United States
Environmental Protection
Agency

Municipal Environmental Research
Laboratory
Cincinnati OH 45268

Research and Development

EPA-600/S2-81-192 Oct. 1981

EPA

Project Summary

Treatment Effectiveness: Oil Tanker Ballast Water Facility

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The large, modern ballast water treatment plant at the Valdez, Alaska, marine terminal was studied using specially developed chemical analytical methods to determine the effectiveness of each unit process and to characterize compositional changes in the process stream. The studies disclosed that the state-of-the-art processes are generally effective in reducing the free oil content of the oily wastewater discharged from arriving tankers. A reduction of more than 99.8% in the organic load of the process stream is realized with ballast water treatment by gravity separation, dissolved air flotation, and retention in polishing ponds.

Less effectively removed, however, are the water soluble fractions of the oily wastewaters, which often include five priority pollutants: benzene, toluene, ethylbenzene, phenol, and naphthalene. Such priority pollutants make up more than 50% of the total organic load in the effluent from the ballast treatment plant, and they are discharged in significant quantities into the receiving waters of Port Valdez. The plant discharges approximately half a metric ton of organic carbon each day. Included in this daily discharge are 102 L of benzene, 91 L of toluene, 45 L of ethylbenzene/xylenes, 27 kg of phenol, and 2.8 kg of naphthalene.

Because benzene, toluene, and ethylbenzene/xylenes constitute a significant fraction of the total organic discharge, their distribution in the receiving waters was studied. During the summer months, when the waters of the fjord are stratified, the effluent does not mix uniformly with the receiving waters, but forms a submerged field of diluted effluent. The aromatic hydrocarbons are contained at a depth of 50 to 70 m in a thin trap zone that spreads horizontally as far as 2 to 3 km from the plant outfall. The top of the trap zone moves progressively farther below the surface as the summer heating season progresses—from 50 m in June to 65 m in September. No aromatic hydrocarbons were found in the fjord outside the confines of the trap zone.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Current technology for the physical treatment of oily wastewater is based on gravity separation followed by air or gas flotation and impoundment. State-of-the-art ballast water treatment plants are designed primarily for removal of suspended organic matter or water-insoluble petroleum (commonly called "free oil"). This assessment of the technology's effectiveness indicates that, when properly operated, the treatment can produce effluents with very low levels of free oil. The water soluble fraction of oily wastes, however, remains essentially unaffected by the treatment and enters receiving waters uncontrolled in significant amounts.

Our studies have shown that the dissolved fraction of oily wastewaters quite often contain five priority pollutants: benzene, toluene, ethylbenzene, phenol, and naphthalene. Because aromatic compounds are toxicologically important and the five principal types found in oily wastewaters are designated as priority pollutants by the U.S. Environmental Protection Agency (EPA), their role in the treatment process and ultimate fate in the receiving environment is of prime environmental concern.

The object of this study was to determine the capabilities and limitations of a modern, state-of-the-art oily waste treatment technology for removing conventional and unconventional pollutants, including priority toxic pollutants. The plant selected for this study is one of the largest on-shore oily wastewater treatment installations. The plant is located in Port Valdez, Alaska, in the northernmost part of Prince William Sound. This plant first came on stream in August 1977, when the TransAlaska Pipeline began operations bringing large tankers with large volumes of ballast to Port Valdez. The oil tankers arrive from southern ports partially loaded with ballast water (up to 40% of the tanker's capacity). The latter is discharged to the plant for treatment and ultimate disposal into Port Valdez, and the tankers are reloaded with Prudhoe Bay crude from the pipeline for shipment south. Average daily water discharge rate of this plant is 40,000 to 45,000 m^3.

The Port Valdez ballast water treatment facility uses gravity separation under quiescent aging conditions in above-ground, 68,000-m^3, steel-cone-roof storage tanks, followed by chemically aided flocculation and a dissolved air flotation process (with capability for a final pH adjustment), and an effluent impoundment basin. Final disposal of the treated water is through a submerged diffuser line laid into Port Valdez.

The effluent from the gravity separators enters a secondary aeration flotation process unit. This system is the effluent recirculation type, in which a side stream of treated water is pressurized, aerated, and mixed with wastewater undergoing treatment.

The separation of oil from water by aeration was initially aided by the addition of flocculating chemical agents (alum and polyelectrolytes). In late 1978, the use of alum and polyelectrolyte was stopped, and the plant switched to using demulsifiers. The effluent from the secondary treatment unit enters the holding ponds before discharge to the receiving waters of Port Valdez. The processing elements are sized for treating the entire contents of the primary separation and storage tanks within a 36-hr period, and effluent impounding facilities are sized to hold the initial average flow for a mean time of approximately 10 hr before its discharge into Port Valdez waters.

Objectives

Objectives of this study included determining the effectiveness of organics removal in a modern oily wastewater treatment operation and characterization of compositional changes in the process stream. To accomplish those objectives, it was necessary to monitor the organic content of the process stream in terms of the total material balance. When the results indicated a substantial discharge of priority pollutants (dissolved aromatics), brief surveys to indicate the distribution of these substances in Port Valdez were also carried out.

Procedures

Preliminary tests carried out on samples of process water from the Alyeska ballast treatment plant disclosed that organic matter present in the stream included volatile organic matter (lower molecular weight [mw] hydrocarbons), dissolved nonvolatile organic matter (including phenolic and naphthalenic compounds), and suspended oil. To develop information on the effectiveness of oil removal and to characterize the compositional changes taking place in the process, it was necessary to measure the concentrations of each organic fraction and to characterize the chemical nature of principal compounds present.

An analytical protocol (Figure 1) was devised that included:

1. Determination and chemical characterization of the volatile fraction,
2. Determination and chemical characterization of the dissoved nonvolatile fraction, and
3. Determination of the suspended organic matter.

The total organic load (TOL) (the overall organic concentration in the process stream expressed in mg C/L) is defined as the sum of the volatile organics, dissolved nonvolatile organic matter, and suspended organic materials. Daily samples were collected from the plant for analysis during three 10-day periods (in August 1978, February 1979, and June 1979).

A more sensitive protocol was also devised for analyzing samples collected from the fjord in June 1979, September 1979, and June 1980.

Results

Treatment

The effectiveness of oily wastewater treatment can be defined as its ability to remove petroleum and related organic matter from the water. Determination of organic load reduction in the process stream can be considered a measure of process effectiveness.

The process stream in a ballast water treatment plant originates with untreated ballast entering from tankers, and it ends with treated effluent leaving through a diffuser laid on the bottom of Port Valdez. During its passage through the plant, ballast water undergoes two principal physical separations: quiescent gravity separation in primary holding tanks, and dissolved air flotation in flowthrough chambers. Consequently, the chemical composition of the process water is expected to be qualitatively and quantitatively different at three major points in the process: incoming ballast, effluent from the gravity separator, and final treated effluent. Those three points were selected as the principal sampling points during this study.

Analyses of primary and final effluents conducted during the study periods of summer 1978, winter 1979, and summer 1979 indicated very little difference (qualitative or quantitative) in the 10-day average chemical compositions of the process streams from season to season. This result was in spite of a large day-to-day fluctuation in the chemical composition of the stream observed during each study sequence. The reason for this may lie in the averaging effect of the large volumes of water processed, consistency of plant operational procedures, and relative similarity in the chemical composition of incoming ballast water. For this reason, all the experimental data

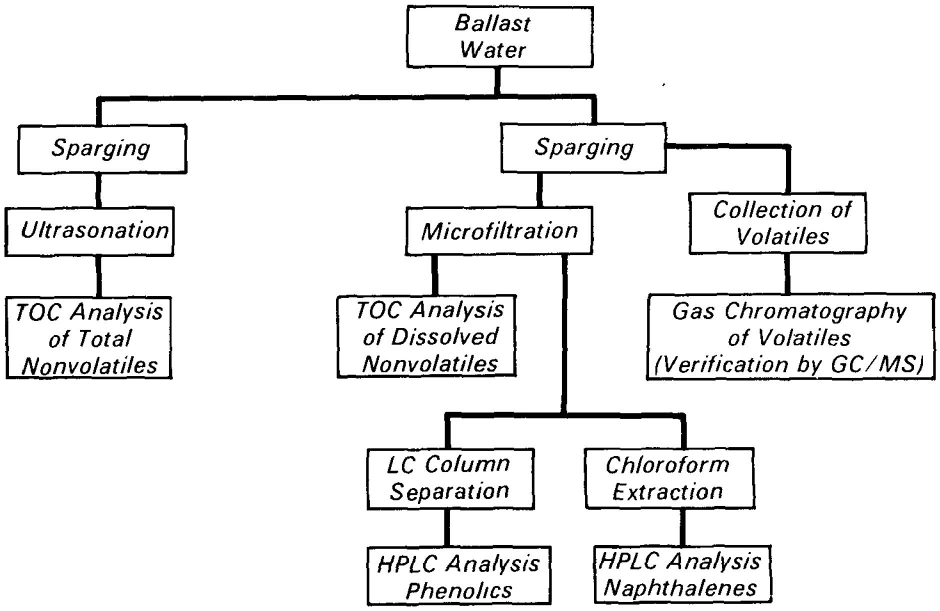

Figure 1. *Protocol for ballast water hydrocarbons analysis*

obtained during this study for primary and final effluent chemical compositions were averaged and used in subsequent discussions. Using these data, it was possible to develop complete organic material balances for the primary and final effluents.

Difficulties were experienced in representative sampling of incoming untreated ballast water. The ballast in taker compartments is heterogeneous, and oil and water are fairly well separated. This fact makes representative sampling of incoming water extremely difficult. The problem was overcome by combined use of plant operating records and the experimental data to produce an organic material balance for incoming untreated ballast waters. The plant records contained information on the amount of water processed and the amount of free oil removed. Based on the 2 years of plant operation records, it was estimated that incoming ballast water contained an average of 7,200 mg C/L of suspended (recoverable) oil. The concentration of dissolved organic matter (volatile and nonvolatile) in the incoming untreated ballast was determined during the 10 days of the winter 1979 study. A combination of those two sources of data provided an organic material balance in the incoming ballast.

The 2-year average for suspended oil was estimated to be 7,200 mg C/L, and the level of all dissolved organics was experimentally determined at approximately 20 mg C/L. Consequently, the total organic load of incoming, untreated ballast is estimated at 7,200 mg C/L. The dissolved organics were composed of approximately 13 mg C/L of volatile hydrocarbons and 5 mg C/L nonvolatile organic compounds. The organic load of incoming ballast was reduced to approximately 17 mg C/L by the gravity separator treatment and then was finally reduced to approximately 11 mg C/L by the secondary treatment of aeration-flotation and in-pond retention. The overall organic load reduction by the treatment plant was on the order of 99.8% to 99.9% (Table 1).

The elimination of suspended organic matter (the oil) was almost complete: 99.97% of it was removed by the process. But the dissolved organic matter was reduced by only 50%. The overall reduction of volatile hydrocarbons was approximately 62%, with reduction of volatile aliphatic hydrocarbons being almost complete (95%). The concentration of the dissolved nonvolatile fraction was reduced by only 20%, however.

The gravity separator reduced the total organic load by 99.8%. The dissolved air flotation unit improved on this reduction by less than 0.1%, as it removed about half of the remaining load.

The effectiveness of plant operation can be summarized in the following manner: the gravity separator removes almost all of the suspended oil, and some of the dissolved (both volatile and nonvolatile) organic compounds. The dissolved aeration-flotation operation contributes to further reduction of volatile organic matter, but it has very little effect on the concentration of dissolved nonvolatile organics.

The studies also disclosed that treated effluent contained a substantial amount of petroleum-derived, dissolved organic matter, including five priority pollutants: benzene, toluene, ethylbenzene, phenol, and naphthalene. The average chemical composition of treated effluent is shown in Table 2.

Volatile aromatic hydrocarbons constitute almost half of all organic compounds present in the treated effluent. The principal compounds present are benzene, toluene, xylenes, and ethylbenzene. The nonvolatile dissolved fraction (35% to 40% of the total organic load) contains significant amounts of phenols and of naphthalene and its derivatives.

Because of the large volume of ballast water processed, significant amounts of aromatic hydrocarbons and nonvolatile organic compounds are discharged daily. The daily average discharge of aromatic hydrocarbons during 2 years of treatment plant operation was estimated at 230 to 260 L.

Disposal

The treated effluent from the terminal facility is discharged into the Port Valdez fjord, which is about 5 km wide by 18 km long, with a mean depth of about 180 m. The port is shaped somewhat like a bathtub, with steep sides on the north and south; it has a nearly horizontal bottom at a depth of about 240 m over three-quarters of its length. The bottom of the easternmost quarter of the fjord rises rather uniformly to the eastern shore at the former townsite of Valdez. The waters of Port Valdez and Valdez Arm exhibit a pronounced annual density cycle, varying between strongly stratified summer and early autumn conditions and a nearly homogeneous state that persists from late fall to early spring.

Treated effluent is discharged from the diffuser about 380 m from the plant depths of 65 to 75 m through dispersion ports as turbulent jets, providing for highly efficient mixing of the effluent and receiving water over a distance of approximately 60 m. The buoyant

Table 1. *Reduction of Organic Content of Process Water by Treatment Process, Port Valdez, Alaska, August 1978 to June 1979*

Type of Organic Material	Untreated Ballast (mg C/L)	% Reduction	Gravity Separator Effluent (mg C/L)	% Reduction	Final Effluent (mg C/L)	Total % Reduction by the Process
1 Volatile hydrocarbons						
Benzene	4	25	3	33	2	50
Toluene	3	0	3	33	2	33
Xylenes/ethylbenzene	2	0	2	50	1	50
Other	4	50	2	90	0 2	95
Total	13	30	9	44	5	62
2 Dissolved nonvolatile organic matter	5	20	4	0	4	20
3. Suspended organic matter (free oil)	~7200	99.9	4	50	2	99 97
Total organic load	~7220		17	35	11	99.8

Table 2. *Average Hydrocarbon Content of Port Valdez, Alaska, Treated Ballast Water, August 1978 to June 1979*

Item	mg C/L	Confidence Interval (E) at 95% limit	% of TOL
Benzene	2.0	0.5	19
Toluene	1.8	0.3	17
Xylenes/ethylbenzene	0.9	0.1	8
Aliphatic hydrocarbons	0.2	0.05	2
Total volatile hydrocarbons	4.9	0.8	46
Total dissolved organics	4.3	0.5	40
Total suspended organics	1.5	0.9	14
Average total organic load of the effluent	10.7	1.6	100

effluent plume will entrain fjord water and will rise toward the surface until it reaches a level with the same density as that of the plume mixture. At this neutral buoyancy level, known as the trap level, the plume spreads horizontally, creating a submerged field of diluted effluent.

Aromatic hydrocarbons in the receiving waters were sampled and analyzed in June to July 1979, September 1979, and June 1980 (Figure 2). In the June-July 1979 study, sampling was carried out at 40- and 60-m depths at Stations 42 and 51 and at a 60-m depth at a station 2 km to the north. Detectable amounts of aromatic hydrocarbons were found at all three stations.

In the September 1979 study, at the end of the summer warm period, an attempt was made to determine the vertical profile of aromatic hydrocarbons on the boundary of the diffuser mixing zone. The arm surface layer at the time extended to the depth of the diffuser (approximately 75 m). Sampling was carried out at Stations 32, 34, 42, 44, and 51. At Station 42, the maximum concentration of 21 µg/L was found at a depth of 77 m (within 2 m of the bottom). The concentration decayed rather rapidly in the vertical plane, and at a depth of 70 m (9 m above the bottom), it was only 2.4 µg/L. The centerline of the contaminated zone was at an average depth of approximately 65 m, or within 10 m of the depth of the diffuser.

In the June 1980 study, a further brief attempt was made to define the position and geometry of the effluent plume. During this period, the low-density surface layer extended to depths of 40 to 50 m. Station 42 on the northwestern border and Station 34 on the northeastern border of the diffuser mixing zone were sampled, plus Stations 45 and 56 (located 175 m from each other). Four to five water samples were collected at each station at 10-m vertical intervals from depths of 40 to 70 m. The centerline (maximum concentration of aromatic hydrocarbons) of the submerged field on the boundaries of the mixing zone was at a depth of 50 m, or approximately 20 m above the mean depth of the diffuser (Figure 3). The submerged hydrocarbon field was contained in a very narrow vertical zone (approximately 10 m) on the boundaries of the mixing zone. A minimum dilution of approximately 1:2600 was achieved approximately 0.5 km from the point of discharge.

Conclusions

This 2-year study of the operation and effectiveness of a large-scale ballast treatment facility at the Port Valdez, Alaska, marine terminal has disclosed that the plant removed more than 99% of all the suspended organic matter (oil) and that volatile aromatic hydrocarbons (primarily benzene, toluene, xylenes, and ethylbenzene) constitute the principal and toxicologically important component of the treated effluent discharged to the environment. Because of the large volume of ballast water processed (40,000 to 45,000 m^3/day), significant quantities of volatile aromatic compounds are discharged daily into the Port Valdez fjord. The average daily discharge of aromatic hydrocarbons was 230 to 260 L, which totaled approximately 175,000 L of aromatic hydrocarbons between August 1977 and August 1979.

Three short-term studies of the aromatic hydrocarbon distribution in the fjord during the summers of 1979 and 1980 indicated that the effluent plume from the diffuser rose to the level of a density discontinuity and then spread horizontally in a thin, pancake-like layer. The depth to the discontinuity was about 50 m in June and 75 m in September. The aromatic layer was some 20 m thick at the diffuser and was found to extend up to 3 km from it.

The full report was submitted in fulfillment of Contract No. 68-03-2648 by Rockwell International Corporation, Newbury Park, CA 91320, under the sponsorship of the U.S. Environmental Protection Agency

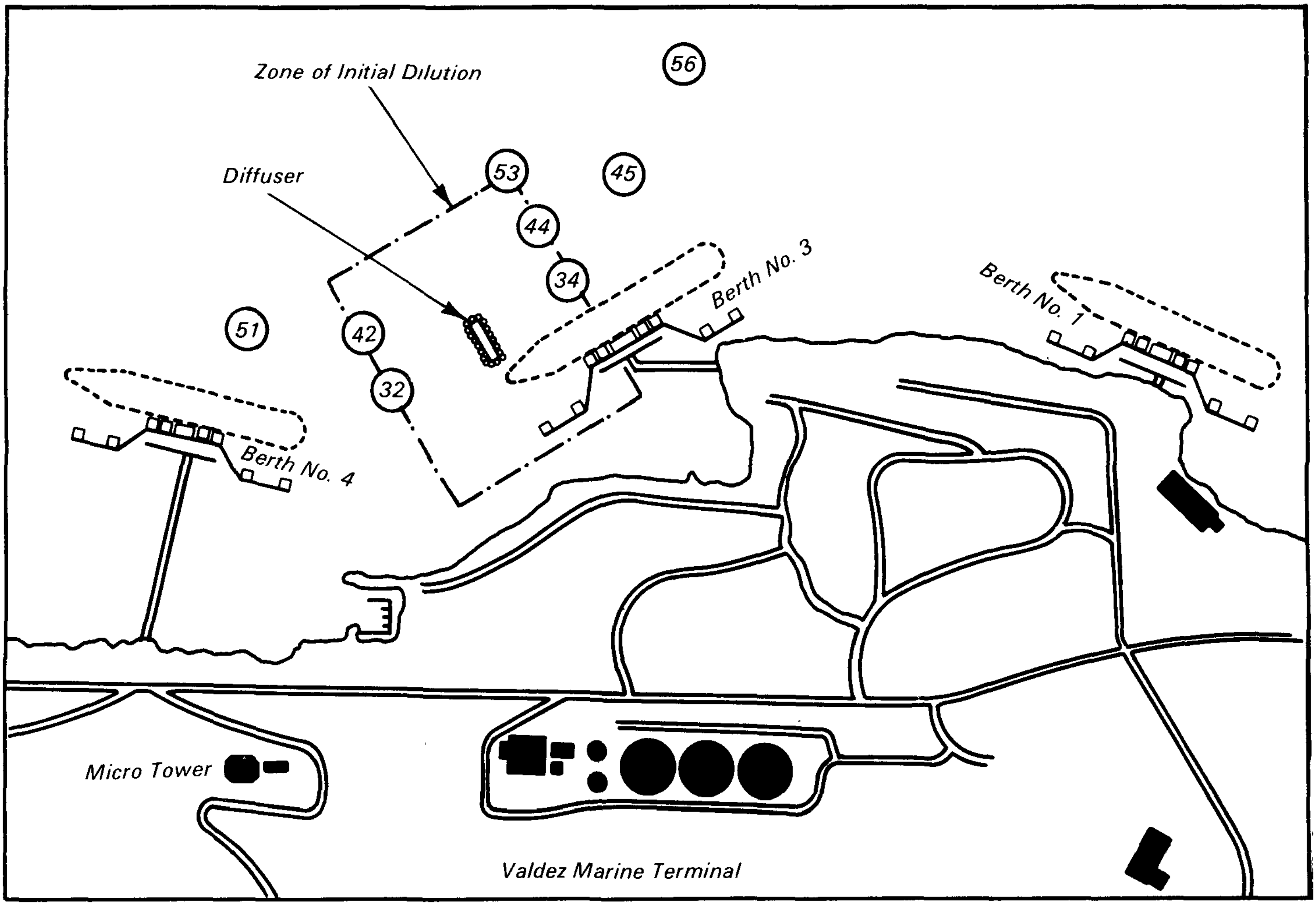

Figure 2. *Hydrocarbon sampling stations nearest the terminal, June 1979, September 1979, and June 1980.*

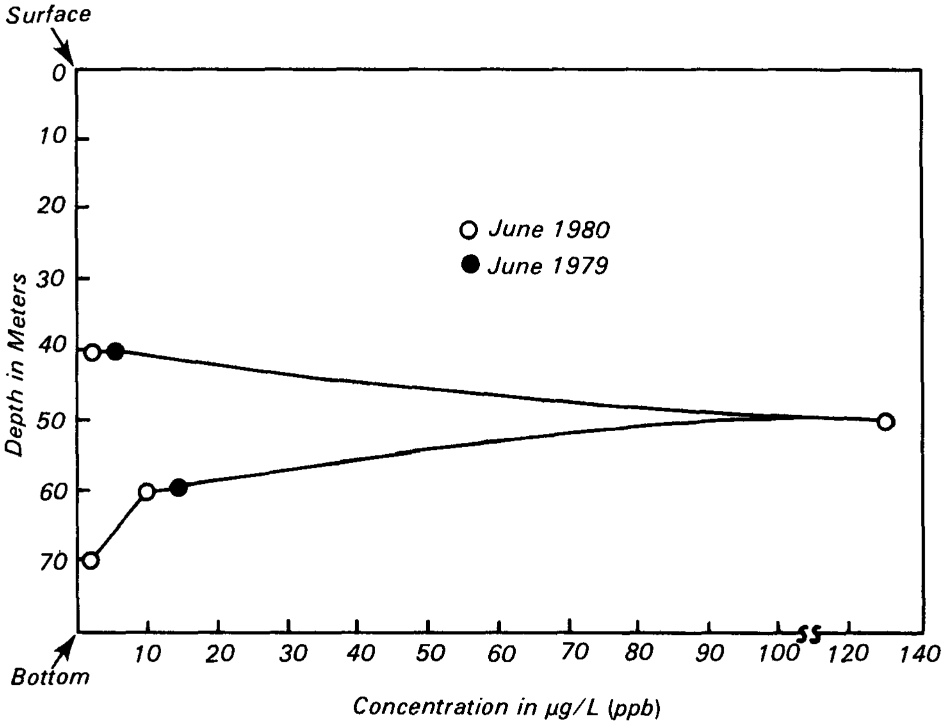

Figure 3. *Vertical distribution of aromatic hydrocarbons at Station 42, Port Valdez, Alaska.*

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***John S. Farlow** is the EPA Project Officer (see below).*

The complete report, entitled "Treatment Effectiveness: Oil Tanker Ballast Water Facility," (Order No. PB 82-101 361; Cost: $15.50, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
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