Life cycle assessment of wastewater reclamation in a petroleum refinery in Turkey

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Abstract
Wastewater reclamation in a petroleum refinery in Turkey was evaluated with life cycle assessment (LCA). The goal of the study was to determine whether or not refinery wastewater reclamation for different industrial purposes, namely boiler feedwater, cooling water and fire water, leads to an overall benefit across different environmental aspects, besides alleviating freshwater resources, when compared to current wastewater disposal practices. The basis for the assessment was the hypothetical scale-up of a demonstration plant tested with real wastewaters during seven months at the Izmit petroleum refinery operated by Tüpraş. This demonstration plant consisted of different treatment modules, including dissolved air flotation, ceramic membrane bioreactor, catalytic wet-air oxidation, advanced oxidation with ozone and hydrogen peroxide, and reverse osmosis. The LCA was conducted following consequential modelling principles, and six environmental indicators were analysed in detail at midpoint level: global warming, respiratory inorganics, marine ecotoxicity, aquatic eutrophication, freshwater consumption and non-renewable energy demand. All three reclamation scenarios (boiler, cooling, fire water) succeeded in achieving a life-cycle freshwater saving. Equally beneficial results were obtained in marine ecotoxicity and aquatic eutrophication. With regard to global warming and non-renewable energy demand, only the boiler feedwater application appeared to involve an improvement over wastewater disposal, thanks to potential thermal energy savings. For cooling makeup water and fire water, impacts were higher in these two indicators when compared to wastewater disposal. Finally, the indicator on respiratory inorganic effects, showed higher impact for all reuse scenarios, due to electricity demand, which is linked to the Turkish electricity production mix with a substantial contribution from coal power plants. A sensitivity analysis shows that that the environmental performance of all scenarios would improve to a great extent when shifting to an electricity mix with a higher share of renewables, as is the current trend in most European countries.

Keywords
Wastewater reclamation, reverse osmosis, dissolved air flotation, advanced oxidation process, ceramic membrane bioreactor, catalytic wet air oxidation

1. Introduction

Petroleum refineries are intensive consumers of water. According to Barthe et al. (2015) the average European refinery uses 5.89 m^3 per tonne of feedstock refined, for a variety of processes including the distillation process, the cracking of hydrocarbons, for steam generation, for cooling systems and for cleaning operations, among others. As a consequence, large volumes of wastewater are generated. Nabzar and Duplan (2010) suggest that a refinery using 400-1,000 m^3/h raw water produces 200-600 m^3/h wastewater to be discharged. These wastewaters are complex and contain a wide variety of pollutants, including aliphatic and aromatic hydrocarbons, emulsified oil and grease as well as inorganic substances, including ammonia, sulfides and cyanides (Al-Khalid and El-Naas 2018). A typical refinery wastewater treatment plant (WWTP) may include a first oil recovery step, using API separators or similar equipment such as a correguated plate interceptor (CPI); a second step for removal of dispersed oil and suspended solids, consisting of a flotation system; a third step for removal of soluble substances, including biological treatment and clarification; finally, advanced treatment operations may be applied, such as sand filtration or membrane-based treatments (Barthe et al. 2015). Nonetheless, several drivers are pushing industries beyond effluent treatment and towards reuse, namely regulatory developments and water scarcity. Although locally and regionally dependent, environmental legislation is gradually becoming stricter and is pushing for water reuse. Also, the most productive areas for the oil and gas industry frequently occur in regions with scarce water resources, leading to an increasing interest in water reuse to relieve this local stress. In Turkey in particular, the company Tüpraş, with the country's biggest oil refining capacity, has made substantial progress in this area, going from a wastewater reuse rate of 15% in 2007 (Tüpraş 2011) to 40% in 2015 (Tüpraş 2019).

Selection of the most appropriate technology or combination of technologies capable of achieving a desired reuse quality is a multicriteria one, requiring performance data but also an assessment of costs and environmental sustainability. The latter is increasingly achieved by means of life cycle assessment (LCA), providing a comprehensive evaluation of the direct and indirect potential environmental impacts associated to a product or service (Finnveden et al. 2009). However, LCA studies in the oil and gas sector with a particular focus on water treatment are scarce. Vlasopoulos et al. (2006) investigated the environmental impact of 20 technologies suitable for treating the water produced during oil and gas extraction, in order to achieve the target water qualities for nine agricultural and industrial end uses, however the study addressed so-called 'produced water' from oil and gas extraction activities, rather than those from refining activities. To our knowledge, there are no published studies applying LCA to the treatment of wastewater from petroleum refineries.

In this article we present the results of an environmental assessment applied to wastewater reclamation in a petroleum refinery, considering the conditions of Turkey, where pilot-scale tests were recently carried out in the framework of the EU-funded research project INTEGROIL® (https://integroil.eu/). The goal of the LCA study was to determine whether or not refinery wastewater reclamation for different industrial purposes (boiler feed water, cooling water, fire water) leads to an overall benefit across different environmental aspects, besides the intrinsic benefit of alleviating pressure on freshwater sources.

2. Materials and methods

2.1. The INTEGROIL® demonstration plant

The purpose of INTEGROIL® was to develop an integrated solution for the oil and gas industry to treat wastewater flows with variable compositions, in order to achieve reuse quality for different applications. This new solution features physical-chemical processes and biological treatment, effectively operated through a Decision Support System (DSS), ensuring optimized operation with minimal process understanding. A demonstration plant with a capacity of approximately 1.5 m^3/h was designed, built and tested with real wastewaters at a Tüpraş refinery in Izmit, Turkey, from November 2018 to May 2019. This demonstration plant consisted of different treatment modules, as can be seen in Figure 1. Wastewater from the refinery's API separator is fed to the dissolved air flotation (DAF) unit, the effluent of which is directed to a biological reactor coupled to a ceramic ultrafiltration unit, effectively constituting a ceramic membrane bioreactor (MBR). The following treatment unit applies catalytic wet-air oxidation (CWAO) in two reactors operating alternately. The next step is an advanced oxidation process based on ozonation combined with hydrogen peroxide dosage. As a final polishing step, a reverse osmosis membrane is used. The DSS was programmed to produce three different types of reclaimed water, complying with Tüpraş quality requirements for fire water, cooling water and boiler feed water (see supplementary material (SM) for details). The most cost-effective combination of treatments to achieve the corresponding qualities was managed on a continuous mode by the DSS, taking into account the variable inlet wastewater composition.

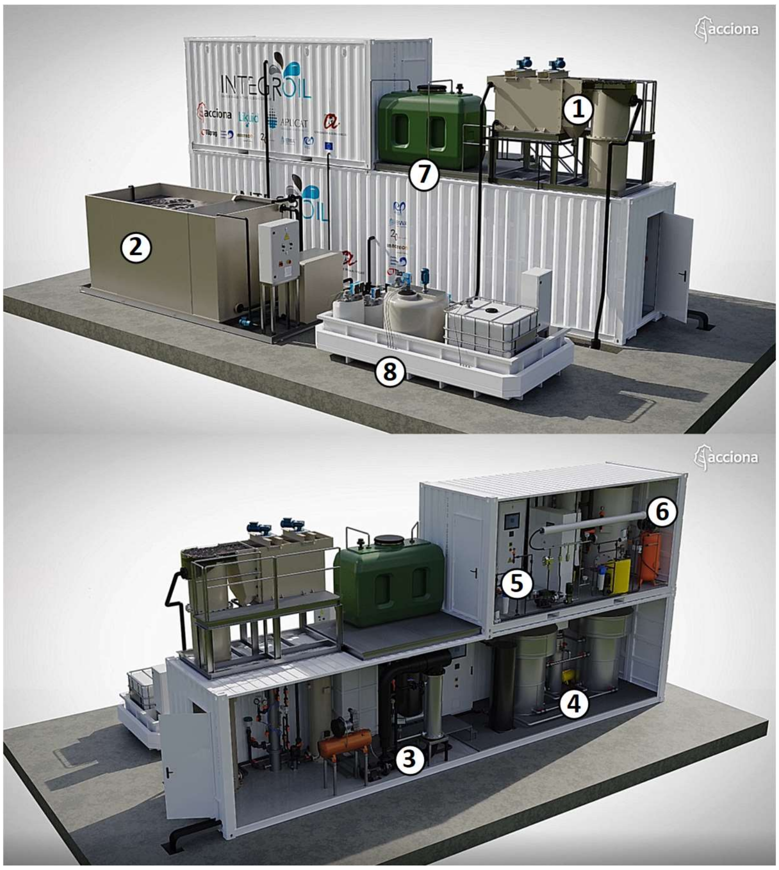

Figure 1. Overview of the INTEGROIL® demonstration plant. 1: dissolved air flotation. 2: bioreactor. 3: ceramic ultrafiltration. 4: catalytic wet-air oxidation. 5: advanced oxidation. 6: reverse osmosis. 7: reclaimed water storage tank. 8: chemical dosing station.

2.2. LCA methods

LCA was carried out with the ISO 14040 and 14044 standards as methodological guidelines (ISO 2006a, 2006b), and consequential modelling was used in the inventory analysis, as defined in Weidema (2003, 2009). The software used to model the life cycle was SimaPro version 8.5 (Pré 2016). The assessment can be considered as prospective in the sense that 1) consequential modelling was used and 2) the assessment takes a step forward from its actual pilot scale to a commercial scale model. These two methodological aspects allow for a more realistic depiction of a potential deployment of this technology in the market.

2.3. Goal and scenarios to be assessed

The goal of the LCA was to determine whether or not the implementation of wastewater reclamation according to the INTEGROIL® technologies leads to an environmental benefit considering three potential uses within the refinery: boiler feedwater, cooling water and fire

water. This is compared to a situation where no reclamation takes place and wastewater is discharged to the environment after a conventional treatment. In such a situation, the refinery is assumed to obtain its process water from freshwater resources. Four scenarios were assessed, namely three INTEGROIL® reclamation scenarios and a reference scenario. In all cases, geographical and technological aspects in the study reflect the situation in Turkey, where the reclamation technologies were tested.
Figure 2 shows a flow diagram outlining the activities included in the study for the reference scenario, which can be considered as representative of current wastewater disposal practices by Tüpraş. Following treatment in an API or CPI separator, wastewater is subject to a dissolved air flotation process, followed by biological treatment with activated sludge and clarification, after which the treated effluent is discharged to the sea. Sludge from these two treatment steps is collected together, dewatered and transported to a cement production plant where it is used as alternative fuel, substituting conventional fossil fuels.

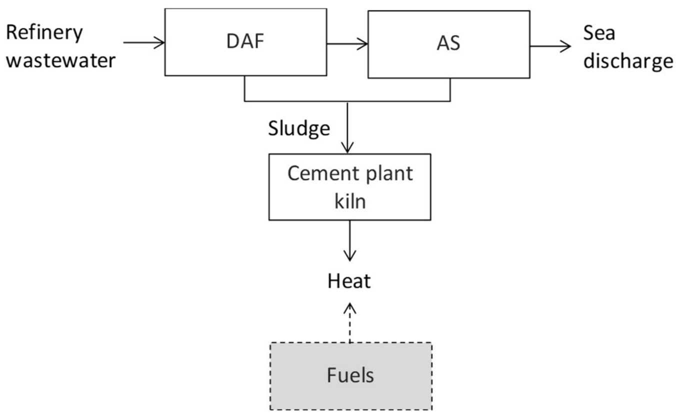

Figure 2. System under study in the reference scenario. DAF: dissolved air flotation. AS: activated sludge. Grey-background boxes indicate substituted activities.

Figure 3 shows a flow diagram outlining the activities included in the study for the INTEGROIL® scenario. Depending on the targeted reuse (boiler, cooling or fire water) the DSS decides the most cost-effective combination of treatments (see Table 1). All combinations always include treatment by DAF and MBR, while the extent to which CWAO, AOP and RO are applied depends on the reuse quality to be achieved and the continuously changing wastewater composition.

Table 1. Distribution of treatment combinations in the demonstration plant according to the reuse application. The utilitzation rate expresses the ratio of m³ treated with a given combination per m³ at the plant inlet.

Scenario	Utilization rate (%)	DAF	MBR	CWAO	AOP	RO-1[a]	RO-2[b]
INTEGROIL, fire reuse	15%	■	■				
	41%	■	■	■			
	28%	■	■	■	■		
	16%	■	■	■	■	■	
INTEGROIL, cooling reuse	4%	■	■			■	
	3%	■	■	■			
	28%	■	■	■		■	
	7%	■	■	■	■		
	59%	■	■	■	■	■	
INTEGROIL, boiler reuse	100%	■	■	■	■	■	■

[a] RO, one pass. [b] RO, second pass.

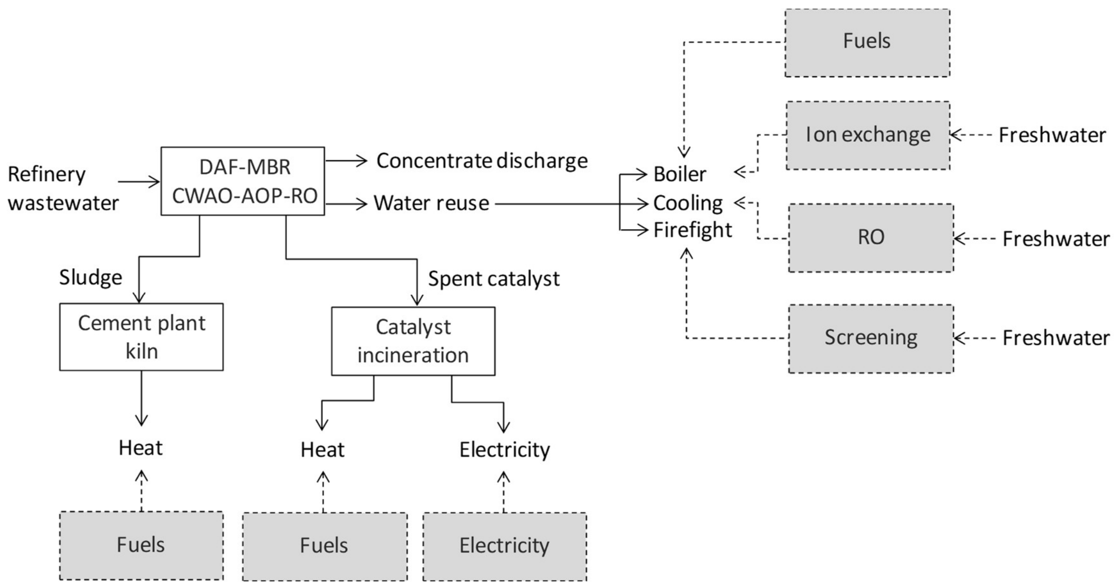

Figure 3. System under study in the INTEGROIL® scenario. DAF: dissolved air flotation. MBR: membrane bioreactor. CWAO: catalytic wet-air oxidation. AOP: advanced oxidation process. RO: reverse osmosis. Grey-background boxes indicate substituted activities.

Several waste flows are generated by these treatments; first, the RO concentrate, containing mainly dissolved salts, is discharged to the sea. Sludge from the DAF and MBR units is considered to be treated together, following the same disposal route as in the reference scenario. The CWAO unit is expected to periodically require replacement of the spent catalyst, which is sent for disposal through incineration with energy recovery. Finally, the treatment supplies three qualities of reclaimed water, which substitute the corresponding conventional treatment of freshwater. Freshwater treatment for use as fire water is assumed to require only a simple screening, while cooling water production requires a more thorough treatment with reverse osmosis. Boiler feedwater requires the most intensive treatment, namely ion exchange. Another substitution effect associated to water reuse as boiler feedwater is related to the fact that the reclaimed water is at an average temperature of 34ºC, while freshwater from a natural body is expected to present a lower temperature. This leads to a potential energy saving, as less thermal energy needs to be supplied to the water in order to achieve the steam system temperature (see US Department of Energy 2012).

2.4. INTEGROIL® plant up-scaling

The environmental assessment was based on a scale-up of the demonstration plant. This is justified on the fact that research scales such as lab- and pilot-scales are not suitable for meaningful assessments (Muñoz et al. 2015; 2019; Gavankar et al. 2015; Piccinno et al. 2016). Data obtained during the operation of the demonstration plant were used for the design and subsequent scale-up of the technologies (e.g. filtration fluxes, hydraulic retention times, chemical dosages, effluent quality achieved in each process, etc.), at the level of equipment (infrastructure) and operation (power demand, chemical dosing, etc.). The scaled-up plant had a capacity of 500 m^3/h, equivalent to that of the real WWTP at the Izmit refinery.

2.5. Functional unit

The function of the system under study was established as providing treatment for refinery wastewater. The INTEGROIL® scenario, however, provides an additional function, namely water for reuse within the refinery. This additional function is dealt with in the LCA by means of substitution. The functional unit and reference flow used in the study is the treatment of 1 m^3 refinery wastewater from the API/CPI separator, with the following composition: 20 mg/L oil and grease, 25 mg/L suspended solids (SS), 370 mg/L chemical oxygen demand

(COD), 166 mg/L biological oxygen demand (BOD), 85 mg/L total organic carbon (TOC), 21 mg/L ammonium, 2 mg/L nitrate and 4 mg/L phosphate.

2.6. Impact assessment method

A comprehensive set of 17 impact categories was included, at mid-point level. In this article, though, we focus on a set of six indicators covering the three areas of protection commonly addressed in LCA, namely use of resources, impacts on human health and impacts on ecosystems. The chosen indicators are the following:

- Global warming, expressed as CO_2-equivalents (eq.) with the global warming potentials for a 100-year horizon from the IPCC fifth assessment report (Myhre et al. 2013).
- Fine particulate matter pollution, measured as kg $PM_{2.5}$-equivalents, based on Goedkoop and Spriensma (2001).
- Aquatic eutrophication, expressed as nitrate-eq. emissions to water, based on Hauschild and Potting (2005).
- Marine ecotoxicity, expressed as 1,4-dichlorobenzene (1,4-DCB) eq. emissions to seawater, based on Huijbregts (2016).
- Water consumption, expressed as a physical volume of water abstracted, i.e. excluding water used in hydropower plants.
- Non-renewable energy demand, expressed in MJ, based on Jolliet et al. (2003).

A particular challenge to address marine ecotoxicity was the lack of a characterization factor for oil and grease, one of the main parameters analysed in the refinery wastewater. We estimated this parameter consists of 49% aliphatic hydrocarbons and 51% aromatic hydrocarbons, and existing characterization factors were applied to these fractions (see details in the SM).

3. Inventory analysis

The life cycle model was built in the SimaPro software using the consequential system model ecoinvent v.3.2 (Ecoinvent 2018) as background database, whereas a variety of primary data sources were used in the inventory analysis. In this section we outline the main figures, data sources and assumptions, whereas detailed inventory data can be found in the SM.

3.1. Electricity production in Turkey

One of the key inputs to all activities in the system is electricity. A prospective analysis of electricity production in Turkey in the period from 2014 to 2030 was carried out in order to define a production mix, following the consequential modelling principles proposed by Muñoz (2019). The resulting electricity mix consists of 38% fossil fuels, 20% nuclear power and 42% renewable sources. Further details are available in the SM.

3.2. Reference WWTP

Construction of a refinery WWTP treating 500 m^3/h was approximated with inventory data for urban WWTPs available in ecoinvent, by interpolating the figures from the two closest capacities (5E+09 L/year and 1E+09 L/year). Disposal of the WWTP materials and equipment at the end-of-life stage was determined based on the amounts quantified for its construction and ecoinvent data sets for waste disposal.
Consumption of iron chloride as coagulant in the DAF unit was quantified as 200 mg/L based on Hernando (2011), while flocculant consumption was established by Tüpraş as 2 mg/L. Consumption of phosphoric acid as nutrient in the biological treatment was estimated at 0.001 kg phosphoric acid (54%) per m^3 wastewater. Concerning energy use, electricity consumption by the WWTP, in kWh/m^3, was communicated as confidential data by Tüpraş.
Emissions of VOCs to the atmosphere from the entire plant were estimated based on the area of the WWTP tanks and emission factors from Barthe et al. (2015), while N_2O emissions from the biological reactor were estimated with an emission factor of 0.005 kg N_2O-N per kg N input to the reactor.

A combined mass balance for the DAF and biological treatment was performed in order to determine the amount of sludge produced (0.18 kg dry mass/m^3), its composition and calorific value, as well as CO_2 emissions from the degradation of BOD in the biological reactor (0.19 kg CO_2/m^3).
Emissions to the sea of oil and grease, COD, SS and ammonium in the treated effluent were quantified considering the discharge limits established by the Water Pollution Prevention Regulation by the Turkish Ministry of Environment and Urban Planning, while other parameters such as nitrate, total organic carbon, etc., were provided by Tüpraş.

3.3. INTEGROIL® WWTP

Infrastructure and equipment for all INTEGROIL® treatment units in a hypothetical WWTP with a capacity of 500 m^3/h was provided by each technology developer as a detailed bill of materials, reporting each component to be installed (piping, valves, tanks, probes, pumps, electrical installations, etc.), its material characterization if applicable and the expected life span of each component, in years. All equipment was modelled either with existing ecoinvent data sets or by adapting some of them, as detailed in the supplementary material. As in the reference scenario, disposal of the WWTP materials and equipment at the end-of-life stage was determined based on the amounts quantified for its construction and ecoinvent data sets for waste disposal.
Operation data were constituted, on the one hand, by a quantification of the expected power demand (kWh/m^3) and the dosage of a total of 14 different chemicals as well as the replacement rate for the CWAO catalyst, taking into account the predicted optimization of this consumption by the DSS. On the other hand, an overall mass balance was carried out, based on the average characterization of the water to be treated and the removal rates by each module according to the demonstration tests.
Emissions of VOCs and N_2O to the atmosphere were estimated with the same procedure described for the reference scenario, while CO_2 emissions originating from either biological degradation in the MBR or chemical oxidation in the AOP and CWAO units was determined based on a TOC balance for the entire plant.
Given that in this scenario the reclaimed water is reused within the refinery, the only direct emissions to the sea are constituted by the RO concentrate, when this treatment unit is used. Based on the above-mentioned mass balance, we quantified emissions of oil and grease, COD, BOD, ammonium and nitrates.
As for solid waste, the INTEGROIL® plant generates 0.11 kg sludge dry mass/m^3, originating from the DAF and MBR units. Production of spent catalyst for disposal was also taken into account, assuming its useful life is 2 years if the CWAO unit is used continuously. The detailed LCI data for all these activities is shown in the supplementary material.

3.4. Sludge disposal

According to Tüpraş, sludge is transported with a dry mass content of 37% to a cement production plant, at a distance of 215 km, but no further data on this process could be obtained. It was assumed that sludge is dried with hot waste gases from the cement kiln and combusted to replace fossil fuels. The average fuel mix used for cement production in Europe, according to ecoinvent, was considered as being substituted. Specific CO_2 emissions for these fuels and sludge were calculated in the inventory, while all other emissions were excluded. The latter implicitly equals the assumption that combustion of sludge in the cement kiln does not affect those other emissions.

3.5. CWAO catalyst disposal

The CWAO unit uses a heterogeneous catalyst, consisting of an active carbon adsorbent incorporating small amounts of metals. Prior to its extraction from the reactor, it is dried to a moisture level of 10%. The expected disposal route for this material, once exhausted, is incineration. This process was modelled with the hazardous waste incinerator model developed by Doka (2007) for ecoinvent v2, programmed as an excel spreadsheet, in which the user enters the composition of the treated waste. This was approximated as the composition of coal containing 80% carbon, 5% hydrogen and 15% oxygen. The resulting inventory covers not only the mass and energy balance of the incinerator, but also the disposal of the ash in a controlled landfill after inertization with cement. According to the model, 0.35 kWh electricity and 17 MJ thermal energy are recovered per kg treated catalyst, which are modelled as substituting grid electricity and industrial thermal energy production in Turkey, the former according to the mix defined in section 3.1 and the latter according to the Rest-of-World (RoW) region in ecoinvent.

3.6. Substituted freshwater treatment

Reclamation and reuse of refinery wastewater leads to the substitution of equivalent treated water, which in the present study is assumed to originate from freshwater. Three water qualities were modelled in the study, namely fire water, cooling makeup water and boiler feedwater.
Fire water production from freshwater was considered to require a simple coarse screening. This process was modelled with a modified version of the ecoinvent process for production of tap water by direct filtration, in which the disinfection step was excluded.
Cooling makeup water requires a more through treatment. In our model this consisted of a physical-chemical process similar to that applied to tap water production (coagulation, flocculation, settling, filtration and disinfection), followed by RO. The first process was approximated with the ecoinvent process for conventional production of tap water in Europe. RO was approximated with the same LCI data used for the reclamation of refinery wastewater through single-pass RO, which has a recovery of 75% over the raw water input.
Boiler feed water requires the most exhaustive treatment, in order to obtain deionized water that prevents damage in boilers. As in the production of cooling water, it was assumed that raw water undergoes a physical-chemical treatment process, after which it is passed through the ion exchange resins. Consumption figures for energy and chemicals for the ion exchange process were obtained from Beardsley et al. (1995), assuming the feed water has a total dissolved solids (TDS) content of 240 mg/L expressed as $CaCO_3$-eq, which is considered as an average case in that study. Consumption of cationic and anionic resins per m^3 product water was obtained from the ecoinvent data set for deionized water.

3.7. Substituted steam production

As mentioned in section 2.3, reuse of RO permeate as boiler feedwater leads to a thermal energy saving, due to the higher temperature of the refinery effluent (34 ºC) compared to freshwater from e.g. a river or lake. This saving is estimated assuming boiler feed water from freshwater has a temperature of 15 ºC, leading to a gap of 19 ºC when compared to the refinery wastewater. With a heat capacity of 4.18 kJ/L/ºC, the energy saving is estimated as 79 MJ/m^3 RO permeate reused. This is modelled as a reduced demand of steam, produced from cogeneration with natural gas.

4. Results and discussion

4.1. Results

Table 2 shows the life cycle impact assessment results for the reference and three reuse scenarios, displaying only the total values obtained for each selected indicator, per m^3 refinery wastewater. In the supplementary material we show the values for the entire set of 17 indicators. As it can be seen, none of the reuse scenarios obtains favourable results in all six indicators at the same time. In greenhouse-gas emissions and non-renewable energy demand, only boiler reuse performs better than the reference, while in aquatic eutrophication only fire reuse achieves a substantially lower impact. In marine ecotoxicity and freshwater consumption, though, all reuse scenarios are preferable to the reference. Finally, in fine particulate matter pollution, all reuse scenarios perform worse than the reference.

Table 2. Life cycle impact assessment results, total values.

Impact category	Unit	Reference	Boiler reuse	Cooling reuse	Fire reuse
Global warming	kg CO_2-eq	1.3	-0.9	2.8	2.7
Fine particulate matter	kg PM2.5-eq	0.008	0.060	0.021	0.019
Marine ecotoxicity	kg 1,4-DCB	1.5	0.3	0.2	0.1
Aquatic europhication	kg NO_3-eq	0.034	0.029	0.027	0.006
Non-renewable energy demand	MJ primary	16	-24	42	40
Freshwater consumption	m^3	0.006	-0.88	-1.04	-0.94

4.2. Contribution analysis

In figure 4 we take a closer look at the results of each indicator, by means of a contribution analysis. The figure shows, for each indicator and scenario, the positive sign (impacts) and negative sign (benefits) contributions from different activities involved in the corresponding supply chains.

In global warming, we see all reuse scenarios have a higher impact than the reference due to the operation of the different treatment units, but when wastewater is reused as boiler feedwater these impacts are completely offset by the benefits from steam substitution, and to a lower extent by those associated to substituted freshwater treatment (ion exchange). As it has been described in the inventory analysis, the warmer nature of the RO effluent, when compared to freshwater, leads to an estimated saving of 79 MJ steam per m^3 wastewater, which would be produced in the refinery by burning fossil fuels. This benefit does not apply to reuse in cooling or firefighting applications, as the water temperature does not play a role in those cases.

In particulate matter pollution we see all reuse scenarios perform worse than the reference. In all cases we see higher emissions associated to the different treatment units, and this is caused by the overall higher electricity demand by these. The electricity production profile considered for Turkey supplies 25% of electricity from coal, leading to substantial emissions of fine particulate matter from power plants. Although the reuse scenarios save electricity by means of substituted freshwater treatment, this seems not to be enough to offset the electricity demand to reclaim the wastewater. In the boiler reuse scenario, we also see that steam substitution, as opposed to what we see in global warming, leads to an impact rather than to a benefit. This is explained by the fact that steam is produced in the refinery in a cogeneration unit, where steam is co-produced with electricity. Since reusing wastewater as boiler feedwater leads to a lower steam demand, this means the cogeneration unit will at the same time produce less electricity as a by-product. This gap is compensated by an increase in electricity production from the national grid, with its relatively high particulate emissions.

Marine ecotoxicity shows a clear preference for all reuse scenarios, as this avoids the direct emissions to the sea from the reference treatment. An analysis of the individual contributions of the emitted substances shows that most of this toxicity is associated to aromatic hydrocarbons of more than 21 carbon atoms, which in our impact assessment have been characterized as anthracene. This compound is representative for this hydrocarbon fraction according to risk assessment practices (Geosphere 2006), however from an LCA perspective this choice can have substantial effects in the results. According to the same source, pyrene and phenanthrene, among others, are also representative compounds, but they have substantially different characterization factors in the marine ecotoxicity model by Huijbregts ey al. (2016) (one order of magnitude above or below that of anthracene). Also, in the inventory we assumed a discharge level for oil and grease equal to the legal limit in Turkey, of 10 mg/L. Actual discharge values in refineries might be below this threshold. As usual, toxicity-related impact categories in LCA remain among the most uncertain, and our study is no exception to this, due to a combination of uncertainties at the inventory and impact assessment levels.

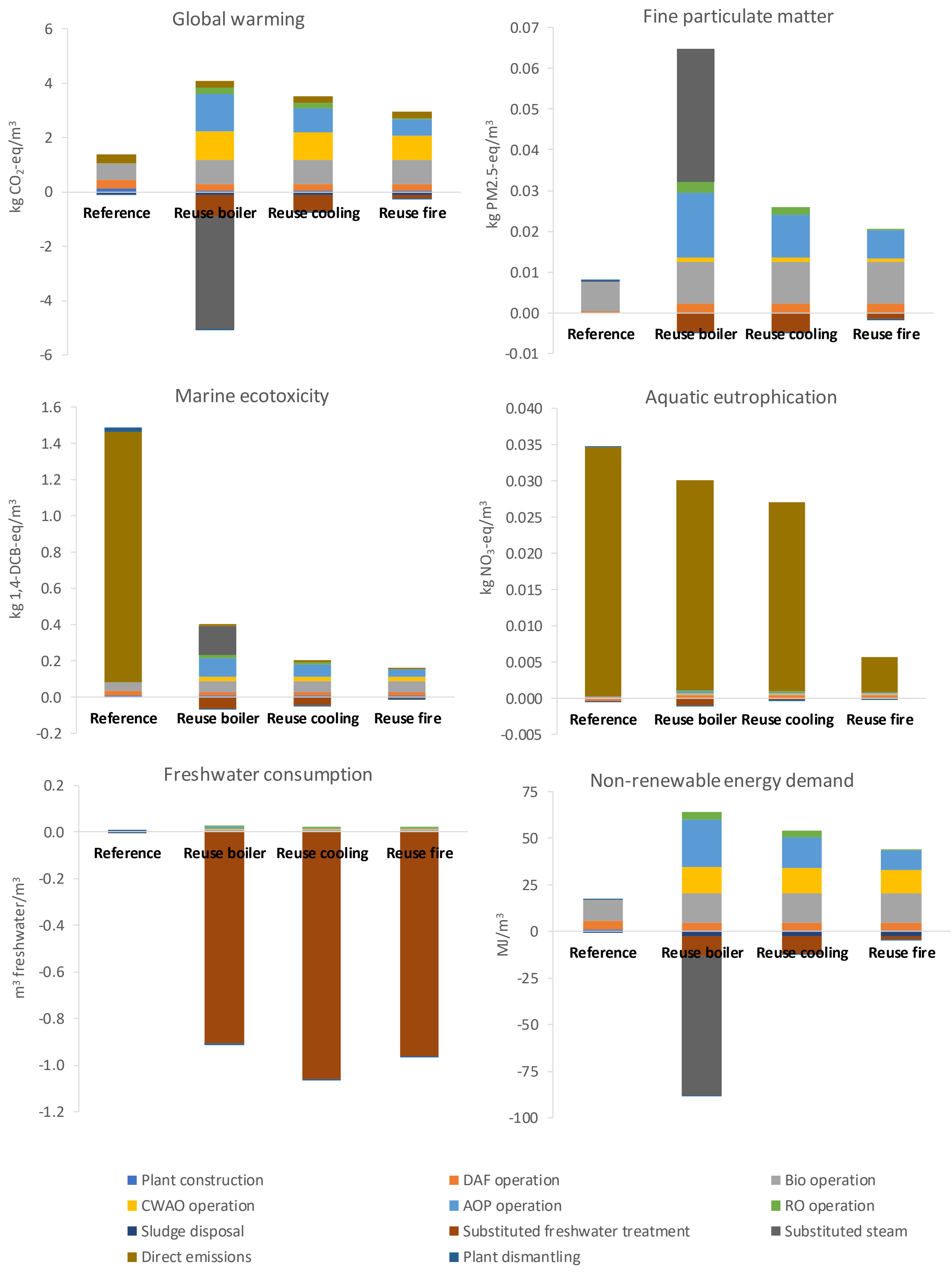

Figure 4. Life cycle impact assessment results, contribution analysis.

In the aquatic eutrophication indicator, we see the main contribution in all scenarios is the direct emission of pollutants from the WWTP. Favourable results can be seen for all reuse scenarios, especially for reuse as fire water. The latter is explained by the fact that this reuse option is the one leading to the lowest amount of liquid effluents being discharged to the sea. In the reference

scenario the entire treated effluent is discharged, with its residual nitrogen content. In the boiler and cooling reuse scenarios most of the water is diverted from discharge, however the RO concentrate, containing any nitrogen compounds left from the biological treatment, is effectively discharged. In the fire reuse scenario, though, only 16% of the wastewater is subject to RO (see table 1), thus minimizing the amount of nitrogen reaching the sea.
Non-renewable energy demand shows a very similar pattern to that observed for global warming. This is expected to some extent, since greenhouse-gas emissions are well correlated to energy consumption, which is what this indicator reflects. On the one hand, we see that refinery wastewater reclamation for reuse as boiler feedwater leads to a net energy saving (40 MJ less per m^3 wastewater when compared to the reference), for the most part due to steam substitution. On the other hand, reuse as cooling or fire water leads to an increased energy demand, due to the electricity consumption by the exhaustive treatment to which wastewater must be subject to achieve the desired quality. This is unfortunately not offset by the avoided energy demand for freshwater treatment.
Finally, the freshwater consumption indicator shows clear benefits for all reuse scenarios, with the three of them showing a net freshwater saving over the reference scenario, of around 1 m^3 per m^3 wastewater, induced by the substituted freshwater treatment. In this way, freshwater savings are not only a fact on-site, but also when one takes into account the entire supply chain of the affected activities.

4.3. Sensitivity analysis on electricity production

The results of the LCA study show that refinery wastewater reclamation through the INTEGROIL® concept is an energy-intensive process, particularly with regard to electricity. As the basis for the study we considered the current conditions in Turkey, including electricity production, however the technology was developed with a European focus. For this reason, we conducted a sensitivity analysis where a different electricity production profile is considered, namely that for Europe, also taking a consequential approach. This mix presents a slightly higher contribution from renewable sources, namely 51%, but most importantly, the contribution of coal to the total supply mix is only 2%. The detailed data for this European marginal electricity mix is shown in the supplementary material.
In this sensitivity analysis we simulate all the scenarios, including the reference, after replacing the Turkish electricity mix by the European one, in order to evaluate the influence in the results, which are shown for this new situation in figure 4.
The results for marine ecotoxicity, aquatic eutrophication and freshwater consumption are largely unaffected by the choice of electricity supply mix, however this is not the case for the remaining three indicators, where we can see that figures drop for all scenarios, including the reference. This drop is of particular relevance in particulate matter pollution, where all figures decrease between 1 and 2 orders of magnitude. Despite this substantial drop, however, we see that the ranking of scenarios under European conditions remains unaffected when compared to Turkish conditions.

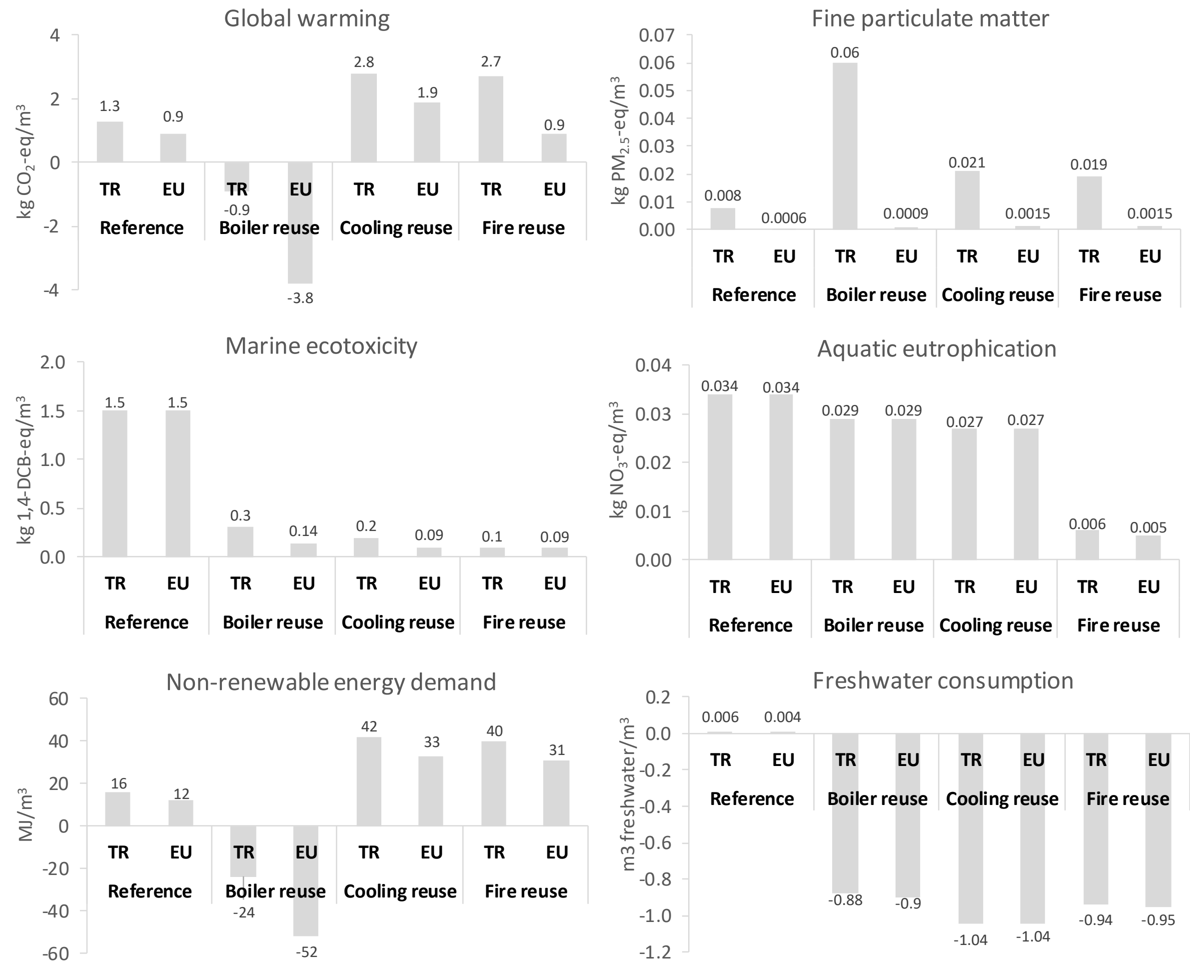

Figure 5. Life cycle impact assessment results, total values for Turkey and Europe.

4.4. Discussion

This study has quantified the environmental performance and trade-offs associated to wastewater reclamation in a refinery. Although the focus has been on Turkey, the sensitivity analysis on electricity production allowed us to also get a view closer to wider European conditions. Wastewater reclamation for reuse within the refinery does achieve the goal of saving freshwater resources taking a life cycle perspective. It appears, though, that when reclamation targets cooling water or fire water as applications, this comes at the price of a net increase in energy consumption, which is not compensated by the avoided energy consumption associated to treating the otherwise used freshwater. Boiler reuse appears to have a better environmental profile in several indicators, such as global warming, thanks to the steam substitution effect. In general, our findings seem to be in accordance with Vlasopoulos et al. (2006), stating that the environmental impact of technologies for treating wastewater in the oil and gas sector is proportional to their energy consumption.

In our study we started from the premise that the refinery would otherwise use freshwater in its boiler, cooling and fire water systems. Some refineries, though, might rely on seawater instead. Our analysis cannot be extrapolated to such conditions; first, because the substituted sea water treatment, at least for cooling and boiler makeup water, would involve desalination, which is known to have higher energy consumption and life cycle impacts (Muñoz and Rodríguez. 2008); second, in a context where sea water is already in use, the motivation to save freshwater resources is not in focus anymore.

Another source of uncertainty in our study was the fact that the INTEGROIL® technologies were assessed based on a hypothetical scale-up of the existing demonstration plant. In spite of this, the up-scaled plant model can be considered as a realistic one in terms of equipment and operation. This is considered to overall reduce uncertainty when compared to relying on the demonstration plant scale.
Finally, in our assessment the treatment intensity has been established by the water quality thresholds established by Tüpraş. Less strict thresholds, especially to produce fire water, would probably lead to a better environmental performance of wastewater reclamation than apparent in our study.

4.5. Conclusions

We assessed the life cycle impacts of wastewater reclamation and reuse in a petroleum refinery, with a focus on Turkey. Three main reuse applications were considered, namely boiler feedwater, cooling and fire water. These options were compared to current refinery disposal practices, under six environmental impact indicators covering use of natural resources, human health and impacts on ecosystems.
All three reclamation scenarios succeed in achieving a freshwater saving, of around 1 m^3 freshwater per m^3 wastewater treated, taking into account the entire supply chain of all affected activities. Equally beneficial results are obtained concerning marine ecotoxicity and aquatic eutrophication. In the former, all reuse scenarios lead to a reduction in the impact from discharge of harmful hydrocarbons to the sea, although the magnitude of this reduction is subject to substantial uncertainty. Concerning aquatic eutrophication, benefits are due to a reduced flow of nitrogen compounds to the sea, especially in the fire water application.
With regard to global warming and non-renewable energy demand, only the boiler feedwater application appears to involve an improvement over disposal. The advantage of this option is that, by providing the boiler system with a treated effluent of higher temperature than freshwater from a natural body, a considerable thermal energy saving can be achieved. For cooling makeup water and fire water, on the other hand, the exhaustive treatment required to achieve the desired quality is not compensated in these two indicators by the substituted freshwater treatment. The indicator on particulate matter pollution shows that all reuse scenarios lead to higher impact than current disposal practices. This is caused by a higher electricity demand, linked to the Turkish electricity production mix with a substantial contribution from coal power plants. A sensitivity analysis has shown that that the environmental performance of all scenarios would improve to a great extent when shifting to an electricity mix with a higher share of renewables, as is the current trend in most European countries.

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