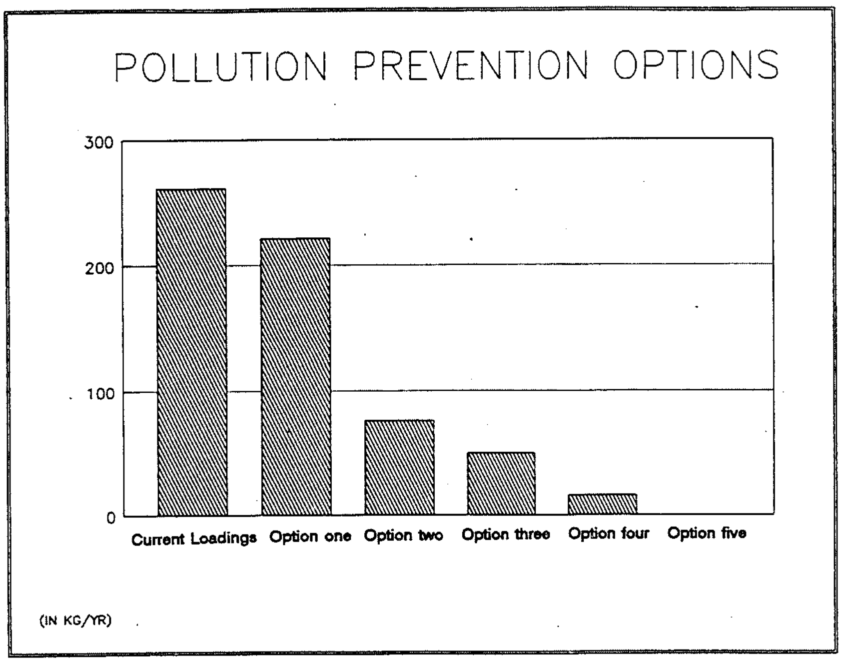
Developing Technology-Based Standards Under the Municipal Industrial Strategy for Abatement in Ontario:

A Case Study of the Petroleum Refining Industry



Canadian Environmental Law Association

Susan Sang, Ph.D.

The Program for Zero Discharge

Canadian Institute for Environmental Law and Policy

February, 1991

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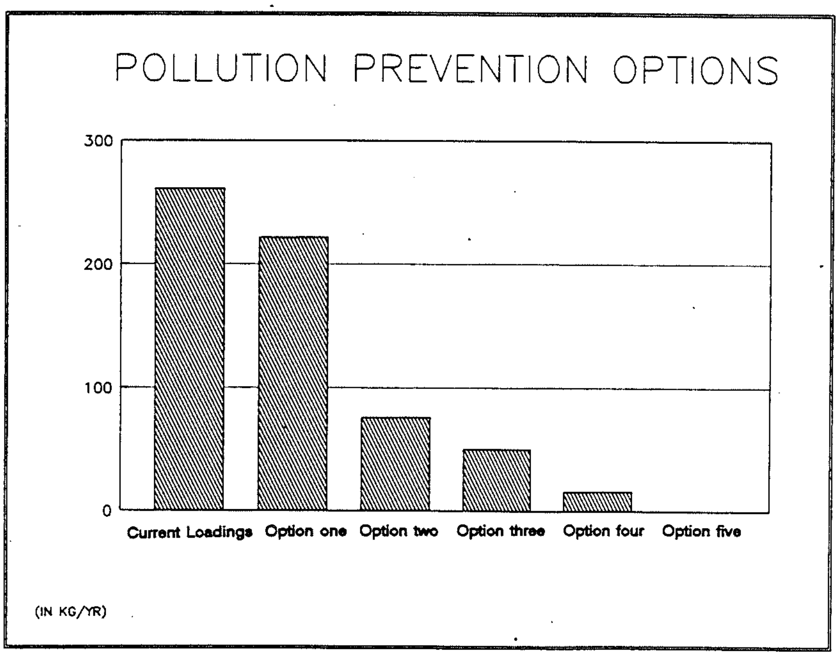

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Table of Contents

List of Tables

List of Figures

1. Introduction

In 1986, the Province of Ontario announced a new initiative to improve the province's water quality - the Municipal Industrial Strategy for Abatement (MISA). The first phase of the MISA program requires wastewater monitoring by industries discharging directly into Ontario waterways. During the second phase, technology-based standards are to be developed in order to set enforceable effluent limits for each of nine categories of industrial dischargers. These effluent limits will be based on the Best Available Technology Economically Achievable (BATEA, or BAT for short).

By the end of 1990, the monitoring regulations for all industrial sectors have been enacted. The first effluent limit regulation, addressing the Petroleum Refining Sector, is due to be released for public review in early 1991.

1.1. Purpose of this Report

This report represent a series of Best Available Technology (BAT) options to deal with petroleum refinery wastewater. The BAT options are based on a review of pertinent technologies and associated effluent data. Compliance with the purposes of the MISA Program and with commitments under the Great Lakes Water Quality Agreement is the primary criterion used in considering the different technologies. It is hoped that this report will benefit the Ministry of the Environment (MOE) in developing an effective effluent control regulation for the petroleum refining sector.

In recognition of MISA's objective to virtually eliminate the discharge of persistent toxic chemicals into Ontario waterways, the primary objectives of this report are:

i. to identify various effluent treatment technologies used in petroleum refineries in North America;

ii. to review and evaluate the existing technologies, and to determine the effectiveness of demonstrated technologies available in North America;

iii. to identify and establish BAT options for the petroleum refining industry; and

iv. to provide additional information to assist in the identification of the Best Available Technology for water pollution control in the Ontario petroleum refining sector.

1.2. Methodology

A comprehensive review of industry literature and available data was conducted to identify pertinent control technologies and practices. Additionally, CIELAP contacted industry experts for their input and advice on BATs for the control of refinery effluents. The scope of the review included worldwide applications of mechanical/chemical treatment control technologies, alternative production processes and best management practices (BMPs).

During the literature search, CIELAP used a system of key words to identify related literature through titles and abstract reviews. The research was conducted in several phases, accessing each of the following sources:

- Science and technology journals;
- Industry texts;
- Industry journals;
- Computer data bases - NTIS, Water Resources, Pollution Abstracts, Enviroline, and Wilson Disc Search;
- Ontario Petroleum Association research papers;
- U.S. Environmental Protection Agency reports; and
- Environment Canada reports.

The selection of three parameters, benzene, chromium and phenol, allowed a quantitative assessment of the various control technology options. CIELAP choose these parameters because of their environmental concern and the availability of discharge data. Choosing three parameters is considered adequate for demonstration purposes.

CIELAP used analyzed discharge data from the literature search, MISA sector data base and the MOE direct dischargers reports for consideration in the modelling component for the three parameters.

2. Background and Overview of MISA

The 1986 White Paper, which initiated MISA, states that, "MISA's ultimate goal is the virtual elimination of toxic contaminants in municipal and industrial discharges into waterways".[1] The MISA strategy divides all direct dischargers into nine industrial sectors and a municipal sector (sewage treatment plants). A three phase approach is then taken to fulfil MISA's objectives.

PHASE ONE is the monitoring program, consisting of a general monitoring regulation for all sectors and a complementary sector-specific monitoring regulation. Each regulation outlines the precise monitoring and reporting requirements for a specified number of pollutants. This data will be used during the second phase of the MISA program.

PHASE TWO consists of developing technology-based effluent limits for each of the ten sectors. These limits are based upon the Best Available Technology Economically Achievable, however, industries may employ any technology as long as the effluent limits are met.

PHASE THREE, the development of water quality standards, was intended to be implemented as a parallel program. Unlike technology-based criteria, water quality based standards dictate the acceptable limits, rather than having the technological limitations dictate the effluent limits. Water quality standards protect the quality of the receiving water where the technological standards are insufficient to do so or where water quality is of primary concern.

According to the 1986 White Paper, the technology-based limits for the industrial sectors were to be in place by mid-1989.[2] However, thus far, no such limits have been established. The first regulation to be released for public review is scheduled for early 1991, with others to follow until all industrial sectors are regulated by late 1992.[3]

Water quality standards were to be implemented between 1988 and 1995, however, their development has been indefinitely postponed due to financial limitations.[4]

2.1. Setting BAT Effluent Limits Under MISA

A technology-based standard is a discharge limit based on the demonstrated performance of a defined technology. Technology-based standards are determined by the availability and feasibility of a technology to control pollutants, and not on ecological requirements. The 1986 MISA White Paper outlines a 14 step process for establishing BAT limits (see Appendix A).

The design of technology-based standards involves a periodic review and assessment of performance. As control technology improves, discharge limits will become more stringent. The frequency of the periodic review has yet to be determined for the MISA program.

3. The Petroleum Refining Industry

The petroleum refining industry processes crude oil into a number of products, including gasoline, petrochemical feedstocks, lubricating oils and asphalts. A petroleum refinery operates 24 hours a day and seven days a week with infrequent shutdowns every one to two years for major maintenance.

This section provides a brief description of the processes associated with petroleum refining and related effluent sources. The currently applied wastewater treatment technologies are also described.

3.1. The Ontario Petroleum Refining Sector

The petroleum refining sector in Ontario consists of one petrochemical plant and six conventional refineries, the former being a petroleum-based producer of primary petrochemical products. The six refineries have a combined annual production capacity of 24 billion litres of end products, while the petrochemical plant produces 1.3 billion kilograms of petrochemical products.[5] Details on production processes and effluent volumes for each plant are given in Table 1 (next page).

In 1985, Ontario petroleum refineries accounted for 31% of the total Canadian crude oil processing capacity, and generated more than $9.2 billion in revenues in 1984.[6] Although petroleum refining is an important industrial sector to the economy, it is also a major discharger of wastewater into Ontario waterways.

3.2. Petroleum Refining Processes

Petroleum refining is a complex and sophisticated operation. Essentially, the process converts crude oil into petroleum products such as gasoline, oil, lubricants and many others. Crude oil is a mixture of many hydrocarbons, which are generally classified into four groups: paraffins, olefins, aromatics and naphthenes. In addition to these hydrocarbons, crude oil contains sulphur, nitrogen and oxygen compounds, trace amounts of metals such as arsenic and chromium, and inorganic salts such as sodium chloride.

The processes employed by one refinery may differ from others depending upon the type of crude oil and the type of products.[7] A 1977 survey conducted by the U.S. Environmental Protection Agency (U.S. EPA) found over 150 separate processes in use throughout the country.[8] Additionally, combinations of those processes may be employed in refineries as well.

Table 1. Description of Petroleum Refineries in Ontario Discharging into the Great Lakes Basin.

Facilities	Processes	Product Line	Crude Oil Processing Rate (m3/d)	Total Effluent Rate (m3/d)	Receiving Water
Esso Petroleum Canada-Sarnia Ontario	Vacuum distillation Thermal operations, Catalytic cracking; reforming; hydrotreating, alkylation, Polymerization, lubes, Hydrogen (MMcfd)	Fuel products, Packaging, Lubricating oil, Petrochemical-operations	20,000	215,700	Lake Erie
Petro-Canada Inc. Clarkson Refinery-Mississauga Ontario	Vacuum distillation, Catalytic reforming; hydrocracking; hydrotreating, Lube, Asphalt, Hydrogen-(MMcfd)	Liquid petroleum gases, Aviation-fuel, Motor-gasoline, Distillates, Residual fuel oils Asphalt, Lubricating oils and greases, Solvents	7,100	260,000	Lake Ontario
Petro-Canada Inc. Trafalgar Refinery-Oakville Ontario	Vacuum distillation, Catalytic cracking; reforming; hydrotreating, Alkylation, Polymerization	Petroleum fuel-products, Liquid Petroleum gases, Aviation gasoline, Motor gasolines, Distillates residual fuel oils, Asphalt, Sulphur	13,600	4,800	Lake Ontario
Petrosar Limited Sarnia, Ontario	Petrochemical-Refiner	Primary petrochemical products (Ethylene, Propylene, Butadiene, Iso-butylene, N-butylene, Benzene, Toluene/Xylene)	27,000	6,580	St.Clair River Lake Ontario
Shell Canada Products Limited Sarnia, Ontario	Vacuum distillation Thermal operation, Catalytic cracking; hydrotreating; reforming; hydrocracking, Alkylation, Polymerization, Aromatic isomerization	Gasoline; Diesel; and Furnace fuel Benzene, Toluene, Xylene, Sulphur, Hydrocarbon-solvents	11,800	234,700	Talford Creek Lake Erie

Table 1 Continued

Facilities	Processes	Product Line	Crude Oil Processing Rate (m3/d)	Total Effluent Rate (m3/d)	Receiving Water
Suncor Sarnia Refinery Sarnia, Ontario	Vacuum distillation Thermal operation, Catalytic reforming; hydrocracking; hydro-treating; hydrorefining, Alkylation, Polymerization, Aromatics isomerization, Hydrogen (MMcfd)	Motor gasolines, Light and heavy fuels, Light Aromatic-products, liquified-gases, Solid sulphur	9,000	119,000	St.Clair River Lake Erie
Esso Canada Nanticoke, Ontario	Vacuum distillation Catalytic cracking; reforming; hydrotreating, Polymerization, Alkylation	Leaded and unleaded gasolines, Jet fuel, Heating Oils, Diesel, Industrial fuels, Liquified Propane, Butane, Sulphur	15,200	6,810	Hickory Creek Lake Erie

Despite this wide range of variables, the processes in petroleum refineries are classified either as *physical separation* or as *chemical conversion* operations. During the separation processes, crude oil is separated into a number of fractions of varying molecular weights. Subsequent conversion processes are required for intermediate and final products. Finished petroleum products are manufactured by blending various intermediate products in the required proportions. The range of processes is summarized in Table 2, while Figure 1 (page 10) illustrates the general processes in a typical petroleum refinery.

Table 2. Typical Petroleum Refining Processes.

CRUDE OIL DISTILLATION	
Atmospheric	separates light hydrocarbons from crude in a distillation column under atmospheric pressure.
Vacuum	separates heavy gas oil from the bottom of the atmospheric distillation under a vacuum.
GAS PROCESSING	separates gases such as LPG, fuel gas, isobutane, butylene and light naphtha from the light ends of the atmospheric distillation unit.
CATALYTIC CRACKING	converts heavy petroleum fractions to lighter products using a high temperature catalytic process.
CATALYTIC REFORMING	converts low octane naphthas into high octane gasoline blending compounds by contacting feedstock with hydrogen over a catalyst.
HYDROCRACKING	converts heavy petroleum fractions to lighter products using catalytic cracking in the presence of hydrogen.
ALKYLATION	catalytically combines an olefin with an isoparaffin to form high octane gasoline blending compounds.

Table 2 (continued). Typical Petroleum Refining Processes

ISOMERIZATION	converts n-butane, n-pentane and n-hexane into respective isoparaffins.
LUBE OIL	removal of aromatics, unsaturated processing naphthenes and asphalts from lubricating-oil base stocks using solvents such as phenol.
HYDROTREATING	removes sulphur, nitrogen and metallic compounds through catalytic treatment with hydrogen.
ASPHALT PRODUCTION	removes asphaltic materials from heavy oil and residual fractions using solvent extraction.
COKING	converts crude oil residue and tar pitch products into gas, oil and petroleum coke by a thermal cracking process.

In addition to these processes, a desalting unit, which does not process crude oil directly, is common to all refineries. In a desalting unit, crude oil is mixed with water and is passed through a chemical or electrical desalter in order to separate the crude oil from inorganic salts and other impurities.

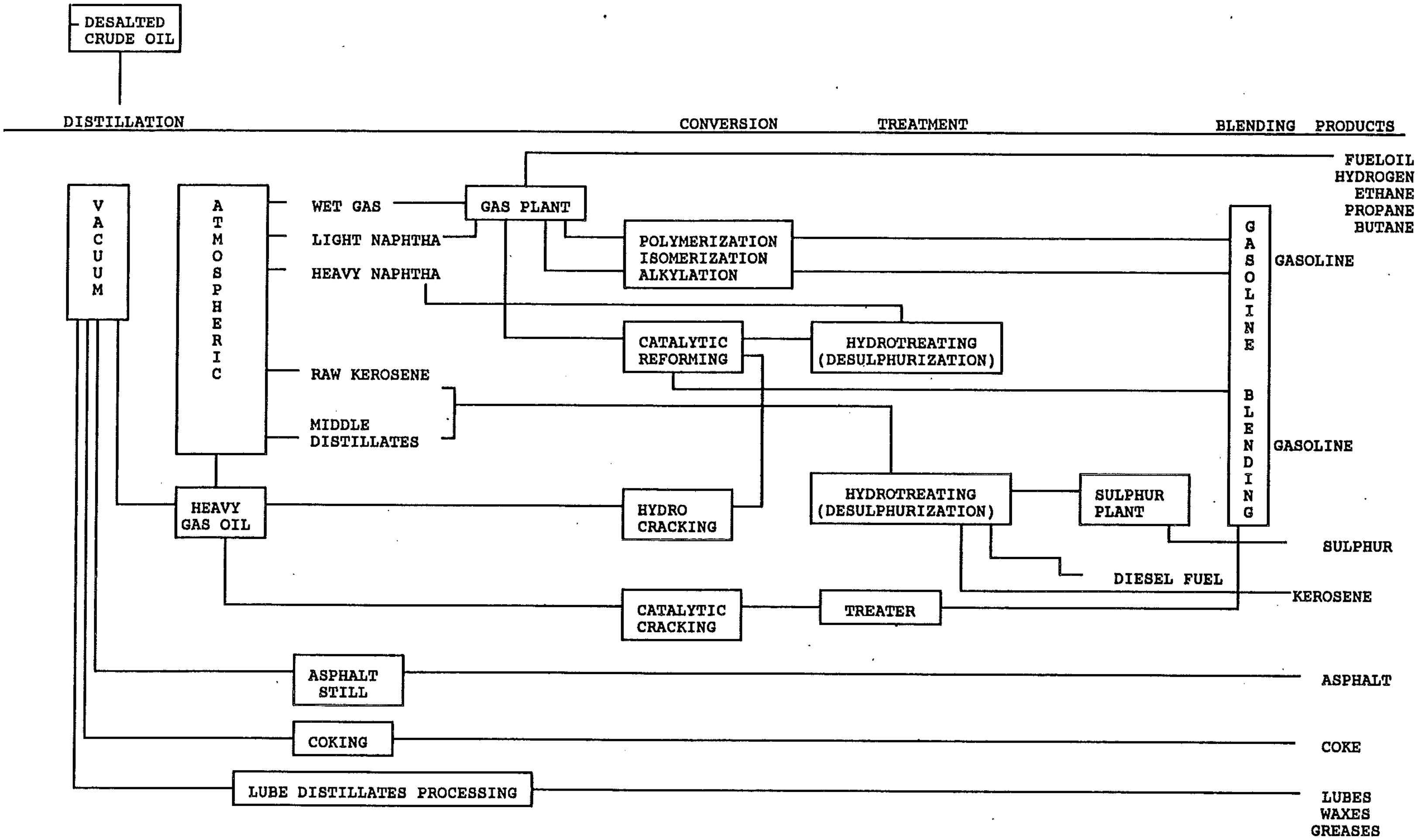

FIGURE 1 : A SIMPLIFIED DIAGRAM OF THE PROCESS FLOW IN AN OIL REFINERY

3.2.1. Sources of Wastewater

The major uses of water in petroleum refineries are associated with steam generation and heat transfer. The volume of water coming into direct contact with refining process streams is small relative to volumes resulting from indirect cooling and heat transfer. There are numerous processes in a refinery which condense steam and in which cooling water comes in contact with petroleum and/or petroleum products. Wastewater generation sources from various refining processes are summarized in Table 3.

Table 3. Wastewater Sources from Various Refining Processes.

Process	Wastewater Sources
desalting	water washing
atmospheric distillation	condensed stripping steam from overhead accumulator
vacuum distillation	jet ejectors, barometric condensers
catalytic reforming	condensed stripping steam from overhead accumulator
catalytic cracking	overhead accumulators and steam strippers on the fractionator, catalyst regeneration
hydrocracking	high and low pressure separators, accumulator on fractionator
alkylation	Overhead accumulator on fractionation tower, caustic washer (sulphuric acid alkylation process)
isomerization	caustic washer
hydrotreating	overhead accumulator on fractionator
coking	contact process water and steam overhead accumulators
asphalt production	steam jet ejectors, condensers

Source: U.S. EPA, 1985.[9]

Leaks and spills are also common and these eventually drain into the central sewer system. Stormwater runoff from process areas is another significant source of wastewater.

The following list summarizes the major sources of contamination to refinery wastewater:

- desalting unit effluent;
- steam processing to remove impurities;
- water accumulated in the bottom of the storage tanks;
- ballast water from petroleum tanker ships;
- contaminated 'once-through-cooling-water' from process leaks;
- cooling water blowdown*; and
- storm water runoff from process areas and tank farms.

Generally, a major source of wastewater in older refineries is Once-Through-Cooling-Water (OTCW) which may account for 90% of a refinery's effluent.[10] In newer refineries, however, the common practice is to install a cooling tower circuit, a system which recycles most of the cooling water. Better still, some refineries use a combination of cooling towers and air coolers. In Ontario, only one refinery (NOVA Petrochemical, Corunna) employs a 100% cooling tower system. Two refineries are using a combination of cooling towers and air coolers (Esso Petroleum, Nanticoke and Petro-Canada, Oakville). The remaining refineries use primarily OTCW (Esso Petroleum, Sarnia and Shell Sarnia), with a small amount of cooling achieved by cooling towers and air coolers (Suncor, Sarnia and Petro- Canada, Mississauga).

Table 4 (next page) summarizes the cooling methods, process and total effluent volumes, and "effluent factors" for all Ontario refineries. The effluent factor describes how many cubic metres of water are discharged for every cubic meter of crude oil processed. It is important to note that the refineries using OTCW have the largest volume of effluent per m^3 of processed oil (see Table 4). The larger effluent volumes translates into larger discharges of toxic substances (see Table 11, page 35). Thus, refineries using OTCW pollutes waters more.

* The dissolved solids content of circulated cooling water is controlled by discharging a portion of it, this is called the blowdown.

Table 4. Effluent Volumes and Effluent Volume per unit Oil Processed for each Ontario Refinery (1988-1989).

Refinery	Cooling Method	Process Effluent m3/day	Total Effluent m3/day	Total Effluent per m3 of Oil Processed
Petro-Canada Mississauga	OTCW	9,299	260,000	36.1
Petro-Canada Oakville	air & cooling tower	4,463	4,800	0.36
Shell Sarnia	OTCW	11,916	234,700	19.9
Esso Sarnia	OTCW	26,253	215,700	10.8
Esso Nanticoke	air & cooling tower	6,696	6,810	0.45
Suncor Sarnia	OTCW	8,600	119,000	13.2
NOVA Petro-chemical (Corunna)	cooling tower	5,727	6,580	0.24

Source: MOE, 1988[11] and MOE, 1989.[12]

OTCW = once through cooling water

3.2.2. Types of Wastewater Contaminants

Contaminants detected in petroleum refinery effluents are classified either as conventional pollutants or as toxic "priority" or pollutants. Refineries in Ontario traditionally monitor the following conventional pollutants in their effluents:[13]

* pH
* Biochemical Oxygen Demand (BOD)
* ammonia-nitrogen
* Total Suspended Solids (TSS)
* Total Organic Carbon (TOC)
* phenolics
* oil and grease
* sulphides

Many toxic pollutants have been detected in the discharges of petroleum refineries, and consequently appear on the U.S. priority pollutants list.[14*] During the development stage of BAT limits in the United States, the EPA conducted a sampling program of 17 refineries.[15] Table 5 presents a list of the most frequently occurring pollutants in the wastewater of U.S. petroleum refineries. Some of these priority pollutants originate from the crude oil, whereas others are by-products of the processes, products of corrosion, or simply additives.

Table 5. Priority Pollutants Found in Treated Effluents of the Petroleum Refineries in the United States.

Contaminant	Frequency of Occurrence (%)
Benzene	25
Chloroform	13
Methylene chloride	69
Toluene	6
Naphthalene	<5
Bis(2-ethylhexyl)phthalate	23
Di-n-butyl phthalate	9
Diethyl phthalate	14
Benzo(a)pyrene	<9
Chrysene	<14
Phenanthrene	<5
Pyrene	<5
Antimony	18
Arsenic	38
Chromium	78
Copper	54
Cyanide	48
Lead	23
Mercury	74
Nickel	22
Selenium	68
Thallium	16
Zinc	80
Total phenols	76
Hexavalent chromium	13

Source: U.S. EPA 1982.[16]

* The U.S. priority pollutants list, developed by U.S. EPA in 1977, consists of 126 potentially persistent and bioaccumulative parameters.

Under MISA's petroleum sector monitoring regulation (amended 1988), Ontario refineries began monitoring their effluents for selected parameters on December 1, 1988 for a 12 month period, ending November 30, 1989. Over 80 pollutants, of the 149 monitored, were found for the entire sector.[17] Of these pollutants, 15 were conventional pollutants (Table 6), and the rest were toxic priority pollutants (Table 7, next page) including four dioxin/furan compounds.

Table 6. Conventional Pollutants Found in Process Effluents of Seven Ontario Refineries.

Parameter	Average Conc./FOD (Dec.88-May 89) ug/l		Average Conc./FOD (June 89-Nov. 89) ug/l	
COD	53,250	100	46,535	100
DOC	13,191	100	13,138	100
Hydrogen ion (pH)	7.6*	93	7.8*	100
Nitrate + Nitrite	1,837		3,472	100
Specific-conductance	1,416.1**	100	1,492.1**	100
TOC	18,991	100	20,011	100
TSS	29,777	99	23,843	100
Total nitrogen	2,817	100	1,947	98
VSS	14,787	98	13,003	97
Total phosphorus	450	83	475	93
Phenolics (4AAP)	13.8	94	9.1	91
Ammonia+Ammonium	1,566	79	1,738	79
Cyanide Total	12.00	84	7.00	79
Sulphide	103.00	72	87.00	77
Oil and Grease	2,545	82	2,030	72

Source: MOE, 1989[18], and MOE, 1990[19].

* NO unit for pH
** Unit of measurement is us/cm
N/A Not Available

FOD = Frequency of Detection Above the Laboratory Detection Limit
COD = Chemical Oxygen Demand
DOC = Dissolved Organic Carbon
TOC = Total Organic Carbon
TSS = Total Suspended Solids
VSS = Volatile Suspended Solids

Table 7. Priority Pollutants Found in the Process Effluent of Seven Ontario Refineries.

Parameter	Average Conc./FOD (Dec.88-May 89) ug/l		Average Conc./FOD (June 89-Nov.89) ug/l	
Zinc	752.664	95	143.403	96
Aluminum	336.272	94	306.340	91
Arsenic	8.542	94	9.313	81
Chromium	125.943	83	86.647	74
Chromium Hexavalent	18.833	83	5.167	50
Selenium	4.165	58	5.123	64
Molybdenum	15.583	35	10.255	49
Nickel	3.188	33	4.085	49
Antimony	0.488	25	0.628	34
Vanadium	2.542	21	13.438	34
Chloroform	0.511	43	0.952	33
Copper	4.021	38	4.815	30
Bis(2-ethylhexyl)-phthalate	0.900	27	0.632	25
Cadmium	0.192	4	0.180	21
Chloromethane	1.593	13	0.971	19
Methylene chloride	1.071	28	1.187	19
Benzylbutyl-phathalate	N/A	--	0.871	18
Hexachlorobenzene	N/A	--	0.029	17
Octachlorodibenzo-p-dioxin	0.054*	8	0.020*	17
Octachlorostyrene	N/A	--	0.040	17
Total H7CDD	N/A	--	0.007*	17
Total PCDF	N/A	--	0.007*	17
Total TCDF	N/A	--	0.019*	17
PCBT	520.00*	10	N/A	--
Toluene	0.590	19	0.400	16
Lead	5.375	8	1.898	13
Thallium	19.354	13	2.383	13
1,1-Dichloro-ethylene	N/A	--	0.180	12
Benzene	0.661	21	0.346	12
Bromomethane	N/A	--	1.321	12
Di-n-butyl-phthalate	0.300	23	0.135	12
o-Xylene	1.348	18	0.366	12
m-Xylene + p-Xylene	0.775	16	0.525	11
Chrysene	0.001	10	0.155	9
Indeno(1,2,3-cd)-pyrene	N/A	--	0.718	9
Mercury	2.542	19	0.009	9

Table 7 (continued): Priority Pollutants Found in the Process Effluent of Seven Ontario Refineries

Parameter	Average Conc./FOD (Dec.88-May 89) ug/l		Average Conc./FOD (June 89-Nov.89) ug/l	
1,1-Dichloroethane	N/A	--	0.023	7
Benz(a)anthracene	0.022	8	0.209	7
Benzo(a)pyrene	N/A	--	0.419	7
Benzo(b)-fluoranthene	0.071	6	0.279	7
Benzo(g,h,i)-erylene	N/A	--	0.698	7
Benzo(k)-fluoranthene	N/A	--	0.419	7
Dibenzo(a,h)-anthracene	N/A	--	0.698	7
Perylene	N/A	--	0.419	7
Pyrene	0.019	6	0.039	7
Cobalt	3.667	25	0.277	6
1,2-Dichloroethane	0.019	6	0.012	5
1,2-Dichloropropane	0.497	17	0.719	5
2,4-Dimethylphenol	0.012	2	0.346	5
1,1,2-Trichloroethane	N/A	--	0.022	3
Ethylbenzene	0.149	8	0.024	3
4-Nitrophenol	0.050	2	0.037	2
Phenanthrene	0.066	4	0.015	2
Phenol	0.441	13	0.044	2

Source: MOE, 1989[20], and MOE, 1990[21].

FOD Frequency of Detection above the laboratory detection limit
N/A Not Available
* Unit of Measurement in ng/l

3.3. Effluent Treatment Technologies

In order to minimize the contaminants produced during the various processes, most petroleum refineries employ several wastewater treatment technologies. These technologies are divided into two broad classes:

(1) in-plant treatment technologies, and

(2) end-of-pipe treatment technologies.

3.3.1. In-Plant Treatment Technologies

In-plant treatment technology facilitates pollutant removal by reducing or eliminating the loadings of a particular pollutant in segregated effluent streams prior to mixing with the main wastewater stream. Also, the overall loadings of pollutants are reduced before being treated by the end-of-pipe treatment systems.[22] The in-plant treatment and control technologies used in Ontario are described below.

A. Sour Water Stripper

Sour water results from the direct contact of hydrocarbon streams with water. This occurs either during desalting of the crude oil or in the steam stripping processes within a refinery. Sour water contains sulphides, ammonia and phenols. The most common in-plant treatment systems for sour water involve sour water stripping and sour water oxidization, or a combination of the two. All Ontario refineries treat the relatively small amount of sour water prior to being discharged into the main wastewater stream.

B. Chemical Substitution

Cooling water may contain chemicals such as chromium, zinc, phosphate and free chlorine, all of which are added to reduce corrosion, scaling and biological growth. Some of these contaminants may be removed by precipitation and sedimentation at an optimal pH level.[23] The level of these contaminants could also be reduced with chemical substitution, such as using organic phosphate or molybdates to replace zinc chromate.[24]

Until recently only two of the Ontario refineries, Esso Petroleum (Nanticoke) and Suncor (Sarnia), were using alternatives to zinc chromate. During the development of the MISA program, after the monitoring period two other Ontario refineries, NOVA Petrochemical (Corruna) and Petro-Canada (Oakville), decided to eliminate the use of chromium based additives as a corrosion inhibitor.[25]

C. Wastewater Reduction

A number of different methods can reduce wastewater production:

(1) replace the practice of "Once-Through-Cooling-Water" (OTCW) with the use of cooling towers;

(2) substitute air cooling devices for water cooling systems; and

(3) applying Best Management Practices (BMPs).

As noted earlier, the use of cooling towers eliminates large volumes of OTCW by allowing cooling water to be reused with the use of heat exchangers. The combination of refinery reusing water and air cooling in Esso Petroleum (Nanticoke) have reduced the water requirements for cooling purposes by 85%.[26]

There are two more advantages in reducing and reusing cooling water. First, the volume of the final effluent generated is reduced, and second, it eliminates the mixing of process wastewater with cooling water, which otherwise results in the pollutants being diluted and therefore more difficult to both detect and remove.

3.3.2. End-Of-Pipe Treatment Technologies

Refineries apply end-of-pipe treatment technologies to remove pollutants from combined refinery effluents. There are several common treatment processes, and the components of such treatment facilities are discussed below.

A. Primary Treatment

Wastewater generated by the refining process has a high oil content. The primary goal of wastewater treatment is to reduce the oil and consequently the organic content of the final effluent. This can be achieved through the use of American Petroleum Institute's (API) gravity separators or by Corrugated Plate Interceptors (CPI).

An API separator consists of a long rectangular basin, allowing most of the oil to float to the surface and be removed. Solids can settle to the bottom of the basin, forming a sludge which can be removed, dewatered and either incinerated or disposed of in a landfill. The sludge is a heavy oily mud, and contains high concentrations of phenols, Cr, Se, Hg, Co, Cu, Zn, Cd, Pb, and Mo.[27]

A CPI separator consists of a number of parallel corrugated plates (between 12 and 48). Wastewater flows downward between the plates, while the oil droplets float upward to form a floating layer, which can be skimmed off.[28]

With the exception of the NOVA Petrochemical plant, which uses the CPI oil removal system, all Ontario refineries use API separators for the treatment of oily water. The Petro-Canada (Mississauga) refinery uses API separators for process water and CPI units for storm water.

B. Intermediate Treatment

Intermediate treatment systems consists of Dissolved Air Flotation (DAF), Induced Air Flotation (IAF), clarifiers or filters. These methods remove additional oil and solids from the wastewater.

The DAF treatment saturates the wastewater with air at high pressure, holding the wastewater at this pressure for a few minutes in a retention tank. Upon reaching atmospheric pressure, it is released to the flotation chamber. The sudden reduction in pressure results in the release of microscopic air bubbles which attach themselves to oil and solid particles. The air-solids mixture rises to the surface, where it is continuously skimmed off and reprocessed.[29]

In an IAF system, air bubbles are produced by mechanical or gas diffusion techniques. The bubbles interact with the suspended solids and oils, and carry them to the surface of the IAF system, where they are removed by a surface skimmer.

Clarifiers are also used to remove oils and solids by using gravitational sedimentation, and are often equipped with skimmers to remove floating oil. Filtration techniques are used to further remove suspended solids.

C. Secondary Treatment

The secondary treatment system is based on biological oxidation processes and is used to remove dissolved organics through oxidative decomposition by micro-organisms. Activated sludge, trickling filters, waste stabilization ponds and aerated lagoons are common secondary treatment processes.

Activated sludge is an aerobic biological treatment system consisting of an aeration tank followed by a sedimentation tank. In this process, high concentrations of micro-organisms are suspended uniformly throughout the aeration tank to which wastewater is added. The organic materials in the wastewater are metabolized by the micro-organisms and the metabolic products are removed from the sedimentation tank.

Trickling filters consist of a large open vessel containing a packed medium that provides a growth site for micro-organisms. Wastewater is applied to the medium by a rotary distributor and the treated wastewater is collected in a drain system. Soluble organics are consumed by the microorganisms and converted to carbon dioxide, water and protoplasm.

Aerated lagoons are medium depth basins, designed for the biological treatment of wastewater on a continuous basis. Oxygen is supplied to the lagoon by mechanical devices such as surface aerators or submerged turbine aerators. Aerated lagoons are often used as a polishing step following removal of organics.

Oxidation ponds consist of shallow basins, which assure an adequate supply of oxygen without mechanical mixing. Aeration is achieved by oxygen transfer at the surface and by photosynthetic action of algae present in the ponds. Microorganisms then cause aerobic degradation of organic contaminants in the water.

D. Tertiary Treatment

To further improve the quality of the wastewater effluent, tertiary processes can be used for removal of some organic pollutants, taste and odour producing substances, and dissolved inorganic substances.[30] The most effective and commonly used tertiary treatment is Granular Activated Carbon (GAC) adsorption, Powder Activated Carbon (PAC) and Granular Media Filters (GMF).

There are several types of Granular Media Filters, such as *sand dual media* and *multimedia* filters. Such filters basically consist of a coarse layer of coal above a fine layer of sand, and a third layer of heavy fine material (usually garnet) beneath the coal to keep the fine particles on the bottom. As wastewater passes through such filters, the suspended matter is caught in the pores.[31]

In the Powdered Activated Carbon (PAC) treatment, powdered carbon is added to the biological treatment systems. The adsorbent quality of carbon aids in the removal of organic materials.[32] PAC treatment also enhances colour removal, clarification, as well as BOD* and COD** reduction.

Granular Activated Carbon filtration removes large organic molecules from the wastewater, while a companion sand filter removes solids. The water flows through a bank of parallel carbon columns where the pollutants are adsorbed by the carbon, gradually filling its pores. At intervals, the carbon is removed, regenerated and the adsorbed substances are incinerated.

Only two Ontario refineries use a tertiary treatment system: Esso (Nanticoke) is using Granular Media Filters and NOVA (Corunna) is utilizing Activated Carbon Filtration.[33] The activated carbon treatment is potentially a very promising and flexible method of tertiary treatment.

Table 8 summarizes the current wastewater treatment facilities utilized by Ontario's petroleum refineries.

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* Biochemical Oxygen Demand (BOD) provides a measure of the amount of biodegradable organic material discharged in the effluents. The BOD loadings can be correlated with the dissolved oxygen levels of the receiving water.

** Chemical Oxygen Demand (COD) provides a measure of the equivalent oxygen required to oxidize the materials present in a wastewater sample.

Table 8. Description of the Wastewater Treatment Facilities in Ontario's Petroleum Refineries.

Plant	Treatment facility Process Water	OTCW	Cooling Tower Blowdown
Esso Petroleum Sarnia P & S	API separator, filters (sand and anthracite), Biological unit, Activated Sludge, Clarifiers	Segregated, API Separators	Combined with OTCW
Petro-Can. Mississauga P & S	API separator, Sand filter, Equalizer, Activated sludge, Clarifiers	Segregated, Oil skimmers	To the API sep. or to the receiving water
Petro-Can. Oakville P & S	API separator, Equalization, IAF separator Activated Sludge, Clarifiers, Surge lagoon	Not Using OTCW	Surface water-lagoon
NOVA Petro-chemicals Corunna P, S & T	Corrugated plate oil separator, Equalization, DAF separator Activated sludge, Clarifier, Activated Carbon, Final ponds	Not Using OTCW	To final ponds, or if needed will be treated
Shell Sarnia P & S	API separator, DAF, Retention tank, Activated sludge Clarifiers, API	API separator	N/A
Suncor Sarnia P & S	API separator, Vertical tube-separator, Equalization basin, IAF, Activated sludge, Impounding Basins	API separator	API separator IAF, to activated sludge
Esso Petroleum Nanticoke P, S & T	API separators, Equalization ponds, DAF, Activated sludge, Clarifiers, Recycle ponds, Dual filters sand/ anthracite, final-impounding basins	Not Using OTCW	N/A

Source: MOE, 1987.[34]
P = Primary; S = Secondary; T = Tertiary
OTCW = Once Through Cooling Water; NA = not available

4. Review of Available Technologies

In this part, additional pollution control technologies which are available, but not necessarily used in Ontario are assessed. There are several key components associated with the technologies which affect refinery effluent quality.

4.1. General and Specific Levels of Assessing of Treatment Technologies

A review of the industry literature clearly indicates that the assessment of pollution control technology performance is generally undertaken on one of two levels.

The first and predominant level is a 'general' assessment of the performance of a technology component. This level attributes parameter concentrations to a general technology component within a refinery. For example, loadings will be attributed only to the presence of a biological treatment facility, an API separator, or a combination of such components. There are uncertainties with such an assessment, since many variables are related to those general components and can not be controlled for or identified.

The second level of assessment attributes parameter concentrations to specific operational procedures. For example, the 'specific' level of assessment will evaluate what parameter concentrations are discharged with which particular type of activated carbon used. Similarly, the length of time an effluent is retained for treatment in a retention pond can identify the optimal retention time for maximum pollutant removal.

Without attributing an efficiency or "polluting" value to a specific process, it is not possible to assess the optimal performance of a technology. It is only through extensive assessments of treatment specifics that the identification and operation of a Best Available Technology will be realized.

Values reported by Short et. al. are related to volumes and refining processes, but are not associated with feedstock types or details of the general treatment process components (see Table 9, next page).[35]

Short et. al. also noted that the phenol discharge values are indicative of the activated sludge efficiencies, depending upon the retention time of the effluent.[36] Tomatsu et. al. considered the performance of several different types of manufactured activated carbon, and the possibility of reactivating spent carbon, for use in the activated carbon adsorption processes. The results indicated that both virgin and reactivated carbon have similar adsorptive capacities.[37] Overall, Tomatsu et. al. suggested that the Carbon systems are an effective measure to treat wastewater from petroleum refineries.

The data reported by Yamaguchi et. al. are generalized and are not supported by details on treatment components (see Table 9).[38] Therefore, it is not clear which aspect of the treatment technology is primarily responsible for the derived discharge values.

Lanouette, however, offers details on the treatment components of phenolic-bearing wastes which are often neglected by other authors.[39] These types of details regarding the treatment facilities and their efficiency in removing pollutants must be considered as they are critical in identifying optimal levels of technology performance.

Table 9. Control Technologies for Phenol.

SITE	TREATMENT	RESULT	SOURCE
56,000 b/d; cracking; Midwest USA	API separator; equalization basin (7.5 hrs); Activated sludge (12 hrs aeration basin detention)	10 ug/l	Short et. al. 1974
90,000 b/d cracking-petrochemical; Southwest USA	API Separator; Equalization Basin (time na); Chemical coagulation; Activated sludge (12 hrs).	10 ug/l	"
35,000 b/d; cracking; Southwest USA	Activated carbon in API separator	13 ug/l	"
35,000 b/d; cracking; Southwest USA	Bio-treated effluent. Polished with activated Carbon Absorption.	3 ug/l 1 ug/l	
ballast and tank drains; Japan	storage; oil separator; coagulator filter; activated carbon; absorber guard basin	20 ug/l	Yamaguchi 1975
N/A	chemical oxidation; - hydrogen peroxide 1:1 H202/COD	100% removal	Lanouette 1977

b/d = barrels per day.

4.2. Research and Development of new Technologies

The literature search indicates that research and development of new technologies is not rapidly developing. The International Joint Commission notes that, although sufficient data exists to initiate regulatory measures pertaining to toxics, this does not "...alleviate the need for continuing research".[40] The current lack of research substantiates the IJC's suggestion that pollution control technology research is indeed not an active field.

The composition of crude oil is changing, and refineries are forced to use heavier crudes which result in a greater portion of residuals.[41] Therefore, it is necessary for the refineries to upgrade both the processing and effluent treatment technologies in order to accommodate such changes.[42] Further research and development activities, aimed at all specifics of the various treatment components, should identify the best performing technology for a given set of operating conditions.

Each petroleum plant employs a group of research scientists and engineers. Such corporate research is considered to be private information, and therefore is not available to either CIELAP in setting BAT standards. However, such research may identify BATs for achieving levels below current regulatory limits.

4.3. Best Available Technologies in the U.S.

The results of CIELAP's literature search show that there has been no recent research by the U.S. EPA to improve the existing BAT. By the time the BAT regulations were promulgated in 1982, most U.S. refineries had already employed the best available technology.[43] BAT development beyond water conservation techniques, and in some cases, installation of Granular Activated Carbon systems, has not occurred in the U.S. because the EPA considered the current Best Practicable Technology (BPT) as the Best Available Technology.[44] The explanation was that the cost involved of going beyond the BPT level of control was very high and the 96 percent reduction in toxic pollutant loadings achieved by BPT seemed reasonable.[45]

4.4. Best Management Practices (BMP)

BMPs in refinery pollution controls tend to address several issues:

(1) the optimization of treatment facility efficiency;[46]

(2) the reduction in water use by recirculating and/or reusing

wastewaters;[47] and

(3) the re-design or replacement of faulty or poorly designed mechanical components within production and effluent treatment processes.[48]

In general, no standard set of BMPs exist, although it appears that BMPs should encompass all actions, components and training which strive to optimize pollution control efficiencies while not impeding the efficiency of production processes. Table 10 summarizes the issues identified during the literature search as likely BMPs.

Table 10. Best Management Practices.

Practice	Result	Source
Scouring of Carbon surfaces for accumulated solids and oils via air scouring and back-washing; 7 day interval optimum	efficiency of carbon maintained	Tomatsu et. al., 1980
minimize effluent volume via recirculation and/or reuse; adopting waste water stripper; oil separator; activated sludge; sand filtration; and, activated carbon adsorption for liquid-waste treatment.	200-300 ug/l phenol	Yamaguchi, 1975
replace inadequate drain covers on storm drains	N/A	Vervalin, 1986
prevents plugging of API units with oily emulsions via more effective emulsifiers.	N/A	"
prevent tank emission losses due to inadequate initial and safety seals.	secondary seal extends life of primary seal	"

The role of BMPs in specifying BATs may be considered complementary to the technology specification. A BMP goes beyond merely acquiring a technology component, and is directed at specifying how to optimally operate that component in a refinery. BMPs should address the operations of a refinery and the various technological components within.

5. Developing BAT Options for Ontario Petroleum Refineries

5.1. Overview

Having reviewed the MISA program, the petroleum refining industry, treatment technologies and related data bases, the report will now identify the best available technology options for the control of effluent contaminants in the petroleum refining industry.

The intent of assessing the BAT is not to set limits, but rather to review the performance of technologies for the purpose of selecting a set of technologies from which such limits may be derived.

The virtual elimination of persistent toxic substances is the ultimate goal in defining a BAT under MISA. However, it is not expected that this goal is achievable immediately, and therefore, a number of successively more stringent standards need to be developed. The first step in attaining virtual elimination then, is to define the BAT which meets an initial limit. In addition the setting of limits requires that specific parameters be selected for regulation. Finally, a set of specific criteria as to what are considered appropriate technologies must be adopted.

5.2. Goal of Zero Discharge

5.2.1. Currently Proposed Definitions & Criteria

According to the 1986 MISA White Paper, the goal of MISA is to "virtually eliminate" the discharge of toxic chemicals from Ontario waterways.[49] In essence, the goal of virtual elimination defines what level of discharge of a specific parameter is safe, and therefore not requiring any further regulations.

MISA's Issues Resolution Process has not yet achieved a consensus on the definition of the term 'virtual elimination'. Three definitions have been proposed as follows:

* *Effect-Based Definition* - virtual elimination is defined as a function of eliminating (or reducing to a defined level) the adverse effects of toxics on water quality and uses, including protection of biota and human health.

* *Detection Level-Based Definition* - where virtual elimination is defined as a function of the analytical detection levels; and

* *Treatment-Based Definitions* - where virtual elimination is defined as a function of the required degree of removal (or

allowable amount of discharge) of toxics associated with a given treatment technology.

All three definitions are consistent in recognizing that virtual elimination cannot be achieved in the first stage of regulations, but through successive stages of effluent limits regulations.

5.2.2. CIELAP's Working Definition

Since the MOE has yet to define virtual elimination, CIELAP has adopted a working definition for the purposes of this report, which may also be considered in the Issues Resolution Process.

CIELAP's proposed definition is consistent with the Great Lakes Water Quality Agreement (GLWQA). CIELAP proposes a definition of virtual elimination that is based upon the GLWQA's distinction between persistent and non-persistent toxic substances.[50] With respect to persistent toxic chemicals,

> *Virtual elimination* is defined as the elimination of all inputs, to any medium, of persistent toxic substances.

This definition suggests that all deliberate inputs of persistent toxic chemicals would be eliminated. The elimination of these substances may not be "absolute", but only "virtual", since toxic chemicals may still be discharged by natural or non-human sources, or by those sources beyond immediate control (such as accidental and illegal discharges).

From a practical point of view, implementation would include the phasing-out from use, manufacture and discharge of certain persistent toxic substances. It is recognized that the goal of virtual elimination may not be realistic within the first "round" of BAT development.

For non-persistent toxic chemicals, it is necessary to develop a set of comprehensive water quality standards. Such standards, as opposed to the technological approach, would determine acceptable levels of discharge based upon concentrations in the water column and in biological indicators (i.e. fish and wildlife).

5.3. Selecting Parameters for Effluent Limits

5.3.1. The MOE Criteria

The MOE IRP Proposal concerning the selection of parameters for effluent limits states:

> "All persistent toxic contaminants should be included unless the effluent data satisfies the following criterion: a parameter should be deleted from the data set for selection if the monitoring data shows (at 95% confidence level) that a statistical proportion of 0.9 of the data are at concentrations less than the value defined as virtual elimination. Virtual elimination may be:
>
> Alternative 1 - at concentrations less than the Regulation Method Detection Limit (RMDL)
>
> Alternative 2 - at concentrations less than the Provincial Water Quality Objective (PWQO)
>
> All non-persistent toxic, conventional, and non-conventional pollutants should be included, unless the effluent data satisfies the following criteria: a parameter should be deleted from the data set for selection if the monitoring data show (at 95% confidence level) that a statistical proportion of 0.9 of the data are at concentrations less than the Provincial Water Quality Objective for that parameter.
>
> Parameters of environmental significance which are not selected according to the above criteria may also be considered for selection through 'Best Professional Judgement'."[51]

5.3.2. Parameters Selected for this Study

The BAT modelling component of this study requires suitable data in order to generate loadings and assess treatment efficiencies. Although several sources of data were investigated, not all of the data was adequate for modelling applications. The quality of the data available imposes limitations on the strength of the conclusions which may be drawn. Variables associated with many of the values were often not available, nonetheless, CIELAP's BAT options provide a useful tool for evaluating pollution control technologies.

This study selects three parameters for the purposes of developing BAT options: benzene, chromium and phenol. These parameters are listed on the U.S. EPA Priority Pollutants List and the Effluent Monitoring Priority Pollutants List (EMPPL)*. These parameters are also included in the MISA petroleum monitoring regulation.[52]

The assessment of only three parameters is less comprehensive than the MOE's plan to model an extensive number of parameters. However, for illustration purposes a small number is considered adequate. The specific characteristics of the selected parameters are detailed below.

Benzene

Benzene (C_6H_6) is a clear, colourless, liquid with aromatic properties and is flammable at room temperature. It is the parent hydrocarbon of the aromatic group and a natural constituent of crude oil. Benzene is almost exclusively produced from petroleum refining operations, however, small quantities may be produced as a by-product in the steel industry, and some benzene may be recovered from coal-based operations.[53]

Benzene is utilized extensively in the manufacture of other chemicals. Generally, benzene is used:

* as a solvent;
* to increase the octane rating of unleaded gasoline;
* in preparation of derivatives for polymers, detergents, pesticides; and
* in the production of pharmaceuticals.[54]

Benzene is associated with extensive health risks because it is recognized as a human leukaemogen and as a carcinogen.[55] The extensive industrial use of benzene results in widespread exposure to workers, which has warranted the setting of acceptable exposure levels in the work place.[56]

In the United States, benzene is one of the few chemicals regulated under Section 112 of the Clean Air Act as a hazardous air pollutant.[57] The potential for health impacts via the ingestion of both contaminated water and aquatic organisms has convinced the EPA to suggest that the ambient water concentration of benzene should be zero.[58] The U.S. EPA assumes a non-threshold limit for benzene, that is, there is no recognized safe

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* EMPPL, the Effluent Monitoring Priority Pollutant List, was initiated by MISA in 1987 and is periodically updated. To date, EMPPL consists of 266 chemicals. The hazard assessment process is based on a chemical's environmental persistence, potential to bioaccumulate, acute and sublethal toxicity to biota (including human) and potential to exist in effluents discharged to surface waters.

concentration for this human carcinogen.

Excessive concentrations of benzene have been reported in untreated wastewater of petroleum refineries and in the sludge collected from primary, intermediate and biological treatment facilities.[59]

The reasons for selecting benzene as a study parameter are that it is:

- produced in refineries as a petrochemical intermediate;
- measured at high concentration in intermediate refinery wastewaters;
- detected in final effluents;
- detected in sludges;
- required to be monitored under MISA;
- and a potential carcinogen and leukaemogen.

Chromium

Chromium occurs naturally in the Earth's crust and trace amounts are found in air and water. Excessive amounts of chromium enter the atmosphere and surface waters through various industrial activities. Chromium is an essential nutritional trace element with the potential to bioaccumulate in indigenous biota.[60,61]

The common forms of the metal in aquatic environments are trivalent and hexavalent chromium. Of the two forms, hexavalent chromium is the most toxic to aquatic organisms. Hexavalent chromium compounds can remain soluble in surface waters near industrial outfalls and are able to persist for extended periods if the concentration of oxidizable material is low. Therefore, the relative availability of hexavalent chromium in aquatic media is site specific.[62]

The carcinogenic health risks of hexavalent chromium to humans have never been demonstrated, however, there is evidence which relates human lung cancer to hexavalent chromium exposure.[63]

About 90% of the chromium effluents of petroleum refineries is from addition of zinc chromate in the cooling tower waters as an anti-corrosive, scale and slime agent.[64] Chromium is also detected in very low concentration in crude oil.[65]

The reasons for selecting chromium in this study are that it is:

- detected in high concentrations in intermediate and final effluents of refineries;
- bioaccumulative
- persistent;
- potential carcinogen; and
- required to be monitored under MISA.

Phenol

Phenol (C_6H_6O) is a non-persistent organic compound and highly soluble in water. It readily forms various phenolic compounds in water, some of which represent potential risks to human health.

The concern with phenol is primarily due to its toxicity to aquatic organisms and its high oxygen demand on receiving streams as they degrade. Phenol is toxic to fish at levels above 2 mg/l.[66] If detected at concentrations far below the toxic level, phenol can cause a taste and odour problem in fish flesh and in drinking water.[67]

The majority of phenol in refinery wastewater originates from the catalytic cracking process; thermal cracking and crude distillation also produce phenolic wastewater.[68]

The reasons for selecting phenol in this study are that it is:

- detected in final effluents;
- detected in refinery sludge;
- required to be monitored under MISA; and
- toxic to aquatic organisms.

5.3.3. Discharge Data for the Selected Parameters

Literature Search Data

Of the three study parameters, only phenol is discussed in the literature. Several of these references attribute phenol concentrations to specific production or treatment components (see Table 9, page 24). However, this phenol data is dated 1970's and tends to be at or below the MISA laboratory detection limit of 10 ug/l. The reliability of data so close to the detection limit is questionable. In addition, the details by which it is derived from the treatment components are often vague. Thus, the use of this data for modelling purposes is not appropriate.

MISA Monitoring Data

The MISA monitoring regulations specified the sampling frequencies of the three parameters for the 12 months period:

Benzene - 150 data points
Chromium - 150 for OTCW; 12 if cooling water is recycled
Phenol - 12 data points

The data points for phenol and chromium (if cooling water is recycled) are considered to be statistically restrictive, and therefore, an assumption is made that the normal distribution best represents the data. There is insufficient information to make any other assumption regarding the applicable distribution. The central tendency of normally distributed data is best represented with the mean value, which was calculated for the chromium and phenol parameters.

A greater temporal density of data for benzene permits a more thorough investigation of the applicable data distributions. A graphical analysis of the data indicates that the log normal curve would be the most representative statistical distribution. The geometric mean is thus the best measure of the average concentrations. The geometric mean, having been derived from a larger data base, more reliably represents the average concentrations of that parameter, and subsequently the derived loadings. In the case of the sparser chromium data, the arithmetic average is a good estimate of the actual average concentration value since all data points are very close.

Overall, CIELAP's assessment of BAT abides by the MISA criteria, however, it differs from MISA by considering the upper 10% of the technology performance and also by treating non-detected values as detection limits.*

5.4. Parameter Loadings

CIELAP obtained the 12 months MISA monitoring data for chromium, benzene and phenol from the Water Resources Branch of the MOE in June of 1990. The data is used to generate the total

* CIELAP assesses the upper 10% of technology performance rather than the 50% advocated by MISA. It is considered that the identification of the Best Available Technology should only consider the best. The incorporation of such a high standard would essentially render 90% of regulated contaminants as being unacceptable, rather than merely 50%. Such a stringent criterion is better suited to identify the technologies which may realize the virtual elimination of toxics.

CIELAP differs from the MOE in its treatment of non-detected (<DL) values. Where the Ministry applies a value of zero to such detections, CIELAP has considered such values as the detection limit and used the data points as they were reported. The rationale is that since the detection limits are laboratory dependent, rather than bias the data downward as the Ministry does with an applied zero value, our application of the detection limit biases the data upward, thus erring on the side of caution during the BAT modelling.

annual parameter loadings in order to assess the effectiveness of the proposed BAT options. Loadings were derived by multiplying the average parameter concentration with the annual effluent volumes.

The total loadings depend on both the effluent volumes and the parameter concentrations. An ideal BAT model would have zero concentrations and zero effluent volumes. The two factors cannot be assessed separately because the target figure should be the final loading of the parameter - the product of the two variables. The loadings of chromium, benzene and phenol for each refinery and for the whole sector were calculated in the same fashion and the results are presented in Table 11.

Table 11. Benzene, Chromium and Phenol Loadings from Ontario Petroleum Refineries into the Great Lakes Basin (in kg/year).

Refinery	Benzene	Total Chromium	Chromium(6+)	Phenol
Esso Petroleum (Sarnia)	78	198	N/A	11.8
Esso Petroleum (Nanti.)	0.44	19.4	35.2	1.1
Shell	134	2,234	N/A	5.3
Suncor	35.5	66	N/A	3.3
Petro-Canada Oakville	.25	74	N/A	5.2
Petro-Canada Mississauga	12.4	776	N/A	4.9
Nova Petrochemicals	0.5	399	N/A	2.3
TOTAL	261	3,766	35.2	33.9

5.5. The MOE Criteria for Selecting BAT Options

Through the Issues Resolution Process (IRP), the MOE has drafted detailed criteria for the selection of BAT.[69] This report uses the following draft criteria from the IRP: contaminants of concern, stream types, available technologies and demonstrated technology*.

The selection of BAT options from the list of demonstrated technologies primarily concerns the contaminant removal ability, and secondarily considers the following at applicable sampling points:

* non-lethal to trout and Daphnia;

* maximum use of reduction, re-use and recycling, and smallest transfer to other media; and

* maximum water conservation.

BAT Selection

In order to be considered by MOE, a list of at least four BAT options should be developed in order to facilitate an economic achievability analysis. The proposed options should reflect the goals and objectives of the MISA program. The following BAT options should be selected, among others:

* A BAT option that utilizes the best technologies currently in use in North America, Europe or Japan;

* The BAT option selected by the U.S. EPA for the sector or sub-sector in question;

* A BAT option that utilizes the best technologies currently in use in Ontario for the sector or sub-sector in question; and

* A BAT option consisting of any technologies or combinations of technologies which advance the sector or sub-sector towards the goals, policies, and objectives as identified during the Issues Resolution Process.

* "Demonstrated technology" means a technology for which data are available to predict its performance.

Subsequent Activities

The list of BAT options will move forward for further analysis including:

* setting effluent limits for those substances controlled by each BAT option;

* a technical cost evaluation of each BAT option; and

* an economic achievability evaluation of each BAT option.

Further to the above criteria, the MISA Advisory Committee (MAC) has recommended that the following also be included:

"* At least one BAT technology will be advanced to meet the requirements for production facilities yet to be built or for major upgrading of existing facilities. This technology shall be in a new source performance standard (NSPS) based on best available demonstrated technology.

* At least one zero discharge of water option should be considered among possible BAT technologies. Although in most cases zero discharge of water may not prove either technically or economically feasible, it provides for virtual elimination and a point of reference for other technologies in terms of effluent reduction, benefits, and cost effectiveness."

5.6. U.S. EPA Percentage Removal Efficiency Data

In 1983, the U.S. EPA released its "Treatability Manual", listing different treatment technologies with their associated removal efficiency factors.[70] The EPA values represent the performance to be expected for refineries employing the same technology under similar operating conditions. Table 12 (next page) lists the removal efficiencies of selected treatment facilities. In conjunction with the loadings derived from the MISA monitoring data, it is now possible to model the performance of several options.

Table 12. Pollutant Removal Efficiencies of End-of-Pipe Treatment Measures.

Parameter	Removal Efficiency (%)			
	GMF	GAC	GMF+GAC	PAC+GMF
Benzene	15	64	69	90
Chromium	31	37	57	94
Phenol	4	75	76	91
TOC	25	47	60	25
TSS	60	40	76	60
Oil and Grease	42	45	68	42
Zinc	43	37	64	43
Toluene	17	69	74	93

Source: U.S.EPA, 1983[71]; SAIC et.al. 1990

GMF = Granular Media Filtration

GAC = Granular Activated Carbon Adsorption

PAC = Powdered Activated Carbon Adsorption

TOC = Total Organic Carbon

TSS = Total suspended Solids

6. BAT Options Identified by CIELAP

This section presents five independent BAT options based on the technology and loadings information obtained in the research phase. The options are developed to demonstrate the expected removal efficiencies of various technological components, or combinations thereof. The option which is best able to realize the virtual elimination of toxic pollutants should be the preferred choice.

The assessment is considered to be of the 'general' level of performance, as more detailed operation specifications and associated data remain unavailable.

CIELAP assessed the performance of the technologies beyond the base control components. Currently, Ontario refineries use the following base control technologies in treatment systems:

* sour water stripping;
* initial oil-water separation (API separator and CPI separator);
* equalization basin;
* further oil-water separation (Dissolved Air Flotation and Induced Air Flotation); and
* biological treatment (activated sludge).

The above components are common to all Ontario refineries, and the current loadings are thus a function of these technologies (in conjunction with other site specific components). As a result, CIELAP quantitatively assessed the effect of the treatment technologies beyond the base control technology components.

The total sector loadings have been calculated and compared against the removal efficiencies of the various BAT options (see Appendix B for a sample calculation). With the three study parameters, CIELAP is demonstrating which BATs may be expected to be more effective in the removal of contaminants from refinery effluents. The key points pertinent to the development of each BAT option are discussed following each option.

OPTION 1
Employ End-of-Pipe Technologies -
Best Available Technology in the U.S.

1. **Base Control Technology**

2. **In-plant Control Measures:**

   Water Conservation

   - substitute cooling towers for Once Through Cooling Water (100%)

   - reuse the sour water in desalter unit

3. **End-of-Pipe Control Measures:**

   - install Granular Media Filtration (GMF)

Option 1 Contaminant Removal Efficiency:

	Removal Efficiency	Current Sector Loadings (in kg/year)	Option 1 Loadings (in kg/year)
benzene	15%	261	222
chromium	31%	3,766	2,599
phenol	4%	34	33

Note: option loadings reflect the application of GMF only.

Option 1: Employ End-of-Pipe Technologies - Best Available Technology in the United States

The Option 1 technologies meet the MOE criteria for BAT selection because they are currently used in Ontario or in the United States. The reduction of flow by substituting cooling towers for OTCW is practised in some Ontario refineries and is one requirement of the U.S. BAT. The Option 1 loading reductions only reflect the removal efficiency of the granular media filters (GMF) as no performance standards are available for the water conservation component for OTCW.

Elimination of OTCW via the recirculation of water through cooling towers is expected to reduce the refineries' water usage by up to 90%.[72] Such a reduction is considered substantial as several of the refineries currently discharge large effluent volumes, indicative of using OTCW.

Possible reuse of sour water as desalter water, process wash water, cooling tower makeup, or boiler makeup, facilitates the reduction of effluent volumes as well. The use of sour water in desalter units is a proven technology.[73] It has the advantage of reducing the fresh water needed and, at the same time, some of the phenols present in the sour water are extracted, while the crude is desalted.[74]

Estimates of total loadings for each refinery and the entire sector are provided in Appendix C, Table 1. The values reflect the expected loadings assuming that all refineries implement the end-of-pipe treatment technology components of Option 1. Some variability may be expected due to the unquantifiable nature of the water conservation components, and due to the performance of components such as Best Management Practices.

OPTION 2
Employ Advanced End-of-Pipe Treatment Technologies

1. **Base Control Technology**

2. **In-Plant Control Measures**

   Water Conservation

   - substitute air cooling devices for water cooling systems (25% air cooling)

   - substitute cooling towers for OTCW

   - reuse of sour water in the desalter unit

   - segregate, collect and separately treat the cooling tower blowdown

3. **End-of-Pipe Control Measures:**

   - installation of Granular Activated Carbon (GAC) adsorption system

Option 2 Contaminant Removal Efficiency:

	Removal Efficiency	Current Sector Loadings (in kg/year)	Option 2 Loadings (in kg/year)
benzene	71%	261	76
chromium	40%	3,766	2,260
phenol	77%	34	8

Note: Option loadings reflect the application of GAC and 25% air cooling.

Option 2: Employ Advanced End-of-Pipe Treatment Technologies

Air cooling systems, replacing existing water based cooling methods, represent a major process change which can drastically reduce wastewater. The Esso Petroleum (Nanticoke) plant is the only refinery in Ontario which employs 85% of the total cooling needs to the air cooling system. Such a system produces lower volumes of wastewater effluent per unit of production, and therefore a less contaminated effluent.

The segregation and separate treatment of cooling tower blowdown has two advantages. First, it reduces the dilution of the process effluent, thereby optimizing the efficiency of the biological treatment system, and second, the treated cooling tower blowdown can be satisfactorily used in cooling towers.[75]

The use of Granular Activated Carbon (GAC) reduces the residual solids and organic compound content in wastewaters for a number of pollutants (See Table 12, page 37). Currently the GAC technology is used only in the NOVA Petrochemical plant.[76] However, GAC is employed by some petroleum refining facilities, municipal wastewater treatment plants and other industrial sectors in the Unites States.[77]

Similar to Option 1, the use of stripped sour water in desalter units reduces the volumes of fresh water required, and eliminates phenolic materials.

Estimates of total loadings for each refinery and the entire sector are provided in Appendix C, Table 2. The values reflect the expected loadings assuming that all refineries implement the Option 2 GAC technology component and application of 25% air cooling. Variability in the loadings may be expected due to variability in Best Management Practices.

OPTION 3
Toxics Use Reduction through Chromium Substitution

1. **Base Technology Components**

2. **In-Plant Control Measures**

   Pollution Prevention

   - substitute non-metallic anti-corrosive substances for metallic ones (i.e. replace zinc chromate with phosphate-based chemicals)

   Water Conservation

   - substitute an air cooling system for the water cooling system (50% air cooling)
   - segregate, treat and reuse cooling tower blowdown
   - replace barometric condensers with surface condensers

3. **End-of-the Pipe Control Measures**

   - install Granular Activated Carbon (GAC) absorption
   - install Granular Media Filtration (GMF)
   - segregate, separate and separately treat process wastewater, ballast water, and stormwater

Option 3 Contaminant Removal Efficiency:

	Removal Efficiency	Current Sector Loadings (in kg/year)	Option 3 Loadings (in kg/year)
benzene	81%	261	50
chromium	85%	3,766	565
phenols	77%	34	8

Note: Option loadings reflect the application of GAC and 50% air cooling.*

* Barometric condensers are used to provide vacuum jet condensing for vacuum distillation towers. The wastewater generated by the barometric condensers is a major source of oil-water emulsions, containing a high organic waste load, and thus is very difficult to treat. Condensers are also an important source of airborne hydrocarbon emissions. Replacement of these units with surface condensers or air fan coolers eliminates a major source of wastewater and air emissions from refineries.

Option 3: Toxics Use Reduction through Chromium Substitution

Segregation and separation of oily and non-oily wastewater optimizes the efficiency of the biological treatment process by eliminating dilution. Generally, refinery wastewater should be segregated into four different types: non-oily water, moderately oily-water, oily-water and sanitary wastewater.

Estimates of total loadings for each refinery and the entire sector are provided in Appendix C, Table 3. The values reflect the expected loadings assuming that all refineries implement the Option 3 component of GMF/GAC, substitute chromium in their cooling system and employ at least 50% air cooling.

OPTION 4
The "Best Performing" Refinery in Ontario

1. **Base Technology Component**

2. **In-Plant Control Measures**

   Pollution Prevention

   - substitute chromium (see option 3)

   Water Conservation

   - substitute an air cooling system for the water cooling system (85% air cooling)

3. **End-of-Pipe Control Measures**

   - install Granular Media Filters (GMF)

4. **Best Management Practices**

   - reuse/recycling of wastewater
   - good housekeeping
   - onsite/offsite waste management
   - spill and leak control
   - risk identification and assessment
   - preventive maintenance
   - employee training
   - optimization of the treatment facilities

5. **Spill Prevention Technology**

   - require the use of best available spill prevention technology

Option 4 Contaminant Removal Efficiency

	Removal Efficiency	Current Sector Loadings (in kg/year)	Option 4 Loadings (in kg/year)
benzene	94%	261	16
chromium	88%	3,766	452
phenols	59%	34	14

Note: Option loadings reflect the application of the Esso (Nanticoke) performance and 85% air cooling.

Option 4: The "Best Performing" Refinery in Ontario

The Esso Petroleum (Nanticoke) refinery was selected as the best performing refinery in Ontario since the MISA monitoring data shows that it produces the lowest levels of contaminants among the Ontario refineries (See Table 11, page 34).

This proposed BAT option is based on the upper 10% of Nanticoke parameter concentrations as derived from the MISA monitoring data, and subsequently applied to the entire petroleum refining sector. This BAT option applies to the process effluent only, as Nanticoke recycles cooling water and employs air cooling system. The average daily process effluent flow was calculated for each of the Ontario refineries. This created an effluent flow figure that was roughly analogous to the Nanticoke refinery. In applying the Nanticoke loadings several key assumptions are made:

1. Although Nanticoke is a more modern, lower capacity refinery, the transfer of water recycling and air cooling methods is technically feasible.

2. The upper 10% of refinery performance is to be used to set BAT standards for concentrations and loadings because this level represents the uppermost level of control technology efficiency.

3. The size and production levels of each refinery do not affect the output data of this model. Although these are very important factors in setting the final BAT standards, a lack of data prevents using these two factors.

Spills occur frequently in Ontario petroleum refineries and cause serious aquatic damage. Thus, it is vital that spills are addressed under Best Management Practices (BMPs) and under the BAT. As part of a BAT, the best available spill prevention technology must be employed by oil refineries. As part of the BMPs, a protocol must be developed describing procedures related to cleaning up a spill effectively and quickly.

Total loadings for each refinery, after applying Option 4, is presented in Appendix C, Table 4.

OPTION 5
Zero Effluent Refinery

1. **Base Technology Components**

2. **Source reduction**

   - reduce petroleum production through mandating alternative fuels
   - redesign or reformulate end products

3. **In-Plant Control Measures**

   - apply chromium substitution (see Option 3)
   - apply water conservation (100% air cooling)
   - reuse sour water (see Option 2)

4. **End-of-Pipe Control Measures**

   - use Powdered Activated Carbon (PAC)
   - apply Granular Media Filters (GMF)
   - wastewater reuse leading to zero effluent: recycle and reuse treated process effluent as well as other wastewater

5. **Best Management Practices (see Option 4)**

6. **Spill Prevention Technology (see Option 4)**

7. **Zero Effluent Measures**

   - closed-loop effluent systems
   - water intake to replace evaporative losses only

Option 5 Contaminant Removal Efficiency:

	Removal Efficiency	Current Sector Loadings (in kg/year)	Option 6 Loadings (in kg/year)
benzene	100%	261	0
chromium	100%	3,766	0
phenols	100%	34	0

Option 5: Zero Effluent Refinery

Option 5 proposes a zero effluent refinery, which is technically achievable, as there are 55 such refineries in the U.S..[78] There remains, however, some question as to the methods used to achieve zero effluent.

The treatment of wastewater in the U.S. zero effluent refineries is typically achieved through the use of evaporation or percolation ponds, leaching beds, surface spraying and disposal wells. The evaporation ponds are sized according to the annual flow, so that inflow, plus incidentally added water such as rainfall, equals evaporative losses. Most U.S. zero effluent refineries are located in arid regions, however, plants located in non-arid regions may also achieve zero discharge through techniques such as forced evaporation (using heat to evaporate the water).[79] The resultant steam is then condensed and reused in the refinery while the brine (slurry) stream is solidified in a flash dryer and disposed.[80]

Although by definition these techniques result in zero 'industrial' effluents, they do not necessarily remove the threat of future aquatic contamination, and therefore, should not be wholly advocated without due consideration. CIELAP currently that considers only the recycling of treated wastewater may provide environmentally sound forms of zero effluents.

6.1 Summary of Options

Table 13 summarizes the components of each option, while the loading models expected from each option are provided in Appendix C, Tables 1 to 4. Table 5 in Appendix C provides a summary of the loadings generated from application of each option. Figures 2 to 4 also illustrate the option loadings.

Table 13. A Map to Zero Discharge.

Option 1 U.S. BAT	Option 2 WATER CONSERVATION	Option 3 CHROMIUM SUBSTITUTION	Option 4 BEST PER-FORMING	Option 5 ZERO EFFLUENT
cooling-towers	water conser-vation	pollution prevention	pollution prevention	pollution prevention
GMF	GAC	GAC	water conser-vation	water conser-vation
		GMF	air cooling	source reduction
			GMF BMP	GMF PAC BMP closed-loop

GMF = Granular Media Filters
GAC = Granular Activated Carbon
BMP = Best Management Practice
PAC = Powdered Activated Carbon

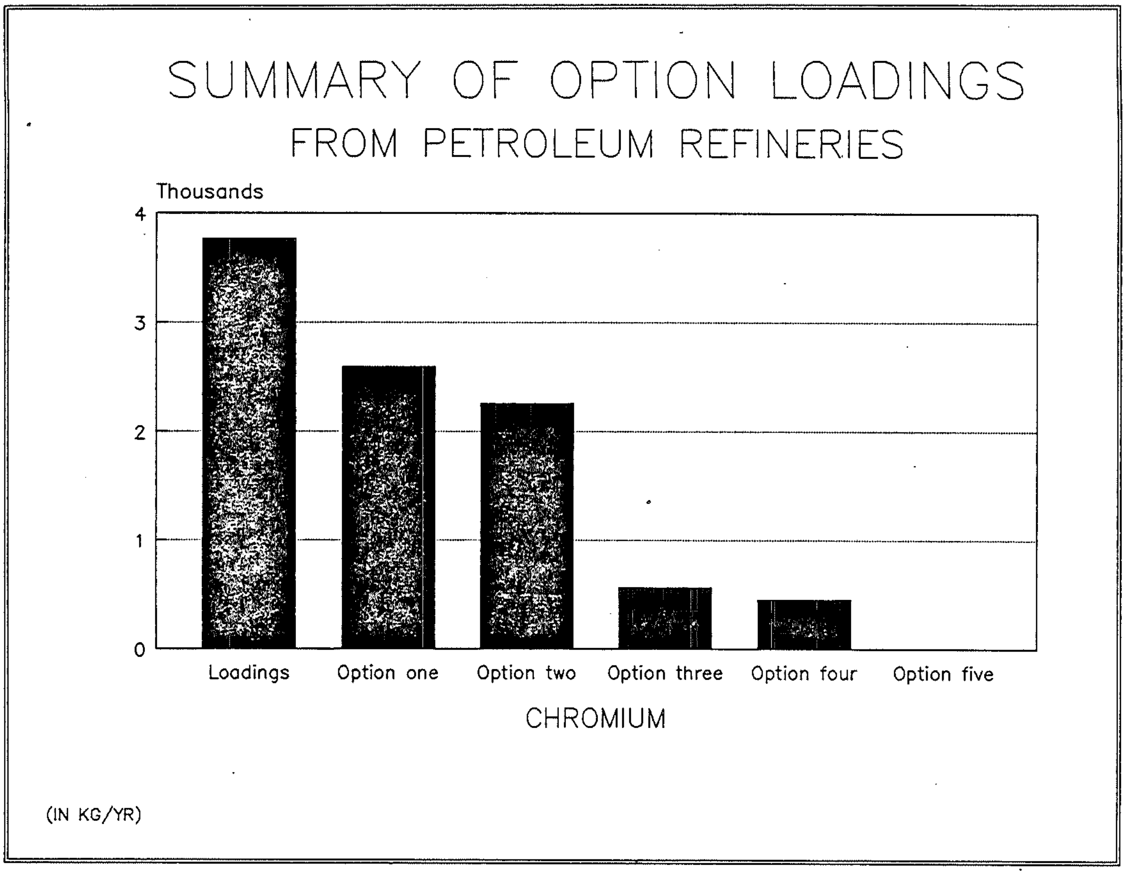

FIGURE 2: Summary of Chromium Loadings from Petroleum Refineries in Ontario, After Application of Each Option

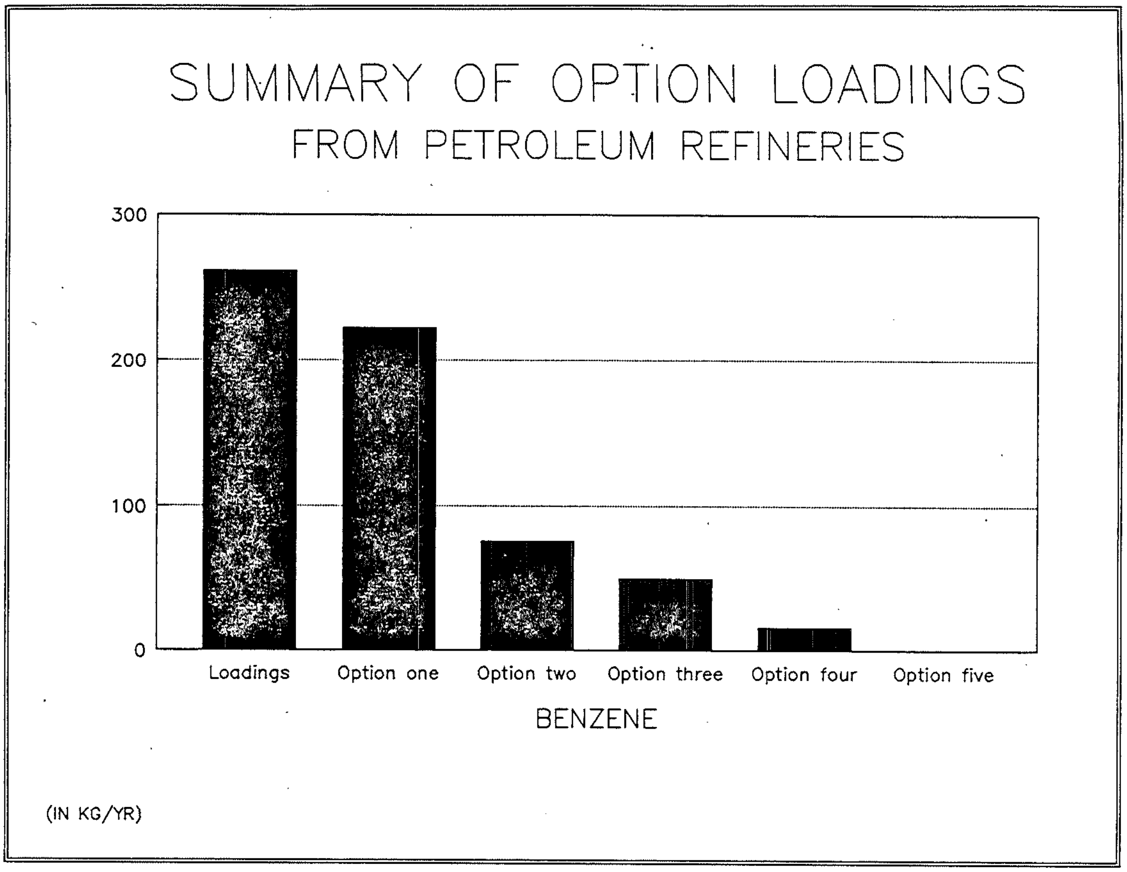

FIGURE 3: Summary of Benzene Loadings from Petroleum Refineries in Ontario, After Application of Each Option

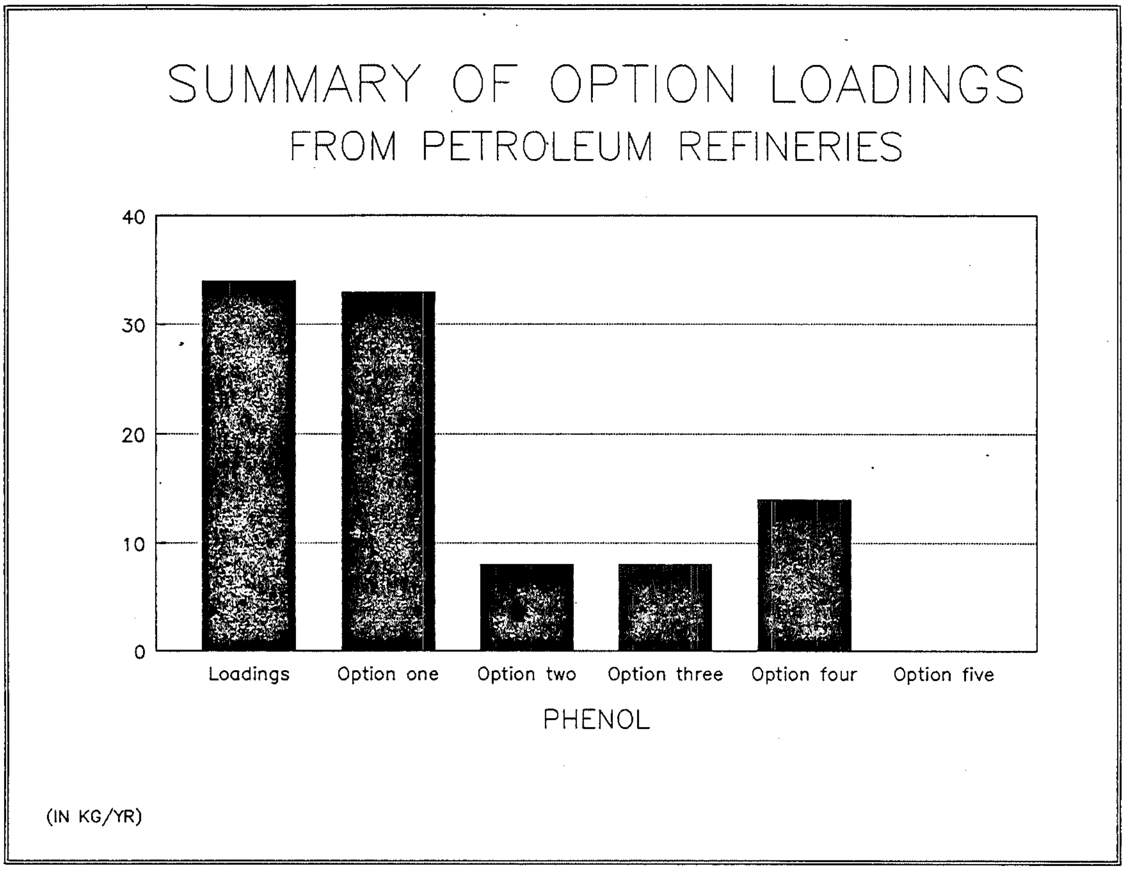

FIGURE 4: Summary of Phenol Loadings from Petroleum Refineries in Ontario, After Application of Each Option

6.2 The Recommended Option

The five options identified are based on restrictive technical and data base information. The modelling exercises must be viewed within the confines of the available research material, and by the assumptions incorporated in the established BAT assessment methods.

Within these limitations, CIELAP recommends adoption of the technology which is best able to realize the MISA goal of virtual elimination of all toxic pollutants. Consequently, the first choice is Option 5, **The Zero Effluent Refinery**. In practical terms, Option 5 can not be immediately imposed on Ontario refineries. However, because there are 55 refineries in the U.S. employing this option, it is our view that it could be adopted as BAT for 1996, with a number of interim BATs. Ultimately, virtual elimination of toxics to all media will require source reduction techniques. Thus CIELAP recommends the following:

RECOMMENDATION 1: Monitoring of Priority Pollutants
Implemented Immediately

Continued monitoring of effluents from oil refineries must be included in the BAT requirement. While the frequency of monitoring does not need to be as extensive as during the monitoring phase of MISA, all persistent toxic chemicals must be monitored periodically (i.e. every two months) until zero discharge refineries are achieved.

RECOMMENDATION 2: Chromium Substitution
Implemented by January, 1992

- Replace zinc chromate with phosphate based-chemicals.

There are viable alternatives to chromium which have an equal effectiveness and are less harmful to the environment. Following is a list of chemicals which can replace chromium.[81]

Phosphate	Azoles
Nitrite	Silicate
Orthophosphate	Molybdate

CIELAP recommends phosphate based-chemicals, since it is a demonstrated technology in the United States and Canada, and poses no harm to the environment.[8283]

RECOMMENDATION 3: <u>Best Management Practices and Spill Prevention Activities</u>
Implemented by January, 1992

- Manage site runoff and drainage from outdoor process and non-process areas resulting from storm water or thaw events
- Control once-through-cooling-water
- Optimize operation of wastewater treatment systems
- Minimize by-passes of the effluent treatment system
- Manage sludge and waste disposal
- Minimize the impact of spills

To be considered an available technology, the BMPs should provide specific effluent performance results. Without an assessment of the effects of a BMP, its importance in pollutant reduction can only be assumed.

RECOMMENDATION 4: <u>Water Conservation</u>
Implemented by January, 1993

Water conservation is the key issue in reducing the contaminated wastewater in a refinery since up to 90% of the contaminants may come from cooling water sources. A major process change which can reduce wastewater is the substitution of air cooling devices for water cooling systems. The elimination of water can increase machinery reliability, reduce capital expenditure for piping and water treatment facilities, and save operating cost.[84] Air cooling systems also reduce the amount of effluent discharged to the wastewater treatment facilities.

RECOMMENDATION 5: <u>Employ Advanced End-of-Pipe Treatment System</u>
Implemented by January, 1994

CIELAP recommends that advanced end-of-pipe treatment systems (tertiary) be employed by all petroleum refineries in Ontario by January 1994. A combination of granular multimedia filtration (GMF) and powdered activated carbon (PAC) or a combination of GMF and granular activated carbon (GAC) is recommended. The percentage removal efficiencies, provided in Table 12, page 37 reveals that a combination of GMF and PAC or GMF and GAC are able to remove pollutants most effectively.

Installation of GMF+PAC or GMF+GAC will reduce total loading by 24,000 to 40,000 kg/year.[85]

RECOMMENDATION 6: <u>Zero Effluent Refineries</u>
Implemented by 1996

CIELAP recommends that the treated process effluent be recycled and reused in the refinery. This would eliminate the discharge of any pollutants into the receiving water. However, recycling the effluent would create contaminated sludge. The conventional sludge disposal practices include: landfilling, landspreading, incineration, deep-well injection and recovery/recycling.[86] Except for recovery/recycling technology, the other methods of sludge disposal are not acceptable, since they are potential sources of air, surface water and ground water contamination. The recovery/recycling method is a feasible technology with economic benefit. Recovery is the reclamation of some valuable constituents in the waste through reprocessing (such as, distillation). In 1978, Canadian refineries recovered a total of 58,100 tonnes of catalysts, alkylation acid, spent caustic products, and scrap metals.[87] Recycling is when waste is being directly reused as raw material or with minor modifications. Therefore CIELAP only recommends the recovery/recycling method of sludges. The remainder of the sludge which cannot be reused should be dewatered and stored, until a safe method of disposal is found.

RECOMMENDATION 7: <u>"True" Source Reduction</u>
Implemented by 1999

- Reduce petroleum use by mandating alternative transportation means (i.e. mandating the use of public transportation in cities, or providing bicycle routes for commuters).
- Use of alternative fuels; an example is the use of alcohol which has been practised in Brazil since the 1970's oil crises.
- Use of electric car engine.

7. Summary and Conclusions

The purpose of this report is to consider the ability of available technologies to achieve zero discharge of all toxic pollutants from the Ontario petroleum refineries. The options proposed in this report are based on a comprehensive review of pertinent technologies and associated effluent data, and in recognition of MISA's goal to virtually eliminate the discharge of toxic chemicals into Ontario waterways. It identifies the processes within a petroleum refinery, the wastewater sources and the contaminants detected in the effluent. The conventional in-plant and end-of-pipe treatment technologies are also discussed.

For the purposes of developing BAT options, three parameters are selected. The assessment of only three parameters is solely for illustration purposes. CIELAP uses the 12 months MISA monitoring data for chromium, benzene and phenol. Total annual loadings of these parameters are generated by multiplying the average parameter concentrations with the annual effluent volumes.

CIELAP is proposing five BAT options based on the technology and data information obtained in our research. In each option, the total sector loadings have been calculated and compared against the removal efficiencies of various end-of-pipe treatment facilities and water use reductions. CIELAP recommends the option which promotes toxic use reduction (i.e. chromium substitution), water conservation (i.e. use of air coolers), and the recycling and reusing of the wastewaters. However the ultimate goal is to reduce the petroleum production and the use of alternative fuels.

Appendix A

Ontario's Approach to the Development of BAT Effluent Limits under MISA.

conducted to establish which technologies were available and their performance levels, especially with respect to treatment efficiencies. Treatment system cost estimates were made to determine the probable costs of achieving BPT or BAT levels for each industry.

It should be noted that the EPA program for developing effluent limits in "rules" is not yet complete; however, proposed rules are available for a number of sectors.

Ontario Approach

The Ministry will be defining BAT effluent requirements for each industrial and municipal sector. The U.S. EPA approach, and the supporting information developed in the process of defining regulations under the U.S. Clean Water Act, will be used where appropriate. Ontario and other Canadian data sources and experiences with technology will be considered where available. The procedure will contain the following steps:

1. Definition and establishment of municipal and industrial sectors (individual companies and municipalities included).

2. Consideration of toxic and conventional contaminants of concern for each sector. This will include literature reviews of existing data and consideration of new data produced during voluntary or regulated monitoring programs. This process will identify candidate pollutants for consideration in the effluent limits regulation.

3. Review of existing treatment technologies in use and the status of each industry with respect to compliance with existing guidelines or control orders.

4. In order to establish best available technology for each sector, a review will first be made of EPA documents for their definition of best available technology for control of toxics and best conventional technology for control of conventional pollutants. Use of EPA data is considered valid since EPA used a large data base for most sectors, and most industries use similar processes in North America.

   Secondly, consideration will be given to technology in use in Ontario and other Canadian provinces that is applicable for each sector, including recent research and demonstration programs in control technology. The review will also establish if substantial differences exist between Ontario industries and U.S. sectors because of differences in raw materials, processes, economics or operating conditions. Several levels and kinds of technology may be defined in this step for consideration in subsequent steps.

5. The performance level for the defined technologies will be established in statistical terms for removal efficiencies of conventional and toxic contaminants. Relationships to units of industrial production, gross water use and pollutant loadings to the treatment system will be established. Final performance levels will be established in units of concentration (mg/l) and either mass loading (Kg/day) or load per unit of production (Kg/day/production unit). Performance will be established statistically for normally well operated plants in terms of long-term average (LTA) performance

and maximum variations in performance normally expected to determine a maximum permissible daily value. (This will require definition of the effluent variability-probability distribution generally established in EPA reports).

6. Up-to-date estimates of costs to achieve technology levels for each individual industry will be calculated from readily available information in the U.S. EPA documents and relevant Canadian data.

7. Parameters for definition of limits will be chosen on the basis of potential environmental impact, relationships to toxics (surrogates), or single toxic compounds representative of groups of toxics, and cost. Ideally, a short list of easy-to-measure toxics and conventional pollutants will form the basis of the limits definition. This is on the assumption that compliance with requirements for the short list would achieve control of the long list of contaminants of concern. This short list will be measured frequently in routine monitoring programs, with less frequent sampling of the long list of toxics to check the validity of assumptions.

8. Based on treatment-efficiency and cost, the best available technology and its abatement performance will be defined. In choosing best technology, the Ministry will consider non-water quality impacts in order not to favour technologies that would transfer equal or greater problems to other media (air or solid wastes).

9. Effluent requirements for toxicity, biomonitoring and mixing zones will be considered.

10. Best management practices for each sector will be defined.

11. Municipal and industrial input to the above steps will be provided by frequent opportunities to comment on the requirements before the regulation is drafted. Opportunities for formal review will also occur when the regulation is circulated in draft form.

12. The Ministry will specify the details of information to be submitted by each industry necessary to identify the effluent requirements of that industry.

13. The Ministry will have in place, through prior implementation of a monitoring regulation for each sector, a data base system and reporting procedure. Sampling, flow measurement and analytical protocols will also have been established.

14. The effluent limits will be framed in terms of performance only. The industry or municipality will have the option to choose the means of achieving the effluent limits. An exception to this is being considered in the case of volatile organic compounds where the industry may not have the option of using technologies that would result in air pollution, but would be required to remove these compounds using specific technologies.

Appendix B

Sample Calculations of Parameter Loadings

The current loadings and option loadings of benzene, chromium and phenol are calculated as follows:

Current Loading: Concentration x Flow

Option 1 Loadings: GMF Removal Efficiency % x Loading

Option 2 Loadings: Total Removal Efficiency % (GAC Removal Efficiency % + 25% Flow Reduction Efficiency) x Current Loading

Option 3 Loadings: Total Removal Efficiency % (GAC and GMFS Removal Efficiency % + 50% Flow Reduction Efficiency) x Current Loading

Option 4 Loadings: Total Removal Efficiency % (GMF Removal Efficiency % + 85% Flow Reductions Efficiency) x Current Loading

Following is a sample calculation of chromium loadings from a refinery before and after the application of Option 2:

Current Loading = 399 kg/yr

Process Effluent = 4859 m^3

Cooling Effluent = 853 m^3

Chromium Concentration = 192 ug/l

$853m^3$ x 25% = 213 m^3 Flow Reduction

$853m^3$ - $213m^3$ = 640 m^3 reduced flow

Total Flow = $4859m^3$ + $640m^3$ = $5,499m^3$

Loading = $5,499m^3$ x 192 ug/l x 365 days x 0.000001 = 386 kg/yr

Loading Reduction = 399 kg/yr - 386 kg/yr = 13.0 kg/yr

Flow Reduction Efficiency = 3.0 %

Total Removal Efficiency = GAC Removal Efficiency + Flow Reduction Efficiency = 37% + 3% = 40%

Appendix C

Benzene, Chromium and Phenol Loadings for all Proposed BAT Options.

Table 1: Estimated Total annual loadings of benzene, chromium and phenol from seven Ontario refineries (kg/yr), after application of GMF; Option 1.

Parameter	Esso Sarnia	Esso Nanticoke	Shell	Suncor	Petro.Can Oakville	Petro.Can Mississauga	NOVA	Total Sector Loadings
Benzene	66.00	0.37	113.90	30.20	0.21	10.50	0.43	221.72
Chromium	136.60	13.40	1541.50	45.50	51.10	535.00	275.31	2598.47
Phenols	11.30	1.10	5.10	3.20	5.03	4.70	2.20	32.60

Table 2: Estimated Total annual loadings of benzene, chromium and phenol from seven Ontario refineries (kg/yr), after application of GAC and 25% air cooler; Option 2.

Parameter	Esso Sarnia	Esso Nanticoke	Shell	Suncor	Petro.Can Oakville	Petro.Can Mississauga	NOVA	Total Sector Loadings
Benzene	22.62	0.13	38.86	10.30	0.07	3.60	0.15	75.73
Chromium	118.80	11.64	1340.40	39.60	44.40	465.60	239.40	2259.84
Phenols	2.72	0.25	1.22	0.759	1.13	1.13	0.53	7.81

Table 3: Estimated Total annual loadings of benzene, chromium and phenol from seven Ontario refineries (kg/yr), after application of GAC, GMF and 50% air cooler; Option 3.

Parameter	Esso Sarnia	Esso Nanticoke	Shell	Suncor	Petro.Can Oakville	Petro.Can Mississauga	NOVA	Total Sector Loadings
Benzene	14.82	0.08	25.46	6.75	0.05	2.36	0.10	49.62
Chromium	29.70	2.91	335.10	9.90	11.10	116.40	59.85	564.96
Phenols	2.72	0.25	1.22	0.76	1.13	1.13	0.53	7.81

Table 4: Estimated Total annual loadings of benzene, chromium and phenol from seven Ontario refineries (kg/yr), after application of Esso (Nanticoke) performance and 85% air cooler; Option 4.

Parameter	Esso Sarnia	Esso Nanticoke	Shell	Suncor	Petro.Can Oakville	Petro.Can Mississauga	NOVA	Total Sector Loadings
Benzene	4.68	0.03	8.04	2.13	0.02	0.74	0.03	15.67
Chromium	23.76	2.33	268.08	7.92	8.88	93.12	47.88	451.97
Phenols	4.84	0.45	2.17	1.35	2.13	2.01	0.94	13.90

Table 5. Summary of Total Sector Loading of Benzene, Chromium and Phenol After Application of Each Option.

	Current Loadings	Opt. 1	Opt. 2	Opt. 3	Opt. 4	Opt. 5
Benzene	261	222	76	50	16	0
Chromium	3,766	2,599	2,260	565	452	0
Phenols	34	33	8	8	14	0

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13. MOE, 1988. Effluent Monitoring Regulations for the Petroleum Refining Sector, page II-35.

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19. MOE, 1990. Second Report on the Monitoring Data for the Petroleum Refining Sector, pages 9 and 10.

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