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Developing Options for Technology-Based Standards for the Petroleum Refining Sector in the Great Lakes Basin

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A Report of

the Program for Zero Discharge

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Introduction

This report examines the role of pollution prevention in attaining zero discharge of persistent toxic pollutants from the petroleum refining industry.

Petroleum refining is a complex combination of inter-dependent operations. The basic function of a refinery is to process crude oil into a variety of petroleum products. There are 13 petroleum refineries (7 in Ontario and 6 in the United States) discharging directly into the Great Lakes basin. These refineries collectively discharge over 1.1 million m^3 per day of wastewater into the Great Lakes.

The objectives of this report are:

(1) to summarize technology-based pollution abatement programs in the U.S. and Canada;

(2) to establish discharge loadings for specific pollutants on a basin-wide level;

(3) to review and assess existing technologies;

(4) to establish best available technology (BAT) options to prevent pollution by a selected group of contaminants; and

(5) to recommend technology-based actions, with the goal of zero discharge, based on pollution prevention.

Pollution Abatement Programs in the Great Lakes Basin

The signing of the Great Lakes Water Quality Agreement in 1972 by Canada and the United States committed the two governments to restoring and maintaining the chemical, physical and biological integrity of the Great Lakes ecosystem. The Agreement was revised and strengthened in 1978 with the addition of a protocol in order to control toxic discharges.

Pollution Abatement Programs in the United States

Water pollution abatement programs in the United States are administered under the authority of the Federal Water Pollution Control Act (FWPCA). Since 1977, the FWPCA, has been known as the Clean Water Act (CWA). In 1972, amendments to FWPCA required the Environmental Protection Agency (U.S. EPA) to develop technology-based effluent limits on a national scale for various industrial sectors. Technology-based effluent standards are standards of performance for specific industrial sectors. These standards are based upon the effectiveness of various technologies in reducing the discharge of pollutants in the final discharges.

The first effluent limits for petroleum refineries were promulgated in 1974. These included best practicable treatment control technology (BPT), new source performance standards (NSPS), pretreatment standards for new sources (PSNS), best available control technology (BAT) and storm-water limits. The current BAT limits were promulgated in 1982 and were revised in 1985. Best conventional treatment technology (BCT) limits and final storm-water limits were also promulgated in 1985.

Pollution Abatement Programs in Canada

In Canada, environmental protection is a shared responsibility of the federal and the provincial governments. The Fisheries Act and the Canadian Environmental Protection Act (CEPA) are the federal laws under which Environment Canada responds to the requirements of the Great Lakes Water Quality Agreement. The Ontario Ministry of the Environment (MOE) uses the Ontario Water Resources Act and the Environmental Protection Act (EPA) to control water pollution.

In 1986, the Ontario government started a new initiative to improve the province's water quality laws - the Municipal Industrial Strategy for Abatement (MISA). This program required industries to monitor their wastewaters at regular intervals for a period of one year. Technology-based effluent standards will be developed based on the data gathered and promulgated as regulations under the EPA.

The Petroleum Refining Industry

Petroleum refineries process crude oil into a number of products, including gasoline, petrochemical feedstock, lubricating oils and asphalt. The processes employed by petroleum refineries may differ depending upon the type of crude oil and the type of product.

The processes in petroleum refineries are generally classified either as physical separation or as chemical conversion operations. During the separation process, crude oil is divided 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.

Wastewater Sources

Wastewater is generated by various refining processes. The major sources of contamination in refinery wastewater include: desalting unit effluents, steam processing, water which has accumulated in the bottom of the storage tanks, ballast water from petroleum tankers, contaminated "once-through-cooling-water," and storm-water run-off from process areas and tankfarms.

Effluent Treatment Technologies

Effluent treatment technologies are divided into two broad classes: (1) in-plant treatment technologies, and (2) end-of-pipe treatment technologies.

In-plant treatment technologies include: sour water stripping, chemical substitution and wastewater reduction.

End-of-pipe treatment technologies include:

* primary treatment: American Petroleum Institute (API) gravity separators or Corrugated Plate Interceptors (CPI) are used to remove oil;
* intermediate treatment: induced air flotation devices, clarifiers or filters are used to remove additional oils and suspended solids;
* secondary or biological treatment: activated sludge, trickling filters, waste stabilization ponds or aerated lagoons are used to remove dissolved organic substances; and
* tertiary treatment: granular activated carbon, powdered activated carbon or granular media filtration are used to remove certain organic pollutants, taste and odour-producing substances, and dissolved inorganic substances.

Developing BAT Options

Three chemicals were selected, benzene, chromium, and phenol, to develop BAT options for the petroleum refining sector. The rationale for choosing these substances can be found in Appendix E.

Technologies are evaluated on their ability to reduce total loadings: using pollutant loadings provides the most illustrative way to show the effectiveness of pollution abatement technologies. The current loadings from refineries are calculated from Ontario MOE's MISA data, and from the U.S. EPA's monthly discharge monitoring reports (DMRs) and permit applications.

As a result, CIELAP has developed five BAT options to evaluate and compare different technologies and their capability to remove contaminants from the wastewater discharge. The options are:

Option 1: *Best available technology in the United States*: employing a granular media filtration system in addition to a secondary treatment system.

Option 2: *Advanced end-of-pipe treatment technology*: employing a granular activated carbon adsorption system. In addition, it is suggested that three measures should be taken to conserve water: (a) by substituting (partially) air cooling for water cooling systems, (b) by substituting cooling towers for once-through-cooling-water, and (c) by reusing sour water.

Option 3: *Toxic use reduction through chromium substitution*: replacing zinc chromate with non-metallic anti-corrosive substances. In addition, it is suggested that advanced end-of-pipe treatment systems, such as granular activated carbon and granular media filtration, are employed.

Option 4: *Best performing refinery in Ontario*: using the same treatment measures as the Esso refinery in Nanticoke:

- o a chromium substitute is used;
- o 85% of cooling is done with air instead of water;
- o the granular media system is used;
- o best management practices are employed; and
- o best spill prevention technology is used.

Option 5: *Closed-loop refinery*: employing all the previously specified in-plant and end-of-pipe control measures. In addition, refineries are required to employ closed-loop systems in order to reuse the process effluents. Thus, in this option no effluents will be discharged into the Great Lakes basin.

Recommendations

The recommendations are divided into three categories: immediate, short-term and long-term recommendations. Continued monitoring and chromium substitution should be done immediately, while option five, the closed-loop option, is recommended in the short-term (by 1996). Long-term recommendations recognize that society's dependence on petroleum products is riddled with negative ecological consequences, from oil drilling and its transportation, to refining and burning the oil product. Consequently, the dependence on this resource has to be reduced significantly, including, the reduction of petroleum use by mandating alternative transportation means, the re-formulation of fuels, and the development and application of alternative energy sources.

1. INTRODUCTION

Petroleum refining is a complex combination of interdependent operations. The basic function of a refinery is to process crude oil into a variety of petroleum products including gasoline, fuel oil, jet oil, heating oils and gases, and petrochemical products.

There are 13 petroleum refining facilities (6 in the United States and 7 in Ontario) directly discharging into the Great Lakes. These 13 facilities discharge more than 1.1 million m3/day (approximately 290 million gallons per day). Table 1 lists the number of refineries in each jurisdiction, the total quantities of crude oil processed each day and the total quantities of wastewater discharges every day.

Table 1. Production Capacity and Wastewater Generation of Petroleum Refineries Discharging into the Great Lakes Basin.

Jurisdiction	Total No. of Plants	Crude Oil Processed m3/day	Wastewater Discharges m3/day
Indiana	1	57,233	51,900
Michigan	1	6,995	1,930
Ohio	3	68,521	210,500
Wisconsin	1	5,405	900
Ontario	7	103,700	847,590
Total	13	241,854	1,112,820

Source: MOE[1], MOE[2] and U.S. EPA[3]

1.1. Purpose of the Report

The purpose of this report is to examine the available technologies to reduce and eliminate the generation, use and release of pollutants from petroleum refineries. The report assumes that the long-term goal for refineries is to meet the goal of zero discharge of persistent toxic chemicals, as articulated and defined under the Great Lakes Water Quality Agreement. This report specifically examines technological capability. It does not examine economic assessments of the proposed technologies, although it is recognized that these are important issues to study.

The primary objectives of this report are:

(1) to summarize technology-based pollution abatement programs in the U.S. and Canada;

(2) to establish discharge loadings for specific pollutants on a basin-wide level;

(3) to review and assess existing technologies;

(4) to establish best available technology (BAT) options to prevent pollution by a selected group of contaminants; and

(5) to recommend technology-based actions, with the goal of zero discharge, based on pollution prevention.

1.2. Methodology

A comprehensive review of the industry literature was conducted to identify pertinent control technologies and practices. Additionally, CIELAP researchers contacted industry experts for their input and advice on technologies for the control of refinery effluents. The review of technologies 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 Ministry of the Environment reports;

- MISA's one year monitoring data;
- Ontario Petroleum Association research papers;
- U.S. Environmental Protection Agency reports; and
- Environment Canada reports.

Using the total loadings of three pollutants, benzene, chromium and phenol, allowed a quantitative assessment of the various technology options. That is, the loadings of the three pollutants was calculated basin-wide from all refineries, leading to the current loadings into the Great Lakes. Using removal efficiencies from the literature, it was then possible to assess the different technologies. Choosing three pollutants is considered adequate for demonstration purposes.

The discharge data was derived from the literature search, from the Ontario Municipal/Industrial Strategy for Abatement (MISA) sector data base, and from the Ontario Ministry of the Environment (MOE) direct discharger reports. The U.S. loadings were derived from the Discharge Monitoring Reports (DMRs) and from the Permit Application Forms, both of which were supplied by the U.S. EPA.

2. POLLUTION ABATEMENT PROGRAMS IN THE GREAT LAKES BASIN

By signing the Great Lakes Water Quality Agreement, the governments of Canada and of the United States have committed themselves to work toward the restoration and preservation of the Great Lakes. Both countries have set a series of standards to fulfil the Agreement and these are generally technology-based. Technology-based effluent standards can be described as effluent limits derived from the average performance of a selected pollution control technology in a specific industrial sector.

The following sections briefly discuss the Great Lakes Water Quality Agreement and the development of technology-based effluent standards for the petroleum refining sector in Canada and the United States.

2.1. The Great Lakes Water Quality Agreement

The Great Lakes Water Quality Agreement was first signed by the national governments of Canada and the United States in 1972. The Agreement was re-negotiated and re-singed in 1978, and the purpose of the Agreement is "to restore and maintain the chemical, physical, and biological integrity of the waters of the Great Lakes Basin Ecosystem".[4] The Great Lakes Water Quality Agreement was renewed and strengthened in 1987 with the addition of a Protocol. A number of provisions outlined in the revised Agreement are aimed at controlling toxic discharges.

2.1.1 Zero Discharge Mandate

Article II of the Agreement establishes a number of policy commitments or hierarchy of obligations. The first paragraph establishes the commitment to eliminate or to reduce to the maximum extent practicable, the discharge of all pollutants.

Article II also mandates a special, more stringent, regime pertaining to toxic substances. It prohibits their discharges in toxic amounts and states that the discharge of all persistent toxic substances should be virtually eliminated.[5]

The qualifying statement, "...to the maximum extent practicable..." is not present in the obligations pertaining to persistent toxic substances. The goal of "virtual elimination" of any such toxic substances, therefore, appears to remain technologically unimpeded, unlike other pollutants. In essence, the optimal use of all technology is permissible.

The clear intention of the Great Lakes Water Quality Agreement is that "virtual elimination" is the overriding goal since many provisions under the Agreement are considered "interim", pending its achievement.[6]

Annex 12 of the Agreement is specifically devoted to persistent toxic substances. This Annex specifically defines "persistent toxic substances," while Annex 1 lists some of these substances.

Annex 12 includes a number of principles which the governments are to abide by when undertaking regulatory strategies to deal with persistent toxic substances. The key principle in this regard is the zero discharge of persistent toxic substances. Annex 12 states that:

> "The philosophy adopted for control of inputs of persistent toxic substances shall be zero discharge;...".[7]

2.2. Pollution Abatement Programs in the United States

Pollution abatement programs in the United States are administered according to the Federal Water Pollution Control Act, FWPCA (since 1977, the FWPCA has been known as the Clean Water Act). In 1972, the amendments to the FWPCA required the Environmental Protection Agency (U.S. EPA) to develop effluent limits on a national scale for various industrial sectors (prior to 1972, effluent treatment requirements for dischargers were set by the individual States, whereas the federal government was only involved in research and development of treatment facilities). The U.S. EPA was also given the responsibility to establish a nationwide discharge permit system called the National Pollutant Discharge Eliminating System (NPDES)*.[8]

The first effluent limits for petroleum refineries were promulgated in 1974; they included Best Practicable Technology (BPT), New Source Performance Standards (NSPS), Pretreatment Standards for New Sources (PSNS), Best Available Technology Economically Achievable (BAT), and storm-water limits. Final BAT effluent limits for petroleum refineries were promulgated in 1982.[9]

The BAT limits were revised in 1985, establishing more stringent treatment requirements for total phenolics, total chromium and hexavalent chromium. Best Conventional Pollutant Control Technology (BCT) limits and storm-water limits were also promulgated in 1985. Figure 1 (page 6) shows the chronological development of technology-based standards, while Table 2 summarizes the pollutants regulated by technology-based

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*NPDES permits are issued under the National Pollutant Discharge Elimination System; every point source discharger to waters of the United States must have a valid NPDES permit that is issued under the statutory authority of the Clean Water Act.

standards.

BAT effluent limits in the U.S. are based primarily on process subcategories and on the crude oil processing capacity of each refinery. Appendix A gives a description of each technology-based standard and the current BAT effluent limits, as developed by the U.S. EPA.

Figure 1: The Chronological Development of Technology-Based Standards for Petroleum Refineries in the U.S.

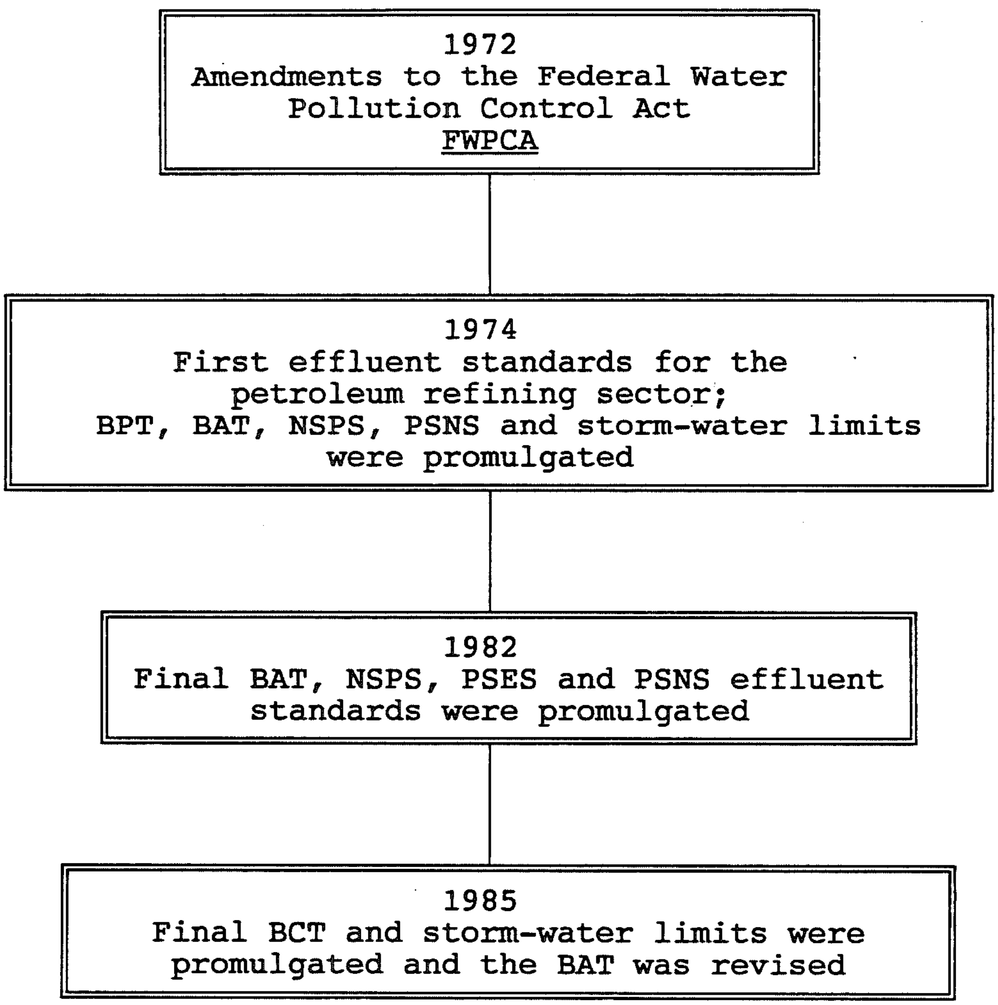

Table 2. Various Technology-Based Standards in the U.S.

BPT	BAT	BCT	PSNS	PSES
BOD5 COD TOC TSS O&G Phenol Ammonia Sulphide Total-chromium Hexavalent-chromium	Phenolics COD Ammonia Sulphide Total-chromium hexavalent-chromium	BOD5 TSS O&G pH	O&G Ammonia Total-chromium	O&G Ammonia

BOD5 the five day biochemical oxygen demand: the 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.
COD chemical oxygen demand: the COD provides a measure of the equivalent oxygen required to oxidize the materials present in a wastewater sample.
TOC total organic carbon
TSS total suspended solids
O&G oil and grease

2.3. Pollution Abatement Programs in Canada

The responsibility for environmental protection in Canada is shared among the federal and provincial governments. The federal government has developed national baseline effluent regulations and guidelines for specific industrial sectors, including petroleum refineries. In Ontario, the provincial government enforces the federal requirements as minimum standards.

2.3.1. Federal Programs

The Fisheries Act and the Canadian Environmental Protection Act (CEPA) are the federal laws under which Environment Canada attempts to fulfil the requirements of the Great Lakes Water Quality Agreement.

Under the Fisheries Act, the *Petroleum Refinery Effluent Regulations and Guidelines* stipulate nationwide standards based on Best Practicable Control Technology (BPT). The Guidelines apply to all refineries commencing operation after November 1973, but do not apply to refineries which operated prior to November 1973. The following substances are regulated in petroleum refineries discharges::

- o oil and grease
- o phenols
- o ammonia
- o total suspended solids
- o sulphides
- o pH

2.3.2. Ontario Programs

Under provincial legislation, the Ontario Ministry of the Environment (MOE) uses the Ontario Water Resources Act and the Environmental Protection Act in an attempt to control water pollution.

Under the Canada-Ontario Agreement Respecting Great Lakes Water Quality, Ontario adopts the federal limits as minimum requirements. Conversely, the province can set and enforce more stringent requirements.

In 1986, the Province of Ontario announced an initiative to improve the province's water quality - the Municipal Industrial Strategy for Abatement (MISA). The first phase of the MISA program required 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 (BAT). Appendix B gives an overview of the MISA program.

By the end of 1990, the monitoring regulations for all industrial sectors had been enacted. The first limit regulation for the Petroleum Refining Sector is due to be released for public review in early 1992, and it is expected that the BAT limits begin applying sometime in 1995.

3. THE PETROLEUM REFINING INDUSTRY

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

This section provides a brief description of the petroleum refineries discharging into the Great Lakes basin, the processes associated with petroleum refining, the related effluent sources and the currently applied wastewater treatment technologies.

3.1. The Ontario Petroleum Refining Sector

The petroleum refining sector in Ontario consists of one petrochemical plant and six conventional refineries, all of which discharge into Great Lakes waters. The petrochemical plant is a petroleum-based producer of primary petrochemical products, with a production capacity of 1.3 billion kilograms of end products; the six refineries have a combined annual production capacity of 24 billion litres of end products.[10] Details on production processes and effluent volumes for each plant are given in Appendix C.

In 1985, Ontario petroleum refineries accounted for 31% of the total Canadian crude oil processing capacity. They generated more than $9.2 billion in revenues in 1984.[11] Petroleum refining is an important industrial sector of Canada's economy.

3.2. U.S. Petroleum Refineries in the Great Lakes Basin

The petroleum refining industry in the United States portion of the Great Lakes basin consists of six refineries. The six refineries undertake a variety of activities and their production processes and effluent volumes are given in Appendix C.

3.3. 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 refineries may differ depending upon the type of crude oil used and the type of products produced.[12] A 1977 survey conducted by the U.S. Environmental

Protection Agency found over 150 separate processes in use throughout the country.[13] Additionally, combinations of these processes may also be used by refineries.

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 a number of intermediate products in the required proportions. The range of processes is summarized in Table 3 (page 11), while Figure 2 (page 12) illustrates the general processes of a typical petroleum refinery.

In addition to the processes listed in Table 3, 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.

Table 3. 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.
ISOMERIZATION	converts n-butane, n-pentane and n-hexane into respective isoparaffins.
LUBE OIL	removal of aromatics, unsaturated processing naphthenes and asphalt 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.

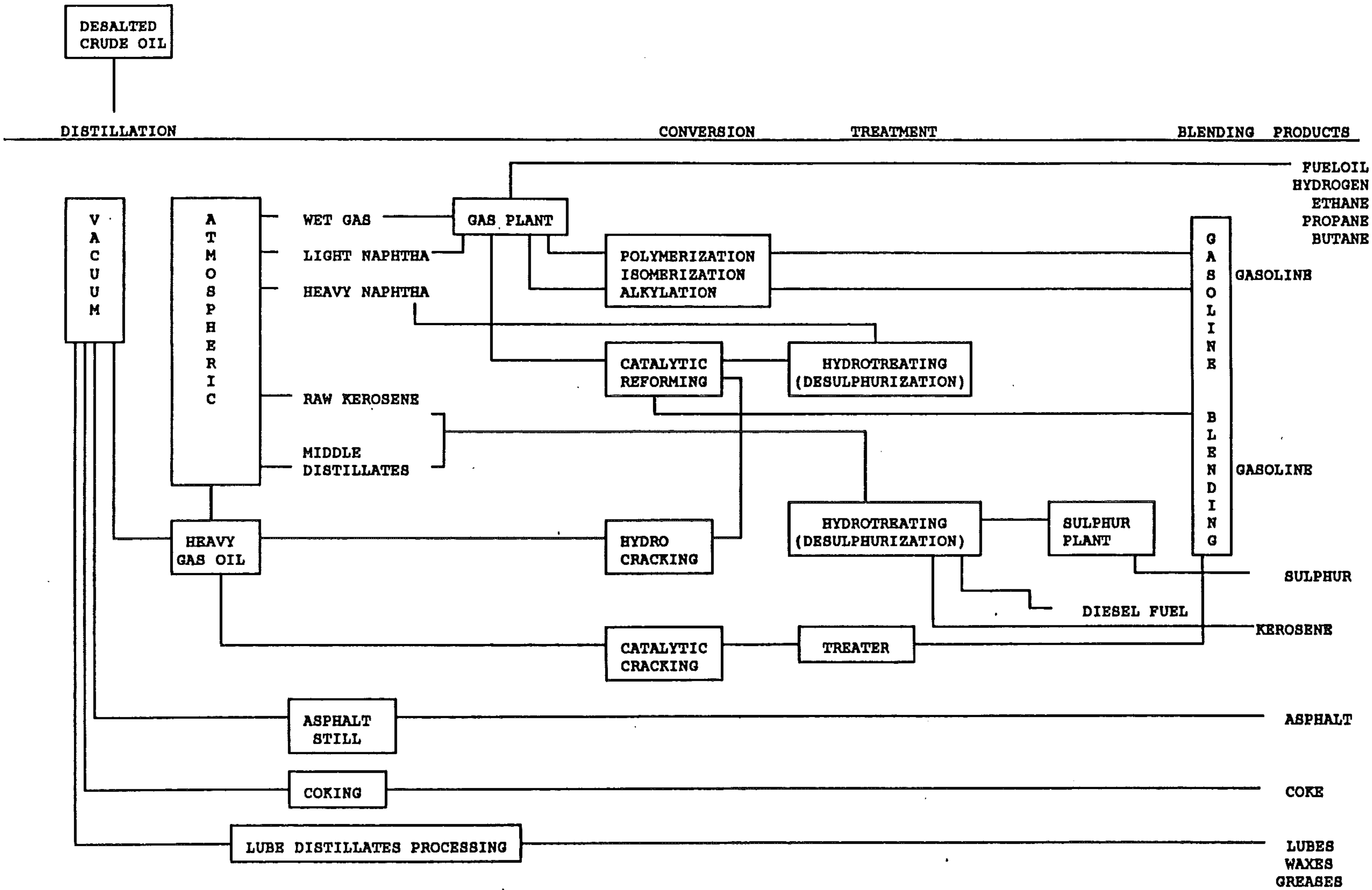

Figure 2: A Simplified Diagram of the Process Flow in an Oil Refinery.

3.3.1. 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 4.

Table 4. 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[14]

Leaks and spills are also common and these eventually drain into the central sewer system. Storm-water run-off 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 run-off from process areas and tank farms.

A major source of wastewater in most older refineries is once-through-cooling-water (OTCW) which may account for 90% of a refinery's effluent.[15] In newer refineries, to cut down on wastewater, 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 in Corunna) employs a 100% cooling tower system (see Table 5, page 15). Two refineries are using a combination of cooling towers and air coolers (Esso Petroleum in Nanticoke and Petro-Canada in Oakville). The remaining refineries use primarily OTCW (Esso Petroleum in Sarnia and Shell in Sarnia), with a small amount of cooling achieved by cooling towers and air coolers (Suncor in Sarnia and Petro-Canada in Mississauga).

As result of U.S. EPA's 1982 BAT regulations, refineries in the U.S. generate lower effluent volumes in comparison to Ontario refineries. All of the U.S. refineries are primarily using cooling towers with a combination of OTCW and air coolers. The amount of cooling provided by the air coolers is generally limited to 5% to 10% of the total cooling system needs.

Table 5 summarizes the cooling methods, total effluent volumes, crude oil processed, and "effluent factors" for all Great Lakes 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. The larger effluent volume translates into larger discharges of toxic substances. Thus, refineries using OTCW discharge more pollution.

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

Table 5. Effluent Volumes and Effluent Volume per unit of Oil Processed for each Great Lakes Refinery (1988-1989).

Refinery	Cooling Method	Processed Crude Oil m3/day	Total Effluent m3/day	Ratio of Total Effluent per m3 of Oil Processed
Petro-Canada Mississauga	OTCW	7,100	260,000	36.6
Petro-Canada Oakville	air & cooling tower	13,600	4,800	0.35
Shell Sarnia	OTCW	11,800	234,700	19.9
Esso Sarnia	OTCW	20,000	215,700	10.8
Esso Nanticoke	air & cooling tower	15,200	6,810	0.45
Suncor Sarnia	OTCW	9,000	119,000	13.2
NOVA Petro-chemical (Corunna)	cooling tower	27,000	6,580	0.24

Table 5. (cont'd) Effluent Volumes and Effluent Volume per unit of Oil Processed for each Great Lakes Refinery (1988-1989).

Refinery	Cooling Method	Processed Crude Oil m3/day	Total Effluent m3/day	Ratio of Total Effluent per m3 of Oil Processed
AMOCO Oil Co. Whiting, Indiana	OTCW air & cooling tower	57,233	60,484	1.1
British-Petroleum Lima, Ohio	air & cooling tower	28,616	18,682	0.65
British-Petroleum Toledo, Ohio	OTCW & cooling tower	20,191	113,619	5.6
Murphy Oil USA, Inc. Superior, Wisconsin	air & cooling tower	5,405	1,269	0.23
Sun Refining & Marketing Toledo, Ohio	OTCW air & cooling tower	19,714	9,739	0.49
Total Petroleum Inc.-Alma, Michigan	air & cooling tower	6,995	1,977	0.28

Source: MOE[16], MOE[17] and personal communication[18].

OTCW = once-through-cooling-water

3.3.2. Types of Wastewater Contaminants

Contaminants detected in petroleum refinery effluents are classified either as conventional pollutants or as toxic pollutants. Refineries in Ontario traditionally monitor the following conventional pollutants in their effluents:[19]

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

Refineries in the United States are required to monitor the following parameters under BAT regulations (toxic pollutants) and under BCT regulations (conventional pollutants):[20]

BAT	**BCT**
phenolics	BOD5
COD	TSS
ammonia	oil and grease
sulphide	pH
total chromium	
hexavalent chromium	

Many toxic pollutants have been detected in the discharges of petroleum refineries and consequently appear on the U.S. priority pollutants list.[21*] During the development stage of BAT limits in the United States, the EPA conducted a sampling program of 17 refineries; Appendix D presents a list of the most frequently occurring pollutants in the wastewater of U.S. refineries.[22] Some of these priority pollutants originate from the crude oil and others are by-products of processes, products of corrosion or simply additives.

Under MISA's petroleum sector monitoring program, Ontario refineries began monitoring their effluents on December 1, 1988 for a 12 month period ending November 30, 1989. Of the 149 pollutants monitored, over 80 were found in refinery effluents.[23] Of these pollutants, 15 were conventional, and the rest were toxic pollutants including four dioxin/furan compounds. Appendix D contains a summary of the concentration of these contaminants.

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

3.4. 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 categories:

(1) in-plant treatment technologies, and

(2) end-of-pipe treatment technologies.

3.4.1. In-Plant Treatment Technologies

The first stage of treatment takes place inside the refinery. The in-plant efforts reduce or eliminate particular pollutants in segregated effluent streams before they reach the main wastewater stream. The second stage, end-of-pipe treatment, then has to deal with a lighter pollutant load.[24] The in-plant treatment and control technologies used in Ontario and the United States are described below.

A. Sour Water Stripper

Sour water results from the direct contact of hydrocarbon streams with water. This occurs either during the desalting stage of crude oil or during 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 resulting from the refining processes, prior to combining it 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.[25] The level of these contaminants can also be reduced with chemical substitution, such as the use of organic phosphate or molybdates to replace zinc chromate.[26]

Until recently, only two of the Ontario refineries, Esso Petroleum (Nanticoke) and Suncor (Sarnia), were using alternatives to zinc chromate. After the MISA monitoring period, the all remaining Ontario refineries decided to eliminate the use of chromium-based additives as a corrosion inhibitor.[27]

C. Wastewater Reduction

A number of different methods can reduce wastewater:

(1) cooling towers can be used instead of once-through-cooling-water (OTCW);

(2) air cooling devices can replace water cooling systems; and

(3) best management practices (BMPs) can be used.

As noted, the use of cooling towers eliminates large volumes of OTCW by allowing cooling water to be reused with the installation of heat exchangers. The combination of reusing water and utilizing air cooling in the Esso Petroleum (Nanticoke) refinery has reduced the water requirements for cooling purposes by 85%.[28]

In addition to reducing the volume of the final effluent, reducing and reusing cooling water eliminates the problem of dilution that makes pollutants harder to detect and remove.

3.4.2. 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.

A. Primary Treatment

Wastewater generated by the refining process has a high oil content. The primary goal of wastewater treatment is to reduce the amount of oil and consequently to reduce 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 that allows most of the oil to float to the surface and be removed. Solids settle to the bottom of the basin, forming a sludge which can be taken away, de-watered and either incinerated or disposed of in a landfill. The sludge is an oily mud and contains high concentrations of phenols, Cr, Se, Hg, Co, Cu, Zn, Cd, Pb, and Mo.[29]

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.[30]

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

B. Intermediate Treatment

Intermediate treatment systems consist 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.[31]

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.

A trickling filter consists of a large open vessel containing a packed medium which 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 micro-organisms 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. Micro-organisms 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 removing certain organic pollutants, taste and odour producing substances, and dissolved inorganic substances.[32] The most effective and commonly used tertiary treatments are Granular Activated Carbon (GAC) adsorption, Powder Activated Carbon (PAC) and Granular Media Filters (GMF).

There are several types of Granular Media Filters and 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.[33]

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.[34] PAC treatment also enhances colour removal and 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 an advanced tertiary treatment system: Esso (Nanticoke) is using Granular Media Filters and NOVA (Corunna) is utilizing Activated Carbon Filtration.[35] Four of the six U.S. refineries in the Great Lakes use sand filtration as a tertiary treatment system; they include Amoco Oil (Whiting, Indiana), British Petroleum (Lima, Ohio and Toledo, Ohio), and Sun Refining and Marketing (Toledo, Ohio). The activated carbon treatment is potentially a very promising and flexible method of tertiary treatment.

Table 6 (page 22) summarizes the wastewater treatment facilities used by refineries around the Great Lakes.

Table 6. Wastewater Treatment Facilities of Ontario Petroleum Refineries Discharging into the Great Lakes.

Plant and Treatment Category	Treatment facility Process Water	Once-Through-Cooling Water	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

Treatment Category: P = Primary; S = Secondary; T = Tertiary
N/A = not available

Table 6. (cont'd) Wastewater Treatment Facilities of U.S. Petroleum Refineries Discharging into the Great Lakes.

Plant and Treatment Category	Treatment facility Process Water	OTCW	Cooling Tower Blowdown
AMOCO Oil Co. Whiting, Indiana P, S & T	API separators, Equalization ponds, DAF, Activated sludge. Clarification, Storm-surge, Multimedia-gravity filtration	N/A	Combined with the Process-Water
British Petroleum Lima, Ohio P, S & T	Sour water stripper, DAF, Biological-treatment, Clarifiers, Sand filters	Not Using OTCW	Treated with Process Effluent
British Petroleum Toledo, Ohio P,S & T	Sour water stripper, API separators DAF, Biological-treatment, Clarifiers, Sand filtration	Gravity-separator	N/A
Murphy Oil USA Inc. Superior, Wisconsin P & S	Sour water stripper, API separators, Settling pond, Aerated-lagoon, Polishing-lagoon	Not Using OTCW	N/A
Sun Refining & Marketing, Toledo, Ohio P, S & T	API separators, DAF, Equalization Tank, Biological treatment Sand filters, Oxygen-treatment	Not Using OTCW	Process-effluent recycled to CT
Total Petroleum Inc.- Alma, Michigan P & S	API separators, Settling ponds, Polishing ponds, Biological treatment, Deep well disposal	Not Using OTCW	Treated with Process Effluent

Source: MOE[36] and personal communication[37].
Treatment Category: P = Primary; S = Secondary; T = Tertiary
CT = Cooling Tower; N/A = not available

4. REVIEW OF AVAILABLE POLLUTION CONTROL TECHNOLOGIES

This section assesses additional pollution control technologies which are currently available and which have been evaluated.

4.1. General and Specific Levels of Assessing 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 pollutant concentrations to a general technology component within a refinery. For example, contaminant 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 cannot be controlled or identified.

The second level of assessment attributes pollutant concentrations to specific operational procedures. For example, the 'specific' level of assessment will evaluate what contaminant 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.

With regard to phenol a number of studies have been undertaken. Short et. al. noted that the phenol discharge values are indicative of the activated sludge efficiencies, depending upon the retention time of the effluent.[38] 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 7, page 25).[39]

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.[40] Overall, Tomatsu et. al. suggested that the carbon systems are an effective means to treat wastewater from petroleum refineries.

The data reported by Yamaguchi are generalized and are not supported by details on treatment components (see Table 7).[41] 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.[42] 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 7. Control Technologies for Phenol.

GEOGRAPHICAL REGION	TREATMENT	PHENOL CONC.	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 Adsorption.	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. Indeed, the International Joint Commission (IJC) notes that although sufficient data exists to initiate regulatory measures pertaining to toxics, this does not "...alleviate the need for continuing research".[43] The current lack of research substantiates the IJC's suggestion that pollution control technology research is indeed not an active field.

The grade type and composition of crude oil is changing as new sources are brought on stream. Refineries are forced to use heavier crudes which result in more residuals.[44] Therefore, it is necessary for the refineries to upgrade processing and effluent treatment technologies in order to accommodate such changes.[45] Further research and development activities, aimed at all specifics of the various treatment components, should attempt to identify the best performing technology for a given set of operating conditions.

4.3. Best Available Technologies in the United States

By the time BAT regulations were promulgated in 1982, most U.S. refineries had already employed the best available technology.[46] BAT development beyond water conservation techniques and 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.[47] 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.[48]

4.4. Best Management Practices (BMP)

Best management practices for refineries tend to address several issues:

(1) the optimization of treatment efficiency;[49]

(2) the reduction in water use by recirculating and/or reusing wastewater;[50]

(3) the re-design or replacement of faulty or poorly designed mechanical components within production and effluent treatment processes;[51] and

(4) operator training, including manuals and certified operators.

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 8 summarizes the issues identified during the literature search as likely BMPs.

The role of BMPs in specifying BATs may be considered complementary to the technology specification. A BMP goes beyond merely acquiring a technology component. It 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 a refinery.

Table 8. Best Management Practices for Refineries.

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
prevent 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	"

5. DEVELOPING BAT OPTIONS FOR PETROLEUM REFINERIES

Having reviewed the technological background of petroleum refineries, this section summarizes the loadings data, and the assumptions and information used to develop best available technology options for the industry.

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

5.1. Current Loadings of Selected Pollutants

This study selects three pollutants for the purposes of developing BAT options: benzene, chromium and phenol. The reasoning for using these pollutants are outlined in Appendix E. The BAT modelling requires suitable data in order to generate loadings and to assess treatment efficiencies. Although several sources of data were investigated, not all were 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, the proposed BAT options provide a useful tool for evaluating pollution prevention and control technologies.

5.1.1. MISA Monitoring Data

The MISA monitoring regulations specified the sampling frequencies (number of data points) of the three pollutants for the 12 month period (December 1988 - November 1989):

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* The proposed definition of "virtual elimination" is based upon the Great Lakes Water Quality Agreement's distinction between persistent and non-persistent toxic substances. 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).

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 chromium and phenol.

A greater amount 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.

The data assessment of MISA data for this report differs from the data assessment done by the Ministry of Environment. This study considers the upper 10% of the technology performance and treats non-detected values as detection limits.*

5.1.2. U.S. EPA Discharge Monitoring Reports (DMRs)

Monthly monitoring reports of the United States petroleum refineries were obtained from the U.S. EPA regional offices for the period of November 1988 to December 1989. The total annual loadings of chromium was calculated using the DMR data base. The data for benzene and phenol were gathered from the Permit

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* 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.

Application Forms of each refinery because monitoring of benzene and phenol is not required under U.S. EPA BAT regulations. However, for permit application requests, the refineries are required to monitor a number of chemicals including benzene and phenol.

5.1.3. Pollutant Loadings

Current loadings were derived by multiplying the average contaminant concentrations by the annual effluent volumes (see Appendix F for a series of sample calculations). The total loadings depend on both the effluent volumes and the pollutant 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 contaminant - 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 9.

Table 9. Benzene, Chromium and Phenol Loadings from Ontario Petroleum Refineries Discharging into the Great Lakes Basin (in kg/year, for 1989/90).

Refinery	Benzene	Chromium Total	Chromium Hexavalent	Phenol
Esso-Sarnia	78.00	198.00	N/A	11.80
Esso-Nanticoke	0.44	19.40	35.2	1.10
Nova-Corunna	0.50	399.00	N/A	2.30
Petro-Canada Oakville	0.25	74.00	N/A	5.20
Petro-Canada Mississauga	12.4	776.00	N/A	4.90
Shell-Sarnia	134.00	2,234.00	N/A	5.30
Suncor-Sarnia	35.5	66.00	N/A	3.30

Table 9. (cont'd) Benzene, Chromium and Phenol Loadings from U.S. Petroleum Refineries Discharging into the Great Lakes Basin (in kg/year, for 1989/90).

Refinery	Benzene	Chromium Total	Chromium Hexavalent	Phenol
Amoco Oil Co. Whiting, Indiana	99.3	278.20	45.50	198.70
British-Petroleum, Lima, Ohio	34.5	534.40	14.70	6.90
British-Petroleum, Toledo, Ohio	N/A	1,304.00	N/A	N/A
Murphy Oil, USA Inc., Superior, Wisconsin	1.50	17.20	4.9	N/A
Sun Refining & Marketing, Toledo, Ohio	16.10	160.00	71.10	32.50
Total-Petroleum Inc. Toledo, Ohio	0.72	0.30	0.04	N/A
Total Sector Loadings (U.S. & Ontario)	**413.20**	**6,060.00**	**171.40**	**271.90**

5.2. 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.[52] The EPA values represent the performance to be expected for refineries employing the same technology under similar operating conditions. Based on the U.S. EPA's manual, SAIC et. al. produced removal efficiencies for different treatment facilities and combinations thereof. Table 10 (page 32) lists the removal efficiencies of selected treatment facilities. In conjunction with the loadings derived from the MISA monitoring data, it is possible to model the performance of several options.

Table 10. Pollutant Removal Efficiencies of End-of-Pipe Treatment Technologies.

Pollutant	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: SAIC et. al.[53]

GMF = Granular Media Filtration
GAC = Granular Activated Carbon Adsorption
PAC = Powdered Activated Carbon Adsorption
TOC = Total Organic Carbon
TSS = Total Suspended Solids

5.3. Other Assumptions

An additional number of assumptions had to be made in order to undertake the comparative analysis, including:

(a) The financial costs and benefits of the BAT options have not been examined. The sole purpose of this report is to identify choices for pollution prevention, and it should be emphasized that BAT standards will not be developed based on costs.

(b) The BAT options are applied across all refineries, regardless of whether a particular refinery already uses one component of the BAT option. This allows a better comparison between the different technologies.

(c) The BAT Options also focus on water discharges only. Sludge management and air pollution from boilers deserve further study.

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

(e) Issues such as energy consumption, secondary air emissions or noise implications have been omitted for the purposes of this study.

Finally, the criteria used by the Ontario MOE and the U.S. EPA to establish BAT standards are summarized in Appendix G. A summary of the nine BAT options developed by the U.S. EPA can also be found in Appendix G.

6. THE BAT OPTIONS

This section presents five BAT options based on the data, assumptions and information gathered in the previous sections. The options demonstrate the expected removal efficiencies of various technological components, or combinations thereof. The option which is best able to achieve virtual elimination of persistent toxic pollutants should be the preferred choice.

The purpose of this section is not to set discharge limits as with the strict definition of BAT, but rather, to recognize choices which can eliminate the use and generation of toxic persistent pollutants. In essence, this is a comparative analysis, comparing various technological options for their ability to remove benzene, phenol and chromium.

The performance of the technologies was assessed beyond the base control components. Currently, refineries in the Great Lakes basin use the following base control technologies in treatment systems:

Base Control Components

- 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 current loadings are thus a function of these technologies in conjunction with other site-specific components. As a result, the technologies of the BAT options are quantitatively assessed beyond the base control technology components.

Using the three study pollutants, it is demonstrated 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 United States

1. **Base Control Components**

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%	413	351
chromium	31%	6,060	4,181
phenol	4%	272	261

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

The Option 1 technologies meet the Ontario 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 of OTCW.

Elimination of OTCW via the recirculation of water through cooling towers is expected to reduce the refineries' water usage by up to 90%.[54]

Possible reuse of sour water as desalter water, as process wash water, as cooling tower makeup, or as boiler makeup, facilitates the reduction of effluent volumes as well. The use of sour water in desalter units is a proven technology.[55] 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.[56]

The loading values after applying this option 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 other components such as best management practices.

OPTION 2
Employ Advanced End-of-Pipe Treatment Technologies

1. **Base Control Components**
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%	413	120
chromium	40%	6,060	3,636
phenol	77%	272	63

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

Air cooling systems which replace existing water-based cooling methods represent a process change which can drastically reduce wastewater. The Esso Petroleum (Nanticoke) plant is the only refinery in Ontario which attains 85% of its total cooling needs from an air cooling system. Such a system produces lower volumes of wastewater effluent per unit of production. This in turn results in a lower volume of contaminated effluent.

The segregation and separate treatment of cooling tower blowdown has two advantages. First, it reduces the degree of dilution of the process effluent, thereby optimizing the efficiency of the biological treatment system. Second, the treated cooling tower blowdown can be satisfactorily used in cooling towers.[57]

The use of Granular Activated Carbon (GAC) reduces the residual solids and organic compound content in wastewaters for a number of pollutants (see Table 10, page 32). Currently the GAC technology is used only in the NOVA Petrochemical plant.[58] However, in the U.S., GAC is employed by several petroleum refining facilities.[59]

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

The resulting loadings are based on the application of GAC and 25% air cooling. The values reflect the expected loadings assuming that all refineries implement the Option 2 GAC technology component and apply 25% air cooling. Some variability may be expected due to the unquantifiable nature of all water conservation components, and due to the performance of other components such as 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-Pipe Control Measures**

- install Granular Activated Carbon (GAC) adsorption
- install Granular Media Filtration (GMF)
- segregate, isolate and separately treat process wastewater, ballast water and storm-water

Option 3 Contaminant Removal Efficiency:

	Removal Efficiency	Current Sector Loadings (in kg/year)	Option 3 Loadings (in kg/year)
benzene	81%	413	79
chromium	85%	6,060	909
phenols	77%	272	63

Note: 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 of the effluent. Generally, refinery wastewater should be segregated into four different types: non-oily water, moderately oily-water, oily-water and sanitary wastewater.

The option loadings reflect the expected loadings assuming that all refineries implement the Option 3 component of GMF/GAC, use a substitute for chromium in their cooling system and employ at least 50% air cooling. Some variability may be expected due to the unquantifiable nature of all water conservation components, and due to the performance of other components such as best management practices.

OPTION 4
The "Best Performing" Refinery in Ontario

1. **Base Technology Components**

2. **In-Plant Control Measures**

   Pollution Prevention

   - substitute chromium

   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
   - preventative maintenance
   - employee training; operator 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%	413	25
chromium	88%	6,060	727
phenols	59%	272	112

Option 4: The "Best Performing" Refinery in Ontario

In applying the Esso Petroleum (Nanticoke) loadings several key assumptions are made:

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

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 assessing the technologies, a lack of data prevents use of these two factors.

Spills occur frequently in Ontario 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 spill prevention technology must be employed by petroleum refineries. In addition, as part of the BMPs, a protocol must be developed describing procedures related to cleaning up a spill effectively and quickly.

This BAT option applies to the process effluent only, as this refinery recycles cooling water and uses an air cooling system. The average daily process effluent flow was calculated for each Great Lakes refinery. This created an effluent flow figure that was roughly analogous to the Esso refinery in Nanticoke. Some variability may be expected due to the unquantifiable nature of all water conservation components, and due to the performance of other components such as best management practices.

OPTION 5
Closed-Loop 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
   - apply water conservation (85% air cooling)
   - reuse sour water

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

   - use Powdered Activated Carbon (PAC)
   - apply Granular Media Filters (GMF)
   - wastewater reuse leading to closed-loop: 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. **Closed-Loop Measures**

   - closed-loop effluent systems (recycle the process-effluent)
   - 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%	413	0
chromium	100%	6,060	0
phenols	100%	272	0

Option 5: Closed-Loop Refinery

Option 5 proposes a closed-loop refinery, which is technically achievable, as there are 55 such refineries in the United States.[60] There remains, however, some question as to the methods used to achieve "closed-loop" refineries in the U.S. because the treatment of wastewater in such 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 equals evaporative losses. Most U.S. "closed-loop" refineries are located in arid regions. However, plants located in non-arid regions may also achieve zero discharge through techniques such as forced evaporation (use of heat to evaporate the water).[61] The resultant steam is then condensed and reused in the refinery while the brine (slurry) stream is solidified in a flash dryer and removed.[62]

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.

All the technical components of Option 5 do not currently exist in any refinery, although several have installed individual components. In addition, 100% air cooling has not been achieved yet on a plant-scale. However, with additional research and development, 100% air cooling should be achievable within the next five years.

6.1. Summary of Options

Table 11 summarizes the components of each option, while figures 3 to 5 also illustrate the resulting option loadings.

Table 11. A Map to Zero Discharge.

Option 1	Option 2	Option 3	Option 4	Option 5
U.S. BAT	WATER CONSERVATION	CHROMIUM SUBSTITUTION	BEST PERFORMING	CLOSED LOOP
cooling-towers	water conservation	pollution prevention	pollution prevention	pollution prevention
GMF	GAC	GAC	water conservation	water conservation
		GMF	air cooling	source reduction
			GMF	GMF
			BMP	PAC
				BMP
				closed-loop

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

Figure 3: Chromium Loadings into the Great Lakes after Applying the Five Technology Options.

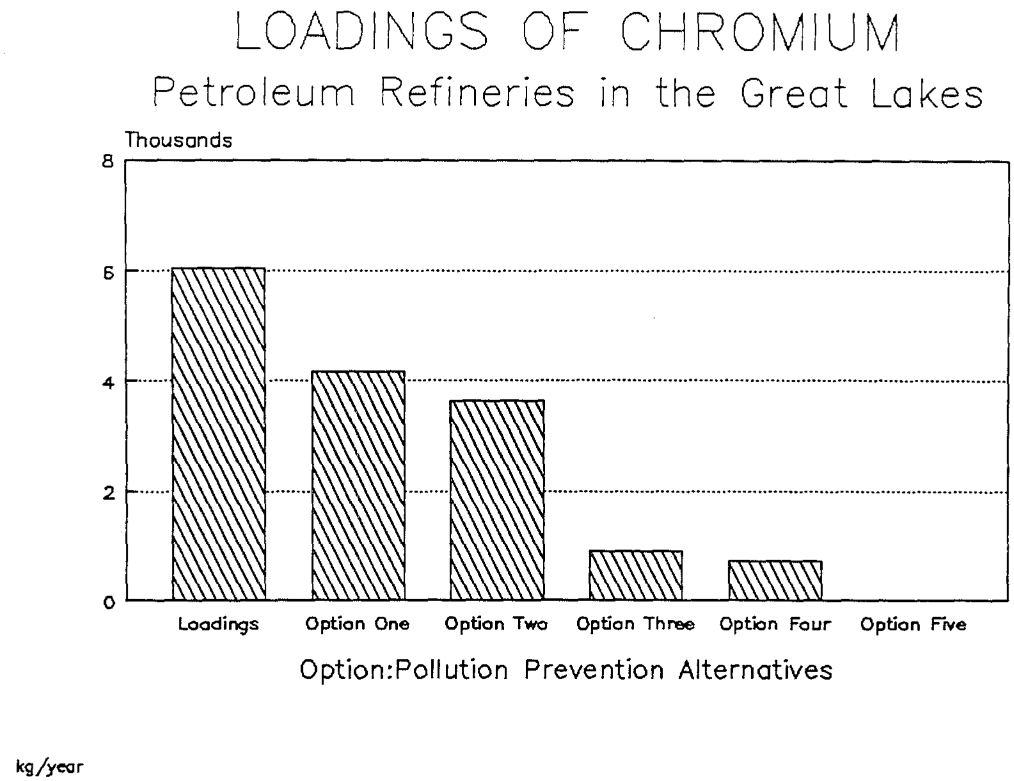

Figure 4: Benzene Loadings into the Great Lakes after Applying the Five Technology Options.

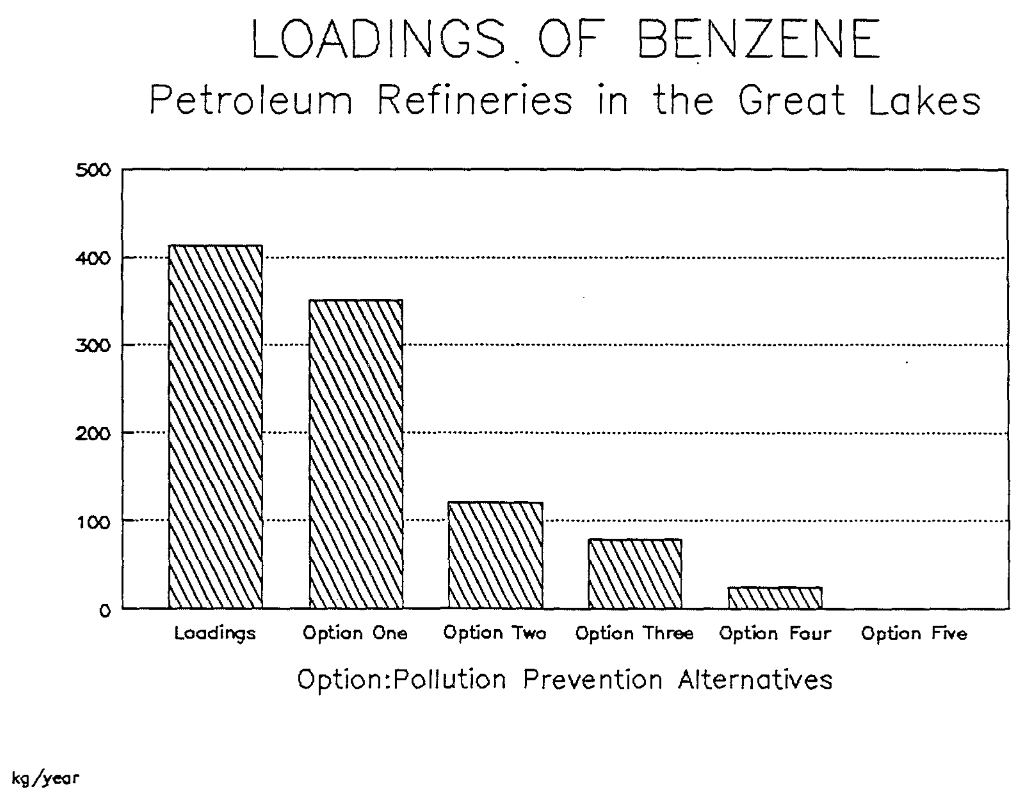

Figure 5: Phenol Loadings into the Great Lakes after Applying the Five Technology Options.

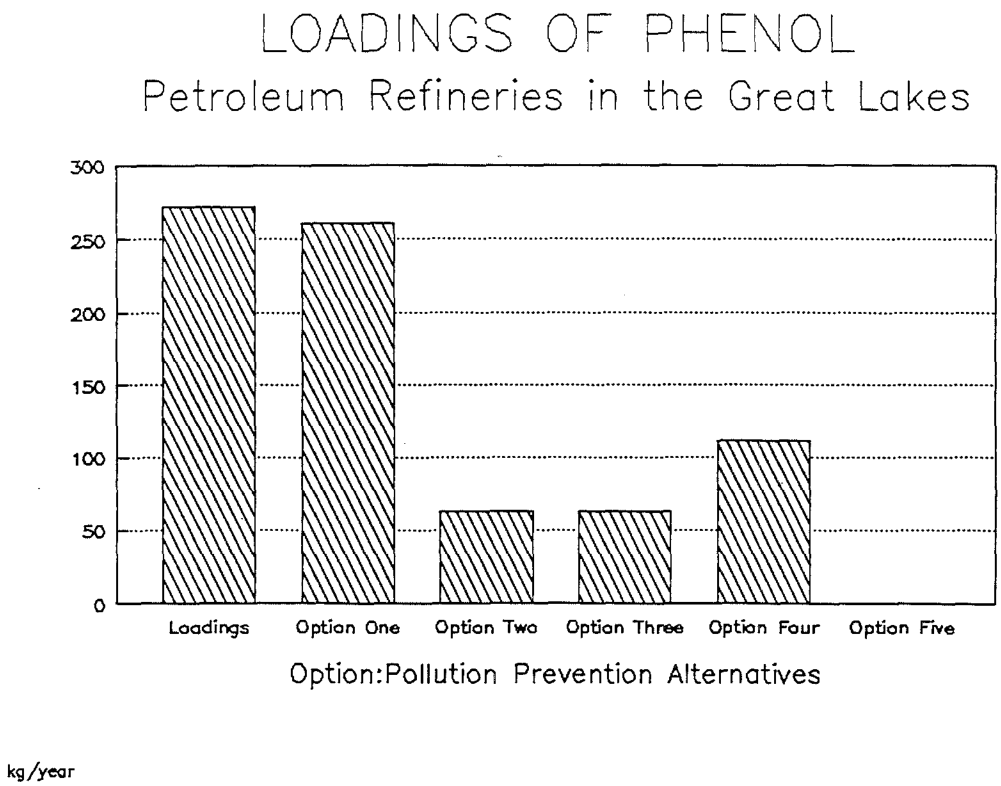

Table 12. Summary of Total Sector Loadings of Benzene, Chromium and Phenol After Application of Each Option (kg/year).

Pollutant	Current Loadings	Opt. 1	Opt. 2	Opt. 3	Opt. 4	Opt. 5
Benzene	413.2	350.9	119.8	78.5	24.8	0
Chromium	6,060	4,181	3,636	909	727	0
Phenol	271.9	261.2	62.6	62.6	111.5	0

6.2. Recommendations

The use of oil and petroleum inherently generates pollution; from extracting and transporting the oil, to refining and burning it. At each step there are many potential sources of contamination; as a result, applying pollution prevention technologies at petroleum refineries can only reduce contamination by a certain degree. It must be recognized that true pollution prevention calls for a reduction of society's dependence on oil.

The five options identified are based on restricted technical information, limited contamination data and are developed with certain assumptions. Furthermore, the options do not provide all the answers for petroleum refineries, but attempts to provide a comparative analysis of the technologies that are effective and available.

With these confines in mind, only those technologies are recommended which are best able to achieve the goal of virtual elimination of persistent toxic pollutants. Consequently, the first choice is Option 5, the Closed-Loop Refinery. In practical terms, Option 5 cannot be immediately imposed on Ontario and United States refineries. However, Option 5 could be adopted as a BAT by 1996, with a number of interim BATs.

Cost analyses of various options are not covered in this report due to the limited nature of this study. The extent of that topic requires a separate, more extensive study.

The following recommendations are made:

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 does not need to be as extensive as during the monitoring phase of MISA, all persistent toxic chemicals should be monitored periodically (i.e. every month) until zero discharge refineries are achieved.

RECOMMENDATION 2: Chromium Substitution
Implemented by December, 1992

Zinc chromate should be replaced with phosphate based-chemicals. There are viable alternatives to chromium which have an equal effectiveness and are less harmful to the environment. The following is a list of chemicals which can replace chromium:[63]

- Phosphate
- Azoles

- o Nitrite
- o Orthophosphate
- o Silicate
- o Molybdate

Phosphate-based chemicals are recommended, since their use is a demonstrated technology in the United States and Canada, and poses little harm to the environment when phosphate removal technologies are included.[64]

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

To be considered as an available technology, the BMPs should provide specific effluent performance results. A numerical assessment of the impacts of BMPs will clarify their importance in reducing contamination. Best management practices include:

- management of site run-off and drainage from outdoor process and non-process areas resulting from storm water or thaw events;
- control of once-through-cooling-water;
- optimized operation of wastewater treatment systems;
- minimized by-passes of the effluent treatment system;
- management sludge and waste disposal; and
- minimized spills impact.

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

Water conservation is the key issue in reducing 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 machine reliability, reduce capital expenditure for piping and water treatment facilities, and save operating costs.[65] Air cooling systems also reduce the amount of effluent discharged to the wastewater treatment facilities. Although 100% air cooling is currently not employed on a plant scale, a focused research and development program should make this technology available.

RECOMMENDATION 5: <u>Advanced End-of-Pipe Treatment Systems</u>
Implemented by December, 1994

Advanced, tertiary end-of-pipe treatment systems should be employed by all petroleum refineries discharging into the Great Lakes basin by December 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 this report reveal that these two combinations remove pollutants most effectively. Installation of GMF+PAC or GMF+GAC will reduce total pollutant loadings from 64,000 to 40,000 kg/year.[66]

RECOMMENDATION 6: Closed-Loop Refineries
Implemented by 1996

Treated process effluents should be recycled and reused in refineries. This would eliminate the discharge of any pollutants into the receiving water. However, recycling the effluent would create contaminated sludge, and conventional sludge disposal practices include: land-filling, land-spreading, incineration, deep-well injection and recovery/recycling.[67]

Except for recovery/recycling technology, these 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.[68] Therefore it is recommended that sludges should be recovered/recycled to the maximum extent possible. The remainder of the sludge should be de-watered and stored, until a safe method of disposal can be found.

RECOMMENDATION 7: "True" Source Reduction
Implemented by 1999

Society's dependence on petroleum products is riddled with negative ecological consequences, from oil drilling and its transportation, to refining and burning the oil product. Consequently, the dependence on this resource has to be reduced significantly, including:

- reducing the petroleum use by mandating alternative transportation means (i.e. mandating the use of public transportation in cities, or providing bicycle routes for commuters);
- re-formulating fuels;
- using alternative energy sources such as solar power, hydrogen, etc.; and
- finding other alternatives to the internal combustion engine.

Appendix A

Description of U.S. Technology-Based Standards and Current U.S. BAT Effluent Limits for Refineries.

Table 1. Development of the Technology-Based Standards in the United States.

Standard	Date	Description
NSPS	1974	New Source Performance Standards (NSPS), are the levels of performance to be achieved by new industrial sources (new is defined as beginning construction after promulgation of the effluent limits guidelines, May 1974). This level of treatment takes advantage of the best technology for reducing wastewater volumes and pollutant loads, thus achieving higher standards of performance than older plants. This level of pollutant control is also referred to as best available demonstrated technology (BADT).
BPT	1974	Best Practicable Technology (BPT) limits represent the average of in-plant and end-of-pipe technologies and practices employed by the industry. In-plant BPTs include: stripping the sour water, eliminating once-through barometric condenser water, segregating sewers for uncontaminated run off and for once-through-cooling-water (OTCW), and eliminating polluted OTCW. End-of-pipe BPTs consist of: equalization of wastewater (e.g. ponds), initial oil and solids removal (e.g. API separator), further oil and solids removal (e.g. air flotation), biological treatment, and filtration (e.g. granular media).
PSNS & PSES	1974 1977	Pretreatment Standards for New Sources (PSNS) and Existing Sources (PSES), for indirect sources discharging into sewage treatment plants, are based on oil/water separation and steam stripping technologies. The pollutants regulated with PSES and PSNS limits are oil and grease, ammonia and chromium.

Table 1. (continued). Development of the Technology-Based Standards in the United States.

Standard	Date	Description
BAT	1982	Best Available Technology (BAT) requirements are the same as for BPT with the addition of water reuse and recycling practices to provide flow reduction. BAT limits control the discharge of toxics (total chromium, hexavalent chromium), and non-conventional pollutants (chemical oxygen demand, phenolics, ammonia, and sulphides).
BAT	1985	The revised BAT is based on the same treatment technology and flow reduction methods that were considered for the previous BAT. The revised BAT only affects the limits for phenolics, total chromium and hexavalent chromium. The limits require flow reduction of 20 to 37.5% with more stringent limits for total chromium.
BCT	1985	Best Control Technology (BCT) limits are used for the control of conventional pollutants (biochemical oxygen demands, total suspended solids, pH, oil and grease). BCT is on the same level as BAT treatment and therefore complements it in controlling all types of pollutants.

Table 2. BAT Effluent Limits for Petroleum Refineries.

(in kg per 1000 cubic meters of feedstock)

Pollutants	Process Type	Maximum for any One Day	Average of Daily values for 30 Consecutive Days
Phenolic Compounds (4AAP)	Crude	0.037	0.009
	Cracking & coking	0.419	0.102
	Asphalt	0.226	0.055
	Lube	1.055	0.257
	Reforming & alkylation	0.377	0.092
Total chromium	Crude	0.030	0.011
	Cracking & coking	0.340	0.118
	Asphalt	0.183	0.064
	Lube	0.855	0.297
	Reforming & alkylation	0.305	0.106
Hexavalent chromium	Crude	0.0019	0.0009
	Cracking & coking	0.0218	0.0098
	Asphalt	0.0117	0.0053
	Lube	0.0549	0.0248
	Reforming & alkylation	0.0196	0.0088

Source: 40 CFR 419

Appendix B

An Overview to Ontario's MISA Program.

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".[69]

The MISA strategy divides all direct dischargers into nine industrial sectors and a municipal sector (sewage treatment plants). The 10 sectors are:

- Electric power generation
- Industrial minerals
- Inorganic chemicals
- Iron and Steel
- Metal mining and refining
- Metal Casting
- Organic chemicals
- Pulp and Paper
- Petroleum refining
- Sewage treatment plants

A three-phase approach is being taken by the MOE to fulfil the MISA 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 is being used for the second phase of the MISA program.

PHASE TWO consists of developing technology-based effluent limits for each of the ten sectors. Even though these limits are based upon the best available technology, 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. In this phase, water-quality based standards are to dictate acceptable effluent limits (rather than having them dictated by technological limits). Water quality standards protect the quality of the receiving water where 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.[70] However, thus far, no such limits have been established. The first regulation to be released for public review is scheduled for early 1992, with others to follow until all industrial sectors are regulated by late 1992.[71]

Water quality standards were to be implemented between 1988 and 1995, however, their development has been indefinitely postponed due to financial limitations.[72]

Setting BAT Effluent Limits Under MISA

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

The design of technology-based standards involves 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.

Ontario's Approach to Setting BAT Standards

The following is taken directly from the 1986 MISA White Paper.

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 C

Production Processes and Effluent Volumes for the 13 Petroleum Refineries Discharging into the Great Lakes Basin

Table 1: Description of Petroleum Refineries in Canada and United States, Discharging to the Great Lakes Basin

Facilities	Processes	Product Line	Effluent treatment	Crude Oil (m3/d)	Effluent Rate (m3/d)	Receiving Water
Esso Petroleum Canada-Sarnia Ontario	Vacuum distillation Thermal operations, Catalytic cracking; reforming; hydro-treating, alkylation, Polymerization, lubes, Hydrogen (MMcfd)	Fuel products, Packaging, Lubricating oil, Petrochemical-operations	Primary treatment, Intermediate treatment, Sand/anthracite-filtration, secondary treatment & clarification, Sour water stripper	20,000	26,253	Lake Erie
Petro-Canada Inc. Lake Ontario 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	Sour water stripper, Primary; Intermediate and Secondary treatment Systems	7,100	9,299	Lake Ontario
Petro-Canada Inc. Lake Ontario Refinery-Oakville Ontario	Vacuum distillation, Catalytic cracking; reforming; hydro-treating, Alkylation, Polymerization	Petroleum fuel-products, Liquid Petroleum gases, Aviation gasoline, Motor gasolines, Distillates residual fuel oils, Asphalt, Sulphur	Sour water stripper, Feed equalization, Primary, Intermediate and Secondary treatment Systems	13,600	4,464	Lake Ontario
Petrosar Limited Sarnia, Ontario	Petrochemical-Refiner	Primary petrochemical products (Ethylene, Propylene, Butadiene, Iso-butylene, N-butylene, Benzene, Toluene/Xylene)	Primary and Secondary treatment systems, Activated Carbon Filtration.	27,000	5,728	St.Clair River, Lake Ontario
Shell Canada Products Limited Sarnia, Ontario	Vacuum distillation Thermal operation, Catalytic cracking; hydrotreating; reforming; hydro-cracking, Alkylation, Polymerization, Aromatic isomerization	Gasoline; Diesel; and Furnace fuel Benzene, Toluene, Xylene, Sulphur, Hydrocarbon-solvents	Sour water stripper, Gravity separator, Equalization tanks, Air flotation unit, Activated sludge, Clarifier, Recycle ponds, Dual media filters	11,800	11,916	Talford Creek, L.Erie

Table 1 Cont.

Facilities	Processes	Product Line	Effluent Treatment	Crude Oil (m3/d)	Effluent Rate (m3/d)	Receiving Water
British Petroleum Lima,Ohio U.S.	Vacuum distillation, Thermal operations, Catalytic cracking; reforming; hydro - reforming; hydro - cracking, Aromatic - isomerization, Lubes, Coke	Propylene, Propane, Butane, Gasoline, Jet fuel, Kerosene, Diesel fuel, Furnace oils, Heavy fuel oils, Coke, Trolumen	Stripper for removal of H2 and ammonia, Gravity separator, Dissolved air flotation, Two aeration zones, (biological treat-ment), Clrifiers, sand filters (tertiary treatment)	28,616	18,500	Ottawa River, Lake Erie
British Petroleum Toledo, Ohio U.S.	Vacuum distillation, Thermal operations, Catalytic cracking; reforming; hydro - cracking; hydro - treating, Alkylation, Polymerization, Asphalt, Coke, Hydrogen (MMcfd)	Gasoline, Furnace Oil, Kerosene, Benzene, Toluene, Asphalt, Sulphur, Liquid propane, Petroleum spirits	Foul condensate stripper, API Separator, Dissolved-air flotation, Biological-treatment, Clarification, Sand filtration, Gravity-separator for once-through cooling water	20,191	41,000	Maumee Bay, Lake Erie
Sun Refining and Marketing, Toledo, Ohio U.S.	Vacuum distillation, Catalytic cracking; reforming; hydro-treating; hydro-cracking, Alkylation, Polymerization, Hydrogen (MMcfd)	Propane, Gasoline (auto, aviation), Heavy fuel oils, Asphalt, Coke, Aromatics, Sulphur	All wastewater through single API separator, DAF, equalization tank, biological treatment in cooling towers (acting as (trickling filters), then flow through sand filters, (tertiary treatment), Oxygen treatment before discharge	19,714	96,000	Otter Creek Lake Erie
Murphy Oil USA Inc.-Superior Wisconsin, U.S.	Vacuum distillation, Catalytic cracking; reforming; hydro-refining, hydro-treating, Alkylation, Polymerization, Asphalt	Gasoline, Diesel fuel, Liquid propane-gas, Asphalt	API separator, Settling-pond, Aerated lagoon, Sour water stripper	5,405	900	Newton Creek, Lake Superior

Table 1 Cont.

Facilities	Processes	Product Line	Effluent Treatment	Crude Oil (m3/d)	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	Primary and Secondary Treatment Systems	9,000	8,933	St.Clair River L.Erie
Esso Petroleum 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	Sour water stripper or Spent caustic neutralization, Feed equalization, Primary and Secondary Treatment Systems Clarifiers, Polishing filters	15,200	6,697	Hickory Creek, L.Erie
Total Petroleum Inc.-Alma, Michigan, U.S.	Catalytic cracking; reforming;hydro-treating, Alkylation, Polymerization, Aromatics isomerization	Gasoline, Regular and unleaded, #1, #2, & #6,Fuel oil, Propane, Mineral Seal Oil	API Separation, settling ponds (Aeration), Polishing ponds, Land disposal of - biological sludges, Deep - well disposal	6,995	1,930	Horse Creek, L.Huron
Amoco Oil Co.- Whiting, Indiana, U.S.	Vacuum distillation, Thermal operations, Catalytic cracking; reforming; hydro-reforming; hydro-refining; hydro-treating, Alkylation, Polymerization, Aromatics isomerization, Asphalt, Lubes, Coke	Chemical grade-propylene, LPG, Leaded and unleaded regular and premium gasoline, Jet fuel, Diesel #1 and #2, Heater oil, Furnace oil, 4 Grades-#6 oil, Industrial and paving asphalt, Lubricating oils; grease and wax, Light-oils, Coke, Sulphur	API Separation, equalization, storm surge, DAF, activated sludge (bio-logical treatment), multimedia gravity filtration (tertiary treatment)	57,233	51,900	Lake Michigan

Appendix D

Concentrations of Pollutants in the Discharges of U.S. and Ontario Refineries

Table 1. Priority Pollutants Found in Treated Effluents of Petroleum Refineries in the U.S.

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[73].

Table 2. Conventional Pollutants Found in the Process Effluents of Ontario Refineries.

Parameter	Average Conc. (Dec.88-May 89) ug/l	FOD	Average Conc. (June 89-Nov.89) ug/l	FOD
COD	53,250	100	46,535	100
DOC	13,191	100	13,138	100
Hydrogen ion (pH)	7.6*	100	7.7*	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[74], and MOE, 1990[75].

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

FOD = Frequency of detection above the detection limit (%)
COD = Chemical Oxygen Demand
DOC = Dissolved Organic Carbon
TOC = Total Organic Carbon
TSS = Total Suspended Solids
VSS = Volatile Suspended Solids
Conc.= concentration

Table 3. Priority Pollutants Found in the Process Effluents of Ontario Refineries.

Parameter	Average Conc. (Dec.88-May 89) ug/l	FOD	Average Conc. (June 89-Nov.89) ug/l	FOD
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 Hex.	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 3 (continued). Priority Pollutants Found in the Process Effluents of Seven Ontario Refineries.

Parameter	Average Conc. (Dec.88-May 89) ug/l	FOD	Average Conc. (June 89-Nov.89) ug/l	FOD
1,1-Dichloroethane	N/A	--	0.023	7
Benzo(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[76], and MOE, 1990[77].

FOD Frequency of detection above the detection limit (%)
N/A Not Available
* Unit of Measurement in ng/l

Appendix E

Pollutants Selected for BAT Modelling

The selected pollutants, benzene, phenol and chromium are listed on the U.S. EPA Priority Pollutants List and on the Effluent Monitoring Priority Pollutants List (EMPPL)* of MISA. These pollutants are also included in the MISA petroleum monitoring regulation.[78]

The assessment of only three contaminants is less comprehensive than the MOE's plan to model an extensive number of contaminants. However, for illustration purposes a small number is considered adequate. The specific characteristics of the selected pollutants 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.[79]

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

- o as a solvent;
- o to increase the octane rating of unleaded gasoline;
- o in preparation of derivatives for polymers, detergents, pesticides; and
- o in the production of pharmaceuticals.[80]

Benzene is associated with extensive health risks because it is recognized as a human leukaemogen and as a carcinogen.[81] 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.[82]

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.[83] The potential for human health impacts by benzene via the ingestion of both contaminated water and aquatic organisms has convinced the EPA to suggest that the ambient water

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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, or potential to bioaccumulate, or acute and sublethal toxicity to biota (including human), and or potential to exist in effluents discharged to surface waters.

concentration of benzene should be zero.[84] The U.S. EPA assumes a non-threshold limit for benzene, that is, there is no recognized safe 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.[85]

The reasons for selecting benzene are:

- produced in refineries as a petrochemical intermediate;
- measured at high concentrations 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.[86]

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.[87]

There is evidence which relates human lung cancer to hexavalent chromium exposure.[88]

About 90% of the chromium in the effluent of petroleum refineries is from addition of zinc chromate in the cooling tower waters as an anti-corrosive, scale and slime agent.[89] Chromium is also detected in very low concentration in crude oil.[90]

The reasons for selecting chromium are:

- detected in high concentrations in intermediate and final effluents of refineries;
- it is bioaccumulative and persistent;
- it is a potential carcinogen; and

- it is required to be monitored under MISA and under the U.S. BAT.

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. Phenol is toxic to fish at levels above 2 mg/l.[91] If detected at concentrations far below the toxic level, phenol can cause a taste and odour problem in fish flesh and in drinking water.[92]

The majority of phenol in refinery wastewater originates from the catalytic cracking process. Thermal cracking and crude distillation also produce phenolic wastewater.[93]

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.

Appendix F

BAT Options Calculations and Sample Calculations of Pollutant 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 G

U.S. and Ontario BAT Selection Criteria and U.S. EPA BAT Options

The MOE Criteria for Selecting BAT Options

Through the Issues Resolution Process (IRP), the MOE has drafted detailed criteria for the selection of BAT.[94] 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:

- o non-lethal effect on trout and <u>Daphnia</u>;
- o maximum use of reduction, re-use and recycling, and smallest transfer to other media; and
- o maximum water conservation.

To be considered by the MOE, a list of at least four BAT options has been developed in order to facilitate an economic achievability analysis. They are:

- o a BAT option that utilizes the best technologies currently in use in North America, Europe and Japan;
- o the BAT option selected by the U.S. EPA for the sector or sub-sector in question;
- o a BAT option that utilizes the best technologies currently in use in Ontario for the sector or sub-sector in question; and
- o 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.

Subsequent MOE Activities

After selection, the chosen BAT options will need to undergo further analysis by the MOE. It will:

- o set effluent limits for those substances controlled by each BAT option;
- o develop a technical cost evaluation of each BAT option;

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

and

- do 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."

U.S. EPA Criteria for Selecting BAT Options

In assessing the BAT limits, the U.S. EPA considered the following criteria[95]:

- the age of the equipment and facilities involved;
- the processes employed;
- the engineering aspects of control technologies;
- process changes;
- the cost of achieving such effluent reduction; and
- non-water quality environmental impacts.

U.S. EPA BAT Options

The U.S. EPA investigated nine control and treatment technology options for selection of BAT criteria. These control and treatment technology options are summarized below:

<u>Option 1</u> **A 27% reduction in discharge flow achieved through greater reuse and recycling of wastewaters, in addition to using BPT treatment. Establish a long term achievable concentration for phenolic compounds at 19 ug/l as the**

base for computing pollutant load.

Flow reduction as a mean of pollution outflow is a viable technology in the petroleum refining sector.

Option 1 was rejected since flow measurement is based on the 1979 proposal which the Agency has decided not to use.

Option 2 **Discharge flow reduction of 52% achieved through greater reuse and recycling of wastewaters, in addition to using BPT control treatment technologies.**

BAT option 2 was developed using the proposed 1979 flow model and it was rejected by Agency.

Option 3 **A Discharge flow reduction of 27% from the proposed model flow per Option 1, plus enhanced BPT treatment with powdered activated carbon to reduce residual toxic organic pollutants.**

The two end-of-pipe treatment technologies that were used to establish Option 3 are rotating biological contactors (RBC) and powdered activated carbon (PAC) treatment. Since the available data from 5 existing refineries showed inconsistent pollution reduction using Option 3, this option is not recommended for this industry.

Option 4 **A discharge flow reduction of 52% from the proposed model flow per Option 2, in addition to BPT treatment, plus segregation and separation treatment of cooling tower blowdown.**

Cooling tower blowdown treatment for metals removal includes: reduction of hexavalent chromium to trivalent chromium;Ph adjustment; precipitation; and settling or clarification.

Option 4 was based on an industry-wide ability to segregate, collect, and separately treat cooling tower blowdown which is the major source of chromium for this industry. However, the recycling/reuse study concluded that for existing sources, it is extremely difficult to segregate cooling water blowdown for chromium treatment.

Therefore this option was rejected for existing refineries. However, refineries which will be built in the future could incorporate separate treatment of cooling tower blowdown into the plant design.

Option 5 A discharge flow reduction of 27% from proposed model flow per option 1, in addition to BPT treatment plus granular activated carbon (GAC) treatment to reduce residual toxic organic pollutants.

BAT Option 5 is an end-of-pipe technology and is based upon the ability of petroleum refineries to install and operate GAC.

The U.S. EPA conducted six pilot plant treatability studies that used GAC to treat refinery wastewater after BPT treatment. Because the levels of toxic pollutants after BPT treatment were so low, it was very difficult for the Agency to quantify the toxic pollutant reductions. Because of these difficulties, removal efficiencies were not estimated for this option. Moreover, considering the marginal benefits and uncertain effectiveness of this technology in treating diluted concentrations of priority pollutants, the Agency decided to reject BAT Option 5.

Option 6 **A "no discharge of wastewater pollutants" (i.e. ZERO DISCHARGE) standard based upon reuse, recycling, evaporation, or re-injection of wastewater.**

Zero discharge of waste water is a demonstrated technology. There are currently 55 refineries in the United States that do not discharge wastewater. However, the technology at these zero discharge refineries is very site specific, e.g. 32 of the 55 use evaporation/percolation basins which rely on special conditions of climate and geology. Therefore some of the technologies in use by the refinery industry cannot be applied in other geographical locations because of meterological conditions, load availability, and other environmental constraints.

Removal of toxic pollutants under this option would be 100% assuming that percolation or injected waste water would not be transported to aquifers and streams.

The Agency rejected BAT Option 5 because of its high capital and operating costs, its generation of large amounts of solid waste, and its very high energy consumption.

Option 7 A discharge flow reduction of 37.5% from a revised model flow achieved through greater reuse and recycling of wastewaters, in addition to BPT treatment.

In order to verify that the 37.5% flow reduction was achievable, the Agency conducted a 15-plant study. The study concluded that this level of flow reduction can be achieved by traditional recycle/reuse schemes. An analysis of the data shows that implementation of Option 7 would have removed an additional 110,000 pounds of toxic pollutants annually beyond BPT treatment levels. This is equivalent to removing an additional 1.5% of toxic pollutants from raw wastewaters beyond BPT treatment levels, or two pounds of toxic pollutants per day per refinery.

The Agency estimated that the capital cost of implementing recycle/reuse technologies is $112 million with an annual additional cost of $37 million. The Agency decided that because of the limited benefit and of the cost involved, Option 7 is not warranted for this industry.

Option 8 **A discharge flow reduction of approximately 20% from a revised model flow achieved through greater reuse and recycling of wastewaters, in addition to BPT treatment.**

The Agency's analysis of available data showed that implementation of Option 8 would remove an additional 1% of toxic pollutants from raw wastewater beyond BAT treatment levels. This translates into an additional removal beyond BPT of 1.3 pounds of toxic pollutants per day, per refinery. The cost of implementing Option 8 is estimated at a capital cost of $77 million and annual cost of $25 million. The Agency believes that, given all of these factors and the costs involved, Option 8 is not warranted for this industry.

Option 9 **Flow equalization, initial oil and solids removal, advanced oil and solids removal, biological treatment, and filtration or other final "polishing" steps.**

This option is based upon the flow model developed for the BPT regulations promulgated by the Agency in 1974. Therefore, the effluent limits are equivalent to the BPT effluent limits.

The cost of implementing Option 9 is effectively zero, since the Act required that all refineries achieve BPT treatment by 1977.

U.S. EPA BAT Selection

Considering the limited pollutant reduction benefits associated with Options 1 through 8, the inability to quantify non-conventional pollutant reduction via Option 1 through 8, the costs involved of going beyond BPT level of control, and the 96% reduction in toxic pollutant loadings achieved by BPT, the Agency has concluded that the BAT level of control should be equivalent to the BPT level of control for the petroleum refining industry.

The U.S. EPA selected Option 9 as Best Available Technology Economically Achievable for the petroleum refining industry. Effluent data from the EPA sampling survey show that present BPT treatment removes 96% of the toxic pollutants, 85% of the conventional pollutants (BOD, TSS, oil and grease), and 74% of the non-conventional pollutants (COD, ammonia, TOC, sulphides, and phenolics). The levels of toxics from the final refinery effluents are extremely low. Also, a separate analysis of the effluent showed that there are no environmentally significant priority pollutants in direct discharges from petroleum refineries at BPT technology levels after application of the 50th percentile average and low flow dilutions. The basis for this determination of environmental significance is the comparison of diluted average plant effluent concentrations with ambient water quality criteria as determined by the U.S. EPA Criteria and Standard Division. Selection of this option would result in no additional cost or secondary impacts beyond that associated with BPT compliance.[96]

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5. Great Lakes Water Quality Agreement, Article II, page 8.

6. For example, the following provisions are interim "pending" the achievement of the goal:

   * the Specific Objectives, in accordance with the Supplement to Annex 1; and
   * the Areas of Concern, Critical Pollutants and Point Source Impact Zones, in accordance with Article IV and Annex 2.

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