

**DOKUZ EYLÜL UNIVERSITY**  
**GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

**LIFE CYCLE ASSESSMENT OF TREATMENT  
OPTIONS FOR AN INDUSTRIAL WASTEWATER**

by

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**February, 2016**

**İZMİR**

# **LIFE CYCLE ASSESSMENT OF TREATMENT OPTIONS FOR AN INDUSTRIAL WASTEWATER**

**A Thesis Submitted to the  
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**by**

**Hatiye FINDIKÇI**

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**İZMİR**

**M.Sc. THESIS EXAMINATION RESULT FORM**

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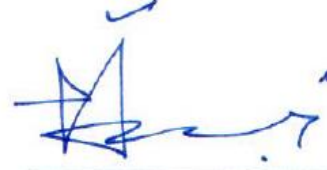
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Hatiye FINDIKÇI

# LIFE CYCLE ASSESSMENT OF TREATMENT OPTIONS FOR AN INDUSTRIAL WASTEWATER

## ABSTRACT

The waste management systems help us to protect the environment, but in contrast to their main commissioned purpose, they can damage the environment through energy consumption, greenhouse gas emission, the utilization of chemicals, and some toxic material outcomes. Therefore, it is very important to design and operate to any waste management systems as to minimize their negative effects to the environment. Life cycle assessment (LCA) is used as a decision support tool to determine the most appropriate wastewater management strategy.

In the scope of this project, different scenarios were generated for leather industry wastewater treatment and the environmental effects of these scenarios were compared using life cycle assessment tool. Scenarios were developed considering especially chromium removal and recovery alternatives. Life cycle assessment studies were carried out by using GaBi 6.0 LCA software. The required data for the operating of the software was obtained from the laboratory experiments, literature, and Eco-invent database which are integrated into the GaBi 6.0 software.

Depending on the studies' results, Scenario-1, in which combined chromium and sulphur flows are treated in the wastewater treatment plant, was determined as the most harmful alternative for the environment. The chromium and sulphur flows were separated in the rest of the scenarios. So, it can be said that, to decrease the wastewater treatment plant loads by the separation of the chromium and sulphur flows in the leather industry, is the environmentally friendly application. In addition, chromium recovery applications reduce the negative environmental effects (Scenario 3 and 4).

**Keywords:** Tannery wastewater, life cycle assessment, sulphur, chromium removal and recovery, GaBi software

# ENDÜSTRİYEL ATIKSULARIN ARITMA SEÇENEKLERİNİN YAŞAM DÖNGÜSÜ ANALİZİ İLE DEĞERLENDİRİLMESİ

## ÖZ

Atık yönetim amacıyla yapılan ve işletilen tesislerde çevre kirliliğine karşı önlem almak amacıyla bir takım işlemler gerçekleştirilirken, kimyasal madde tüketimi, aşırı enerji tüketimi, sera gazları salınımı, ötrofikasyona neden olma gibi doğal çevrenin yapısını bozacak özelliklerin bulunması tezatlık yaratmaktadır. Bu nedenle herhangi bir atık yönetimi ile ilgili tesisin en verimli ve doğaya en az zarar verecek tasarımının yapılması ve işletilmesi, bu tesislerin kurulma amacına doğru hizmet etmesi bakımından çok önemli bir husustur. Yaşam döngüsü analizi (YDA), en iyi atıksu yönetim stratejisini belirlemek için bir karar destek aracı olarak kullanılmaktadır.

Bu proje çalışması kapsamında, deri endüstrisi atıksularının arıtılmasında uygulanabilecek olan yöntemler için farklı senaryolar oluşturulmuş ve bu senaryolarda çevreye olan etkiler yaşam döngüsü analizi çalışmaları gerçekleştirilerek karşılaştırılmıştır. Senaryolar oluşturulurken özellikle krom giderimi ve geri kazanımı yöntemleri dikkate alınmıştır. Yaşam döngüsü analizleri GaBi 6.0 LCA yazılım program ile gerçekleştirilmiştir. Programın çalıştırılması için gerekli veri, proje çalışması kapsamında yürütülen laboratuvar denemeleri, literatür bilgileri ve GaBi 6.0 yazılım program içerisinde yer alan Eco-invent veri tabanı ile elde edilmiştir.

Yapılan çalışmalar sonucunda, üretilen senaryolarda krom hattı ve sülfür hattının birleşik olarak arıtma tesisine gelmesi ve üretimde oluşan tüm atıksuyun birlikte arıtılması durumunda uygulanabilecek arıtma ünitelerinin kullanıldığı Senaryo-1, tüm senaryolar içerisinde çevreye en fazla zarar verecek uygulama olarak belirlenmiştir. Senaryo-1 haricindeki tüm uygulamalarda krom ve sülfür hattı ayrılmıştır. Buna göre, deri endüstrisinde krom ve sülfür hattının ayrılarak, sonraki kademelerde arıtma tesisinin yükünü azaltmak çevresel etkileri oldukça azaltan bir

uygulamadır. Krom geri kazanımı uygulanan senaryolarda (Senaryo 3 ve 4), olumsuz çevresel etkiler en aza inmiştir.

**Anahtar kelimeler:** Deri atıksuyu, yaşam döngüsü analizi, sülfür, krom giderimi ve geri kazanımı, GaBi yazılımı



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# CHAPTER ONE

## INTRODUCTION

### 1.1 Introduction

In the 18<sup>th</sup> and 19<sup>th</sup> centuries Industrial Revolution, is defined the realization of new innovations and the impact on production of this invention with the developing industry, has been gained rapid momentum to development of the industry in Europe. Besides increased in the yield of products has begun diversity. Overmuch producing and consuming society structure became dominated to developed and developing countries. Therefore, overconsumption has caused so many problems. At the beginning of these problems, the increase of raw material needing and accordingly to start to observed decrease in natural resources appear. Increasing of natural resources consumption and excessive production causes negative environmental conditions. Because of occurred liquid, solid and gaseous waste.

Worth living features of the Earth badly is affected from rise of waste amount. Aware of this situation developed countries enhanced “environmental management” and “waste management” terms. Waste management, which decrease human impacts on the environment, allow the self-renewal of the natural balance and expose problems due top revent degradation of the natural balance is aimed to increase society’s environmental protection consciousness. The waste management systems help us to protect the environment, but in contrast to their main commissioned purpose, they can damage the environment through energy consumption, greenhouse gas emission, the utilization of chemicals, and some toxic material outcomes.

With the global growing economy, both of environmental pollution and owning cost simultaneously need to optimize. In this way, the idea of review process which is examined from extraction of raw material to returns to the nature of the raw material was emerged. Then, assessment systems were developed for it.

In the recent times, Life Cycle Assessment (LCA) term, assess many environmental impacts associated with all the stages of process from cradle to grave, is evaluating system.

## **1.2 Aim and Scope of the Thesis**

Life cycle assessment (LCA) approach was applied as a decision support tool to determine the most appropriate wastewater management strategy in this thesis. The present study is, to the best of our knowledge, the first LCA focusing on leather industry wastewater treatment plants. LCA methodology was applied to compare the environmental performance of alternative treatment methods for tannery wastewaters.

In the scope of this study, different scenarios were generated for leather industry wastewater treatment and the environmental effects of these scenarios were compared using life cycle assessment tool. Scenarios were developed considering especially chromium removal and recovery alternatives.



## CHAPTER TWO

### WASTEWATER MANAGEMENT IN TANNERY INDUSTRY

#### 2.1 Tannery Industry

Tannery (Leather) industry is one of the most important industrial sectors in Turkey. In particular, a significant portion of the sheep/goat skins produced in the world is handled by the Turkish leather sector. Leather is processed thereabout 600 tons per day in Turkey. The processing of bovine leather areas are İstanbul-Tuzla, İzmir-Menemen, Niğde-Bor, Bolu-Gerede and Çorlu in Turkey. Besides, the processing of small cattle areas are Isparta-Yalvaç, Uşak and İzmir-Menemen (Öztürk, n.d.).

In the leather sector, the all process includes a successiveness of complex chemical reactions and mechanical processes. The operations falling in pre-tanning, tanning and post-tanning operations are depicted in the Figure 2.1.

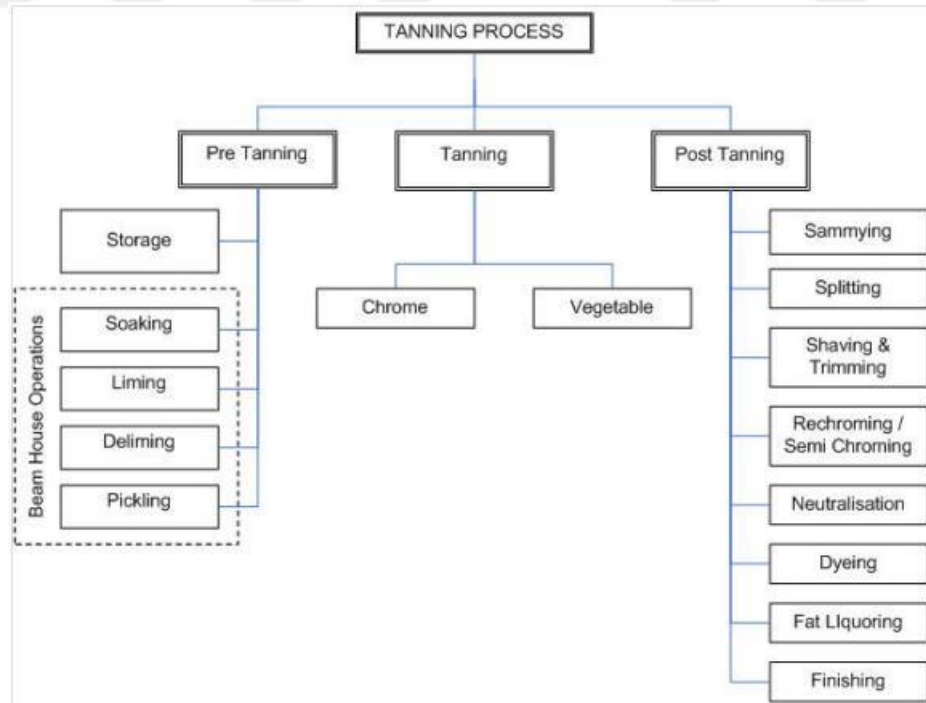


Figure 2.1 Tannery industry processes (MoEF, 2010).

These steps manufacture a final product with specific properties: stability, appearance, water resistance, temperature resistance, elasticity, and permeability (MoEF, 2010). In the leather sector various types of finished leather is processed from salted raw skins. Approximately 130 different types of chemicals are used in leather manufacturing which ranges from widespread salt to very costly chrome sulphate (Chattha & Shaukat, 1999).

## **2.2 Treatment of Tannery Wastewater**

### ***2.2.1 Identification and Classification of Tannery Wastewater***

Leather industries use large amount of water. Approximately 20-80 m<sup>3</sup> water is used by tanning industries per ton of raw skin (Krishnamoorthi, Sivakumar, Saravanan & Prabhu, 2009).

Tanning production operations are soaking, liming/reliming/unhairing, fleshing, pickling, chrome tanning, splitting, shaving, trimming, rechroming, dyeing, fat liquoring and dry finishing. These steps and their inputs and outputs are depicted in the Figure 2.2. Water consumption is too much to these steps. Water is used as the carrier for chemicals to provide the cleaning of raw skins. Volume of wastewater and its characteristics vary from tannery to tannery. They may also vary within the same tannery from time to time. But, approximately 30-50 litres wastewater is occurred by tanning industries per kilogram of raw skin (Krishnamoorthi, Sivakumar, Saravanan & Prabhu, 2009).

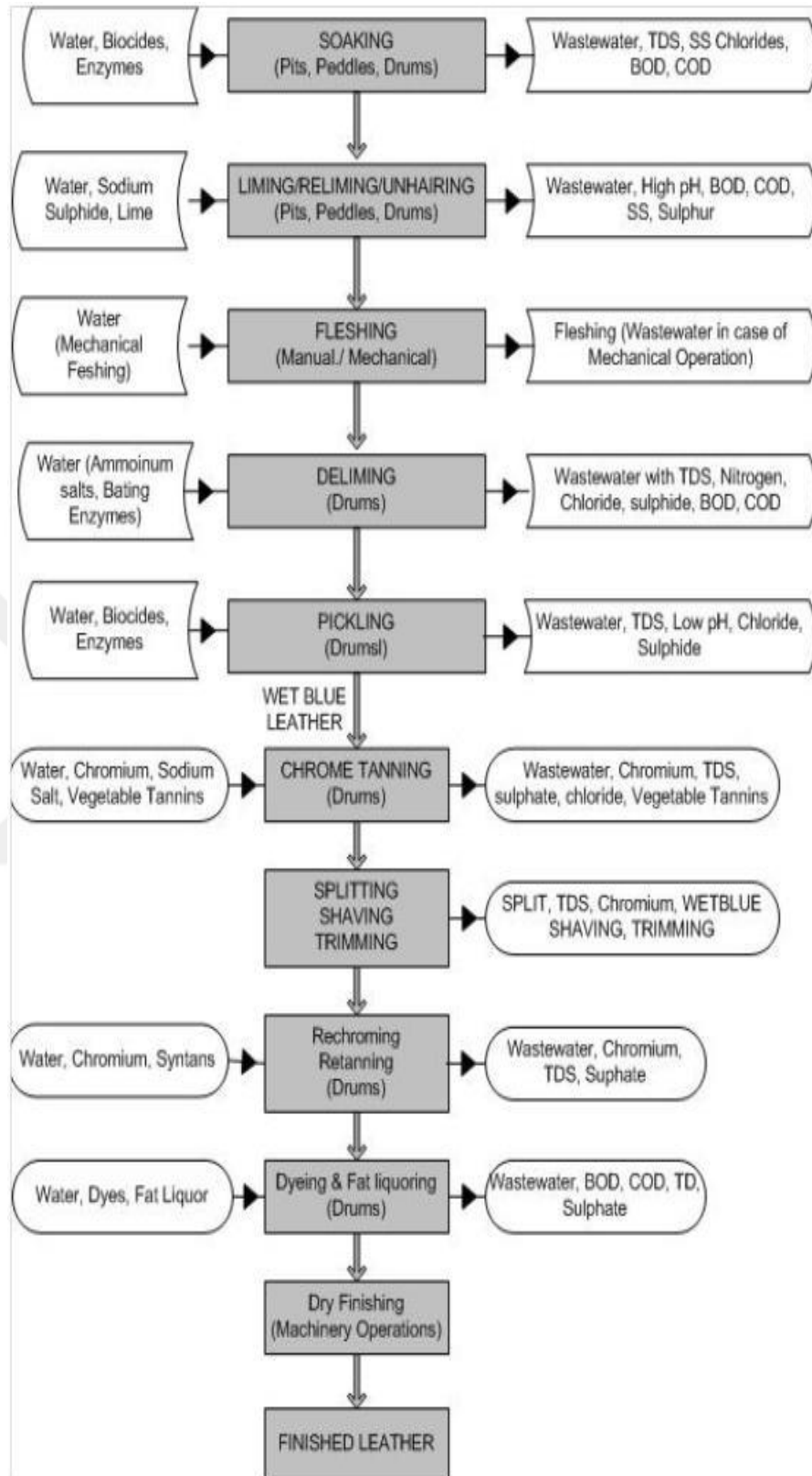


Figure 2.2 Inputs and outputs in tannery industry (MoEF, 2010).

The leather industry produces wastewaters containing high strength toxic chemicals and chromium and sulphur are the main pollutants. In order to treat wastewaters effectively, sulphur and chromium containing flows should be separated and each flow should be treated separately. Most methods for treating sulphur rely on the oxidation with various oxidants, such as air, chlorine, hydrogen peroxide, ozone.

There are several chromium treatment methods, such as chemical precipitation, adsorption, ion exchange, membrane systems, electrochemical methods, and among them chemical precipitation is the most popular method. However, chromium containing sludge is difficult to handle since it is classified as a hazardous waste. Nowadays, the recovery of chromium from chemical sludge has become more common method since this application has both environmental and economic advantages (Fahima, Barsoumb, Eida & Khalila, 2006).

## **CHAPTER THREE**

### **LIFE CYCLE ASSESSMENT (LCA) APPROACH**

#### **3.1 Introduction to LCA**

As has been demonstrated in various ways, the capacity of the globe to snugly maintain is not possible, because our industrial activities have already gone over the limit. We need urgent action to alter this critical case to a sustainable one (Takata, 2007). This situation has led to emergence the notion of Life Cycle Assessment (LCA).

LCA is a technique to assess environmental impacts associated with a product over its life cycle; extraction of raw materials, manufacture, distribution, materials processing, manufacturing, transport, repair, maintenance, use, re-use and recycling (Charters, 2010).

#### **3.2 LCA Methodology**

Life Cycle Assessment is a technique that makes the evaluation of all potential environmental impact of all activities. Turkish Standards Institute (TSE) published “Environmental Management – Life Cycle Assessment – Principles and Frame” Standard in 19.06.2007. According to this standard, Life Cycle Assessment, goods and services obtained from a particular material and energy in goods and services system. As UNEP (1997) explains it “the aim of LCA is to suggest more sustainable forms of production and consumption”. LCA is science-based, quantitative and integrative (Schuurmans-Stehmanna, 1994).

Life Cycle Assessment is generally applied in order to determine the environmental impact of industrial production all stage which is obtaining the raw material, using of product and then disposal of used product (Dagnew, Parker, Seto, Waldner, Hong, Bayly & Cumin, 2011). A life Cycle Assessment which describe energy use, material input, product obtain from raw material and disposal of product

periods uses “cradle-to-grave” approach. LCA principles by ISO 14040 Standards and LCA conditions by ISO 14044 Standards are defined.

There are mainly four types of LCA approaches:

- Cradle-to-grave is the full Life Cycle Assessment from resource extraction ('cradle') to use phase and disposal phase ('grave').
- Cradle-to-gate is an assessment of a partial product life cycle from resource extraction (cradle) to the factory gate (i.e., before it is transported to the consumer)
- Cradle-to-cradle is a specific kind of cradle-to-grave assessment, where the end-of-life disposal step for the product is a recycling process. It is a method used to minimize the environmental impact of products by employing sustainable production, operation, and disposal practices and aims to incorporate social responsibility into product development.
- Gate-to-gate is a partial LCA looking at only one value-added process in the entire production chain.

LCA framework steps:

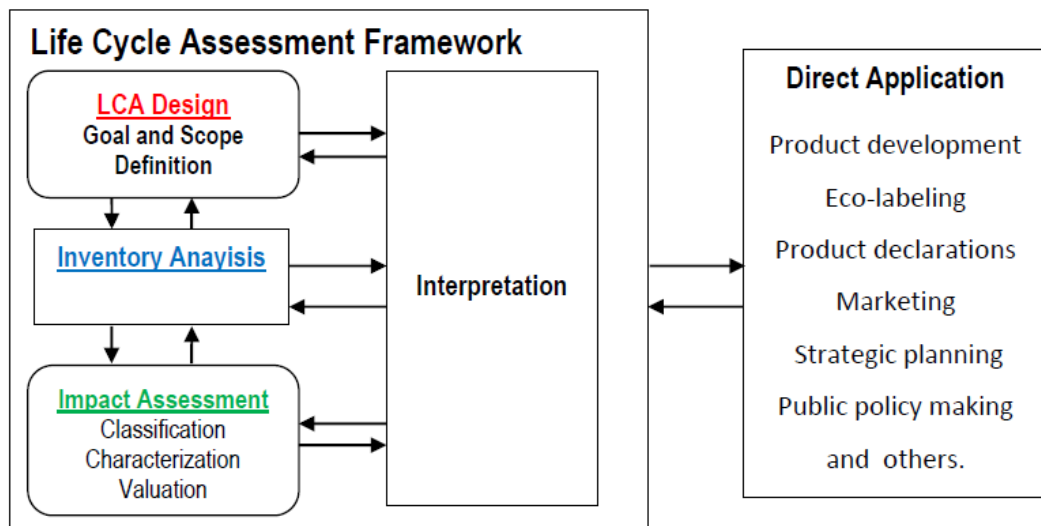


Figure 3.1 Life cycle assessment framework (Chaosakul, 2005).

### ***3.2.1 Goal and Scope Definition***

The prime and quite likely most important step of a LCA is the Goal and Scope definition. Present part is defined the reason to make the assessment (Ramirez, 2012). The system boundaries of a system are identified by an input and output flow diagram. All operations that promote to the life cycle of the product, process, or activity fall within the system boundaries (Roy et al., 2009).

Functional unit and system boundaries are very important for definition and compassion. The functional unit is the quantified definition of a function of a product system associated with physical unit. The system boundaries are described by the cut off criteria. Cut off criteria permit us to define which parts and materials of the product system will be included in or excluded from the total system and which are excluded from the system (Spatarb, Betz, Florin, Baitz & Faltenbacher, 2001)

### ***3.2.2 Life Cycle Inventory Analysis***

The inventory analysis accumulates all the data of the unit processes in a product system and depends on them to the functional unit of the study (Ramirez, 2012). This phase is the most work compacted and time consuming compared to other phases in an LCA, because of data collection. The data collection can be less time consuming if good databases are procurable and if customers and suppliers are willing to help (Roy et al., 2009). On the other words, the inventory model is defined algebraically, in order to reveal the model structure and in order to demonstrate the precision of results to variation in model parameters (Boyd, 2012).

### ***3.2.3 Life Cycle Impact (LCI) Assessment***

Impact assessment is the step that forms an estimate of the effects of the environmental impacts registered in the inventory table. There is little agreement considering a standard methodological framework; The SETAC Code of Practice proposes:

- classification,
- characterisation,
- evaluation

which have been defined in detail in their report from the SETAC workshop "Integrating Impact Assessment into LCA" (SETAC, 1994)

Classification is the appointment of the LCI results to the impact categories hand-picked. Characterization is the assessment of the significance of potential impacts of each inventory flow into its corresponding environmental impact. Characterization ensures a way to directly contrast the LCI results within each category. Valuation is the assessment of the relative significance of environmental loads described in the classification, characterization stages by assigning them weighting which permits them to be contrasted or rounded up (Roy et al., 2009; Ramirez, 2012).

#### ***3.2.4 Interpretation***

Interpretation where final assessment is made is the last phase in LCA. The aim here is to draw consequences that can support a decision or can ensure a readily comprehensible result of the LCA. Interpretation results to be a systematic technique to identify and quantify, control and evaluate information from the conclusions of the Life Cycle Impact and Life Cycle Impact Assessment, and communicate them influentially (Ramirez, 2012).

### **3.3 Use of software in LCA studies**

It has been developed to be used various software like SimaPro, CML 2000, Eco Indicator 99, EDIP 96, EPS, Ecopoints 97, EarthSmart, Sustainable Mind, Umberto 5.5, GaBi and etc. These softwares must be purchased commercial. But some free softwares are also available.

SimaPro life cycle analysis software can take into account a carbon footprint of various kinds of product and systems. It can detect the potential environmental



impact that a system or service produced with statistical accuracy with its ability to detect key performance indicators and subject full environmental (Loijos, 2012).

GaBi permits you to design your ideas in its interworking. It can come to someone's rescue in designing product with particularly more environmentally friendly components. Using GaBi's process recording property, you can save data across whole point of the design process and determine clearly where efficiencies occur (Loijos, 2012).

EarthSmart is a young piece of software. It reports property permits rapid creation of professional reports that can be updated almost immediately. It automatically takes into account ends of life predicated on expert-selected end of life scenarios (Loijos, 2012).

Sustainable Minds is optimized for conducting life cycle assessment at the design and product advancement stage. It can be used all the way from the whole product systems level down to the particular part level to assess environmental efficiency. This software has articulable procedures (Loijos, 2012).

### **3.4 Case studies on LCA**

Vlasopoulos et al. (2006) defined the execution of life cycle assessment to analyze the environmental impact of 20 technologies appropriate for treating large scaled volumes of water produced during the oil and gas extraction processes. Their life cycle environmental impacts have taken stock of over 15 year time period. The baseline for this study is on the treating of a volume (10,000 m<sup>3</sup> per day) of process water to give a final volume of treated water at suitable water quality levels for a kind of end uses. These 20 technologies are grouped into 4 different treatment stages basing on their quality to treat the oily wastewater in Table 3.2.

Table 3.1 Categorisation of treatment technologies (Dillon, 2003)

Stage 1	Stage 2	Stage 3	Stage 4	Additional
Dissolved air flotation (DAF)	Rotating biological contactors (RBC)	Dual media filtration (DMF)	Reverse osmosis (RO)	Ion exchange (ION)
Hydrocyclones (HYDRO)	Absorbents (ABS)	Granular activated carbon (GAC)	Electrodialysis reversal (EDR)	
	Activated sludge (AS)	Slow sand filtration (SSF)		
	Trickling filters (TF)	Ozone (OZO)		
	Air stripping (AIR)	Organoclay (ORG)		
	Aerated lagoons (AL)	Ultrafiltration (UF)		
	Wetlands (CWL)	Nanofiltration (NF)		
	Microfiltration (MF)			

Treatment train is normally composed of one option from each of the four stages. In total, more than 600 different systems were occurred and investigated. The life cycle impact assessment of the technologies was applied depend on the ISO 14040 series of standards. SimaPro 6 was used for assessment.

The environmental impact was quantified with accord to technologies' contribution for their construction and use phases. For the construction phase, the use of plastic construction materials, namely GRP and PVC, in wetlands, trickling filters, rotating biological contactors, sand filtration and dual media filtration technologies

was reached to be liable for a comparatively higher environmental impact in this phase of the life cycle. The use phase impacts are related to the energy generation processes that supply the used up energy, it is apparent that the mix of energy sources used to generate the electricity is critical to the calculation of the use phase environmental impacts. The use of higher shares of hydropower, solar power and gas in the overall energy mix is anticipated to decrease the environmental impact of the use phase of each technology (Vlasopoulos, Memon, Butler & Murphy; 2006).

In a study performed by Zang, Li, Wang, Zhang and Xionghas made a review of the LCA studies touching on biological (activated sludge) WWTPs, with the aim to ensure qualitative comment of the related environmental impact categories: eutrophication potential, global warming potential, toxicity-related impacts, energy balance, water use, land use and other impact categories (Zang, Li, Wang, Zhang & Xiong, 2015).

In another study performed by Rodriguez-Garcia et al. is life cycle assessment of nutrient removal technologies for the treatment of anaerobic digestion supernatant. The aim of this study is to comment the environmental profile of three different options for the treatment of the anaerobic supernatant. These are a CANON reactor, a sequencing batch reactor based on the NSC, and a struvite crystallization process (SCP) reactor. The main objective of side stream technologies is the removal of N and P compounds. Therefore, they chose, as functional unit (FU), the reduction of the eutrophication potential (EP) as defined by the CML methodology. Reduction of the eutrophication potential impact is shown in below Figure 3.2.

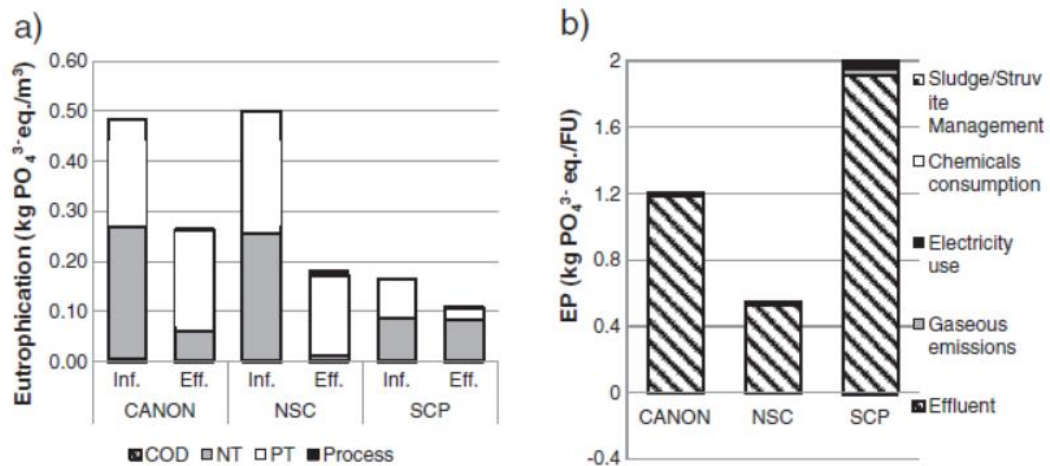


Figure 3.2 Eutrophication impact of the influent and the effluent + the process of the reactors under study (per m<sup>3</sup>) and b) eutrophication potential impact per FU (1 kg PO<sub>4</sub><sup>3-</sup> eq. rem.) (Rodriguez-Garcia et al., 2014)

In this paper, 4 scenarios occurred: CANON, NSC, SCP and CANON+SCP. Finally, P-removal technologies, namely the combination of CANON + SCP, were reached to be the best applicable upgrades for the treatment of the anaerobic digestion supernatant (Rodriguez-Garcia et al., 2014).

Li et al. assessed the environmental benefits and drawbacks of a municipal WWTP (in Kunshan, China) in contrasting with other wastewater treatment plants using different advanced treatment processes (Beijing Green Lake Constructed Wetland Park and the 5-stage Bardenpho simulated process). The approximate influent flow at the Kunshan WWTP is 10<sup>5</sup> m<sup>3</sup>/d, and the lifetime of this WWTP is 50 years. This WWTP features a reactor using Anaerobic/Anoxic/Oxic (A2O) process and a V-shaped sand filter for advanced wastewater treatment. The LCA study of the Kunshan WWTP was carried out from a “cradle-to-grave” perspective. In this study, CMLBaseline2000 method was used for life cycle impact assessment using SimaPro7.0 software. Results are shown in Table 3.2.

Table 3.2 Impact assessment of the Kunshan WWTP

<b>Criterion</b>	<b>Unit</b>	<b>Construction</b>	<b>Operation and maintenance</b>	<b>Transportation</b>	<b>Total</b>
Abiotic resource depletion	kg Sb eq.	1.76E+05	1.72E+06	1.81E+04	1.91E+06
Global warming	kg CO <sub>2</sub> eq.	1.86E+07	5.24E+08	2.25E+06	5.45E+08
Terrestrial ecotoxicity	kg 1,4-DCB eq.	1.11E+05	6.93E+05	-	8.04E+05
Photochemical oxidation	kg C <sub>2</sub> H <sub>4</sub> eq.	4.09E+03	9.34E+04	7.75E+03	1.05E+05
Acidification	kg SO <sub>2</sub> eq.	4.76E+04	2.41E+06	6.11E+04	2.52E+06
Eutrophication	kg PO <sub>4</sub> eq.	4.78E+03	2.00E+07	9.21E+03	2.00E+07

Different environmental impacts created during construction, operation and maintenance, and transportation of chemicals was quantified. It was indicated that eutrophication, global warming and waterborne suspended particles are the most expensive impacts of the Kunshan WWTP. The LCA consequence of Kunshan WWTP taking renewable energy (wind power) as the energy source proposed that improving the effluent quality will decrease the environmental (Li, Luo, Huang, Wang & Zhang, 2013).

## **CHAPTER FOUR**

### **MATERIAL AND METHODS**

#### **4.1 Laboratorial Analyses**

For the characterization of the tannery wastewater samples Chemical oxygen demand (COD), biological oxygen demand (BOD), total nitrogen (TN), total phosphorus (TP), total solids (TS), total volatile solids (TVS), total suspended solids (TSS), pH, electrical conductivity (EC), chromium and sulphur analyses were carried out. TN and TP analyses were measured by using test kits (Merck 14537 – 14543). pH and EC were measured by using WTW Model 340i Multi Analyzer. Chromium was analyzed using Perkin Elmer ICP-OES OPTIMA 7000DV analyzer. The analyses of the other parameters were done according to procedures given in Standard Methods that published by American Public Health Association, American Water Works Association, & Water Environment Federation. Total solid concentration of the sludge and the organic material fraction of the solid material measurements were also done according to Standard Methods (APHA, AWWA, WEF, 2005).

After the characterization studies, treatability and recovery of chromium studies were carried on. Jar tests experiments were performed for this aim.

#### **4.2 Life Cycle Assessment Studies**

##### ***4.2.1 GaBi Software and Used Data Set***

Life cycle assessment studies were carried out by using GaBi 6.1 LCA software. Program mainly has been prepared for manufacture of a product. For this reason, the numbers of available processes are very limited for wastewater treatment. The required data for the software was obtained from the previous laboratory experiments, literature, and Eco-invent database which are integrated into the

GaBi6.1 software. One of the most important details is mass balance while process is created. Mass balance is achieved between the inputs and outputs are not able to perform the correct process production.

When the scenario is created in program, the plans were created with subdivided their plans. Then, the scenario was obtained by combining them. For example; created of first scenario which works without chromium recovery and is constructed in form of chromium and sulphur combined line was formed by the combination of three plans: Equalization unit, chemical treatment unit and biological treatment unit. Creating mass balance screenshot is given to equalization tank in Figure 4.1.

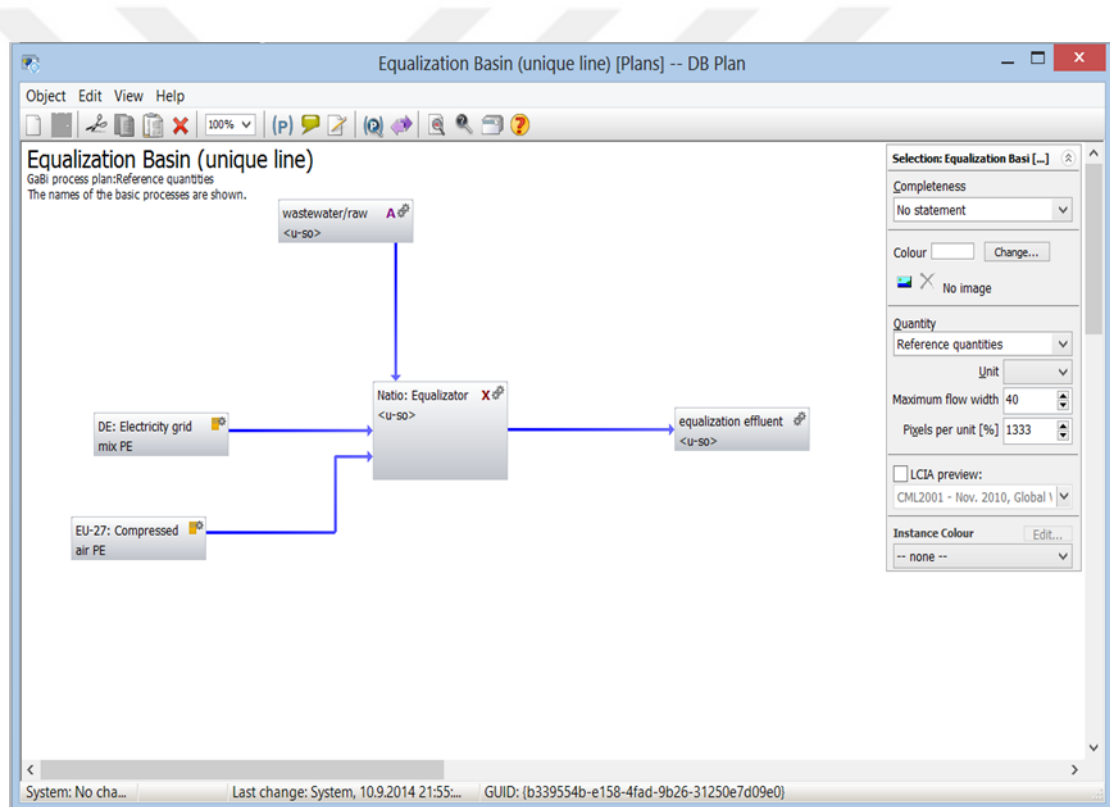


Figure 4.1 Equalization tank flow diagram

As shown in Figure 4.1, equalization tank's inputs are raw wastewater, energy for using mixing and energy for aeration. System output only is aerated wastewater. After the flow diagram has been created, the process content has been created. Creating input-output screenshot is given to equalization tank in Figure 4.2.

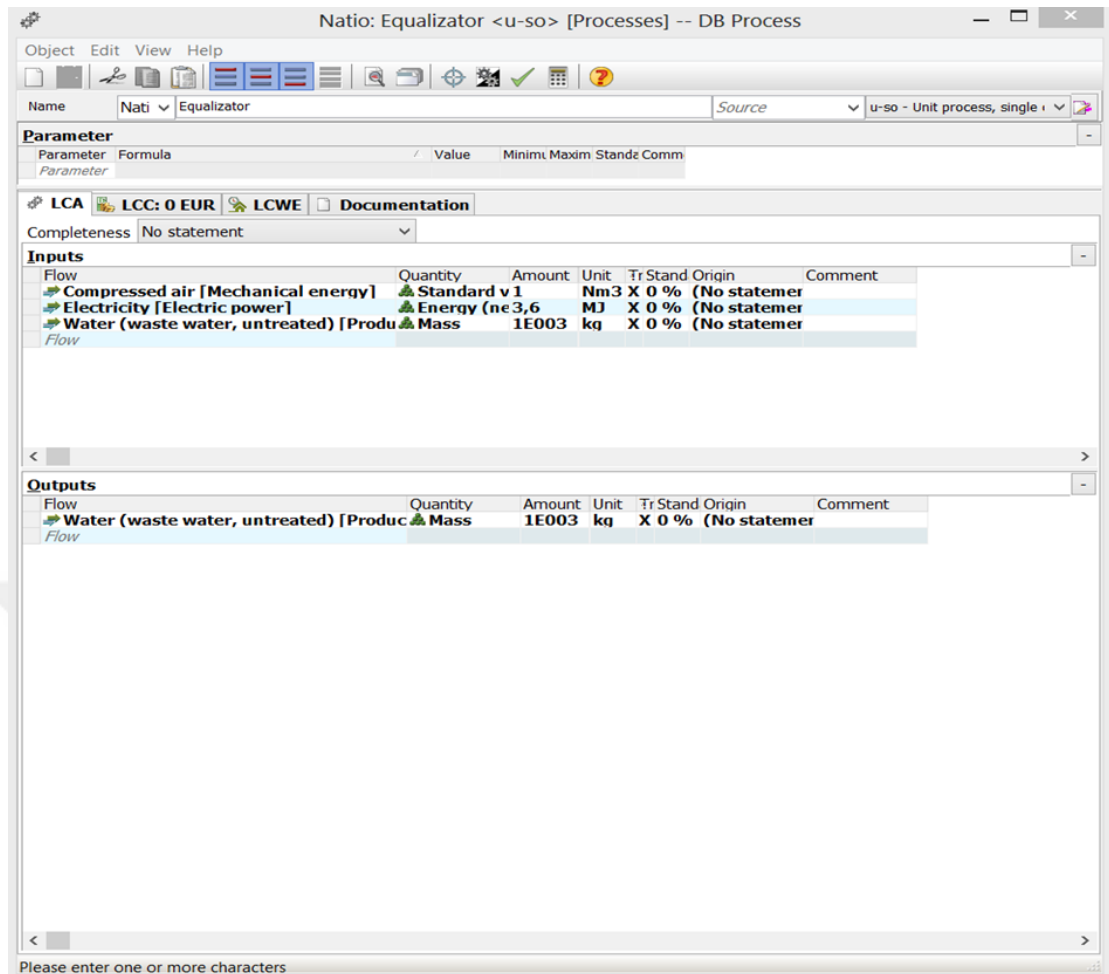


Figure 4.2 The process content created for equalization tank

CML 2001 (Institute of Environmental Sciences, Leiden University) impact assessment method was used to determine the environmental impacts. Eleven environmental impact categories were taken into consideration: global warming potential, acidification potential, eutrophication potential, ozone layer depletion potential, abiotic depletion elements, abiotic depletion fossil, fresh water aquatic ecotoxicity potential, human toxicity potential, marine aquatic ecotoxicity potential, photochemical ozone creation potential, and terrestrial ecotoxicity potential.



## ***4.2.2 Goal and Scope of the Study***

The goal of the study was to identify the environmental impacts of some leather industry wastewater treatment alternatives. For this aim four different scenarios were generated considering chromium removal/recovery option.

### *4.2.2.1 Functional Unit*

The functional unit is defined to quantify the environmental impact associated with the various management regimes and thus provide a basis for comparing the results. All data used in scenarios should be interconnecting with functional unit. In this study, functional unit is significant for input-output balance. Used commercial software doesn't perform of function with incompatible input-output balance. The main functional unit was chosen the cubic meter of wastewater treated. All parameters used to describe wastewater characterization express contamination in one cubic meter of wastewater.

### *4.2.2.2 System Boundaries*

The most of great weight stage in LCA study is system boundaries. After determining the four main scenarios, these scenarios were elaborated in themselves. At this stage, system boundaries were identified considering applicable database in Gabi 6.1 software. A "gate to gate" approach was considered. This means that study only focuses on the operation of the wastewater treatment plant, the environmental load of the construction phase and sludge management units were neglected. As shown in Figure 4.3, mechanical treatment unit, chemical treatment unit and biological treatment unit are incorporated into system boundaries.

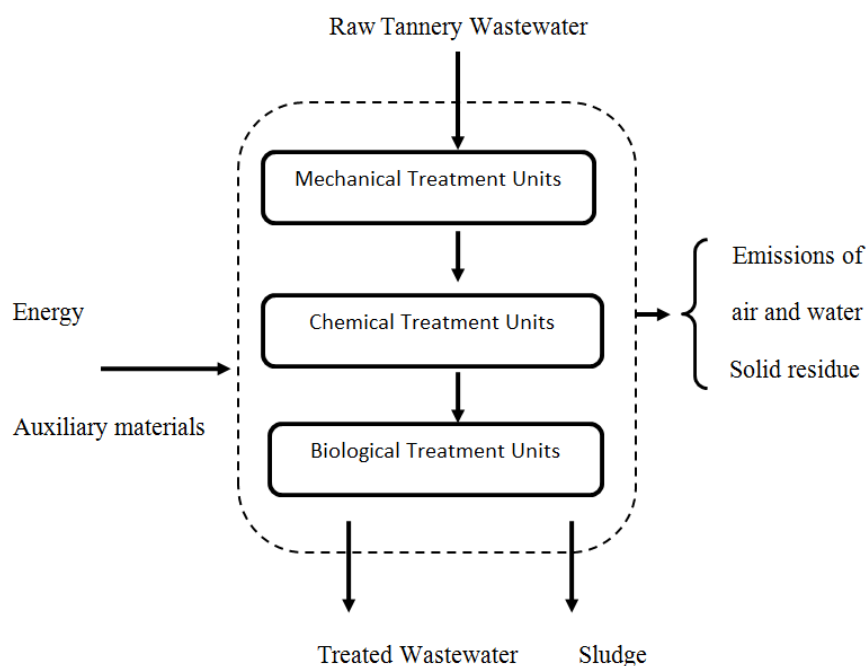


Figure 4.3 The study of system boundaries

Energy consumptions were calculated for the treatment of one cubic meter of wastewater for each unit. There are several energy input types in the database depending on the country and the types of the energy generation techniques. In this study, electricity grid mix energy for Turkey was chosen from the database. The energy consumptions of coagulation and flocculation units are accepted as 0.00504 MJ and 0.00468 MJ, respectively. For biological treatment systems, aeration unit consumption and precipitation unit consumptions are 1.66 MJ and 0.324 MJ, respectively.

#### 4.2.2.3 Assumptions

- A “gate to gate” approach was considered, so that wastewater treatment was evaluated. Leather production steps and occurring of wastewater steps have not been taken into account.
- The raw wastewater properties were accepted considering the wastewater characteristics of a leather industry fabric in Menemen, Izmir City.

- Energy consumption which is required for treatment options data was taken from literature.
- Sludge treatment options were excluded from assessment of system.
- The main functional unit was chosen the cubic meter of wastewater treated.
- The parameters taken into consideration in the treatment unit are chemical oxygen demand, sulphur, chromium, and energy consumption.

#### 4.2.3 Inventory Analysis of Study

The goal of the study was to identify the environmental impacts of some leather industry wastewater treatment alternatives. For this aim four different scenarios were generated considering chromium removal/recovery options (Figure 4.4). Since, there are two main process wastewater flows, namely sulphur-rich lime liquors and chromium-containing liquors, in leather industries, scenarios were generated depends on either these flows are segregate or not in the plant.

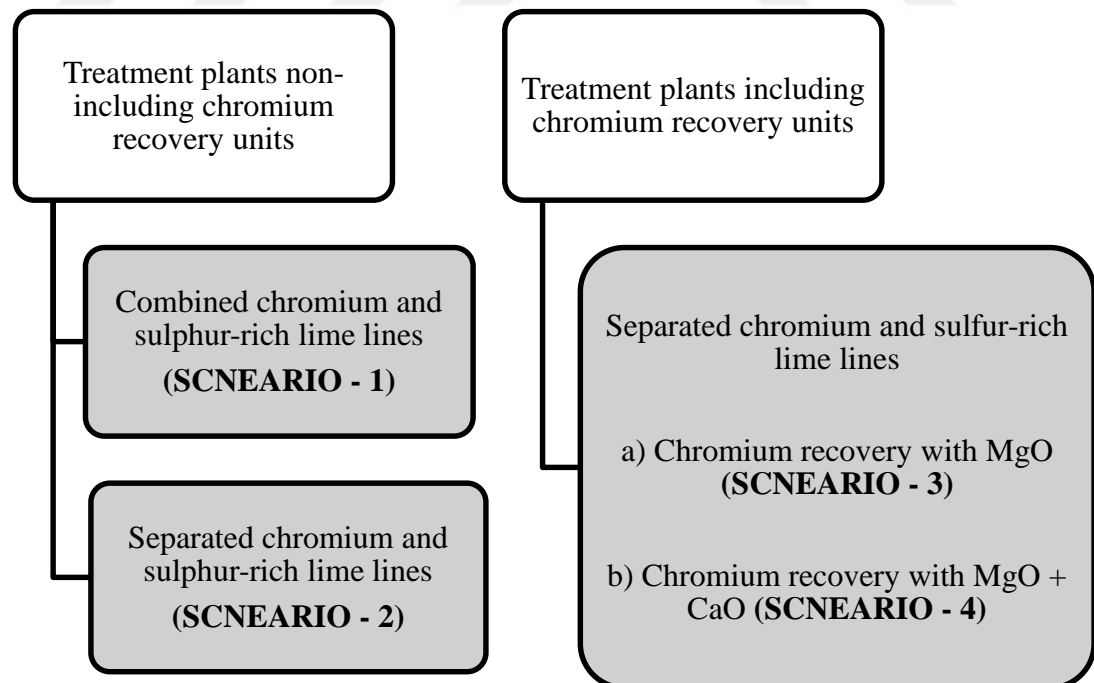


Figure 4.4 Produced scenarios scheme

#### *4.2.3.1 Produced Scenarios*

In leather industry wastewaters, main significant pollutants are organic matter, solids, oil, chromium, and sulphur. Typically, coarse and fine screening, oil removal, and primary sedimentation are applied as primary treatment units to remove coarse and suspended solids and oil. Then equalization tank is used for the homogenization and sulphur oxidation by applying sufficient amount of oxygen. After then the chemical treatment is used for the chromium and suspended and colloidal matter removal. In most cases, conventional activated sludge unit follows chemical treatment to reduce the amount of organic matter. Considering these treatment options, treatment plant flow schemes were developed for each scenario. Since screening, oil removal and primary sedimentation is applied for all scenarios, the effects of these units are not considered. Impact assessment calculations were started with equalization basin for each flow scheme. For the combined scenario (Scenario 1), single equalization basin was used, whereas two different equalization basins were used for each flow, namely sulphur-rich lime liquors and chromium-containing liquors, for the segregated scenarios.

The detailed flow scheme for each scenario is given in Figure 4.5 – 4.7.

4.2.3.1.1 Treatment Plants Non-Including Chromium Recovery Units

4.2.3.1.1.1 Combined Chromium and Sulphur-Rich Lime Line (Scenario-1)

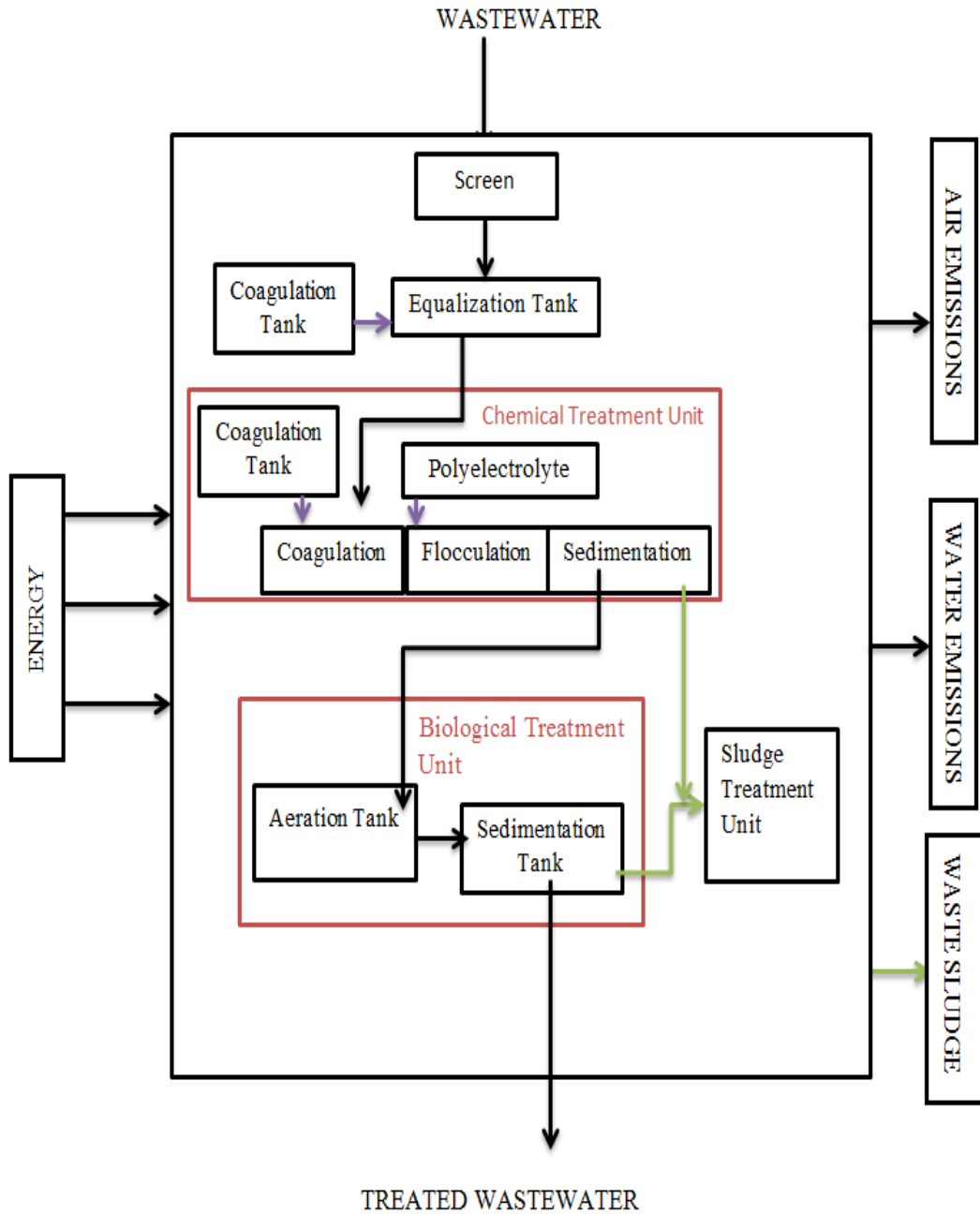


Figure 4.5 Scenario-1 flow scheme

4.2.3.1.1.2 Separated Chromium and Sulphur-Rich Lime Lines (Scenario-2)

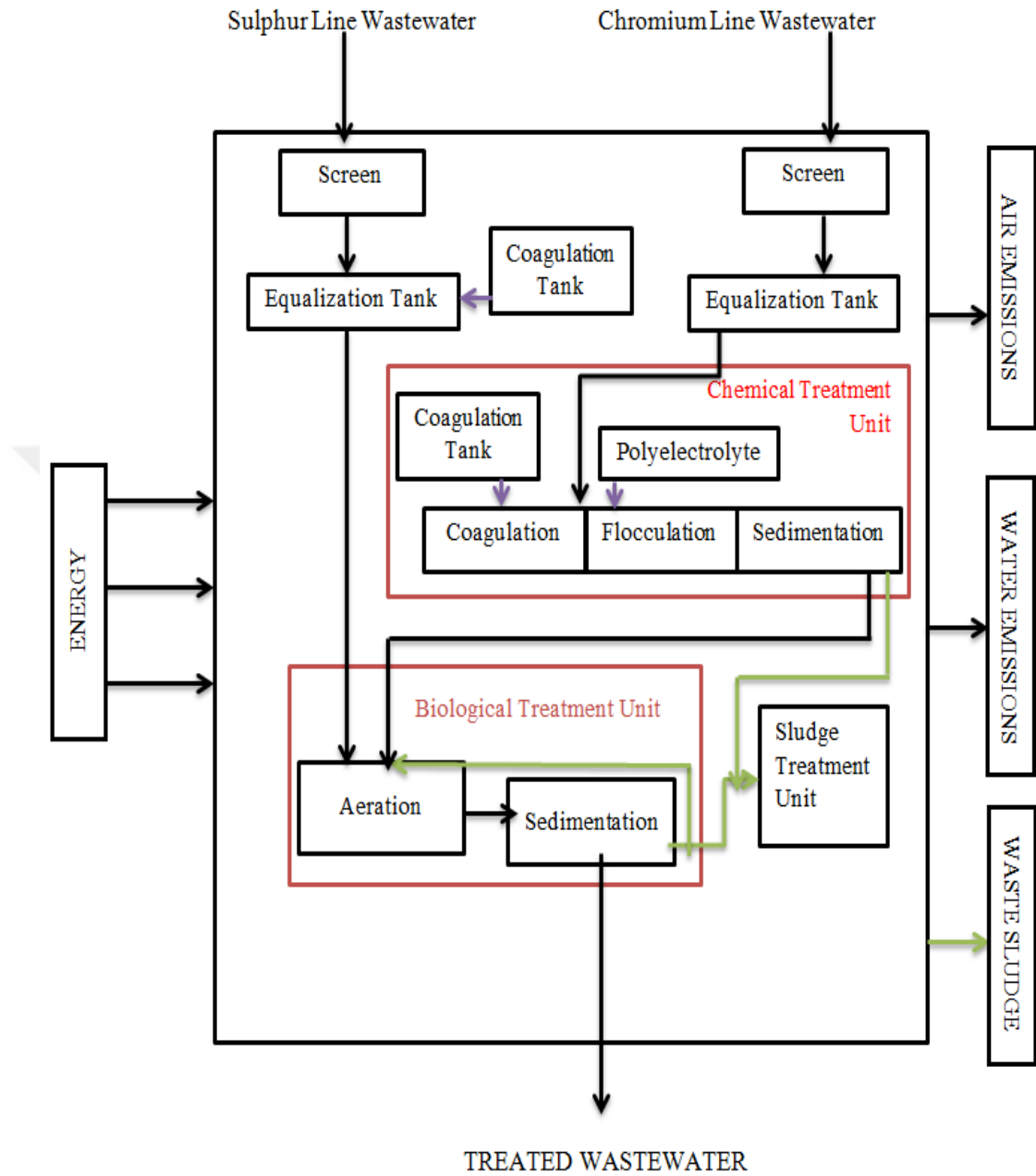


Figure 4.6 Scenario-2 flow scheme

4.2.3.1.2 Treatment Plants Including Chromium Recovery Units

4.2.3.1.2.1 Separated Chromium and Sulphur-Rich Lime Line (Scenario-3/4)

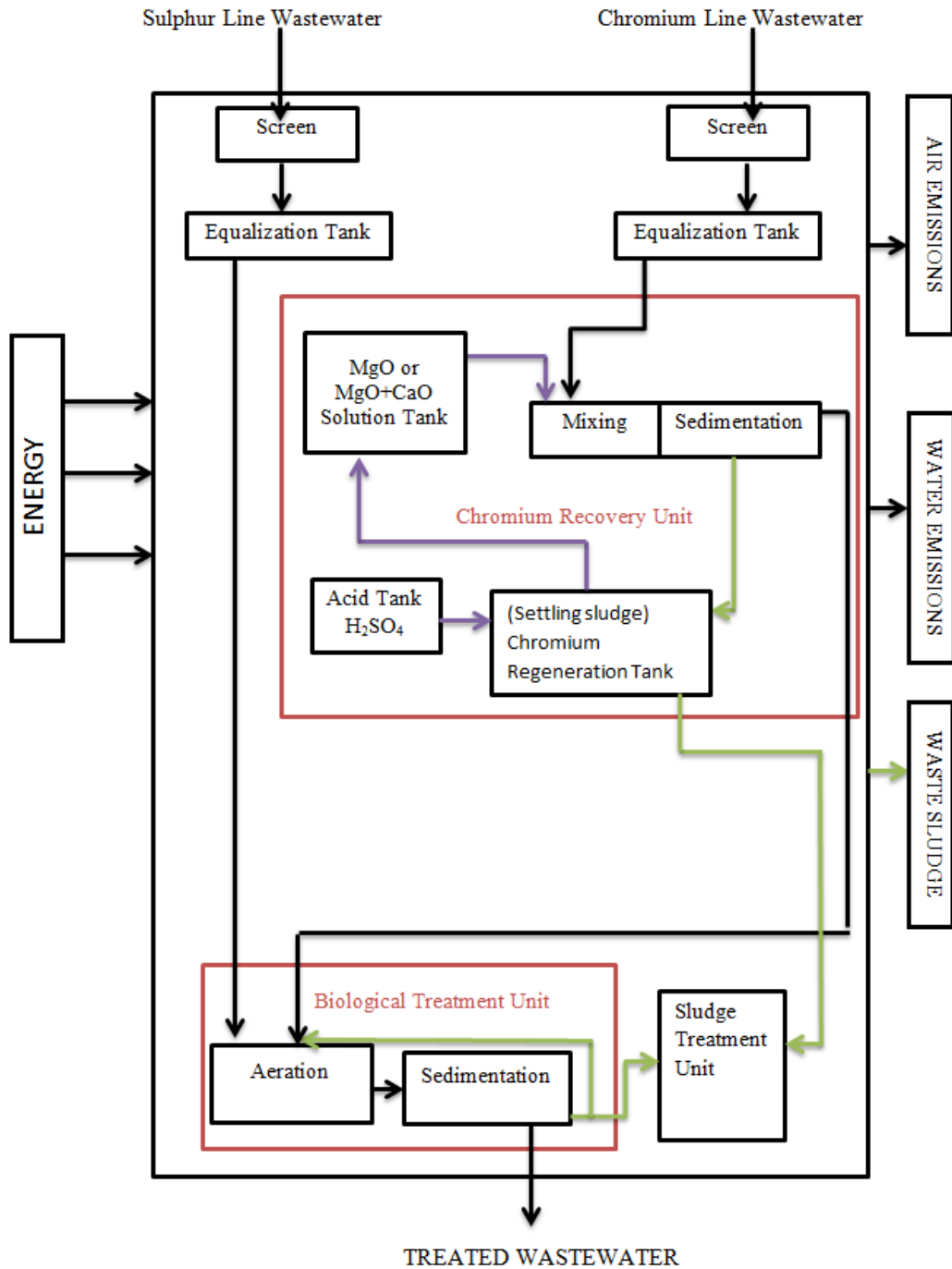


Figure 4.7 Scenario-3/4 flow scheme

## CHAPTER FIVE

### RESULTS AND DISCUSSION

#### 5.1 Results of the Laboratory Studies

##### 5.1.1 Wastewater Characterization

The parameters taken into consideration in the treatment units are chemical oxygen demand (COD), sulphur (S), chromium (Cr), and energy consumption. The raw wastewater properties were accepted considering the wastewater characteristics of a leather industry fabric in Menemen, Izmir City.

Wastewater samples took from Equalization tank (E) and Chromium Tank (C) in the Wastewater Treatment Plant. Performed characterization studies are given in Table 5.1, 5.2 and 5.3.

Table 5.1 Temperature, pH and conductivity analysis results

CODE	Temperature	pH	Conductivity (mS/cm)
E	22.3 ± 0.1	8.78 ± 0.02	21.20 ± 0.1
C	26.9 ± 0.1	3.65 ± 0.01	70.50 ± 0.02

Table 5.2 TS, VS, SS and VSS analysis results

CODE	TS (mg/L)	VS (mg/L)	SS (mg/L)	VSS (mg/L)
E	17525 ± 250	2950 ± 60	3180 ± 20	480
C	9190 ± 70	2078 ± 60	3080 ± 20	1460 ± 20

Table 5.3 COD, BOD, phosphorus, nitrogen and sulphur analysis results

CODE (1, 2)	COD (mg/L)	BOD (mg/L)	Phosphorus (mg/L)	Nitrogen (mg/L)	Sulphur (mg/L)
E	10400	1490	25.2	120	56
C	8000	-	9.5	120	-



### 5.1.2 Chromium Removal and Recovery Experiments

Used of in chrome tanning and +3 value chromium, brought to pH 8-10 by addition of a alkaline substance can be removed from wastewater in the form of precipitated chromium hydroxide. Lime is often used as alkaline chemicals.

Scope of the thesis, the effect of different coagulants was investigated for chromium removal. For this purpose,  $\text{FeSO}_4$ ,  $\text{FeCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  coagulants were analysed by adding different doses of chromium concentration. 10% solutions were prepared for each coagulant.

#### Results of the study carried out with Combined Line ( Equalization Tank):

Jar testing was performed by studying different doses of coagulants in 500 ml sample while testing Combined Line. Jar test was performed speed mixing for 2 minutes, slow mixing for 30 minutes and rest for 30 minutes in the same manner for all samples.

Lime was used as auxiliary coagulant while Jar Test was performed with  $\text{FeSO}_4$ . Provided of being in the same amount for all samples, 4 ml lime solution was added. The values obtained in the Jar test results are given in Table 5.4. The study of the experimental setup and the sample images are provided in Figure 5.1.

Table 5.4  $\text{FeSO}_4$  Jar test results

<b>CODE</b>	<b>Used Coagulants</b>	<b>COD (mg/L)</b>	<b>Settled Sludge (mL)</b>
3	Control + 4 mL lime solution	8800	0
4	10 mL $\text{FeSO}_4$ added + 4 mL lime solution	6400	180
5	15 mL $\text{FeSO}_4$ added + 4 mL lime solution	4800	200
6	20 mL $\text{FeSO}_4$ added+ 4 mL lime solution	5600	140
7	25 mL $\text{FeSO}_4$ added + 4 mL lime solution.	6400	160



Figure 5.1 Jar testing kits and FeSO<sub>4</sub> application image

Polyelectrolyte was used as auxiliary coagulant while Jar Test was performed with FeCl<sub>3</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. Provided of being in the same amount for all samples, 2 ml lime solution was added. So it aimed to facilitate flocculation. The values obtained in the Jar test results are given in Table 5.5 and Table 5.6. The study of the experimental setup and the sample images are provided in Figure 5.2 and Figure 5.3.

Table 5.5 FeCl<sub>3</sub> Jar test results

CODE	Used Coagulants	COD (mg/L)	Settled Sludge (mL)
8	Control + 2 mL polyelectrolyte	5440	40
9	10 mL FeCl <sub>3</sub> + 2 mL polyelectrolyte	3440	195
10	15 mL FeCl <sub>3</sub> + 2 mL polyelectrolyte	3760	200
11	20 mL FeCl <sub>3</sub> + 2 mL polyelectrolyte	3520	195
12	25 mL FeCl <sub>3</sub> + 2 mL polyelectrolyte	3280	190



Figure 5.2 Jar testing kits and FeCl<sub>3</sub> application image

Table 5.6 Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> Jar test results

CODE	Used Coagulants	COD (mg/L)	Settled Sludge (mL)
13	Control + 2 mL poly. Solution	7200	25
14	10 mL Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 2 mL polyelectrolyte	4800	170
15	15 mL Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 2 mL polyelectrolyte	6400	180
16	20 mL Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 2 mL polyelectrolyte	7200	190
17	25 mL Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 2 mL polyelectrolyte	6400	170



Figure 5.3 Jar testing kits and  $\text{Al}_2(\text{SO}_4)_3$  application image

Results of the study carried out with Chromium Line:

Jar testing was performed by studying different doses of coagulants in 300 ml sample while testing Chromium Line. Jar test was performed speed mixing for 2 minutes, slow mixing for 30 minutes and rest for 30 minutes in the same manner for all samples.

Lime and polyelectrolyte were used as auxiliary coagulants while Jar Test was performed with  $\text{FeSO}_4$ ,  $\text{FeCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$ . Provided of being in the same amount for all samples, 15 ml lime from 10% lime solution and 2ml polyelectrolyte from 1% polyelectrolyte solution were added. The values obtained in the Jar test results are given in Table 5.7, Table 5.8 and Table 5.9. The study of the experimental setup and the sample images are provided in Figure 5.4, Figure 5.5 and Figure 5.6

Table 5.7 Jar test results of FeSO<sub>4</sub>

CODE	Used Coagulants	COD (mg/L)	Settled Sludge (mL)
18	Control + 15 mL lime + 2 mL poly.	8800	130
19	10 mL FeSO <sub>4</sub> + 15 mL lime + 2 mL poly.	5600	190
20	20 mL FeSO <sub>4</sub> + 15 mL lime + 2 mL poly.	4800	210
21	30 mL FeSO <sub>4</sub> + 15 mL lime + 2 mL poly.	4800	200
22	40 mL FeSO <sub>4</sub> + 15 mL lime + 2 mL poly.	6400	180



Figure 5.4 Jar testing kits and FeSO<sub>4</sub> application image

Table 5.8 Jar test results of FeCl<sub>3</sub>

CODE	Used Coagulants	COD (mg/L)	Settled Sludge (mL)
23	Control + 15 mL lime + 2 mL poly.	9600	190
24	10 mL FeCl <sub>3</sub> + 15 mL lime + 2 mL poly.	6400	240
25	20 mL FeCl <sub>3</sub> + 15 mL lime + 2 mL poly.	4800	170
26	30 mL FeCl <sub>3</sub> + 15 mL lime + 2 mL poly.	6400	100
27	40 mL FeCl <sub>3</sub> added + 15 mL lime + 2 mL poly.	7200	180



Figure 5.5 Jar testing kits and FeCl<sub>3</sub> application image

Table 5.9 Jar test results of  $\text{Al}_2(\text{SO}_4)_3$

CODE	Used Coagulants	COD (mg/L)	Settled Sludge (mL)
28	Control + 15 mL lime + 2 mL poly.	9600	180
29	10 mL $\text{Al}_2(\text{SO}_4)_3$ +15 mL lime + 2 mL poly.	5600	220
30	20 mL $\text{Al}_2(\text{SO}_4)_3$ +15 mL lime + 2 mL poly.	7200	190
31	30 mL $\text{Al}_2(\text{SO}_4)_3$ +15 mL lime + 2 mL poly.	4800	150
32	40 mL $\text{Al}_2(\text{SO}_4)_3$ +15 mL lime + 2 mL poly.	7200	100



Figure 5.6 Jar testing kits and  $\text{Al}_2(\text{SO}_4)_3$  application image

Jar testing was performed by studying different doses of  $\text{MgO}$  in 500 ml sample for chromium recovery while it tested Chromium Line. But used in the tanning process of chromium salts is reacted with leather from 65 to 70%. Approximately 30-

35% of the remaining chromium mixed in wastewater. Movement of this case, Chromium settled as  $\text{Cr}(\text{OH})_3$  when wastewater containing of chromium was treated with  $\text{MgO}$ .  $\text{H}_2\text{SO}_4$  was added to occurring sludge ( $\text{Cr}(\text{OH})_3$ ) for ensured the dissolution of the chromium recovery process. The values obtained in the Jar test results are given in Table 5.10 The study of the experimental setup and the sample images are provided in Figure 5.7

Table 5.10 Jar testing results of  $\text{MgO}$

CODE	Used Coagulants	COD (mg/L)	Settled Sludge (mL)	Added $\text{H}_2\text{SO}_4$ (mL)
33	50 mL $\text{MgO}$	7200	145	17.5
34	62.5 mL $\text{MgO}$	6400	147	21.5
35	75 mL $\text{MgO}$	4800	160	26



Figure 5.7 Jar testing kits and  $\text{MgO}$  application image



Another chromium recovery method is MgO and CaO using of together. MgO is very expensive chemical substance. When CaO compare to MgO, CaO is much cheaper than MgO. If both of them use together mixed in certain ratio, it is possible to achieve better efficient and economic results. According to the results of some studies that optimal ratio CaO / MgO is given as 4/1. (Öztürk, n.d.) Based on this information, the solutions were prepared at 10 %. Chromium settled as Cr(OH)<sub>3</sub> when wastewater containing of chromium was treated with MgO and CaO. H<sub>2</sub>SO<sub>4</sub> was added to occurring sludge (Cr(OH)<sub>3</sub>) for ensured the dissolution of the chromium recovery process. The values obtained in the Jar test results are given in Table 5.11. The study of the experimental setup and the sample images are provided in Figure 5.8.

Table 5.11 Jar testing results of MgO + CaO

CODE	Used Coagulants	COD (mg/L)	Settled Sludge (mL)	Added H <sub>2</sub> SO <sub>4</sub> (mL)
36	37.5 mL MgO + CaO	9600	310	13
37	50 mL MgO + CaO	4800	300	17.5
38	62.5 mL MgO + CaO	3200	425	21.5

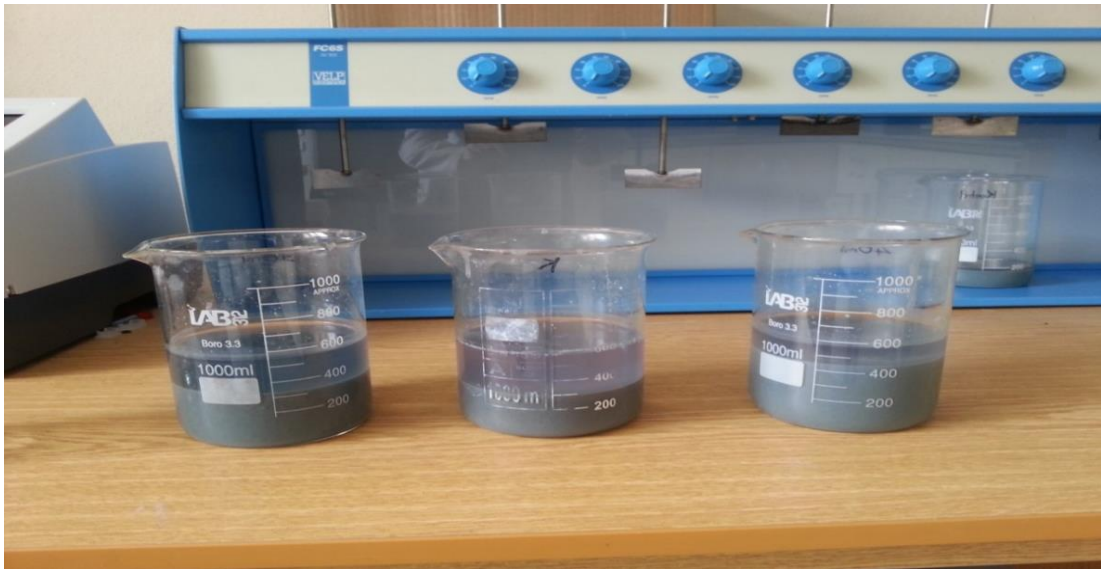


Figure 5.8 Jar testing kits and MgO + CaO application image

### 5.1.3 Sulphur Oxidation Experiments

In leather industry used of orpiment (arsenic) for trichome removal process yields of sulphur in wastewater. Mainly oxidation methods are used for the sulphur removal. For this purpose, many oxidant substance uses like chlorine, ozone, peroxide etc. But, the most widely used method of oxidation is air oxidation. Reaction of sulphur with oxygen is very low and depends on the pH. pH value smaller than 6, reaction rate is very slowly. The oxidation rate reaches the maximum value on pH range 8-8.5. Used wastewater pH value was above 8.5 ( $8.78 \pm 0.02$ ). Thus, pH adjustment was not made because of a very close value. Sulphur analyses were performed with direct and periodically taken wastewater from equalization tank. Sulphur concentrations of the experimental obtained results of the study are given in Table 5.12.

Table 5.12 Sulphur analyses results of oxidation

<b>Oxidation time (minute)</b>	<b>Sulphur concentration (mg/L)</b>
0-30	36
30-60	20
60-120	12
120-180	8

The chromium amount in the final occurred samples obtained in all experimental work carried out was analysed. For this purpose, PerkinElmer OPTIMA 7000DV ICP-OES was used. All results obtained are given in Tables 5.13 and Table 5.14.

Table 5.13 The results obtained from samples taken from the equalization tank

INPUT	Sample Characteristic	COD		Chromium	
		Effluent (mg/L)	Efficiency (%)	Effluent (mg/L)	Efficiency (%)
<b>SAMPLES TAKEN FROM THE EQUALIZATION TANK</b> (COD <sub>influent</sub> : 10400 mg/L, C <sub>influent</sub> : 125 mg/L)	Kontrol + 4 mL lime	8800	15	47	
	10 mL FeSO <sub>4</sub> + 4 mL lime	6400	38	48	62
	15 mL FeSO <sub>4</sub> + 4 mL lime	4800	54	45	64
	20 mL FeSO <sub>4</sub> + 4 mL lime	5600	46	42	66
	25 mL FeSO <sub>4</sub> + 4 mL lime	6400	38	48	62
	Control + 2 mL polyelectrolyte	5440	48	125	
	10 mL FeCl <sub>3</sub> + 2 mL poly.	3440	67	71	43
	15 mL FeCl <sub>3</sub> + 2 mL poly.	3760	64	93	26
	20 mL FeCl <sub>3</sub> + 2 mL poly.	3520	66	70	44
	25 mL FeCl <sub>3</sub> + 2 mL poly.	3280	68	58	54
	Control + 2 mL polyelectrolyte	7200	31	58	
	10 mL Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 2 mL poly.	4800	54	45	64
	15 mL Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 2 mL poly.	6400	38	51	59
	20 mL Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 2 mL poly.	7200	31	49	61
	25 mL Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 2 mL poly.	6400	38	52	58

Table 5.14 The results obtained from samples taken from the chromium tank

INPUT	Sample Characteristic	COD		Chromium	
		Effluent (mg/L)	Efficiency (%)	Wastewater (mg/L)	Sludge (mg/kg)
SAMPLES TAKEN FROM THE CHROMIUM TANK (COD <sub>influent</sub> : 8000 mg/L, Cr <sub>influent</sub> : 4200 mg/L)	Control + 15 mL lime + 2 mL polyelectrolyte	8800	-	2795	
	10 mL FeSO <sub>4</sub> + 15 mL lime + 2 mL poly.	5600	30	3500	
	20 mL FeSO <sub>4</sub> + 15 mL lime + 2 mL poly.	4800	40	2312	
	30 mL FeSO <sub>4</sub> + 15 mL lime + 2 mL poly.	4800	40	2500	
	40 mL FeSO <sub>4</sub> + 15 mL lime + 2 mL poly.	6400	20	4278	
	Control + 15 mL lime + 2 mL polyelectrolyte	9600	-	883	
	10 mL FeCl <sub>3</sub> + 15 mL lime + 2 mL poly	6400	20	4885	
	20 mL FeCl <sub>3</sub> + 15 mL lime + 2 mL poly	4800	40	7255	
	30 mL FeCl <sub>3</sub> + 15 mL lime + 2 mL poly	6400	20	8990	
	40 mL FeCl <sub>3</sub> + 15 mL lime + 2 mL poly	7200	10	11966	
	Control + 15 mL lime + 2 mL polyelectrolyte	9600	-	4143	
	10 mL Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 15 mL lime + 2 mL poly.	5600	30	431.6	
	20 mL Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 15 mL lime + 2 mL poly.	7200	10	5326	
	30 mL Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 15 mL lime + 2 mL poly.	4800	40	6970.9	
	40 mL Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 15 mL lime + 2 mL poly.	7200	10	9065	
	50 mL MgO	7200	10	49.9	62143
	62.5 mL MgO	6400	20	49.2	52217
	75 mL MgO	4800	40	49.9	49379
	37.5 mL MgO + CaO	9600	-	163	22892
	50 mL MgO + CaO	4800	40	95	26227
62.5 mL MgO + CaO	3200	60	198	8100	

## 5.2 Impact Assessment of the Study

In this part, experimental results obtained as a result of the studies described in detail above, literature information and database of GaBi program based on the assumptions made on basis of the information and results are generated for each scenario. Stage on Life Cycle Impact Analysis (LCIA), potential human health and environmental effects of discharge evaluates. Impact assessment considers also the consumption of natural resources as well as health and environmental values.

### 5.2.1 Scenario 1

Chromium and sulphur come to plant with combined line and non-including chromium recovery units. The chemical and biological treatment are applied in order to treatment after equalization tank in this scenario. Figure 5.9 shows the created process plan for scenario 1. It was created separately flow sheets for each treatment unit and all movements are combined afterwards. For instance, the chemical treatment flow diagram is given in Figure 5.10. Figure 5.10 shows the chemical treatment unit content, as shown in Figure 5.9. Energy inputs, used of chemicals and occurred sludge mass introduced to software for each step. Created scenario and plans were defined in this way. In other scenarios and plans were created by the same method.

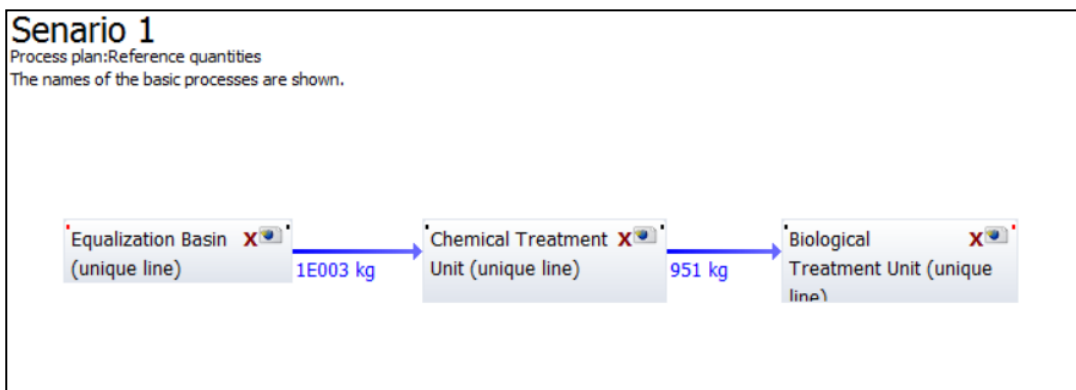


Figure 5.9 Created flow diagram image for Scenario 1

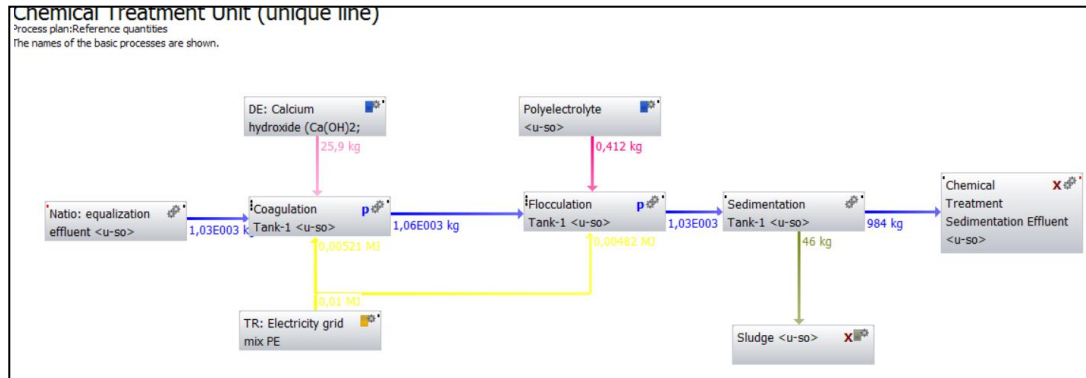


Figure 5.10 Created pre-flow diagram for chemical treatment unit

GaBi software ran on according to created flow diagram and introduced inputs and outputs. Acquired results is given among Figure 5.11 and Figure 5.22. In Figure 5.11, process inputs massive contribution is shown for basic units in scenario. In Figure 5.11 to 5.22, the whole units and system effects are seen according to environmental impact categories in GaBi software. The effects of biological treatment is very small than chemical treatment in all graphs. Because, in biological treatment only energy consumption is concerned. In chemical treatment , energy consumption, chemicals and occurred sludge of environmental impacts are concerned. The total environmental impact of Scenario 1 was presented in Table 5.15.

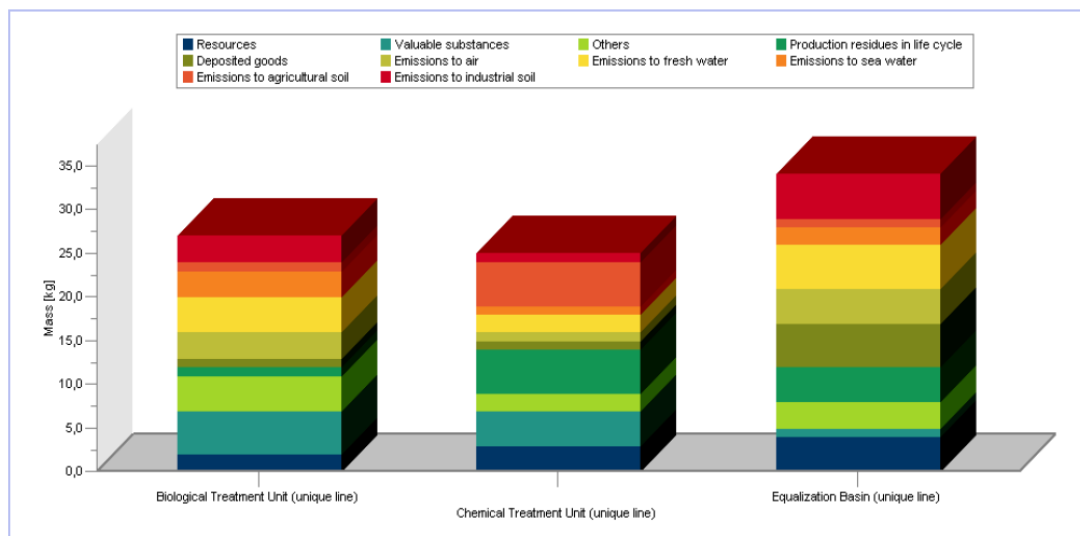


Figure 5.11 Massive contribution of used basis unit in Scenario 1

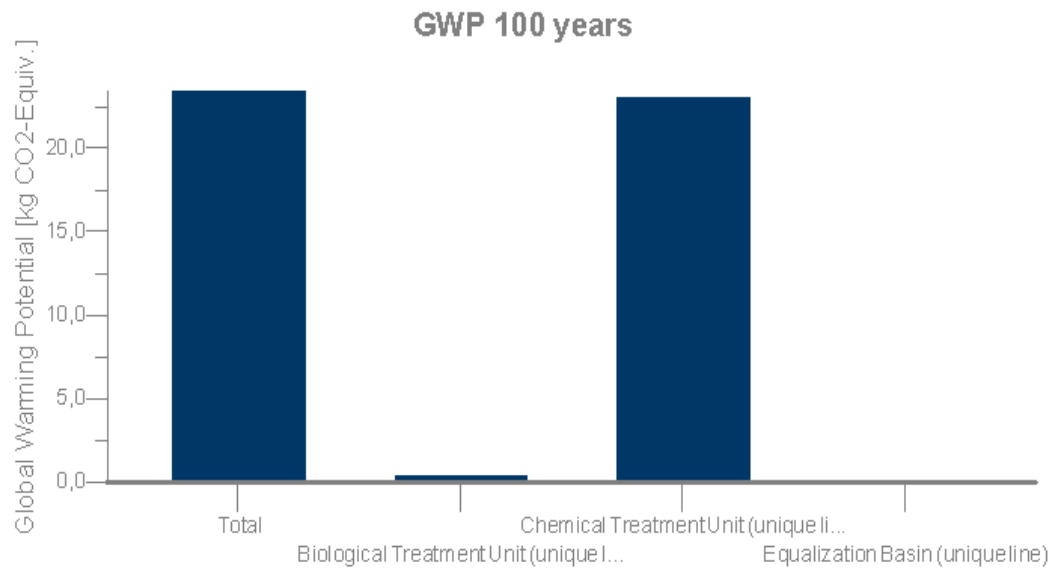


Figure 5.12 Global warming potential effects in Scenario 1

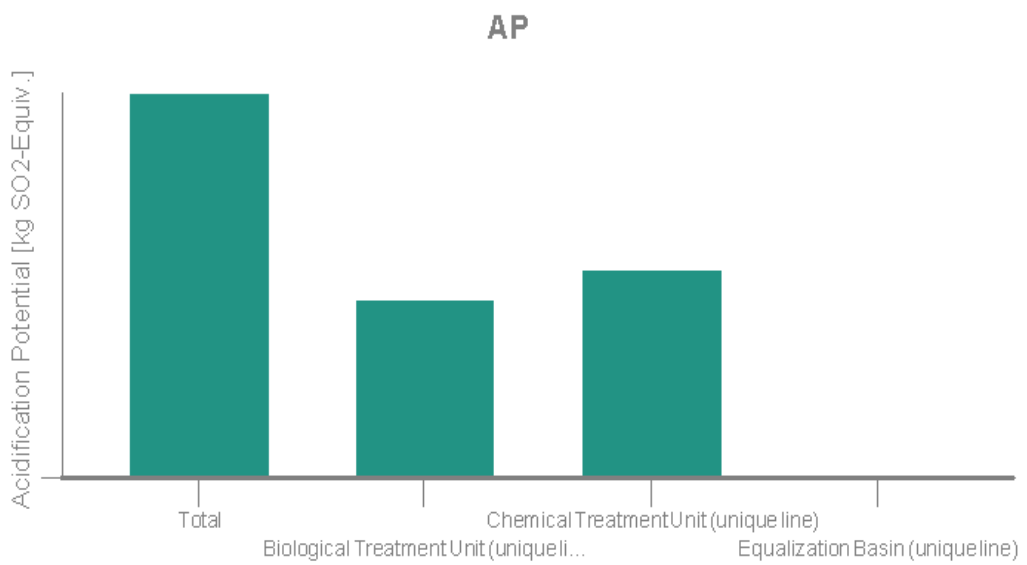


Figure 5.13 Acidification potential effects in Scenario 1

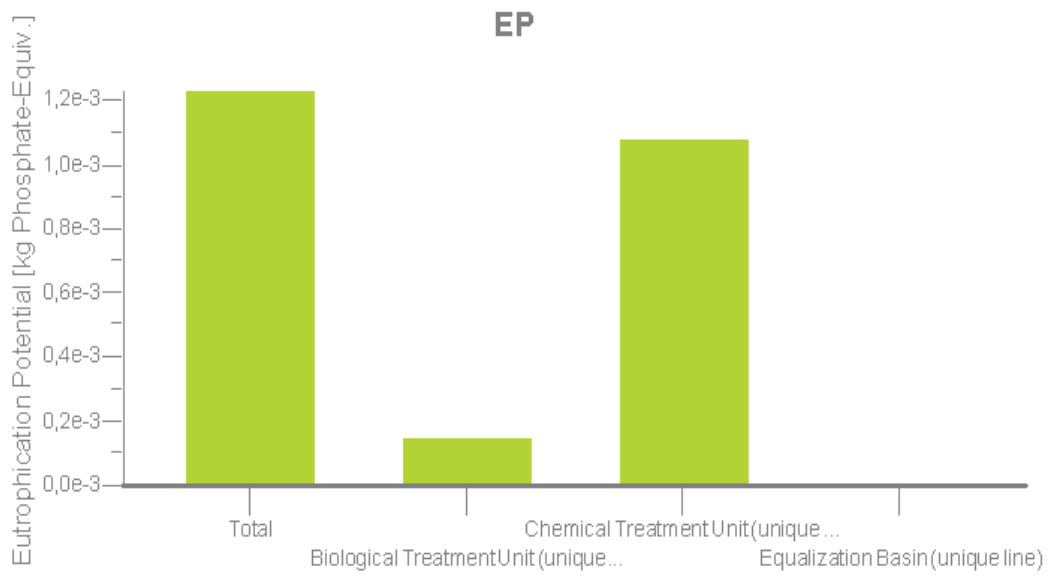


Figure 5.14 Eutrophication potential effects in Scenario 1

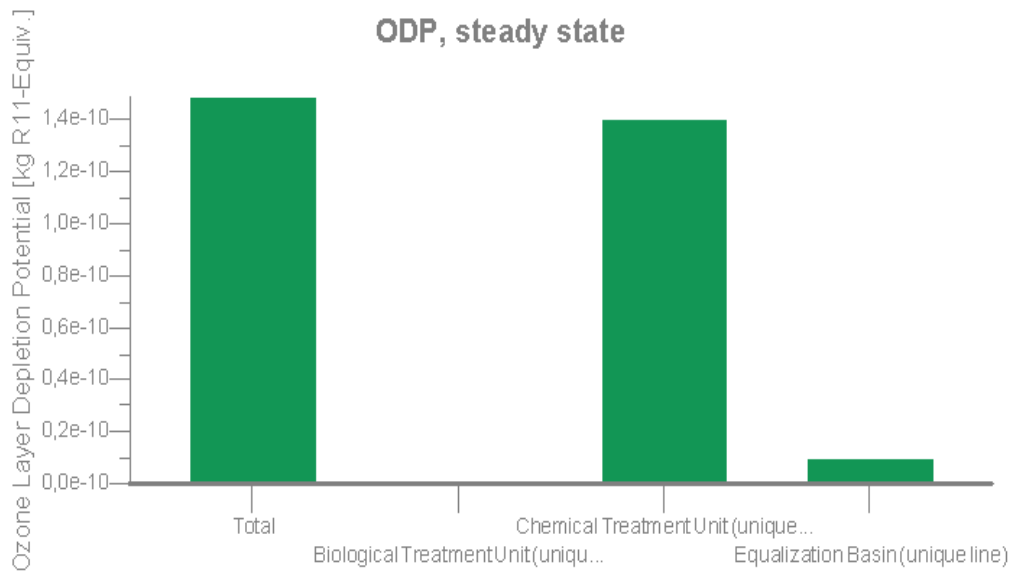


Figure 5.15 Ozone layer depletion potential effects in Scenario 1



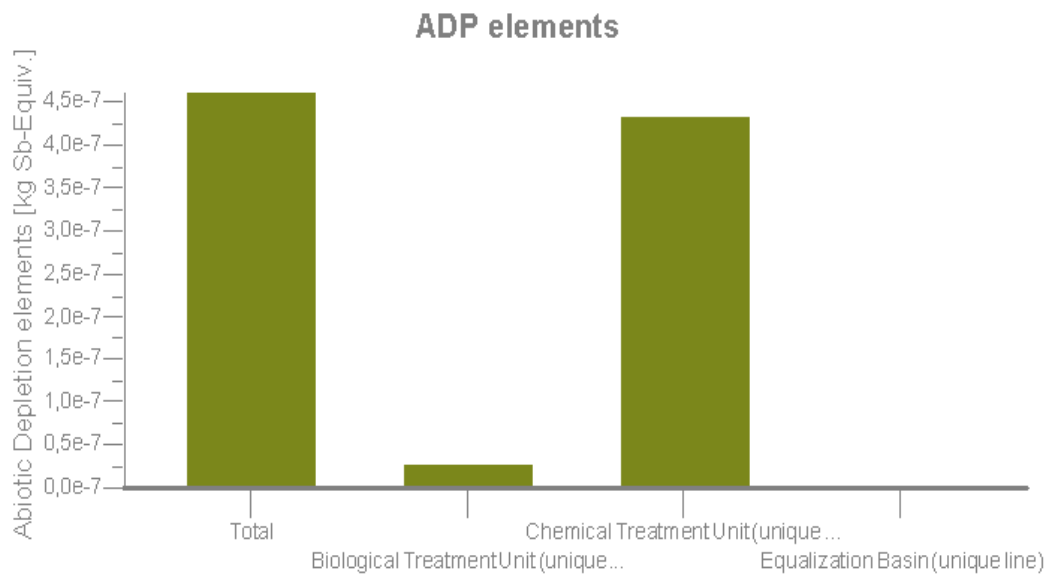


Figure 5.16 Abiotic depletion elements effects in Scenario 1

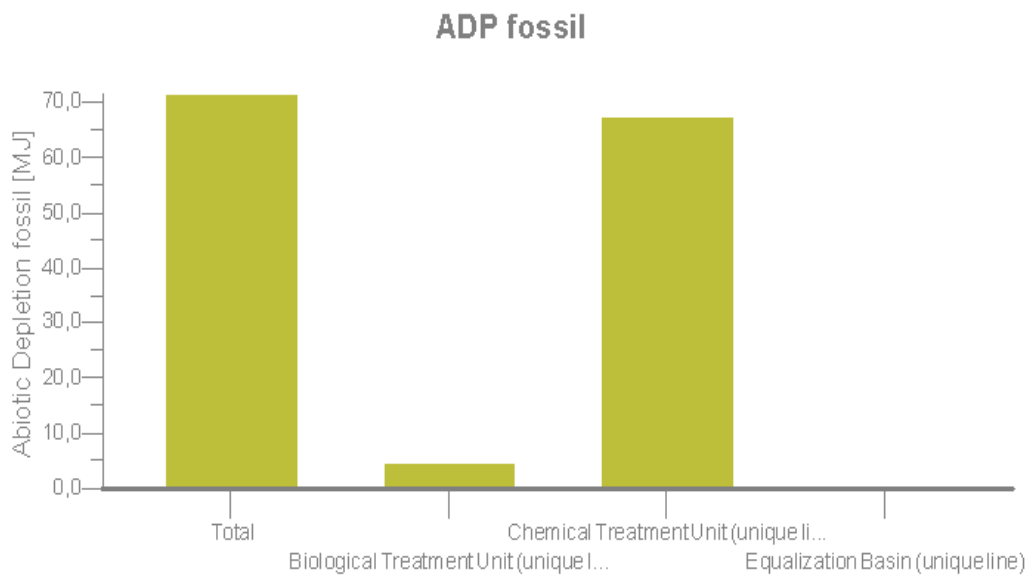


Figure 5.17 Abiotic depletion fossil effects in Scenario 1

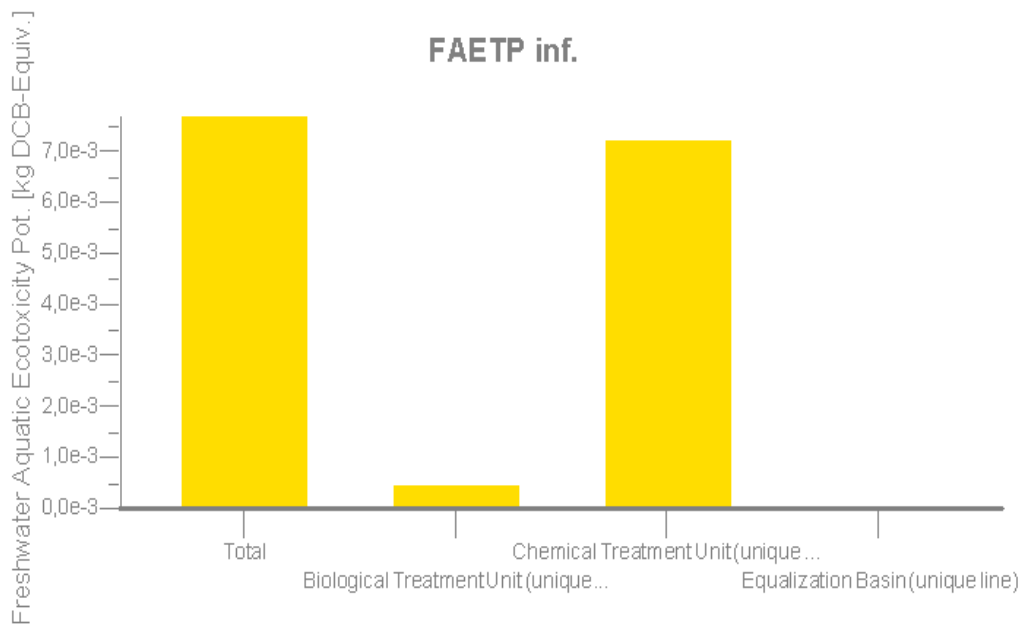


Figure 5.18 Freshwater ecotoxicity potential effects in Scenario 1

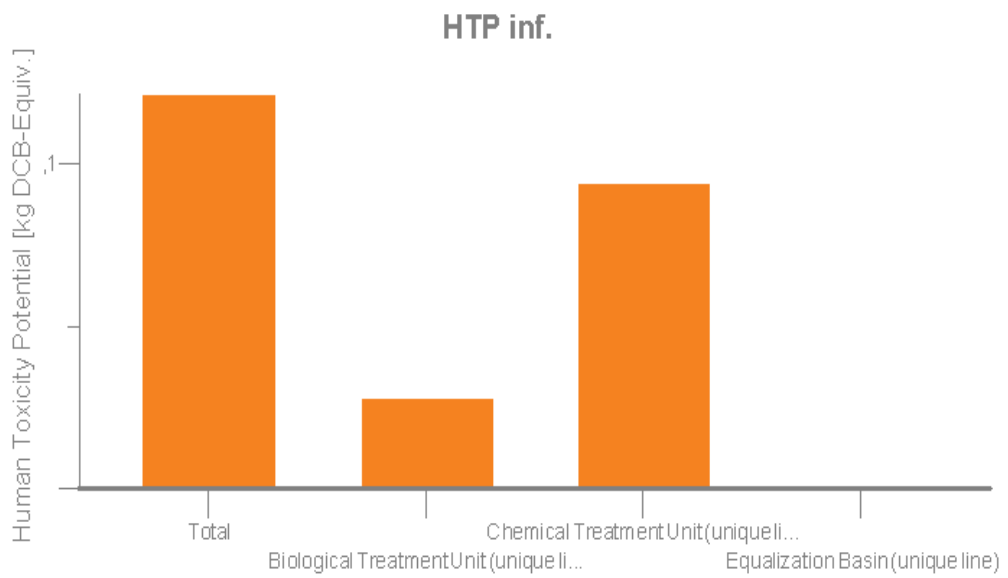


Figure 5.19 Human toxicity potential effects in Scenario 1

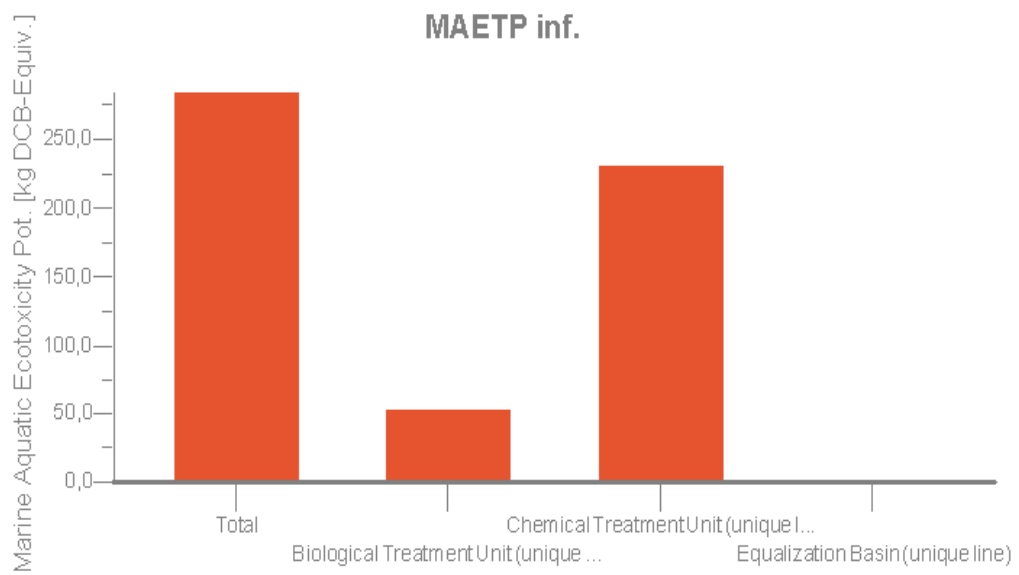


Figure 5.20 Marine aquatic ecotoxicity potential effects in Scenario 1

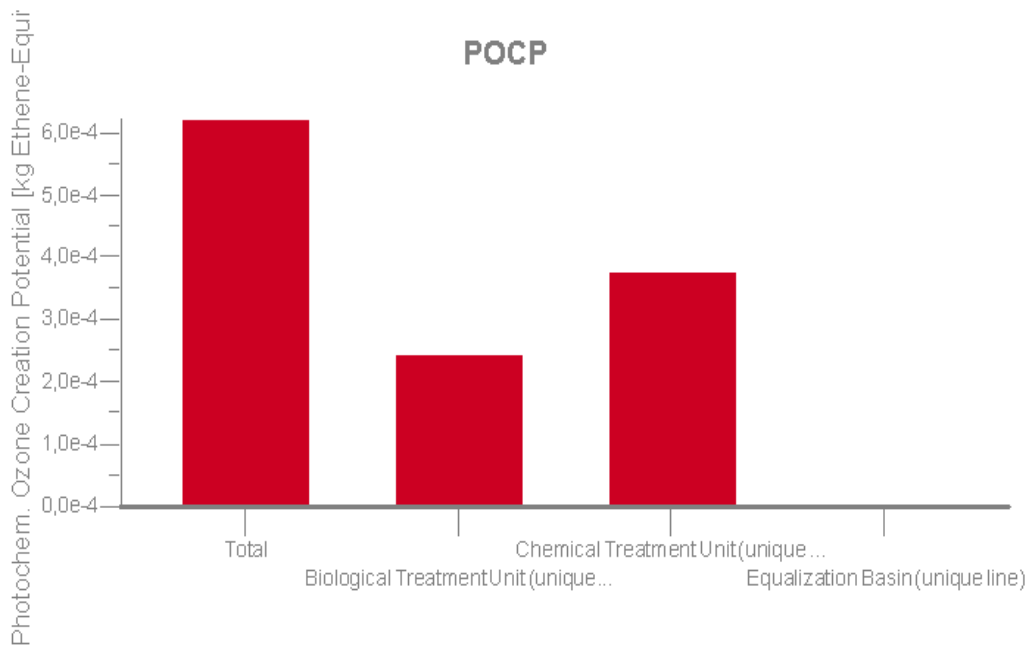


Figure 5.21 Photochemical ozone creation potential effects in Scenario 1

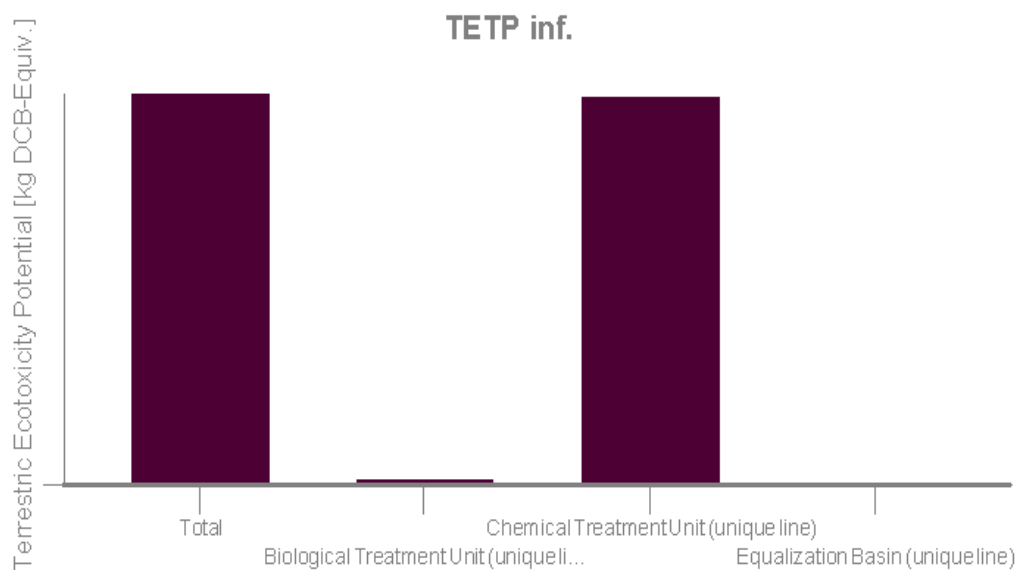


Figure 5.22 Terrestrial ecotoxicity potential effects in Scenario 1

Table 5.15 Environmental impacts of Scenario 1

Environmental Impact Categories	Unit	Value
Global Warming Potential	kg CO <sub>2</sub> equiv.	23.4
Acidification Potential	kg SO <sub>2</sub> equiv.	0.0111
Eutrophication Potential	kg PO <sub>4</sub> <sup>-2</sup> equiv.	0.00123
Ozone Layer Depletion Potential	kg R11 equiv.	1.49x10 <sup>-10</sup>
Abiotic Depletion Elements	kg Sb equiv.	4.6x10 <sup>-7</sup>
Abiotic Depletion Fossil	MJ	71.5
Freshwater Ecotoxicity Potential	kg DCB equiv.	0.00768
Human Toxicity Potential	kg DCB equiv.	0.121
Marine Aquatic Ecotoxicity Potential	kg DCB equiv.	285
Photochemical Ozone Creation Potential	kg C <sub>2</sub> H <sub>4</sub> equiv.	6.22x10 <sup>-4</sup>
Terrestrial Ecotoxicity Potential	kg DCB equiv.	0.0649

### 5.2.2 Scenario 2

Chromium and sulphur come to plant with separated line and non-including chromium recovery units in Scenario 2. Sulphur oxidation is made in equalization tank is placed sulphur line. Chromium is treated with chemical treatment in chromium line and then both of lines are combined in biological treatment unit. Figure 5.23 shows the created process plan for scenario 2.

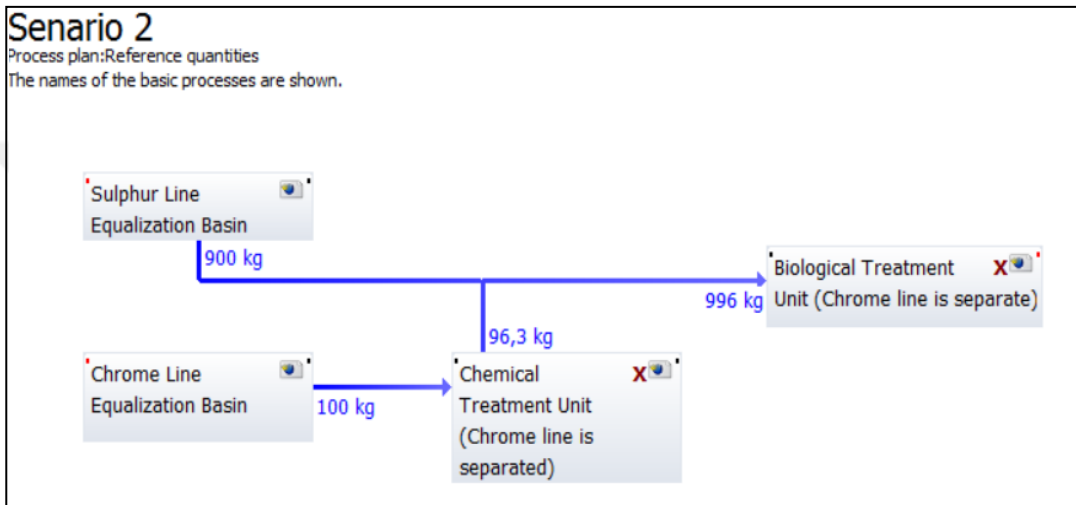


Figure 5.23 Created flow diagram image for Scenario 2

Acquired results are given among Figure 5.24 and 5.35. In Figure 5.24, process inputs massive contribution is shown for basic units in scenario. In Figure 5.24 to 5.35, the whole units and system effects are seen according to environmental impact categories in GaBi software.

The effects of biological treatment is very small than chemical treatment in all graphs, because energy consumption only is concerned in biological treatment. In chemical treatment, energy consumption, chemicals and occurred sludge of environmental impacts are concerned. The total environmental impact of Scenario 2 was presented in Table 5.16.

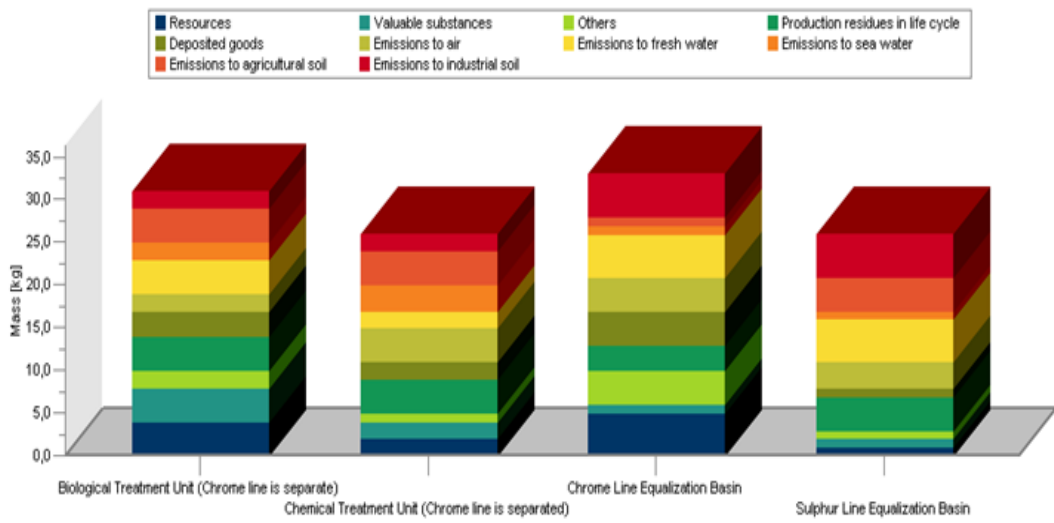


Figure 5.24 Massive contribution of used basis unit in Scenario 2

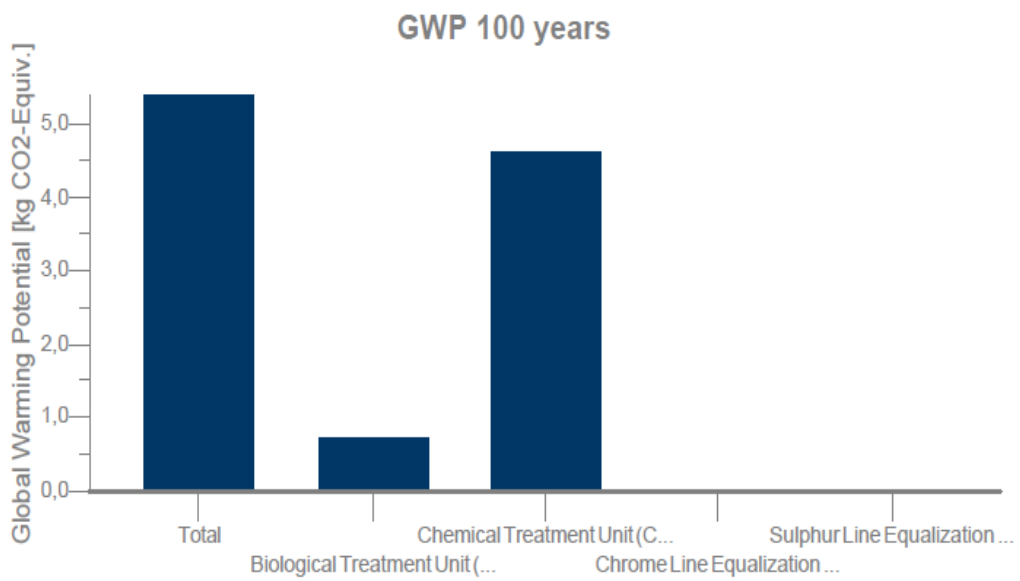


Figure 5.25 Global warming potential effects in Scenario 2

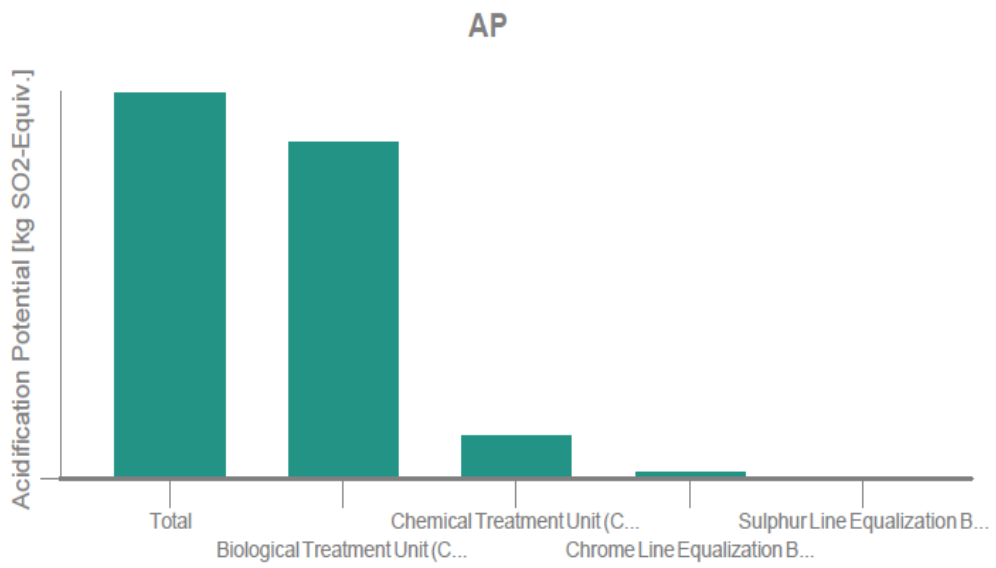


Figure 5.26 Acidification potential effects in Scenario 2

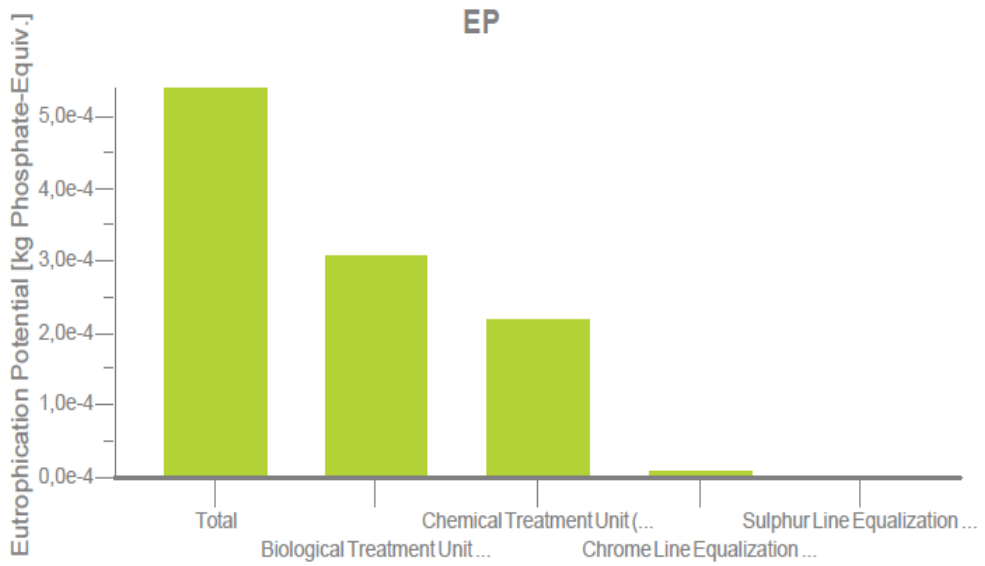


Figure 5.27 Eutrophication potential effects in Scenario 2

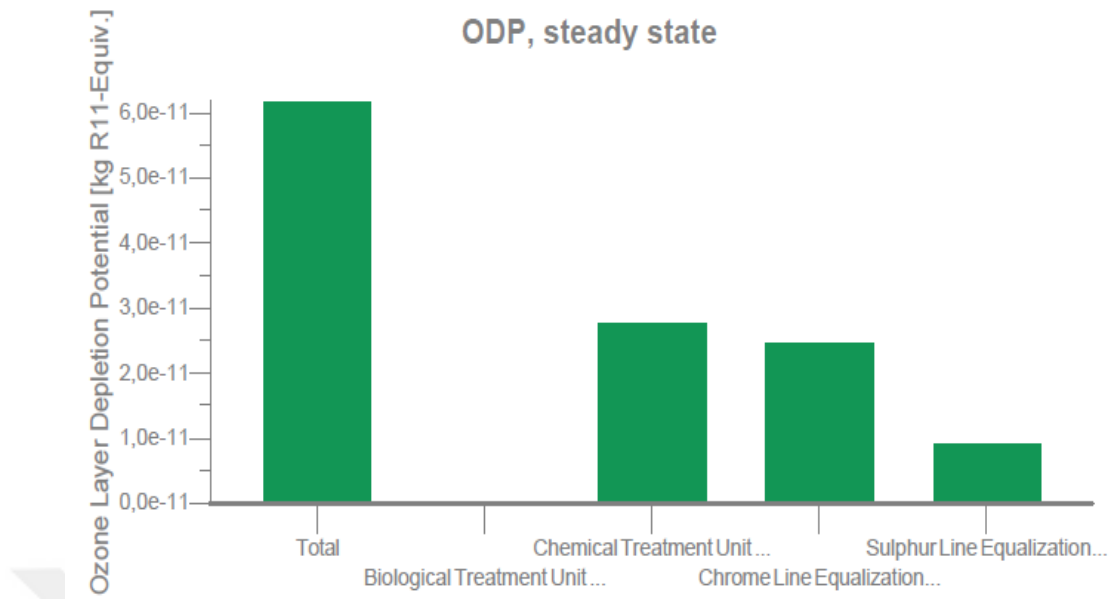


Figure 5.28 Ozone layer depletion potential effects in Scenario 2

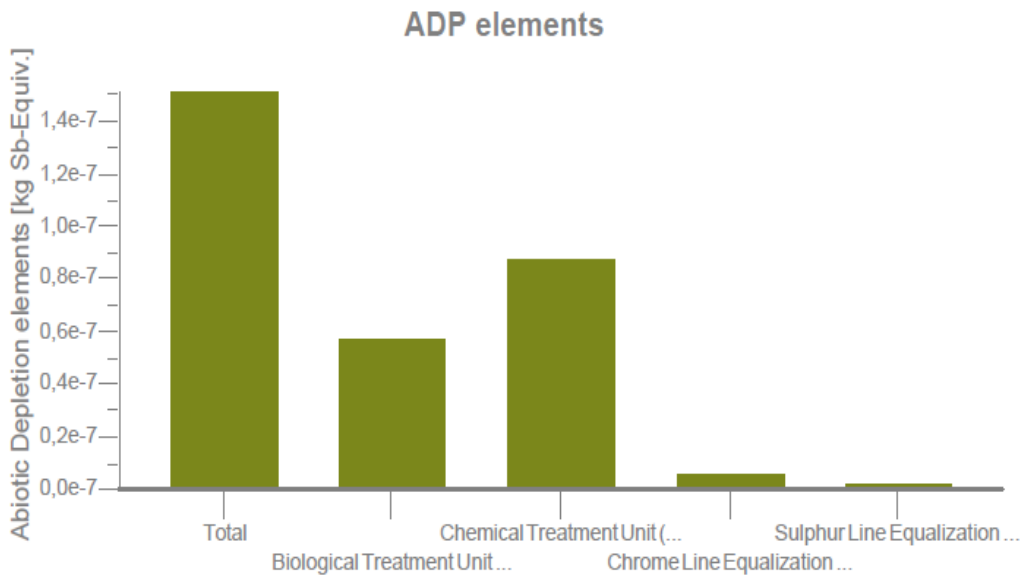


Figure 5.29 Abiotic depletion elements effects in Scenario 2



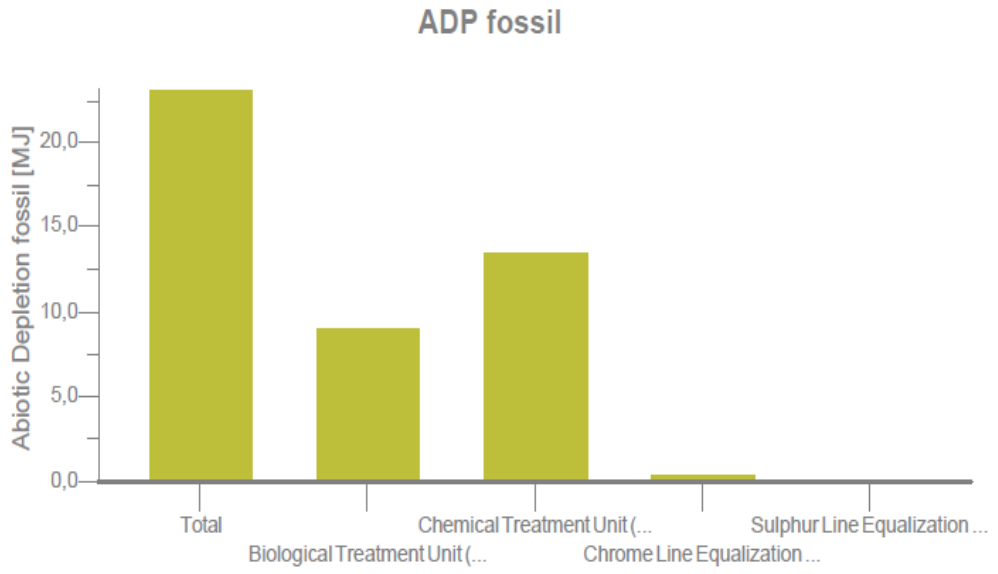


Figure 5.30 Abiotic depletion fossil effects in Scenario 2

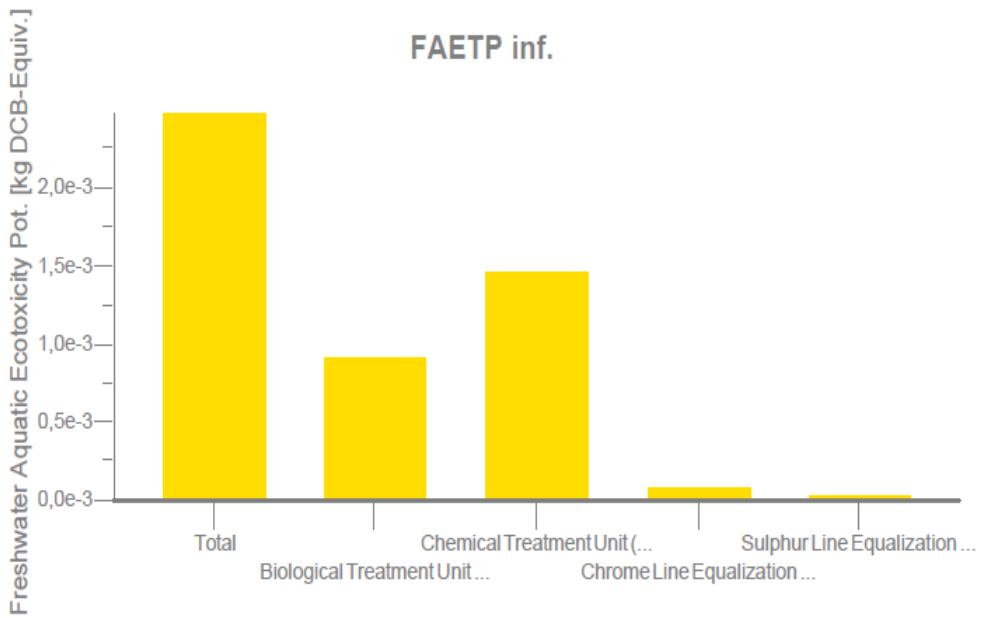


Figure 5.31 Freshwater aquatic ecotoxicity potential effects in Scenario 2

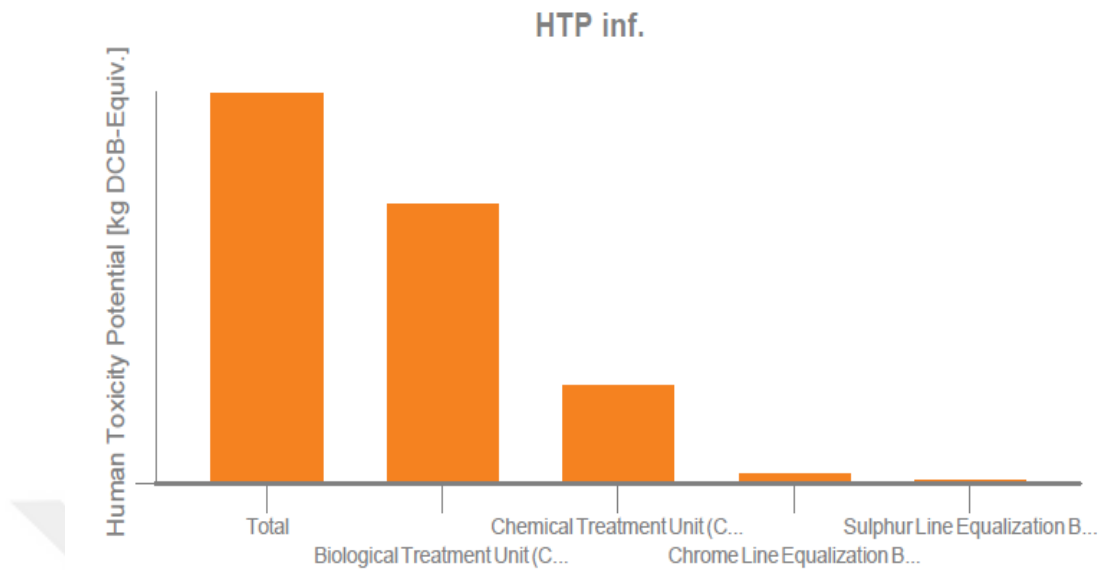


Figure 5.32 Human toxicity potential effects in Scenario 2

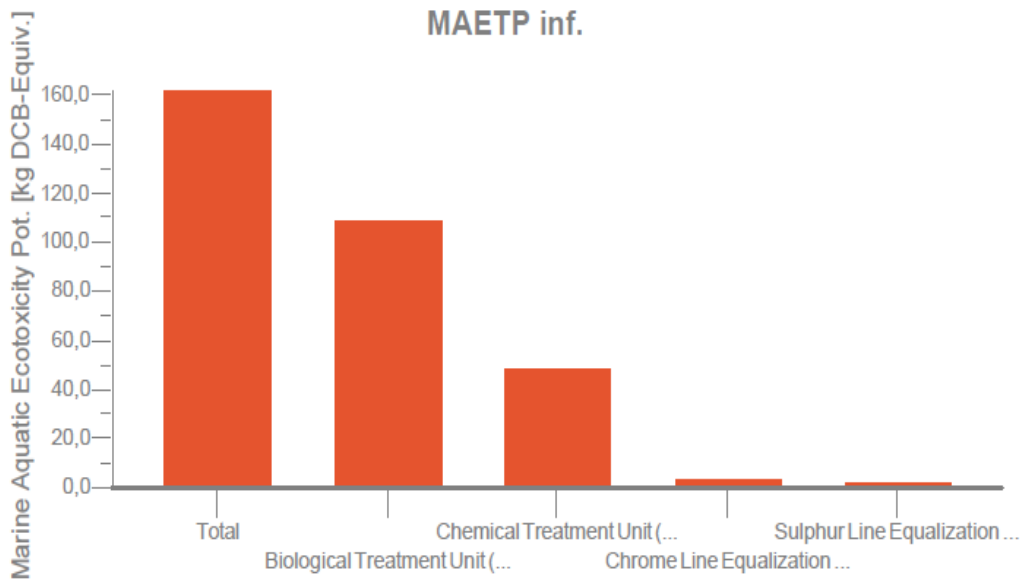
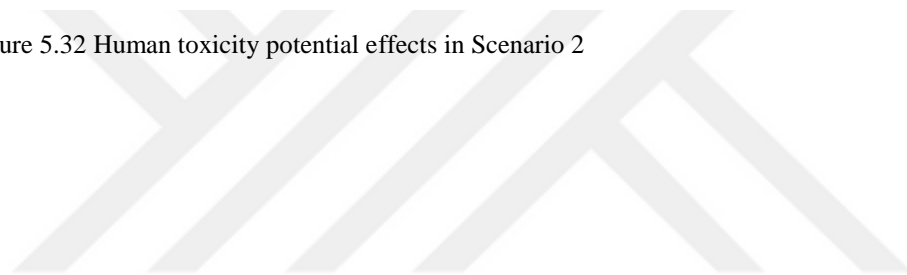


Figure 5.33 Marine aquatic ecotoxicity potential effects in Scenario 2

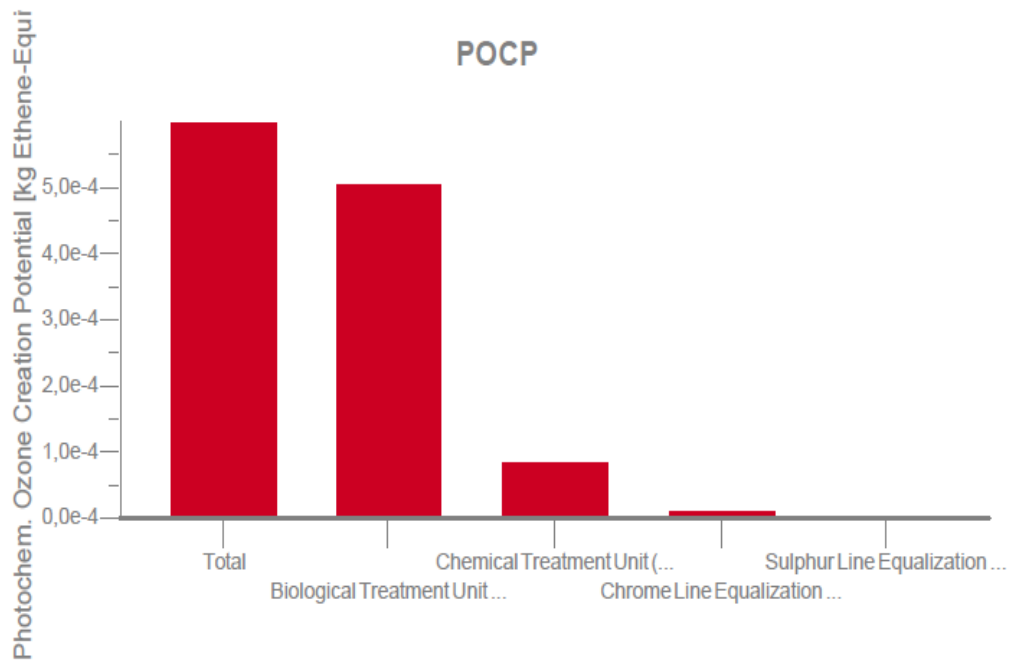


Figure 5.34 Photochemical ozone creation potential effects in Scenario 2

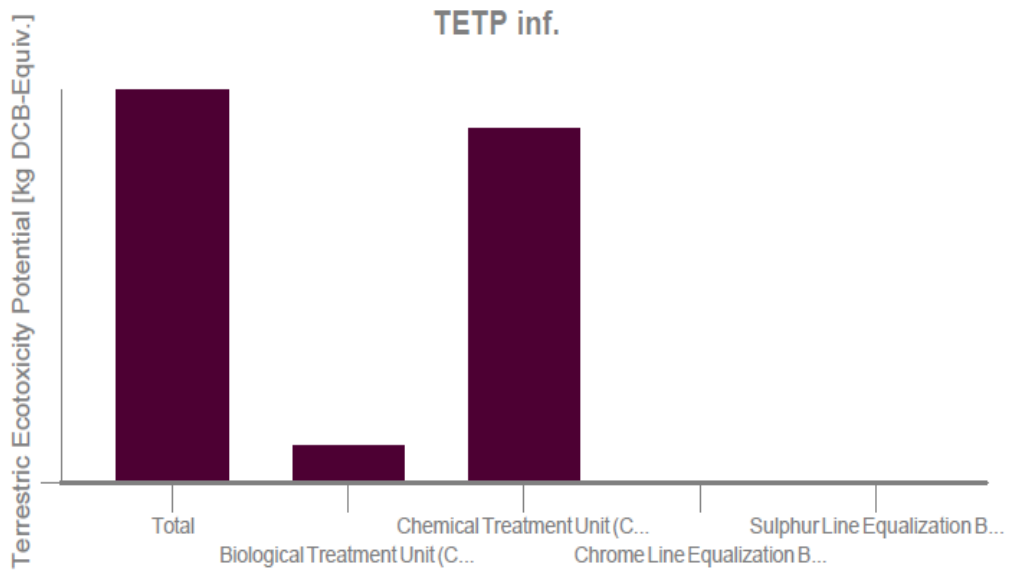


Figure 5.35 Terrestrial ecotoxicity potential effects in Scenario 2

Table 5.16 Environmental impacts of Scenario 2

Environmental Impact Categories	Unit	Value
Global Warming Potential	kg CO <sub>2</sub> equiv.	5.39
Acidification Potential	kg SO <sub>2</sub> equiv.	0.0121
Eutrophication Potential	kg PO <sub>4</sub> <sup>-2</sup> equiv.	0.00054
Ozone Layer Depletion Potential	kg R11 equiv.	6.19x10 <sup>-11</sup>
Abiotic Depletion Elements	kg Sb equiv.	1.51x10 <sup>-7</sup>
Abiotic Depletion Fossil	MJ	23.1
Freshwater Ecotoxicity Potential	kg DCB equiv.	0.00248
Human Toxicity Potential	kg DCB equiv.	0.0784
Marine Aquatic Ecotoxicity Potential	kg DCB equiv.	162
Photochemical Ozone Creation Potential	kg C <sub>2</sub> H <sub>4</sub> equiv.	6x10 <sup>-4</sup>
Terrestrial Ecotoxicity Potential	kg DCB equiv.	0.0143

### 5.2.3 Scenario 3

Chromium and sulphur come to plant with separated line and including chromium recovery units in Scenario 3. Sulphur oxidation is made in equalization tank is placed sulphur line. Chromium is treated with MgO and recovery of chromium in chromium line and then both of lines are combined in biological treatment unit. Figure 5.36 shows the created process plan for scenario 3.

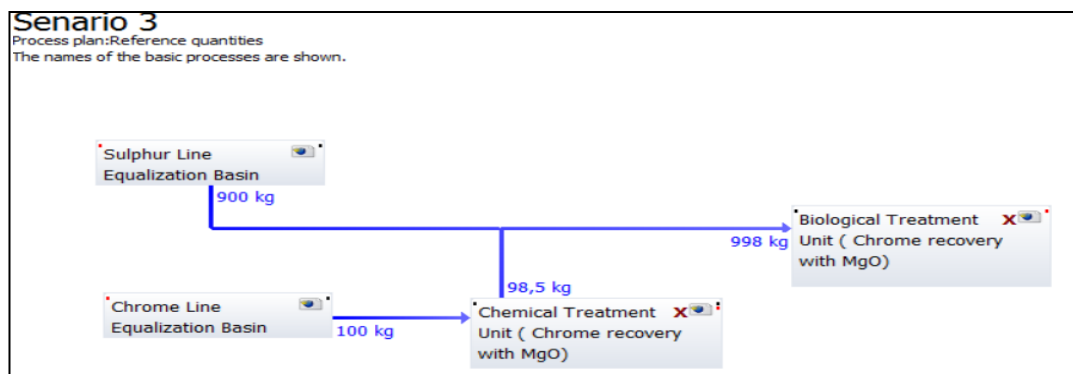


Figure 5.36 Created flow diagram image for Scenario 3

Acquired results are given among Figure 5.37 to 5.48. In Figure 5.37, process inputs massive contribution is shown for basic units in scenario. In Figure 5.38 to 5.48, the whole units and system effects are seen according to environmental impact categories in GaBi software.

The effects of biological treatment is very small than chemical treatment in all graphs. Because only consumed energy is considered in this scenario in view that GaBi database don't include information about of MgO. The total environmental impact of the scenario 3 as presented in Table 5.17.

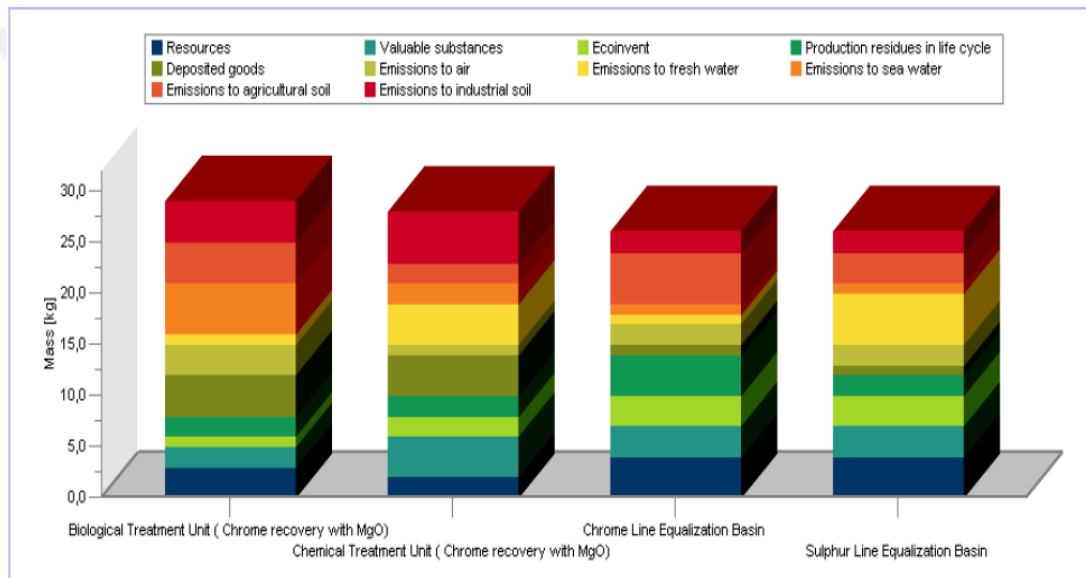


Figure 5.37 Massive contribution of used basis unit in Scenario 3

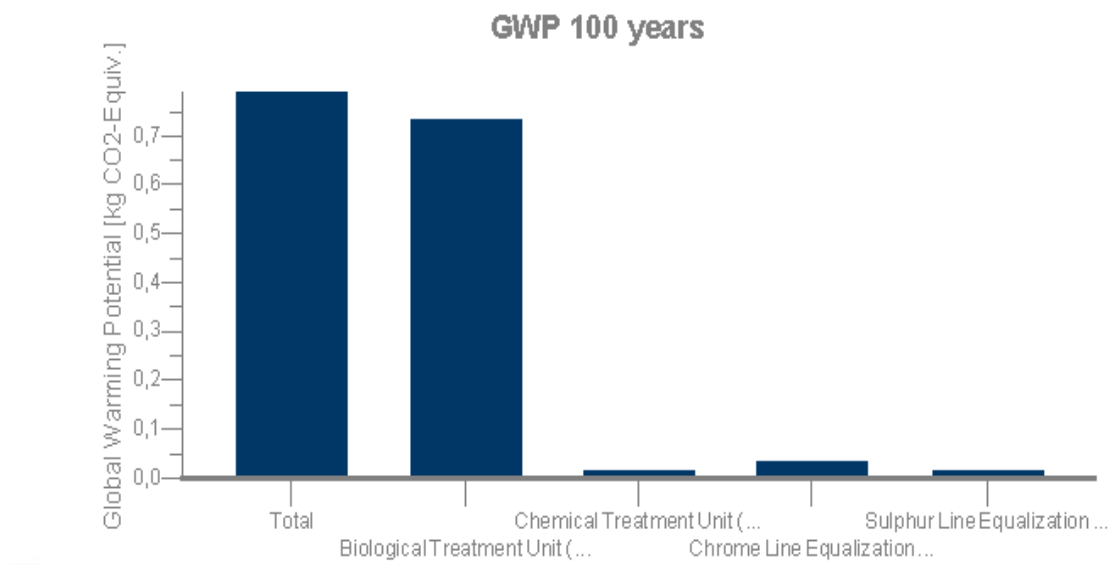


Figure 5.38 Global warming potential effects in Scenario 3

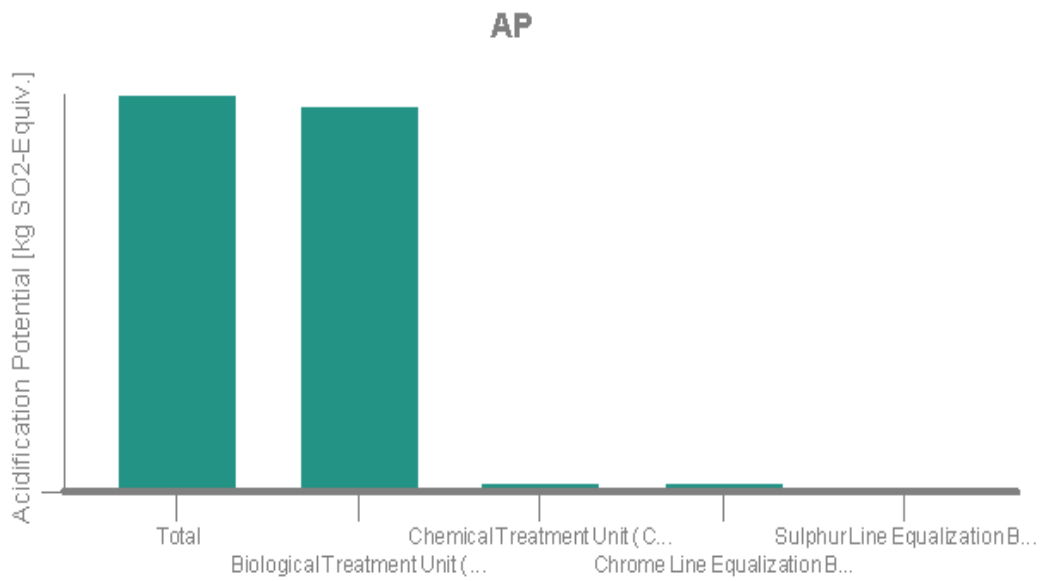


Figure 5.39 Acidification potential effects in Scenario 3

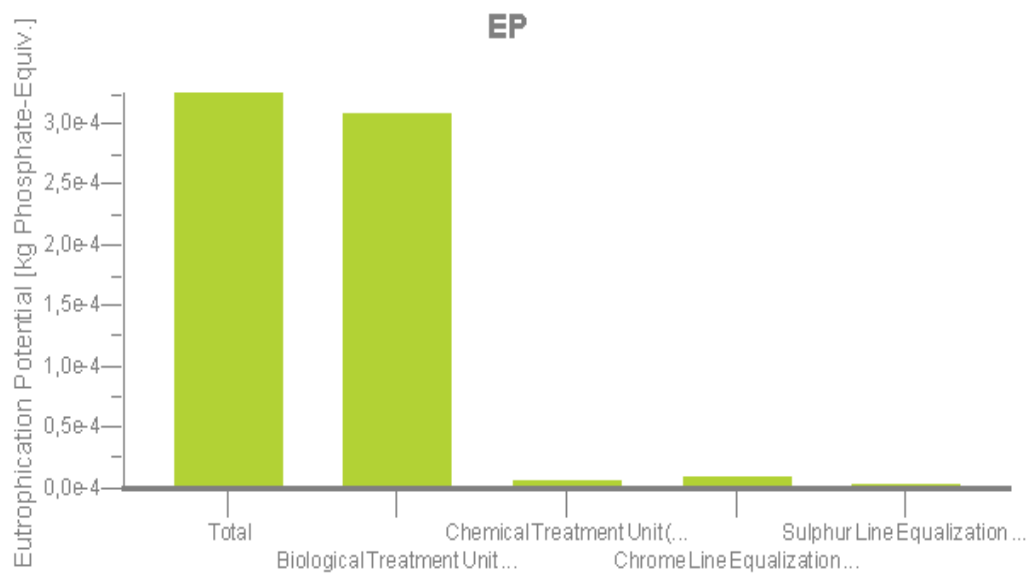


Figure 5.40 Eutrophication potential effects in Scenario 3

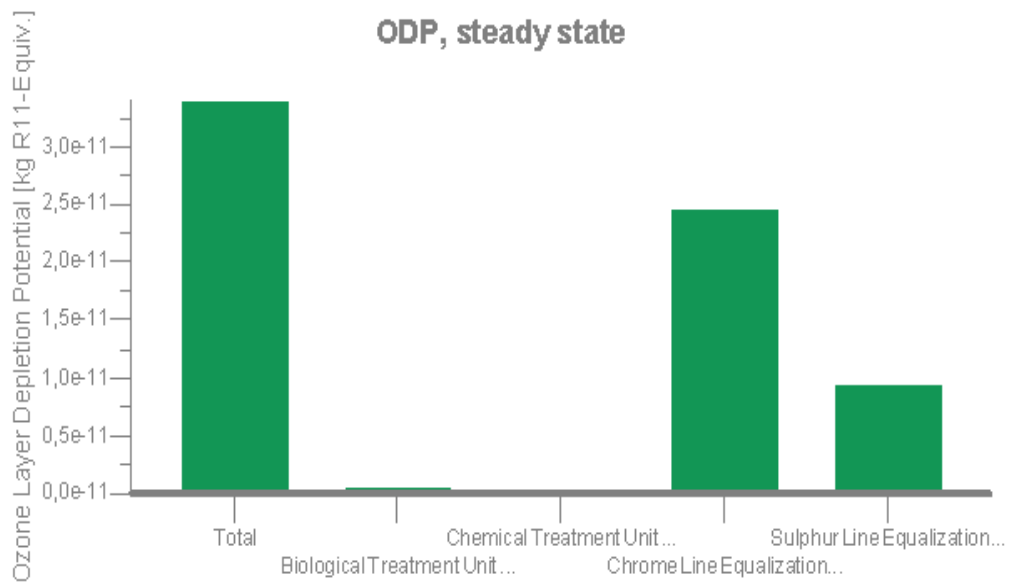


Figure 5.41 Ozone layer depletion potential effects in Scenario 3

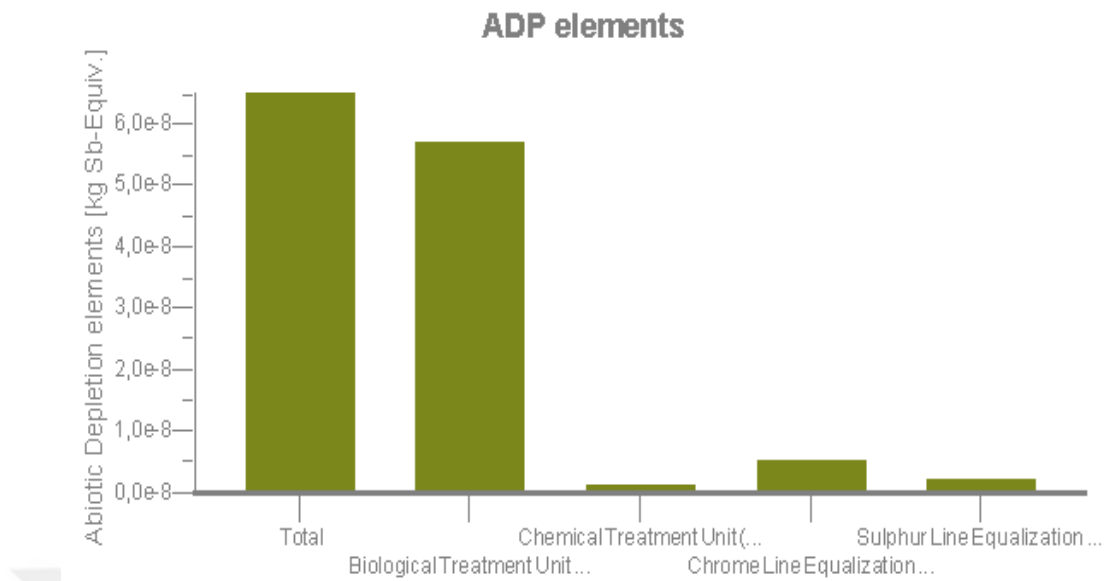


Figure 5.42 Abiotic depletion elements effects in Scenario 3

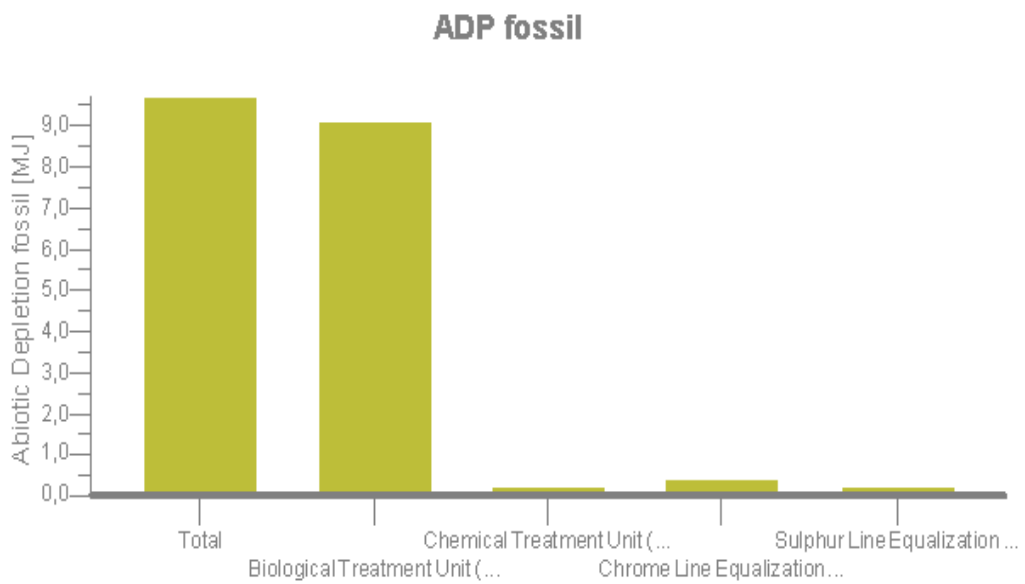


Figure 5.43 Abiotic depletion fossil effects in Scenario 3



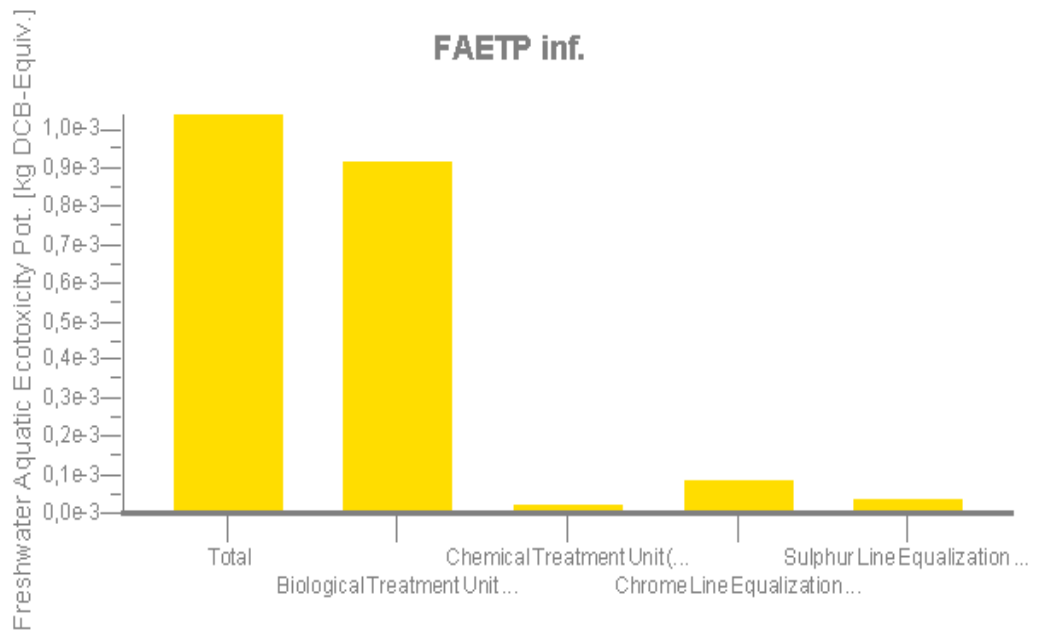


Figure 5.44 Freshwater aquatic ecotoxicity potential effects in Scenario 3

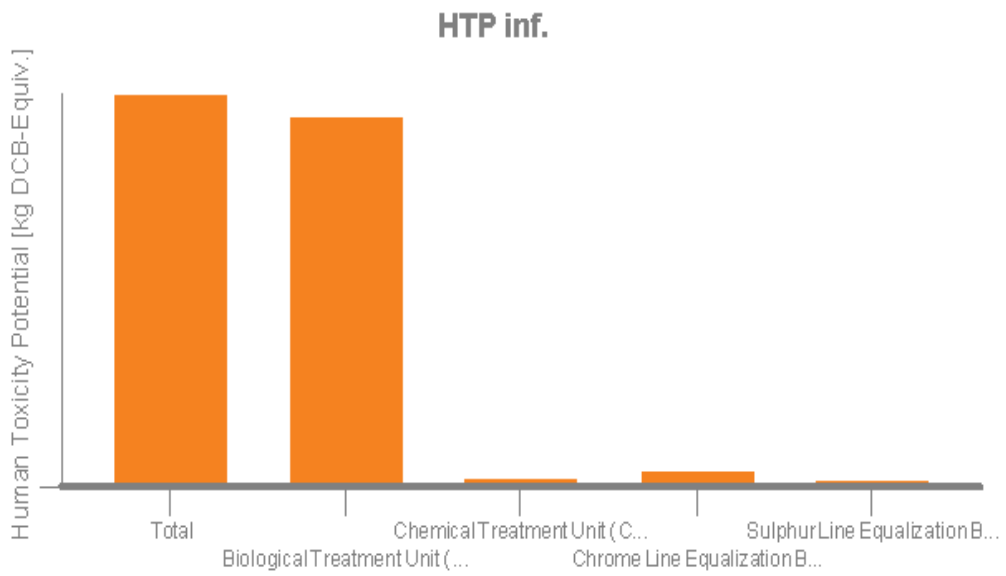


Figure 5.45 Human toxicity potential effects in Scenario 3

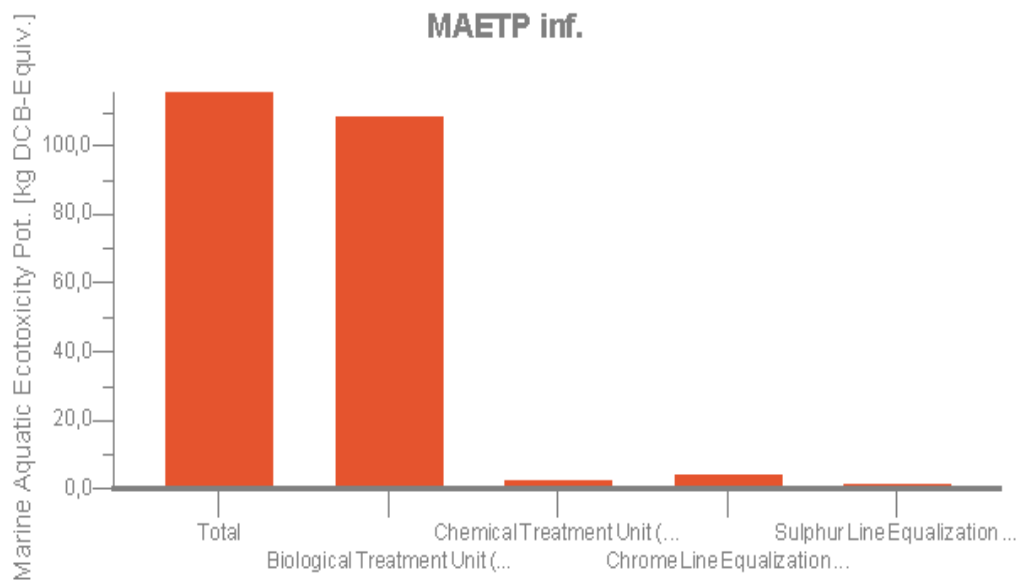


Figure 5.46 Marine aquatic ecotoxicity potential effects in Scenario 3

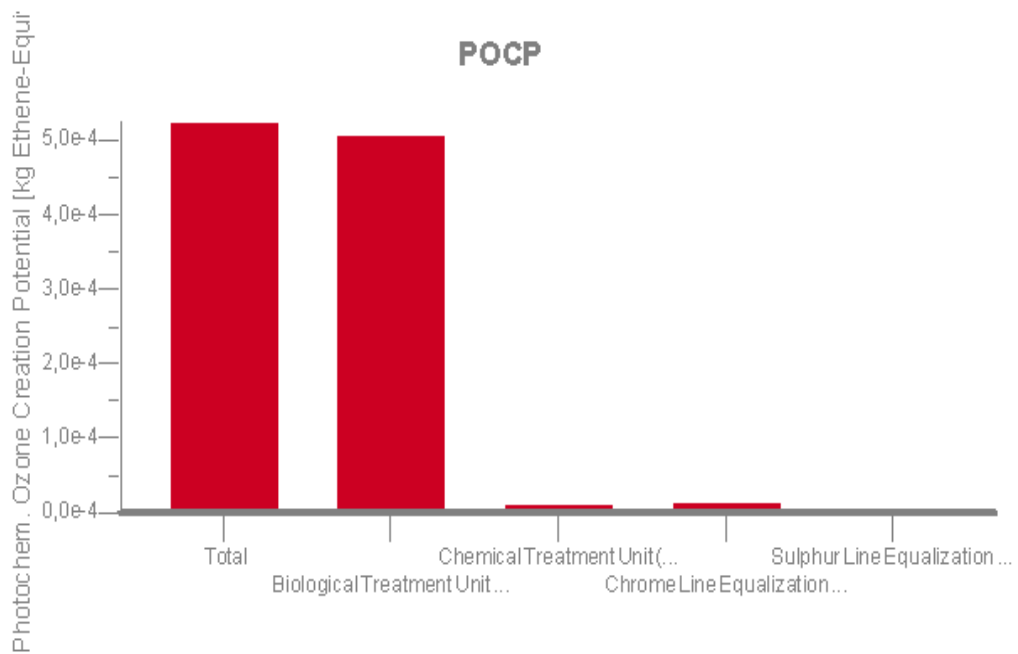


Figure 5.47 Photochemical ozone creation potential effects in Scenario 3

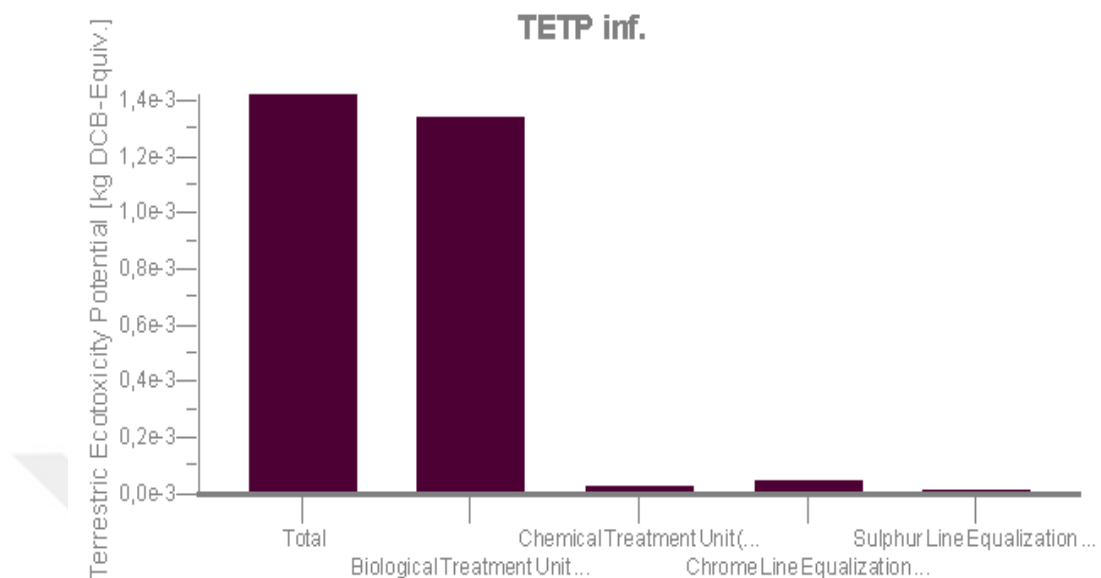


Figure 5.48 Terrestrial ecotoxicity potential effects in Scenario 3

Table 5.17 Environmental impacts of Scenario 3

Environmental Impact Categories	Unit	Value
Global Warming Potential	kg CO <sub>2</sub> equiv.	0.79
Acidification Potential	kg SO <sub>2</sub> equiv.	0.0109
Eutrophication Potential	kg PO <sub>4</sub> <sup>-2</sup> equiv.	0.000325
Ozone Layer Depletion Potential	kg R11 equiv.	3.41x10 <sup>-11</sup>
Abiotic Depletion Elements	kg Sb equiv.	6.5x10 <sup>-8</sup>
Abiotic Depletion Fossil	MJ	9.73
Freshwater Ecotoxicity Potential	kg DCB equiv.	0.00104
Human Toxicity Potential	kg DCB equiv.	0.0597
Marine Aquatic Ecotoxicity Potential	kg DCB equiv.	116
Photochemical Ozone Creation Potential	kg C <sub>2</sub> H <sub>4</sub> equiv.	5.25x10 <sup>-4</sup>
Terrestrial Ecotoxicity Potential	kg DCB equiv.	0.00142

#### 5.2.4 Scenario 4

Chromium and sulphur come to plant with separated line and including chromium recovery units in Scenario 4. It was accepted that MgO only was used in Scenario 3. But, chromium is treated with MgO + CaO mixing and recovery of chromium in chromium line and then both of lines are combined in biological treatment unit in Scenario 4. Because mixing of specific ratio of MgO and CaO is considered to be economical and effective solution. CaO is much cheaper than MgO. Sulphur oxidation is made in equalization tank is placed sulphur line. Figure 5.49 shows the created process plan for scenario 4.

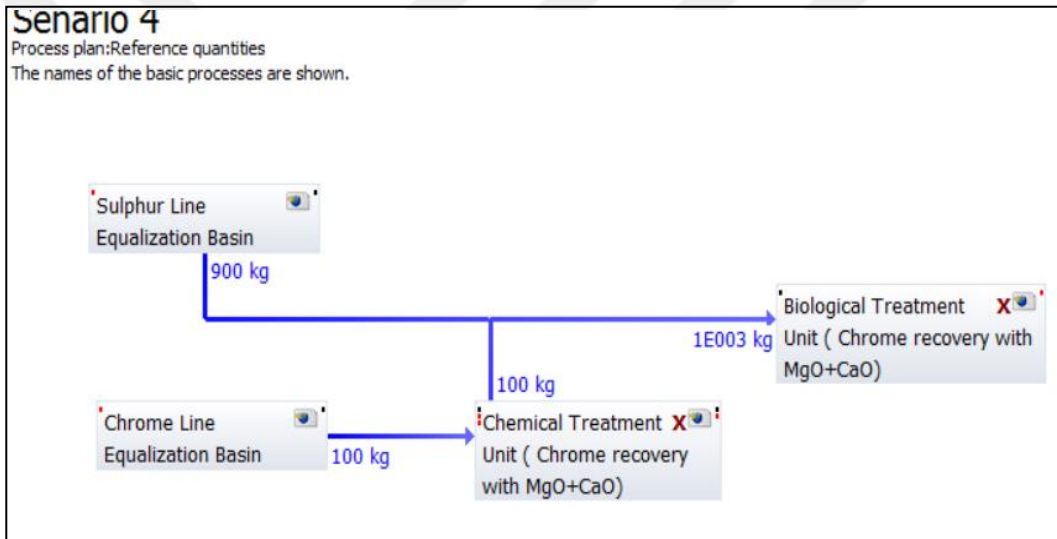


Figure 5.49 Created flow diagram image for Scenario 4

Acquired results are given among Figure 5.50 to 5.61. In Figure 5.50, process inputs massive contribution is shown for basic units in scenario. In Figure 5.51 to 5.61, the whole units and system effects are seen according to environmental impact categories in GaBi software.

The effects of biological treatment is very small than chemical treatment in all graphs. Because only consumed energy is considered in this scenario in view that GaBi database don't include information about of MgO. The total environmental impact of the Scenario 4 is presented in Table 5.18.

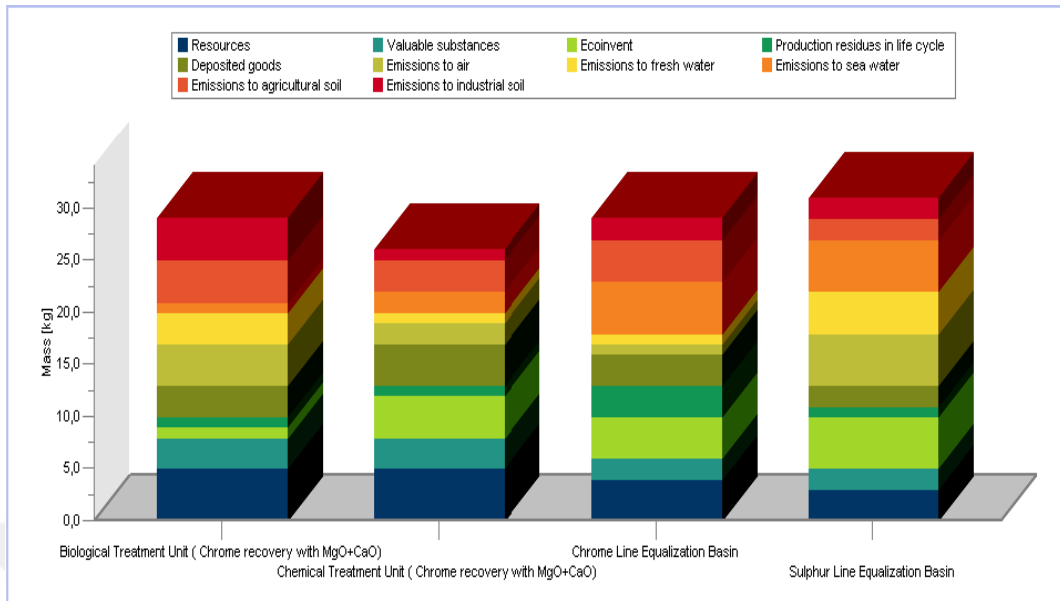


Figure 5.50 Massive contribution of used basis unit in Scenario 4

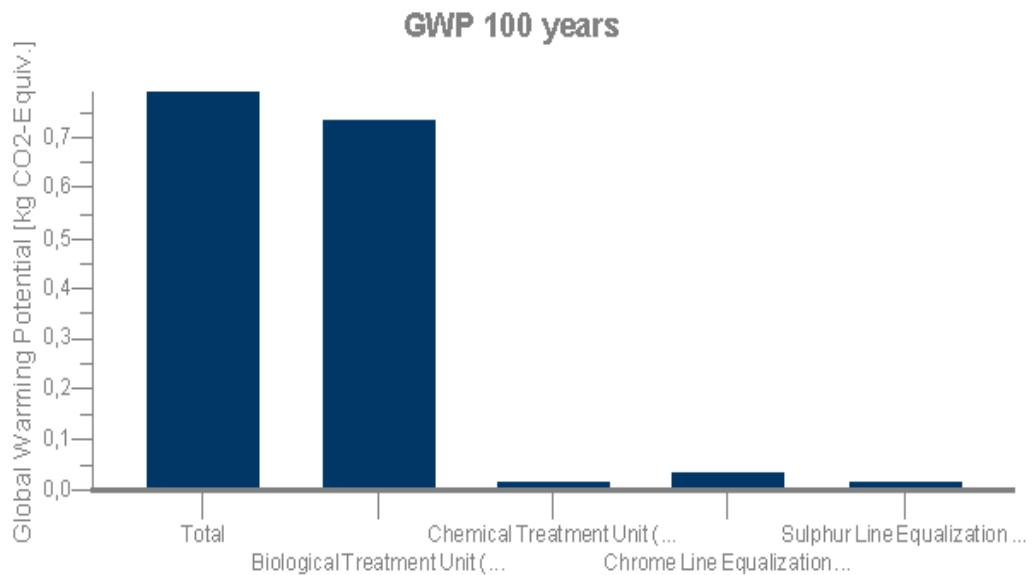


Figure 5.51 Global warming potential effects in Scenario 4

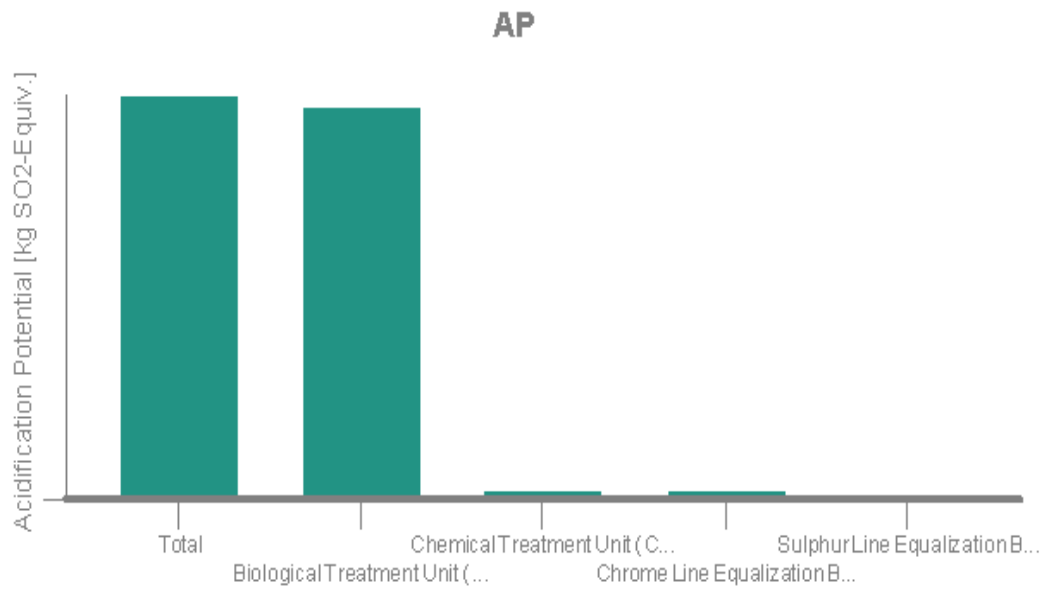


Figure 5.52 Acidification potential effects in Scenario 4

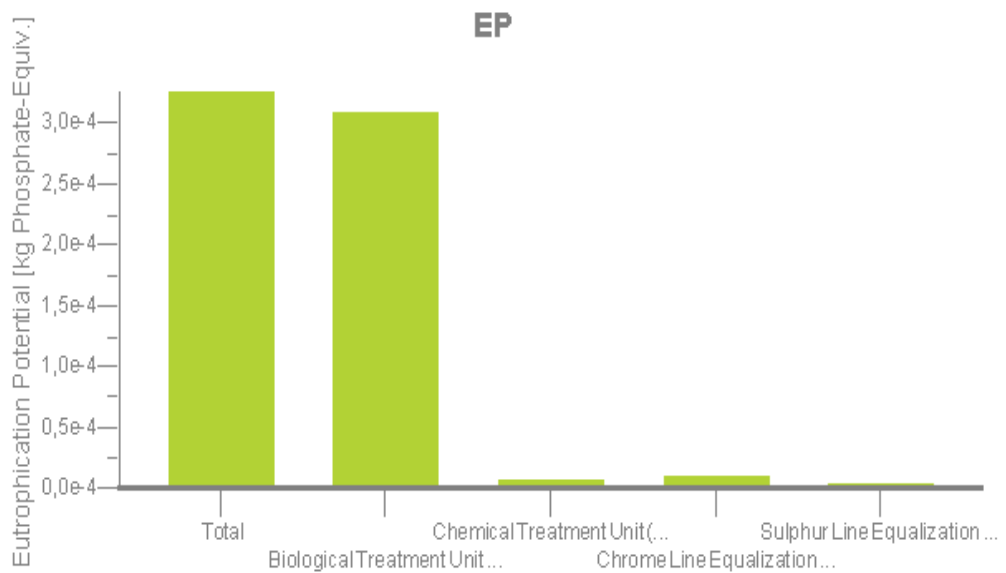


Figure 5.53 Eutrophication potential effects in Scenario 4

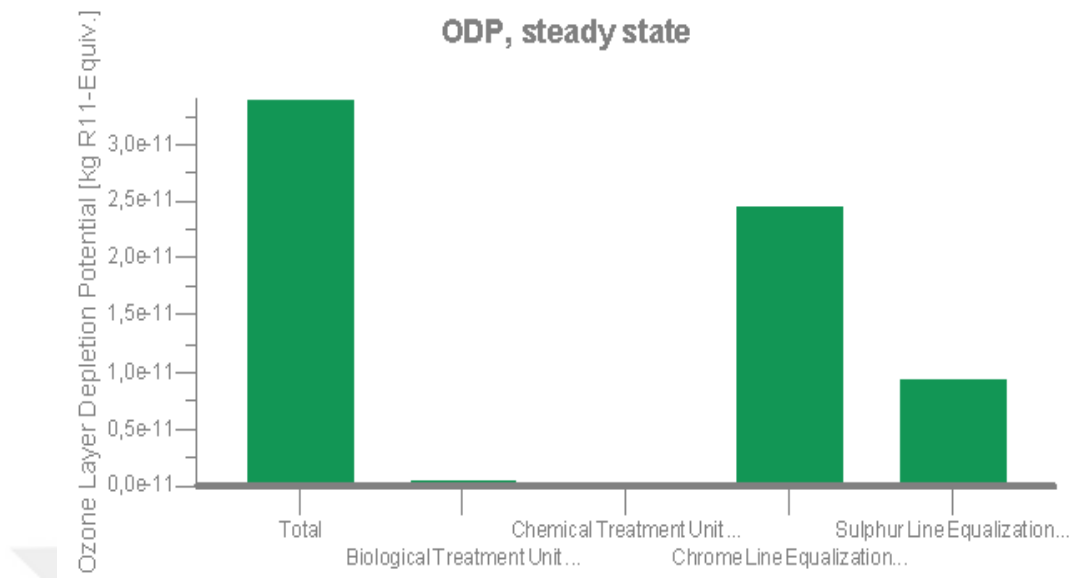


Figure 5.54 Ozone layer depletion potential effects in Scenario 4

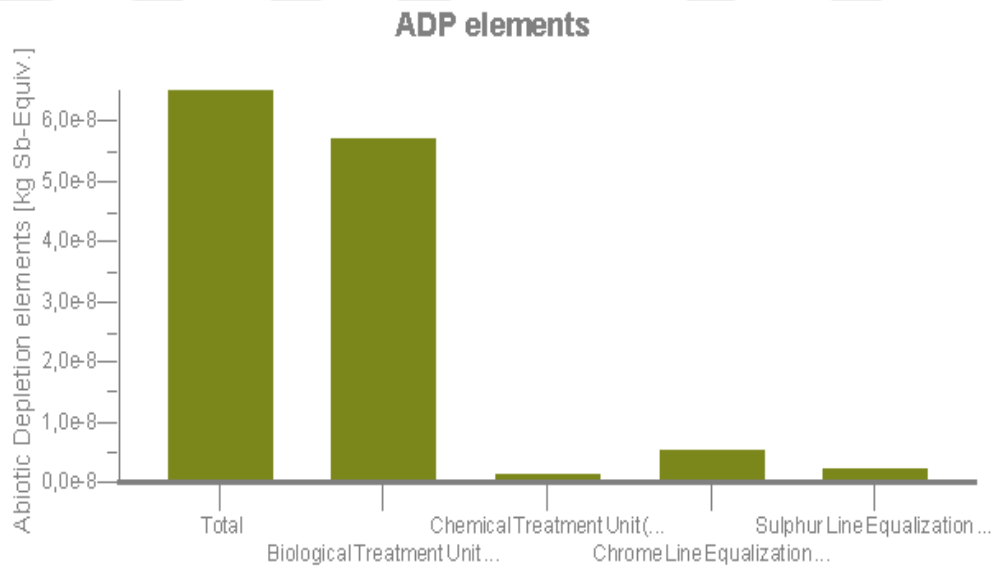


Figure 5.55 Abiotic depletion elements effects in Scenario 4

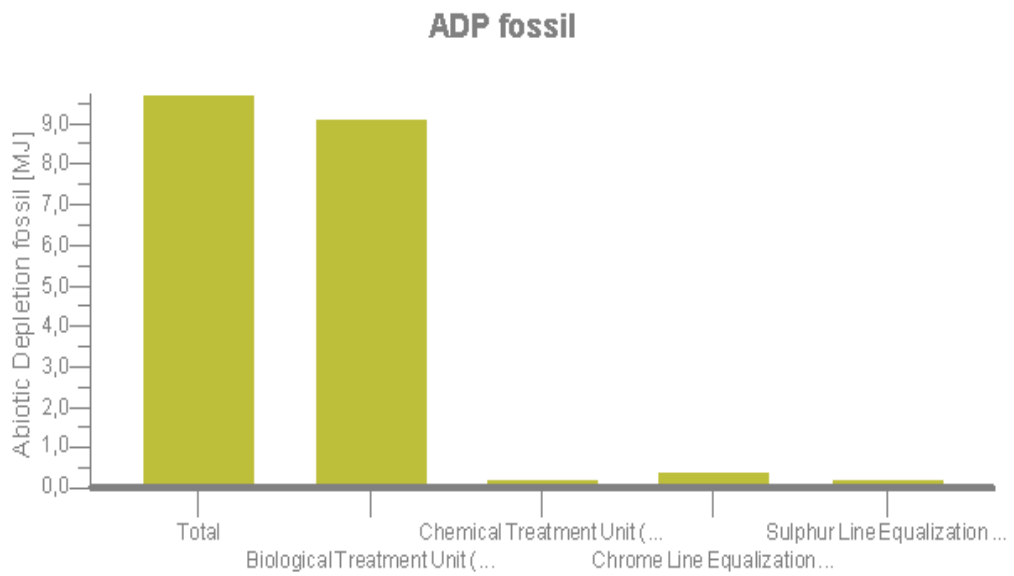


Figure 5.56 Abiotic depletion fossil effects in Scenario 4

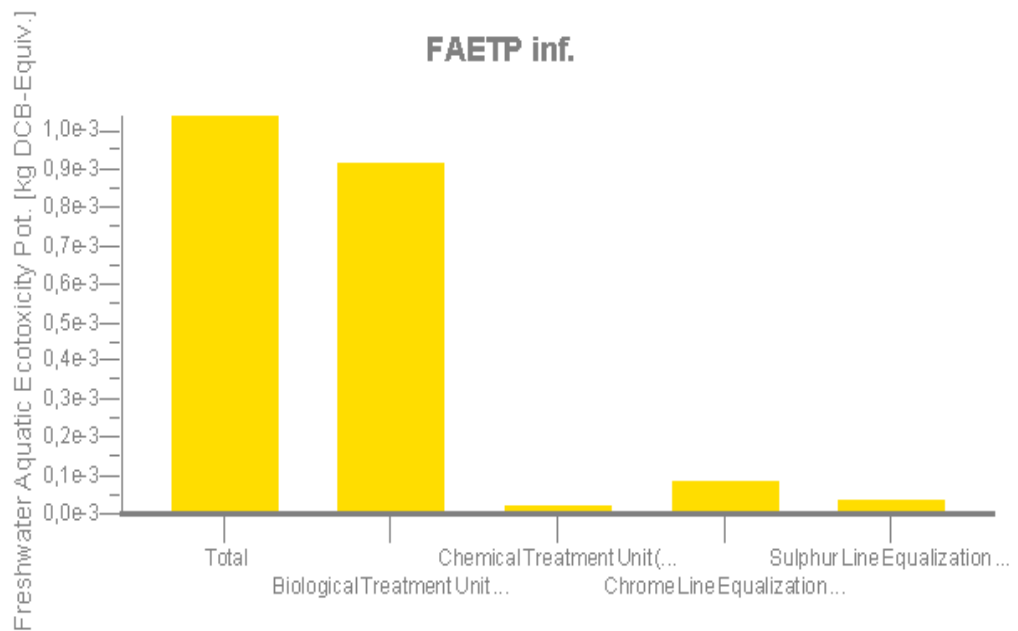


Figure 5.57 Freshwater aquatic ecotoxicity potential effects in Scenario 4



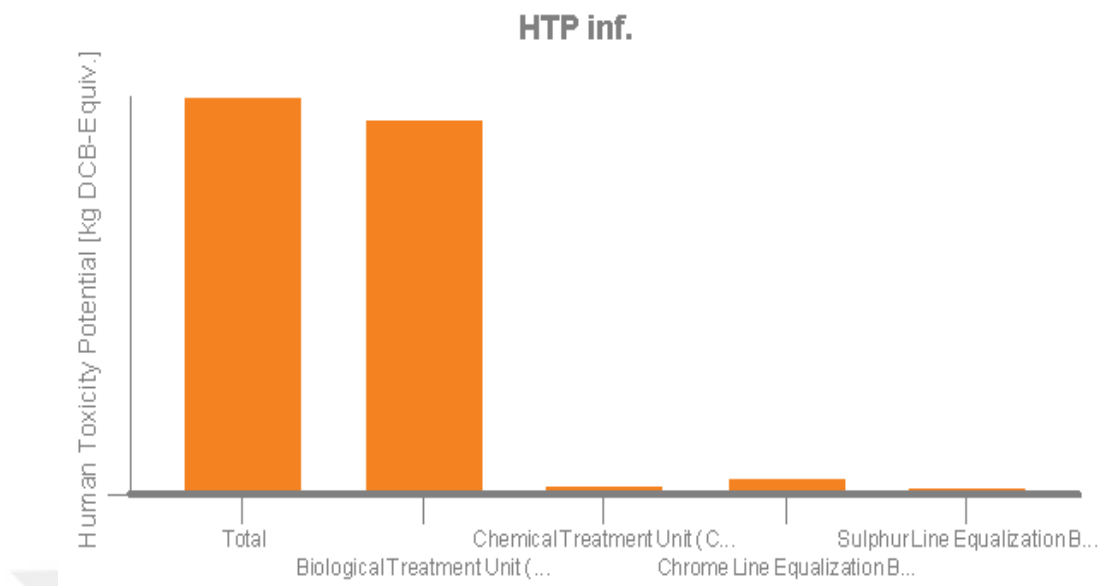


Figure 5.58 Human toxicity potential effects in Scenario 4

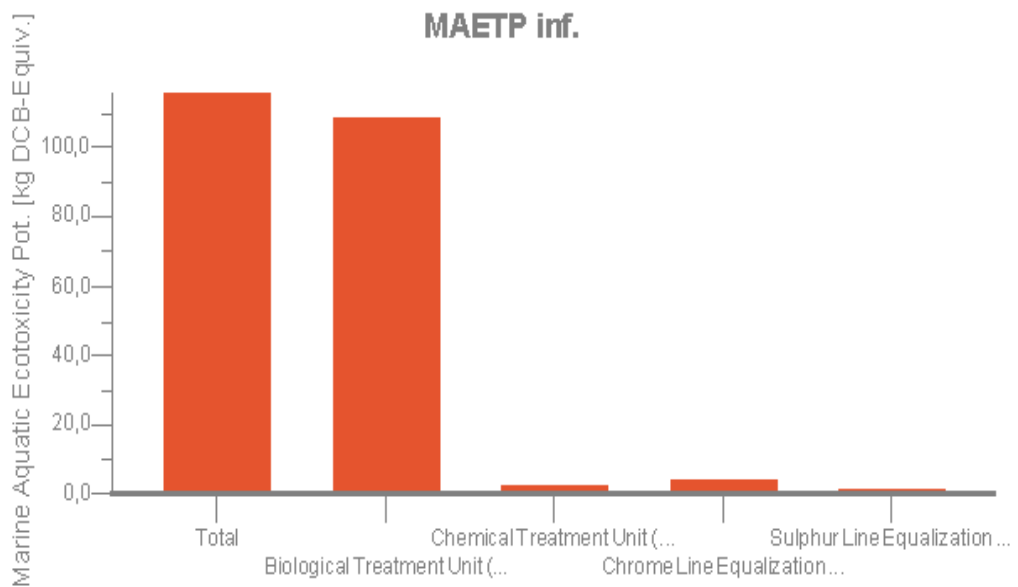


Figure 5.59 Marine aquatic ecotoxicity potential effects in Scenario 4

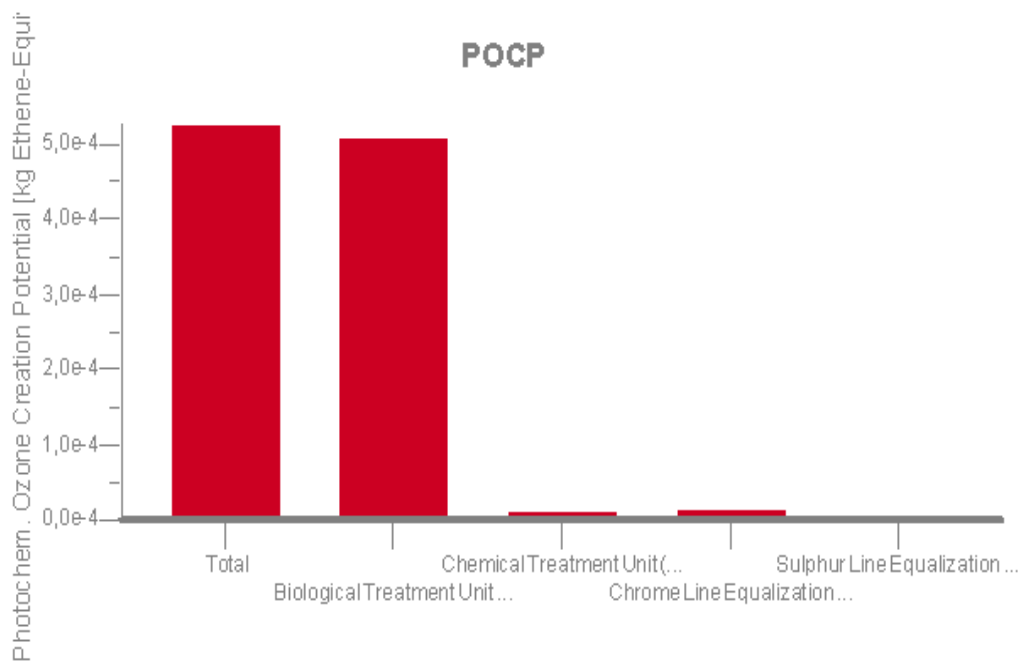


Figure 5.60 Photochemical ozone creation potential effects in Scenario 4

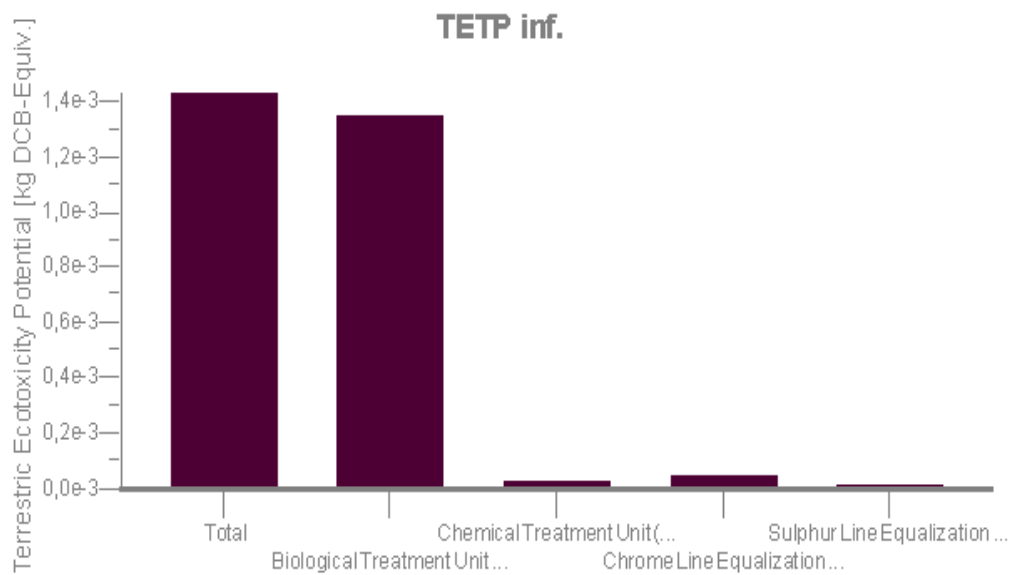


Figure 5.61 Terrestrial ecotoxicity potential effects in Scenario 4

Table 5.18 Environmental impacts of Scenario 4

<b>Environmental Impact Categories</b>	<b>Unit</b>	<b>Value</b>
Global Warming Potential	kg CO <sub>2</sub> equivalent	0.791
Acidification Potential	kg SO <sub>2</sub> equivalent	0.011
Eutrophication Potential	kg PO <sub>4</sub> <sup>-2</sup> equivalent	0.000326
Ozone Layer Depletion Potential	kg R11 equivalent	3.41x10 <sup>-11</sup>
Abiotic Depletion Elements	kg Sb equivalent	6.51x10 <sup>-8</sup>
Abiotic Depletion Fossil	MJ	9.75
Freshwater Ecotoxicity Potential	kg DCB equivalent	0.00104
Human Toxicity Potential	kg DCB equivalent	0.0599
Marine Aquatic Ecotoxicity Potential	kg DCB equivalent	116
Photochemical Ozone Creation Potential	kg C <sub>2</sub> H <sub>4</sub> equivalent	5.26x10 <sup>-4</sup>
Terrestrial Ecotoxicity Potential	kg DCB equivalent	0.00143

### 5.3 Evaluation of the Results

Considering the life cycle analysis of the generated scenarios, their environmental impacts are presented in Table 5.19. The results clearly show that the separation of chromium and sulphur-rich lime line and recovery of chromium provides the reduction in all environmental effects. The comparison of all impacts of each scenario is given in Figure 5.62 to 5.72.

Table 5.19 Environmental impacts of all used scenarios

<b>Environmental Impact Categories</b>	<b>Unit</b>	<b>Scenario-1</b>	<b>Scenario-2</b>	<b>Scenario-3</b>	<b>Scenario-4</b>
Global Warming Potential	kg CO <sub>2</sub> equiv.	23.4	5.39	0.79	0.791
Acidification Potential	kg SO <sub>2</sub> equiv.	0.0111	0.0121	0.0109	0.011
Eutrophication Potential	kg PO <sub>4</sub> <sup>-2</sup> equiv.	0.00123	0.00054	0.000325	0.000326
Ozone Layer Depletion Potential	kg R11 equiv.	1.49x10 <sup>-10</sup>	6.19x10 <sup>-11</sup>	3.41x10 <sup>-11</sup>	3.41x10 <sup>-11</sup>
Abiotic Depletion Elements	kg Sb equiv.	4.6x10 <sup>-7</sup>	1.51x10 <sup>-7</sup>	6.5x10 <sup>-8</sup>	6.51x10 <sup>-8</sup>
Abiotic Depletion Fossil	MJ	71.5	23.1	9.73	9.75
Freshwater Ecotoxicity Potential	kg DCB equiv.	0.00768	0.00248	0.00104	0.00104
Human Toxicity Potential	kg DCB equiv.	0.121	0.0784	0.0597	0.0599
Marine Aquatic Ecotoxicity Potential	kg DCB equiv.	285	162	116	116
Photochemical Ozone Creation Potential	kg C <sub>2</sub> H <sub>4</sub> equiv.	6.22x10 <sup>-4</sup>	6x10 <sup>-4</sup>	5.25x10 <sup>-4</sup>	5.26x10 <sup>-4</sup>
Terrestrial Ecotoxicity Potential	kg DCB equiv.	0.0649	0.0143	0.00142	0.00143

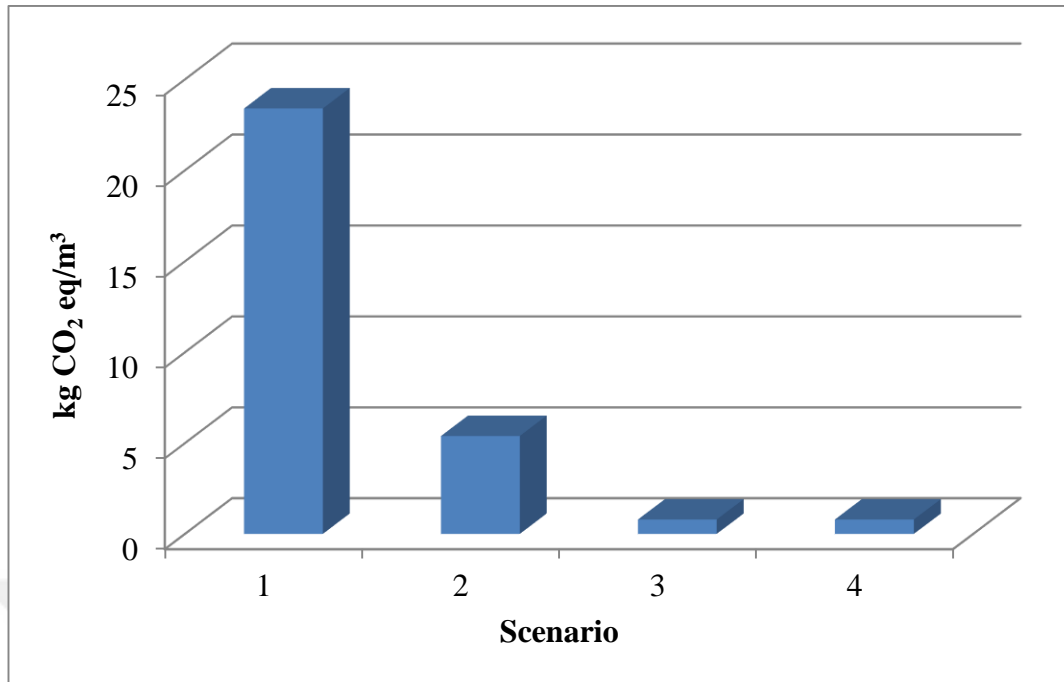


Figure 5.62 Global warming potential effects for all scenarios

The global warming potential (GWP) impacts are directly related with electricity use. Direct electrical consumption by the wastewater treatment plants (WWTP) makes the most significant contribution to GWP and other some environmental impacts, such as abiotic resource depletion, photochemical oxidation, and acidification, and this is a common finding for WWTP, with energy consumption (e.g. pumping and aeration) often dominating the environmental impacts (Li et al., 2013). As seen in Figure 5.62, the combined scenario, compared to the other options, significantly increase the global warming potential (23.4 kg CO<sub>2</sub>eq/m<sup>3</sup>). 77% and 96.6% better GWP result was achieved with the separation of these lines and chromium recovery, respectively. The lowest impact, 0.79 kg CO<sub>2</sub>eq/m<sup>3</sup>, was obtained for the chromium recovery options (Scenario 3 and 4).

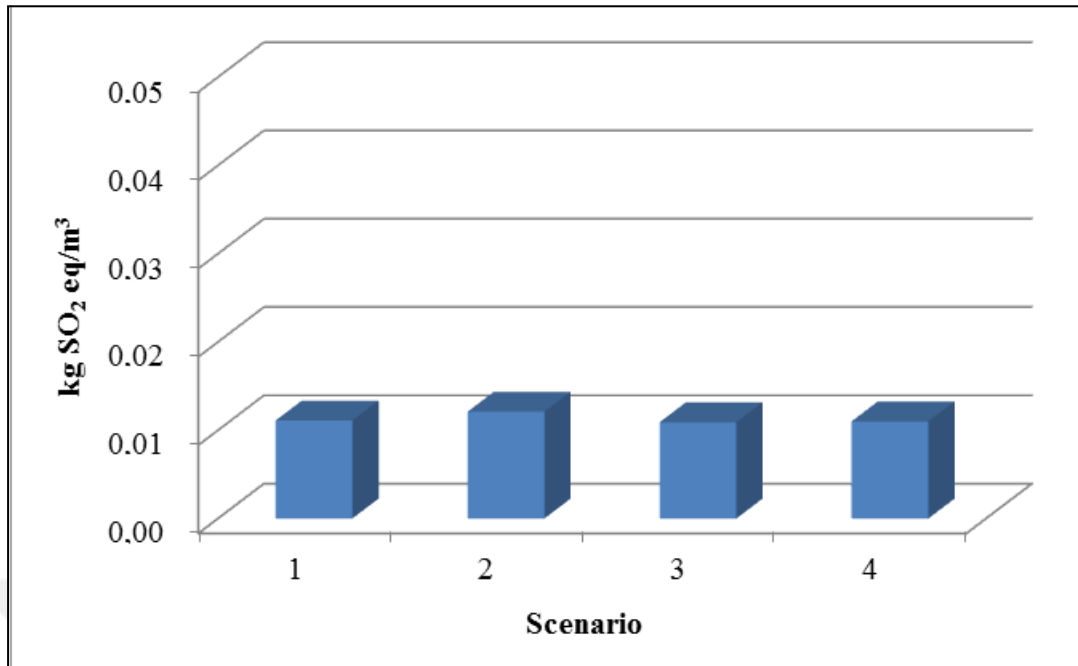


Figure 5.63 Acidification potential effects for all scenarios

Acidification has a regional/local effects on the environment and it is commonly associated with atmospheric pollution. Acidification potentials of all scenarios are almost the same and very low (0.0109 – 0.0121 kg SO<sub>2</sub>eq/m<sup>3</sup>). The Scenario 1 generates higher impacts for all the impact categories analyzed, but in acidification potential, the impacts are almost equivalents. The results show that combination or separation of chromium and sulphur-rich lime line and chromium recovery has no effect on the acidification potential (Figure 5.63).

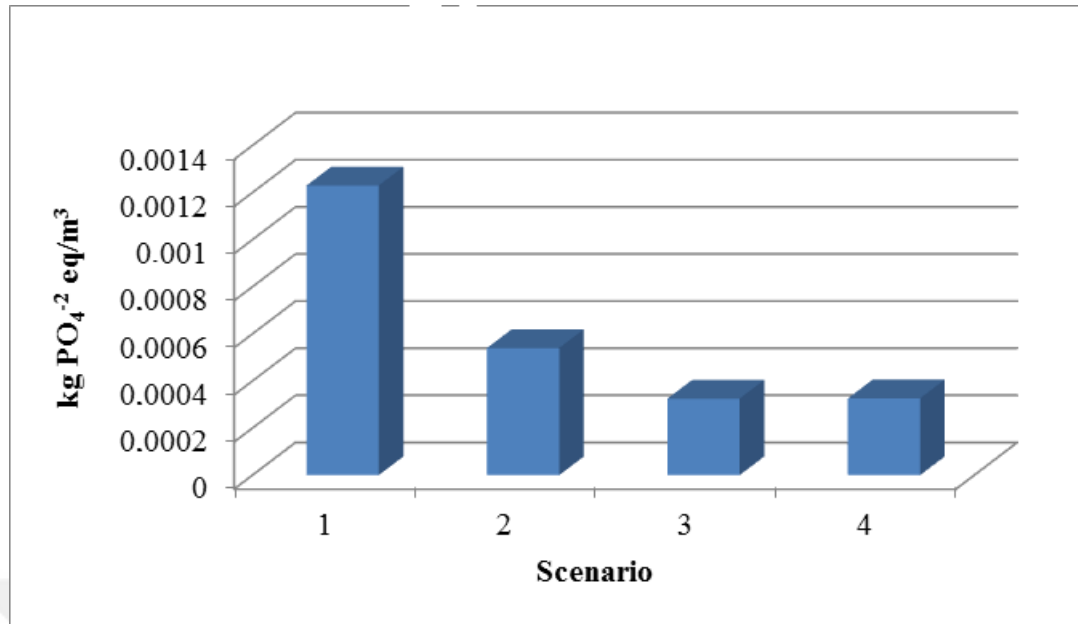


Figure 5.64 Eutrophication potential effects for all scenarios

Eutrophication potential due to the remaining nutrients in the effluent has been considered the most relevant environmental issue when performing environmental evaluation of WWTPs. It is demonstrated that the eutrophication potential impact category of a WWTP is mostly associated with the emissions to water, mainly due to the phosphorus (P), nitrogen (N) and to a lower extent, degradable organics (COD) in wastewater effluent (Zang et al., 2015). However, since the nitrogen and phosphorus are not significant parameter for the leather industry wastewater, these parameters are not used in LCA calculations in this study. So, the eutrophication potentials of all scenarios are very low (0.000325 – 0.00123 kg PO<sub>4</sub><sup>-2</sup> eq/m<sup>3</sup>). But, eutrophication impact of Scenario 1 is higher comparing to other scenarios. This result may be related to the higher concentrations of COD in the treated effluent (Figure 5.64).

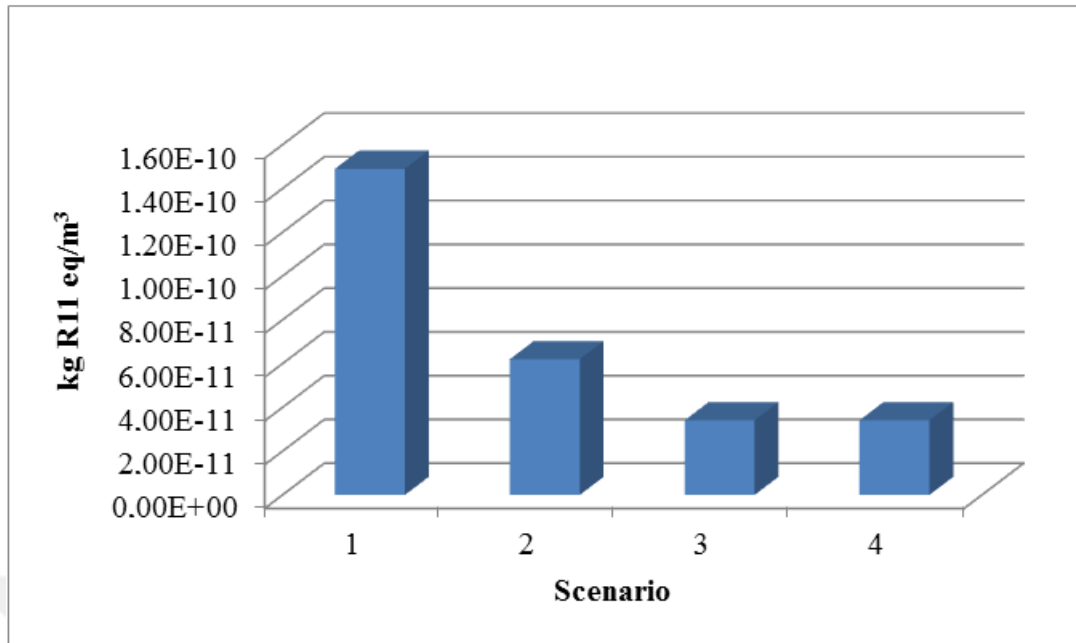


Figure 5.65 Ozone layer depletion effects for all scenarios

The ozone layer depletion is caused by the release of ozone-depleting substances, such as chlorofluorocarbons and bromofluorocarbons, in the stratospheric ozone layer (Itsubo & Inaba, 2012). Abiotic resource depletion is the decrease of availability of the total reserve of potential functions of resources (Oers et al., 2002). Abiotic resource depletion is grouped as the depletion of elements and the depletion of fossil fuels. The impact of the generated scenarios in the categories ozone layer depletion and abiotic depletion-elements is considerably lower than those of the other categories. Anyway, the higher impacts were determined for the combined scenario comparing to other scenarios for both categories (Figure 5.65 and 5.66).

The main contributor to the impact category abiotic depletion-fossil is the consumption of energy of the treatment systems. Since the energy consumption is higher than in Scenario 1, the abiotic depletion-fossil of this scenario is higher than the others (Figure 5.67). The results show that the separated scenario significantly decreases the abiotic depletion-fossil impacts and almost 67% lower impacts were determined for the Scenario 2 (23.1 MJ) comparing to Scenario 1 (71.5 MJ). The lowest abiotic depletion-fossil impact was determined for the chromium recovery options (9.73 MJ).



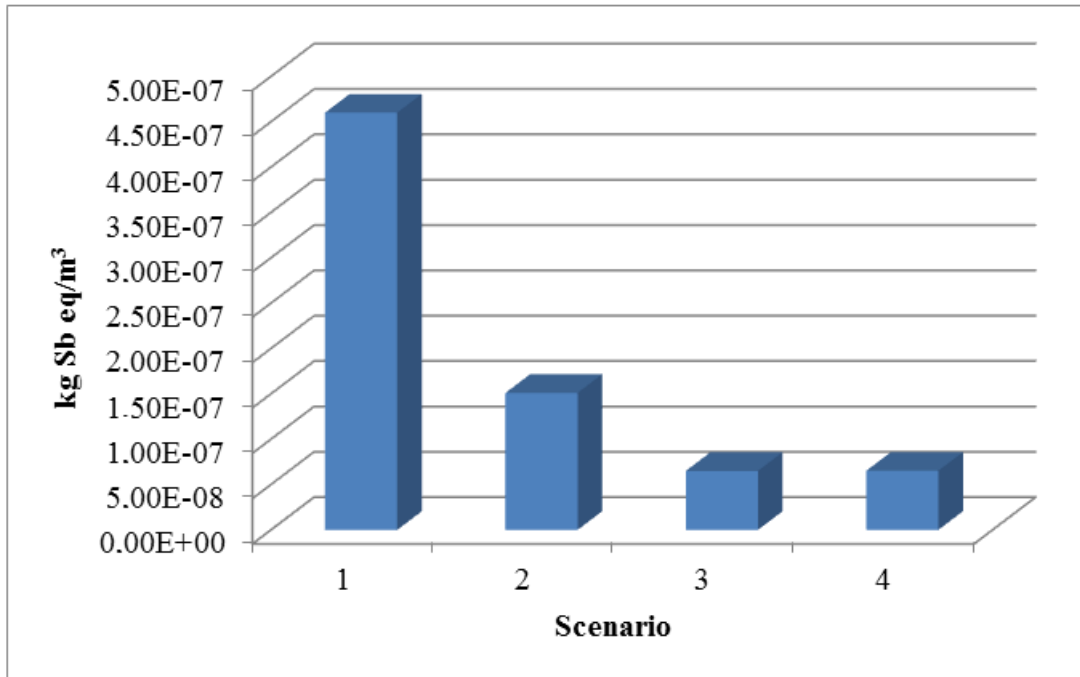


Figure 5.66 Abiotic depletion elements effects for all scenarios

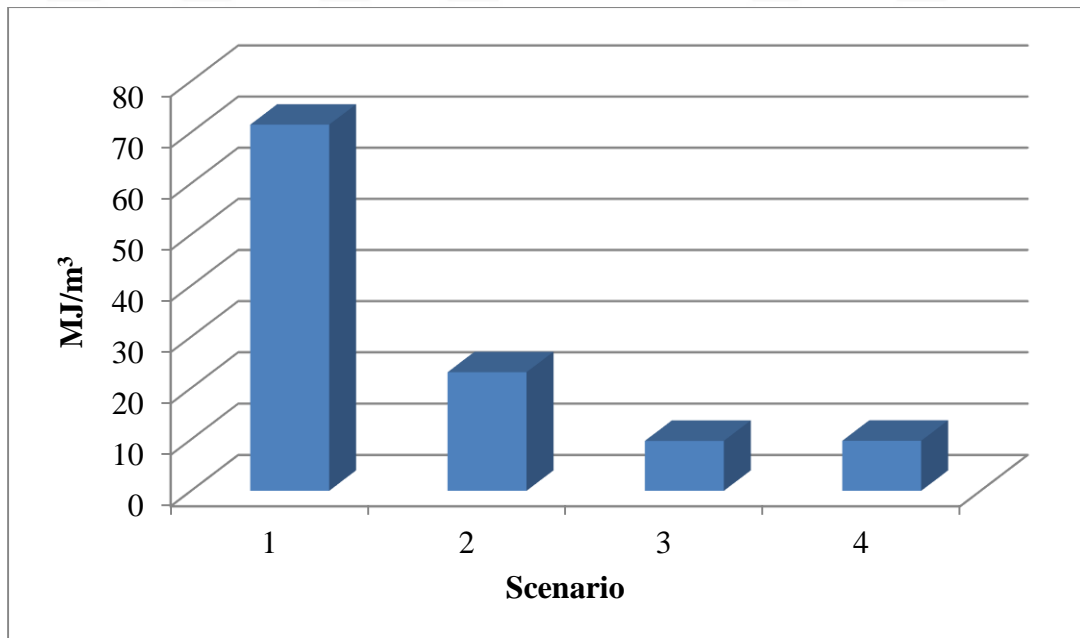


Figure 5.67 Abiotic depletion fossil effects for all scenarios

Toxicity can impact humans, and the environment, such as water, soil. In the scope of this study, toxicity potentials for the four impact categories freshwater aquatic ecotoxicity, human toxicity, marine aquatic ecotoxicity, and terrestrial ecotoxicity were calculated for each scenario. Human toxicity category concerns effects of toxic substances that effect humans. Freshwater aquatic ecotoxicity, marine ecotoxicity, and terrestrial ecotoxicity describes the amount of water, marine, and soil pollution, respectively. As seen from Figure 5.68 – 5.71, Scenario 1 has the highest toxicity impacts for all categories comparing to other scenarios. Any generated scenario which includes segregated flows was found to be the less toxic for both human and environment for all kinds of toxicities.

Photochemical Ozone Creation Potential (POCP), also known as summer smog potential, is a measure of how much a unit mass of harmful trace gases, such as nitrogen oxides and hydrocarbons, contributes to the formation of ground level (tropospheric) ozone in the presence of UV radiation. Although all scenarios have very low POCP effects; among the generated scenarios, Scenario 1 has the highest POCP effects (Figure 5.72).

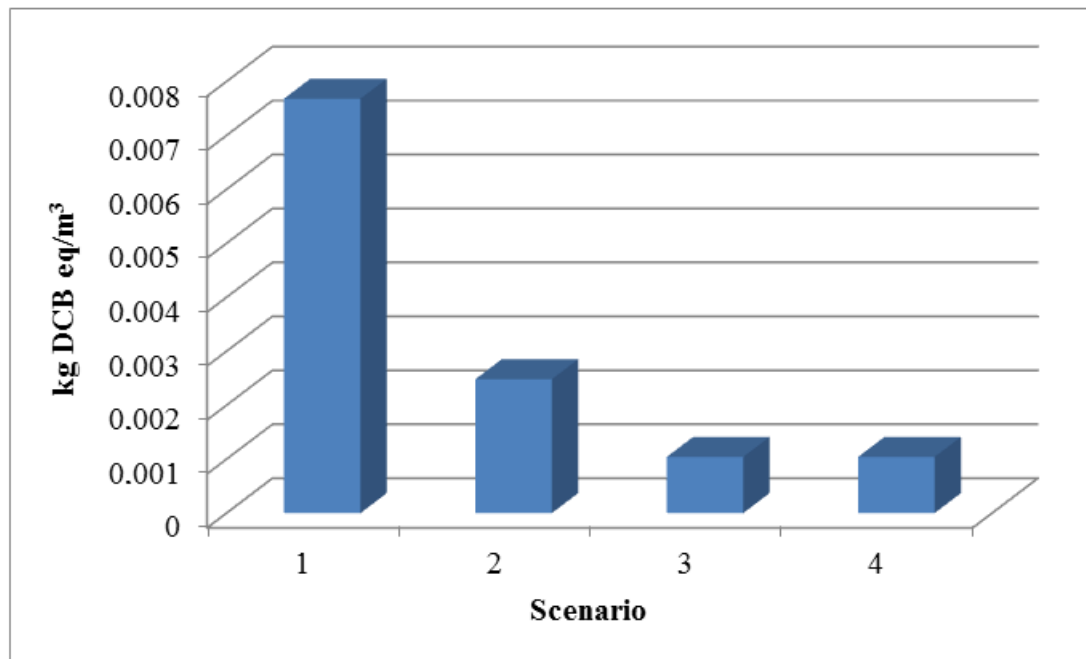


Figure 5.68 Freshwater ecotoxicity potential effects for all scenarios

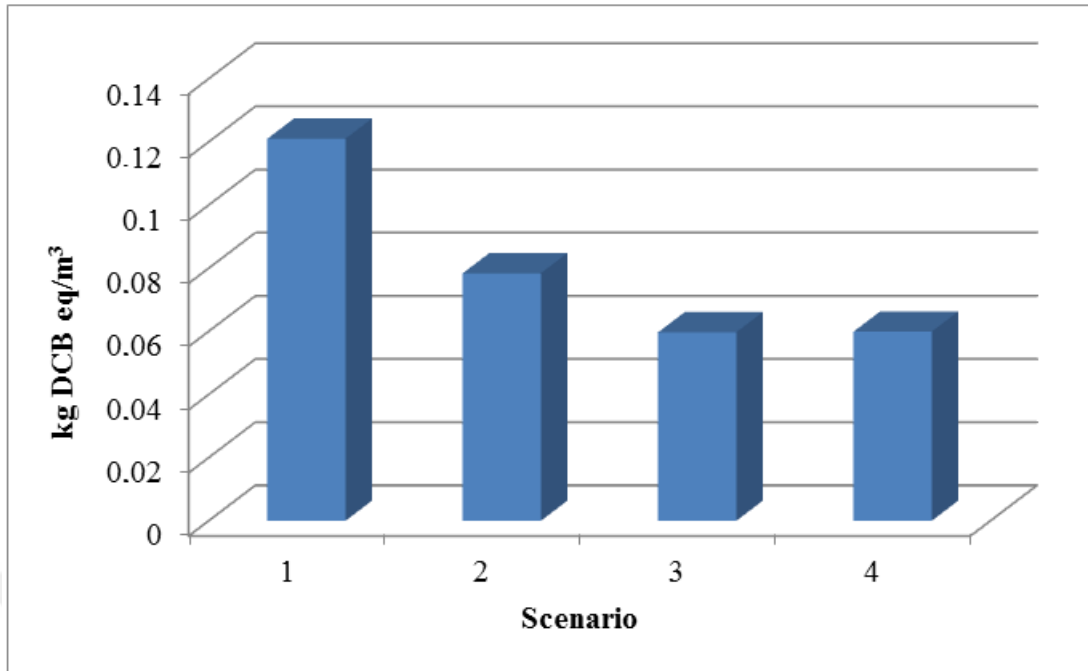


Figure 5.69 Human toxicity potential effects for all scenarios

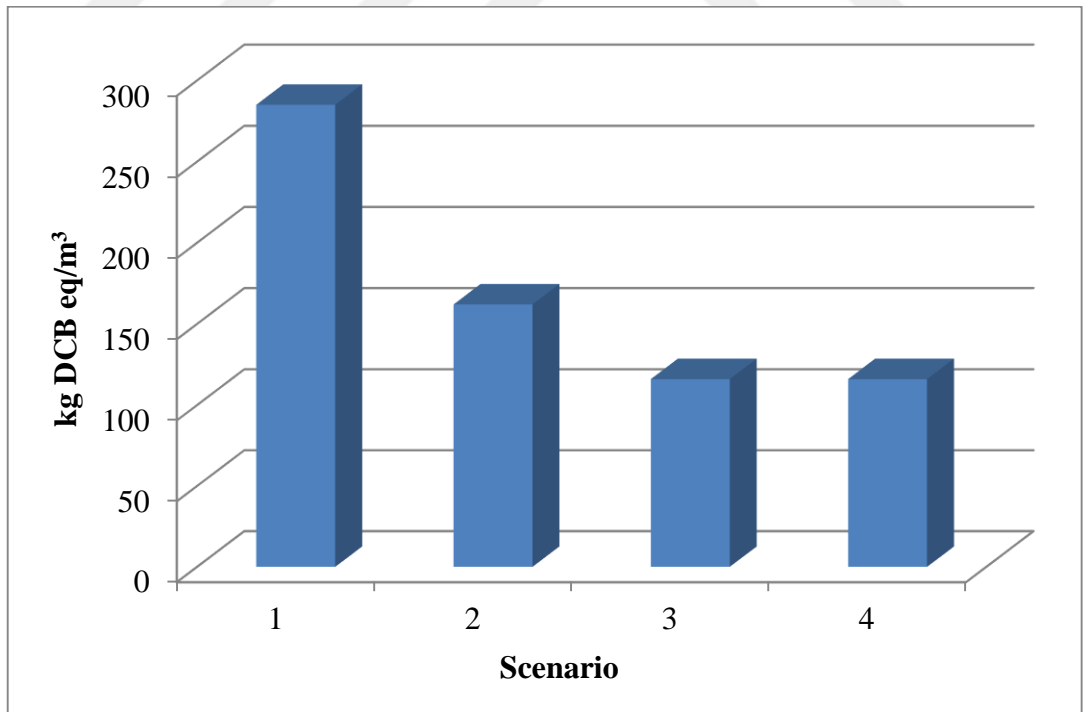


Figure 5.70 Marine aquatic ecotoxicity potential effects for all scenarios

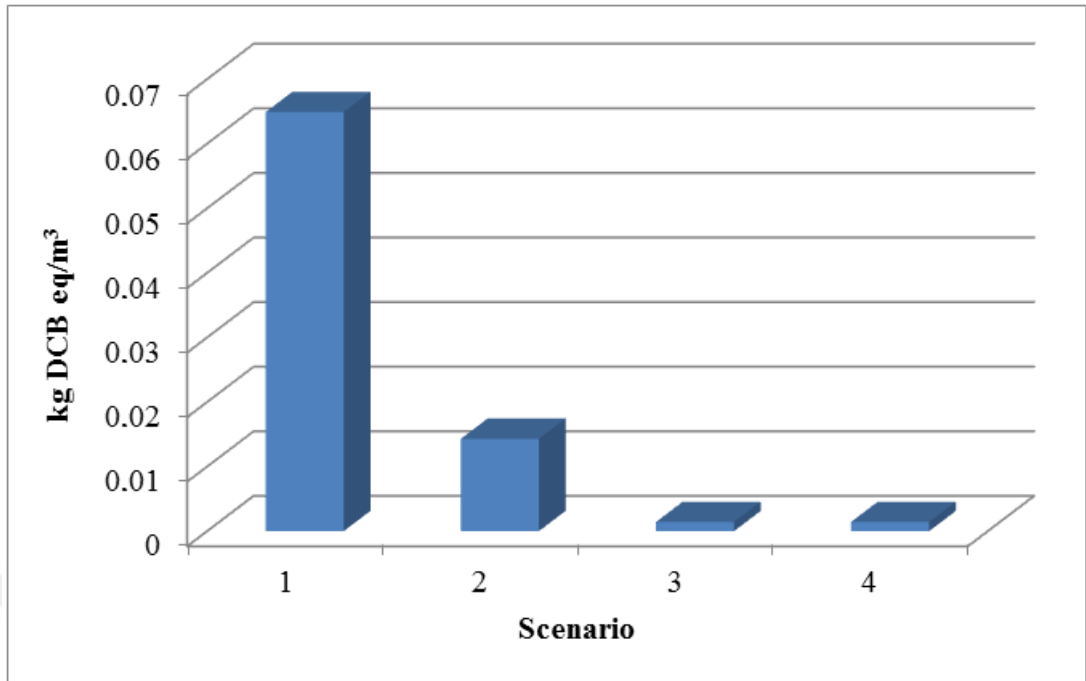


Figure 5.71 Terrestrial ecotoxicity potential effects for all scenarios

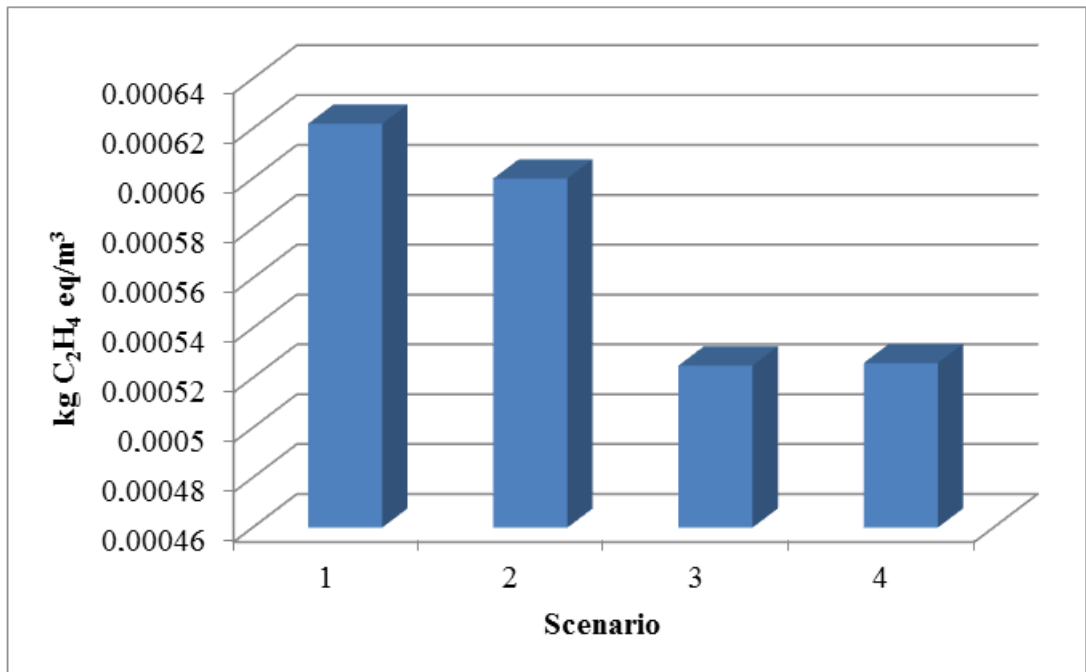


Figure 5.72 Photochemical ozone creation potential effects for all scenarios

## **CHAPTER SIX**

### **CONCLUSIONS AND RECOMMENDATIONS**

#### **6.1 Conclusions**

Life cycle assessment (LCA) has been widely used as a decision support tool to determine the most appropriate wastewater management strategy. In the scope of this thesis, different scenarios were generated for leather industry wastewater treatment and the environmental effects of these scenarios were compared using life cycle assessment tool. Scenarios were developed considering especially chromium removal and recovery alternatives. In accordance with this study, the following conclusions were obtained:

- Depending on the studies' results, Scenario-1, in which combined chromium and sulphur flows are treated in the wastewater treatment plant, was determined as the most harmful alternative for the environment. The chromium and sulphur flows were separated in the rest of the scenarios.
- The separation of chromium and sulphur-rich lime line and recovery of chromium considerably improve the environmental performance of the treatment plant. Therefore, if combined system is not necessary for some reasons, separated flows should be preferred.
- Chromium recovery applications reduce the negative environmental effects (Scenario 3 and 4).
- The LCA results show that energy use is the dominant factor in the environmental impacts of WWTP.
- Any generated scenario which includes segregated flows was found to be the less toxic for both human and environment for all kinds of toxicities.

## 6.2 Recommendations

LCA studies can play significant roles to determine the most appropriate wastewater management strategy. In the scope of this study, most of the processes, such as, construction, sludge management, etc., were considered outside the system boundaries. To determine the most appropriate scenarios, more detailed studies should be implemented and the LCA studies' results should be supported with the economical factors.

In this study, the LCA studies were carried out using the GaBi 6.1 Software. CML 2001 (Institute of Environmental Sciences, Leiden University) impact assessment method was used to determine the environmental impacts. The required data for the software was obtained from the previous laboratory studies, literature, and Eco-invent database which are integrated into the GaBi 6.1 software, as software was developed product-oriented. Therefore we forced creating new processes. Since it is not possible to obtain specific data for all processes, we didn't find useful data for wastewater treatment process phases and some calculations based on theory have been done. Software doesn't directly focus on wastewater treatment stages. It only gives the unit process for the conventional treatment process and it does not let to interference in. For this reason, software should be developed with data that can be obtained from similar studies.

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