LBL-13665

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

EARTH SCIENCES DIVISION

RECEIVED
LAWRENCE
BERKELEY LABORATORY

OCT 28 1982

LIBRARY AND
DOCUMENTS SECTION

Presented at the 4th Conference on Water Chlorination, Pacific Grove, CA, October 18-23, 1981

BROMOFORM PRODUCTION IN TROPICAL OPEN-OCEAN WATERS: OTEC CHLORINATION

Eric O. Hartwig and Richard Valentine

September 1981

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

LBL-13665 c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL 13665

BROMOFORM PRODUCTION IN TROPICAL OPEN-OCEAN WATERS: OTEC CHLORINATION

Eric O. Hartwig[1]

Richard Valentine[1,2]

[1]Marine Sciences Group
Earth Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

[2]Sanitary, Environmental, Coastal and Hydraulic Engineering
Civil Engineering Department
University of California
Berkeley, CA 94720

September 1981

This work was supported by the Assistant Secretary for Conservation & Renewable Energy, Office of Solar Power Applications, Division of Ocean Energy Systems, Department of Energy under contract number W-7405-ENG-48.

INTRODUCTION

Ocean Thermal Energy Conversion (OTEC) is an energy production process utilizing the temperature differential between cold, deep and warm, surface ocean waters. A closed cycle OTEC plant is depicted in Figure 1. Warm surface water is used to evaporate a working fluid (e.g., NH_3) which expands and drives a turbine to generate power. Cold, deep water is used to condense the working vapor back into a liquid.[1]

In the study reported here the bromoform, and other volatile organics produced while chlorinating both the evaporator and condenser seawater during operation of the one megawatt (1 MW) OTEC-1 test facility are reported. Although many halogenated compounds might be produced as a result of chlorination, the quantitative analyses in this study focused on volatile EPA priority pollutants. Bromoform is the compound specifically recognized as a potential pollutant. Its concentration may be indicative of other halogenated species. Glaze et al.[2] observed a relationship between the concentration of trihalomethanes and the concentration of total halogenated organic compounds in chlorinated water.

Determining the proper chlorination schedule and dose is important to the viability of an OTEC plant for three reasons.

1. Maintaining the heat transfer coefficient at a high value.

2. Parasitic power losses from chlorine production.

3. Environmental consequence of dosing chlorine to the marine environment.

These reasons are discussed below.

The first reason (maintaining a high heat transfer coefficient) involves the use of chlorine as a biofouling control agent. For OTEC to be economically feasible, biofouling control is required to maintain the thermal resistance of fouling (R_f) between 1.8×10^{-5} to 9.0×10^{-5} m^2 $^oK/W$ (0.0001 to 0.0005 ft^2 hr $^oF/BTU$)[3,4]. By contrast heat exchanger design in the process industries commonly operate at an R_f = 1.8×10^{-4} m^2 $^oK/W$ (0.001 ft^2 hr $^oF/BTU$). A biofouling layer 50 um thick corresponds to an R_f = 9.0×10^{-5} m^2 $^oK/W$ (0.0005 ft^2 hr $^oF/BTU$) and would reduce OTEC heat exchange efficiency by 15-25%[4]. The heat exchangers constitute about one-third the total capital cost of an OTEC plant[5]. To compensate for the loss of heat transfer efficiency due to biofouling the heat exchangers would have to be even larger and more expensive.

The total (Carnot) efficiency for an OTEC heat engine is a function of the absolute temperature (degrees Kelvin) of the warm and cold water. For surface water of 25°C and deep water of 5°C the Carnot efficiency is 6.7% [Carnot efficiency = $(^oK_2 - ^oK_1 / ^oK_2) \times 100$]. The actual efficiency of operating OTEC plants is expected to be 3-5% as the entire temperature difference cannot be extracted due to engineering constraints and reduction of heat transfer efficiency due to biofouling. A temperature difference (T) of 20°C between warm surface and cold deep water (800-1200m) is required for economic operation of a closed cycle OTEC plant[1]. Figure 2 shows those regions of the Pacific and Indian Oceans where the temperature difference between surface waters and 1000m deep water is 20°C or greater.

The second reason (chlorination parasitic power losses) involves

the electrical requirement of chlorine production. An operating OTEC plant has such a low total efficiency it cannot lose 15-25% of its heat transfer efficiency and produce exportable power economically. The parasitic losses of pumping water, pumping working-fluid, chlorine production, other power equipment and hotel needs would utilize almost all available power. For example, the estimated power requirement for the water pumps alone is 22-26% of gross power production[6]. Table 1 summarizes parasitic power requirements for a proposed 100 megawatt (MW) OTEC plant operated with continuous and intermittent (1 hr/day) low and high chlorine doses of 0.20 and 1.6 mg/l, respectively. Total parasitic power losses due to chlorination are projected to range from 0.13 to 25.6%. It is desirable to keep parasitic power losses to a minimum.

The third reason (environmental consequences) involves the impact of dosing chlorine into the marine ecosystem. This impact must be further elucidated[8]. The implications of chlorine dosing are more apparent to those persons used to working in the freshwater environment if one considers that chlorinating the water flow of a 100 MW OTEC plant is like chlorinating the entire flow of the Missouri River (390 m^3 min^{-1} MW^{-1}). With this analogy it is easier to grasp the importance of identifying and quantifying the environmental loading rates of potentially deleterious halogenated products.

METHODS

OTEC-1 Test Facility

The OTEC-1 test facility was mounted in the vessel Ocean Energy Converter (OEC) off the island of Hawaii (Figure 3). The plant withdrew

deep-ocean water from 640 m and surface water from 8 m and had a mixed discharge at 8 m.

Figure 4 is a water flow schematic of the OTEC-1 plant and Table 2 gives flow rates, and water transit times. Also, depicted are the sampling ports and the chlorination points for the evaporator and condenser. The evaporator and condenser system were individually chlorinated for one hour each day permitting higher chlorine doses as the effluents (one chlorinated, the other not chlorinated) were combined before being discharged. Chlorination was achieved using a commercially available (Chloropac) electrolytic chlorine generator.

Total Residual Oxidants

The proper term for the oxidizing chemicals present after chlorination of seawater is "residual oxidants", as chlorine reacts with organic molecules, ammonia and the bromide ion present in seawater to produce a variety of chlorine and bromine containing products and oxidants[9]. Total residual oxidant (TRO) analyses were done immediately after sampling using either the amperometric or iodiometric (colorimetric) back-titration standard methods[10] as described by Carpenter, et al.[11] Duplicate residual oxidant analyses were performed to compare amperometric against iodiometric (colorimetric) end-point detection.

Data comparing the amperometric versus the iodiometric end-point detection method is presented in Table 3. The amperometric method under actual OTEC-1 operating conditions (i.e., at sea with a contracted technician) gave somewhat lower mean values and was less variable. To reduce variance TRO was determined using the amperometric method.

Total Residual Oxidant Demand

Water samples for oxidant demand testing were taken in 1 liter glass bottles when chlorination was not being done and brought to room temperature in the onboard lab. A small known volume of the hypochlorite output from the chlorinator was taken during the daily chlorination period. A small volume of the product hypochlorite was placed in 300 ml glass BOD bottles. The volume of hypochlorite added was sufficient to produce a TRO concentration in blank distilled water of between 0.5 and 0.8 mg/l. To replicate bottles 200 ml water samples were added for 2 and 5 minute contact times. After the required contact time, phenylarsine oxide (PAO) was added to the test bottles, and the contents were analyzed for TRO. The difference between the TRO oxidant levels in the blanks and in the samples was the oxidant demand.

Ammonium

Samples for ammonium analysis were taken in clean 1 liter glass bottles and returned to the OEC laboratory. An aliquot of the sample was transferred to a clean 125 ml polyethylene bottle and frozen. Analyses for ammonium were done using the alkaline hypochlorite method[12].

pH

The pH of seawater samples was analyzed onboard using an Orion Model 901 digital pH meter and Orion glass pH and reference electrodes[13].

Total Organic Carbon

Samples for total organic carbon (TOC) analysis were taken in

chromic acid-washed, distilled water rinsed Pyrex bottles fitted with Teflon -lined screw caps. Samples were frozen immediately, and shipped frozen to the shore-based laboratory. TOC analysis was done using a modification of the method described in Strickland and Parsons[13], utilizing the Oceanography International non-dispersive infra-red TOC analyzer.

Volatile Organic Compounds

The procedures and methodologies used in the analysis of volatile organic compounds, including bromoform, were based on EPA Method 624[14]. Samples were taken on two successive days in order to examine the variability of bromoform production. The day to day variability of the chemistry of the evaporator and condenser water is as great as week to week or month to month variability (unpublished data from OTEC-1, NPDES permit monitoring). Therefore, sampling on two successive days is a satisfactory method to examine a range of bromoform production values.

Samples were taken in precleaned and dried vials and capped with Teflon -lined silicone rubber septa. One set of samples was treated with sodium thiosulfate (3.0 mg/40 ml vial) to stop formation of organohalides after samples were taken; a replicate set of samples was not so treated. Samples were kept refrigerated and allowed to react for 17 to 20 days before anaylsis by GC/MS (analyses performed by Science Applications, Inc., La Jolla, CA).

The analytical method involved sparging volatile compounds from the liquid sample using an inert gas and trapping these compounds on a sorbent resin trap (Tenax-GC). Using thermal desorption the volatiles

were transferred to a gas chromatographic column which separated the sample mixture prior to detection by mass spectrometry. Quantification was accomplished by comparing the intensity of fragment ions specific to each compound to the response of an internal standard. Standard mixtures of volatile priority pollutants were analyzed to generate a response factor which was then applied to compounds identified in the sample. Qualitative identification (tentative) was made using a 26,000 entry computer library search program.

Modifications made to Method 624 included the use of cryogenic focusing and separation by fused silica high resolution gas chromatography. The mass spectrometer was maintained as the detector system for these analyses. Deuterium labeled benzene, toluene and ethylbenzene were employed as laboratory quality control mechanisms. In addition, a 25 ml aqueous sample was used instead of the normal 5 ml sample that is called for in Method 624. The effective limit of detection was lowered from 20 ug/l to 1 ug/l.

Non-Volatile Organic Compounds

Analysis (analyses performed by Tracor Instruments, Austin, TX) of non-volatile organo-halide compounds was by high performance liquid chromatography (HPLC). Four water samples from the OTEC system were analysed; evaporator and condenser inlets both before and during chlorination. Samples were taken in clean, 4 liter amber glass bottles fitted with Teflon-lined screw tops. The bottles and caps were hexane-washed and triple rinsed with deionized-distilled water before being filled.

The analytical procedure was as follows: sample volumes of 250 ml

were concentrated onto a short (7 cm x 4.6 mm I.D.) column packed with 60 um octadecylsilyl-bonded silica. The column was then backflushed into the chromatographic stream using a linear sixty minute gradient from 1:1 methanol:water to 1:1 methanol:isopropanol. Similarly, a 200 ml standard containing chlorobenzene, 1,4-dichlorobenzene, 1,2,3-trichlorobenzene, and hexachlorobenzene, each at 10 ppb, was concentrated and eluted.

RESULTS

Oxidant Demand

The oxidant demand (2 and 5 minute) of the evaporator, condenser and mixed discharge system waters is shown in Table 4. The oxidant demand in all three systems was low. At similar dosed chlorine levels Eppley et al.[15] and Goldman et al.[16] found a much higher oxidant demand than found in this study. The initial high demand of seawater samples is generally attributed to organic demand. The coastal water samples used by Eppley, et al.[15] and Goldman et al.[16] have a higher organic content than open ocean tropical waters. The lower organic content may be the reason a lower demand was measured in the present study.

Total oxidant demand was a function of the water sample type, i.e., evaporator, condenser or mixed discharge. The oxidant demand of condenser water was significantly lower than demand of evaporator water, while the mixed discharge oxidant demand reflected a mixture of the two.

Volatile Organic Compounds

The results of GC/MS analysis of the 16 samples for volatile organ-

ics are presented in Table 5. Quantitative values are listed for all compounds that were included in the standard mixture. Compounds that were tentatively identified using computer search routines (in many cases, these compounds were less than 10% of the intensity of the internal standard) are listed with a "+" and had a concentration of less than 2 ug/l. Of the compounds listed that were quantitatively identified, dichloromethane and benzene are the only normal laboratory contaminants that are seen routinely. Levels of up to 8 ug/l for dichloromethane and 2 ug/l of benzene are normal contamination levels. Benzene reported in Blank #18 and in sample Condenser #13 would appear to be unusually high levels of contamination.

Bromoform is the compound that was specifically recognized as a potential pollutant expected in these samples. Indeed, bromoform was found and quantified in ten of the eighteen samples that were analyzed. Bromoform was not detected in either of the field blanks nor in the instrument blanks that were analyzed prior to sample analysis. The limit of detection for bromoform is 1 ug/l.

In general, the levels of observed organohalides were similar between the two sample dates. The levels of volatile organic compounds in nonchlorinated water (Sample Numbers 13-16) was low. Bromoform was the only compound which occurred in significant concentrations after chlorination, although several compounds not present in the nonchlorinated water were found after chlorination. Samples to which thiosulfate had been added had much lower levels of bromoform than those which were not so treated indicating that there was a time lag between chlorination

and maximum bromoform production.

Non-Volatile Organohalides

Four chlorinated benzene compounds were detected (Figure 5): chlorobenzene, 1,4-dichlorobenzene, 1,2,3-trichlorobenzene and hexachlorobenzene. The chromatograph peaks were not quantified, however, it appears that there was no change in concentration of the four compounds after chlorination.

DISCUSSION

Bromoform has been identified as the major halogenated organic compound produced as a result of chlorinating seawater at less than 1 mg/l[9,17]. Results presented in Table 5 from this study are consistent with this observation. Halogenated species, other than bromoform, were not found in concentration significantly higher than background levels.

The bromoform concentration was studied as a function of the TRO level in the evaporator, condenser and mixed discharge system water samples (Table 6). Significantly greater quantities of bromoform were produced in the evaporator water as compared to the condenser water as a function of TRO in both chlorinated and dechlorinated stored samples.

No immediate (11 second transit time, Table 2) bromoform production was detected in the dechlorinated condenser water while a low (1-2 ug/l) but significant amount was immediately produced in the dechlorinated evaporator water. Bromoform levels greatly increased in all samples after storage in the presence of TRO. Highest bromoform production was in the evaporator samples (Table 6).

The amount of bromoform produced in stored samples containing evaporator water (i.e., mixed discharge and evaporator system water) and in the condenser water was directly related to the TRO level (Figure 6). The amount of bromoform produced per quantity of TRO (i.e., ug bromoform per mg TRO) was greater in samples containing evaporator water (96 ug/mg) than in the condenser water (44 ug/mg). Both of these slopes (Figure 6) are significant at less than the 0.001 level with a y-intercept not significantly different ($p<.001$) than zero (0).

The results are consistent when water quality differences are considered. Oxidant demand (Table 3) and TOC (Table 7) are higher in samples containing evaporator water. Higher chlorine dosages were needed for the evaporator water (higher evaporator oxidant demand, Table 3) in order to achieve OTEC-1 plant operating TRO levels (unpublished OTEC-1 chlorine dosing records). This could result in higher bromoform precursor concentrations and higher bromoform concentrations in the same time period. Evidence for this is the immediate production of 1-2 ug/l of bromoform in the dechlorinated evaporator samples, while the dechlorinated condenser samples had no detectable bromoform and both had an 11 second transit time.

The bromoform concentration discrepancy between dechlorinated evaporator and condenser water could also be the result of pH, TOC and temperature differences. The <u>in situ</u> temperature and pH differences between surface and deep ocean waters are significant. Evaporator water is warmer and more basic than condenser water (Tables 2 and 7), 25°C, pH 8.1 and 5.6°C, pH 7.6 respectively. The haloform reaction is temperature dependent and strongly base catalyzed[18] and one would expect higher

bromoform production rates with increasing temperature and pH. Other investigators have observed the pH effect in which trihalomethane (THM) formation during water chlorination increases 2-3 fold going from pH 7 to pH 10[19,20].

The data show that bromoform precursor has not become limiting during storage as higher TRO residuals result in an increase in bromoform concentration (Figure 6). This effect has been observed in fresh water[21]. Accordingly, the highest concentration of bromoform (32 ug/l) produced in the evaporator water (Table 6) is not the maximum possible, and the line drawn in Figure 6 could be extended. Additionally, if the TRO went to zero in the stored bromoform samples then the bromoform production per unit of initial TRO for the condenser water samples (44 ug/mg) and evaporator containing water samples (96 ug/mg) is a maximum for the conditions described.

Using the above data the daily potential bromoform production by the OTEC-1 plant can be estimated. OTEC-1 had a mixed discharge, therefore, discharged water contained evaporator water with a potential bromoform production of 96 ug bromoform/mg TRO.

$$96 \text{ ug/mg} \quad 0.2 \text{ mg TRO/l} \quad 3.49 \times 10^{7} \text{ l/hr} \quad 2 \text{ hrs chlorination/day}$$
$$= 1.3 \times 10^{9} \text{ ug bromoform/day.}$$

If OTEC plants used higher TRO values, chlorinated longer and/or had a higher volume flow the bromoform production would be proportionately greater.

The potential bromoform production will be diluted when it is discharged into the ocean. The OTEC-1 discharge initially was diluted

ten fold[22] and within two hours is estimated to be diluted 20 fold. Therefore, the bromoform concentration contained in the diluted discharge water will be:

$$1.3 \times 10^{9} \text{ ug bromoform} \quad [3.49 \times 10^{7} \text{ l/hr} \quad 2 \text{ hrs} \quad 20 \text{ (dilution)}]$$
$$= 0.93 \text{ ug bromoform/l}$$

With careful technique and larger water samples, this concentration could be detected in the plume water. The main problem would be to know where the chlorinated water would be two hours after discharge.

ACKNOWLEDGEMENTS

We wish to acknowledge the analytical services of AECOS, Inc. of Honolulu, HI., and in particular Dr. David Ziemann for his assistance throughout the OTEC-1 deployment. Mr. Daniel Estrella of the Marine Sciences Group, Lawrence Berkeley Laboratory (LBL) assisted in compiling and tabulating the data. This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Solar Power Applications, Division of Ocean Energy Systems, United States Department of Energy under contract number W-7405-ENG-48.

REFERENCES

1. U.S. Department of Energy, Program Summary, Ocean Energy Systems. Fiscal Year 1979. DOE/ET-0118, 276 p. Lawrence Berkeley Laboratory Report (LBL-12951), 116 p. (May 1981).

2. Glase, W.H., G.R. Peyton and R. Rawley. "Total Organic Halogen as a Water Quality Parameter: Adsorption-Microcoulometric Method," Envir. Sci. and Tech. 11: 685 (1977).

3. Perrigo, L.D., R.H. Gray, G.A. Jensen, W.W. Laity and R.G. Moles. "An Overview of the OTEC Biofouling and Corrosion Program," In: Proceedings of the Ocean Thermal Energy Conversion (OTEC) Biofouling and Corrosion Symposium, R.H. Gray, Ed. (Washington, D.C.: U.S. Department of Energy,

4. Bell, K.J. "The Effect of Fouling on OTEC Heat Exchanger, Design, Construction, and Operation," In: Proceedings of the Ocean Thermal Energy Conversion (OTEC) Biofouling and Corrosion Symposium, R.H. Gray, Ed. (Washington, D.C.: U.S. Department of Energy, Oct. 10-12, 1977), pp. 19-29.

5. Curto, P.A., "An Update of OTEC Baseline Design Costs," In: Proceedings of the 5th Ocean Thermal Energy Conversion Conference, Vol 1, A. Lavi and T.N. Veziroglu, Eds. (Washington, D.C.: U.S. Department of Energy, Feb. 20-22, 1978) pp. II 77-93.

6. Miller, R.T., J.J. Gertz and S. Cunninghis. "Preliminary Designs of 10MWe and 50 MWe Power Modules," In: Proceedings of the 6th Ocean Thermal Energy Conversion Conference, Vol. 1, G.L. Dugger,

Ed. (Washington, D.C.: U.S. Department of Energy, June 19-22, 1979), pp 8.1-1 - 8.1-11.

7. Fava, J.A., and D.L. Thomas. "Use of Chlorine for Antifouling on Ocean Thermal Energy Conversion (OTEC) Power Plants," In: Proceedings of the Ocean Thermal Energy Conversion (OTEC) Biofouling and Corrosion Symposium, R.H. Gray, Ed. (Washington, D.C.: U.S. Department of Energy, Oct. 10-12, 1977), pp. 107-125.

8. Hartwig, E.O. "OTEC Environmental Biological Oceanographic Program," In: Eighth Ocean Energy Conference- June 7-11, 1981. (In press). Glaze, W.H., G.R. Peyton and R. Rawley. "Total Organic Halogen as a Water Quality Parameter: Adsorption-Microcoulometric Method," Envir. Sci. and Tech. 11: 685 (1977).

9. Carpenter,J.H., E.A. Smith and R.G. Zika. "Reaction Products from the Chlorination of Seawater," In: Water Chlorination: Environmental Impact and Health Effects, Vol. 3, R.L. Jolley et al., Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc. 1980) pp. 379-385.

10. APHA, AWWA, WPCF. Standard Methods for the Examination of Water and Wastewater. 14 Ed. Washington, D.C. 1193 p. (1976).

11. Carpenter, J.H., C.P. Moore, and D.L. Macalady. "Errors in the Determination of Residual Oxidants in Chlorinated Seawater," Envir. Sci. and Tech. 11: 992-994 (1977).

12. Solorzano, L. "Determination of Ammonia in Natural Waters by the Phenolhypochlorite Method," Limnol. Oceanogr. 14: 799-801, (1969).

13. Strickland, J.D.H. and T.R. Parsons. "A Practical Handbook of Sea-water Analysis," Bulletin 167 (Second Edition). Fish. Res. Bd. Canada. 310 p. (1972).

14. U.S. Environmental Protection Agency. Purgeables - Method 624. Federal Register 44 (233): 69532-69539, (1979).

15. Eppley, R.W., E.H. Renger and P.M. Williams. "Chlorine Reactions with Sea-water Constituents and the Inhibition of Photosynthesis of Natural Marine Phytoplankton," Est. Coastal Mar. Sci. 4:147-161 (1976).

16. Goldman, J.C., H.L. Quinby and J.M. Capuzzo. "Chlorine Disappearance in Sea-Water," Water Research 13:315-323 (1979).

17. Bean, R.M., R.G. Riley and P.W. Ryan. "Investigation of Halogenated Components Formed from Chlorination of Marine Water," In: Water Chlorination: Environmental Impact and Health Effects, Vol. 2. R.L. Jolley, et al., Eds. (Ann Arbor, MI: Ann Arbor Sciences Publishers Inc., 1978), pp.223-234.

18. Morris, J.C., "Formation of Halogenated Organics by Chlorination of Water Supplies," EPA Report No. EPA 600/1-75-002, (Washington, D.C.: U.S. Environmental Protection Agency, March 1975).

19. Rook, J.J. "Formation of Haloforms During Chlorination of Natural Waters," Water Treat. Exam. 23: 234-243 (1974).

20. Stevens, A.A., C.J. Slocum, D.R. Seeger and G.G. Rubeck. "Chlorination of Organics in Drinking Water," J. Amer. Water Wks. Assoc. 68: 615-620 (1976).

21. Trussel, A.R. and M.D. Umphres. "The Formation of Trihalomethanes," J. Amer. Water Wks. Assoc. 70: 604-612 (1978).

22. Noda, E.K., P.K. Bienfang, W.J. Kimmerer and T.W. Walsh. Plume Survey, OTEC-1 Mixed-Water Discharge, April 11-12, 1981. Oct. 10-12, 1977), pp. 13-18.

Table 1. Chlorine, Power and Percent of Parasitic Power Loss Required by 4 Chlorination Schedules for a 100 MW OTEC Plant (Based on the Flow Rate for Proposed 1 MW Test Unit)[a]

System	Low Chlorine Dose[b]		High Chlorine Dose[c]	
	Continuous	Intermittent	Continuous	Intermittent
Evaporator System				
Flow rate (liters per min)	22.7 M	22.7 M	22.7 M	22.7 M
Chlorine (kg per day)	6,532	727	52,254	2,177
AC Power (kWhr/day)[d]	36,000	1,500	288,000	12,000
Parasitic power loss (%)	1.5	0.06	12.0	0.50
Condenser System				
Flow rate (liters per min)	25.7 M	25.7 M	25.7 M	25.7 M
Chlorine (kg per day)	7,403	308	59,221	2,468
AC power (kWhr/day)	40,800	1,700	326,400	13,600
Parasitic power loss (%)	1.7	0.07	13.6	0.57
Total 100 MW plant				
Flow rate (liters per min)	48.45 M	48.45 M	48.45 M	48.45 M
Chlorine (kg per day)	13,934	581	111,475	4,645
AC power (kWhr/day)	76,800	3,200	614,400	25,600
Parasitic power loss (%)	3.2	0.13	25.6	1.07

[a]From reference 6.
[b]Chlorine dose of 0.20 mg/l resulting in a chlorine residual of 0.1 mg/l.
[c]Chlorine dose of 1.6 mg/l resulting in a clorine residual of 0.1 mg/l.
[d]Based on 2.5 kWhr per 0.45 kg of chlorine produced by onsite hypochlorite generation.

Table 2. Water Flow and Transit Times in the OTEC-1 Test Facility

System	*ΔT	Total Water Flow (m^3/sec)	Transit Time Point to Point
Evaporator (warm water inlet = 25.0°C)	1.7°C	5.2	Warm Water Inlet (1) [chlorination] to Evaporator Inlet Sample Port (2) ≃ 11 sec. Evaporator Inlet Sample Port (2) to Mixed Water Discharge Sample Port (5) ≃ 28 sec Warm Water Inlet (1) to Mixed Water Discharge (6) ≃ 54 sec
Condenser (cold water inlet = 5.6°C)	+2.5°C	4.3	Cold Water Inlet (3) [chlorination] to Condenser Inlet Sample Port (4) ≃ 11 sec. (4)=11 sec Condenser Inlet Sample Port (4) to Mixed Water Discharge Sample Port (5) ≃ 41 sec Cold Water Inlet (3) to Mixed Water Discharge (6) ≃ 67 sec

*ΔT: Water temperature change across heat exchanger. Nominal mixed water discharge temperature = 17.9°C

Table 3. Comparison of Amperometric vs. Iodiometric End-Point Detection for Total Residual Oxidant (values in mg/l).

Test # System		Ampero-metric	Iodio-metric	Test # System		Ampero-metric	Iodio-metric
(1) 1 COND		.14	.15	10 COND		.13	.16
		.12	.18			.11	.15
	(3) $\bar{x}$	.13	.17		$\bar{x}$	.12	.16
(2) 2 EVAP		.21	.21	11 EVAP		.18	.24
		.22	.24			.18	.23
	$\bar{x}$	.22	.23		$\bar{x}$	.18	.24
3 EVAP		.19	.19	12 COND		.12	.16
		.19	.20			.09	.15
	$\bar{x}$	.19	.20		$\bar{x}$	.11	.16
4 COND		.09	.12	13 COND		.09	.13
		.09	.14			.10	.10
	$\bar{x}$	.09	.13		$\bar{x}$	.10	.12
5 COND		.10	.06	14 EVAP		.19	.16
		.08	.11			.18	.20
	$\bar{x}$	.09	.08		$\bar{x}$	.19	.18
6 EVAP		.18	.15	15 EVAP		.20	.20
		.18	.21			.19	.20
	$\bar{x}$	.18	.18		$\bar{x}$	.20	.20
7 EVAP		.16	.21	16 COND		.07	.12
		.17	.18			.08	.08
	$\bar{x}$	.17	.20		$\bar{x}$	.08	.10
8 COND		.13	.17	17 COND		.10	.13
		.12	.18			.10	.07
	$\bar{x}$	.13	.18		$\bar{x}$	.10	.10
9 COND		.13	.16	18 EVAP		.24	.19
		.11	.15			.21	.20
	$\bar{x}$	.12	.16		$\bar{x}$	.23	.20

[1] COND: Condenser water
[2] EVAP: Evaporator water
[3] $\bar{x}$: Mean

Table 4. Oxidant Demand (values in mg/l)

Date	Evaporator 2 min	Evaporator 5 min	Condenser 2 min	Condenser 5 min	Mixed Discharge 2 min	Mixed Discharge 5 min
12/23/80	0.12	0.11	0.03	0.04	0.07	0.08
12/24/80	0.12	0.13	0.06	0.07	0.07	0.08
12/25/80	0.12	0.15	0.06	0.07	0.04	0.11
12/26/80	0.11	0.13	0.05	0.06	0.10	0.11
12/27/80	0.10	0.10	0.04	0.05	0.06	0.05
12/28/80	0.11	0.13	0.04	0.06	0.08	0.07
12/29/80	0.08	0.11	0.03	0.03	0.06	0.07
12/30/80	0.10	0.12	0.05	0.05	0.10	0.12
12/31/80	0.13	-	0.05	-	0.09	-
01/01/81	0.12	-	0.06	-	0.08	-
01/02/81	0.12	-	0.05	-	0.09	-
01/03/81	0.13	0.15	0.06	0.09	0.10	0.10
01/04/81	0.13	0.15	.08	0.09	0.11	0.13
01/05/81	0.11	0.14	0.07	0.09	0.09	0.10
n	14	11	14	11	14	11
Mean	0.11	0.13	0.05	0.06	0.07	0.09
*SE	0.004	0.005	0.004	0.006	0.007	0.008

*SE: Standard error of the mean.

Table 5. Data Summary for Analysis of Volatile Organic Compounds (μg/l)

System	[1]COND	[2]COND	EVAP	EVAP	[3]COND MD	COND MD	COND	COND	EVAP	EVAP	EVAP MD	EVAP MD	COND	COND	EVAP	EVAP	BLANK	BLANK
Sample No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
[4]Day	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2		
[5]Cl_2	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	-	-	-	-	-	-
[6]THIO	✓	✓	✓	✓	-	-	-	-	-	-	-	-	-	-	-	-	✓	✓
COMPOUND																		
BROMOFORM	[7]ND	ND	1.1	2.0	8.0	6.7	13.6	22	26	32	21	21	ND	ND	ND	ND	ND	ND
DICHLOROMETHANE	2.5	5.9	<1	2.1	2.1	4.1	1.3	5.5	1.2	7.5	3.8	8.1	2.4	6.6	8.3	7.6	1.8	7.1
BENZENE	<1	<0.5	<1	<0.5	<1	<0.5	ND	<0.5	<0.5	<0.5	<0.5	<0.5	37.5	<0.5	<0.5	<0.5	1.1	6.7
CHLOROBENZENE	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<1
META & PARA XYLENE	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	ND	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<1	<1
DIBROMOCHLORO METHANE	ND	<0.5	ND	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	ND	<1
BROMODICHLORO METHANE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
HEXANE	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		+
2-PROPANONE		+		+	+	+		+										
BUTANOL		+		+		+					+				+			+
PENTANONE		+				+		+										
DIMETHYLPENTANONE						+		+		+								
METHYLOXIRANE										+								
BUTANENITRILE	+		+	+	+		+		+	+	+						+	+
ETHENYL BENZENE																	+	+

(1) COND: Condenser inlet water sample
(2) EVAP: Evaporator inlet water sample
(3) MD: Mixed discharge water sample with either Condenser or Evaporator being chlorinated
(4) Day: Day 1 or 2 of experimental sampling
(5) Cl_2: Chlorinated (✓ = yes; - = no)
(6) THIO: Thiosulfate added to sample (✓ = yes; - = no)
(7) ND: Not detected

Table 6. Summary Table of Bromoform Production

	(1) Cl_2	(2) THIO	(3) TRO (mg/L)	Bromoform (ug/L)	Temp (°C)	NH_4 (ug-at/L)
Condenser	+	+	0.41	ND(4)	5.6	.30
	+	+	0.40	ND	5.8	.37
	+	-	0.41	14	5.6	.30
	+	-	0.40	22	5.8	.37
	-	-	0.00	ND	5.6	.30
	-	-	0.00	ND	5.8	.37
Evaporator	+	+	0.29	1.1	25.2	.40
	+	+	0.33	2.0	24.9	.32
	+	-	0.29	26	25.2	.40
	+	-	0.33	32	24.9	.32
	-	-	0.00	ND	25.2	.40
	-	-	0.00	ND	24.9	.32
Mixed Discharge						
(5) Cond	+	-	0.08	8.0	18.9	.29
	+	-	0.06	6.7	17.8	.32
Evap	+	-	0.19	21	18.7	.29
	+	-	0.18	21	17.3	.32

(1) Cl_2: System being chlorinated: + = yes
(2) THIO: Thiosulfate added to sample bottle: + = yes
(3) TRO: Total residual oxidant
(4) ND: Not detected
(5) Particular system being chlorinated at time of sampling

Table 7: Mean pH and Total Organic Carbon (TOC) Values

		pH	TOC (ug/L)
Evaporator	Mean	8.27	1.17
	Std Dev	0.056	0.306
	#Samples	16	8
Condenser	Mean	7.64	0.758
	Std Dev	0.151	0.197
	#Samples	15	7
Mixed Discharge	Mean	8.06	0.914
	Std Dev	0.141	0.148
	#Samples	15	10

FIGURE CAPTIONS

1. Schematic diagram of closed cycle OTEC power system.

2. OTEC thermal resource in Pacific and Indian Oceans.

3. Location of the OTEC-1 test power plant off Hawaii.

4. Schematic of OTEC-1 water flow showing chlorination points and sampling ports.

5. Presence of non-volatile organo-halides in:

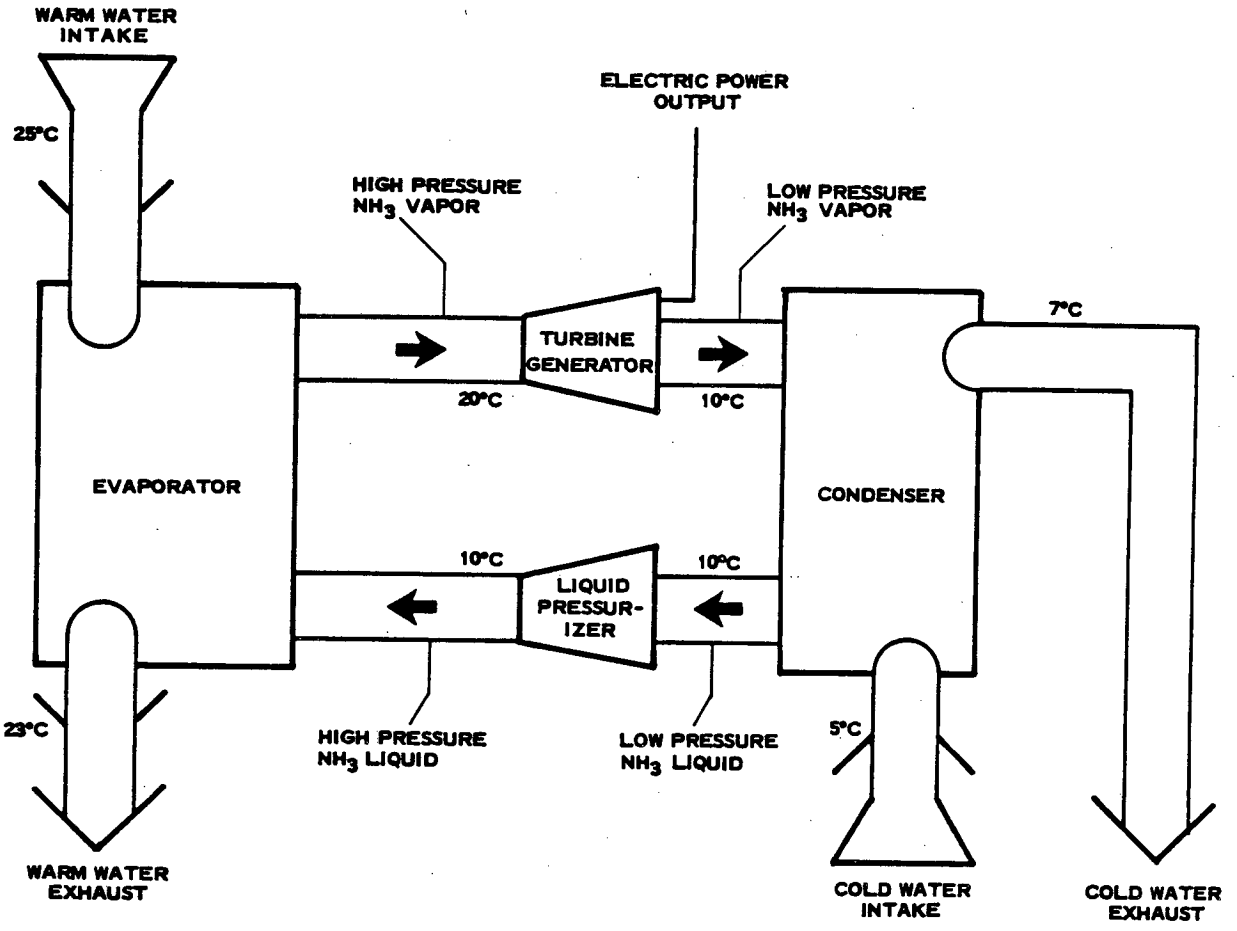
    1. 10 ppb Standards
    2. Evaporator Inlet Water - Unchlorinated
    3. Evaporator Inlet Water - Chlorinated
    4. Condenser Inlet Water - Unchlorinated
    5. Condenser Inlet Water - Chlorinated

    Y-axis unlabeled, but all compounds in all inlet water samples were at less than 10 ppb.

6 Bromoform production (Y: ug/l) Per Unit of TRO (X: mg/l).
$Y = 0.81 + 95.7 X$: Evaporator containing water samples.

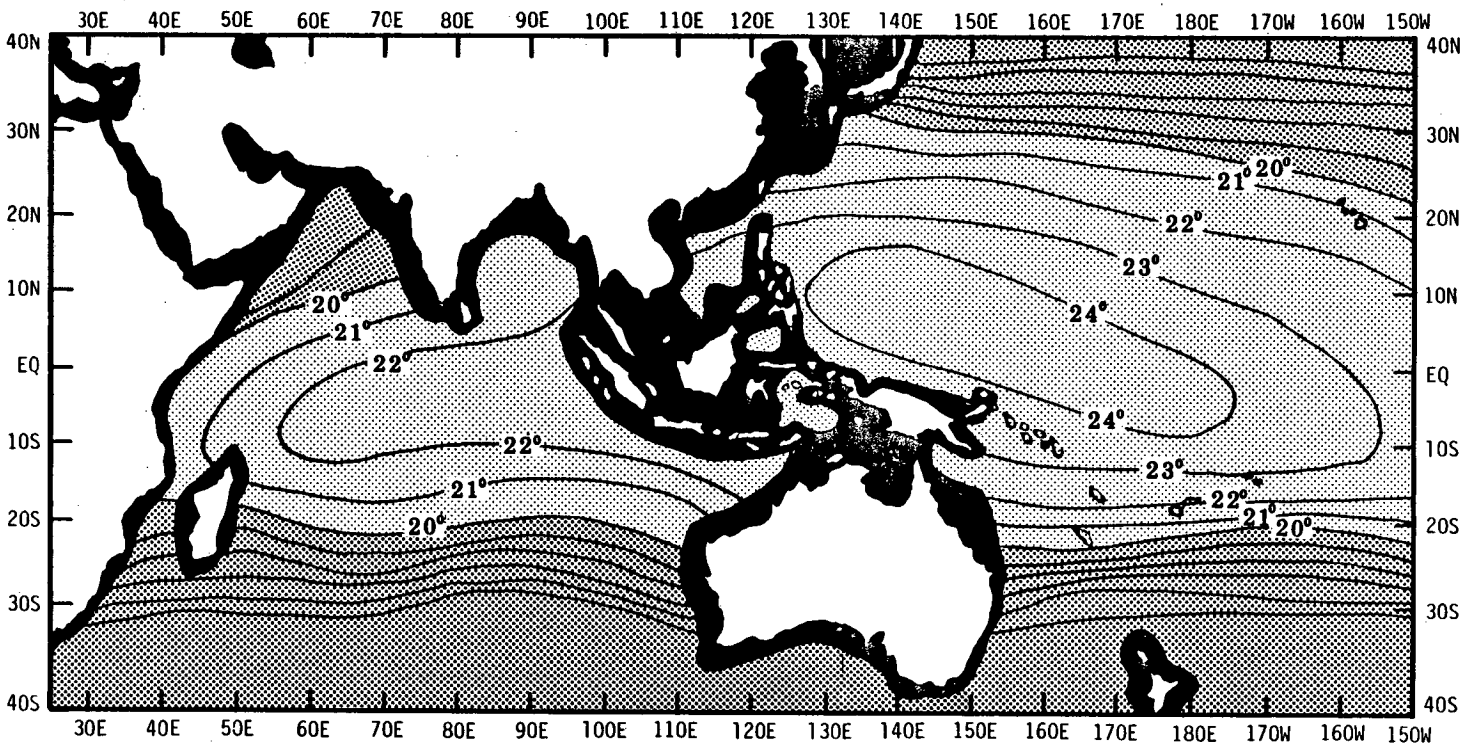
$Y = 0.06 + 43.7 X$: Condenser water samples.

FIGURE 1
SCHEMATIC DIAGRAM OF CLOSED CYCLE OTEC POWER SYSTEM



XBL 804-9276

LARGE SCALE DISTRIBUTION OF
OTEC THERMAL RESOURCE
ΔT (°C) BETWEEN SURFACE AND 1000 METER DEPTH



SCALE AND ACCURACY

This global scale chart shows the gross resource availability and does not adequately portray features whose size is less than 200 miles. Local values are considered accurate to less than 1°C in dense data areas, but may be less precise in regions of large horizontal gradients.

Wherever the gray areas (ΔT > 20°C) intersect the black area (water depth < 1000 meters), there will be some portion of the black area in which a ΔT of 20°C exists at depths shallower than 1000 meters.

XBL 819-1980

Figure 2. OTEC thermal resource in Pacific and Indian Oceans

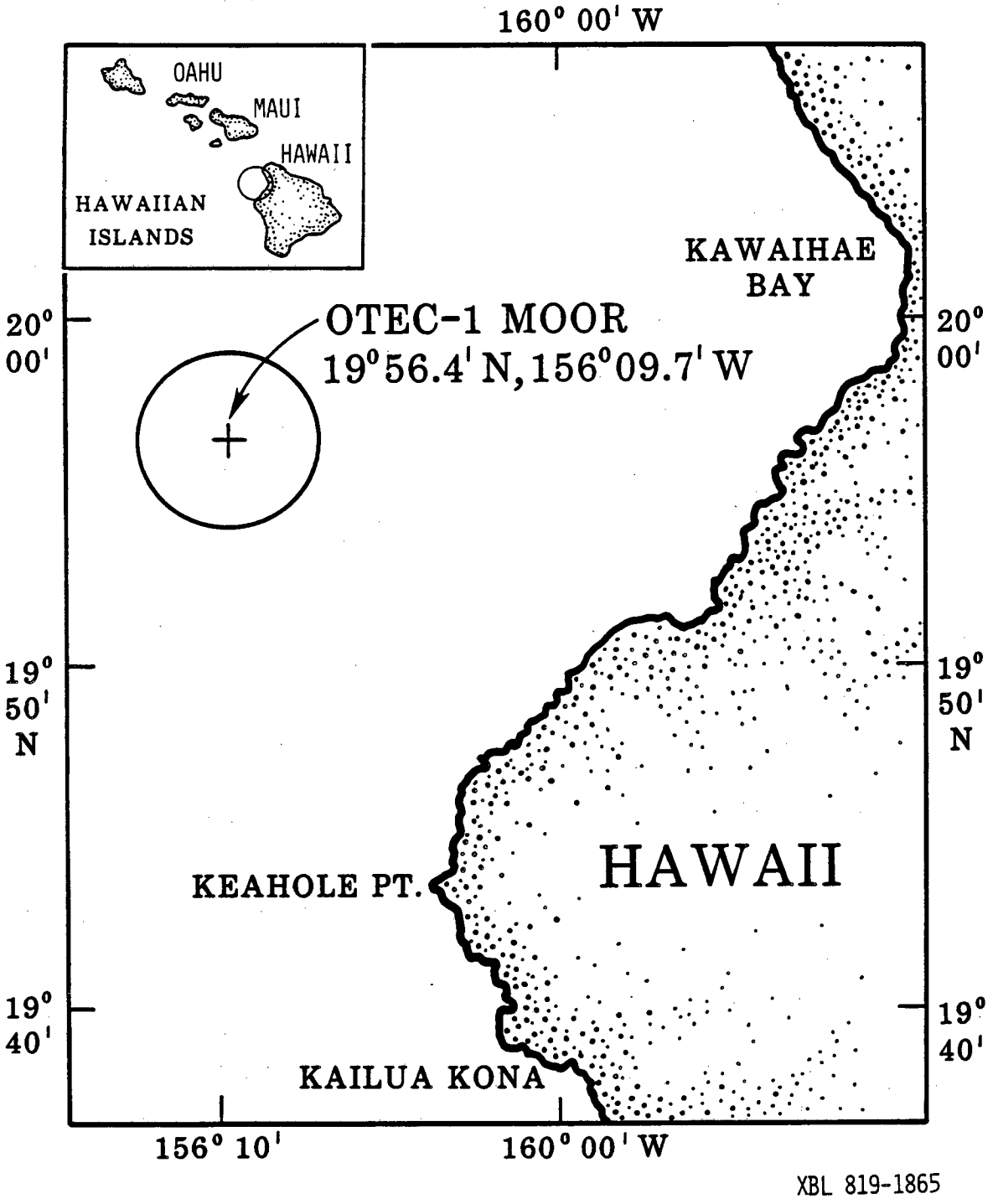


Figure 3. Location of the OTEC-1 test power plant off Hawaii

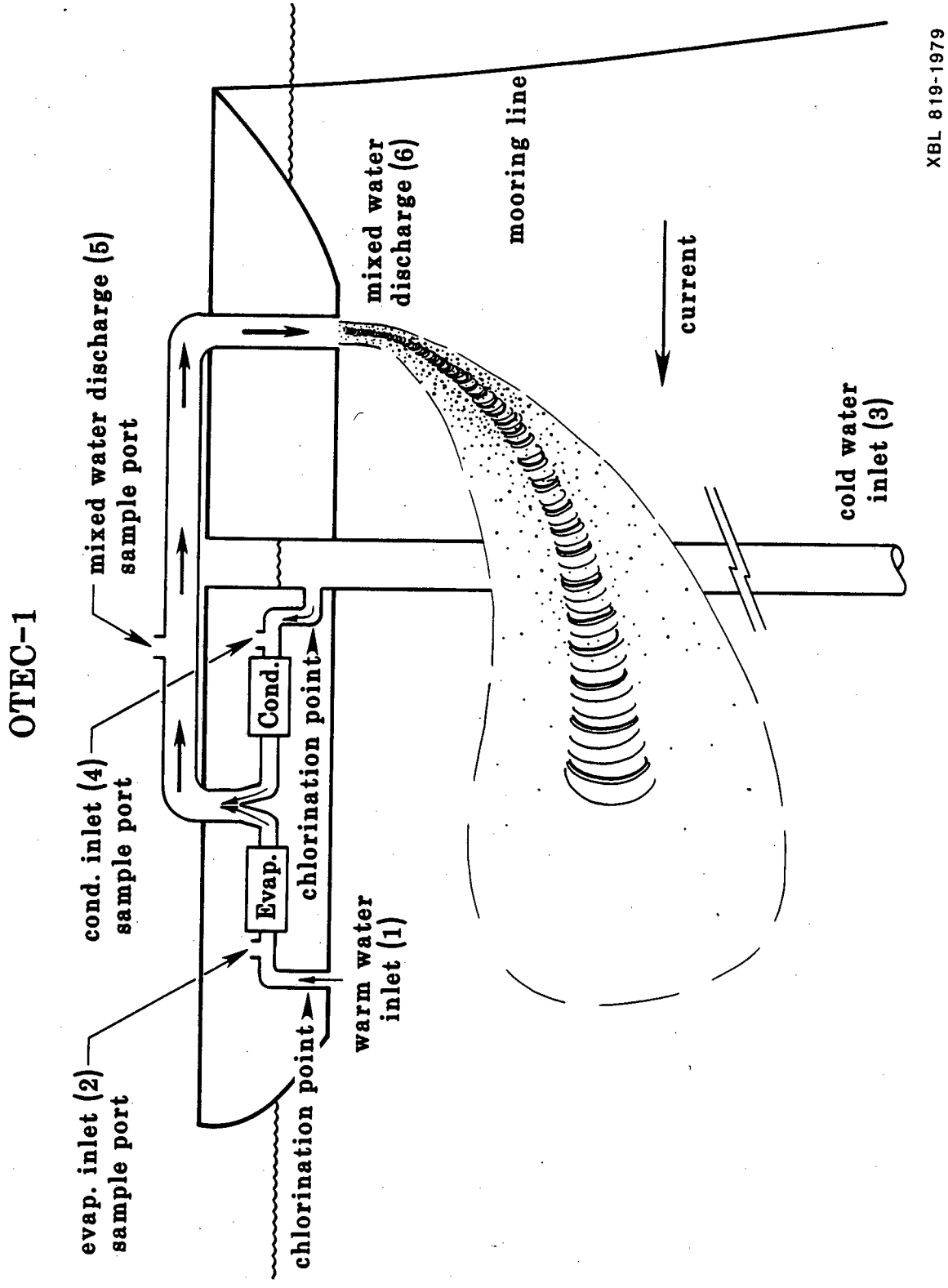


Figure 4. Schematic of OTEC-1 water flow showing chlorination points and sampling ports

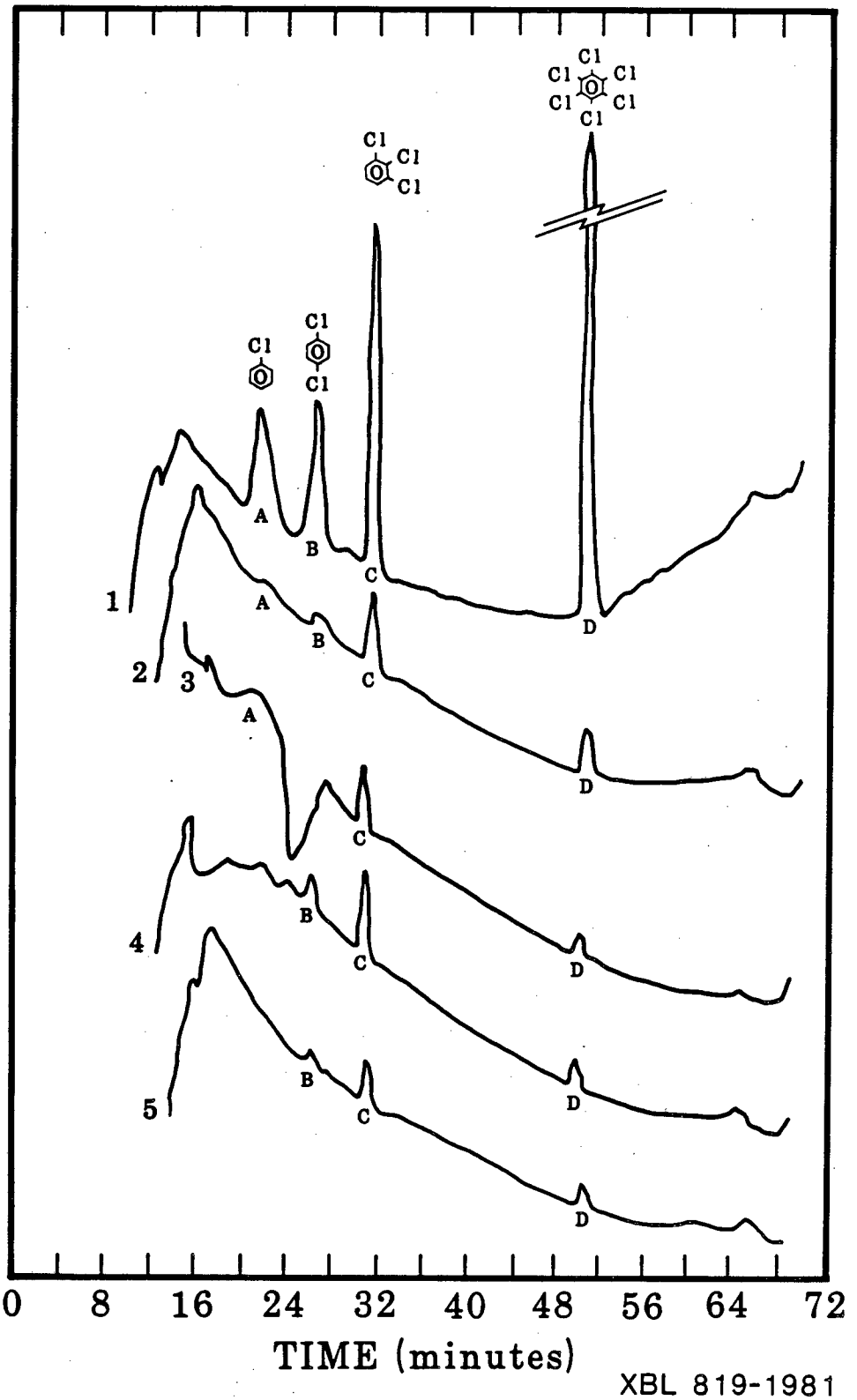


Figure 5. Presence of non-volatile organo-halides in: 1. 10 ppb Standards; 2. Evaporator Inlet Water - Unchlorinated; 3. Evaporator Inlet Water - Chlorinated; 4. Condenser Inlet Water - Unchlorinated; 5. Condenser Inlet Water - Chlorinated. Y-axis unlabeled, but all compounds in all inlet water samples were at less than 10 ppb.

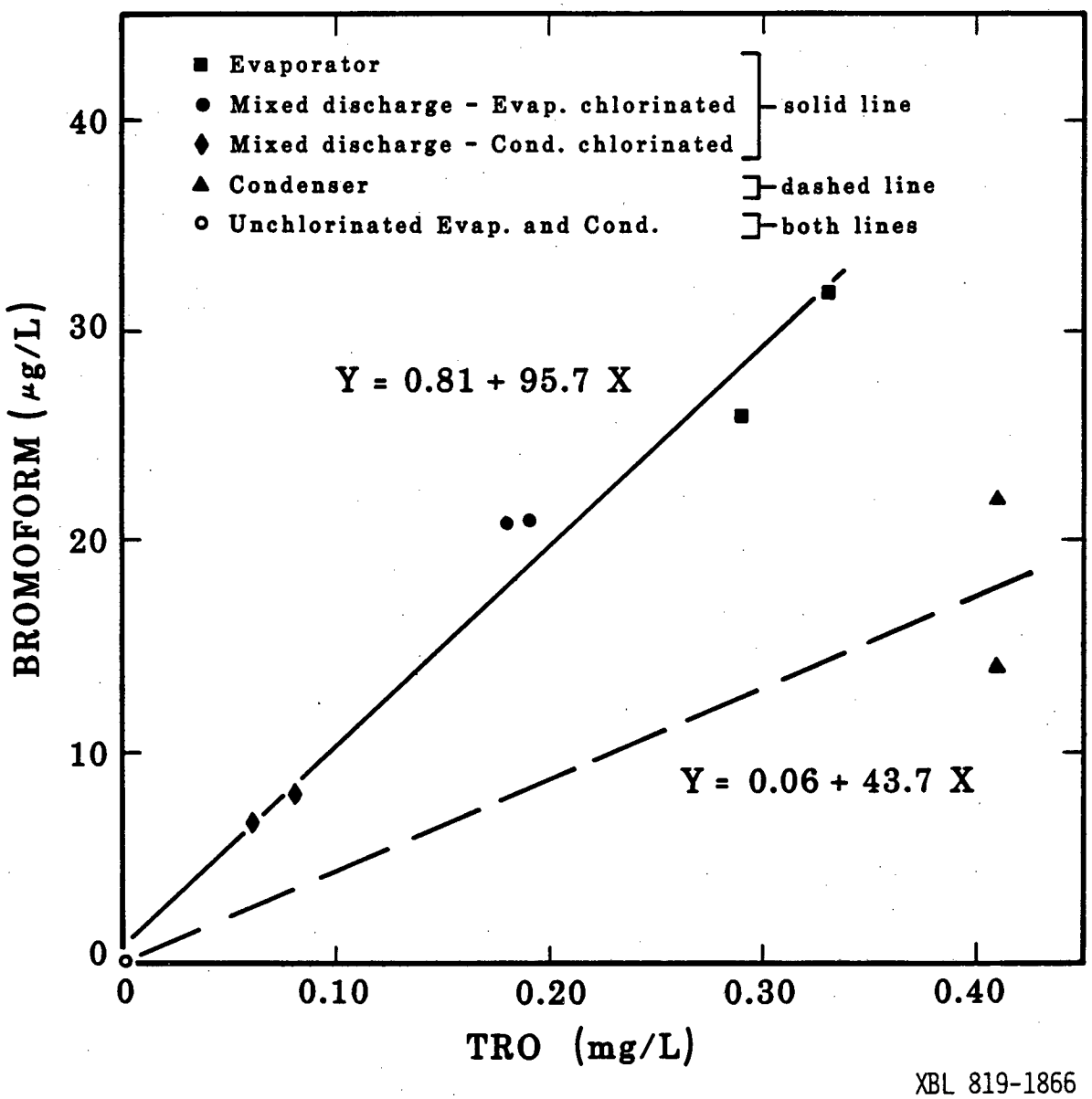


Figure 6. Bromoform production (Y: ug/l) Per Unit of TRO (X: mg/l).
Y = 0.81 + 95.7 X: Evaporator containing water samples.
Y = 0.06 + 43.7 X: Condenser water samples.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720