POLITECNICO DI MILANO

School of Civil, Environmental and Land Management Engineering

Master of Science in Environmental and Land Planning Engineering

WATER FOOTPRINT: APPLICATION OF DIFFERENT METHODS TO THE CASE STUDY OF THE BENEFICIATION PROCESS OF MANGANESE ORES

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Academic Year 2019/2020

DEDICATION

Mine

“And, when you want something, all the universe conspires in helping you to achieve it”

– Paulo Coelho, The Alchemist

ACKNOWLEDGEMENTS

This Master of Science degree academic adventure has been a truly extraordinary and an unforgettable experience. I made many new friends and received overwhelming support from my family and close friends throughout all the moments of doubt and difficulty. I, therefore, would like to wholeheartedly thank all those who made this thesis work possible.

First of all, I would like to express sincere gratitude to both my supervisors Prof. Lucia Rigamonti and Dr. Sara Pantini for giving me the opportunity to work with them. Through all the moments of consultation, they accorded me patience, unwavering support, and wonderful guidance which eventually led to massive improvement in the quality of this thesis report.

Special thanks from the bottom of my heart also goes to all the members of staff and students of the Department of Civil and Environmental Engineering of Politecnico di Milano for sharing the last few years with me through all the good and difficult moments as I embarked on this academic journey.

Above all, I would like to thank the Almighty God for giving me the wisdom and tenacity to successfully complete this thesis and achieve this academic milestone.

Emmanuel Nyero
Milan, April 2021**.**

ABSTRACT

Water is an indispensable resource for all known forms of life. It covers around 70% of our planet’s surface, mostly in seas and oceans. Only 2.5% of the worlds water resources is available as freshwater with a distribution that is not ubiquitous due to spatiotemporal variability. That notwithstanding, barely 1% of the freshwater resource is available for consumption since a substantial portion of it is frozen in glaciers and polar ice caps. This signifies pressure on the available resource resulting from global population growth and industrial development leading to increase in freshwater consumption. In the present day, water scarcity is already a far-reaching problem that our societies are facing. As a result, the water footprint (WF) concept developed by Hoekstra and Hung (2002) as an indicator for quantifying water use has become a vital pillar to ameliorate the situation.

A comprehensive literature review was conducted to analyse and better understand the WF concept. The WF concept was introduced and the different WF terminologies were defined, two main WF frameworks were discussed and a comparison between them was also done. An overview of water flows from the inventory and the main impact mechanisms related to water were highlighted. Furthermore, a general description of WF accounting methods was done by explaining several inventory databases and methods. Adopting the inside-out perspective, a total of 15 pre-selected computational WF methods were then classified into three main groups i.e., 9 water depletion methods, 3 future efforts methods and 3 thermodynamic accounting methods, based on the underlying impact mechanisms and the water use issues addressed.

These WF methods were reviewed and then split into two groups based on their levels on the impact pathway i.e., midpoint and endpoint methods. The two groups were thereafter summarized in a tabular format by considering the fundamental elements: the scope of the method and modelling choices, sources of documentation / data, temporal representativeness, geographical representativeness, and main limitations. Following an explicitly stated criteria, five (5) midpoint methods that only assess the impact category of water scarcity, and that are already available to be used in LCA software (SimaPro) were selected for case study application. The selected methods considered most suitable for case study application were: Pfister et al., 2009; Boulay et al., 2011b; Hoekstra et al., 2012; Berger et al., 2014 and AWARE method (2016). These methods used the same units (m^3) despite having different characterisation factors (CFs), this simplified comparison of results from the case study.

The beneficiation process of Manganese (Mn) ores available in the ecoinvent module was selected as a case study to better understand the environmental impacts of water use as a result of this process considering different WF methods and geographical locations. The cradle-to-gate WF analysis was conducted on the case study using the 5 selected WF midpoint methods. The total scores from the indicators of all the methods influenced by their respective CFs were interpreted, followed by the identification of WF hotspots. The spatial variation of the results was tested by considering Poland (Europe) and Gabon (Africa). Sensitivity analyses were performed using three different calculation set ups created by the modification of the WF inventory and CFs of the WF methods to evaluate the reliability of results.

All the 5 WF impact assessment methods showed that WF was higher in Poland than Gabon, and both country-specific WF results were lower than the global reference set up. The results from the WF analysis of the case study were then used to make conclusions and recommendations for future developments and research.

Key words: water footprint, water scarcity, impact category, impact pathway, beneficiation

SOMMARIO

L'acqua è una risorsa indispensabile per tutte le forme di vita conosciute. Copre circa il 70% della superficie del nostro pianeta, principalmente nei mari e negli oceani. Solo il 2,5% delle risorse idriche mondiali è disponibile come acqua dolce con una distribuzione che non è onnipresente a causa della variabilità spazio-temporale. Ciò nonostante, appena l'1% della risorsa di acqua dolce è disponibile per il consumo poiché una parte sostanziale di essa è congelata nei ghiacciai e nelle calotte polari. Ciò significa pressione sulla risorsa disponibile derivante dalla crescita della popolazione globale e dallo sviluppo industriale che porta ad un aumento del consumo di acqua dolce. Al giorno d'oggi, la scarsità d'acqua è già un problema di vasta portata che le nostre società stanno affrontando. Di conseguenza, il concetto di impronta idrica (WF) sviluppato da Hoekstra e Hung (2002) come indicatore per quantificare l'uso dell'acqua è diventato un pilastro fondamentale per migliorare la situazione.

È stata condotta una revisione completa della letteratura per analizzare e comprendere meglio il concetto di WF. È stato introdotto il concetto di WF e sono state definite le diverse terminologie di WF, sono stati discussi due framework principali di WF ed è stato anche fatto un confronto tra di loro. È stata evidenziata una panoramica dei flussi d'acqua dall'inventario e dei principali meccanismi di impatto relativi all'acqua. Inoltre, è stata eseguita una descrizione generale dei metodi contabili WF spiegando diversi database e metodi di inventario. Adottando la prospettiva rovesciata, un totale di 15 metodi computazionali WF preselezionati sono stati quindi classificati in tre gruppi principali, ovvero 9 metodi di esaurimento dell'acqua, 3 metodi di sforzi futuri e 3 metodi di contabilità termodinamica, basati sui meccanismi di impatto sottostanti e l'acqua utilizzare i problemi risolti.

Questi metodi WF sono stati rivisti e poi suddivisi in due gruppi in base ai loro livelli sul percorso dell'impatto, ovvero metodi midpoint ed endpoint. I due gruppi sono stati successivamente sintetizzati in formato tabellare considerando gli elementi fondamentali: ambito del metodo e scelte modellistiche, fonti di documentazione / dati, rappresentatività temporale, rappresentatività geografica e principali limitazioni. Seguendo un criterio esplicitamente dichiarato, cinque (5) metodi intermedi che valutano solo la categoria di impatto della scarsità d'acqua e che sono già disponibili per essere utilizzati nel software LCA (SimaPro) sono stati selezionati per l'applicazione del caso di studio. I metodi selezionati considerati più idonei per l'applicazione dei casi di studio sono stati: Pfister et al., 2009; Boulay et al., 2011b; Hoekstra et al., 2012; Berger et al., 2014 e il metodo AWARE (2016). Questi metodi utilizzavano le stesse unità (m^3) nonostante avessero diversi fattori di caratterizzazione (CF), questo confronto semplificato dei risultati dal caso di studio.

Il processo di arricchimento dei minerali Manganese (Mn) disponibili nel modulo ecoinvent è stato selezionato come caso di studio per comprendere meglio gli impatti ambientali dell'uso dell'acqua come risultato di questo processo considerando diversi metodi WF e posizioni geografiche. L'analisi WF dalla culla al cancello è stata condotta sul caso di studio utilizzando i 5 metodi del punto medio WF selezionati. Sono stati interpretati i punteggi totali degli indicatori di tutti i metodi influenzati dai rispettivi CF, seguiti dall'identificazione degli hotspot WF. La variazione spaziale dei risultati è stata testata considerando la Polonia (Europa) e il Gabon (Africa). Le analisi di sensibilità sono state eseguite utilizzando tre diverse configurazioni di calcolo create dalla modifica dell'inventario WF e CF dei metodi WF per valutare l'affidabilità dei risultati.

Tutti i 5 metodi di valutazione dell'impatto del WF hanno mostrato che il WF era maggiore in Polonia rispetto al Gabon, ed entrambi i risultati del WF specifici per paese erano inferiori al set di riferimento globale. I risultati dell'analisi WF del caso di studio sono stati quindi utilizzati per trarre conclusioni e raccomandazioni per futuri sviluppi e ricerche.

Parole chiave: impronta idrica, scarsità idrica, categoria di impatto, percorso dell'impatto, arricchimento

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LIST OF ACRONYMS

ADP - Abiotic Depletion Potential

AMD - Availability Minus Demand

AoP - Area of Protection

AWARE - Available WAter REmaining Method

BIER - Basin internal evaporation recycling

CEENE - Cumulative Exergy Extraction from the Natural Environment

CExD - Cumulative Exergy Demand

CF - Characterization factor

CF_{AWARE} - CF of the AWARE method

CF_{WD} - CFs for water deprivation

CTA - Consumption-To-Availability

DALY - Disability adjusted life years

DTA - Demand-To-Availability

EC-JRC - European Commission Joint Research Centre

EF - Effect factor

EWR - Environmental Water Requirements

FF - Fate factor

FU - Functional unit

GA - Gabon

GIS - Geographical Information System

GLO - Global

GWS - Groundwater stocks

HDF - Human Development Factor

HDI - Human Development Index

HWC - Human Water Consumption

ILCD - International Reference Life Cycle Data System

IMnI - International Manganese Institute

IO - Input-output framework

ISO - International Organization for Standardization

I_{WD} - Impacts on the water deprivation

JRC-IES - Joint Research Centre - Institute for Environment and Sustainability

LCA - Life Cycle Assessment

LCI - Life Cycle Inventory

LCIA - Life Cycle Impact Assessment

MEDLI - Model for Effluent Disposal Using Land Irrigation

MJ - Megajoules

NO_X - Nitrogen oxides

NPP - Net Primary Production

OECD - Organisation for Economic Co-operation and Development

PAF - Potentially Affected Fraction

PDF - Potentially Disappeared Fraction

PL - Poland

R_{act} - Actual runoff

RED - Relevant for Environmental Deficiency

SED - Solar Energy Demand

SEF - Solar Energy Factor

SETAC - Society of Environmental Toxicology and Chemistry

SO_X - Sulphur oxides

SRB - Sub-river basin

SRF - Strongly Regulated Flow

SSD - Species Sensitivity Distribution

STE - Surface-time equivalent

SWS - Surface water stocks

TTI - Temperature tolerance interval

UNEP - United Nations Environment Programme

UN-Water - United Nations Water

USGS - United States Geological Survey

VF - Variation factor

VPBD - Vulnerability of vascular plant species biodiversity

WAVE - Water Accounting and Vulnerability Evaluation

WBCSD - World Business Council for Sustainable Development

WDI - Water Depletion Index

WF - Water Footprint

WFA - Water Footprint Assessment

WFSA - WF sustainability assessment

WHYMAP - World-wide Hydrogeological Mapping and Assessment Programme

WPL - Water Pollution Level

WS_{blue} - Blue water scarcity index

WS_{green} - Green water scarcity index

WSI - Water stress index

WTA - Withdrawal-To-Availability

WULCA - Water Use in LCA

CHAPTER ONE: INTRODUCTION

1.1 Background

Water is an indispensable resource for all known forms of life. It covers around 70% of our planet's surface, mostly in seas and oceans. Only 2.5% of the world water resources is available as freshwater with a distribution that is not ubiquitous due to spatiotemporal variability. This renders water abundant in some locations, and scarce in other parts of the world. The availability of freshwater has a great impact on human well-being, mediates economic growth, influences ecosystem functions and biodiversity (Xu and Li, 2019). That notwithstanding, barely 1% of the freshwater resource is available for consumption since a substantial portion of it is frozen in glaciers and polar ice caps. This signifies pressure on the available resource resulting from global population growth and industrial development leading to increase in freshwater consumption.

According to the UN-Water projections made in 2014, more than 40% of the world population will be living in regions facing severe water scarcity in 2050. In the present day, water scarcity is already a far-reaching problem that our societies are facing. This is manifested by the intense competition for the available freshwater mainly from agricultural, industrial, and domestic uses. This dire situation can be ameliorated by significantly improving water management, lest mankind faces major challenges in securing enough water to support the growing world population, and to meet environmental needs. As a result, the water footprint (WF) concept was developed by Hoekstra and Hung (2002) as an indicator for quantifying water use. Since the availability of freshwater is geographically dependent, the WF results can vary between different nations or areas.

The potential impacts associated with water use can be evaluated by life cycle assessment (LCA) using commercial software e.g., SimaPro, Gabi, OpenLCA, etc. LCA is a tool used to assess the potential environmental impacts and resources used throughout a product's life cycle i.e., the cradle-to-gate analysis. LCA identifies and quantifies energy consumption, material use, and emissions to the environment. LCA can also be conducted considering only partial life cycles. LCA has gained scientific approval over the years in several production sectors e.g., mining, energy, etc. Owing to that, the leading standards for conducting LCA i.e., ISO 14040 and ISO 14044 were developed in 2006 by the International Organization for Standardization (ISO). Many LCA practitioners have shone a spotlight on the impacts assessment of water use through continuous research. This has led to many WF methodological advances for assessing and evaluating the environmental impacts of water use adopting different perspectives.

1.2 Problem statement

The mining sector is viewed by many nations as a key engine of economic development, it provides inputs for industrial use, however, it is highly water intensive. Manganese (Mn) is a crucial raw material consumed in many industrial applications, especially for steel and alloy making. Now more than ever, the priority of all Mn based industries is to obtain high grade Mn ores as raw materials. On the other hand, most of the Mn ores contain significant amounts of gangue content. This creates a need for identification and selection of a suitable beneficiation process to upgrade the low-grade Mn ores.

However, the beneficiation process of Mn ores has significant environmental impacts resulting from but not limited to water use, felt at both local and global scales, that have become a substantial burden. As a result, there is a need to better understand the hotspots of the beneficiation process of Mn ores contributing the most to WF considering different WF methods and geographical locations. This information can then be used by decision makers for water management to better understand the most suitable WF method to apply for assessing the water use impacts on a case-by-case basis.

1.3 Main objective

The main objective of this study is to conduct a review of selected computational WF methods by indicating their strengths and drawbacks, to provide some recommendations for application-dependent use of methods in LCA-based WF studies.

1.4 Scope of the study

There are many WF methods available, however, this study only covered the review of fifteen (15) available computational WF methods classified in three categories i.e., water depletion methods, future effort methods and thermodynamic accounting methods, and pre-selected based on a comprehensive literature review. The pre-selected WF methods only looked at environmental impacts, therefore social and economic impacts were not considered in this study. Not all the computational WF methods were studied because of time constraints.

The beneficiation process of Mn ores using the ecoinvent dataset was selected as a case study. The WF analysis was conducted on the case study using five (5) clearly described and evaluated midpoint methods already incorporated in the LCA software SimaPro. Only the midpoint effects of water use were assessed because the damages at endpoint level and areas of protection (AoPs) were beyond the scope of the methods used for analysis. The spatial variation of the results was tested by considering Poland (Europe) and Gabon (Africa).

1.5 Structure of the thesis

In this section, a description of the core methodology followed in this thesis is summarized. Chapter 1 gives the foundation for the study, and provides a brief background, problem statement, main objective, and scope of the study. In chapter 2, a comprehensive literature review was conducted: it looked at the WF concept and terminology, many WF methods were reviewed in accordance with the main study objective and 5 midpoint WF methods were selected for application on a case study. Chapter 3 deals with the case study, i.e., beneficiation process of Mn ores, and it explains why the particular case study was selected, and all the details of the phases of the LCA required for WF analysis. SimaPro software is used to conduct WF analysis on the case study using the pre-selected methods for impact assessment. In chapter 4, the results of the WF analysis are presented and thoroughly analysed. Chapter 5 is where conclusions and recommendations were made based on the overall findings from the study conducted in the thesis.

CHAPTER TWO: LITERATURE REVIEW

2.1 Introduction to WF: concepts and definitions

The WF concept was developed by Hoekstra and Hung (2002) as an indicator to evaluate human consumption of water resources with a volumetric perspective, considering both direct and indirect water uses (Hoekstra et al., 2011). According to Hoekstra and Hung (2005), WF can assist decision makers in forming a basis for a better management of the globe's freshwater resources. WF was built from the virtual water concept introduced by Allan (1997), to quantify the "virtual water flows" related to international trade in products and commodities. A WF differs from the typical measure of water use, i.e., the amount of water withdrawn from its source for a specific purpose, because a WF only accounts for consumptive water use, which is water that becomes unavailable locally in the short term due to evaporation, product incorporation or quality decline (Dourte and Fraisse, 2012) through pollution assimilation.

The WF concept has been further developed as a multidimensional indicator for assessing water resource consumption and pollution caused by anthropogenic activities in different geographical (global, national/regional, and local/corporate level) and temporal (short-term 0-25 years; mid-term 25-100 years; or long-term 100 years-infinite) dimensions (Hoekstra et al., 2011). According to Hoekstra et al. (2011), the WF can be divided into three components; blue, green, and grey WFs according to the "water colours" implying different water sources and uses as in **section 2.1.1**. The blue WF measures the volume of surface and groundwater consumed to produce goods or services. The green WF measures the volume of rainwater consumed by crops due to evapotranspiration, and the grey WF measures the volume of freshwater that is required to assimilate pollutants to meet specific water quality standards.

WF can be calculated for almost any product or organizations (Chapagain and Hoekstra, 2007; Dourte and Fraisse, 2012), human being (Hoekstra, 2009), as well as ecosystem services (Karabulut et al., 2016). Depending on the objective of the study and spatiotemporal scale chosen for the analysis, WF studies can be conducted using methods that are standalone or embedded in LCA. WF also provides a clearer picture about global water use by integrating economic (benefits from water use must outweigh the costs) and social (equity in allocation of water prioritising environmental and basic human water needs) considerations onto water consumption trends. Chenoweth et al. (2014) found the WF concept to be helpful in terms of highlighting hydrological interdependencies between nations or regions in simple terms, and also for identifying hot spots of environmental impact relating to their water use.

However, using the WF concept comes with several limitations, among which are the following:

- Rockström (2007) points the difficulty in distinguishing between blue and green water because it has been illustrated that in the hydrological system water can change condition from green to blue or vice-versa (Wichelns, 2011). Precipitation causes run off which is considered blue water but on the other hand, when the runoff percolates and becomes soil moisture, then it is considered to be green water (Ali, 2019).
- According to Ridoutt and Pfister (2010), the main concern is the fact that WF represents only the quantity of water used with total disregard to the environmental impacts.
- Chapagain and Tickner (2012) also noted that the results from WF analyses can help to highlight interconnections and risks but do not provide solutions, and its potential is too unclear to create a clear link between WF and policy (Hastings and Pegram, 2012).
- The lack of consistent terminology arising from the numerous research developments on WF which reflects the diverse interests concerned in water issues, some of which are financial and do not genuinely addressing water problems.

Despite these methodological qualms, the WF concept has had notable success in raising awareness about water use (Chenoweth et al., 2014).

2.1.1 WF Terminology

Many different researchers around the world have studied the WF concept and its application, this has resulted to a lack of consistent WF terminology. All the WF terminology used in this thesis have been adopted from the definitions proposed by the UNEP/SETAC working group on water (Pfister et al., 2009; Bayart et al., 2010), and the WF ISO standard (ISO 14046:2016), to enhance consistency in the document. According to these publications, some of the main terminology used in relation to WF include the following:

1. **Virtual water:** amount of water evaporated in the production of, and incorporation into, agricultural products, neglecting runoff (Pfister et al., 2009)
2. **Fresh water:** water having a low concentration of dissolved solids (ISO 14046:2016). This term specifically excludes sea water and brackish water.
3. **Surface water:** water in overland flow and storage, such as rivers and lakes, excluding seawater (ISO 14046:2016).
4. **Groundwater:** water, which is being held in, and can be recovered from, an underground formation (ISO 14046:2016).
5. **Sea water:** water in a sea or an ocean (ISO 14046:2016).

6. **Fossil water:** groundwater that has a negligible rate of natural recharge on the human time scale (ISO 14046:2016). It is also sometimes referred to as non-renewable water.
7. **Blue water:** fresh surface and groundwater, i.e., the water in freshwater lakes, rivers and aquifers. (Hoekstra et al. 2011)
8. **Green water:** the precipitation on land that does not run off or recharge the groundwater but is stored in the soil or temporarily stays on top of the soil or vegetation (Hoekstra et al. 2011)
9. **Grey water:** the amount of fresh water required to dilute concentrations in polluted water, caused by a certain process step, back to its natural water quality (Hoekstra et al., 2011).
10. **Water use:** use of water by human activity. This includes water withdrawals, water releases, or any other human activities within a drainage basin (ISO 14046:2016)
11. **In-stream (non-withdrawal) freshwater use:** use of water in situ (e.g., navigational transport on a river) (Bayart et al., 2010)
12. **Off-stream (withdrawal) freshwater use:** Use of water that requires human removal from a natural body of water or groundwater aquifer (e.g., pumping or diversion of water for municipal, agricultural, or industrial purposes) (Bayart et al., 2010)
13. **Freshwater consumptive use:** Use of freshwater when release into the original watershed does not occur because of evaporation, product integration, or discharge into different watersheds or the sea (Bayart et al., 2010)
14. **Freshwater degradative use:** withdrawal of water and discharge into the same watershed after the quality of the water has been altered (includes both quality deterioration and improvement) (Bayart et al., 2010)
15. **Water quality:** physical (e.g., thermal), chemical and biological characteristics of water with respect to its suitability for an intended use by humans or ecosystems (ISO 14046:2016)
16. **Water scarcity:** extent to which demand for water compares to the replenishment of water in an area, e.g., a drainage basin, without considering the water quality (ISO 14046: 2014).
17. **Water availability:** extent to which humans and ecosystems have sufficient water resources for their needs. Water quality can also influence availability (ISO 14046:2014).
18. **WF profile:** compilation of impact category indicator results addressing potential environmental impacts related to water (ISO 14046: 2014).

19. **Elementary water flow:** water entering the system being studied that has been drawn from the environment, or water leaving the system being studied that is released into the environment (ISO 14046: 2014)

2.1.2 WF methodological frameworks

Due to the need for standardization of WF studies around the world, two main methodological approaches for assessing WF as a basis for a more sustainable management of water resource currently exist. The first approach **(section 2.1.2.1)** was developed by the Water Footprint Network (WFN) to measure the human consumption of water resources according to the water footprint assessment (WFA) manual (Hoekstra et al., 2011) by mapping three WF components (blue, green, and grey water). This approach is generally adopted to assess the efficiency and equitability of water uses for a product system or an organization. However, since the water issue has been multifaceted, the International Organization for Standardization (ISO) developed the second approach **(section 2.1.2.2)**, ISO 14046 standard (ISO, 2014), a methodological framework that is used to determine the potential environmental impacts related to water use along the life cycle.

2.1.2.1 WF according to the WFN framework

The WFN is an international organisation which promotes WF thinking and application to contribute to sustainable water management. They have developed the WFA manual (Hoekstra et al., 2011), which aims to set a global standard for how to calculate and evaluate a WF for a product system. The WFA framework is based on the concept of virtual water (Allan, 1997), it defines specific guidelines (Hoekstra, 2010) for quantifying in volumetric terms (m^3) the freshwater necessary to produce or, in other terms, embedded in goods and services that are consumed by individuals or communities (Lovarelli et al., 2016). According to the WFA manual, there are three types of water based on “colour” (blue, green, and grey water), and these act as indicators for the three components of WF (blue, green, and grey WF), as defined earlier in **section 2.1**. Blue water is defined as fresh surface water and groundwater, green water is defined as precipitation and plant-soil “evapo(transpi)rated” freshwater, and grey water refers to the amount of fresh water required to dilute concentrations in polluted water, caused by a certain process step, back to its natural water quality (Hoekstra et al., 2011). The WFN framework defines the WF of a product, as the result of accounting for the total volume of the freshwater that is used directly or indirectly to produce the product, and it is generally calculated in different steps: the set of the goal and scope, the WF accounting, the WF sustainability assessment (WFSA), and the WF response formulation are shown in **Figure 1.**

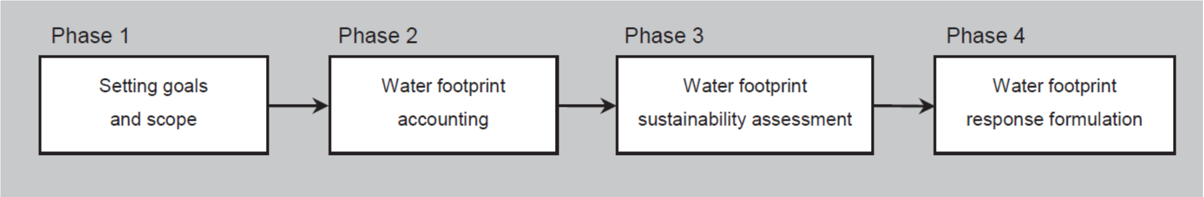

Figure 1. Four distinct phases in water footprint assessment (Source: Hoekstra et al., 2011)

The first step aims to clarify the purpose of the study and to determine the processes to be included in the assessment, a WF study can be undertaken for many different reasons (Hoekstra et al., 2011). In the second step, three dimensions are investigated to distinguish among different types of water: the blue and the green WFs, related to consumptive water user use, and the grey WF, related to degradative water use, these indicators are assessed for each process step in the study (Manzardo et al., 2015). The third step further investigates the environmental, social, and economic aspects and is called the sustainability assessment of the WF. The last step consists of the analysis of hotspots and the identification of options, strategies, or policies to reduce the WF; this assessment is based on the results of the sustainability assessment (Manzardo et al., 2015).

According to WFA manual, WFs can be calculated at different levels of scale: WF of a process step, WF of a product, WF of a consumer or group of consumers, WF within a geographically delineated area, National WF accounting (internal and external WF), WF accounting for catchments and river basins, WF accounting for municipalities, provinces, or other administrative units, and WF of a business. Hoekstra et al. (2011) developed a generic midpoint method for WF accounting based on the methodological framework outlined in the WFA manual. The method characterizes each water type (blue, green and greywater use) with separate scarcity indexes which are disaggregated, allowing each water type to be applied individually to each AoP (human health, ecosystem quality, and resources) (Kounina et al., 2013).

The blue WF is an indicator of consumptive use of fresh blue water resources (surface water and ground water), and it can be quantified based on the volume of surface and groundwater consumed as a result of the production of a good or service (e.g., domestic, industrial, power production, irrigation etc.) (Hoekstra et al., 2011; Rodrigues et al., 2014). The green WF refers to consumption of green water resources (rainwater stored in the soil as soil moisture) during the growing period of the crop, and it can be estimated using any crop model suitable for estimating evapotranspiration based on input data on climate, soil, and crop characteristics (Hoekstra et al., 2011) e.g., the CROPWAT model (FAO, 2010). Grey WF is computed using ambient water quality standards for the receiving freshwater body, i.e., standards with respect to maximum allowable concentrations in the water bodies.

For the environmental sustainability pillar of WFSA, to assess water scarcity within a catchment (x) during a given time period (t), ratios of consumption (WF) to availability (WA) are used for blue and green water scarcity indexes (WS_{blue} and WS_{green}) as in **Equations 1** and **2**. The presumptive standard for environmental flow protection developed by Richter et al. (2012) is an appropriate method for assessing the availability of blue water by satisfying the environmental flow requirement (Hoekstra et al., 2012), it states that the extraction of available water (river flow) above 20 percent will cause ecosystem degradation and environmental inequality. For grey water, the water pollution level (WPL) is calculated by taking the ratio of total grey WF in the catchment to the actual runoff as in **Equation 3**. Environmental water sustainability will be violated if any of WS_{green}, WS_{blue} or WPL exceeds 100%. The social and economic sustainability pillars of WFSA deal with a fair allocation of water (equity) while guaranteeing a minimum amount for basic human needs, and economically efficient allocation of water, respectively. However, there are no proper methods available for conducting social and economic WFSA (Quinteiro et al., 2018).

$$\mathbf{WS_{blue}[x,t]} = \frac{\sum \mathbf{WF_{blue}\,[x,t]}}{\mathbf{WA_{blue}[x,t]}} \quad [-] \qquad (\mathbf{1})$$

$$\mathbf{WS_{green}[x,t]} = \frac{\sum \mathbf{WF_{green}\,[x,t]}}{\mathbf{WA_{green}[x,t]}} \quad [-] \qquad (\mathbf{2})$$

$$\mathbf{WPL[x,t]} = \frac{\sum \mathbf{WF_{grey}\,[x,t]}}{\mathbf{R_{act}[x,t]}} \quad [-] \qquad (\mathbf{3})$$

2.1.2.2 WF according to the ISO framework

This approach has been developed by the LCA community by implementing water use-related impact categories and inventory methods within LCA studies (Kounina et al., 2013). The LCA community identified “Water Use” as a very important variable for environmental impact assessments (Lovarelli et al., 2016). The efforts of the LCA community in the field allowed for the recent publication of a new ISO standard on WF, ISO 14046 to provide standardisation of the WF calculation method and a common ground with the LCA approach as prescribed in ISO 14044:2006. ISO 14046 Environmental management includes the principles, requirements, and guidelines to perform WF as a standalone study or as part of a more comprehensive LCA where consideration is given to a set of environmental impacts and not only impacts related to water

(ISO, 2014). According to ISO14046, a WF assessment needs to include the four phases of an LCA, i.e., goal and scope definition, WF inventory analysis, WF impact assessment and the interpretation of the results as illustrated in **Figure 2** below.

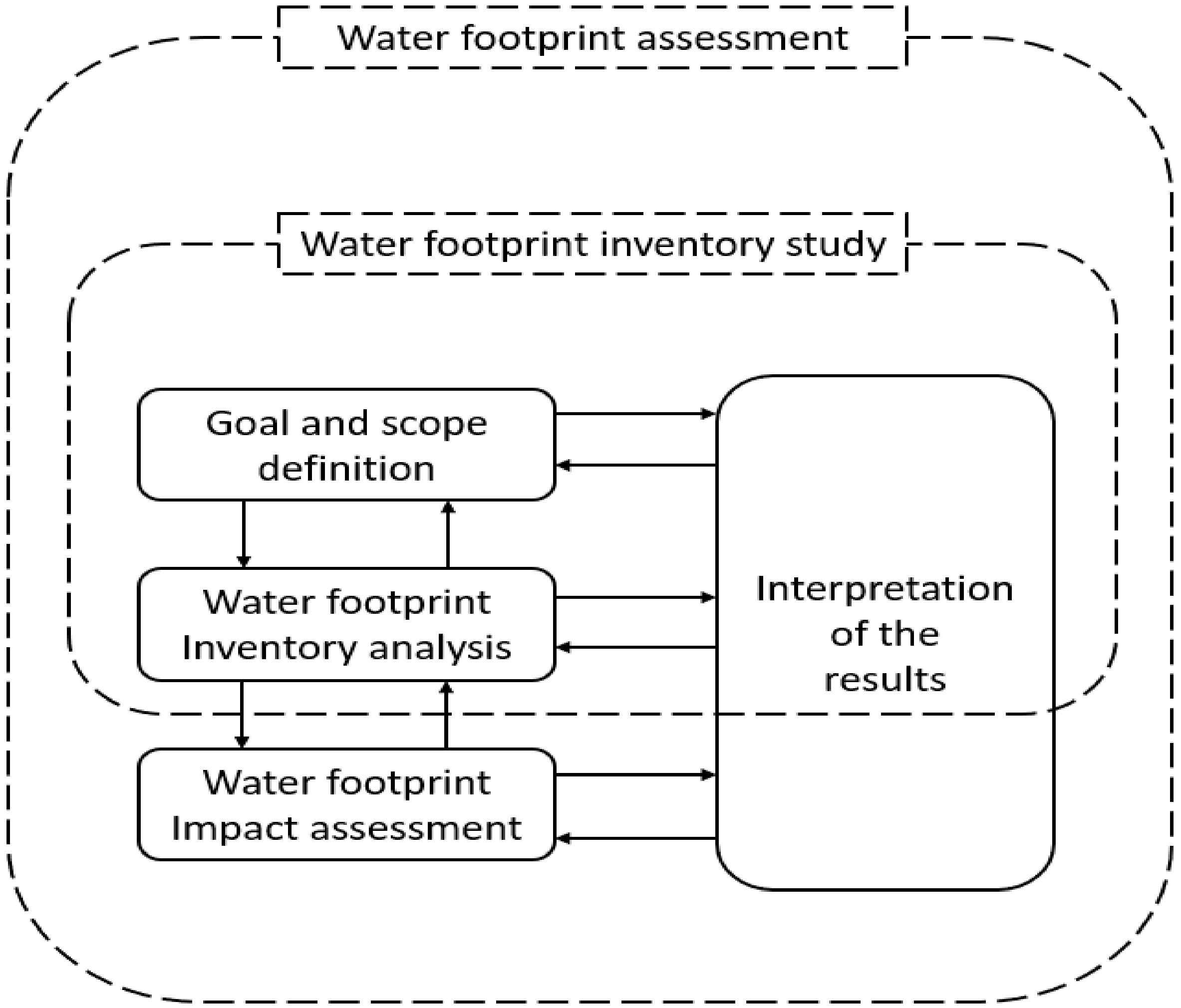

Figure 2. Phases of a water footprint assessment (Source: BS EN ISO 14046:2016)

From **Figure 2**, it can be observed that a study is a WF inventory analysis if the WF impact assessment phase is not considered. To account for the impacts of blue water consumption from a lifecycle perspective, all the four phases of an LCA as stated in ISO 14044 must be followed. The goal and scope definition phase deals with defining the purpose of the study and the determination of the boundaries of the product system. The goal is set by determining the intended application of the study and the intended audience for the results. The scope of the study must be consistent with the goal, it has to account for the uncertainties and limitations of the study and discuss which cause-effect chains and potential environmental impacts are covered in the WF assessment (ISO, 2014). The inventory analysis consists of the collection of all of the elementary flows as listed in section 5.3.2 of the ISO 14046 standard, and information related to the goal of the study. The WF impact assessment phase consists of the quantification of the potential impacts related to water through classification and characterization (Manzardo et al., 2015). According to ISO 14046, a WF impact assessment method may include several category indicators related to different environmental mechanisms. Each impact category assessed will have its own WF indicator results, e.g., water scarcity footprint, water eutrophication footprint, etc. A WF profile is comprised of several impact category related indicator results.

Finally, the interpretation of results phase deals with the identification of the significant issues based on the results of the WF assessment, e.g., processes with a significant contribution to the calculated water footprints, environmental mechanism(s) mainly affected, elementary flows that have highest contribution to the result(s) of the WF assessment (ISO, 2014). Interpretation of results should also include an evaluation of the completeness of the assessment, including sensitivity and consistency check. A sensitivity analysis should be conducted to determine the range of changeability of the acquired results (ISO 14046, 2016).

2.1.2.3 Comparison of the two WF methodological frameworks

Several researchers have analysed and compared the WFN and ISO 14046 methodological approaches for assessing WF (Pfister et al., 2009; Hoekstra et al., 2011; Pfister and Ridoutt, 2014). The WFN and ISO are the current methodological frameworks indicating how to quantify the indicator for water uses in practice, but with a different scope/perspective. Both approaches can have the same applications (Pfister and Ridoutt, 2014), despite the methodological differences. According to Boulay et al. (2013) the two approaches fulfil complementary goals even if they can both be used to define solutions to reduce the anthropogenic impact on the environment.

In summary, the WFA approach is more focused on accounting for water use along supply chains and it is mainly applied for supporting water resources management, including its use and allocation. It has played an important role in the awareness raising of water issues in the past decade (Boulay et al., 2013). Instead, the ISO 14046 approach is a standard (based on the LCA standard ISO14044), and it is more oriented towards an embedded LCA-assessment type approach with the aim of estimating the environmental impacts related to water use (scarcity and pollution). Neither the WFN nor the ISO 14046 indicates the computational method to calculate WF; the choice of most appropriate method is referred to practitioner based on the scope of the WF analysis.

2.2 Overview of water flows and impact mechanisms

This section links the different water types/uses defined in **section 2.1.1** to the environmental pathways considered during water accounting for each unit process in the inventory level. The WULCA working group (Bayart et al., 2010; Kounina et al.,2013) identified four types of water resources which are currently used in LCA to model water flows: surface water (river, lake, and sea), groundwater (renewable, shallow, and deep), precipitation (or water stored as soil moisture - also called green water), and fossil groundwater, referring to groundwater coming from fossil aquifers (Sala et al., 2019), basing on the hydrological nature of water flows.

ISO 14046:2016 states that data related to water which represent elementary flows may be directly collected from unit processes or derived from data which represent material flows. **Figure 3** qualitatively shows the inventory of input and output water flows for each unit process part of the product system being considered in terms of quantities of water used (volume), types of water resources, water use, and water quality as recommended in section 5.3.2 of ISO 14046:2016. In general, the total input of water into a product system is referred to as 'water use'. As part of the water input is released from the product system as wastewater, the remaining part which has become unavailable due to evaporation or product integration is referred to as water consumption (Berger and Finkbeiner, 2010).

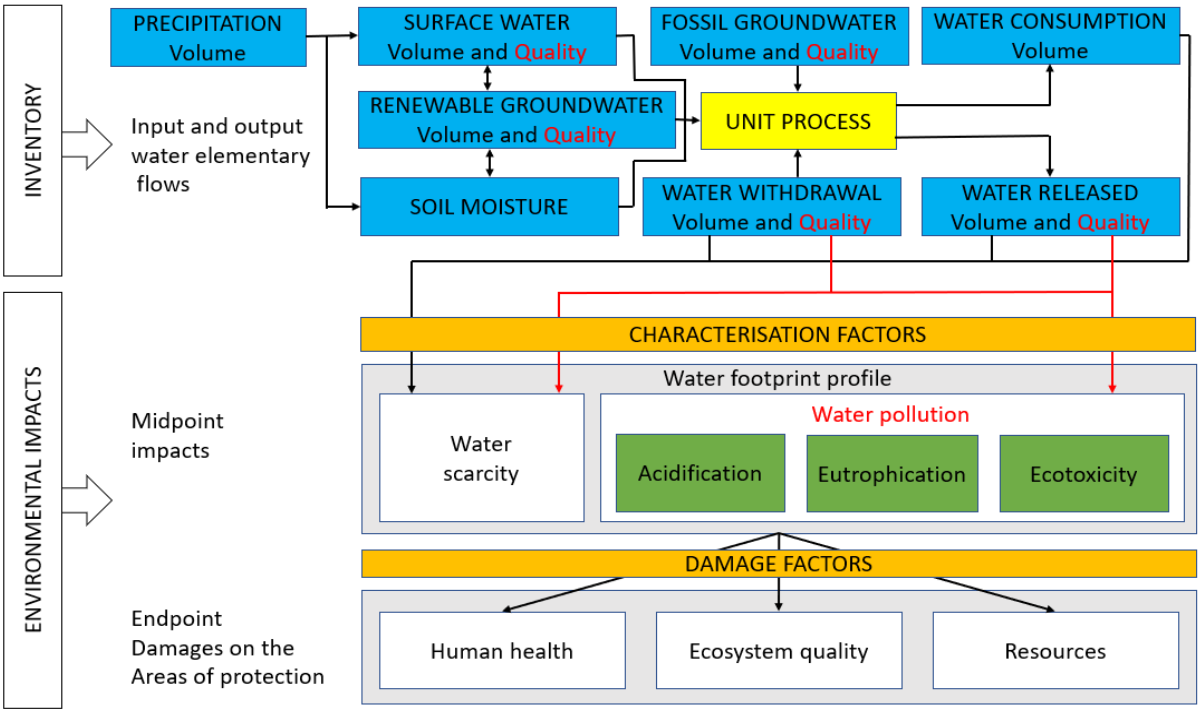

Figure 3. Inventory of water flows for each unit process, and the environmental impact categories at midpoint level and damages on the three areas of protection at endpoint level (adapted from Payen, 2019).

All the inputs and outputs (resources extraction and emissions to the environment) associated with the product system are inventoried in the WF accounting stage (**section 2.2.1**), then, each water flow for the impact pathway considered is converted to environmental impacts indicators (**section 2.2.2**) thanks to characterization factors (CFs). These impacts (at midpoint level) can be further aggregated into damage indicators at endpoint level on the three areas of protection (AoPs) as defined by Jolliet et al. (2004): human health, ecosystems quality and resources.

The Midpoint level deals with environmental issues which the WF analysis should address, includes indicators which are part way along the impact pathway, such as global warming, acidification, land use, resource use. The Endpoint level looks at the damages on areas of protection (AoP), with indicators like increased malnutrition in relation to human health; damage to aquatic species in relation to ecosystem quality; and increased extraction costs in relation to natural resources.

2.2.1 WF accounting

WF accounting is the first step of the impact pathways, and it constitutes the compilation and quantification of all inputs and outputs of water related to products, processes or organizations as defined in the goal and scope (ISO, 2014). An appropriate flow must be determined for each unit process (ISO 14046). Inventory on each water elementary flow should include quantity, source, quality, form of water use, geographical location, and temporal aspects. The distinction between the input and output water flows is essential for an adequate assessment of the potential impacts of water use (Jeswani and Azapagic, 2011). The overview of existing inventories and methods shown in **Figure 4** was based on the work of Kounina et al. (2013) updated with new LCI databases and methods.

Several databases and methods which provide data on water consumption are discussed into two separate sections: **section 2.2.1.1** related to databases and **section 2.2.1.2** related to inventory methods. Data validity must be checked during data collection and evidence needs to be availed that the data quality requirements have been met for the intended application. This can be achieved through performing a water balance analysis of the process/system being studied. Understanding the water inventory methodologies will result in more detailed and clarified water inventory and consequently a more thorough impact assessment will be possible (Mack-Vergara and John, 2017).

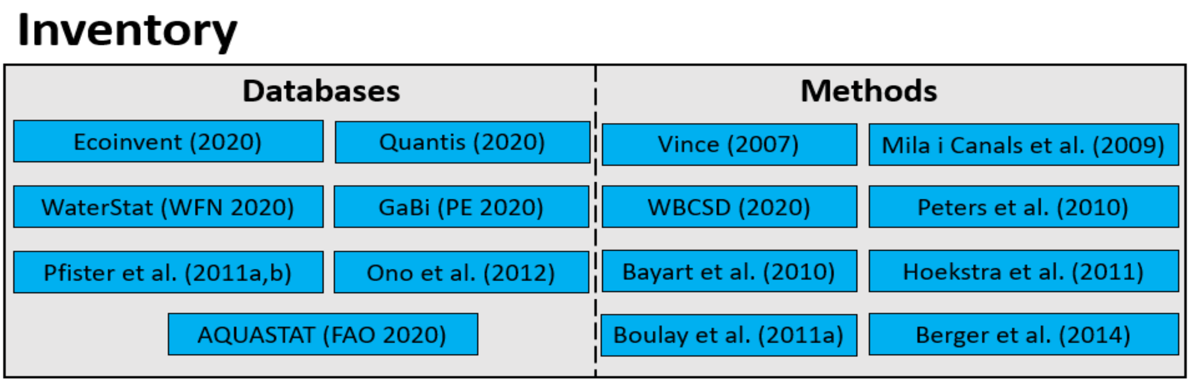

Figure 4. Water footprint accounting databases and methods (partially adapted and updated from Kounina et al., 2013)

2.2.1.1 Inventory databases

There are a number of databases containing water consumption inventory data for use within the LCA domain depending on the scope behind the model development. According to Berger (2013), the databases can be classified into typical life cycle inventory (LCI) databases like GaBi (PE International 2020) and Ecoinvent (Ecoinvent centre 2020), sector and country specific databases (FAO 2020; Pfister et al. 2011a; Pfister et al. 2011b; Ono et al. 2012) and distinct water footprint databases like the Quantis Water Database (Quantis 2020) or the WaterStat database (WFN 2020).

The Ecoinvent database (Frischknecht et al., 2004; Ecoinvent 2007) and GaBi database (PE 2020) are widely used databases and contain elementary flows for freshwater withdrawal and turbined water (Kounina et al., 2013), allowing to differentiate the water inputs based on their source i.e., surface water (lake and river) and groundwater (renewable and fossil). The Quantis Water Database was derived from the Ecoinvent 2.2 which segregates all flows into inputs and outputs and uses a water balance for final assessment (Quantis 2012). It was created to provide LCA practitioners with a complete database for easier application within all the different existing water impact assessment methodologies (Kounina et al., 2013).

The Pfister et al. (2011) database allowed for assessing the water consumption (green and blue water footprint) for 160 crops at the country level. It provides scarcity-weighted water consumption values reported as RED (Relevant for Environmental Deficiency) water, which includes consideration for full-irrigation water consumption, deficit water consumption and expected water consumption (Kounina et al., 2013; Pfister et al., 2011). The WaterStat database developed by WFN contains the water consumption flows of various crops and derivative products, farms, etc., that are estimated based on the WFN method (Hoekstra et al., 2011). It is used to evaluate the consumption of water retained in the soil as moisture due to evapotranspiration and the consumption of surface and deep water (WFN, 2020).

Ono et al. (2012) developed a water consumption inventory database focusing on eight Asian countries using an input-output (IO) framework. For agricultural products, water consumption was estimated by modelling, while for other sectors, statistical reports were used for estimation. AQUASTAT is a free database that provides up-to-date, validated, and reliable national-level data on water resources (internal, transboundary, total), water use (by sector, by source, wastewater) and irrigation. It contains many variables and indicators that can be searched and extracted for all countries and for different regions over an extensive time period (FAO, 2014).

2.2.1.2 Inventory methods

The reviewed inventory methods generally suggest concepts for a systematic classification of freshwater elementary flows according to their type (surface water, groundwater, precipitation water stored as soil moisture, whether intake water quality is considered, etc.) without providing respective data (Kounina et al., 2013). Vince (2007) provides an LCI scheme which allows water quality to be accounted for. The Mila i Canals et al. (2009) method proposes differentiating between inputs of green water (soil moisture), blue water (ground and surface water), fossil blue water (non-renewable groundwater), and water use due to land use changes by categorizing water inventory data into ‘evaporative’ and ‘non-evaporative’ use (Meyer, 2017). The global water tool of WBCSD (2020) provides inventory tools for organizations (Kounina et al., 2013) to help in the integration of water values and costs into decision making.

The Peters et al. (2010) method classified water use LCI data in the Australian red meat sector in a manner consistent with contemporary definitions of sustainability in normal LCA practice, this made the results reflect better the environmental issues. This was achieved by providing detailed hydrological modelling using MEDLI model, and classification of freshwater use data (flows) in specific sectors (Kounina et al., 2013). Bayart et al. (2010) published a comprehensive framework for assessing off-stream freshwater use (consumptive and degradative) in LCA to distinguish between the water types, using resource type (e.g., groundwater, surface water) and water quality as parameters. According to their method, the inventory flows represent a set of water types each one representing an elementary flow with its own characterisation factors (CFs) for impact assessment using parameters like resource type (e.g., groundwater, surface water) and water quality to distinguish between consumptive and degradative water use. This helped to fix the methodological limitations of previous LCI.

The Boulay et al. (2011a) inventory method is an upgrade on Vince (2007) and Bayart et al. (2010). The method gives 17 water categories based on source, quality, and potential users, it also handles the issue of degradative water use in life cycle impact assessment (LCIA) by providing the elementary flows needed to evaluate how degradative return flows translate to lost functionality to human users (Boulay et al., 2011a). The Hoekstra et al. (2011) inventory method reports the virtual water consumed (both green and blue water) and polluted during the production of a product, or throughout a process; the values are primarily used as a water inventory. Application of the method towards assessing impacts in an LCA, though possible, are challenging (Meyer, 2017). The LCI accounting scheme of Berger et al. (2014) additionally considers effects of atmospheric moisture recycling within basins (Berger, 2013).

2.2.2 Impact categories related to WF

A WF profile considers a range of potential environmental impacts associated with water (ISO 14046). These impacts may address both the effects of water quantity and quality change on the environment. According to Kounina et al. (2013), both the degradative use and the consumption of water can lead to water deprivation for other users because of changes in availability (scarcity), modifications of functionality (i.e., degradation), and reduction of the renewability rate. **Figure 3**. shows four of the water-related environmental impact categories depicting the effects of anthropogenic activities, and these were: water scarcity, acidification, eutrophication, and eco-toxicity. However, there are numerous water-related environmental impact categories depicting the effects of anthropogenic activities. Other impact categories include thermal pollution, human toxicity, etc. The impact mechanisms (both existing and potential) link water type and use to potential impacts at the midpoint and endpoint level and, ultimately, to the related AoPs, with different perspectives. According to ISO 14046, a WF impact assessment method may include several category indicators related to different environmental mechanisms. Each impact category assessed will have its own WF indicator results with a qualifier, e.g., water scarcity footprint, water eutrophication footprint, etc.

2.2.2.1 Water scarcity

This is an indicator of the relative comparison of water demand and water replenishment of a specified area e.g., drainage basin, without accounting for water quality. Water scarcity describes the availability, or lack of availability, of water either due to physical shortage or due to lack of access caused by poor infrastructure or failure by institutions to provide regular supply (UN-Water, 2017).

2.2.2.2 Acidification

This is an indicator of the potential acidification on water due to the release of gases such as nitrogen oxides (NO_X) and sulphur oxides (SO_X). Acidification of water bodies is caused by atmospheric pollutants and agricultural land use. Atmospheric pollutants modify the acidity of soils and surface water through acidic precipitation and dry deposition (Curran, 2006).

2.2.2.3 Eutrophication (aquatic)

This is an indicator of the enrichment of the aquatic ecosystem with nutritional elements, due to the emission of nitrogen or phosphor containing compounds. According to Yang et al. (2008), eutrophication of water is assessed by determining the concentrations of nitrogen and phosphorus, algal chlorophyll, dissolved oxygen and evaluating water transparency.

2.2.2.4 Eco-toxicity (freshwater and marine)

This is an indicator of the impact that the concentration of toxic substances emitted to the environment will have on water organisms. According to Tiwary (2001), aquatic ecotoxicity is caused when unwanted chemicals leach into a water body, e.g., heavy metal runoff from mining activities leaching into surface water.

2.3 Overview of WF LCIA methods

Several reviews on WF methods have been conducted by many researchers (Berger and Finkbeiner, 2010; Jeswani and Azapagic, 2011; Berger and Finkbeiner, 2012; Kounina et al., 2013; Boulay et al., 2015c; Quinteiro et al., 2018; Sala et al., 2019). However, many more new methods keep on mushrooming as the research and application of WF advances. The existing methods assess the environmental impacts of water use at the midpoint and/or endpoint level of the cause-effect chain. Midpoint category indicators are either scarcity (e.g., Pfister et al., 2009) or availability indicators (e.g., Boulay et al., 2011b); some are specific to one AoP (Mila i Canals et al., 2008) while others cover all AoPs (e.g., Pfister et al., 2009). Across all available methods, endpoint category indicators addressing the same AoP are neither identical, nor complementary (Payen, 2019).

Hitherto, there is no single method for performing a comprehensive impact assessment of all possible impacts due to water use. WF methods address different issues related to water use with two perspectives (i.e., Inside-Out and Outside-In) and temporal and geographical coverage. Berger et al. (2020) defined the two perspectives in their study related to mineral resources, and these definitions were adapted and applied to WF in this study. The Inside-Out perspective focuses on how the use of water resources in a product system can affect the opportunities of future users to use resources, whereas the Outside-In perspective focuses on how environmental and socioeconomic conditions can affect the accessibility of water resources for a product system. With reference to the Inside-Out perspective, that is the most common approach for LCA, a thorough literature review was conducted basing on original publications to identify the WF accounting methods**,** that allow quantifying and modelling water use at the LCI phase **(section 2.2.1)**, and the impact assessment (LCIA) methods for WF that allow evaluating midpoint and endpoint impact indicators **(section 2.4)**.

2.3.1 Classification of WF LCIA methods

According to Berger (2013), basic volume is not sufficient for the application of impact assessment methods that evaluate the consequences of the water consumption determined from the LCI models. This is a major limitation of methods based on WFN framework, hence the decision to focus on ISO framework compliant WF methods for review in this study. The ISO framework methods can be used to account for total water withdrawn as well as just water consumed and uses CFs to find the impact of water use. The most common LCIA methods consistent with the ISO framework were pre-selected and classified into three categories, depending on the impact pathways modelled and, thus, on the effects of water use they want to assess: water depletion methods, future efforts methods (modelling water degradation) and thermodynamic accounting methods, as shown in **Figure 5**. These types of methods answer the question “how can I quantify the relative contribution of a product system to changing opportunities of future generation to use water resource(s) due to current water resource(s) use?” with different perspectives.

2.3.1.1 Water depletion methods

These methods are based on the resource depletion concept, that is often used as a proxy of the availability of water resources. They assess the relative contribution of a product system to water depletion. Among this category, a distinction into three different sub groups can be made:

- Consumption-To-Availability (CTA) methods which are based on a CTA ratio calculated as the fraction between amount of water consumed and available water (midpoint: Boulay et al., 2011a,b; Hoekstra et al., 2012; Loubet et al., 2013; Berger et al., 2014, endpoint: Motoshita et al., 2010; Boulay et al., 2011b)
- Withdrawal-To-Availability (WTA) methods are based on a WTA ratio calculated as the fraction between total water withdrawals for off stream use and available water (midpoint: Pfister et al., 2009; Milà i Canals et al., 2009; Ecological Scarcity method (2013), endpoint: Pfister et al., 2009).

- Demand-To-Availability (DTA) method accounts for both ecosystem water demand and human consumption (midpoint: AWARE method (2016))

2.3.1.2 Future efforts method

This category includes methods that model the degradation of water quality and the consequences (from an energetic or economic point of view) of water quality degradation on societal efforts to use the resource in the future (e.g. economic externalities of water use) (endpoint: Verones et al., 2010; Amores et al., 2013; Pfister and Suh, 2015).

2.3.1.3 Thermodynamic accounting methods

These quantify the impact of water use based on thermodynamic losses (midpoint: Cumulative Exergy Extraction from the Natural Environment (CEENE) method (2007), endpoint: Cumulative Exergy Demand (CExD) method (2007)) and thermodynamic costs (midpoint: Solar Energy Demand (SED) method (2011)).

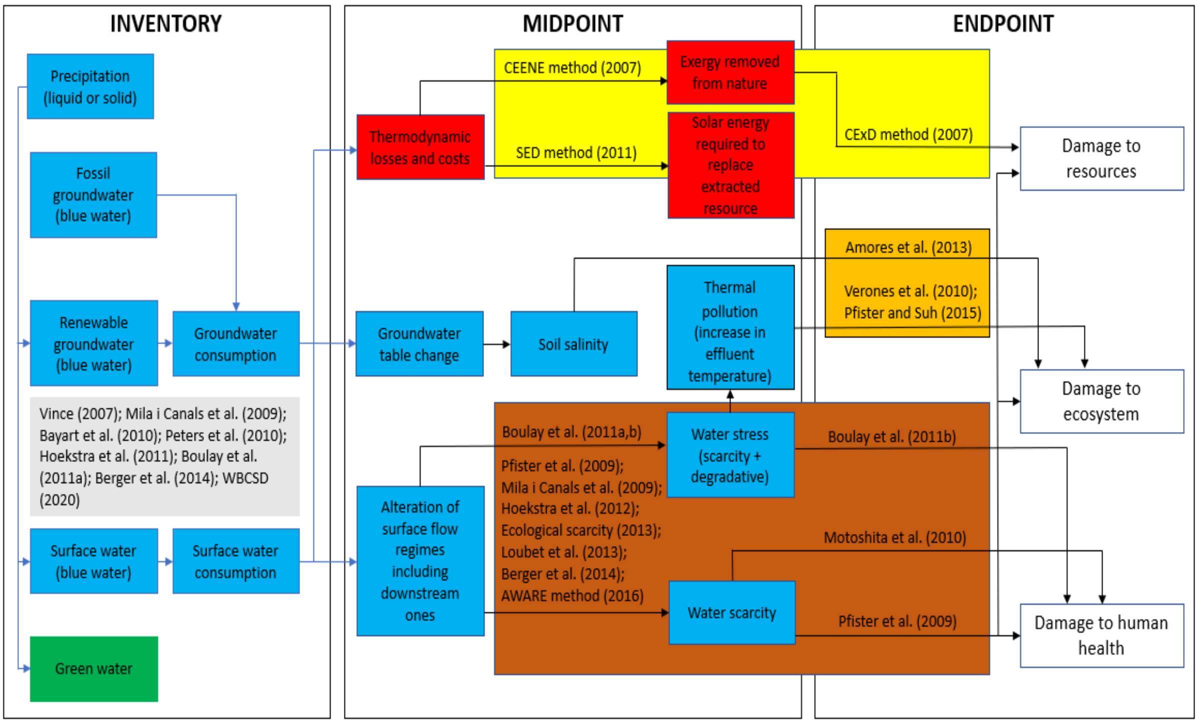

Figure 5. Summary of pre-selected WF methods in relation to the underlying impact mechanism (inventory-midpoint-endpoint) (adapted from Quinteiro et al., 2018). Blue and green arrows show blue and green water flows, respectively; black arrows indicate the impact pathways. Grey area represents inventory methods; brown area represents methods based on water depletion; orange area shows methods based on future efforts; yellow area indicates methods based on thermodynamics.

2.4 Detail analysis of WF LCIA methods

In this study, the most common computational WF methods based on the ISO framework were pre-selected for deep analysis following a comprehensive literature review. As introduced previously they were classified into three categories **(section 2.3.1),** based on the underlying impact pathways, that are further discussed below in a review as follows: water depletion methods (**section 2.4.1**), future efforts methods (**section 2.4.2**) and thermodynamic accounting methods (**section 2.4.3**)**.**

The pre-selected methods are deeply analysed by considering the fundamental elements highlighted below:

- the scope of the method and modelling choices (e.g., level of cause-effect chain, water use, water functionality for human or ecosystem, underlying equations, etc)
- sources of documentation/data (e.g., papers, official reports, websites, etc)
- temporal representativeness (short-, mid-, and long-term)
- geographical representativeness (local, national, or global scale)
- main limitations

The review of considered computational WF LCIA methods is presented, along with an indication an indication of their strengths and drawbacks, to provide some recommendations for application-dependent use of methods in LCA-based WF studies.

2.4.1 Water depletion methods

The nine (9) water depletion methods reviewed in this study are listed in **Table 1** showing their subgroups and levels of impact assessment on the impact pathway.

Table 1. List of the reviewed water depletion methods and their respective subgroups

Water Depletion method	Subgroup	Level on the impact pathway
Pfister et al. (2009)	WTA	Midpoint and Endpoint
Milà i Canals et al. (2009)	WTA	Midpoint
Ecological scarcity method (2013)	WTA	Midpoint
Motoshita et al. (2010)	CTA	Endpoint
Boulay et al. (2011b)	CTA	Midpoint and Endpoint
Hoekstra et al. (2012)	CTA	Midpoint
Loubet et al. (2013)	CTA	Midpoint
Berger et al. (2014)	CTA	Midpoint
AWARE method (2016)	DTA	Midpoint

2.4.1.1 The Pfister et al. (2009) method

The method developed by Pfister et al. (2009) is LCA-based belonging to the group of WTA methods. It enables a comprehensive impact assessment of freshwater consumption on both midpoint and endpoint level (Berger and Finkbeiner, 2010). The method only accounts for blue water consumptive use, and the impact at midpoint level is based on the "water deprivation" impact category (Fardi, 2013). The characterization factor (CF) for measuring water deprivation is the water stress index (WSI) which is based on WTA ratios, using data in a geographical information system (GIS)-based database at 0.5º grid cell. CFs for watershed and country level can be found on the website http://www.worldwater.org/data.html. **Equation 4** shows the WTA ratio for a watershed *i* (WTA*i*) quantifying annual freshwater availability (WA*i*) and withdrawals for different users *j* (WU*ij*) e.g., agriculture, industry, etc.

$$\mathbf{WTA_i = \frac{\sum_j WU_{ij}}{WA_i}} \qquad (4)$$

To calculate WSI, the WaterGAP2 global model based on data from the so-called climate normal period (1961-1990) (Alcamo et al., 2003) was used to get an annual average, describing the WTA ratio of more than 10 000 individual watersheds (Pfister et al., 2009). To account for the nonlinear relationship between water stress and WTA, a variation factor (VF) was adopted to compute a modified WTA ratio (WTA*) as in **Equation 5**. According to Nilsson et al. (2005), VF differentiates water watersheds with strongly regulated flows (SRF). The adjusted WSI is then calculated according to the following logistic function **(Equation 6)** in order to reach CFs that vary continuously from 0.01 to 1 (Berger and Finkbeiner, 2010). The midpoint impact indicator, called water deprivation, can be calculated multiplying the blue freshwater consumptive flows by the WSI (Fardi, 2013).

$$\mathbf{WTA^* = \begin{cases} \sqrt{VF} \times WTA & \text{for SRF} \\ VF \times WTA & \text{for non} - \text{SRF} \end{cases}} \qquad (5)$$

$$\mathbf{WSI\ (m^3\ water\ eq) = \frac{1}{1 + e^{-6.4 \cdot WTA*}\left(\frac{1}{0.01} - 1\right)}} \qquad (6)$$

At the endpoint level, the method focuses on potential environmental damages of water use on all three AoPs; human health, quality of ecosystems and resource depletion. CFs are developed at 0.5º grid cell in a GIS based database at watershed and country level (Quinteiro et al., 2018). This assessment is implemented based on the eco-indicator 99 framework (Berger and Finkbeiner, 2010). To assess the damage to human health, Pfister et al. (2009) focused on the effects of water deprivation on food production, because competition in water scarce areas ultimately affects irrigation. Thus, the method only describes the malnutrition impact pathway: the damages of water deprivation for agriculture use leading to malnutrition (Quinteiro et al., 2018). **Equation 7** shows the human development factor (HDF) which relates human development index (HDI) and the vulnerability of society to malnutrition based on socio economic factors. Furthermore, HDF is considered to estimate the damage on human health based on DALY indicator as shown in **Equation 8** for a watershed or country *i*.

$$\mathbf{HDF_{mal}} = \begin{cases} \mathbf{1} & \mathbf{for} \quad \mathbf{HDI < 0.30} \\ \mathbf{2.03HDI^2 - 4.09HDI + 2.04} & \mathbf{for} \quad \mathbf{0.30 \leq HDI \leq 0.88} \\ \mathbf{0} & \mathbf{for} \quad \mathbf{HDI > 0.88} \end{cases} \qquad (7)$$

$$\mathbf{\Delta HH_{mal,i}\ (DALY)} = \underbrace{\underbrace{\mathbf{WSI_i \cdot WU_{\%,agric,i}}}_{\mathbf{WDF_i}} \cdot \underbrace{\mathbf{HDF_{mal,i} \cdot WR_{mal}}^{-1}}_{\mathbf{EF_i}} \cdot \mathbf{DF_{mal}}}_{\mathbf{CF_{mal,i}}} \cdot \mathbf{WU_{con,i}} \qquad (8)$$

Where Δ $HH_{mal,i}$ is the damage to human health from malnutrition (DALY); $CF_{mal,i}$ (DALY/m^3 consumed) is the expected specific damage per unit of water consumed; WDF_i is the water deprivation factor ($m^3_{deprived}/m^3_{consumed}$); EF_i is the effect factor which quantifies the annual number of malnourished people per water quantity deprived (capita · yr/m^3 deprived); WSI_i is the Water Stress Index (-); $WU_{\%,agric,i}$ represents the fraction of water used in agriculture at watershed (-); $HDF_{mal,i}$ is the human development factor (-); $WR_{malnutri}^{-1}$ is the per capita water requirement to prevent malnutrition (m^3/year. person) calculated from the minimum direct human dietary requirements from blue and green water; DF_{mal} represents the damage due to malnutrition (DALY/year. person); $WU_{con,i}$ is the blue water consumption (m^3)

In relation to damage to ecosystem quality, Pfister et al. (2009) assessed the effects of freshwater consumption on terrestrial ecosystem quality (ΔEQ (m^2 · yr)) following the Ecoindicator-99-method (EI99, Goedkoop and Spriensma 2001). The damage to ecosystem quality is expressed in units of potentially disappeared fraction of species (PDF), which are a measure for the vulnerability of vascular plant species biodiversity (VPBD) (Berger and Finkbeiner, 2010). The vulnerability of that kind of plants is significantly correlated to net primary production (NPP). It stands for the quantity of carbon, which is caught and stocked by plants while photosynthesis. Thereby, the fraction of NPP, which is limited by freshwater availability ($NPP_{wat\text{-}lim}$), represents the vulnerability of an ecosystem to a lack of water. It is used as an approximation of PDF (Eléonore, 2010). As shown in **Equation 9,** the damage to ecosystem quality (ΔEQ) is determined by multiplying $NPP_{wat\text{-}lim}$ by the ratio of water consumption ($WU_{consumptive}$) to mean annual precipitation (P), similarly to the assessment of land use impacts within EI99 (Pfister et al.,2009). The ratio of $WU_{consumptive}$ and P denotes the theoretical area-time equivalent (A·t) which would be needed to recover the amount of consumed water by natural precipitation (Berger and Finkbeiner, 2010), and CF_{EQ} is the ecosystem damage factor ($m^2 \cdot yr/m^3$).

$$\mathbf{\Delta EQ\ \ (m^2 \cdot yr) = CF_{EQ} \cdot WU_{consumptive} = \underbrace{NPP_{wat-lim}}_{PDF} \cdot \underbrace{\frac{WU_{consumptive}}{P}}_{A \cdot t}} \qquad (9)$$

For the damage to natural resources, Pfister et al. (2009) stated that water stock exhaustion can be caused by the extraction of fossil groundwater or the overuse of other water bodies. Pfister et al. (2009) adopted the concept of back-up technology introduced by Stewart and Weidema (2005) for assessing abiotic resource depletion in Ecoindicator99 (Goedkoop and Spriensma, 2001) for evaluating damage to freshwater resources, as endpoint indicator (Sala et al., 2019). This indicator assesses the contribution of freshwater overexploitation to damage on natural resources (Pradinaud et al., 2019). **Equation 10** shows how to determine damage to resources (ΔR) resulting from water consumption ($WU_{consumptive}$) expressed in “surplus energy” (MJ). The energy demand for desalination of seawater ($E_{desalination}$) as back-up technology multiplied by the fraction of water consumption contributing to freshwater depletion ($F_{depletion}$) (which doubles as CF for midpoint indicator freshwater depletion) as shown in. While $E_{desalination}$ is fixed to a value of 11 MJ/m³ (Fritzmann et al., 2007), $F_{depletion}$ for a particular watershed i is dependent on the WTA ratio as in **Equation 11**. When the WTA ratio is above one (the modelled withdrawal is larger than the modelled availability), then the share of water use above renewability is the depleted share (Pradinaud et al. 2019).

$$\mathbf{\Delta R\ \ (MJ) = E_{desalination} \cdot F_{depletion} \cdot WU_{consumptive}} \qquad (10)$$

$$\mathbf{F_{depletion,i}\ (-) = \begin{cases} \frac{WTA\ -1}{WTA} & \text{for WTA} > 1 \\ 0 & \text{for WTA} \leq 1 \end{cases}} \qquad (11)$$

After determining the damage of freshwater consumption on human health, ecosystem quality, and resources, a normalization and then weighting based on weighting factors in the eco-indicator 99 method can be accomplished to reach a single-score indicator (Eléonore, 2010). This indicator is a measure of the overall damage caused by freshwater consumption. It can be compared and aggregated to damage from other environmental interventions such as waste or emissions, which are caused by the product system investigated (Berger and Finkbeiner, 2010).

2.4.1.2 The Milà i Canals et al. (2009) method

Among the Withdrawal-To-Availability methods, the approach of Milà i Canals et al. (2009) proposed a midpoint impact category named freshwater depletion, acknowledging that the consumption of an overexploited groundwater resource (stock or fund resource) could damage the natural (freshwater) resources AoP (Pradinaud et al., 2019). The impact pathway considered is the one of direct groundwater use causing reduced long-term (fund and stock) freshwater availability. Freshwater is an abiotic resource (Finnveden, 1996), which can be depleted at least temporally and spatially (Eléonore, 2010) if the water use is greater than the renewability rate of the affected water resources. The midpoint impact category freshwater depletion assesses the reduced availability of the resource freshwater for future generations if the water use exceeds the renewability rate of the respective body of water.

In terms of LCI modelling, the method of Milà i Canals et al. (2009) requires a specific inventory for freshwater depletion: the water elementary flows have to be categorized distinguishing water stocks (groundwater/fossil water) and over-abstracted water funds (groundwater/aquifers) from the other water flows (Pradinaud et al. 2019). As surface watercourses such as rivers usually have a high renewability rate, it is assumed that only the consumption of water from aquifers (evaporative use) and fossil water (evaporative and non-evaporative use) can contribute to that impact category (Berger and Finkbeiner, 2010). Mila i Canals et al. (2009) consider that the Guinée approach on abiotic resources (baseline method) in the CML guidelines 2001(Guinée et al. 2002) is the most relevant to assess freshwater depletion (Eléonore, 2010).

Therefore, the Abiotic Depletion Potential (ADP) should be adapted to freshwater resource to provide a CF for a water resource *i* e.g. groundwater from an aquifer (ADP*i*), as shown in **Equation 12** where ER_i is the extraction rate of resource *i* (m^3/year); RR_i is the regeneration rate of resource *i*; R_i is the ultimate reserve of resource *i* (m^3/year); R_{Sb} is the ultimate reserves of the reference resource for ADP (Sb, Antimony); DR_{Sb} is annual depletion rate of the reference resource for ADP (Sb, Antimony) (Berger and Finkbeiner, 2010, Sundberg, 2012). Underexploited groundwater bodies (i.e., with RR>ER) would not lead to freshwater depletion and therefore are neglected.

$$\mathbf{ADP_i}\ \ (\mathbf{m^3\ water\ eq/m^3\ \ groundwater}) = \frac{\mathbf{ER_i - RR_i}}{(\mathbf{R_i})^2} \times \frac{(\mathbf{R_{Sb}})^2}{\mathbf{DR_{Sb}}} \qquad (\mathbf{12})$$

Generally, groundwater resources are seldom quantified in terms of their relative abundance compared to potential use (except for small aquifers), and this creates a knowledge constraint. Groundwater is considered to be renewable in most cases and neglected from the ADP impact category. However, Milà i Canals et al. (2009) suggest that if there is knowledge that the relevant aquifer is being over-abstracted, or that fossil water is being used, then the LCA practitioner should find the necessary values to develop ADP factors for the specific water bodies in question (Sala et al., 2019). On the basis of the data published by Custodio (2002) on groundwater consumption and availability, Milà i Canals et al. (2009) estimated ADP values for Califorina and Almeria over-exploited aquifers. The resulting factors are of several orders of magnitude higher than those of scarce resources such as fossil fuels or metals. Unfortunately, CFs have not been calculated for other aquifers (Sala et al. 2019).

2.4.1.3 The Ecological scarcity method (2013)

The Ecological Scarcity method is a single-score midpoint impact assessment method which does not cover a specific AoP (Kounina et al., 2013), although, results of the assessment are measured in single-score (eco-points), which is typical for endpoint approaches (Grinberg et al., 2012). The 2013 version of this method (Frischknecht and Büsser Knöpfel, 2013) is an update of the previous ones (Frischknecht et al., 2006; 2008; 2009) to expand its scope of use based on ISO standard revisions and recent developments in scientific knowledge, accounting also for recent European legislation and environmental targets. This method is based on the distance-to-target principle as defined by SETAC (Udo de Haes, 1996) and provides eco-factors (CFs) for various environmental impacts including water use (Frischknecht et al., 2009).

The eco-factors are calculated by considering the actual flows of pollutants and resources, as well as the maximum allowed or critical flows. In its basic form, Eco-factors are calculated and expressed as EP/m^3 or EP/kg according to the following three elements in accordance with ISO Standard 14044 (ISO, 2006b): characterization, normalization, and weighting (Grinberg et al., 2012). The formula used in the Swiss ecological scarcity method (Frischknecht and Büsser Knöpfel, 2013) is given below **(Equation 13)** and characterisation is optional and politically determined, unlike in ISO 14044 where it is mandatory.

$$\mathbf{Eco-Factor\ (EP/m^3)} = \underbrace{\mathbf{K}}_{\mathbf{Characterization}} * \underbrace{\frac{\mathbf{1 * EP}}{\mathbf{F_n}}}_{\mathbf{Normalization}} * \underbrace{\left(\frac{\mathbf{F}}{\mathbf{F_K}}\right)^{\mathbf{2}}}_{\mathbf{Weighting}} * \underbrace{\mathbf{C}}_{\mathbf{Constant}} \qquad (\mathbf{13})$$

where: K - Characterization factor of a pollutant or of a resource; EP − Eco-point (the unit of assessed impact); F_n − normalisation factor for water consumption (with Switzerland as a system boundary); F is the current flow in the reference area and F_K is the critical flow in the analysed region. The current and critical flows should be measured in the same units and be determined with the same system boundaries (Frischknecht & Büsser Knöpfel, 2013).; C - constant (10^{12}/yr) for obtaining presentable numerical quantities with no technical meaning. Flow is used to express the quantity of a resource, the load of a pollutant or the intensity of an environmental impact (Frischknecht et al., 2009).

The Eco-factor for water use refers to the total input of freshwater into a product system, but there is no characterization done for water quality or type of water source (Berger and Finkbeiner, 2010). Impacts from a released pollutant to freshwater or use of freshwater resources are assessed based on the maximum legal water withdrawal, called critical flow (Frischknecht et al., 2006). In weighting (spatiotemporal scale) for assessment of water use, this method incorporates the relevant political and environmental policy objectives of preventing water stress.

The OECD measures the scarcity (pressure on the fresh-water resources) by calculation of the ratio of the water withdrawal (irrigation, industrial use, drinking water) to the available resources of renewable water (WTA). If this is 20%, it is regarded as an acceptable pressure (Frischknecht et al., 2009, Berger and Finkbeiner, 2010). The water pressure classification ranges encompassing the whole range of scarcity and resulting weighting factor assuming a critical load of 20% are shown in **Table 2** varying in six levels from low to extreme, with each level attributed an individual weighting factor (Frischknecht et al., 2006). The squared ratio of current and critical flow expresses the weighting on basis of the distance to target as shown in **Equation 14.**

The method can be applied at the country, region, or watershed level (Jeswani and Azapagic, 2011) in the short term (e.g., monthly, seasonally, yearly). Due to lack of data, it cannot be applied at all locations of the world (Pfister and Hellweg, 2011; Flury et al., 2011), however, the country-specific eco-factors for freshwater consumption for OECD and non-OECD countries calculated from AQUASTAT data (FAO 1998-2010) are available (Frischknecht and Büsser Knöpfel, 2013).

$$\mathbf{Weighting} = \left(\frac{\mathbf{Current\ flow}}{\mathbf{Critical\ flow}}\right)^{\mathbf{2}} = (\mathbf{WTA})^{\mathbf{2}}\left(\frac{\mathbf{1}}{\mathbf{20\%}}\right)^{\mathbf{2}} \qquad (\mathbf{14})$$

Table 2. Water pressure ranges and resulting weighting factor considering a critical load of 20% (Adapted from Frischknecht et al., 2006).

Water pressure classification ranges		**WTA used for calculation**	**Weighting factor**
Low	< 0.1	0.05	0.0625
Moderate	0.1 to < 0.2	0.15	0.563
Medium	0.2 to < 0.4	0.3	2.25
High	0.4 to < 0.6	0.5	6.25
Very high	0.6 to < 1.0	0.7	16.0
Extreme	≥ 1.0	1.5	56.3

2.4.1.4 The Motoshita et al. (2010) method

This is an endpoint method based on the Consumption-To-Availability approach, developed by Motoshita et al. (2010), which handles the AoP of damage to human health by assessing the disability adjusted life years (DALY) as indicator. It aims to assess the damage of domestic water scarcity (low accessibility to safe water) caused by water consumption; however, freshwater degradation is unaccounted for. The method models the health damage assessment of infectious diseases (ascariasis, trichuriasis, hookworm disease, and diarrhoea) caused by domestic water scarcity and calculates damage factors on a country scale. The cause-effect chain modelling is based on hydrological and socio-economic data. The cause-effect chain of domestic water scarcity was composed of two steps, including assessments of water accessibility and health damage caused by intake of unsafe water (Motoshita et al., 2010).

Compensation mechanism for the level of economic development is included through the parameter house connection rate to freshwater supply and sanitation. By combining the two steps (domestic water scarcity, and health damage assessment), the damage factors (expressed in DALY per m^3 of water consumed) are given at a country level (where there is statistical data for the analysis) and are available at http://www.worldwater.org/data.html. They were developed based on non-linear multiple regression analysis (modelling relationships between freshwater scarcity, accessibility to safe water and damage to health caused by infectious diseases) (Quinteiro et al., 2018), this was because the relationship between subjective and explanatory variables may not always be a linear relationship.

2.4.1.5 The Boulay et al. (2011b) method

This is both a midpoint and endpoint method for assessing water scarcity based on Consumption-To-Availability (CTA) concept and modelling direct impacts on human health. At Midpoint level, the WSI at watershed and country level is proposed as the indicator and the CF values are available at http://www.worldwater.org/data.html. This water stress model is based on a CTA ratio, calculated using statistical low-flow to account for seasonal variations, and modelled using a logistic function (S-curve) in order to obtain resulting indicator values between 0 and 1 m^3deprived/m^3consumed (Sala et al., 2019). The curve is tuned using accepted OECD water stress thresholds (OECD, 2003), which define moderate and severe water stress as 20% and 40% of withdrawals, respectively and converted with an empirical correlation between WTA and CTA. Water consumption and availability data for surface and ground water are taken from the WaterGap v2.2 model (Alcamo et al., 2003). It accounts for inflow and outflow freshwater quality (consumptive and degradative use) through 137 quality parameters by weighing the stress of each water type. The midpoint CF is given by the water stress, α_i, and it is used to aggregate the results of each flow as shown in **Equation 15**.

$$\mathbf{WSI\ (m^3\ water\ eq)} = \sum_{\mathbf{i}} (\boldsymbol{\alpha}_{\mathbf{i}} \times \mathbf{V}_{\mathbf{i,in}}) - \sum_{\mathbf{i}} (\boldsymbol{\alpha}_{\mathbf{i}} \times \mathbf{V}_{\mathbf{i,out}}) \qquad (\mathbf{15})$$

Where WSI expresses the midpoint result in m^3 equivalent of water, αi the stress index of water category i (in m^3 of water equivalent per m^3 of water of category i withdrawn/released) and Vi (in and out) the volumes of water category i entering and leaving the process or product system (i.e., elementary flows (in m^3)). It represents the equivalent amount of water of which other competing users are deprived as a consequence of water use (Boulay et al., 2011b).

Boulay et al. (2011b) proposed endpoint CFs at the watershed and country level, accounting for the local freshwater stress, the extent to which users will be affected by a change in freshwater availability (quality and seasonal variations), the adaptation capacity, and the importance of human health impacts caused by a freshwater deficit for a user (Quinteiro et al., 2018). Gross national income classification (World Bank 2008) was chosen as adaptation capacity (compensation mechanism) of freshwater deficit for other users (Boulay et al. 2011a) for the level of economic development. This model evaluates the potential impacts of water unavailability as a result of consumptive or degradative use, solely focusing on human users in an LCA context. According to Boulay et al (2010), human users are identified according to domestic use, agricultural use, fisheries, industry, cooling, transport, hydropower, and recreational use.

However, this method only considers the impacts from freshwater deprivation for agriculture (irrigation), aquaculture (fisheries), and domestic uses (hygiene and ingestion) at the endpoint level. These potential environmental impacts are modelled using three impact pathways leading to direct human health impacts (in DALY) caused by malnutrition and disease (Boulay et al., 2011b) namely malnutrition from water deprivation for agricultural users, malnutrition from water deprivation for fisheries, and water-related diseases associated with a lack of water for domestic use. The human health impacts are computed following the difference between resource extraction and emission into the environment, as per **Equation 16.**

$$\mathbf{HH_{impact}}\ (\mathbf{DALY}) = \sum_{\mathbf{i=1}}^{\mathbf{17}} (\mathbf{CF_i} \times \mathbf{V_{i,in}}) - \sum_{\mathbf{i=1}}^{\mathbf{17}} (\mathbf{CF_i} \times \mathbf{V_{i,out}}) \qquad (\mathbf{16})$$

Where, HH_{impact} expresses the human health impacts in DALY, CF_i is the characterization factor of water category *i* for the human health impact category (in DALY/m^3 of water category (i) and V_i (in and out) is the volume of water category *i* entering and leaving the process or product system, i.e., the elementary flows (in m^3) (Boulay et al., 2011b).

2.4.1.6 The Hoekstra et al. (2012) method

This is a midpoint method developed for assessment of global water scarcity by combining three innovations: use of water consumption instead of water withdrawal, explicit incorporation of environmental flow requirements and a monthly time-step. The Hoekstra et al. (2012) allows for water scarcity footprint assessment and computes the blue water scarcity indicator at the river basin level, on a monthly basis, using hydrological data. It is based on a CTA ratio calculated as the fraction between consumed (referred to as blue WF) and available water.

Monthly blue WF of 405 river basins accounting for 69 percent of global runoff were analysed for the period 1996–2005 using data from Mekonnen and Hoekstra (2011). For the calculation of blue WF of industries and domestic use, FAO (2010) statistics were used. Water availability was calculated as 'natural runoff' minus the water demand from ecosystem i.e., environmental water requirements. The data for water runoff is from Fekete et al. (2002) and re-adjusted by Hoekstra et al. (2012) so to approximate the natural un-depleted run-off (Sala et al., 2019).

To account for ecological health and the ecosystem services in water scarcity assessment, Hoekstra et al. (2012) adopted the ''presumptive environmental flow standard'' as proposed by Richter et al. (2011); it is used only when site-specific scientific investigation of environmental flow needs has not been undertaken. The presumptive standard is a precautionary approach to estimating environmental flow requirements. It states the following thresholds for conducting any river environmental flow assessment for ecological health:

- A high level of ecological protection will be provided when daily flow alterations are no greater than 10%; a high level of protection means that the natural structure and function of the riverine ecosystem will be maintained with minimal changes.
- A moderate level of protection is provided when flows are altered by 11–20%; a moderate level of protection means that there may be measurable changes in structure and minimal changes in ecosystem functions.
- Alterations greater than 20% will likely result in moderate to major changes in natural structure and ecosystem functions, with greater risk associated with greater levels of alteration in daily flows.

The findings were that in 201 basins with 2.67 billion inhabitants there was severe water scarcity during at least one month of the year, this corresponded strongly with documented ecological declines in some of the world's most heavily used river basins. **Equation 17** shows how the CF i.e., blue water scarcity index (WSI) is computed. The CFs are available at both watershed and country scales; however, the coverage of the world area is lower in comparison to other models, as it only covers major world catchments (Sala et al., 2019) e.g., Po river basin in Italy, the Danube river basin in Central and Eastern Europe and the Congo river basin in Central Africa.

$$\mathbf{WSI\ (m^3\ of\ water\ eq)} = \frac{\mathbf{CU}}{\mathbf{WR - EWR}} \qquad (\mathbf{17})$$

Where: CU – Consumptive use of water; WR – Water Resources; EWR - environmental water requirement; and WSI - Blue water scarcity index (Sala et al., 2019).

2.4.1.7 The Loubet et al. (2013) method

Loubet et al. (2013) proposed this method to derive midpoint CFs for water deprivation (CF_{WD}) accounting for downstream cascade effects within a single river basin in LCA. The method is premised on a two-step approach. First, water scarcity is defined at the sub-river basin scale with the CTA ratio. Second, CF_{WD} are calculated, integrating the effects on downstream sub-river basins. The available water (WA) is estimated as regulated discharge (Fekete et al., 2002) to which the share of environmental water requirements (EWR) estimated by Smathkin et al. (2004) are subtracted (Sala et al., 2019) as shown in **Equation 18**. The river basin or watershed (Pfister et al., 2009) to be assessed has to be split into sub-river basins (SRBi) which are defined based on their relative location within the river basin. The CTA ratio **(Equation 19)** was used because water consumption is more relevant compared to water withdrawal when water scarcity issues are being addressed in LCA due to the fact that released water is made available again in the ecosystem for new users (Bayart et al., 2010). According to Loubet et al. (2013), the major difference between "water withdrawal" and "water consumption" is that water consumption considers water that is returned to the flow (i.e., withdrawal minus release).

Furthermore, the method notes that the water consumed at a specific location only affects SRBs downstream from this location: specific water consumption in SRB_i will affect SRB_i to SRB_n. This causes a cascade effect on potential downstream usages and ecosystems, something that is not captured by water scarcity indicators. The CF_{WD} are based on freshwater scarcity at sub-river basin considering weighting parameters for downstream sub-river basin which are; *i)* area, using data from the HYDRO1K drainage basin database (U.S.G.S. 2012); *ii)* river volume (Hanafiah et al., 2011); and *iii)* number of inhabitants, estimated using the GPWV3 database (CIESIN/CIAT 2005). At the last, the CF_{WD} **(Equation 20)** is measured by the weighted sum of downstream CTA ratios, as was done for two case studies in France (Seine river basin) and Spain (Guadalquivir river basin) selected due to their diverse climatic conditions. However, CF_{WD} values are not available for all river basins at a worldwide scale, and this is a limitation of this method.

Potential midpoint impacts on the water deprivation (I_{WD}) of a studied system are calculated based on the difference between water withdrawal and water release, characterized by their respective CF_{WD} values **(Equation 21),** as previously done by Boulay et al. (2011).

$$\mathbf{WA_i = (1 - \%EWR) \cdot D_i^{reg}} \qquad (\mathbf{18})$$

$$\mathbf{CTA = \frac{tWC}{WA}} \qquad (\mathbf{19})$$

$$\mathbf{CF_{WD,i} = \frac{1}{\overline{\overline{p} \cdot N_{down}}} \sum_{j=1}^{n} (CTA_j \cdot p_j)} \qquad (\mathbf{20})$$

$$\mathbf{I_{WD} = WW \cdot CF_{WD,A} - WR \cdot CF_{WD,B}} \qquad (\mathbf{21})$$

Where: i= the assessed sub river basin (SRB*i*); WA= available water (m^3) in the river basin; %EWR= percentage of total available water (tWA) that can be consumed without causing any change to the ecosystems; D^{reg} = regulated discharge is that in which natural discharge is altered by reservoir operations; CTA = Consumption-To-Availability ratio; tWC = total water consumption; CF_{WD} = characterization factor for downstream water deprivation; $\overline{p}$ = the average value of the weighting parameters among all the SRBs within the river basin; $\overline{N}_{down}$ = the average number of SRBs downstream from each SRB within the river basin; CTA_j = downstream CTA ratio; p_j = the chosen weighting parameter of downstream SRB (SRB_j); I_{WD} = the midpoint impact of water deprivation (m^3 equivalent); WW = the water withdrawal volume of the studied system that occurs at location A (m^3); WR = the water release volume of the studied system that occurs at location B (m^3); $CF_{WD,A}$ and $CF_{WD,B}$ characterize locations A and B, respectively

2.4.1.8 The Berger et al. (2014) method

Berger et al. (2014) developed an LCA-based midpoint method, i.e., the water accounting and vulnerability evaluation (WAVE) model, to consider water consumption and the vulnerability of basins to freshwater depletion. The WAVE model does not focus on predicting potential impacts on freshwater resources, and it does not account for freshwater degradation (Quinteiro et al., 2018). On the inventory level, the model considers atmospheric evaporation recycling effects within drainage basins which potentially reduce water consumption volumes by up to 32%. The method therefore gives a more realistic water consumption volume by introducing the effective water consumption (Berger et al., 2014).

The water depletion index (WDI) is the CF, and it is derived from the CTA ratio (Boulay et al., 2011b), which relates annual water consumption (C) to annual availability (A); the model relies on data from more than 11000 basins, available on a global level and obtained from the WaterGAP2 model (Alcamo et al., 2003).
Compared to other CTA methods, here the CTA ratio is modified as CTA* according to **Equation 22** by including two stocks:

1. Annually usable surface water stocks (SWS) are added to A in order to consider lakes, wetlands, and dams as available water resources.
2. As volumes of groundwater stocks (GWS) are not available on a global level, an adjustment factor (AF_{GWS}) defined on geological structure and annual recharge (WHYMAP - Richts et al., 2011) was introduced to account for availability of groundwater (Berger et al., 2014).

$$\mathbf{CTA^{*}} = \frac{\mathbf{C}}{\mathbf{A+SWS}} \cdot \mathbf{AF_{GWS}} \qquad (22)$$

$$\mathbf{WDI\ (m^3\ water\ eq.\ depleted)} = \frac{\mathbf{1}}{\mathbf{1+\ e^{-40 \cdot CTA^{*}}\left(\frac{1}{0.01}-1\right)}} \qquad (23)$$

Based on local blue water scarcity, WDI represents an equivalent volume of depleted water resulting from a volume of water consumption. To avoid mathematical artifacts of previous indicators that deserts are regarded uncritical if consumption is close to zero, Berger et al., 2014 set WDI equals to 1 above a CTA* of 0.25, the threshold of extreme water stress (Richter et al., 2011) to account for relative scarcity (UNEP, 1997), and absolute freshwater shortage. Assessing the vulnerability of a drainage basin to freshwater depletion is the core objective of the WDI **(Equation 23)** and the CFs are available at http://www2.worldwater.org/data.html in both watershed and country scale with yearly resolution. The vulnerability of basins to freshwater depletion, i.e., the indicator, is determined by multiplying the effective water consumption in each basin and the corresponding WDI. The indicator values range between 0.01 and 1.00.

2.4.1.9 The AWARE method (2016)

This is a midpoint method for characterizing water use and its resulting environmental impacts in LCA that was developed as a result of the UNEP-SETAC Life Cycle Initiative founded Water Use in Life Cycle Assessment (WULCA) working group consensus. It evaluates the water left available (per unit area) in the catchment area once the demand for water by humans and ecosystems has been satisfied, answering the question: "What is the potential to deprive another user (human or ecosystem) when consuming water in this area?" (Boulay et al., 2015a). This method assumes that less water remaining within an area after human and ecosystem requirements are met leads to deprivation among other users within the same area (Boulay et al., 2016), and it is popularly known as the "AWARE" method because it assesses the impacts of water consumption based on available water remaining (AWARE) as an indicator.

However, to avoid the risks of double counting with water quality indicators, deprivation due to water degradation was not considered since the availability of water resources, from a hydrological point of view, corresponds to precipitation minus evapotranspiration. The indicator is calculated at the sub-watershed level and monthly time-step; the underlying hydrological model from which water availability and human consumption of water are estimated is WaterGAP v2.2 (Schmied et al., 2014) using data from 11000 global river basins, whereas the water demand for ecosystems (EWR) is approximated to the value of water needed for aquatic systems and relies on values estimated by Pastor et al. (2013) (Sala et al., 2019).

According to Boulay et al. (2016), AWARE represents the only shared methodological approach to date to determine water consumption in LCA or the water scarcity footprint, as defined in the ISO 14046: 2014 standard because the indicator is calculated per unit area (m^3water / (m^2 * month)) to allow comparability between different regions. When potential impacts from water use started to be integrated in LCA, indices based on the ratio of water WTA were used as CFs (Frischknecht et al., 2008; Pfister et al., 2009). However, following the consensus of the WULCA experts, the AWARE method adopted a demand-to-availability (DTA) ratio approach as it accounts for both ecosystem water demand and human consumption, in order to better answer the overarching question identified in Boulay et al. (2015c) through the 1/AMD criteria. First, the water Availability Minus the Demand (AMD) of humans and freshwater ecosystems in relation to the area (m^3 m^{-2} $month^{-1}$) is calculated, and then the result is normalized with the world average AMD (AMD_{GLO} = 0.0136 m^3 water m^{-2} $month^{-1}$) which is calculated as a-weighted average (Meyer, 2017) then it is inverted. Once inverted, 1/AMD can be interpreted as a surface-time equivalent (STe) to generate unused water in this region (Sala et al., 2019), with values ranging from 0.1 to 100 (Boulay et al., 2016), and the units are dimensionless.

The CFs of the AWARE method (CF_{AWARE}) are expressed as 1/AMDi and available on the website http://www.wulca-waterlca.org/aware.html at watershed-month scale as well as country and/or annual scales, for agricultural and non-agricultural water use as well as unknown use. The main equations underlying the AWARE method are **24, 25, 26,** and **27** where: AMD = Availability-Minus-Demand per area; Demand = HWC + EWR; HWC = human water consumption; EWR = environmental water requirements for freshwater ecosystems; STe = Surface-Time equivalent required to generate one cubic meter of unused water i.e., 1/AMDi (Boulay et al., 2016). The potential impact (water scarcity footprint) is calculated as the product of the inventory flow (amount of water consumed) for the CF_{AWARE} as shown in **Equation 28.**

$$\mathbf{AMD_i = \frac{(Availability\ -\ HWC - EWR)}{Area}} \quad (24)$$

$$\mathbf{CF_{AWARE} = \frac{STe_i}{STe_{world,avg}} = \frac{AMD_{world,avg}}{AMD_i}\ for\ Demand < \ Availability} \quad (25)$$

$$\mathbf{CF_{AWARE} = \ Max\ = 100, for\ Demand \geq Availability\ or\ AMDi < 1\% \times AMD_{world,avg}} \quad (26)$$

$$\mathbf{CF_{AWARE} = \ Min = \ 0.1, for\ AMDi > 10 * AMD_{world,avg}} \quad (27)$$

$$\mathbf{Water\ Scarcity\ Footprint = \ Water\ consumption\ (inventory)\ \times CF_{AWARE}} \quad (28)$$

From **Equations 25**, values CF <1 indicates regions with less water scarcity problems than the world average, while CF = 10 means that the water available per unit area in the region is 10 times less than the world average.

As shown in **Equations 26** and **27**, the AWARE method establishes the following cut-off criteria:

1. Upper cutoff: in case the local water demand is greater than the availability (negative AMD, corresponds to 33% of world consumption on a monthly scale) or the value of AMDi is 100 times smaller than AMDworld, avg (corresponds to 5% of the world average consumption), the method assigns the maximum value of 100 to the CF (because the equation underlying the model would no longer have meaning, Boulay et al. 2018).
2. Lower cutoff: if the value of AMDi is greater than 10 times AMDworld, $m^3_{world,eq}/m^3_i$. The upper cutoff criteria could be a limitation of the model since it impacts around 33% of water consumption.

The main limitations of the AWARE method highlighted by Boulay et al. (2018) are connected to the model implemented to quantify the water demand for ecosystems (Pastor et al., 2013); this model was chosen as the only one, at present, that provides EWR on a monthly scale and that has been validated for different eco-regions and habitats but has inherent limitations. In fact, the monthly EWRs vary only according to the water flow and not to other environmental factors and the algorithm that calculates the global EWR does not consider local aspects such as river width, aquatic fauna, etc. Furthermore, although the data underlying the model also includes information related to dams, there are some uncertainties about how these infrastructures are managed; in some cases, dam management includes specific releases of water to allow for vital flows downstream.

Another limitation is linked to the global hydrological model which is very uncertain, especially for the monthly scale and this uncertainty propagates both in the estimation of water availability and in the assessment of water demand. Boulay et al. (2018) also underline the issues related to the temporal and spatial representativeness of the CF calculated with the AWARE method due to the aggregation data procedure; in particular, they highlighted significant differences between the monthly and annual scales, especially in central Asia, Spain, North and South Africa, Western Australia, the Middle East, and part of China.

Ansorge and Berankova (2017) found that CF_{AWARE} values calculated at the country or river basin level may not be suitable for local studies because conditions in a country can be very heterogeneous. Although water represents a global resource, the problem related to its availability / scarcity is of a purely local or regional nature, and therefore the impact deriving from the use of water varies according to local conditions and time and should be calculated on regional basis.

2.4.2 Future efforts methods

2.4.2.1 The Verones et al. (2010) method

This is an endpoint method which assesses the potential adverse effects on aquatic species due to thermal pollution. The thermal regime of a water body is a crucial factor for Ecosystem Quality (Caissie, 2006) because of the limited temperature tolerance of most aquatic animal species (Coutant, 1999). The Verones et al. (2010) method deals with the impact of cooling freshwater (blue water) discharges on aquatic ecosystems. Verones et al. (2010) applied a fate and effect model which calculates the CFs for quantifying the potential disappearance of freshwater aquatic species due to thermal discharges.

For the calculation of the fate factor (FF), the model QUAL2Kw (version 5.1) was applied (Pelletier et al., 2006). It describes the change in ambient river profile temperature ($°C_{river}·m^3_{river}$) due to a change in thermal discharges ($°C_{cw}·m^3_{cw}$/day). On the other hand, the effect factor (EF) which reflects the change in the potentially disappeared fraction (PDF) of aquatic species for direct temperature-induced mortality due to a change in ambient temperature ($°C_{river}$) for each river section was calculated by means of a species sensitivity distribution (SSD) following a normal temperature-response function using data for 36 species (De Vries et al., 2008). EF is measured in PDF/$°C_{river}$.

Cumulative CFs were computed through space and time explicit integration of the partial FF and corresponding EF as shown in **Equation 29.** The CF for assessing thermal pollution was calculated following the LCIA characterization scheme according to Pennington et al. (2004), and it is given in PDF·days·m^3_{river}/($°C_{cw}·m^3_{cw}$). The inclusion of different time periods (e.g., months) reflects the variability in environmental conditions throughout the year. Combining the CF with the inventory parameters, that is, the set of the amount of cooling water (m^3) and (calculated) surplus temperature above the natural water temperature ($°C_{cw}$) returns Ecosystem Quality damage scores in the unit PDF·day·m^3_{river} (Verones et al. 2010). The CFs are only available for cooling water from the nuclear power plant Muehleburg in Switzerland to two rivers (Aare and Rhine), and this is a limitation of this method.

$$\mathbf{CF_{cumulative,t}} = \sum_{\mathbf{j}} \mathbf{CF_{j,t}} = \sum_{\mathbf{j}} \mathbf{FF_{j,t}} \cdot \mathbf{EF_{j,t}} \qquad (\mathbf{29})$$

Where $CF_{cumulative,t}$ is the sum of all the partial CFs along the distance of the river, $FF_{j,t}$ is the fate factor ($days \cdot m^3_{river} \cdot °C_{river}/(°C_{cw} \cdot m^3_{cw})$) and $EF_{j,t}$ the effect factor ($PDF/°C_{river}$) for river section *j* in time period *t*.

2.4.2.2 The Amores et al. (2013) method

This is an LCA-based endpoint method specific to AoP "ecosystem quality". It was developed to evaluate the environmental impact associated with salinity increases due to water consumption on biodiversity, with application in a Spanish coastal wetland. Amores et al. (2013) used fate and effect modelling to develop CFs and use the Potentially Affected Fraction of species (PAF) as indicator. The impact indicator represents how the change in PAF of species varies with groundwater consumption ($PAF.m^3.yr.m^{-3}$), which affects the salinity content via altered amounts of groundwater and seawater infiltration into the wetland. The method considered the coastal wetland of Albufera de Adra containing two lagoons (Nueva and Honda lagoon as the study area), and due to data constraints, only 18 species from Nueva lagoon (13 plants, 3 fish, 1 alga, and 1crustacean) were within the scope.

The FF was calculated from seasonal (wet and dry months) water balances of the wetland Albufera de Adra (Nueva Lagoon was selected since it is closer to the sea and thus affected by seawater intrusions). The EF was obtained from the fitted curve of the potentially affected fraction of native wetland species due to the ecological damage from increased salinity and can be applied to other wetlands with similar species composition (Amores et al., 2013). The developed CFs for salinity impact in a coastal wetland were applied to calculate the impacts on wetland biodiversity due to the irrigation of the existing greenhouse crops close to the study area as shown in **Equation 30**.

$$\mathbf{CF} = \mathbf{FF} \cdot \mathbf{EF}\ [\mathbf{m^3} \cdot \mathbf{PAF} \cdot \mathbf{yr} \cdot \mathbf{m^{-3}}] \qquad (\mathbf{30})$$

Results converted into ecosystem quality damage using the ReCiPe method (Goedkoop et al., 2008) were compared to other categories such as climate change, freshwater eutrophication, freshwater ecotoxicity etc, to better understand the relative importance of salinity impacts on ecosystem quality. However, local conditions should be considered to account for the varying freshwater species density, this could improve the results obtained from the freshwater species density estimates of the ReCiPe model.

2.4.2.3 Pfister and Suh (2015) method

This is an endpoint method used to assess the damage to ecosystem resulting from thermal pollution in freshwater aquatic biota. The Pfister and Suh (2015) method, like Verones et al. (2010), also deals with the impact assessment of cooling freshwater discharges on aquatic ecosystems (Quinteiro et al., 2018), with the aim to address water-use related environmental impacts within LCA or WF study. The impacts are measured as the potentially disappeared fraction (PDF) of species in the affected freshwater ecosystem volume over time (Pfister and Suh, 2015). Pfister and Suh (2015) developed a spatially explicit fate and effect model, a generic fate model (based on water body temperature, river discharge, river width, flow velocity and distance to sea) was used to determine CFs at a 0.5° grid cell for United States power plants (Quinteiro et al., 2018).

The effect model for characterising the impact of increased river temperature on the ecosystem was assessed based on a temperature tolerance interval (TTI) of aquatic species (including fish, molluscs, meduzosa, crustacean, and annelida) from de Vries et al. (2008) and Verones et al. (2010). The river was partitioned into sections and a two-step approach was adopted to capture both the short-range and long-range thermal effects. These were:

1. Calculation of non-linear, temperature-based factors for local fate ($FF_{local,i}$) and effect ($EF_{local,i}$) in the model cell of heat release *i*,
2. Development of energy-based factors for fate ($FF_{river,i}$) and effect ($EF_{river,i}$) downstream of the cell of heat release until the river mouth.

The characterization factor (CF_i) for thermal emissions in each grid cell *i* was calculated using **Equation 31** where $CF_{local,i}$ is the factor summarizing fate and effect in the grid cell of thermal emission and needs to be calculated as a function of the emission rate, while $CF_{river,i}$ is a linear combination of $FF_{river,i}$ and $EF_{river,i}$ for downstream effects (Pfister and Suh, 2015).

$$\mathbf{CF_i} = \underbrace{\mathbf{FF_{local,i}} \times \mathbf{EF_{local,i}}}_{\mathbf{CF_{local,i}}} + \underbrace{\mathbf{FF_{river,i}} \times \mathbf{EF_{river,i}}}_{\mathbf{CF_{river,i}}} \qquad (\mathbf{31})$$

In addition to thermal impacts, the Pfister and Suh (2015) method also considered freshwater eutrophication, freshwater ecotoxicity, and freshwater acidification impacts (which are degradative impacts from emissions) and water consumptive effects on the ecosystem.

2.4.3 Thermodynamics accounting methods

2.4.3.1 The CExD method (2007)

This endpoint method evaluates potential damage on the AoP "resources" (Kounina et al., 2013) through the exergy content of the resource. Based on the exergy concept, Bösch et al. (2007) applied the Cumulative Exergy Demand (CExD) indicators for LCIA to the ecoinvent database (Wernet et al., 2016) in LCA to portray the total exergy removed from nature (CFs) to deliver a product. Exergy (measured in megajoules) is work or ability to produce work (Wall 1993) and it is utilised as entropy is produced following the second law of thermodynamics (Szargut 2005).

Exergy is computed using **Equation 32** where: Ex is Exergy (MJ); T_0 is the Temperature of the surroundings (K) and S is the Entropy (MJ/K) (Bösch et al., 2007). There are limitations to the Szargut model, primarily the complexity of the chemical exergy calculations when states other than the standard state is considered but also potential inaccuracies associated with the lithosphere calculations (Fitzsimons, 2011). Another limitation of the CExD method is that its cause-effect chain is not clear in the inventory and it does not reflect water scarcity, also it is not spatially differentiated (Kounina et al., 2013).

$$\boldsymbol{\delta}\mathbf{Ex}\ (\mathbf{MJ}) = \mathbf{T_0} \sum \Delta \boldsymbol{S} \qquad (\mathbf{32})$$

CExD considers 8 resource categories in the inventory, among which is water. All types of water resources excluding water turbined in hydroelectric power plants are considered. CExD assigns the same exergy score CFs (50 MJ/m^3 of water) for all the freshwater resources, irrespective of the type of source (e.g., from river, lake, ground etc) compared to the reference state (baseline) and seawater is considered the standard environment. However according to Fitzsimons (2011), the chemical exergy of water is sensitive to changes in location and time, in terms of relative humidity and temperature for areas remote to the sea.

The CExD is defined as the sum of exergy of all energy and material resources required to provide a process or product (Gulotta et al., 2018). The mathematical notation of CExD **(Equation 33)** was chosen by Bösch et al. (2007) to stress the similarities to Cumulative energy demand (CED). CExD may be compared to CED, both being indicators of life cycle energy demand. The difference between these two methods is that the CED represents the direct and indirect energy use throughout the life cycle while the CExD calculates the whole exergy input to a system by computing exergy of fuels and chemical potential (Gulotta et al., 2018).

CExD is stated in MJ-equivalents to highlight that it is an impact assessment indicator and not an inventory elementary flow, while Exergy is stored in resources in the form of chemical, thermal, kinetic, potential, nuclear and radiative energy (Szargut 2005). CExD uses the second law of thermodynamics rules when calculate the exergy, that is why it has a higher scientific robustness than CED (which uses energy, based on the first law of thermodynamics) and a higher number of CFs (Alvarenga et al., 2016).

$$\mathbf{CExD\ (MJ\ of\ exergy\ eq)} = \sum_{\mathbf{i}} \mathbf{m_i} * \mathbf{Ex_{(ch),i}} + \sum_{\mathbf{j}} \mathbf{n_j} * \mathbf{r_{ex-e(k,p,n,r,t),j}} \qquad (\mathbf{33})$$

Where CExD is the cumulative exergy demand per unit of product or process (MJ-eq); m_i is the mass of material resource i (kg); $Ex_{(ch),i}$ = exergy per kg of substance i (MJ-eq/kg); n_j is the amount of energy from energy carrier j (MJ); $r_{ex-e(k,p,n,r,t),j}$ represents the exergy to energy ratio of energy carrier j (MJeq/MJ); ch is chemical exergy; k is kinetic exergy; p is potential exergy; n is nuclear exergy ; r is radiative exergy and t is thermal exergy (Bösch et al., 2007).

2.4.3.2 The CEENE method (2007)

This is a thermodynamic-based LCIA method derived from the concept of exergy. It uses consistent exergy data on fossils, nuclear and metal ores, minerals, air, water, land occupation, and renewable energy sources with well-defined system boundaries (Dewulf et al., 2007). CEENE consists in an update and refinement of the CExD (Bösch et al., 2007) and, according to Dewulf et al. (2007), is the most comprehensive resource indicator which evaluates energy carriers, non-energetic resources (including water) and land occupation (Sala et al., 2019).

The resource indicator CEENE is seen as an improvement (more elementary flows with a higher number of CFs) towards the previous CExD method because it is more consistent (Dewulf et al. 2007). CEENE depicts total exergy removal from nature to provide a product, summing up the exergy of all resources required and is computed using **Equation 34** where $CEENE_j$ is the cumulative exergy extracted from the natural environment for a product *j* (in MJ_{ex}), calculated as the summation (over all resource reference flows) of the products of the X_i factor of the i^{th} reference flow (X_i in MJ_{ex}/kg, MJ_{ex}/MJ, MJ_{ex}/Nm^3, MJ_{ex}/m^2a) and the cumulative amount a_{ij} from reference flow i (kg, MJ, Nm^3, m^2.a) necessary to obtain product j (Dewulf et al., 2007).

$$\mathbf{CEENE_j\ (MJ\ of\ exergy\ eq)} = \sum_{\mathbf{i=1}}^{\mathbf{184}} \left(\mathbf{X_i} \times \mathbf{a_{ij}}\right) \qquad (\mathbf{34})$$

According to De Meester et al. (2006), the chemical exergy of any species can be calculated from the exergy values of the reference compounds, considering its reference reaction. The CEENE method is based on thermodynamics and water scarcity is not accounted for (Sala et al., 2019). Water is therefore characterized because of its chemical and potential exergy, based on the reference state for water defined by Szaegut et al. (1988). CEENE is coupled to a comprehensive state of the art LCI database, ecoinvent (www.ecoinvent.org), and these data in the ecoinvent database version 1.2 from the 184 reference flows of the resources considered are used to establish conversion factors, called X factors which help in quantifying the exergy extracted from natural ecosystems and is thus called the CEENE. For water resources, reference flows and their recommended X factors, are shown in **Table 3**. The CFs have been tested over a number of case studies, however they are not spatially differentiated (Sala et al. 2019).

Table 3. Ecoinvent reference flows for water resources and their recommended X factors (Dewulf et al., 2007)

Reference flow (or category)	**Unit**	**X MJ_{ex}/Unit resource**
Water, cooling, unspecified natural origin	m^3	5.0×10^1
Water, lake	m^3	5.0×10^1
Water, river	m^3	5.0×10^1
Water, salt, ocean	m^3	0.0
Water, salt, sole	m^3	0.0
Water, turbine use, unspecified natural origin	m^3	0.0
Water, unspecified natural origin	m^3	5.0×10^1
Water, well, in ground	m^3	5.0×10^1

2.4.3.3 The SED method (2011)

The Solar Energy Demand (SED) model was developed by Rugani et al. (2011) as a midpoint model for assessing and improving the environmental management of natural resources. It is a single score LCIA indicator derived from the broader emergy method (Odum 1996) with some adjustments to introduce a thermodynamic or solar energy-based indicator (i.e., SED) for resource consumption. SED represents the direct and indirect solar energy (in mega-joule solar energy, MJ_{se}-eq) required by a product or service during its life cycle. SED is not the same as emergy since emergy analysis uses computation rules that differ from those of LCA (Liao et al., 2012). Furthermore, SED, in contrast to emergy, does not account for human labour, information, and many ecosystem services.

Compared to CED and CExD, SED expands the system boundaries for the evaluation from the primary resources (i.e., reference states in exergy and energy) back to the primary energy of the sun (Rugani et al., 2011). According to Alvarenga et al. (2016), SED has a high number of CFs, but they are not regionalized. Rugani et al. (2011) measured and quantified the SED of the extraction of 232 atmospheric, biotic, fossil, land, metal, mineral, nuclear, and water resources. CFs measure the amount of solar energy that would be needed to replace the resource that is extracted from the environment (Sala et al., 2019). The SED of a particular process can be defined as the summation of the product of solar energy of the ith reference flow of resource (SEF_i) and the quantity of resource flow *i* involved as input in the production of the good or service p ($M_{p,i}$) as shown in **Equation 35** where SED_p shows the total solar energy required to produce the good or service (Rugani et al., 2011).

$$\mathbf{SED_p(solar\ energy\ joules) = \sum_i SEF_i * M_{p,i}} \qquad (\mathbf{35})$$

The solar energy factor (SEF) for any resource can be calculated by assuming the baseline as ‘free energy’ that feeds and sustains each of the resource flows. In general, SEF (measured in MJse/unit) can be calculated using **Equation 36** (Rugani et al., 2011) where: S represents the annual baseline of energy that flows in the geobiosphere, i.e., sum of emergy in sun, tide, and crustal heat (Campbell 2000), and F_i is the annual flow of the resource *i* (e.g., kg/year), estimated by the ratio of the stored quantity and its turnover time (Odum 1996).

$$\mathbf{SEF_i = \frac{S}{F_i}} \qquad (\mathbf{36})$$

The SED model groups elementary flows using the LCI data in the ecoinvent database, version 2.1 into 8 resource categories: (1) atmospheric and gaseous resources; (2) land resources; (3) renewable energy resources; (4) fossil resources; (5) metal ores; (6) minerals and mineral aggregates; (7) nuclear energy resources; (8) water resources. Categories 2, 3, and 8 refer to renewable resources, while those included in the other categories were considered non-renewable (Rugani et al., 2011). The turnover time is used to make a distinction between renewable resources and non-renewable resources (Odum 1996). Since the baseline is defined on an annual basis, resources having a turnover time of less than one year are defined as renewable, whereas resources having a turnover time over one year as non-renewable (Sala et al., 2019).

For water resources, there are nine reference flows, and all SEFs were derived from a comprehensive emergy evaluation of global and regional water uses according to Buenfil (2001) and they are shown in **Table 4.** Transformities of global water storages and flows are calculated by assuming these as coproducts, respectively, of the baseline (Rugani et al., 2011). SEFs equal to zero were assigned to 'seawater flows' since seawater is considered "ground state" with no chemical potential energy. The SEF of water in turbines of hydropower plants was also set to zero to avoid double counting for hydroelectric power (Buenfil, 2001).

Table 4. Overview of the Solar Energy Factors (SEFs) for water resources coupled to the ecoinvent database v2.1 (adapted from Rugani et al., 2011).

Key elementary flows (n = number of total resources within each group)	Units	Type[a]	Solar energy factors[b] MJse/unit	Source of original flow
Water, lake	m^3	R	2.22×10^5	Freshwater lakes
Water, river	m^3	R	3.09×10^5	Rivers and streams
Water, well	m^3	R	1.10×10^6	Fresh groundwater
Water, unspecified (n.2 flows)	m^3	R	5.44×10^5	Average of lake, river, and well waters
Salt water (n.2 flows); water in turbines	m^3		0	g.s.[c]

[a]R = Renewable resource; [b]Values refer to the baseline $9.26*10^{18}$ MJ_{se}/year (Campbell 2000); [c]Ground-state resource.

2.5 Summary of the reviewed LCIA methods for WF

A total of 15 common LCIA methods for WF selected thorough a through literature review were considered in the scope of this study, and they were classified into three categories in view of their perspectives: water depletion methods (9), future efforts methods (modelling water degradation) (3) and thermodynamic accounting methods (3). The pre-selected methods under each category were discussed in **sections 2.4.1**, **2.4.2 and 2.4.3** by analysing the fundamental elements of each i.e., the scope of the method and modelling choices (e.g., level of cause-effect chain, water use, water functionality for human or ecosystem, underlying equations, etc); sources of documentation/data (e.g., papers, official reports, websites, etc); temporal (short-, mid-, and long-term) and geographical representativeness (local, national, or global scale) and main limitations. In this section, all the analysed LCIA methods for WF have been separated into two sets based on their level of cause-effect chain i.e., midpoint and endpoint methods and each set was summarized in a table format (**i.e., Tables 5 and 6** respectively) highlighting the different principal elements of each to facilitate comparison and the better understanding of the WF methods for application in the LCA case study as per the objectives of the WF assessment.

2.6 Selection of WF methods for case study application

In the document "ILCD recommendations for LCIA in the European context", the European Commission (EC-JRC–IES, 2011) analysed several methods for LCIA (including several reviewed in this study) and made some effort towards harmonization. Starting from the first pre-selection of existing methods and the definition of criteria, a list of recommended methods for each impact category at both midpoint and endpoint was produced.

The set of specific criteria which are selected for evaluating LCIA methods and/or models assessing water depletion is explicitly designed for the evaluation of midpoint models and not for endpoint models, because of the relatively low level of development and maturity which characterizes the endpoint models (Sala et al. 2019). Owing to that, all the endpoint methods reviewed in this study were not considered for the case study application. Furthermore, thermodynamic accounting methods were not considered because their CFs did not account for spatial and temporal variations. They were deemed more suitable for assessing and comparing different impacts from a variety of resources i.e., metal, fossil, water, land, nuclear, etc., and this was beyond the scope of this case study.

The principal objective of the case study application was to use SimaPro software for comparing WF results using different methods and testing the spatial variation of results considering Poland (Europe) and Gabon (Africa). The only viable selection criteria to achieve the objective was to consider midpoint WF methods (already embedded in SimaPro) that assess water scarcity. Above all else, the WF methods also assessed water scarcity using the same units (m^3) despite having different CFs and this simplified comparison when interpreting results from the case study.

Against this background, five (5) midpoint methods that only assess the impact category of water scarcity, and that are already available to be used in SimaPro were selected for case study application in this study. These were: Pfister et al., 2009; Boulay et al., 2011b; Hoekstra et al., 2012; Berger et al., 2014 and AWARE method (2016). In a nutshell, the methods (already embedded in SimaPro) selected, and the criteria used are summarized in **Table 7.**

Table 7. Summary of selected WF methods and the criteria used for selection

WF Method	**Criteria considered for selection**		
	CF (m^3)	**Impact category assessed**	**Level on the impact pathway**
Pfister et al. (2009)	WSI	Water scarcity	Midpoint
Boulay et al. (2011b)	WSI	Water scarcity	Midpoint
Hoekstra et al. (2012)	WSI	Water scarcity	Midpoint
Berger et al. (2014)	WDI	Water scarcity	Midpoint
AWARE method (2016)	Water Remaining	Water scarcity	Midpoint

Table 5. Summary of the principle elements of the reviewed pre-selected midpoint LCIA methods for WF

Method	Classification	Water uses covered	Geographic resolution and timeframe	Impact assessment model/mechanism	Main limitations
The Pfister et al. (2009) method	Water depletion method under the subgroup WTA	The method only accounts for off-stream consumptive use[3] i.e., withdrawals of surface and ground water	CFs are available at both watershed and country scales, on annual basis, covering the majority of the globe[1]	The impact on water deprivation is measured by the water stress index (WSI) (expressed in m^3 water equivalent) which is based on WTA ratios.	The method considers water withdrawals and not consumption[1] The spatial resolutions do not account for arid areas[1] Water quality issues cannot be assessed[2]
The Milà i Canals et al. (2009) method	Water depletion method under the subgroup WTA	Evaporative and non-evaporative water use exceeding the renewability rate; only fossil and aquifer groundwater use	CFs values can be easily calculated at sub-watershed scale in the short-, medium-, and long-term, however maturity is low[1]	The impact on freshwater depletion is assessed through the reduced availability of the freshwater for future generations[3] when the renewability rate is exceeded. The CFs are called Abiotic Depletion Potentials (ADP) and expressed in m^3 of water equivalent / m^3 of groundwater	The spatial resolutions do not account for arid areas[1] The method fails if water quality needs to be assessed[2] Limited data on groundwater resources in terms of their relative abundance compared to potential use (except for small aquifers) CFs are only available for Califorina and Almeria over-exploited aquifers[1]

If the reference is not stated here, then information source is the original publication of each method already included in the Bibliography, otherwise: **1.** Sala et al. (2019); **2.** Quinteiro et al. (2018); **3.** Berger and Finkbeiner (2010); **4.** Pfister and Hellweg (2011)

Table 5. Summary of the principle elements of the reviewed pre-selected midpoint LCIA methods for WF (Continuation I)

Method	Classification	Water uses covered	Geographic resolution and timeframe	Impact assessment model/mechanism	Main limitations
The Ecological scarcity method (Frischknecht and Büsser Knöpfel, 2013)	Water depletion method under the subgroup WTA	Withdrawal uses of freshwater e.g., irrigation, industrial use, etc.	Eco-factors (CFs) are available for OECD and non-OECD countries, at country, region, or watershed level in the short term (e.g., monthly, seasonally, yearly).	It applies the distance-to-target principle to assess eco-factors (CFs); it covers various environmental impacts, including water use, and results are provided as single-score (eco-points).	The method does include water quality issues or type of water source i.e., surface or groundwater Due to lack of data, it cannot be applied at all locations of the world[4] The method is not suitable for mid- and long-term evaluation.
The Boulay et al. (2011b) method	Water depletion method under the subgroup CTA	Consumptive and degradative use of surface and ground water (including fossil ground water)[1]	Water stress indicators (CFs) are available at watershed and country level, on annual basis, covering the majority of the globe[1]	The water stress indicator is based on a CTA ratio, calculated using statistical low-flow to account for seasonal variations, and modelled using a logistic function (S-curve) to obtain values between 0 and 1 m^3deprived / m^3consumed (Sala et al., 2019)	The method is based on CTA and does not account for desert areas[1] The method is not suitable for mid- and long-term evaluation
The Hoekstra et al. (2012) method	Water depletion method under the subgroup CTA	Consumptive use of surface and ground water[1]	Blue water scarcity index (CFs) developed at the river basin and country level on a monthly basis for major world catchments	Water scarcity is derived from CTA ratio considering the blue water scarcity as indicator (expressed in m^3 equivalent)	Arid areas are not reflected since the CFs available only covers major world catchments[1] The method is not suitable for mid- and long-term evaluation

If the reference is not stated here, then information source is the original publication of each method already included in the Bibliography, otherwise: **1.** Sala et al. (2019); **2.** Quinteiro et al. (2018); **3.** Berger and Finkbeiner (2010); **4.** Pfister and Hellweg (2011)

Table 5. Summary of the principle elements of the reviewed pre-selected midpoint LCIA methods for WF (Continuation II)

Method	Classification	Water uses covered	Geographic resolution and timeframe	Impact assessment model/mechanism	Main limitations
The Loubet et al. (2013) method	Water depletion method under the subgroup CTA	Consumptive use of freshwater (agriculture, industry, and domestic use) in the sub-watershed or river basin Both surface and ground water use are considered, however fossil groundwater is excluded[1]	CFs values are calculated at sub-watershed scale**[1]**, but only for two case studies in France (Seine river basin) and Spain (Guadalquivir river basin)[1] Evaluation in the short-, medium-, and long-term are possible	Potential impacts on water deprivation (expressed in m^3 equivalent) in downstream sub watersheds due to water consumption are calculated based on CTA ratio	CFs are not available except for two case studies in France and Spain, there are no CFs for other river basins The spatial resolution is thus very limited Arid areas are not reflected, water quality is also not considered[1]
The Berger et al. (2014) method	Water depletion method under the subgroup CTA	Blue water consumption mainly due to evapo(transpi)ration or product integration of ground and surface water.	CFs are available in both watershed and country scale with yearly resolution**[1]**	The water depletion index (WDI) is derived from the CTA ratio (expressed in m^3 equivalent) Atmospheric evaporation recycling within drainage basins is considered giving a more accurate estimates of water consumption volumes	The model only assesses the vulnerability of watersheds to freshwater depletion, it does not focus on predicting potential impacts on freshwater resources The method does not account for freshwater quality degradation**[2]** The method does not assess the vulnerability to human health and ecosystem impacts (Berger, 2013)

If the reference is not stated here, then information source is the original publication of each method already included in the Bibliography, otherwise: **1.** Sala et al. (2019); **2.** Quinteiro et al. (2018); **3.** Berger and Finkbeiner (2010); **4.** Pfister and Hellweg (2011)

Table 5. Summary of the principle elements of the reviewed pre-selected midpoint LCIA methods for WF (Continuation III)

Method	Classification	Water uses covered	Geographic resolution and timeframe	Impact assessment model/mechanism	Main limitations
The AWARE method (Boulay et al., 2016)	Water depletion method under the subgroup DTA	Surface and ground water consumption (agricultural and non-agricultural water use as well as unknown use)[1]	CFs are calculated at the sub-watershed level and with monthly time-step, as well as at country and/or annual scales [1]	A demand-to-availability (DTA) ratio approach is applied to assess the impacts of water consumption in relation to the available water remaining (AWARE) per area in a watershed after the demands of humans and aquatic ecosystems have been met The result is normalized with the world average, allowing for the comparability between different regions	The main limitations are connected to the model for estimating water demand of ecosystems (Pastor et al., 2013) and are summarized in **section 2.5.1.9** Significant differences between the monthly and annual scales of the CFs may exist due to the aggregation procedure especially in central Asia, Spain, North and South Africa, Western Australia, the Middle East, and part of China (Boulay et al., 2018). CF_s at country or river basin level may not be suitable for local studies (Ansorge and Berankova, 2017)

If the reference is not stated here, then information source is the original publication of each method already included in the Bibliography, otherwise: **1.** Sala et al. (2019); **2.** Quinteiro et al. (2018); **3.** Berger and Finkbeiner (2010); **4.** Pfister and Hellweg (2011)

Table 5. Summary of the principle elements of the reviewed pre-selected midpoint LCIA methods for WF (Continuation IV)

Method	Classification	Water uses covered	Geographic resolution and timeframe	Impact assessment model/mechanism	Main limitations
The Cumulative Exergy Extraction from the Natural Environment (CEENE) method (Dewulf et al., 2007)	Thermodynamic accounting method	Both consumptive and degradative uses of blue water are modelled Exergy based on the reference state for water defined by Szaegut et al. (1988).	Exergy factors (CFs) on annual basis, and it is not spatio-temporally differentiated	Total exergy removal from nature to provide a product, summing up the exergy of all water flows. Exergy values are based on the reference state for water defined by Szaegut et al. (1988) and summed-up to compute the CEENE indicator (Unit: Joules of exergy)	Being based on thermodynamics, water scarcity is not accounted for[1] CFs are not spatially and temporally differentiated in the assessment[1]
The Solar Energy Demand (SED) method (Rugani et al., 2011)	Thermodynamic accounting method	Consumptive water use. Only blue water (water used in fisheries, irrigation water, urban use water, raw wastewater, and treated wastewater) is included.	SEFs (CFs) are on a global scale, and do not allow spatially and temporally explicit evaluation[1]	SED is an impact indicator for natural resource consumption, It measures the amount of solar energy (direct and indirect) that would be needed to replace the resource that is extracted from the environment (Sala et al., 2019) and it is expressed in solar energy Joules.	The method does not account for spatial and temporal differentiation in the assessment[1] Being based on thermodynamics, water scarcity is not accounted for[1] Results are highly uncertain as calculations all depend on a specific baseline[1]

If the reference is not stated here, then information source is the original publication of each method already included in the Bibliography, otherwise: **1.** Sala et al. (2019); **2.** Quinteiro et al. (2018); **3.** Berger and Finkbeiner (2010); **4.** Pfister and Hellweg (2011)

Table 6. Summary of the principle elements of the reviewed pre-selected endpoint LCIA methods for WF

Method	Classification	Water uses covered	Geographic resolution and timeframe	Impact assessment model/mechanism	Main limitations
The Pfister et al. (2009) method	Water depletion method under the subgroup WTA	The method only accounts for blue water off-stream consumptive use**3**	CFs are developed at 0.5° grid cell in a GIS based database at watershed and country level**2**, on annual scale (short term perspective)	The method assesses potential damages of water use on all three AoPs; human health, quality of ecosystems and resource depletion (our focus) The method adopted the concept of back-up technology introduced by Stewart and Weidema (2005) for assessing ADP in Ecoindicator99 for assessing damage to freshwater resources (ΔR) leading to deletion, expressed in "surplus energy" (MJ)	The model is specific in scope and only works for resource depletion**1** The spatial resolutions do not account for arid areas**1** The method fails if water quality needs to be assessed**2** The CFs are not fully available for the indicator at midpoint level (freshwater depletion)**1**
The Boulay et al. (2011b) method	Water depletion method under the subgroup CTA	Consumptive and degradative use of freshwater i.e., agricultural, aquaculture, and domestic water use	CFs are available at the watershed and country level, on annual basis**1**	The method assesses the impact on human health (i.e., malnutrition) and water-related diseases due to freshwater deprivation based on DALY	The method does not consider the impacts from freshwater deprivation due to industry, cooling, transport, hydropower, and recreational use at the endpoint level.

If the reference is not stated here, then information source is the original publication of each method already included in the Bibliography, otherwise: **1.** Sala et al. (2019); **2.** Quinteiro et al. (2018); **3.** Berger and Finkbeiner (2010); **4.** Pfister and Hellweg (2011)

Table 6. Summary of the principle elements of the reviewed pre-selected endpoint LCIA methods for WF (Continuation I)

Method	Classification	Water uses covered	Geographic resolution and timeframe	Impact assessment model/mechanism	Main limitations
The Motoshita et al. (2010) method	Water depletion method under the subgroup CTA	Surface and ground water consumptive use	The damage factors (expressed in DALY per m^3 of water consumed) are given at a country level[2]	The human health damage caused by infectious diseases (ascariasis, trichuriasis, hookworm disease, and diarrhoea) from domestic water scarcity It is based on the concept of disability adjusted life years (DALY), used as an indicator.	The damage factors are only available for countries where there is statistical data for the analysis The method fails if water quality needs to be assessed[2]
The Verones et al. (2010) method	Future efforts method	Both consumptive and degradative use of blue water (cooling water)[2]	Local geographical level: CFs are available only for cooling water from a nuclear power plant in Switzerland to two rivers, on a monthly basis to account for the variability in environmental conditions throughout the year	The method assesses the impact of cooling freshwater (thermal discharges) on aquatic ecosystems (measured in PDF.m^3.day) as a result of the changes in river temperature. Three Areas of Protection are covered: human health, quality of ecosystems and resource depletion	The method cannot be applied regionally or globally The method only works using data for 36 species which occur in temperate climates (De Vries et al., 2008). It fails for species in different climatic zones.

If the reference is not stated here, then information source is the original publication of each method already included in the Bibliography, otherwise: **1.** Sala et al. (2019); **2.** Quinteiro et al. (2018); **3.** Berger and Finkbeiner (2010); **4.** Pfister and Hellweg (2011)

Table 6. Summary of the principle elements of the reviewed pre-selected endpoint LCIA methods for WF (Continuation II)

Method	**Classification**	**Water uses covered**	**Geographic resolution and timeframe**	**Impact assessment model/mechanism**	**Main limitations**
The Amores et al. (2013) method	Future efforts method	Consumptive use of ground water i.e., irrigation	Locally specific geographical resolution, on a short-term basis CFs are available only for the wetland Albufera de Adra in Spain, on annual basis, using data from wet and dry months	Change in aquatic species (plants, fish, algae, and a crustacean) due to groundwater consumption for crop irrigation causing salinity increase (quality degradation) in a coastal wetland in Spain (measured in PAF.m^3.yr.m^{-3})	The method cannot be applied regionally or globally The method only considered 18 of the 30 indigenous species reported to be found in the Nueva lagoon. Can only be applied in similar geographical context with same species
The Pfister and Suh (2015) method	Future efforts method	Both consumptive and degradative use of blue water (cooling water)^2	Local (watershed level) and Regional level (CFs at a 0.5º grid cell for United States power (coal and natural gas) plants), on annual scale	The damage to ecosystem due to thermal pollution in freshwater aquatic biota (measured in PDF.m^3.year) in the affected ecosystem volume over time. The method also considers freshwater eutrophication, freshwater ecotoxicity, and freshwater acidification impacts and water consumptive effects on the ecosystem	The method only works for power plants in the USA and fails to facilitate a global assessment. The method does not account for thermal impacts on coastal regions or oceans

If the reference is not stated here, then information source is the original publication of each method already included in the Bibliography, otherwise: **1.** Sala et al. (2019); **2.** Quinteiro et al. (2018); **3.** Berger and Finkbeiner (2010); **4.** Pfister and Hellweg (2011)

Table 6. Summary of the principle elements of the reviewed pre-selected endpoint LCIA methods for WF (Continuation III)

Method	Classification	Water uses covered	Geographic resolution and timeframe	Impact assessment model/mechanism	Main limitations
The Cumulative Exergy Demand (CExD) method (Bösch et al., 2007)	Thermodynamic accounting method	In- and off-stream freshwater consumptive uses, and in-stream degradative water use[3] All types of water resources (e.g., from river, lake, ground etc) excluding water turbined in hydroelectric power plants are considered	Exergy factors (CFs) are not spatially and temporally differentiated[1]	The method evaluates potential damage on the AoP "resources" (Kounina et al., 2013) through the exergy content of the resource using CExD indicator to portray the total exergy removed from nature (CFs) to deliver a product Seawater is considered the standard environment.	Based on thermodynamics and water scarcity is not accounted for[1] The method does not account for spatial and temporal differentiation in the assessment[1]

If the reference is not stated here, then information source is the original publication of each method already included in the Bibliography, otherwise: **1.** Sala et al. (2019); **2.** Quinteiro et al. (2018); **3.** Berger and Finkbeiner (2010); **4.** Pfister and Hellweg (2011)

CHAPTER THREE: CASE STUDY APPLICATION

3.1 Overview for the beneficiation process of Manganese ores

Manganese (Mn) is a crucial raw material consumed in many industrial applications, for the most part in the production of structural steel and alloys. 95% of the Mn ore produced annually is consumed by the steel industry with the other 5% used by the other non-metallurgical applications like chemical, paint, fertilizer, and battery industries (Roskill, 2015). The Mn industry is global, with the majority of mining and smelting distributed between Asia, Africa, Australia, and Europe (Westfall et al., 2016). The total land-based Mn reserves are about 26 t/km^2 of continental crust (Singh et al., 2019). According to the United States Geological Survey (USGS) report 2014, global Mn reserves are about 570 million tonnes, and these are mainly distributed in South Africa (~26%), Ukraine (~24%), Australia (~17%), with the lesser amount in Brazil, India, China, Gabon, and Mexico. The Mn resources are classified into three major categories, i.e., oxide, siliceous, and carbonate ores, and their different mineralogy is summarised in **Table 8.**

Table 8. Mineralogy of the three categories of Mn ores (adapted from Singh et al., 2019)

Mn Ore Type	Major minerals	Typical Gangue minerals
Oxide ores	Pyrolusite, Ramsdellite, Nsutite, Cryptomelane, Hollandite, Bixbyite	Quartz, Garnet, Magnetite, Kaolinite
Siliceous ores	Braunite, Tephroite, Spessartine	Quartz, Kaolinite, Hematite, Goethite
Carbonate ores	Rhodochrosite, Kutnahorite	Feldspars, Dolomite, Pyrite, Other metallic impurities

Mn ore is typically classified into three grades based on the Mn content of the ore. High grade ores contain 44% and above, while medium and low-grade ores contain 30 - 44%, and less than 30% Mn, respectively. For economical ferroalloy production, the Mn content of the ore should be at least 40% (Elliott and Barati, 2020). According to the International Manganese Institute (IMnI) statistics (2019), the world's output of manganese ore increased in 2018 for the second consecutive year, on rising demand from manganese alloy smelters. It reached 20.3 million dry metric tonnes (Mn contained), up by 6% or 1.2 million dry metric tonnes from 2017, exceeding 2014 production of 19.3 million metric tonnes and marking a new record high as shown in **Figure 6.** The additional supply mostly came from Africa and Australia, driven by China, where output decreased because of mine depletion and stricter safety regulations. In 2018, the leading Mn ore producer countries were South Africa (32%), Australia (17%), Gabon (12%), Ghana (12%), Brazil (6%), and China (6%) (IMnI, 2019).

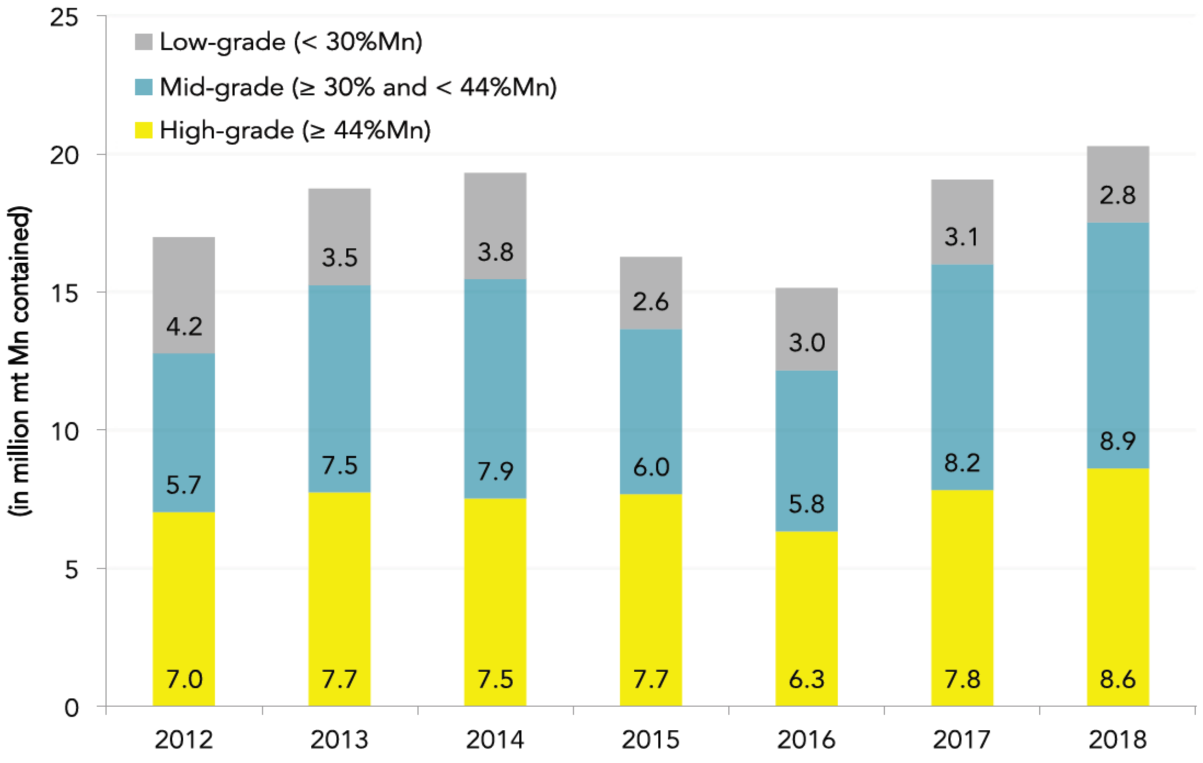

Figure 6. Global Mn ore production 2012 – 2018 (Source: IMnI, 2019)

The mining of Mn ore is conducted using either conventional surface or underground methods, and these have significant environmental impacts resulting from but not limited to water use, felt at both local and global scales. Unlike Gabon that has predominantly medium to high grade Mn ores (USGS, 2015), most of the other ore producer countries have low grade ores. Hence, the mining of low-grade ore now exceeds that of high-grade ore on a tonnes-manganese-metal basis (Elliott et al., 2018). According to Singh et al. (2019), this poses several challenges for the Mn based industries e.g., unavailability of high-grade raw materials, technoeconomic difficulties during processing of low-grade ores, and the environmental restriction on ore processing technologies, such as CO_2 emission, waste disposal, etc. Now more than ever, the priority of all industries is to obtain high grade Mn ores as raw materials.

The solution, therefore, is the identification and selection of a suitable beneficiation process to upgrade the low-grade Mn ores. The beneficiation process helps to enrich the grade of the Mn ore and to eliminate gangue components from the ore, thereby lessening the significant variability in grades as well as in mineralogical characteristics. The selection of a beneficiation process largely depends on the impurities present in the ores (**Table 8**) and the intended application of the produced concentrates (Singh et al., 2019). According to Wellbeloved et al. (2000), the three most important areas of application of Mn ores and the specific requirements, are as follows:

1. Metallurgical grade ore for the iron and steel industry, which generally contains 38 - 55 % Mn. The phosphorus content should preferably be below 0.1 %, and the concentrations of Al_2O_3, SiO_2, CaO, MgO, and S are important. The manganese/iron ratio is critical; a 7.5 : 1 ratio, for example, is required for a standard ferromanganese alloy with 78 % Mn.
2. Battery grade ore, containing 70 - 85 % MnO_2 (44 - 54 % Mn). The ore should generally contain less than 0.05 % of metals more electronegative than zinc, such as copper, nickel, cobalt, and arsenic. The suitability of manganese dioxide for use in batteries depends on a number of factors, including the crystal structure, surface area, pore size distribution, particle shape and size, electrical conductivity, surface conditions, chemical composition, and structure defects.
3. Chemical grade ore whose specifications vary considerably depending on the end use. Included in this category are feed stocks for electrolytic manganese and manganese dioxide, manganese chemicals, colorants and, in the Republic of South Africa, an oxidant in uranium extraction.

During the Mn ore beneficiation, gravity separation, magnetic separation, and flotation can be applied. According to Singh et al. (2019), gravity separation is the oldest and easiest process to upgrade the low-grade Mn ores. This method is applied to remove the low-density silica and clay-bearing minerals in siliceous ores. However, it is not suitable for the beneficiation of oxide and carbonate Mn ores. Magnetic separation is best suited for the beneficiation of siliceous and oxide Mn ores that are rich with iron-bearing impurities such as hematite, goethite, limonite, whereas for carbonate ores, it can used for removal of ferro and paramagnetic iron-bearing minerals. Flotation has been reported by various researchers to be capable of upgrading complex carbonate Mn ores (Abeidu 1973; Yongping and Mulong, 1988; Andrade et al. 2012; Zhou et al. 2015; Calderon-Rodarte et al. 2017). That notwithstanding, most of the flotation studies carried out for upgradation of Mn carbonate ores could not be able to produce very high-grade ore concentrate and it was mainly due to fine granular and chemical association of gangue minerals (Singh et al., 2019). Whenever suitable, it is also possible to use a combination of all the available beneficiation strategies depending on the nature of gangue content in the Mn ore. However, the beneficiation techniques require water due to the combinations of washing, wet screening, cycloning, etc, and the environmental impacts resulting from water consumption could be massive.

3.2 LCA of the Case Study using SimaPro Software

This LCA study investigates the variability and consistency of WF results for the beneficiation process of Mn ores as a case study, using the SimaPro software version 9.0.0 released in November 2018. SimaPro is an LCA software created by a Dutch company called PRé Sustainability. SimaPro is used to calculate and identify the pertinent environmental impacts associated with products and services throughout their life cycle (Goedkoop et al., 2016). SimaPro also facilitates easy modelling and analysis of complex life cycles in a systematic and transparent way, in accordance with the ISO14040 and ISO14044 LCA standards (ISO, 2006). It also allows for the identification of hotspots in every link of your supply chain, from extraction of raw materials to manufacturing, distribution, use, and disposal.

SimaPro 9.0.0 is equipped with several LCI databases including the ecoinvent database version 3.7 released in September 2020, which is selected for the analysis of the Mn- case study. It was selected because it is recognized as one of the most extensive LCI international databases with more than 10.000 processes relative to a wide range of sectors including mining. SimaPro also allows for the using of several calculation methods to provide results for midpoint and/or endpoint environmental impact categories as well as for single score impacts as carbon footprint or WF. With the purpose of assessing the WF of the selected case study on Mn-ores beneficiation, 5 different WF methods among those analysed in Chapter Two were tested, and these are: Pfister et al., 2009; Boulay et al., 2011b (water scarcity); Hoekstra et al., 2012; Berger et al., 2014 and AWARE method (2016). These methods are already embedded in the SimaPro software version 9.0.0 thus speeding the comparison.

To test the variability and consistency in WF results among the different WF methods with the geographical contexts, some sensitivity analyses were performed for Poland and Gabon according to the summarized description of the considered calculation setups in **Table 9.** The selected WF methods that were used to perform the calculations have CFs that transform data from the WF inventories to environmental impacts. For the case study of this thesis, the mining and beneficiation process of Mn ores to produce a commercial Mn-concentrate suitable for pyrometallurgy, was modelled by using the ecoinvent dataset "Manganese concentrate {GLO}| production | Cut-off, U". The case study description is structured according to the four phases of LCA (i.e., goal and scope, inventory, impact assessment, results interpretation) and is reported in the **sub-sections 3.2.1** to **3.2.4**.

Table 9. Summarized description of the sensitivity analyses performed in the study

Calculation Setups	WF inventory	WF impact assessment
Reference Setup	Global dataset	WF methods with global CFs
First Setup	Global dataset modified by replacing the global elementary flows (GLO) with those of Poland (PL) and Gabon (GA), wherever applicable, and keeping all other GLO inputs the same	WF methods with global CFs
Second Setup	Global dataset modified by replacing the global elementary flows (GLO) with those of Poland (PL) and Gabon (GA), wherever applicable, and keeping all other GLO inputs the same	WF methods modified by replacing global CFs with those of Poland (PL) and Gabon (GA)

3.2.1 Goal and Scope definition

This is a standalone WF assessment which analyses only the midpoint environmental impacts under the water scarcity impact category which was the most relevant in reflecting the single issue of the studied system as stipulated in the LCA ISO standards. The goal of this WF study is to analyse the cradle-to-gate environmental impact of Mn ores considering the current technological level worldwide. The study covers partial life cycle stages of metal production, since it considers the "intermediate product" i.e., Mn-concentrate without considering the manufacturing of the final metal products, its use phase and end-of-life management. This is an internal LCA study purely for academic purposes whose results are intended to identify all the hotspots in the mining and beneficiation process of Mn ores, as a result of water consumption.

The primary function of the system under study is the production of marketable Mn-concentrate for pyrometallurgy. Consequently, the functional unit (FU) is 1 kg of that Mn-concentrate produced globally. It represents the reference flow for the LCI (all inputs and outputs are computed with respect of this FU) as well as for the impact assessment step (LCIA), thus presenting the WF score per kg of Mn-concentrate. The system boundary, which ensures that the results comprehensively characterize the life cycle of the product, includes all the activities starting from manganese ore in ground until the production of Mn-concentrate, as illustrated in **Figure 7.**

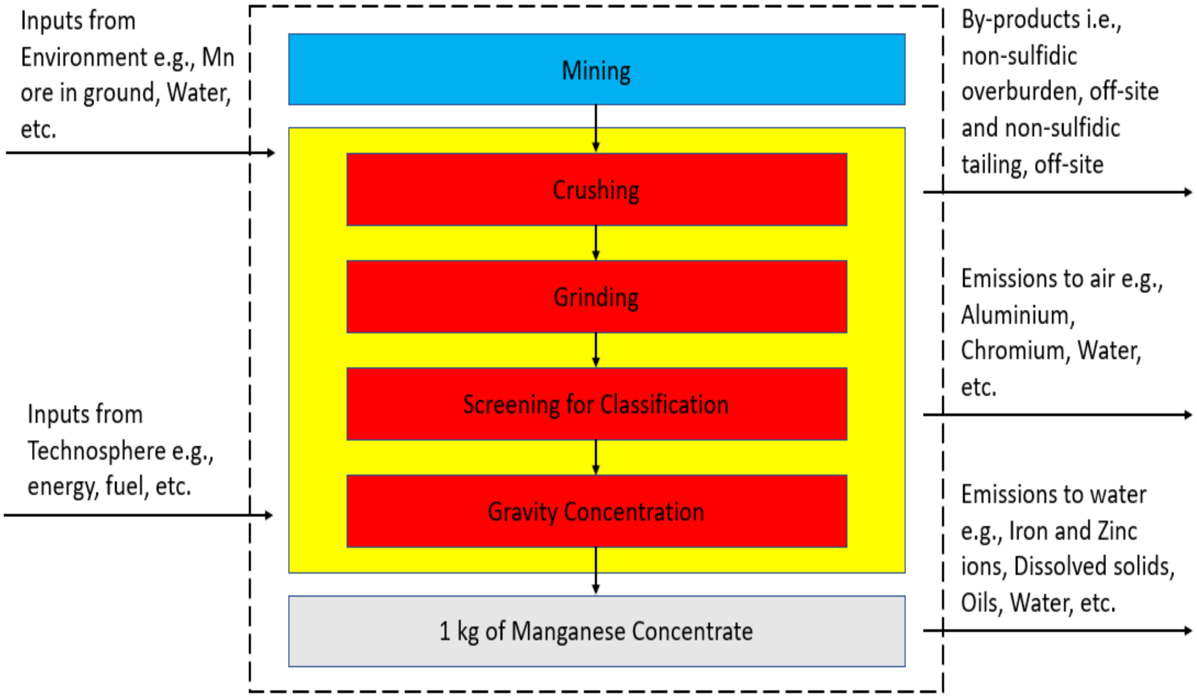

Figure 7. System boundaries and main inputs and outputs as listed in the ecoinvent module being studied for WF analysis. Yellow area shows the steps in the beneficiation process of Mn ores.

In the ecoinvent dataset, the mining process is done 70% open pit and 30% underground. After mining, the ore is first crushed in several stages with jaw and / or cone crushers, and then subsequently ground with rod and / or ball mills and finally screened for classification. In a second step the classified material it is subjected to gravity concentration to separate the metal-bearing particles from the unwanted minerals. For this, drum separators and de-watering screens for lumps are used, and cone separators and a high-gradient magnetic separator for fine material. No flotation is done (Adelhardt and Saiger, 1999). The end-gate of the system is Mn concentrate suitable for commercialization, just prior to sending it to either on-site pyrometallurgy or hydrometallurgy to produce Mn metal. Note that the metallurgical step is not included in this WF assessment, since it is out of the scope.

Due to the strong dependence of WF from water consumptions patterns and climate at local level, the spatial resolution of the pre-selected midpoint WF methods as well as the variability of results were tested by assuming two different locations, one in Africa (Gabon) and one in Europe (Poland).

3.2.2 WF inventory analysis

The WF inventory analysis phase involves the quantification of all inputs as resources use and material uses, and all outputs as wastes (by-products) and emissions to the environment (air, water, and soil), with respect to the selected FU of the product system. The LCI thus lists all the flows entering and living the unit processes in the system as generic datasets (not specified for each unit process) within the system boundary considered in relation to the scope of the study.

The WF inventory step as stated in ISO 14046 is mandatory for any WF assessment. In this case study the completed LCI has not been created since the one available in the ecoinvent 3.7 database under "Manganese concentrate {GLO}| production | Cut-off, U" was used. The dataset refers to the production of 1 kg of Mn concentrate, at plant, for a world-wide production average in 2017 (the dataset was created by extrapolating data of 2003 and accounting for uncertainty due to temporal variability).

The inventory of the ecoinvent 3.7 dataset used to model the foreground system was developed by experts as per the ecoinvent quality guidelines. It is available at a global level, and it was modified to make the sensitivity analyses on the geographical context, considering Poland and Gabon. The dataset documentation in **Table 10** shows in detail the by-products, the inputs from technosphere (e.g., energy, fuels) and from environment (e.g., water, Mn-ores), as well as the emissions to air and surface water (river) for 1 kg of Mn concentrate.

Table 10. The dataset documentation of the global Mn-module showing the unit processes (Source: Ecoinvent center, 2020)

Reference product	**Amount**
Manganese concentrate	1 kg
Inputs from technosphere: materials/fuels	Amount
aluminium hydroxide factory {GLO}| market for | Cut-off, U	1.44E-11 p
Blasting {GLO}| market for | Cut-off, U	0.000452 kg
conveyor belt {GLO}| market for | Cut-off, U	1.3E-7 m
diesel, burned in building machine {GLO}| market for | Cut-off, U	0.0799 MJ
electricity, high voltage {RoW}| electricity production, hydro, run… | Cut-off, U	0.00453 kWh
electricity, medium voltage {GLO}| market for | Cut-off, U	0.00302 kWh
mine infrastructure, open cast, non-ferrous metal {GLO}| market for | Cut-off, U	1.94E-11 p
mine infrastructure, underground, non-ferrous metal {GLO}| market for | Cut-off,	8.3E-12 p
steel, chromium steel 18/8, hot rolled {GLO}| market for | Cut-off, U	0.000515 kg
Inputs from nature	**Amount**
Manganese, in ground	0.613 kg
Occupation, mineral extraction site	9.01E-5 m^{2}a
Transformation, from unspecified	3.0E-6 m^2

Transformation, to mineral extraction site	3.0E-6 m^2
Water, river, GLO	0.00139 m^3
Outputs to technosphere: waste and emissions to treatment	**Amount**
non-sulfidic overburden, off-site	2.61 kg
non-sulfidic tailing, off-site	0.71 kg
Emissions to air	**Amount**
Aluminium	3.95E-9 kg
Chromium	2.05E-10 kg
Iron	5.86E-6 kg
Magnesium	1.54E-9 kg
Particulates, < 2.5 um	1.18E-8 kg
Particulates, > 10 um	1.22E-7 kg
Particulates, > 2.5 um, and < 10um	1.06E-7 kg
Silicon	1.03E-7 kg
Water/m^3	0.0002085 m^3
Emissions to water	**Amount**
Arsenic, ion	1.13E-10 kg
BOD5, Biological Oxygen Demand	1.13E-7 kg
COD, Chemical Oxygen Demand	1.7E-7 kg
Copper, ion	1.13E-10 kg
DOC, Dissolved Organic Carbon	6.64E-8 kg
Iron, ion	3.96E-9 kg
Lead	1.13E-10 kg
Oils, unspecified	1.13E-8 kg
Suspended solids, unspecified	5.66E-8 kg
TOC, Total Organic Carbon	6.64E-8 kg
Water, GLO	0.0011815 m^3
Zinc, ion	1.13E-10 kg

The WF inventory for the global Mn-dataset was the reference calculation set up, it was then modified to create Mn-datasets for Poland and Gabon as described in **Table 9** to perform sensitivity analyses. In detail, for Poland, the value of the input from nature "water, river, (GLO)" was replaced by "water, river, (PL)", inputs from technosphere "electricity, high voltage (RoW)" and "electricity, medium voltage (GLO)" were replaced by "electricity, high voltage (PL)" and "electricity, medium voltage (PL)", respectively, and emission to water "Water, GLO" was replaced by "Water, PL". For Gabon, the values of the input from nature "water, river, (GLO)" was replaced by "water, river, (GA)", input from technosphere "electricity, medium voltage (GLO)" was replaced by "electricity, medium voltage (GA)", and emission to water "Water, GLO" was replaced by "Water, GA". All the other inputs and outputs kept the same values as modification was not applicable due to missing country-specific datasets for both Poland and Gabon. Water balance analyses were done on the global Mn-module inventory, and the inventory for its modified versions to check for data consistency.

3.2.3 WF impact assessment

Table 11 shows the WF methods (with their years of release) used to determine the WF of the beneficiation process of Manganese ores.

Table 11. Comparison of the WF methods used for impact assessment in SimaPro 9.0.0.

WF method	Version	Year of release	CF	Units
Pfister et al. (2009)	1.02	August 2014	WSI	m^3
Boulay et al. (2011b)	1.02	August 2014	WSI	m^3
Hoekstra et al. (2012)	1.02	August 2014	WSI	m^3
Berger et al. (2014)	1.00	March 2014	WDI	m^3
AWARE method (2016)	1.01	March 2017	Water Remaining	m^3

Furthermore, two copies each of all the 5 WF methods were created and modified by substituting CFs at global level (**Table 12**) with country-specific CFs for Poland and Gabon as in **Tables 13** and **14**, respectively. The global CFs are higher than the country-specific CFs for Poland and Gabon, and this is due to the non-uniform distribution of water resources which places many people at risk globally hence compounding the already existing water scarcity problem. Water use has been growing globally at more than twice the rate of population increase, and an increasing number of regions are reaching the limit at which water services can be sustainably delivered. Demographic growth and economic development are putting unprecedented pressure on water resources, especially in arid regions.

Comparing the CFs of Poland and Gabon shows that Poland is more critical in terms of water availability. This can be explained by the differences in climatic conditions between the two countries and how they influence the hydrological cycle. Gabon with a moist and hot climate receives higher annual rainfall ranging from 1500 – 2000 millimetres due to the condensation of moist air, resulting from the meeting of the cold Benguela Current from the south and the warm Guinea Current from the north. On the other hand, Poland receives an average annual precipitation of only about 600 mm due to the temperate climate with very cold winters caused by polar cold waves, coming from the Russian Arctic or Siberia.

According to Boulay et al. (2016), CF_{AWARE} is limited to a range from 0.1 to 100, with a value of 43 meaning that the water available per unit area in the region is 43 times less than the world average. Considering the other midpoint methods, CFs varied from two orders of magnitude (0.01–1) for Pfister et al. (2009) and Berger et al. (2014), and up to 5 and 7 orders of magnitude for Boulay et al. (2011b) and Hoekstra et al. (2012), respectively, excluding the zero values. The Boulay et al. (2011b) method has CFs of zero for all elementary flows in Gabon, and this signifies no water stress. The CFs also reveal that all the considered WF LCIA methods assess only the freshwater consumption and use, with no CFs for sea water.

Table 12. Global CFs of the different WF methods used for impact assessment

Compartment	**Sub compartment**	**Substance**	**Characterisation Factor (m^3/m^3)**				
			Pfister et al. (2009)	**Boulay et al. (2011b)**	**Hoekstra et al. (2012)**	**Berger et al. (2014)**	**AWARE Method (2016)**
Raw	Unspecified	Water cooling unspecified natural origin, GLO	0.606	0.7098	1.3928	0.592	43
Raw	Unspecified	Water, lake, GLO	0.606	0.6582	1.3928	0.592	43
Raw	Unspecified	Water, river, GLO	0.606	0.6582	1.3928	0.592	43
Raw	Unspecified	Water, turbine use, unspecified natural origin, GLO	0.606	0.7098	1.3928	0.592	43
Raw	Unspecified	Water, unspecified natural origin, GLO	0.606	0.7098	1.3928	0.592	43
Raw	Unspecified	Water, well, in ground, GLO	0.606	0.694	1.3928	0.592	43
Water	Unspecified	Water, GLO	-0.606	-0.7098	-1.3928	-0.592	-43
Water	Ocean	Water, GLO	-	-	-	-	0

Table 13. CFs for Poland of the different WF methods used for impact assessment

Compartment	**Sub compartment**	**Substance**	**Characterisation Factor (m^3/m^3)**				
			Pfister et al. (2009)	**Boulay et al. (2011b)**	**Hoekstra et al. (2012)**	**Berger et al. (2014)**	**AWARE Method (2016)**
Raw	Unspecified	Water cooling unspecified natural origin, PL	0.07	0.0148	0.2604	0.038	1.96
Raw	Unspecified	Water, lake, PL	0.07	0.0157	0.2604	0.038	1.96
Raw	Unspecified	Water, river, PL	0.07	0.0157	0.2604	0.038	1.96
Raw	Unspecified	Water, turbine use, unspecified natural origin, PL	0.07	0.0148	0.2604	0.038	1.96
Raw	Unspecified	Water, unspecified natural origin, PL	0.07	0.0148	0.2604	0.038	1.96
Raw	Unspecified	Water, well, in ground, PL	0.07	0	0.2604	0.038	1.96
Water	Unspecified	Water, PL	-0.07	-0.0148	-0.2604	-0.038	-1.96
Water	Ocean	Water, PL	-	-	-	-	0

Table 14. CFs for Gabon of the different WF methods used for impact assessment

Compartment	**Sub compartment**	**Substance**	**Characterisation Factor (m^3/m^3)**				
			Pfister et al. (2009)	**Boulay et al. (2011b)**	**Hoekstra et al. (2012)**	**Berger et al. (2014)**	**AWARE Method (2016)**
Raw	Unspecified	Water cooling unspecified natural origin, GA	0.0101	0	0.001431	0.01	1.09
Raw	Unspecified	Water, lake, GA	0.0101	0	0.001431	0.01	1.09
Raw	Unspecified	Water, river, GA	0.0101	0	0.001431	0.01	1.09
Raw	Unspecified	Water, turbine use, unspecified natural origin, GA	0.0101	0	0.001431	0.01	1.09
Raw	Unspecified	Water, unspecified natural origin, GA	0.0101	0	0.001431	0.01	1.09
Raw	Unspecified	Water, well, in ground, GA	0.0101	0	0.001431	0.01	1.09
Water	Unspecified	Water, GA	-0.0101	0	-0.001431	-0.01	-1.09
Water	Ocean	Water, GA	-	-	-	-	0

The data from the LCI phase was used to evaluate the water use impacts by implementing the above-mentioned methods one per time in the simulations. The potential environmental impacts from water use were calculated through the use of CFs derived from the 5 considered LCIA methods for WF related to the water scarcity impact category. In this study, the long-term emissions were excluded from the impact assessment calculations because they suffered from high uncertainty, and mainly impacted the end-of-life stage which was beyond the scope.

3.2.4 Interpretation of the results

This is the final phase of the LCA procedure, and it is mandatory for an LCA study. The WF results for the case study at the LCI and LCIA levels were interpreted in accordance with the ISO 14044 specification and the JRC technical report guide (Zampori et al., 2016). Basing on the goal and scope of this study, the significant issues were identified through hotspot analysis, and an evaluation considering completeness, sensitivity and consistency checks was conducted and documented in Chapter 4. All these eventually formed the cornerstone for making informed conclusions, limitations, and recommendations in Chapter 5.

CHAPTER FOUR: RESULTS AND DISCUSSION

In this chapter, the results of the WF analysis of the Case study described in Chapter 3 were presented and discussed thoroughly. The results of the analysis were evaluated in three parts: evaluation of WF inventory results **(section 4.1),** evaluation of WF impact assessment results **(section 4.2),** and sensitivity analysis of the results **(section 4.3).**

4.1. Evaluation of WF inventory results

The LCI used for this Case study was that of the global Mn-dataset obtained from the ecoinvent 3.7 database. ISO 14044 demands that a check on data validity is performed through a water balance analysis based on the laws of conservation of mass for a closed system. Water balance analysis showing water uptake and release in the beneficiation process of Mn ores was done using the global Mn-dataset inventory, and the inventory for its two modified versions for Poland and Gabon (**Table 15**). The country-specific inventories were made to account for differences in hydrological conditions. This further doubled up as a sensitivity check to evaluate the reliability of the LCI results.

Table 15. LCI results for the WF inventory used for impact assessment

WF Inventory	Water balance		Change in storage	Unit
	Uptake	Release		
Global dataset	3.18×10^{-1}	3.18×10^{-1}	2.32×10^{-5}	m^3
Modified Global dataset for Poland	3.04×10^{-1}	3.04×10^{-1}	9.43×10^{-5}	m^3
Modified Global dataset for Gabon	3.73×10^{-1}	3.72×10^{-1}	9.03×10^{-4}	m^3

Water balance allows the quantification of changes in freshwater availability and use. The volume of water at any point in a hydrologic system can be viewed simply as the difference between the inflow (release) and outflow (uptake) of the system and the resulting change of storage. It was observed that the uptake was slightly higher than the release for all three inventories despite appearing to border equilibrium like a perfectly closed system when expressed in scientific notation after rounding off. The negligible values of the change in storage indicate water losses in the hydrological cycle possibly due to evapo(transpi)ration, interception, infiltration, and runoff. These results are influenced by the local climatic conditions i.e., the levels of precipitation and evapotranspiration. The Mn-dataset for Gabon had the highest value for residual water due to the rainforests and moist and hot climate typical of tropical regions. The change in storage of Poland was an order of magnitude lower and this was influenced by the temperate climate with cold winters. The global module was the least since it reflects the global average of different climatic zones ranging from arid to wet.

The detailed water balance showing all the relevant uptake and release elementary flows forming part of the WF inventory is shown in the **Tables 16** and **17,** respectively. Sea water was included as an uptake elementary flow in the inventory because it is considered a water supply alternative in several countries that use desalination technology despite the high energy demand. Exchange of moisture between the oceans and land also plays a critical role for water resource availability. According to the results in **Table 16**, the most relevant elementary flow considering all three inventories is "Water, turbine use, unspecified natural origin" which contributes more than 95% of total water, and this signifies that electric energy intensive processes (e.g., manufacturing, processing, etc.,) in general, are hotspots in WF assessment for the considered geographical locations. However, for the case study specifically, the most crucial elementary flow for WF is "Water, river" which is indicated as an input from nature in **Table 10.**

Table 16. WF inventory showing water uptake for the global dataset and modified global datasets for Poland and Gabon

Substance	**Compartment**	**Total (m^3)**		
		Global	**Poland**	**Gabon**
Water, cooling, unspecified natural origin	Raw	4.77×10^{-4}	1.03×10^{-3}	2.55×10^{-5}
Water, lake	Raw	1.19×10^{-6}	8.47×10^{-7}	8.25×10^{-7}
Water, river	Raw	1.42×10^{-3}	1.42×10^{-3}	1.41×10^{-3}
Water, salt (ocean and sole)	Raw	3.99×10^{-6}	3.94×10^{-6}	4.10×10^{-6}
Water, turbine use, unspecified natural origin	Raw	3.16×10^{-1}	3.01×10^{-1}	3.72×10^{-1}
Water, unspecified natural origin	Raw	2.48×10^{-5}	2.48×10^{-5}	2.51×10^{-5}
Water, well, in ground	Raw	9.44×10^{-6}	1.33×10^{-5}	7.14×10^{-6}
Total Water Uptake	-	3.18×10^{-1}	3.04×10^{-1}	3.73×10^{-1}

Table 17. WF inventory showing water release for the global dataset and modified global datasets for Poland and Gabon

Substance	**Compartment**	**Total (m^3)**		
		Global	**Poland**	**Gabon**
Water, all countries	Water	3.18×10^{-1}	3.04×10^{-1}	3.72×10^{-1}
Water/m^3	Air	2.82×10^{-4}	2.88×10^{-4}	2.72×10^{-4}
Total Water Release	-	3.18×10^{-1}	3.04×10^{-1}	3.72×10^{-1}

4.2. Evaluation of WF impact assessment results

Using SimaPro and case study data from the ecoinvent 3.7 database, a standalone LCA i.e., WF analysis was conducted within the defined system boundaries using the pre-selected WF methods shown in Section 3.2.3. This brought about the results shown in **Table 18** depicting the environmental burdens and/or credits associated with the beneficiation process of Mn ores on a global scale to produce 1 kg of Mn concentrate (FU). It was observed that all the WF methods generate a positive score, thus meaning the existence of environmental burdens associated with water consumed by the system.

Table 18. Total score results from SimaPro using the different WF methods with reference to 1 kg of Mn-concentrate

WF Method	Indicator	Total score with Global CF	Unit
Pfister et al. (2009)	Water stress	0.17×10^{-3}	m^3
Boulay et al. (2011b)	Water scarcity	0.12×10^{-3}	m^3
Hoekstra et al. (2012)	Blue water scarcity	0.38×10^{-3}	m^3
Berger et al. (2014)	Water depletion	0.17×10^{-3}	m^3
AWARE method (2016)	User deprivation potential	0.12×10^{-1}	m^3

The results are influenced by the global CFs (**Table 12)** of each method used for WF impact assessment. The AWARE method (2016) which indicates the user deprivation potential had a total score 2 order of magnitude higher than those of the other methods. The CF_{AWARE} value of 43 in **Table 12** signified a region where there is 43 times less water remaining per area within a certain period of time as the world average, assuming a given level of water demand. Hence, the higher final impact as compared to the other WF methods.

The Pfister et al. (2009) method and Berger et al. (2014) had the same total score due to an almost equal CF value (i.e., 0.606 and 0.592, respectively) modelled using the same hydrological data in more than 11000 basins based on WaterGAP2 global model and fitted on a logistic function (S-curve) to achieve values between 0.01 and 1.00, notwithstanding the different indicators (i.e., water stress and water depletion respectively).

The Boulay et al. (2011b) method showed the lowest total score because the inventory procedure integrates the functionality of withdrawn and released water based on quality, the released water and its corresponding functionalities are considered to be returned to the environment, avoiding an overestimation of the potential impacts by considering that the water was consumed.

The Hoekstra et al. (2012) method with blue water scarcity result less than 100% signified a low blue water scarcity globally, and that the presumptive environmental flow requirements specified by Richter et al. (2011) are not violated i.e., the blue WF is lower than 20% of natural runoff and does not exceed blue water availability.

Additionally, a hotspot analysis was conducted to determine the most relevant unit processes contributing to WF. This helps decision makers to pinpoint the activity where they should focus their attention in order to improve the environmental sustainability of the studied system. In this case study, the result of the hotspot analysis for the AWARE method (2016) is shown in **Figure 8**, and it revealed that the most relevant WF hotspots contributing more than 80% cumulatively are as summarized in **Table 19**. These impacts are associated with the input from nature of water, river, GLO as in **Table 10,** consumed during the process. The single most important WF hotspot considering the reference set up was the “Manganese concentrate {GLO}| production” process contributing 75% to WF according to the hotspot analysis.

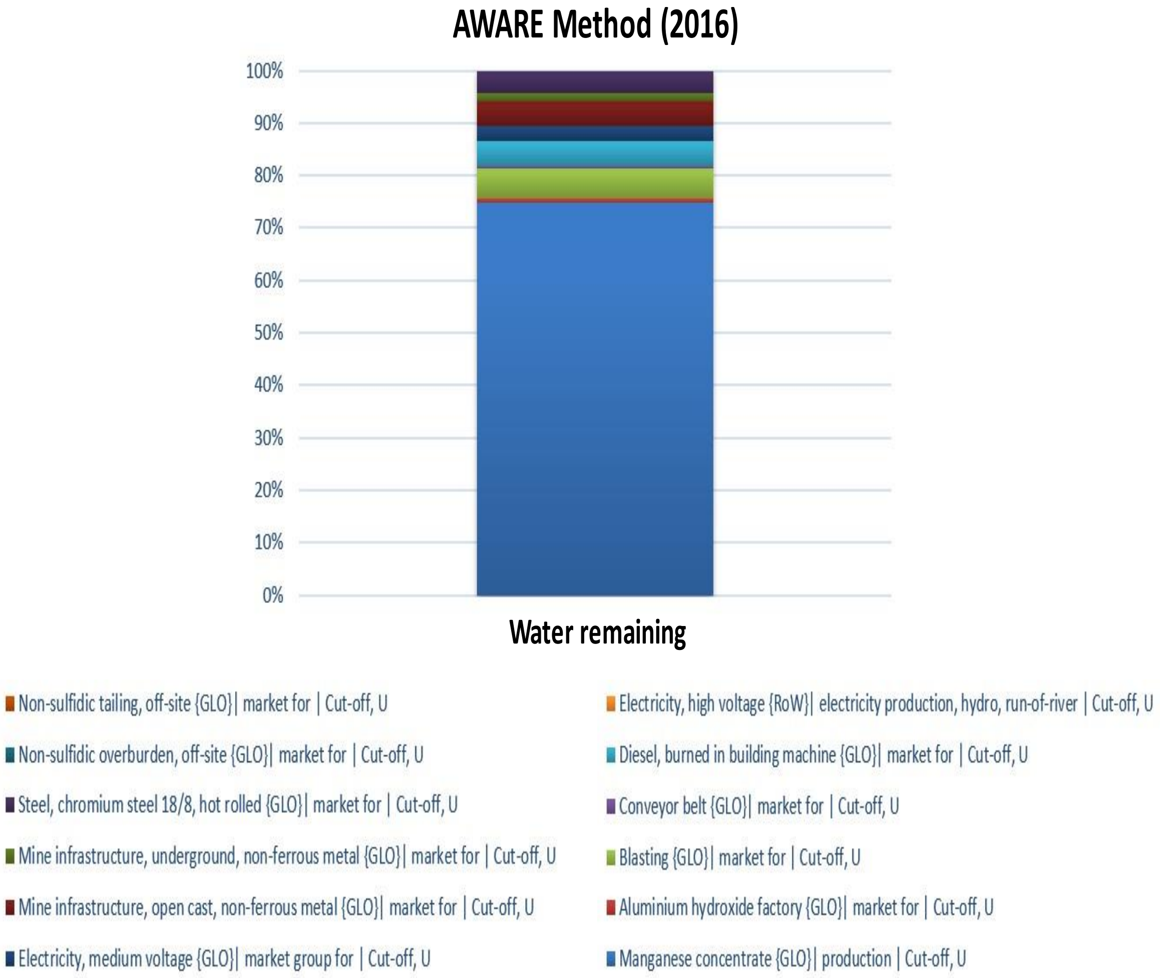

Figure 8. Results from the hotspot analysis of the AWARE Method (2016) considering the reference set up

Table 19. Summary of the most relevant WF hotspots considering the reference set up

Most relevant WF hotspot	**Contribution to WF (%)**
Manganese concentrate {GLO}| production	75
Blasting {GLO}	6
Diesel, burned in building machine {GLO}	5
Mine infrastructure, open cast, non-ferrous metal {GLO}	5
TOTAL	**91**

The results from the AWARE method (2016) was selected to illustrate the hotspot analysis because it is the most recent method based on the WULCA consensus accounting for both human and ecosystem water needs. However, the findings from the WF analysis of the other 4 methods used for WF assessment all followed the same pattern as for the AWARE method (2016), as portrayed in **Figure 9.** This validates the results generated from the WF impact assessment of the case study.

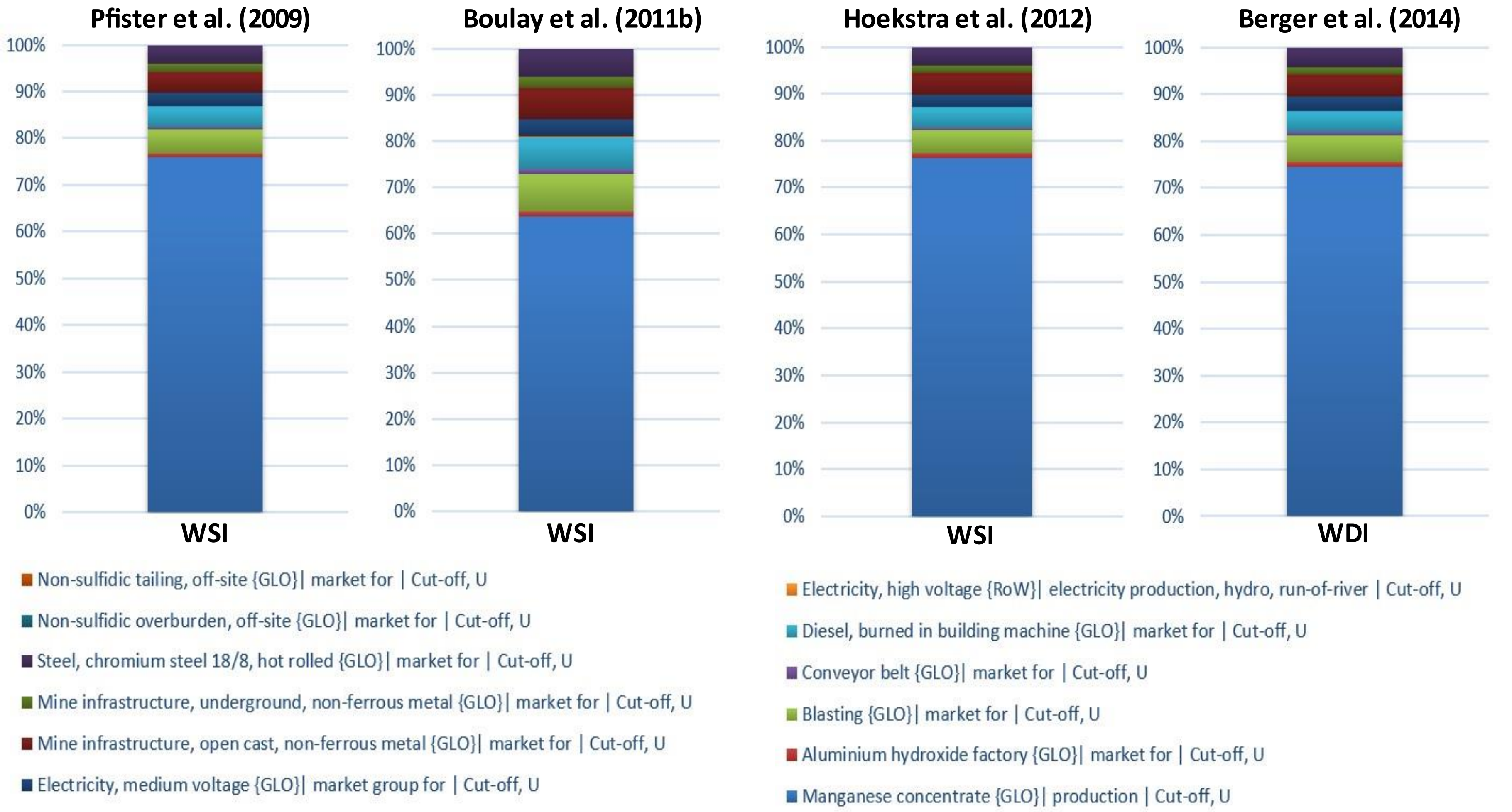

Figure 9. Results from the hotspot analysis of the Pfister et al. (2009), Boulay et al. (2011b), Hoekstra et al. (2012), and Berger et al. (2014) methods considering the reference set up

4.3 Sensitivity analysis

Sensitivity analysis was performed to assess the variation and reliability of the acquired WF results using different calculation set ups. For the sensitivity analysis carried out in this study, three (3) different calculation set ups were chosen including a reference set up. The details of each calculation set up are clearly explained in **Table 9.** A detailed characterized result of WF LCIA for Poland and Gabon using the 5 WF methods and the 3 calculation setups are shown in **Table 20.** This was done to determine the influence of different geographical locations on WF. Results for the reference set up was already deeply analysed in **section 4.2** and the results considering the first and second set up are analysed in **sections 4.3.1 and 4.3.2,** respectively.

Table 20. Sensitivity analysis results from the three different calculation set ups with reference to 1 kg of Mn-concentrate

WF methods	**Reference set up**	**First set up**		**Second set up**	
	Global (m^3)	**Poland (m^3)**	**Gabon (m^3)**	**Poland (m^3)**	**Gabon (m^3)**
Pfister et al. (2009)	0.17×10^{-3}	0.59×10^{-4}	0.38×10^{-4}	0.58×10^{-4}	0.37×10^{-4}
Boulay et al. (2011b)	0.12×10^{-3}	0.48×10^{-4}	0.40×10^{-4}	0.47×10^{-4}	0.39×10^{-4}
Hoekstra et al. (2012)	0.38×10^{-3}	0.16×10^{-3}	0.82×10^{-4}	0.16×10^{-3}	0.79×10^{-4}
Berger et al. (2014)	0.17×10^{-3}	0.52×10^{-4}	0.41×10^{-4}	0.51×10^{-4}	0.40×10^{-4}
AWARE method (2016)	0.12×10^{-1}	0.35×10^{-2}	0.30×10^{-2}	0.34×10^{-2}	0.29×10^{-2}

4.3.1 First calculation set up

Results of the WF analysis (**Table 20**) considering the first set up indicated a positive score for all the WF methods in both Poland and Gabon. This meant that there were environmental burdens associated with the beneficiation process of Mn ores. There was no single important WF hotspot like in the reference set up, rather different WF contributions from several subprocesses that are uniquely concatenated. These impacts are associated with the consumption of the input from nature of “water, river, PL”, and “water, river, GA”, considering Poland and Gabon, respectively. However, the impacts in both Poland and Gabon were lower than that of the global reference set up despite using global CFs for impact assessment. This is because using country-specific LCI data accounts for strictly the local climatic and hydrologic conditions, whereas the global LCI is an average of different climatic conditions ranging from wet to arid.

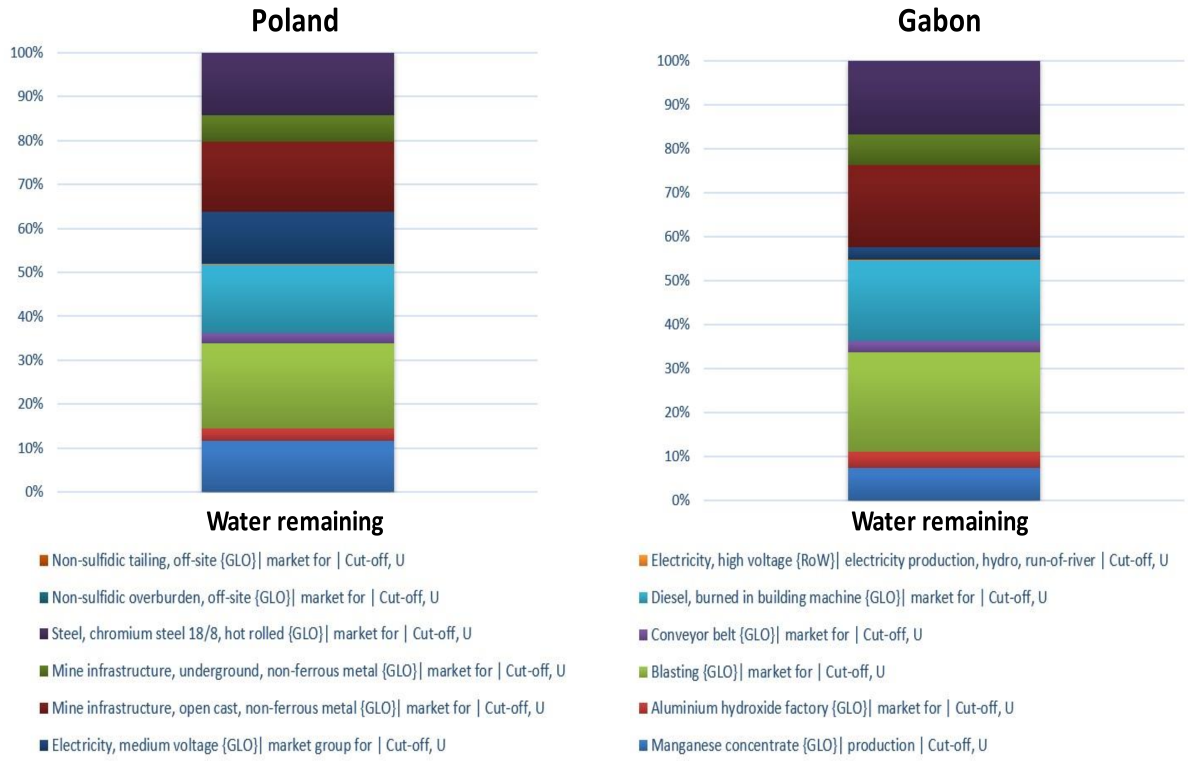

Figure 10. Results from the hotspot analysis of the AWARE Method (2016) comparing Poland and Gabon considering the first set up

The WF results from comparing Poland and Gabon revealed that the impacts in Poland were slightly higher than in Gabon despite using the same global CFs for impact assessment. This can be attributed to the differences in water balance data. **Figure 10** shows the contribution analysis considering the AWARE method: from that the most relevant WF hotspots for Poland and Gabon were identified and summarized below in **Table 21.**

Table 21. Summary of the most relevant WF hotspots for Poland and Gabon considering the first calculation set up

Most relevant WF hotspot	**Contribution to WF (%)**	
	Poland	**Gabon**
Manganese concentrate {GLO}| production	12	8
Blasting {GLO}	19	23
Diesel, burned in building machine {GLO}	16	18
Electricity, medium voltage {PL}	12	-
Mine infrastructure, open cast, non-ferrous metal {GLO}	16	19
Steel, chromium steel 18/8, hot rolled {GLO}	14	17
TOTAL	**89**	**85**

The results of the other four methods used for WF assessment followed the patterns as shown in **Figures 11** and **12** for Poland and Gabon, respectively.

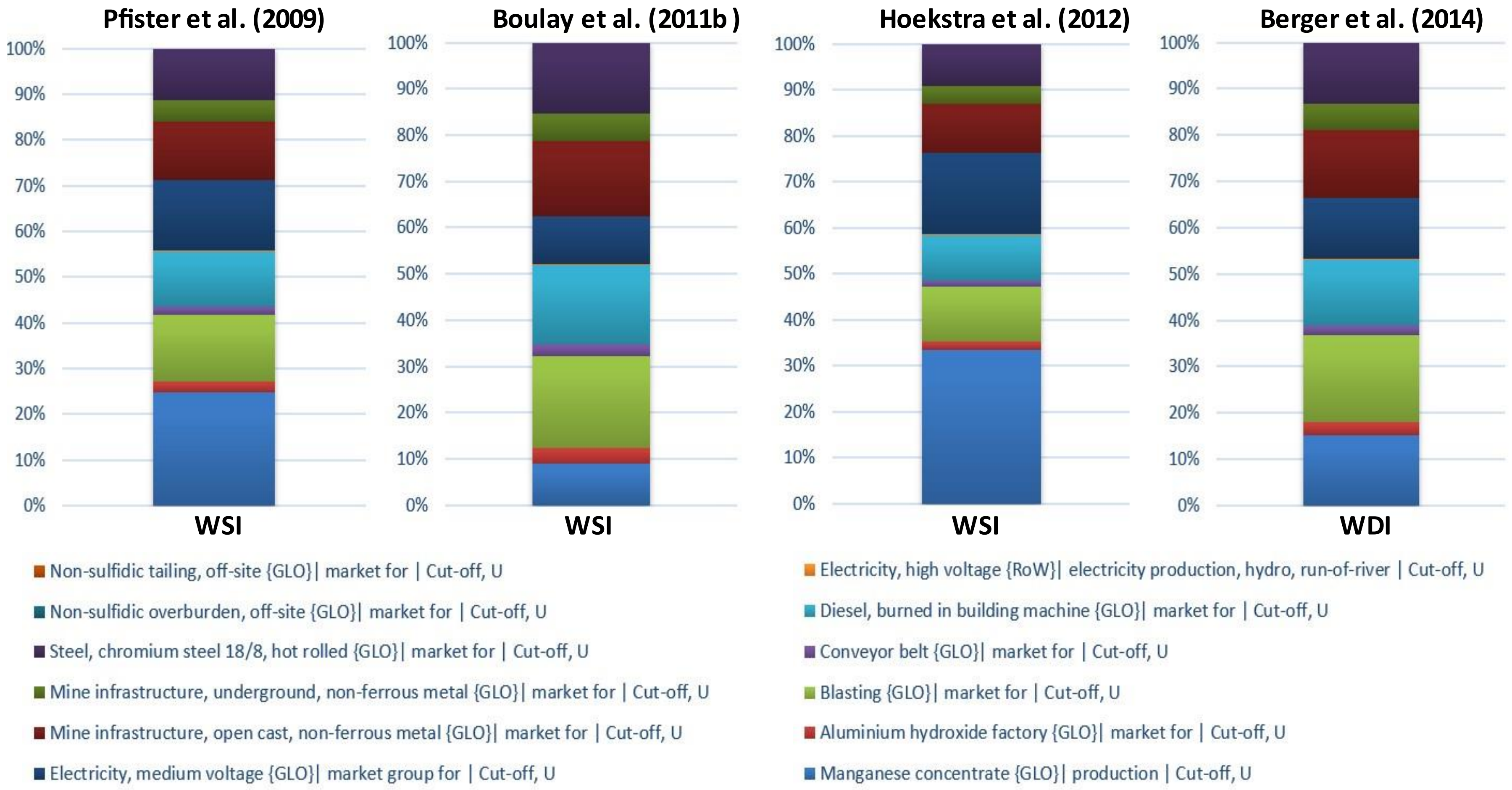

Figure 11. Results from the hotspot analysis of the Pfister et al. (2009), Boulay et al. (2011b), Hoekstra et al. (2012), and Berger et al. (2014) methods for Poland considering the first set up

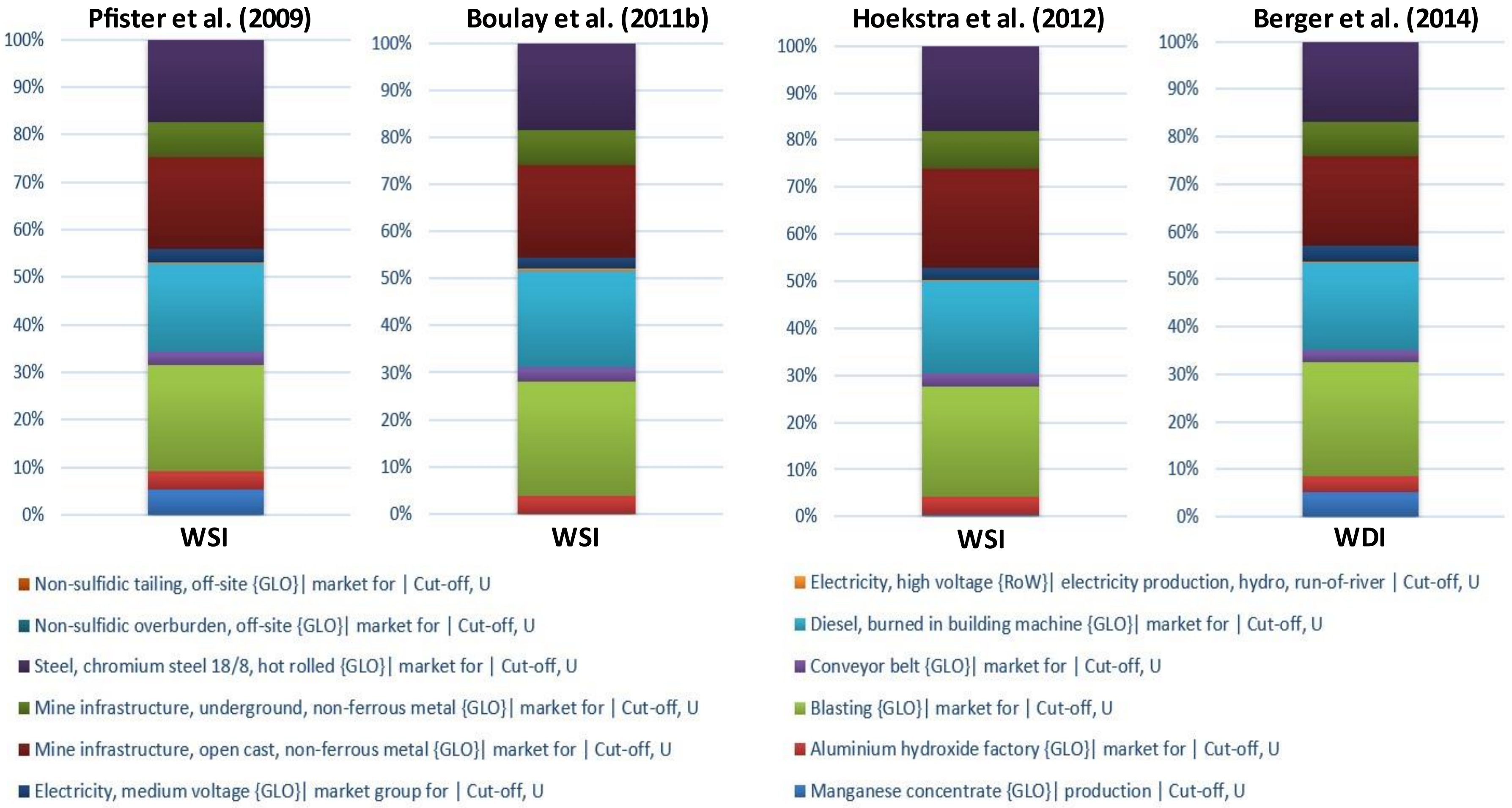

Figure 12. Results from the hotspot analysis of the Pfister et al. (2009), Boulay et al. (2011b), Hoekstra et al. (2012), and Berger et al. (2014) methods for Gabon considering the first set up

4.3.2 Second calculation set up

Comparing results between Poland and Gabon for the second calculation set up **(Table 20)** revealed a difference in the WF levels (as in the first calculation set up) because the impacts of water use, and consumption strongly depend on the region and its hydrological conditions. Notwithstanding the similarity in the pattern, the results from the second set up were slightly lower than those in the first calculation set up due to difference in the CFs used for impact assessment i.e., global CFs in the first set up and country specific CFs in the second set up. These impacts are again associated with the consumption of the input from nature of "water, river, PL", and "water, river, GA", considering Poland and Gabon, respectively.

Comparing the two countries, the results of WF impacts in Poland when applying the AWARE method were higher than in Gabon. This was because of the CFs used i.e., 1.96 and 1.09 as in **Tables 13** and **14** to account for the local climatic conditions of Poland and Gabon, respectively.

Figure 13 shows results from the hotspot analysis of the AWARE Method (2016) comparing Poland and Gabon considering the second set up.

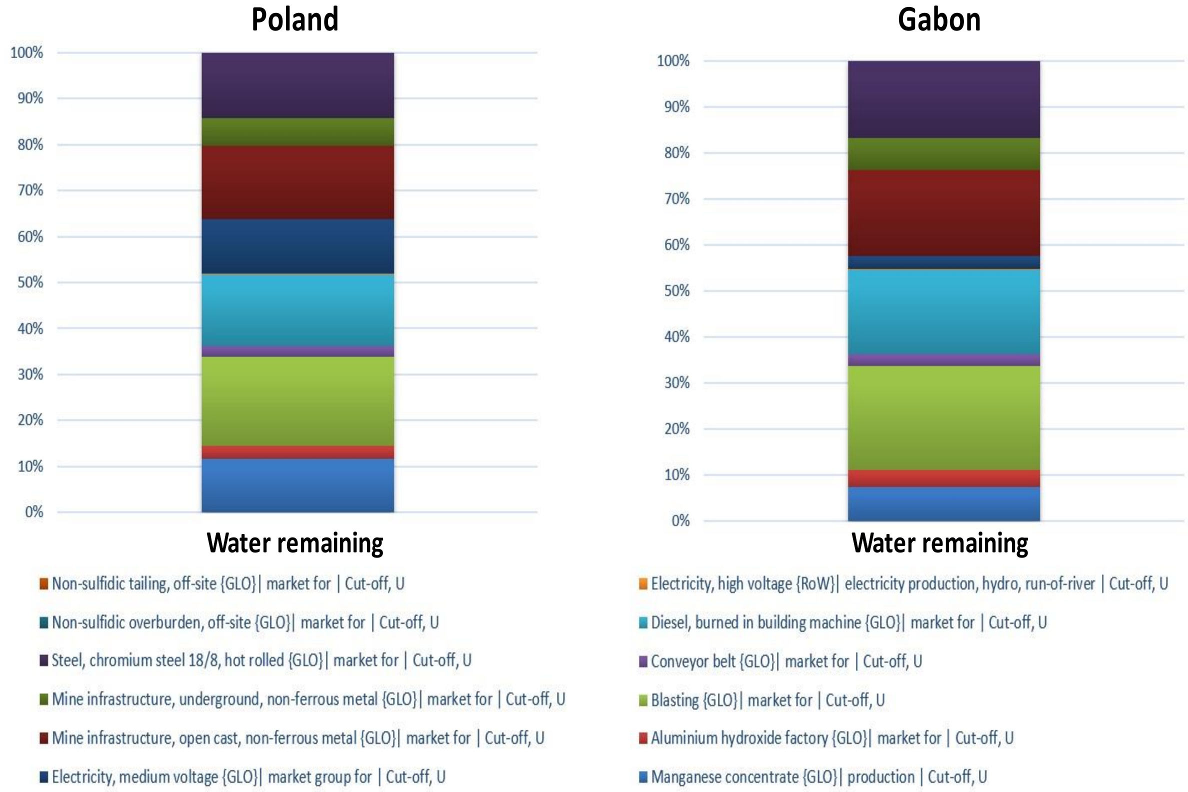

Figure 13. Results from the hotspot analysis of the AWARE Method (2016) comparing Poland and Gabon considering the second set up

From **Figure 13,** the most relevant processes (hotspots) contributing cumulatively more than 80% to WF for Poland and Gabon are listed in **Table 22.** The hotspots were found to be the same to the ones in the first calculation set up with slight variations in the percentages of contribution to WF.

Table 22. Summary of the most relevant WF hotspots for Poland and Gabon considering the second calculation set up

Most relevant WF hotspot	**Contribution to WF (%)**	
	Poland	**Gabon**
Manganese concentrate {GLO}| production	12	8
Blasting {GLO}	20	23
Diesel, burned in building machine {GLO}	17	20
Electricity, medium voltage {PL}	12	-
Mine infrastructure, open cast, non-ferrous metal {GLO}	16	19
Steel, chromium steel 18/8, hot rolled {GLO}	12	14
TOTAL	**89**	**84**

The results of the other four methods used for WF assessment followed a similar pattern to those in the first calculation set up (i.e., **Figures 11** and **12**), as shown in **Figures 14** and **15** for Poland and Gabon, respectively. The results of the different WF methods were influenced by their country-specific CFs as in **Tables 13** and **14,** for Poland and Gabon, respectively.

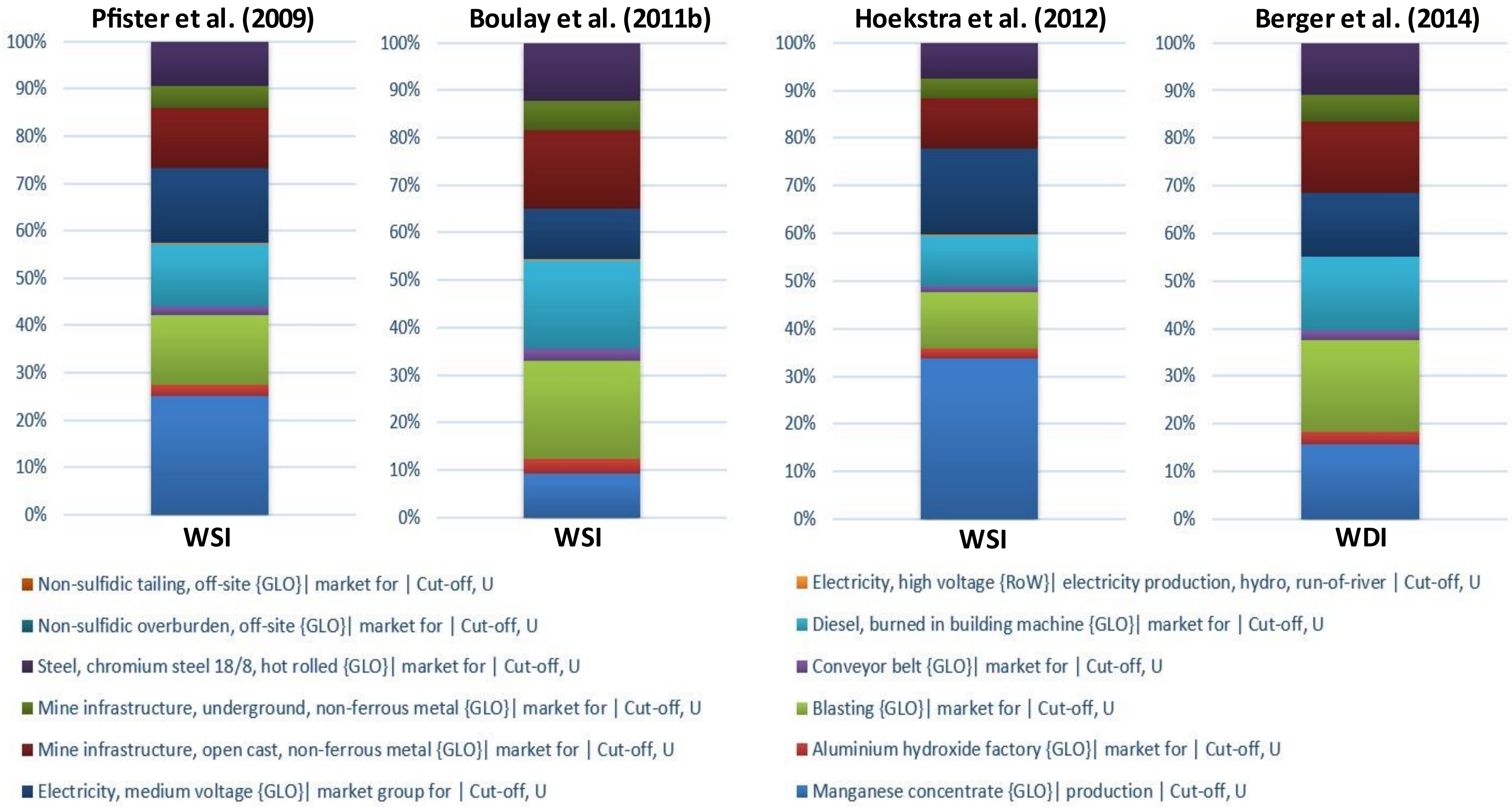

Figure 14. Results from the hotspot analysis of the Pfister et al. (2009), Boulay et al. (2011b), Hoekstra et al. (2012), and Berger et al. (2014) methods for Poland considering the second set up

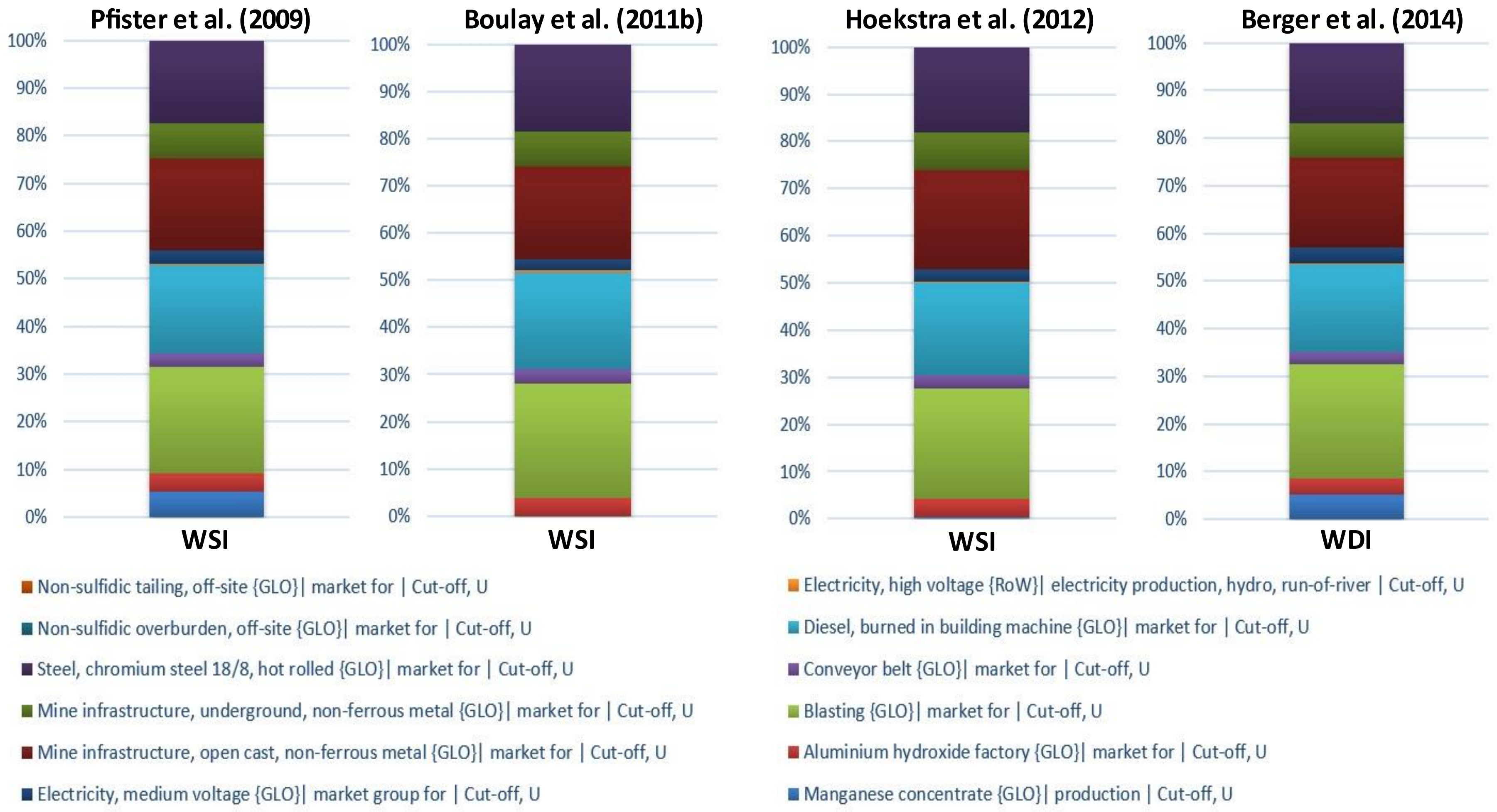

Figure 15. Results from the hotspot analysis of the Pfister et al. (2009), Boulay et al. (2011b), Hoekstra et al. (2012), and Berger et al. (2014) methods for Gabon considering the second set up

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study on the WF concept was conducted in two parts. The main aim of the first part was to conduct a thorough review of WF methods and summarize them in a tabular format by considering the fundamental elements, thereafter, select a few methods for case study application. The notable aims of the second part of this study were to analyse the WF associated with the beneficiation process of Mn ores as a case study, identify the major hotspots behind the environmental impact, and recommend possible avenues for further development.

In this thesis, 5 different WF methods were applied to the case study of the beneficiation process of Mn ores to understand how the results would behave. However, the WF methods only tested for freshwater impacts since CFs for seawater were not available. The impacts of water use were then analysed, and the WF hotspots identified. The results from the WF analysis from the different WF methods followed a consistent pattern despite the differences in modelling choices and CFs, and this validated the findings.

The results from the AWARE method (2016) were used to discuss the findings and compare the spatial variation of results considering Poland and Gabon since it was the easiest to understand, and the method was developed most recently after the WULCA consensus. The single most important WF hotspot considering the reference set up i.e., globally was found to be the “Manganese concentrate {GLO}| production” process. The impacts of this WF hotspots were mainly due to the direct water use from the input from nature “water, river, GLO”.

Furthermore, a sensitivity analysis was conducted by considering two different set ups. Results of the WF analysis considering the first set up indicated the environmental burdens associated with several subprocesses of the beneficiation process of Mn ores. These impacts are associated with the consumption of the input from nature of “water, river, PL”, and “water, river, GA”, considering Poland and Gabon, respectively. However, the impacts in both Poland and Gabon were lower than that of the reference set up despite using global CFs for impact assessment.

Results from the second set up followed a similar pattern to those from the first set up with no single important WF hotspot contribution as in the reference set up, rather contributions from subprocesses. However, the results were slightly lower than those in the first calculation set up due to difference in the CFs used for impact assessment i.e., global CFs in the first set up and country-specific CFs in the second set up. In a nutshell, impacts of WF in Poland were higher than in Gabon due to variations in climatic conditions and amounts of water available.

5.2 Recommendations

Considering that the results of WF analysis from the case study using different WF methods can allow for more improvements, future developments and research should consider:

- The development of CFs for seawater because it is already being used as an alternative water supply source in many parts of the world through desalination technologies. It would therefore be prudent to understand the impacts associated with that.
- The WF analysis of other countries with different climatic conditions e.g., in South America, Australia, or Asia to understand better the variations of results for all the studied climatic and hydrological conditions
- The integration of renewable energy generation resources in the beneficiation process of Mn ores to reduce on the high impacts associated with energy consumption, which in turn reduces the impacts on water use.
- The comparison of WF analysis results with the impacts associated with other impact categories e.g., land use, climate change, etc, to understand the relative importance of each impact category in the beneficiation process of Mn ores.

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