.

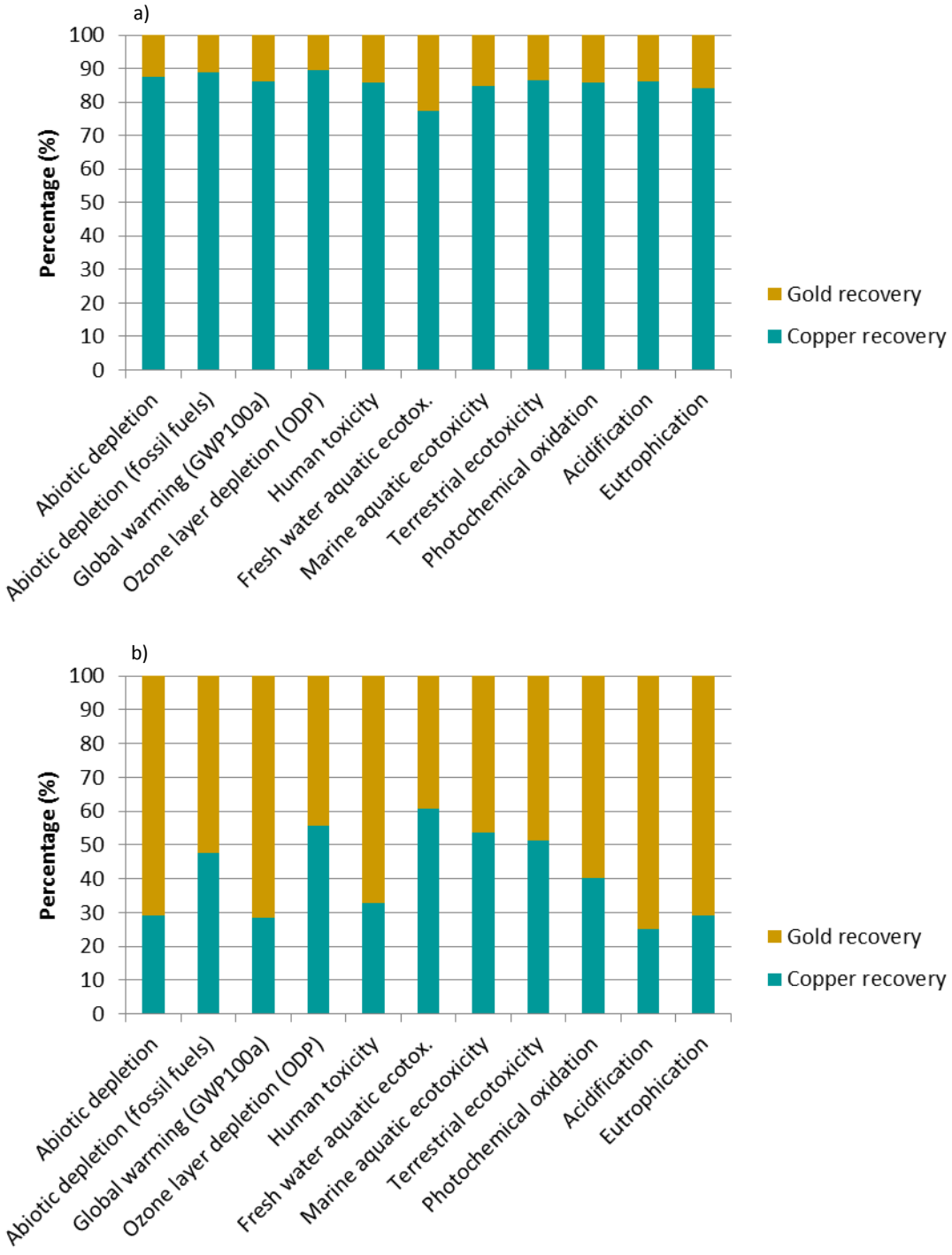

Figure 11 - Impacts comparison between copper and gold recovery for a) mass allocation and b) economic allocation.

6. Conclusions

The environmental impacts of a hydrometallurgical pilot plant aimed at treating small electronic wastes have been estimated through the LCA methodology. The obtained outcomes allow to point out the critical steps of the process and consequently improve the eco-design phase of the plant. This study has considered all the stages of the WEEE treatment, from collection to the recovery of the secondary raw materials.

The results obtained by CML method show that the core process has the highest impacts. Unfortunately, to the current state-of-the-art it is not possible to intervene on the most impacting step of the core process, that is the nitric acid leaching, without compromising the efficiencies or the reaction time. On the other hand, environmental performances could be improved by optimizing the adsorption step. Effective improvement will be evaluated in the pilot plant, by testing different sorbents and their real lifetime.

For future developments, a suitable economic allocation has to be applied, since preliminary analyses show that the results are greatly affected by the allocation method. Furthermore, it would be worthwhile to compare different end-of-life scenarios and improve the related data quality. Finally, the studied hydrometallurgical process could be compared with other treatments, as pyrometallurgy or biometallurgy, but in this case further research and primary data are needed.

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