

Review

A Review of the Carbon Footprint of Cu and Zn Production from Primary and Secondary Sources

Anna Ekman Nilsson ¹, Marta Macias Aragonés ^{2,3}, Fatima Arroyo Torralvo ³, Vincent Dunon ⁴, Hanna Angel ⁵, Konstantinos Komnitsas ⁶ ⁽¹⁾ and Karin Willquist ^{5,*}

- ¹ Research Institutes of Sweden, Division of Bioscience and Materials, Agrifood and Bioscience, Ideon, SE-22370 Lund, Sweden; anna.ekman.nilsson@ri.se
- ² Fundación Corporación Tecnológica de Andalucía (CTA), C/Albert Einstein, Edif. Insur, 4th Floor, 41092 Seville, Spain; marta.macias@corporaciontecnologica.com
- ³ Departamento de Ingeniería Química y Ambiental, Escuela Superior de Ingeniería, Universidad de Sevilla, Camino de los Descubrimientos S/N, 41092 Seville, Spain; fatimarroyo@us.es
- ⁴ ARCHE Consulting, Liefkensstraat 35D, BE-9032 Ghent, Belgium; vincent.dunon@arche-consulting.be
- ⁵ Research Institutes of Sweden, Division of Build Environment, Energy and Circular Economy, Ideon, SE-22370 Lund, Sweden; hanna.angel@ri.se
- ⁶ School Mineral Resources Engineering, Technical University Crete, GR-73100 Chania, Greece; komni@mred.tuc.gr
- * Correspondence: karin.willquist@ri.se; Tel.: +46-10-5165963

Received: 13 July 2017; Accepted: 9 September 2017; Published: 13 September 2017

Abstract: Copper (Cu) and zinc (Zn) with their unique properties are central for economic growth, quality of life, and the creation of new jobs. The base-metal producing sector is, however, under growing public pressure in respect to energy and water requirements and needs to meet several challenges, including increased demand and lower ore grades, which are generally associated with larger resource use. The development of technologies for metal production from secondary sources is often motivated by increased sustainability, and this paper aims to provide further insights about one specific aspect of sustainability-namely, climate change. The paper presents a review of carbon footprints (CF) for Cu and Zn produced from primary and secondary raw materials by analyzing data taken from scientific literature and the Ecoinvent database. Comparisons are carried out based on the source of data selected as a reference case. The data available in the literature indicate that secondary production of Cu and Zn has the potential to be more beneficial compared to primary production regarding the impact on climate change. However, the technologies used today for the production of both metals from secondary sources are still immature, and more research on this topic is needed. The general variation of data suggests that the standardization of a comparison is needed when assessing the environmental benefits of production in line with the principles of waste valorization, the zero waste approach, and circular economy.

Keywords: Cu; Zn; circular economy; carbon footprint; mining; secondary materials; metal production

1. Introduction

The sector of non-ferrous metals, with a turn-over of EUR 116.09 billion (1.8%) in 2010, accounts for 1.25% (EUR 19.91 billion) of EU manufacturing. Among non-ferrous metals, copper (Cu) and zinc (Zn) are very important for the EU's industry, and their smooth supply guarantees economic growth, quality of life, and the creation of new jobs. Cu and Zn possess unique physical, chemical, thermal, electrical, and isolating properties and are used in many industrial sectors including automotive, aerospace, construction, electricity, energy, electronics, and mechanical engineering. They differentiate from steel due to their high conductivity (valid for Cu) and resistance to corrosion and non-magnetic



properties (valid for Zn). Cu is considered the third most important metal for industry after iron and aluminum, with a yearly production of 10 Mt. It has been predicted that the market of Cu will reach 30 Mt during the period 2030–2040, which is approximately 8% higher than the predicted metal production for the same period [1]. By taking into account the decreasing ore grades, some studies indicate that Cu mining will reach its peak around 2050 [1–3], giving economic incentives to mine secondary sources. Primary and secondary Cu sources considered in this review are summarized in the Supplmentary Materials.

Zn has been identified as one of the fifty-four metals that are important to the EU's economy. China (39%), Australia (11%), and Peru (10%) are the top three producers of Zn, predominantly by primary mining. Europe has produced approximately 1 Mt of Zn in 2014, which is 8% of the total worldwide output [4]. In the developing world, Zn demand is expected to grow at an average rate of 2.2% per annum until 2035 [5]. A summary of Zn sources considered in this review is provided in the Supplmentary Materials.

The EU's non-ferrous metal sector depends mainly on imported raw materials; thus, its longevity relies on continuous supply, the use of innovative and energy efficient technologies for the production of the respective metals, and the maximization of the use of secondary raw materials. Probably this is one of the reasons that the European recycling industry is among the most advanced in the world when compared to other developed countries such as the US, Canada, and Japan [6]. Also, by taking into account their high recycling potential, their continuous utilization will definitely contribute to an improvement of the sustainability of several industrial sectors, as well as in achieving the EU's resource efficiency and energy goals [7].

For instance, while the global average demand for secondary raw materials for Cu production was approximately 35% in 2011, the respective figure in the EU was close to 40% [8]. In the case of Zn, nearly 70 per cent of Zn is recycled from end-of-life products in the EU [9]. Regarding Cu, almost 40% of the world's demand is met using recycled material [10] and, at present, approximately 30% of global Zn production comes from secondary sources. In Europe, these figures are higher, 50% in the case of Cu [11] and 60%–70% in the case of Zn [12].

The future challenges of the sector, in order to maintain its competitiveness, minimize carbon and water footprint [13], and achieve sustainable growth include aspects related to exploitation and access of new resources, trade, research and innovation activities, and the reduction of energy and water requirements [14].

Moreover, the decreasing ore grades result in environmental concerns such as large waste/metal ratio and larger resource use in respect to the use of energy, explosives, and water [14]. The metal producing sector is, on the one hand, under growing public pressure, while on the other hand it needs to overcome several burdens such as, for example, increased demand for metals and the treatment of lower ore grades [15]. This increases the environmental incentives for mining secondary sources. Primary Cu is mined both from open pit and underground mines [16]. Cu ores normally occur as either oxides or sulfides [17]. Upgrading processes to produce high-grade Cu include the stages of concentrating, smelting, and refining [18]. Cu can also be recovered from the majority of its end-products and returned to the production process without loss of quality during recycling. The production of secondary Cu is based on the direct melt of "new scrap" (waste resulting from either metals discarded in semis fabrication or generated during the initial manufacturing process) and/or the recycling of "old scrap" (obsolete end-of-life products or structures) [19]. Old scrap is often contaminated to a certain degree, depending mainly on its origin and the efficiency of its collection systems [20]. Scrap metal recycling involves a number of steps such as recovery, sorting, brokering, baling, shearing, and smelting [19]. Pyrometallurgical and hydrometallurgical processes are similar to those used in primary metal production. A detailed description of the production technologies is given in the Supplmentary Materials.

Primary Zn is also mined from underground and/or open pit mines [21] and extracted from Zn-Pb ores, or from other ores containing Cu, Au, or Ag. Zn is mainly recovered through the

pyrometallurgical or hydrometallurgical route. In the case of ZnS ore, a hydrometallurgical approach is followed, where the ore is concentrated by froth flotation and roasted to convert the zinc sulfide to oxide, which is then leached out with sulfuric acid to provide a leach solution that can be purified before recovering Zn by electrowinning. In the case of Zn-Pb ores, a pyrometallurgical approach is followed in blast furnaces [21,22], and the main steps involve sintering, smelting, refining, and casting. Zn can be also recovered from different secondary resources with different levels of impurities including, among others, ash, zinc dross, flue dusts of the electric arc furnace and brass smelting, automobile shredder scrap, rayon industry sludge, and cathodic tubes from WEEE. Recovery from these sources eliminates the option of disposal, which today is considered expensive and environmentally unacceptable because of the increasingly stringent environmental protection regulations. Furthermore, most of these materials are classified as hazardous wastes due to their increased toxicity as a result of the presence of different metals including Pb, Cd, As, and Cr. In view of the above, there has been an increasing interest in developing new processes for the recovery of Zn from these secondary sources in order both to valorize these wastes and reduce the environmental risk associated with their disposal. Usually, pyrometallurgical and hydrometallurgical processes are employed for treating such secondary materials, but they are not widely used for low-concentration streams. Regarding the pyrometallurgical approach, its main concept relies on the reduction of zinc oxide using carbon and the distillation of the metallic Zn from the resulting mix in a carbon monoxide atmosphere. A detailed description of the production technologies is provided in the Supplmentary Materials.

The development of new technologies for metal production from secondary sources should be mainly motivated by increased sustainability, and this paper aims to provide further insights about one specific aspect of sustainability: climate change. It presents a review of carbon footprints (CF) for Cu and Zn produced from primary and secondary raw materials by analyzing data taken from the scientific literature and the Ecoinvent database. All studies that are included have a cradle-to gate perspective, which for primary metal production includes mining, concentration, and refining, and for secondary sources collection of raw materials, concentration of the target metals, and upgrading. Another objective of this paper is to identify key factors affecting the CF of Cu and Zn production by comparing CO_2 emissions based on country (for primary sources) and technology (for primary and secondary sources).

During the life cycle of base metals production, a large share of the environmental impacts is associated with the use of energy (thermal or electrical) in various processes. Thermal energy is mainly produced from the combustion of fossil fuels, while electricity may be produced from various sources in thermal, nuclear, and hydro power plants, as well as from renewable sources. Thus, the overall environmental impact of energy generation may differ broadly among countries and regions, even among different parts of the same country. Base metal production also contributes considerably to other environmental impacts such as depletion of resources, water consumption, and emissions of hazardous substances to the environment; these are, however, not included in this review.

2. Carbon Footprint and LCA

Life Cycle Assessment (LCA) is a methodological tool used to assess the potential environmental impacts of a product or service through its life cycle [23]. LCA can also be used to calculate the environmental impacts of an entire sector such as non-ferrous metals. The results generated by LCA can be used for sustainability reporting and for exploring possibilities to improve environmental performance by assessing and mapping environmental impacts and their causes. LCA is standardized by ISO in the standards 14040 and 14044 and includes four main steps, namely, goal and scope definition, life cycle inventory analysis, impact assessment, and interpretation [24,25].

According to ISO 14040-14044 standards, the Life Cycle Inventory (LCI) is an inventory of the input/output data pertinent to the system studied. In this respect, energy, materials use, and associated emissions over the life cycle of the entire metal production systems need to be identified and assessed.

Given the contribution of the base-metal sector, including Cu and Zn production to global warming, mass flow analysis (MFA) and substance flow analysis (SFA) need to be properly defined and integrated [26].

Since 2013, there has been a separate ISO standard for carbon footprint, ISO 14067 [27], which defines the principles, requirements, and guidelines for its quantification and communication. In general, it can be said that CF is often used for communication purposes because this specific environmental impact category can be more easily grasped by the general public. Full LCAs are more commonly used for research and development purposes when a more nuanced picture of a product or process is required. The main difference between CF and LCA is that CF only considers the emissions of CO₂-equivalents (CO₂-eq), while LCA covers a broader spectrum of impact categories. According to the ISO standard, CF is expressed as global warming potential, in CO₂-eq. This means how potent a GHG is compared to CO₂. GWP factors recommended in ISO 14067 [27] are derived from the IPCC Fourth Assessment Report. Examples of GHGs considered are CO₂, CH₄, N₂O, SF₆, HFCs, and PFCs.

The product environmental footprint (PEF) and the organization environmental footprint (OEF) were inaugurated by the European Commission as a way to measure environmental performance. Between 2013 and 2016, PEF and OEF have been tested in a variety of pilots, of which the production Metal Sheets is one pilot for PEF and the Cu sector is one pilot for OEF [28].

Methodology

The data used in this review paper were mainly obtained through searches in scientific databases such as Science Direct and Scopus. Also, Google Scholar and commonly used LCI databases were used to extract data. Several combinations of key words were considered to extract the most appropriate publications. Data for the production of Cu and Zn from primary sources was extracted from scientific papers and the Ecoinvent v3.3 database. For Cu and Zn production from secondary sources, data were extracted from the scientific literature. It is important to mention that no pertinent data was found in databases such as Ecoinvent v3.3, Open LCA nexus Web, the European Life Cycle Database (ELCD), the CPM database from the Swedish Life Cycle Center, and the United States LCI database. Data from non-scientific reports published by, e.g., professional and industrial organizations, were not included in this review.

This study reviews the available literature pertinent to the calculation of the CF of metal production using a "cradle-to-gate" approach and does not consider other impact categories. As the produced metal can be an intermediate product, most CF reports and scientific literature are based on this approach, which considers all production processes involved, from raw materials extraction (i.e., the cradle) to the production in the form of Cu anode, Cu cathode, Cu blister, or Zn which are available to a manufacturing sector (i.e., the gate) [29]. For Zn, metal at the factory gate in the reviewed studies refers to refined Zn, Zn ingot, and special, high-grade Zn with a purity of more than 99.99%. The functional unit used for the comparisons is 1 kg metal. Figure 1 shows the system boundaries for studies included in this review.



Figure 1. System boundaries used for base-metal production Life Cycle Assessment (LCA) studies.

3. Results and Discussion

3.1. Copper

A great variety of LCA publications on Cu production from primary sources are available, however only a few describe the production of Cu metal in a cradle-to-gate approach. Therefore, both the pyrometallurgical and hydrometallurgical processes are included in this review, which produce either anode or cathode copper. Figure 2 shows the calculated CF for Cu production according to the geographical region and the metallurgical production process. The CF ranged from 1.1 to 8.5 kg CO_2 -eq/kg Cu. Average CFs retrieved from the Ecoinvent 3.3 database [30] ranged from 2.1–8.0 kg CO₂-eq/kg Cu, and this range is consistent with what was retrieved from the literature. Data on the contributions of the different process steps is scarce for high-grade Cu production, and the reviewed data did not show any correlations between the geographical production of Cu and the CF, nor between the metallurgical production process and CF. Northey et al. [1] concluded that the main factors for the variation in CF values are the use of different ore grades and fuel sources for the heating and generation of electrical energy. The type of the ore, the mining method, and the smelting technology used were identified as critical factors determining the overall energy consumption by Norgate et al. [22]. A similar observation was made by Adachi and Mogi [31], showing the high CF variability of Cu production from different mining sites. The authors also found that 30%-70% of the CF resulted from the mining and processing processes. Overall, more harmonization of CF for Cu-production is needed, in order to provide more detailed information on the different process steps.



Figure 2. Overview of carbon footprints (CFs) of copper (Cu) production (cradle-to-gate) from primary sources. The CFs are grouped by geographical region. *X* axis indicates the type of metallurgical processes used in each case: Pyrometallurgy, P; Hydrometallurgy, H; and Combined, C.

Recently, there has been growing interest in the study of secondary Cu production, but only a few studies estimated the CF of these processes. The processes used for obtaining secondary Cu are similar to those used in primary metal production (Figures 1 and 2). The main differences are linked to the first steps of the processes, namely, mining and beneficiation (in the case of primary Cu and collection), disassembly, sorting (according to different levels of purity), and transportation (in the case of secondary Cu production). A summary of CFs for Cu produced from secondary sources is given in Figure 3. CF values vary from 0.2 to 1.9 kg CO₂-eq/kg Cu. The data indicates that the variation depends on the quality of the source material and the metallurgical process used. In addition, studies have shown that transport is a key factor in secondary Cu production in terms of CF, and, depending

on the transport distance of the raw materials, recycling may not be as environmental friendly as expected [32].



Figure 3. CFs of Cu production from secondary sources grouped by source material. Waste electrical and electronic equipment, WEEE; municipal solid waste incinerator, MSWI; low grade, LG; high grade, HG; mixed grade, MG; at refinery, AR; LED lamp, LL; mechanical dismantling in Europe, MDE; manual dismantling in Europe, HDE; mechanical dismantling in India, MDI; and manual dismantling in India, HDI.

Grimmes et al. [33] showed that the CF of processing low grade scrap was approximately three times higher than that of high grade scrap. Slightly higher is the value estimated by Nuss and Eckelman [34], based on a Cu recovery process considered by Nassar et al. [35]; however, transport was not included in the assessment. In the work of Giurco and Petrie [36], the CF to obtain 1 kg of Cu from an ore (0.45% Cu) was estimated to be 7kg CO₂-eq; however, when Cu was obtained from a mix of 25% Number 1 scrap (99% Cu), 37.5% of Number 2 scrap (95% Cu), and 37.5% of low quality scrap (30% Cu), the CF was estimated to be reduced to 0.65 kg CO₂-eq.

Various recycling methodologies for e-waste were analyzed in the work of Eisinger et al. [37], in which the manual and mechanical dismantling of personal computers was compared for India and Europe. The lowest CFs were calculated when mechanical dismantling was performed in Europe (Figure 4). Almost the same CF was reported by Reuter and Van Schaik [38] in the case of producing Cu from an eco-designed, light-emitting diode lamp. The authors compared the results with the environmental impact of obtaining 1 kg of blister Cu from a 1% ore in an EU-27 country with the use of concentrator and smelter (Flash smelting and Flash Converting). The highest CF, 1.9 kg CO₂-eq/kg Cu, was reported by Boesch et al. [39], who assessed the recovery of metals from the fly ash and the slag produced in a municipal solid wastes incinerator in Switzerland. The Cu content in the MSWI slag was 1 kg Cu/t.

To the best of our knowledge, there are only two publications regarding the recovery of Cu from printed circuit board (PCB) using the electrochemical processes. In the work of Soares et al. [40], two electrochemical processes for recovering Cu from PCB scrap were compared using LCA methodology; one involves sulfuric acid and the other aqua regia (nitric and chloridric acid). In the paper of Fogarasi et al. [41], the environmental impacts related to direct electrochemical oxidation were compared with the mediated electrochemical oxidation using Fe^{2+}/Fe^{3+} redox couple.

The data presented in Figures 2 and 3 are insufficient to justify a statistically viable benefit of treating secondary materials in respect to primary sources due to the high variation in terms of purity and ease of processing. For example, the average CF calculated by Nuss and Eckelman [34] for global production of Cu was considerably lower (2.80 kg CO₂-eq/kg Cu) than that derived from the Ecoinvent database (6.62–8.00 kg CO₂-eq/kg Cu). Both primary and secondary sources were included, along with

various production processes. These results highlight clearly the complexity in assessing the benefits of Cu production from different sources.

3.2. Zinc

The carbon footprints of Zn produced from primary sources are summarized in Figure 4. The CFs are grouped either by technology used or by geographical region. However, there is not enough data available to draw any clear conclusions about the importance of each factor. Data used by van Genderen et al. [42], Qi et al. [43], and Ecoinvent 3.3 were obtained from the industry, while other studies used only literature data. Van Genderen et al. [42] aimed for a representative global average CF, but in certain regions too few producers provided data for the result to be fully representative and reliable. Qi et al. [43] used data from one specific production site in China. In the Ecoinvent 3.3 database, different datasets are available for Zn production. However, only one dataset was considered representative and included in this study. This represents a global average CF for Zn. Since Zn is not the single product produced from the process, allocation of environmental impact was applied in all studies reviewed except for Adachi and Mogi [31]. Ecoinvent 3.3 applies as a default alternative the principle of allocation at the point of substitution. Nuss and Eckelman [34] applied economic allocation, whereas the other studies applied physical allocation based on either mass [22,43] and/or metal content [42]. In all studies, it can be seen that metal production has a larger contribution to CF than ore mining and concentration. The contribution from metal production varied between 51% and 80% of the total CF. According to Norgate et al. [22], 100% coal-based electricity was assumed for Zn production in Australia, which could can why these emissions are rather high. Norgate et al. [22] only mention that metal production and refining stages made the greatest contribution to CF. In the study by Werder and Steinfeld [44], approximately 20% of CF was caused by mining and concentration and 80% by refining. Of the process stages used for refining, electrolysis has the single highest contribution. Van Genderen et al. [42] calculated 30% of CF to be due to mining, 5% due to the transportation of concentrate, and 65% due to smelting. In the study of Qi et al. [43], less than 10% was due to mining, 65% were caused by electricity production, and 25% were due to the use of natural gas. Adachi and Mogi [31] studied the CF of Zn production from imported concentrate in a smelter in Japan, and they estimated that the contribution of mining was 40%-50% of the total, while the contribution of mineral processing was 20%–30%. Data derived from the EcoInvent Database do not allow the accurate assessment of the contribution of single production phases. The CF of Zn production in Sweden is low, but the metal is considered as a by-product of the treatment of Au-Ag-Zn-Pb-Cu ore with the use of low-carbon electricity.



Figure 4. Overview of CFs of zinc (Zn) production (cradle-to-gate) from primary sources. The CFs are grouped by geographical region. *X* axis indicates the type of metallurgical processes used: Pyrometallurgy, P; Hydrometallurgy, H; Electrometallurgy, E; and Combined, C.

During the last decade, many papers have been published on Zn production from secondary sources focusing on process feasibility, sustainability, or economics. Since the number of potential secondary sources is big, papers usually focus on some of them, for example, Ng and co-workers [4] focused on wastes and conducted a multilevel sustainability assessment for Zn recovery. Figure 5 presents the CFs of Zn production from secondary sources grouped by source material. Available information about CF is mostly related to Zn recovery from scrap and fly ash produced after municipal solid waste (MSW) incineration, while only a few papers are available for the production of Zn from waste electrical and electronic equipment (WEEE) [45]. Boesch and co-workers [39] investigated the recovery of Zn from MSW fly ash considering combustion in a grate incinerator, the use and recovery from slag and fly ash, and the landfilling of residues. Until now, this approach has been mostly followed in Switzerland and Sweden. Concerning the rest of Europe, ash from MSW incineration is also increasingly recognized as a potential source for materials of high importance to the economy [46]. Boesch et al. [39] studied also the sensitivity of LCA results to the electricity mix used, and concluded that the savings from energy recovery vary considerably depending on assumptions related to the substituted energy production systems. Substituting the average Swiss electricity mix provides the lowest savings. Savings from substituting the average European electricity mix or marginal electricity production (natural gas power plants in the case of Switzerland) are considerably larger (by one order of magnitude). As for the metal recovery approach, a hydro-chemical process can be applied, which involves the use of the acidic scrub water obtained from the wet flue gas treatment to mobilize and extract metals from the alkaline fly ash. The acidic fly ash leaching process produces a metalliferous filtrate and a low metal filter cake. The filtrate contains elevated concentrations of Zn, Pb, Cu, and Cd and can be further processed directly at a MSWI for Zn recovery (FLUREC process) or sent to a specific Zn-oxide recycling facility (FLUWA process) [47]. When LCIs of fly ash treatment with and without metal recovery are compared, metal recovery through acidic fly ash scrubbing is preferable over landfilling of solidified fly ash or underground disposal [39]. Moreover, according to the reviewed CFs state-of-the art Zn recovery, directly at the MSWI is the environmentally preferred process. The largest benefits of this approach include savings in neutralization agents and credits for Zn recovery. The main differences in CFs between conventional (FLUWA) and integrated Zn recovery at the MSWI (FLUREC) arise from the associated burdens and recovery efficiency of the processes (pyro-metallurgical and electrowinning, respectively) [39]. Hence, when considering the CF of Zn production in this case, figures averaged around 0.30 kg CO₂-eq/kg Zn, with values ranging from 0.23 [48,49]) to 0.33 kg CO₂-eq/kg Zn [50].



Figure 5. CFs of Zn production from secondary sources grouped by source material. In (**A**), the CFs of Zn production from scrap and waste electrical and electronic equipment (WEEE) are given. (**B**) shows the CFs for Zn production from municipal solid waste incinerator (MSWI ash).

Regarding Zn production from scrap recycling and clean and mixed scrap can be treated by sweating, whereby the scrap is heated at 360–420 °C to melt and recover Zn (e.g., using dezincing, Waelz Kiln, or DC-furnace based processes), directing other impurities such as Cu, Al, and Fe in slag. Zn alloy scrap can also be processed by using a similar route to recover the metal as a new, pure alloy, while Zn oxide residues can be converted to Zn by dissolving them in sulfuric acid and recovering the metal by electrowinning, e.g., in the EZINEX process. It has been shown that the dezincing process has a CF around 4.6 kg CO₂-eq/kg, while the EZINEX process accounts for 0.7–1.4 kg CO₂-eq/kg [33].

For WEEE, as recovery processes are still under development with only some of them going for pilot scale, just a few references have been found, which highlight research activities carried out in the frame of projects such as the HydroWEEE, funded by the European Commission [51]. An LCA was applied to hydrometallurgical treatment carried out using the developed new portable prototype plant for the recovery of valuable metals. The plant treated the WEEE residues derived from physical processes applied for the recycling of fluorescent lamps, cathode ray tubes (CRTs), Li-ion accumulators, and printed circuit boards (PCBs). Leaching with sulfuric acid, followed by metal recovery through selective precipitation, were the main steps considered. The final step involved treatment of wastewater with lime. The recovered metals included Y, Zn, Co, Li, Cu, Au, and Ag. In the case of Zn, which is contained in CRTs (30–35% Zn, as oxide and sulfur compound), an estimated CF of 5.5 kg CO₂-eq/kg Zn was calculated [45]. Concerning Zn production from steel dust, only one paper has been found, while the CF analysis does not provide specific information [52].

In comparison to Cu, less information is available for the CF of Zn production. Based on literature data, it seems that the CF of Zn produced from secondary sources is a magnitude lower than the CF of Zn produced from primary sources. However, as in the case of Cu production, there is a large variation of CF values depending on the source of data selected for comparison.

4. Conclusions

Cu and Zn are of great importance for the world economy and the increasing need for their production contributes significantly, as the entire base-metal sector, to global warming, both due to the extraction of resources and the production of metals. In this review, the production of both metals from primary and secondary sources was studied and compared. In general, LCI-data for metals production from primary sources is more often available in databases, whereas data for their production from secondary sources from the scientific literature.

Production of metals from secondary sources is promising, but more research and development in all stages of their life cycle is needed to provide truly sustainable solutions in the frame of circular economy. From the analysis of data, it is deduced that no clear trend could be seen between the CF for metals produced from primary sources and their geographical origin or the technology used for processing. With few exceptions, the production of metals from secondary sources has generally been reported to have lower CFs than the production from primary sources. However, the variations in each case are large. For example, the CF of Cu production from MSWI slag was in the same range as several of the reviewed CFs from primary sources, whereas the CF for Zn from MSWI fly ash was significantly lower than all the reviewed CFs from primary sources. The variation is large, and depends on the metal content in the resource and how easily it can be extracted.

The technologies used for the extraction of metals from secondary sources are less mature than the technologies used for their extraction from primary sources, and this may have a negative impact on the results. One can expect that as technology matures and systems are optimized, the CFs of metal production from secondary sources will be reduced. On the other hand, as ore grades are becoming lower, one can expect that the CFs for the production of metals from primary sources will be increased over time. Similarly, as the technologies for the extraction and logistics needed for efficient recovery of metals from secondary sources are improved, CFs for metals production from secondary sources will most likely decrease over time. Hence, the general variation of data suggests that standardization of the comparison approach is needed for the assessment of environmental impacts of metal production, the reliable evaluation of the existing technologies used (in terms of water and energy requirements), and the development of more environmentally friendly and cost-efficient approaches. Finally, it is important to highlight that this review only presents literature data on CF without the ambition of including other environmental impact categories such as marine and terrestrial eco-toxicity, acidification, and water footprint. The inclusion of these categories may result in larger differences between metal production from primary and secondary sources. However, the number of studies that include, for example, water footprint is low and more studies are needed to provide a more comprehensive picture of the environmental impact of metal production from primary and secondary sources.

Supplementary Materials: The following are available online at www.mdpi.com/2075-163X/7/9/168/s1; Figure SI1. Summary of Cu sources and main recovery process and Figure SI2. Summary of Zn sources and main recovery methods.

Acknowledgments: The authors would like to acknowledge the financial support of European Commission in the frame of Horizon 2020 project "Metal recovery from low-grade ores and wastes", <u>www.metgrowplus.eu</u>, Grant Agreement n° 690088.

Author Contributions: A.E.N. was responsible for the writing process and performed a literature research and analyzed data of metal production from primary sources. K.W. took initiative to the paper and has contributed to the literature search and composition of the paper. M.M.A. and F.A.T. drafted the sections corresponding to secondary sources and contributed to literature search and paper review. V.D. and H.A. performed a literature search and analyzed the data of primary resources. K.K. performed a literature search, critically analyzed results and revised the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Northey, S.; Mohr, S.; Mudd, G.; Weng, Z.; Giurco, Y.D. Modelling future copper ore grade decline based on a detailed assessment of copper resources and mining. *Resour. Conserv. Recycl.* **2014**, *83*, 190–201. [CrossRef]
- 2. Brown, L. Plan B. 2.0: Rescuing a Planet Under Stress and a Civilization in Trouble; W.W. Norton: New York, NY, USA, 2006.
- 3. Vieira, M.D.; Goedkoop, M.J.; Storm, P.; Huijbregts, M.A. Ore grade Decrease as Life Cycle Impact Indicator for Metal Scarcity: The Case of Copper. *Environ. Sci. Technol.* **2012**, *46*, 12772–12778. [CrossRef] [PubMed]
- 4. Ng, S.; Head, I.; Premier, G.; Scott, K.; Yu, E.; Lloyd, J.; Sandhukhan, J. A multilevel sustainability analysis of Zn recovery from wastes. *Resour. Conserv. Recycl.* **2016**, *113*, 88–105. [CrossRef]
- 5. Zinc Investing News. Available online: http://investingnews.com/category/daily/resource-investing/ base-metals-investing/zinc-investing/ (accessed on 13 July 2017).
- 6. Eugster, M. External Costs in the European Copper Value Chain. A Comparison of Copper Primary Production and Recycling. Master's Thesis, ETH Zürich, Zürich, Switzerland, 2008.
- 7. Boulamanti, A.; Moya, Y.J. Production costs of the non-ferrous metals in the EU and other countries: Copper and Zinc. *Resour. Policy* **2016**, *49*, 112–118. [CrossRef]
- 8. ECORYS. 2011. Available online: http://www.ecorys.com (accessed on 13 July 2017).
- 9. ASM Recycling. 2015. Available online: http://www.asm-recycling.co.uk/blog/the-world-of-metal-recycling-the-facts/ (accessed on 13 July 2017).
- 10. Chao, D. *BIR Annual Report 2016, Non-Ferrous Metal Division;* Bureau of International Recycling BIR: Brussels, Belgium, 2016.
- 11. E.C. Institute. 2017. Available online: http://copperalliance.eu/about-copper/recycling (accessed on 13 July 2017).
- 12. Graedel, T.E. Recycling Rates of Metals—A Status Report, A Report of the Working Group on the Global Metal Flows to the International Resource Panel; UNEP: Athens, Greece, 2011.
- 13. Song, X.; Pettersen, J.B.; Pedersen, K.B.; Roberg, S. Comparative life cycle assessment of tailings management and energy scenarios for a copper mine: A case study in Northern Norway. *J. Clean. Prod.* **2017**, *164*, 892–904. [CrossRef]
- 14. Norgate, T.; Jahanshahi, S. Reducing the greenhouse gas footprint of primary metal production: Where should the focus be? *Miner. Eng.* **2011**, *24*, 1563–1570. [CrossRef]

- 15. Eckelman, M. Facility-level energy and greenhouse gas life-cycle assessment of the global nickel industry. *Resour. Conserv. Recycl.* **2010**, *54*, 256–266. [CrossRef]
- 16. Dudka, J.; Adriano, Y.P.; Dudka, S.; Adriano, D. Environmental Impacts of Metal Ore Mining and Processing: A Review. J. Environ. Qual. **1997**, *26*, 590–602. [CrossRef]
- 17. CDAA (Copper Development Association Africa), Sources of Copper Ore. 2016. Available online: http: //www.copper.co.za/copper-education/sources-of-copper-ore/ (accessed on 20 April 2017).
- 18. Northey, S.; Haque, N.; Mudd, G. Using sustainability reporting to assess the environmental footprint of copper mining. *J. Clean. Prod.* **2013**, *40*, 118–128. [CrossRef]
- 19. ICSG (International Copper Study Group). The World Copper Factbook. 2014. Available online: http://www.icsg.org (accessed on 13 July 2017).
- Muchova, L.; Eder, P.; Villanueva, A. End-of-Waste Criteria for Copper and Copper Alloy Scrap: Technical Proposals. Report EUR 24786 EN. Available online: http://publications.jrc.ec.europa.eu/repository/ bitstream/JRC64207/reqno_jrc64207_pdf (accessed on 20 August 2017).
- 21. IZA. International Zinc Association Website. Available online: http://www.zinc.org/basics/ (accessed on 13 July 2017).
- 22. Norgate, T.; Jahanshahi, S.; Rankin, W. Assessing the environmental impact of metal production processes. *J. Clean. Prod.* **2007**, *15*, 838–848. [CrossRef]
- 23. Finnveden, G.; Hauschild, M.; Ekvall, T.; Guinée, J.; Heijungs, R.; Hellweg, S.; Koehler, A.; Pennington, D.; Suh, S. Recent developments in life cycle assessment. *J. Environ. Manag.* **2009**, *91*, 1–21. [CrossRef] [PubMed]
- 24. ISO. Environmental Management—Life Cycle Assessment—Principles and Framework, ISO14040; The International Organization for Standardization: Geneva, Switzerland, 2006.
- 25. ISO. Environmental Management—Life Cycle Assessment—Requirements and Guidelines, ISO 14044; The International Organization for Standardization: Geneva, Switzerland, 2006.
- 26. Raugei, M.; Ulgiati, S. A novel approach to the problem of geographic allocation of environmental impact in life cycle assessment and material flow analysis. *Ecol. Indic.* **2009**, *9*, 1257–1264. [CrossRef]
- 27. ISO. Greenhouse Gases—Carbon Footprinting of Products-Requirements and Guidelines for Quantification and Communication; The International Organization for Standardization: Geneva, Switzerland, 2013.
- 28. European Commission. 2017. Available online: http://ec.europa.eu/environment/eussd/smgp/ef_pilots. htm (accessed on 13 July 2017).
- Bartzas, G.; Komnitsas, K. Life cycle assessment of ferronickel production in Greece. *Resour. Conserv. Recycl.* 2015, 105A, 113–122. [CrossRef]
- 30. Swiss Centre for Life Cycle Inventories. *Ecoinvent Life Cycle Inventory Database v3.3*; Ecoinvent: Zurich, Switzerland, 2016.
- Adachi, T.; Mogi, G. Life Cycle Inventory for Base Metal Ingots Production in Japan Including Mining and Mineral Processing Processes by Cost Estimating System Database. *Trans. Nonferrous Met. Soc. China* 2007, 17, 131–135.
- 32. Barba-Gutierrez, Y.; Adenso-Diaz, B.; Hopp, M. An analysis of some environmental consequences of European electrical and electronic waste regulation. *Resour. Conserv. Recycl.* **2008**, *52*, 481–495. [CrossRef]
- 33. Grimes, S.; Donaldson, J.; Cebrian Gomez, G. *Report on the Environmental Benefits of Recycling*; Bureau of International Recycling: Brussels, Belgium, 2008.
- Nuss, P.; Eckelman, M.J. Life Cycle Assessment of Metals: A Scientific Synthesis. *PLoS ONE* 2014, 9, e101298. [CrossRef] [PubMed]
- 35. Nassar, N.; Barr, R.; Browning, M.; Diao, Z.; Friedlander, E. Criticality of the Geological Copper Family. *Environ. Sci. Technol.* **2011**, *46*, 1071–1078. [CrossRef] [PubMed]
- 36. Giurco, D.; Petrie, J. Strategies for reducing the carbon footprint of copper: New technologies, more recycling or demand management? *Miner. Eng.* 2007, *20*, 842–853. [CrossRef]
- 37. Eisinger, F.; Chakrabarti, R.; Krüger, C.; Alexeew, J. *Carbon Footprint of E-Waste Recycling-Scenarios in India, Version 1.0;* Adelphi: Berlin, Germany, 2011.
- Reuter, M.; van Schaik, A.; Gediga, J. Simulation-based design for resource efficiency of metal production and recycling systems: Cases-copper production and recycling, e-waste (LED lamps) and nickel pig iron. *Int. J. Life Cycle Assess.* 2015, 20, 671–693. [CrossRef]

- Boesch, M.; Vadenbo, C.; Saner, D.; Huter, C.; Hellweg, S. An LCA model for waste incineration enhanced with new technologies for metal recovery and application to the case of Switzerland. Waste Manag. 2014, 34, 378–389. [CrossRef] [PubMed] 39.
- Soares Rubin, R.; Soares de Castro, M.; Brandão, D.; Schalch, V.; Ometto, A. Utilization of Life Cycle Assessment methodology to compare two strategies for recovery of copper from printed circuit board scrap. J. Clean. Prod. 2014, 64, 297–305. [CrossRef] 40.
 - Fogarasi, S.; Imre-Lucaci, F.; Ilea, P.; Imre-Lucaci, A. The environmental assessment of two new copper recovery processes from Waste Printed Circuit Boards. J. Clean. Prod. 2013, 54, 264-269. [CrossRef] 41.
- Van Genderen, E.; Wildnauer, M.; Santero, N.; Sidi, N. A Global Life Cycle Assessment for Primary Zinc Production. Int. J. Life Cycle Assess. 2016, 21, 1580–1593. [CrossRef] 4
 - Qi, C.; Ye, L.; Ma, X.; Yang, D.; Hong, J. Life cycle assessment of the hydrometallurgical zinc production chain in China. J. Clean. Prod. 2017, 156, 451–458. [CrossRef] 43.
 - Werder, M.; Steinfeld, A. Life cycle assessment of the conventional and solar thermal production of zinc and synthesis gas. Energy 2000, 25, 395-409. [CrossRef] 44.
 - Rocchetti, L.; Veglio, E.; Kopacek, B.; Beolchini, F. Environmental Impact Assessment of hydrometallurgical Processes for Metal Recovery from WEEE Residues Using a Portable Prototype Plant. Environ. Sci. Technol. 2013, 47, 1581–1588. [CrossRef] [PubMed] 45.
- Morf, L.; Gloor, R.; Haag, O.; Haupt, M.; Skutan, S.; Lorenzo, F.; Böni, D. Precious metals and rare earth elements in municipal solid waste-sources and rate in a Swiss incineration plant. Waste Manag. 2013, 33, 634-644. [CrossRef] [PubMed] 46.
- Fly Ash Scrubbing 'FLUWA', a Trendsetting Procedure in Waste I; Swiss Federal Office for the Environment: Verfahren, ein Zukunftsweisendes Verfahren in der Abfallverbrennung (Recovering Heavy Metals from Fly Ash: Acidic Bühler, A.; Schlumberger, S. Schwermetalle aus der Flugasche Zurückgewinnen: Saure Flugaschenwäsche—FLUWA Bern, Switzerland, 2010. 47.
- from Swedish MSWI fly ashes. In Proceedings of the Second Symposium on Urban Mining, Bergamo, Italy, Karlfeldt Fedje, K.; Andersson, O.; Modin, P.; Frändegard, P.; Pettersson, A. Opportunities for Zn recovery 19-21 May 2014. 48.
- Willquist, K.; Johansson, I.; Andersson, S.; Angel, H.; Harfeldt, L.; Karfeldt Fedje, K. Critical metal extraction from municipal solid waste incineration ashes and the impact on a circular economy. In Proceedings of the 5th International Slag Valorisation Symposium, Leuven, Belgium, 3–5 April 2017. 49.
- Bjurström, H.; Steenari, B.M. Wet Treatment of Ashes, a Survey of Methods; Värmeforsk Service AB: Stockholm, Sweden, 2003. 50.
 - HYDROWEEE Project-Innovative Hydrometallurgical Processes to Recover Metals from WEEE including Lamps and Batteries. Available online: http://cordis.europa.eu/result/rcn/45388_en.html (accessed on 13 July 2017). 51.
- Salmi, O.; Wierink, M. Effects of waste recovery on carbon footprint: A case study of the Gulf of Bothnia steel and zinc industries. J. Clean. Prod. 2011, 19, 1857-1864. [CrossRef] 5



© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).