Analysis and improvement proposal of a wastewater treatment plant in a Mexican refinery

Master's thesis in Infrastructure and Environmental Engineering

ANA ISABELLA NAVARRETE PÉREZ

Department of Civil and Environmental Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2015
Master's thesis 2015:101

Analysis and improvement proposal of a wastewater treatment plant in a Mexican refinery.
CHALMERS, 2015.

SUMMARY

Water scarcity is a problem that is currently lived in several countries of the world. The level of water scarcity will be different depending on the region of the world where one is located, and the amount and type of contaminants found in water bodies will rely on the different industrial activities realized in the area, the urban development and, the type of treatment facilities found around it. In Mexico, one of the most important industrial activities is the extraction and processing of crude oil; petroleum refining is among the ones that consume the higher amount of water per barrel of crude oil. In this project, the analysis of the state of a wastewater treatment plant in a Mexican refinery (Refinery 1) was done based on interviews and collected information about water quality parameters in the different streams.

REPORT 2015:101

Analysis and improvement proposal of a wastewater treatment plant in a Mexican refinery

Ana Isabella Navarrete Pérez

Department of Civil and Environmental Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2015

Analysis and improvement proposal of a wastewater treatment plant in a Mexican refinery
ANA ISABELLA NAVARRETE PÉREZ

Department of Civil and Environmental Engineering
Chalmers University of Technology
SE-412 96 Göteborg
Sweden
+ 46 (0)31-772 1000

Cover:
[Mexican refinery at night, PEMEX. Mexico, 2014.]

Göteborg, Sweden. 2015.

Abstract

Water scarcity is a problem that is currently lived in several countries of the world. The level of water scarcity will be different depending on the region of the world where one is located, and the amount and type of contaminants found in water bodies will rely on the different industrial activities realized in the area, the urban development and, the type of treatment facilities found around it. In Mexico, one of the most important industrial activities is the extraction and processing of crude oil; petroleum refining is among the ones that consume the higher amount of water per barrel of crude oil. In this project, the analysis of the state of a wastewater treatment plant in a Mexican refinery (Refinery 1) was done. Interviews, information about water quality parameters in the different streams was collected and a visit to the plant took place in order to do so. The treatment plant consists of sumps, API separator, Dissolved Air Flotation (DAF) units, oxidation lagoons and a stabilization lagoon. Most of the treatment units are being impacted by the high concentration of oil and grease present in the process wastewater entering the plant and its inefficient recovery in the different units. The DAF units are non-functional and thus smaller oil droplets (oil emulsions) are not being removed efficiently. A thick layer of oil in the oxidation ponds and the lack of functioning aerators provide a mostly anaerobic environment which is less effective for pollutant removal than an aerobic one. Ammonia, phenol, sulfur and oil and grease concentrations in the wastewater leaving the treatment plant are above to what it is required in the next treatment step (activated sludge). Parameters such as BOD_5, total nitrogen, TSS, and oil and grease of the treated wastewater that is discharged into the water body have shown to be above or very close to the limits recommended by the World Bank for refineries. An intense maintenance and repair is needed in the treatment plant to get a better pollutant removal and the sampling plan is recommended to be analyzed in order to be able to fully understand what is happening exactly in each unit as the amount of data was very limited.

Keywords: Oil refining, process wastewater treatment, oil and grease separators, water quality analysis, pollutant concentration limits, refineries.

Acknowledgement

A special thanks to my family for their amazing unconditional love and support, words cannot express how grateful I am to have you.

I would also like to thank my friends and mentors, Fidel Mejía and Mario Nuñez for all their guidance, counseling and support ever since my journey in the environmental field started.

Also, special thanks to Oskar Modin, for all his help and guidance throughout the development of the project.

Thanks to all the engineers and personnel working in Refinery 1 that were very kind to receive me in the installations and kindly provide information and support.

I would also use the opportunity to thanks Mr. Lars Eriksson, I will always feel honored and grateful for your support and trust during my year of studies in Chalmers.

And finally, to God and all my beautiful angels up there.

Thank you for believing in me.

Table of content

1. Introduction

Water scarcity is a problem that is currently lived in every continent of the world. This is a phenomenon that is caused by nature, as water is not evenly distributed in the planet, but also by anthropogenic activities as its use has been managed very poorly (UN-Water, 2007). Water resources are being overexploited and their use is being reduced due to bad quality problems caused by discharges of contaminated water and runoff.

Some of the major sources of water pollution come from urban, industrial and agricultural discharges. Industries dump an estimate of 300-400 million of tons of polluted waste in water bodies every year and around 80% of the sewage in developing countries is discharged directly without being treated (UN-Water, 2013). Also, nitrogen and phosphorous present in agricultural runoff cause eutrophication problems in rivers, lakes and coastal areas.

Water contamination not only affects negatively the natural ecosystems by decreasing its biodiversity but it also affects human health as the amount of people dying or getting sick by its consumption increases with it. Wastewater from industries can infiltrate into the ground and contaminate aquifers and wells which are normally used as a source for drinking water. Also, economic activities that depend on water are strongly affected when water quality and quantity values are below the minimum required; this could easily impact the annual Gross Domestic Product of a country (UNEP, 2010).

The level of water scarcity will be different depending on the region of the world where one is located, and the amount and type of contaminants found in water bodies will depend on the different industrial activities realized in the area, the urban development, and the type of treatment facilities found around it.

In Mexico, different types of industrial activities can be found along the country such as mining, textile industry, wood, pulp and paper, chemical production, automobile manufacturing, among others. One activity that has a high environmental relevance is the extraction and processing of crude oil as most of the yearly environmental emergencies that affect water and soil are directly related to it (Volke & Velasco, 2002). Also, crude oil and gas processing are quite important activities in the country as around 85% of the total energy produced in Mexico comes from it (SENER, 2011).

The different procedures needed for oil extraction and processing require a great amount of water and, as a consequence, a big volume of wastewater is generated. One example of this can be seen in crude oil refineries, where the amount of wastewater generated can be 0.4-0.6 times the amount of crude oil processed in the installation (Coelho et al., 2006). Wastewater coming from refineries is normally composed of oil, grease and many other toxic organic compounds that can be very harmful to the environment. Mexico counts with a total of 6 petroleum refineries that are owned by PEMEX which is a state-owned company created in 1938. The exact composition of the wastewater coming from them will depend on the different processes being done in each of the plants. The polluted water is normally treated in wastewater treatment plants and further discharged into water bodies such as rivers and the ocean, where people develop different economic and recreational activities. In Mexico, surface water is mostly used for irrigation purposes and, to a lesser extent, distributed for households activities (CONAGUA,2013). In 2013, 244 tons of oil and grease, 1,080 tons of total suspended solids, 424 tons of total nitrogen and 12 tons of heavy metals where discharged in total by the 6 refineries into water bodies (PEMEX, 2013).

More than half of Mexico's area face either high or extremely high water stress (amount of water withdrawn/amount of renewable water). This is due to the fact that most of the industrial activities can be found in the northern and central part of the country where the average water precipitation is much less compared to that in the southern part (CONAGUA, 2013). Four out of the six refineries found in the country are located in areas that have high water stress and thus, it is important that water of good quality is discharged into the water bodies and treated wastewater is reused in order to preserve the natural resource.

According to CONAGUA (2013), a population increase of 20.4 million people is expected for Mexico by 2030. The highest percentage of population growth is expected to happen in places where water stress is already high. The later will cause a reduction in the amount of water available per capita to about 1000 m^3/person/year in these areas, which would make them zones of extremely high water stress. Also, due to climate change, the quality of the available water sources is expected to decrease considerably. Awareness needs to be raised and actions need to be taken around the limited amount of freshwater resources in the country and the need to protect them in terms of quantity and quality.

In this project, the focus will be on analyzing the performance of a process wastewater treatment plant found in one of PEMEX's refineries and, proposing improvement actions in order to increase the quality of the effluents.

2. Theory

2.1 Characteristics of wastewater from refineries

In the refining process of crude oil, the oil is converted into more than 2,500 products by using several chemical processes such as distillation, cracking, alkylation, polymerization, coking, hydrotreating, among others. Wastewater is generated in several of these different processes done daily in the refinery and, based on where this polluted water is generated, it can be classified into two types: process and non-process wastewater. Process wastewater is the one that is generated during the refining process itself and that has been in direct contact with hydrocarbons whilst non-process wastewater normally comes from cooling towers, surface water runoff, equipment flushing, containers cleanse and office facilities (Benyahia, et al., 2006). Normally, these streams are separated in order to accomplish the best treatment possible and to avoid the contamination of a higher volume of water with harsh pollutants.

Process wastewater is produced due to the fact that water is already present in the crude oil when this is received in the refinery. Water can be found in suspension or emulsified with the oil in the well where it was extracted. Moreover, water could have been injected in the well in a liquid or gas form to stimulate the oil's flow up the well (Martel-Valles, et al., 2013). Process wastewater is also produced because water vapor is commonly used as a stripping medium or as a diluent in processes like distillation and cracking units, and because liquid water is used in the desalting units (IPIECA, 2010).

Process wastewater is normally composed of oil, inorganic substances and many other toxic organic compounds. Oil and grease are determined as a group of compounds rather than just one in particular and thus it is the source of many different toxic compounds found in refinery wastewater such as polyaromatic hydrocarbons (PAH), benzene and phenols. Oil is not soluble in water but the nature of the oil phase will depend on the different environmental conditions, for instance, oil can be hydrolyzed under anaerobic conditions into acetate.

The pollutants found in the wastewater will depend on the type of oil being refined, the plant configuration and the processes found in the installation (Saien & Nejati, 2007). For instance, when water vapor is used for distillation and/or cracking units, the vapor is condensed in an environment where hydrocarbons that contain hydrogen sulphide and ammonia are present, thus the produced wastewater has a high concentration of them. Also, when cokers are being used in the installation they can generate wastewater with a high amount of phenols and cyanides. In table 1, the different processes being done in refineries and the possible pollutants present in their wastewater are presented. Because effluents coming from different refineries have diverse characteristics, there isn't a standardized treatment train that could be applied to all.

Table 1. Different refinery's processes and possible pollutants present in their wastewater (Leavitt, et al., 2004).

Process	Possible pollutants in wastewater
Distillation	Sour water (hydrogen sulfide, ammonia, suspended solids, chlorides, mercaptans and phenol)
Fluid catalytic cracking	Sour water (hydrogen sulfide, ammonia, suspended solids, oil, phenols and cyanides)
Catalytic reforming	Sour water (hydrogen sulfide, ammonia, suspended solids, mercaptans, oil)
Alkylation	Spend potassium hydroxide stream (hydrofluoric acid)
Crude desalting	Desalting wastewater (salts, metals, solids, hydrogen sulfide, ammonia, and phenol)
Thermal cracking/visbreaking	Sour water (hydrogen sulfide, ammonia, suspended solids, dissolved solids and phenol)
Catalytic hydrocracking	Sour water (hydrogen sulfide, ammonia and suspended solids)
Coking	Sour water (hydrogen sulfide, ammonia and suspended solids)
Isomerization	Sour water (hydrogen sulfide and ammonia) and caustic wash water (calcium chloride)
Catalytic hydrotreating	Sour water (hydrogen sulfide, ammonia, suspended solids and phenol)
Sulfur removal	Sour water (hydrogen sulfide and ammonia)
Lubricating oil manufacture	Steam stripping wastewater (oil and solvents) and solvent recovery wastewater (oil and propane)

The presence of oil and grease in the treated water discharged into water bodies is detrimental for the aquatic life as a layer of oil is formed in the water surface that decreases the penetration of light and consequently reduces photosynthetic activity and oxygen production. Also, this layer decreases the dissolution of oxygen from the atmosphere into the water affecting the amount of dissolved oxygen present and impacting the amount of species that can survive under those conditions. Furthermore, environmental health is affected as several of the compounds that are found in oil contaminated water are detrimental for life, mutagenic and/or carcinogenic (Alade, et al., 2011).

In general, the contaminants that are found in oily wastewater coming from refineries and that are of concern are: suspended solids, phenols, benzene, ethylbenzene, xylenes, sulphides, ammonia, polyaromatic hydrocarbons (PAH) and chemical oxygen demand (IPIECA, 2010) (Ishak, et al., 2012). If all these compounds are discharged continuously over time in a water body, they can affect quite drastically the health of the ecosystem (Otokunefor & Obiukwu, 2005).

Phenols are compounds that can be highly toxic for humans even when consumed at small concentrations. Chronic toxicity of phenol can cause sour mouth, diarrhea, impaired vision and dark urine in humans and it is also highly toxic for aquatic fauna (Kulkarni & Kaware, 2013). These compounds are very soluble in water and can serve as precursors for the formation of other toxic compounds (El-Naas, et al., 2010). Benzene, toluene, ethylbenzene and xylenes (BTEX) are compounds that are usually found in crude oil. These compounds can be absorbed through the skin when showering or bathing with polluted water or be ingested in contaminated water. Some effects of consumption of benzene in drinking water over a long period of time can be anemia, a decrease in blood platelets and even cancer. If ethylbenzene is consumed instead of benzene, the health effects could be liver and/or kidney failures. Toluene causes the same health effects as ethylbenzene but it can also affect the person's nervous system and xylene consumption can cause damages to the nervous system (USEPA, 2013).

Polycyclic aromatic hydrocarbons (PAH) are rarely produced commercially but are commonly found in crude oil. They are normally formed as a byproduct due to the incomplete combustion of fossil fuels and some sources of PAH in refineries can be cracking operations and crude oil storage (USEPA, 2004). Their solubility in water is dependent on their molecular weight; the higher their molecular weight, the lower their solubility in water. PAH biodegrade slowly under aerobic conditions in aquatic environments, however, if the compounds have a high number of aromatic rings the degradation is decreased quite drastically; they can remain in the environment from 100 days to a couple of years. Since these compounds are liposoluble, they can be stored in the fat of certain animals and be consumed by humans. Some PAH's have shown to have carcinogenic and genotoxic effects in mice (WHO, 2003).

When ammonia is present in high concentrations in surface water it can cause direct toxic effects in the aquatic life established in it, such as the reduction of oxygen in the blood of fish. Its toxicity to animals can vary depending on different parameters such as temperature and pH as this will help to change the oxidation state of the molecule (USEPA, 2013). Long exposure to nitrates and nitrites can provoke hemorrhage of the spleen and cause the displacement of oxygen in the blood (USEPA, 2006). Hydrogen sulfide is a very toxic and corrosive gas that is formed in aqueous environments that have sulfate and organic matter. This compound is highly toxic for aquatic life, even when it is present in small concentrations, and causes obnoxious odors (Altas & Büyükgüngör, 2008).

Some studies have been made to determine the impact of water effluents coming from refineries. Wake (2005) has shown that refinery effluents are toxic at different concentrations for algae, invertebrates and fish; some species being more sensitive than others and the toxicity varies depending on the life cycle of the organism. Also, the area around where the discharges were taking place normally showed a low diversity and quantity of fauna due to the tough environment created by these discharges. An enrichment of algae and biomass can also be seen due to the increase of organic chemicals, like ammonia, in the water. However, as explained before, each refinery effluent pollutant content will depend on the operations being made and the crude oil being treated, and thus the effects to the environment will be different for each case.

2.2. Commonly used treatment techniques

Wastewater coming from refineries cannot be discharged directly into water bodies and thus it requires a primary, secondary and tertiary treatment to remove the contaminant load found in it. With a primary treatment all the settleable and floating material found in the wastewater (like suspended solids and oil) are removed using physical and chemical operations; using a secondary treatment all the dissolved contaminants are removed from the water mostly by chemical/biological processes and with a tertiary treatment the effluent is conditioned to meet the different final discharge standards (Bagajewicz, 2000).

With a primary treatment pollutants principally oil, grease and solids are removed; this is an extremely important and critical step since the presence of oil, either free, dissolved or emulsified, can affect quite drastically the efficiency of the consecutive treatment units and thus affecting the quality of the effluent discharged in the water body (Schultz, 2006). Primary treatment is normally done in refineries using the American Petroleum Institute (API) separators coupled with Dissolved Air Flotation (DAF). API separators work by splitting the compounds and solids in the water based on their specific gravity; compounds that have a specific gravity lower than water will float and be removed using a skimmer, whilst heavy materials will sink in the bottom of the tank and be removed from time to time. There are different configurations of API separators, like corrugated plate interceptors (CPI) or parallel plate separators (PPS).

In DAF units, small size bubbles are used to remove suspended particles in the water; the bubbles attach to the particles and make them float to the surface where a foam/pollutant layer is formed. The foam/pollutant layer is frequently skimmed off in order to avoid the sedimentation of solids. One requirement for the use of DAF is that the water must be pretreated with a coagulation/flocculation procedure in order to stabilize the charges of the pollutants and encourage the formation of small aggregation which will improve the efficiency of pollutant removal in the unit (Russell, 2006). Normally after this, an equalization stage or unit is used in order to regulate the amount of water and the amount of pollutants going into the secondary treatment step; the latter is to avoid any toxic shock that could affect the efficiency of contaminants' removal. Flow regulation tanks and lagoons are common examples of equalization units.

When using a secondary treatment, dissolved organic pollutants are being removed from wastewater mostly through microbiological activity. Microbes can grow suspended in the wastewater (suspended growth) or attached to surfaces with the formation of biofilms (attached growth). When suspended growth techniques are used, microbes are kept in suspension in the wastewater where they degrade the organic matter in order to grow and reproduce. Suspended growth techniques can be done in an aerobic or anaerobic environment, being the first ones the most commonly used in refineries. Some examples of aerobic suspended growth techniques found in this type of installations are activated sludge reactors and aerated lagoons. When attached growth techniques are used, microorganisms grow attached to a packing material that is put in the reactor. This material can be made out of plastic, gravel, rock or other synthetic material. Examples of this type of process are trickling filters and rotating biological contactors (IPIECA, 2010).

Nitrification/denitrification reactions are very important for the reduction of ammonia or nitrogen found in the wastewater. These chemical reactions are also microbiological driven; nitrifying bacteria convert ammonia (NH_3) in the water into nitrate (NO_3), and denitrifying bacteria convert nitrate (NO_3) into nitrogen gas (N_2). Each reaction needs different environmental conditions for them to happen, and thus two different tanks are needed for this purpose: an aerated tank where nitrification occurs and an anoxic tank where denitrification reactions occur.

Tertiary treatment encompasses techniques that would help to meet discharge standards and remove all the remaining compounds that could not be eliminated via primary and secondary treatment. Examples of tertiary techniques are activated carbon filters, oxidation processes, granular filtration and membrane filtration. With these units, total suspended solids, chemical oxygen demand and other non- biodegradable compounds such as dissolved metals and PAH’s can be removed from the wastewater (IPIECA, 2010).

Sludge is generated as a byproduct in most of the wastewater treatment units such as the API separators, DAF and activated sludge. This sludge needs to be treated before its discharge or reuse due to the amount of pollutants present in it. Some of these contaminants found are petroleum hydrocarbons, metals, solids, organic compounds, among others. The composition at which these contaminants can be found in the sludge depend on the type of crude oil being processed in the refinery, the processes used for oil-water separation and the amount of sludge being mixed with existing oily sludge coming from the refining processes . The most common organic compounds present in the sludge are alkenes, benzene, xylene, toluene, ethyl-benzene, phenols and polycyclic aromatic hydrocarbons (Kriipsalu, et al., 2008).

2.3. Legislation for pollutant discharge coming from refinery effluents

The United States Environmental Protection Agency (USEPA) determined in 1974 some guidelines and standards for effluents coming from petroleum refineries; these limits were modified several years after they were stablished, 1985 being the last year when this was done. In the guideline, the different processes done in the refineries are divided into 5 different categories; each category has different limits for the different pollutants produced in the wastewater effluents. In table 2, the amount of pollutants permitted when applying currently available best practice control technologies for the category that integrates all the water discharges produced in any facility that manufactures petroleum derived products can be seen. These values need to be further multiplied by a factor depending on the process' configuration of the refinery and the amount of barrels per day that are treated in the installations, and by the refinery's feedstock rate to obtain the allowed kg/day of pollutant that can be discharged.

Table 2. Pollutant concentration limits for effluents coming from petroleum refineries (USEPA, 2012).

Pollutant	Maximum for any 1 day (kg/1000 m^3 of feedstock)	Average of daily values for 30 days (kg/1000 m^3 of feedstock)
Biochemical Oxygen Demand (BOD_5)	54.4	28.9
Total Suspended Solids (TSS)	37.3	23.7
Chemical Oxygen Demand (COD)	388.0	198.0
Oil and grease	17.1	9.1
Phenolic compounds	0.40	0.192
Ammonia as N	23.4	10.6
Sulfide	0.35	0.158
Total chromium	0.82	0.48
Hexavalent chromium	0.068	0.032
pH	6-9	6-9

The European Union parliament created a water framework directive that aims to safeguard the EU's water quality and quantity; they established a strategy against water pollution and determined a list of priority pollutants found in wastewater effluents based on their risk to the environment. The directive 2013/39/EU list has the maximum allowable concentration and the annual average of pollutants such as benzene, phenol, and polyaromatic hydrocarbons depending whether if it's inland surface water or other surface water. Another directive, the directive 91/271/EEC, determines that the concentration of parameters such as BOD_5, COD and total suspended solids coming from urban sewage discharges should be 25 mg/l of O_2, 125 mg/l of O_2 and 35 mg/l (>10,000 people) respectively and, total phosphorous and nitrogen concentrations of 1-2 mg/ l and 10-15 mg/l. Furthermore, in the directive 2013/39/EU the environmental quality standards for priority substances and other pollutants are stated (see Annex I. Table 1).

Similarly, the International Finance Corporation (IFC) of the World Bank Group establishes guides on environment, health and safety for different types of industries; these guides serve as a technical reference as they contain certain examples of the current and recommended international practices that would help to have a good environmental performance. In the guide for the oil refining industry, they determine the limit concentration for certain pollutants in the effluents coming from refineries (see table 3.). These limits are based on what has been stablished in certain countries that are members of the IFC and that have a recognized normative frame (IFC, 2007).

Table 3. Limits for pollutants found in effluents coming from refineries according to the World Bank Group (IFC, 2007).

Pollutant	Value	units
pH	6-9	
BOD_5	30	mg/l
COD	150	mg/l
TSS	30	mg/l
Oil and grease	10	mg/l
Total chromium	0.5	mg/l

Hexavalent chromium	0.05	mg/l
Copper	0.5	mg/l
Iron	3	mg/l
Total cyanide	1	mg/l
Lead	0.1	mg/l
Nickel	0.5	mg/l
Mercury	0.02	mg/l
Vanadium	1	mg/l
Phenol	0.2	mg/l
Benzene	0.05	mg/l
Sulfides	1	mg/l
Total nitrogen	10	mg/l
Total phosphorous	2	mg/l
Temperature increment	<3°	°C

In Mexico, the official norm NOM-001-SEMARNAT-1996 establish the different limits of water quality parameters commonly measured in all types of effluents being discharged to water bodies; these limits are determined based on the type of water body where the discharge is taking place and the different activities for what the water from this water body is being used (see Annex I. Table 2.). Specific limits for pollutants discharge can be determined by the National Commission of Water in special cases where possible harmful contaminants are not specified in the previously mentioned norms and/or when the environmental state of the receiving water body is poor; discharges from Mexican refineries are mostly regulated by either Particular Discharge Conditions (PDC) or by the NOM-001.

The Mexican Federal Law of Rights in Terms of National Water (Ley federal de Derechos en Materia de Aguas Nacionales) stablishes the payment of a quota for the right to discharge water into a water body, depending on the type of water body receiving, and penalties when the concentration of pollutants in discharges of different type of industries or users exceed the limits stablished by the NOM-001-SEMARNAT-1996 or its own PDC; the amount to be paid would depend on the concentration of COD and TSS found in the discharged water, the type of water body where it was discharged and the water availability in the zone.

3. Background

PEMEX is a company that cooperates with the state but it is not part of its administration (a mixture of a public and private owned company); it is the only company in charge of the exploration, exploitation and sales of the Mexican oil and gas. So far, PEMEX's environmental protection strategies for water usage in refineries have been focused in the reuse of their own treated wastewater in some of their processes as a way to decrease the amount of fresh water extracted and used, and to reduce the amount of water discharged into water bodies. All of the Mexican refineries are equipped with treatment plants that allow the reuse of wastewater coming from their own processes either in cooling towers and/or in boilers for steam production. Some refineries also treat municipal wastewater in order to satisfy their processes' demand of water and reduce their fresh water consumption.

In 2013, refineries contributed to a large proportion of contaminants discharged into water bodies, 34% of the total amount of pollutants discharged by all PEMEX's installations (PEMEX, 2013). Before 2012, the wastewater treatment plants located in the refineries were operated by external third parties. The treatment plants are now being operated by PEMEX's personnel and, according to PEMEX's sustainability report (2013), there was a 4.5% increase in the overall raw water consumption of the company from 2012-2013 because of all the adjustments done due to the later. The company's personnel had to be trained and prepared in order to take care of the wastewater treatment plants; adjustments are still being made in some of the wastewater treatment installations.

The wastewater treatment plant that will be analyzed is found in Refinery 1. Refinery 1 is located in an area of Mexico that is considered to have a high water stress as determined by the National Commission of Water (CONAGUA). Water reuse and discharge are very critical for the region being studied due to the water scarcity present. In Refinery 1, the wastewater treatment process is divided into two sections or treatment trains: an "effluents' treatment" plant (ETP) and a "process wastewater treatment" plant (PWTP). In the ETP, the oil, grease and solids are separated from the water with the use of sumps, API units, CPI units, DAF, oxidation and stabilization ponds; a regulation pond is also used between the CPI separators and the DAF units. In figure 1, a diagram of the ETP can be observed.

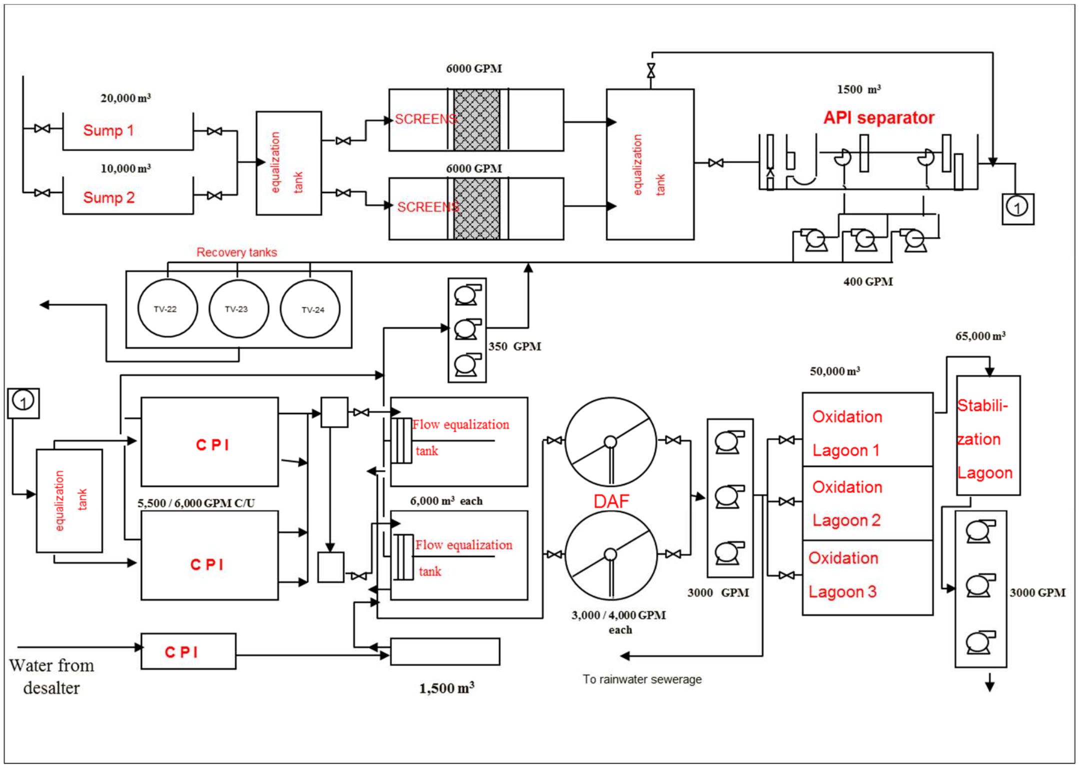


Figure 1. Diagram of "effluent treatment" plant (ETP)

In the PWTP, the wastewater coming from the ETP goes through an activated sludge unit, then to a sedimentation tank and finally to a chlorination basin. Afterwards, a portion of this treated water is discharged into a nearby water body, used for firefighting and/or for irrigation activities; the remaining treated water is combined with treated municipal wastewater to be used as water make-up in the cooling towers.

The mixture of treated municipal wastewater and process water is further processed with cold lime softening, followed by recarbonation with CO_2 and chlorination before its use in the cooling towers. Cooling towers blowdown is then treated for its use in steam production boilers; the water goes through a warm lime softening process, recarbonation with CO_2, filtration and reverse osmosis in order to be suitable for its use in the units. It is important to mention that the municipal wastewater used for the cooling towers water make-up comes from a treatment plant close to the refinery installations (see figure 2).

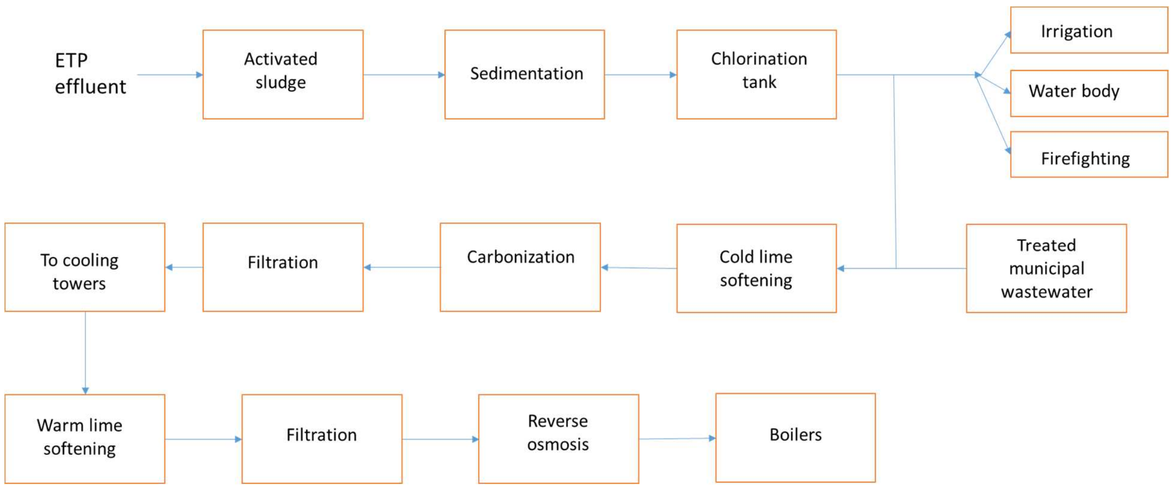


Figure 2. Diagram of "process wastewater treatment" plant (PWTP)

The pollutant discharges limits coming from Refinery 1 into water bodies are determined by a Particular Discharge Conditions (PDC) established by the National Commission of Water (CONAGUA).The PDC parameters to be measured and their limits are based on what is stablished in the Official Mexican Norm NOM-001-SEMARNAT-1996 but with some clear modifications; the exact limits can be seen in table 4.

Table 4. Pollutant concentration limits for discharges from Refinery's 1 wastewater (CNA, 1997).

Parameter	Monthly average	Daily average	units
Temperature	40	40	°C
Oil and grease	15	25	mg/l
Floating material	absent	Absent	
Settleable solids	1	2	ml/l
TSS	150	200	mg/l
BOD_5	150	200	mg/l
Total nitrogen	40	60	mg/l
Total phosphorous	20	30	mg/l

Arsenic	0.2	0.4	mg/l
Cadmium	0.2	0.4	mg/l
Cyanide	2	3	mg/l
Copper	4	6	mg/l
Chromium	1	1.5	mg/l
Mercury	0.01	0.02	mg/l
Nickel	2	4	mg/l
Lead	0.5	1	mg/l
Zinc	10	20	mg/l
Fecal coliforms	1000	2000	MPN/100 ml
pH	between 5-10	between 5-10	

Refinery 1 was built around the 70's and the effluent treatment plant was constructed with it. The ETP was originally designed to treat around 3,000 gpm (189 l/s) of wastewater, this considering that the refinery would be treating around 235,000 barrels per day of crude oil. The plant was designed to treat wastewater with a maximum amount of oil and grease of 60,000 mg/l, a maximum phenol content of 1-3 mg/l, maximum temperature of 35°C and a pH of 6-8.5. The original design consisted of the sumps, CPI separators, DAF and the oxidation and stabilization ponds; these were supposed to treat all the process wastewater such as those from pumping stations, process areas, purges coming from storage tanks, laboratories, etc. Rain water was not considered to be treated in the effluent treatment plant and wastewater from the desalter was considered to be treated separately. Years later, some new process units were installed in Refinery 1; some of them were alkylation units, coking units and hydrogen sulfide removal units. The later helped to increase the processing capacity of the refinery from 235,000 to 275,000 barrels per day of crude oil. API separator units were added to the ETP but no other major changes were done to the plant.

Several problems have been registered for some years about the quality of the water leaving the ETP from Refinery 1, most of them related to the amount of crude oil and grease contained in the water that is received in the activated sludge process at the PWTP. Also, problems with the water quality of the effluent going into the water body have been registered in previous years; concentration of oil and grease, total nitrogen, ammonia and salts very close to the established PDC limits and over them have been presented very often. Similarly, ammonia and salts concentration have shown to be above the limits for its reuse as water make-up in cooling towers after its tertiary retreatment in the PWTP plant.

According to PEMEX's sustainability report (2014), Refinery 1 was the 2nd major contributor of total pollutants discharged into water bodies and also one of the biggest contributors of oil and grease, and total suspended solids discharged in that year (only considering oil refining installations).

Because of the later, a focus will be done in the ETP area as the water treated in here goes into a biological treatment in the PWTP before it is discharged into the water body and a failure the ETP could affect the efficiency of the treatment units in the PWTP.

4. Materials and methods

4.1. Interviews

A visit was made to Refinery 1 in order to obtain all the information about the effluent treatment plant. Data about plant design, laboratory analysis, maintenance and physical aspects of the plant were collected and analyzed. A visual inspection was done through the ETP and the PWTP to check the physical state of the plants and different meetings were held with the people in charge of the maintenance of the plant and the operators.

An operations' engineer of the ETP was in charge of the visit around the facilities and the one who was interviewed about the normal operation of the different units, maintenance being done and common problems found in them. Also, he was questioned about the conditions of the equipment and future maintenance planned for the plant. An engineer of the process engineering area was also interviewed to obtain information about the design, plant's layout and different operation parameters of the units in the ETP.

The chief manager of the environmental protection department in Refinery 1 was also interviewed. He was questioned about previous environmental studies done in the ETP, law requirements for the effluents coming out of the refinery, environmental audits done by the government, registered discharges and previous problematics or lawsuits that they have received due to the quality of their discharges into the water body.

The refinery has a certified laboratory which is in charge of measuring different parameters along the ETP. The area engineer and the engineers in charge of doing the measurements were questioned about the parameters that were analyzed in the ETP, the different sampling points, the frequency at which these were taken, the procedures by which these parameters were measured and how they were recorded.

The operations' engineer of the PWTP was also interviewed; questions about the common problems found in the plant, the operation of the units, maintenance done, and parameters measured were done. This same person was in charge of showing the facilities of such plant. This area counts with a laboratory were they measure certain parameters in the PWTP but this one is not certified; every once in a while, an external certified laboratory is called to corroborate the measurements being done in the lab.

4.2. Laboratory analyses

People from the refinery's certified laboratory measure parameters in the ETP once a week, on Thursdays; these are normally taken in the morning. Parameters such as ammonia, pH, oil and grease content, COD, sulfur, phenol, TSS and BOD_5 are analyzed. The only exception is with oil and grease measured in the effluent of the API separator and the pumping sump that goes into the oxidation lagoon which is measured daily at 0:00, 7:00 and 15:00 hours. The parameters measured depend on the unit being analyzed and the sample point (see table 5). All the different analysis are performed based on Mexican norms that determine the procedures that need to be done in order to obtain the parameter's values; such norms are shown in table 6.

Table 5. Sampling points and parameters measured in ETP.

Sample point	Parameters measured
Influent to API separator	pH
	Oil and grease
Effluent of API separator	pH
	Oil and grease
Effluent of flow equalization tank	pH
	TSS
Effluent of DAF	Oil and grease
	pH
	Ammonia
	COD
	TSS
	BOD_5

Effluent of oxidation ponds	pH
	Ammonia
	Oil and grease
	COD
	TSS
	BOD_5
Effluent of stabilization pond	pH
	Ammonia
	COD
	Phenol
	TSS
	BOD_5

Table 6. Mexican norms that specify the procedures for the measurement of each parameter.

Parameter	Mexican norm
COD	NMX-AA-030-SCFI-2001
BOD_5	NMX-AA-028-SCFI-2001
Oil and grease	NMX-AA-005-SCFI-2013
phenol	NMX-AA-050-SCFI-2001
pH	NMX-AA-008-SCFI-2001
TSS	NMX-AA-034-SCFI-2001
Total nitrogen/ammonia	NMX-AA-026-SCFI-2010

The values of this parameters from 1st of January of 2014 until the 23rd of March of 2015 were provided by the certified laboratory. The absence of measurement of these parameters and lack of data are due to the fact that the samples were not taken by the operator in turn, the operator was absent that day, the sample was not considered representative, the levels of explosivity in the sewer were too high, the actual conditions of the place of measurement were too risky for the operator, the sample was contaminated or the amount of crude oil in the sample was too high. When not enough data was obtained for certain streams in this time range, information from 2007-2009 or from 2010-2013 was used.

4.3. Statistical analysis

The monthly average, standard deviation, maximum and minimum values were calculated for each parameter in the mentioned range of time. The averages were compared with the design specifications of each treatment unit and their removal performance was analyzed.

Also, a statistical analysis was done to determine whether there is a significant difference between the concentration of certain parameters in the influent and effluent in some of the units of the ETP. This was realized by using the concentration measurements done in the same day for the influent and effluent of each unit and with the application of a paired t-test using Microsoft Excel. A single sided or one tail test was used in most of the cases as there is an expected reduction of the parameters in each units. For the analysis, the obtained one tail probability was compared with a level of significance (α) of 0.05.

Some correlations were also done for certain parameters in some of the streams in the ETP. The latter was done by plotting the parameters against each other with the use of Microsoft Excel.

5. Results and discussion

The ETP is currently receiving process wastewater coming from the desalter units, pretreated sour water, coking units, hydrodesulfuration units, distillation units, purges from cooling towers and even water coming from the rain detention basins when the capacity of these units is exceeded.

The plant does not have any measuring devices between the units, but it has a flow meter at the end to check the amount of water leaving the ETP and entering the PWTP. According to analyses previously done, the flow of wastewater entering the ETP is on average 186 l/s, which is around what the plant is supposed to be treating by design. Next a description of the state of the plant will be presented for each unit of the ETP.

5.1. Physical state of the plant

5.1.1. Sumps

Two sumps in parallel are at the entrance of the ETP, receiving the wastewater coming from the process area. The first sump (sump 1) has a capacity of 20,000 m^3 while the second (sump 2) has a capacity of 10,000 m^3. The main function of these two sumps is the regulation of flow into the ETP especially during the rainy season or when there is a big volume of water being discharged from the process area. Both of the sumps are covered with a liner in order to avoid wastewater infiltration into the ground.

One of the first problems that was evident in sump 1 was the presence of large gas bags formed between the liner and the sump's bottom; this doesn't just decrease its capacity but, because the liner was detached in several parts around the sump, it increases the risk of contaminated water infiltrating the ground. This gas bag formation happen mostly because of wastewater leaking through the liner and microbes in the soil start forming gases (Scheirs, 2009).

The incorrect placement of sump's lining also represents a major risk because sump 1 is used as a collection basin for all the oil and grease collected along the units present in the ETP. This is due to the fact that most of the units don't have a fully operational oil and grease skimmer or don't have a skimmer at all. Also, because there is a provisional pumping system that takes the oil and grease accumulated in sump 1 into the oil recovery tanks. The recovery tanks are frequently drained and the separated oil is sent back to process units for further treatment.

Oil and grease from the flow equalization ponds, and the oxidation and stabilization ponds are discharged into sump 1 with the use of a supersucker vacuum truck. This type of discharges into sump 1 can create turbulence in the water and as a consequence emulsions can be formed. The creation of emulsifications before the API separator can affect greatly the degree of oil and grease recovery in such units, as the separation there is done by gravity and depends on the droplet size. API are designed to remove oil and grease with droplet size of 150 µm or higher; smaller oil droplets won't be removed as they would require a longer residence time to be separated in an efficient way (Schultz, 2005).

The difference between sump 2 and sump 1 besides its capacity (10,000 m^3) is that this one counts with a gas vent system that helps to remove the formed gas and keep it without any gas bags. Sump 2 sometimes receives the oil and grease coming from the flow equalization ponds that is recovered with a supersucker vacuum truck, and then it is further pumped into the sump 1 for its recuperation in the recovery tanks.

Based on an operation report of the ETP done in March 27th 2015, the level of oil in sump 1 is around 1.35 m and the level of water is around 1.05 m. The total height of sump 1 is 2.62 m but, by design and during normal operation conditions, the level of water should be around 2 m. The level of oil in sump 2 is around 1.05 m with a water level of 1.30 m. The total height of the sump is 2.47 m but it should be normally operating with a water level of 1.85 m.

Taking into consideration the area of sump 1 and 2, approximately 13,613 m^3 (85,625 bls) of oil are contained in sump 1 while 6,300 m^3 (39,630 bls) are floating in sump 2; the later represents an approximate 31% and 14% of the daily crude oil processing in refinery 1 (275,000 bpd).

5.1.2. API separation units

Before the wastewater enters the API separators it has to go through a pair of screens that help to remove big solids and garbage that could be present. The screens are made of stainless steel and have an orifice size of 3/8 inches (0.95 cm). These screens are supposed to remove the solids and be self-cleansing, however, the mechanism by which this is done is damaged in one of the screen and thus the cleaning has to be done manually if the screen get clogged; the traction chains of the motor are missing and operators mention that it has not being working for some years. The second screen is normally non-operational but is in good conditions for it.

The API separator has 4 cells or channels; all of the channels have a metallic cover and oil and grease is removed with the use of a half-pipes skimmers installed close to the outlet of each cell. API separators receive wastewater coming from sumps 1 and 2, but also has a direct discharge of wastewater coming from the desalter unit in the refinery.

The API separators found in Refinery 1 are in an extremely poor state and only 3 of the 4 cells are functioning. The covers of the units have a high degree of corrosion and the solids' dredge is non-operational. The floating oil and grease is collected with the half-pipes and pumped into the recovery tanks. There is not any measurement equipment in the API so the operators don not know for sure the amount of water coming into the unit, the residence time of the water, or the amount of oil being recovered. When the half-pipes of the separators are clogged or for some reason are not working a supersucker vacuum truck is used to remove the oil and grease and sent to sump 1 for its further pumping into recovery tanks.

According to the operators, the dredge hasn't been functional for more than 5 years and thus the amount of accumulated solids can be high as they haven't been removed. Based on some rough measurements done by them, they estimate that the height of the solids' layer in the units is around 70 cm. Also, the separator doesn't count with a fully functional sludge removal mechanism which is one of the most important parts of the unit. All of the screw conveyors present in the API separator are currently non-operational and the same goes to the sludge pumping system. The plant counts with a sludge hopper were the settled solids from the API separators should be pumped. The hopper is corroded and hasn't been receiving solids ever since the conveyors failed.

5.1.3. CPI and flow equalization lagoons

After the water has passed through the API units it is supposed to go to a series of CPI separators. According to the operators, these units haven't been operational for quite some time (more than 12 years) and thus the valves leading to these units are closed. They mentioned that the units used to get clogged frequently which lead to the installation of the API units and the discontinued use of the CPI units. Instead of going to the CPI separator, the water goes to a pair of flow equalization lagoons with volume capacity of 6,000 m^3 each.

The flow equalization lagoons have a noteworthy layer of oil in the surface due to the poor oil removal efficiency of the API separator. According to a report done by the operations area in March 27th 2015, a layer of oil around 0.24 m and 0.3 m can be found respectively in each lagoon. The lagoons count with half-pipes for the removal of the floating oil and grease which should be then pumped to the recovery tanks, however, the half-pipes are overflowed and some of them are non-functional due to damages in their structure. Supersucker vacuum trucks are used to remove the oil from the lagoons, which is then sent to the sumps and then into the oil recovery tanks. After the wastewater has passed through the flow equalization lagoons, they go to the DAF units.

5.1.4. DAF units

The ETP counts with a pair of DAF units with a capacity of 3,000 gpm (189.3 l/s) each; these DAF units were constructed considering that the concentration of oil in the wastewater entering was going to be around 70 mg/L with a maximum of 300 mg/l. The effluent coming from these units was expected to have an oil concentration of 5- 10 mg/l.

The DAF units are currently not functioning and they are used basically as retention basins, where the water only passes through the tanks; air is not being injected in to the tanks and the pressurized system to create the bubbles is also not working. Both of the tanks are overflowed with oil and a thick layer of oil and grease can be seen on top of the units. According to the refinery's personnel, the DAF units have been non-operational and have remained the same for more than 12 years.

5.1.5. Oxidation lagoons and stabilization lagoon

The plant counts with 3 oxidation lagoons that altogether have a volume of 50,000 m^3 and are 306 m long and 65.5 m wide. The oxidation lagoons were designed to receive a flow of wastewater of 6,000 gpm (378.5 l/s) with a BOD_5 content of 270 mg/L, a temperature of 30°C and a pH of 6-8.5; the residence time expected in the lagoons based on the design was 4.2 days.

Currently, one of the three oxidation ponds is out of service due to maintenance work being done. The lagoons used to have superficial aerators to help the oxidation and degradation of the pollutants in water (3 in each lagoon), however, the 9 aerators were damaged and thus are not working in any of the oxidation lagoons. The company just purchased barometric hyper aerators that are waiting to be installed but for that they need to remove the sediments from the pond as their level is already too high and make installation of the equipment difficult.

Stripped water is being received in the oxidation ponds, together with the effluent coming from the DAF units. In both of the lagoons, a thick layer of oil can be seen. According to an operation report done on March 27th 2015, one of the oxidation ponds has a level of oil of 0.20 m and 2.22 m of water; the other oxidation pond has a level of oil of 0.25 m and a water level of 2.14 m. Using the dimensions of the lagoons, the latter means that a total of 9,019 m^3 (56,720 bbl) of oil are currently floating in both of the lagoons.

To reduce the amount of TSS and oil and grease in the wastewater different quantities of a coagulant and a flocculant are being added to the stabilization pond and an emulsion breaker is added in the first oxidation pond. This is being done by an external company that was hired to do so.

After the water has passed the oxidation lagoons, it is discharged by gravity into a stabilization lagoon that has a capacity of 65,000 m^3. This lagoon was designed to treat 6,000 gpm (378.5 l/s) of wastewater, with a BOD_5 content of 60 mg/l and a pH of 6-8.5 and have retention time of 1.56 days. In the stabilization pond, a thin layer of oil and grease can still be observed some parts of the unit, but in the rest just iridescence can be perceived.

5.2 Water quality analysis

The different units were designed and built to provide an effluent with a certain water quality. Some of these design parameters are presented in table 7.

Table 7. Design parameters for ETP in Refinery 1.

Stream	parameter	value	Unit
Influent API separator	Oil and grease	6	% vol
Effluent API separator	Oil and grease	0.03	% vol
Effluent Flow equalization lagoon	Oil and grease	300	mg/l
	TSS	350	mg/l
Effluent DAF	Oil and grease	15	mg/l
	TSS	100	mg/l
	BOD_5	270	mg/l
	phenol	3	mg/l
Effluent Oxidation lagoons	Oil and grease	10	mg/l
	BOD_5	60	mg/l
	phenol	0.05	mg/l
Effluent Stabilization lagoon	Oil and grease	10	mg/l
	BOD_5	20	mg/l
	COD	100	mg/l
	NH_3	25	mg/l

From the analysis of historical data, the calculated monthly average of parameters in the different streams can be seen in the table 8. For some of the parameters, data from 2007-2009 and from 2010-2013 was used due to the fact that information about some parameters were not available for the time lapse being studied.

Table 8. Average concentration of different parameters in ETP effluents from 2014-mar 2015.

Influent API separator	**Effluent API separator**	**Effluent DAF**	**Effluent oxidation lagoon**	**Effluent stabilization lagoon**	**Discharge to water body**

	(desalter only)					
Oil and grease (mg/l)[2]	66.8 %[1]	15.35 %	7.11 %	95.29	52.99	12.03
COD (mg/l)	ND	ND	478.8[5]	442.28	384.40	153.70
TSS (mg/l)	ND	ND	162.8[1]	70.13	55.67	66.69
BOD$_5$ (mg/l)	ND	ND	137.53[5]	84.30	85.85	36.42
Ammonia (mg/l)	ND	ND	130.22[3]	81.39	84.36	46.13[4]
Sulfide (mg/l)	ND	ND	3[3]	ND	2.84	ND
Phenol (mg/l)	ND	ND	16.8[3]	ND	4.43	0.14

ND: No data available

1. Average concentration from data of 2007-2009
2. Except for influent and effluent of API and DAF effluent which unit is % vol.
3. Average concentrations found in stripped water coming into the oxidation pond
4. Total nitrogen
5. Average concentration from data of 2010-2013

5.2.1. Oil and grease

Because there is no information about the quality of the wastewater entering the API separators in the time range being studied, information from 2007-2009 was used as a reference to have an idea of the quality of the water that is coming into the unit. The later was done only taking into account the water from the desalter that enters directly into the API separator as there is no information about the quality of the water coming from the sumps.

As it can be seen from the table, the percentage of oil and grease being received by the API separator is more than 10 times that what it was designed to handle. The characteristics of the wastewater coming from the desalter can vary frequently and the amount of oil present in it can be quite high if the pH in the desalter unit is not frequently controlled. When the pH in the desalter is high, the formation of oil/water emulsion increases thus leading to a high concentration of oil and grease in the wastewater (IPIECA, 2010).

Even though the amount of oil is quite high, there is still a reduction of around 77% of oil in the API separator which is still low to what it was considered as designed to be the efficiency of the unit. The concentration of oil obtained in the effluent of the unit is still elevated to what it was designed for.

There is also a reduction of a bit more than half of the concentration of oil and grease in the DAF unit. Since these units are only working as gravity separation tanks, it is obviously not giving the removal efficiency that they were designed for. It is important to remember that before the DAF units there are two flow regulation tanks where oil and grease is also separated. Because of the lack of data about the effluent quality from the flow equalization tanks, it is not possible to determine how much of the concentration of oil and grease is reduced in those units compared to the DAF units.

The biggest reduction of oil and grease is taking place in the oxidation lagoons, where there is a removal of 98% of the oil concentration. This could be due mostly to storage of oil in the surface of the pond as there is a thick layer of oil floating in both of the units. The latter is based on the fact that the aerators are currently not working, and thus the only source of oxygen for microorganisms comes from the diffusion of air into the pond which is most likely to be reduced due to the presence of the thick layer of oil. The lack of oxygen will affect the efficiency and activity of aerobic microbial degradation of pollutants and thus it’s most likely that the current conditions are not promoting this type of bacterial activity. Even though it is commonly known that the degradation of hydrocarbons is done mostly by aerobic bacteria, it has been found that anaerobic bacteria can also degrade them; this could be contributing to the reduction and degradation of contaminants in a certain way (Heider & Schühle, 2013).

Same situation applies for the stabilization pond, however, the reduction in the concentration of oil and grease is much less than that in the oxidation lagoons (around 45%). The quality of the effluent coming out of the stabilization pond still doesn’t comply with the design specifications of 10 mg/l of oil and grease. After the water has gone through the PWTP is when the effluent quality complies with the requirements; even so, the concentration of oil and grease present in the effluent is high compared to what is recommended by the IFC. The standard deviation, maximum and minimum values are shown in table 9.

It can be seen that the values of oil and grease in the oxidation pond effluent are spread out over a wider range compared to the values found in the other effluents. This could be due to the lack of data obtained from this particular unit, as only 11 measurements were done during the time period studied.

Table 9. Standard deviation, maximum and minimum values for data from 2014-mar 2015 for oil and grease.

	Effluent API		Effluent DAF		Effluent oxidation pond		Effluent stabilization pond		Discharge water body	
AVERAGE	15.35	%	7.11	%	95.29	mg/l	52.99	mg/l	12.03	mg/l
STANDARD DEVIATION	7.03	%	3.41	%	48.56	mg/l	6.41	mg/l	4.65	mg/l
MAX	28.57	%	13.52	%	177.90	mg/l	67.36	mg/l	22.16	mg/l
MIN	7.75	%	3.52	%	43.00	mg/l	44.73	mg/l	8.73	mg/l

A statistical analysis was done to determine whether there was a significant difference in the concentration of oil and grease in the influent and effluent of the DAF, the oxidation lagoon and the stabilization lagoon. The analysis was not done for the API separator as the information about the concentration in the influent of this unit was not available.

In table 10, the results of a t-test can be seen for the DAF unit + flow equalization lagoon. Using the probability of a single tail, there is indeed a statistical significant difference between the concentration in the influent and the effluent of the DAF unit + flow equalization lagoon as the p value is less than α value of 0.05, being a higher concentration of pollutant in the influent.

Table 10. T-test results for the influent and effluent concentrations in DAF units.

	influent	effluent
Mean	15.13	7.10
Variance	220.97	74.63
Observations	441.00	441.00
P(T<=t) one-tail	3.4808E-26	

t critical one-tail	1.65	
P(T<=t) two-tails	6.9616E-26	
t critical two-tail	1.97	

In table 11, the results of the t-test can be seen for the oxidation pond unit. Using the probability of a single tail, there is a statistical significant difference between the concentration in the influent and the effluent of the oxidation unit as the p value is less than α value of 0.05, being higher in the influent of the pond.

Table 11. T-test results for the influent and effluent concentrations in oxidation ponds.

	Influent	effluent
Mean	43712.12	85.06
Observations	11	11
P(T<=t) one-tail	0.0021142	
t critical one-tail	1.81	
P(T<=t) two-tails	0.0042284	
t critical two-tail	2.23	

In table 12, the t-test results for the stabilization pond unit are shown. It can be seen that there is a statistical significant difference between the concentration in the influent and the effluent of the stabilization unit as the p value for one tail is less than the α value of 0.05. Even though the main goal of the stabilization pond is the settling of solids and equalization of the wastewater, there is still a good decrease of oil and grease content, mostly due to the amount of this pollutant reaching this point and its storage in the surface of the unit.

Table 12. T-test results for the influent and effluent concentrations in the stabilization pond.

	Influent	effluent
Mean	85.06	53.15
Variance	2474.54	27.78
Observations	11	11

P(T<=t) one-tail	0.03146286	
t critical one-tail	1.81246112	
P(T<=t) two-tails	0.06292572	
t critical two-tail	2.22813885	

5.2.2. COD

Since this parameter is only measured in the oxidation and stabilization lagoons effluents, it is difficult to determine the degree of COD removal occurring in the DAF and API separator units. Information from 2010-2013 was used to make an estimation of the concentration of COD entering the oxidation lagoons; according to the data, the average concentration of COD entering the ponds was around 478.83 mg/l during that time. An estimated removal of 8% is being obtained in the oxidation ponds, which is really low considering that with the use of this type of lagoons a removal of up to 60-75% of the COD concentration can be obtained (Shalaby, et al., 2003) (Chamorro, et al., 2009). A slightly higher reduction, 13%, of the COD concentration can be seen in the stabilization pond; a higher and faster COD removal can be obtained under aerobic conditions and it is more likely than the concentration of oxygen in the stabilization lagoon is higher than in the oxidation lagoons because it doesn't have a thick layer of oil and grease in the surface. Also, volatilization of short chain molecules can be increasing the reduction of COD concentration.

The effluent being discharged into the water body barely complies with what it is recommended by the IFC of the World Bank Group and the amount of permitted COD discharge is not specified in the Mexican PDC. The standard deviation shows that the data being analyzed is dispersed and spread in a wide range of values in the oxidation and stabilization pond as it can be seen in table 13.

Table 13. Standard deviation, maximum and minimum values for data from 2014-mar 2015 for COD.

	Effluent oxidation pond		Effluent stabilization pond		Discharge water body	
AVERAGE	442.28	mg/l	384.40	mg/l	153.70	mg/l
STANDARD DEVIATION	224.24	mg/l	108.85	mg/l	18.54	mg/l

MAX	766.21	mg/l	552.00	mg/l	186.00	mg/l
MIN	128.00	mg/l	240.00	mg/l	127.80	mg/l

In the next graph, the concentration of COD and oil and grease in the effluent of the oxidation pond measured in the same days are plotted against each other. This shows that there seems to be a positive correlation between both of the parameters; this would make sense as the COD measurement is related to the amount of oxygen required for the oxidation of organic compounds (biodegradable and non-biodegradable) and oil and grease found in the water is a mixture of different type of hydrocarbons.

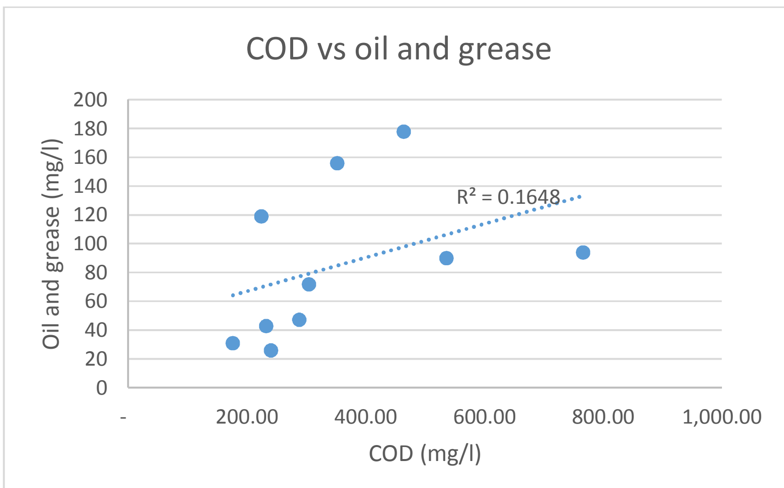


Figure 3. COD vs oil and grease concentration in oxidation ponds' effluent.

Also, the correlation between COD and ammonia in the effluent of the oxidation pond was analyzed. It can be seen in the graph that there is also a positive correlation between both of the parameters, this is expected as COD includes the oxygen demand required by ammonia for its conversion into nitrate (Metcalf & Eddy, 2014).

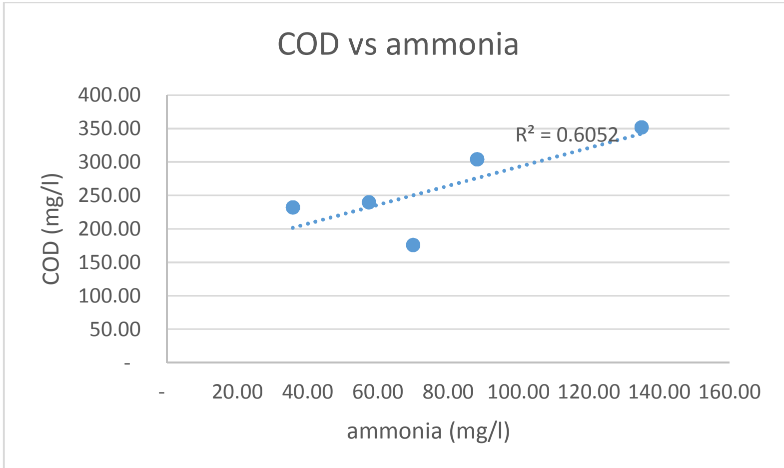


Figure 4. COD vs ammonia concentration in oxidation ponds' effluent.

5.2.3. TSS

The TSS concentration in the wastewater is an important design and operation parameter for API separators and DAF units, however, there is no available data on the value of such parameters.

Data about the concentration of TSS found in the influent going to the oxidation pond is missing for the time lapse being analyzed. Information of the concentration of TSS from 2007-2009 is used to estimate the percentage of removal happening in the ponds system. There is an overall estimated 66% removal of TSS in the ponds' system, with a higher percentage of removal happening in the oxidation ponds. The concentration of TSS leaving the oxidation pond is inside the range of values that is expected to get from such units (30-150 mg/l) (USEPA, 2011). The settlement of TSS could also be the cause of the reduction in COD concentration as some studies have shown that there is a positive correlation between these two parameters in wastewaters (Maha, et al., 2011) (L'Altrella, 2007).

The average concentration of TSS in the effluent coming from the stabilization ponds and in the water being discharged in the waster body comply with the limits stated in the PDC. The standard deviation, maximum and minimum values are shown in the next table. It is important to mention that the amount measurements for TSS for the oxidation and stabilization pond in the studied time period were very few (7 and 9 values) and went from values of 110-50 mg/l and 81-20 mg/l.

Table 14 Standard deviation, maximum and minimum values for data from 2014-mar 2015 for TSS.

	Effluent oxidation pond		Effluent stabilization pond		Discharge water body	
AVERAGE	70.13	mg/l	55.67	mg/l	66.69	mg/l
STANDARD DEVIATION	19.99	mg/l	21.88	mg/l	16.59	mg/l
MAX	100.00	mg/l	81.00	mg/l	84.00	mg/l
MIN	50.67	mg/l	20.00	mg/l	36.00	mg/l

In table 15. the t-test results for the TSS concentration in the stabilization pond can be seen. It can be seen that there is not a statistical significant difference between the concentration in the influent and the effluent of the stabilization unit as the p value for one tail is more than the α value of 0.05. The main goal of the stabilization pond is the settling of the remaining TSS in the effluent before the wastewater enters into the PWTP, but the statistical analysis shows a different outcome. It is important to mention that the number of observations used for the analysis were only 6 and very different from each other, which might influence the result obtained. Also an improper removal could be happening due to anaerobic reactions going on in the sediment layer at the bottom of the pond, causing the formation of gases that could resuspend the already settled sludge.

Table 15. T-test results for the influent and effluent concentrations in the stabilization pond.

	Influent	effluent
Mean	62.33	56.67
Variance	387.87	609.07
Observations	6	6
P(T<=t) one-tail	0.29	
t critical one-tail	2.02	

P(T<=t) two-tails	0.57	
t critical two-tail	2.57	

5.2.4. BOD_5

Information about the concentration of BOD_5 in the influent to the lagoon system is not available, but the same procedure used with COD will be used by estimating a reduction percentage based on information form 2010-2013. An average of 137.56 mg/l of BOD_5 was entering the oxidation pond during that time; an estimated 39% removal of BOD_5 is happening in the lagoon. This value is far from the expected removal by the oxidation pond (around 78%). Again, the lack of aeration in the oxidation pond is certainly affecting the degradation of organic pollutants. Also, the average concentration of this parameter in the effluent from both ponds is higher than what they were expected by design. According to the design parameters, there should be a 66% decrease in the concentration of BOD_5 in the stabilization pond.

The BOD_5 concentration in the effluent from the stabilization pond is slightly higher than that from the effluent coming from the oxidation lagoon. The operator mentioned that water from the rain sumps is sent into the stabilization ponds whenever the capacity of the sumps is exceeded; this could be increasing the BOD_5 concentration if water is slightly polluted with organic material or compounds. Also, if there is hydrolysis of particulate material in the stabilization pond under anaerobic conditions, that could increase the BOD_5 concentration in the effluent of the unit (Metcalf & Eddy, 2014) (Young, et al., 2005).

In the next table, the standard deviation, maximum and minimum values are presented. It is important to mention that the amount of BOD_5 measurements for the oxidation and stabilization pond in the studied time period were very few (around 9 values) and went from values of 55-110 mg/l which might not be enough data to come to a clear conclusion to what is exactly happening in the lagoons.

Table 16. Standard deviation, maximum and minimum values for data from 2014-mar 2015 for BOD_5

	Effluent oxidation pond		Effluent stabilization pond		Discharge water body	

AVERAGE	84.30	mg/l	85.85	mg/l	36.42	mg/l
STANDARD DEVIATION	22.34	mg/l	21.09	mg/l	9.93	mg/l
MAX	110.00	mg/l	114.00	mg/l	58.65	mg/l
MIN	55.50	mg/l	63.57	mg/l	26.65	mg/l

The BOD_5 and ammonia concentrations in the effluent of the oxidation pond were plotted to see if there was any relation between these two parameters. According to the data used, there seems to be a negative correlation between them. This goes against to what is expected as low levels of BOD_5 would promote nitrification processes to occur and thus the level of ammonia present in this situation would be low (Metcalf & Eddie, 2014). However, stripped sour water that still contains a considerable concentration of ammonia, is being discharged into this pond; this could be having a toxic effect on the bacteria present reducing the concentration of BOD_5 in the wastewater (Gerardi, 2005). The same was done for the effluent in the stabilization pond effluent and the negative correlation is still happening (see figure 6).

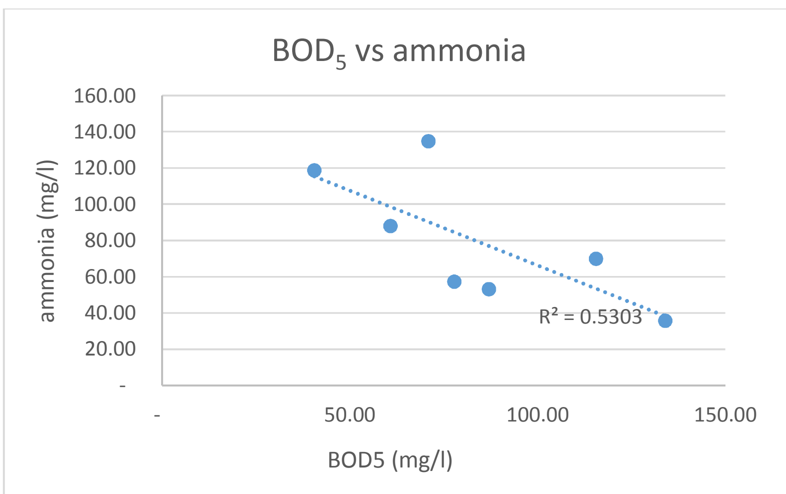


Figure 5. BOD_5 vs ammonia concentration in oxidation ponds' effluent.

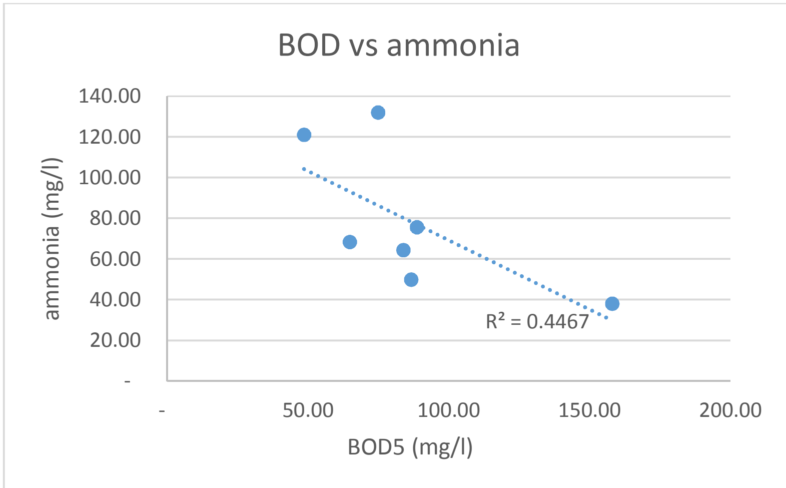


Figure 6. BOD_5 vs ammonia concentration in stabilization pond's effluent.

5.2.5. Ammonia

Taking into account the amount of ammonia present in the stripped sour water that is coming into the oxidation pond, a rough estimation of how much it is removed from the wastewater can be done; the latter because data about the ammonia content in the wastewater coming from the DAF units is not available. Around a 37% of the ammonia concentration is being removed in the oxidation pond, this could be due to ammonia volatilization as this compound volatilizes at pH>8 and the average pH has been around 8.5 for March 2015 in the stabilization pond effluent (Freney, et al., 1983). Also, partial or complete nitrification process could be going on even at low oxygen levels but this could be hindered by the high concentration of ammonia in the wastewater (Bellucci, et al., 2011). It would be ideal to keep track of the amount of dissolved oxygen and the microbial ecology present in the lagoons in order to understand in a better way the possible microbial processes happening; at least 1.5 mg/l of dissolved oxygen is needed for nitrification processes to be happening (Gerardi, 2005).

There is a slightly higher concentration of ammonia in the stabilization pond effluent than in the oxidation lagoon, which could be due to the anaerobic production of ammonia in the sediments present in the stabilization pond by biomass hydrolysis. The concentration of ammoniacal nitrogen in the effluent of the stabilization pond is higher than what it was designed for (25 mg/l) and the concentration of total nitrogen being discharged to the water body is higher than what it is required in the PDC. The standard deviation, maximum and minimum values are presented in the next table.

Table 17. Standard deviation, maximum and minimum values for data from 2014-mar 2015 for ammonia.

	Effluent oxidation pond		Effluent stabilization pond		Discharge water body[1]	
AVERAGE	81.39	mg/l	84.36	mg/l	46.13	mg/l
STANDARD DEVIATION	63.30	mg/l	58.87	mg/l	27.92	mg/l
MAX	252.00	mg/l	241.00	mg/l	95.20	mg/l
MIN	35.00	mg/l	35.10	mg/l	2.75	mg/l

1. Total nitrogen

5.2.6. Hydrogen sulfide

From table 18, it can be seen that the average concentration of hydrogen sulfide is being reduced only by a 5% in the lagoons. Oxygen is required for the oxidation of sulfide to sulfate by the sulfur oxidizing bacteria; since the aerators in the oxidation ponds are not working there might not be enough oxygen for the bacteria to grow and metabolize the compound. However, a slightly higher concentration of oxygen could be present in the stabilization pond, due to the lack of a thick oil layer in the surface that blocks the dissolution of oxygen in the water which might be enough to allow a slight decrease of H_2S concentration.

There was no information available for the period of study about the concentration of sulfide being discharged to the water body but the concentration of sulphide in the effluent of the ETP is more of the double of what is recommended by the IFC of the World Bank Group. In the table below, the standard deviation, maximum and minimum values can be seen.

Table 18. Standard deviation, maximum and minimum values for data from 2014-mar 2015 for H_2S

	Stripped water		Effluent stabilization pond	
AVERAGE	3.00	mg/l	2.84	mg/l

STANDARD DEVIATION	1.20	mg/l	1.99	mg/l
MAX	4.33	mg/l	7.60	mg/l
MIN	0.80	mg/l	0.50	mg/l

5.2.7. Phenol

Considering the average concentration of phenol present in the stripped sour water coming into the oxidation ponds, there is an overall 74% reduction of the average phenol concentration in the lagoons' system. This could be happening because of aerobic biodegradation of the compound in the stabilization ponds, due to photodegradation/photolysis of the compound in such unit at wavelengths between 200-300 nm and/or because of the adsorption of this compound into the TSS and its removal via sedimentation (Chun, et al., 2000) (Van Schie & Young, 2000) (Kulkarni & Kaware, 2013) (Basha, et al., 2010). Studies have shown that up to 70% of phenol can be removed from wastewater with the use of stabilization ponds which is around what is being obtained in this case (Almasi, et al., 2014). The concentration of phenol being discharged into the water body is below the limit of what is recommended by the IFC of the World Bank Group.

In the next table the standard deviation, maximum and minimum values are shown. The range of the values found in the effluents of the stripped water, effluent of the stabilization pond and discharge to the water body is high, especially for the stripped water. Again, the amount of data provided was very limited for each parameter.

Table 19. Standard deviation, maximum and minimum values for data from 2014-mar 2015 for phenol.

	Stripped water		Effluent stabilization pond		Discharge water body	
AVERAGE	16.81	mg/l	4.43	mg/l	0.14	mg/l
STANDARD DEVIATION	25.49	mg/l	4.64	mg/l	0.13	mg/l
MAX	76.70	mg/l	14.40	mg/l	0.40	mg/l
MIN	2.01	mg/l	1.36	mg/l	0.04	mg/l

5.2.8. Quality requirements for PWTP

The PWTP has certain quality requirements for the effluent coming from the ETP to avoid damaging the performance of the activated sludge process. Operators of the PWTP commented that there have been several times on which the activated sludge reactor has been affected by shock loads of oil entering the unit, which can still be seen in the walls of the tanks.

The specifications requires the presence of less than 1 mg/l of sulfur, less than 70 mg/l of ammonia, less than 40 mg/l of oil and grease, less than 1.5 mg/L of phenol, less than 400 mg/l of COD and a pH of 6-9. As it can be seen in table 20, all the average values of the parameters with exception of the COD, exceeded the specified values for the entrance of water to the PWTP. However, the BOD_5/COD average ratio present in the effluent is around 0.23 which makes the water hardly biodegradable (Srinivas, 2008). This could be affecting the performance of the activated sludge treatment as the reduction of some of the contaminants are not being enough to comply with what is recommended by the IFC to discharge into water bodies.

Table 20. Stablished limits for water quality parameters entering the PWTP compared to actual averages.

	limit	**average**
Ammonia (mg/l)	70	84.36
Phenol (mg/l)	1.5	4.43
Sulfur (mg/l)	1	2.84
COD (mg/l)	400	384.4
Oil and grease (mg/l)	40	52.99

5.3 Suggested Improvements

5.3.1. Sumps

The stress caused by the gas bags could lead to the liner being ripped or damaged, and thus increase the probability of contaminated water infiltrating into the ground. In order to avoid the formation of gas bags in sump 1, a double liner could be installed: geotextile can be placed under the liner and an under drain and/or gas vents can be installed in between them. This will help to drain the gasses formed and water leaked, and decrease the risk of soil and groundwater pollution (Giroud & Gourc, 2015). However, the use of underdrains will require the presence of a slope in the pond that will facilitate the recollection of wastewater or else the use of a small pumping station would be required. The gas vents should be placed at the top of the slopes or in high areas to avoid the entrance of water into the system.

Some gas ventilation/under drain systems consist of several perforated tubes that just need to be laid below the liner; the tubes are covered with a non-woven geotextile that helps to avoid tube clogging. The latter will help to decrease cost of installation as the placement of a geotextile cover underneath the liner will be unnecessary. This could be a considered a good option for the refinery sump (see figure 7).

Figure 7. Multi-vent underliner for gas venting (Underwater warehouse, 2013).

Oil and grease separation is taking place in sump 1 and 2 due to gravity and thus the proper removal of oil in this first step could help to reduce the amount of oil going further down in the treatment train. Floatable oil skimmers could be used to remove the oil present in this units and decrease the amount of water being carried with the oil into the recovery tanks.

It's important to mention that the installation of proper oil and grease skimmers in the different units downstream and a functional piping and pumping system into the recovery tanks will help to reduce the amount of oil being discharged with super sucker trucks, and avoid increasing the oil-water emulsification in the sumps.

5.3.2. API separators

API separators are ideal units when the influent has a high amount of solids and oil; API separators help to reduce the amount of oil in the wastewater but also a certain percentage of

TSS is removed. A well designed API can give quite a relatively consistent effluent quality independently of the influent's quality (Schultz, 2005).

API efficiency will depend on the temperature of the water, the density and size of the oil droplets and the characteristics of the TSS (Wong & Hung, 2005). According to previous analysis done in the influent of the ETP, the wastewater coming from the sump 1 and 2 had an average TSS concentration of 203 mg/l, while the water from the desalter had an average of 416 mg/l (IAENL, 2010); the latter makes the API an ideal oil/water separator as the amount of solids it can handle can range from 300-10,000 mg/l of TSS. If CPI units were to be used, a lower load of TSS (<200 mg/L) is needed because solids can foul the plates and thus affect their oil/water removal performance (SIEMENS, 2006). API have been preferred in refinery installations as they can take shock loads of oil and higher flows of oil than a CPI, even though the space required and retention time in the unit is larger than in a CPI (Wong & Hung, 2005). Based on the observed amount of oil present in the influent coming to the ETP, it is highly recommended to use an API separator instead of CPI as the oil and solids can clog and foul the plates.

Oil collection and removal from the API separator is crucial for its proper functioning and to avoid oil going into the next units. Currently, the API separator cells only count with half-pipes or rotary pipe skimmers to collect the separated oil, however, the skimmers are overflowed in all cells. This type of skimmers can overload quite easily as they have a very limited capacity, and normally collect a high amount of water with the recovered oil (around 80-90% if skimmer is not frequently adjusted) (Liu & Liptak, 1999).

An upgrade that could be done in order to reduce the amount of water present in the recovered oil and to increase the amount of oil collected is the installation of a rotating drum skimmer. This drum skimmer works by adhering the oil in its specially treated surface as it is normally made with oleophilic materials that helps to attract the oil; then the oil is removed off the drum by some scrapers and falls in a channel that will send the recovered oil into the pumping system and into the recovering tanks. The rotational speed of the drum will depend on the amount of oil that is needed to removed and the viscosity of it but the optimal is around 0.15 - 0.46 m/s (American Petroleum Institute, 1990); also the level of submergence is not important as long as the skimmer is in contact with the oil layer. This drum skimmer is normally placed before the pipe skimmer and so the latter helps as a back-up oil removal device (see figure 8).

Figure 8. From left: Drum skimmer, followed by a pipe skimmer, underflow baffle and overflow weir (Monroe Environmental, 2012).

To avoid the escape of volatile organic compounds (VOC's) into the atmosphere, a cover is needed for all the cells in the API separator as the current ones are already perforated in some areas due to extreme corrosion. There are two types of covers: fixed ones and floating ones. The first ones stand high above the surface whilst the floating ones are floating in the surface of water. In order to avoid interferences with the skimming units, a fixed cover would be a good option in this case. The trapped gasses could be send back to the refinery installations for their treatment and exploitation if the technology is available to do so. The installation of these covers difficult the observation of the oil and water levels in the separator but the presence of certain hatches or entrances close to the effluent and skimming area can help the inspection of the unit and separation process.

The API separator doesn't count with a mechanism by which the settled solids can be removed. The lack of solids removal in an API separator is the most common cause of why these units do not work properly (Schultz, 2005). A drag conveyor is needed to carry the settle solids into the chamber close to the inlet where solids can be removed with the use of a hopper and screw conveyor. When the recovered sludge is taken out of the API separator by the screw conveyor, it should go into a sludge collection basin where it could later be sent to further treatment; this sludge is considered as hazardous material and thus it needs to be disposed and treated as one.

There are several materials by which the solids drag conveyor (shafts and chain) can be made of; plastic conveyors are recommended in this case in order to avoid frequent damages of its structure due to the corrosive nature of the components in the water. The resistance of the plastic will depend on the characteristics of the wastewater being received and the plastic by which they are made; currently, there are high-tech plastic conveyors manufactured specially to resist petrochemical/refining wastewater conditions (PROBIG, s.f.).

All of the screw conveyors present in the API separator and the sludge pumps need maintenance or full replacement in the 4 cells. Since the sludge can be very thick and viscous, positive displacement pumps are recommended to avoid plugging and ease the sludge transport (Schultz, 2005).

One fact that could also be affecting the efficiency of API separators might be that the characteristics of the crude oil being treated in the refinery have changed. The crude oil that was being processed some years before could have been lighter than the one that is being processed actually. Currently, the refinery treats heavy crude oil (20-21° API) and light crude oil (32-33° API); around 89 thousand barrels per day of the first one and around 84 thousand barrels per day of the second one (PEMEX, 2014). The heavier crude oil has a specific gravity that is more similar to the water specific gravity making it harder and taking longer to separate compared to the lighter crude oil. The specific gravity of the crude oil removed from the supernatants in the ETP has shown to be around 0.94.

In order to check if the design of an API separator is correct, the vertical velocity of the oil needs to be determined. This vertical velocity is the oil droplet rising velocity and it's affected by the difference of the specific gravity of the water and the oil. The formula used to determine this velocity is:

$$v = \frac{Q}{A} = \frac{g}{18} * \frac{S_w - S_o}{\mu} * d^2$$

Where Q is the design flow, A is the horizontal area of the separator, v is the vertical velocity, Sw is the specific gravity of the water, So is the specific gravity of the oil, μ is the absolute viscosity of the water, d is the particle diameter and g is the gravity (Stephenson & Blackburn, 1998). The specific gravity of the oil in Refinery 1 is around 0.94 g/cm^3, since temperature is not measured in the effluent arriving to the ETP, a value of 35°C will be used which is the designed value of the unit. At this temperature the viscosity of water is 0.7191 mPoise and its specific gravity is 0.994 g/cm3 (Metcalf & Eddy, 2014). The diameter of particle that is used for this type of oil and grease separators is 150 microns or 0.015 cm. The later gives a vertical velocity of 0.0919 cm/s.

The horizontal velocity in the separator is calculated multiplying the vertical velocity by 15. The horizontal velocity should be equal or less than 1.524 cm/s based on operational experience of API separators (API, 1990). In this case the horizontal velocity is 1.378 cm/s; this horizontal velocity can be multiplied by the API's cross sectional area to determine the adequate flow rate needed. Then, with the following formula, the retention time required for oil separation in the current conditions can be calculated:

$$t = \frac{volume\ of\ unit}{flow\ rate}$$

This retention time can be compared with the actual retention time in the unit; If the actual retention time is lower than what is needed in the current conditions, the flow rate should be decreased in order to allow the oil droplets to reach the surface before leaving the API separator.

API separators need to comply with different design criteria in order to operate in a proper way. A minimum length to width radio of 5:1 is required to get plug flow conditions, a minimum depth to width ratio of 0.3:0.5 is necessary to reduce the time needed for oil particles to float to the surface, maximum channel width of 20 ft (6.1 m) and depth of 8 ft (2.44 m), minimum width and depth of 6 ft (1.83 m) and 3 ft (0.91 m) and horizontal velocity of 3 ft/s (0.91 m/s) to minimize turbulence (Schultz, 2005).

Wastewater reaches the ETP in Refinery 1 mostly by gravity which is good in order to avoid the creation of emulsions, but these can also be formed within some parts of the refining process like in the desalter units (Wong & Hung, 2005). The presence of emulsions increase the amount of oil arriving to the ETP and decreases the efficiency of oil/water separation in the API as they strongly depend on the size of the oil droplets and particle size. Wastewater coming from the desalter units is normally the primary source of wastewater into treatment plants; it normally has a great amount of suspended solids, free oil and dissolved salts but its characteristics vary widely. Because wastewater coming from the desalter enters directly into the API separators, one recommendation would be to pretreat the wastewater coming from the desalter in a different oil/water separation unit before entering the API unit. The latter will help to reduce the amount of oil arriving into the ETP and increase the amount of valuable oil recovered.

One way to do this is by making it go through a storage unit such as a floating roof tank; a residence time of one day would be enough to help the emulsified oil to be separated, to remove the suspended solids present and reduce the amount of crude oil that will be entering the ETP (IPIECA, 2010). The tank should be equipped with a floating oil skimmer, an outlet for the wastewater that will be sent to the API separator, and a sludge removal system. The skimmed oil can be reprocessed in the refinery, the settled sludge can be dewatered and then disposed accordingly, and the wastewater can be send to the ETP for its treatment.

Another way to decrease the amount of oil and grease going into the ETP is by having a better control of the oil and grease emulsion interface in the desalter units; this could be done by controlling the pH in the unit. When the pH increases in the desalter (>7.5), the formation of oil/water emulsions is augmented and thus, more oil is discharged with the wastewater (Baker Hughes, 2011). However, pH <6.5 can induce to the presence of corrosion problems in the downstream units. Keeping the pH in between this values by adding acid or a base would help to improve the separation of oil and water, and thus less water will be in the recovered oil and less oil will be in the wastewater. The installation of probes to measure oil content and pH in the desalter unit could help to have a faster response to drastic changes in the process.

5.3.3. CPI and flow equalization lagoons

As explained before, the use of the API separator is better in this case as the amount of oil and grease and TSS entering the units is high, which could cause frequent clogging between the coalescent plates. Because of this, it's recommended to keep them out of service and keep using API separators as a primary oil and grease separation process.

In the case of the flow equalization lagoons, their main purpose is to reduce drastic changes in the flow rate and to give the wastewater a certain stable composition. This is ideal for the DAF units, as this will keep parameters that are crucial for its function, such as pH, oil and grease, and TSS, in a fairly constant state. These units are being highly impacted by the poor performance of the API separator as one of the mayor problems was the high level of oil in the wastewater surface; also the lack of a functioning oil and grease recovery skimmers increases the level of oil stored. The pipe skimmers or half-pipes present in the units need to be repaired as the manual device to adjust them is not working. The pumping system for the recovered oil is still functional.

To increase the amount of oil and grease being recovered and reduce the amount of water present in the recovered oil, the use of a floating drum skimmer is recommended. The units could be used as a backup measure to skim the oil when high loads of this contaminant are leaving the API separator or when the skimmers are not working properly. These units have the advantage of adjusting quite easily to any wastewater level in the units and can be transported and removable with little difficulty. The skimmed oil can be sent with hoses into the pumping sump that takes the recovered oil from this equalization lagoons into the recovery tanks. This kind of skimmer, since it's transportable, can be also used in any other units such as the lagoons.

5.3.4. DAF

Because API separators can only remove big droplet size particles (bigger than 0.015 µm), another treatment step is needed to remove the finer oil droplets and avoid problems in the biological treatment units. The latter can be achieved with the use of a DAF unit which would enhance the quality of the effluent. DAF units can function properly with an oil concentration of 300 mg/l and TSS concentration of more than 800 mg/l. If the previous mentioned improvements are done in the API separators and sumps, an oil concentration of less than 300 mg/L could be easily obtainable as properly operated gravity separators can provide an effluent quality of 30-150 mg/L (Parkash, 2003) (Rajaram & Melchers, 2005) (Wang, et al., 2005).

DAF units also help to remove the remnant suspended solids present after the water has gone through the API separators and oil emulsions can also be removed by adding coagulants that will help to destabilize the molecules and increase the particle size. When coagulants/flocculants are not used in the DAF units, a solids and oil and grease removal percentage of 50-80% and 60-80% can be achieve respectively. DAF units with the addition of flocculants/coagulants can help to obtain an oil and grease concentration of 5-25 mg/l in the effluent, a BOD_5-COD removal of

30-50 % and a 95% removal of solids (Wang, et al., 2005) (Wong & Hung, 2005). Since the DAF unit can reduce COD concentrations it would help to reduce the BOD_5/COD ratio and make the wastewater more easily biodegradable for the oxidation lagoons and activated sludge units (Srinivas, 2008).

The most commonly used coagulants and flocculants are iron and aluminum salts and activated silica (Yu, et al., 2013) (Metcalf & Eddy, 2014). In order to determine the proper amount of coagulant and/or flocculant that needs to be added, a jar test needs to be performed where different pH, chemicals and amount of chemicals are tried with the wastewater. Another benefit of using DAF is that the sludge from such units is more concentrated than the sludge coming from gravity separators. The latter depends on the type of coagulant being used; organic coagulants can give a solids concentration of 80-200 mg/l in the sludge while an inorganic one can give a concentration of 50-100 mg/l (Berne & Cordonnier, 1995). Floating sludge needs to be frequently skimmed as the accumulation of this layer on top of the unit can lead to their sedimentation due to gravity and increase the amount of TSS in the effluent.

The four most important components in a DAF unit are the air supply, a pressurizing pump, a retention tank and a flotation basin. The influent is pressurized in the retention tank using the pressurizing pump in order to increase air solubility in it. Then it is sent to the flotation tank that is at an atmospheric pressure and thus a pressure drop occurs, generating air microbubbles (Wang, et al., 2005). There are three different types of DAF units depending on the amount of the influent that is pressurized; the most commonly used and recommended in refineries is the recycle flow pressurization system on which a portion of the effluent is pressurized and sent back to the flotation basin. The portion recycled is normally around 15-50% of the DAF's effluent; this type of configuration can be used in Refinery 1 to avoid the use of raw water.

Some important factors to maintain a good pollutant removal in the DAF units are to avoid drastic changes in the pH, have proper flow rates and have a good A/S ratio. The presence of the flow regulation tank previous to this unit is ideal to keep the wastewater's characteristics fairly constant or without mayor changes. To design a proper DAF unit, several laboratory and pilot tests need to be done in order to determine the right amount of air that needs to be dissolved in the water to obtain a good solids removal.

The pressure at which the water is exposed will affect its air saturation and the size of the formed bubbles; normally, a higher pressure will give a better supernatant formation and less TSS in the effluent of the unit but there's a limit at which this can apply (Wang, et al., 2005). Also, a certain air to solids ratio (A/S) is required to maintain for a good performance in the unit as this can affect the solids rise rate; an A/S ratio of around 0.008 has shown to be an ideal value but tests need to be done to determine the optimum one for each case (Metcalf & Eddy, 2014).

It would be recommended that the DAF units should be protected with a roof or a cover, to avoid that meteorological factors such as wind and rain affect the separation by disturbing the layer of separated solids in the surface of water. Also, this would help to avoid the scape the volatile organic compounds (VOC's) that will be removed or stripped from the wastewater. Even though this technology is good for wastewater treatment, it is more energy intensive, might require chemical addition and needs the presence of a qualified operator.

As it was mentioned before, an external company was hired to add a flocculant, coagulant and emulsion breaker into the stabilization and oxidation lagoons. The use of an emulsion breaker in the oxidation pond is decreasing any chance of bacterial degradation of oil, as the microorganisms need the presence of oil in an emulsified form to be able to degrade them, but increases its skimming possibilities (Das & Chandran, 2011). The addition of flocculant and coagulant to destabilize emulsions in the stabilization pond increases the formation of a sludge layer in the bottom; because there is no additional mixing in the pond besides that driven by air currents, the coagulation/flocculation process might be inefficient as they strongly depend in the degree of mixing provided for particle collision and each requires a different mixing velocity (Metcalf & Eddy, 2014). The average concentration of TSS is reduced in only a 9% from the oxidation effluent to the stabilization pond, which supports the previous idea. When coagulation/flocculation techniques are applied correctly, they can provide a TSS removal and COD removal of more than 90% (Irfan, et al., 2013). If the DAF is rehabilitated and used properly, there will be no need to keep doing this as this unit will decrease the TSS, COD and oil concentration in the effluent.

5.3.5. Oxidation and stabilization lagoons

When the ETP was built during the 70's, the use of an activated sludge unit was not considered and thus the secondary treatment of wastewater was going to be done by the use of oxidation and stabilization lagoons.

Stabilization ponds are a good secondary treatment method for wastewater that contains a high concentration of organic substances but their efficiency will depend strongly on the climate present in the place where they are located as they are open to any weather inclemency (Veeresh & Veeresh, 2010). The advantages of using this type of system for biological treatment are low operation and maintenance costs, low sensibility to hydraulic and organic shock loads, low energy requirements and no use of additional chemicals (Mayo, et al., 2014).

There are 3 types of stabilization ponds: aerobic/oxidation, anaerobic and facultative. If stabilization ponds are meant to be used as a method of secondary treatment, the best way is to combine an anaerobic pond, followed by a facultative pond and an aerated pond. Anaerobic ponds are normally used when strong raw wastewaters are meant to be treated (BOD5>300 mg/l, TSS>200 mg/l, oil and grease>150 mg/l) (FAO, 1992). However, since the wastewater in the ETP will go through some previous treatment units, aerobic or facultative ponds can be used to treat medium and low strength wastewaters without the use of an anaerobic one.

The installation of the new hyperaerators will improve the amount of dissolved oxygen in the lagoons, as the previous ones (surface aerators) were constantly failing. One recommendation will be to remove all the settled solids from the lagoons as a way to avoid any type of early damage or clogging to the aerators, avoid zones of insufficient mixing and to increase the active volume of the oxidation pond. Also, a frequent analysis of the stripped sour water stream should be done as high concentrations of ammonia and hydrogen sulfide can be toxic for the nitrifying bacteria present in the pond. A higher control and regulation is needed in the sour water stripper units as they have shown to produce stripped water with higher concentration of ammonia that what they were designed for (25 mg/l of NH_3 and 5 mg/l of H_2S) and their low performance can impact the efficiency of wastewater treatment in the oxidation ponds.

The presence of the thick layer of oil in the ETP's oxidation ponds doesn't let the light and air go through the pond and this has an effect on the type of bacteria and algae that can develop and grow in the unit. The latter decreases the opportunity of pollutant removal via microbial degradation which is the main purpose of the oxidation lagoons and thus the removal of the thick layer of oil and grease is required. The removal can be done with the use of a the portable floatable oil skimmers to avoid dragging too much water with the oil; then the recovered oil can be sent to the oil pumping sumps and into the recovery tanks.

Ideally, the microbiota developing in the aerated lagoon should be studied and monitored every once in a while, as the process going on in the unit will highly depend on the type of microorganisms present. The same would be with the amount of dissolved oxygen, temperature and pH in the lagoons, as they will impact in the microbial activity. The oxidation/stabilization lagoons could also work as a regulation tank were the quality of the water can be homogenized; this could be important because the PWTP doesn’t count with a primary clarifier or a regulation tank where this could be done.

The presence of activated sludge and the oxidation and stabilization lagoons might be redundant but when there is not enough capacity in the PWTP to receive the effluent from the ETP, the water after the lagoon’s treatment could be discharged into the water body without representing a major danger to the environment. A study made by Xavier et al. (2009) shows that the removal percentage of certain pollutants such as BOD_5 and COD in activated sludge and an aerated lagoons is quite similar, but it has shown to be higher in the activated sludge.

Further adjustments might be needed if the proposed improvement methods for the ETP are applied to determine, based on the quality of the water obtained, whether the oxidation/stabilization ponds should still be used or not. Xavier et al., (2009) Showed that in an activated sludge system the compounds/pollutants suffer a complete removal whilst in an aerated lagoon they are transformed into lower molecular weight compounds. Thus, the use of an activated sludge would be preferred over lagoons or ponds systems in terms of pollutant removal.

However, the oxidation/stabilization lagoons could work as a regulation tank were the quality of the water can be homogenized before entering the PWTP. The latter could be important because the PWTP doesn’t count with a primary clarifier or a regulation tank where this could be done.

5.4 General recommendations

5.4.1. Measurements

The amount of data provided by the company's laboratory was very limited for most of the parameters measured in different parts of the ETP in the time lapse studied. As it was mentioned in the methodology part, this was mostly due to contamination problems in the sample, high concentration of oil, lack of personnel, among others. The behavior of the processes and the performance of the units cannot be assessed if the monitoring system of the plant is not working or not being done properly.

One recommendation would be to analyze and evaluate the sampling methodology and plan being used by the laboratory in the ETP. One thing that could be observed during the collection of some samples, was the lack of sample preservation immediately after their collection. According to the EPA, the wastewater samples should be preserved by adding a chemical or keeping them at a low temperature in less than 15 min after their collection to avoid changes in sample's integrity. Also, the samples were taken by interns of the lab who lack the criteria to determine whether a good sample was taken or not. The success of a sampling program is directly related to the care that is taken during the collection process; better performance will be achieved if trained and experienced personnel is the one taking the samples (USEPA, 1982).

It is important to mention that Mexican regulations do not demand the industries to measure the COD and a minimum value for this parameter is not even established in the NOM-001-SEMARNAT-1996. This parameter is of extremely importance since it can give a realistic assessment of the amount of organic pollutants that can be oxidized that are discharged in the water body (Amiry, et al., 2008). COD is also known to be a major contaminant in the oil industry as it can be found in high concentrations in refinery effluents and so it would be convenient to determine the COD of the effluents coming from Refinery 1 frequently (El-Naas, et al., 2010). This parameter would also be helpful decide if further adjustments are needed in the units downstream the ETP, as a good BOD/ COD ratio is needed for an efficient biological treatment (Metcalf & Eddy, 2014). In this case, the laboratory in charge of measuring the water quality parameters in the effluents doesn't have the COD measurement as a certified practice and thus it's not officially approved. One recommendation will be to obtain the certification of COD measurement and use it as a tool for the correct operation of the plant, even when the legislation does not require it.

Also, parameters such as phenol, and certain priority pollutants (BTEX) that are known to be common in refinery effluents should be measured even if the authority does not demand; the latter in order to determine if further treatment is needed after the PWTP to keep the receiving water body in a good environmental state. If the concentrations of this priority pollutants is high, further steps need to be taken such as the installation of tertiary or polishing steps like activated carbon filters. The USEPA's Clean Water Act can be used as a methods' reference as they specify different approved techniques for the measurement of this pollutants in wastewater.

Reported data of the water quality parameters of discharge into the water body for refinery 1 effluent are presented in Annex II. The different limits recommended or stablished by the IFC from World Bank, the NOM 001 and the Particular Discharge Conditions of Refinery 1 are compared with each other. In those graphs it can be seen that the PDC for the refinery are very relaxed compared with what is recommended by the other organizations and, in several cases, the values presented in Refinery 1 effluents are well above them. Considering the actual state of water stress in that area, it would be reasonable to consider that the environmental legislation will go towards a more strict control of what is being discharged into water bodies. Thus it will be good for the refinery to consider the compliance of other organization limits such as those by the USEPA or the IFC of the World Bank.

5.4.2. Sludge dewatering

In order to avoid expenses due to hazardous waste disposal, the sludge coming from the ETP units could be treated to remove as much oil and water as possible and reduce the volume of hazardous waste that needs to be treated and disposed. The later will also help to recover valuable oil that could be reprocessed and reused in the refinery and facilitate solids disposal techniques.

The design of dewatering/drying units depends on the characteristics of the sludge that will be treated. The sludge coming from refineries is composed by stable emulsions of oil and water, solids, petroleum hydrocarbons and metals; the proportion at which the contaminants are present in the sludge will vary constantly and thus its characteristics such as viscosity, density and heat value will fluctuate as well (Hu, et al., 2013). Recovery techniques such as centrifugation, surfactant oil recovery, freeze/thaw, and bio-slurry have shown to be suitable for oily sludge treatment that has a high moisture content (Tuncal & Uslu, 2014).

One suggestion for Refinery 1 is that the sludge coming from the different ETP units could be dewatered with the use of centrifuges. Centrifugation is a technique on which rotational forces help to separate the components based on their different densities. This units have been used extensively in the petroleum industry to dewater oily sludge as they have shown to be fast, efficient and easy to apply. However, before the sludge can go through a separation unit, it needs to be conditioned to facilitate the separation of solids, water and oil. This is normally done by the addition of a demulsifying compound, organic solvents and/or sludge heating, to mention a few. Normally, sludge is heated up to help reducing the viscosity of the sludge and at the same time help to decrease the centrifuge's energy consumption.

Besides heating up the sludge, the addition of demulsifiers has shown to be an effective conditioning technique but they tend to be costly and their chemical nature makes them hazardous for the environmental as they are mostly refractory organic polymers. The use of biodemulsifieres have shown to be good replacement for chemical demulsifiers, as they have low toxicity, have a good performance, don't affect the biological degradation and have no secondary pollution effects (Long, et al., 2013). Rhamnolipids have shown to be effective demulsifiers when used with sludge coming from refineries with over 98% of oil recovery (Long, et al., 2013); Yan et al., (2012) pretreated oily sludge from a refinery with rhamnolipid and used centrifugation to dewater the sludge at a pilot scale and obtained an oil recovery of 91.5% which shows its potential use. Rhamnolipids are commercially available as they are produced at a high scale which increases its potential use in refineries.

This type of biodemulsifiers could be used coupled with centrifugation for Refinery 1 sludge treatment. Recovered oil can be sent to the recovery tanks and be processed, water can be send back to the ETP and the dewatered sludge can be then disposed. Further studies would be required to determine the economic feasibility of the proposed process.

5.4.3. Unregistered discharge

The operators mentioned that when the wastewater treated in the ETP cannot be send to the PWTP, they send it to a rainwater sump which discharges into a small creek (this discharge is not registered as an official water discharge from Refinery 1). Rainwater in the refinery doesn't receive any chemical or physical treatment besides gravity sedimentation, because it is considered to be water with a good quality.

Some of the rainwater sumps have a slight pollution of oil and iridescence or a small layer of crude can be seen in the surface of water. Because of the later and due to the fact that effluent from the ETP is being mixed with relatively clean water, the quality of the wastewater that goes into the creek has shown to have a bad quality that doesn't comply with what is required by law (see Annex III). The fact that this is not registered and that the concentration of pollutant present in the discharge is high, could lead to strong legal actions against refinery 1, penalties and high economic fines.

A way to reduce the amount of water entering the ETP is by using the stripped water that is being discharged to the oxygenation ponds in the desalter units. Up to 7% of the volume of oil that is being processed in the refinery can be used of water in the desalter, as this is currently done in other PEMEX's installations. In this case, up to 3,070 m^3 of stripped water a day could be used as wash water in the desalter unit. However, the quality of the stripped water should comply with certain parameters in order to avoid corrosion problems in the units; an ammonia concentration of less than 50 mg/l and sulfide of less than 30 mg/l is recommended (PTQ, 2011). The ammonia concentrations present in the effluent from the strippers has shown to be higher than what it is required, and thus it is recommended to do a performance analysis of the stripper units or consider the use of a two-step stripping process.

The refinery should avoid at all cost the pollution of rain water as its quality makes it disposable without any further treatment. The practice of sending effluent from the ETP into the rain sumps should be eluded, instead, as much water as possible should be treated; if the recommended improvements and maintenance actions are done, the quality of the wastewater leaving the ETP would be enough for the disposal of excess water into water body but only when it is strictly necessary.

5.4.4. PWTP

The PWTP, as explained before, utilizes an activated sludge unit to biodegrade the pollutants present in the wastewater coming from the ETP. All of the biological treatment being used in the refinery are mostly aerobic; under this conditions the presence of nitrification processes is promoted. However, the concentration of nitrogen being discharge into the water body has been higher than what it is required by law. One way to reduce the concentration of this pollutant in the treated water is by combining nitrification/denitrification processes. Denitrification processes allows the removal of nitrate as nitrogen gas from the water and it's done by a certain type of microorganisms.

For nitrification/denitrification process to occur, different tanks are required as the microbes in charge of doing each process are different and thus have different growth conditions. Denitrifiers are anaerobic organisms that require the presence of organic carbon for their growth and reproduction; nitrifers are aerobic microorganisms that use inorganic carbon (CO_2) as a major carbon source. One proposed configuration would be the addition of an anoxic tank prior the activated sludge unit. Ammonia is converted to nitrate in the activated sludge unit, this nitrate would be then recirculated and converted into nitrogen gas in the anoxic tank. The configuration of the process should be as the one present in figure 9. It is important to mention that the level of BOD_5 in the anoxic tank should be enough to promote the growth of the denitrification bacteria (Keffala, et al., 2011). The use of a denitrification tank can also help to remove sulfur and carbon from the wastewater; Reyes-Avila et al. (2004) found that removal efficiencies in a denitrifying reactor under steady state was more than 90% for carbon and nitrogen, whilst sulfide was removed as elemental sulfur by up to 99%.

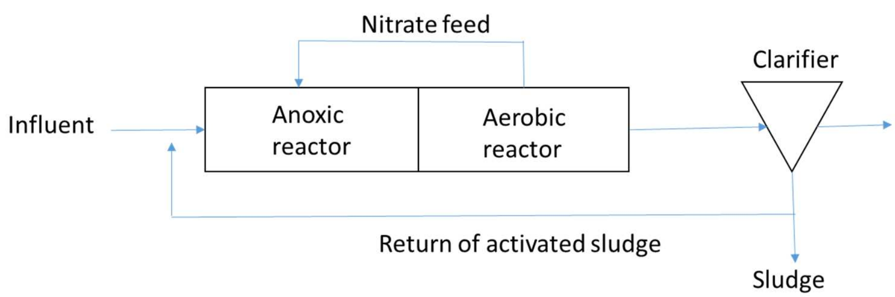


Figure 9. Pre-anoxic denitrification configuration (Metcalf & Eddy, 2014).

The PWTP doesn't have a unit to remove residual constituents coming from the secondary treatment (considering that the sedimentation basin is part of the activated sludge process). As it can be seen from table 8 (see results, section 5.2). The concentration of TSS in the discharge to the water body is higher than that present in the effluent of the ETP, meaning that there are some solids being added by the activated sludge unit. An additional treatment is required to remove organic and inorganic suspended ad colloidal particular matter, biological constituents, and dissolved organic and inorganic pollutants that can still be present. The installation of a granular media filter would help to remove the amount of suspended solids, BOD_5, oil and grease and phosphorous, but it also helps to condition the water for a further disinfection or polishing unit (Metcalf & Eddy, 2014). The filter could be a dual filter media with anthracite and sand, as it would avoid clogging problems and as it is the commonly used one in wastewater treatment plants. A conventional activated sludge plus a filtration unit can give effluents with COD concentration of 30-70 mg/l, BOD_5 of 5-20 mg/l and TSS of 2-8 mg/l (Metcalf & Eddy, 2014).

The presence of organic acids, such as humic acids, in the effluent should be checked as their presence can lead to the formation of chlorination byproducts such as trihalomethanes and holoacetic acids. This should be assessed as some of this disinfection byproducts have shown to be carcinogenic and detrimental for human and animal health (Metcalf & Eddy, 2014). If the presence of organic acids is positive, then a different disinfection technique should be considered to use; one possible alternative if the treated water is clean enough (low turbidity and TSS) could be the use of UV lamps.

6. Conclusions

Treatment of process wastewater coming from refineries is crucial due to the presence of toxic compounds that, if discharged directly into water bodies, can harm the flora and fauna present in it. Its improper treatment could also affect its potential recycling and safe use in other processes or activities.

One of the major problems of ETP in refinery 1 is the high amount of oil entering the units. The removal of oil and grease in the ETP of refinery 1 is a crucial step as the high concentration of oil impacts the performance of all the treatment process downstream the train. The installation of a pretreatment unit for the wastewater coming from the desalter and the improvement of the oil recovery/skimmers present in each treatment unit could help to decrease the concentration of oil in the wastewater reaching the plant.

The ETP counts with a good treatment train that has the potential to decrease the pollutant concentration in the wastewater, however, an intense maintenance and rehabilitation program is needed as most of the units present have not been changed or modified since its construction in the 70's and present high physical deterioration. Also, a better control during the sampling and parameters' analysis is required to be able to understand how each treatment unit is working and when the unit is not working properly. The latter due to the fact that the presence of limited amount of data was mostly due to contamination of the samples, lack of personnel, and risky situation for the operator, among others.

Wastewater treatment plants in refineries are normally seen as a non-profitable process or area which might be the cause of its negligence by the company. However, since environmental legislations and requirements are becoming more stringent every day, the inattention of this process could lead to strong monetary fines, lawsuits and legal actions that could harm to the company's finances and reputation and at the same time, lead to irreparable damage to the limited natural resources of the country. That's why it is extremely important to have a better control in the quality of the treated wastewater discharges coming from this type of industry.

References

Alade, A. et al., 2011. Removal of oil and grease as emerging pollutants of concern in wastewater stream. *IIUM Engineering journal,* 12(4), pp. 161-169.

Almasi, A. et al., 2014. Effect of the retention time and the phenol concentration on the stabilization pond efficiency on the treatment of oil refinery wastewater. *Fresenius environmental bulletin,* 23(10), pp. 2541-2548.

Altas, L. & Büyükgüngör, H., 2008. Sulfide removal in petroleum refinery wastewater by chemical precipitation. *Journal of hazardous materials,* Volume 153, pp. 462-469.

American Petroleum Institute, 1990. *Monographs on refinery environmental control-management of water discharges.* sl:sn

Amiry, H., Sutherland, H., Martin, E. & Goodsell, P., 2008. Environmental management and technology in oil refineries. In: *Environmental tecnology on the oil industry.* sl:Springer, pp. 281-314.

API, 1990. *Monographs on refinery environmental control- management of water discharges,* sl: API publication.

Bagajewicz, M., 2000. A review of recent desing procedures for water networks in refineries and process plants. *Computers and chemical engineering,* Volume 24, pp. 2093-2113.

Bai, Z., Wang, H. & Tu, S., 2011. Oil-water separation using hydrocyclones enhanced by air bubbles. *chemical engineering research and design,* 89(1), pp. 55-59.

Baker Hughes, 2011. *Improve crude oil desalting capabilities.* sl:sn

Basha, K., Rajendran, A. & Thangavelu, V., 2010. Recent advances in biodegradation of phenol: a review. *Asian journal of expermiental biological sciences,* 1(2), pp. 219-234.

Belila, A. et al., 2013. Sulfur bacteria in wastewater stabilization ponds periodicaly affected by the red-water phenomenon. *Applied microbiology and biotechnology,* 97(1), pp. 379-394.

Bellucci, M. et al., 2011. Low dissolved oxygen nitrifying systems explicit ammonia oxidizing bacteria with unusually high yields. *Applied environmental microbiology,* 77(21), pp. 7787-7796.

Benyahia, F., Abdulkarim, M., Embaby, A. & Rao, M., 2006. Refinery wastewater treatment: A true technological challenge. *The seventh annual U.A.E. university research conference,* pp. 186-193.

Berne, F. & Cordonnier, J., 1995. *Industrial water treatment.* Houston: Gulf publishing company.

Chamorro, S., Xavier, C., Becerra, J. & Vidal, G., 2009. Aerobic removal of stigmasterol contained in kraft mill effluents. *Electronic journal of biotechnology,* 12(2).

Chun, H., Yizhong, W. & Hongxiao, T., 2000. Destruction of phenol aqueous solution by photocatalysis or direct photolysis. *Chemosphere,* Volume 41, pp. 1205-1209.

CNA, 1997. *Título de concesión de descarga.* sl:sn

Coelho, J., Castro, A., Dezotti, M. & Sant'Anna, G., 2006. Treatment of petroleum refinery sourwater by advanced oxidation processes. *Journal of Hazardous Materials,* Volume 137, pp. 178-184.

CONAGUA, 2013. *Estadísticas del agua en México,* Mexico city: Comisión Nacional del Agua.

Das, N. & Chandran, P., 2011. Microbial degradation of petroleum hydrocarbon contaminants: an overview. *Biotechnology research international,* pp. 1-13.

El-Naas, M., Al-Zuhair, S. & Alhaija, M., 2010. REduction of COD in refinery wastewater through adsoprtion on date-pit activated carbon. *Journal of hazardous materials,* 173(1), pp. 750-757.

El-Naas, M., Al-Zuhair, S. & Alhaija, M., 2010. Removal of phenol from petroleum refinery wastewater through adsorption on date-pit activated carbon. *Chemical engineering journal,* Volume 162, pp. 997-1005.

EU council, 1991. *Council directive concerning urban waste water treatment,* sl: Official Journal of the European Communities.

FAO, 1992. *Wastewater treatment and use in agriculture.* [Online]
Available at: http://www.fao.org/docrep/t0551e/t0551e00.htm#Contents
[Geopend 2015 march 20].

Freney, J., Simpson, J. & Denmead, O., 1983. Volatilization of ammonia. *Develpments in plant and soil sciences,* Volume 9, pp. 1-32.

Gerardi, M., 2005. *Nitrification and denitrification in the activated sludge process.* sl:John Wiley and Sons.

Giroud, J. & Gourc, J., 2015. The first doubel geomembrane liner 40 years later. *Geosynthetics,* 33(1), pp. 14-24.

Heider, J. & Schühle, K., 2013. Anaerobic biodegradation of hydrocarbons including methane. In: *The prokaryotes- Prokaryotic physiology and biochemistry.* sl:Springer, pp. 605-634.

Hu, G., Li, J. & Zeng, G., 2013. Recent development in the treatment of oily sludge from petroelum industry: a review. *Journal of hazardous materials,* Volume 261, pp. 470-490.

IAENL, 2010. *Estudio de modernización de la planta de tratamiento de efluentes.* Cadereyta: sn

IFC, 2007. *Guías sobre medio ambiente, salud y seguridad para la refinación del petróleo,* sl: sn

IPIECA, 2010. *Petroleum refining water/wastewater use and management,* London: IPIECA.

Irfan, M. et al., 2013. the removal of COD, TSS and colour of black liquor by coagulation-flocculation process at optimized pH, settling and dosing rate. *Arabian journal of chemistry.*

Ishak, S., Malakahmad, A. & Isa, H., 2012. Refinery wastewater biological treatment: a short review. *Journal of scientific & industrial research,* 71(4), pp. 251-256.

Keffala, C., Galleguillos, M., Ghrabi, A. & Vasel, J., 2011. Investigation of nitrification and denitrification in the sediment of wastewater stabilization ponds. *water air and soil pollution,* Volume 219, pp. 389-399.

Kriipsalu, M., Marques, M. & Maastik, A., 2008. Characterization of oily sludge from a wastewater treatment plant flocculation-flotation unit in a petroleum refinery and its treatment implications. *Journal of material cycles and waste management,* Volume 10, pp. 79-86.

Kulkarni, S. & Kaware, J., 2013. Review on research for removal of phenol from wastewater. *International journal of cientific and research publications,* 3(4), pp. 1-5.

Kulkarni, S. & Kaware, J., 2013. Review on research for removal of phenol from wastewater. *International journal of scientific and research publications,* 3(4).

L'Altrella, C., 2007. *Stormwater runoff from elevated highways: prediction of COD from feld measurments and TSS.* New Orleans: sn

Leavitt, M. et al., 2004. *Technical support document for the 2004 effluent guidelines program plan,* Washington: USEPA.

Lee, L. et al., 2004. Two stage SBR for treamtnet of oil refinery wastewater. *water science and technology,* 50(10), pp. 243-249.

Liu, D. & Liptak, B., 1999. *Environmental engineers' handbook.* sl:CRC press.

Long, X. et al., 2013. Application of rhamnolipid as a novel biodemulsifier for destabilizing waste crude oil. *Bioresource technlogy,* Volume 131, pp. 1-5.

Maha, A., Aziz, A., Abdulqahar, M. & Kutaiba, A., 2011. Estimating and modelling the interrelationships between physcochemical pollutants of samara drug factory wastewater. *European journal of scientific research,* 61(2), pp. 230-241.

Martel-Valles, J. et al., 2013. Effect of the application of produced water on the growth, the concentration of minerals and toxic compounds in tomato under greenhouse. *Journal of environmental protection,* Volume 4, pp. 138-146.

Mayo, A., Hanai, E. & Kibazohi, O., 2014. Nitrification-denitrificaiton in a coupled high rate. water hyacinth ponds. *physics and chemistry of the earth ,* Volume 72-75, pp. 88-95.

Metcalf & Eddy, 2014. *Wastewater engineering: treatment and reuse.* fifth edition red. sl:McGraw Hill.

Monroe Environmental, 2012. *Water & wastewater treatment.* Michigan: sn

Norouzbahari, S., Roostaazad, R. & Hesampour, M., 2009. Crude oil desalter effluent treatment by a hybrid UF/RO membrane separation process. *Desalination,* Volume 238, pp. 174-182.

Otokunefor, T. & Obiukwu, C., 2005. Impact of refinery effluent on the physicochemical properties of a water body in the Niger delta. *Applied ecology and environmental research,* 3(1), pp. 61-72.

Parkash, S., 2003. *Refining processes handbook.* sl:Elsevier.

PEMEX, 2013. *Informe de Sustentabilidad 2013,* México, D.F.: sn

PEMEX, 2014. *Informe de sustentabilidad,* sl: sn

PEMEX, 2014. *PEMEX- Base de datos institucional.* [Online]
Available at: http://ebdi.pemex.com/bdi/bdiController.do?action=cuadro&cvecua=RPROREF
[Geopend 25 March 2014].

Pescod, M., 1992. *wastewater treatment and use in agriculture.* sl:FAO.

PROBIG, sd *high quality non-metallic scraping systems.* [Online]
Available at: http://www.probig.com/en/products/api-scrapers/
[Geopend 01 May 2015].

PTQ, 2011. *Petroleum technology: The refining, gas & petrochemicals processing website.* [Online]

Available at: http://www.eptq.com/article_index.aspx?intContentID=10
[Geopend 18 march 2015].

Rajaram, R. & Melchers, R., 2005. waste management. In: *Sustainable mining practices: a global perspective.* sl:Taylor and Francis group, pp. 193-230.

Reyes-A, J., Razo-Flores, E. & Gomez, J., 2004. Simultaneous biological removal of nitrogen, carbon and sulfur by denitrification. *Water research,* Volume 38, pp. 3313-3321.

Rizk, S., Mageed, A. & Abu-ali, M., 2010. dewaterign the sludge generated from water treatment plants with two hydrocyclones in series. *journal of engineering sciences,* 38(3), pp. 797-806.

Russell, D., 2006. Dissolved air flotation and techniques. In: *PRactical wastewater treatment.* New Jersey: John Wiley & Sons.

Saien, J. & Nejati, H., 2007. Enhanced photocatalytic degradation of pollutants in petroleum refinery wastewater under mild conditions. *Journal of Hazardous Materials,* Volume 148, pp. 491-495.

Scheirs, J., 2009. *A guide to polymeric geomembranes: A practical approach.* UK: Wiley.

Schultz, T., 2005. Get the most out of API separators. *Chemical Engineering,* 112(7), pp. 38-42.

Schultz, T., 2006. Improve oily wastewater treatment. *Hydrocarbon processing,* p. 1.

SENER, 2011. *Balance nacional de energía,* Mexico city : sn

Shalaby, I. et al., 2003. Assessment of the effectiveness of the aeration lagoons system in sewage treatment with reference to the removal of protozan cysts and helmith eggs. *Egyptian journal of zoology,* Volume 40, pp. 203-224.

SIEMENS, 2006. *Petroelum refinery, ethylene and gas plant wastewater treatment.* sl:sn

Srinivas, T., 2008. *Environmental biotechnology.* New Delhi: New Age International.

Stephenson, R. & Blackburn, J., 1998. *The industrial wastewater system handbook.* sl:CRC Press LLC.

Tuncal, T. & Uslu, O., 2014. A revie of dehydration of various industrial sludges. *Drying technology: an international journa,* 32(14), pp. 1642-1654.

Underwater warehouse, 2013. [Online]
Available at: http://www.underwaterwarehouse.com/Multi-Vent-Underliner-System-Pond-Liner-and-Sealants-sc-4192.html
[Geopend 30 March 2015].

UNEP, 2010. *Clearing the waters: A focus on water quality solutions,* Oakland, CA: UNEP.

UN-Water, 2007. Coping with water scarcity. Challenge of the twenty-first century.

UN-Water, 2013. *Water quality factsheet.* sl:sn

USEPA, 1982. *Handbook for sampling and sample preservation of water and wastewater,* sl: USEPA.

USEPA, 2002. *Wastwater technology fact sheet: Anaerobic lagoons,* Washington, DC: sn

USEPA, 2004. *Technical support document for the 2004 effluent guidelines progrma plan ,* Washington, DC: USEPA.

USEPA, 2006. *Consumer factsheet on nitrates/nitrites,* Washington: USEPA.

USEPA, 2011. *Principles of design and operations of wastewater treatemnt pond systems for plant operators, engineers and managers,* Washington, D.C.: USEPA.

USEPA, 2012. *Effluent guidelines and standards- Petroleum refining point source category ,* sl: USEPA.

USEPA, 2013. *Aquatic life ambient water quality criteria for ammonia- freshwater,* Washington: sn

USEPA, 2013. *Basic information about regulated drinking water contaminants and indicators.* [Online]
Available at: http://water.epa.gov/drink/contaminants/basicinformation/
[Geopend 20 01 2015].

Van Schie, P. & Young, L., 2000. Biodegradation of phenol: mechanisms and applications. *Bioremediation journal,* Volume 4, pp. 1-18.

Varón, M. & Mara, D., 2004. *Waste stabilization ponds,* Delft: IRC international water and sanitation center.

Veeresh, M. & Veeresh, A., 2010. Dynamics of industrial waste stabilization pond treatment process. *Environmental monitoring assessment,* Volume 169, pp. 55-65.

Volke, T. & Velasco, J. A., 2002. *Tecnologías de remediación para suelos contaminados.* México: Instituto Nacional de Ecología.

Wake, H., 2005. Oil refineries: a review of their ecologial impacts on the aquatic environment. *Estuarine, coastal and shelf science,* Volume 62, pp. 131-140.

Wang, L., Fahey, E. & Wu, Z., 2005. *Physicochemical treatment processes.* sl:Humana Press.

WHO, 2003. *Polynuclear aromatic hydrocarbons in drinking water,* Geneva: sn

Wong, J. & Hung, Y., 2005. Treatment of oilfield and refinery wastes. In: *Waste treatment in the process industries.* sl:Taylor & Francis Group, pp. 235-306.

World Health Organization (WHO), 2002. *World Health Report: Reducing risk, promoting healthy life,* France: sn

Xavier, C. et al., 2009. Activated sludge versus aerated lagoon treatment of kraft mill effluents containing beta-sitosterol and stigmasterol. *journal of environmental sciences and health. Part A, toxic/hazardous substances & environmental engineering,* 44(4), pp. 327-335.

Yan, P. et al., 2012. Oil recovery from refinery oily sludge using rhamnolipid biosurfactant-producing Pseudomonas. *Bioresoure technology,* Volume 116, pp. 24-28.

Young, J., Clesceri, L. & Kamhawy, S., 2005. Changes in the biochemical oxygen demand prcedure in the 21st edition of standard methods for the examination of water and wastewater. *Water enviornment research,* 77(4), pp. 404-410.

Yu, L., Han, M. & Fang, H., 2013. A review of treating oily wastewater. *Arabian journal of chemistry,* pp. 1-10.

Annex I.

Table 1. EU limit of pollutants found in industrial wastewater discharges

Substance	Annual average-Inland surface waters (µg/l)	Annual average-Other surface waters(µg/l)	Maximum allowable concentration-Inland surface waters(µg/l)	Maximum allowable concentration-Other surface waters(µg/l)
Alachlor	0.3	0.3	0.7	0.7
Anthracene	0.1	0.1	0.1	0.1
Atrazine	0.6	0.6	2	2
Benzene	10	8	50	50
Brominated dyphenylethers	-	-	0.14	0.14
Cadmium*	<0.08	0.2	<0.45	<0.45
Carbon tetrachloride	12	12	-	-
C10-13 Chloroalkanes	0.4	0.4	1.4	1.4
Cyclodiene pesticides	0.01	0.005	-	-
DDT	0.025	0.025	-	-
1,2-dichloroethane	10	10	-	-
dichloromethane	20	20	-	-
DEHP	1.3	1.3	-	-
Fluoranthene	0.0063	0.0063	0.12	0.12

Hexachlorobenzene			0.05	0.05
Lead and its compounds	1.2	1.3	14	14
Mercury and its compounds			0.07	0.07
Naphtalene	2	2	130	130
Nickel and its compounds	4	8.6	34	34
Nonylphenols	0.3	0.3	2	2
Octylphenols	0.1	0.01	-	-
Pentachlorobenzene	0.007	0.0007	-	-
Pentachlorophenol	0.4	0.4	1	1
PAH	-	-	-	-
Simazine	1	1	4	4
Tetrachloroethylene	10	10	-	-
Trichloroethylene	10	10	-	-
Tributyltin compounds	0.0002	0.0002	0.0015	0.0015
Trichlorobenzenes	0.4	0.4	-	-
Trifluralin	0.03	0.03	-	-
PFOS	6.5*10^-4	1.3*10^-4	36	7.2
Aclonifen	0.12	0.012	0.12	0.012
Bifenox	0.012	0.0012	0.04	0.004
HBCDD	0.0016	0.0008	0.5	0.05
Terbutryn	0.065	0.0065	0.34	0.034

*depends on water hardness classes, values presented are for class 1 hardness

Table 2. Mexican limits for pollutants in wastewater discharges

Parameters mg/l (except when specified)	Rivers						Artificial and natural reservoirs				Coastal waters						Soil			
	Irrigation		Municipal distribution		Aquatic life protection		irrigation		Municipal distribution		Fishing, navigation, others		Recreational		Estuary		irrigation		wetlands	
	M.A	D.A	M.A	D.A	M.A	D.A	M.A	D.A	M.A	D.A	M.A	D.A	M.A	D.A	M.A	D.A	M.A	D.A	M.A	D.A
Temperature (°C)	-	-	40	40	40	40	40	40	40	40	40	40	40	40	40	40	-	-	40	40
Oil and grease	15	25	15	25	15	25	15	25	15	25	15	25	15	25	15	25	15	25	15	25
Floating material	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Settleable materials (ml/l)	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	-	-	1	2

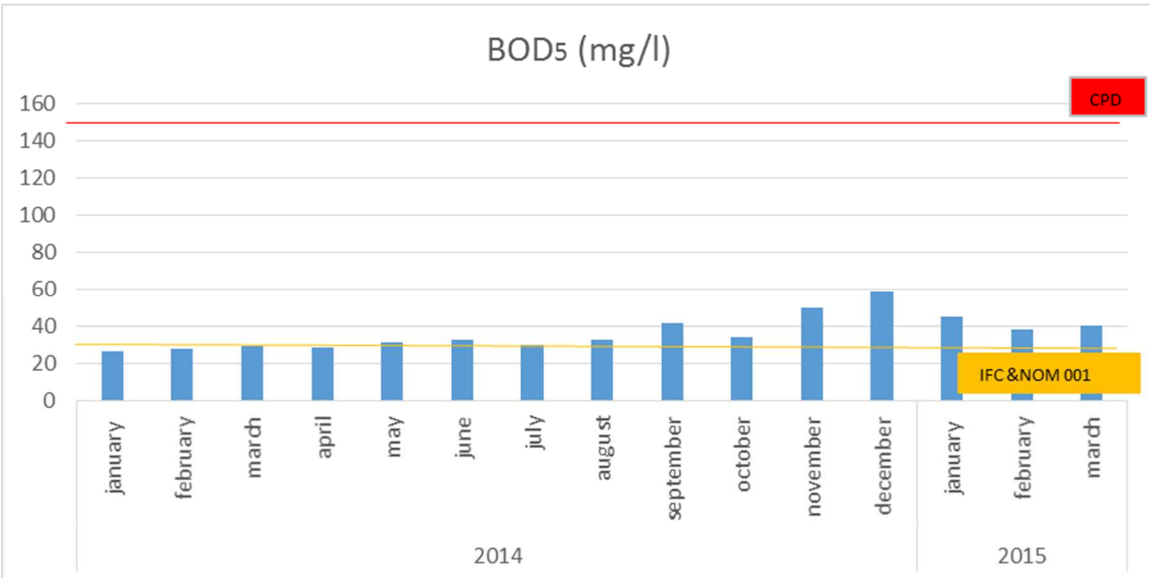
Total suspended solids	150	200	75	125	40	60	75	125	40	60	150	200	75	125	75	125	-	-	75	125
Biochemical Oxygen Demand 5	150	200	75	150	30	60	75	150	30	60	150	200	75	150	75	150	-	-	75	150
Total nitrogen	40	60	40	60	15	25	40	60	15	25	-	-	-	-	15	25	-	-	-	-
Total phosphorous	20	30	20	30	5	10	20	30	5	10	-	-	-	-	5	10	-	-	-	-
Arsenic	0.2	0.4	0.1	0.2	0.1	0.2	0.2	0.4	0.1	0.2	0.1	0.2	0.2	0.4	0.1	0.2	0.2	0.4	0.1	0.2
Cadmium	0.2	0.4	0.1	0.2	0.1	0.2	0.2	0.4	0.1	0.2	0.1	0.2	0.2	0.4	0.1	0.2	0.05	0.1	0.1	0.2
Cyanide	1	3	1	2	1	2	2	3	1	2	1	2	2	3	1	2	2	3	1	2
Copper	4	6	4	6	4	6	4	6	4	6	4	6	4	6	4	6	4	6	4	6
Chromium	1	1.5	0.5	1	0.5	1	1	1.5	0.5	1	0.5	1	1	1.5	0.5	1	0.5	1	0.5	1
Mercury	0.01	0.02	0.005	0.01	0.005	0.01	0.01	0.01	0.005	0.01	0.01	0.02	0.01	0.02	0.01	0.02	0.005	0.01	0.005	0.01
Nickel	2	4	2	4	2	4	2	4	2	4	2	4	2	4	2	4	2	4	2	4
Lead	0.5	1	0.2	0.4	0.2	0.4	0.5	1	0.2	0.4	0.2	0.4	0.5	1	0.2	0.4	5	10	0.2	0.4

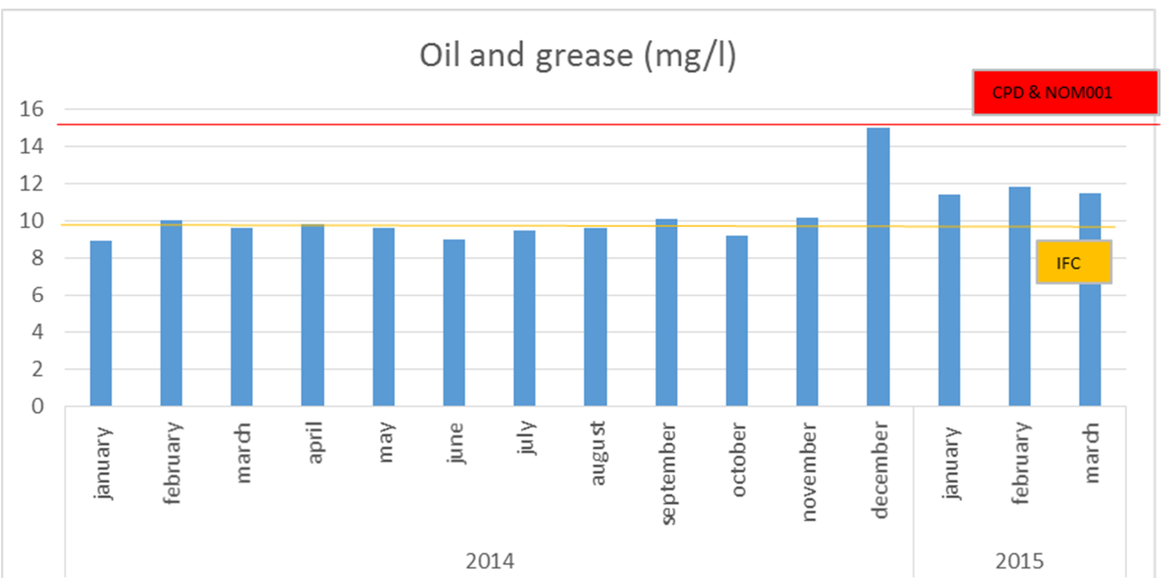
Zinc	10	20	10	20	10	20	10	20	10	20	10	20	10	20	10	20	10	20	10	20

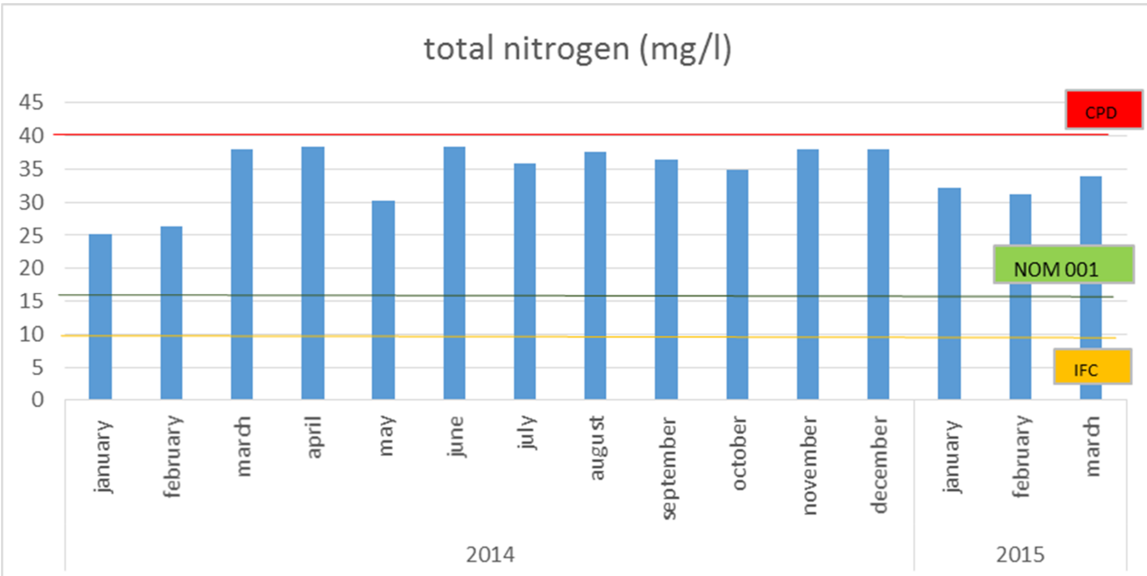
D.A: daily average, M.A.: monthly average

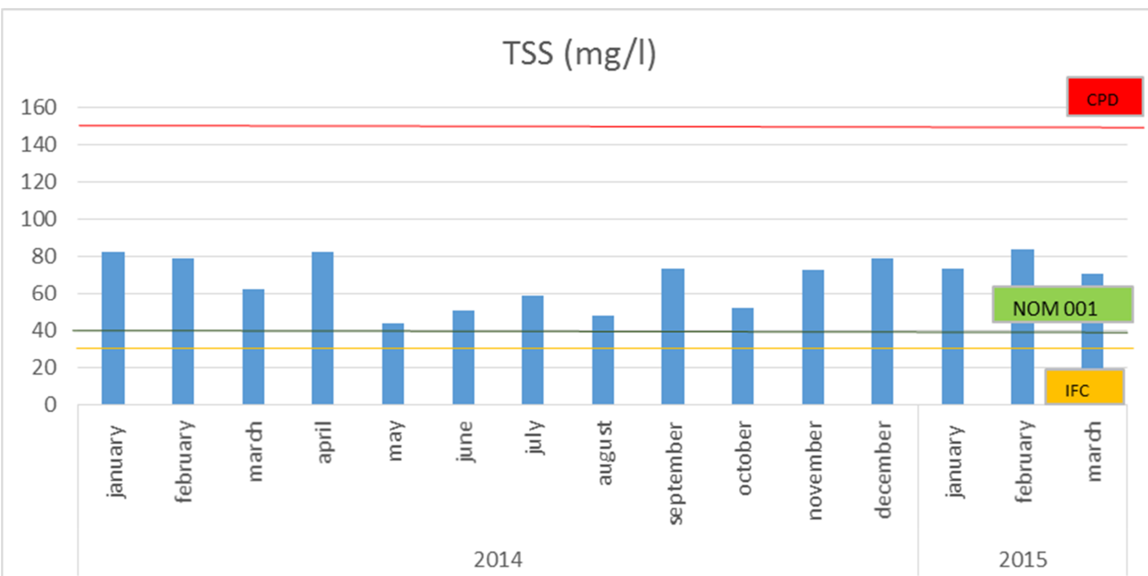
Annex II.

Comparison of different parameter's limits and data of Refinery 1 concentration from 2014-2015






total nitrogen (mg/l)
45
40
35
30
25
20
15
10
5
0
CPD
NOM 001
IFC
january
february
march
april
may
june
july
august
september
october
november
december
january
february
march
2014
2015


TSS (mg/l)
160
140
120
100
80
60
40
20
0
CPD
NOM 001
IFC
january
february
march
april
may
june
july
august
september
october
november
december
january
february
march
2014
2015

Annex III.

Table 1. Monthly average concentration of pollutants in the unregistered discharge of Refinery 1 in the period from January 2014-March 2015

	Discharge to water body	Unregistered discharge
Oil and grease (mg/l)[2]	12.03	79.27
COD (mg/l)	153.70	363.84
TSS (mg/l)	67.83	ND
BOD_5 (mg/l)	36.45	ND
Total nitrogen (mg/l)	46.13	53.36
Sulfur (mg/l)	ND	ND
Phenol (mg/l)	0.14	5.27