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ENERGETICA**

Water consumption in industrial and energy processes

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Index

Introduction

1. Water footprint

- 1.1 *Water footprint assessment..... pg 6*
- 1.2 *Goal and scope of water footprint assessment..... pg 6*
- 1.3 *Accounting..... pg9*
 - 1.3.1 *Water footprint of a product..... pg 11*
 - 1.3.2 *Water footprint of a business..... pg 13*
- 1.4 *Sustainability assessment..... pg 14*
 - 1.4.1 *Geographical assessment..... pg 15*
 - 1.4.2 *Sustainability of a process and a product..... pg 17*

2. Water saving solutions

- 2.1 *Textile sector..... pg 18*
- 2.2 *Steel and metals industries..... pg 20*
- 2.3 *Paper industry..... pg 24*
- 2.4 *Cooling systems..... pg 26*

3. Water pinch analysis

- 3.1 *Introduction to water pinch analysis..... pg 28*
- 3.2 *Water pinch analysis implementation..... pg 28*
 - 3.2.1 *Water flowrate determination..... pg 29*
 - 3.2.2 *Contaminant concentration determination..... pg 29*
 - 3.2.3 *Data extraction..... pg 30*
- 3.3 *Maximum water recovery targets..... pg 30*
 - 3.3.1 *MWR target for a single pure freshwater source..... pg 32*

3.3.2	<i>MWR target for a single impure freshwater source...</i>	<i>pg 35</i>
3.3.3	<i>MWR target for multiple freshwater sources.....</i>	<i>pg 35</i>
3.4	<i>Water network design/ retrofit.....</i>	<i>pg 36</i>
3.4.1	<i>Source/ sink mapping diagram (SSMD).....</i>	<i>pg 36</i>
3.4.2	<i>Source and sink allocation curves (SSAC).....</i>	<i>pg 37</i>
3.5	<i>Comparison and parallels with heat pinch analysis.....</i>	<i>pg 38</i>
3.5.1	<i>Composite curves.....</i>	<i>pg 38</i>
3.5.2	<i>Problem table.....</i>	<i>pg 39</i>
3.6	<i>Water pinch analysis of a cooling network.....</i>	<i>pg 39</i>

4. Water footprint of the energy sector

4.1	<i>Italian energy sector.....</i>	<i>pg 43</i>
4.1.1	<i>Method and critical points of the study.....</i>	<i>pg 43</i>
4.1.2	<i>Method application to the Italian energy sector.....</i>	<i>pg 45</i>
4.1.3	<i>Inventory phase.....</i>	<i>pg 46</i>
4.1.4	<i>Impact evaluation.....</i>	<i>pg 49</i>
4.2	<i>European energy sector.....</i>	<i>pg 51</i>
4.2.1	<i>Inventory phase.....</i>	<i>pg 52</i>
4.2.2	<i>Impact evaluation.....</i>	<i>pg 53</i>

5. Future prospects: water footprint of hydrogen production

5.1	<i>Introduction.....</i>	<i>pg 55</i>
5.2	<i>Hydrogen production methods.....</i>	<i>pg 56</i>
5.2.1	<i>Water footprint of hydrogen production: gasification</i>	<i>pg 61</i>
5.2.2	<i>Water footprint of hydrogen production: electrolysis</i>	<i>pg 65</i>
5.2.3	<i>Water footprint of electrolysis: SIMAPRO analysis...</i>	<i>pg 71</i>

Conclusions

Bibliography

Introduction

The subject of water usage and consumption, while it was always considered important, has not gained as much attention as it has recently. This is due, mostly, to the extreme changes in climate that the world is experiencing, with dramatic temperature increase and subsequent droughts. As a matter of fact, Europe, and Italy in particular, have suffered an extremely dry summer in 2022 leading to an array of issues, ranging from crop and cattle production to industrial and energy sectors. That is because water is an extremely valuable and indispensable resource for human activities and its misuse or overuse can lead to a negative chain reaction in the economy of a nation. Considering just the industrial sector, water is an essential component in the processing of many products: chemicals, fuels, steel, plastics, textile products, paper, etc. and such industries require electricity to operate, especially energy intensive sectors like metal works. The production of electricity is tied with water consumption as well, since fossil fuel powered plants use it for cooling, nuclear plants for moderation of the core and cooling and even some renewable sources make extensive use of water (namely hydroelectric and geothermal plants). A lack of water will lead to a lack of electric energy as these plants won't meet the required conditions for cooling or production therefore shutting down, thus weighing down all the industries highly dependent on electricity. Naturally, preserving water resources is also a matter of humanitarian concerns. Precisely for this reason, finding solutions to reduce the consumption and the footprint of the industrial sector can only be beneficial even in that matter, since the amount of available fresh water would, potentially, increase or, at the very least, be preserved within acceptable boundaries.

The objective of this thesis is to tackle this issue and explore the current situation for a few major water intensive industrial sectors, analysing their water consumption and impact, presenting case studies for potential solutions and observing how such implementations affect the overall impact on the industry, their feasibility and potential issues that come from implementing a system instead of another, especially since some are more on an experimental level and not yet commercially mature.

The first part of this thesis will explain the concept of water footprint and what it entails, explaining the differences between its three main components, as well as the relevant equations for calculating it for a singular product, a whole business and their sustainability, and then delving into some of the main industries that have a great impact on water (high consumption, due to cooling, incorporating it into the product and/or great indirect use, tied to the energy used by the plant, as well as contamination that

prevents the water from returning entirely into the environment). These industries are mostly tied to modern consumer goods, like paper, textile and electronics, and many more could've been included, however time constraints demanded a select choice and as such, alongside these sectors, another two water intensive processes were selected, namely steel production and cooling via cooling towers. The energy sector is also highly water intensive, especially considering fossil fuel powered plants and some green energy power plants, as previously said, and so it will be treated more at length further down the line, in the second part of this thesis. Said part will also include an introduction to water pinch analysis as a general method that can be applied, potentially, to any sector that we wish to optimise in regards to water consumption and impact, with the most natural application being water cooling networks, since there're a lot of similarities with the thermal pinch analysis that is conducted for heat exchangers networks (HENs).

Finally, in the last part of the thesis, a brief analysis on hydrogen production is presented, with case studies and also an investigation conducted using SIMAPRO software in the university. This section is potentially the most interesting on a water and energy perspective as the future economy is shifting to greener options as well as less impacting on the water resources, given the high potential of hydrogen in such a scenario.

1. Water footprint

1.1 Water footprint assessment

The water footprint is an indicator of freshwater use, accounting for both direct and indirect use, showing water consumption and pollution by source/type of pollutants specified by time and geographical area. The water footprint assessment is about quantifying the water consumption of a process/product, producer/consumer, in a specific time and/or geographical area, establishing the impact on the environment of said consumption and finally formulate a response in this regard [1].

To achieve this, the assessment follows four steps:

- Setting goal and scope
- Accounting
- Sustainability assessment
- Response

1.2 Goal and scope of water footprint assessment

The goals of the assessment are numerous and can be applied to different situations and contexts, each requiring its own scope of analysis: water footprint of a process, a product, a consumer (or group thereof, or localised in a specific geographical area), a specific location, an industry (or a whole industrial sector), etc.

The following checklist can be used as guidance in specifying the goal of the analysis [1].

General

- What is the ultimate target? Awareness-raising, hotspot identification, policy formulation or quantitative target setting?
- Is there a focus on one particular phase? Focus on accounting, sustainability assessment or response formulation?
- What is the scope of interest? Direct and/or indirect water footprint? Green, blue and/or grey water footprint?
- How to deal with time? Aiming at assessment for one particular year or at the average over a few years, or trend analysis?

Process water footprint assessment

- What process to consider? One specific process or alternative, substitutable processes (in order to compare the water footprints of alternative techniques)?
- What scale? One specific process in a specific location or the same process in different locations?

Product water footprint assessment

- What product to consider? One stock-keeping unit of a particular brand, one particular sort of product or a whole product category?
- What scale? Include product(s) from one field or factory, one or more companies or one or more production regions?

Consumer or community water footprint assessment

- Which community? One individual consumer or the consumers within a municipality, province or state?

Assessment of the water footprint within a geographically delineated area

- What are the area boundaries? A catchment, river basin, municipality, province, state or nation?

- What is the field of interest? Examine how the water footprint within the area is reduced by importing virtual water and how the water footprint within the area is increased by making products for export, analyse how the area's water resources are allocated over various purposes, and/or examine where the water footprint within the area violates local environmental flow requirements and ambient water quality standards?

National water footprint assessment (water footprint within a nation and water footprint of national consumption)

- What is the scope of interest? Assess the water footprint within a nation and/or the water footprint of national consumption? Analyse the internal and/or the external water footprint of national consumption?
- What is the field of interest? Assess national water scarcity, sustainability of national production, export of scarce water resources in virtual form, national water saving by import of water in virtual form, sustainability of national consumption, impacts of the water footprint of national consumption in other countries and/or dependency on foreign water resources?

Business water footprint assessment

- What is the scale of study? A company unit, whole company or a whole sector? (When the scale of interest is the product level, see above under product water footprint assessment.)
- What is the scope of interest? Assess the operational and/or the supply chain water footprint?
- What is the field of interest? Business risk, product transparency, corporate environmental reporting, product labelling, benchmarking, business certification, identification of critical water footprint components, formulation of quantitative reduction targets?

Fig. 1.1 Water footprint checklist for guidance [1].

Once the goal has been defined, the scope of the accounting should be addressed. The inventory boundaries must be clearly defined depending on the study, choosing to include or exclude the different types of footprint (blue, green, grey), where to stop in the supply chain, the spatiotemporal application and period of data.

As to where to stop along the supply chain, the general rule of thumb is to include all processes that contribute significantly to the water footprint (agricultural and industrial products have a significant contribution). The spatiotemporal application is divided in various levels based on the detail: global average from database, national level, regional level, water basin level, etc.

The next step is the scope of the sustainability assessment, which can be made on a geographical perspective or from the product, process, consumer, producer perspective. The first is the sustainability of the total footprint within the defined area, while the latter is the sustainability of the individual contribution.

1.3 Accounting

While it's true that the global water cycle always has a positive balance, with freshwater on land being constantly replenished, the availability is not infinite: the yearly consumption for anthropic uses cannot exceed the replenishment rate. The water footprint expresses the volume that is consumed for human activities and the basic unit for any accounting is the footprint of a process step, the sum of which will return the overall footprint of a process or a product [1].

- The water footprint of a product = the sum of the water footprints of the process steps taken to produce the product (considering the whole production and supply chain).
- The water footprint of a consumer = the sum of the water footprints of all products consumed by the consumer.
- The water footprint of a community = the sum of the water footprints of its members.
- The water footprint of national consumption = the sum of the water footprints of its inhabitants.
- The water footprint of a business = the sum of the water footprints of the final products that the business produces.
- The water footprint within a geographically delineated area (for example, a municipality, province, state, nation, catchment or river basin) = the sum of the process water footprints of all processes taking place in the area.

Fig. 1.2 Definitions of water footprint on different scale levels [1].

Within the footprint of a process step, one can distinguish three separate water footprints based on the origin of the water: blue, green and grey:

Blue water footprint expresses the consumption of freshwater (surface and groundwater), happening in one of the following ways:

- Evaporation
- Incorporation in the product
- Return to a different catchment area
- Return in a different time period

Evaporation is the most relevant and common component, however in some cases the other three must be accounted for. Evaporation refers to all evaporating water during the process considered, from storage and transport to the actual processing and disposal. The blue water footprint is calculated as follows:

$$WF_{process_{blue}} = Evaporation_{blue} + Incorporation_{blue} + Return_{lost}$$

The last component refers to the water that is not available for reuse within the same catchment area either because it was returned in a different time, or because it was returned to a different area. On the subject of reuse and recycle, the recycle refers to using the water on site for the same purpose, while reuse can be done elsewhere. The reduction of blue water footprint by reuse and/or recycle is instrumental when there's an actual decrease in water consumption.

Green water footprint expresses the use of green water, which is the precipitation that is not run off or replenishing the blue water sources, but is temporarily stored on the soil or within it. This indicator is particularly important for agriculture and forestry, as rainwater is an important resource for these two sectors, while it's less relevant (if relevant at all) for industrial use.

Grey water footprint is expressed the degree of freshwater pollution of the process step and it's a little different compared to the other indicators, in the fact that it's not a direct measurement of polluted water, but rather the quantity of freshwater needed to absorb the contaminants and keep their concentration below certain levels defined by laws and norms.

The grey water footprint is calculated by dividing the pollutant load by the difference between the water quality standard (maximum acceptable value of pollutant in the water) and its natural concentration, for that pollutant:

$$WF_{process_{grey}} = \frac{Load}{C_{max} - C_{nat}}$$

The most common threshold considered for pollutants in the water is drinking water quality, therefore keeping concentrations to a level where water is still considered drinkable.

A more accurate calculation can be done if there's a direct release of chemicals in the water through an effluent. Water recycling and reuse can have an impact on the grey water footprint as well as there is potentially no effluent released in the environment, even though reused/recycled water will be returned at some point, so the most likely event is a reduction in the effluent. Similarly, but in an opposite way, evaporation can become a source of pollution: as the water quantity is reduced, the concentration of the pollutants will increase, thus it's equivalent to adding a certain quantity of the pollutants [1].

1.3.1 Water footprint of a product

The water footprint of a product is the total amount of freshwater that is consumed both directly and indirectly, considering the whole production chain, to make said product. It can be measured in m³/€ or m³/piece and it breaks down into the three main components that have been explored above. To establish the WF of a product it's important to understand how it's made, identifying its production system and the process steps that make said system. Usually, a production system will involve multiple inputs and process steps, so it won't be a linear chain, but more like a process tree or even a circular one. For this reason, it's necessary to limit the process steps, by choosing the most relevant ones.

The calculation of the WF of a product can be done in two ways: chain-summation and stepwise accumulative approaches. While the former is simpler it's restricted to a process with a single output product:

$$WF_{prod}[p] = \frac{\sum_{s=1}^k WF_{process}[s]}{P[p]}$$

Where $[s]$ is the step, $[p]$ is the product and P is the production quantity [1].

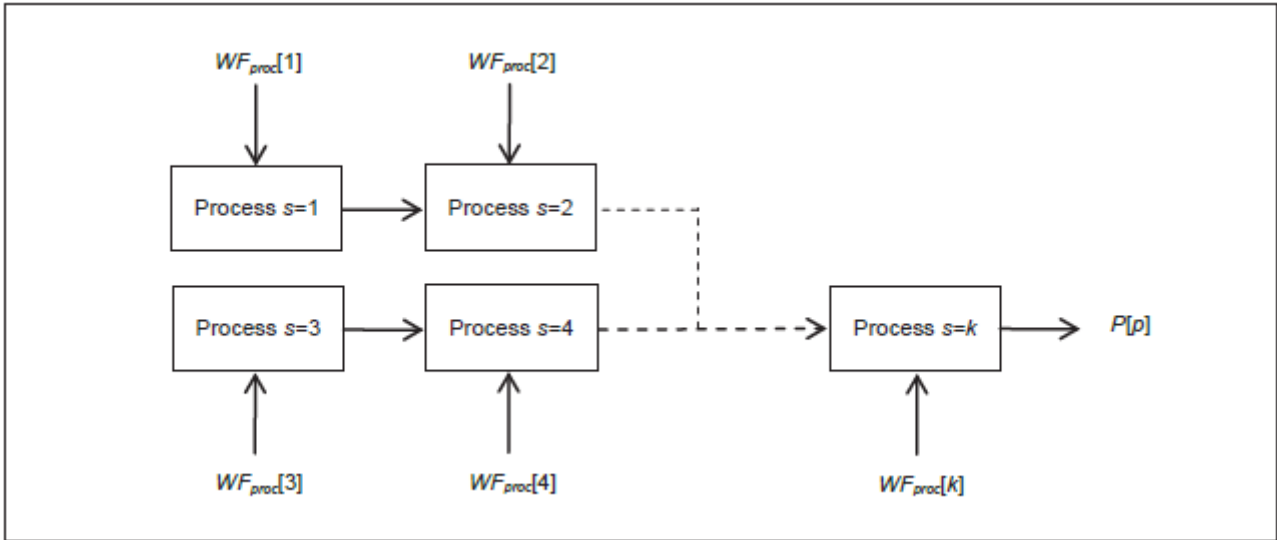


Fig. 1.3 Scheme of production of product p from k process steps (chain-summation) [1].

The stepwise accumulative approach, on the other hand, is a generic calculation method using the WF of inputs used in previous steps and the WF of the step.

$$WF_{prod}[p] = (WF_{process}[p] + \sum_{i=1}^y \frac{WF_{prod}[i]}{f_p[p, i]}) \cdot f_v[p]$$

With

$$f_p[p, i] = \frac{w[p]}{w[i]}$$

Where w is the quantity (mass), and

$$f_v[p] = \frac{price[p] \cdot w[p]}{\sum_{p=1}^z (price[p] \cdot w[p])}$$

That are respectively the product fraction and the value fraction [1].

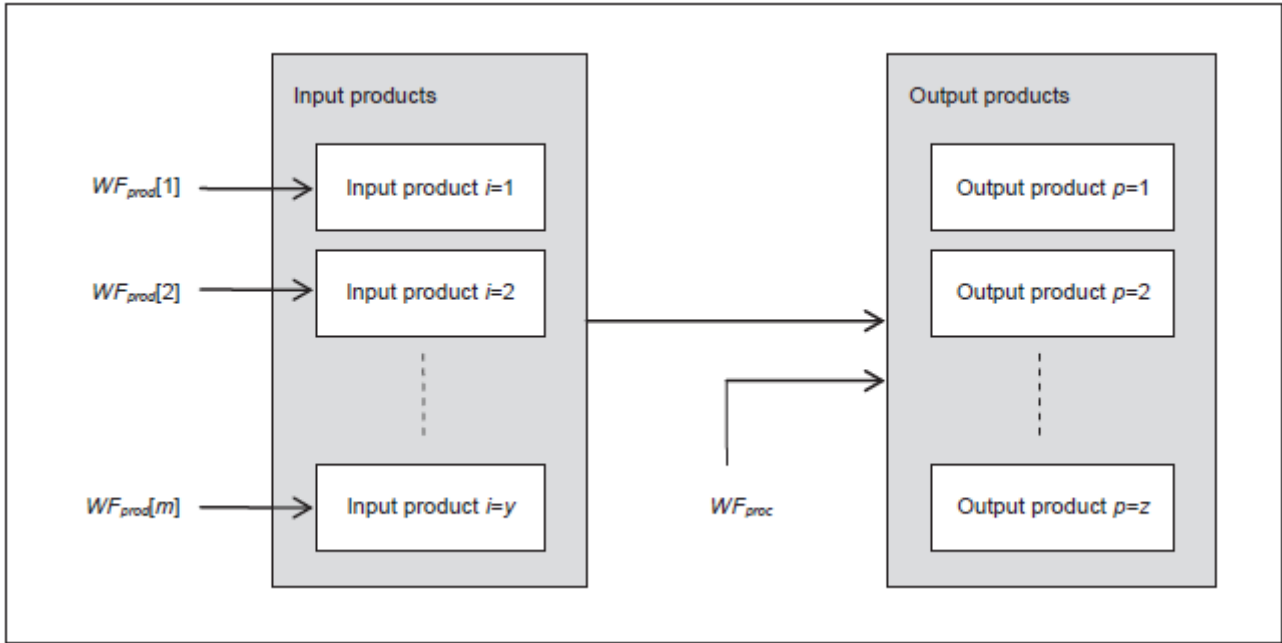


Fig. 1.4 Last process step to obtain product p (stepwise accumulative approach) [1].

1.3.2 Water footprint of a business

The WF of a business is defined as the total quantity of freshwater consumed directly and indirectly to run the business in question. It is divided into two main components, an operational (direct, water consumed or polluted by the business operation) WF and a supply chain (indirect, water consumed or polluted in making the goods and services in input) WF. The business WF is also divided into the three main water components previously mentioned and is, essentially, the sum of the WF of all the products of said business plus their inputs. To correctly assess it, the boundaries of the business must be specified clearly.

$$WF_{business} = WF_{bus,op} + WF_{bus,sup}$$

$$WF_{bus,op} = WF_{op,input} + WF_{op,overhead}$$

$$WF_{bus,sup} = WF_{sup,input} + WF_{sup,overhead}$$

Where overhead refers to the necessary water consumption to keep the business going, not directly related to the production of a particular product [1].

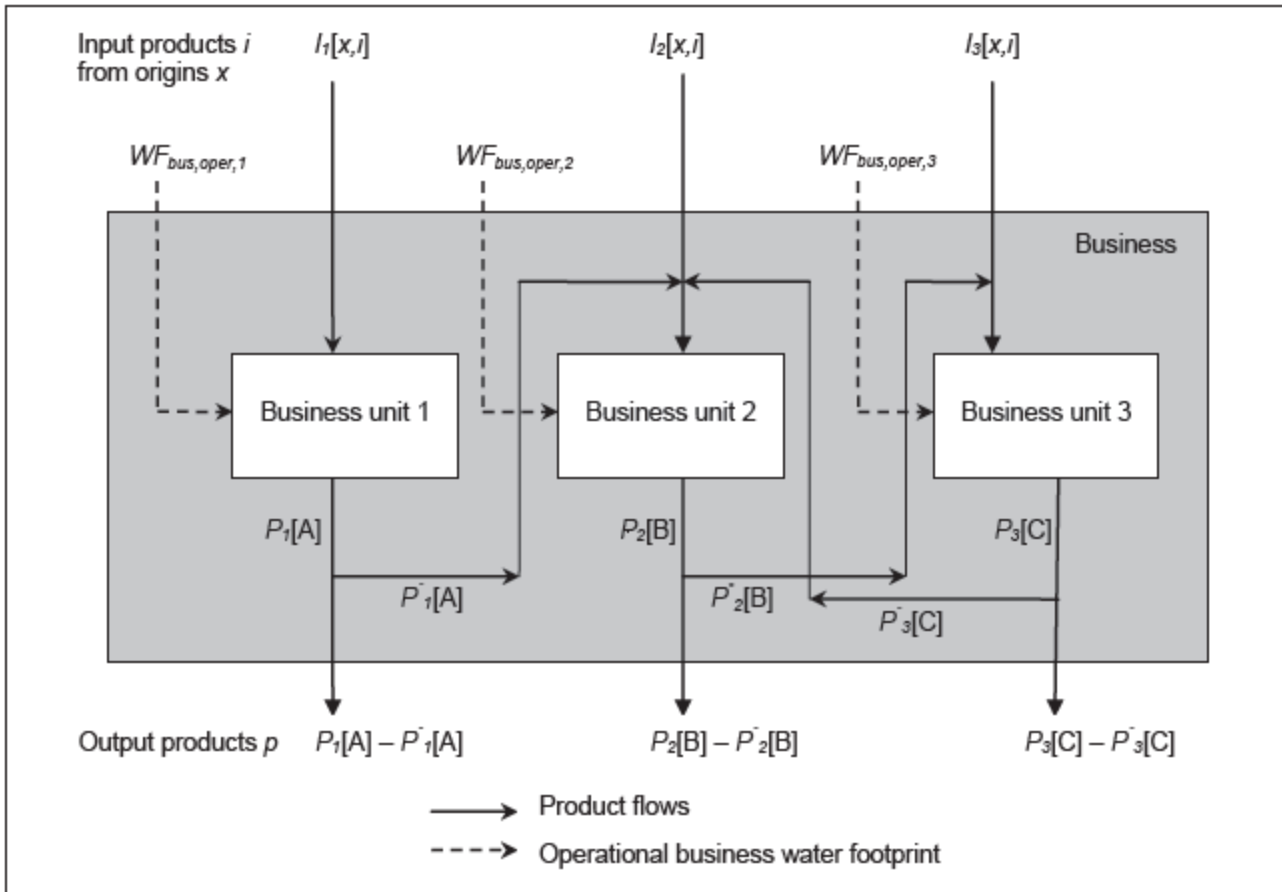


Fig. 1.5 Scheme of business divided into multiple business units generating different products and relative water footprints [1].

Blue water footprint is obviously the main focus as the freshwater source is scarce and precious, however in some applications green water can be a substitute of freshwater and, since green water is also limited, including it in the analysis can be beneficial.

1.4 Sustainability assessment

The WF sustainability assessment consists in taking the results of the previous step calculations and analyse them comparatively: confronting the human footprint with what the earth can support sustainably. Sustainability, however, is a broad concept that can be considered under many different points of view: from a geographical, specific process, product, producer's and a consumer's point of view. The geographical point of view is intertwined with the others, as their sum leads to a water shortage, so it is very important to analyse [1].

1.4.1 Geographical assessment

Establishing the sustainability in a specific geographic area is easier considering the catchment or basin, as it allows to compare the blue, green and grey WF to their respective availabilities in said area. The geographical sustainability can be assessed in three different fields: environmental, social and economic, with specific criteria to be established for each of them. This is the first step, the second one entails the identification of so called hotspots (specific periods of the year in a specific area in which the WF is not sustainable) within the area and the third and fourth steps are the quantification of primary and secondary impacts in the hotspots, with the former being changed water flow and quality and the latter being ecological, social and economic goods or services that are weakened as a result of the primary impacts [1].

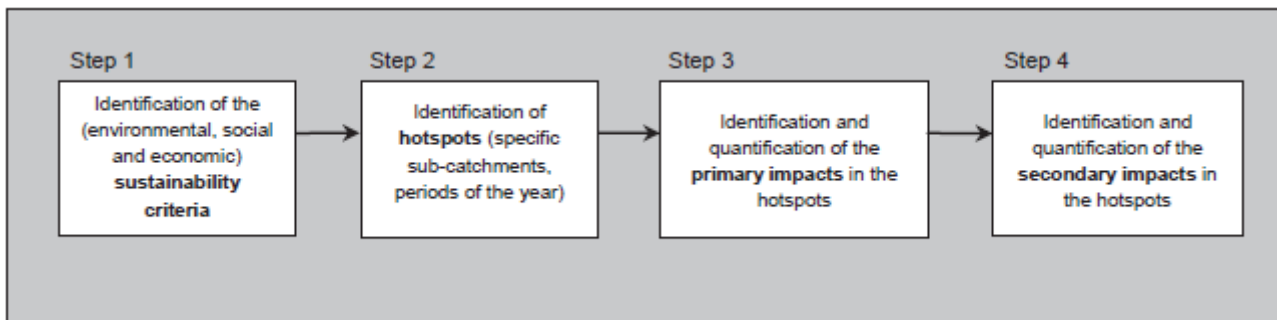


Fig. 1.6 Steps to assess the water footprint within a catchment area [1].

The WF is environmentally unsustainable if environmental water needs or pollution absorption capabilities are exceeded, thus creating a hotspot. The severity can be expressed through the green and blue water scarcity and pollution level indicators: whenever these are above 100% it's a hotspot.

The green water scarcity can be calculated as follows: first establishing the green water availability in a certain area x during a certain time of the year t .

$$WA_{green}[x, t] = ET_{green}[x, t] - ET_{env}[x, t] - ET_{unprod}[x, t]$$

The availability is the total evapotranspiration of rainwater, minus the quantity reserved for plants and the quantity that can't be made productive.

$$WS_{green}[x, t] = \frac{\sum WF_{green}[x, t]}{WA_{green}[x, t]}$$

A water scarcity of 100% indicates full consumption of the available green water, while values above it, means that the WF is unsustainable.

A similar process is done for the blue water scarcity:

$$WA_{blue}[x, t] = R_{nat}[x, t] - EFR[x, t]$$

The blue water availability is the total run-off in the catchment minus the environmental flow requirement.

$$WS_{blue}[x, t] = \frac{\sum WF_{blue}[x, t]}{WA_{blue}[x, t]}$$

Values above 100% indicate an unsustainable WF [1].

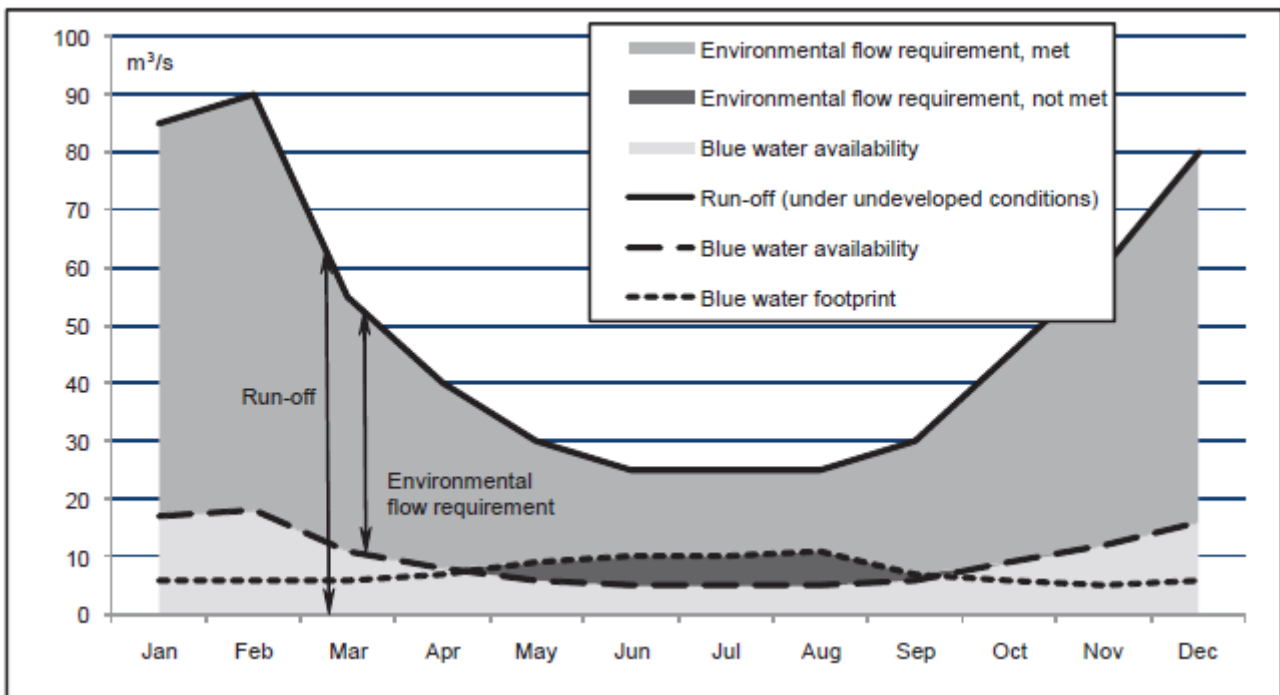


Fig. 1.7 Blue water footprint compared to blue water availability [1].

Lastly, the water pollution level:

$$WPL[x, t] = \frac{\sum WF_{grey}[x, t]}{R_{act}[x, t]}$$

Where R_{act} is the actual run-off of the catchment. When values are above 100%, the environmental quality standards are not respected.

1.4.2 Sustainability of a process and a product

The sustainability of a process depends on two factors: the geographic context (the process is unsustainable when situated in a hotspot) and the characteristics of the process itself (unsustainable when the WF could be avoided or diminished). The sustainability has to be separately evaluated for the three main components of the WF.

As the WF of a product is equal to the sum of the WF of the different processes involved in the making of said product, its sustainability depends on the different steps taken in the production. As such, the sustainability of a product is divided into the single component and each of them can be assessed with two criteria: component located in an identified hotspot and if the WF is avoidable or diminishable in any way. Once again these are calculated for the three separate WF components and the final assessment is expressed in a percentage of how much sustainable the product is, as some steps may be unsustainable singularly [1].

2 Water saving solutions

The available solutions for water saving are numerous and varied and their applicability depends on the industry and the objective that needs to be reached. Water intensive industries like textile ones, have also a great output of wastewater due to the multiple stages of washing the products. In such cases, both water reuse and water recycling can be applied to achieve some degree of water saving. Water reuse is the practice of using the output water of a process into a different stage of the industry, while water recycling is the treatment and reuse of wastewater even outside the plant in question.

The type of industry and product also dictate the quality of the water that needs to be used during production and thus what kind of water saving solution to apply: a fruit juice factory requires drinking water quality to wash the bottles [9], therefore treatment is mandatory, while a clothing factory can reuse lower quality wastewater from a process into the next one, provided that the chemicals are below the required threshold [2] [3]. To better understand this, some practical examples and case studies are provided in the following paragraphs.

2.1 Textile sector

The textile sector is one of the major consumers of water among industries, with an average of 230 to 270 tons of water consumed per ton of textile material produced, and one of the major contributors of water pollution, with 20% of global wastewater originating from the textile sector, mainly due to the dyeing process (80% of wastewater generation of the textile sector). As such, the potential for water reuse is great and can bring about quite the resource saving in the process: by using membrane processes like reverse osmosis a good quantity of wastewater can be treated and recovered, however the generated brine still poses quite the environmental issue. As such, a case study has been made in Turkey to recover water and salt from the brine obtained from a textile mill: the company uses about 6000m³ a day of freshwater for the overall operation (includes all uses) and generates about 5000m³ of wastewater treated in an on-site plant (60% needs further treatment), generating the brine and recovered water [2].

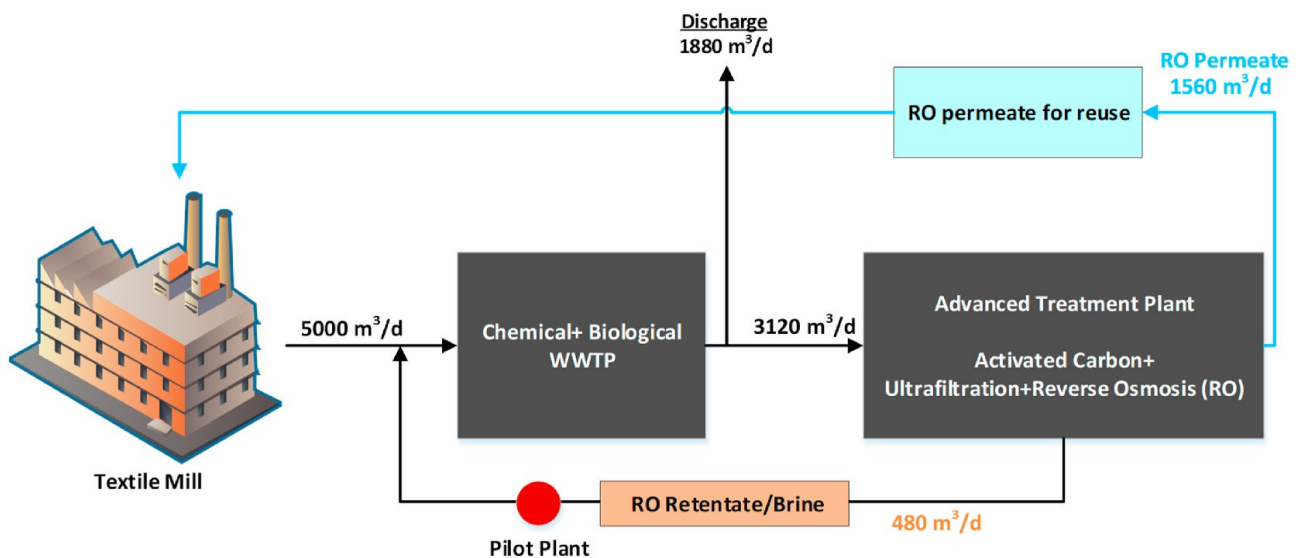


Fig. 2.1 Scheme of water reuse process of the case study textile mill [2].

The brine recovery plant has a capacity of 2 to 4m³ a day and consists of three different stages: pre-treatment, concentration and softening.

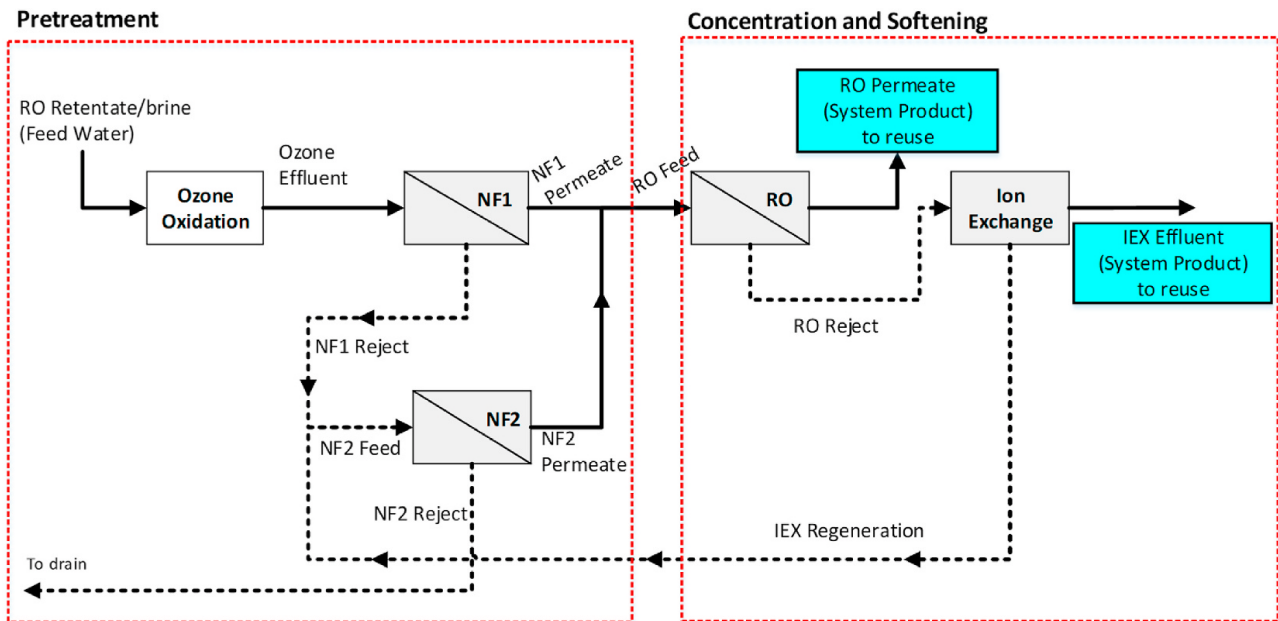


Fig. 2.2 Process flow of wastewater and brine treatment and reuse [2].

The clean water recovery of such an application reaches 77% and if the concept is applied to a full scale plant, the potential process water recovery would reach about 115000m³ per year and, considering the potential reuse in the dyeing process (the most water intensive), the overall yearly water reduction for the textile mill would reach 142000m³, which equates to 15% water reduction for its operation [2].

The European textile sector is one of the largest consumers of freshwater (600 million m³) among the different industries, yet not many factories have applied water saving solutions despite the huge potential. This is because textile products require chemical treatment, thus implying the wastewater is highly contaminated and the majority of the factories are medium-small enterprises that can't afford the treatment required to recycle it. Moreover, the composition and characteristics of the wastewater are variable, adding to the difficulty of treating it [3].

That being said, some solutions for bigger realities have been implemented:

- FOTOTEX: photo oxidation process to remove biodegradable and non-biodegradable components from the wastewater. The method is simple and requires only lighting and specific chemicals, however it's also incomplete and should be paired up with a filtration membrane.
- PROWATER: physical and chemical pre-treatment, followed by ultrafiltration and ozonation processes. It's technically and economically suitable as well as efficient at removing dyeing agents and surfactants from the wastewater (98% and 62%

respectively).

- ADOPBIO: UV-activated photolysis of hydrogen peroxide, thermal activated oxidation and bioflotation.
- BATTLE: based on effluent studying and separating it into reusable and non-reusable streams, then treating with membrane filtration and biological treatment. The pilot plant received 500m³/day of wastewater and recovered 374m³/day.
- PURIFAST: uses the same principles of ADOPBIO, but with the addition of an ultrafiltration step. High efficiency at removing contaminants (90% dyeing agents, 80% COD abatement and TSS reduction), making the resulting treated water suited to be reused as is for some finishing processes or mixed with a share of freshwater to be reused at the beginning of the chain.
- AQUAFIT4USE: Separation of streams based on the concentration of pollutants and combination of treatment technologies. Ultrafiltration pre-treatment, nanofiltration, UV-activated photolysis of hydrogen peroxide. The distillate has a high potential for reuse and leads to 40% less freshwater consumption. The downside is the necessity of small-scale tailor made solutions with combined technologies to achieve it [3].

2.2 Steel and metals industries

Steel making is a prominent industrial sector in many countries in the world and has always been an energy intensive industry. During the past decades improvements in efficiency have been made and nowadays 96% of raw materials are successfully converted into steel. Despite this, the water consumption is still high at an estimated 129m³/ton of steel as it's involved in different processes, namely: rolling, coking, iron making and casting. The latter is of particular interest as continuous steel casting constitutes 95% of the world steel production and uses a significant amount of water. While it is possible to substitute the conventional, coal or gas fired furnaces with electric ones (thus achieving 10 to 16% water saving) this would potentially increase the electric energy consumption of the plant. Thus, solutions for saving water in the casting process have been developed, in particular regarding the cooling of the steel bars once formed [4].

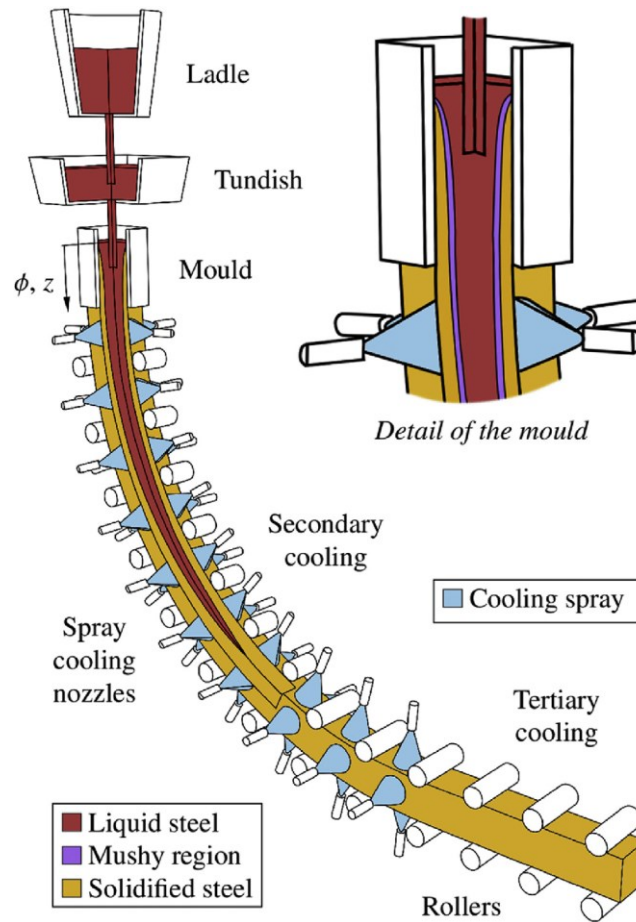


Fig. 2.3 Continuous steel casting process and relative cooling [4].

The first, simplest solution is the optimization of the water spray cooling already in place in continuous steel casting. This allows for 10% water saving and also prevent a drop in steel quality. This requires determining the flowrate of the nozzles and heat transfer coefficients between the water and the steel surface (increasing with water flow density up until $12\text{kg}/\text{m}^2\text{s}$), to minimise the difference between the actual temperature of the surface and the set point temperature [4].

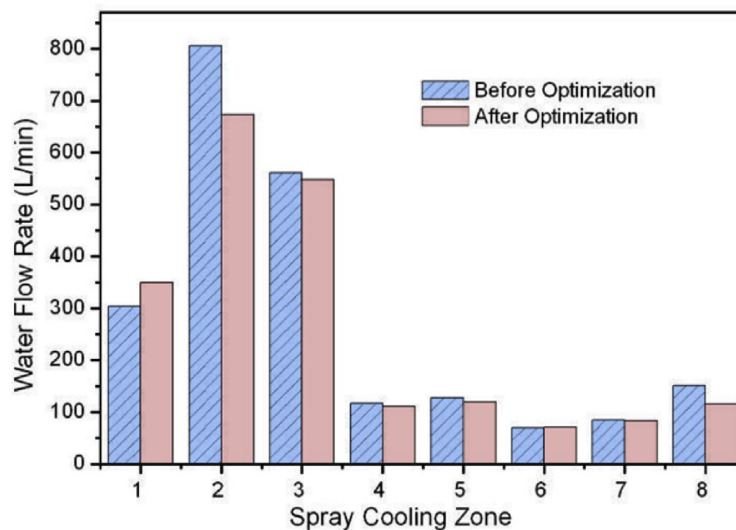


Fig. 2.4 Diagram displaying effects of cooling optimization [4].

A second solution would be using nano additives mixed in the water stream. In particular a mix of copper and aluminium additives in a 4:1 ratio at 160ppm would grant a 17% higher heat flux and 15% better heat exchange coefficient than standard cooling. This method, while convenient in theory, is complicated to apply in practice as there're health concerns regarding the wastewater generated and the high costs of the nano additives, thus making it not viable for most industries in the sector [4].

A third method would be to use dry and fog cooling. This solution would reduce the amount of sprayed water, by introducing a closed loop circuit for cooling the steel rod. The fog cooling refers to the initial water misting part, as some still is required to achieve good quality steel. The water in the closed loop would flow through the rollers shaping the steel, cooling it, and circling back to release the heat. While this system does require a much bigger starting water quantity, 95% of it remains in the circuit, effectively being reused, saving 48% compared to the classic open loop nozzle system [4].

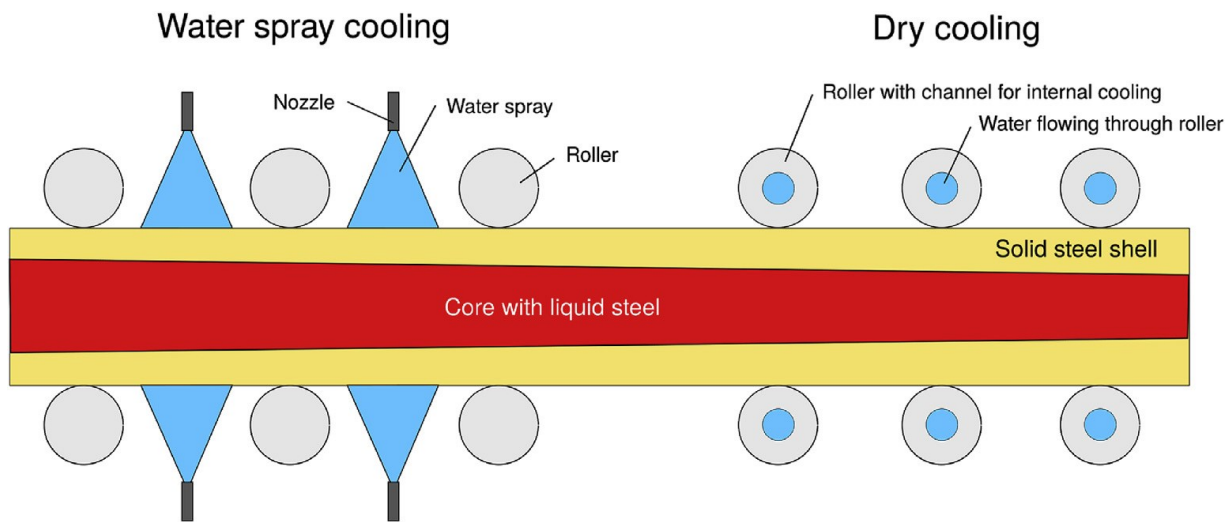


Fig. 2.5 Dry cooling process [4].

Another worldwide relevant sector tied in with metal production is the electronics one, especially since they've become an integral part of our daily lives on so many levels and applications. Electronics require many different metals to functions, some of which are rarer than others, and their extraction and processing are very energy and water intensive, especially because their manufacturing happens in water stressed areas, rising the water footprint even further. Water is not only used directly in their creation (91m³ of freshwater per ton of copper processed pyrometallurgically), but also indirectly in many other related activities like cooling, maintenance and, of course, in the production of the required energy to make the process itself function [5].

With this in mind, a case study considering the production of two extremely common and widespread electronics, namely a smartphone and a laptop, has been conducted, first by analysing the water consumption and impact with a kg of the main metals required for

their manufacture and afterwards by switching to a per product focus [5]. The study showed three potential scenarios to reduce the water footprint of the production of said electronics:

- Alternate supply chains: impact reduction achieved by obtaining the required gold through different supply chains, from regions with lower water stress
- Material substitution: switching some materials used for the construction (like the laptop case) with lower impact ones (plastics instead of aluminium for example)
- Material recovery in circular economy: recycling gold and aluminium from electronics waste

The analysis on a per kg of metal returned very different results depending on the metal selected, as one might expect: rarer metals require a much higher water quantity to be extracted and refined, given their low percentage in the ores excavated. As such, the water footprint of gold is 46% for direct use (mining and processing) and 36% indirect use (energy requirements), while for aluminium it's 6% and 84% respectively [5].

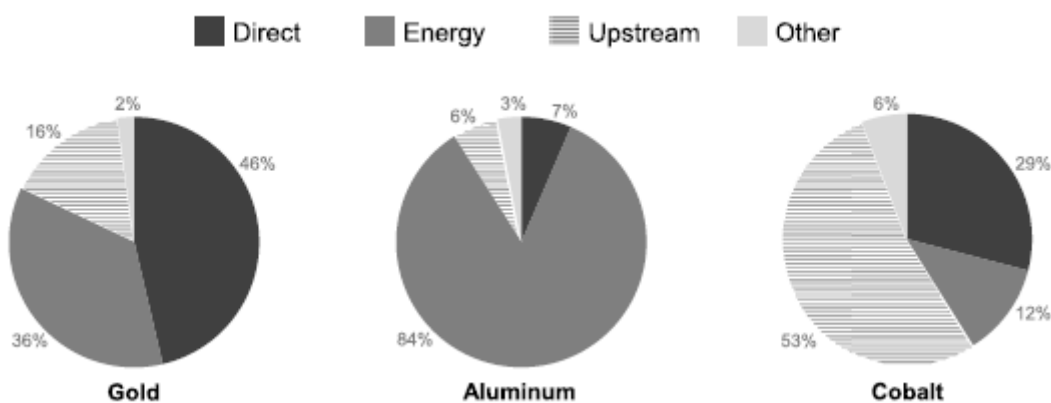


Fig. 2.6 Water footprints of different metals, both direct and indirect [5].

Switching on a per product focus returns similar, yet different results, due to the different metals required for the production of the electronics chosen, with the smartphone taking a 45% overall impact from gold, 28% from aluminium, while the laptop has similar figures, but with different metals (aluminium and copper 45%, palladium and gold 31%) [5].

Exploring the three different scenarios previously proposed, one can obtain different degrees of water saving: the alternate supply chain can achieve between 19 and 28% of reduction in the water footprint, however it's not easily applicable as supply routes are hard to change and they would rely only on Canada, Brazil and Russia for the global gold production (which brings about a series of problems, also on a political level). The material

substitution would achieve around 17% of WF reduction, by substituting aluminium with abs plastic and magnesium, however it introduces the need for chemical additives and so it must be analysed properly. The material recovery is dependent on how much recycled material can be used and as such, as this percentage increases, so does the water saving (between 10 and 20% WF reduction with 35 to 70% of recycled gold for a smartphone, 11 to 22% WF reduction with 45 to 90% of recycled aluminium for a laptop), however such recycling processes are not yet feasible on large scale [5].

2.3 Paper industry

The paper industry is a notoriously water and energy intensive sector, given the high quantities required to prepare the paper paste that will then become paper. The majority of said water will be highly contaminated during the production phase by chemical additives, ink and other substances and, normally, gets disposed of after some treatment to lower the pollutant contents enough to allow discharge in the environment. These wastewater streams have the potential to be reused, after adequate treatment, within the industry itself. As paper quality depends also on the quality of the water used to prepare the paste, the treated wastewater streams could potentially be used to integrate the freshwater streams, instead of substituting them entirely, keeping the quality high enough to not impact the final product, while at the same time saving a relevant amount of freshwater in the process [6].

Another important waste product of the paper industry is paper sludge, what remains of paper production, made of cellulose fibres and ash with 40% or more of moisture. A typical paper mill will make roughly 83kg of paper sludge (wet weight) per ton of paper produced and is normally disposed of at the landfill, with great impact on the environment as well as the water footprint of the industry. A possible solution is to recycle this waste material to reclaim as much water from it as possible, as well as some energy: by fermenting and digesting the paper sludge, biogas can be produced and used for energy purposes of the industry itself, as well as reclaiming water. The fermentation and digestion process will require more water, but, as it doesn't need to be high quality, wastewater streams from the same industry can be used here as well, as make up water (at

optimum conditions the fermentation process will yield more than the 40g/l threshold of economic ethanol production). A case study has been conducted in South Africa: the process is made of two phases, with the first one producing ethanol through fermentation and the second one using the resulting stillage to make biogas through digestion [6].

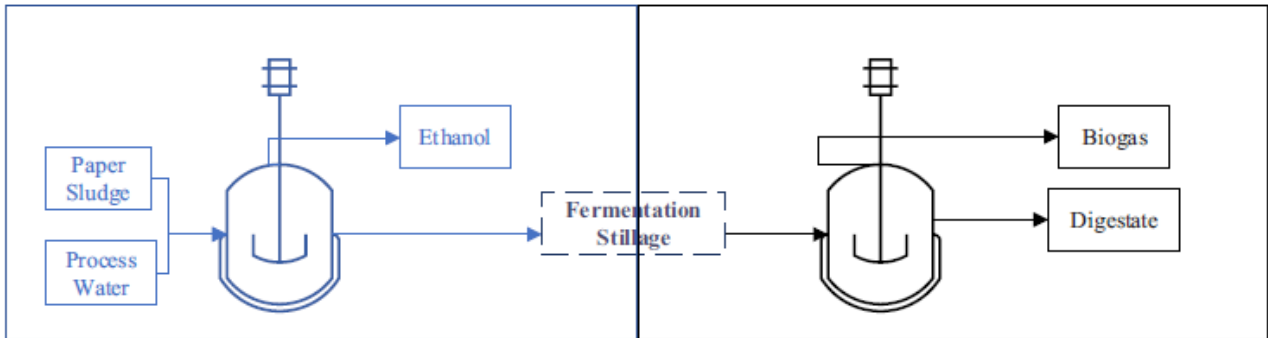


Fig. 2.7 Scheme of paper sludge recycling through fermentation [6].

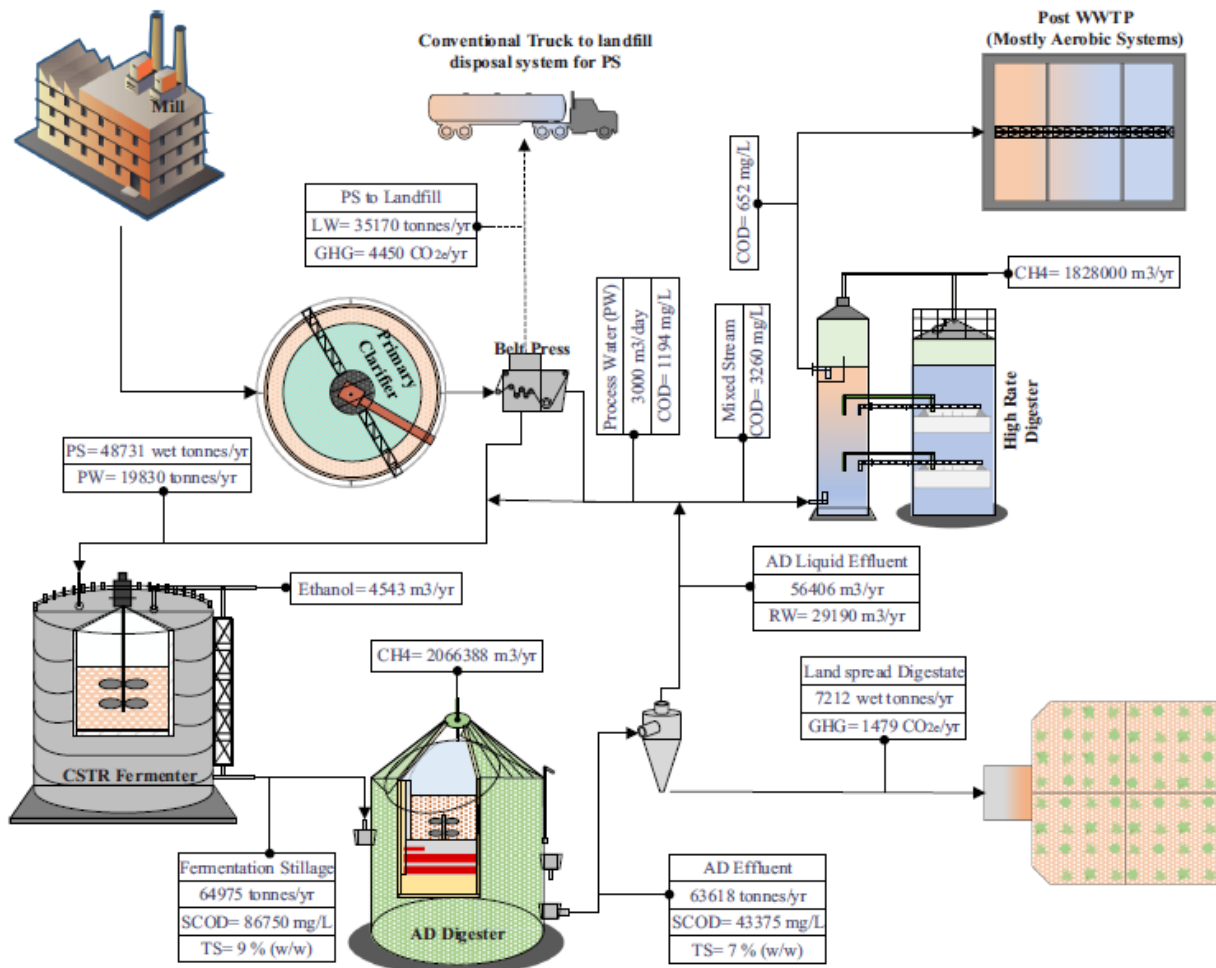


Fig. 2.8 Complete process flow of treatment of process water and paper sludge [6].

The water reclaimed through fermentation and sequential digesting and processing of the paper sludge is between 65 and 85% (at Mondi Richards Bay mill, of the over 35000m³ of water that would've ended at the landfill through disposal of sludge, 29000m³ were reclaimed), however the quality considerably worsened and subsequent treatment is required before considering its reuse [6].

2.4 Cooling systems

Cooling towers are necessary in many industrial applications but are also one of the major factors of water consumption, as they normally rely on freshwater to operate. Moreover, the wastewater coming from the cooling towers cannot be reused without treatment, given its high salinity and the contamination with other components and chemicals. While standalone techs would manage to reduce the contamination, a combination of such solutions would regenerate the water stream to usable conditions [7] [8].

One proposed solution for treatment is through the use of so-called constructed wetlands, an artificially made wetland environment that works as a pre-filtration method. The plants in the wetlands reduce the content of phosphates, nitrates and benzotriazole, but lead to a higher amount of carbon components and salinity. However, adding further treatment steps, like nanofiltration, electrochemical oxidation and reverse osmosis, grants an almost total neutralization of such issues and renders the wastewater usable again, thus saving on water consumption [7].

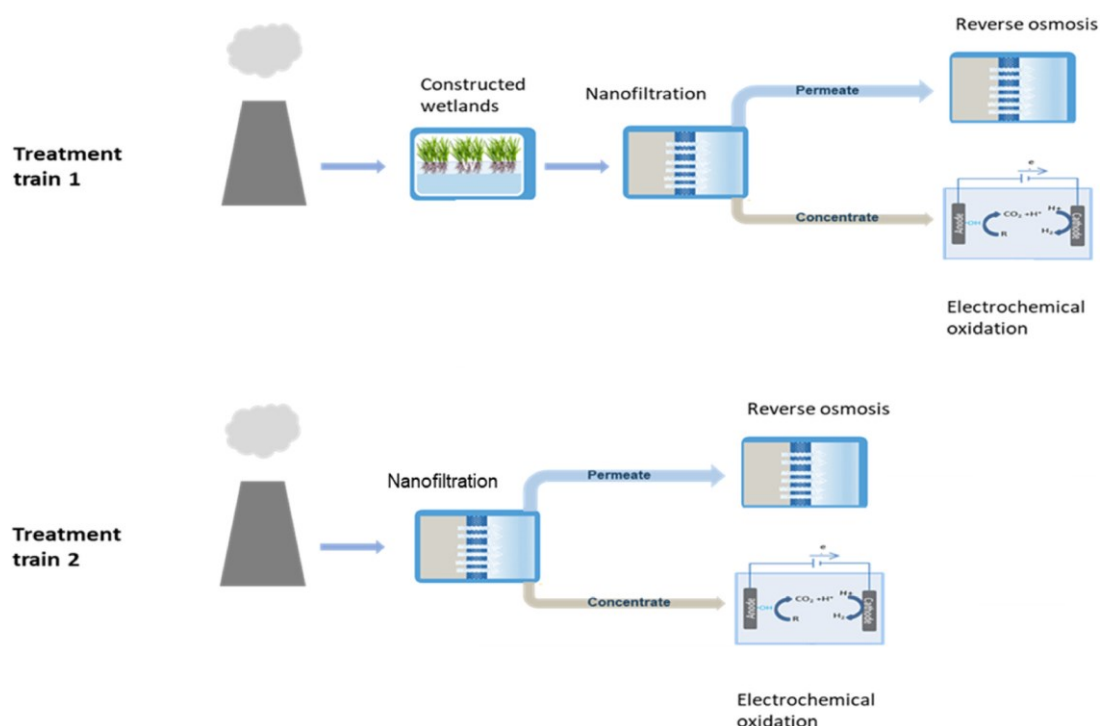


Fig. 2.9 Treatment process with and without the constructed wetlands [7].

A different approach can be taken: instead of treating and reusing the wastewater coming from the cooling tower, treating the wastewater from a process and feed it to the tower. This is doable, for example, in the food industry as it uses a lot of freshwater for health reasons. A practical example involved a juice factory, reusing the water from the washing process of the packaging in the cooling tower. As said previously, such water cannot be fed as is, because it would lead to maintenance issues, namely corrosion (due to the presence of biocides such as H_2O_2). As such, treatment is required: while classic solutions like the use of a membrane, enzymes or microorganisms are good in theory, they aren't in practice as they wouldn't be able to keep up with the volumes required and would deteriorate at a fast pace, requiring frequent maintenance. The applied treatment solution for this specific case was the use of activated carbon filters: the reaction with the biocides leaves non-toxic, easy to dispose components and allows for a stationary continuous regime operation. The filters themselves are relatively cheap to purchase and change, with a quick return on investment, leading to an overall positive saving of water and money in the long run [8].

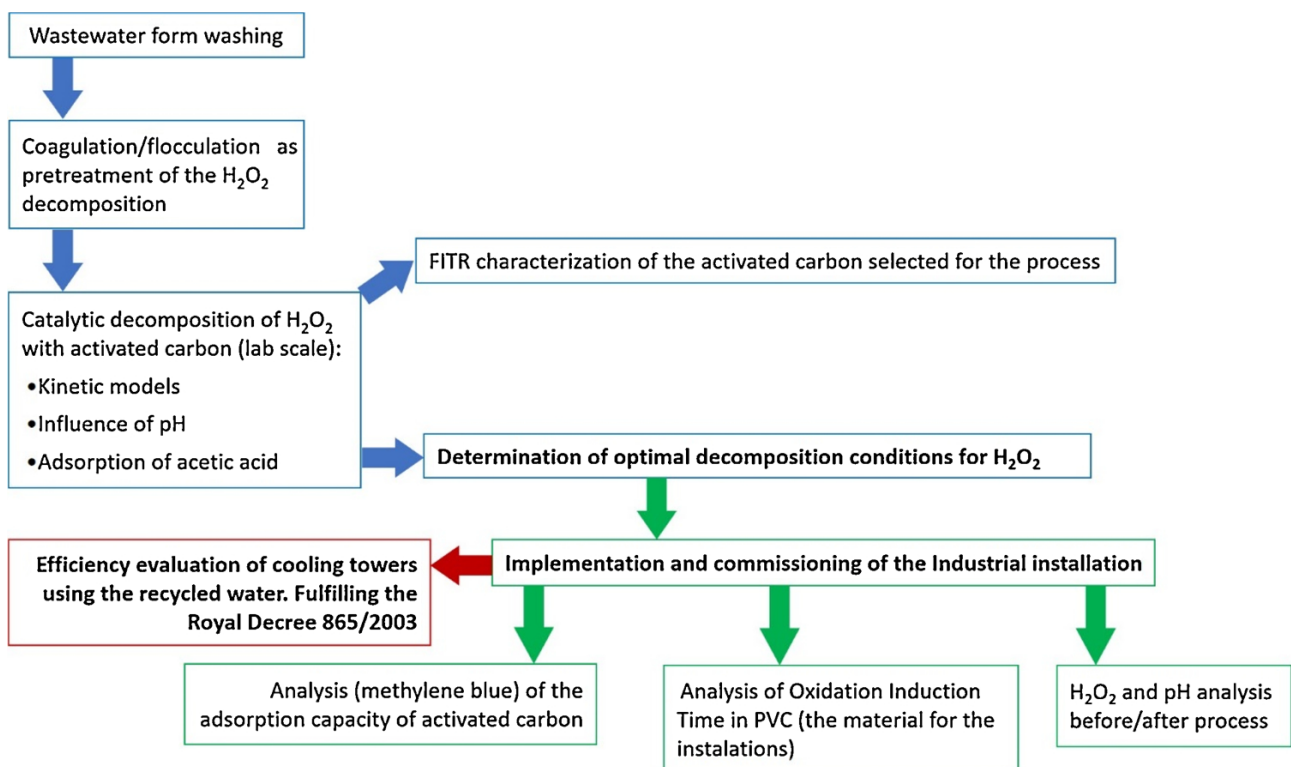


Fig. 2.10 Experimental process implemented in the juice factory for water reuse in the cooling tower [8].

3 Water pinch analysis

3.1 Introduction to water pinch analysis

As the need for water saving has risen during the years, and many methods to achieve it have been developed, the majority have been focused on specific industrial sectors or processes. The WPA was developed to approach the problem from a wider and more general perspective, to tackle the reality that industries have many different processes that need freshwater and produce wastewater. Originally, the method was adapted from the concept of mass exchange networks, where water was used as a mass separating agent to remove impurities from a stream (a fixed load case: the target was the minimum freshwater needed to get rid of impurities). This scenario assumes no changes in the freshwater quantity (freshwater used = wastewater generated). WPA was then extended, in the following years, to nonmass transfer-based systems (fixed flowrate case): these include water evaporation losses and water used or generated in reactions, among others. Thus, WPA can be defined as a method to achieve maximum water efficiency by implementing water minimization.

Similarly to the heat pinch analysis, which has many parallels with WPA as it will be discussed further on, the term pinch is related to the limits of water recovery [9] [10].

3.2 Water pinch analysis implementation

WPA involves five steps:

- Step 1: Analysis of water network
Identifying all water using operations and processes, developing their water balances
- Step 2: Data extraction
Identification of water sources and sinks as well as extraction of limiting water flowrate and limiting concentration data
- Step 3: Setting minimum utility targets
Minimum freshwater requirement and wastewater generation or maximum water recovery targets are set through graphical or numerical methods
- Step 4: Water network design/retrofit
Design of a new network/retrofit of the existing one to achieve the set targets

- Step 5: Economics and technical evaluations
Accounting for costs of the operation as well as technical constraints. A preliminary evaluation can be made by calculating the payback time of the investment

The second step deserves a more detailed analysis as the water flowrate and limiting concentration are required for each of the water streams and extracting this data is not as easy as it sounds [9].

3.2.1 Water flowrate determination

Normally, freshwater is taken from water mains and distributed throughout the industrial facility, while wastewater is collected in a common drain. As such, no specific devices installed to measure such flows and the quantity of mixed wastewater is known only when it reaches the treatment plant, which makes it already unusable for WPA purposes as the quality is too low at that point. Therefore, using existing material balances of the process, computer monitoring, routine measurements and laboratory reports can lead to the extraction of the needed data. In some situations, installation of measuring devices is needed however this is not always possible, in which case estimates can be made. In any case, the data should be gathered during normal operation of the plant and to account for all waterflows (aiming at mapping at least 80% of the site water balance), prioritizing the streams with the bigger flowrates [9].

3.2.2 Contaminant concentration determination

Having similar issues in determining the data for the contaminant concentration, the limits related to water sinks (water stream entering a process) can be extracted from equipment specifications, literature, estimates or manufacturer's design data. Other constraints may come from physical limitations based on the operations and plant and technical constraints to avoid specific phenomena (like corrosion, precipitation, explosions and fires etc.).

Data for water sources (wastewater stream leaving a process) can be obtained through samples and lab tests [9].

3.2.3 Data extraction

After the water balances have been developed the limiting water data can be extracted, choosing processes that are close and chemically related to reduce piping and pumping costs as well as facilitating water integration and regeneration. To simplify matters, use of aggregated contaminants is common, allowing the modelling of a single contaminant system using multiple quality factors. The primary contaminants that prevent the reuse of the stream are chosen for WPA implementation and the rest of the elements are double checked to ensure that they're within the limits for reuse. The extracted data is obtained considering the worst-case scenario, to account for every possible outcome [9].

3.3 Maximum water recovery targets

Once the data extraction has been completed, the maximum water recovery targets can be set. This can be done with a variety of methods, reported below, some of which will be discussed more amply in the following paragraphs.

- Limiting composite curves: Processes using water are plotted on a concentration-flowrate diagram and can be used for both fixed flowrate and fixed load problems

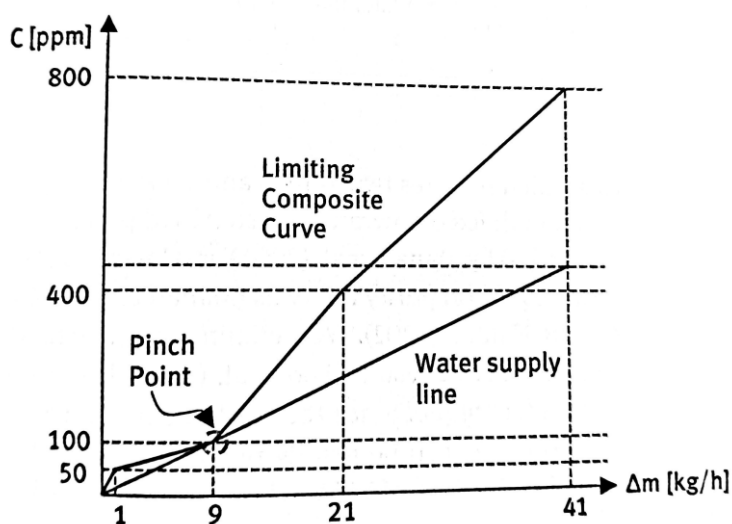


Fig. 3.1 Example of limiting composite curve [9].

- Water surplus diagram (WSD): Using a concentration-flowrate diagram once again to plot the water sources and sinks, establishing the water surplus and deficit. These are summed to form the water surplus diagram and, through an iteration, the

targets are set. Works for both fixed flowrate and fixed load problems

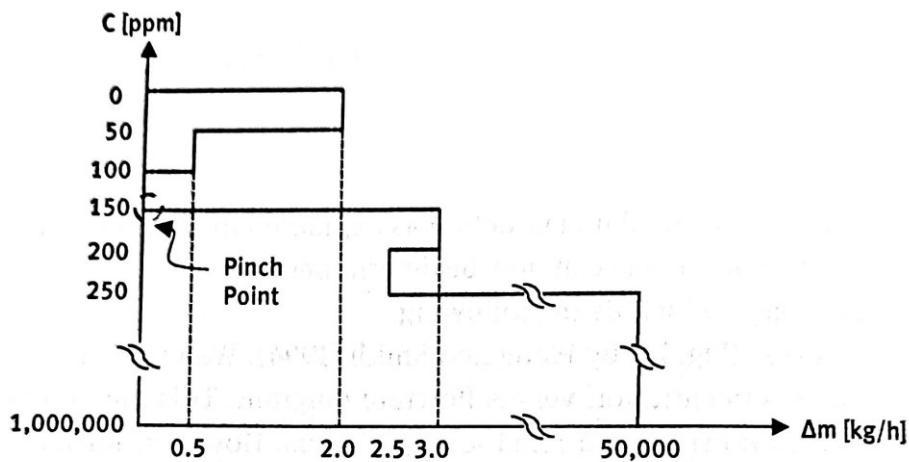


Fig. 3.2 Example of WSD [9].

- Source/sink composite curves (SSCC): The graph is a contaminant mass load-flowrate this time, plotting water sources and sinks, it's an improved method based on the previous one, getting rid of the iterative process

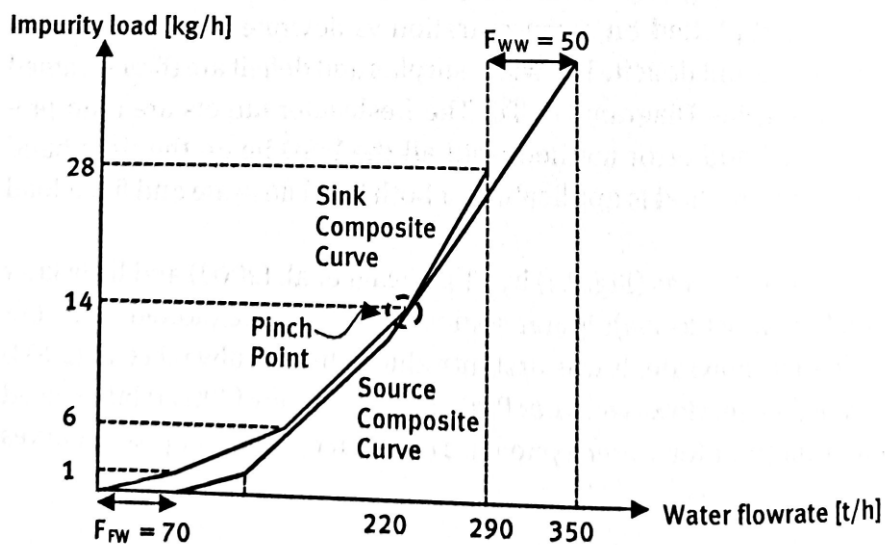


Fig. 3.3 Example of SSCC [9].

- Water cascade analysis (WCA): Based on purity intervals, it's another improvement of WSD, returning more accurate results
- Algebraic targeting approach: Numerical version of SSCC
- Source composite curves: A mix of graphical and numerical approaches, uses a similar cascading method as WCA to then plot composite curves on a

concentration-mass load diagram. This method can predict the average wastewater concentration

These methods apply for continuous processes, however it's possible to use them for batch processes as well. To do so, it's necessary to make use of water storage tanks as water sources can be generated at different times compared to when the water sink needs them, hence the need for storage.

Of the previously mentioned methods, the two most used for MWR targets setting are WCA and SSCC. The former, especially, is easy to set up and run since it's algebraic and returns accurate results [9].

3.3.1 MWR target for a single pure freshwater source

WCA and SSCC methods fall within this category. The WCA is a numerical method used to determine the overall freshwater requirement and wastewater generation, after assessing the possibility of using available water sources, within the examined process, to cover the water sinks. As such, the net flowrate, surplus and deficit are required: they need to be established at the different concentration levels within said process [9].

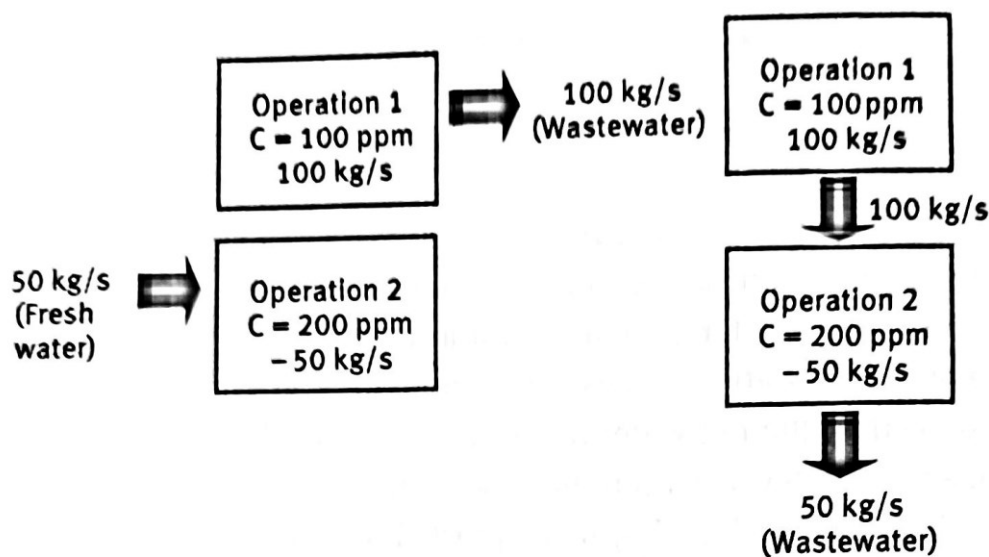


Fig. 3.4 Example of cascading process, with wastewater flows and contaminant loads [9].

The cascading method allows for a reduction of freshwater needs and therefore of wastewater generation: by coupling the outlet of an operation within the process to the inlet of the next one, the water need can be at least partially covered without drawing more freshwater from the external source. If the quality of wastewater from operation 1 is high enough to feed operation 2, there's no need for freshwater at all, otherwise, a certain amount can be fed to dilute the contaminants and raise the quality until it's usable. To calculate all of this, the water cascade table is constructed, by ordering the contaminant

concentrations in ascending order, water sinks (negative values) and water sources (positive values). The sum of sinks and sources at each concentration interval (obtained as difference of concentration levels between $n+1$ and n values) returns the surplus (positive values) and deficit (negative values) at the respective levels. At this point the cumulative water flowrates are calculated by cascading the surplus/deficit values, with a null value as a starting point. The cumulative flowrate is then multiplied by the concentration levels (mass load) and this is also cumulated for each level, thus proceeding to calculate the interval freshwater flowrate. If there're negative values, it means that the impurity level is too high and more freshwater is needed. The biggest negative value is taken as reference point and substituted with a null value, cascading the whole column again starting with the taken quantity. The initial and final values of this column are, respectively, the freshwater requirement and wastewater generated (target values). Incidentally, the pinch point is located at the null value (the former biggest negative value). The following figure shows an example of a water cascading table [9].

C_k , ppm	ΔC_k , ppm	$\sum F_{SKi}$, t/h	$\sum F_{SRj}$, t/h	$\sum F_{SKi+}$ $\sum F_{SRj}$, t/h	F_C , t/h	Δm , kg/h	Cum. Δm , kg/h	$F_{FW,cum}$, t/h	F_C , t/h
0				0			0		F_{FW} = 70
20	20				0	0	0	0	70
50	30	-50		-50	-50	-1.5	-1.5	-30	20
100	50	-100	50	-50	-100	-5.0	-6	-65	-30
150	50	-80	100	20	-80	-4.0	-10	-70	-10
200	50		70	70	-10	-0.5	-11	-55	(PINCH) 60
250	50	-70		-70	-80	-4.0	-15	-60	-10
			60	60	-20	0	-15		F_{WW} = 50

Fig. 3.5 Example of water cascading table, where the pinch point has been identified [9].

SSCC is a graphical method plotting mass load-flowrate, used to target the minimum usage of fresh sources for material recycle/reuse. The sink and source composite curves need to be constructed: the sink curve is obtained by connecting every sink with the corresponding mass load and flowrate, ordered by ascending concentration. Similarly, the source curve is obtained by connecting all sources with their mass loads and flowrates in ascending concentration order. The source curve is then shifted towards the right until it

enters contact with the sink curve (this is the pinch point). The minimum freshwater and wastewater targets are the distance difference, on the flowrate axis, between the beginning and ending points of the two curves respectively.

The figure below portrays the composite curves before (a) and after (b) the shift.

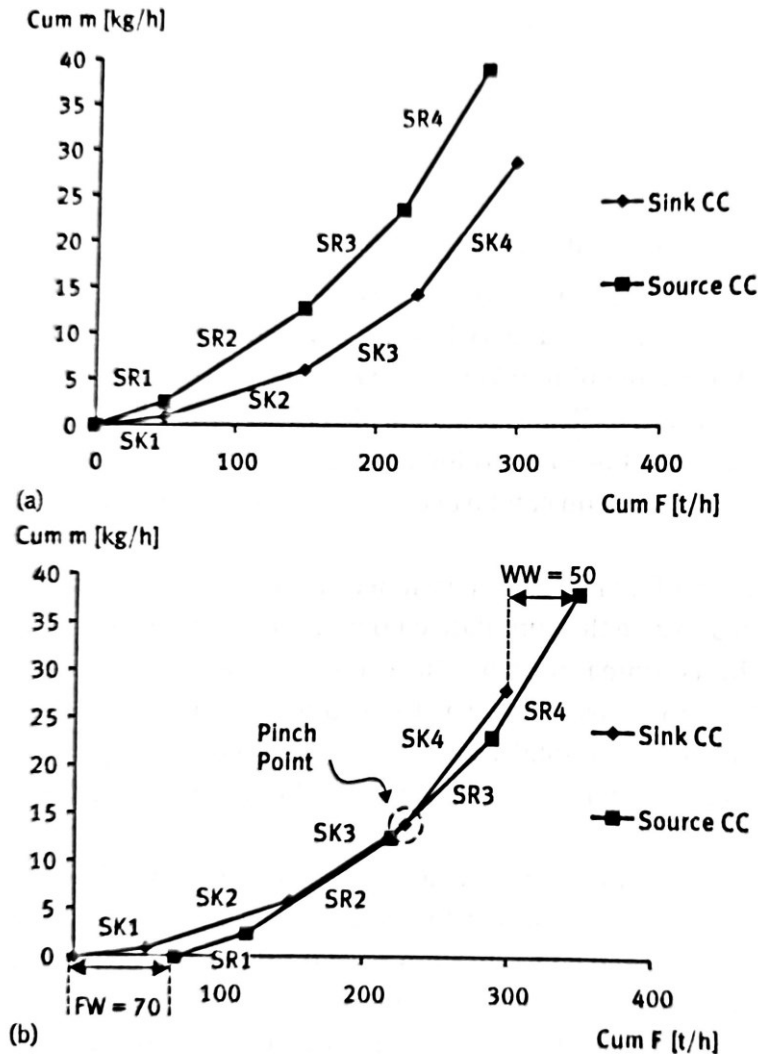


Fig. 3.6 (a) composite curves prior the shift, (b) composite curves after the shift. The pinch point is identified at the minimum distance between the two [9].

The pinch point is critical for the design of the network: it divides the graph into two (or more if there're multiple pinch points) different regions with different concentration levels. The region below the pinch has lower concentration and the whole sink mass load should be satisfied by local water sources or freshwater (no wastewater is generated), while above the pinch the concentration is higher (no freshwater should be added). The excess water sources are discharged as wastewater. Between the regions (saddling the pinch point) there should be no freshwater addition nor wastewater generation with sources satisfying the sinks completely. Basically, no source should traverse the pinch point to avoid incurring in a water penalty [9].

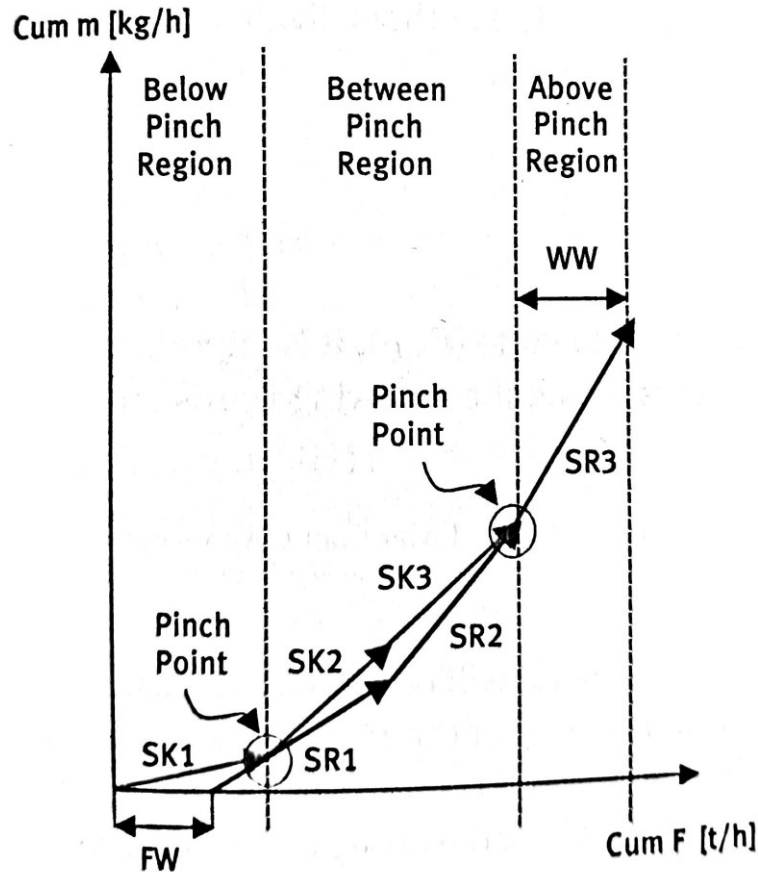


Fig. 3.7 Example of region subdivision by multiple pinch points, with external wastewater and freshwater sources [9].

3.3.2 MWR target for a single impure freshwater source

This case can be divided into pinched problems and threshold problems. Pinched problems are based on the following heuristic: A water source can be considered as a utility if its concentration is lower than the pinch concentration. This is to prevent the generation of additional wastewater, which would be the result of using a utility with higher concentration than the pinch. In pinched problems the new utility flowrate can be obtained by moving the source lines above and below the utility line.

A threshold problem is defined by having freshwater or wastewater as a utility. In these problems the pinch point may or may not exist. If it does, the utility targeting technique for pinched problems is used [9].

3.3.3 MWR target for multiple freshwater sources

In the case of multiple available utilities, both freshwater and regenerated wastewater, the use of the higher quality utilities should be minimised as they're more valuable, thus

maximising savings. This can be done by using the water composite curves to obtain the new utilities flowrate, from cleanest to dirtiest water sources. This implies the use of the SSCC method for the cleanest new utility, then moving on by adding the next if its concentration is lower than the highest pinch concentration. This is repeated until all utilities have been used [9].

3.4 Water network design/retrofit

When the targets have been selected, the design/retrofit process of the network can begin. There are two main methods for designing a network capable of reaching the targets: the source/sink mapping diagram (SSMD) and source and sink allocation curves (SSAC) [9].

3.4.1 Source/sink mapping diagram (SSMD)

Systematic mixing of source streams with each other and with freshwater, if needed, to meet the needs of each of the sinks for both quality and quantity parameters. The quantity to be sent to the contaminated source depends on the contaminant load associated with the sink and as such, three scenarios are possible:

- 1) The quantity is equal to the required value; thus, no freshwater is required
- 2) The quantity is less than the sink and some freshwater will be needed
- 3) The quantity is more than the sink, therefore the sink can accept a higher contaminant load from another source

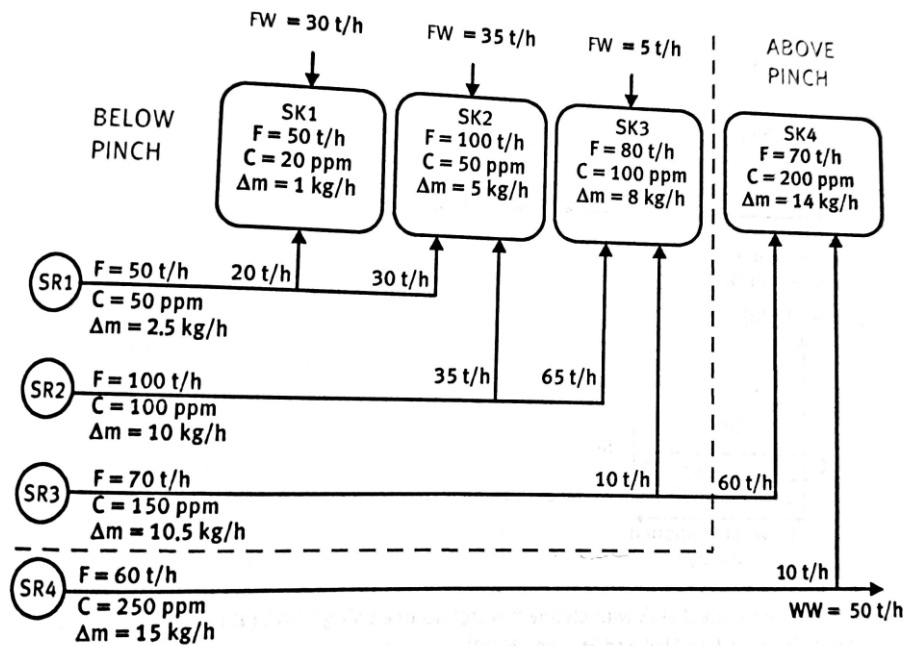


Fig. 3.8 Example of HEN design with defined pinch regions, water flows and contaminant loads [9].

The previous figure shows an example of network design by SSMD [9].

3.4.2 Source and sink allocation curves (SSAC)

Originally the SSAC method was used to solve issues of flowrate deficit cases (mass load satisfied), with a cleanest to cleanest rule between sources and sinks, however it has been updated to account for mass load deficit cases as well (flowrate satisfied), by using the cleanest and dirtiest sources combined in the pinch region while satisfying the pinch point and utility targets [9].

This method is divided into three steps:

- Step 1: Plotting sources and sinks from cleanest to dirtiest forming the SSCC
- Step 2: Drawing SSAC for the different pinch regions following these rules
 - a) Matching sources and sinks below and between pinches, starting with the cleanest source and cleanest sink, then proceeding depending on the cases:

If freshwater or utility purity is greater than all of the other streams and mass load is satisfied, add utility until the flowrate of the sink is also satisfied. Vice versa, if the mass load is not satisfied, using the dirtiest source to reach the mass load target before moving on.

If freshwater or utility purity is not greater than all of the other streams, the utility should be treated as a source and use cleanest and dirtiest sources to satisfy the sinks' mass load and flowrate.

b) Matching sources and sinks above the pinch, satisfying the sinks' flowrate with sources in ascending concentration order, however the mass load will always be less and requires the input of higher purity sources.

- Step 3: Draw the network allocation diagram (NAD)

3.5 Comparison and parallels with heat pinch analysis

Although water tends to be regarded on the same level as fuels or raw resources for an industrial process, this view is not comprehensive of water's nature. While it's true that water use can be compared to the consumption of raw resources, it's also, especially in water intensive industries, a constant stream required to keep the process running. This second nature is more akin to electricity or heat fluxes and the latter comparison is especially fitting when dealing with water saving solutions and methods. Water pinch analysis and heat pinch analysis share many common aspects and even the main goal, albeit for different purposes, has the same focus: integrating locally available sources with sinks to save as much utilities as possible [9] [10].

3.5.1 Composite curves

In heat pinch analysis, the objective is to build a heat exchanger network (HEN) to save as much energy as possible: this is done by using the maximum energy recovery principle (MER), through different available methods, both graphical and numerical. The graphical method makes use of composite curves built for the cold and hot streams, plotted in a temperature-enthalpy difference diagram. The hot composite curve (HCC) and cold composite curve (CCC) are constructed by identifying the temperature intervals and coupling them with the relative heat fluxes and their thermal capacities. MER conditions are achieved when, by shifting the HCC right, the two curves enter contact: that's the location of the pinch point and the distance difference on the enthalpy axis between the beginning of HCC and CCC and the end of HCC and CCC are, respectively, the cold utility and the hot utility. The pinch point is critical and divides the graph into two separate regions: below the pinch it's a heat well and above the pinch it's a heat source. To maintain MER conditions no heat flux should traverse the pinch point to avoid a heat flux penalty.

3.5.2 Problem table

The numerical method for heat pinch analysis consists in a cascading sum of heat fluxes from sources to sinks to satisfy the heat needs. To calculate this, the problem table is constructed by following these steps: ordering the temperature intervals in decreasing order, summing the thermal capacities of fluxes traversing said intervals and multiply the sum by the respective temperature difference, obtaining the heat surplus/deficit (positive/negative values respectively). The results are cascaded starting with a null value at the beginning of the cascade and the biggest negative value is identified. This will be the reference point and substituted with a null value, adding the negative amount at the beginning of the cascade and repeating the calculation once again. The starting and ending points of the cascade are the hot and cold utility targets, representing the heat that needs to be supplied to the process and the one that must be discarded at the end of it. The pinch point is located at the null value.

Both the graphical and numerical methods are an almost perfect parallel with the respective ones for water pinch analysis, even sharing virtually the same goal in principle (MWR vs MER). The construction process for the composite curves and the theory behind what should or should not happen (e.g., fluxes/streams crossing the pinch point) are alike with the SSCC method, whilst the problem table, its construction and calculations are almost identical to WCA and the water cascading table, even reaching similar conclusions. This presents a great advantage: by studying and understanding the mechanisms of heat exchange and recovery, the same train of thoughts and ideas can be adapted with relative ease into a water saving and recovery network and vice versa, granting a good degree of versatility for an energy engineer.

3.6 Water pinch analysis of a cooling network

The water pinch analysis, while useful for a variety of applications, finds its most natural use in water cooling networks. These can be considered integrated networks composed of three main components: heat exchangers network, recirculation system and the cooling tower, which is the principal component as it allows for the heat release from the cooling water into the air. As a result of this process as well as blowdown to avoid buildup of unnecessary and potentially harmful material in the system, part of the cooling water evaporates, requiring make up water to keep the cooling network functioning properly [10].

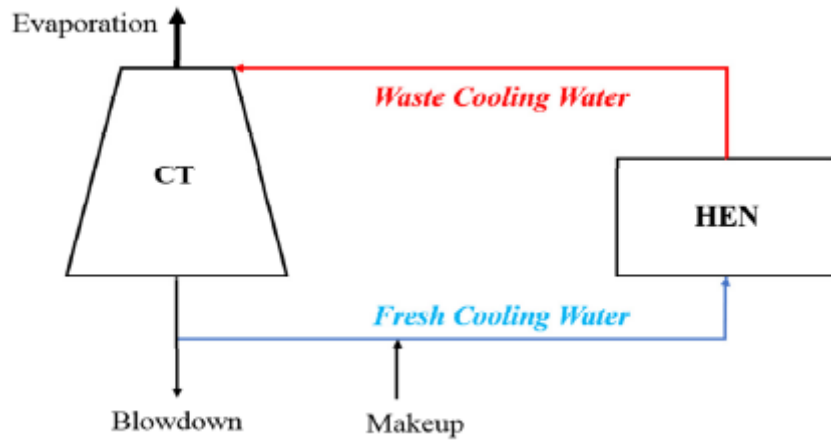


Fig. 3.9 Simple representation of cooling circuit [10].

The HEN is made of various heat exchangers, each of which is considered to be operating in counter-current with a ΔT_{\min} between the heat source and the cooling water: the heat source is supplied to the exchanger and is cooled from the maximum inlet temperature ($T_{hs,i}$) to the maximum outlet temperature ($T_{hs,o}$), while the cooling water is heated from maximum inlet temperature ($T_{cw,i}$) to the maximum outlet temperature ($T_{cw,o}$).

$$Q = CP_{hs}(T_{hs,i} - T_{hs,o}) = CP_{cw}(T_{cw,o} - T_{cw,i}) = \Delta H$$

The inlet cooling water stream is considered as demand and the outlet as a source, to target the fresh cooling water flow rate and waste cooling water temperature.

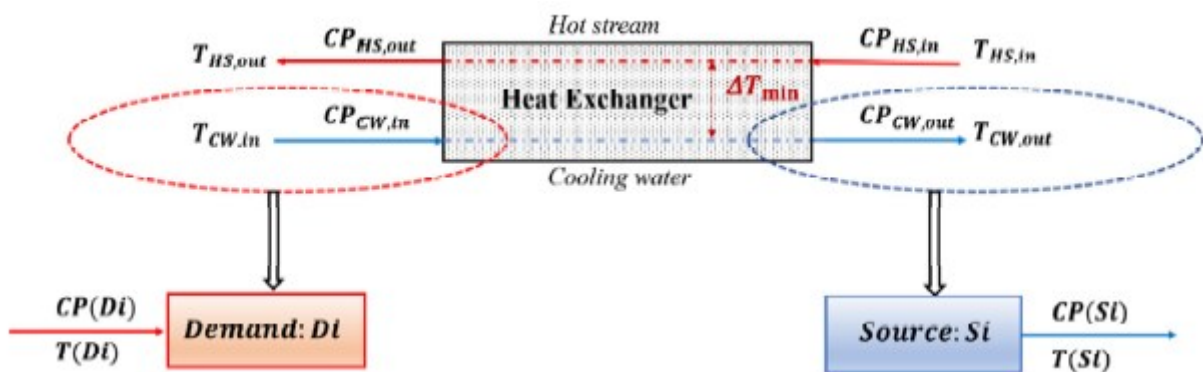


Fig. 3.10 Heat exchange process with heat flows and temperatures: inlet and outlet flows of cooling water are considered as demand and source [10].

The minimum ΔT is 10°C and the temperature of the fresh water is 20°C . The inlet temperature of the cooling water is equal to the heat source outlet temperature minus 10°C and the cooling water outlet temperature is equal to the heat source inlet temperature minus 10°C .

Table 1: Limiting cooling water data

Heat Exchanger	Inlettemperature (°C)	Outlettemperature (°C)	HCFR (kW/°C)	Enthalpy change (kW)
HE1	20	40	20	400
HE2	30	40	100	1 000
HE3	30	75	40	1 800
HE4	55	75	10	200

Table 2: Limiting cooling water data as demands and sources

Cooling water demands			Cooling water sources		
Demand	Temperature (°C)	HCFR (kW/°C)	Source	Temperature (°C)	HCFR (kW/°C)
D1	20	20	S1	40	20
D2	30	100	S2	40	100
D3	30	40	S3	75	40
D4	55	10	S4	75	10

Table 3: Targeting of FCW heat capacity flow rate and WCW temperature

T_k (°C)	$CP_k(Dj)$ (kW/°C)	$CP_k(Sj)$ (kW/°C)	CP_k (kW/°C)	$\sum_k CP_k$ (kW/°C)	$T_k \sum_k CP_k$ (kW)	$\sum_k T_k CP_k$ (kW)	H_k (kW)	$CP_{F,k}$ (kW/°C)	$T_{CWSL,k}$ (°C)
20	20	0	20	20	400	400	0	0	20
30	140	0	140	160	4800	4 600	200	20	22.2
40	0	120	-120	40	1600	-200	1800	90	40
55	10	0	10	50	2750	350	2400	68.6	46.7
75	0	50	-50	0	0	-3400	3400	61.8	57.8

Fig. 3.11 Tables detailing the WPA calculations taken to obtain the composite curves [10].

After obtaining the above tables by following the water pinch analysis procedures previously explained, the demand composite curve can be plotted.

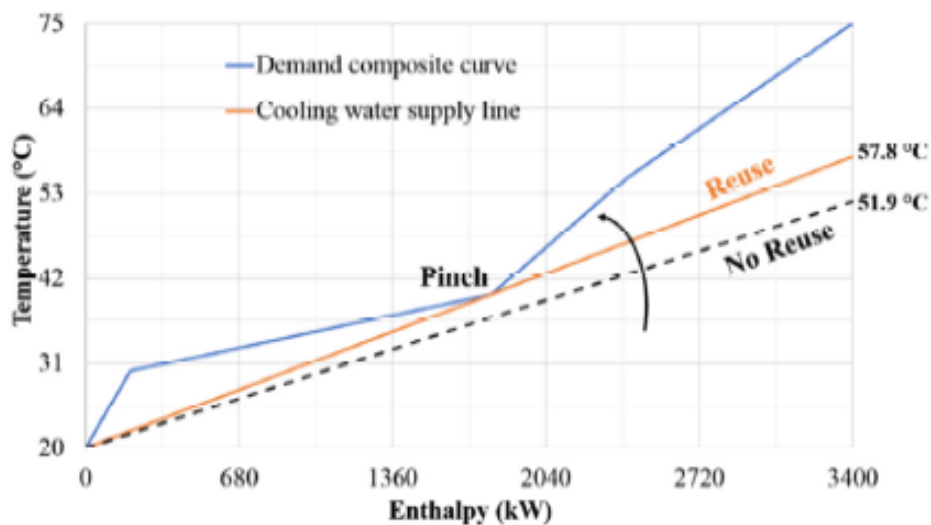


Fig. 3.12 Composite curves of the case study [10].

The pinch point is the point of contact between the cooling water supply line and the demand composite curve (40°C pinch temperature). The maximum reuse limit corresponds to the maximum slope of the cooling water supply line, while the no-reuse limit corresponds to the minimum slope of the supply line.

Designing the HEN requires the temperature diagram, obtained by following three steps: a) arranging all the heat exchangers from the lowest to the highest inlet temperature levels, b) each HE is located in its temperature range by arrows moving from maximum inlet to maximum outlet temperature, c) the temperature diagram is divided into two areas, one above and one below the pinch point [10].

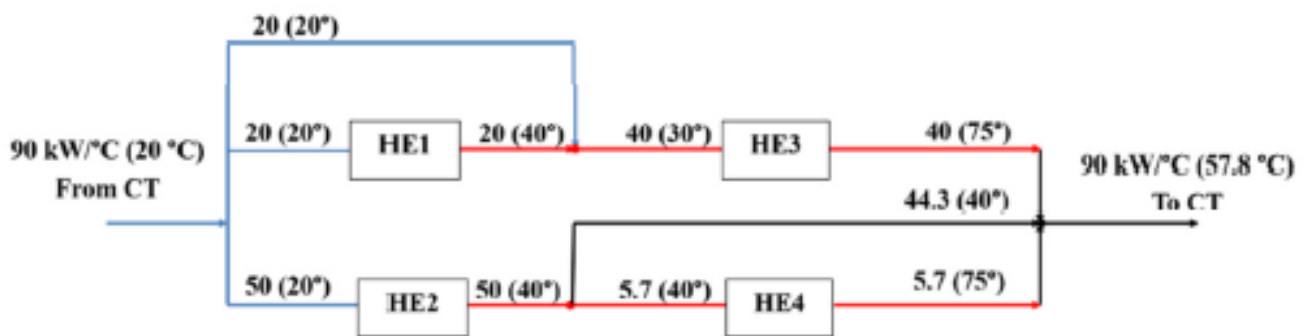
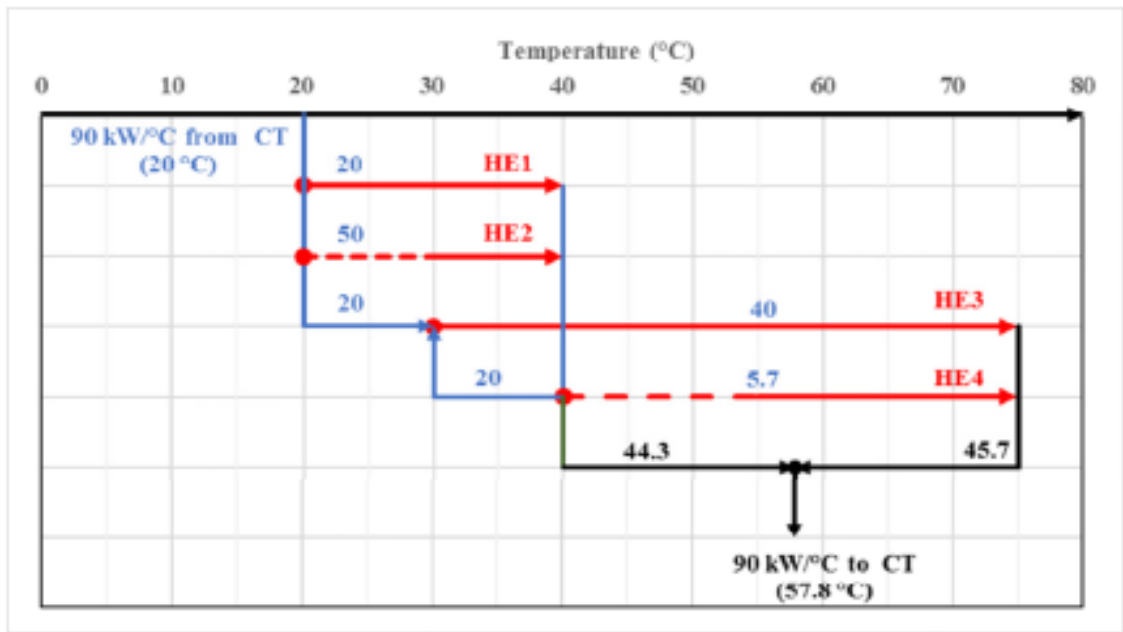


Fig 3.13 Temperature diagram and flowsheet of the HEN network designed from the previous calculations [10].

4 Water footprint of the energy sector

4.1 Italian energy sector

As the issue of water scarcity becomes more concerning, several studies related to it have been made and one of particular interest is related to the energy production sector.

Considering the current situation, water is used in the majority of the power production plants as a cooling liquid (fossil powered plants) or as “fuel” itself (hydroelectric plants). This is problematic, as the current trends from IEA showed a future increase in water consumption and, according to EU estimates, it can be as high as 68% of water withdrawals for energy production (between 2000 and 2050). According to Mekonnen et al. a substantial increase in solar and wind power production would offset these values and EU prediction with similar solution show a decrease of water withdrawals of 33% (2000-2050).

Even if water scarcity wasn't an issue, major withdrawals would negatively impact on the basin and one must also consider the issue of the water footprint embedded in the imported/exported energy quota (in the specific Italian case it's important as the imported electricity is quite relevant) [11].

4.1.1 Method and critical points of the study

The chosen methodology for the study is the water footprint based on LCA (ISO 14040) and as such it follows the same steps: not only it evaluates the water consumption during the lifetime of the plant, but it also weighs them to express them as an impact. The main phases are:

- Goal definition and field of application (definition of objectives, functional unit, boundaries of the system and processes)
- Inventory (all inputs and outputs of the system regarding matter and energy fluxes)
- Impact evaluation (inventory data gets grouped and organised through classification and characterisation)
- Results analysis

The most relevant aspects to account for are, obviously, related to the water source: quality and quantity, changes in the regime after withdrawal, seasonal changes, usage of storage and other temporal related changes, type of consumption (evaporation, incorporated into a product, released to a different basin, to quote a couple), etc.

Because of that, the inventory phase is extremely important, but at the same time one of the more critical points of the method as it is the heaviest part of the process in terms of workload. It requires the collection of data of all input and output water fluxes: they're numerous and varied and as such they must be divided by type of source (groundwater, sea water, surface water, etc.) and, most importantly, by geographical location as the evaluation of water scarcity is related to the location of the water source.

The selected method has been applied to a test study in 2016, consisting of a gas-powered combined cycle plant, representing the Italian production park. The reference unit chosen is 1kWh of electric energy produced in such a plant, accounting for all phases of the life cycle. The majority of the water consumption was during the operation of the power plant, with another relevant quote, albeit inferior, during the supplying phase of the natural gas.

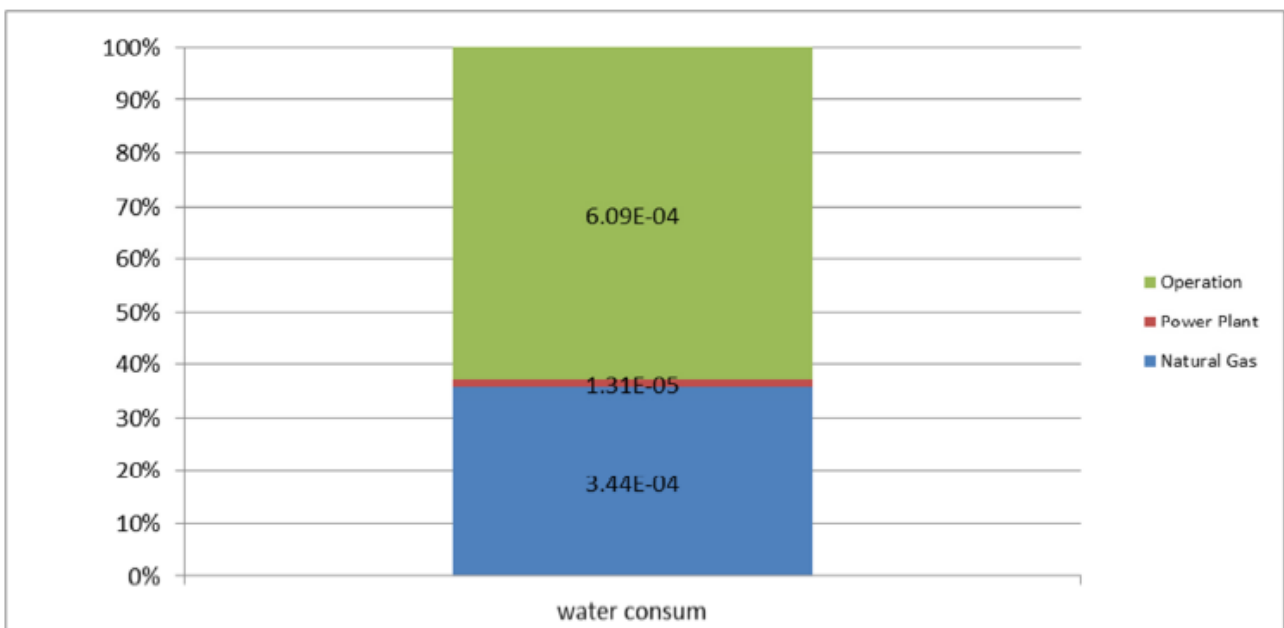


Fig. 4.1 Water consumption of natural gas extraction, plant construction and its operation [11].

As previously mentioned, the location is as important as the footprint itself. The study shows that, while the majority of the impact is located in Italy (during operation), the quota related to the supplying is split between Europe, Russia and Rest of the World (RoW).

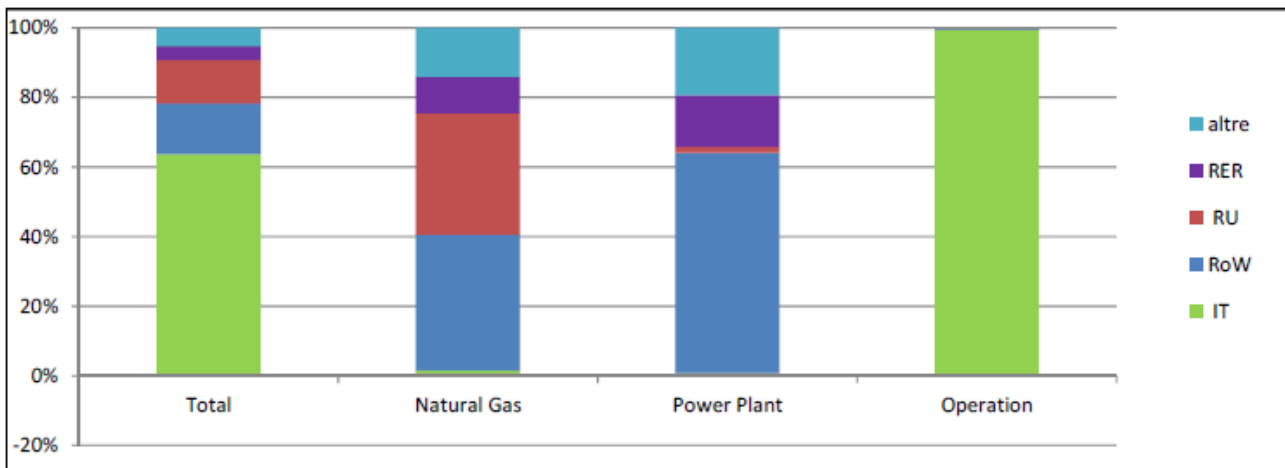


Fig. 4.2 Water consumption divided by phase and geographical location [11].

While there're similarities, there're also differences. The main one is in the type of footprint, as the classic water footprint distinguishes between blue, green and grey water footprints, while the ISO 14046 is more accurate in terms of the pollutant impact evaluation: while the WFA measures the grey footprint as a volume of water necessary to absorb a certain quantity of pollutant agents, the ISO requires the definition of specific impacts like eutrophication and acidification. Moreover the green water footprint is not included in the ISO as it's not environmentally relevant and any potential impact on soil conditions is evaluated within a specific category of the LCA [11].

4.1.2 Method application to the Italian energy sector

The application of the ISO 14046 follows the previously mentioned steps, starting with the goal definition, which is the evaluation of the water footprint of the Italian energy mix. For completeness, the energy supplied to the network is considered, therefore energy imports have been included. The functional unit selected is 1 MWh of energy supplied to the electric network and the boundaries include all phases of the life cycle of all the available technologies for energy production, ranging from the extraction of raw resources to the dismantling of the plants.

The selected footprint evaluation is AWARE, based on the 1/AMD (availability minus demand) indicator. AWARE evaluates the impact in terms of water scarcity for both humans and ecosystems, using characterisation factors to determine if an additional consumption in a determined geographical area will compromise the water use for another entity.

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

$$STe_i = \frac{1}{AMD_i}$$

$$CF = \frac{STe_i}{STe_{world\ avg}} = \frac{AMD_{world\ avg}}{AMD_i}, \text{ for Demand} < \text{Availability}$$

$$CF = \text{Max} = 100, \text{ for Demand} \geq \text{Availability in region } i \text{ or } AMD_i < \frac{AMD_{world\ avg}}{100}$$

$$CF = \text{Min} = 0.1, \text{ for } AMD_i > AMD_{world\ avg}$$

Fig. 4.3 Calculation of AMD and CFs [11].

CFs are calculated for agricultural use, non-agricultural use and generic (unknown) use. A CF of 10 means that the water resource availability is 10 times lower than the world average.

This evaluation method presents some critical points, for example the cut-off at 100 for the CF, however the information loss is acceptable. The second point is the quantification of the ecosystem water requirement (EWR), which has to be made by consulting experts and making hypotheses on ecosystem conditions. The third point is the matter of application of AWARE: the method is only valid for situations in which the water availability of the region considered is not modified, in other words, for marginal water consumption, in the case of processes that generate an additional consumption compared to the current availability [11].

4.1.3 Inventory phase

This section of the method gathered data regarding both the energy mix and the water cooling of the production plants. The following picture shows the Italian energy mix by type of technology of the required energy on the network (as of 2014) [11].

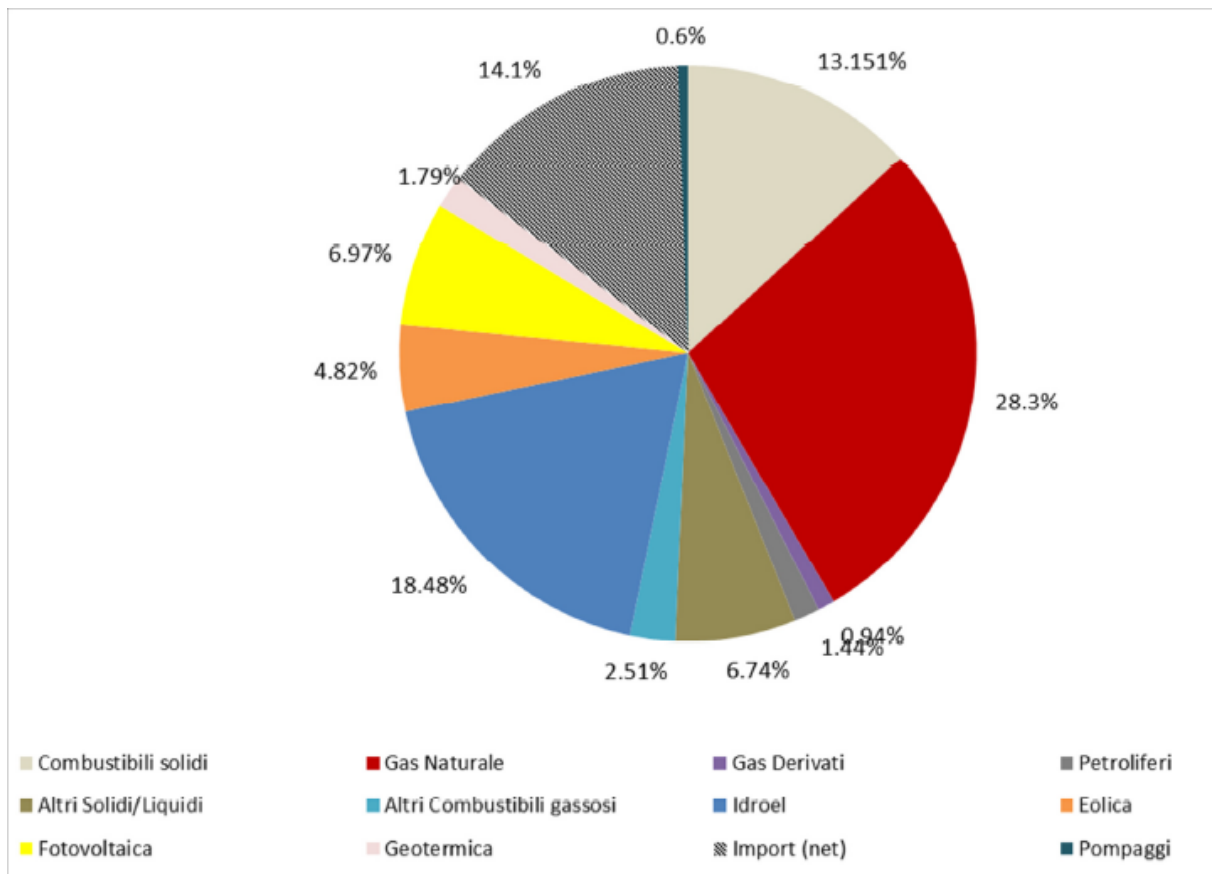


Fig. 4.4 Italian energy mix of 2014 [11].

The main contribution is from natural gas (28%), followed by hydroelectric, import and solid fuels. Solar and wind power are both at less than 10%. The different technologies considered are obtained from statistical reports from the electric network operator TERNA:

- Energy production only: Internal combustion (CI), gas turbine (TG), steam condensation (C), combined cycle (CC), repowered (RP)
- Combined energy and heat production: CIC, TGC, CCC, counterpressure steam (CPC), steam condensation with extraction (CSC)

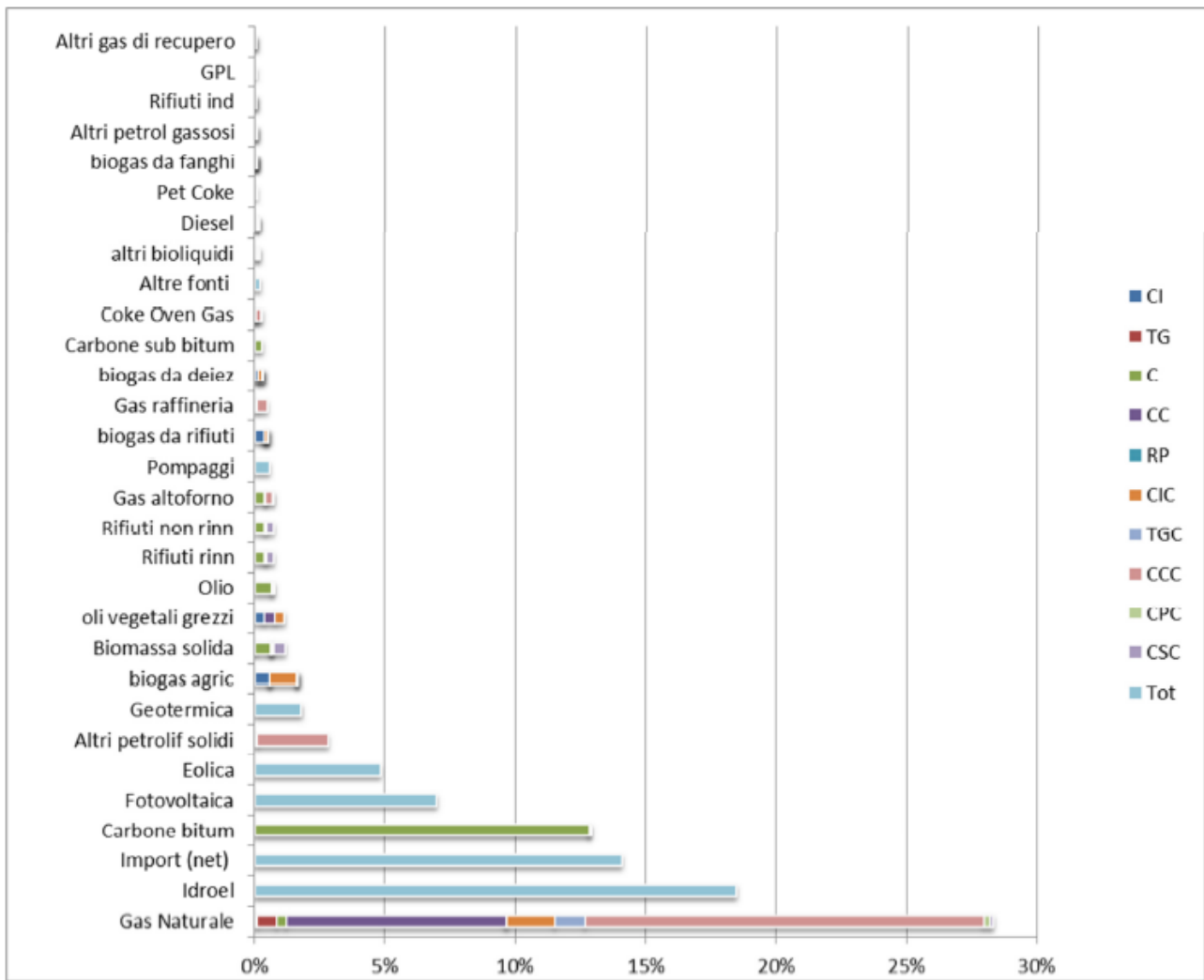


Fig. 4.5 Energy demand of 2014 divided by technology type [11].

Regarding the cooling systems, the ECOINVENT table has been used, with the following formula:

$$C_i = (C_{i_{rec}} \cdot f_{i_{rec}}) + (C_{i_{once}} \cdot f_{i_{once}})$$

Where $C_{i_{rec}}$ and $f_{i_{rec}}$ represent, respectively, the consumption of recirculating systems and the percentage of plants that use a recirculating system, while $C_{i_{once}}$ and $f_{i_{once}}$ represent the same data for once-through systems.

This information is integrated with the type of fluid used in the cooling system (freshwater, sea water or air), dividing the coal and gas powered plants accordingly and recalculating the cooling water consumption [11].

Tipologia di raffreddamento	Ecoinvent (Flörke et al. 2011)	RSE Impianti CC Gas Naturale	RSE Impianti a Carbone
A passaggio singolo (once-through)	73%	40%	0%
Ciclo chiuso (recirculating)	27%	20%	1%
Acqua di mare/aria	0%	40%	99%

Table 4.1 Percentage of Italian power plants making use of the respective cooling technology, both from literature and from RSE databank [11].

4.1.4 Impact evaluation

The results obtained from AWARE are as follows: for every MWh of energy supplied to the network, 4.6m³ of water are consumed of which roughly 3m³ are from hydroelectric plants and 1m³ is from energy import. Excluding the latter, 3.55m³ of water are consumed for each MWh of produced energy, of which 80% are from hydroelectric plants, 5% gas powered plants and 4.5% from photovoltaic plants. The impact of the Italian energy mix is obtained by applying the CFs (by geographical area) to the input and output water fluxes in the inventory, thus returning the impact values: 78% from hydroelectric and 8% from import. Analysing just the electric production, the values change to 85% hydroelectric, 3.9% natural gas and 2.9% PV, as reported in the following pictures [11].

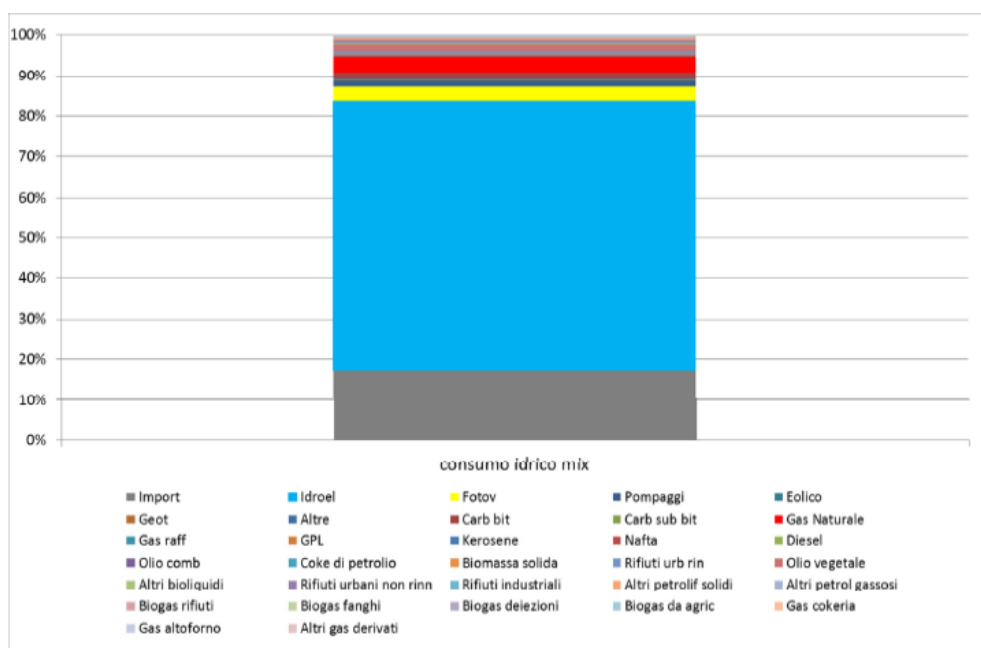


Fig. 4.6 Water consumption of the Italian energy mix [11].

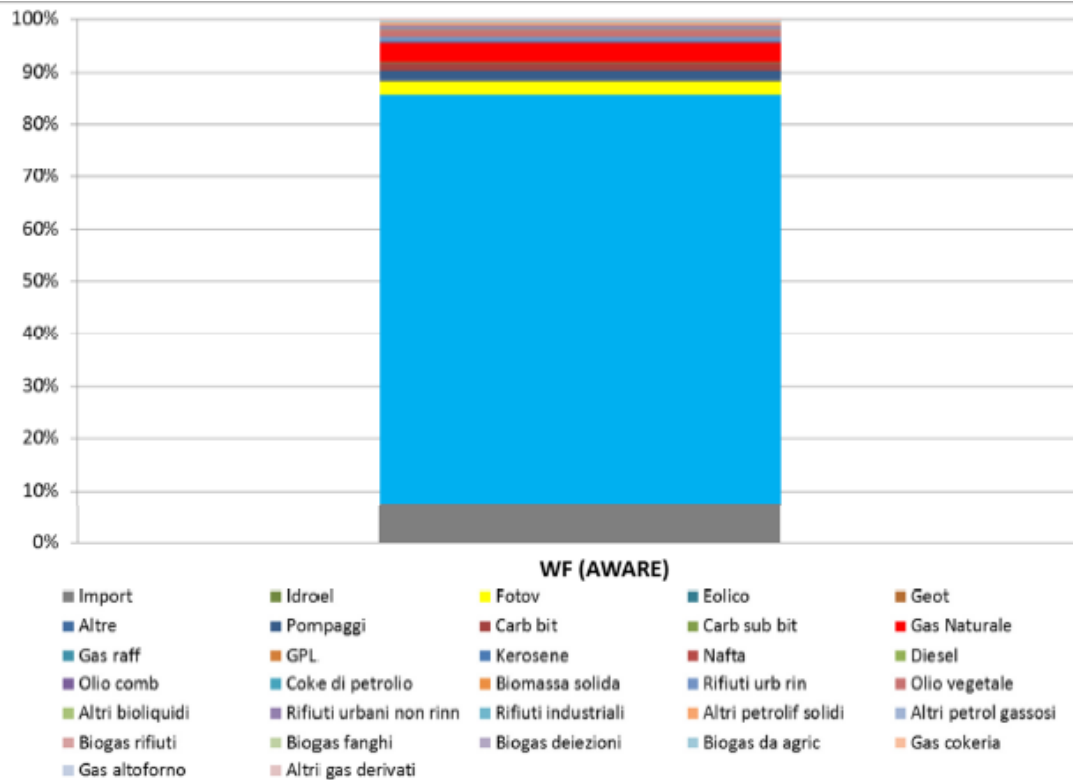


Fig. 4.7 Water footprint of the Italian energy mix, calculated with AWARE [11].

Hydroelectric plants impact more than other technologies despite their relatively low contribution (18%, 10% if only reservoir plants are considered) to the energy mix, because their specific consumption is higher: $16\text{m}^3/\text{MWh}$ for a single plant, compared to $0.627\text{m}^3/\text{MWh}$ for a gas plant. For this reason it's useful to switch from a energy mix consumption analysis to a specific consumption by technology, to compare them. By doing so, the hydroelectric technology has the maximum consumption, as expected, however an interesting comparison can be made between coal and gas powered plants: natural gas plants have higher efficiencies and therefore a reduced water consumption, compared to coal technology, however in the specific Italian case the consumptions are roughly equal as the majority of coal powered plants use sea water for cooling, which is not included in the impact analysis [11].

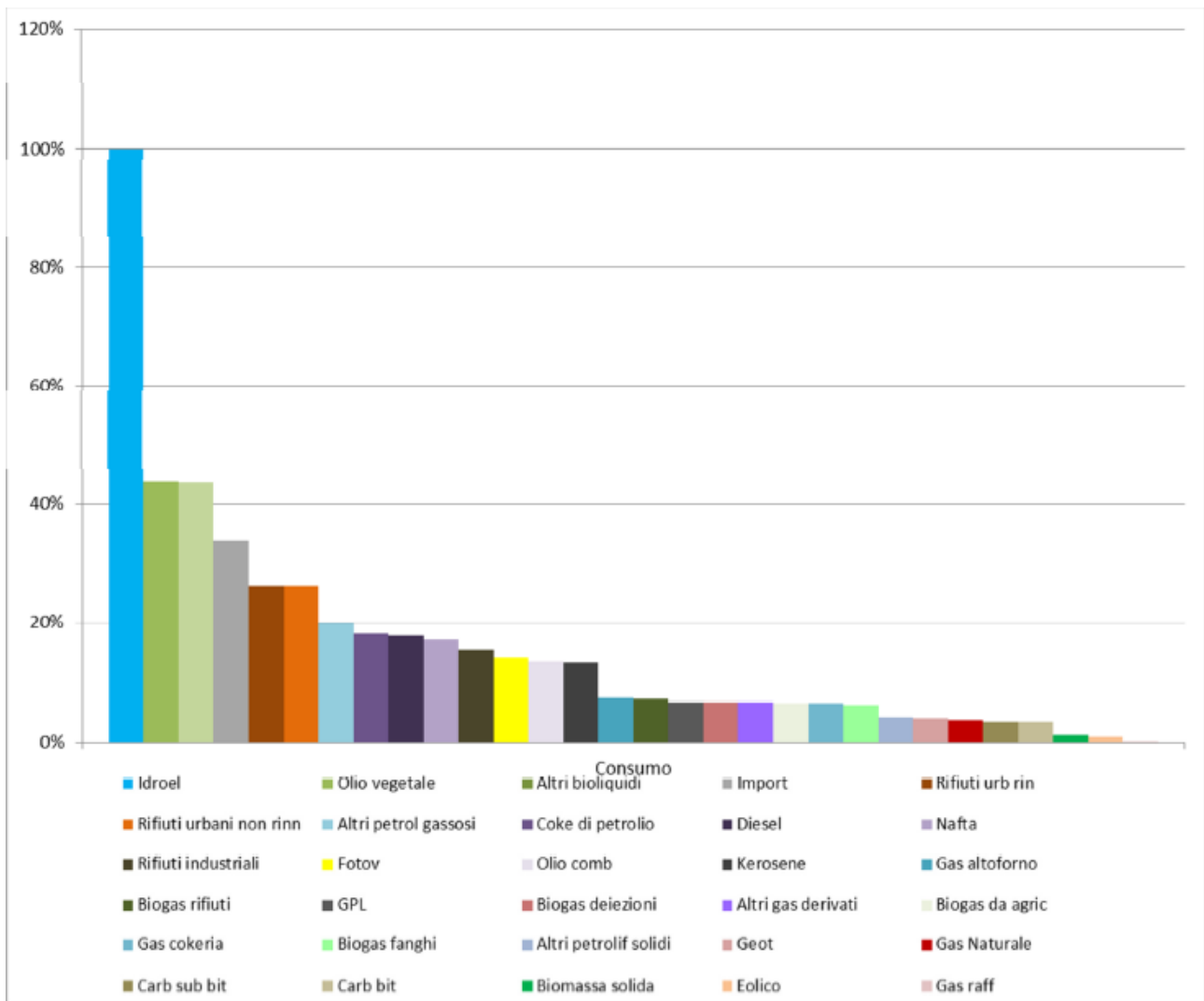


Fig. 4.8 Specific water consumption of different power plant technologies [11].

4.5 European energy sector

The energy sector on a European level is responsible for over 55% of total water withdrawals, mostly tied to cooling systems and hydroelectric plants [11] [12]. As the climate crisis worsens, the issue of water scarcity affects the power generation sector immensely. In the past few years, high temperatures and absence of precipitations have caused severe droughts in some areas of Europe, Italy included, resulting in problems to the social-economical tissue of the countries and the power sector as well, with many fossil and nuclear power plants shutting down momentarily. While a transition to green energy would be beneficial under many environmental aspects, water abstraction included, it is not true that the issue would be solved, as hydroelectric plants have shown to be the most consuming in terms of water withdrawals. Thus a water footprint assessment of current power generating technologies in Europe has been conducted, to help with future decisions in that matter [12].

4.5.1 Inventory phase

As the databases used for the compilation of the power plants was extremely vast, it was narrowed down to plants above 50MW of power located in Europe (EU member states plus the Balkans, Turkey, Switzerland, Ukraine, Iceland, UK and Norway). The cut-off is appropriate as lower power capacities utilise a negligible amount of water due to the dry cooling that most of them use. As such, 3276 power plants have been considered, of which 895 (27.3%) are gas powered, 852 (26%) coal powered, 835 (25.5%) hydroelectric, 302 (9.2%) oil powered, 150 (4.6%) nuclear and the remaining 7.4% are other technologies combined. Despite weighing heavily on water withdrawals singularly, geothermal power plants have been excluded as their numbers are few and far between and thus the overall contribution negligible [12].

In addition to the type of plant considered, their location is also important to establishing the impact on water sources. The GSHHG database was used to link the power plants with water bodies in their vicinity (Geographic Information System analysis), assuming that plants within 5km of rivers and lakes make use of their freshwater for cooling, plants within 20km of the sea coastline use sea water and plants with unknown water sources have been assumed to be using ground freshwater as a cooling source. The picture below shows the different types of plants that have been identified and considered [12].

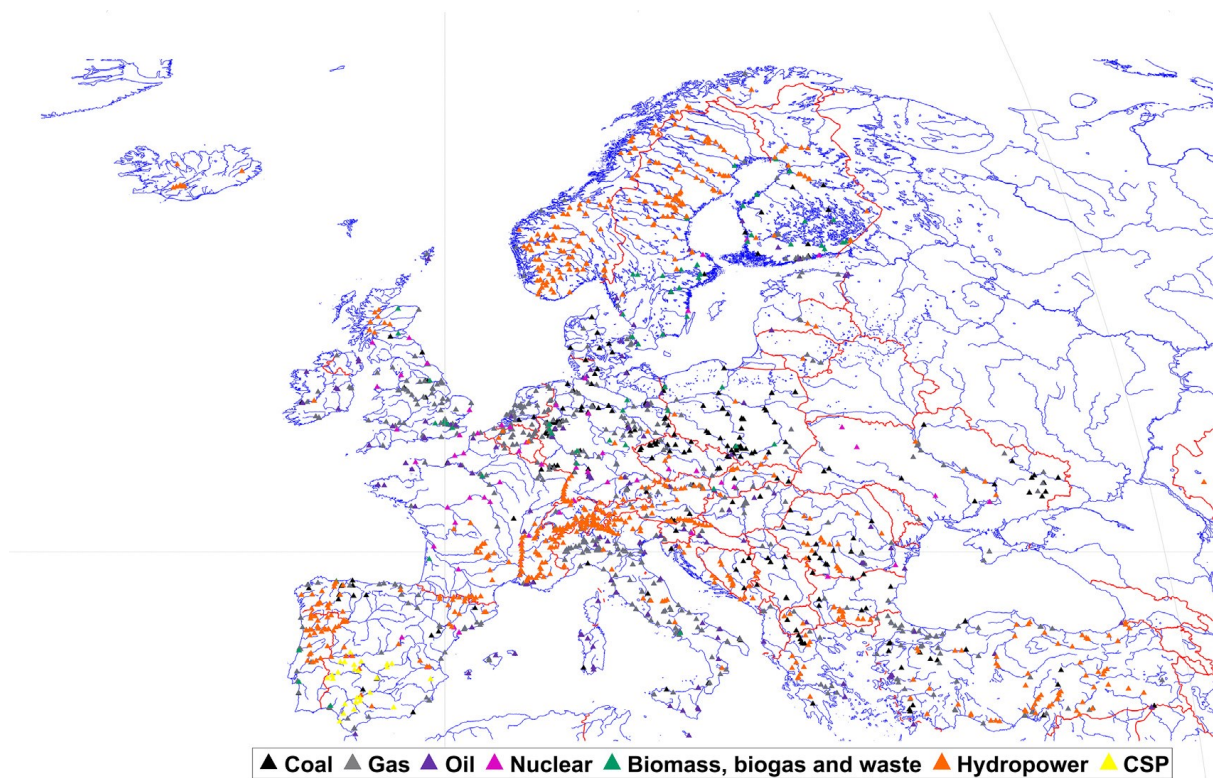


Fig. 4.9 Map displaying the identified and chosen power plants for the study [12].

To assess the water footprint of the plants, the type of cooling employed by them is also crucial. Therefore, integrating the initial database on cooling plants with satellite imagery to recognize the type, five technologies have been considered: dry cooling (direct and indirect air cooling), once-through (open loop), recirculating tower (cooling towers with natural or mechanical induced draft), recirculating pond and inlet cooling systems.

4.5.2 Impact evaluation

The water footprint on a power plant level has been calculated with the following equation:

$$WF = AC \cdot FLH \cdot WUI$$

Where AC is the active capacity in MW, FLH is full load hours of power generation, WUI water use intensity factor in m³ per MWh. The water footprint on a country level is obtained as a sum of all power generation facilities located within it and the sum of the countries WF is the regions' one [12].

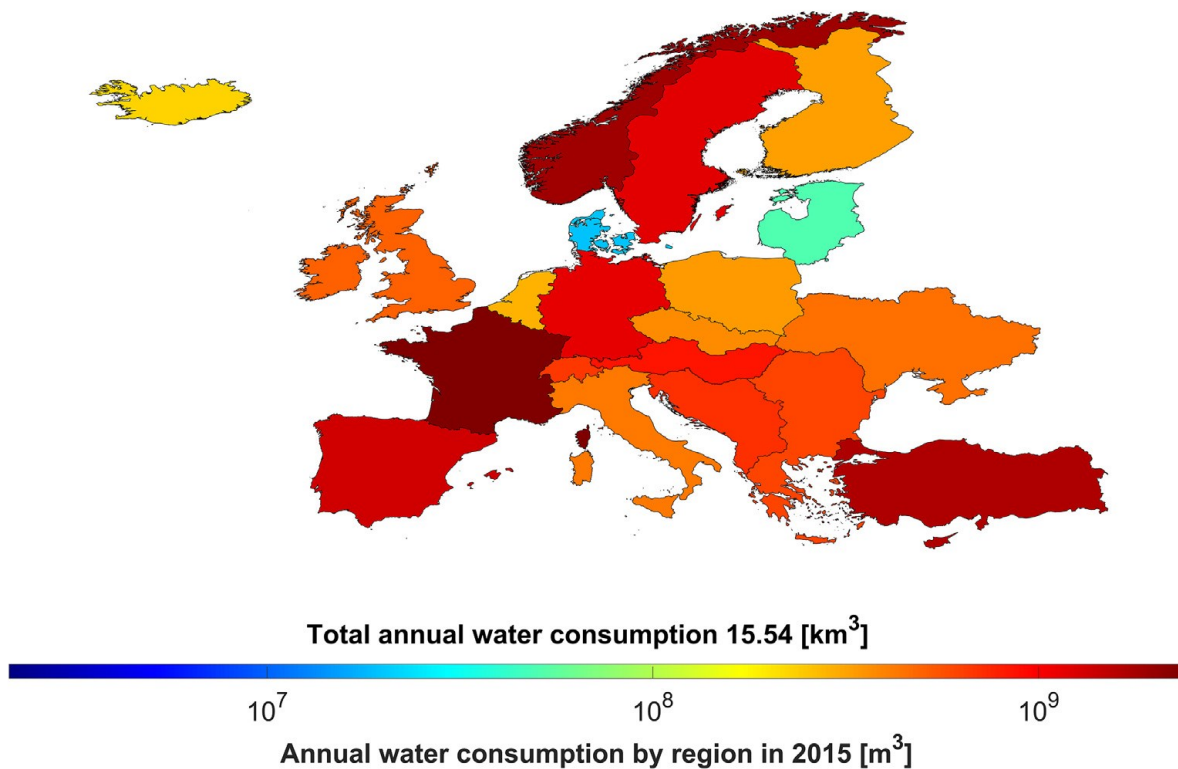


Fig. 4.10 Water consumption by country, in Europe, with the overall total quantity displayed [12].

The picture above shows the results of the WF evaluation. The total water consumption was of 1.554.000 m³, with the highest impact from hydropower plants (61.5%), while coal and nuclear plants have contributed with 19.4% and 15.5% respectively and all the other technologies combined amount to a measly 3.6%. The share of European electricity from hydropower was only 14%, despite the high consumption of water source and this is due to the fact that the water consumption factor is the highest among power generation technology, as previously stated. It can be up to 68m³ per MWh (upper limit of the min-max water consumption interval), making it 21 times more impactful on water sources than a nuclear power plant. Much like the Italian case, gas power plants in Europe contribute little to the water footprint due to the cooling system employed: while Italian plants make use mostly of sea water, European plants utilise dry cooling and both have very little impact on freshwater sources [12].

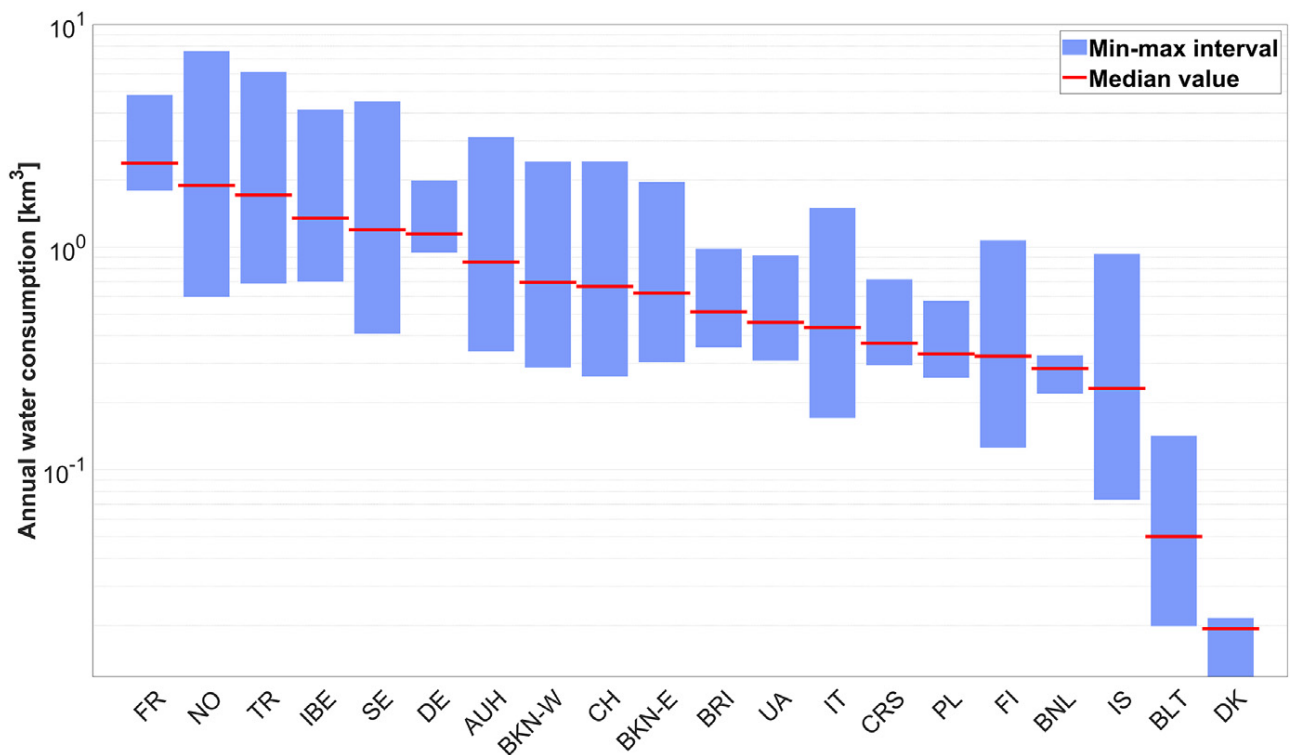


Fig. 4.11 Min-max intervals per region, with the Y axis in log scale [12].

5 Future prospects: water footprint of hydrogen production

5.1 Introduction

Since the world became more aware of the dangers and issues concerning global warming and water scarcity, governments have shifted towards a greener focus on both energy and economy, with the aim of reducing the usage of fossil fuels and resources for energy production and eventually cutting them off completely. This approach is especially evident and talked about in the automotive industry, with plans from the EU to completely stop the selling of combustion engine cars by 2035. As these scenarios slowly develop, new sources have been proposed to substitute the standard engines, namely electric cars and hydrogen powered vehicles.

While electric motors and technology are already well established and keep on improving, hydrogen applications are few and far between in the automotive sector, with only some experimental applications so far. This is also true in the energy production sector, where hydrogen is used very rarely and in small plants, an example of which would be the Italian power plant at Fusina that recently installed some small hydrogen turbines as a support for the main production. The fuel needed for the operation is coming from the nearby chemical pole as a byproduct of their processes, so, for all intents and purposes, it's a waste reuse operation.

While hydrogen is not a well developed resource for energy and automotive sectors, it's mainly used for chemical processes and productions, so the vast majority of its market is the chemical industry and even then the quantities are relatively small, such that the impact on the environment and the water footprint is, at least for now, limited.

However, if it is deemed a viable vector in substitution of fossil fuels, this may change. For this reason it's important to evaluate the water consumption and impact of such a production.

As it stands, there are two main methods for hydrogen production on an industrial scale, both well developed commercially: Steam reforming and electrolysis [\[13\]](#) [\[14\]](#) [\[15\]](#) [\[16\]](#).

While other methods are available and can potentially become significant in the future, like extracting hydrogen from coal or waste biomass, steam-methane reforming is, by far, the most common one.

5.2 Hydrogen production methods

Hydrogen production can be divided into four main categories, depending on the sources used for the process and their impact on the environment [13] [14]:

- Grey: fossil fuel usage and high impact (GHG)
- Blue: fossil fuel usage, but improved emissions of GHG
- Turquoise: fossil fuel usage, but no production of CO₂ as a by-product
- Green: renewable resources and water are used

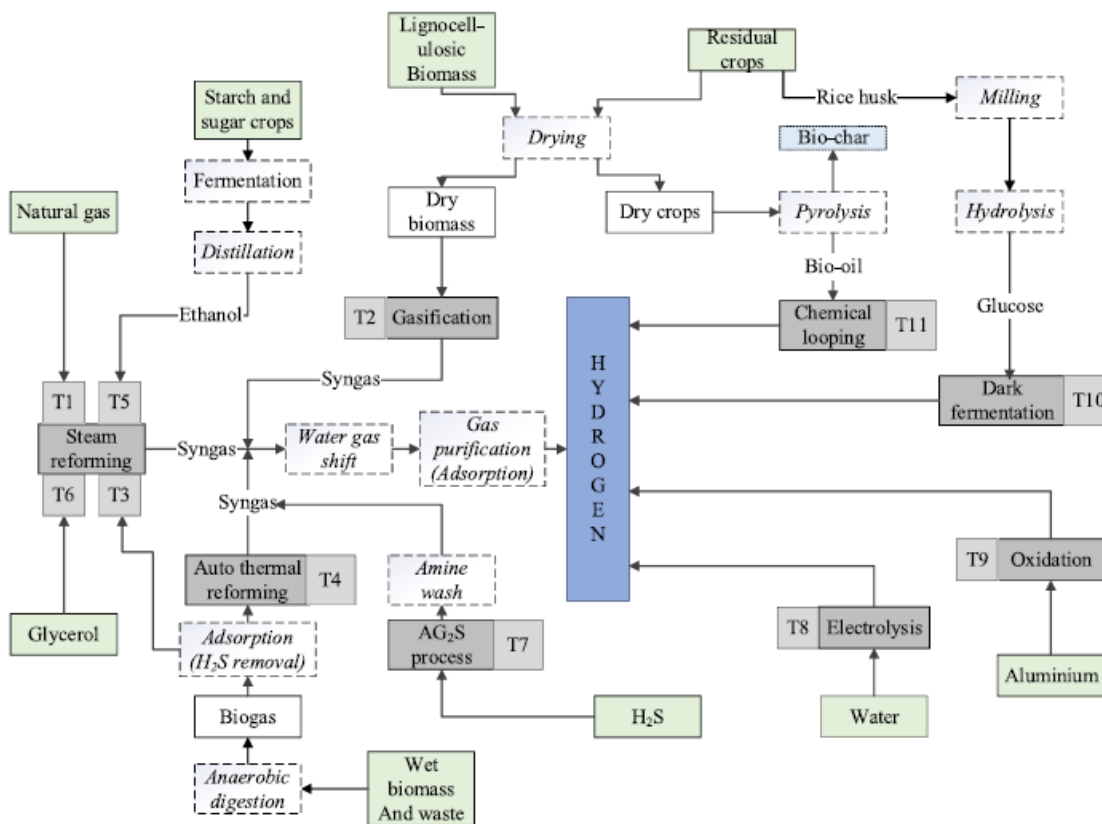


Fig. 5.1 Comprehensive scheme of different hydrogen production technologies, the majority of which are green [14].

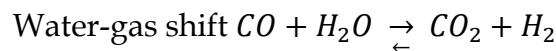
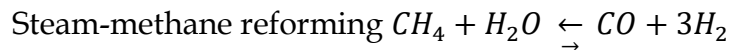
The figure above shows different hydrogen production technologies, some of which are still in an experimental phase or not commercially available. Apart from the natural gas steam reforming, all other technologies are considered as part of the green category.

As it stands, grey technologies are the most common and commercially available, with steam-methane reforming being the most mature technology for hydrogen production in

large plants, accounting for 76% overall global production, and will still work well for short term as the hydrogen industry expands [13] [14].

It consists of applying high temperature steam to methane to obtain syngas mixtures, steam and electric power. The production starts with raw natural gas, pretreated to remove the sulfur compounds, sent to the steam reformer where it gets transformed into syngas and hydrogen. These are fed to a high and low temperature shifts where more hydrogen gets extracted.

The two main processes are:



With this production method, the steam and electric power can be used for other operations as well, so it's flexible, but still reliant on fossil sources.

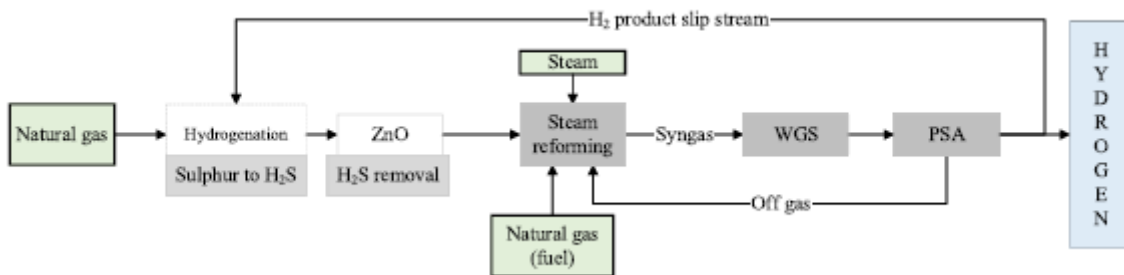
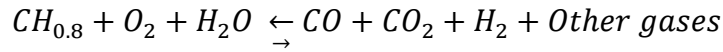


Fig. 5.2 Flowsheet of a common steam-methane reforming process [14].

Another fossil based technology of interest, mainly for economic reasons is coal gasification. This process produces hydrogen by reacting coal with oxygen and steam under high pressures and temperatures to obtain syngases, much like in steam reforming. This solution can be especially attractive in certain economies (for example China) where there's an abundance of coal and thus leading to a cheap production, albeit fairly impactful on both the environment and the water sources. As countries shift from a coal based power generation system to greener solutions, they might consider coal as a cheap transition towards a green hydrogen production, given the simplicity of the technology required [13] [14] [15].



Biomass and biofuels are an attractive alternative to fossil sources for hydrogen production as they are effectively CO₂ neutral, or close to neutrality, and their water impact can be kept low if the materials used are from agricultural waste (producing biomass specifically for hydrogen production is not convenient and counterproductive on the scope of reducing impacts and water footprint). The gasification of solid biomass (lignocellulosic residual biomass from forestry operations) requires high temperatures without combustion (500 to 1400°C), while liquid and gaseous biofuels like ethanol and biogas use reforming, similar to methane [14] [15].

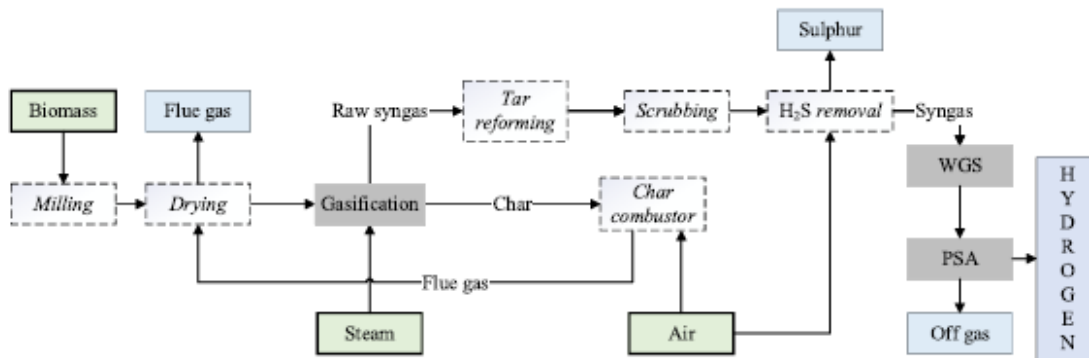


Fig. 5.3 Biomass gasification and reforming processes [14].

Biogas as a source of hydrogen is a viable and interesting option, provided that it is obtained from waste. Silage from agriculture, food waste, animal sludge are all good options to consider, since they won't impact the environment nor require additional water for their production. The process to convert biogas to hydrogen can be carried out like steam-methane reforming, or through autothermal reforming. The latter uses less electricity and is more efficient, however they're both very similar in nature. The biogas is pretreated to eliminate the many components that hinder the reaction and then sent to either reforming unit, depending on the plant used [14].

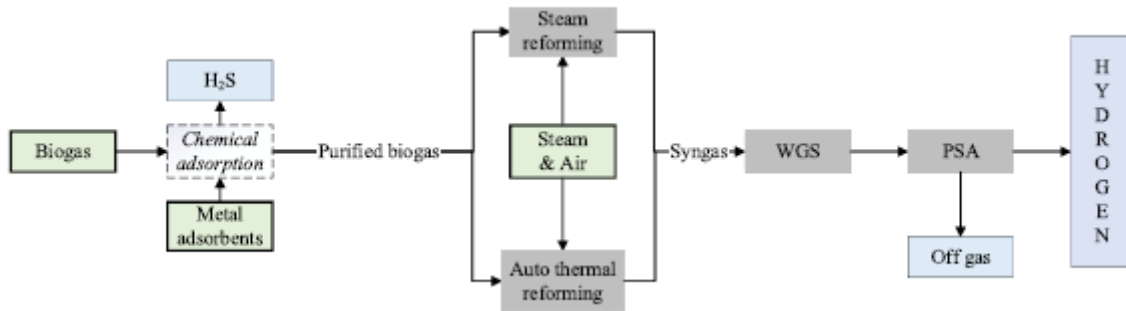


Fig. 5.4 Biogas reforming for hydrogen production [14].

Alcoholic waste is mainly made of ethanol which can be converted to hydrogen through steam reforming. The alcoholic waste is mixed with water into a 1:5 ethanol-water ratio and then warmed up and evaporated. The vapours head to the reformer where they become syngas and then undergo a water-gas shift to extract more hydrogen [14]:

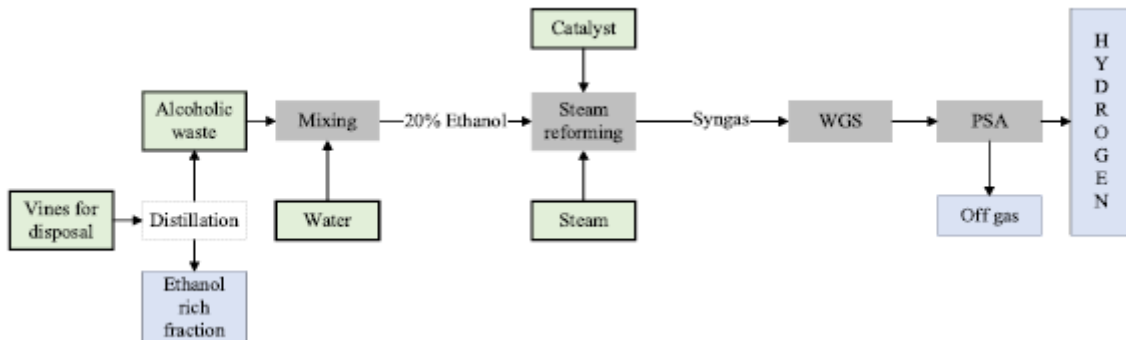
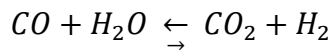
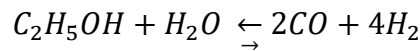
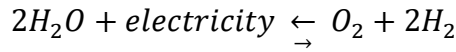


Fig. 5.5 Alcoholic waste evaporation and reforming [14].

Electrolysis of water is, potentially, the greenest method to obtain high quality hydrogen. The reaction requires electric energy and takes place in electrolyzers, units made of a cathode, an anode and an electrolyte. At the moment, there are low and high temperature electrolyzers available industrially (PEM and SOEC technologies, operating at 70-90°C and 650-850°C respectively) [13] [14] [16]. The reaction is quite simple:



The main advantage of operating at high temperature is the fact that part of the required energy can be supplied in the form of thermal energy, making it a highly viable and efficient process, but the PEM operating at lower temperatures is more flexible, couples better with dynamic systems and has a faster cold start.

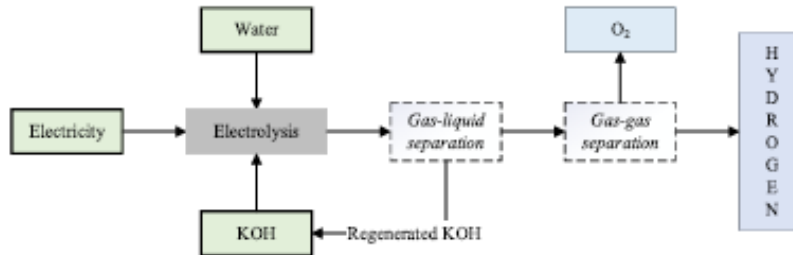


Fig 5.6 Electrolysis of water for hydrogen production [14].

Table 1. Resources required to produce 1 kg of H₂ from different production technologies and pathways.

Type	Thermo-Chemical				Electrolysis			Biological		
Conversion pathway	Steam methane reforming	Coal Gasification	Biomass Gasification	Biomass Reformation	Proton exchange membrane (PEM)	Solid oxide electrolysis cells (SOEC)	Dark fermentation + microbial electrolysis cell (MEC), w/out ER	Dark fermentation + microbial electrolysis cell (MEC), w/ER	Dark fermentation + microbial electrolysis cell (MEC), w/H ₂ recovery	
Abbreviation	SMR	CG	BMG	BDL-E	E-PEM	E-SOEC	DF-MEC w/out ER	DF-MEC w/ER	DF-MEC w/H ₂ recovery	
Feedstock	Natural gas	Coal	Corn Stover	Ethanol	Electricity	Electricity	Corn Stover	Corn Stover	Corn Stover	
Natural gas (MJ/kg H ₂)	165	-	6.228	-	-	50.76	22.9	-	-	
Coal (kg/kg H ₂)	-	7.8	-	-	-	-	-	-	-	
Biomass (kg/kg H ₂)	-	-	13.5	6.54	-	-	23.0	23.0	23.0	
Electricity (kWh/kg H ₂)	1.11	1.72	0.98	0.49	54.6	36.14	21.6	6.03	21.6	
Water (kg/kg H ₂) ¹	21.869	2.91	305.5	30.96	18.04	9.1	104.225	104.225	104.225	
Ammonia (kg/kg H ₂)	-	-	-	-	-	-	0.102	0.102	0.102	
Sodium hydroxide (kg/kg H ₂)	-	-	-	-	-	-	0.389	0.389	0.389	
Sulfuric acid (kg/kg H ₂)	-	-	-	-	-	-	0.207	0.207	0.207	
Glucose (kg/kg H ₂)	-	-	-	-	-	-	0.335	0.335	0.335	
Corn liquor (kg/kg H ₂)	-	-	-	-	-	-	0.008	0.008	0.008	
Diammonium phosphate (kg/kg H ₂)	-	-	-	-	-	-	0.015	0.015	0.015	

Table 5.1 Quantities of resources needed for the production of 1kg of Hydrogen, for different technologies [13].

5.2.1 Water footprint of hydrogen production: gasification

As previously mentioned, natural gas accounts for the majority of the current hydrogen production and is a widespread technology. As the hydrogen generation expands, however, coal could become a more prominent source, especially as a short-term transition solution until other green hydrogen plants are established. Coal can be found in greater and cheaper quantities compared to natural gas and nations that have a natural abundance of it like China, are probably heading in that direction. This, however, brings forth a variety of issues, specifically related to the environmental impact and the water consumption and as such, while it may be acceptable as a technology for the time being, other alternatives must be considered. The use of waste and residual biomass could be a very promising solution as they're pretty flexible as far as applications are concerned, depending on the nature of the biomass itself [15].

In the following paragraphs a comparison between coal and biomass gasification is made as the technology is relatively similar and leads to comparable hydrogen qualities. The study has been carried out in China using wheat straw as the biomass source and 1MJ of hydrogen as a functional unit for the WF analysis. The system boundaries were defined as shown in the below picture.

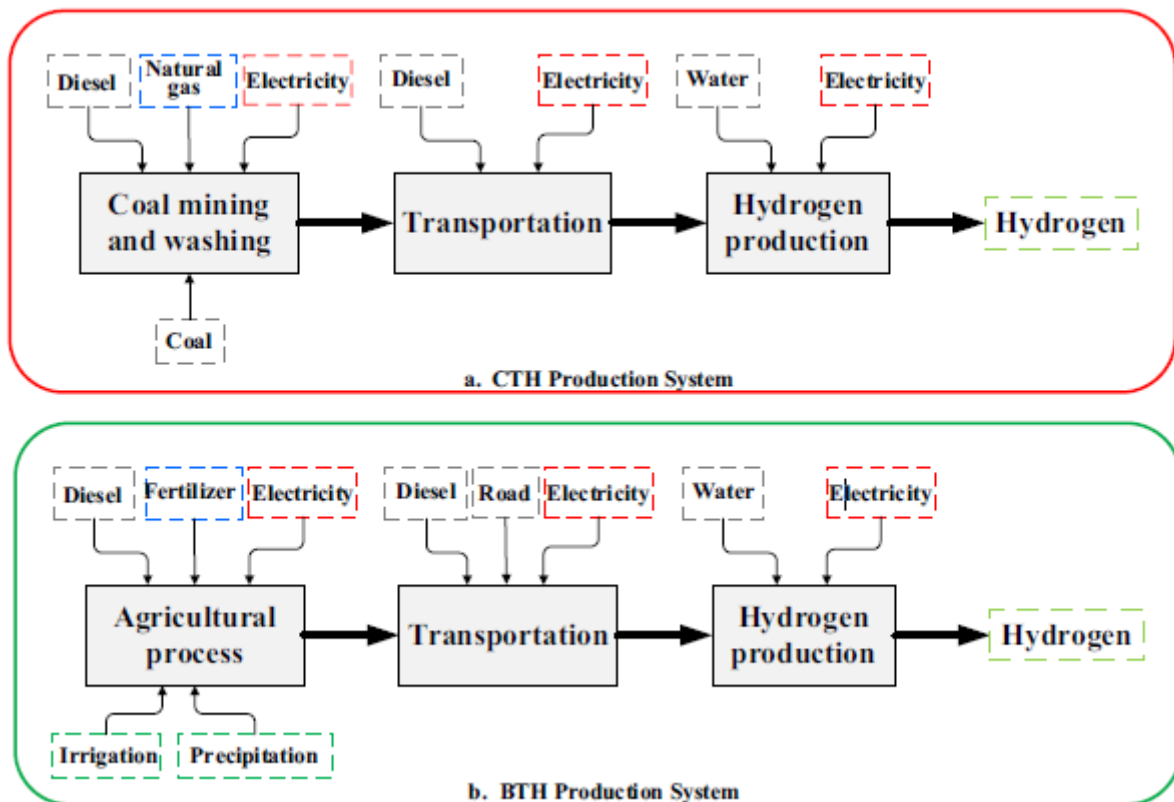


Fig. 5.7 Flowsheets of coal and biomass gasification and reforming for hydrogen production [15].

In regards to the biomass production, the majority of the water used is, as one might think, allocated to the growth of the wheat crop from which straw is obtained: while precipitation water does contribute to the development of the crop, it is not sufficient alone for its maturation. As such, irrigation water is provided, in the case of this study up to 2300 m³/ha (which roughly mirrors the average expected precipitation water quantity that the crops will receive during the year). Other water consumption data is related to the operation of agricultural machinery and the processes relative to the harvesting of the crop and baling of the straw.

In regards to coal production, the majority of the water is, instead, used during the washing process after extraction of the mineral. Coal mining operations are mostly underground in China and consists of mainly six phases: 1) exploitation of the coal mine fields; 2) stoping process; 3) tunnelling and supporting; 4) mine ventilation and safety; 5) coal mine transport system; and 6) coal washing and preparation. While the last process is the most water intensive one, operation of machinery, cooling, dust prevention and other such operations also make use of fresh water.

The production process makes use of an air separation unit to remove impurities and other harmful elements through pure oxygen as an oxidant, reducing the pollution discharge into the environment, and a pressure swing adsorption unit (PSA) to separate hydrogen from other components. The water consumption related to these two steps is mainly related to the power used and is, thus, indirect, or the cooling systems: 1.33t water/t coal is consumed by the air separation unit while the overall gasification unit consumes 1.12t water/t coal. This is due to the fact that some water has to be used in the coal slurry preparation, but given the low quality requirements, it can be recycled water from other sources.

The results of the study showed that the difference in water quantity between the two processes is quite relevant: the growth of the wheat crop alone accounts for 99% of the water used in the base case scenario, with a higher water utilization rate than coal gasification. In contrast, the majority of the water consumption related to coal usage is allocated to the transportation through the mine and the direct water uses mentioned above related to the tunnelling operations.

Overall, however, the coal gasification process uses more water and electricity than the biomass gasification process, due to the high quantity of water used in the circulation and cooling systems [15].

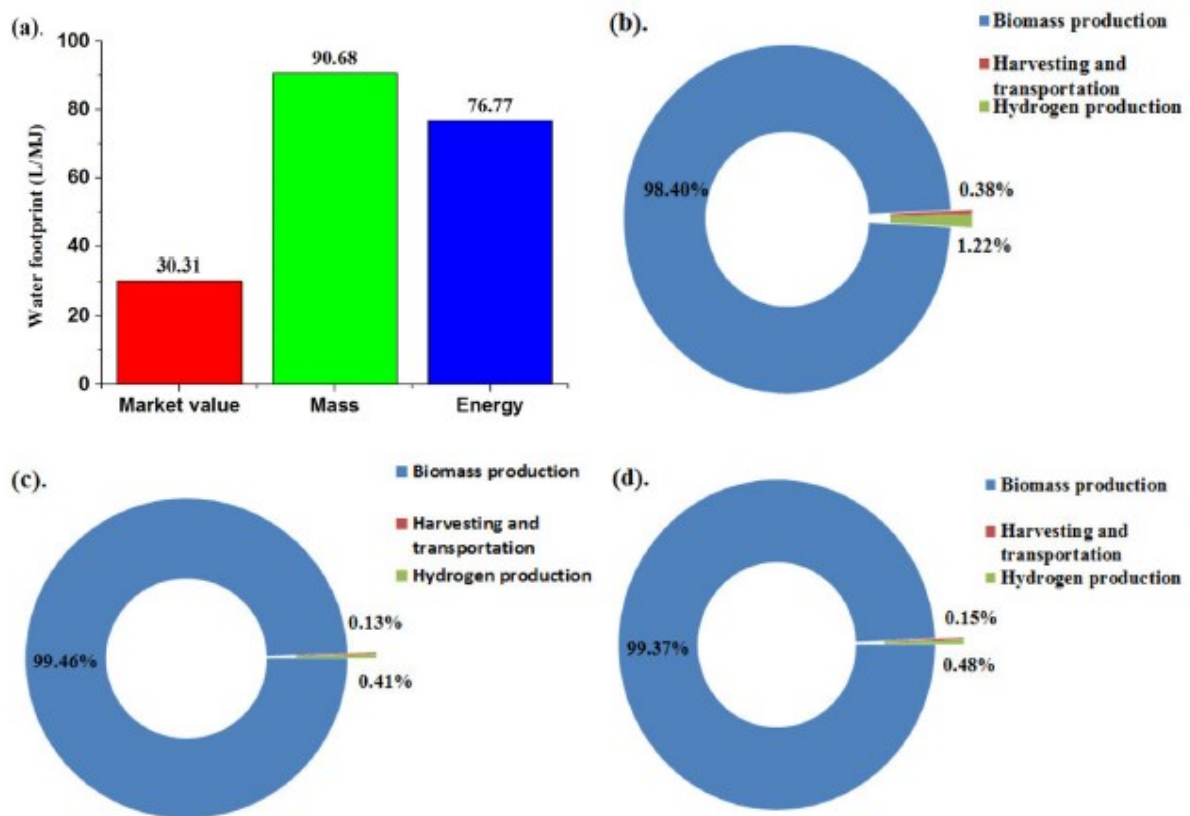


Fig. 5.8 Water footprint of biomass gasification and reforming, by scenario [15].

Apart from the base case scenario, the WF related to the biomass gasification process can vary sensibly depending on the distribution coefficients that are chosen for the analysis: the above figure shows the changes in WF based on different coefficients benchmarks, respectively market value (b), mass (c) and energy (d). The last two, in particular, have a much higher total WF compared to the base case scenario (118% and 39.5%).

Another important parameter related to water consumption was, of course, electricity usage in the processes. The indirect WF of power generation accounted for the majority of the overall indirect WF, with significant differences in values of water intensity of electricity based on raw materials used and technology employed in the power generation [15].

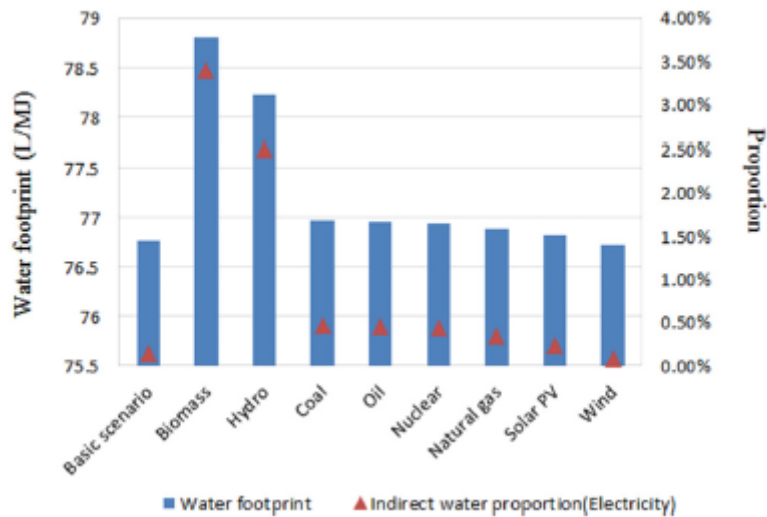


Fig. 5.9 Water footprint and indirect proportion of power generation for BTH process [15].

The figure above shows the water footprint of power generation and its indirect proportion for the biomass gasification process. As the vast majority of the WF is allocated for the growth of the crops, the impact of power usage isn't as significant as the coal gasification process, which is portrayed in the figure below. The hydroelectric and biomass powered plants are the heaviest in terms of WF and indirect proportion for coal gasification, greatly affecting the overall WF of the process [15].

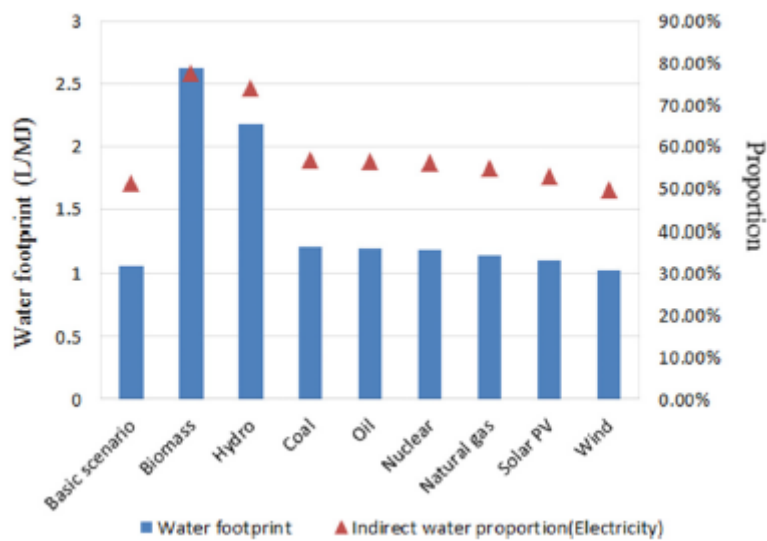


Fig. 5.10 Water footprint and indirect proportion of power generation for CTH process [15].

The results of the study, therefore, suggest that, while both methods are viable and, under an environmental concern, the biomass gasification is to be preferred, the amount of water consumed for its production is very significant and thus making it problematic to implement: while coal is potentially available in most areas of the world, waste straw is not as abundant and is closely linked to the geography of the considered country (even choosing Italy as an example, only a few areas like Pianura Padana can be cultivated extensively with wheat or comparable crops and even in that case, not all land can be

cultivated with wheat only). Moreover, precisely because of the high WF value related to the cultivation and growth of the crop, specifically planting wheat or other plants with the intention of generating additional biomass is not convenient and quite stressing on the freshwater sources.

As such, biomass is convenient and a considerable alternative if it is from crop waste or other waste sources (forestry, animal sludge etc).

5.2.2 Water footprint of hydrogen production: electrolysis

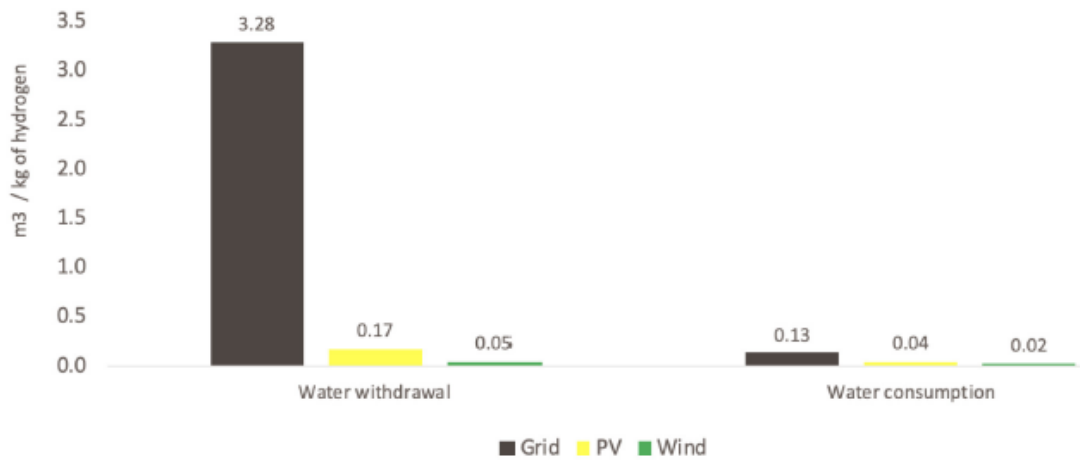
Water electrolysis as a mean to obtain hydrogen is becoming increasingly attractive and is getting more and more focus in recent years in an attempt to find alternative solutions to decarbonisation and fossil fuel. As hydrogen is an energy vector that can potentially be developed to the level comparable of an electric power grid (as far as energy vector is concerned), means of producing it without relying on fossil sources are highly sought after and electrolysis has the potential to be the main method of production in the not so far future. Because, as previously explained, electrolysis uses water and electricity to produce hydrogen, an analysis on the water footprint of this technology is in order:

While, theoretically, the reaction uses 9kg of water to obtain 1kg of hydrogen (stoichiometric balance), in reality the consumption is much higher [16]. This is due to the fact that the cell has a certain efficiency and there're losses at play, as well as all the indirect water used in the electricity production as well as the manufacturing process of the cell components, their transport, their cooling etc.

So if 1Nm³ of hydrogen would require 0.81L of water in theory, it can be expected that the actual practical consumption is 25% higher than that and the indirect consumption can be as much as 20 times the direct consumption (depending on the electricity supply chain). As such, depending on the origin of the power used on the cell, the water consumption can range between roughly 9m³ to 220m³ (wind and grid power respectively), thus making the source of energy a major contributor to the WF and a key element to consider when thinking about creating an industrial system for the production of green hydrogen: the electricity input itself varies greatly between different electrolysis technologies (alkaline, PEM, SOEC etc.), brands and scale of operation, with average consumptions of 50-65 kWh [16].

To better visualize the impact of this and the WF, a case study on hydrogen production in Australia is used as example: an expected increase in export is, in fact, predicted by 2040 for Australia, reaching 4% of the total global hydrogen demand.

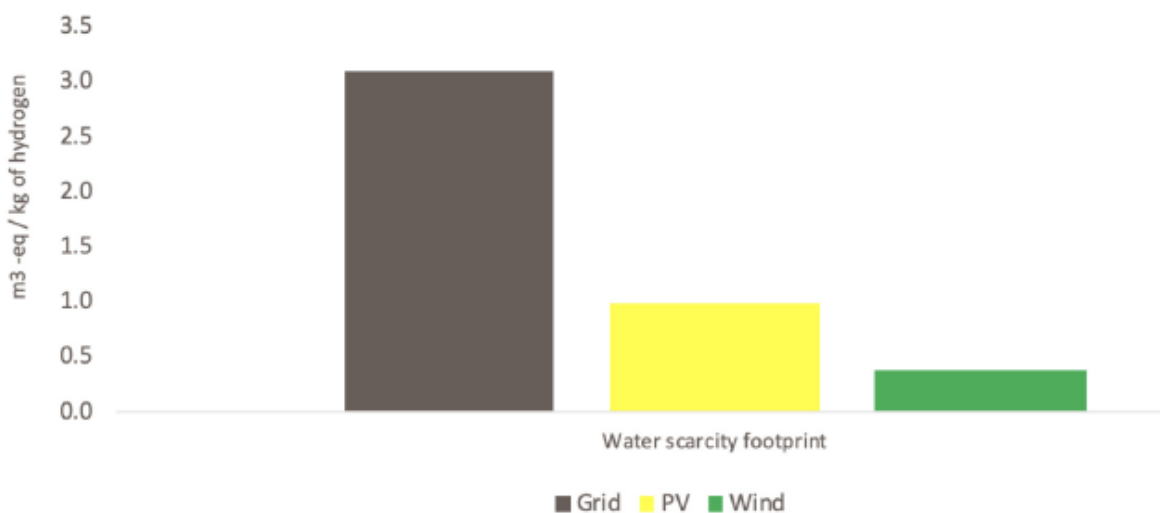
The generation of 1kg of hydrogen in such an environment, consumes 0.13m³ of water when using energy from the grid, 0.04m³ when using photovoltaic energy and 0.02m³ when using wind power [16]. Naturally, this data reports the actual water consumption, however the overall water withdrawal is much higher: while this implies that the majority of the water abducted from the environment will be returned to it, it is still impactful from a WF standpoint as it may not be returned in the same spot, can be returned after an extensive period of time elapsed or the overall quality could be lower than when abducted.



Note: kg = kilogram, m³ = cubic meter, PV = photovoltaic.

Fig. 5.11 Comparison of water withdrawal and water consumption of different power supply options for electrolysis [16].

As it can be seen from the figure above, there's a huge difference in water quantities between different power supplying technologies, with energy coming from the power grid being the most water intensive of the three. This is expected, as the energy mix of Australia relies on water intensive technologies, mostly tied to cooling.



Notes: kg = kilogram, m³-eq = cubic meter equivalent, PV = photovoltaic.

Fig. 5.12 Water footprint of different technologies for electrolysis power supply [16].

The water scarcity footprint follows a similar pattern to the water consumption and withdrawal graphs.

When analysing the water consumption and scarcity across different regions, it can be seen how just a part of the actual water consumption happens locally, with varying degrees of percentage depending on the technology considered. In particular, the photovoltaic accounts for only 25% of local water consumed, while the rest is coming from outside Australia and the power grid has a 73% of locally acquired water. In contrast, still considering photovoltaic hydrogen production, China has a 34% of locally sourced water and this is to be expected: the vast majority of cells and wafers are produced in China and as such, the related WF will count as indirect and will have a much higher weight the further away the country using PV panels for hydrogen production is [16]. The below figure depicts just that.

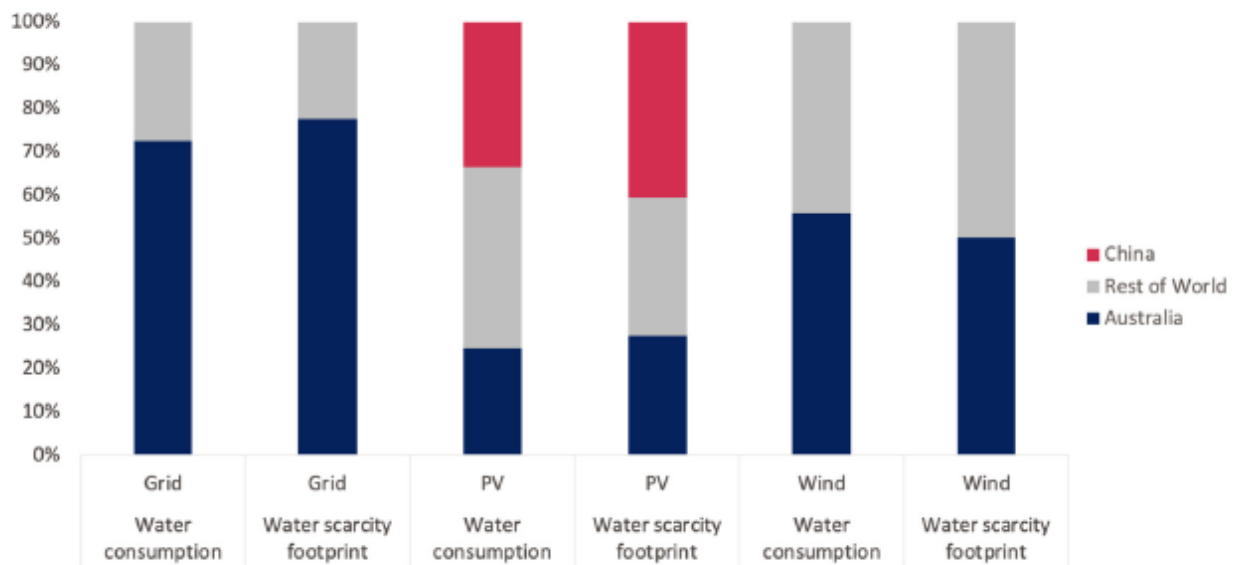


Fig 5.13 Distribution of water consumption and footprint in different regions, for different power supply technologies [16].

While the power necessary for the operation of electrolyzers has a heavy weight in terms of WF, the water for hydrogen production itself has to be considered as well: depending on the source it can impose a significant strain on the water availability of a certain region and other constraints (social and legal) could be tightened as a result of climate change and emergency situations that could occur in the future due to it (for example, the extended drought suffered recently in Italy). As such, another case study set in Portugal (which doesn't have a huge water availability and aims at preserving its water sources as best as possible) is considered [17].

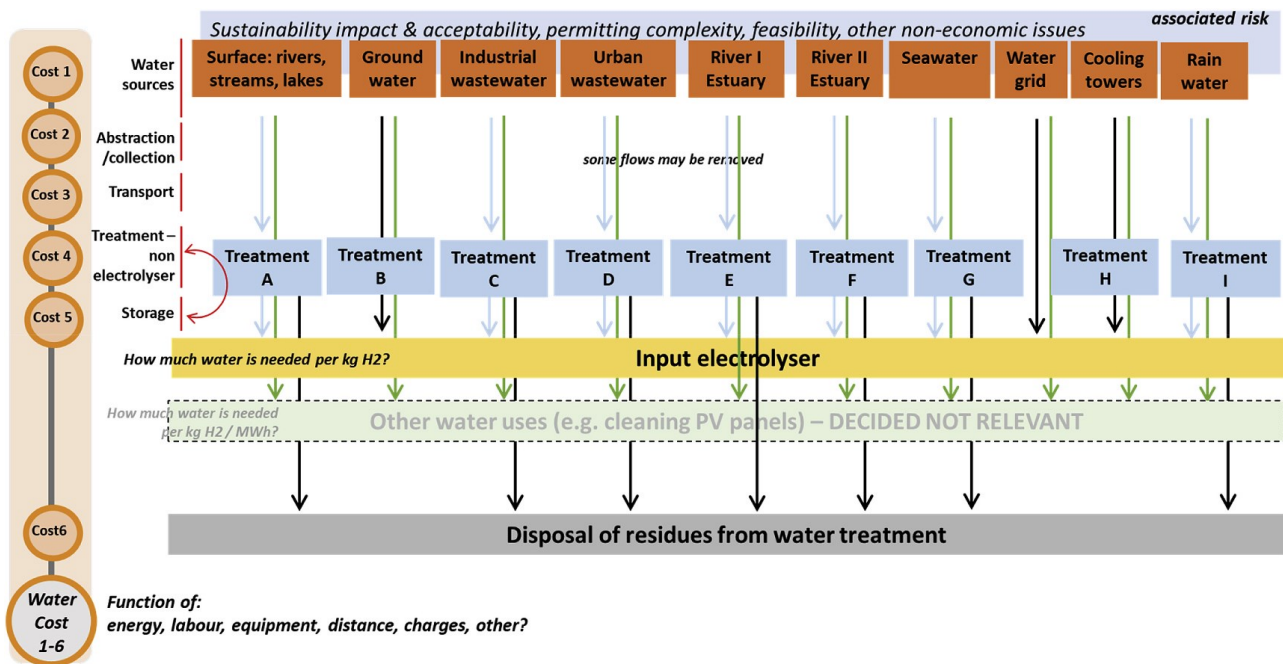


Fig. 5.14 Overview of case study approach to assess water sources for electrolysis [17].

The study considered the 4 main electrolysis technologies and 9 potential water sources to supply the electrolyzers with:

- Alkaline electrolyzers: cheapest, most mature, functions by transporting OH ions through the electrolyte to the anode, hydrogen is produced on the cathode
- SOEC: operating at higher temperatures uses solid ceramic materials as the electrolyte, higher costs
- MEC: same principle as microbial fuel cells, but opposite functions, utilises biomass
- PEM: wider dynamic range, more flexible, faster cold start, twice as expensive as alkaline

The water sources identified as a supply are:

- Seawater
- Estuaries
- Surface water (creeks, streams, rivers and lakes)
- Groundwater
- Rainwater

- Public grid water
- Urban wastewater
- Industrial wastewater
- Cooling tower water

For all these sources the steps assumed to be taken for their use are abstraction/collection, transport, storage, treatment and disposal of residue [17].

As electrolyzers require high purity water to function, the treatment step is of utmost importance and can vary greatly depending on the water source considered: deionised water is usually the typical requirement and sources like public grid water (essentially tap water), are already treated for human consumption and as such have to undergo minimal treatment, while wastewater from industrial areas will require a more thorough process to eliminate all impurities and other dissolved elements [17]. Just as important, at least in some cases, are the transport and storage: public grid water and wastewaters already have an established infrastructure for their transportation and as such don't require extensive efforts in that aspect, same for storage, however sources like seawater require brand new piping systems and storage that will definitely increase the indirect WF as well as the environmental impact of the whole operation, something to keep in mind.

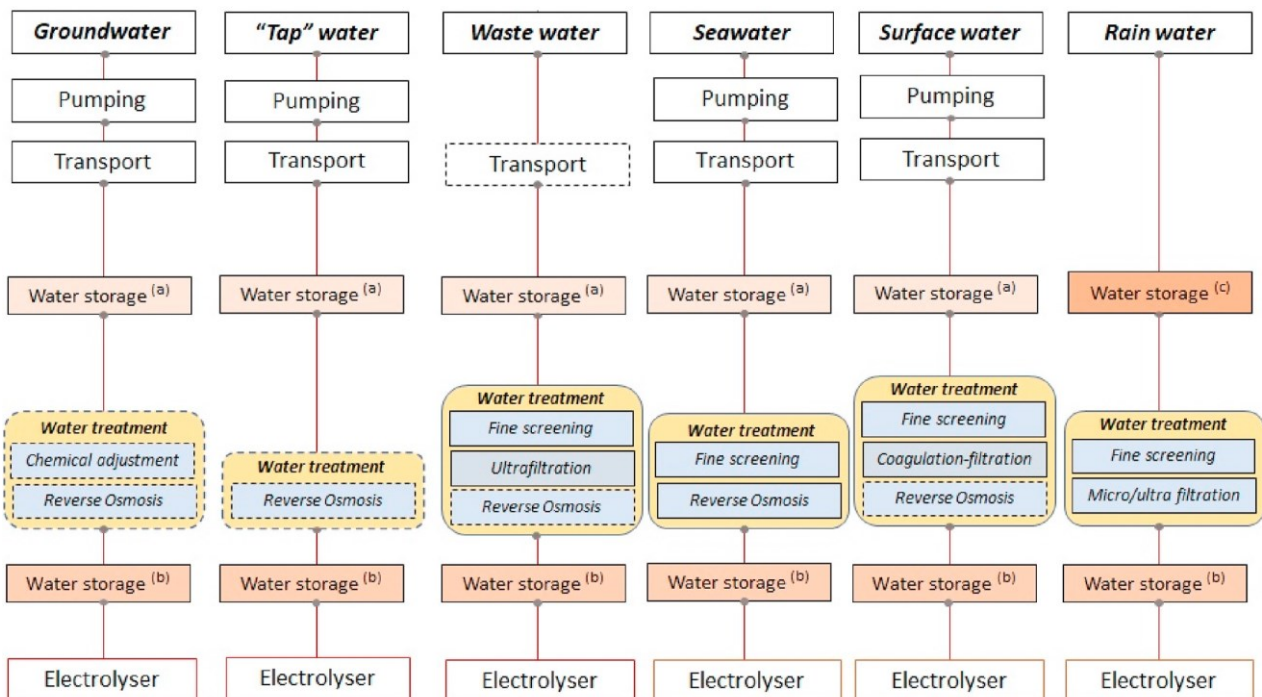


Fig. 5.15 Supply steps for different water sources [17].

Making use of previous considerations, plus adding a 10% additional water losses, the required water to be inputted in the electrolyser is around 14-15 l/kgH₂ depending on the technology chosen (alkaline or PEM as they're the most common commercially nowadays). This means that for a 60MW electrolyser, almost 400m³ of water are needed per day and assuming a load of 60% of the year, it amounts to the total of roughly 85000m³ of water for roughly 6000t of hydrogen produced.

The total water needs are 85% on top of the stoichiometric needs for the reaction and are split between losses in abstraction/collection (5%), losses in transportation (10%), treatment losses (15-40% depending on treatment required), evaporation (10%), cleaning and maintenance (25%) and an extra 10% for insurance on preventing shortages in the supply chain [17].

Keeping these values in mind, the choice of which water source to use has to be done considering a variety of parameters, not just in terms of availability, costs and impacts, but also social and legal. Considering all the criteria, the previously mentioned water sources have been evaluated using two different hydrogen producing plants as reference (**A** located in a urban, highly populated area and **B** in an industrial zone) and the results of the analysis provided an interesting perspective that, while geographically bound to Portugal, can prove useful in carrying out similar evaluations in other countries, as they may incur in similar scenarios and issues [17].

The most expected result is probably the high qualitative value of tap water for plant A, given the low treatment requirements as well as ease of access from already established infrastructure and laws regarding its use. Similarly, the high value for urban and industrial wastewater for either plant (A and B respectively, given their geographical position) is also to be expected for similar reasons, even though they require more intensive treatment before usage. Industrial wastewater does, however, bring uncertainties regarding the supply since it's tied to weather and climate change impacts, which is also a problem for cooling tower water, groundwater and surface water. As such, these sources are not highly valued and groundwater in particular is cause for competition between different sectors (agriculture, industry etc), making it more difficult to use and thus more unattractive. Seawater and rainwater could be great alternatives as their impact is low, there's no competition and the treatment is significant, but less so than wastewater, however they present a geographical and quantitative challenge: seawater can really be competitive if the plants are nearby the coast as laying all the required infrastructure is definitely a big impact in terms of environment and WF, while rainwater has a very unreliable availability due to its strong dependence on weather and climate changes [17].

Performance of water sources according to qualitative assessment of selected value analysis criteria.

Criteria/water source	Site A									Site B					
	Surface: rivers, streams, lakes	Groundwater	Industrial wastewater	Treated urban wastewater	Seawater	Estuary	Water grid	Cooling towers	Rainwater	Surface: rivers, streams, lakes	Groundwater	Industrial wastewater	Treated urban wastewater	Water grid	Rainwater
Reliability of availability (short time: weather)	1	2	2	4	4	2	4	1	1	3	2	2	4	4	1
Reliability of availability (climatic effect)	1	2	3	4	3	1	4	2	1	2	2	3	4	4	1
Reliability of availability (continuity of supply)	2	2	1	4	3	2	4	1	1	3	2	1	2	4	1
Competition with other uses [water collection]	1	1	4	4	4	3	4	4	4	1	1	4	4	4	4
Complexity of abstraction/ collection	2	2	2	3	1	1	4	1	1	2	2	3	3	4	1
Transport distance	2	3	2	2	1	1	4	2	4	3	3	2	2	4	4
Treatment needed	1	2	1	3	1	1	4	3	3	3	2	1	3	4	3
Social acceptance	2	1	4	4	2	2	4	4	4	4	1	4	4	4	4
Complexity of permitting process	2	1	3	3	1	1	4	3	3	2	1	3	3	4	3
Total points	14	16	22	31	20	14	36	21	22	23	16	23	29	36	22
Total classification (%)	39	44	61	86	56	39	100	58	61	63	44	64	81	100	61

Table 5.2 Performance scores of different water sources for plant A and B of the considered case study [17].

While these results are significant in this specific way only for Portugal, they provide a meaningful insight into the method to use when considering which water source to use in hydrogen production via electrolysis as well as the impacts and issues related to them.

5.2.3 Water footprint of electrolysis: SIMAPRO analysis

After all the previous considerations and studies, a simple and brief investigation of WF for electrolysis has been conducted using the SIMAPRO software. The aim was to analyse the values of water consumption related to this method of hydrogen production, using different scenarios and calculation methods.

By using a reference process in the ecoinvent library, namely electrolysis for liquid hydrogen production of 1kg of hydrogen, with library data referring to the Canadian region of Quebec, as a starting point, the software calculated the related WF using both RECIPE and AWARE methods. The obtained values have been used as a baseline for further considerations.

The database values used the Canadian energy mix, and thus power grid supply, for hydrogen production. These were subsequently modified, by creating 3 different

processes, that differ for their water sources and power generation, while keeping all other meaningful data, like the materials for the cells, unchanged for simplicity and on the assumption that similar technologies would be employed in Italy as well.

As such, first a process where the energy mix is kept Canadian, but the water source is Italian, then a process where both the energy mix and the water are from Italian sources and finally a process using Italian water and photovoltaic panels to provide the required energy for hydrogen production. The quantities of the different inputs and outputs used for the analysis of the different processes remain the same.

The reference process chosen is the membrane cell electrolysis, which outputs 1kg of hydrogen in liquid form. The water and energy inputs, the focus of this investigation, are, respectively for cooling or as feed for the cell itself (water of unspecified natural origin). The cooling water used to obtain 1kg of hydrogen is 0.62m³, while the unspecified natural origin amounts to 0.12m³. The energy is assumed to be from the Canadian energy mix, therefore the database lists it as market for electricity, medium voltage and the quantity is roughly 19kWh. Other components used are mostly metals and other chemical substances like barite, calcium chloride, acids (sulfuric and hydrochloric) etc. The emissions are of various chemical nature both in air and water (carbon oxide, chlorine, solvents etc.) and the water that is returned to the environment is about 0.4m³

The first modification to this database process was the usage of water of Italian origin, while keeping everything else unchanged, while the second modification made use of both water and energy of Italian origin: the source of energy is the Italian energy mix, as stated in the process information of SIMAPRO, grouping producers and imports of electricity (if relevant and in the case of Italy they very much are, considering the quantities imported from France and Switzerland, coming mostly from their nuclear power plants), for the medium voltage network (production volume of 257.21*10⁹ kWh). The third and final modification was done by using Italian water and photovoltaic cells as a supply of energy: these cells are supposed to be grid connected single-Si panels, low voltage, building integrated (on slanted roof) of 3kWp from 2012 (production volume of 3.6*10⁹ kWh). The module is chosen as a base unit and can be enlarged by assembling multiple ones together. The dataset includes the water used for washing and maintenance purposes.

These processes have been confronted and WF values were calculated with AWARE and RECIPE methods, then compiled into tables to investigate the major players, besides the direct water consumption in the electrolytic cell itself.

As the methods used are different and express the water consumption in different ways, namely the AWARE method weighs the values using coefficients specific to the country in question, a confrontation between the two values has been done, as well as observing the separate results. The following tables report as such in the following order: Italian water with Canadian energy mix, both Italian water and energy mix, Italian water and photovoltaic energy.

Tipologia	Rapporto stringhe H2O IT	Rapporto stringhe Database
Water, cooling, unspecified natural origin, IT	43,21000065	43,21000107
Water, cooling, unspecified natural origin, RoW	42,95000026	42,95000026
Water, turbine use, unspecified natural origin, CA-NF	1,379999966	1,380000037
Water, turbine use, unspecified natural origin, CA-ON	0,830000012	0,830000003
Water, turbine use, unspecified natural origin, CA-QC	0,870000014	0,869999996
Water, turbine use, unspecified natural origin, CN-FJ	7,840000341	7,839999593
Water, turbine use, unspecified natural origin, CN-GS	68,24999796	68,25000051
Water, turbine use, unspecified natural origin, CN-GX	1,179999988	1,180000019
Water, turbine use, unspecified natural origin, CN-GZ	0,690000005	0,690000005
Water, turbine use, unspecified natural origin, CN-HE	34,95000029	34,95000029
Water, turbine use, unspecified natural origin, CN-JL	0,048280897	0,048280897
Water, turbine use, unspecified natural origin, CN-LN	0,013022436	0,013022436
Water, turbine use, unspecified natural origin, CN-NX	86,96999694	86,96999694
Water, turbine use, unspecified natural origin, CN-QH	0,40186182	0,40186182
Water, turbine use, unspecified natural origin, CN-SA	75,81000016	75,80999988
Water, turbine use, unspecified natural origin, CN-SC	0,900000009	0,900000004
Water, turbine use, unspecified natural origin, CN-SX	89,47000002	89,47000478
Water, turbine use, unspecified natural origin, CN-XJ	73,49999975	73,49999975
Water, turbine use, unspecified natural origin, CN-YN	1,52000002	1,52000002
Water, turbine use, unspecified natural origin, CN-ZJ	11,02999988	11,03000009
Water, turbine use, unspecified natural origin, IT	43,21000099	43,21000099

(a)

Tipologia	Rapporto stringhe uguali H2O EN IT	Rapporto stringhe Database
Water, cooling, unspecified natural origin, IT	43,20999851	43,21000107
Water, cooling, unspecified natural origin, RER	40,96000078	40,9600007
Water, cooling, unspecified natural origin, RoW	42,95000069	42,95000026
Water, turbine use, unspecified natural origin, CA-NF	1,379999984	1,380000037
Water, turbine use, unspecified natural origin, CA-ON	0,829999999	0,830000003
Water, turbine use, unspecified natural origin, CA-QC	0,869999993	0,869999996
Water, turbine use, unspecified natural origin, CH	0,969999986	0,970000003
Water, turbine use, unspecified natural origin, CN-FJ	7,839999802	7,839999593
Water, turbine use, unspecified natural origin, CN-GS	68,24999772	68,25000051
Water, turbine use, unspecified natural origin, CN-GX	1,179999998	1,180000019
Water, turbine use, unspecified natural origin, CN-GZ	0,689999999	0,690000005
Water, turbine use, unspecified natural origin, CN-HE	34,95000012	34,95000029
Water, turbine use, unspecified natural origin, CN-JL	9,269999992	9,269999893
Water, turbine use, unspecified natural origin, CN-LN	33,30999946	33,31000053
Water, turbine use, unspecified natural origin, CN-NX	86,96999838	86,96999694
Water, turbine use, unspecified natural origin, CN-QH	69,44999986	69,44999901
Water, turbine use, unspecified natural origin, CN-SA	75,80999987	75,80999988
Water, turbine use, unspecified natural origin, CN-SC	0,900000021	0,900000004
Water, turbine use, unspecified natural origin, CN-SX	89,47000127	89,47000478
Water, turbine use, unspecified natural origin, CN-XJ	73,49999857	73,49999975
Water, turbine use, unspecified natural origin, CN-YN	1,520000046	1,52000002
Water, turbine use, unspecified natural origin, CN-ZJ	11,03000012	11,03000009
Water, turbine use, unspecified natural origin, FR	8,150000037	8,15000006
Water, turbine use, unspecified natural origin, IT	43,21000034	43,21000099

(b)

Tipologia	Rapporto stringhe PV IT	Rapporto stringhe Database
Water, cooling, unspecified natural origin, IT	43,21000025	43,21000107
Water, cooling, unspecified natural origin, RER	40,96000109	40,9600007
Water, cooling, unspecified natural origin, RoW	42,94999972	42,95000026
Water, turbine use, unspecified natural origin, CA-NF	1,379999998	1,380000037
Water, turbine use, unspecified natural origin, CA-ON	0,829999993	0,830000003
Water, turbine use, unspecified natural origin, CA-QC	0,870000001	0,869999996
Water, turbine use, unspecified natural origin, CN-FJ	7,840000008	7,839999593
Water, turbine use, unspecified natural origin, CN-GS	68,25000099	68,25000051
Water, turbine use, unspecified natural origin, CN-GX	1,18	1,180000019
Water, turbine use, unspecified natural origin, CN-GZ	0,690000006	0,690000005
Water, turbine use, unspecified natural origin, CN-HE	34,95000014	34,95000029
Water, turbine use, unspecified natural origin, CN-HU	0,280000008	0,279999994
Water, turbine use, unspecified natural origin, CN-JL	9,270000049	9,269999893
Water, turbine use, unspecified natural origin, CN-LN	33,31000062	33,31000053
Water, turbine use, unspecified natural origin, CN-NX	17,68794051	15,54273935
Water, turbine use, unspecified natural origin, CN-QH	3,402405131	3,396783253
Water, turbine use, unspecified natural origin, CN-SA	332,8155382	331,4331326
Water, turbine use, unspecified natural origin, CN-SC	2,824301291	2,786509467
Water, turbine use, unspecified natural origin, CN-SX	105,4997321	109,6232871
Water, turbine use, unspecified natural origin, CN-XJ	11,01094997	10,72288982
Water, turbine use, unspecified natural origin, CN-YN	1,520000035	1,52000002
Water, turbine use, unspecified natural origin, CN-ZJ	11,03	11,03000009
Water, turbine use, unspecified natural origin, IT	43,21000083	43,21000099

(c)

Fig. 5.16 Comparisons of database values and values obtained by changing the parameters: Italian water (a), Italian water and energy mix (b), Italian water and photovoltaic energy (c).

Among the data results, the biggest numbers were found to be related to cooling and direct water consumption in both scenarios, with the AWARE method reporting the highest values, as expected, given the weighing process the method goes through during calculations. The weighing itself returned results compatible with the Italian coefficients reported in the AWARE database, accessible through ecoinvent library. These values vary greatly between the scenarios, as one would expect, depending on the origin of the water: the case with Italian water and Italian energy mix had the highest water cooling quantity coming from Italy at 50m³, almost double the case of photovoltaic and Canadian energy mix. Interestingly as well, the quantity of water consumed in the Italian water and energy mix case reported with RECIPE is lower than the quantity in the base scenario (everything of Canadian origin), implying a heavier impact on the WF: this is as expected, considering the different coefficients between the two countries. The tables reported above depict exactly this fact, with the comparison between the values ending up very similar.

The second biggest category of data was all the indirect water consumption related to energy, as underlined by the “turbine use” category, with values that varied depending on the scenario: in particular, the Italian water and energy mix case has the highest quantity of water consumed from Italy (at over 2000m³ with AWARE), compared to the other two cases. This is natural as the Italian energy mix contains a relatively high percentage

coming from hydroelectric sources, which are the most WF intensive, as well as natural gas plants and coal plants. In contrast, the quantity in the photovoltaic scenario is extremely close to the base case value (10 vs 8 m³ with AWARE), as one would expect, given the negligible WF of photovoltaic panels (inherently tied to their production process and maintenance).

On another note, in all three cases, it's interesting to see how a pretty big group of data is coming from Chinese regions, with relatively important numbers as well, all listed as "turbine use" and as such related to energy production.

Given how it's unlikely that this energy is used directly in the electrolyzers for hydrogen production, since China isn't nearby either Italy nor Canada and powerlines reaching either country are unlikely if not outright impossible, further investigation was needed. The software was used again to calculate the WF of every single process separately using AWARE method and, since the process tree was unavailable given the presence of cycles in the processes, the network of all three cases was examined, choosing a cutoff value of 0.35%.

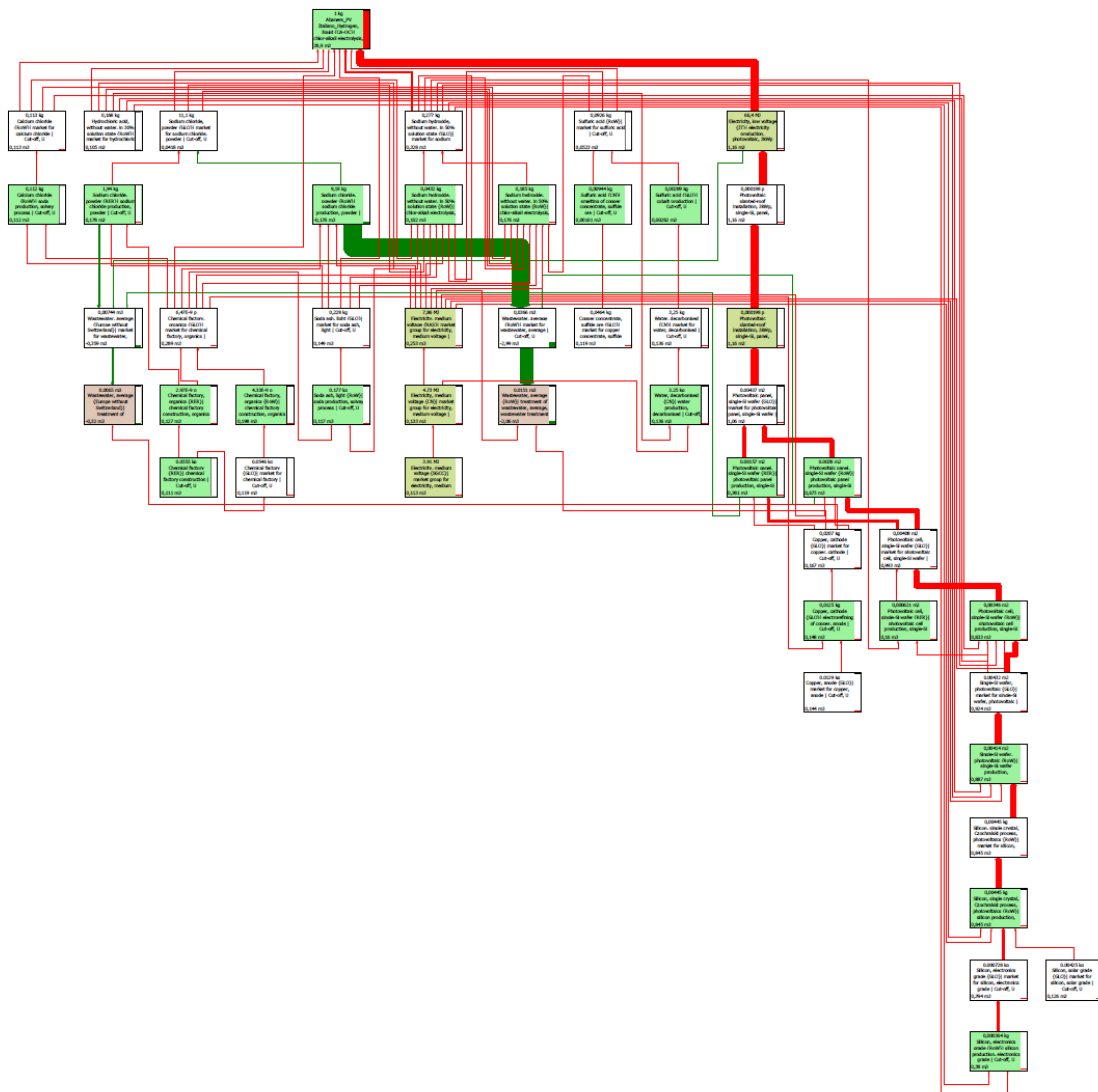


Fig. 5.17 Example of network for the Italian water and photovoltaic energy case

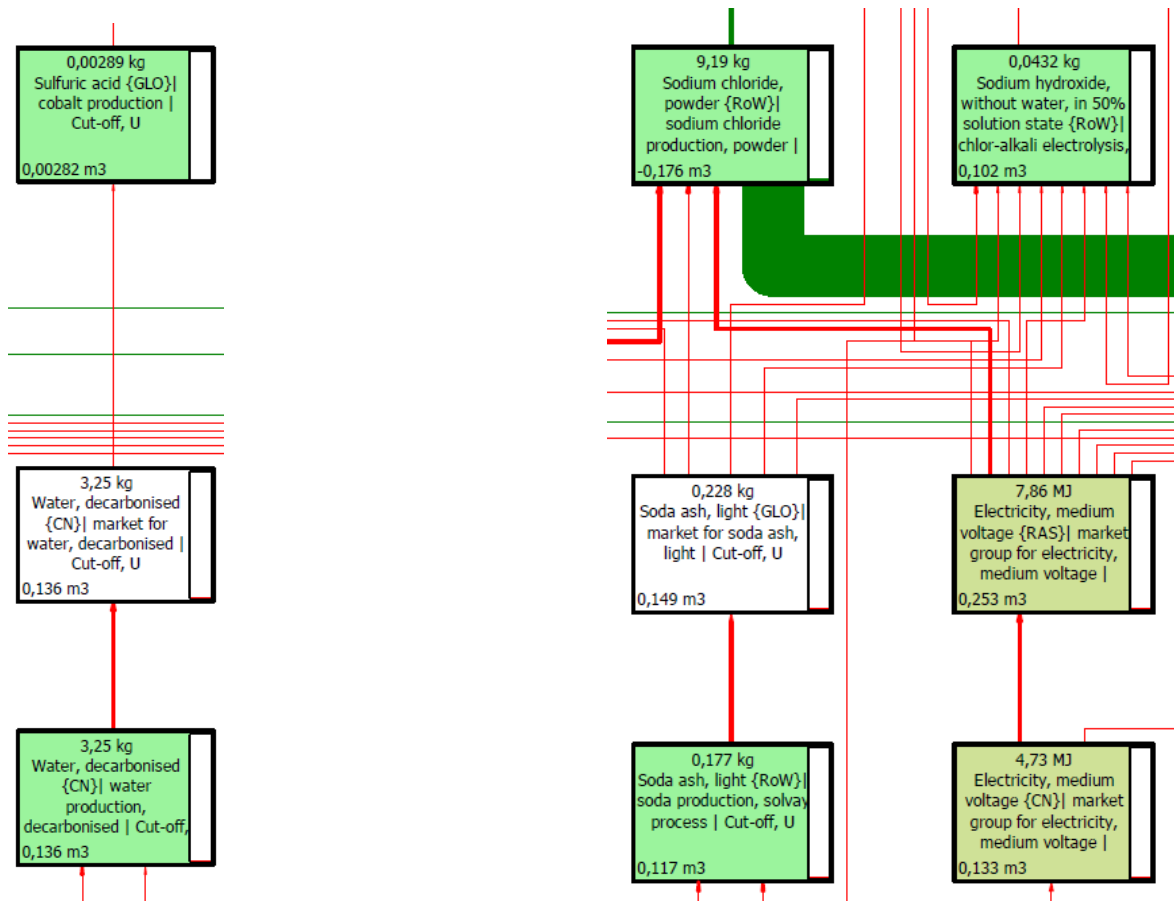


Fig. 5.18 Close up of the previous network. Notice the connection between the Chinese water quantities and the chemical productions.

Doing so, it's possible to see the connections between the Chinese water and the whole process: the "turbine use" is indeed related to power generated in China, however this energy is then used in the production of different components that make up the electrolysers, for the most part.

The higher values reported in the photovoltaic case are also unsurprising since, as stated before in the Australian case study, China is one of the largest manufacturers of cells and wafers for photovoltaic use and as such, the panels that have been used in this case are also likely made in China, or a good part of their components are, on top of the ones related to the electrolysers themselves.

Conclusions

Water is becoming more and more important and under more attention nowadays than in the past, given the impending shift to a greener economy in Europe and the rest of the western world, as well as the risks that climate change has painfully made us aware of, with extended periods of intense heat and droughts followed by short bursts of extremely unpredictable and wet climate, leading to vast floods in some areas. Such a scenario, which was almost unthinkable a few years ago, has become almost the norm in hydro-geological risk areas like Italy (the flood of Emilia Romagna last month), that are also, ironically, becoming more and more water stressed as the climate keeps changing for the worst. This, naturally, garners a lot of public attention and is perceived as a matter to be solved with urgency, especially by the people hit by those extreme events, and rightfully so, however the issue needs to be addressed with objectivity: rushing in a panic after extreme events in an attempt to solve the issue will only cause further problems down the line.

To prevent worsening the current conditions and, potentially, invert the trend in the next future, water saving, recycling and reuse technologies can and should be implemented and used in the most water intensive industrial sectors. While the agricultural and domestic areas are also responsible for the water stress, the possible solutions for reducing their consumptions are already well known and commercially available or need to be conducted by the public sector (maintenance of piping, rainwater catchment and storage, improved irrigation systems, etc.) and as such were not the focus of this paper. Industries, and especially those that use a lot of water both directly and indirectly like the metallurgic, paper and textile businesses to mention a few and, by consequence, the energy sector should strive to implement solutions to save as much water as it's feasible economically and technologically and the government should walk the same path by adapting and creating norms that will make it easier to reach such a goal.

Going specifically into the energy sector and, thus, into new prospects like hydrogen production, it is important to not rush things in the name of saving the planet through a greener economy: hydrogen has enormous potential to become the energy vector of the future, coupled with electricity, for a sustainable energy production and a new generation of zero or near zero impact vehicles and means of transportation and it's likely that it will garner more and more interest as the years progress. It's, however, worth mentioning that public interest and experimentation on hydrogen has been oscillating heavily in the past, ranging from a full commitment and projects to shift the automotive industry and energy sector to a fully hydrogen powered production, to completely forgetting such a solution is a possibility. As such, the current prospects are still unknown and the technology for its production still not that diversified: while many manufacturing methods are indeed available and showing promising results, like said in the previous part, most of them are still either experimental or not commercially mature, with the main contributor being still fossil fuel reforming.

While public interest for hydrogen as an energy vector is growing once again and many claim it would solve many problems and lead us toward a greener future, since

electrolysis would generate no GHG impacts (and ignoring or forgetting the fact that the cells do generate other types of environmental impacts however small they may be), the water consumption that this will lead to is often not discussed or glossed over, potentially because seawater is abundant and the general public will assume that it can be freely used for this purpose.

This thesis, however, proved that it is not exactly the case and that water supply is indeed an important issue of large scale hydrogen production and not just for its direct use, which is surely the bulk of the overall consumption: depending on the type of water source and the geographical location of the plant, some sources are more suited than others, as well as easier to treat and process before feeding them to the electrolyzers. Sea water in particular (but this issue can apply to surface water just as much), will require an enormous effort in terms of transportation (new infrastructure needs to be constructed) and depuration (salts and contaminants have to be removed), which would make it a possibility as a feasible source only for plants relatively close to the coast, to keep costs and impacts low.

Keeping all that has been said so far in mind, it is the duty of energy engineers to analyse and assess the situation correctly and objectively, giving the public the means to interpret correctly what solutions can be employed to solve the issue at hand: governments should not wait until tragedy strikes to act, only to discover studies and warnings have been issued by the scientific community, but should cooperate and listen to prevent such events from occurring. At the same time, however, it is not safe to rush for a solution either, as it will present its own sets of issues and unpredictability, both environmentally and economically, like in the case of a hydrogen driven power and automotive sectors.

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