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Water Quality of The Tula River related to the petroleum refining industry: accumulation factors and treatments

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Abstract

The petroleum refining processing counts on two main phases and a wide number of different operations to generate fuels and other useful products. The first phase is to eliminate salts and then, to distil a lot of compounds or fractions. The second phase includes three kinds of processes: to combine, to separate and to structure. Even if the petroleum refineries apply currently water treatments to eliminate the pollutant substances before the river dumping, in some countries, like Mexico, there are cities or towns near the petroleum refining installations and it is very important to develop monitoring programs to avoid human health problems related to industrial pollution. The Tula River is an important closed basin that flows to The Endhó Dam and to several aqueducts. The aim of this paper was to establish pollutant emission factors from the refining industry to estimate the influence of the Miguel Hidalgo Refinery in the water quality of this river. Two sampling campaigns were carried out in the dry and the wet seasons, considering the industrial effluent after the treatment and in ten sampling stations in The Tula River. The levels of the main environmental parameters at this aquatic ecosystem, like pH, temperature, suspended matter, flow, grease and oil, total nitrogen, settled solids, suspended solids, Biochemical Oxygen Demand, fecal coliform bacteria, cyanide, arsenic, mercury, cadmium, copper, chromium, nickel, lead, zinc, phosphorus, contemplated by the Mexican legislation,

were compared to the levels found in the effluent. According to the sampling results, the main kinds of wastewater treatments were analyzed and a numerical efficiency analysis was developed for the best option selection to be applied to diminish the pollution in the water column of The Tula River in the Mexican Hidalgo State, to reach a sustainable management.

1 Introduction

The petroleum refining industry has a wide number of operations to generate fuels and other useful by-products. The first phase is to eliminate salts and to distil a lot of compounds or fractions. The second phase includes three kinds of processes: to combine, to separate and to structure. Even if the petroleum refineries apply currently water treatments which eliminate the pollutant substances before the river dumping, in some countries, like Mexico, there are cities or towns near the petroleum refining installations and it is very important to develop monitoring programs to avoid human health problems related to industrial pollution. The distilling process separates different boiling points hydrocarbons; there are two types of it: atmospheric and by vacuum distilling. The petroleum is separated in fractions to produce different products, to be sold later in the international market, e.g. gasoline, gas; fuels for jets, industrial and heavy vehicles. However some pollutants are produced during the different processes [1] (Table 1), which have to be eliminated by means of effective wastewater treatments including primary, secondary and tertiary ones [2].

One way to state the effects of the refinement industry in its surroundings influence zone is by measuring the levels of some main pollutants inside and outside the refineries as well as to calculate emission factors, which can be compared with the values found in the air, soil and water bodies, determining the spatial affectation of this industrial activities.

The Tula River has an extended basin among the Hidalgo and Mexico States, its flow is controlled by dams built over the river and its tributaries, as Requena and Endhó. The main affluent forming Tula River are: Tepeji, el Salto, Tlautla, Rosas and el Salado. In its lowest place, after passing by Ixmiquilpan and El Tasquillo Valleys receives other important tributaries to form the Moctezuma River, and later The Panuco River, to end up into the Gulf of Mexico [3]. The Valley of Mexico contributes to the river basin with 1´636,43 mm^3/year, from which, 943,91 mm^3/year are of wastewaters from the metropolitan zone of Mexico city and some pluvial water. In The Tula River, the sampling was made in the shore, 10 km to the south and 15 km to the north of the population of Tula de Allende where several populations are located unloading their residual waters with no processing into The Tula River, since plants of wastewater processing do not exist. For over 70 years, this river has received an important volume of wastewaters from different sources, mainly textile, refinement, hydroelectricity and cement industries ones, besides municipal waters containing high volumes of fecal feces. The Tula River water is used for agricultural irrigation: pasture, grains, fruit trees and vegetables, this practice represents a high sanitary risk though, due to the levels of bacteria associated to the wastewaters containing pathogenic gas producing bacteria, as coliform, that lives in the mammals digestive tracts [4].

Table 1. Main pollutants produced by the petroleum refinement [1].

Aluminum oxide	Molybdenum
Amine	Naftenes
Ammonium	Nickel
Aromatics	Nitrogenous compounds
Benzene	Nitrogenous substances
Calcium chloride	Oil with disulfur
Carbon monoxide	Organic chloride
Caustic substances	Other hydrocarbons
Cobalt	Phenol
Corrosive caustics	Phosphoric acid
Dust	Platinum
Haloid	Propane
Heavy metals	Sodium chloride
Hydrochloric acid	Sour gas and water
Hydrosulphuric acid	Sulfides
Hydrofluoric acid	Sulfuric acid
MEC–toluene	Sulfur
Mercaptanes	Dioxide of sulfur
Metil-etil-cetone	Sulfurous acid
Metil-isobutil cetone	Tungsten

2 Objectives

This paper was developed to determine the refinement industry effects in the surrounding environment, and to establish emission factors based on inventories of the main pollutants unloaded in wastewaters, final effluents and in a river, inwalls and outwalls the Miguel Hidalgo of Tula, Hgo. Refinery, to develop recommendations associated with the wastewater treatment optimization, within other corrective actions, to lead the Mexican refineries towards a sustainable development.

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3 Methodology

Inventories were carried out to determine the refinement industry effects in the surrounding environment, and the emission factors from the main remainders in wastewaters, inwalls the Miguel Hidalgo of Tula, Hgo. Refinery: a) wastewater from the main processes (discharge), b) wastewater treatment (treatment) and c) final effluent; and in outwalls in ten sampling sites before and after in The Endhó Dam at The Tula River, which is the diffuser receptor (Figures 1 and 2).

Two sampling campaigns were carried out, representative of the extreme seasons, in inwalls and outwalls areas from the refinery, considering residual unloadings evaluation and the characterization of the hydrology as well as the pollution conditions in The Tula River, Hgo., Mex.

This evaluation was based on the Mexican regulation, specifically the NOM-001-ECOL-1996, and methods to analyze wastewater internationally accepted [5, 6].

Within the parameters determined are pH, temperature, suspended solids, total nitrogen, greases and oil, biochemical oxygen demand, cyanide, total phosphorus, heavy metals (Cd, Cr, Cu, Ni, Pb, Zn, As, Hg), total-fecal coliform bacteria and flow. Moreover, in The Tula River, were considered physical-chemical characteristics, other water column and sediment pollutants; same are being prepared to be published in another journal on its hydrology.

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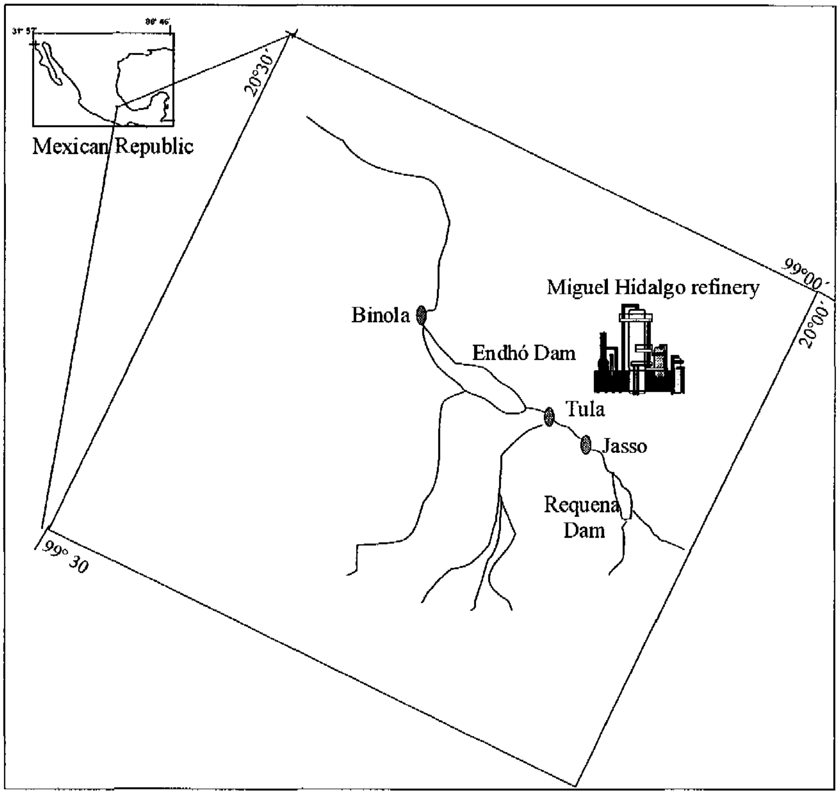

Figure 1: Study area, inwalls at Miguel Hidalgo Refinery discharges, and outwalls at The Tula River (before and after in The Endhó Dam).

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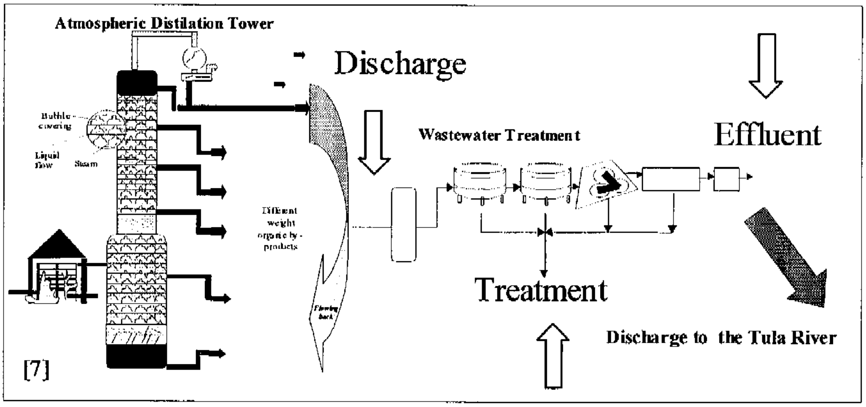
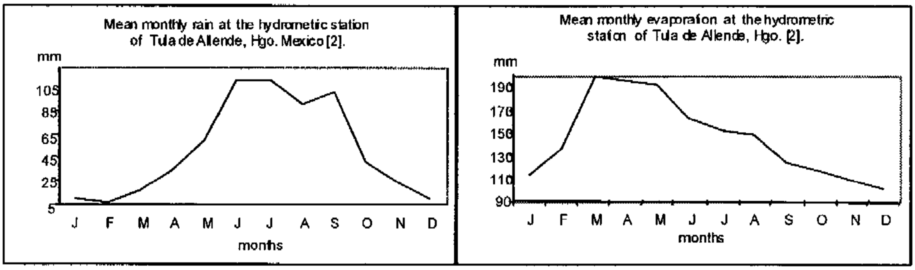


Figure 2: On July 2000 inwalls samples were taken from The Miguel Hidalgo Refinery wastewaters, after the main processes (discharge), during the wastewater treatment (treatment) and at the river diffuser (effluent).



3.a) 3.b)

Figure 3: a) Rain and b) evaporation regime at Tula, Hidalgo, Mexico.

Taking into account the climatic regime in Tula, Hidalgo, climatic seasons were selected; the wet (July 2000) and the dry (March 2001) in order to consider the extreme conditions related to a dilution or a concentration of pollutants in The Tula River (Figure 3).

In both campaigns the samples from the refinery discharges and the water column and sediments from The Tula River were taken simultaneously. The sampling sites into the river were divided by The Endhó Dam before and after.

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4 Results

Table 2 includes the results of the measurements developed in July 2000 and March 2001, representative of the wet and dry extreme climatic seasons in Tula, Hgo. Mexico.

The Miguel Hidalgo refinery treatment system efficiency evaluated on July 2000 had a variation from 0 to 77.6 % for the total suspended solids, from 74.1 to 89.13 % for the greases and oil elimination and from 86.9 to 96.4 % to the BOD_5 removal.

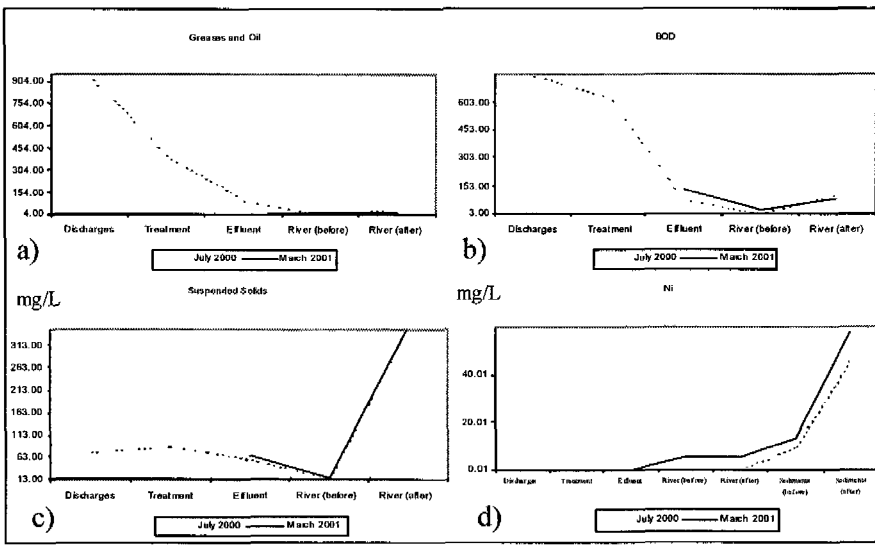

Figure 4. a) Greases and oil, b) BOD, c) Suspended Solids and d) Nickel at the Miguel Hidalgo refinery and The Tula River. July 2000, March 2001.

In order to improve the water quality discharged to The Tula River and to give some proposals on the refinery system treatment optimization, and suggestions to solve the regional pathogenic pollution, an analysis on the different available solutions was developed, granting a specific weight from 1 to 3 to the treatment system recommended for agricultural irrigation and final disposition into The Tula River. The highest efficiencies corresponding to stabilization lagoons plus disinfect for agricultural irrigation in populations lesser than 3000 inhabitants as Tula de Allende (95 %); anaerobic treatment plus aerobic and disinfect for different population densities in relation to the river unloading (70-85 %); the second higher efficiencies were for: trickling filters to unloading the waters to The Tula River (97 %), aerated lagoons plus disinfect to agricultural irrigation with different population densities (80 %). The lowest efficiencies included oxygen activated sludge plus disinfect for agricultural irrigation for the two different densities given (Table 3). The efficiency weighing was granted depending on the cost of the implementation, operation and management, the regional specific requirements related to the pollution existing and the removal efficiencies.

Table 2. Mean values of the refinery Miguel Hidalgo discharges from API separators, after the treatments, and wastewaters before the river; Tula River from the water colum and the sediments. July 2000 and March 2001. Tula, Hidalgo. Mexico.

July 2000.							
Parameter	Discharges	Treatment	Effluent	River (before)	River (after)	Sediments (before)	Sediments (after)
pH	8.36	8.94	8.11	7.32	7.13		
Temperature (oC)	50.00	26.45	22.77	21.87	21.20		
Suspended Solids (mg/L)	71	85	56.3	13	350		
N-TOT (mg/L)	594	391	91.84	3.89	33.24		
Greases and Oil (mg/L)	932	401.4	89	4.71	32.31		
BOD	744.44	625	72.22	2.27	95.91		
CN (mg/L)	0.007	0.006	0.01	0.01	0.008		
P-TOT (mg/L)	0.124	0.08	0.379	3.95	0.48		
Cd (mg/L)	< 0.01	< 0.01	< 0.01	<0.005	0.006	<0.50	2.03
Cr (mg/L)	< 0.01	< 0.01	< 0.01	0.072	0.051	18.14	44.94
Cu (mg/L)	< 0.01	< 0.01	< 0.01	0.012	0.04	11.96	113.17
Ni (mg/L)	< 0.01	< 0.01	< 0.01	<0.005	0.05	9.06	45.41
Pb (mg/L)	< 0.01	< 0.01	< 0.01	<0.01	<0.01	<5.00	64.95
Zn (mg/L)	< 0.01	0.15	< 0.01	0.013	0.313	52.58	290.09
As (mg/L)	0.017	0.038	0.044	0.003	0.009	1.08	3.06
Hg (mg/L)	0.002	0.001	< 0.0002	<0.0002	<0.0002	0.464	0.667
TCB / 100 mL	< 30	1825	1'896,667	43,000	90'100,000		
FCB / 100 mL	< 30	73.33	15,000	9,447	2'009,257		
FLOW m3/s	20.00	23.68	295.73	165'622,680			
March 2001							
Parameter	Effluent			River (before)	River (after)	Sediments (before)	Sediments (after)
pH	8.76			7.32	7.13		
Temperature (oC)	22.53			21.87	21.20		
Suspended Solids (mg/L)	64.33			13	349.71		
N-TOT (mg/L)	64.75			3.6	33.05		
Greases and Oil (mg/L)	4.75			7.85	19.07		
BOD	126.67			18.75	75		
CN (mg/L)	< 0.001			<1	<1		
P-TOT (mg/L)	0.49			3.95	4.22		
Cd (mg/L)	< 0.005			14.30	13.2	<0.50	3.28
Cr (mg/L)	0.012			0.02	0.022	0.02	0.026
Cu (mg/L)	0.007			36.2	64.2	10.36	94.94
Ni (mg/L)	< 0.005			<5	<5	13.01	57.82
Pb (mg/L)	0.021			55.03	62.8	19.99	76.69
Zn (mg/L)	0.19			78.33	115.37	37.54	106.57
As (mg/L)	0.05			<5	38.3	1.88	10.75
Hg (mg/L)	0.008			<5	<5	0.04	1.31
TCB MPN / 100 mL	52,700			183	1'267,143		
FCB MPN / 100 mL	766.67			36.66	147,300		
FLOW m3/s	1.87			165'622,680			

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Table 3. Recommended treatment system for two river water uses and their efficiencies [9, 10].

Population	Treatment system	Treated water use	Efficiency
< 3000 inhabitants	oxygen actived sludge+disinfect	agricultural irrigation	85-95 % (3)
< 3000 inhabitants	aerated lagoons+disinfect	agricultural irrigation	80 % (2)
< 3000 inhabitants	stabilization lagoons+disinfect	agricultural irrigation	95 % (1)
< 3000 inhabitants	anaerobic treatment+aerobic+disinfect	unloading to The Tula River	70–85 % (1)
< 3000 inhabitants	percolation filters	unloading to The Tula River	97 % (2)
Tula de Allende 82,333 inh.	anaerobic treatment+aerobic+disinfect	unloading to The Tula River	70-85 % (1)
82,333 inh.	oxygen activated sludge	agricultural irrigation	85–95 % (3)
82,333 inh.	ventilation lagoons+disinfect	agricultural irrigation	80 % (2)
82,333 inh.	stabilization lagoons+disinfect	agricultural irrigation	95 % (1)

5 Discussion

A measure of the strength of the wastewater is biochemical oxygen demand, or BOD_5. The BOD_5 measures the amount of oxygen microorganisms require in five days to break down sewage. Considering that untreated sewage has a BOD_5 ranging from 100 mg/L to 300 mg/L [8] the levels in the effluent denote an intermediate efficiency of the treatment system, considering mean values from 72 and 127 mg/L.

Pathogens or disease-causing organisms are present in sewage. Coliform bacteria are used as an indicator of disease-causing organisms. Sewage also contains nutrients (such as ammonia and phosphorus), minerals, and metals. Ammonia can range from 12 to 50 mg/l and phosphorus can range from 6 to 20 mg/l in untreated sewage [8].

The high volume of municipal wastewater from Mexico City represent a lot of compounds including pathogenic organism, gasoline, diesel remainders, nitrogen and phosphorus, etc. The results obtained are not enough to determine the pollution accumulation factors from the petroleum refining industry due to the great interference of the other discharges, which are not characterized and can not be differentiated from The Tula Refinery discharge.

There were some differences among the levels of pollutants in the final discharge to The Tula River and the levels measured before in The Endhó Dam. The sediments after the dam presented the biggest concentrations of the majority of pollutants, compared to the river water column before it.

Regarding the seasonal variability, the levels in the dry period, characterized by a greater evaporation and scarce rain, are higher (Figure 3).

The main problems detected in the refinery discharge and in the river were high levels of the total and fecal coliform bacteria, suspended solids, nitrogen and BOD_5.

The high level of nitrogen presented into the final unload of the refinery, has its origin in the wastewater of the sweetening processes. The solution is a depletion tower to remove total nitrogen before mixing with the total volume of the processing system.

There are a lot of discharges other than that of the refinery, from textile, electrical and cement industries, hospitals and municipalities; they include high loads from wastewaters from Mexico City, originating a big sanitary trouble related to extreme levels of total and fecal coliform bacteria. This kind of pollution represents an additional risk as the wastewaters are employed for irrigation waters at the Tula of Allende Agricultural District.

The refinery wastewater treatment will be improved considering the proposals with the aim of optimizing the water quality of the final disposal to The Tula River. However, it is necessary to make the authorities aware of decision making while establishing wastewater treatments for all the different discharges before their disposal into any water body; this is the only way to adequately solve the important pollution problem existing in Tula de Allende at The Tula River.

6 Conclusion

The quality of the water at The Tula River was bad due to the high loads of municipal wastewaters discharged into it without any kind of treatment. The main pollutants are the suspended solids, the total-fecal coliform bacteria, the suspended solids and the total nitrogen from the anthropogenic unloads. The pollution accumulation factors from the petroleum refining industry can not be determined for The Tula River due to the interference of a lot of discharges, which are not characterized and can not to be differentiated from the Tula Refinery discharge. There were some effects or accumulation of pollutants related to the Miguel Hidalgo Refinery into The Tula River. It is necessary to improve the treatment system, because of this an analysis and quantification of the efficiency was developed on the different available treatments to be applied and to get a better quality in that refinery before the final disposition of the industrial wastewaters to this river. The main trouble is that the municipal pollution is worse than the industrial one, as the former discharges were not treated and they needed to be.

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