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Implementation of the effluent limitations based on the best practicable control technology for the petroleum refining industry in Korea

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ABSTRACT

The effluent limitations of wastewaters discharged from various industrial facilities are based on uniform regulatory criteria in Korea. However, an individual effluent limitation on each effluent discharging industry is widely applicable for regulation of industrial wastewater in the USA and European Union (EU). The main objectives of this study were; (1) to suggest the method and procedure for establishing effluent limitations for the petroleum refining facilities on the basis of treatment technology to implement the most appropriate effluent limitations reflecting wastewater characteristics and the level of treatment technologies and (2) to estimate the effluent limitations based on the Best Practicable Control Technology (BPT) currently available. To decide an individual effluent limitation, Technology-Based Effluent Limitation (TBEL) was derived for the petroleum refining industry based on BPT in this study. It was suggested that effluent limitations were $BOD_5 5.0 \text{ mg/L}$, $COD_{Mn} 11.0 \text{ mg/}$ L, SS 4.0 mg/L, TN 7.0 mg/L, and TP 0.3 mg/L and BPT for the petroleum refining facilities in Korea was oil separation, coagulation and floatation, activated sludge treatment, and sand filter (or activate carbon filter). In order to implement new effluent limitations and BPT suggested in this study, institutional complements of separate effluent limitations for individual industrial sectors are urgently required in Korea.

Keywords: Effluent limitation; Technology Based Effluent Limitations (TBEL); Best Practicable control Technology currently available (BPT); Petroleum refining industry; National Pollutants Discharge Elimination System (NPDES)

1. Introduction

A set of comprehensive effluent limitations for industrial wastewater has been applied regardless of

wastewater characteristics, types of industries, and the level of treatment technology in Korea. The application of uniform effluent limitations was considered as an appropriate policy in the past since there were no substantial differences among the amounts of

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pollutants from discharge facilities. However, uniform limitations cannot properly accommodate the rapidly developing modern industrial environments, and also cannot reflect the differences in treatment technologies and management abilities among the discharge facilities with similar scales and industries when there is no appropriate way to apply the same limitations of similar scale industries [1].

In order to determine the individual effluent limitations for various industrial sectors according to the wastewater discharge characteristics, sufficient data, time, and specialized processes for technology evaluation for wastewater discharge characteristics, the level of treatment techniques applied, and water quality impact are required. The most appropriate limitations for related discharge facilities are adopted through technology evaluations by experts for various industries, and the effluent limitations are finally determined by authorized agencies. After the interim effluent limitations are established, they need to be periodically updated to reflect the management policies and environmental changes.

For this reason, National Pollutants Discharge Elimination System (NPDES) [2] by the USA and Integrated Pollution Prevention and Control (IPPC) [3] Directives by the European Union (EU) are determining the effluent limitations considering the wastewater characteristics, level of treatment technologies, and water quality impacts, and considered these as the basic procedure for the permission processes of discharge facilities.

In the USA, Environmental Protection Agency classified the industrial sectors in detail (500 subcategories over 56 categories) and proposed guidelines for separate effluent limitation for each industrial sector for the purpose of managing properly and reducing industrial wastewater pollutants. Based on these guidelines, individual discharge permits for discharge facilities are being issued by state governments. In order to issue the individual guidelines, geographic locations and the kinds and amount of products of the discharge facilities and the concentrations and kinds of pollutants in the wastewater from those facilities are investigated. Secondly, Technology-Based Effluent Limitation (TBEL) based on the level of wastewater treatment technologies and Water Quality-Based Effluent Limitation (WQBEL) based on the regional characteristics of water bodies, compliance with water quality standards, effect on the human health and aquatic organisms, were determined. Finally, NPDES specifying the final effluent limitations including post-management plan is issued on the basis of various opinions among relevant stakeholders.

Several TBELs currently used in the USA are summarized in Table 1 [4].

In Europe, the IPPC Directive was adopted by EU to secure a high level of environmental protection in 1996 [3]. The directive categorized over six main industrial activities: energy, metal production and processing, mineral industry including ceramics and glasses manufacturing, chemical industry, waste management, and other activities including pulp and paper, tanning, and certain agricultural activities [3]. IPPC Directive has evaluated the integrated management methods of various pollutants from those facilities in accordance with Best Available Technology (BAT). Investigation parameters are the kinds and industrial activities of discharge facilities, raw and subsidiary materials, and energy for industrial activities, pollution sources, regional conditions, the amount and characteristics of pollutants discharged into the environment and impacts, technologies for pollutant emission prevention and reduction, methods for waste

Table 1	
Summary of TBEL proposed by USEPA	

Section	Description	
BPT	Best Practicable Control Technology Currently Available	Existing Source, Direct Discharge, Conventional, Toxic, Non-conventional pollutants, Average performance of treatments
BCT	Best Conventional Pollutant Control Technology	Existing Source, Direct Discharge, Conventional pollutants
BAT	Best Available Technology Economically Achievable	Existing Source, Direct Discharge, Toxic and Nonconventional pollutants, Best performance of treatments
NSPS	New Source Performance Standards	New Source, Direct Discharge, Conventional, Toxic, Nonconventional pollutants
PSES	Pretreatment Standards for Existing Source	Existing Source, Indirect Discharge, Toxic pollutants
PSNS	Pretreatment Standards for New Source	New Source, Indirect Discharge, Toxic pollutants

recycling and prevention, the duty of the operator and the action plans, and monitoring plans. After the evaluation of these parameters in accordance with the relevant guidelines (BAT Reference, BREF), authorized agencies colligate the opinions from advisory bodies and related limitations, and then set up the Emission Limit Values (ELVs), and finally approve the integrated effluent limitations [3].

In the case of the USA, effluent limitations are being revised in every two years, and central government is establishing national effluent limitations due to the expertise of limitation establishment and postmanagement. However, the permission and management of wastewater discharge facilities are carried out by provincial government in Korea. In order to introduce separate effluent limitations for various industrial sectors, the fields of requiring expertise (i.e. establishment of effluent limitations) needs to be implemented by central government. Recently, studies on improving related institutions have been carried out in Korea[5]. These studies evaluated the technical feasibility for applying effluent limitations based on technology.

With this research background, the main objectives of this study are: (1) To suggest the method and procedure for establishing effluent limitations for the petroleum refining facilities on the basis of treatment technology in order to the most appropriate effluent limitations reflecting wastewater characteristics and the level of treatment technologies and (2) To estimate the effluent limitations based on the Best Practicable Control Technology Currently Available (BPT).

2. Materials and methods

2.1. Steps of technology evaluations for effluent limitation establishment

General steps to establish individual effluent limitations for discharging facilities can be consisted of three stages: (1) survey data, (2) technology assessment, and (3) examination of current criteria [6] (Fig. 1).

In the first survey data stage, the basic data on types and concentrations of pollutants, types and levels of applied treatment technologies are obtained. Water quality data such as national watershed monitoring networks near the discharge facilities are investigated, and then potentially dischargeable pollutants are figured out by the notified data on the amount of discharged hazardous chemicals from the facilities. Additional site investigation and water quality analysis can be possible.

At the technology assessment stage, TBEL or WQBEL is finally determined for implementation on

the basis of data surveyed in the first stage. In accordance with the Anti-Backsliding principle, established limitations on the basis of WQBEL or TBEL cannot exceed the currently applied limitations, and more strict limitation among TBEL and WQBEL is adopted, in principle.

Institutional legitimacy and technical feasibility for established limitations are re-examined at the final examination of current criteria stage. Effluent limitations are determined and notified to the competent authority, Regional Environmental Office of Korea (REOK).

After that, final effluent permission reflecting on the final effluent limitations is issued by REOK through examining the presented limitations.

2.2. Establishment of effluent limitation based on technology and water quality

As suggested by researchers from Korea and other countries [6–8], methods for establishing effluent limitations can be divided into TBEL and WQBEL (Table 2).

TBEL-based method, often referred to as BAT, is characterized by a thorough analysis of the industry types including treatment facilities, as well as effluent characteristics [5]. Long-term water quality data are commonly used for deriving limitation values with BPT level through statistical analysis. Basic statistical approaches such as regressional analysis [9] and 95th percentile approach [10] have been adopted for TBEL implementation [5].

The methodology for establishing WQBEL contains the principle of risk assessment. WQBEL was established on the basis of the drinking water standards and the economical and technical availability [5]. The three lowest annual averages among 10 years of measured data from the nearest point to the designated facilities in the national monitoring network are used to set up WQBEL. In addition, another WQBEL method utilizes water quality criteria for human toxicity and the protection of aquatic organisms, and the other WQBEL method establishes limitation values with the amount of streamflow and pollutant concentrations monitored at the upstream and downstream in the long term, and amount of wastewater and pollutant concentrations of the discharge facilities [11].

More details on these two methods can be found elsewhere [5,7]. In order to successfully implement these methods, enough data for a long term is essential, but not yet sufficiently accumulated by individual facilities and even by regional and central government in Korea. For this reason, the TBEL-based effluent

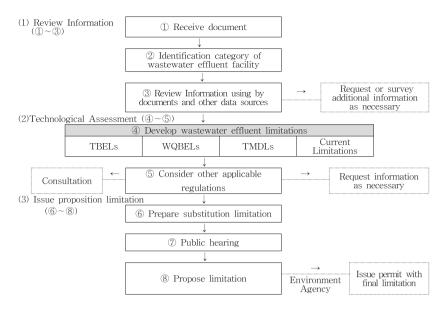


Fig. 1. Major steps of technological assessment to determine effluent limitations.

limitations were derived by the data obtained through limited field investigations and expert survey.

2.3. Establishment of TBEL in Korea

In this study, method four among those methods for establishing effluent limitations (Table 2) was applied for the petroleum products manufacturing facilities in Korea, and then effluent limitations based on the practical best available treatment technology (BPT) were derived. Effluents from five big petroleum refining facilities were analyzed (Table 3 and 4). Even though various heavy metals and Volatile Organic Compounds (VOCs) were detected in the effluents, this study focused on conventional water pollutants because long-term monitoring data on other toxic materials are not yet enough to derive any effluent limitations.

The first step to achieve this goal was to collect water quality data from the facilities currently being operated properly, and then TBEL were estimated in the BPT level based on statistical analysis. On the basis of the data collected, concentration values corresponding to 95% (X_{95}) and 99% (X_{99}) in the lognormal distribution were considered as the limitation values for the monthly average and daily maximum, respectively. Those values are applied in accordance with the characteristics of discharge facilities in the USA, while the representative values of treated water quality are estimated by the average values measured twice per 30 min in water quality investigations without applying average water quality concepts in Korea.

In this study, the daily maximum value (X_{99}) was applied for estimating TBEL considering the stability of the treated water quality. Variability factors (VF) were also applied to reflect the variability of treated water quality on establishing effluent limitations [7]. Procedures for establishing TBEL by individual discharge facilities are as follows:

- Gathering data on treated long-term water quality
- Screening available data: extremely high or low values and values from abnormal conditions are excluded.
- Estimating average water quality concentrations (X₉₅ and X₉₉) and VF
- Estimating TBEL-based discharge permit standards

Effluent limitations = arithmetic (or geometric) average \times VF

3. Results and discussion

3.1. Current status of petroleum refining industry in Korea

Petroleum refining industry, the one of the Korea's major industries, is the process from importing crude oil to producing petroleum products including gasoline, diesel, and kerosene using large-scale devices and facilities [12]. The number of wastewater discharge facilities registered in 2010 was 48,266, and the total amount of industrial wastewater from those facilities was 3,446,857 ton/day in Korea. Among those facilities, 112 facilities were registered as wastewater discharge facilities, and 71,208 ton/day of wastewaters were released to water bodies after treat-

Section	Methods 1 (use water quality monitoring data)
WQBEL	New facility: use monitoring water quality data in stream
	 Numerical average for the lowest three years in decennary
	• Existing facility: do not over TMDL in stream
	Methods 2 (use ambient water quality criteria)
	$^{*}AWQC = RfD \times RCS \times \frac{BW}{DI + (FI \times BAF)}$
	Methods 3 (suppose steady state, complete mix)
	$C_{\rm r}Q_{\rm r} = Q_{\rm s}S_{\rm s} + Q_{\rm d}C_{\rm d}$
	• $C_{\rm d} Q_{\rm d}$: Concentration of pollutants and quantity of wastewater from facility
	• $C_{r}Q_{r}$: Concentration of pollutants and quantity of water in lower stream
	• $C_{s}Q_{s}$: Concentration of pollutants and quantity of water in upper stream
TBEL	Methods 4 (use variability factor)
	• Effluent limits = numerical average × VF
	 Monthly average concentration VF = X.95/E(X)
	• Daily maximum concentration VF = X.99/E(X)
	Methods 5 (use average performance of treatments)
	• Effluent water quality data from treatment facility to be operated normally (BPT)
	 Numerical average+(Max-Lower)/2 or geometric average (Max-Lower)/2

*AWQC—Ambient Water Quality Criteria; RfD—Feference Dose; BW—Body Weight; RSC—Relative Source Contribution; DI—Drinking water Intake; FI—Fish Intake; BAF—Bioaccumulation Factor.

Items	Conditions
P&T	Velocity xpt purge and trap, TELEDYNE TEKMAR
Trap	Tekmar trap K(vocarb 3,000), SUPELCO
Pre perge	0.50 min
Purge	40 °C at 11 min
Dry purge	40 °C
Desorbe	4 min at 250 °C
Bake	6 min at 250 °C
GC/MS	7890A/5975C, AGILENT TECHNOLOGIES
Inlet temp.	220°C
Split ratio	20:1
Column	DB-624 (Agilent J&W GC Columns),
	$30 \mathrm{m} \times 0.320 \mathrm{mmID} \times 1.80 \mathrm{\mu m}$
Column temp.	5 min at 35°C,
*	20 min at 195°C(8°C/min),
	4 min at 245°C (25°C/min)
Column flow	1.4 mm/min
Carrier gas	H ₂ (99.999%, flow rate 60psi)

Table 3 GC/MS operating conditions for analysis of VOCs

Table 4

Concentration of toxic pollutants in treated wastewater from petroleum refining facilities

Toxic pollutants	Concentration in treated wastewater (mg/L)
Cu	0.009–0.021
Cr	0.001-0.009
Mn	0.088-0.774
Fe	0.005-0.439
Ni	0.005-0.031
Zn	0.006-0.124
Sn	0.002-0.034
Ba	0.01-0.143
Se	0.01-0.14
Toluene	0.001-0.006
Ethylbenzene	0.002-0.004
Xylene	0.002–0.004

ment [13]. The percentage of petroleum refinery was only 0.23%, but the percentage of wastewater discharge was 2.07%. It indicated that the amount of wastewater discharged from petroleum refining facilities is relatively high considering the number of facilities (Table 3).

Petroleum refinery wastewater usually contains several aromatic compounds and inorganic substances, which have hindering effects in the treatment process [14]. Currently, N-hexan, phenol, Zn, Fe, Cr⁺⁶, Polychlorinated Biphenyls, and Trichloroethylene are classified as water pollutants in Korea in addition to general pollutants such as Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Suspended Solid (SS), Total Nitrogen (TN), and Total Phosphorus (TP) (Korean Ministry of Environment, 2004). Results from previous studies indicated that wastewaters were discharged during petroleum refining processes such as distillation, desulfurization, and desalination (Fig. 2), and COD concentrations were substantially higher than those of BOD in the input wastewaters (Table 4).

3.2. Implementation of effluent limitations based on the applicable BPT

3.2.1. Evaluation of treated water quality

In order to estimate the BPT-based effluent limitations applicable for the petroleum refining facilities, nine facilities were selected and current status of wastewater treatments and technology was determined (Table 5). BOD_5 , COD_{Mn} , SS, TN, and TP of final treated wastewater from selected discharge facilities are summarized in Table 6. Pollutant concentrations of final treated wastewater varied depending on the concentration of influent wastewater and removal efficiencies applied treatment methods for the facilities. The average concentration of BOD₅, COD_{Mn}, SS, TN, and TP in final treated wastewaters from nine selected facilities was 8.1, 27.6, 13.1, 10.1, and 0.3 mg/ L, respectively. The concentrations of COD_{Mn} were relatively higher considering BOD₅ concentrations.

A (fourth) petroleum refining facility represented the best treatment efficiency among those nine facilities. In this facility, the average concentration of BOD_5 was 3.82 mg/L, COD_{Mn} was 7.74 mg/L, SS was 2.64 mg/L, TN was 5.24 mg/L, and TP was 0.18 mg/L, respectively. The concentrations of these five parameters were under the current effluent limitations in Korea.

3.2.2. Selection of applicable BPT

The wastewater treatment technologies being utilized in nine petroleum refining facilities are classified with similar processes and summarized in Table 6. The main treatment processes of petroleum refining facilities are coagulation and sedimentation and activated sludge, and minor unit processes such as oil separation, sand filter, and activated carbon filter are added before or after the main processes, and then being operated in multi-step processes.

The wastewater treatment process of facility A is presented in Fig. 3. As illustrated in Fig. 3, treatment processes are composed of oil separation, in which oil components in the wastewater are removed; coagulation and floatation for eliminating organic and inorganic compounds in petroleum and biological activated sludge; and sand filter or activated carbon filter process for removing particulate materials in the wastewater. As we discussed in previous section, the treatment efficiency of facility A was the best among the nine chosen facilities in this study, and facility A was selected as the BPT for the petroleum refinery industry in Korea (Fig. 4).

3.2.3. Implementation of effluent limitation for petroleum refining facilities

According to the result of analyses of treated water quality mentioned above, suggested BPT and TBEL for petroleum refinery industry in Korea are estimated and summarized in Table 7. The VF of BOD₅ was 1.32, COD_{Mn} was 1.39, SS was 1.58, TN was 1.37, and TP was 1.55, respectively. The lowest average concentrations for selected parameters were as follows: BOD₅ was 3.82 mg/L, COD_{Mn} was 7.74 mg/L, SS was

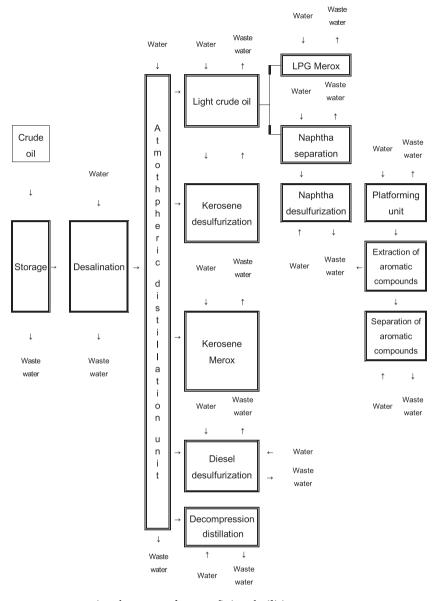


Fig. 2. Diagram of wastewater generation from petroleum refining facilities.

Table 5 Status of wastewater discharge from the petroleum refining facilities in KOREA in 2010

Total	Amount of	Amount of
facilities	wastewater generation	wastewater discharge
(unit)	(ton/day)	(ton/day)
112	71,418	71,208

2.64 mg/L, TN was 5.24 mg/L, and TP was 0.18 mg/L. BPT-based effluent limitations for petroleum refining facilities were estimated through multiplying those two values. Effluent limitations of BOD₅ was 5.05 mg/L, COD_{Mn} was 10.78 mg/L, SS was 4.18 mg/L, TN

was 7.16 mg/L, and TP was 0.28 mg/L, respectively. These values were substantially low compared with current limits (Table 8). The values of current limit for BOD₅ was 10 mg/L, COD_{Mn} was 40 mg/L, SS was 10 mg/L, TN was 60 mg/L, and TP was 8 mg/L, respectively. These results indicate that TBEL for petroleum refining industry suggested in this study need to be more strict than the universal limitations currently being used for all industries in Korea (Table 9).

Kim et al. [5] suggested a using economically available BAT. The evaluation processes of BAT include environmental factors except water quality (e.g. contaminant concentration in the atmosphere),

Characteristics of raw wastewater from petroleum refining facilities							
Pollutants(mg/L)	TN	TP					
Average	94.6	2,746.9	1,308.9	35.5	103.3	0.91	
Max	609.6	44,864.4	15,360.0	279.1	1,527.4	5.68	

 Table 6

 Characteristics of raw wastewater from petroleum refining facilities

the amount of energy used, and legal requirements to meet [4]. However, parameters only related to treated water quality were considered here because one of the main objectives of this study was to estimate the BPT-based effluent limitations on the basis of treatment technologies currently used in discharge facilities and achievable water quality level.

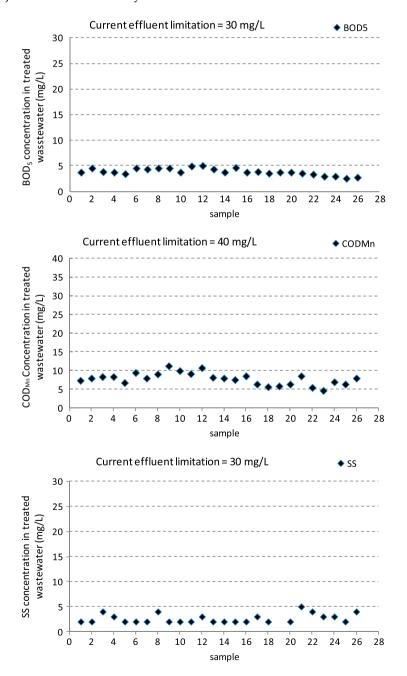


Fig. 3. Pollutants concentration in treated wastewater from facility A.

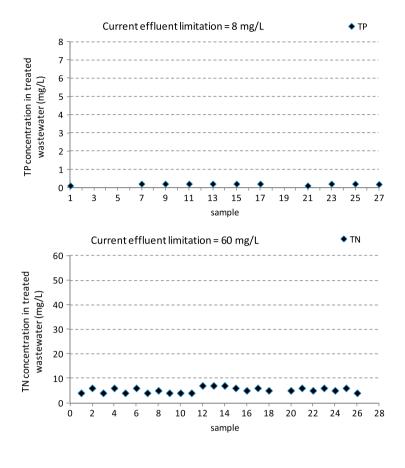


Fig. 3. (Continued)

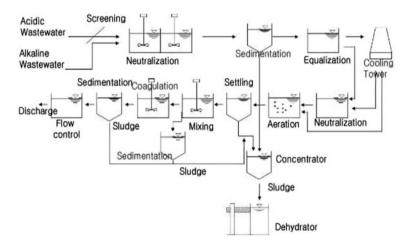


Fig. 4. Diagram of wastewater treatment processes as BPT for petroleum refining industry (oil separation \rightarrow coagulation and flotation \rightarrow activated sludge \rightarrow sand filter (activated carbon filter)).

4. Conclusions

In this study, BPT-based effluent limitations for petroleum refining facilities were estimated considering the wastewater characteristics and treatment technologies. The estimated effluent limitations for selected parameters were: BOD_5 was 5.5 mg/L, COD_{Mn} was 10.78 mg/L, SS was 4.18 mg/L, TN was 7.16 mg/L, and TP was 0.28 mg/L, respectively. The BPT for petroleum refining facilities in Korea was oil separation \rightarrow coagulation and floatation \rightarrow biological activated sludge \rightarrow sand filter or activated carbon filter.

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Facilities	BOD ₅	COD _{Mn}	SS	TN	TP
1	-	182.6	69.7	4.9	1.39
2	1.2	3.4	1.8	-	-
3	-	15.5	5.0	-	_
4(A)	3.8	7.7	2.6	5.2	0.18
5	4.1	9.1	2.8	6.3	0.20
6	-	19.9	8.5	6.4	0.28
7	27.1	31.2	28.7	1.2	0.06
8	15.3	77.6	26.3	8.1	1.50
9	2.4	21.8	6.7	28.2	0.54

Table 7
Average concentrations of water pollutants in treated wastewater from petroleum refining industry

Table 8

Summary of wastewater treatment processes of petroleum refining industry

Facilities	Treatment process
1	Oil separation + activated sludge + coagulation and flotation + sand filter(activated carbon filter)
2	Aeration + oil separation + activated Sludge + sedimentation + activated carbon filter
3	Coagulation and sedimentation or activated sludge
4	Coagulation and sedimentation + activated sludge
5	Coagulation and sedimentation + activated sludge + sand filer
6	Activated sludge + coagulation and sedimentation + sand filer

Table 9

BPT and TBEL of petroleum	refining	industry
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		Parameters (mg/L)				
Best practicable control technology currently available for petroleum refining industry	Items	BOD ₅	COD _{Mn}	SS	TN	TP
Oil separation ↓	Total average concentration in category	8.1	27.6	13.1	10.1	0.3
Coagulation and Flotation	Variability factor (VF)	1.32	1.39	1.58	1.37	1.55
Ļ	Lower average concentration in category	3.82	7.74	2.64	5.24	0.18
Activated Sludge						
\downarrow Sand filter (activated carbon filter)	Technology Based Effluents Limits (TBEL)	5.05	10.78	4.18	7.16	0.28
	Current limits	10	40	10	60	8

It is not yet realistic to directly apply the BPT suggested in this study to other petroleum refining facilities since uniform effluent standards for those parameters are being applied to all discharge facilities. Thus, in order for TBEL to be settled, the institutional complement applying different effluent limitations for various industrial areas in accordance with the wastewater discharge characteristics and the level of treatment technology is urgently needed. Our results indicated that pollutants from petroleum refining facilities can be removed more efficiently if BPT suggested in this study can be applied to those facilities.

Implementation of separate effluent limitations in accordance with the various characteristics of discharge facilities may strengthen the rationality of environmental regulations, and induce the voluntary development of technology and reduction of pollutant discharge by various industrial sectors. Efforts to secure national data are needed to pinpoint current status of wastewater discharge including the type and concentration of contaminants, treatment technologies, and management situations.

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