This document is part of Appendix A, and includes Small Boat Engine Wet Exhaust: Nature of Discharge for the "Phase I Final Rule and Technical Development Document of Uniform National Discharge Standards (UNDS)," published in April 1999. The reference number is EPA-842-R-99-001.

Phase I Final Rule and Technical Development Document of Uniform National Discharge Standards (UNDS)

Small Boat Engine Wet Exhaust: Nature of Discharge

April 1999

NATURE OF DISCHARGE REPORT

Small Boat Engine Wet Exhaust

1.0 INTRODUCTION

The National Defense Authorization Act of 1996 amended Section 312 of the Federal Water Pollution Control Act (also known as the Clean Water Act (CWA)) to require that the Secretary of Defense and the Administrator of the Environmental Protection Agency (EPA) develop uniform national discharge standards (UNDS) for vessels of the Armed Forces for "...discharges, other than sewage, incidental to normal operation of a vessel of the Armed Forces, ..." [Section 312(n)(1)]. UNDS is being developed in three phases. The first phase (which this report supports), will determine which discharges will be required to be controlled by marine pollution control devices (MPCDs)—either equipments or management practices. The second phase will develop MPCD performance standards. The final phase will determine the design, construction, installation, and use of MPCDs.

A nature of discharge (NOD) report has been prepared for each of the discharges that has been identified as a candidate for regulation under UNDS. The NOD reports were developed based on information obtained from the technical community within the Navy and other branches of the Armed Forces with vessels potentially subject to UNDS, from information available in existing technical reports and documentation, and, when required, from data obtained from discharge samples that were collected under the UNDS program.

The purpose of the NOD report is to describe the discharge in detail, including the system that produces the discharge, the equipment involved, the constituents released to the environment, and the current practice, if any, to prevent or minimize environmental effects. Where existing process information is insufficient to characterize the discharge, the NOD report provides the results of additional sampling or other data gathered on the discharge. Based on the above information, the NOD report describes how the estimated constituent concentrations and mass loading to the environment were determined. Finally, the NOD report assesses the potential for environmental effect. The NOD report contains sections on: Discharge Description, Discharge Characteristics, Nature of Discharge Analysis, Conclusions, and Data Sources and References.

2.0 DISCHARGE DESCRIPTION

This section describes the small boat engine wet exhaust discharge and includes information on: the equipment that is used and its operation (Section 2.1), general description of the constituents of the discharge (Section 2.2), and the vessels that produce this discharge (Section 2.3).

2.1 Equipment Description and Operation

Small boat engines commonly use seawater to both cool and quiet their exhaust. Seawater passes through the heat exchanger, gear oil cooler, and aftercooler (if equipped), and is then injected into the exhaust. When injected, some of the gaseous and solid components of the exhaust transfer into the cooling water. The cooling water then discharges into the receiving water. Any cooling water that is not injected into the exhaust is directed overboard.[1] For purposes of this analysis, it was assumed that all cooling water cycled through the engine is injected into the air exhaust.

Small boats are powered by either inboard or outboard engines. Inboard engines usually develop greater power than outboards. In addition, inboard engines are generally diesel fueled while outboard engines typically use gasoline. Inboard and outboard engines can be either two- or four-stroke. The majority of small boat outboard engines are two-stroke gasoline engines. The moving parts of gasoline-powered, two-stroke outboard engines are lubricated with oil that is pre-mixed with gasoline. Thus, the oil is continuously burned with the gasoline. In four-stroke engines, lubricating oil is circulated and not intentionally introduced into the combustion chamber.[2]

A diagram of a typical two-stroke diesel engine air system is included as Figure 1. A diagram of a typical inboard wet-exhaust system is included as Figure 2. Although engine design may vary based on boat class, general process flow will be similar for all water-cooled, small boat engines.

2.2 Releases to the Environment

This discharge consists of water injected as a cooling stream into the exhaust system of small boat engines. Exhaust constituents generated during the operation of the engines can be transferred to the engines' water cooling streams and discharged as wet exhaust. Inboard engines usually discharge wet exhaust above the water line. Outboard engines generally discharge their wet exhaust underwater through the propeller hub.

2.3 Vessels Producing the Discharge

There are approximately 3,300 Navy, 1,560 U.S. Coast Guard (USCG), 209 Army, and 1,454 Marine Corps small boats currently using seawater for cooling engine exhaust. Of the total number of small boats in the military fleet, 3,822 have inboard engines and 2,701 have outboard engines.[3] Air Force and Military Sealift Command (MSC) small boats have not been included in this analysis; however, their inclusion does not significantly affect this reports conclusion.

3.0 DISCHARGE CHARACTERISTICS

This section contains qualitative and quantitative information that characterizes the discharge. Section 3.1 describes where the discharge occurs with respect to harbors and near-shore areas, Section 3.2 describes the rate of the discharge, Section 3.3 lists the constituents in the discharge, and Section 3.4 gives the concentrations of the constituents in the discharge.

3.1 Locality

Based on their limited range, all small boats are expected to operate within 12 nautical miles (n.m.).[1]

3.2 Rate

Approximately one-third of the small boat fleet is equipped with outboard engines. Based on engine specifications, outboard engines can discharge up to 20 gallons per minute (gpm).[4] This rate was used as the fleet-wide average for outboard-driven small boats.

Inboard diesel engines generally have a higher discharge rate than outboard engines, and can discharge up to 100 gpm.[5] This estimate assumes that all cooling water flows through the engine and is discharged into the exhaust. Many small Armed Forces boats have twin engines, yielding a total flow rate up to 200 gpm per vessel. However, to take into account vessels with single engine installations, and for vessels with engines discharging less than 100 gpm per engine, a flow rate of 150 gpm per vessel was used as the average fleet-wide flow rate for boats with inboard engines.

Table 1 summarizes the estimated annual small boat engine wet exhaust flow rate by service. Flow rates were calculated for each service based on a monthly average operating time of 25 hours, and each vessel discharging 150 gpm of wet exhaust for inboards and 20 gpm for outboards.[4,5,6] The total fleet-wide discharge is approximately 11 billion gallons per year.

3.3 Constituents

The main constituents from all engines are oxides of nitrogen (NO_x), organic compounds (including hydrocarbons (HCs)), carbon monoxide (CO), and particulates. The HC constituents are primarily the result of incomplete combustion. Since diesel fuels have a different composition than regular gasoline, the distribution of constituents in the exhaust differ between the two engine types. In general, diesel engines produce higher particulate emissions and lower organic emissions than gasoline-powered engines.[7]

3.3.1 Outboard Engines

As mentioned in Section 2.1, almost all outboard engines are two-stroke gasoline powered engines. Some limited studies have been done on the impact of engine exhaust on water quality. A 1995 study measured the rate of introduction of volatile organic compounds (VOCs) into water during the operation of gasoline powered two-stroke and four-stroke outboard engines. In this study, a 10-horsepower (hp) outboard engine of each type was operated in an enclosed tank, and the increase in VOCs such as benzene was measured. The results were given in terms of milligram (mg) of compound per 10 minutes (min) of operation (e.g. 2800 mg benzene/10 min). Therefore, the number was a bulk measurement of the rate of accumulation of the compound in the water.[8]

The study reported that the VOC compounds found in water for both two-stroke and four-stroke engines were almost exclusively aromatic hydrocarbons. In most cases, other types of HCs were not found. The amount of VOCs found in the water on a power basis (grams per horsepower-hour (g/hp-hr) was equivalent to approximately 10% of the total HCs emitted in the exhaust. The VOC compounds measured in the 1995 study and the rate of accumulation are shown in Table 2.[8] Of the compounds listed in Table 2, benzene, toluene, ethylbenzene, and naphthalene are priority pollutants. No bioaccumulators are suspected to be present in this discharge.

3.3.2 Inboard Engines

To support the air quality management planning process, EPA has published emission factors for various industrial sources, including stationary diesel engines up to 600 hp. These emissions factors relate quantities of released materials to fuel input, as nanogram per joule (ng/J) fuel input, or power output, as in g/hp-hr. Although intended for stationary diesel engines, these emission factors may be used to approximate diesel engine emissions for small boats and craft for the following reasons:

- For diesel engine families with 1994 emissions certification, more than 90 percent have HC emissions of 0.5 g/hp-hr or less.[9] According to the manufacturer's specification sheet, the HC emissions rate for a typical diesel engine in use by the Armed Forces is 0.45 g/hp-hr.[5] This demonstrates that the emissions from the typical diesel engine used by the Armed Forces is similar to industry standard diesel engines.

- The EPA emission factor for total organic carbon (TOC) emitted by diesel engines is approximately 1.1 g/hp-hr.[7] Because HCs are a subset of TOC, these emissions rates appear to be appropriate for an order of magnitude estimate.

Table 3 lists the emission factors for constituents present in the air exhaust of diesel engines.[7] Through contact with the cooling water, many of these constituents have the potential to be introduced into the water. Of the compounds shown in Table 3, benzene, toluene, acrolein, naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene are priority pollutants. None of the constituents listed in Table 3 are bioaccumulators.

3.4 Concentrations

3.4.1 Outboard Engines

The 1995 study measured the VOC accumulation in water from the exhaust of 10-hp (7.3 kilowatt (kW)) two-stroke engines. Because the typical two-stroke outboard engine used by the Armed Forces is a 100 hp (74.6 kW) engine, the results from the 10-hp engine are not directly transferable. However, one pertinent observation was reported in the 1995 study which permits the results of the smaller engine to be "scaled" up for a larger engine. This observation was that the concentration of VOC in the water was related primarily to the level of HC emissions in the exhaust. The higher the level of HC emissions in the engine air exhaust, the higher the level of VOC found in the water.[8] This indicates that if the level of total HC emissions for a larger engine can be estimated, the VOC concentrations for the compounds given in the 1995 study can reasonably be estimated by comparing the total HC emission rates.

In 1996, EPA published a rule regulating the emissions of gasoline-powered marine engines. The rule gives an equation for HC output which describes the current emission rates of two-stroke engines for the power output range from 2 hp to 300 hp. This equation is given as:

$$HC = [151+(557/P^{0.9})], \text{ or } 300 \text{ g/kW-hr, whichever is lower.}$$

In this expression, P is the power in kW, and HC is the hydrocarbon emissions rate in g/kW-hr.[10] The relationship between power and emissions is different for 4-stroke and 2-stroke engines. However, in the absence of a similar equation for 4-stroke engines, it was assumed that 4-stroke engine emissions follow the same trend in emissions output on a normalized basis (power basis) as two-stroke engines.

Using the typical two-stroke outboard engine size of 100 hp and the EPA equation, the normalized output for HC is 162.5 g/kW-hr. Therefore, the total emissions rate is approximately 12,122 g/hr. Using the 7.3 kW engine power and the 267 g/kW-hr HC emissions rate reported in the 1995 study for the two-stroke engine, the total HC emissions rate is 1,949 g/hr. The ratio of HC emissions for these two engine sizes can be calculated as shown below:

Estimate the hydrocarbon emissions ratio for a 100 hp (74.6 kW) engine
Total emissions rate (7.3 kW engine): = (HC)(P) = (267 g/kW-hr) (7.3 kW) = 1,949 g/hr
Projected emissions rate (74.6 kW engine): = (HC)(P) = (162.5 g/kW-hr)(74.6 kW) = 12,122 g/hr
Emissions ratio = 12,122/1,949 = 6.2

If it is assumed that there is a direct relationship between the HC emissions rate and the VOC introduction rate, the rates of VOC introduction measured in the 1995 study can be multiplied by the HC emissions ratio. Using this approach, Table 4 provides the estimated VOC introduction rates for two-stroke outboard engine wet exhaust. An example calculation for benzene is provided below:

Benzene introduction rate for a 7.3 kW engine is 2800 mg/10 min (from 1995 study)
Hydrocarbon emissions ratio for a 74.6 kW engine equals 6.2 (from above calculation)
Benzene introduction rate equals (6.2)(2800 mg/10 min) = 17,360 mg/10 min

A similar procedure can be followed to estimate the VOC introduction rate for four-stroke engines. For these engines, a typical engine size is 90 hp. Again, using the EPA equation, the normalized output for HC in a 90 hp (67.1 kW) engine is 163.6 g/kW-hr. Therefore, the total emissions rate is approximately 10,961 g/hr. Using the 7.3 kW engine power and the 267 g/kW-hr HC emissions rate reported in the 1995 study for the two-stroke engine, the total HC emissions rate for the two-stroke engine in the 1995 study is 1,949 g/hr. For a 90 hp engine, the hydrocarbon emissions ratio therefore is 10,961/1,949 or 5.62. Using this ratio, Table 4 shows the estimated VOC introduction rate for four-stroke outboard engines. A sample calculation for the introduction rate of benzene is given below:

Benzene introduction rate for a 7.3 kW engine is 110 mg/10 min (from 1995 study)
Hydrocarbon emissions ratio for a 67.1 kW engine equals 5.62 (from above calculation)
Benzene introduction rate equals (5.62)(110 mg/10 min) = 618.2 mg/10 min

To estimate the concentration of the constituents in the wet exhaust, the flow rate must be used. From Section 3.2, the approximate wet exhaust flow rate for outboard engines is 20 gpm. The constituent concentration can be estimated by assuming all the VOCs introduced into the exhaust enters the water. Table 4 shows the estimated concentrations for the constituents in both two-stroke and four-stroke outboard engines. A sample calculation is presented below:

Wet Exhaust Flow rate:	20 gpm
Benzene introduction rate:	17,360 mg/10 min
Concentration = (17,360 mg/10 min)(1 min/20 gal)(1 gal/3.7854 L) = 22.9 mg/L	

3.4.2 Inboard Engines

The constituent concentrations for the discharge of inboard engines were determined through a multi-step calculation. Using emission factors for mid-size stationary diesel engines given in Table 3 and diesel engine output specifications, the concentrations in air exhaust were estimated. The transfer of air exhaust constituents into the water was estimated using Henry's Law, which relates the partial pressure of a gas in the atmosphere to the concentration of the gas in water. Table 5 provides the estimated constituent concentrations in the inboard engine wet exhaust. A sample calculation for the concentration of benzene is presented in the calculation sheet at the end of the report.

4.0 NATURE OF DISCHARGE ANALYSIS

Based on the discharge characteristics presented in Section 3.0, the nature of the discharge and its potential impact on the environment can be evaluated. The estimated mass loadings are presented in Section 4.1. In Section 4.2, the concentrations of discharge constituents after release to the environment are estimated and compared with the water quality standards. In Section 4.3, the potential for the transfer of non-indigenous species is discussed.

4.1 Mass Loadings

The estimated mass loadings shown in Table 6 and Table 7 were based on the total number of small boats in the Navy, USCG, Army, and Marine Corps; on a monthly average operating time of 25 hours; and each boat discharging 150 gpm of wet exhaust for inboards and 20 gpm for outboards.[4,5,6] The concentration data for two-stroke engines were used because the majority of Armed Forces outboard engines are two-stroke. This approach is conservative because constituent concentrations in two-stroke engine wet exhaust are higher than concentrations in four-stroke engine exhaust.

Mass loading sample calculations:

Table 6, Outboard Engine for benzene is:

(22.93 mg/L)(0.97 billion gallons/yr)(3.785 liters/gallon)(1 kg/10^6 mg) = 84,186 kg/yr

Table 7, Inboard Engine for benzo(a)pyrene is:

(7.69×10^{-5} mg/L)(10.31 billion gallons/yr)(3.785 liters/gallon)(1 kg/10^6 mg) = 3.0 kg/yr

4.2 Environmental Concentrations

The concentrations and mass loading estimates described above are likely an overestimate because of non-equilibrium effects. The method used to estimate the concentrations of the diesel exhaust components in wet exhaust using Henry's Law assumed sufficient residence time inside the engine for the aerosols in the exhaust to reach equilibrium with the cooling water. However, due to the short residence time of both air and water in the exhaust system, equilibrium conditions are unlikely. Residence time in the exhaust system is expected to be less than one second. Because equilibrium conditions are unlikely, less constituents will dissolve in the cooling water.

Based on cited research, chemical constituents in the wet exhaust from small boat engines can be present at concentrations that exceed water quality criteria (WQC). Table 8 summarizes estimated discharge concentrations and WQC for constituents of this discharge. Benzene, toluene, ethylbenzene, and naphthalene in two stroke outboard engines exceed the most stringent state WQC. Benzene and ethylbenzene in four-stroke outboard engine wet exhaust, and total PAHs in inboard engine wet exhaust each exceed the most stringent state WQC.

4.3 Non-Indigenous Species

The residence time of cooling water in small boat engines is very short; therefore, the wet exhaust is discharged within yards of where the cooling water was taken aboard. Because seawater is not transported during small boat operations, it is unlikely that the operation of small boat engines could transport or introduce non-indigenous species.

5.0 CONCLUSIONS

Constituents found in small boat engine wet exhaust discharge are estimated to be discharged in significant amounts that exceed water quality criteria. Therefore, this discharge has the potential to cause adverse environmental effects.

6.0 DATA SOURCES AND REFERENCES

To characterize this discharge, information from various sources was obtained. Process information, equipment specifications, average annual use, and fleet-wide inventories were considered in estimating the rate of discharge. Estimated constituent concentrations were calculated using solubility principles and published emissions data. Additional constituent concentrations were obtained from previously completed research. Table 9 shows the sources of data used to develop this NOD report.

Specific References

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MARCORSYSCOM. Totals for Marine Small Boat/Watercraft. 14 February 1997.

Committee Print Number 95-30 of the Committee on Public Works and Transportation of the House of Representatives, Table 1.

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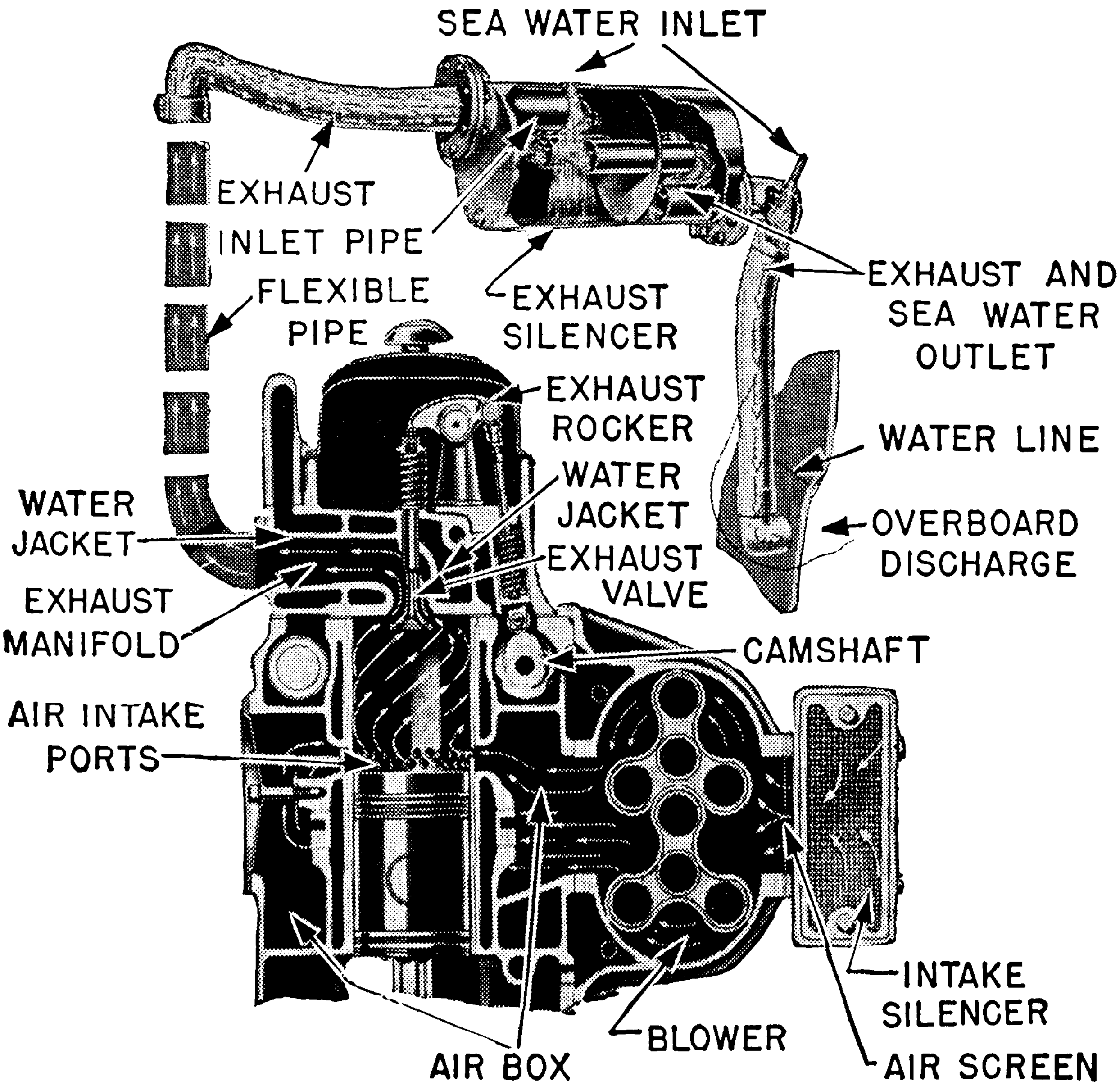

Figure 1. Air Systems of a Two-Stroke Cycle Engine (GM71)[11]

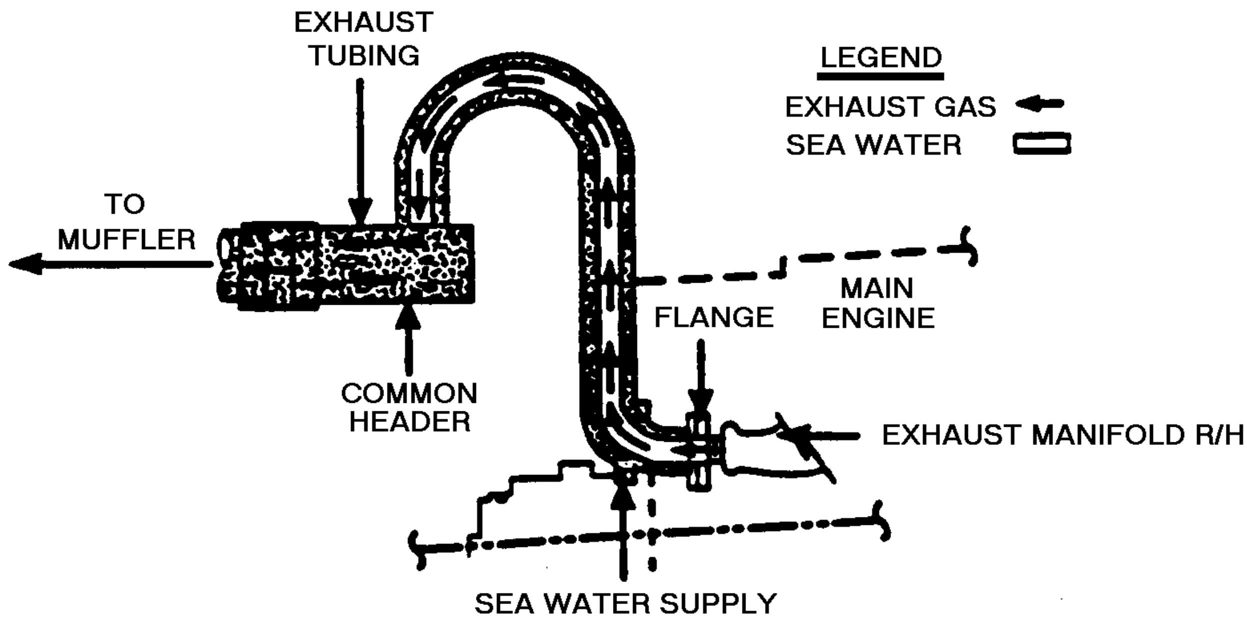

Figure 2. Typical Water Jacketed Elevated Loop[12]

Table 1. Estimated Annual Small Boat Wet Exhaust Discharge Flow Rates[3,4,5,6]

Service (fleet)	Number of Small Boats	Estimated Annual Discharge* (billions of gallons)
Navy (inboard)	2,500	6.75
Navy (outboard)	800	0.29
USCG (inboard)	620	1.67
USCG (outboard)	940	0.34
Army (inboard)	152	0.41
Army (outboard)	57	0.02
Marine Corps (outboard)	904	0.32
Marine Corps (inboard)	550	1.48
Totals (inboard)	3,822	10.31
Totals (outboard)	2,701	0.97
Totals (combined)	6,523	11.28

* Based on 150 gpm for vessels with inboard engines, 20 gpm for vessels with outboard engines, and an average operating time of 25 hours/month.

Table 2. Wet Exhaust Constituents Emitted from Two and Four-Stroke 10 Horsepower Gasoline Outboard Engines[8]

Constituent	Amount in Wet Exhaust from Two-Stroke Outboard Engines (mg/10 min)*	Amount in Wet Exhaust from Four-Stroke Outboard Engines (mg/10 min)
Benzene	2800	110
Toluene	8500	260
Ethylbenzene	2000	22
p/m-Xylene	6900	71
o-Xylene	3600	37
3 4-Ethyltoluene	3400	26
Mesitylene	1200	10
2-Ethyltoluene	870	8.7
Pseudocumene	4500	40
Hemellitene	1200	13
Indane	840	4.7
Indene	270	6.5
Naphthalene	1400	13
2-Methylnaphthalene	930	5.5
1-Methylnaphthalene	350	2.7
Formaldehyde	970	100

***Note:** Majority of small boat outboard engines in the Armed Forces are two-stroke engines

Table 3. Organic Compound Emission Factors for Diesel Engines[7]

Constituent	Emission Factor	
	(lb/MMBtu)*	(ng/J)
Benzene	0.000933	0.40119
Toluene	0.000409	0.17587
Xylenes	0.000285	0.12255
Formaldehyde	0.00118	0.5074
Acetaldehyde	0.000767	0.32981
Acrolein	0.0000925	0.039775
No_x	4.41	1896.3
CO	0.95	408.5
CO_2	164	70520
Naphthalene	0.0000848	0.036464
Acenaphthylene	0.00000506	0.0021758
Acenaphthene	0.00000142	0.0006106
Fluorene	0.0000292	0.012556
Phenanthrene	0.0000294	0.012642
Anthracene	0.00000187	0.0008041
Fluoranthene	0.00000761	0.0032723
Pyrene	0.00000478	0.0020554
Benzo(a)anthracene	0.00000168	0.0007224
Chrysene	0.000000353	0.00015179
Benzo(b)fluoranthene	9.91E-08	0.000042613
Benzo(k)fluoranthene	0.000000155	0.00006665
Benzo(a)pyrene	0.000000188	0.00008084
Indeno(1,2,3-cd) pyrene	0.000000375	0.00016125
Dibenz(a,h) anthracene	0.000000583	0.00025069
Benzo(g,h,i) perylene	0.000000489	0.00021027

* lb/MMBtu = pounds per million British thermal units

Table 4. Estimated Concentrations of Wet Exhaust Constituents from Two- and Four-Stroke Gasoline Outboard Engines

Constituent	Introduction Rate Two-Stroke Engines (mg /10 min)*	Introduction Rate Four-Stroke Engines (mg /10 min)*	Estimated Concentrations in Engine Wet Exhaust (mg/L)	
			Two-Stroke	Four-Stroke
Benzene	17360	618.2	22.93	0.82
Toluene	52700	1461.2	69.62	1.93
Ethylbenzene	12400	123.64	16.38	0.16
p/m-Xylene	42780	399.02	56.51	0.53
o-Xylene	22320	207.94	29.48	0.27
3 4-Ethyltoluene	21080	146.12	27.85	0.19
Mesitylene	7440	56.2	9.83	0.07
2-Ethyltoluene	5394	48.89	7.13	0.06
Pseudocumene	27900	224.8	36.86	0.3
Hemellitene	7440	73.06	9.83	0.1
Indane	5208	26.41	6.88	0.035
Indene	1674	36.53	2.21	0.048
Naphthalene	8680	73.06	11.47	0.1
2-Methylnaphthalene	5766	30.91	7.62	0.04
1-Methylnaphthalene	2170	15.17	2.87	0.02
Formaldehyde	6014	562	7.94	0.74

*Note: The majority of small boat outboard engines in the Armed Forces are two-stroke engines.

Table 5. Estimated Concentrations of Wet Exhaust Constituents from Diesel Inboard Engines

Constituent	Concentration in Air Exhaust (moles/ft^3)	Concentration in Discharge (mg/L)
Benzene	3.21E-08	1.87E-04
Toluene	1.19E-08	6.78E-05
Xylenes	7.22E-09	4.91E-05
Formaldehyde	1.06E-07	7.58E-01
Acetaldehyde	4.68E-08	4.83E-02
Acrolein	4.44E-09	6.15E-04
Nox	3.95E-04	1.82E-02
CO	9.11E-05	1.97E-03
CO2	1.00E-02	1.11E+01
Naphthalene	1.78E-09	2.19E-04
Acenaphthylene	8.93E-11	2.16E-06
Acenaphthene	2.47E-11	6.58E-06
Fluorene	4.72E-10	3.81E-04
Phenanthrene	4.43E-10	8.17E-04
Anthracene	2.82E-11	3.46E-05
Fluoranthene	1.01E-10	3.84E-06
Pyrene	6.35E-11	4.43E-04
Benzo(a)anthracene	1.98E-11	9.18E-04
Chrysene	4.15E-12	2.13E-04
Benzo(b)fluoranthene	1.05E-12	5.28E-06
Benzo(k)fluoranthene	1.65E-12	2.49E-06
Benzo(a)pyrene	2.00E-12	7.69E-05
Indeno(1,2,3-cd) pyrene	3.65E-12	3.45E-03
Dibenzo(a,h) anthracene	5.63E-12	5.05E-03
Benzo(g,h,i) perylene	4.75E-12	5.80E-03

Table 6. Estimated Annual Fleet-Wide Mass Loading of Wet Exhaust Constituents from Outboard Engines

Constituent	Concentrations (mg/L)	Estimated Mass Loading (kg/yr)	Estimated Mass Loading (lbs/yr)
Benzene	22.93	84,196	185,600
Toluene	69.62	255,595	562,500
Ethylbenzene	16.38	60,140	132,600
p/m-Xylene	56.51	207,483	456,400
o-Xylene	29.48	108,252	238,700
Naphthalene	11.47	42,098	92,800
2-Methylnaphthalene	7.62	27,965	61,700

* These values were based on an annual flow rate of 0.97 billion gallons/year (see Section 4.1). Mass loadings are based on estimated emissions from a 100 HP, two-stroke engine.

Table 7. Estimated Annual Fleet-Wide Mass Loading of Wet Exhaust Constituents from Diesel Inboard Engines

Constituent	Concentration in Discharge (mg/L)	Annual Mass Loading (Kilograms)	Annual Mass Loading (Pounds)
Polyaromatic Hydrocarbons (PAHs)			
Naphthalene	2.19E-04	8.56E+00	18.9
Acenaphthylene	2.16E-06	8.44E-02	0.186
Acenaphthene	6.58E-06	2.57E-01	0.566
Fluorene	3.81E-04	1.49E+01	32.8
Phenanthrene	8.17E-04	3.19E+01	70.3
Anthracene	3.46E-05	1.35E+00	2.98
Fluoranthene	3.84E-06	1.50E-01	0.330
Pyrene	4.43E-04	1.73E+01	38.1
Benzo(a)anthracene	9.18E-04	3.58E+01	79.0
Chrysene	2.13E-04	8.32E+00	18.3
Benzo(b)fluoranthene	5.28E-06	2.06E-01	0.454
Benzo(k)fluoranthene	2.49E-06	9.72E-02	0.214
Benzo(a)pyrene	7.69E-05	3.00E+00	6.61
Indeno(1,2,3-cd) pyrene	3.45E-03	1.35E+02	297
Dibenzo(a,h) anthracene	5.05E-03	1.97E+02	434
Benzo(g,h,i) perylene	5.80E-03	2.26E+02	499

* These values were based on an annual flow rate of 10.31 billion gallons/year (see Section 4.1)

Table 8. Comparison of Estimated Concentrations of Wet Exhaust Constituents and Water Quality Criteria (μg/L)

Constituent	Estimated Discharge Concentration	Federal Acute WQC	Most Stringent State Acute WQC
Outboard Engines			
Two-Stroke			
Benzene	22,930	None	71.28 (FL)
Toluene	69,620	None	2,100 (HI)
Ethylbenzene	16,380	None	140 (HI)
Naphthalene	11,470	None	780 (HI)
Four-Stroke			
Benzene	820	None	71.28 (FL)
Ethylbenzene	160	None	140 (HI)
Inboard Engines			
Acenaphthylene	2.16E-03	None	0.031 (FL)[1]
Phenanthrene	8.17E-01	None	0.031 (FL)[1]
Chrysene	2.13E-01	None	0.031 (FL)[1]
Benzo(a)pyrene	7.69E-02	None	0.031 (FL)[1]
Benzo(a)anthracene	9.18E-01	-	0.031 (FL)[1]
Benzo(b)fluoranthene	5.28E-03	-	0.031 (FL)[1]
Benzo(k)fluoranthene	2.49E-03	-	0.031 (FL)[1]
Indeno(1,2,3-cd) pyrene	3.45	-	0.031 (FL)[1]
Dibenzo(a,h) anthracene	5.05	-	0.031 (FL)[1]
Benzo(g,h,i) perylene	5.80	-	0.031 (FL)[1]
TOTAL PAHs (Inboard Engines)	16.3 [1]		0.031 (FL)[1]

Notes:
Refer to federal criteria promulgated by EPA in its National Toxics Rule, 40 CFR 131.36 (57 FR 60848; Dec. 22, 1992 and 60 FR 22230; May 4, 1995)
Where historical data were not reported as dissolved or total, the metals concentrations were compared to the most stringent (dissolved or total) state water quality criteria.

FL = Florida
HI = Hawaii

1: Florida criteria for total PAHs is for the total of the following individual PAH compounds: acenaphthylene, benzo-(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene, and phenanthrene. Estimated discharge concentrations for total PAHs represent a sum of these chemicals.

Table 9. Data Sources

	Data Source			
NOD Section	**Reported**	**Sampling**	**Estimated**	**Equipment Expert**
2.1 Equipment Description and Operation	X			X
2.2 Releases to the Environment	X		X	X
2.3 Vessels Producing the Discharge	UNDS Database			X
3.1 Locality	X			X
3.2 Rate	X		X	X
3.3 Constituents	X		X	X
3.4 Concentrations	X		X	
4.1 Mass Loadings			X	
4.2 Environmental Concentrations	X		X	
4.3 Potential for Introducing Non-Indigenous Species			X	

Calculation Sheet
Benzene

Background:

Henry's Law was used to estimate the concentration of components in wet exhaust from small boat inboard diesel engines. This calculation sheet shows the calculation for the concentration of benzene in the wet exhaust. Calculations for the other exhaust components were similar.

A heat balance was used to determine the approximate wet exhaust equilibrium temperature. The temperature was determined using an air exhaust flow rate of 2,190 cfm at 870 °F, and a water injection rate of 100 gpm at 60 °F. 60 °F is believed to be an appropriate average because most large military ports are located in areas with similar average water temperatures. For this calculation, we assume the exhaust gas to have thermal properties similar to air.

ΔH: Change in enthalpy, m: mass of air or water, Cp: Specific heat capacity of air or water

$\Delta H_{exhaust\ gas} = \Delta H_{water}$

$\Delta H_{exhaust\ gas} = mCp\ (200\ °F - T)$

$= (2{,}190\ ft^3/min)\ (0.0601\ lb_m/ft^3)\ (0.24\ Btu/lb_m°F)\ (870\ °F - T)$

$= 31.59\ Btu/°F\ min.\ (870\ °F - T)$ **(1)**

$\Delta H_{water} = mCp\ (T - 60\ °F) = (100\ gal/min)\ (8.345\ lb_m/gal)\ (1\ Btu/\ lb_m\ °F)\ (T - 60\ °F)$

$= 834.5\ Btu/°F\ min\ (T - 60\ °F)$ **(2)**

Setting (1) = (2) we obtain the following:

$31.59\ Btu/°F\ (870\ °F - T) = 834.5\ Btu/°F(\ T - 60\ °F)$

$31.59\ (T) + 834.5\ (T) = 870\ °F\ (31.59) + 834.5\ (60\ °F)$

T = **89.5 °F** = (9/5) °C + 32 = **32 °C**

This temperature was then used to determine the appropriate values for Henry's Law constants, which vary with temperature.

At dilute concentrations, the concentration of benzene dissolved in water can be found from Henry's Law:

$$X_{exhaust} = (H_a)\ (X_{water})\ /\ (P_t)$$

Where:

$X_{exhaust}$: Mole Fraction of Benzene in Exhaust
H_a: Henry's Law Constant (Adjusted Reference 7)
X_{water}: Mole Fraction of Benzene in Water
P_t: Total Exhaust Pressure (atm)

Rearranging, Henry's Law can be rewritten as:

$$X_{water} = (X_{exhaust})\ (P_t)\ /\ H_a$$

The mole fraction of benzene in exhaust can then be converted into a concentration of benzene in the wet exhaust in mg/L using the molecular weight of benzene.

Given Conditions and Assumptions:

55.56 moles H_2O in 1 liter, [(1000 g/liter) (mole H_2O / 18 g) = 55.56 moles H_2O / liter]
Exhaust temperature of 870 °F
2,190 cfm air exhaust flow rate for 228 kW diesel engine
0.401 ng/J generation rate of benzene
Backpressure (P_t) on engine is approximately 1.147 atm
Molecular weight of benzene is 78.11 grams per mole (78,110 mg/mole)
Based on a water temperature of 32 °C (305.15 K), Henry's Law constants (in atm) for the constituents are the following:

Constituent	**H_a (atm)**
Benzene	**6.52E+02**
Toluene	7.94E+02
Xylenes	7.64E+02
Formaldehyde	2.05E-01
Acetaldehyde	2.09E+00
Acrolein	1.98E+01
No_x	6.81E+04
CO	1.37E+05
CO_2	3.85E+03
Naphthalene	5.09E+01
Acenaphthylene	3.08E+02
Acenaphthene	2.84E+01
Fluorene	1.01E+01
Phenanthrene	4.74E+00
Anthracene	7.11E+00
Fluoranthene	2.61E+02
Pyrene	1.42E+00
Benzo(a)anthracene	2.41E-01
Chrysene	2.18E-01
Benzo(b)fluoranthene	2.47E+00
Benzo(k)fluoranthene	8.19E+00
Benzo(a)pyrene	3.22E-01
Indeno(1,2,3-cd) pyrene	1.43E-02
Dibenzo(a,h) anthracene	1.52E-02
Benzo(g,h,i) perylene	1.11E-02

The conversion of Henry's Law constants into common units is presented at the end of the calculation sheet.

Solution:
1) Total number of moles per cubic foot in the air exhaust, including constituents and circulated air, n_t

The number of moles per cubic foot can be determined using the ideal gas law; $PV = n_tRT$

Where:
P: Pressure within the exhaust piping, 1.147 atm
V: Volume of space occupied by gas (assume 1 ft^3)
R: Gas constant, 0.08206 L-atm/ K-mol
T: Temperature, 305.15 K

Rearranging the ideal gas law equation and solving for n_t/V:

$$n_t /V = P/RT$$

$$n_t /V = (1.147\text{atm}) / ((0.08206 \text{ L-atm/ K-mol}) (1 \text{ ft}^3 /28.32 \text{ L}) (305.15 \text{ K}))$$
$$= 1.30 \text{ moles/ ft}^3$$

2) Concentration of benzene in air exhaust, A_b

A_b= (0.401 ng/J) (228 kW) (3.6×10^6 J/kW-hr) (10^{-9}g/ng) (1000 mg/g) (min./2190 f^{t3}) (hr/60 min)

= 2.50×10^{-3} mg/ft^3

= (2.50×10^{-3} mg/ft^3) (mole benzene/78,110 mg) = 3.2×10^{-8} moles benzene/ft^3 exhaust

3) Mole fraction of gas in exhaust, P_a

$P_a = A_b$ / total molar concentration

P_a = (3.2×10^{-8} moles benzene/ ft^3 exhaust) / (1.30 total moles/ ft^3 exhaust)

$P_a = 2.46 \times 10^{-8}$ moles benzene/ mole exhaust

4) Mole fraction of gas in water, X_{water}

$X_{water} = (X_{exhaust}) (P_t) / H_a$

$X_{water} = (2.46 \times 10^{-8})$ (1.147 atm) / (652 atm)

$X_{water} = 4.33 \times 10^{-11}$ moles benzene/ mole water

5) Concentration of gas in water:

Per 1 liter of water;

Moles benzene = (4.33×10^{-11} moles benzene/mole H_2O)(55.56 moles H_2O/ 1 liter) = 5.19×10^{-9} moles/L

= (2.4×10^{-9} moles/L) (78,110 mg benzene/mole) = **1.87×10^{-4} mg/L benzene**

Determination of Henry's Constants

Henry's constants for the constituents were available, but units and temperature for the constants varied between the references used. Henry's constants with the following units were available:

1) H_1, atm
2) H_2, atm-m^3/mol

For purposes of clarity, the same calculation was used for each constituent. It was therefore necessary to convert all of Henry's constants to atm units, (1).

1) Conversion H_2 (atm-m^3/mol) to H_1 (atm):

$H_1 = (H_2 \text{ atm-m}^3/\text{mol})\ (55.6 \text{ mol water / L})\ (\text{ L / } 10^{-3} \text{ m}^3 \text{ water}) = (H_2)\ (55{,}600)$

Henry's constants with the following temperatures in degrees Celsius were available:

(1) 20 ^{o}C
(2) 24 ^{o}C
(3) 25 ^{o}C
(4) 40 ^{o}C
(5) 32 ^{o}C

Henry's constants increase on average about threefold for every 10 ^{o}C rise in temperature for most volatile hydrocarbons.[a] Therefore, with an increase in temperature the constants increase by a factor of $\Delta H = 3^{(\Delta T/10)}$. All of the constants were converted to 32 ^{o}C constants using the following conversions.

For Henry's constant at 32 ^{o}C and converting from Henry's constants at 20 ^{o}C , 24 ^{o}C, 25 ^{o}C, and 40 ^{o}C respectively:

$H_{32} = (H_{20})\ (3.74)$,

$H_{32} = (H_{24})\ (2.41)$,

$H_{32} = (H_{25})\ (2.16)$, and

$H_{32} = (H_{40})\ /\ (2.41)$

Example - Henry's Constant Calculation

For Acrolein, Henry's constant was available in atm-m^3/mol for 20^{o}c ($H_a = 9.54 \times 10^{-5}$)
H_a (atm) = $(9.54 \times 10^{-5}$ atm-m^3/mol) (55,600 mol/m^3) (3.74)
H_a = 19.8 atm

Using these methods, the constants were converted to atm units as shown in the table on the following page.

Table of Henry's Constants

Degrees **Source** **Units**	32 degrees Cooper atm	20 degrees USEPA (atm*m³/mol)	25 degrees Mackay (atm*m³/mol)	25 degrees Mackay Kpa m³/mol	40 degrees CH2M Hill (atm*m³/mol)	**32 degrees** **Henry's Constants** **atm**
Benzene				**5.50E-01**		**6.52E+02**
Toluene				**6.70E-01**		**7.94E+02**
Xylenes				**6.45E-01**		**7.64E+02**
Formaldehyde		**9.87E-07**				**2.05E-01**
Acetaldehyde					**9.05E-05**	**2.09E+00**
Acrolein		**9.54E-05**				**1.98E+01**
Nox	**3.18E+04**					**3.18E+04**
CO	**6.35E+04**					**6.35E+04**
CO2	**1.95E+03**					**1.95E+03**
Naphthalene		1.15E-03	**4.24E-04**	4.30E-02		**5.09E+01**
Acenaphthylene		**1.48E-03**				**3.08E+02**
Acenaphthene		9.20E-05	**2.37E-04**	2.40E-02		**2.84E+01**
Fluorene		6.42E-05	**8.39E-05**	8.50E-03		**1.01E+01**
Phenanthrene		1.59E-05	**3.95E-05**	4.00E-03		**4.74E+00**
Anthracene		1.02E-03	**5.92E-05**	6.00E-03		**7.11E+00**
Fluoranthene		6.46E-06	**2.17E-03**	2.20E-01		**2.61E+02**
Pyrene		5.04E-06	**1.18E-05**	1.20E-03		**1.42E+00**
Benz(a)anthracene		**1.16E-06**				**2.41E-01**
Chrysene		**1.05E-06**				**2.18E-01**
Benzo(b)fluoranthene		**1.19E-05**				**2.47E+00**
Benzo(k)fluoranthene		**3.94E-05**				**8.19E+00**
Benzo(a)pyrene		**1.55E-06**				**3.22E-01**
Indeno(1,2,3-cd) pyrene		**6.86E-08**				**1.43E-02**
Dibenz(a,h) anthracene		**7.33E-08**				**1.52E-02**
Benzo(g,h,i) perylene		**5.34E-08**				**1.11E-02**

Bold: Original Referenced Number

Sources:

a. Kavanaugh, M. C. and R. Rhodes Trussell, "Design of Aeration Towers to Strip Volatile Contaminants from Drinking Water" Journal of the American Water Works Association, December, 1980.

b. Cooper, D. and F. Alley, Air Pollution Control, A Design Approach. Waveland Press, Inc., 1986.

c. United States Environmental Protection Agency, Office of Air Quality Planning and Standards. Ground-Water and Leachate Treatment Systems Manual. R-94, January 1995.

d. Mackay, D. and W. Y. Shiu, "A Critical Review of Henry's Law Constants for Chemicals of Journal of Phys. Chem. Ref. Data. Vol. 10, No. 4, pp. 1175-1199. 1981.

e. CH_2M Hill Inc., Bay Area Sewage Toxic Emissions Model. Version 3, 1992.