⊕EPA

Research and Development

MERCURY IN PETROLEUM AND NATURAL GAS: ESTIMATION OF EMISSIONS FROM PRODUCTION, PROCESSING, AND COMBUSTION

Prepared for

Office of Air Quality Planning and Standards

Prepared by

National Risk Management
Research Laboratory
Research Triangle Park, NC 27711

Foreword

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources, protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

E. Timothy Oppelt, Director
National Risk Management Research Laboratory

EPA REVIEW NOTICE

This report has been peer and administratively reviewed by the U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

Mercury in Petroleum and Natural Gas: Estimation of Emissions from Production, Processing, and Combustion

by

S. Mark Wilhelm
Mercury Technology Services
23014 Lutheran Church Rd.
Tomball, TX 77375

EPA Project Officer
David A. Kirchgessner
National Risk Management Research Laboratory
Research Triangle Park, NC 27711

Prepared for:

U.S. Environmental Protection Agency
Office of Research and Development
Washington, DC 20460

Abstract

Mercury is a trace component of all fossil fuels including natural gas, gas condensates, crude oil, coal, tar sands and other bitumens. The use of fossil hydrocarbons as fuels provides the main opportunity for emissions of the mercury they contain to the atmospheric environment but other avenues also exist in production, transportation and in processing systems. These other avenues may provide mercury directly to air, water or solid waste streams. This document examines mercury in liquid and gaseous hydrocarbons that are produced and/or processed in the United States for the purpose of estimating, to the extent possible, emissions of mercury to the U.S. environment from petroleum and natural gas.

Although the masses of petroleum and natural gas processed and consumed in the U.S. are very large, only limited amounts of information are available concerning mercury in gas and oil processed domestically. This report compiles existing information and data on mercury in petroleum and natural gas and examines the current state of knowledge of the amounts of mercury in petroleum and gas produced and imported to the U.S. In addition, the distribution and transformation of mercury in production, transportation and processing are considered relative to the determination of mercury in air emissions, wastewater, and products from oil and gas processing facilities. Finally, the fates of mercury in combusted gas and liquid fuel products are examined.

The mercury associated with petroleum and natural gas production and processing enters the environment primarily via solid waste streams (drilling and refinery waste) and via combustion of fuels. In total the amount may exceed 10,000 kg yearly but the present estimates are uncertain due to lack of statistical data. The amounts in solid wastes and atmospheric emissions from combustion are estimated to be roughly equal. Solid waste streams likely contain a much higher fraction of mercuric sulfides or other insoluble compounds than water soluble species and thus the bioavailability of mercury from this category is much more limited than that which derives from combustion.

This report is intended to assist in the identification of those areas that require additional research, especially the needs associated with measuring the concentrations of the various chemical species of mercury in the various feedstocks and waste streams associated with the oil and gas industry. Acquisition of additional information will be necessary if accurate estimates of the magnitudes of mercury emissions associated with U.S. petroleum and natural gas are to be accomplished.

Contents

Tables

Figures

Abbreviations

API	American Petroleum Institute
BP	Boiling Point
bpd	barrels per day
bpy	barrels per year
CVAA	Cold Vapor Atomic Absorbance
CVAF	Cold Vapor Atomic Fluorescence
DFO	Distillate Fuel Oil
DOE	(U.S.) Department of Energy
EOR	Enhanced Oil Recovery
EPA	(U.S.) Environmental Protection Agency
GF	Gulf (of Mexico)
HPLC	High Performance Liquid Chromatography
ICP	Inductively Coupled Plasma
LNG	Liquefied Natural Gas
Mg	Megagram (10^6 grams)
MS	Mass Spectroscopy
NAA	Neutron Activation Analysis
NGL	Natural Gas Liquids
NPDES	National Pollutant Discharge Elimination System
OAR	Office of Air and Radiation (U.S. EPA)
OPEC	Organization of Petroleum Exporting Countries
ORD	Office of Research and Development (U.S. EPA)
OSWER	Office of Solid Waste and Emergency Response (U.S. EPA)
OW	Office of Water (U.S. EPA)
PBT	Persistent, Bioaccumulative, Toxic
RFO	Residual Fuel Oil
SCF	Standard Cubic Foot
TDS	Total Dissolved Solids
TEG	Triethyleneglycol
TMDL	Total Maximum Daily Load
TRI	Toxic Release Inventory
USGS	United States Geological Survey
UV	Ultraviolet
VP	Vapor Pressure

Acknowledgements

Chapter 1
Introduction

Discharges of mercury to the environment from industrial sources are recognized as significant contributors to the accumulations of mercury in aquatic ecosystems. The reasons are many but they mainly stem from the current understanding of the global mercury cycle and the chemical and biological mechanisms that account for the transformation of atmospheric mercury and mercury in industrial wastewaters to the methylmercury in fish (U.S. EPA/ATSDR 1996). Further, the toxicity of methylmercury to humans and piscivorous mammals and the effects of inorganic mercury species on aquatic organisms are now firmly established (NRC 2000, U.S. EPA 1996). The comprehensive reviews of the geochemical aspects of mercury (EPA 1997a, Porcella 1994, Morel et al. 1998) strongly suggest that mercury originating from human activities is a major contributor to the global cycle and hence to the resultant methylmercury in the aquatic food chain. A general overview of the geochemical mercury cycle and its anthropogenic contributions are provided in Chapter 2.

Mercury and its common chemical forms are officially designated by the U.S. EPA as persistent, bioaccumulative and toxic (PBT) pollutants, which are defined as those substances that are persistent (months to years) in the environment, accumulate and concentrate in biota and that are toxic to organisms (EPA 1997b, EPA 1999). Mercury and its compounds are thus the subjects of numerous regulations that originate from both federal and regional agency jurisdictions. The statutes that regulate mercury discharges to the environment include provisions based on both human and aquatic life concerns.

Under the general program to develop action plans for PBT pollutants, the U.S. EPA has constructed an action plan for mercury that focuses on regulatory actions, enforcement and research to characterize and reduce the risks associated with mercury. As part of the mercury action plan, U.S. EPA Office of Research and Development (EPA/ORD) has developed a mercury research and monitoring strategy to facilitate coordination and direction of research efforts involving mercury. Some of the research topics currently under investigation include source evaluation, emission characterization, atmospheric transport and fate, deposition, fate in terrestrial and aquatic media, bioaccumulation, ecological toxicity, health effects, exposure, monitoring, risk management, control and remediation.

The EPA/ORD research plan includes the development and evaluation of emission control technology for coal-fired utilities and other mercury emitters in support of the Office of Air and Radiation (OAR) and the Office of Solid Waste and Emergency Response (OSWER) programs. This effort includes attention to speciation issues, control option costs and the disposal of the mercury-containing wastes resulting from the control options. Also included are research efforts directed to the development of fate, transport and transformation data in support of the Office of Water (OW) determinations of total maximum daily loads (TMDLs) for mercury.

While the issues involving mercury emissions from coal and waste combustion are currently under intensive investigation, U.S. EPA acknowledges that little is known about mercury emissions from the petroleum and natural gas industries (EPA 1997b). Given the magnitude of petroleum and natural gas consumption in the U.S., it would seem prudent to have accurate data on the ranges and mean amounts of mercury in petroleum and gas produced in, and imported to, the U.S. In addition, the distribution and transformation of mercury in production, transportation and processing are likewise important to the determination of mercury in air emissions, wastewater, and products from oil and gas processing facilities. Finally, the fate of mercury in combusted fuel products needs definition.

EPA/ORD has initiated a program to better define the issues related to mercury in the natural gas and oil industries. This document was commissioned by U.S. EPA/ORD to document the current level of understanding of the factors that influence the role of petroleum and natural gas as contributing sources of

mercury. Several major questions are addressed in the discussion to follow:

- What are the estimated ranges and mean amounts of mercury (total) in oil and natural gas?

- What are the major sources of mercury in hydrocarbons as categorized by geology, location of origin and hydrocarbon type?

- What chemical species of mercury are present in petroleum and natural gas and how do they distribute in production, processing and refining systems?

- What is the current knowledge concerning the amounts of mercury that exist in the major egression pathways from petroleum processing including wastewater, air emissions, solid waste and fuel products?

- What are the estimated magnitudes of water and atmospheric mercury emissions from petroleum processing?

- What are the major deficiencies in the current knowledge and what data are required to improve understanding?

Strategies to reduce anthropogenic mercury emissions should be based on the known amounts of mercury in industrial emissions. The compilation of information that follows is intended to assist government and industry to define the research and data gathering that may be necessary to improve the current level of understanding concerning mercury in fossil fuels.

In the discussion to follow, an effort has been made, when referring to the concentration of mercury in liquids and solids, to apply the units "ppb" meaning parts per billion by weight with correction for density of liquids and solids. Such concentrations are referred to as THg meaning total mercury per unit weight of the matrix. This designation derives from the fact that mercury analysis methods typically do not distinguish forms and all forms of mercury in a sample are summed in the procedures employed. Thus the term THg (ppb) means the summed (by the analytical method) concentration of mercury in a sample of measured or calculated weight.

For gases, the units are typically $\mu g/m^3$ meaning μg per standard cubic meter of the gas. It is acknowledged that many gas concentrations reported in the literature are not corrected to standard conditions (which have different interpretations for chemists and engineers). No attempt has been made to attempt such corrections, which are negligible in comparison to the analytical uncertainties for such values. The term THg for gases is not applied as gas analysis methods (as historically practiced) are incapable to distinguish volatile forms. Gas concentrations infer total amounts in that particulate mercury is seldom encountered in analysis of natural gas streams. Exceptions do exist and are acknowledged but are not typically identified in the text.

References

Morel, F., Kraepiel, A., and M. Amyot, 1998, The Chemical Cycle and Bioaccumulation of Mercury, *Annu. Rev. Ecol. Syst.*, 29:543.

National Research Council, 2000, Toxicological Effects of Methylmercury, National Academy Press, Washington, DC.

Porcella, D., 1994, Mercury in the Environment, Biogeochemistry in Mercury Pollution, Integration and Synthesis, Watras, C. and J. Huckabee, eds., Lewis Publishers, Boca Raton, FL.

U.S. EPA, 1996, 1995 Updates: Water quality criteria documents for the protection of aquatic life in ambient water, EPA/820/B-96/001 (NTIS PB98-153067), Office of Water, Washington, DC.

U.S. EPA, 1997a, Mercury Study Report to Congress, EPA/452/R-97/003 (NTIS PB98-124738), Office of Air Quality Planning and Standards, Research Triangle Park, NC and Office of Research and Development, Washington, DC.

U.S. EPA, 1997b, EPA Strategic Plan, EPA/190/R-97/002 (NTIS PB98-130487), Office of the Chief Financial Officer, Washington, DC.

U.S. EPA, 1999, PBT Final Rule Effective for Reporting Year 2000, 64 FR 58666, October 29, 1999, Washington, DC.

U.S. EPA and Agency for Toxic Substances and Disease Registry (ATSDR), 1996, National Alert on Metallic Mercury Exposure, Washington, DC.

Chapter 2
Background

The geochemical mechanisms by which mercury cycles in the environment are generally known in concept but some aspects of the cycle are incompletely understood in detail. The level of understanding, however, has improved markedly over the last 10 years and many of the aspects of the cycle can be described with a fair degree of confidence. The term cycle is used because of the movement of mercury between major pools (major pools are air and water; geologic mercury is not considered a pool but contributes to the cycle) at significant rates of flux (see Table 2-1). The movement is coincident with chemical transformations of mercury that are produced by physical, chemical and biologic forces. While the total amount of mercury in the world as a whole is constant, the amount in the biosphere is not. The amount of mercury mobilized and released into the biosphere has increased markedly over time, especially from human activities since the beginning of the industrial age.

Contributions of mercury to the biosphere originate from both natural and anthropogenic sources. The natural sources are volcanic activity; erosion of terrain; dissolution of mercury minerals in oceans, lakes and rivers; and a variety of other avenues that are not related to human activities. Mercury also enters the biosphere from industrial activities through its use as a raw material and from combustion of fossil fuels and waste. The use of mercury as an ingredient in manufactured products has been reduced in recent years and likely will be completely discontinued within the next decade or two.

The atmosphere is considered important because it is the mobilizing pathway for mercury deposition to remote regions not contiguous with industrial activities and thus provides the avenue for introduction of mercury to otherwise pristine environments. The estimate of the total annual global input to the atmospheric pool from all sources including natural, anthropogenic, and oceanic emissions is approximately 5,000 Mg (see Table 2.1, evasion 2,000 Mg, terestrial 3,000 Mg).

Most of the mercury in the atmosphere exists as elemental mercury vapor, which can circulate in the atmosphere for more than a year and thus can be transported to regions far from the source of emission. Mercury in rainfall is the primary avenue of egress from the atmosphere to the surface. Mercury in surface waters can be re-emitted back to the atmosphere as a vapor (evasion). From land, mercury re-enters the atmosphere from the transpiration of plants or as mercury adsorbed to mobilized particles. As it cycles between the atmosphere, land, and water, mercury undergoes numerous chemical and physical transformations, some of which are not completely understood in a quantitative fashion.

While most of the mercury in the atmosphere is elemental, most of the mercury in water, soil, sediments, or plants and animals is in the form of inorganic mercury salts and organometallics (mostly methylmercury). Bacteria in sediments produce most of the methylated form of mercury but the exact mechanisms have yet to be completely defined. Although its concentration is a very small percentage of the amount in water, methylmercury concentrates in the aquatic food chain. Predatory organisms at the top of the aquatic food web acquire and accumulate the methylmercury in their diets and present elevated concentrations. While the concentration at the bottom of the aquatic food chain may be at the low parts per trillion level, at the top, fish tissue can present mercury concentrations in excess of 1 ppm. Bioconcentration factors are thus on the order of 10^4 to 10^5.

Inorganic mercury (oxidized and elemental) is less efficiently absorbed and more readily eliminated from the body than methylmercury and, therefore, does not tend to bioaccumulate in fish or other organisms. Inorganic mercury (mercuric ion, mercury complexed to inorganic ligands) is toxic to organisms, however, and is the dominant toxic species in water. Although environmentally important, the toxicity of inorganic mercury is secondary in consideration to its role as the

species that is acted on by bacteria to produce methylmercury that concentrates in the aquatic food chain. It is the rising amount of methylmercury in fish and the known effects of inorganic mercury on aquatic organisms that are the principal reasons to reduce the human contribution to the mercury cycle. Since natural emissions are largely outside the domain of human influence, attention is focused on man's contribution and on ways to minimize it.

The vast majority of the mercury that enters the global mercury cycle from human activities comes from combustion of waste and fuels. According to the U.S. EPA (1997) estimates (see Table 2-2), of the approximately 140 Mg of mercury emitted to the environment in the U.S. from point sources in the year analyzed (1994-95), fully 125 Mg originated from combustion. According to the EPA estimates, the breakdown for combustion is roughly 50/40/10 percent for coal burning, waste incineration and fuel oil combustion (U.S. EPA 1997).

The U.S. total mercury emissions from point sources of 125 Mg/y compares to approximately 2,000 Mg/y globally. The U.S. percentage of the world mercury emission total is less than the U.S. percentage of its energy usage. The discrepancy derives from the fact that waste disposal and coal combustion are more prevalent in countries outside the U.S.

Major R&D efforts are now being directed to developing systems and process modifications to reduce mercury emissions from U.S. combustion sources. For waste incinerators and coal-fired boilers, some of the new technology is now being applied. The use of mercury removal equipment for coal-fired boilers was recently mandated and full implementation should occur by 2005. Extension of regulations to oil-fired boilers is currently under review.

U.S. EPA (1997) acknowledges that the estimates for mercury in petroleum (fuel oil) are highly suspect due to the fact that data are lacking both for mercury in crude oil and in many of the fuel products derived from it. Given that the amount of oil consumed in the U.S. is roughly the same as the amount of coal burned, it would seem prudent to obtain a more precise estimate of mercury in crude oil so as to be able to estimate atmospheric mercury emissions that originate from refineries and liquid fuels.

References

U.S. EPA, 1997, Mercury Study Report to Congress, EPA/452/R-97/003 (NTIS PB98-124738), Office of Air Quality Planning and Standards, Research Triangle Park, NC and Office of Research and Development, Washington, DC.

**Table 2-1 – Estimate of Mercury Cycling in the Biosphere
(U.S. EPA 1997)**

	Rates, Amounts, Concentrations
Pools	
Ocean	11×10^6 kg (0.5 - 3 ppt ocean; 1 – 10 ppt fresh water)
Air	5×10^6 kg (1 - 10 ng/m^3; mean lifetime > 1 year)
Flux (yearly)	
Ocean to Air	2×10^6 kg/y (evasion)
Air to Ocean	2×10^6 kg/y (marine deposition)
Air to Ground	3×10^6 kg/y (terrestrial deposition)
Ground to Air	3×10^6 kg/y (natural 1 + man 2)
Human Production	4×10^6 kg/y (local 2 + air 2)
Sink (yearly)	
Marine precipitation	0.2×10^6 kg/y

Table 2-2 - Estimate of Point Source Mercury Discharge
(U.S. EPA 1997)

U.S. year 1994-95	Mg/y	% of Total (1)
Point Sources	**141.0**	**96.9**
Combustion sources	125.3	86.9
Utility boilers	*47.2*	*32.8*
Coal	(47.0)	(32.6)
Oil	(0.2)	(0.1)
Natural gas	(<0.1)	(0.0)
Municipal waste incinerators	*26.9*	*18.7*
Commercial/industrial boilers	*25.8*	*17.9*
Coal	(18.8)	(13.1)
Oil	(7.0)	(4.9)
Medical waste incinerator	*14.6*	*10.1*
Hazardous waste incinerator	*6.4*	*4.4*
Residential boilers	*3.3*	*2.3*
Oil	(2.9)	(2.0)
Coal	(0.4)	(0.3)
Sewage Sludge Incinerators	*0.9*	*0.6*
Wood-fired boilers	*0.2*	*0.1*
Crematories	*<0.1*	*0.0*
Manufacturing Sources	14.4	10.0
Miscellaneous Sources	1.3	0.9

(1) Total for percentage amounts includes non-point sources

Chapter 3
Oil And Gas Processed in the United States

Fossil fuels include coal, petroleum, natural gas, shale oil and several other forms of bituminous fuel materials that were produced by the decay of plant remains over geological time (Speight 1999). Most of the world's energy is derived from the fossil fuels with smaller amounts of energy coming from nuclear, wind, solar and hydroelectric sources. Fossil fuels are projected to be the major sources of energy for the next 50 to 100 years.

Mercury is a trace component of all geologic hydrocarbons. Its origin relative to the origin of the oil and gas in which it is found, and the geological reasons for its occurrence in the various types of fossil fuels are largely unexplored topics. In the effort to account for mercury in petroleum and natural gas, it is useful to examine mercury in the context of petroleum chemistry in general and in the context of the extraction and product manufacturing processes for petroleum and natural gas (Chapter 4). Although of interest from a geological standpoint, the quantities of fuels produced from shale oil, tar sands, and other forms of bitumen are small relative to coal, crude oil and natural gas. The occurrence of mercury in shale oil and tar sands is largely undocumented and will not be discussed.

Chemistry of Oil and Natural Gas

The distinction between petroleum (taken to mean liquid hydrocarbons when extracted from the earth) and natural gas (taken to mean material in a purely gaseous state when extracted) is somewhat arbitrary and inconvenient. The industrial processes that convert liquids to products are different from those that separate gases, however, and the distinction is preserved for discussion of processing. It should be stated that liquids and gas are co-produced from almost all gas and petroleum reservoirs and the distinction between a gas field and an oil field rests on the relative proportions of produced phases and the molecular weight distribution of the compounds produced.

Crude oils are complex mixtures containing many different hydrocarbon compounds. The chemical composition and physical properties of crude oil vary dramatically from one field to another. Crude oils range in consistency from water-like liquids to semi-solids, and in color from clear to black. An average crude oil contains about 84% carbon, 14% hydrogen, 1-3% sulfur, and less than 1% each of nitrogen, oxygen, metals, and salts. The types of organic molecules contained in crude oils are numerous (more than 10,000 have been detected) but the major types are saturated and unsaturated straight chain and cyclic hydrocarbons with lesser amounts of substituted (for carbon or hydrogen) molecules. Substitutional moieties include (in order of occurrence) sulfur, oxygen, nitrogen and metals.

Crude oils are generally classified as paraffinic, naphthenic, or aromatic based on the proportional dominance of hydrocarbon molecules in these categories. Crude oil assays are used to classify crude oils and are based on either the distillation profile or on specific gravity and boiling points. More comprehensive crude assays determine the value of the crude (i.e., its yield and quality of useful products) and processing parameters. Crude oils are usually grouped according to the products they yield. Table 3-1 provides examples of typical characteristics of common crude oils according to the compositional categories.

Paraffinic hydrocarbon compounds found in crude oil are saturated (maximum hydrogen bonding) and can be either straight chains (normal) or branched chains (isomers) of carbon atoms. The lighter, straight-chain paraffin molecules (alkanes) are found in gases and paraffin waxes. Isomer paraffins are usually found in heavier fractions of crude oil.

Aromatics are unsaturated compounds having at least one benzene ring as part of their molecular structure. Naphthalenes are fused double-ring aromatic compounds. Complex aromatics containing three or more fused aromatic rings are found in heavier crude

oil fractions. Cyclic saturated hydrocarbons (napthenes) are found in all fractions of crude oil and include monocycloparaffins (mostly C4-C6) and dicycloparaffins (mostly C6-C10)

Crude oils are also defined in terms of American Petroleum Institute (API) gravity, which is a measure of density. Crude oils with lower percentages of carbon (lighter density, less viscous, higher API gravity) are richer in paraffins and yield greater proportions of gasoline and light petroleum products. Crude oils with higher percentages of carbon (heavier, more viscous, lower API gravity) usually have greater amounts of aromatics. Crude oils that contain hydrogen sulfide or other reactive sulfur compounds are referred to as "sour." Those with less reactive sulfur are called "sweet."

Sulfur in crude oil can take the form of hydrogen sulfide, as mercaptans, sulfides, disulfides and thiophenes or as elemental sulfur. All crude oils contain sulfur but in differing amounts and types. Heavier crude oil fractions typically contain more total sulfur. Oxygen compounds such as phenols, ketones, and carboxylic acids also occur in crude oils in varying amounts but usually in much lesser proportions than sulfur compounds. Nitrogen is found in lighter fractions of crude oil as basic compounds, and more often in heavier fractions of crude oil as non-basic compounds.

Several trace metals (in addition to mercury) are sometimes present in crude oil and these include nickel, iron, arsenic and vanadium. Crude oils often contain inorganic salts such as sodium chloride, magnesium chloride, and calcium chloride in suspension or dissolved in entrained water (brine). Crude oils when extracted from the earth contain suspended inorganic material including silicates (sand) and carbonates. The distribution of particle sizes varies considerably from colloids to fine sand. The more viscous the oil the more suspended material it typically holds.

Natural gas generally is predominantly methane (usually > 90%) with lesser amounts of propane and butanes (C1 – C5, 1 - 5 carbon atoms per molecule). Liquids co-produced from natural gas are mostly C5 to C10 and have little aromatic character. Carbon dioxide and hydrogen sulfide are common components of natural gas. Mercury (elemental) is a unique metallic component of natural gas because of its volatility.

Natural gas is geologically different from most oil in the sense that it is a less mature material. Less mature means that gas hydrocarbon reservoirs have been subjected to subterranean temperature and pressure over shorter periods of geologic time. As a result the liquids co-produced with natural gas are less diverse as compared to light crude oils and contain much higher percentages of paraffinic compounds.

Table 3-1 – Typical Characteristics of Crude Oil
(Speight 1999)

Crude source	Paraffins (% vol)	Aromatics (% vol)	Naphthenes (% vol)	Sulfur (% wt)	API gravity
USA -Mid-continent	-	-	-	0.4	40
North Sea -Brent	50	16	34	0.4	37
Nigeria -Light	37	9	54	0.2	36
Saudi Arabia -Light	63	19	18	2.0	34
USA -W. Texas Sour	46	22	32	1.9	32
Venezuela -Light	52	14	34	1.5	30
Saudi Arabia -Heavy	60	15	25	2.1	28
Venezuela -Heavy	35	12	53	2.3	24

World Oil Production

Tables 3-2 and 3-3 compile the world production of petroleum liquids (crude oil and natural gas liquids, NGL) and natural gas for 1998 (U.S. DOE 2000). Within regions of the world, oil and gas vary considerably in composition reflecting the geological characteristics of the strata of origin. The world produces about 27 billion barrels (1 barrel = 159 liters) of oil and about 80 trillion standard cubic feet (SCF = 0.0283 standard m^3) of gas yearly. Major exporting countries (producing and selling more oil and gas than they consume) are those in the Middle East, Venezuela and in Africa. Major importing countries are Japan, China, India and the United States. Gas is imported primarily in liquid form (LNG, liquefied natural gas) and mainly by Japan and Singapore as feeds to petrochemical manufacture.

While global reserves of both oil and gas continue to increase, the recent rate of natural gas discovery and production has increased more rapidly due to its preference as a clean fuel and the improving infrastructure for its transportation to markets (USGS 2000). In the U.S. this is especially true with gas fields accounting for the majority of new hydrocarbon reserves.

Table 3-2 - World Production of Crude Oil, NGL and Other Liquids (1998)
(U.S. DOE 2000)

Region/Country	Rate (1000 b/d)
North America	**15,495**
Canada	2,694
Mexico	3,523
United States	9,278
Central & South America	**6,974**
Western Europe	**6,999**
Eastern Europe & Former U.S.S.R.	**7,454**
Middle East	**22,454**
Africa	**7,851**
Far East & Oceania	**7,926**
World Total	**75,152**

Table 3-3 - World Natural Gas (dry) Production (1998)
(U.S. DOE 2000)

Region/Country	Rate (10^{12} SCF/y)
North America	**26.17**
Canada	6.04
Mexico	1.27
United States	18.86
Central & South America	**3.09**
Western Europe	**9.66**
Eastern Europe & Former U.S.S.R.	**25.16**
Middle East	**6.61**
Africa	**3.70**
Far East & Oceania	**8.58**
World Total	**82.97**

United States Oil and Gas Production and Imports

The United States currently produces about 40 percent of the liquids processed by U.S. refineries (U.S. DOE 2000). About 60 percent of crude oil processed by U.S. refineries is imported. A smaller amount of natural gas is imported as a percentage of gas processed. Total amounts of oil and gas produced in U.S. are compiled in Table 3-4 and by State in Table 3-5. The top 30 U.S. oil and gas fields by production in 1998 are listed in Tables 3-6 and 3-7.

About 30 major fields account for about half of U.S. crude oil production (see Table 3-6). Most of these fields were discovered prior to 1990. Newer production is found mostly offshore in either State or Federal waters, mostly in the deeper waters of the Gulf of Mexico. The range of geology of U.S. production spans numerous formation types. Field size is characterized by recoverable reserves defined as the amount of oil calculated to be obtainable by conventional extraction techniques. The largest producing oil fields in the U.S. at present are located on the North Slope of Alaska.

Large gas reserves are found in New Mexico, Texas and offshore Gulf of Mexico, with the newer production originating offshore. The relationship between gas production rates and gas reservoir size (field size) is more uniform than that for oil because of the variability of oil viscosity and weight as opposed to gas. Gas production from the top 30 gas fields (Table 3-7) accounts for about one third of total U.S. production (1998).

The trend toward increasing U.S. imports of oil is due to the fact that the terrestrial regions of the continental U.S. have been thoroughly explored and the majority of major fields have been discovered. Those that may remain are more likely to be found in deep offshore waters and in arctic regions. The cost of U.S. frontier oil exploration and production translates to a price per barrel that is higher than the price of oil that can be presently purchased in world markets. Since refineries naturally purchase oil having the lowest cost, the trend to imports is likely to continue as long as the supply and quality of oil in the global market is high and as long as imported oil is lower in cost than new domestic supplies.

Imported crude oils are compiled in Table 3-8. The major sources of crude oil imported to the United States are those that originate in the Middle East, Venezuela, the west coast of Africa, Canada and Mexico. Imported crude oil accounts for about 60 percent of crude oil processed by U.S. refineries and is roughly equally divided between OPEC (oil producing and exporting countries) and non-OPEC sources.

Table 3-4 – U.S. Production and Reserves of Crude Oil, NGL and Natural Gas (1998) (U.S. DOE 2000)

	Production	Reserves
Oil (million barrels)	1,991	21,034
Natural Gas (billion SCF)	18,720	164,041
Gas Liquids (million barrels)	833	7,524
Imported (OPEC [1]) Oil (million barrels)	1,500	
Imported (Non- OPEC) Oil (million barrels)	1,600	

(1) OPEC – Organization of Petroleum Exporting Countries

Table 3-5 – U.S. Crude Oil Reserves and Production
(1998, 10^6 Barrels)
(U.S. DOE 2000)

State or Region	Reserves 12/31/97	Production 1998
Alaska	**5,161**	**437**
Lower 48 States	**17,385**	**1,554**
Alabama	47	7
Arkansas	45	7
California	3,750	270
Colorado	198	20
Florida	91	6
Illinois	92	10
Indiana	10	1[b]
Kansas	238	34
Kentucky	20	2
Louisiana	714	83
Michigan	68	8
Mississippi	183	19
Montana	159	14
Nebraska	21	3
New Mexico	735	59
North Dakota	279	33
Ohio	43	6
Oklahoma	605	62
Pennsylvania	17	1
Texas	5,687	417
Utah	234	14
West Virginia	26	1
Wyoming	627	58
Federal Offshore	3,477	417
Pacific (California)	528	45
Gulf of Mexico (Louisiana)	2,587	336
Gulf of Mexico (Texas)	362	36
Miscellaneous	19	2
U.S. Total (1998)	**22,546**	**1,991**

Table 3-6 - Top Thirty U.S. Oil Fields
(U.S. DOE 2000)

Rank by Reserves	Field Name	Location	Discovery Year	1998 Production (10^6 barrels)
1	Prudhoe Bay	AK	1967	222.0
3	Kuparuk River	AK	1969	91.8
2	Midway-Sunset	CA	1901	49.6
15	Point McIntyre	AK	1988	47.6
6	Kern River	CA	1899	46.8
4	Belridge South	CA	1911	44.9
9	Mississippi Canyon Block 807	GF [1]	1989	43.2
40	Garden Banks Block 426	GF	1987	26.5
10	Milne Point	AK	1982	20.4
18	Green Canyon Block 244	GF	1994	20.2
13	Spraberry Trend Area	TX	1950	20.1
5	Yates	TX	1926	19.3
8	Elk Hills	CA	1919	19.3
23	Wilmington	CA	1932	19.0
50	Viosca Knoll Block 990	GF	1981	18.6
44	Niakuk	AK	1984	18.5
61	Ewing Bank Block 873	GF	1991	18.1
21	Cymric	CA	1916	17.7
14	Endicott	AK	1978	17.0
60	Giddings	TX	1960	16.7
54	Viosca Knoll Block 956	GF	1985	16.5
7	Wasson	TX	1937	16.3
11	Slaughter	TX	1937	14.9
12	Hondo	CA	1969	13.9
28	East Texas	TX	1930	13.8
24	Lost Hills	CA	1910	11.5
35	Seminole	TX	1936	11.5
25	Pescado	CA	1970	11.1
58	Eugene Island SA Block 330	GF	1971	10.2
14	Levelland	TX	1945	10.0
Total Production of Top 30				**927**

(1) GF = Gulf of Mexico

Table 3-7 - Top Thirty U.S. Natural Gas Fields
(U.S. DOE 2000)

Rank by Reserves	Field Name	Location	Discovery Year	1998 Production $(10^9$ SCF)
1	Blanco / Ignacio-Blanco	NM & CO	1927	718.1
2	Basin	NM	1947	662.6
3	Hugoton Gas Area	KS & OK & TX	1922	468.6
4	Prudhoe Bay	AK	1967	252.7
15	Giddings	TX	1960	225.6
6	Carthage	TX	1936	222.7
7	Mobile Bay	AL	1979	149.4
11	Antrim	MI	1965	136.0
12	Panhandle West	TX	1918	123.2
10	Wattenburg	CO	1970	100.9
79	Matagorda Island Block 623	GF [1]	1980	100.3
21	Elk Hills	CA	1919	98.0
46	Garden Banks Block 426	GF	1987	92.8
19	Panoma Gas Area	KS	1956	92.7
52	McAllen Ranch	TX	1960	84.7
51	Anschutz Ranch East	UT & WY	1980	80.1
25	Whitney Canyon	WY	1978	76.2
37	Viosca Knoll Block 956	GF	1985	74.6
45	Bob West	TX	1990	74.3
53	Indian Basin	NM	1963	73.4
43	McArthur River	AK	1968	72.5
36	Vaquillas Ranch	TX	1978	71.6
27	Strong City District	OK	1972	70.5
22	Spraberry Trend Area	TX	1953	69.2
23	Oak Hill	TX	1967	66.5
29	Mocane-Laverne Gas Area	OK & KS & TX	1947	66.3
17	Red-Oak Norris	OK	1910	64.6
41	Watonga-Chickasha Trend	OK	1948	64.6
26	Gomez	TX	1963	63.5
66	Waltman	WY	1959	56.6
Total of Top 30				**4573**

(1) GF = Gulf of Mexico

Table 3-8 – Oil Imports to U.S. Refineries
(U.S. DOE 2000)

	Crude Oil 1000 b/d	LPG 1000 b/d
Arab OPEC	**2,053**	**53**
Algeria	10	50
Iraq	336	
Kuwait	300	
Qatar	1	
Saudi Arabia	1,404	3
United Arab Emirates	3	
Other OPEC	**2,116**	**11**
Indonesia	50	
Nigeria	609	
Venezuela	1,377	11
Non OPEC	**4,427**	**87**
Angola	465	
Argentina	80	
Australia	31	
Brunei	23	
Cameroon	1	
Canada	1,209	108
China, PRC	25	
China, Taiwan	-7	
Colombia	349	-1
Congo	70	
Ecuador	98	-1
Egypt	11	
Gabon	207	
Guatemala	23	
Japan	-5	
Korea	-24	
Malaysia	26	
Mexico	1,321	-23
Norway	221	6
Peru	41	
Russia	9	
Trinidad and Tobago	53	
Turkey	0	
United Kingdom	161	6
Yemen	4	
Other	34	-8
TOTAL	**8,596** $(3.1 \times 10^9$ b/y)	**151** $(0.06 \times 10^9$ b/y

Geologic Origin of Mercury in Oil and Natural Gas

It would be useful to understand the geologic origin of mercury in hydrocarbons so as to obtain some predictive capability for estimation of the amounts in regional sources. At present this task is difficult because of the lack of data on total mercury and species concentrations in many of the major oil and gas fields in the world. In addition, much of the data that does exist are uncertain in accuracy (discussed in Chapter 5) and insufficiently documented as to exact geologic origin.

Petroleum and natural gas occur throughout the upper portion of earth's crust. Most oil and gas has been discovered at depths that do not exceed 10,000 meters. The earth's crust is divided into strata that are categorized in order of age (Table 3-9). These divisions are distinguished by compositions that are specific to the conditions of formation and include the nature and type of organic debris, fossils, minerals, and other characteristics they contain. Carbonaceous materials, including oil and natural gas, occur in all geological strata from the Precambrian onward (Tiratsoo 1984).

Crude oil and natural gas originate from geological formations associated with ancient basins (locations of accumulation of ancient organic material). The basin geology is referred to as the source rock. Basins are characterized as marine (salt water), lacustrine (fresh water) or terrestrial. It is generally believed that the accumulation of petroleum in reservoirs occurred by transformation (maturation) of the source organic material to molecular hydrocarbons with the process being assisted by heat and pressure from burial of the original deposits. Subsequent hydrocarbon fluid migration to locations of accumulation (traps) accounts for the discovery of petroleum in porous reservoirs. The chemical and geologic factors that account for the origin of petroleum and its location of discovery are the focus of a wide body of science and technology, so large in fact that a concise summary is not possible here.

There are few if any attempts in published literature to account for the origin of mercury in petroleum. Mercury in coal is associated with pyrites that are both syngenic and epigenic with coal (Toole-O'Neil et al. 1999). One possible syngenic origin of mercury in petroleum and coal is atmospheric deposition to the region of organic genesis. Rates of ancient atmospheric mercury deposition are unknown, however. Present day rates of atmospheric mercury deposition are on the order of 10 ug/m^2-year, but ancient rates are likely lower. Volcanic activity is a possible source of atmospheric deposition also.

As will be discussed in later sections, the range of total mercury concentrations in oil is thought to be wider than that for coal and this variation suggests that atmospheric deposition to genetic organic material, being globally uniform, cannot account for the mercury in petroleum. The more likely hypothesis is that mercury in oil and gas originated from mercury in the earth's crust that was liberated by geological forces (heat and pressure) and migrated as a vapor to the traps in which oil and gas accumulated.

Although of mostly academic interest, the geological mechanisms that account for mercury in oil and natural gas await definition. At present, there is insufficient data on mercury at specific locations and geologies to draw any definite conclusions.

References

Speight, J. G., 1999, *The Chemistry and Technology of Petroleum*, Marcel Dekker, New York, NY.

U.S. Geological Survey, 2000, USGS World Petroleum Assessment 2000, Description and Results, U.S. Dept. of Interior Digital Data Series, U.S. DOI, Washington, DC.

U.S. DOE 2000, Energy Statistics for 1998, Energy Information Administration, National Energy Information Center, Washington, DC.

Tiratsoo, E. N., 1984, *Oilfields of the World*, Scientific Press Ltd. Beaconsfield, UK.

Toole-O'Neil, B., Tewalt, S., Finkleman, R., and D. Akers, 1999, Mercury concentration in coal - unraveling the puzzle, *Fuel*, 78: 47.

Table 3-9 - Nomenclature and Age of Geological Strata
(Speight 1999)

Era	Period	Epoch	Age (years X 10^6)
Cenozoic	Quaternary	Recent	0.01
		Pleistocene	3
Cenozoic	Tertiary	Pliocene	12
		Miocene	25
		Oligocene	38
		Eocene	55
		Paleocene	65
Mesozoic	Cretaceous		135
	Jurassic		180
	Triassic		225
Paleozoic	Permian		275
	Carboniferous		
	Pennsylvanian		350
	Mississippian		
	Devonian		413
	Silurian		430
	Ordovician		500
	Cambrian		600
Precambrian			800

Chapter 4
Petroleum and Natural Gas Processing

In the effort to construct the routes of mercury in geologic hydrocarbons to the biosphere, it is useful to examine oil and gas processing steps and to account for the possible pathways of mercury in the various process streams. A tremendous variety of processing schemes exists for refining crude oil and for natural gas separation but the majority of gas and oil processing facilities are similar in their basic designs and configurations.

Produced fluids from both oil and gas wells enter separators where the primary phase separations occur. In almost all cases, primary phase separations produce a water stream that is disposed of (most commonly by re-injection to the reservoir), a gas stream and a liquid hydrocarbon stream that are processed separately. Oil is transported to refineries in pipelines, tankers (or barges) and sometimes by truck. Raw natural gas is usually treated close to the wellhead to partially remove water and H_2S before transport by pipeline to a gas treatment/processing facility. The initial treatments are necessary to prevent corrosion of the pipeline.

The feed to a refinery is a blend of oil from numerous fields and usually from several overseas sources. Refineries are usually configured to process either sour or sweet crude but usually not both, so the feeds to a refinery are selected to match the process configuration. A significant aspect of refinery configuration is the process needed to separate large quantities of sulfur contained in sour crude. The same is true for gas in that sour gas requires special treatment steps and a contiguous facility to process separated H_2S into sulfur for sale.

In general, the processing of oil is directed to maximize gasoline manufacture while gas processing is directed to separate methane (sales gas) from other gas components. The major differences in processing steps that are utilized depend on the composition of produced hydrocarbon and the local market. Gas plants that process both gas and condensate usually separate liquids (C5+) that are used either as feeds to petrochemical plants or sent to a refinery where they are processed along with crude oil. The gas that is generated in a crude oil refinery is most often used to fuel the refinery and less often processed to separate methane for sale.

Petroleum Refining

Petroleum refining involves the distillation, or fractionation, of crude oils into separate hydrocarbon groups or cuts. Chemical modification and blending of cuts results in products that are sold. The types of products and the relative amounts of products that are obtained in refining are directly related to the chemical characteristics of the crude processed and to the processing steps employed to modify chemical structure (Speight 1999). A schematic of the typical integrated refining processes is shown in Figure 4-1.

The principal steps in oil refining are the primary (Figure 4-2) and vacuum (Figure 4-3) distillations that produce the major streams that are subsequently treated and modified. Table 4.1 provides an overview of the feeds and separated fractions.

Intermediates from distillations are subjected to numerous treatment and separation processes such as extraction, hydrotreating, and sweetening to remove undesirable constituents and improve product quality. Integrated refineries incorporate distillation, conversion, treatment, and blending operations (see Figure 1). Distillation cuts are converted into products by changing the structure of the hydrocarbon molecules through cracking, reforming, and other conversion processes and by blending streams to optimize desired characteristics.

Conversion processes (Tables 4-2 and 4-3) change the size and structure of hydrocarbon molecules to optimize the amount and quality of products. These processes include molecular decomposition by thermal and catalytic cracking, molecular combination by alkylation and polymerization and molecular rearrangement by isomerization and catalytic reforming.

Many variations on these basic unit processes have been developed and many are proprietary to individual companies. For the catalytic processes, refinery efficiency is achieved by optimizing catalyst performance relative to feed characteristics.

Treatment processes (Table 4-4) are applied to process intermediates and to products and are used to remove impurities and contaminants (sulfur, metals) and to separate undesirable constituents (wax, aromatics, naphthenes). Treatments involve both chemical and physical separation and include desalting, drying, hydrodesulfurizing, solvent refining, sweetening, solvent extraction, and dewaxing.

Formulating and blending combine hydrocarbon fractions, additives, and other components to produce finished products with specific properties. Other refinery unit operations include light-ends recovery (still gas); sour-water stripping; sludge treatment; wastewater treatment; acid and tail-gas treatment; and sulfur recovery.

Major product types and yearly amounts of products from U.S. refineries are shown in Table 4-5. Transportation fuels (combusted in engines as opposed to furnaces) include gasoline, jet fuel and diesel. Naphthas are primarily used as feeds to petrochemical processes. Fuel oil is primarily used for residential heating and to fire industrial boilers. Asphalts and heavy oils are used for a variety of non-combusted products (construction materials, road materials, lubricants) and combusted products (wax).

A typical refinery generates approximately 10-15 gallons of process wastewater for every barrel of oil processed (API 1977). Water contacts oil in washing operations such as desalting, in steam stripping and in aqueous treatments (alkylation). A typical refinery uses a segregated water treatment system as described schematically in Figure 4-4. The water treatment system consists of initial oil and solids removal (clarifiers, separators), additional oil and solids removal (air flotation, filters), and waste removal (activated sludge, aerated lagoons, oxidation ponds, trickling filters). Following biological treatment, granular filtration and polishing are employed to eliminate dissolved solids (Sittig, 1978). The main function of wastewater treatment systems is to remove hydrocarbons so that water can be discharged to meet regulatory criteria.

A wide variety of solid waste streams are generated in conjunction with crude oil refining. These streams include tank bottoms, slop oil, spent catalysts, filter cake from water treatments and numerous others. The nature and type of refinery residuals is documented in periodic compilations (API 1998) and regulatory reviews (U.S. EPA 1996).

Table 4.1 – Distillation Processes
(OSHA 2000)

Process	Action	Method	Purpose	Feedstocks	Products
Atmospheric distillation	Separation	Thermal	Separate fractions	Desalted crude oil	Gas, gas oil, distillate, residual
Vacuum distillation	Separation	Thermal	Separate w/o cracking	Atmospheric tower residual	Gas oil, lube stock, residual

Table 4-2 – Decomposition Processes
(OSHA 2000)

Process name	Action	Method	Purpose	Feedstocks	Products
Catalytic cracking	Alteration	Catalytic	Upgrade gasoline	Gas oil, coke distillate	Gasoline, petrochemical feedstock
Coking	Polymerize	Thermal	Convert vacuum residuals	Gas oil, coke distillate	Gasoline, petrochemical feedstock
Hydrocracking	Hydrogenate	Catalytic	Convert to lighter HC's	Gas oil, cracked oil, residual	Lighter, higher-quality products
Hydrogen steam reforming	Decompose	Thermal/ catalytic	Produce hydrogen	Desulfurized gas, O_2, steam	Hydrogen, CO, CO_2
Steam cracking	Decompose	Thermal	Crack large molecules	Atm. tower hvy fuel/ distillate	Cracked naphtha, coke, residual
Visbreaking	Decompose	Thermal	Reduce viscosity	Atmospheric tower residual	Distillate, tar

Table 4-3 – Unification and Rearrangement Processes
(OSHA 2000)

Process	Action	Method	Purpose	Feedstock	Products
Alkylation	Combining	Catalytic	Unite olefins & isoparaffins	Tower isobutane/ cracker olefin	Iso-octane (alkylate)
Grease compounding	Combining	Thermal	Combine soaps & oils	Lube oil, fatty acid, alky metal	Lubricating grease
Polymerizing	Polymerize	Catalytic	Unite two or more olefins	Cracker olefins	High-octane naphtha, petrochemical stocks
Catalytic reforming	Alteration/ dehydration	Catalytic	Upgrade low-octane naphtha	Coker/ hydro-cracker naphtha	High-octane Reformate/ aromatic
Isomerization	Rearrange	Catalytic	Convert straight chain to branch	Butane, pentane, hexane	Isobutane/ pentane/ hexane

Table 4-4 – Treatment Processes

(OSHA 2000)

Process	Action	Method	Purpose	Feedstocks	Products
Amine treating	Treatment	Extraction	Remove acidic contaminants	Sour gas, HCs w/CO_2 & H_2S	Acid free gases & liquid HCs
Desalting	Dehydration	Extraction	Remove contaminants	Crude oil	Desalted crude oil
Drying & sweetening	Treatment	Adsorption Thermal	Remove H_2O & sulfur compounds	Liquids, LPG, alkylation feedstock	Sweet & dry hydrocarbons
Furfural extraction	Solvent extraction	Absorption	Upgrade mid distillate & lubes	Cycle oils & lube feedstocks	High quality diesel & lube oil
Hydrodesulfurization	Treatment	Catalytic	Remove sulfur, contaminants	High-sulfur residual/gas oil	Desulfurized olefins, HCs
Hydrotreating	Hydrogenation	Catalytic	Remove impurities, saturate HC's	Residuals, cracked HCs	Cracker feed, distillate, lube
Phenol extraction	Solvent extraction	Adsorption Thermal	Improve viscosity & color	Lube oil base stocks	High quality lube oils
Solvent deasphalting	Treatment	Absorption	Remove asphalt	Vacuum tower residual, propane	Heavy lube oil, asphalt
Solvent dewaxing	Treatment	Cool/ filter	Remove wax from lube stocks	Vacuum tower lube oils	Dewaxed lube basestock
Solvent extraction	Solvent extraction	Absorption precipitation	Separate unsat. oils	Gas oil, reformate, distillate	High-octane gasoline
Sweetening	Treatment	Catalytic	Remove H_2S, convert mercaptan	Untreated distillate/gasoline	High-quality distillate/gasoline

Table 4-5 - Refined Products
(U.S. DOE 2000)

Specific Gravity g/mL	Refined Products	Barrel/y (10^9)	kg/y (10^{11})
0.75	Transportation fuels (60%)	3.7	4.4
0.80	Naphthas (5%)	0.3	0.4
0.85	Residual fuel oil (5%)	0.3	0.4
0.85	Distilled fuel oil (21%)	1.3	1.8
1.10	Petroleum coke (3%)	0.2	0.3
0.90	Asphalt, Heavy oils (3%)	0.2	0.3
0.55	Still Gas (3%)	0.2	0.2
	TOTAL	**6.2**	**7.8**
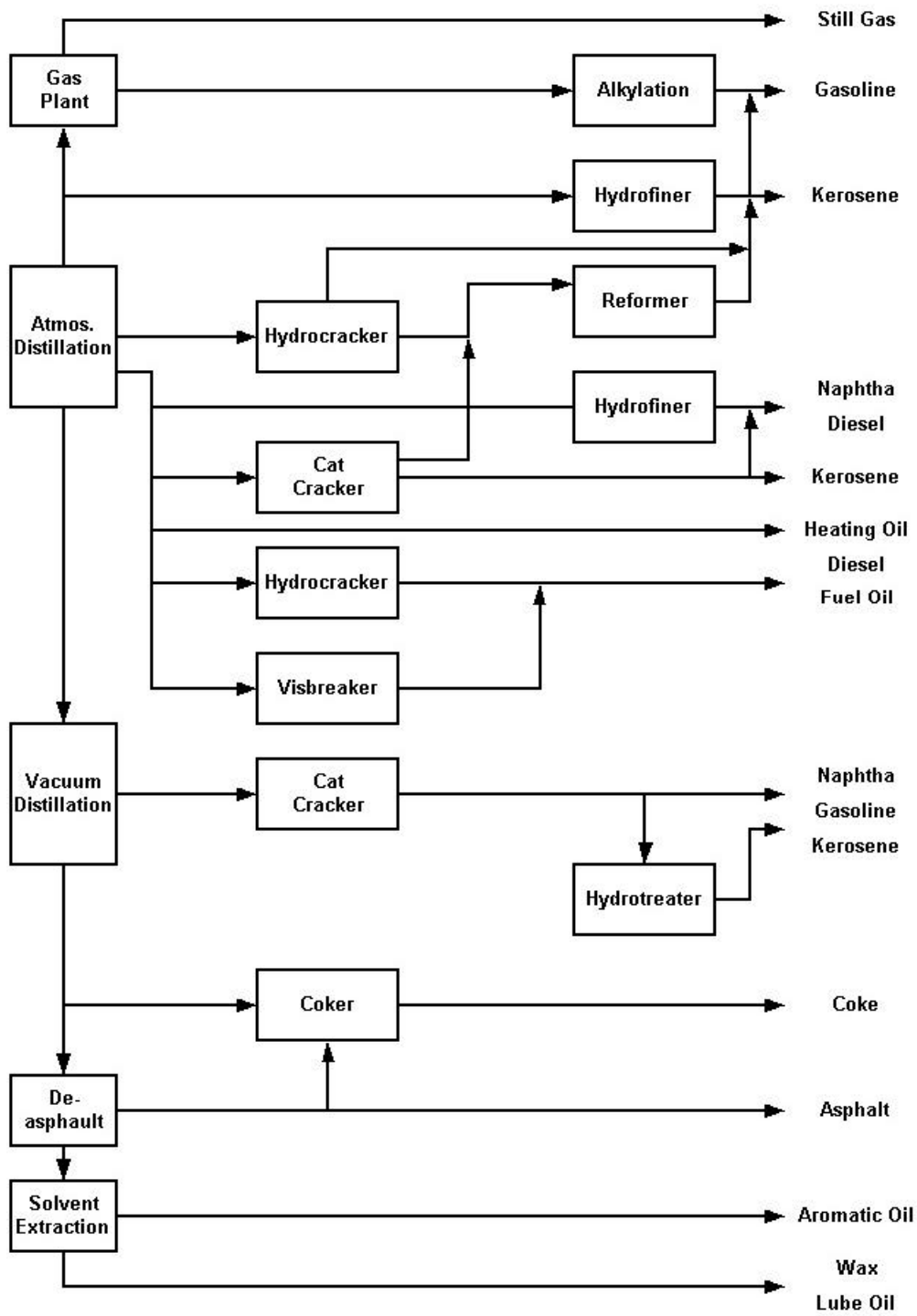
Figure 4-1 - Typical Refining Process
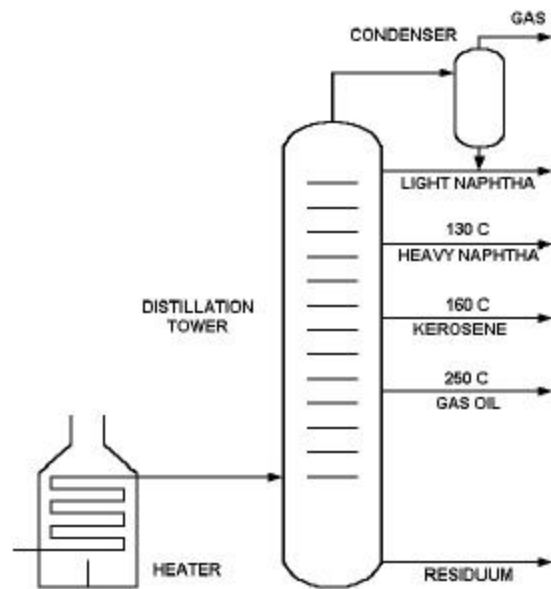
Figure 4-2 − Primary Distillation
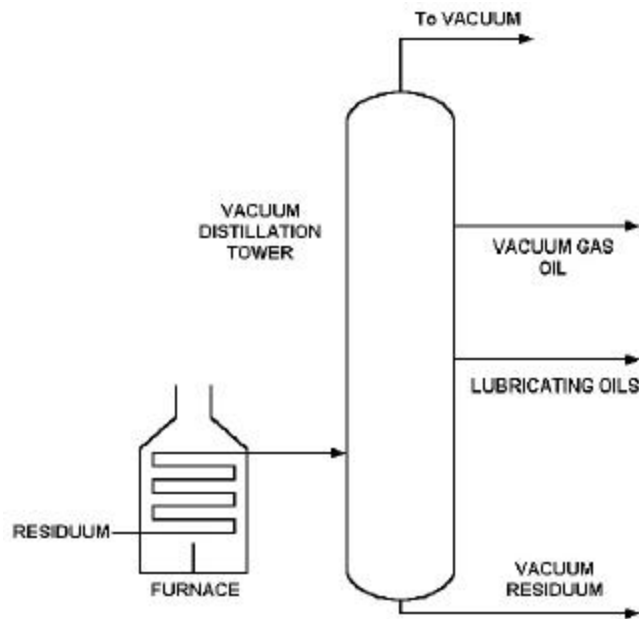
Figure 4-3 − Vacuum Distillation
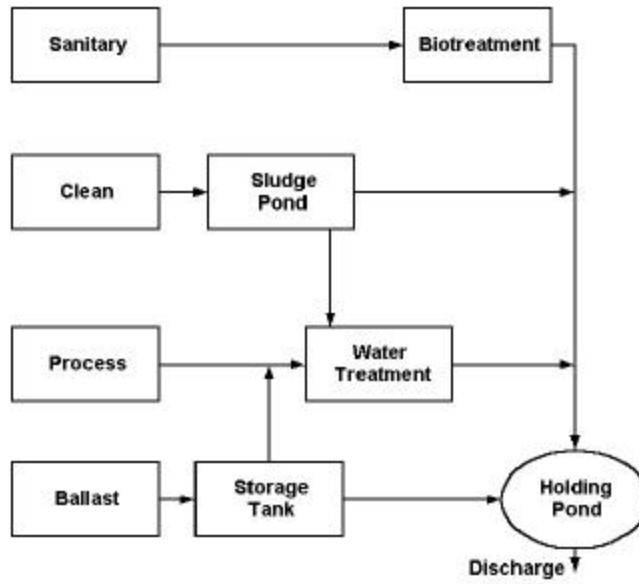
Figure 4-4 – Segregated Water Treatment System for a Typical Refinery

Gas Processing

Figure 4-5 shows a typical gas processing plant that provides pipeline sales gas (methane) and petrochemical feedstocks. Several other types of gas processing are common including plants that optimize liquefied petroleum gas (LPG, C3 and C4) separation, liquefied natural gas (LNG, C1), natural gas liquids (NGL, C3+). Certain aspects of gas treatment are common to all gas processing schemes.

Unlike refining, gas processing attempts no molecular transformations to produce salable products. Gas processing is more accurately termed a treatment and separation process. The treatments are designed to remove unwanted constituents (CO_2, H_2S, H_2O) and trace contaminants (metals). The separations are typically cryogenic utilizing selective condensation of fractions (C2, C3, C4) by removal of heat.

Water removal (dehydration) treatments are applied to all natural gas and several processes are common. Glycol dehydration contacts gas with triethyleneglycol (TEG) that absorbs water. The TEG is regenerated in a continuous process that boils off the water. Molecular sieve (mol-siv) water adsorbents are also employed. Mol-siv water sorbents are regenerated with hot gas in a

dual contactor arrangement (lag-lead regeneration). Acid gas removal (AGR) involves contacting gas with amine solutions that selectively adsorb H_2S and some CO_2. CO_2 is removed by contacting gas with carbonate solutions.

The gas separation process involves cooling gas (Joule-Thompson) to liquefy C2 – C5. The cryogenic heat exchanger is referred to as a cold box and is typically manufactured from aluminum. Mercury removal units containing sorbents specific to mercury are applied upstream of the cold box to prevent condensation of mercury and subsequent damage to the aluminum welds (Wilhelm 1994).

Mercury removal (see Figure 4-5) may or may not be employed at gas processing plants. The decision is based on the amount of mercury in feeds, whether aluminum heat exchangers are utilized and on whether downstream customers of gas products have specifications for mercury. Mercury removal units are required for virtually all LNG plants because of the sensitivity of cryogenic heat exchanges to mercury deposition (Wilhelm 1994) and because the low temperatures required to liquefy gas usually condense mercury as well.

The individual products (propane, butane, C5+) are separated in towers by warming and pressure reductions. The resulting liquid product streams (butane, propane) are typically feeds to petrochemical manufacture with methane sold as a pipelined product (sales gas). Ethane is typically the feed to ethylene manufacture; propane to propylene; butane to MTBE (methyl-tertbutylether, a gasoline additive). The C5+ product may be sold to a refinery or to other types of petrochemical manufacture (aromatics, olefins).

References

American Petroleum Institute, 1977, Water Reuse Studies, API Publication No. 949. Washington, DC.

American Petroleum Institute, 1998, Management Of Residual Materials: 1997, Petroleum Refining Performance, API Publication No. 352, Washington, DC.

Sittig, M., 1978, *Petroleum Refining Industry - Energy Saving and Environmental Control*, Noyes Data, Park Ridge, NJ.

Speight, J. G., 1999, *The Chemistry and Technology of Petroleum*, Marcel Dekker, New York, NY.

U.S. EPA, 1996, Waste Minimization for Selected Residuals in the Petroleum Refining Industry, Office of Solid Waste and Emergency Response, EPA/530/R-96/009 (NTIS PB97-121180), Washington, DC.

U.S. DOE, 2000, Energy Statistics for 1998, Energy Information Administration, National Energy Information Center, Washington, D.C.

U.S. Occupational Safety and Health Administration, 2000, OSHA Technical Manual, Section 4: Petroleum Refining, U.S. Dept. of Labor, Washington, DC.

Wilhelm, S., 1994, Methods to Combat Liquid Metal Embrittlement in Cryogenic Aluminum Heat Exchangers, *Proceedings 73rd GPA Convention*, New Orleans, LA.
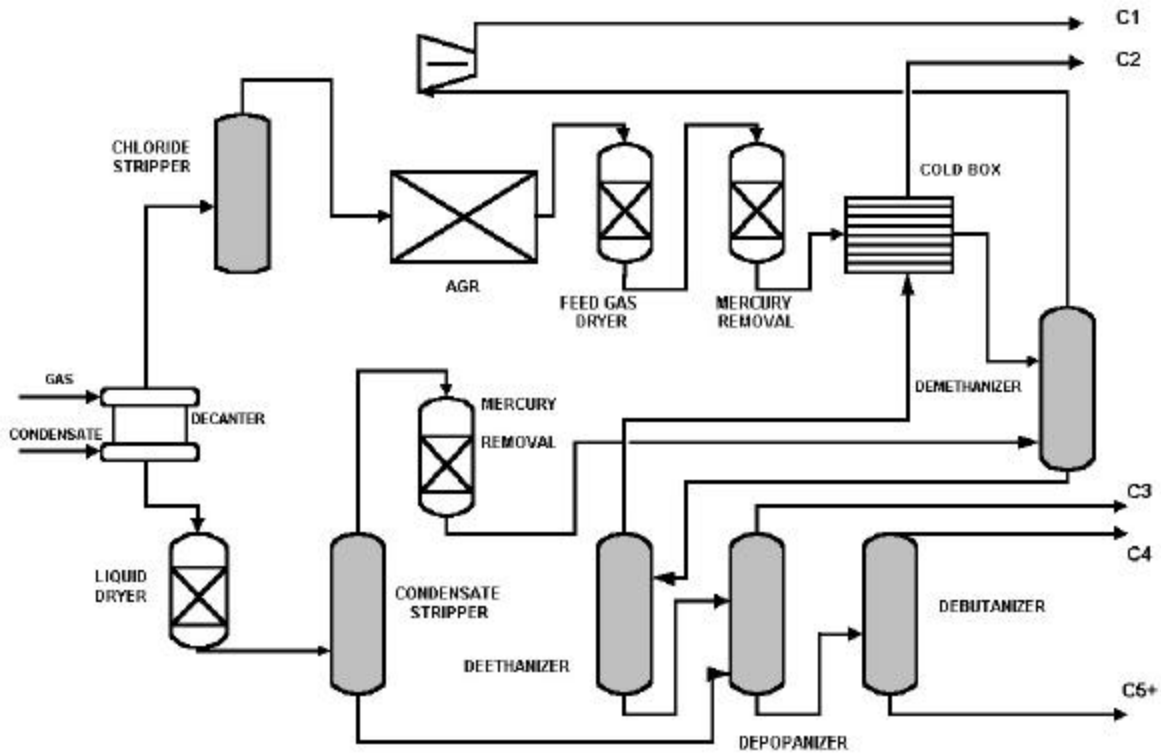
Figure 4-5 – Gas Process Schematic

Chapter 5
Mercury in Petroleum and Natural Gas

Properties of Mercury and Mercury Compounds

The common physical properties of elemental mercury are listed in Table 5.1. Elemental mercury is a liquid at ambient conditions. Its melting point is -38.87 C and it has a boiling point of 357 C. Elemental mercury is quite dense (13.5 times more than liquid water under ambient conditions). The high density, the low saturation vapor pressure and high surface tension control the behavior of elemental mercury in solid, liquid and gaseous matrices.

Mercury occurs in nature in the zero (elemental), +1 (mercury[I] or mercurous), or the +2 (mercury[II] or mercuric) valence states. Mercurous compounds usually involve Hg-Hg bonds and are generally unstable and rare in nature.

Mercury occurs most prevalently in the elemental form or in the inorganic mercuric form. Common mercuric compounds include mercuric oxide, mercuric chloride, mercuric sulfide and mercuric hydroxide. Organic mercury forms also exist and consist of two main groups: R-Hg-X compounds and R-Hg-R compounds, where R = organic species, of which methyl (-CH_3) is prominent, and X = inorganic anions, such as chloride, nitrate or hydroxide. The R-Hg-X group includes monomethylmercury compounds. The most prominent R-Hg-R compound is dimethylmercury.

Table 5-1 – Physical Properties of Elemental Mercury

Atomic number	80
Atomic weight	200.59 atomic mass units
Boiling point	357 C (675 F)
Boiling point/rise in pressure	0.0746 ^{0}C/torr
Density	13.546 g/cm^3 at 20 C (0.489 lb/in^3 at 68 F)
Diffusivity (in air)	0.112 cm^2/sec
Heat capacity	0.0332 cal/g at 20 C (0.060 Btu/lb at 68 F)
Henry's law constant	0.0114 atm m^2/mol
Interfacial tension (Hg/H$_2$O)	375 dyne/cm at 20 C (68 F)
Melting point	-38.87 C (-37.97 F)
Saturation vapor pressure	0.16 N/m^3 (pascal) at 20 C (68 F)
Surface tension (in air)	436 dyne/cm at 20 C (68 F)
Vaporization rate (still air)	0.007 mg/cm^{2}hr for 10.5 cm^2 droplet at 20 C

Mercury is difficult to oxidize in the natural environment and spilled mercury (in soil for instance) retains the elemental form indefinitely absent moisture and bacteria until evaporation. Mercury can be oxidized by the stronger oxidants including halogens, hydrogen peroxide, nitric acid and concentrated sulfuric acid. Mercury is oxidized and methylated in sediments by sulfate-reducing bacteria.

Selected solubility and volatility data for elemental mercury and some mercury compounds in water are compiled in Table 5-2. It is important to note that sulfides of mercury are largely insoluble in water (and oil) and, as pollutants are less available to receptors.

Under ambient conditions, silver, gold, copper, zinc, and aluminum readily form amalgams with elemental mercury. The solubility of these metals in elemental mercury is relatively low. The solubility of zinc in mercury is approximately 2 g Zn/100 g Hg, while gold solubility in mercury is only 0.13 g Au/100 g Hg. Silver, copper, and aluminum have even lower solubilities than gold. The affinity of mercury for gold is important in analytical procedures that trap vapor phase mercury on gold collectors.

Table 5-2 – Solubilities and Volatilities of Mercury Compounds

Formula	State	Volatility	Hg Solubility in H_2O; 25 C	Name
Hg^0	Liquid	Boiling Point 357 C Vapor Pressure 25 mg/m^3 (25 C)	50 ppb	Elemental
$HgCl_2$	Solid	Boiling Point 302 C	70 g/L	Mercuric chloride
$HgSO_4$	Solid	decomposes 300 C	0.03 g/L	Mercuric sulfate
HgO	Solid	decomposes 500 C	0.05 g/L	Mercuric oxide
HgS	Solid	Sublimes under vacuum; decomposes 560 C	- log Ksp[1] = 52	Mercuric sulfide
$HgSe$	Solid	Sublimes under vacuum, decomposes 800 C	- log Ksp ~ 100	Mercuric selenide
$(CH_3)_2Hg$	Liquid	Boiling Point 96 C	< 1 ppm	Dimethylmercury
$(C_2H_5)_2Hg$	Liquid	Boiling Point 170 C	< 1 ppm	Diethylmercury

(1) Ksp = solubility product

Mercury In Hydrocarbons

Elemental mercury and mercury compounds occur naturally in geologic hydrocarbons including coal, natural gas, gas condensates and crude oil. Table 5-3 provides a listing of the mercury species that have been detected and their relative abundance in hydrocarbon matrices (Wilhelm and Bloom 2000). Since analytical speciation techniques do not exist for all of the matrices (especially coal), considerable uncertainty exists for the relative abundance of some species.

In natural gas, mercury exists almost exclusively in its elemental form and at concentrations far below saturation suggesting that no liquid mercury phase exists in most reservoirs. One gas reservoir is known (Texas) that produces gas at saturation (with respect to elemental mercury) and produces condensed liquid elemental mercury as well suggesting that, in this single example, the gas is in equilibrium with a liquid mercury phase in the reservoir.

The prevalence of dialkylmercury in natural gas is largely unknown but thought to be low (less than 1 percent of total) based on the limited speciation data reported in the literature for gas condensates (Tao et al. 1998). Organic mercury compounds in produced gas would be expected to partition to separated hydrocarbon liquids as the gas is cooled. Therefore, if dialkylmercury is present in the reservoir, it would be found mostly in condensate, less so in gas, in those situations where hydrocarbon liquids separate due to natural cooling. Likewise in gas processing, little organic mercury would be expected in sales gas due its partition to liquid streams.

Crude oil and gas condensate can contain several chemical forms of mercury, which differ in their chemical and physical properties.

1. Dissolved elemental mercury (Hg^0) – Elemental mercury is soluble in crude oil and hydrocarbon

liquids in atomic form to a few ppm. Elemental mercury is adsorptive and adsorbs on metallic components (pipes and vessels), suspended wax, sand and other suspended solid materials in liquids. The measured concentration of dissolved elemental mercury typically decreases with distance from the wellhead due to adsorption, reaction with iron, conversion to other forms and loss of the suspended fraction.

2. Dissolved organic mercury (RHgR and RHgX, where R = CH_3, C_2H_5, etc. and X = Cl^- or other inorganic anion) – Dissolved organic mercury compounds are highly soluble in crude oil and gas condensate. Organic mercury compounds are similar to elemental mercury in adsorptive tendencies but differ in their boiling points and solubilities and thus they partition to distillation fractions in a different fashion from Hg^0. This category includes dialkylmercury (i.e., dimethylmercury, diethylmercury) and monomethylmercury halides (or other inorganic ions).

3. Inorganic (ionic) mercury salts ($Hg^{2+}X$ or $Hg^{2+}X_2$, where X is an inorganic ion) -Mercury salts (mostly halides) are soluble in oil and gas condensate but preferentially partition to the water phase in primary separations. Mercuric chlorides have a reasonably high solubility in organic liquids (about 10 times more than elemental mercury). Ionic salts also may be physically suspended in oil or may be attached (adsorbed) to suspended particles.

4. Complexed mercury (HgK or HgK_2) – Mercury can exist in hydrocarbons as a complex, where K is a ligand such as an organic acid, porphyrin or thiol. The existence of such compounds in produced hydrocarbons is a matter of speculation at present depending in large part on the particular chemistry of the hydrocarbon fluid.

5. Suspended mercury compounds – The most common examples are mercuric sulfide (HgS) and selenide (HgSe), which are insoluble in water and oil but may be present as suspended solid particles of very small particle size.

6. Suspended adsorbed mercury – This category includes elemental and organic mercury that is not dissolved but rather adsorbed on inert particles such as sand or wax. Suspended mercury and suspended mercury compounds can be separated from liquid feeds to the plant by physical separation techniques such as filtration or centrifugation.

There is considerable debate in the scientific community as to the prevalence of dialkylmercury compounds in produced hydrocarbons. Their existence is inferred when analysis for total mercury in a liquid matrix does not mass balance with speciated forms. Dialkylmercury compounds have been directly detected in a few instances but at very low concentrations possibly inferring an analytical artifact.

Gas and liquid processing can cause transformation of one chemical form of mercury to another. A common example is the reaction of elemental mercury with sulfur compounds. The mixing of gas and/or condensate from sour and sweet wells allows reaction of elemental mercury with S_8 or ionic mercury with H_2S to form particulate HgS that can settle out in tanks and deposit in equipment. In theory, high temperature processes such as hydrotreating in refineries should convert dialkylmercury and complexed mercury to the elemental form.

The partitioning of mercury into product and effluent streams in petroleum processing is largely determined by solubility. Table 5-4 provides the approximate solubility of the common species in several liquid matrices. The solubility of elemental mercury in normal alkanes (IUPAC 1987) as a function of temperature is shown in Figure 5-1.

Crude oil and gas condensate, when sampled soon after primary separation of water and gas, can contain significant amounts of suspended mercury compounds and or mercury adsorbed on suspended solids. The suspended compounds usually are mostly HgS but include other mercury species adsorbed on silicates and other suspended colloidal material. The amount of suspended mercury can be a substantial percentage of the total concentration of mercury in liquid samples of produced hydrocarbons and they must be separated (filtered) prior to any analytical speciation of dissolved forms.

The term gas condensate refers to liquids that can originate at several locations in a gas processing scheme. A generic unprocessed condensate is the hydrocarbon liquid that separates in the primary separator, either at the wellhead or at the gas plant. Processed condensate is the C5+ fraction that is a product from a gas separation plant. Naphthas typically originate from the primary distillation of oil in the range of 50 to 150 C. The distribution of hydrocarbon compounds in both condensates and naphthas are similar and mostly in the range C5 to C10. Processed condensate and naphthas typically do not contain

26

suspended mercury compounds while unprocessed condensate can contain some amount.

Published total Hg concentrations in condensate, naphthas and crude oil often do not fully disclose sampling procedures or analytical processing steps (filtration, centrifugation, exposure to air). For these reasons, some data are suspect in that the total mercury concentrations reported may or may not include a contribution from suspended forms. In addition, the distribution of compounds could reflect species conversion due to aerobic processing of samples that is suspected to promote oxidation of Hg^0 to ionic forms and thus to alter the distribution of species.

Reported total Hg concentrations in liquid hydrocarbons (compiled in Chapter 7) vary considerably. Some condensates and crude oils are close to saturation with respect to Hg^0 at concentrations of 1 - 4 ppm as determined by sparging of fresh, filtered samples. Adding suspended, ionic and organic forms, total mercury concentrations in crude oil over 5 ppm are known. Gas condensates in Southeast Asia have dissolved total Hg concentrations in the 10 - 800 ppb range. Most crude oils processed in the U.S. have relatively low (<10 ppb) mercury concentrations. The range of total mercury concentration in oil processed in the U.S. is estimated to be 1 to 1000 ppb (wt.) with the mean close to 5 ppb (see Section 7 and Wilhelm 2001).

Data for total Hg in naphthas (Tao et al. 1998) are similar to condensates and range between approximately 5 and 200 ppb. High concentrations have not been reported in the limited published data. Naphthas originating from distillations would be expected to have lower concentrations than the raw produced liquids from which they originate.

Only limited data are available that allow examination of the distribution of concentrations of mercury compounds in hydrocarbon liquids. Of interest are the natural abundance of mercury compounds, the relative distribution of compounds in liquid samples, the partitioning of compounds in separations and distillations and transformation of species during processing.

The data of Tao et al. (1998) on gas condensates, naphthas and a crude oil, are shown graphically in Figure 5-2. The origin (process location) of samples analyzed by Tao were not disclosed. Tao's data indicate that ionic mercury was the dominant species in the condensates examined. Hg^0 did not exceed 25 percent of the total in any of the condensate samples. The dialkyl species was detected (>10%) in some condensates. The monoalkyl species was detected but

at very low concentrations. Hg^0 was not seen in naphthas as would be expected assuming a normal distillation profile. The more volatile Hg^0 would be expected to partition to the lighter gas fraction. RHgR appeared to be the dominant species in one naphtha sample. Ionic forms of mercury were seen in all of the samples.

Zettlitzer et al. (1997) used two methods to measure concentrations of mercury species. The method for monoalkylmercury provided suitable detection limits. The concentrations of monoalkylmercury in the condensate analyzed by Zettlitzer were low and generally agree with the data of Tao. A gas chromatographic (separation) and mass spectrometer (detection) method was used to examine RHgR but the detection limit was high and the methodology suspect. In Zettlitzer's procedure, extracting condensate with HCl was postulated to remove ionic and organic forms. The concentration of acid-extractable mercury was operationally defined as the difference between the total amount extracted using HCl and the sum of ionic and monoalkylmercury determined independently.

Zettlitzer's distributions of compounds, using operationally defined values for extracted mercury, are compiled in Table 5-4. The unprocessed condensate sample exhibited a 2 ppm concentration of Hg^0 which is close to the saturation value for elemental mercury in hydrocarbon liquids. These data do not show the dominance of ionic species seen in the data of Tao.

Frech et al. (1996) analyzed two condensates and found most of the total mercury in ionic form. The dialkyl form accounted for approximately 10 percent and the monoalkyl form less than 1 percent. Similarly Schlickling and Broekaert (1995) analyzed 2 condensates and found mostly ionic compounds. Bloom's (2000) operationally defined speciation (Table 5-6) data account for the majority of total dissolved mercury as either Hg^0 or KCl extractable (mostly ionic).

In spite of the fact that dialkylmercury has been detected in some samples, the concentrations found for this class of compounds are very low (< 10 ppb) excepting one naphtha (Tao et al. 1998) in which it was found at a concentration of approximately 50 ppb. Based on the limited data, it is by no means apparent at this point in time that dialkylmercury is prevalent in petroleum.

Snell et al. (1998) examined the stabilities of mercury species in synthetic gas condensate and demonstrated conclusively that Hg^0 and $HgCl_2$ react to form Hg_2Cl_2 that is insoluble in hydrocarbons and precipitates.

$$Hg^0 + HgCl_2 \rightarrow Hg_2Cl_2 \downarrow$$
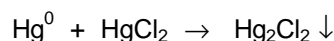
The reaction exhibited a half-life on the order of about 10 days at ambient temperature. Most condensate samples contain both species thus implying, given the clearly defined observations of Snell, that species conversion is likely in gas condensate samples. Bloom (2000) likewise examined sample stability and found standard solutions of Hg^0, $HgCH_3^+$ and $Hg(CH_3)_2$ stable in paraffin oil stored in glass. $HgCl_2$ was not stable in paraffin oil and Hg^0 and $HgCl_2$ were unstable in natural crude oil. Bloom's data generally support those of Snell.

Oxidative mechanisms may operate in hydrocarbon samples that are exposed to oxygen, that contact metal surfaces or that are treated with impure reagents as part of the analytical method. If this is the case, then the high concentrations of ionic forms in some samples may be an artifact of collection procedures, sample age and analytical processing methodologies. The author's experience with crude oils and gas condensate samples is that very fresh samples typically exhibit the dominance of the Hg^0 species. No reductive mechanisms are known that would account for generation of Hg^0 in samples of geologic hydrocarbons; hence, the transformation of ionic or organic species to elemental mercury is not likely.

The primary separation of water in gas or oil production would be expected to segregate the majority of ionic species naturally present to the water phase. Produced water that has low dissolved mercury content is associated with co-produced hydrocarbon liquids containing high concentrations of ionic species (analyzed days after collection). Such high percentage concentrations of ionic species in the hydrocarbon liquid are not expected based upon the rationalization that the ionic species should partition to the separated water phase during primary separations.

If one compares the concentrations of Hg^0 in co-produced hydrocarbon liquid and gas, Hg^0 typically is dominant in both. This suggests that Hg^0 is the dominant species in the reservoir and the ionic forms derive from it. Reaction mechanisms associated with sample stability certainly require further investigation. If the ionic content of liquid samples is merely an artifact of sample aging, then the distribution of mercury compounds previously cited is suspect.

There is also considerable doubt that dialkylmercury exists abundantly in crude oil and condensate. Monoalkylmercury is not found in petroleum. If dialkylmercury were abundant, then the monoalkyl species would be expected to be similarly abundant. Given the very low concentrations of $HgCH_3^+$ in condensate, it is unlikely that discharges of produced water to the ocean would contain significant amounts and thus would not have any direct contribution to monomethylmercury levels in sediments or in fish in proximity to platforms.

**Table 5-3 – Approximate Natural Abundance of
Mercury Compounds in Hydrocarbons**

	Coal	Natural Gas	Gas Condensate	Crude Oil
Hg^0	T	D	D	D
$(CH_3)_2Hg$	?	T	T, (S?)	T, (S?)
$HgCl_2$	S?	N	S	S
HgS	D	N	Suspended	Suspended
HgO	T?	N	N	N
CH_3HgCl	?	N	T?	T?

Abundance: *D (dominant) - greater than 50 percent of total;*
              S (some) - 10 to 50 percent
              T (trace) - less than 1 percent
              N (none) – rarely detected
              ? indicates that data not conclusive

Table 5-4 - Approximate Solubility of Mercury Compounds in Liquids; 25 C

Species	Water (ppm)	Oil (ppm)	Glycol (ppm)
Hg^0	0.05	2	<1
XHgX	?	miscible	>1
$HgCl_2$	70,000	>10	>50
HgS	0.01	< 0.01	< 0.01
HgO	50	low	
CH_3HgCl	>10,000	1,000	>1,000

Table 5-5 - Concentrations of Mercury Compounds in Natural Gas Condensates (μg/liter Hg) (Zettlitzer et al. 1997)

Sample	Hg^0	$HgCl_2$	Other	RHgCl	Sum (a)	Total	HgS
Low-Temp. Separator	250	400	644	6	1300	3500	2200
(percent)	19.2	30.8	49.5	0.5	100.0		
Ambient temp. Separator	2000	400	2600	100	5100	5500	400
	39.2	7.8	51.0	2.0	100.0		
Storage tank	200	200	1250	50	1700	4300	2600
	11.8	11.8	73.5	2.9	100.0		

(1) Sum $= Hg^0 + HgCl_2 + RHgCl + $ other; other = acid extracted - $HgCl_2$; HgS = Total- sum

Table 5-6 - Operational Hg Speciation in Petroleum Samples (Bloom 2000)

	unfiltered Hg, ng/g		0.8 μfiltered Hg, ng/g		
Sample ID	Total	Hg^0	dissolved total	Hg(II)	CH_3Hg
condensate #1	20,700	3,060	5,210	2,150	3.74
condensate #2	49,400	34,500[1]	36,800	2,370	6.24
crude oil #1	1,990	408	821	291	0.25
crude oil #2	4,750	1,120	1,470	433	0.26
crude oil #3	4,610	536	1,680	377	0.27
crude oil #4	4,100	1,250	1,770	506	0.62
crude oil #5	15,200	2,930	3,110	489	0.45
crude oil #6	1.51	0.09	1.01	0.39	0.15
crude oil #7	0.42	0.17	0.41	0.02	0.11

(1) This sample was contained particulate Hg^0 that was re-dissolved in hexane.
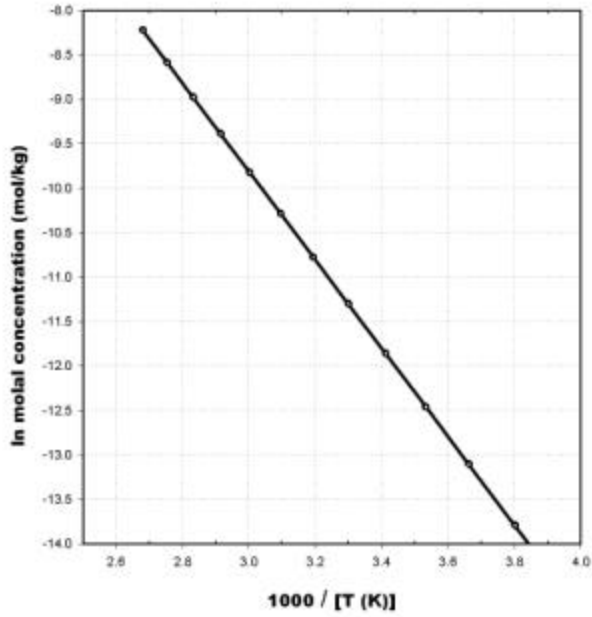
Figure 5-1 – Solubility of Elemental Mercury in Normal Alkanes as a Function of Temperature
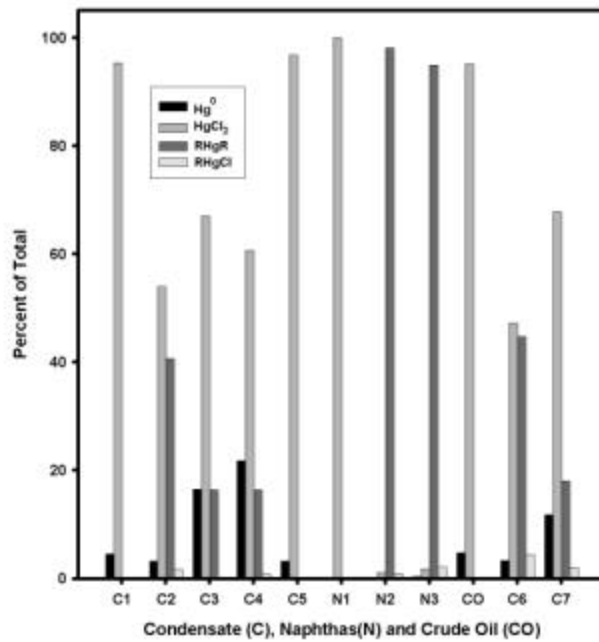

Figure 5-2 – Distribution of Mercury Compounds in Liquids (Tao et al. 1998)

Analytical Methods for Mercury in Hydrocarbon Matrices

Advances in analytical techniques over the last decade have allowed extremely accurate determinations of mercury and mercury species in virtually all matrices. The advances have been made in both technique and instrumentation. The most important contributions were the development and application of ultraclean sample handling techniques (Bloom 1995; Fitzgerald and Watras 1989) and the development of more sensitive analytical methods, such as amalgamation pre-concentration (Bloom and Crecelius 1983; Fitzgerald and Gill 1979) and cold vapor atomic fluorescence spectrometry, or cold vapor atomic fluorescence (CVAF) (Bloom and Crecelius 1983; Goddon and Stockwell 1989). The CVAF method for total Hg determination in water was adopted by U.S. EPA as Method 1631 (U.S. EPA 1995).

Speciation techniques for mercury compounds in water have evolved along with the development of the very sensitive detectors. Mercury and its compounds can now be measured in aqueous media at below parts per trillion (ng/L) levels. Essentially all environmentally important mercury species, including methylmercury, dimethylmercury $[(CH_3)_2Hg]$, inorganic mercury, particulate mercury, and elemental mercury (Hg^0), can be accurately measured in aqueous environmental media. Clevenger et al. (1997) provides an excellent review of the variety of methods used to detect and speciate mercury in environmental media (water, sediments, atmosphere) and the limits of detection presently achieved.

Determination of mercury in hydrocarbon matrices has likewise evolved over the last decade primarily as a result of the major improvements accomplished for water. In hydrocarbon samples, lower detection has been achieved by better sampling techniques and new methods for separating mercury from the hydrocarbon matrix. Improvements have also been obtained by a better understanding of the chemistry of mercury in petroleum and gas and from understanding how the various species distribute in phases during sampling and analysis.

Sampling of low molecular weight hydrocarbon liquids (C2-C5) for mercury analysis is difficult to accomplish when the process stream is at elevated temperature and/or pressure. In samples taken from elevated temperature liquids, Hg^0 can segregate to the vapor phase in a sample container thus causing a lower than actual analytical result of the liquid phase. Losses of volatile mercury also occur when sampling pressurized fluids. When samples of pressurized fluids are taken into a vessel at ambient pressure, volatile mercury (Hg^0) escapes to the gas phase when the fluid is partially depressurized. This problem is especially important for sampling of condensed gases such as propane and butane. The sampling techniques for volatile liquids often do not account for volatile mercury components thus placing some of the reported data in doubt.

Mercury concentrations in metal containers used for pressurized liquid samples can exhibit lower than actual results due to adsorption or reaction with corrosion products on container walls. The material of construction for pressurized sample containers must be selected carefully to obtain quantitative samples. Stainless steel containers minimize reactive loss of mercury but can introduce errors due to adsorption, especially if the mercury concentrations are low.

For multiple-phase samples (water, hydrocarbon liquid and gas), mercury will partition to the various phases disproportionately with elemental mercury equilibrating between gas and liquid and other forms remaining mostly in the liquids. The amount of elemental mercury that partitions to water is usually a small percentage of the total mercury concentration in coexisting phases because of the low solubility of elemental mercury in water. Ionic mercury compounds, if a large percentage of the total mercury concentration in crude oil, will partition to the water phase. Acidic water can encourage formation of a particle rich layer at the water/oil interface that can be very high in mercury concentration. Sampling and analysis protocols often are not designed to take these factors into account, thus supplying additional uncertainty to reported data.

Gas

Mercury in a hydrocarbon gas matrix at low concentrations is difficult to detect directly by spectroscopic methods (UV, visible, IR, X-ray) because of interference by the hydrocarbon. Pre-concentration of the mercury in gas to a collector facilitates analysis. Collection methods for mercury in natural gas are used primarily because of the low concentrations that are often present. By using a collector, the total amount of mercury present in a large volume of gas can be concentrated into a liquid or solid matrix.

A prevalent wet collection method is to bubble gas (containing mercury) through a permanganate solution where all mercury species are converted to mercuric ion. Mercuric ion is then reduced to elemental mercury and separated by volatilization into an inert gas stream

for quantitative detection. Detection methods are typically UV atomic absorbance or UV atomic fluorescence. This method is accurate and reasonably sensitive if sufficient volumes of gas are used, but the apparatus required to collect the samples is somewhat cumbersome and the required sample volumes are large.

A common dry collection method is to flow gas across a gold collector (sputtered gold on quartz). The gold amalgamates with mercury to scavenge elemental mercury. Organic mercury amalgamates as well but slower than elemental necessitating low flow rates and long sampling times if the total mercury concentration is required. The mercury/gold amalgam is heated in an inert (Ar) gas stream to volatilize mercury for detection. The collection method is very effective for light, dry gas. If the stream to be sampled contains heavier components, hydrocarbon condensation is minimized by heating the traps slightly (100^0 to 200^0 C) without compromise of quantitative mercury collection.

Iodated carbon carbon impregnated with potassium iodide is also used to scavenge mercury from gas matrices resulting in concentration of a sufficient quantity of mercury on the solid adsorbent for routine digestive analysis. Iodated carbon traps are less sensitive to contaminants in hydrocarbons than gold traps. Iodated carbon traps also have complete capture capability for elemental and dialkyl mercury and a high capacity. In view of these attributes, the iodated carbon trap is used for unprocessed gas where reasonably high concentrations are expected.

Liquids

Analytical methods for total mercury in hydrocarbon liquids vary considerably and include combustion/trap (Liang et al. 2000), vaporization/trap (Shafawi et al. 1999), acid digestion (reviewed by Liang et al. 2000) and oxidative extraction (Bloom 2000). Combustion techniques (Liang et al. 2000) oxidize and vaporize the entire liquid matrix and mercury in the combustion vapors is trapped by amalgamation on gold. Mercury on gold is then thermally desorbed and detected using CVAF. The thermal vaporization/trap method (Shafawi et al. 1999) is similar to the combustion method excepting that the hydrocarbon liquid is not combusted and the matrix is retained but in vapor form. The vaporized liquid is passed over a gold trap in the same fashion as the combustion method.

Acid digestion methods chemically oxidize mercury to mercuric ion that separates to the aqueous solution. The important considerations in wet digestive methods are to avoid losses to vaporization if the digestion is hot and to avoid introduction of mercury from impure reagents or the air. Mercuric ion in acid solution is quantified by acid neutralization, reduction ($SnCl_2$) to Hg^0, evolution by sparging, trapping on gold and detection by CVAA or CVAF. Acid digestions are reported using mixtures of nitric, hydrochloric, sulfuric acids and perchloric acids.

Extractive methods (Bloom 2000) also employ oxidants, most typically BrCl, but as opposed to digestions do not chemically decompose the matrix. Thus typically less heat is required and losses due to thermal evolution of volatile mercury forms do not occur. The mercuric ion in the aqueous extract is treated in the same manner as acid digestates (reduction, sparging, trap on Au, detect CVAF). For extractive methods, an important consideration is that the period of time that the extracting solution contacts the sample must be long enough to accomplish complete oxidation and separation of the entirety of the mercury present in the sample. Formation of emulsions with some hydrocarbon liquids can complicate extractive techniques and procedures such as centrifugation are used to break oil/water emulsions.

Digestates and extracted liquids are treated chemically to transform mercuric ion into a species that can be detected. This is accomplished in a variety of ways, but the most common is to reduce mercuric ion to elemental mercury (in water) using stannous chloride or sodium borohydride. The elemental mercury is evolved from the solution using inert gas and either sent directly to a detector or collected on a trap (amalgamation) and then thermally evolved into an inert gas stream for detection.

The most common forms of detection are UV absorbance and UV atomic fluorescence. In cold vapor atomic absorbance (CVAA), a mercury lamp and optical flux detector are employed to measure absorbance of UV light by mercury atoms in argon or nitrogen. The fluorescence (CVAF) technique is similar but measures emission (in argon) following absorbance at 90° to the excitation light path thus avoiding several spectral interferences and other optical limitations. CVAF is the most sensitive detection method (10^{-13} g).

For CVAF the overriding attribute is the low detection limit meaning that quantitative analysis can be achieved with very small gas sample volumes. By using double amalgamation, extremely low concentrations of mercury in gas or liquids can be measured (1 ppt or less). The low detection limits also dramatically reduce matrix effects common to other methods and allow extreme dilution prior to analysis to reduce interferences.

Other methods of total mercury analysis in hydrocarbon liquids include inductively coupled plasma (ICP) followed by mass spectrometry (ICP-MS) (Olsen et al.1997) or atomic emission spectrometry (ICP-AES) detection (Snell et al. 1996). The ICP technique avoids digestion of the sample, hence minimizing some of the potential errors that can occur in multi-step wet chemical processing of liquid samples. The ICP procedure involves dilution of the sample with a solvent and injection of a known quantity directly into a torch that produces a gaseous plasma. A portion of the plasma is then fed directly to the MS or AES detector.

Neutron activation analysis (NAA) methods, in which samples are irradiated in a nuclear reactor and the decay radiation (gamma) is quantitatively counted, have been used successfully to measure total mercury concentration in crude oil (Musa et al. 1995). The cost and availability of this method have limited its application to only very specialized circumstances but the NAA method eliminates essentially all sample preparation and blank requirements and is essentially free of interferences.

Gas chromatography (GC) and high performance liquid chromatography (HPLC) (Schickling and Broekaert 1995) in conjunction with an element specific detector such as ICP/MS (Tao et al. 1998) or ICP/AES (Snell et al. 1996) have been used to directly measure volatile mercury compounds in hydrocarbon liquids. These compounds include elemental mercury, dialkylmercury compounds and monoalkylmercury compounds (determined either directly or after alkylation). Dialkylmercury compounds are separated from other forms chromatographically and can be quantitatively measured in simple matrices. The application of these techniques to actual petroleum is limited to refined products.

Analysis for total mercury in a liquid hydrocarbon matrix provides the sum of both dissolved and suspended species. If samples are not filtered prior to analysis, the result obtained from total mercury analysis includes the contribution from suspended mercury compounds and thus can be artificially high and variable because the distribution of suspended mercury in liquid samples is seldom homogeneous.

Operational speciation of liquid samples (Bloom 2000) involves multiple and sequential analyses for the various forms and a mass balance exercise.

$$THg = Hg^0 + (RHgR + HgK) + Hg^{2+} + suspended\ Hg$$

Suspended mercury is quantitatively determined by measuring total mercury of an agitated sample followed by measuring total mercury of a filtered portion of the agitated sample. Ionic forms are determined by non-oxidative extraction. The volatile elemental form (Hg^0) is determined by sparging and collecting the volatile component on a trap. Total mercury concentration typically is determined by combustion, extraction or acid digestion. The sum of the concentrations of dialkylmercury and complexed mercury (RHgR + HgK) often is estimated from the discrepancy in the mass balance. To determine the exact concentration of the organic forms, more sophisticated techniques (GC-CVAF, GC-ICP/MS) are required.

References

Bloom, N. S., 1995, Mercury as a case study of ultra-clean sample handling and storage in aquatic trace metal research, *Environ. Lab.,* March/April:20.

Bloom, N. S., 2000, Analysis and Stability of Mercury Speciation in Petroleum Hydrocarbons, *Fresenius' J. Anal. Chem.,* 366:5.

Bloom, N. S., and E. Crecelius, 1983, Determination of mercury in seawater at sub-nanogram per liter levels, *Mar. Chem.*, 14:49.

Clevenger, W. L., Smith, B. W., and J. D. Winefordner, 1997, Trace Determination of Mercury: a Review, *Crit. Rev. Anal. Chem.*, 27(1):1.

Fitzgerald, W. F., and G.A. Gill, 1979, Subnanogram determination of mercury by two-stage gold amalgamation applied to atmospheric analysis, *Anal. Chem.*, 46:1882.

Fitzgerald, W. F., and C. J. Watras, 1989, Mercury in surficial waters of rural Wisconsin lakes, *Sci. Tot. Environ.* 87/88:223.

Frech, W., Baxter, D., Bakke, B., Snell, J., and Y. Thomasson, 1996. Determination and Speciation of Mercury in Natural Gases and Gas Condensates, *Anal. Comm.,* 33:7H (May).

Goddon, R. G., and P. Stockwell, 1989, Atomic fluorescence spectrometric determination of mercury using a filter fluorimeter, *J. Anal. Atom. Spectrom.* 4:301.

IUPAC, 1987. Mercury in Liquids, Compressed Gases, Molten Salts and Other Elements, Volume 29; Solubility Data Series, Pergamon Press, H. Clever, editor, New York, NY.

Liang, L., Lazoff, S., Horvat, M., Swain, E., and J. Gilkeson, 2000, Determination of mercury in crude oil by in-situ thermal decomposition using a simple lab built system, *Fresenius' J. Anal. Chem.*, 367:8.

Musa, M., Markus, W., Elghondi, A., Etwir, R., and E. A. Arafa, 1995, Neutron Activation Analysis of Major

and Trace Elements in Crude Petroleum, *J. Radioanal. Nucl. Chem.*, 198(1), 17.

Olsen, S., Westerlund, S., and R. Visser, 1997, Analysis of Metals in Condensates and Naphthas by ICP-MS, *Analyst*, 122:1229.

Schickling, C., and J. Broekaert, 1995, Determination of Mercury Species in Gas Condensates by On-line Coupled HPLC and CVAA Spectrometry, *App. Organomet. Chem.*, 9:29.

Shafawi, A., Ebdon, L., Foulkes, M., Stockwell, P., and W. Corns, 1999, Determination of total mercury in hydrocarbons and natural gas condensate by atomic fluorescence spectrometry, *Analyst*, 124:185.

Snell, J. P., Frech, W., and Y. Thomasson, 1996, Performance Improvements in the Determination of Mercury Species in Natural Gas Condensate Using an On-line Amalgamation Trap or Solid-phase Micro-extraction with GC-MIP-AES, *Analyst*, 121:1055.

Snell, J., Johansson, M., Frech, W., and K. Smit, 1998, Stability and reactions of mercury species in organic solution, *Analyst*, 123:905.

Tao, H., Murakami, T., Tominaga, M., and A. Miyazaki, 1998, Mercury speciation in natural gas condensate by gas chromatography-inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.*, 13:1085.

U.S. EPA, 1995, Method 1631: Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry, EPA/821/R-95/027, Office of Water, Washington, DC.

Wilhelm, S., and N. Bloom, 2000, Mercury in Petroleum, *Fuel Proc. Technol.*, 63:1.

Wilhelm, S., 2001, An Estimate of Mercury Emissions from Petroleum, in press, *Environ. Sci. Tech.*

Zettlitzer, M., Scholer, R., and R. Falter, 1997, Determination of Elemental, Inorganic and Organic Mercury in North German Gas Condensates and Formation Brines, *Proceedings of Symposium: Oil and Gas Chemistry*; Houston, TX, SPE Paper No. 37260.

Chapter 6
Fate Of Mercury in Refining and Gas Processing

It would be useful to understand how mercury partitions in separations, distillations and catalytic processes so as to be able to predict the amounts of mercury in emissions or effluents as a function of the known amount in feeds. Optimally one would have this type of information for each of the various mercury species present in hydrocarbon feeds to processing. Very little data are presently available that provide evidence as to the fate of mercury in refining and gas processing. Most of the reported information concerning mercury in processes is anecdotal and consists of observations of mercury deposition in equipment and detection of mercury in certain waste streams.

In some situations, computational methods have been used to estimate the distribution of mercury and mercury compounds in processes. Computer models can predict locations where mercury can condense or accumulate in cryogenic processes and the distribution of volatile species in distillations. Calculations of the distribution of mercury in a process require accurate information on the concentrations of the various dissolved and suspended forms that exist in liquid and gas feeds as well as vapor pressures, solubilities and gas/liquid partition ratios of Hg species as a function of temperature and pressure.

Vapor pressure and solubility for elemental mercury are reasonably well known or easily estimated. The solubilities of dialkylmercury compounds in hydrocarbons are assumed to be infinite over the range of temperatures encountered in most petrochemical processes. Partitioning of mercury species between liquid and gas phases can be estimated using chemical approximation principles and some limited empirical data (Edmonds et al. 1996, Bloom 2000).

In low temperature processes, chemical reactions to transform one mercury species to another typically do not occur so a species mass balance is assumed. Oxidation of Hg^0 to ionic compounds and/or HgS likely occurs in some high temperature refinery processes, thus making predictive calculations more difficult. Distillations and separations produce major redistribution of mercury compounds in refining as does blending crude feeds having differing amounts of reactive sulfur compounds.

Predictions of redistribution of mercury species based on assumptions of thermodynamic equilibrium do not account for some major kinetic factors. Rates of condensation and dissolution of Hg^0 are slow in liquids at low temperature. Likewise, the rates of redistribution of mercury and organic mercury to separated phases are slow compared to the rates of phase separation. Purely thermodynamic models thus require major corrections for non-equilibrium conditions and empirical verification.

Extraction

Oil and gas production systems provide limited opportunities for loss of mercury from produced fluids that are typically mixtures of hydrocarbon liquids, gas and produced water. Essentially all production systems employ separators to accomplish the primary phase separation so that produced water can be disposed of. Multiple stages of separation are typical as oil or gas is transported to a processing facility.

A typical separator schematic is shown in Figure 6-1 and, although the internals (not shown) are quite complicated, the obvious result is that hydrocarbon liquid, natural gas and water phases are separated. The mercury in the fluid produced at the wellhead will contain both the dissolved and suspended forms. Strictly based on gravity, most of the suspended mercury will be retained in the liquid phases that separate.

The distribution of dissolved and suspended forms of mercury in the produced fluid to separated phases is

difficult to predict but some broad generalities are possible. The amounts of mercury that enter the separated phases depend on physical, chemical and kinetic factors. The distribution of suspended mercury depends on particle size and whether the suspended (colloidal) material is hydrophilic or oleophilic. That amount of suspended mercury that is attached to large particles is either removed in the water phase or retained in the separator as sludge and is then removed when the separator is periodically cleaned. A high percentage of truly colloidal mercury is retained by the liquid hydrocarbon phase in separations.

The distribution of dissolved forms depends on numerous factors including the differences in solubility of each species in the various phases, the chemical composition of the hydrocarbon phases, pressure, temperature and kinetic considerations. Distribution coefficients have been measured by Bloom (2000). In Bloom's study, equal volumes of paraffin oil spiked with the particular species and water were shaken vigorously for 2, 6, or 12 minutes, and then allowed to separate. The results of these experiments are shown in Table 6-1 and agree reasonably well with expectations. The expected coefficient for Hg^0 is approximately 20, based upon the relative solubilities of Hg^0 in water (60 ng/mL) and paraffin oil (1200 ng/mL) at room temperature. The trend to lower K_{OW} (octanol/water partition ratio) for elemental mercury was thought to be due, in part, to oxidation (possibly by oxygen in air) of Hg^0 that produces ionic mercury that partitions to water.

In general, purely ionic (un-complexed) mercury should partition preferentially to the water phase while elemental and organic forms should be retained by the liquid hydrocarbon phase. Henry's law (applied to condensate) determines the amount of mercury in the gas phase (to a first approximation). In practice the accuracy of computations to predict the distribution of mercury in separations is complicated by kinetic factors because the residence time in a separator is short and complete equilibrium is seldom reached.

Table 6-1 - Oil-Water Distribution Coefficients (Bloom 2000)

Shaking Time	Analytical measure	Hg^0	$HgCl_2$	CH_3HgCl
	oil [Hg], ng/mL	170.6	5.5	32.2
2 min	water [Hg], ng/mL	5.0	160.2	98.9
	K_{ow} [1]	34.1	0.034	0.33
	oil [Hg], ng/mL	167.0	1.7	32.7
6 min	water [Hg], ng/mL	12.2	167.6	98.3
	K_{ow}	13.7	0.010	0.33
	oil [Hg], ng/mL	151.8	0.85	33.4
12 min	water [Hg], ng/mL	18.9	169.9	99.4
	K_{ow}	8.0	0.005	0.34

(1) K_{OW} (oil/water partition ratio)
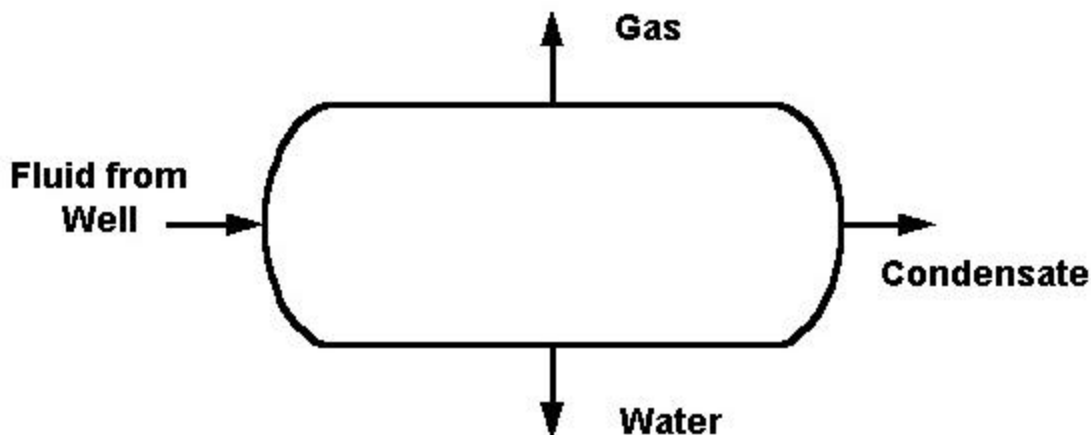
Figure 6-1 – Primary Separation

Transportation

In most cases, mercury is not lost in the movement of fluids to the processing facility, especially mercury in oil. For gas, a notable exception to this statement is transport of slightly wet gas in steel pipelines from primary separations. Elemental mercury reacts with steel corrosion products to form a mercury-rich layer on pipe surfaces. For example, natural gas produced offshore that contains low mercury concentration (1-20 ppb) when measured at the wellhead, may not present any mercury at the processing facility initially. The time to detect mercury at the end of the pipeline is dependent on the length of the pipeline, the amount of moisture in the gas and numerous other factors. The lag in presentation is due to the reaction of the elemental mercury with the non-stoichiometric iron oxide/sulfide corrosion products on pipe surfaces, with participation of H_2S in gas, if present.

Refining

Desalting is the process by which oil is washed with water to remove soluble salts (Figure 6-2) and is applied upstream of the atmospheric distillation. The partition of mercury in desalting is similar to that which occurs in primary phase separations. The greater amount of water and the longer residence time of crude oil in the desalter make it more efficient to remove suspended mercury and those ionic species that have affinity for water. As a result, the mercury in crude oil after application of desalting should be depleted of some fraction of ionic species and contain higher percentages of the elemental and complexed species.

Mercury in desalter sludge was examined by U.S. EPA (1996) at four U.S. refineries. The examined refineries are a small subset of the total number (approximately 100) of U.S. refineries and hence the sampling is not statistically predictive. Total mercury concentrations are reported in Table 6-2.

The distribution of total mercury in (filtered) crude oil to primary distillation products (Sarrazin et al. 1993; Wilhelm and Bloom 2000) is shown in Figure 6-3 and generally trends toward lower concentration in the higher temperature fractions. Suspended HgS was not present in the filtered crude examined by Wilhelm (unknown for Sarrazin et al. 1993). For crude feeds that contain large amounts of suspended mercury, the non-volatile HgS would tend to remain with the bottom fractions in the primary distillation and with the heavy oil and coke in the vacuum distillation. The HgS in resid and other bottom fractions used to fire boilers is converted in combustion to volatile forms (Hg^0, HgO) that can be emitted to the atmosphere.

The amount of mercury in petroleum coke is known with some certainty. As part of the U.S. EPA study of fuel feeds to coal-fired utilities, a large database has been developed that contains the total mercury concentration of petroleum coke consumed as fuel in coal-fired boilers at electric generating facilities (U.S. EPA 2000). Analysis of these data (Wilhelm 2000) allows a clear and accurate determination of the mean amount of mercury in coke. The mean is is approximately 50 ppb. The distribution of concentrations is shown in Figure 6-4. The origin of crude feeds in the refineries that produced the coke is not reported.

It is likely that the mercury in coke is HgS or HgSe because the process to produce coke includes both atmospheric distillation (350 C) and vacuum distillation (500^0 - 550^0 C). Coke is the solid residual material from the vacuum still and other coking processes. The volatilization (sublimation) temperature for mercuric sulfide is approximately 560^0 C, hence, in the vacuum distillation and coking processes, the sulfides and selenides of mercury would be expected to concentrate in residuum.

Little is known concerning the fate of mercury in unit processes at refineries. Such processes include catalytic cracking, visbreaking, alkylation, hydrotreating, etc. Based on purely chemical considerations, any organic or ionic mercury in feeds to hydrotreaters would be expected to be converted to Hg^0, which would then incorporate to the separated gas streams (H_2S, H_2, C1-C4).

Mercury in refinery wastewater has been examined by Ruddy (1982) but prior to the development of the more accurate and sensitive analytical methods previously discussed (Chapter 5). The early estimate was that, on average, refinery wastewater contains approximately 1 ppb total mercury, but the precise range and mean were not obtained from a statistical sampling. This amount is consistent with the removal of the majority of hydrophilic mercury species in the desalter.

Table 6-2 – Total Mercury in Desalter Sludge
(U.S. EPA 1996)

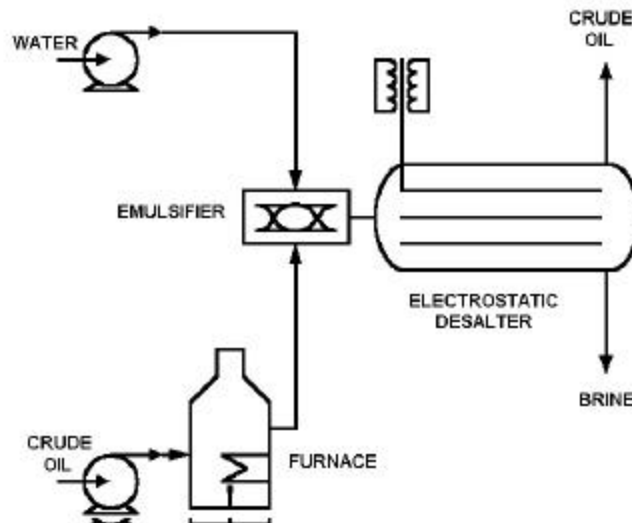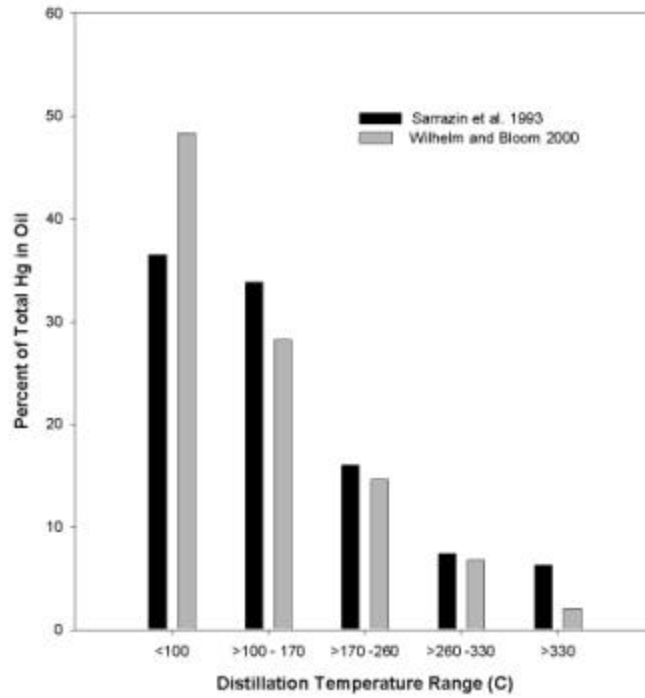| Refinery	THg (ppm)
1	41
2	4
3	39
4	0.01

Figure 6-2 – Crude Oil Desalting

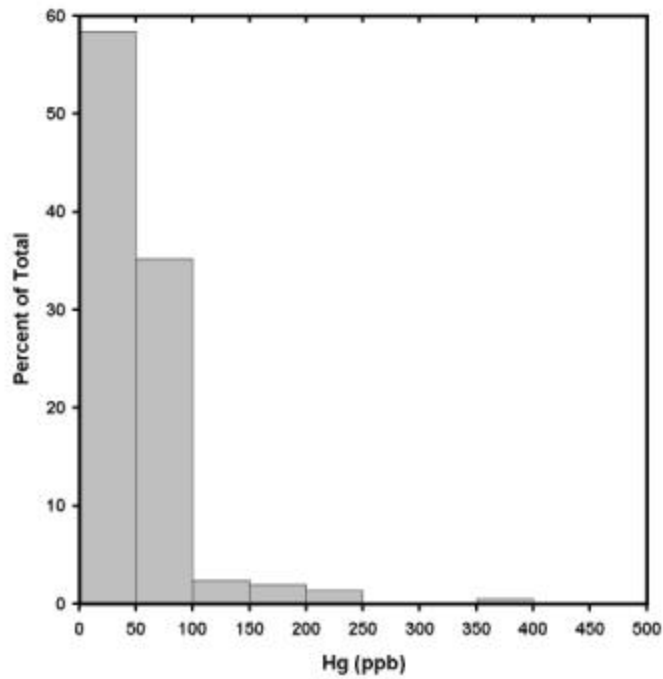**Figure 6-3 – Mercury (Total) in Distilled Products**

Figure 6-4 – Distribution of Mercury (Total) Concentrations in Petroleum Coke

Gas Processing

The fate of mercury in gas processing is easier to predict because the process is simpler and less inclined to cause transformation of the species initially present. Gas is subjected to primary separation, treatments to remove contaminants and cryogenic separation or liquefaction. Distribution of mercury compounds in the primary phase separation process has been discussed, however, produced fluids from most gas wells typically contain lesser amounts of suspended and ionic mercury compounds than those found in crude oil of similar total mercury content (on a mass percentage basis). Some heavy condensate feeds to gas separation processes can contain significant amounts of suspended and oxidized forms, but still less than that seen in crude oil on a percentage basis.

In treatments for contaminants, the elemental mercury in gas will dissolve in the liquid glycol in glycol dehydrators and increase in concentration until equilibrium is reached. Some portion of elemental mercury in a glycol dehydrator is removed in the regen cycle. If the concentration of mercury in gas is sufficiently high, elemental mercury vapor can condense in the glycol reboiler vapor condenser. In amine systems, it is postulated that mercury may react with the H_2S scavenged by the amine and thus be removed from the process as HgS in the amine filters.

The separation process for gas products is typically cryogenic and provides the opportunity for condensation (precipitation) of elemental mercury, if the concentration is sufficiently high to allow this to occur. Such condensation is reported for gas separation plants having mercury in feeds in excess of approximately 10-20 ug/m^3.

LNG plants and many gas separation plants employ mercury removal systems to minimize problems associated with mercury condensation and mercury attack of heat exchangers. Mercury attack of aluminum heat exchangers caused numerous failures in the 1970's and 1980's but newer process designs, the use of mercury removal technology and new heat exchanger designs have succeeded in mostly eliminating the problem (Wilhelm 1994).

Mercury Removal Systems

One approach to minimize the amount of mercury that appears in effluents from petroleum processing operations is to remove the mercury from upstream hydrocarbons. Mercury removal close to the production well, in concept, would eliminate downstream problems.

Unfortunately, removal systems for mercury are ill suited to treating unconditioned hydrocarbons due to the fact that raw produced hydrocarbons contain numerous contaminants that interfere with the successful operation of mercury removal systems. Offshore production facilities are not designed, nor intended, to have the capability of mercury removal beds as part of the primary treatment (dehydration) system. Mercury removal systems are large and, more importantly, heavy which precludes their use offshore in most cases (Wilhelm, 1999).

Mercury removal systems are most often located at gas processing facilities that produce the feedstock materials for downstream chemical manufacturing plants. The removal systems, if properly designed and operated, can eliminate mercury from plant products and thus substantially reduce the impact of mercury on downstream plants. Gas processing plants vary considerably in design depending on the composition of the feed and the market for products. Plants are optimized to make particular products such as LNG, LPG, NGL, ethane, propane, butane and/or C5+ depending on the feed to the plant and the consumer market. There is less incentive to remove mercury at plants configured to make fuels than for plants designed to produce feedstocks for chemical manufacture.

The principal method to prevent mercury contamination at processing facilities is to remove mercury from the various feeds to the plant. Several commercial processes (see Table 6-3) are available for this purpose. Mercury removal sorbent beds or treaters are employed in which the removal material is specially designed for the particular application. Sorbents consist of an inert substrate (support) onto which is chemically or physically bonded a reactive compound that reacts to form a stable mercury compound that is retained by the sorbent bed.

The substrates (supports) are designed to selectively adsorb mercury compounds but do not react with them directly; the reactant compound is designed for this task. Most supports (activated carbon, aluminas, zeolites) are porous with the pore size carefully controlled to selectively adsorb mercury and to avoid adsorption of high molecular weight hydrocarbons. For efficient mercury removal bed function, the adsorptive capacity of the support is equal in importance to the reactive nature of the mercury-scavenging compound.

Some commercial mercury removal systems are targeted at gas phase treatment and some are targeted at liquids. Gas phase treatment systems primarily consist of sulfur impregnated carbon, metal sulfide on

carbon or alumina, and regenerative molecular sieve (zeolite) onto which is bonded a metal that amalgamates with mercury.

In a gas treatment system that utilizes sulfur-impregnated activated carbon (Nishino et al. 1985, Matviya et al. 1987), mercury (Hg^0) physically adsorbs and then reacts to form non-volatile mercuric sulfide. The reaction between Hg^0 and sulfur is a redox reaction in which mercury is oxidized and sulfur is reduced. Because the percentage amount of organic mercury in gas is usually very low, the efficiency to react with organic mercury is less critical. Sulfur is soluble in liquid hydrocarbon and is removed by contact with liquid hydrocarbon rendering it ineffective. Sulfur/carbon sorbents are relatively less effective to treat heavy gas where some liquid condensation is possible.

Metal sulfide (MS) systems for gas (Sugier et al. 1978; Barthel et al. 1993) have the advantage that the metal sulfide is not soluble in liquid hydrocarbon and has less sensitivity to water. The MS systems are therefore more suited to moist feeds or those in which hydrocarbon carry over or condensation may occur. In a metal sulfide mercury removal system for gas having an alumina (Al_2O_3) support, mercury reacts with the metal sulfide directly, adsorption on the alumina substrate is less kinetically favored than for carbon and is not required for the reaction to occur.

Mol-siv sorbents (Markovs 1988) that contain metals (silver) selectively capture mercury by an amalgamation process. Mol-sieve treaters serve a dual role to dehydrate and to remove mercury. The mercury is released as mercury vapor upon heating in the regen cycle. The regen gas in these systems is treated with a conventional mercury removal bed to prevent sales gas contamination or a mercury condensation system is employed in the regen cycle.

Liquid removal processes consist of iodide impregnated carbon, metal sulfide on carbon or alumina, silver (on zeolite), mol-sieve and a two step process consisting of a hydrogenation catalyst followed by metal sulfide captation. The carbon/iodide system (McNamara, 1994) consists of an iodide-impregnated carbon having a large pore diameter. In the iodide system, mercury must oxidize to react with iodide. In theory the oxidation step is assisted by carbon, which provides catalytic assistance to the oxidation step. The metal sulfide and mol-sieve (Markovs, 1993) mercury removal systems for condensate are conceptually equivalent to those employed for gas.

Organic mercury (dialkylmercury) is more prevalent in hydrocarbon liquids. The ability of sorbents to react with the organic variety is less certain. One system addresses this situation by using a two-step process in which the first step is hydrogenation of the dialkyl mercury using a catalyst and hydrogen (Roussell et al. 1990; Cameron et al. 1993). The dialkyl mercury is converted to elemental mercury that is scavenged in the second step using a metal sulfide sorbent.

References

Barthel, Y., Cameron, C., and P. Sarrazin, 1993, Mercury removal from wet natural gas, Proc. of European Gas Processors Association, 10th Continental Meeting.

Bloom, N. S., 2000, Analysis and Stability of Mercury Speciation in Petroleum Hydrocarbons, *Fresenius' J. Anal. Chem.,* 366: 5.

Cameron, C., Courty, P., Boitiaux, J-P., Varin, P., and G. Leger, Method of Eliminating Mercury or Arsenic From a Fluid in the Presence of a Mercury/Arsenic Recovery Mass, U.S. Patent 5,245,106 (1993).

Edmonds, B., Moorwood, R., and R. Szczepanski, 1996, Mercury Partitioning in Natural Gases and Condensates, Proceedings: GPA European Chapter Meeting, London, UK (March).

Markovs, J., 1988, Purification of Fluid Streams Containing Mercury, U.S. Patent 4,874,525.

Markovs, J., 1993, Removal of Mercury from Process Streams, U.S. Patent 5,223,145.

Matviya, T., Gebhard, R., and M. Greenbank, 1987, Mercury Adsorbent Carbon Molecular Sieves and Process for Removing Mercury Vapor from Gas Streams, U.S. Patent 4,708,853.

McNamara, J., 1994, Process for Removal of Mercury From Liquid Hydrocarbon, U.S. Patent 5,336,835.

Nishino, H., Tanizawa, Y. and T. Yamamoto, 1985, Process for Removal of Mercury Vapor and Adsorbent Therefor, U.S. Patent 4,500,327.

Roussell, Courty, P. Boitiaux, J-P., and J. Cosyns, 1990, Process for Removing Mercury and Possibly Arsenic in Hydrocarbons, U.S. Patent 4,911,825.

Ruddy, D., 1982, Development Document for Effluent Limitations Guidelines, New Source Performance Standards, and Pretreatment Standards for the Petroleum Refining Point Source Category, EPA/440/1-82/014 (NTIS PB83-172569), Office of Water Regulations and Standards, Washington, DC.

Sarrazin, P., Cameron, C., and Y. Barthel, 1993, Processes prevent detrimental effects from As and Hg in feedstocks, *Oil and Gas J.*, (Jan. 25).

Sugier, A., and F. la Villa, 1978, Process for Removing Mercury from a Gas or Liquid by Absorption on a Copper Sulfide-Containing Solid Mass, U.S. Patent 4,094,777.

U.S. EPA, 1996, Waste Minimization for Selected Residuals in the Petroleum Refining Industry, Office of Solid Waste and Emergency Response, EPA/530/R-96/009 (NTIS PB97-121180), Washington, DC.

U.S. EPA, 2000, Unified Air Toxics Website: Electric Utility Steam Generating Units, Section 112 Rule Making, Office of Air Quality Planning and Standards, Research Triangle Park, NC. www.epa.gov/ttn/uatw/combust/utiltox/utoxpg.html

Wilhelm, S. M., 1994, Methods to Combat Liquid Metal Embrittlement in Cryogenic Aluminum Heat Exchangers, Proceedings 73rd GPA Convention, New Orleans, LA.

Wilhelm, S. M., 1999, Conceptual Design of Mercury Removal Systems for Hydrocarbon Liquids, *Hydrocarbon Processing,* 78(4):61.

Wilhelm, S. M., and N. S. Bloom, 2000, Mercury in Petroleum, *Fuel Proc. Technol.,* 63:1.

Table 6-3 - Mercury Removal Systems for Hydrocarbons

Reactant	Substrate	Complexed Form	Application
Sulfur	Carbon	HgS	Gas
Metal Sulfide	Al_2O_3; Carbon	HgS	Gas, Condensate
Iodide	Carbon	HgI_2	Condensate
Hydrogen, Metal Sulfide	Al_2O_3	HgS	Condensate
Ag	Zeolite	Ag/Hg amalgam	Gas, Condensate
Metal Oxide	Sulfided metal oxide	HgS	Gas, Condensate

Chapter 7
Mercury Emissions from Oil and Natural Gas Production and Processing

Mercury in produced hydrocarbons may escape to the environment by several avenues of egress. These avenues may be generally categorized as wastewater, solid waste streams and air emissions. Wastewaters originate in production operations in the form of produced water and in refining and gas processing as wastewater. Solid waste streams are generated in production, transportation and in refining. Air emissions originate from fugitive emissions from process equipment and from combustion, with combustion thought to be vastly dominant as a possible avenue by which mercury in oil and gas may be transferred from produced hydrocarbons to the environment.

It is useful, therefore, to examine the major pathways (solids, liquids and gas) and to further categorize mercury emissions by industry segment, meaning production, transportation, and processing systems. Mercury in combusted fuels is examined in detail as this is considered to be the dominant avenue of transfer of mercury in fossil fuels to the atmosphere based on the existing data and based on the analogy to coal combustion recently developed (U.S. EPA 1997a, Brown et al. 1999).

The industry distinguishes between upstream and downstream operations. The upstream category refers to primary production and whatever processing is necessary to place the produced fluids in the transportation system. The term downstream operations refers to refining and gas processing to produce salable products. Natural gas is transported exclusively via pipeline in the U.S. while crude oil is transported by a variety of ways with pipelines and tankers conveying the overwhelming majority.

Mercury Emissions to Water

The main wastewater streams that derive from petroleum production and processing are produced water from both oil and gas production and refinery wastewaters. Very minor amounts of water (relative to produced water and refinery wastewater) derive from gas processing and these are mainly water from separators at gas plants (essentially produced waters) and condensed water from dehydration. No wastewater streams originate from transportation systems other than the very small amounts that come from pipeline pigging operations and tanker ballast. The discussion that follows will concentrate on the major streams as mercury in water data are not reported for the minor sources.

Produced Water

Normal production operations of both crude oil and natural gas involve primary separation of water, gas and oil. Separated water (referred to as produced water when separated close to the well) is either discharged (to an ocean, lake or stream or evaporation pond) or re-injected (usually to the formation it came from). Re-injection is utilized to enhance oil recovery (EOR) or to comply with regulatory requirements stemming from environmental concerns.

Produced water is the largest waste stream in the oil and gas industry. Produced water varies greatly in composition and salinity, depending on the geologic source of the water, type of production, and the treatment of the water once brought to the surface. The salinity of produced water ranges from essentially fresh water to brines that are several times more saline than seawater. Produced waters typically have total dissolved solids (TDS) concentrations between 2,000 to 300,000 mg/L (natural seawater is about 34,000 mg/L). The predominant cation in produced waters is sodium and chloride is usually the predominant anion.

Some states allow surface discharge of produced water, but many do not. Produced water originating on offshore platforms can be discharged to the ocean unless the platforms are located in sensitive areas or

the water is unusually hazardous due to a particular characteristic (salinity, hydrocarbon content, toxicity). In sensitive coastal areas of the U.S., produced water is closely regulated with permit requirements that severely limit options for discharge thus necessitating treatment or re-injection.

The U.S. EPA establishes controls on produced water discharges into U.S. waters through provisions of the Clean Water Act (CWA; 33 U.S.C. 1251) that established the National Pollutant Discharge Elimination System (NPDES). EPA issues effluent limitation guidelines (ELGs) and discharge permits for produced water discharged to waters under Federal jurisdiction. A permit is required for discharge of water both onshore (issued by individual States) and to offshore waters under Federal or State jurisdictions. Granting of a permit is contingent on testing to criteria (including metals) set by the various States but which are based on the human and aquatic life criteria contained in the CWA and Safe Drinking Water Act. Application of the Best Practicable Control Technology for waters exceeding specifications is required and applied on a case-by-case basis.

Only limited data are available concerning mercury in produced waters and essentially none concerning speciation. Produced waters may contain suspended HgS, elemental Hg^0 and/or oxidized forms but the relative amounts in any produced waters are not reported relative to the forms that occur in co-produced hydrocarbons. HgS and Hg^0 are the dominant forms found in produced water associated with gas production in the Gulf of Thailand (Frankiewicz and Tussaneyakul 1997). Gas condensates originating in the Gulf of Thailand contain between 100 and 1000 ppb total mercury (mostly elemental).

Total mercury concentrations in U.S. produced waters were only recently reported as, prior to approximately 1990, analytical methods were insufficient to detect the low ppb and ppt levels typically now found. Tables 7-1 and 7-2 summarize the available data. Petrusak et al. (2000) has estimated the amounts and fate of waters produced onshore for the year 1995. Approximately 18 billion barrels of water were produced by onshore U.S. oil and gas wells in 1995. 71 percent of this water was re-injected for EOR and 21 percent was disposed of in Class II injection wells. Of the remaining 8 percent (0.23 trillion liters), 3 percent was discharged, 2 percent was put to beneficial use and 3 percent was disposed of using miscellaneous methods (public water treatment works, evaporation ponds, etc.).

Waters produced offshore are more likely to be discharged to the ocean unless the platform is located in a sensitive coastal area. Approximately 2 billion barrels of water are produced annually in offshore

areas under Federal and State jurisdiction (about 1 billion bpy in the Gulf of Mexico and 1 billion bpy elsewhere, Stephenson 1992). About 70 percent of the offshore produced water is discharged to the ocean (approximately 0.3 trillion liters annually).

At this point in time it is not possible to assign either a mean or range to mercury concentrations in produced and discharged water. It may be possible eventually to obtain such a mean amount by accessing the NPDES databases of the individual states that require reporting of mercury concentrations. As discussed previously, the analytical methods recently adopted by the U.S. EPA (EPA Method 1631, U.S. EPA 1999) are slowly being applied under statute and it may be some time before sufficient data are available to obtain an accurate estimate of the amount of mercury in produced water that is discharged to the environment. The mercury species present in produced waters are unknown but likely include higher percentages of suspended forms (HgS) and ionic forms than the produced crude oil.

Applying an estimated mean mercury concentration in produced water of 1 ppb to 0.5 trillion liters (0.2 onshore and 0.3 offshore yearly), one obtains the result that on the order of 250 kg mercury may enter the aqueous environment annually from waters associated with U.S. oil and gas production.

Refinery Wastewater

The chemical compositions of refinery wastewaters vary widely, as do the volumes of water (per barrel of oil processed) produced by refineries. Major water compositional differences stem from process configuration (products produced) and from the type of crude oil that is processed (high sulfur crude, sweet crude). The wastewater that enters water treatment systems at refineries is a composite of water discharges from individual processing units that differ in type and function. Water streams from process units are differentiated and categorized as waters that contact hydrocarbons (including condensed steam from stripping) and cooling waters that typically do not contact hydrocarbons directly but may contain some hydrocarbon contamination from leakage.

The following post-secondary treatment wastewater characteristics are typical (API 1977, 1978, 1981). Additional details are contained in Table 7-3.

- 1-10 MMgal/D secondary treatment process wastewater
- Total mercury at up to 1 ppb, species unknown (Ruddy 1982)
- Residual petroleum compounds present (10 - 40 ppm Total Organic Carbon typical)

44

- 10-100 ppb each of any trace metal(s): Cu, Zn, Pb, V, Se, Ni, Cr, Fe, As, etc.
- Ammonia (1 - 20 ppm), cyanide, chelating agents possibly present
- Total Suspended Solids at 10-30 ppm

Speciation of mercury in refinery wastewater is largely unknown. Post-biological treatment waters from municipal sewage treatment (similar in process to refinery biological water treatment) generates mercury compound speciation such that less than 5 percent (of the total mercury concentration) exists as monomethylmercury, less than 0.01 percent as dialkylmercury, less than 0.1 percent as Hg^0, possibly 10-30 percent suspended particulate Hg, less than 10 percent labile Hg(2+), and between 60 and 90 as organochelated Hg(2+). The concentration of total mercury in effluents from (municipal) sewage treatment facilities is in the range of 5-20 ng/L (Bloom and Falke 1996).

The mean and range of mercury concentration in refinery wastewater cannot be stated with certainty. Very little information is available in the published literature that speaks directly to this issue. The EPA study of refinery effluents from the early 80's (Ruddy 1982) provides a mean close to 1 ppb but the methodology to arrive at this number is poorly documented. The advances in mercury analysis procedures that have occurred since that time (U.S. EPA 1999) may allow a more accurate estimate in the future, but now it can only be stated that the mean is likely less than 1 ppb and that the level varies from refinery to refinery and with the amount of mercury in processed crude.

The amount of refinery wastewater discharged to the environment (rivers, lakes and oceans) is approximately 1.5 billion barrels yearly (for year 1998, U.S. DOE 2000, U.S. EPA 1996). Applying the 1982 EPA mean value of 1 ppb (max.) to this amount yields approximately 250 kg as an upper limit to the total amount of mercury discharged in refinery wastewater.

Table 7-1 – Mercury in Produced Waters

Location		Discharge Rate (10⁹ L/y)	THg (ppb)	Reference
Gulf of Mexico	Ocean	0.64	<0.010	Ray 1998
Gulf of Mexico	Ocean	0.40	<0.010	Ray 1998
Gulf of Mexico	Coastal LA	1.74	0.007 - 27; Mean 7.08; SD 11.26	Meinhold et al. 1996
North Sea	Brent		<3	Jacobs et al. 1992
North Sea	Northern		<3	Jacobs et al. 1992
North Sea	Central		<3	Jacobs et al. 1992
North Sea	UK		<1	Jacobs et al. 1992
North Sea	Dutch		4	Jacobs et al. 1992
Gulf of Mexico	Coastal	140	<0.01 – 0.2, n = 37	Trefry et al. 1996

Table 7-2 - Mercury Concentrations in Produced Water
(Southern CA, year 1990)
(Raco 1993)

Platform	No. Samples	Volume (10^6 L/y)	THg (ppb)
Elly	2	1	<1
Edith	1	176	<1
Hogan	2	225	<1
Hillhouse	1	361	<1
A	2	1184	0.5
B	2	726	2.5
C	2	836	<1
Habitat	1	21	<1
Irene	4	608	0.5
Grace	2	139	1
Gail	5	273	1.6
Gilda	2	704	<1
		5,254	

Data from National Pollutant Discharge Elimination System discharge monitoring reports submitted to US EPA Region 9, San Francisco.

Table 7-3 – Pollutant Concentrations for a Typical Refinery Wastewater

Parameter	Value (mg/L)	Basis
Trace Metals		
Arsenic	0.0050	API (1978; 1981)
Chromium	0.0680	API (1978; 1981)
Copper	0.0180	API (1978; 1981)
Mercury	0.0009	Ruddy (1982)
Nickel	0.0100	API (1978; 1981)
Selenium	0.0172	Ruddy (1982)
Zinc	0.0610	API (1978; 1981)
Trace Organics		
Benzene	0.0005	API (1978; 1981)
Toluene	0.0005	API (1978; 1981)
Ethylbenzene	0.0008	API (1978; 1981)
Acenaphthene	0.0011	Ruddy (1982)
Benz[a]anthracene	0.0004	API (1978; 1981)
Benzo[a]pyrene	0.0007	API (1978; 1981)
Chrysene	0.0003	API (1978; 1981)
Phenanthrene	0.0002	Ruddy (1982)
Pyrene	0.0005	API (1978; 1981)
2,4-Dimethylphenol	0.0022	API (1978; 1981)

Mercury Emissions to Air

The primary opportunities for atmospheric emissions of mercury in oil and gas production and processing operations are fuel combustion (discussed in subsequent Sections), mercury in fugitive emissions and gas flares at primary production operations.

The amount of gas that is flared annually in the U.S. is approximately 7 billion cubic meters (for year 1996, U.S. DOE 1999) and the trend is downward. Flared gas typically originates from gas co-produced with oil production in situations where economics dictate that flaring is less expensive than collection and transport. The mercury concentration in flared gas is not reported. If one assumes flare gas contains on the order of 1 ug/m^3 then the annual amount emitted in flared gas is on the order of 7 kg. This order of magnitude estimate does not include mercury in flares at refineries. In most refineries, gas used to regenerate catalysts (some catalysts collect mercury and release it when regenerated) is sent to flares and may contain higher amounts of mercury than typical for other types of gas flares.

Approximately 9 billion m^3 of methane is emitted annually by the gas industry (Kirchgessner et al. 1997). Approximately 90 percent of emitted gas is non-combusted methane and about 10 percent compressor discharge. The concentration of mercury in wellhead natural gas is likely higher than in pipeline gas by a factor of 2-3 based on the distribution of mercury in gas processing (Wilhelm 1999). Assuming an upper limit of 1 μg/m^3 mercury in wellhead gas, the amount of mercury in fugitive natural gas emissions is on the order of 10 kg.

Approximately 1 million metric tons of methane (equivalent) are estimated to be emitted from petroleum production, transportation and processing (year 1999, U.S. DOE 1999). 90 percent of such emissions are associated with production and about half of the production related amount is from vents on oil tanks. While the amount of mercury in such emissions is not known, a rough estimate is possible. The distribution of mercury in oil to vented gases can determined by Henry's law. Henry's constant for mercury in oil is the solubility divided by the vapor pressure (2 ppm/25 mg/m^3). The upper limit amount of mercury in 1 million metric tons (1.5 billion m^3 methane) would be no greater than approximately 185 kg if the mean mercury in oil concentration is 10 ppb.

The Clean Air Act (CAA; 42 U.S.C. 85) requires the U.S. EPA to develop national emission standards for hazardous air pollutants (NESHAP) for source categories. The CAA implements NESHAP via requirements for maximum achievable control technology (MACT). Mercury is a listed hazardous air pollutant (HAP) under Section 112 of the CAA. The source categories that are of interest to petroleum producers and refiners are boilers, certain refining process units and miscellaneous combustion sources.

NESHAP for petroleum refineries apply to catalytic cracking units (CCU), catalytic reforming units (CRU), and sulfur plant units (SPU). Of these, only process vents associated with CRU catalyst regeneration are scrutinized relative to mercury. While EPA has identified particulate metals (PM = antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, and nickel) as HAPs from CRU process vents, mercury is not included because it is volatile in atomic form and not easily controlled by existing particulate control technology. EPA, as of 1998, concluded that because mercury is not well controlled by PM air pollution control devices (ESPs as well as PM scrubbers), the MACT floor for Hg in CCU process vents is determined to be no control for both new and existing units. Data are not available to estimate mercury emissions from either CCUs or CRUs.

Metal emission factors are used to estimate air pollutant emissions to the atmosphere of volatile or particulate metals or metal compounds (U.S. EPA 1997c). They relate the quantity of pollutants released from a source to an activity associated with those emissions. For metals in refinery unit processes, emission factors are usually expressed as the weight of pollutant emitted divided by a unit weight or volume of the activity emitting the pollutant (e.g., pounds of mercury emitted per gallon of fuel oil burned). Emission modification factors are used to estimate a source's emissions by the general equation:

$$EMF = A \times EF \times [1-(ER/100)]$$

where:

EMF = emissions modification factor,
A = activity rate,
EF = uncontrolled emission factor, and
ER = emission reduction efficiency in % for pollution control.

California Assembly Bill 2588 (entitled the Air Toxics Hot Spots Information and Assessment Act of 1987) required petroleum processing facilities in California to inventory their air emissions of designated toxic materials (including mercury) for the purpose of assessing the health risks to surrounding communities.

Data for compliance with the California statute are compiled and reported by the American Petroleum Institute and Western States Petroleum Association (API and WSPA 1998). Emission factors were developed for externally fired boilers and heaters, internal combustion engines, gas turbines and direct-fired processes. The test method used for mercury involved isokinetic collection of particulate and gaseous mercury in potassium permanganate ($KMnO_4$) solution. In the method employed, the collected mercuric form (produced by oxidation by the permanganate) was reduced to elemental Hg and then sparged from the solution into an optical cell and measured by atomic absorption spectrometry.

Table 7-4 summarizes the emission factors reported in the API/WSPA study (1998). The compiled list represents data from ongoing activities and includes only a small fraction of the unit operations and process systems that are potential sources. The California program that examined air toxic emissions from refineries adopted priorities based on suspected sources for a large number of pollutants. Thus, although mercury was examined as a part of the program, it was (and is) not necessarily the primary focus or priority. The data do provide some clues and insights into certain refinery operations and the magnitude of their mercury emissions.

The asphalt blowing process polymerizes asphaltic residual oils by oxidation with air. The objective is to increase the melting temperature and hardness of the asphalt and thus achieve improved properties depending on the type of asphalt product (road materials, construction materials, roofing material, etc) desired. The process involves blowing heated air through the oils in a batch or continuous process to oxidize the polycyclic aromatic compounds that comprise the majority of the asphaltic material. The process operates at approximately 400-450^0 C and thus may partially volatilize HgS. The distribution of mercury compounds emitted in asphalt blowing is unknown.

Process heaters or furnaces are used to heat feed materials to the required reaction or distillation temperature levels. The fuel burned may be still gas, natural gas, residual or distillate fuel oils, or combinations, depending on economics, operating conditions, and emission requirements. Assuming mercury in distillate and residual fuel oils is the elemental form, then one would expect that the emitted mercury species would be the elemental form and mercury oxides, the relative percentage of each depending upon furnace type and efficiency.

Coke calcining is a high temperature pyrolysis treatment of raw petroleum coke with the primary objective to produce coke properties suitable for a particular end use. In the calcining process, moisture and volatile material are removed and carbonization and aromatization processes that started in the coker are completed. The calciner can be heated by a variety of fuels and to a variety of temperatures depending on product properties but typically in the range of 400 to 500^0 C. These temperatures are sufficient to cause partial volatilization of HgS in coke.

In Table 7-4, the mercury emissions factors are calculated from crude fired steam generators in three tests using 3 crude sources. One source has elevated mercury (5×10^{-3} lb/Mgal, 700 ppb) while the other two were much lower (5×10^{-5}, 9×10^{-6} lb/Mgal; 7 ppb, 1 ppb).

Some additional evidence for fuel oils is available from U.S. EPA studies (U.S. EPA 1998) of mercury emission factors for utility boilers. EPA measured mercury emission factors for several furnace types used by utilities. In this study, U.S. EPA (1998) cited mercury in residual fuel oil as 0.6 lb per trillion Btu based on analysis of 4 samples of fuel oil (mean standard deviation = 0.3). The conversion factor applied was 150,000 Btu/gallon of density 8.2 lb/gallon, thus yielding a mean mercury concentration of approximately 10 ppb.

Table 7-4 - Mercury Emission Factors for Refinery Processes
(API/ WSPA 1998)

Process	Fuel	APC [1]	Emission Factor	Units	No. of Tests	Hg [2]	Units
Asphalt Blow	Gas	TO	9.00E-03	lb/MMcf	1	146 [3]	$\mu g/m^3$
Boiler	Fuel Oil	None	1.03E-05	lb/Mgal	1	1.4	ppb
Boiler	Still Gas	None	3.23E-04	lb/MMcf	1	5.2	$\mu g/m^3$
Boiler	Still Gas	SCR	3.23E-04	lb/MMcf	1	5.2	$\mu g/m^3$
Coke Calcining	Gas	SD/FF	4.63E-05	lb/ton coke	1	23	ppb
Heater	Fuel Oil	None	1.72E-05	lb/Mgal	1	2.4	ppb
Heater	Still Gas	DeNOx	2.02E-04	lb/MMcf	1	3.3	$\mu g/m^3$
Heater	Still Gas	None	2.02E-04	lb/MMcf	1	3.3	$\mu g/m^3$
Heater	Still Gas	SO2 Scrub	2.02E-04	lb/MMcf	1	3.3	$\mu g/m^3$
Steam Generator	Crude	None	2.19E-03	lb/Mgal	3	327	ppb
Steam Generator	Crude	SO2 Scrub	2.19E-03	lb/Mgal	3	327	ppb
Turbine	Still Gas	SCR/COC	4.63E-03	lb/MMcf	2	75	$\mu g/m^3$
Turbine	Still Gas	COC	2.15E-02	lb/MMcf	1	348	$\mu g/m^3$

(1) APC – air pollution control; COC - CO Oxidation Catalyst; DeNox (SNCR) - Selective Non-Catalytic NOx Reduction; FF - Fabric Filter; SCR - Selective Catalytic NOx Reduction; SD - Spray Dryer; TO - Thermal Oxidizer.
(2) Calculated concentration in the fuel assuming the emission ratio (THg out/ THg in) is 1.
(3) Calculated Hg concentration in air emitted to the atmosphere.

Mercury Emissions Via Solid Waste Streams

Under the Resource Conservation and Recovery Act (RCRA; 42 U.S.C. 321), materials containing mercury or mercury compounds are regulated as hazardous solid waste if they meet the regulatory definition of solid waste and the definition of hazardous waste. The hazardous category is achieved if the material exhibits either a defined characteristic or is specifically listed by EPA as hazardous. At present, U.S. EPA does not list waste streams from exploration, production or refining as hazardous according to any mercury content criteria.

Solid wastes directly associated with exploration and crude oil or natural gas production are exempted from regulation as hazardous wastes. The exempted categories include drilling fluids and other wastes directly related to production. For this reason, such wastes are infrequently scrutinized for metals content and data are scarce upon which one might estimate the totals for this category.

Wastes are designated as characteristically hazardous based on the concentration of mercury in waste leachate as determined by the Toxicity Characteristic Leaching Procedure (TCLP). Refinery solid waste streams are routinely examined using TCLP for metals leachability characteristics and treated according to

RCRA requirements. In general, solid waste streams from refineries are not characteristically hazardous due to mercury content. RCRA data on TCLP are not typically reported unless the waste stream does not pass and then they are reported under TRI (see discussion below).

Drilling wastes primarily consist of the extracted cuttings and drilling mud from the boreholes of exploratory wells (also workovers and injection wells). The drilling industry generated approximately 24 billion liters of such waste in 1995 (API 1995). Petrusak et al. (2000) reports statistics for drilling wastes produced onshore in the U.S. About 13 percent of such wastes are re-injected, 47 percent are evaporated on site and most of the remainder is buried on site.

Data on mercury content of drilling wastes are not generally reported but TCLP test results typically do not identify this category of waste as characteristically toxic due to mercury content. The reason for this fact is that subterranean mercury (as would be in the cuttings from drilling operations) is found almost exclusively as HgS or as a substitutional element in minerals (mostly pyrites). In addition most of the mercury in drilling muds comes from the mineral ingredients (barite) used to make the mud, not from the drill cuttings, except in rare situations. In these mineral forms mercury is not water soluble and thus not extractable by TCLP.

Mulyono et al. (1996) reported analysis of four water-base drilling muds (Indonesia) as having mercury concentrations between 144 and 2141 ppb (mean 750 ppb). These concentrations were for fresh mud and the concentrations did not change after use. Approximately 20 percent of the mercury was nitric acid extractable.

Under the Emergency Planning and Community Right-to-Know Act (EPCRA; 42 U.S.C. 116), companies that manufacture, process, or use toxic chemicals must report annually a Toxic Release Inventory (TRI) to both the U.S. EPA and the appropriate state agency. Mercury and mercury compounds are included in the list of more than 650 chemicals that must be reported. Although petroleum production is generally excluded, refineries are not if they process crude oil containing more than the threshold reporting amount. Prior to this year (2000) the threshold was sufficiently high to exclude reporting of mercury in crude oil and refined products.

In 1997, the U.S. EPA expanded the types of companies that report TRI to include electric utilities and petroleum bulk terminals and stations (amongst others). In 1999, under EPA's PBT Chemicals Initiative, EPA created a new PBT group within TRI, and then significantly modified the TRI reporting requirements for this group of chemicals by lowering the thresholds that trigger reporting. The final rule (EPCRA, Section 313) criterion for PBTs was promulgated this year (2000) and defines the threshold reporting amount for mercury as 10 pounds.

In the new rules promulgated for 2000 for PBT pollutants, EPA also eliminated the de minimis exemption of 0.1 percent that previously excluded reporting of trace constituents of chemical feedstocks. Thus refineries, bulk terminals and some other petrochemical processors must now report mercury if it exceeds the yearly threshold amount of 10 pounds. Given the new requirements it is likely that it will soon be possible to estimate the contribution of mercury in solid waste from petroleum and gas production and processing to the global burden based on a better statistical database. At this point in time it is not possible to accomplish this task with any confidence as to accuracy.

Mercury in Crude Oil

Crude oil contains both dissolved and suspended mercury compounds and, although analysis for total mercury in crude oil yields the sum of both forms, the concentration of suspended forms that is obtained from sampling crude oil is highly dependent on the location that samples are taken in the production and refining process. Furthermore, given that the fates of suspended forms (HgS) and dissolved forms are different, the concentration of each is important to predicting the fate of mercury in a refinery.

Filby and various colleagues (Shah, Filby and Haller 1970, Filby and Shah 1975, Hitchon, Filby and Shah 1975, Hitchon and Filby 1983) measured mercury in crude oils using neutron activation analysis. This early work was directed to associating chemical characteristics of crude oil with geologic origin for exploration purposes.

Shah et al. (1970) report concentrations for 10 crude oils as shown in Table 7-5. The procedure involved pre-filtration (1 μm pore size) of the oil; hence mercury existing as particulates above 1 μm was not measured. One of the crude oils examined by Shah (California Cymric) was unusual in having had a total mercury concentration above 10 ppm. This crude was popularly analyzed during the 1970's because the high mercury concentration was advantageous to analytical method development and thus it became popular amongst analysts in the early studies.

Shah's data are the basis for U.S. EPA early estimates (Brooks 1989) of ppm levels for the mean amount of mercury in crude oil. The exercise (by EPA) to arrive at a mean amount involved averaging the mean or median of the range of concentrations from the early studies of Shah and Filby. The inclusion of Cymric in all of the early compilations provided a disproportionate emphasis of this anomalous source.

Filby and Shah (1975) report crude oil data for four samples identified by country of origin (see Table 7-6). It is not known if the California oil analyzed by Filby and Shaw is Cymric, but likely so. Hitchon and Filby (1983) measured total mercury in 86 crude oils (and two tar sands) from Alberta, Canada. Thirty-seven samples had mercury concentrations below the detection limit (DL) of 2 ppb. Forty-nine samples were above DL with a mean of 50.0 ppb (maximum concentration of 399 ppb). The data are summarized in Table 7-7. The average of 86 crude oils (22 ppb) was calculated by assigning a value of half the DL to those exhibiting total mercury (THg) below the detection limit.

Musa et al. (1995) reported total mercury in Libyan crude oils to be in the range of 0.1 to 12 ppb (Table 7-8). Liang et al. (2000) reported the mean concentration of mercury in 11 crude oils (source not identified) as 4 ppb (range = 1 to 7 ppb). Magaw et al. (1999) reported data on 26 crude oil types purchased by U.S. west coast refineries as less than 10 ppb (the detection limit of the CVAA instrument). Magaw et al.'s data (Table 7-

9) span the major U.S. crude streams and include both domestic and imported crudes. Magaw et al. report one California crude oil (Cymric) as having 1.5 ppm THg.

Bloom (2000) found total Hg in unfiltered crude oils ranging between sub-ppb levels to over saturation (several ppm, see Table 7-10). The mean concentrations for total mercury in crude oil (1.5 ppm) that Bloom reported is much higher than other reported data. This is due to the fact that the data set contains a large number of samples from one field that presented processing difficulties and hence was extensively analyzed. Bloom's reported mean is derived from the number of samples analyzed in his laboratory and not based on crude oil sources. The crude oil samples in the upper half of Bloom's data come mostly from one field in South America producing less than 30,000 bpd. The mean of the lower half of Bloom's data for crude oils is 1 ppb.

Much of Bloom's condensate data reflects samples from the Gulf of Thailand. These Asian condensates are not processed in the U.S. but are prevalent in reported data (Tao et al. 1998, Shafawi et al. 1999, Bloom 2000) because they are problematic to petrochemical manufacture. The mean concentration of the lower half of condensate samples that were analyzed in Bloom's laboratory was reported as approximately 20 ppb.

The New Jersey Department of Environmental Protection Mercury Task Force, in a recently completed study of oil processed in New Jersey refineries, reported mercury concentrations in crude oil compiled in Table 7-11 (Morris 2000). The reported data identified crude oil origin. The number of samples

analyzed and standard deviations were not reported. According to Morris' data, the mean amount of mercury in crude oil imported to the U.S. East Coast refineries is less than 5 ppb.

Environment Canada (2000) has compiled a database on oil properties that includes metals analysis using ASTM method D 5185 (Inductively Coupled Plasma Atomic Emission Spectrometry; ICP-AES). Table 7-12 compiles the reported mercury concentrations in the EC database. The ICP-AES method has a detection limit for mercury of 15 ppb.

Duo et al. (2000) reports analytical data for 8 crude oils that are representative of 50 percent of all crude oil processed in Canada. The exact origins of the crude oils were not divulged but many of these same oils are also processed in the U.S. The method used was a variation of digestion/CVAA. The method had a minimum detection limit for mercury of 2 ppb. Most of the data are below this amount as shown in Table 7-13.

Total mercury concentrations in crude oil (summarized in Table 7-14) cannot be statistically treated at present, in part because of the uncertainties in the analytical data, and also due to the fact that much of the data reported in the literature are not well documented as to origin. While the majority of recently reported data are less than 20 ppb total mercury there are exceptions in the ppm range, notably Bloom 2000, Shah et al. 1970 and Magaw et al. 1999 (one sample from California). The data for condensates are generally higher than for crude due to a preponderance of data on Asian condensates that are more frequently analyzed due to their difficulty in processing.

Table 7- 5 – Total Mercury Concentrations in Crude Oil by NAA
(Shah et al. 1970)

Source	Amount (ppb)	SD (ppb)	Notes Detection Limit 4 ppb
California	114	2.8	
California	81	1.9	
California	88	3.0	
California	29,688	103.9	Cymric
California	78	2.4	
Libya	2,079	11.9	
Libya	62	5.1	
Libya	75	1.7	
Louisiana	23	1.8	
Wyoming	77	3.4	
Mean	**3,200**		**Range 23 – 30,000 ppb**

Table 7-6 – Total Mercury Concentrations in Crude Oils by NAA
(Filby and Shah 1975)

Source	THg (ppb)	Notes
California (Tertiary)	23,100	5 Replicates; Mean = 21,200; S.D. 0.36
Venezuelan (Boscan)	27	
Alberta (Cretaceous)	84	
Libya	<4	Detection Limit 4 ppb
Mean	**5,803**	

Table 7- 7 - Total Mercury Concentrations in Alberta Crude Oils
(Hitchon and Filby 1983)

Stratigraphic Era	Number of Samples	Number Above DL	High (ppb)	Low (ppb)	Mean [2] (ppb)	Median (ppb)	SD
Upper Cretaceous	21	11	202	<2 [1]	17.6	2.5	46.0
Lower Cretaceous	18	7	138	<2	17.1	1	38.1
Jurassic	3	0	1	<2	1	1	
Triassic	4	2	6	<2	3	2.5	2.4
Carboniferous	8	4	19	<2	5	1.5	6.3
Devonian	32	13	399	<2	36	1	92.5
Total	**86**	**37**	**399**	**<2**	**21.9**	**1**	**63.6**

(1) Detection limit = 2 ppb
(2) Calculated by assuming <DL = 1 ppb

Table 7-8 – Total Mercury Concentrations in Libyan Crude Oils
(Musa et al. 1995)

Field	THg (ppb)	SD (ppb)	Notes
Hamada	0.10	0.01	DL < 0.10
Sabah	2.1	0.23	
Brega	3.19	0.15	
Zella	0.314	0.024	
Aswed	0.368	0.025	
Oxyblend	3.353	0.39	
Agip	12.20	0.34	
Mean	**3.1**		**Range 0.1 to 12.2**

Table 7-9 – Mercury Concentrations in U.S. West Coast Crude Oils
(Magaw et al. 1999)

Region	Number of Samples	Range (ppb)	Mean (ppb)
Middle East	2	<10 [1]	<10
Africa	4	<10	<10
North America	11	<10 – 1,560	146
Asia	4	<10	<10
South America	4	<10	<10
North Sea	1	<10	<10
	26	**ND – 1,560**	**65**

(1) DL = 10 ppb

Table 7-10 - Total Mercury Concentrations in Crude Oils
(Bloom 2000)

Number of Samples	Range (ppb)	Mean (ppb)	SD	Notes
76	NR [1]	1,505	3,278	All
37	NR	1	1.49	Lowest 37 samples
39	NR	3,000	4,140	Top 39 samples

(1) NR – not reported

**Table 7-11 – Mercury Concentrations in Crude Oils
Processed in New Jersey Refineries
(Morris 2000)**

Type	Mean THg (ppb)	Field
Africa (Angola)	2.7	Palanca
Africa (Angola)	1.5	Soyo
Africa (Congo)	1.8	Kitina
Africa (Gabon)	1.8	Rabi
Africa (Nigeria)	1.0	Escravos
Africa (West)	3.2	
Africa (West)	1.5	
Arabia (Dubai)	2.9	Nemba
Canada (Newfoundland)	1.9	
Mexico	2.7	
Mexico	0.1	
Mixed	3.1	
North Sea	3.4	
North Sea	9.3	Ecofisk
North Sea	2.5	Gullfaks
North Sea	4.7	Norne
Saudi Arabia	5.7	
South America (Columbia)	12.3	
South America (Columbia)	2	
South America (Venezuela)	4.8	
South America (Venezuela)	5.1	
South America (Venezuela)	0.8	
South America (Venezuela)	6	
MEAN	**3.5**	**Range = 0.1 – 12.3**

Table 7-12 - Total Mercury Concentrations in Crude Oils
(Environment Canada 2000, Cao 1992)

Field Name	Location	THg (ppb)	Notes
Alberta Sweet	Canada (Alberta)	<15 [1]	Crude
Cold Lake Bitumen	Canada (Alberta)	<15	Bitumen
Transmountain Blend	Canada (Alberta)	<15	Crude
Terra Nova	Canada (Newfoundland)	<15	Crude
Bent Horn A-02	Canada (NWT)	<15	Crude
Taching	China	<15	Crude
Iranian Heavy	Iran	<15	Crude
Maya	Mexico	<15	Crude
Ninian Blend	North Sea	<15	Crude
Oseberg	North Sea	<15	Crude
Arabian Light	Saudi Arabia	<15	Crude
California (API 11)	U.S. (CA)	<15	Crude
Carpinteria	U.S. (CA)	<15	Crude
Dos Quadras	U.S. (CA)	<15	Crude
Hondo	U.S. (CA)	<15	Crude
Platform Irene	U.S. (CA)	<15	Crude
Port Hueneme	U.S. (CA)	<15	Crude
Santa Clara	U.S. (CA)	<15	Crude
Sockeye	U.S. (CA)	<15	Crude
W. Texas Intermediate	U.S. (TX)	<15	Crude
W. Texas Sour	U.S. (TX)	<15	Crude
Alaska North Slope	U.S. (AS)	<15	Crude
BCF 24	Venezuela	<15	Crude
Boscan	Venezuela	<15	Crude
Lagomedio	Venezuela	<15	Crude

(1) *DL = 15 ppb*

Table 7-13 - Mercury Content of Crude Oils Processed in Canada
(Duo et al. 2000)

Crude Oil	Concentration (ppb)		
	Minimum	Maximum	Mean
A	<2	<2	<2
B	<2	<2	<2
C	<2	<2	<2
D	<2	9	2
E	<2	<2	<2
F	<2	<2	<2
G	<2	<2	<2
H	<2	7	4
Mean			1.5

Table 7-14 - Summary of THg in Crude Oils and Gas Condensates

Reference	Type	Number of Samples	Range (ppb)	Mean (ppb)	SD	Notes
Shah et al. 1970	Crude Oil	10	23 - 29,700	3,200		U.S. and imports
Hitchon and Filby 1983	Crude Oil	86	<2 - 399	22	63.6	Canada
Filby and Shah. 1975	Crude Oil	4	<4 - 23,100	5,803		U.S. and imports
Musa et al. 1995	Crude Oil	6	0.1 - 12.2	3.1	4.2	Libyan
Tao et al. 1998	Crude Oil	1		<1		Asia
Magaw et al. 1999	Crude Oil	26	<10 - 1,560	65		West Coast Refineries
Bloom 2000	Crude Oil	76	NR[1]	1,505	3,278	Origins not reported
Liang et al. 2000	Crude Oil	11	1.6 – 7.2	4.4	1.0	Origins not reported
Morris 2000	Crude Oil	23	0.1 - 12.2	3.5		New Jersey Refineries
Cao 1992	Crude Oil	24	All <DL = 15	8		Canada and Imports
Duo et al. 2000	Crude Oil	8	<2 - 9	1.6	1.6	Canadian Refineries
Olsen et al. 1997	Condensate	4	NR	15		Origins not reported
Bloom 2000	Condensate	18	NR	3,964	11,665	Mostly Asian
Shafawi et al. 1999	Condensate	5	9 - 63	30	18.6	S.E. Asia
Tao et al. 1998	Condensate	7	15 - 173	40		Asian

(1) NR – not reported

Mercury in Refined Products

Recently reported data for mercury in refined products are compiled in Table 7-15. Bloom (2000) reported mercury in U.S. light distillates and fuel oil close to 1 ppb (46 samples). Liang et al. (1996) reported mercury in U.S. gasoline and diesel less than 5 ppb.

A statistical ensemble for mercury in refinery products exists in only one case. Total mercury in petroleum coke was reported as part of the U.S. EPA reporting requirements on fuel feeds to utility boilers (U.S. EPA 2000) and the mean is approximately 50 ppb (1000 data points, 2 million tons). The distribution of mercury concentrations in petroleum coke is shown in Figure 6.4.

Table 7-16 summarizes the data for mercury concentrations in fuel oil. The U.S. EPA emissions estimates used in the Report to Congress (U.S. EPA 1997a) are not well documented as to the origin of fuel oil concentration data. Details are discussed in the Section titled U.S. EPA Estimates.

Table 7-15 - Summary of THg in Refined Products

Reference	Type	Number of Samples	Range (ppb)	Mean (ppb)	SD	Notes
Liang et al. 1996	Gasoline	5	0.22 – 1.43	0.7	NR [1]	U.S.
Liang et al. 1996	Gasoline	4	0.72 – 3.2	1.5	NR	Foreign
Liang et al. 1996	Diesel	1	0.4	0.4	NR	U.S.
Liang et al. 1996	Diesel	1	2.97	2.97	NR	Foreign
Liang et al. 1996	Kerosene	1	0.04	0.04	NR	U.S.
Liang et al. 1996	Heating Oil	1	0.59	0.59	NR	U.S.
Bloom 2000	Light distillates	14	NR	1.32	2.81	U.S.
Bloom 2000	Utility fuel oil	32	NR	0.67	0.96	U.S.
Bloom 2000	Asphalt	10	NR	0.27	0.32	U.S.
Olsen et al. 1997	Naphtha	4	3 - 40	15	NR	
Tao et al. 1998	Naphtha	3	8 - 60	40	NR	Asian
U.S. EPA 2000	Petroleum Coke	1000	0 - 250	50	NR	U.S.

(1) NR – not reported, ND – not detected

Table 7-16 – Summary of Mercury Concentrations in Fuel Oils

Reference	Type	Number of Samples	Range (ppb)	Mean (ppb)	SD	Notes
Liang et al. 1996	Heating Oil	1	0.59	0.59	NR [3]	U.S.
Bloom 2000	Utility fuel oil	32	NR	1	0.96	U.S.
EPA 1997b	RFO 6	6	2 - 6	4 [1]		
EPA 1997b	DFO 2	3		<120 [2]		
EPA 1997a	Utility RFO			10		Measured
EPA 1997a	Commercial RFO/DFO			100		Calculated
EPA 1997a	Residential RFO/DFO			100		Calculated
EPA 1998	RFO	4		10	0.3	

(1)Median (2) Average (3) ND – not detected

Estimate of Mercury Emissions from Refineries

Wilhelm (2001 in press) constructed an estimate of mercury emissions from petroleum in the U.S. for the year 1999. The macro-analysis Wilhelm constructed (Table 7-17) considered the amount of mercury in crude oil, the distribution of mercury in the refining process as well as the combustion processes for the fuel products derived from crude oil. Wilhelm drew attention to the fact that analytical uncertainties and lack of information on sample origin obfuscate calculation of the mean concentration of mercury in crude oil and many refined products. The estimation model was constructed to provide a framework to identify major streams that require statistical definition as to mercury concentration.

In Table 7-17, estimates of the total yearly amount in major crude oil streams were calculated by multiplying the source crude feedstock amounts (year 1999; U.S. DOE 2000) by estimated mean concentrations of mercury reported for regional crude oil sources, both domestic and imported. Wilhelm based his estimates of the mean concentration of mercury in major crude streams on the recently reported data of Morris (2000), Environment Canada (2000) and Magaw et al. (1999) but acknowledged that the actual mean concentrations for crude oil from some sources could be an order of magnitude higher or lower than those used in Table 7-17.

The model predicted that, if the amount of mercury in crude oil (including condensates) processed in the U.S. is close to 10 ppb on average, then the total amount of mercury in crude oil is approximately 8,500 kg. Of this amount, approximately 7,000 kg resides in refinery products. Approximately 15 percent of refinery products (asphalt, lube oils, solvents) are not burned, leaving approximately 6,000 kg emitted to the atmosphere mainly by combustion (Wilhelm included refinery fuel combustion and assumed an emission factor of 1). The mean amount of mercury in U.S. transportation fuels (gasoline + diesel + jet fuel) had a major impact on the estimate (due to the fact that half of refined products fall into this category). The mean was considered to be no greater than 3 ppb based on the data of Liang et al. (1996) and data for other distillates.

Wilhelm estimated atmospheric emissions of mercury from refineries from a mass balance with other avenues of egress from refineries and assumed that combustion of fuels accounts for the primary path of emission. From energy usage at U.S. refineries (U.S. DOE 2000) compiled in Table 7-18 and the estimated total mercury concentrations in refined products, Wilhelm estimated the amount of mercury in air emissions from fuel burning at all U.S. refineries to be no more than approximately 1,500 kg/year or about 25 percent of the total amount of mercury in refinery combusted fuel products (6,000 kg/year). The higher percentage amount assigned to refineries appears to be due to the fact that the major fuels utilized at refineries (coke, still gas) have higher, on average, mercury concentrations than other fuel products. While the concentration of mercury in coke is known, the amount in still gas is much less certain.

Wilhelm argued that mercuric sulfide, originating as either suspended in crude oil or as the reaction product of other forms of mercury with sulfur in the refining process, is suspected to concentrate in the heavier fractions so the known amount in coke (50 ppb, U.S. EPA 2000) seemed reasonable (to Wilhelm) relative to the amount in lighter fractions. Even if mercury does not concentrate in coke, its concentration is known with some confidence and should serve as an upper limit to the amount in crude oil, given that light distillates exhibit relatively lower mercury concentrations (<5 ppb). It was argued that if elemental mercury in crude oil partitions to still gas, then the mercury concentration in light distillates would be expected to be elevated as well. Based on these arguments, it was concluded that mercury in distillates likely reflected the amount of volatile elemental mercury in crude oil and the amount in coke reflected the amount of HgS and other suspended forms.

Perturbation of the proposed model to a lower mean concentration for mercury in crude oil actually produces a somewhat better fit to the existing data. As an example, if one applies the origin specific concentrations in Table 7-11 (Morris 2000) to the volumes of oil that derive from known major import sources, then one may calculate with better confidence that 35 percent of all crude processed by U.S. refineries contains no more than approximately 1,500 kg total mercury as opposed to approximately 3,000 estimated by Wilhelm based on an upper limit of 10 ppb in crude oil. These calculations are shown in Table 7-19. The mean concentration applied to imported oil streams is rounded to 5 ppb due to the lack of statistical details.

Numerous major uncertainties exist in the cited analysis including the estimates for refinery wastewater and solid waste (previously discussed), data for mercury in refined products, and discrepancies between crude oil data obtained by differing analytical methods. Wilhelm rightly cautioned that any estimation model for mercury in petroleum should be viewed with skepticism until additional data are obtained and in light of the fact that a complete statistical understanding of the amounts of

mercury in crude oil or in refined products is not presently available. In addition, Wilhelm cautions that mercury emission factors for many combustion sources that burn liquid fuels are not now (2000) known.

Duo et al. (2000) examined emissions from Canadian refineries. The method Duo applied was similar to Wilhelm's but did not consider mercury in wastewater or solid waste streams in his mass balance. Duo concluded

that the amount of mercury emitted from Canadian refineries (to the atmosphere) was the difference between mercury in crude oil and mercury in refined products. Based on Liang et al.'s (1996) data for refined products, Duo concluded that greater than 90 percent of mercury in Canadian crudes is emitted during the refining process.

Table 7- 17 – Estimates of Mercury in Crude Oil and Refined Products
(for year 1999, Wilhelm 2001)

	Type (U.S. DOE 2000)	bpy (U.S. DOE 2000) (10^9)	kg/y (10^{11})	THg ppb	Estimated Total kg/y
Crude Oil					
Domestic (40%)	Alaska (18%)	0.4	0.5	<10	500
	GOM (20%)	0.5	0.7	<10	700
	Other (62%)	1.5	2.0	<10? [1]	*2,000?*
Imported (60%)	Canada (15%)	0.5	0.7	<10?	*700?*
	Mexico (15%)	0.5	0.7	<10	700
	Middle East (20%)	0.8	1.1	<10	1,100
	Other (50%)	1.8	2.4	<10?	*2,400?*
Total (IN)		**6.0**	**8.1**		**8,100**
Refined Products					
d = 0.75	Motor fuels (60%)	3.7	4.4	<2?	*900?*
d = 0.80	Naphthas (5%)	0.3	0.4	<5	200
d = 0.85	Residual fuel oil (5%)	0.3	0.4	<10?	400
d = 0.85	Distilled fuel oil (21%)	1.3	1.8	<5	900
d = 1.10	Petroleum coke (3%)	0.2	0.3	50	1,500
d = 0.90	Heavy oils (3%)	0.2	0.3	50	1,500
d = 0.55	Still Gas (3%)	0.2	0.3	<30?	*900?*
		6.2	**7.9**		**6,300**
Wastewater (Ruddy 1982)		1.5	2.5	1	250
Solid waste (U.S. EPA 1996)			0.3	40?	*1,200?*
Air (Table 7-12)					*(1,500)* [2]
Air (fugitive)					250?
Total (OUT)					**8,000**

(1) question marks indicate major uncertainties in the estimated mean concentration
(2) from fuels used in refineries, included in total for all refinery products

60

Table 7- 18 - Fuels from Crude Oil Used by Refineries
(U.S. DOE 2000)

Fuel Type	bpy (10⁶)	kg/y (10⁹)	THg (ppb)	Amount (kg Hg/y)
LPG	4	0.4	<10	4
Still gas	235	20.6	<30?	600
RFO/DFO [1]	6	0.8	<10	86
Heavy Oils	6	0.9	50	5
Coke	90	15.8	50	800
Total				**1,500**

(1) residual fuel oil/distillate fuel oil

Table 7-19 - Mercury in Major Crude Oil Imports
(Calculated from the data of Morris 2000)

Source	bpy (1999) (10⁹)	Percent of U.S. Total (6 x 10⁹ bpy)	THg (ppb)	Yearly amount (kg Hg/y)
Venezuela	0.50	8	5	359
Middle East	0.74	12	5	531
African	0.22	4	5	158
Mexico	0.48	8	5	345
North Sea	0.15	3	5	108
Total	**2.1**	**35**	**5**	**1,500**

Mercury in Combusted Gas and Estimated Emissions

Only limited data are available that provide specific concentrations of mercury in gas or gas condensate processed in the U.S. Chao and Attari (1993) surveyed U.S. pipeline gas using gold collection and CVAA to measure mercury. The sample volumes and detector sensitivity combined to produce relatively high limits of detection. Chao's data are reported in Table 7-20 and, although the gas distribution system in the U.S. is well covered, the reported concentrations do not provide exact concentrations, only upper detection limits.

U.S. dry gas consumption in 1999 was approximately 525 billion cubic meters (U.S. DOE 2000). Using Chao and Attari's higher concentration (THg<0.2 ug/m³) then the maximum amount of mercury released to the atmosphere from burning natural gas would be approximately 100 kg. Using the lower number (THg<0.02 ug/m³) the maximum amount would be approximately 10 kg. Although the estimate for gas provides some reassurance that natural gas is clean and preferable to other types of fossil energy, the actual mean amount of mercury in U.S. gas supplies remains to be demonstrated.

Table 7-20 - Total Hg Concentration in U.S. Pipeline Gas
(Chao and Attari, 1993)

Pipeline Composition (Source)	Mean THg (ug/m^3)
70-75% Gulf Coast, 25-30% Mid-continent	<0.2
70-75% Mid-continent, 25-30% Rocky Mountain	<0.2
Offshore Gulf Coast	<0.2
Offshore Gulf Coast	<0.2
Coal Seam	<0.2
Appalachian	<0.2
Appalachian Shale	<0.2
Illinois Basin	<0.2
San Juan Basin	<0.2
55% Permian, 15% NM, 6 % Anadarko, 24% San Juan	<0.2
56% San Juan, 44% Permian	<0.2
75% Rocky Mountain, 25 % Canadian	<0.2
California	<0.1
California	<0.1
Canadian	<0.1
Canadian	<0.02
80% Permian, 20% San Juan	<0.02
Gulf Coast	<0.02
Guff Coast	<0.02

U.S. EPA Estimates

U.S. EPA estimates of mercury emissions from fuel oil and gas are summarized in Table 7-21. Estimated emissions of mercury to the atmosphere from combusted fuels were compiled in the 1997 Mercury Report to Congress (U.S. EPA 1997a). The EPA estimated that approximately 11 tons of mercury originated from burning fuel oil in boilers (utility, commercial, residential) in the year analyzed (1994-95). The method of estimation involved calculating an emission factor (lb Hg/Btu) and applying this factor to the yearly fuel oil consumption.

The estimate for mercury emissions from utility boilers in the EPA Mercury Report to Congress was based on an ongoing (at that time) investigation of hazardous air pollutants (HAPs) in fossil fuel fired utility boilers (U.S. EPA 1998). The results of the utility toxics study were published the year following the EPA mercury report to Congress. In the utility HAP study, EPA analyzed for mercury in fuel oil as part of an exercise to calculate emission factors for utility boilers. The data for this exercise are not published; however, the mean amount used in calculations was approximately 10 ppb, which translated to an annual emission amount from all U.S. utility boilers that burn fuel oil of approximately 200 kg.

Emissions data were obtained from 58 emission tests conducted by U.S. EPA, the Electric Power Research Institute (EPRI), the Department of Energy (DOE), and individual utilities. The mercury concentration in as-fired oil and natural gas was estimated from emissions test data for boilers burning these fuels. In the estimation of mercury emissions, all oil-fired units were assumed to burn residual oil because trace element data were available only for residual oil. An average density of 8.2 lb/gal was chosen to represent all residual oils. Trace element analysis of natural gas was performed for only two available emissions tests; these concentrations were averaged. The calculated mercury concentration in the oil and natural gas multiplied by the fuel feed rate resulted in an estimate of the amount of mercury (in kg/year) entering each oil- and natural gas-fired boiler.

The emission ratios and modification factors for pollution control devices (EMFs) were calculated by dividing the amount of mercury exiting either the boiler or the control device by the amount of mercury entering the boiler. The average EMF for specific boiler configurations and control devices was calculated by taking the geometric mean of the EMFs for that type of configuration or control device. (The geometric mean was chosen rather than the arithmetic mean because the distribution of emission factors followed a lognormal distribution.) To calculate the control efficiency, the EMF was subtracted from 1. Boiler-specific emission estimates were then calculated by multiplying the calculated inlet mercury concentration by the appropriate EMF for each boiler configuration and control device.

Mercury emissions for oil combustion in commercial/industrial boilers were estimated on a per-state basis using an emission factor of 6.8 lb/10^{12} Btu for residual oil and 7.2 lb/10^{12} Btu) for distillate oil and the oil consumption estimates for States. The total annual emission for oil-fired commercial/industrial boilers was estimated as 7 Mg/yr (7.7 tons/yr). No estimate was given for mercury emissions from gas fired industrial boilers.

Mercury emissions for oil combustion in residential boilers were estimated on a per-state basis using an emission factor of 6.8 lb/10^{12} Btu for residual oil and 7.2 lb/10^{12} Btu) for distillate oil and the oil consumption estimates for States. The total annual estimated emissions for oil-fired residential boilers is 2.9 Mg/yr (3.2 tons/yr).

It is thought that the emissions estimates reported in the 1997 EPA Mercury Report to Congress (U.S. EPA 1997a) were based on ongoing studies that were reported independently. One report, issued the same year, compiled data specific to mercury as part of the ongoing EPA Air Toxics program.

U.S. EPA (1997b) estimated concentrations of mercury in fuel oil based on data compiled by Brooks (1989). Brooks assembled data for fuel oils and crude oils from studies conducted in the 70's and early 80's. The EPA report admitted no comprehensive oil characterization studies had been done, but cited data in the literature for the range of mercury concentrations in crude oil between 0.023 to 30 ppm wt, and the range of concentrations in residual fuel oil as 0.007 to 0.17 ppm wt. Because only a single mean value was found in the literature for mercury concentration in distillate fuel oil, no conclusions were drawn about the range of mercury in distillate oil.

Table 7-22 lists the values for mercury in oils used by U.S. EPA (1997a) to calculate emission factors. The numbers used were obtained by taking the average of the mean values found in the literature (Shah et al. 1970). The value for distillate oil was the single data point found in the literature and was not considered as representative as the values for residual and crude oils.

Additional evidence concerning mercury in fuel oils is available from the U.S. EPA studies of hazardous air pollutants from electric utility boilers (U.S. EPA 1998). U.S. EPA (Radian 1993 as contractor to EPRI) measured mercury emission factors for several furnace types used by utilities. In this study, U.S. EPA cited mercury in residual fuel oil as 0.6 pounds per trillion Btu based on analysis of 4 samples of fuel oil (mean standard deviation = 0.3). The conversion factor applied was 150,000 Btu/gallon of density 8.2 lb/gallon, thus yielding a mean mercury concentration of approximately 10 ppb. The mercury in gas concentration utilized in calculation of emission factors was 0.5 ug/m^3 but its origin was not documented.

The origin of the EPA estimate for mercury from oil combustion (11 tons) cited in the Report to Congress derives mainly from the estimate for mercury concentrations in residual and distillate fuel oil cited for commercial and residential boilers (7 lb/trillion Btu). These concentrations (100 ppb) are an order of magnitude higher than those derived from emission measurements for utility boilers (U.S. EPA 1997a) and for the mean cited in U.S. EPA, 1997b, Locating And Estimating Air Emissions From Sources Of Mercury And Mercury Compounds and with the amount cited in U.S. EPA 1998 (0.6 lb/trillion Btu).

Table 7-21 – U.S. EPA Estimates of Mercury in Fuel Oil

Boiler	Btu/year (10^{12})	Fuel Type	Fuel Oil Amount (10^{10} L/year)	Emission Factor (kg/10^{12} Btu)	Hg (kg/year)	THg in Fuel (ppb)
Utility	840	RFO	2.4	0.24	200	10
Industrial	2,178	RFO/DFO	6.2	3.09/3.27	7,000	100
Residential	890	RFO/DFO	2.5	3.09/3.27	2,900	100
Total					**10,100**	

Table 7-22 - Mercury Concentration In Oils Used as Fuels (U.S. EPA 1997b)

	Number of samples	Mercury concentration Range (ppb)	Mean (ppb)
Residual (No. 6)	6	2 - 6	4 [1]
Distillate (No. 2)	3		<120 [2]
Crude Oil	46	7 – 30,000	3,500 [3]

(1) Midpoint of the range of values. (2) Average of data from three sites.
(3) Average of 46 data points was 6,860; if the single point value of 23,100 is eliminated, average based on 45 remaining data points is 1,750. However, the largest study with 43 data points had an average of 3,200 ppb wt. A compromise value of 3,500 ppb wt was selected as the best typical value.

References

American Petroleum Institute, 1977, Water Reuse Studies, API Publication No. 949, Washington, DC.

American Petroleum Institute, 1978, Analysis of Refinery Wastewaters for the EPA Priority Pollutants, API Publication No. 4296, Washington, DC.

American Petroleum Institute, 1981, Refinery Wastewater Priority Pollutant Study – Sample Analysis and Evaluation of Data, API Publication No. 4336, Washington, DC.

American Petroleum Institute, 1995, Management of Residuals, API Publication No. 4296, Washington, DC.

American Petroleum Institute and Western States Petroleum Association, 1998, Air Toxic Emission Factors For Combustion Sources Using Petroleum Based Fuels, Final Report, Volume 2 - Development of Emission Factors Using CARB Approach, API Publication No. 348, Washington, DC.

Bloom, N. S. and A. Falke, 1996, The Importance of Chemical Speciation in the Assessment and Treatment of Hg, As, and Se Contaminated Waste Streams, Pacific Northwest Pollution Control Association Conference, Boise, ID, October 27-30.

Bloom, N. S., 2000, Analysis and Stability of Mercury Speciation in Petroleum Hydrocarbons, *Fresenius' J. Anal. Chem.*, 366(5):438.

Brooks, G., 1989, Estimating Air Toxics Emissions from Coal and Oil Combustion Sources, EPA-450/2-89-001 (NTIS PB89-194229), U.S. EPA, Office of Air Quality and Standards, Research Triangle Park, NC. April.

Brown, T., Smith, D., Hargis, R., and W. O'Dowd, 1999, Critical Review - Mercury Measurement and Its Control: What We Know, Have Learned, and Need to Further Investigate, *J. Air & Waste Manage. Assoc.*, June, pp. 1-97.

Cao, J. R., 1992, Microwave Digestion of Crude Oils and Oil Products for the Determination of Trace Metals and Sulphur by Inductively-Coupled Plasma Atomic Emission Spectroscopy, Environment Canada Manuscript Report Number EE-140, Ottawa, Ontario, Canada.

Chao, S. and A. Attari, 1993 Characterization and Measurement of Natural Gas Trace Constituents, Part 1: Natural Gas Survey, Institute of Gas Technology Report to Gas Research Institute, Contract No. 5089-253-1832 (November), GRI, Chicago, IL.

Duo, W., Guthrie, T., and W. Edwards, 2000, Mercury Emissions from The Petroleum Refining Sector In Canada, for Environment Canada, Trans-boundary Air Issues Branch, Hazardous Air Pollutants Program, Ottawa, Canada, EC Contract: K2216-9-0078.

Environment Canada, 2000, Properties of Crude Oils and Oil Products - 12/99, Emergencies Science Division, Ontario, Canada.

Filby, R. H., and K. R. Shah, 1975, Neutron Activation Methods for Trace Metals in Crude Oil, in *The Role of Trace Metals in Petroleum*, by T. F.Yen, Ann Arbor Science Publishers, Ann Arbor, MI.

Frankiewicz, T. C and S. Tussaneyakul, 1997, Upgrading production facilities on the Funan platform to remove hydrocarbons and heavy metals from produced water, Proceedings: Offshore Technology Conference, May 1997, pp. 299-310.

Hitchon, B., Filby, R. H., and K. R. Shah, 1975, Geochemistry of Trace Elements in Crude Oils, Alberta, Canada, in *The Role of Trace Metals in Petroleum*; by T. F. Yen, Ann Arbor Science Publishers: Ann Arbor, MI.

Hitchon, B. and R. Filby, 1983, Geochemical Studies – Trace Elements in Alberta Crude Oils, Open File Report 1983-02, Alberta Research Council for Alberta Energy and Utilities Board and Alberta Geological Survey.

Jacobs, R., Grant, R., Kwant, J., Maequine, J., and E. Mentzer, 1992, The Composition of Produced Water from Shell Operated Oil and Gas Production in the North Sea, in *Produced Water, Technological and Environmental Issues and Solutions*, Ray, J., ed., Plenum Press, New York, NY.

Kirchgessner, D. A., Lott, R. A., Cowgill, R. M., Harrison, M. R., and T. M. Shires, 1997, Estimate of Methane Emissions from the U.S. Natural Gas Industry, *Chemosphere*, 35, 6:1365.

Liang, L., Horvat, M., and P. Danilchik, 1996, A Novel Analytical Method for Determination of Picogram Levels of Total Mercury In Gasoline and Other Petroleum Based Products, *Sci. Tot. Environ.*, 187:57.

Liang, L., Lazoff, S., Horvat, M., Swain, E., and J. Gilkeson, 2000, Determination of mercury in crude oil by in-situ thermal decomposition using a simple lab built system, *Fresenius' J. Anal. Chem.*, 367:8.

Magaw, R., McMillen, S., Gala, W., Trefry, J., and R. Trocine, 1999, Risk evaluation of metals in crude oils, Proceedings SPE/EPA Exploration & Production Environmental Conference, SPE Paper No. 52725.

Meinhold, A., DePhillips, M., and S. Holtzman, 1996, Final Report: Risk Assessment for Produced Water Discharges to Louisiana Open Bays, Brookhaven National Laboratory Report No. BNL-62579 for U.S. DOE, Brookhaven, NY.

Morris, R., 2000, New TRI Reporting Rules on Mercury, Proceedings National Petroleum Refiners Association Meeting, San Antonio, TX, (September).

Mulyono, M., Desrina, R., Priatna, R., Sudewo, B., and M. Sawolo, 1996, Heavy Metals in Water Base Drilling Muds Used in Several Locations of Oil Fields in Indonesia, SPE paper No. 35980.

Musa, M., Markus, W., Elghondi, A., Etwir, R., Hannan, A., and E. Arafa, 1995, Neutron Activation Analysis of Major and Trace Elements in Crude Petroleum, *J. Radioanal. Nucl. Chem.*, 198(1):17.

Olsen, S., Westerlund, S., and R. Visser, 1997, Analysis of Metals in Condensates and Naphthas by ICP-MS, *Analyst*, 122:1229.

Petrusak,R., Freeman, B., and G. Smith, 2000, Baseline Characterization of U.S. Exploration and Production Wastes and Waste Management, SPE Paper No. 63097 presented at the SPE Annual Technical Conference and Exhibition, Dallas, TX, October.

Raco, V., 1993, Estimated Discharges from Offshore Oil Platforms in the Southern California Bight (Santa Barbara Channel and Santa Maria Basin) in 1990, Southern California Coastal Water Research Project Annual Report 1992-93, Los Angeles, CA.

Radian Corporation, 1993, Preliminary Draft Reports on Field Chemical Emissions Monitoring Project. Prepared for Electric Power Research Institute from the following reports: Site 10, October 6, 1992; Site 11, October 6, 1992; Site 12, November, 23, 1992; Site 15, October 6, 1992; Site 21, May 14, 1993. Austin, TX.

Ray, J. P., 1998, Findings of the Offshore Operators Committee Produced Water Bioaccumulation Study, SPE Paper No. 46838, Society of Petroleum Engineers, Dallas, TX.

Ruddy, D., 1982, Development Document for Effluent Limitations Guidelines, New Source Performance Standards, and Pretreatment Standards for the Petroleum Refining Point Source Category, EPA/440/1-82/014 (NTIS PB83-172569), Office of Water Regulations and Standards, Washington, DC.

Shafawi, A., Ebdon, L., Foulkes, M., Stockwell, P., and W. Corns, 1999, Determination of total mercury in hydrocarbons and natural gas condensate by atomic fluorescence spectrometry, *Analyst*, 124:185.

Shah, K. R., Filby, R. H., and W. A. Haller, 1970, Determination of Trace Elements in Petroleum by Neutron Activation Analysis, Journal of Radioanalytical Chemistry, 6:413.

Stephenson, M., 1992, A Survey of Produced Water Studies, *Produced Water: Technological and Environmental Issues and Solutions*, Ray, J., ed., Plenum Press, New York, NY.

Tao, H., Murakami, T., Tominaga, M., and A. Miyazaki, 1998, Mercury speciation in natural gas condensate by gas chromatography-inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.*, 13:1085.

Trefry, J., Trocine, R., Naito, K., and S. Metz, 1996, Assessing the Potential for Enhanced Bioaccumulation of Heavy Metals from Produced Water Discharges to the Gulf of Mexico, in Produced Water 2, Environmental Issues and Mitigation Technologies, Reed, M. and Johnsen, S., eds., Plenum Press, New York, NY.

U.S. DOE, 1999, Estimation of Greenhouse Gases, Energy Information Administration, National Energy Information Center, Report EIA/DOE-0573(99).

U.S. DOE, 2000, Energy Statistics for 1998, 1999, Energy Information Administration, National Energy Information Center, Washington, D.C.

U.S. EPA, 1996, Waste Minimization for Selected Residuals in the Petroleum Refining Industry, Office of Solid Waste and Emergency Response, EPA/530/R-96/009 (NTIS PB97-121180), Washington, DC.

U.S. EPA, 1997a, Mercury Study Report to Congress, EPA/452/R-97/003 (NTIS PB98-124738), Office of Air Quality Planning and Standards, Research Triangle Park, NC and Office of Research and Development, Washington, DC.

U.S. EPA, 1997b, Locating And Estimating Air Emissions From Sources Of Mercury And Mercury Compounds, EPA-454/R/97-012 (NTIS PB98-117054), Office of Air Quality Planning and Standards, Research Triangle Park, NC.

U.S. EPA, 1997c, Procedures For Preparing Emission Factor Documents, EPA/454/R-95-015, Office of Air Quality Planning and Standards, Research Triangle Park, NC.

U.S. EPA, 1998, Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units - Final Report to Congress, EPA/453/R-98/004a (NTIS PB98-131774), Office of Air Quality Planning and Standards, Research Triangle Park, NC.

U.S. EPA, 1999, Method 1631: Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry, EPA/821/R-95/027 (NTIS PB95-252433), Office of Water, Washington, DC.

U.S. EPA, 2000, Unified Air Toxics Website: Electric Utility Steam Generating Units, Section 112 Rule Making, Office of Air Quality Planning and Standards, Research Triangle Park, NC. www.epa.gov/ttn/uatw/combust/utiltox/utoxpg.html

Wilhelm, S. M., 1999, Conceptual Design of Mercury Removal Systems for Hydrocarbon Liquids, Hydrocarbon Processing, 78(4):61-73.

Wilhelm, S. M., 2001, An Estimate of Mercury Emissions from Petroleum, in press, *Environ, Sci. Tech.*

Chapter 8
Data Requirements to Estimate Mercury Emissions

Mercury extracted from the earth in oil and gas including that in associated waste streams contributes to the global mercury cycle. While the amount of mercury that derives from burning coal can be stated with reasonable confidence, the amount that derives from petroleum cannot be stated with equal confidence at present. The estimates compiled in this report merely provide a framework upon which one can gain a rough, but preliminary, idea of the amounts that may be involved. With additional data inputs to the estimates, it may eventually be possible to estimate the total amounts of mercury emissions from oil and gas with better accuracy. Table 8.1 summarizes the estimates compiled and discussed in this report.

Currently available data for total mercury (dissolved and suspended) in petroleum and fuel products, when applied to a mass balance for mercury in the U.S. refining system, provide an order of magnitude estimate of the contribution of mercury in oil and gas to U.S. anthropogenic emissions (Wilhelm 2001). The model finds the mean amount of mercury in petroleum refined in the U.S. to be close to 10 ppb and predicts that the amount of mercury in fuel products burned in the U.S. is on the order 6000 kg/y. The amount of mercury in U.S. fuel oil was estimated to be approximately 1,500 kg/y, assuming a 10 ppb mean mercury concentration in crude oil. This number is in conflict with current U.S. EPA estimates of mercury in fuel oil (10,000 kg/year, see EPA Estimates, Chapter 7).

While the estimates compiled in this report are useful in the present timeframe, they are insufficient to answer some major issues and questions that are important to the determination of the contribution of mercury in petroleum to global pools and fluxes. For example, data on refined products are scarce and undocumented as to the refineries from which they originate. Thus it remains uncertain as to whether the mercury in crude oil is mainly accounted for by the amount in products (> 50 percent) or if it distributes more prevalently to other avenues of egress from refineries (solid waste, wastewater, fugitive emissions).

It does appear, based on currently available data, that approximately half of the entire amount of mercury associated with oil and gas (exploration, production, transportation, processing, fuel combustion) enters the atmosphere in fuel combustion. Some unknown portion of this amount is captured by pollution control equipment but the total is less than 6 Mg/y (if the mean amount of mercury in crude oil is less than 10 ppb). This would suggest that, while oil and gas account for approximately the same mass of fossil fuel burned yearly in the U.S., the amount of mercury in combusted petroleum and gas is about 10 times less that that which derives from coal (66 Mg/y, U.S. EPA 1997).

The above estimate of course depends on the mean amount of mercury in petroleum. Data are somewhat limited on mercury in crude oil of known origin, age and condition, all of which are important to calculation of an accurate mean concentration in crude oils processed in the United States. The statistical ensemble of mercury concentrations in coal that was developed in 1999 (U.S. EPA 2000) serves as an example of the rigor that could be applied to petroleum. Given the estimated amount in crude oil presently available, one could certainly argue that some lesser amount of data would suffice to obtain an accurate mean and distribution of total mercury concentration in petroleum.

Wilhelm and Bloom (2000) and Bloom (2000) point out that analytical uncertainties exist with currently published data. Of major importance are the percentage and species identities of suspended forms of mercury. If, as suspected, mercuric sulfide is a major component of the total mercury in crude feeds to refineries, or if it is produced in the refining process at the expense of other forms, then one can rationalize the amount of mercury in petroleum coke and thus achieve better confidence in the distribution of mercury to heavy products and waste streams.

The chemical stability and fate of elemental mercury in refining are also important and largely unknown. Almost certainly, any mercury that is found in light distillates is volatile in the crude and enters light fractions in the primary distillation. The elemental form is thought to be the dominant volatile, but it remains uncertain as to whether dialkylmercury is a major component in crude oil or if dialkyl or other volatile species are generated in the refining process.

The distribution of mercury to effluents and air emissions in the refining process is an important issue as well and little data are available upon which any conclusions can be drawn relative to refinery emissions. Insufficient data are available for many of the major streams including wastewater, solid waste, still gas, treatment fluids and products. If one were to attempt to obtain a firm understanding of the fate of mercury in refineries, it would be necessary to examine individual unit processes. Some of these have been previously discussed (Chapter 6) and include desalting, distillations, hydrotreating and catalytic cracking. In each case, the attempt to determine the distribution of mercury would require tracking the various species of mercury (volatile, oxidized, inert) through the process and to measure concentrations of each species in all of the streams that enter and exit the process in question.

The relationship of mercury and sulfur in the refining process may be essential to the task of understanding the fate of mercury in hydrocarbon processing. Little is known at present, but given mercury's affinity for sulfur, it would seem likely that sulfides of mercury are more likely produced than consumed in the refining and gas separation processes. If so, understanding the chemical reactions that occur would help account for the amount known to exist in petroleum coke as opposed to gasoline, for example.

The fate of mercury in gas processing also remains uncertain, but this question may be less important than the questions that relate to the fate of mercury in refining. All current estimates for the amount of mercury in natural gas conclude that the amount is very small, at least relative to the amount in crude oil. The precise mean amount and range of concentrations of mercury in natural gas remain to be exactly determined, however. Thus while the data of Chao and Attari (1993) and the EPA estimates (U.S. EPA 1998) infer that the amounts are insignificant, it would be useful to have better data upon which to calculate the contribution of mercury in natural gas to the global cycle more exactly.

An interesting point to be made relative to the gas issue is that mercury removal systems are commercially available and widely applied to gas having sufficient mercury concentration to affect petrochemical processing. The percentage of gas that is subjected to mercury removal treatments as a percentage of the total amount processed in the U.S. is not known. Secondly, pipelines are quite efficient scavengers of mercury in gas and it is likely that major portions of mercury that enter a pipeline, never exit but are retained on pipe interior surfaces indefinitely. Thus the concentration of mercury at the point of consumption will always be less than the concentration upstream of compressors at gas processing facilities.

Of minor importance, but still of some curiosity, is the fate of mercury in gas treatment systems such as glycol dehydration, amine treaters and sorbents. Glycol in particular is suspected to remove mercury by transfer to the glycol regen gas and water vapor vents. The reactions of mercury in amine systems remain unstudied.

Even with knowledge of the amounts of mercury in fuels, and their chemical identities, little is known concerning the fate of mercury in liquid fuel combustion processes. It seems unlikely that mercury is retained in internal combustion engines in any major proportion, but some could be. The amount in used motor oil as compared to new, and the amounts possibly retained by emission controls (catalytic converters) would then need to be determined to answer this question conclusively.

Emission factors for a limited number of refinery processes are discussed in the previous section of this report. While these data are useful and informative, they are insufficient to allow major conclusions as to the fate of mercury in refineries or in other types of liquid fuel combustion processes. In addition, speciation of mercury in liquid fuel combustion processes is not reported and detailed investigations would be necessary to establish the forms of mercury that are emitted in boilers and heaters that burn liquid fuels.

The evolving database on mercury in both crude oil and refined products is optimistic to the conclusion that mercury that derives from petroleum is small in absolute terms, and especially when compared to that which derives from coal. The eventual conclusions to be reached regarding mercury in oil and natural gas and the amounts and avenues of incorporation to the global cycle await focused studies that account for the various species of mercury, the reactions that occur in processing and the fate of mercury in the various combustion process in which petroleum products are consumed.

References

Bloom, N., 2000, Analysis and Stability of Mercury Speciation in Petroleum Hydrocarbons, *Fresenius' J. Anal. Chem.*, 366(5):438.

Chao, S. S. and A. Attari, 1993, Characterization and Measurement of Natural Gas Trace Constituents, Part 1: Natural Gas Survey, Institute of Gas Technology Report to Gas Research Institute, Contract No. 5089-253-1832 (November), GRI, Chicago, IL.

Ruddy, D., 1982, Development Document for Effluent Limitations Guidelines, New Source Performance Standards, and Pretreatment Standards for the Petroleum Refining Point Source Category, EPA/440/1-82/014 (NTIS PB83-172569), Office of Water Regulations and Standards, Washington, DC.

U.S. EPA, 1997, Mercury Study Report to Congress, EPA/452/R-97/003 (NTIS PB 98-124738), Office of Air Quality Planning and Standards, Research Triangle Park, NC and Office of Research and Development, Washington, DC.

U.S. EPA, 1998, Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units - Final Report to Congress, EPA/453/R-98/004a (NTIS PB98-131774), Office of Air Quality Planning and Standards, Research Triangle Park, NC.

U.S. EPA, 2000, Unified Air Toxics Website: Electric Utility Steam Generating Units, Section 112 Rule Making, Office of Air Quality Planning and Standards, Research Triangle Park, NC. www.epa.gov/ttn/uatw/combust/utiltox/utoxpg.html

Wilhelm, S., and N. Bloom, 2000, Mercury in Petroleum, *Fuel Proc. Technol.*, 63:1.

Wilhelm, S. M., 2001, An Estimate of Mercury Emissions from Petroleum, in press, *Environ. Sci. Tech.*

Table 8-1 – Summary of Estimates for Mercury Emissions from Oil and Gas Production and Processing

Type	Industry Segment	Category	Amount of Discharge (10^9 kg/year)	THg (ppb)	Estimated Annual Emission Rate (kg/year)
Water					
	Oil and Gas Production	Produced Water	500	1? [1]	500
	Oil Refining	Refinery Wastewater	250	1?	250
	Oil Transportation	Tanker ballast	?	1?	?
Total					**>750**
Solid Waste					
	Oil and Gas Exploration	Drilling Waste	50	100?	5,000
	Oil refining	Refinery Waste	30	50?	1,200
Total					**6,200**
Air					
	Oil Production	Flared gas	4.5	1.5?	10
	Oil Production	Fugitive	1	185?	185
	Gas Production and Transmission	Fugitive	5.9	?	?
	Oil	Fuel Combustion	790	<8	6,000
	Gas	Fuel Combustion	341	<0.3?	100
Total					**>6,300**
TOTAL					**13,250**

(1) Question marks indicate that the mercury concentrations utilized are not based on definitive data

TECHNICAL REPORT DATA
(Please read instructions on the reverse before completing)

1. REPORT NO. EPA-600/R-01-066	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Mercury in Petroleum and Natural Gas: Estimation of Emissions from Production, Processing, and Combustion		5. REPORT DATE September 2001
		6. PERFORMING ORGANIZATION CODE
7. AUTHORS S. Mark Wilhelm		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Mercury Technology Services 23014 Lutheran Church Road Tomball, Texas 77375		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. EPA Purchase Order
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Air Pollution Prevention and Control Division Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 10/00-5/01
		14. SPONSORING AGENCY CODE EPA/600/13
15. SUPPLEMENTARY NOTES APPCD Project Officer is David A. Kirchgessner, Mail Drop 63, 919/ 541-4021.		

16. ABSTRACT   The report gives results of an examination of mercury (Hg) in liquid and gaseous hydrocarbons that are produced and/or processed in the U.S. The Hg associated with petroleum and natural gas production and processing enters the environment primarily via solid waste streams (drilling and refinery waste) and the combustion of fuels. In total, the amount exceeds 10,000 kg yearly, but present estimates are uncertain due to lack of statistical data. The amounts in solid wastes and atmospheric emissions from combustion are estimated to be roughly equal. Solid waste streams likely contain a much higher fraction of mercuric sulfides or other insoluble compounds than water-soluble species; thus, the bioavailability of Hg from this category is much more limited than that which derives from combustion. The report should help identify Hg-related areas that require additional research, especially the needs associated with measuring the concentrations of the various chemical species of Hg in the various feedstocks and waste streams associated with the oil and gas industry. Additional information is necessary if the magnitudes of Hg emissions associated with U.S. petroleum and natural gas are to be estimated accurately.

17.	KEY WORDS AND DOCUMENT ANALYSIS	
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Processing Mercury (Metal) Combustion Emission Crude Oil Natural Gas Hydrocarbons Production	Pollution Control Stationary Sources	13B 13H 07B 21B 14B 11H, 08G 21D 07C 14G
18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (*This Report*) Unclassified	21. NO. OF PAGES 78
	20. SECURITY CLASS (*This Page*) Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE