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ASSESSMENT OF OCEAN DUMPING NORTH OF PUERTO RICO

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UNITED STATES
DEPARTMENT OF COMMERCE
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#### EXECUTIVE SUMMARY

This assessment report has four purposes: (1) To document, in a single volume, the results of all National Oceanic and Atmospheric Administration (NOAA)-sponsored studies between 1978 and 1982 which related to ocean dumping of pharmaceutical wastes 74 km north of Puerto Rico; (2) to conclude from those studies what environmental costs were borne by the practice of ocean dumping between 1973 and 1981, and to estimate whether replacement of that practice with an ocean outfall yielded an environmental benefit; (3) to discuss what oceanographic information remains to be obtained if the oceandumping disposal option is again considered for Puerto Rico; and (4) to discuss the usefulness of the information that was obtained in assessing the consequences of ocean dumping. This last consideration will be useful if new or uninvestigated ocean dumping These purposes are interrelated and practices are scrutinized. The bulk of this report documents NOAA-sponsored intertwined. studies made in the context of measuring costs of ocean dumping. Considerations of present ocean discharge practice is limited because of limited data. Discussion of further needs is brief because the conclusions are inherent in the preceding considerations.

Environmental costs of dumping pharmaceutical wastes were small. Chemically, the wastes were characterized by organic compounds which were operationally volatile because they were extracted from wastes or seawater samples by purging with inert gas. While specific compounds responsible for waste toxicity were not identified, it was evident that two plant wastes of the seven which were combined to form the composite ocean-dumped wastes were considerably more toxic than the others. Laboratory tests of composite waste toxicity were run with phytoplankton, zooplankton, other invertebrates, and fish. The most sensitive response was

found to be a decrease in the rate of zooplankton egg production which occurred in the presence of wastes as dilute as 1 part in  $10^6\,$ parts seawater (ppm, v/v). Field studies did reveal phytoplankton and zooplankton responses to waste within waste plumes, but beyond these short-term effects over small spatial scales, no biological changes induced by ocean dumping were found. A lack of chronic responses was consistent with dumping which occurred in such amounts that circulation in the dumpsite area was adequate to dilute wastes below toxic levels. The amount dumped was relatively small--about ten dumps per month equating to  $10^3 \, \mathrm{m}^3$  (265,000 gallons) per day. The flushing rate was adequate for wastes of this toxicity dumped in that amount, however, that flushing rate remains unquantified. Circulation is not continuous to the west as initially expected on the basis of current charts. From chemical, bacterial, and physical evidence, the site appears to be in an area where circulation is predominantly influenced by eddies of undetermined size or The physical oceanography of the area translational velocity. should be better understood before ocean dumping is resumed, especially if wastes are to be discarded in larger amounts than in the past. Scientific assessments of ocean dumping should, in fact, require more physical oceanographic information than they have in the past, and can safely obtain it at the expense of decreased emphasis on laboratory toxicity data.

The wastes which were formerly ocean-dumped are now part of the inflow to a secondary waste treatment facility where effluent is discharged 0.8 km offshore. Effects of this effluent cannot be solely attributed to pharmaceutical wastes since the plant treats other industrial as well as municipal wastes. While ocean dumping occurred in an area of low resource value, the marine resources north of Puerto Rico are nearshore. On the basis of chemical and bacteriological evidence as well as some current meter data, it appears that effluent from this outfall can contaminate coastal waters to the shoreline.

#### Introduction

The Puerto Rico Dumpsite, located 74 km north of Arecibo, Puerto Rico, is approximately 500 km² (19°10' to 19°20'N and 66°35' to 66°50'W) 6000 to 8000 m in depth (Figure 1). From 1973 to August 1981, it received annually about 3.5 x  $10^5 \,\mathrm{m}^3$  of industrial wastes (Table 1). Until 1979, approximately 15 percent of the total volume was an alkaline solution containing sulfide generated by a hydrocarbon refining company. Prior to 1979, 85 percent of the wastes, and after 1979 all of the wastes, were derived from seven pharmaceutical plants. The sulfide solution was dumped separately while the pharmaceutical wastes (except one) were mixed together before being loaded into the dumping barge. These wastes, trucked to Arecibo from the various plants, accumulated in a holding tank until on 2 or 3 consecutive days they were dumped in 2.5 x  $10^3 \,\mathrm{m}^3$  lots.

Dumping of sulfide waste stopped when the plant ceased operations. Pharmaceutical wastes began to be transported to a secondary sewage treatment plant at Barceloneta, Puerto Rico, in August 1981. Prior to that time, the plant did not have the capacity to secondarily treat large volumes of industrial wastes. Effluent from the plant is discharged to the ocean by a pipeline diffuser terminating 0.8 km offshore.

Assessing the environmental consequences of ocean use for waste disposal depends, basically, on four considerations. Two of them, waste quality and quantity, are specific to the waste and its generation. The third, its method of discharge, has a large influence on waste distribution but is essentially independent of specific waste characteristics and the fourth critical consideration, discharge location. The discharge location determines the oceanic distribution of wastes and exposure of marine organisms or humans to them.

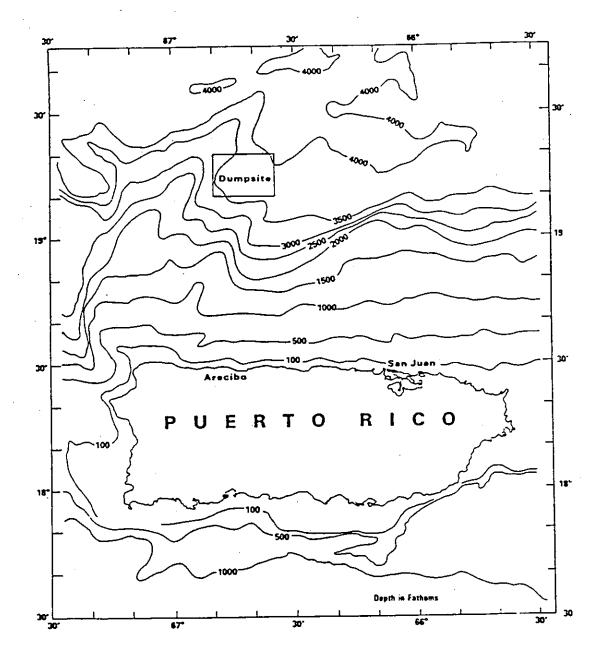


Figure 1. Location of Puerto Rico Dumpsite.

Table 1. Yearly volumes of wastes discharged at Puerto Rico Dumpsite. a

Year	Volume $b (10^5 m^3)$
1973	0.38
1974	2.31
1975	2.52
1976	3.60
1977	3.14
1978	3.60
1979 <sup>C</sup>	3.33
1980	3.61
1981	2.4

Data from U.S. Environmental Protection Agency Report to Congress on Ocean Dumping 1981.

Data are given in terms of wet metric tons. Since waste specific gravities are close to 1.0, a wet metric ton is assumed equivalent to  $1.0~{\rm m}^3$ .

Prior to 1979, about 15 percent of total volume was an alkaline solution of hydrogen sulfide, the remaining 85 percent being pharmaceutical wastes. Since 1979 all wastes were pharmaceutical.

This report will discuss physical and chemical properties of pharmaceutical wastes and their toxicity as measured under controlled conditions. The initial dilution of them as achieved by discharge from moving barges will be described. Attributes of this disposal strategy, which are unique to the ocean north of Puerto Rico will be considered. Finally, some comparisons will be made between dumping 74 km offshore and discharging, after treatment, nearshore.

#### Waste Generation and Chemistry

Five of the seven pharmaceutical plants contributing to the formerly ocean-dumped wastes are strictly chemical plants. Their products are either synthesized drugs or purified versions of raw drugs supplied to them. Two plants, Upjohn and Shering, produce drugs through fermentation processes. Table 2 is a list of the seven plants, their products, and the proportion of their wastes to the total composite waste volume.

A condition of the ocean-dumping permit was that monthly bulk chemical analyses of the composite (not individual) wastes be submitted to Region II of the U.S. Environmental Protection Agency (EPA). These reports are summarized in Table 3 for the years 1978 through 1980. The waste, were essentially an aqueous suspension of near neutral pH, at about the density of seawater, containing approximately 1 percent suspended solids (by weight) and 2 percent organic carbon. While ocean-dumped wastes are required to be analyzed for high molecular weight organochlorines (such as polychlorinated biphenyls and some pesticides), these compounds were not characteristic of pharmaceutical wastes. since (except for one plant which uses scrap iron as a catalyst) transition and other trace elements are not used in the processes of these plants, elemental analysis of this waste was not particularly revealing. An analysis by Presley et al. (1981) of a composite waste sample yielded the following concentrations in units of mg]<sup>-1</sup>: Cd (0.0006), Hg (0.0004), Cu (0.01), Fe (170),

Table 2. Sources of pharmaceutical wastes to Puerto Rico Dumpsite<sup>a</sup>

Company	% of Total Waste Volume <sup>a</sup>	Product
Upjohn Manufacturing Co.	46.	Lincomycin, clinomycin
Merck Sharp and Dohme Quimica		
de P.R. Inc.	20	l-methyl dopa
Shering Corp.	15	Gentamycin, sisomycin
Cyanamid Agricultural		•
de P.R. Inc. <sup>b</sup>	9	Veterinary drugs
Pfizer Pharmaceutical Inc.	5	Diabinese, sinequon, bonine
Bristol Alpha Inc.	3	Ampicillin, other penicillins
Squibb Manufacturing Inc.	2	Penicillin, cephadine

Calculated from total yearly volume on permits issued by U.S. EPA Region II for 1978. Logs of actual dumped volumes in 1978 and subsequent years show the same relative contributions from individual plants.

b This division of American Cyanamid is sometimes referred to as CAPRI.

Table 3. Bulk waste characteristics<sup>a</sup>.

### Characteristics in percent by weight

	Av.	<u>S.D.</u> (1	<u>n) M</u>	edian <u>M</u> a	эх. <u>м</u>	in.
Water b Total Suspended Solids Total Organic Carbon Total Phosphorus Ammonia Nitrogen Total Kjeldahl Nitrogen Specific Gravity pH	95.9 0.8 1.4 0.005 0.15 0.45 1.026 6.92	2.6 1.4 1.1 0.003 0.07 0.23 0.005 0.48	(9) (9) (9) (9) (9) (9)	96.1 0.2 1.0 0.005 0.12 0.49 1.026 6.92	99.7 4.2 3.5 0.001 0.31 0.85 1.037 7.78	92.1 0.04 0.9 0.01 0.05 0.08 1.020 6.23
Mater b Total Suspended Solids Total Organic Carbon Total Phosphorus Ammonia Nitrogen Total Kjeldahl Nitrogen Specific Gravity pH	94.2 1.8 2.2 0.02 0.14 0.44 1.026 6.74	2.4 2.1 1.4 0.04 0.07 0.11 0.011 0.82	(11) (11) (9) (11) (11) (11) (11) (11)	93.4 1.0 1.8 0.007 0.13 0.48 1.022 6.70	97.2 5.3 5.0 0.15 0.26 0.52 1.048 8.22	90.4 0.02 0.8 0.003 0.04 0.24 1.011 5.08
Water b Total Suspended Solids Total Organic Carbon Total Phosphorus Ammonia Nitrogen Total Kjeldahl Nitrogen Specific Gravity pH	95.0 0.5 1.3 0.01 0.04 0.10 1.022 6.73	1.2 0.5 0.5 0.01 0.04 1.20 0.007	(10) (10) (9) (10) (10) (10) (10)	94.9 0.3 1.3 0.005 0.02 0.04 1.023 6.75	96.8 1.4 2.6 0.04 0.1 0.4 1.031 7.42	92.7 0.07 0.8 0.002 0.002 0.02 1.012 5.83
1981 Water Total Suspended Solids Total Organic Carbon Total Phosphorus Ammonia Nitrogen Total Kjeldahl Nitrogen Specific Gravity pH	95.1 0.6 1.5 0.008 0.09 0.3 1.026 6.43	0.9 0.6 0.7 0.005 0.17 0.5 0.005 0.49	(8) (7) (7) (8) (8) (8)	95.2 0.3 1.1 0.006 0.03 0.1 1.024 6.65	96.4 1.7 2.9 0.02 0.5 1.5 1.037 6.96	93.8 0.1 0.7 0.004 0.002 0.004 1.020 5.64

a Summarized from monthly reports submitted to U.S. EPA Region II.

Total solid concentrations, not water, were reported. Percent water was calculated by difference.

Mn (5.2), Ni (0.3), Pb (0.09), Ag (<0.02), Al (<30), As (<0.15), Co (<1.0), Cr (<0.5), Mo (<1), Sb (<0.01), and Zn (<0.5).

Investigating the distribution and effects of pharmaceutical the ocean required a more detailed wastes chemical identification than is afforded by the bulk analyses summarized in Table 3. Atlas et al. (1981) performed extensive extractions and gas chromatographic (GC)--mass spectrometric (MS) analyses of a composite sample collected in 1978. Most individual compounds were extractable into acidic or neutral media and were saturated or unsaturated fatty acids and fatty acid esters. Some normal hydrocarbons, C15 to C32, were found, and in the basic extract the major compound was N.N-dimethyl analine. Using similar analytical techniques Hatcher and Harvey (1978) found the same array of compounds. The distribution of fatty acids was indicative of microbial organisms which was not unexpected since the composite waste contained fermentation waste.

Analysis of individual plant waste samples by Atlas et al. (1981) found major compounds in those wastes as follows: Upjohn, fatty acids and fatty acid esters; Merck, methoxy-4-hydroxyphenyl acetone; Bristol, N,N-dimethyl aniline; American Cyanamid,  $(\pm)$ -2,3,5,6-tetrahydro-6-phenyl imidazol [2, 1-b] thiazole; Pfizer, unidentified nitrogen-containing compounds; and Shering, no compounds extracted.

Operationally, there are two major difficulties with the types of analyses performed by Atlas et al. (1981) and Hatcher and Harvey (1978). (1) They require elaborate extraction procedures, and, when done with seawater samples, require collection of 20 liters or larger volumes in glass-lined or aluminum containers. (2) The extractions include a concentrating step whereby extracts are evaporated to near dryness. This forces a loss of lighter weight compounds.

The lighter compounds are readily extracted by purging them from aqueous solution with inert gas onto an adsorptive resin for subsequent GC or GC-MS analysis. This purge-and-trap technique yields analyses for compounds with boiling points in the range of 65° to 260°C (Schwab et al., 1981). Compounds so isolated are considered to constitute the volatile fraction of organic material in a sample. It should be understood that they are volatilized by purging and heating the sample, they are not necessarily readily volatilized under natural conditions. Unlike analyses for the higher molecular weight compounds the purge-and-trap procedure is relatively simple; it can be done at sea, and only small volumes of seawater (2 liters or less) are necessary. The volatile compounds in pharmaceutical wastes were used in October 1978, and May 1979 (Harvey, NOAA/AOML, unpublished data), October 1979 (Brooks et al., 1983a), November 1980 (Brooks et al., 1983b), February 1981 and June 1981 (Brooks, Texas A&M, unpublished data) as indicators of wastes in waters north of Puerto Rico.

Unlike high-molecular-weight organic compound analyses of wastes which were done only once, a series of volatile compound analyses of composite wastes have been made. These are summarized in Table 4. The GC spectra produced in October 1978 and May 1979 were simpler than others because the 10-ml samples of diluted waste, the volume used in a commercial purge-and-trap system for seawater samples at those times, yielded less detail than the 2-liter samples obtained at the other times. There was some change in the composition of the volatile compound fraction during 1978 1980 period. Low-molecular-weight dichloromethane and toluene remained as major compounds. Chloroform and methyl isobutyl ketone increased in importance. Carbon tetrachloride appeared in 1980, and dimethyl aniline last appeared in 1979. These types of change are evident from comparisons of spectra in Figure 2 which are from Brooks et al. (1983a), and were generated in 1978, 1979, and 1980.

Table 4. Compounds identified in volatile fraction of pharmaceutical waste samples collected at various times. The designation "M" indicates that compound yielded one of the six highest peaks on the appropriate gas chromatogram. The designation "P" indicates that compound was present.

	Feb 78	0ct _78	May _79	0ct 	Feb <u>80</u>	Nine samples collected between July and December 1980 <sup>b</sup>
Acetone and other ketones	М	М	М	М	М	P
Ethyl mercaptan Dichloromethane n-propanol	P M P			М	М	М
Chloroform Ethyl acetate	P P	М	М	М	М	
Tetrahydro furan Benzene Carbon tetrachloride	P P	M	М	Р	М	М
n-butanol Trichloroethylene	M P	М	М		••	М
Methyl isobutyl ketone Toluene	P M P	M	М	M M	M M	M (?)
Isobutyl acetate Ethyl benzene m-p-xylene	P P			P P	P P	
o-xylene Propyl benzene		P	÷	Р	P	
Cumene Mesitylene C <sub>3</sub> -benzene		P			P P P	
Dimethyl pyridine Dimethyl aniline	. Р М	М	М			
C <sub>4</sub> -benzenes		Р			Р	
Butyl benzene Naphthalene C <sub>5</sub> -benzenes	Р	М		P	Р	
Ethyl-cumene	Р					

Sources: Feb. 78, Oct. 79, and Feb. 80 (Brooks et al., 1983a)
Oct. 78 and May 79 (Harvey, personal communication, 1980).
Nine samples between July and December 1980 (Brooks and Kennicutt, 1982).

Among the nine samples collected in the latter half of 1980, five unidentified compounds appeared in the volatile fractions. Four of those were more volatile (eluted earlier) than acetone. One compound, indicated here as methyl isobutyl ketone by "M(?)" eluted between propanol and benzene. It was identified as a ketone which was of lower molecular weight than methyl isobutyl ketone.

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Figure 2. GC/MS spectra of pharmaceutical wastes collected in February 1978(a), October 1979(b), February 1980(c), and a seawater sample collected in a waste plume during February 1978(d). Compounds corresponding to numbered peaks on (a) and (d) are listed below. (Brooks et al., 1983a).

Peak #	Compound
1	Acetone
2	Many possible alcohols and ketones
3	Ethyl mercaptan
4	Dichloromethane
5	n-proponal
6	Unknown
7	Chloroform
8	Ethyl acetate
9	Tetrahydro furan
10	Benzene
11	n-butanol
12	Trichloroethylene
13	Methyl isobutyl ketone
14	Toluene
15	n-butyl or isobutyl acetate
16	Column bleed
17	Ethyl benzene
18	m-, p-xylenes
19	o-xylene
20 ·	C <sub>3</sub> -benzene
21	Column bleed
22	Dimethyl pyridine
23	Dimethyl aniline
24	C <sub>4</sub> -benzene
25	Alkenyl (C <sub>4</sub> ) benzene
26	Naphthalene
27	C <sub>5</sub> -benzene
28	Ethyl cumene
29	Unknown

GC/MS ION SPECTRUM Pure Waste – direct injection

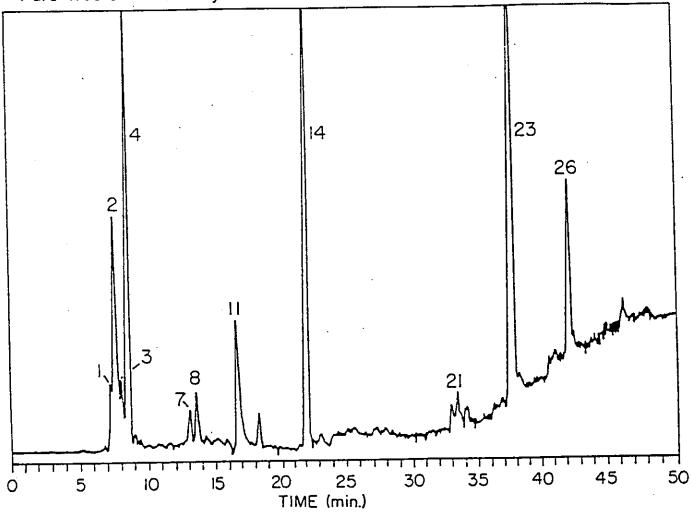


Figure 2a

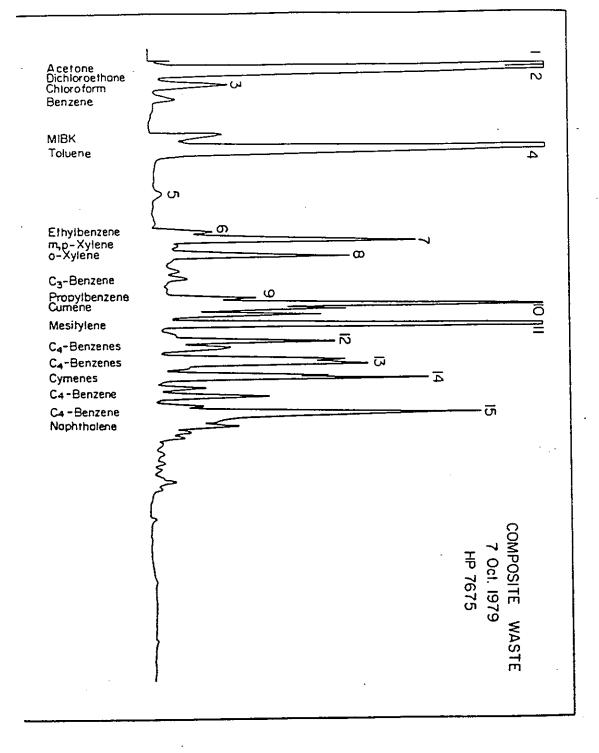


Figure 2b

Figure 2c

20 25 TIME (min.)

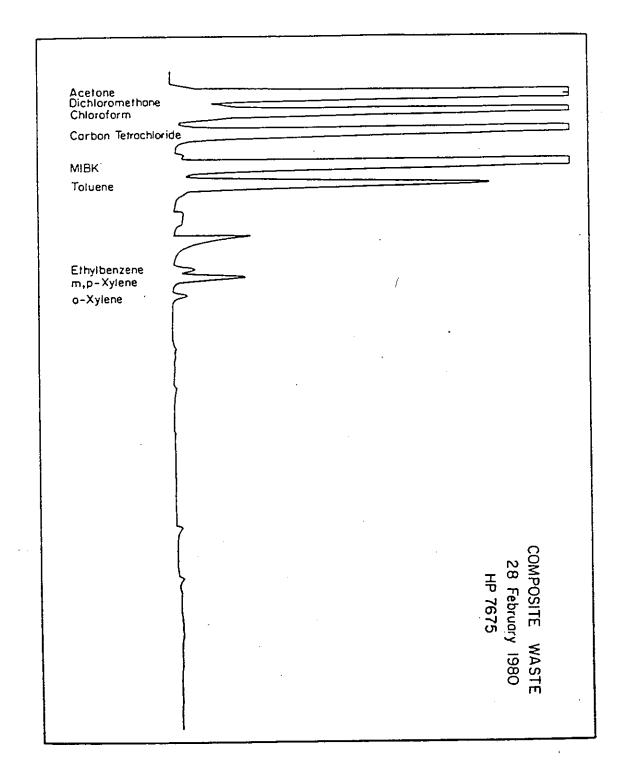


Figure 2d

Those spectra can be viewed as "fingerprints" of pharmaceutical wastes. They have been used, qualitatively, to identify the presence of wastes in the ocean. Quantitatively, however, the absolute and relative concentrations of volatile compounds cannot be used to define the extent to which wastes have been diluted. Such use would require a constant composition of wastes which, as Brooks et al. (1983a) have indicated, was not the case.

In general, the volatile fraction of pharmaceutical wastes is a mixture of common industrial solvents. One prominent unique compound, N,N-dimethyl aniline appeared in 1978 and early 1979 to be an ideal tracer of wastes (Because of its relatively high molecular weight and abundance it appeared in both volatile and non-volatile analyses.) However, even though it still appeared in a 1980 analysis of Bristol waste (Brooks et al, 1983a), its only source, it no longer appeared in the composite waste to which Bristol was a minor contributor (Table 2).

#### Waste Toxicity

To gain some idea of the environmental costs of ocean required permit holders to run periodic dumping, the EPA laboratory toxicity tests. Results of those tests for the period 1978 through 1981 are summarized in Table 5. The method by which pharmaceutical wastes were dumped generated initial 5000-fold dilutions of wastes yielding concentrations of the order of 100 ppm (waste volume per seawater volume). Except for tests with the diatom, Skeletonema costatum, after December 1978, the average and median LC50s in Table 5 exceeded 2000 ppm. There would be little reason to predict a biological response to ocean disposal of pharmaceutical wastes on the basis of these data. serious consequences were found, two pieces of toxological information should be added to that provided by the required (1) large variation in sensitivity to contamination exhibited by phytoplankton species and clones within a species,

Table 5. Summary of toxicity test results reported to EPA<sup>a</sup>. Concentrations are 96-hour LC50s for the sea urchin, <u>Tripneustes esculentus</u>, and shrimp, <u>Mysidopsis bahia</u>, and 96-hour EC50s for the phytoplankter, <u>Skelotenema costatum</u>.

	•	Conce	ntrations	$s (mg l^{-1})$		
Test organism	_Av.	<u>s.D.</u>	<u>(n)</u>	Median	Max.	Min.
1978						
T. esculentus	3500	795	(9)	3800	4450	1950
M. bahia S. costatumb	6725	5034	(6)	5500	13000	1550
1979						
T. esculentus  M. bahia  S. costatum	3514 2324 49	1340 613 70	(11) (9) (10)	3200 2400 11	6600 2800 210	2100 1000 2
1980						
T. esculentus M. bahia S. costatum	4390 5791 214	1921 7838 416	(10) (11) (11)	3725 3150 88	7500 28000 1445	2100 215 15
1981						
<pre>T. esculentus M. bahia S. costatum</pre>	4657 505 26	1761 595 32	(7) (8) (8)	4200 305 11	7400 1500 85	2400 18 5

a Summarized from monthly reports submitted to U.S. EPA Region II.

Does not include results of test run with December 1978 sample where EC50 was 13 mg  $1^{-1}$ .

and (2) sublethal effects on animals, which are important if they could decrease the reproductive potential of populations.

A 100-fold decrease in the concentration of pharmaceutical wastes required to halve the observed growth in 96 hours of S. costatum occurred in the toxicity tests in December 1978. Through October of that year the average EC50 was 6725 ppm (Table 5); in December, the EC50 was 13 pp. The average EC50s for 1979, 1980, and 1981 were 49, 214, and 26 ppm, respectively. In November of 1978, it was necessary to replace the cultured population of  $\underline{S}$ . costatum because the one used until that time was lost because of a power failure (Sandza, personal communication, 1979). The new culture, obtained from a different source than the original, was probably a different strain of the organism. Murphy and Belastock (1980) and Murphy et al. (1983) have demonstrated that sensitivities to ocean-dumped wastes can vary widely among clones of a single species. The data in Table 6 are particularly relevant because they demonstrate the clone-specific sensitivity using pharmaceutical wastes (collected in 1978) as the contami-The parameter measured was the autofluorescence of chlorophyll which, under these controlled conditions, is approximately proportional to biomass. A fivefold variation in response is evident, with clones isolated from the open ocean or from neritic, but pristine, areas being more sensitive. extreme, a clone (3H) isolated from a contaminated coastal area was not affected by pharmaceutical wastes at a concentration of 100 ppm, while an oceanic strain (58-102) displayed only 16 percent of the control fluorescence after 72 hours' exposure to the same concentration.

Since only a single concentration was used in those tests, no EC50s can be calculated. It is not clear whether a change in strain of a given species could account for the 100-fold decrease in EC50. However, assuming that test procedures did not change, it is unlikely that the waste itself increased in toxicity. The yearly average of total suspended solids and total organic carbon

Table 6. Fluorescence relative to control (F1 [test]/F1 [control]) at 72 hours for Thalassiosira pseudonana cultures in the presence of pharmaceutical waste at a concentration of 100 ppm (v/v). Eleven clones of the species were tested.

Clone designation	<u>Source</u> b	Fl(test)/Fl(control)	Relative growth 79 <sup>c</sup>
3Н	neritic-contaminated	$0.98 \pm 0.12$	.89
W	neritic-contaminated	$0.71 \pm 0.09$	
C5	neritic-clean	$0.72 \pm 0.12$	
STX-97	neritic-clean	$0.53 \pm 0.07$	
Swan-1	neritic-clean	$0.40 \pm 0.08$	.78
13.1	oceanic	$0.32 \pm 0.03$	.28
58-102	oceanic	$0.16 \pm 0.02$	
35-10b	oceanic	$0.30 \pm 0.05$	
35-11a	oceanic	$0.21 \pm 0.04$	
35-81	oceanic	$0.74 \pm 0.07$	
35-128b	oceanic	0.49 ± 0.14	

<sup>&</sup>lt;sup>a</sup> Murphy et al. (1982).

Actual times and locations of original isolation of clones are in Murphy et al. (1982). A differentiation is made among oceanic and neritic areas and nominally "clean" or "contaminated" neritic areas.

Relative growth rates (Table 8) of these clones exposed to a waste sample collected in 1979. The tests with all eleven clones were conducted with wastes collected in 1978.

between 1978 and 1979 doubled (Table 3). The month-to-month variation, however, was large for both these parameters, and standard deviations around yearly means overlapped. The toxic concentrations relative to  $\underline{S}$ .  $\underline{costatum}$  were distinctly different between 1978 and 1979. They did not vary at all relative to the sea urchin Tripneustes esculentus.

Phytotoxicities of wastes collected in 1978, 1979, and 1980 of three have been determined usina the same cultures (Van Baalen and Batterton, 1979; Van phytoplankton species Baalen, 1980, 1981). The results in Table 7 indicate year-to-year and within-year variations, but not so wide a range as 100-fold for a given organism. There is evidence among the species, that an EC50 of 6750 ppm could apply to the green alga and sometimes to the diatom while the blue-green would be greatly affected at There was no evidence that concentrations near 10 ppm affected any of the three organisms.

Many phytoplankton species and clones were tested against a 1979 sample of pharmaceutical wastes by Murphy et al. (1983). At a concentration of 100 ppm, an oceanic strain of a centric diatom suffered more than a 50 percent decrease in growth (Table 8). This is the only indication of any sensitivity as great as that shown in the permit-holder toxicity test (also done with a centric The major conclusion from the disparate results of toxicity tests with phytoplankton, summarized in Tables 5 through 8, is that decreased growth will be experienced by some species when pharmaceutical wastes are present at a concentration of 10 ppm, but that others may be stimulated at concentrations of 10,000 ppm. Many species will not grow when the concentrations are somewhere within that three-order-of-magnitude range. toxicity determination using a single clone of phytoplankton species means nothing in terms of environmental effects of waste disposal.

Table 7. Growth rates relative to controls for selected phytoplankton species exposed to pharmaceutical wastes collected at various times. a,b

	Year of waste			Conc	entrati	on (ppr	n, v/v)		
Species	collection	<u>50</u>	<u>150</u>	<u>250</u>	<u>500</u>	1000	<u>2500</u>	5000	10000
Agmenellum	1978(I) <sup>C</sup>	1.0		0.90		0			
quadruplicatum,	1978(II)	0.98		0.71		0			
a blue-green	1979			0.51	0.53		0		
alga, strain PR-6	1980(I)	<u> </u>		0.57	0.66		0		
	1980(II)		0.94	0.74	0				
	1980(III)			0.62	0.58		0		
<u>Cylindrotheca</u> <u>spp</u> , a diatom,	1978					0.94		0.83	0
strain N-1	1980(I)		<del></del>	0.85	.88	<del></del>	0.60	0	
	1980(II) 1980(III)			0.85	.75 .75		0.55	0 0.65	
Chlorella	1978(I)	· · · · - · · · · · · · · · · · · · · ·	·		-			<u></u>	1.7
autotrophica,	1978(II)		<u></u>	<del></del>			<del> </del>		0.72
a green alga,	1980(I)			1.0	0.96		0.96	0.92	
strain 580	1980(II)			1.0	0.96		0.91	0.88	
	1980(III)			1.0	1.0		1.0	1.0	

a Van Baalen and Batterton (1979), Van Baalen (1980 and 1981).

b For clarity, precision on ratios is not shown. Control growth rates in terms of generations per day varied by 6 to 10 percent.

<sup>&</sup>lt;sup>C</sup> The designations I, II, or III indicate separate waste samples collected during a given year.

Table 8. Growth rates relative to controls of a range of phytoplankton groups, species, and clones in the presence of pharmaceutical wastes (1979 sample).

Species (clone, area of isolation)	100 ppm (v/v)	1000 ppm (v/v)
Bacillariophyceae (Diatoms [centric]),		
Thalassiosira pseudonana (3H, np)	$0.89 \pm 0.02$	0
Thalassiosira pseudonana (Swan-1, nc)	$0.78 \pm 0.06$	0
Thalassiosira pseudonana (13-1, 0)	0.28 ± 0.03	0
Bacillariophyceae (Diatoms [pennate]),		
Phaeodactylum tricornutum (Phaeo, np)	$1.08 \pm 0.03$	$0.91 \pm 0.15$
Nitzschia breviostus (0-1, nc)	$1.02 \pm 0.09$	$0.15 \pm 0.15$
Fragillaria pinnata (13-3, 0)	1.10 ± 0.08	0
Dinophyceae (Dinoflagellates),  Scrippsiella trochidea (Peri, np)	0.80 ± 0.12	0
Chlorophyceae (Greens), <u>Dunaliella tertiolecta</u> (Dun, np)	1.02 ± 0.03	1.10 = 0.02
Eustigmatophyceae,	1.02 ± 0.07	0
Monallantus salina (GSB, np)	1.02 ± 0.07	0
Monallantus salina (Say 3, np)	1.02 ± 0.03	v
Prymnesiophyceae,	0.87 ± 0.05	0.05 ± 0.09
Isochryrsis galbana (Iso, np)	$0.62 \pm 0.02$	0.03 2 0.03
Pavlova lutheri (Mono, nc)	$0.62 \pm 0.02$ $0.63 \pm 0.06$	0
Pavlova spp. (Nep, 0)	0.03 ± 0.00	v

a Murphy et al. (1983).

Murphy et al. (1983) discussed recent work demonstrating that effects of contamination on phytoplankton are more likely to be evident as changes in community structure than as loss of biomass. The range of sensitivities toward pharmaceutical wastes is one more example of community structure changes being a possible phytoplankton response to ocean waste disposal. Such changes were sought in the context of this disposal operation.

While toxicity tests with phytoplankton isolates have no value in predicting actual effects in the ocean, they can be used to compare toxicities among wastes or to determine whether the toxicity in a given waste changes with time. Table 9 is a summary of toxicity test results using a single phytoplankton isolate and samples of individual plant wastes collected in 1979 and 1980. It is evident that the phytotoxicity of the ocean-dumped wastes is due to two of its seven sources, Upjohn and Bristol. waste is the more toxic. The 1979 individual plant samples were also tested against the phytoplankters Cylindrotheca spp. Only the Bristol waste and Chlorella autotrophica (5800). decreased the growth rate of  $\underline{C}$ .  $\underline{autotrophica}$  at a concentration of 5000 ppm. There was no growth in the presence of Bristol waste at 250 ppm. The Cylindrotheca spp. was unaffected by any waste, except Bristol, at 500 ppm. At that level there was no growth in the presence of Bristol waste, and growth was decreased to 51 percent of control at 250 ppm (Van Baalen, 1980).

The obvious hypothesis—that mixed pharmaceutical waste toxicity was due to uniquely toxic individual components—was tested by preparing artificial mixtures (Van Baalen, 1981). The proportions of individual wastes were those representative of the actually dumped waste (Table 3), and, if a waste was omitted, its proportion was replaced with distilled water. No mixture was tested in which both Upjohn and Bristol wastes were omitted; however, omission of Upjohn alone dramatically decreased the measured toxicity (Table 10). The 1980 Bristol sample allowed no growth of A. quadruplicatum (R-6) when present at 7 ppm. Since

Table 9. Growth rates relative to control of the blue-green alga, Agmenellum quadruplicatum (strain PR-6) in the presence of various concentrations of individual pharmaceutical wastes collected in 1979 and 1980.

Waste Sourc	e (year) <sup>b</sup>		Concent	tration (ppm	n, v/v)	·
		<u>150</u>	<u>250</u>	500	<u>2500</u>	<u>5000</u>
Upjohn	(1979) (1980)	1.00	0 0.57	0 0	0	0 0
Merck	(1979) (1980)		0.92 1.02	0.92 1.02	0.81 1.02	0.47 0.98
Shering	(1979) (1980)		0.83 1.02	0.81	0.43 1.00	0.21 0.92
American Cyanamid			1.02 1.02	1.02 1.02	1.02 1.02	0.94 0.98
Pfizer	(1979) (1980)		0.98 1.02	0.96 1.02	0.96 1.02	0.96 1.02
Bristol	(1979) <sup>C</sup> (1980)	0	0	0 0	0 0	0 0
Squibb	(1979) (1980)		1.00 1.40	1.00 1.00	0.85 1.00	0.77 0.96

a Van Baalen (1980,1981).

Companies listed in descending order of their percentage contribution to the total waste volume.

The alga did not grow when the concentrations of this waste were 50 and 7 ppm for the 1979 and 1980 samples, respectively. They did grow at lower concentrations in both cases.

Table 10. Growth rates relative to controls of the blue-green alga, Agmenellum quadruplicatum, (strain PR-6) in the presence of various concentrations of mixtures of individual pharmaceutical wastes. a,b,c

	Con	centration_	(ppm, v/v)	
Waste Mixture <sup>d</sup>	250	<u>500</u>	2500	5000
All components (I) (II)	o <sup>e</sup> 0.90	0.65 0.74	0	0 0
Upjohn omitted (I) (II)	0.94 1.08	0.94 1.08	0.90 0.96	0.67 0.72
Bristol omitted (I) (II)	0.84 0.78	0.74 0.72	0	0 0
Merck omitted (I) (II)	0.67 0.82	0.73 0.68	0	0 0
Shering omitted (I) (II)	0.80 0.86	0.69 0.78	0 0	0 0
American Cya- (I) namid omitted (II)	0.73 0.80	0.71 0.78	0	0

a Van Baalen (1981).

Wastes mixed in the proportions listed on Table 3. Omitted wastes were replaced by the appropriate volume of distilled water.

Individual samples collected in 1980. Measures of their individual toxicity are given on Table 9.

d Two sets of experiments were conducted with the same set of individual waste samples.

e Growth did eventually occur after a long lag period.

its proportion to the total waste volume was 3 percent, the mixture with Upjohn waste omitted when present at 2500 ppm, for example, included Bristol waste at 75 ppm. Since that mixture had minimal affect on growth rate (0.90 and 0.96 of control), it may be that, upon being mixed with the other wastes, the compounds responsible for the toxicity of Bristol waste are somewhat neutralized. (A sharp diminution of toxicity would be expected if Bristol waste were very acidic or basic and altered the pH of seawater unless neutralized by other wastes. However, the pH of a Bristol sample was measured to be 4.7, and it did not affect the pH of seawater when present at 100 ppm [Kennicutt, personal communication, 1982].)

While the volatile compounds in mixed pharmaceutical wastes were used as tracers of the wastes they were not necessarily responsible for its toxicity. Van Baalen (1981) observed the same growth rates of A. quadruplicatum when exposed to concentrations of 125 and 250 ppm regardless of whether the waste was first purged for 24 hours with nitrogen. This same treatment removed 28 percent of the total organic carbon in that waste sample (Brooks, personal communication, 1980). Similarly, Murphy (personal communication, 1980) found that bubbling waste overnight did not alter its toxicity to phytoplankton. While purging waste (or dilutions of it) did extract compounds for analysis, it did not strip them entirely from a sample. Some of the compounds listed in Table 4 could have been responsible for the waste's toxicity but that has not been shown.

While compounds responsible for the observed toxicity have not been identified, it is clear that Upjohn and Bristol wastes were the most toxic with Upjohn waste exerting the more influence simply because it constituted about half the waste volume. The presence of N,N-dimethyl aniline in Bristol waste was thought to have been the source of its uniquely high toxicity but a study of aniline toxicity toward phytoplankton growth (Batterton et al., 1978) found this compound to be non-inhibitory. Inhibition was

evident in the presence of aniline itself, and methyl or ethyl substituted anilines when the substitution was on the aromatic ring or singly (not doubly) on the nitrogen atom.

The EPA-required toxicity tests (Table 5) did not show pharmaceutical waste to be particularly toxic to animals. 96 hour LC50's for sea urchins and shrimp were in the 1000's of ppm range except for the shrimp in 1981 when the average LC50 was fourteen species of survival of Measures invertebrates (Lee and Nicol, 1981) summarized in Table 11 are consistent with those results. One species of amphipod, M. finmarchicus, both as adult and juvenile, was more sensitive than all other adult invertebrates; and larval grass shrimp, P pugio, adults 96-hour sensitive. Among the most order of magnitude from varied an over concentrations approximately 5,000 to 50,000. This is less than the sensitivity range displayed among species or among strains of a species for phytoplankton. No specific tests have been made of pharmaceutical However, in the course of wastes' lethal toxicity to fish. examining waste effects on fish respiration, (Table 12) Wohlschlag and Parker (1983) found all individual red snapper, Lutjanus campechanus unable to survive a 48-hour exposure to pharmaceutical wastes at 5,000 ppm, and when fish were forced to swim, the concentration of 2,500 ppm was similarly lethal.

individual toxicity of the lethal estimate of An pharmaceutical wastes is available from Lee (1983). experiment, summarized in Table 13, red fish (Sciaenops ocellatus) eggs and larvae were exposed to three individual wastes. About 90 percent of eggs exposed to Merck and Squibb wastes at 1000 ppm for 29 hours yielded live larvae. The same success occurred in the presence of Bristol waste, but at concentrations 200 ppm. Moreover, those larvae which developed from Bristol-waste-exposed eggs showed behavioral and morphological abnormalities. 48-hour LC50 of red fish larvae (from eggs hatched in clean water)

Table 11. Toxicity of pharmaceutical wastes to invertebrates. a,b

Invertebrate (waste batch) <sup>C</sup>		ur LC50 , v/v)	Highest tested conc. showing no lethality over 96 hours	
Amphipod, Caprella penantis (I)	5	500	4000	
Amphipod, Amphitoe valida (I, II, III)	5300, 3	5000, 3200	4000, 30000, 2000	
Amphipod, Parhyate hawaiensis (II)	3	5000	30000	
Amphipod, Marinogammarus finmarchicus (II)	> 1000	< 5000	1000 (15% dead)	
Shrimp, Palaemonetes pugio (II)	3	5000	30000	
Isopod, Sphaeroma quadridentatum (I)	1	4200	10000	
Anemone, <u>Anemonia sargassensis</u> (I)	. 4	900	4000	
Crab, Callinectus similis (I)	> 10000	< 50000	10000	
Worm, Platyneresis dumerili (I)	5	2000	40000	
Pelecypod, <u>Donax varabilis</u> (I)	1	4100	10000	
Jellyfish, <u>Nemopsis</u> <u>bachei</u> (I)	> 1000	< 10000	1000	
Gastropod, <u>Haminoea</u> antillarium (I)	> 1000	< 10000	1000	
Gastropod, <u>Littorina</u> <u>lineolata</u> (I)	4900	00(192h)	40000(192h)	
Mixed Zooplankton, (primarily <u>Temora</u> <u>turbinata</u> ) (II)	> 1000	< 10000	1000 (70h)	
Juvenile amphipod, M. finmarchicus (II)	> 1000	< 5000	1000 (10% dead)	
Larval shrimp, P. pugio (I)			1000 (37% and 60% dead, two tests)	

a Lee and Nicol (1981).

b Nicol et al. (1980) is a more detailed presentation of same information in ref. a.

C Three separate 1978 batches of wastes were available.

Table 12. Effect of pharmaceutical wastes on respiration rate of fish. a,b

Red snapper, <u>Lutjanus</u> campechanus, exposed for 48 hours to pharmaceutical wastes at four concentrations.

Respiration Rate	(mg	$0_2 kg^{-1}h^{-1}$	1)c
------------------	-----	---------------------	-----

Waste Conc. (ppm, v/v)	(A) at rest	(B) at maximum sustained swim speed	(C) Scope or (B-A)
0 625(I) 625(II) 1250(I) 2500(I) 5000(I)	50 50 50 50 70 Died	560 520 480 340 Died	510 470 430 290 -

Spotted sea trout, <u>Cynoscion nebulosus</u>, exposed to individual or mixed (as received) wastes at listed concentrations until first sign of behavioral or respiratory stress (listed times), then tested for respiration rates in clean seawater.

# Respiration Rate (mg O<sub>2</sub>kg<sup>-1</sup>h<sup>-1</sup>)<sup>d</sup>

Waste Source	Pretest Exposure (ppm, min.)	(A) at <u>rest</u>	(B) at max. sust. swim speed	(C) Scope <u>(B-A)</u>			
None Mixed Upjohn Merck Am. Cyan. Pfizer Bristol Squibb	no exposure 5000, 60 5000, 120 5000, 25 5000, 120 5000, 120 63, 120 5000, 110	200 290 230 360 230 280 270 300	610 540 640 650 570 600 540	410 250 410 290 340 320 270 240			

Wohlshlag and Parker (1983), L. <u>campechanus</u> tests with 1978 wastes, C. <u>nebulosus</u> with 1979 wastes.

b Fish tested individually with 15 to 35 individual tests per treatment.

Rates are those for a fish with the average weight of all fishes at a given treatment.

Rates are those for a fish with the average weight of all fishes used in all treatments.

Table 13. Effects of three individual pharmaceutical wastes on fish eggs and larvae.

Fraction of redfish, <u>Sciaenops ocellatus</u>, eggs which yielded live larvae during 24-hour exposure to individual pharmaceutical wastes.

			Cor	ncentra	ation (	opm, v/v	<u>/)</u>	
Waste Source	200	<u>400</u>	<u>600</u>	<u>800</u>	1000	5000	10,000	50,000
Merck					0.92	0.96	0.40	0
Squibb					0.88	0.04	0	0
Bristol	0.96	0.84	0.84	0				

LC50s of redfish larvae exposed to individual pharmaceutical wastes for 48 hours.

Waste Source	<u>LC50</u>
Merck	4900 ppm (v/v)
Squibb	4200
Bristol	450

a Lee (1983).

Each experiment run with 25 eggs initially in the late gastrula stage. Larvae which hatched from these eggs were transferred to clean water for observation through the 48-hour yolk-sac stage. Those hatched from eggs exposed to Merck or Squibb wastes showed high survival and no behavioral aberrations. Those hatched from eggs exposed to Bristol waste at 200 ppm showed considerable evidence of behavioral or morphological aberrations.

Experiments were initiated with eggs newly hatched in clean seawater, and extended through the 48-hour yolk-sac stage. Larvae appeared normal at lowest Merck and Squibb waste exposures (1000 ppm). Larvae were altered behaviorally and morphologically at the lowest Bristol waste exposure (200 ppm).

in Bristol waste (450 ppm) was 10 times lower than those of Merck or Squibb wastes.

Pharmaceutical wastes were not found in the ocean at concentrations of the order of 1000 ppm. If there were to be responses to it by invertebrates or fish, they would more likely be of a subtle rather than lethal nature. A decrease in the rate by which organisms consume oxygen is a sign that the respiratory system is affected by wastes. Alternatively, an increased rate of respiration indicates that the ability to respire is unimpaired, but that the organism is having to expend energy in order to deal with exposure to wastes. Wohlschlag and Parker (1983) used a rather elaborate experimental system to measure the effect of pharmaceutical wastes on fish respiration. Rates of oxygen consumption were measured while fish were at rest and while they were forced to swim at their maximum sustained speed. They refer to the difference between these rates as the metabolic scope.

Their results, summarized in Table 12, showed that red snapper, <u>Lutjanus campechanus</u>, in the presence of wastes at a concentration of 1250 or 625 ppm, showed little respiratory rate change while at rest. There was, however, a concentration-dependent decrease for swimming fish. That dependence becomes evident after raw data are treated to remove the 80 percent of variation in respiratory rate among fishes, which is due to variation in fish sizes. (Rates listed in Table 12 result from regression equations interrelating empirical data in terms of log oxygen consumption, log fish weight, and swim speed). It appears that lower than lethal levels of wastes did affect the ability of red snapper to generate energy when necessary for maximum locomotion.

Continuous exposure of fish to 625-ppm waste concentrations was unlikely but short exposures followed by swimming in clean water was possible. Wohlschlag and Parker (1983) subjected spotted sea trout, Cynoscion nebulosus, to short-term,

high-concentration exposures to mixed pharmaceutical wastes and to individual wastes (Table 12). Independent of the respiratory rate measurements, some qualitative observations from this experiment All exposures were to concentrations of are of interest. 5000 ppm, except that using Bristol waste. The objective was to visibly stress, but not kill, the fish. With Bristol waste, that required using a concentration about 100 times less than with all other wastes. Again, there is evidence that Bristol waste was uniquely toxic. Moreover, a 5000-ppm concentration of mixed waste (not mixed in the laboratory, but as received) contains about 150-ppm Bristol waste. Thus, as with phytoplankton tests using manipulated mixtures (Van Baalen, 1981), Bristol waste may have lost toxicity upon being mixed with other wastes. If fish had not been removed from their exposures to any wastes at the first sign of stress, they would have eventually died. (A 5000-ppm waste mixture was lethally toxic to red snapper over 48 hours). No briefly-exposed spotted sea trout died after removal into clean water, but at the end of 4 days over which the respiration measurements were made, they were approaching morbidity and showed a high incidence of fin and tail rot. Short-term exposures to high concentrations were obviously detrimental to spotted sea trout. In terms of respiration rates, the increases over controls while fish were at rest indicate a need to expend energy in an attempt to recover from exposure. The decreases in metabolic scope probably indicate an inability of fish to fully adjust energy consumption rate in order to swim at their maximum speed. In the ocean, such an effect could impair ability to forage for food and could therefore affect the size of fish populations. While episodic exposure to wastes is possible for fish, concentrations as high as 5000 ppm did not exist because of the manner in which wastes were dumped.

Planktonic organisms, unlike fish, have very limited mobility, and, if they are in water which becomes contaminated, they are likely to be continuously exposed to decreasing (as waste disperses) concentrations. Lee and Nicol (1981) found no

increased deaths relative to controls when a natural zooplankton community dominated by the copepod, Temora turbinata, was exposed to pharmaceutical wastes at 1000 ppm (Table 11). However, Lee and Bird (1983) have shown that the fecundity of T. turbinata can be decreased by a factor of about 5 by pharmaceutical wastes at a concentration of 1 ppm (Table 14). Over the concentration range of 0 to 100 ppm, the feeding rates of  $\underline{T}$ .  $\underline{turbinata}$  were not Copepods from eggs hatched and grown in systems different. containing 0- to 10-ppm wastes for 15 days had the same survival rates. The rates of development were initially slightly higher, then slower at the concentrations of 1 and 10 ppm compared with 0 and 0.1 ppm, and organisms at the lower concentrations were The major effect, however, was slightly larger. production.

Capuzzo (1982) found a 96-hour LC50 of pharamaceutical wastes to the copepod, Labidocera aestiva, of 104 ppm, indicating a higher toxicity toward copepods than reported by Lee and Nicol (1981). However, like Lee and Nicol (1981), Capuzzo found low concentrations to evoke losses of fecundity. At a concentration of 10 ppm, egg production decreased by 49 percent, and concomitantly respiration decreased by 43 percent. Capuzzo and Lancaster (1983), working with wastes dumped at the only other U.S. deep ocean site, also found that low concentrations, which did not affect survival did dramatically lower egg production. However, adult copepods that developed from those fewer eggs did not exhibit decreased fecundity if they grew in uncontaminated Decreases in egg production have obvious negative water. implications for the maintenance of zooplankton populations. It appears that the effect can be minimized if wastes are well enough dispersed so that fecundity decreases are not compounded through consecutive generations.

Table 14. Effect of pharmaceutical wastes on egg through adult development and fecundity of the copepod, <u>Temora turbinata</u>.

	Concentration (ppm, w/w)			
	<u>o</u>	0.1	1.0	10
Fraction surviving at day 15 <sup>b</sup>	0.68	0.63	0.72	0.66
Fraction as nauplii (day 5)	0.27	0.04	0.00	0.00
Fraction as adults (day 10)	0.92	0.97	1.00	0.84
Fraction as adults (day 15)	1.00	1.00	1.00	.98
Eggs per female (days 10 to 15)	15.4 ± 4.8	27.1 ± 10.9	2.7 ± 1.6	$5.5 \pm 4.3$

Separate experiments with the same waste and organism showed no differences among feeding rates with exposures to concentrations of 0, 0.1, 1.0, 10, and 100 ppm.

<sup>&</sup>lt;sup>a</sup> Lee and Bird (1983), waste sample collected in 1980.

Experiments were begun with 60 test systems (15 at each concentration), each containing 25 eggs and continued for 15 days. Four or five systems were sacrificed for measurements at 5-day intervals. Fractional survival is relative to the 25 original eggs. During the first 5 days, the animals at the higher concentrations proceeded more quickly through the various nauplii and copepidite stages than at the lowest and control concentrations; later development was slower at the higher concentrations. Average lengths of animals at day 10 were slightly higher for those in control or 0.1 ppm systems than for those at the higher concentrations (1077 um control, 1020 um at 10 ppm).

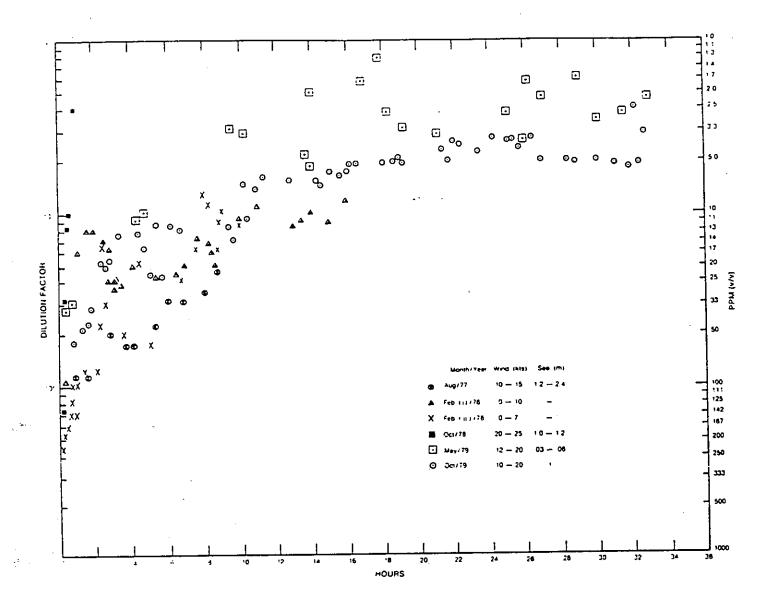


Figure 3. Minimum dilution factors (maximum concentrations) observed in experiments where dyed pharmaceutical waste was dumped. In all cases the dye concentration (Rhodamine-WT) in the waste was 20 ppm. Data from August 1977 were collected by Raytheon (1977). All other data are from Icihye (in preparation).

## Waste Distribution

The dilution histories of six waste plumes (Figure 3) were determined by tracking the concentration of rhodamine-WT dye added to barge loads of wastes. They showed wastes to be diluted by factors of  $10^4$  to about  $4 \times 10^5$  (waste concentrations 100 to 2 ppm, v/v) between 30 minutes to 36 hours after dumping events. Dilution during that period is due to oceanic processes, but the initial dilution is controllable.

Csanady (1981) interpreted initial dilution of wastes dumped at the 106-Mile Site to be simply predictable from the dimensions of the discharging vessel and, more importantly, from the distance traversed per unit volume of wastes discharged. Pharmaceutical wastes were discharged by gravity at a rate of 70  $\mathrm{m}^3~\mathrm{km}^{-1}$ , so that a single load of 2.5 x  $10^3$  m $^3$  was emptied over a distance of 35 km. The volume into which the wastes were initially mixed was that distance multiplied by a cross-sectional area equal to about 3 times the barge draft, and 2.5 times its width or 350  ${\rm m}^2$ . Mixing 2.5 x  $10^3$  m<sup>3</sup> of waste into that volume (35 x  $10^3$  x 350 =  $1.25 \times 10^7 \text{ m}^3$ ) dilutes it by a factor of 5000, thus achieving the dilution factors at the beginnings of the dilution histories in Figure 3. Discharging a barge load of wastes over 35 km required about 4 hours. It could have been done, for example, over 10 times less or 10 times more distance in 15 minutes or 40 hours, respectively. The initial dilutions would have been 500 and (Since pharmaceutical wastes are very 50,000, respectively. similar to seawater in density, dumping them quickly would not have produced a sinking waste mass that would behave independently from the ambient seawater until it entrained enough seawater to lose its effective density difference.) Beyond the initial mixing induced by dumping subsequent dilution is due to oceanic processes. The shape of the dilution versus time curves in Figure 3 would not differ if wastes had been dumped more or less quickly but the dilution factors and concentrations on the y-axis would be shifted up or down, respectively.

Waste dispersion through oceanic mixing is a continuous process whereby plumes grow to fill progressively larger volumes at progressively lower concentrations. At some point, determined by the frequency of dumping and the flow characteristics of the dumpsite region, concern is for the cumulative effect of many dumps rather than the details of how a single plume becomes diluted. On a smaller scale, dumpsite location is irrelevant. The concentration versus time curves shown in Figure 3 could well have been obtained by following dyed liquid wastes dumped at any oceanic site. O'Connor and Park (1982) summarized data yielding very similar curves for wastes dumped at the 106-Mile Site.

Oceanic mixing is due to turbulence. It is similar to nonturbulent molecular diffusion in its dependence on statistically random processes and its direct variation with concentration However, the effect of turbulence is to provide stirring so that concentration gradients at the molecular level are continuously subject to being increased. Molecular diffusion is entirely predictable because it results from the random translocations of a very large number of particles (molecules). Turbulent diffusion is not so predictable because it depends on a continuous physical entrainment of plume parcels with parcels of The size and energy of eddies responsible for this seawater. meteorological stochastic by determined mixing oceanographic factors. The dilution history of a given plume is one manifestation of that arrangement of oceanic eddies and plume is another different dilution of a energy; manifestation, and it need not mimic the first in all details. Despite being less understood than molecular diffusion, turbulent diffusion is the overwhelmingly dominant process mixing wastes into seawater. Csanady (1973), for example, indicates that a turbulent diffusion coefficient (eddy mixing coefficient) of 103 cm<sup>2</sup> s<sup>-1</sup> can conservatively describe the horizontal mixing rate of plumes into large bodies of water. Mathematically, molecular diffusion coefficients have the same meaning and dimensions but are of the order of  $10^{-5}~{\rm cm}^2~{\rm s}^{-1}$ , eight orders of magnitude smaller.

observations number of Results from distributions, which covered time scales of hours to months and horizontal length scales of meters to kilometers (no single distribution was observed over those entire scales), were found by Okubo (1971) to fit an analytical expression whereby horizontal eddy diffusion coefficients increased with the size of the area containing the tracer. There is a theoretical basis for assuming that coefficients should increase with size of tracer field because oceanic "eddies" should exist over a range of sizes. When the tracer field is small, it is simply transported "in toto" by large eddies. As the tracer mixes over larger scales, it becomes subject to being mixed (not simply transported) by the energy in ever larger eddies. Theoretically, coefficients should increase with the length scale (1) of the tracer field increased to the 4/3 power. Okubo (1971) found the exponent of 1.15 to best-fit the observations.

Csanady (1973), on the other hand, has recommended use of constant (scale-invariant) eddy diffusion coefficient of  $10^3~{\rm cm}^2~{\rm s}^{-1}$  to predict early stages of plume growth. Ichiye et al. (1981) found a coefficient of  $10^4~{\rm cm}^2~{\rm s}^{-1}$  to describe the first 12 hours of dispersion of a cluster of drogues deployed at the Puerto Rico Dumpsite. An alternative to diffusion coefficients that is often applicable to the growth of plumes is to invoke diffusion velocities with dimensions of cm s<sup>-1</sup>. The basis for doing so is that under the influence of vertical variations in horizontal velocity (vertical shear), a tracer field will grow, effectively, in a linear fashion with time rather than with the square root of time. As Csanady (1981) has pointed out, shear-induced dispersion can be most efficient in enlarging the scale (and decreasing the concentration) of a tracer until at some point at very large

scales the diffusion is again describable with an eddy coefficient but one which is of the order of  $10^6\ {\rm cm}^2\ {\rm s}^{-1}$ .

Applying any of these models to waste plumes is simplified by having to consider only diffusion in a horizontal direction lateral to a plume. Plumes are initially long, thin ribbons of wastes. Pharmaceutical waste plumes, for example, are typically 35 km long (by design) and 50 km wide after initial mixing. Diffusion by any mechanism requires a concentration gradient, and except at the two ends no such gradient exists along a plume. (Wastes are is not discharged at a perfectly uniform rate, but for practical purposes diffusion along a plume can be neglected.)

Vertical mixing does occur but is effectively limited to the depth of water above the first major pycnocline. Vertical profiles of water temperature and salinity obtained in the months of February and August are shown in Figure 4. In each case, as with all such profiles of ocean water, there are depths where salinity or temperature or both begin to change rapidly with depth. The existence of these halo-or-thermo-clines is evidence for vertical mixing to be severely limited. Otherwise the gradients would not persist. Turbulent mixing is inhibited because, as the term pycnocline implies, the gradients are density gradients and deeper, heavier water has little tendency to rise into overlying, lighter (less salty and/or warmer) water.

Waters north of Puerto Rico are characterized by a salinity maxima at about 100 m (Carnes et al., 1980). This can be considered the base of a permanent pycnocline. Shallower limits to vertical mixing are created by annual cycles in atmospheric temperature or precipitation which will heat or cool surface waters and change salinity. The profiles in Figure 4 indicate mixed layers of 70 and 30 m for February and August, respectively. Other profiles (Carnes et al., 1980) indicate a 50-m deep mixed layer during successive Octobers and a 10-m limit in May (this

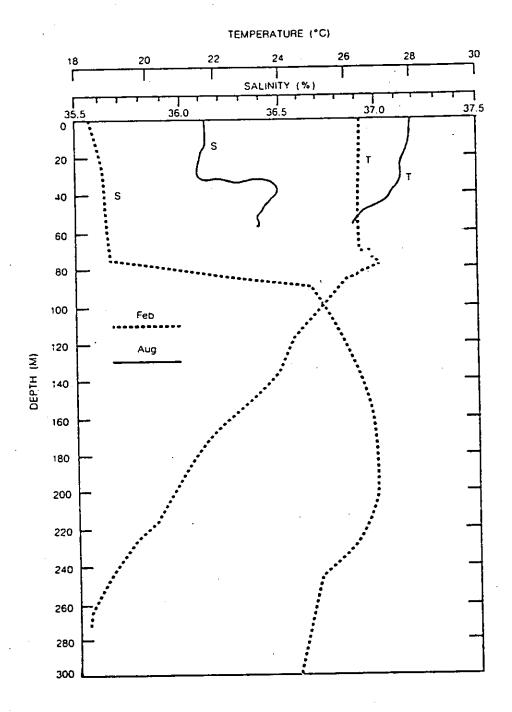


Figure 4. Temperature and salinity versus depth curves obtained at the Puerto Rico Dumpsite in August 1977 (Raytheon, 1977) and February 1978 (Schwab et al., 1981).

last limit was determined by a very weak temperature gradient which may have been transitory).

Vertical limits of plumes have been found to approximately coincide, with mixed layer depths. Raytheon (1977) in August 1977 found evidence of dye (previously added to a waste load) down to a depth of 50 m with the bulk of it being between the surface and 30 m. Ichiye (in preparation) observed dye distributions after dumping events in February 1978 and in May and October of 1979. Again the vertical limits of dye were the depths of the upper mixed layer.

Because pharmaceutical wastess contain suspended particles, they can be detected in the ocean (until they become too dilute) by a high frequency acoustic technique. Basically, a signal is transmitted downward, and the intensity of the return is a complex function of particle size, concentration, and impedence (Orr and Baxter, 1983). Proni and Hansen (1981) using this method found particles of pharmaceutical wastes to be distributed within the upper 30 m after a February 1978 dumping event. technique showed particles limited to the upper 15 m in October of At that time the first major pycnocline began at  $50\ \text{m}$ . Because of a persistent and intense storm, considerable rain had fallen which may have created a thin surficial layer overriding the mixed layer. There were indications in vertical temperature profiles (XBT's) of such a layer which, although weakly defined, may have been sufficient to limit vertical mixing of wastes. Observations of dye during that October 1978 experiment were sporadic and indicative of rapid extensive dilution under the influence of the storm.

The remaining evidence for limited vertical mixing of waste plumes comes from transmissometer lowerings in February 1978. Decreases in transmissivity due to increases in suspended solids concentrations were measured by Schwab et al. (1981). Decreases

were observed only at depths of 40 m or less with the major decreases occurring in the upper  $20\ m_{\odot}$ 

The fact that acoustic and transmissivity indications of waste particles showed them to be constrained to the mixed layer is evidence that the particles are very small and/or light. Their gravitational settling is overwhelmed by oceanic turbulence which tend to homogenize their vertical distribution. Lavelle and Ozturgut (1981) in modeling the behavior of particles discharged to the ocean, in the context of manganese nodule mining, calculated that particles with the settling velocities of the order of  $10^{-3}$  cm s<sup>-1</sup> would be essentially unaffected by gravity under oceanic conditions. Such settling velocities are common to a large fraction of sewage sludge particles (Faisst, 1981) and may be typical of pharmaceutical wastes. Presley et al. (1981) qualitatively observed pharmaceutical wastes solids to be very fine grain because of the length of time required to filter the wastes. On a mass basis, these wastes were low in suspended solids (Table 3) relative to other waste suspensions, but the number of particles was relatively large. The same authors observed that most of the iron in these wastes were associated with particles and that iron concentrations in a 50:1 seawater: waste mixture decreased very slowly in the upper 3-cm of a 30 cm settling column. The decrease was about 3 percent in 10 hours, 15 percent in 40 hours, and 50 percent in 200 hours. (Particles falling as fast as  $10^{-3}$  cm s<sup>-1</sup> would descend through 3 cm in 0.8 hours.)

No measures of the vertical distribution of dye or waste particles indicated uniform concentrations. There were gradients of those tracers within the mixed layer. While plume dispersion can be considered primarily a matter of plume widening, it is not to be understood that the vertical distribution is static.

Diffusion of waste lateral to the plumes created by dumping events can be described by any of three equations corresponding to the models discussed above:

(I) 
$$\overline{U}_t = \overline{U}_o + \sqrt{2Kt}$$
  
(II)  $\overline{U}_t = \overline{U}_o + wt$   
(III)  $\overline{U}_t = \overline{U}_o + \sqrt{2tc\ell}^X$ 

In these equations the symbol "G" denotes the standard deviation of the cross plume distribution of wastes. In that view, at a given depth, the concentration profile of wastes is Gaussian (or "normal" in the statistical sense) with the maxima at the center. Just as in the statistical sense, the standard deviation of the waste distribution is the second "moment" of that distribution. The distance of 4  $\overline{G}$  (actually 3  $\sqrt{2}$  times  $\overline{G}$ ) which is bisected by the plume center is the distance over which concentration rises from and returns to 10 percent of its maximum value. It is also the distance which 96.5 percent of the wastes are contained. The symbol  $\sigma_{_{\mathrm{O}}}$  is the initial plume standard deviation. Actually the initial distribution is not Gaussian but is more or less a flat with sharp lateral gradients. The initial widths are of the order of 40 m which can be used for  $\sigma_{o}$ . The discrepancy between the actual and a Gaussian initial distribution becomes inconsequential as the plume grows and  $\overline{\mathcal{O}_{\mathbf{t}}}$  becomes much larger than the initial Equation I describes  $\mathfrak{G}_+$  as increasing with a constant . eddy diffusion coefficient, K. Equation (II) assumes a constant diffusion velocity, w. In Equation (III), K is replaced with the term cl x where £ is the plume width or 4 \( \tau\_{\text{,}} \) c is a constant, usually 0.01 (Okubo, 1971), and x is an exponent accounting for an increased diffusion coefficient with increasing width.

The major difference between these equations is their predictions of how plume widths will depend on time. Equation (I) has  $\sigma_t$  increasing with the square root of time. Equation (II) has it increasing linearly in time. In Equation (III), the time dependence is determined by the exponent "x". If x were 1.0,

would depend linearly on time as with Equation (II). With x equal to 1.15 or 4/3,  $\sigma$  increases with time raised to approximately powers of 1.1 or 1.2, respectively. Using oceanographically reasonable values for constants in these equations, dilution versus time curves have been calculated and superimposed on observed plume histories (Figure 5). While it is conventional and theoretically more revealing to plot such data on log-log axes, it is nevertheless evident that the three models do portray different time dependencies which cause the curves to diverge more as times become longer.

It is not possible or necessary to choose a single equation and set of constants to describe the short-term dilution of waste plumes. The "4/3" does imply faster dilution than observed and the constant eddy diffusion coefficient model (Equation (I)) appears to underestimate diffusion. Equations (II) and (III) with an exponent of 1.15 appear closer to the observations. Ichiye (in preparation) found concentration to decrease (equivalent to  $\sigma$ increase) with time to the 0.8 power for the October 1979 data set which argues against Equation (III) but is closer to Equation (II) than to (I). The general practice of using Equation (II) with a diffusion velocity of 1.0 cm s<sup>-1</sup> (Pritchard and Okubu, 1969) yields a reasonable estimate of the observations. Csanady (1981) found the short-term diffusion history of a plume created at the 106-Mile Site to be approximated by Equation (II) with a diffusion velocity of 0.2 cm s<sup>-1</sup>. He suggested that such a low constant can be expected under very calm conditions, and that as wind increases and therefore oceanic turbulence increases the constant could rise to a value of  $2.0 \text{ cm s}^{-1}$ .

The reason for using semi-log plots (linear time axis) in Figures 3 and 5 is to demonstrate that actual observations and models (except the 4/3 law) define oceanic waste diffusion as a slow process. After 36 hours, wastes may be diluted by only about 40 times beyond the 5000-fold dilution achieved in the dumping process. Similarly, the plumes remain rather narrow for long

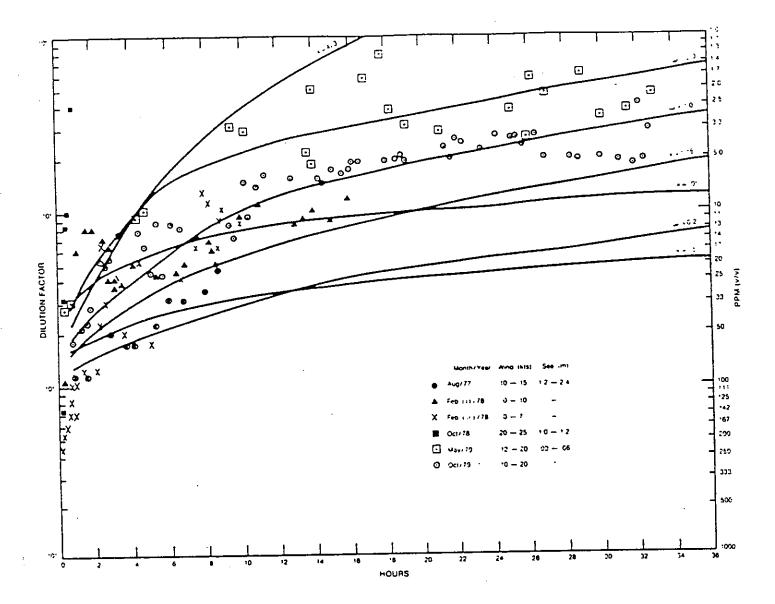


Figure 5. Minimum dilution (maximum concentration) versus time curves calculated by Equations (I), (II), and (III). Data points are also shown in Figure 3. Equation (I) used with  $K = 10^{\circ}$  and  $10^{\circ}$  cm  $s_1^{\circ}$ . Equation II used with  $K = 10^{\circ}$  and  $10^{\circ}$  cm  $s_1^{\circ}$ . Equation III used with  $K = 10^{\circ}$  and  $K = 1.15^{\circ}$  and  $K = 1.15^{\circ}$ 

periods after dumping. Width is difficult to measure from a ship because a given crossing of a plume (i.e., the distance over which dye is detected) need not be the shortest distance. However, analysis of crossing distances along with navigation information can be used to estimate plume growth. Data from such analyses for dyed-waste dumps in August 1977, May 1979, and October 1979 are shown in Figure 6 along with a calculated plume growth curve using Equation (II) with  $w = 1.0 \text{ cm s}^{-1}$  (plume "width" is equal to  $4 \times 6$ ). As with comparisons between calculated and observed dilution factor curves, it appears reasonable to estimate plume behavior with that diffusion velocity.

No single plume was tracked north of Puerto Rico for more than 36 hours. Simple application of a 1.0 cm s<sup>-1</sup> diffusion velocity can be used to predict plume size and concentration at any time. Table 15 is a listing of plume widths and areas and maximum concentrations so calculated for selected times from It is unrealistic, however, to 1 hour to 1 week after a dump. describe plume behavior by so simple a model for 1 week. First, even the simple model shows a plume becoming almost as wide as it is long after 1 week, so one-dimensional horizontal diffusion is no longer appropriate. More importantly, all simple models in Equations (I), (II), and (III) assume that the plume remains intact. They also assume that an initially thin ribbon grows into a relatively large patch. Under the influence of inhomogeneities (shear) in the horizontal current structure, plumes can be divided into a number of small pieces each subject to diffusion in two Such drastic destruction of intact plumes can, dimensions. presumably, occur under the influence of storms which transfer turbulent energy to the sea. Such an event cannot be demonstrated from shipboard observation because, in effect, a plume not seen may, nevertheless, exist. However, a plume tracking experiment in October 1978 succeeded in detecting dye only sporadically and only for 1 hour after a dump. As noted on Figure 3 the winds were stronger than during any other plume tracking experiment. The stormy conditions during that experiment had existed for several

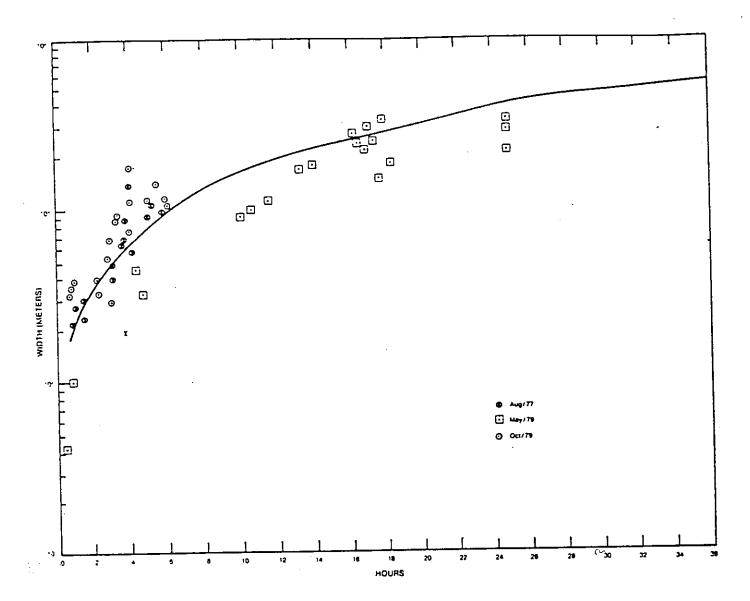


Figure 6. Plume widths versus time as observed in three experiments and as calculated by Equation (II) with  $w=1.0~{\rm cm~s}^{-1}$ .

Table 15. Calculated plume width, area, and maximum concentrations at selected times after a dump (assuming that plume is not broken into many separate sections by horizontal shear or not mixed by extensive storm-induced turbulence).

•			
<u>Time</u>	Width (km)	Area (km²)	Max. conc. (ppm v/v)
1 hour	0.2	6.3	53
10 hours	1.5	52	10
1 day	3.5	123	4
2 days	7.0	243	3
1 week	24	847	0.6

$$G_{+} = 4000 + (1.0)t$$

where 4000 cm is initial plume width, 1.0 is a diffusion velocity (cm  $s^{-1}$ ) and t is time(s).

a Calculation of standard deviation across plume by;

b Width is 46.

C Area calculated using a plume length equal to a dumping track of 35 km.

Maximum concentration calculated by using 100 ppm as the concentration after initial mixing and multiplying by  $C_0/C_+$  where  $C_0$  is 40 m.

days prior to the dump. Similar experiences of plumes' being unsuccessfully tracked under stormy conditions also pertain to studies at the 106-Mile Site (O'Connor and Park, 1982).

Csanady (1981) has concluded that a low diffusion velocity constant can describe plume behavior but that plumes are primarily diluted by episodic storm events. In essence, pharmaceutical wastes or any other ocean-dumped liquid wastes are extensively diluted by the dumping process and by storms. In between those events, it is reasonable to approximate the slow growth of plume with diffusion velocity of  $1.0~{\rm cm~s}^{-1}$ . Assessing the consequences of this waste disposal method at any given location requires a knowledge of the flow regime in the dumpsite area. This, along with dumping frequency, determines the area and intensity of contamination which is created by the disposal operation. In this context, the fate of any single plume becomes irrelevant.

## Flow North of Puerto Rico

Defant, 1961) show surface waters north of Puerto Rico to be within the westward flowing Antilles Current. The U.S. Naval Oceanographic Atlas (USNAVOCEANO, 1970) indicates currents north of the island to be predominately towards the west at a velocity of 25 cm s<sup>-1</sup>. In such a system, waste plumes within the Puerto Rico dumpsite would be expected to move about 22 km westward within a day of being created. Even plumes laid down on the eastern edge of the 27-km-wide site would be expected to be clear of the site in about a day.

Initially chemical, then bacteriological, and finally physical oceanographic evidence was obtained that is at variance with this simple flow structure. Wastes have been detected at the dumpsite in the absence of dumping events. It has been found south, west, and north of the site. Calculations of flow based on

the distribution of water density (geostrophic calculations) have indicated meridional (north-south rather than zonal (east-west) currents. Trajectories of drogues have revealed gyre-like circulation on relatively small scales. The average residence time of water and wastes north of Puerto Rico has not been established, but it is clear that the area is not simply flushed by a continuous westward flow.

Figure 7a to 7e indicates where water samples were taken on seven separate cruises and at which locations chemical evidence of pharmaceutical wastes were found. The first five of these seven cruises included studies of dumping events; the last two sets of samples were collected as an ancillary part of cruises conducted for reasons independent of ocean dumping. No sampling locations shown in Figure 7 were within fresh plumes. The locations were sampled prior to specific dumping events if such did occur during a cruise.

Two sets of water samples were taken (Figure 7a) prior to dumping events in February 1978. This was done primarily to test techniques, but later analysis showed N,N-dimethyl aniline to be present in water taken from depths of 1 or 50 m (Hatcher and Harvey, 1978). This compound was also found in samples of wastes collected at that time and has no apparent source to the ocean other than waste dumping. Its occurrence east of the site and within the site a day after the most recent dumping was unexpected in light of a presumed Antilles Current. Even allowing for a slow westward flow, the presence of wastes at an arbitrary location within the dumpsite was considered unlikely. As indicated in Table 15, a waste plume could, on an average, occupy 125 km² after 1 day. The dumpsite is 4 times larger than that, thus the chance of finding that waste plume, even if it remained within the dumpsite, is only one in four.

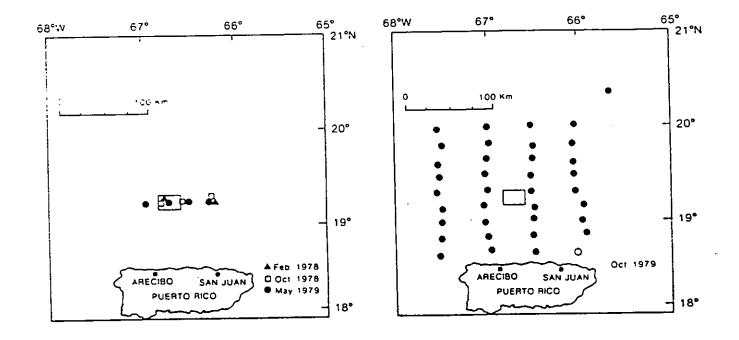
Despite these two "anomalous" observations, no evidence of wastes was found at three locations east of or within the dumpsite

Figure 7. Sampling locations (open and closed symbols) and indications of the presence of pharmaceutical waste (closed symbols) for seven cruises north of Puerto Rico with sampling not within fresh waste plumes.

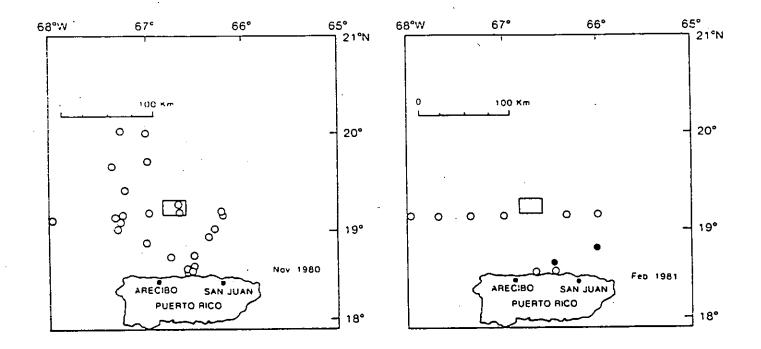
<u>Fig</u> .	Month/year	Sampling day(s)	Three most previous dumps <sup>a</sup>	Source
7 a	Feb/78 (Δ)	2/5	1/29, 1/30, 2/4	Hatcher and Harvey, 1978
7 a	Oct/78 (º)	10/27	10/15, 10/18, 10/25	Harvey, pers. comm., 1979
7a	May/79 (o)	5/5 to 5/6	9/27., 5/3, 5/3	Harvey, pers. comm., 1979
7b	Oct/79 (o)	10/8 to 10/13	10/4, 10/5, 10/7	Brooks et al., 1983a
7c	Nov/80 (o)	10/27 to 11/30	10/18, 10/19, 10/20	Brooks et al., 1983b
7d	Feb/81 (o)	2/14 to 2/15	2/12, 2/13, 1/14	Brooks, pers. comm., 1982
7e	May/81 (o)	5/5 to 5/6	4/30, 5/1, 5/2	Brooks, pers. comm., 1982

Dumping logs submitted to U.S. EPA, Region II by Pollution Control Industries.

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Figures 7a and 7b



Figures 7c and d

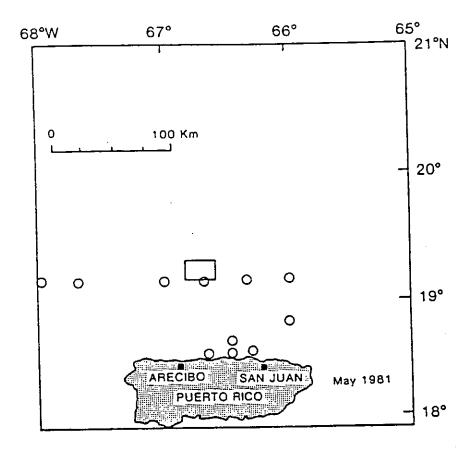


Figure 7e

in October 1978 (Figure 7a) (Harvey, personal communication 1979). Negative data reveal nothing, but are consistent with a westward flow. Collection of samples for bacteriological analysis began in May 1979. To chemically differentiate clean from contaminated locations, subsamples of water obtained at depths of 1 to 50 m in sterile Niskin bags were stored for later analysis of volatile organic compounds. On the basis of chromatogram peaks generated in analysis of a May 1979 waste sample and by those subsamples (e.g., peaks due to methyl isobutyl ketone, cyclohexanone, ethyl acetate, n-butanol, toluene, and N,N-dimethyl aniline), Harvey (personal communication, 1979) found evidence of wastes to the east of, and within, the dumpsite (Figure 7a).

A major objective of a cruise in October 1979 was to discern the areal extent of oceanic contamination due to waste dumping. Samples were taken at 10 m in 2-liter glass bottles at 37 stations over a more that  $20,000 \text{ km}^2$  grid (Figure 7b). On the basis of volatile organic compounds (primarily xylenes but also chlorinated methanes, toluene, ethyl benzene, propyl benzene, mesitylene, cumene,  $C_4$ -benzenes and naphthalene) wastes were identified at all but the most southeast station (Brooks et al., 1983a). This cruise confirmed that wastes were not continuously flushed away from the dumpsite area, but did not find spatial limits to contamination.

A cruise in November 1980 began from Key West, Florida, with samples taken along the track to Puerto Rico. As shown in Figure 7c, no wastes were found at any predump sampling location. Waste detection in 1980 was made more difficult by the volatile organic signature of the wastes having become simpler than in previous years (Figure 2). While wastes could be identified by the presence of N,N-dimethyl aniline in February 1978 and May 1979 and by an array of compounds in 1979, wastes dumped in 1980 and 1981 were generally characterized by a large toluene component and lesser amounts of low-molecular weight ketones. However, the predump samples collected in November 1980 contained no amounts or

trace amounts (less than 10 ng  $\rm kg^{-1}$ ) of toluene and no other compounds (Brooks et al., 1983b). Concentrations of about 20 ng  $\rm kg^{-1}$  have been found in many oceanic areas (Sauer, 1981; Gschwend et al., 1982), so the low levels observed in November 1980 have not been attributed to pharmaceutical waste dumping. Therefore, instead of extending the limits of the waste distribution found in October 1979, the November 1980 cruise indicated that on some time scale the surface waters north of Puerto Rico were cleansed of wastes.

In February and May of 1980 samples were collected (Figures 7d and 7e) from a ship of opportunity, again using glass bottles and a 10-m sampling depth. Wastes were detected in only 2 of the 21 samples. Both of those samples, collected in February 1981, had toluene concentrations in excess of 80 ng kg<sup>-1</sup> (actually 185 and 249 ng 1<sup>-1</sup>). There were also peaks in the chromatograms for those samples corresponding to benzene and xylenes which do occur in pharmaceutical wastes. Nevertheless, given the sparce number of positive indications of wastes, it is concluded that pharmaceutical wastes were not a source of wide-spread contamination in either February or March 1981. Thus, on seven occasions chemical evidence that the area was not being readily flushed of wastes was sought, and on three occasions wastes were found.

Bacterial cultures of individual plant waste samples collected in 1979 and mixed wastes in 1978 and 1979 showed the following results in terms of colonies per ml of wastes grown at 25° on a tripton-based agar medium: Upjohn waste 390 ml<sup>-1</sup>, Shering 10000 ml<sup>-1</sup>, Squibb 20 ml<sup>-1</sup>, mixed waste (1978) 2000 ml<sup>-1</sup>, mixed waste (1979) 300 ml<sup>-1</sup>, with none in wastes from Merck, American Cyanamid, or Pfizer (Colwell, 1980). This was expected since some of the individual wastes were derived from plants employing a fermentation process. It was, therefore, possible that the presence of terrestrial, as opposed to marine, bacteria in waters near the dumpsite could be used to reveal the presence

of wastes. In addition to sampling during cruises of May 1979, October 1979, and November 1980, in conjunction with other work, bacterial samples were collected in December 1979, February 1980, and June 1981 (Peele et al., 1981; Singleton et al., 1983; Grimes et al., 1983).

In all cases, total numbers of viable bacteria in surface waters were in the range of  $1 \times 10^5$  to  $3 \times 10^5$  ml<sup>-1</sup>, as determined by acridine orange direct counts (AODC). No effect of waste dumping on those total counts could be discerned. Evidence for the presence of wastes was implied in the types and numbers of bacteria which could be cultured on marine agar or plate-countagar (same as marine agar but not amended with salt). Though the number of colony forming units (CFU) per ml were in the range of less than 1 to about 100 and were low relative to AODC data, the concentrations of plate-count-agar culturable (non-salt requiring) or gram-positive bacteria were sometimes in excess of what was expected in open-ocean seawater.

Figure 8, taken from Peele et al. (1981), illustrates that numbers of culturable bacteria were at a maximum north of the dumpsite in December 1979, with most of those being culturable on plate-count agar. The fact that most culturable bacteria did not require a salt-amended media and that in three cases the majority of cultured colonies were gram-positive has been taken to imply that wastes were present north of the dumpsite. Gram-positive bacteria were common in pharmaceutical wastes, but are usually not found in open-ocean seawater (Peele et al., 1981). Within a waste plume sampled during October 1979, the culturable bacteria concentrations varied from 25 to 108 CFU ml<sup>-1</sup>, with 70 to 90 percent being cultured on plate count agar (Peele et al., 1981). The distribution of culturable bacteria observed in December 1979. if attributed to waste dumping, is an indication that the dumpsite is not flushed by a continuous westward flow. Two stations were sampled for bacteria in October 1979 prior to a dumping event, one 16 km east of the site and the other 144 km to the northeast.

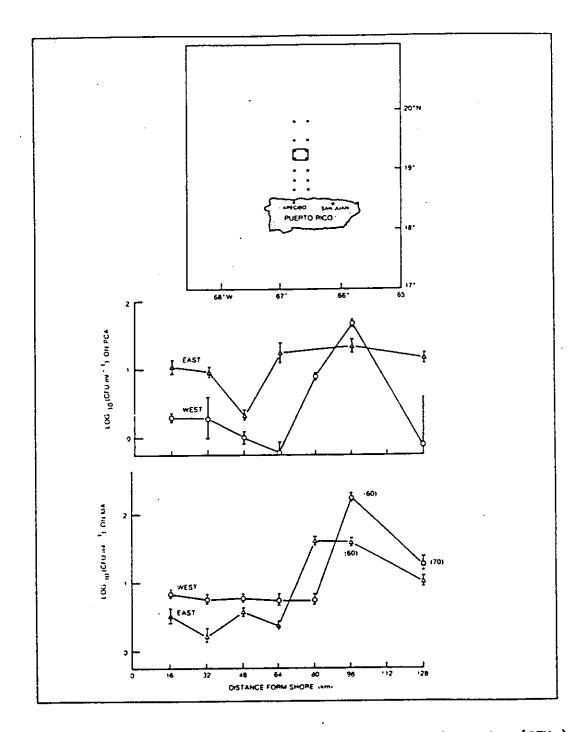


Figure 8. Concentrations of bacterial colongy forming units (CFUs) per ml in surface waters along transects from near shore to and beyond the Puerto Rico Dumpsite in December 1979. Station locations are shown in insert. The southern and northern limits of the dumpsite are 64 and 80 km from shore, respectively. CFU concentrations were determined for samples plated on marine agar (MA) and plate-count agar (PCA). The number associated with three of the MA-cultured concentrations is the percentage of cultured colonies which were gram-positive. In all other cases, MA-cultured colonies were entirely gram-negative.

These did show high concentrations of culturable bacteria (57 and greater than 100 CFU ml<sup>-1</sup>) which could be due to bacteria having entered the ocean by dumping. The chemical data from that cruise (Figure 7b) indicated a widespread distribution of wastes. In February 1980, bacteria were sampled along three parallel transects, one identical to the western transect of December 1979, and one each 40 km west and east of the dumpsite. Large increases in culturable bacteria concentrations, like those found in December 1979, were not observed, but concentrations of marine-agar culturable bacteria were higher north and northwest of the dumpsite than elsewhere, except for a sample taken 6.4 km north of San Juan.

Bacteriological sampling over large scales was conducted in November 1980 and June 1981 (Figure 9) (Grimes et al., 1983). Chemical sampling failed to indicate the presence of wastes in November 1980 (Figure 7c), and, except at the near shore stations (3 and 4, Figure 9a), concentrations of CFUs were  $5 \text{ ml}^{-1}$  or less. Near the discharge of the Barceloneta regional waste treatment plant (station 3, Figure 9a), concentrations of marine-agar culturable bacteria reached 460 ml<sup>-1</sup>. In June 1981, the highest concentrations of culturable bacteria (11 to 50 CFU  ${
m ml}^{-1}$ ) were observed at the three Caribbean stations, and the lowest concentrations (1 to 3 CFU  $ml^{-1}$ ) at the three most northern At the center of the dumpsite the Atlantic stations. concentration was 10 CFU  $ml^{-1}$ , while nearer to shore the concentrations were between 6 and 9 CFU  $ml^{-1}$ , and further north concentrations decreased from 9 to 5 CFU ml<sup>-1</sup>. Among three stations (two within the dumpsite and one 55 km north of the site), the percentage of culturable bacteria which were cultured on plate-count-agar ranged from 5 to 10 percent. Except for the station nearest to shore (D, Figure 9b) where it was 4 percent, the percentage of plate-count-agar culturable bacteria ranged from less than 1 to 2.5 percent. Therefore, on the basis of total culturable bacteria concentrations or the fraction of those cultured on non-salt amended media, there may have been evidence

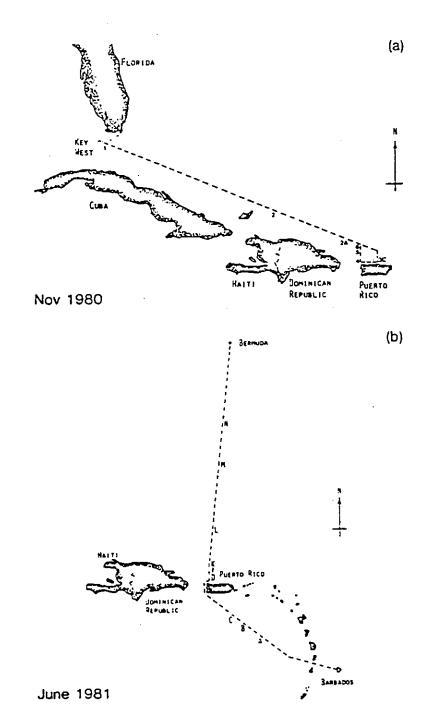


Figure 9. Locations of bacteria sampling stations in (a) November 1980 and (b) June 1981. [Between stations D (18°34.8'N, 66°47.9'W) and K (20°00.0'N, 66°48.0'W) in June 1980 stations E and F were south of the dumpsite (Grimes et al., 1983].

for a northerly distribution of wastes as far 50 km north of the dumpsite.

Bacteriological evidence for the presence of pharamceutical wastes is based on results of culturing a fraction of the total bacteria and differentiating "contaminated" from "clean" water on the basis of total culturable counts, plate-count-agar culturable counts or the presence of gram-positive bacteria among those cultured. None of those parameters alone is indicative Plate-count-agar culturable and wastes. pharmaceutical gram-positive bacteria can be found in very low numbers anywhere in the ocean. The chemical indications of waste are more specific. The earlier samples, February 1978 and May 1979, included N,N-dimethyl aniline among the compounds attributed to wastes. That compound was in waste samples collected at those times and it is unlikely that it could have another source. indications of wastes in October 1979 and February 1981 were based on 1) low-molecular-weight ketones and simple alkylated benzenes and 2) the mixtures of compounds bearing a similarity with their distribution in waste samples. These indices are consistent with the presence of pharmaceutical wastes, but the compounds are not unique to wastes. They are common industrial chemicals and most appear in water contaminated by oil spills or simply from ship The alkyl benzenes found by periodic analyses of volatile organics in Vinyard Sound, Massachusetts, by Gschwend et al. (1982) include those found in pharmaceutical wastes. There is no such unique waste source to Vinyard Sound. While the distributions of volatile organic compounds reported by Brooks et al. (1983a) and by Brooks (personal communication, 1982) are strongly indicative that pharmaceutical wastes' were the source, their connection with these wastes is buttressed by their being consistent with physical oceanographic data.

Carnes et al. (1980) measured vertical profiles of water salinity and temperature during October 1979 at the same station locations occupied for chemical sampling (Figure 7b). Converting

that data to dynamic heights relative to a depth of 1500 m (i.e., defining areas of high and low pressure relative to a depth of no motion which is analogous to high and low pressure regions on the earth's surface used on weather charts) and calculating the direction of surface flow consistent with those dynamic heights yielded Figure 10 (Carnes et al., 1980). A ridge of maximum dynamic height was evident along the 67°W meridian. Calculated flows were to the south on the eastern (dumpsite) side of the ridge and to the north on the western side. There were indications of a gyre-like flow in the dumpsite region which is consistent with an accumulation of ocean-dumped wastes. November 1981, on the other hand, when wastes were not found in the surface waters (Figure 7c), the current calculated from salinity and temperature data was towards the west (Ichiye, in preparation). This flow is consistent with an Antilles Current and imply that on this occasion the flow of new (not recirculated) water could have been sufficient to have removed chemical evidence of wastes.

Two separate sets of physical data indicate that flow can be as expected on the basis of an Antilles Current, or the dumpsite can be embedded within a gyre. This aperiodic type of flow was also observed in the behavior of sets of buoys deployed in October 1979, March 1980, and August 1980 (Hernandez-Avila, University of Puerto Rico, in preparation). On each occasion 12 buoys were set in the water at the dumpsite with two drogued at each of the following depths; 1, 10, 40, 70, 100, and 150 m. The trajectories of the buoys were then followed with radio direction finders at two coastal sites. Each experiment lasted up to 15 days, the lifetime of batteries which powered a buoy's radio beacon. buoys were not successfully located at any time; others were located only sporadically. Six days after the March deployment, no buoys could be located after a severe thunderstorm passed through the area. Nevertheless, a considerable amount of short-term data was obtained and is graphically summarized in Figure 11.

## SURFACE DYNAMIC TOPOGRAPHY (db). REFERRED TO 1500db (Oct. 8-16, 1979)

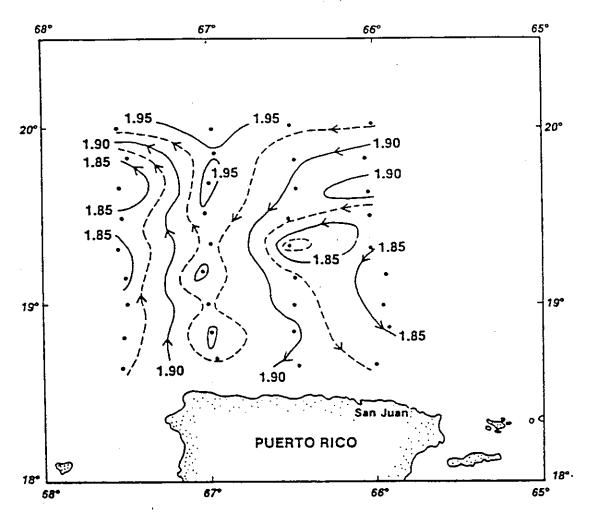


Figure 10. Dynamic heights relative to 1500 m calculated from STD data obtained at indicated locations over period of October 8 to 13, 1979, and current structure derived from dynamic height distribution (Carnes et al., 1980).

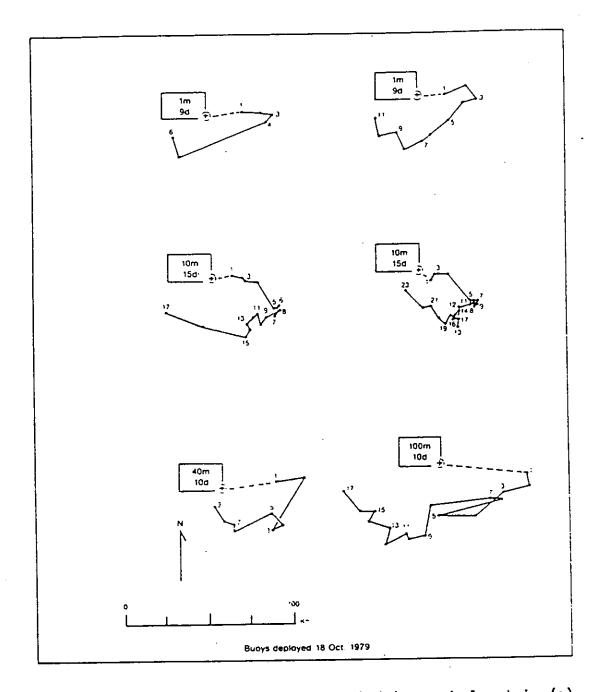


Figure 11. Trajectories of radio-tracked buoys deployed in (a) October 1979, (b) March 1980, and (c) August 1980. Rectangle represents the limits of the dumpsite. Buoys were put into the water at the point marked "X". Buoys were drogued at the depths indicated and followed for the indicated number of days (e.g., the buoy which described the track in the upper left of (a) was drogued at 1 m and followed for 9 days). The numbered points along the tracks are the locations defined by consecutive radio fixes. On some days two fixes were made; on other days no fixes were made. Dashed lines between the origin X and the first fix indicate that 2 or 3 days sometimes elapsed before the first radio fix could be made (Hernandez-Avila, in preparation).

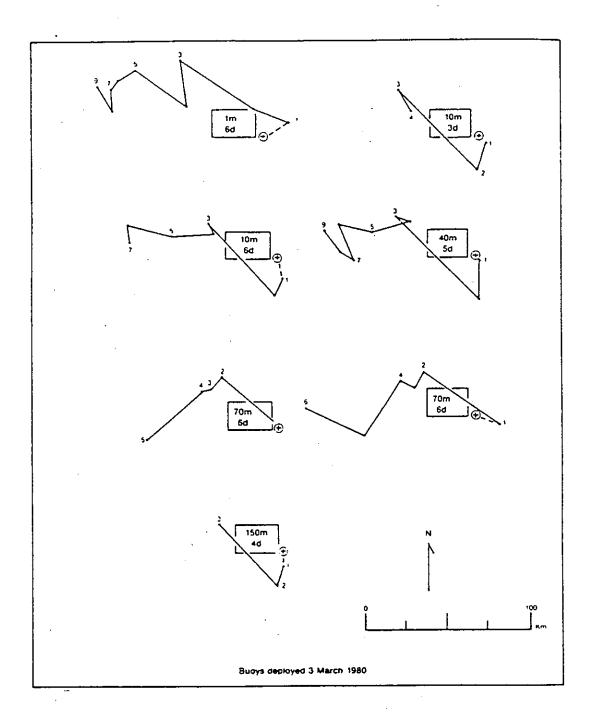


Figure 11b

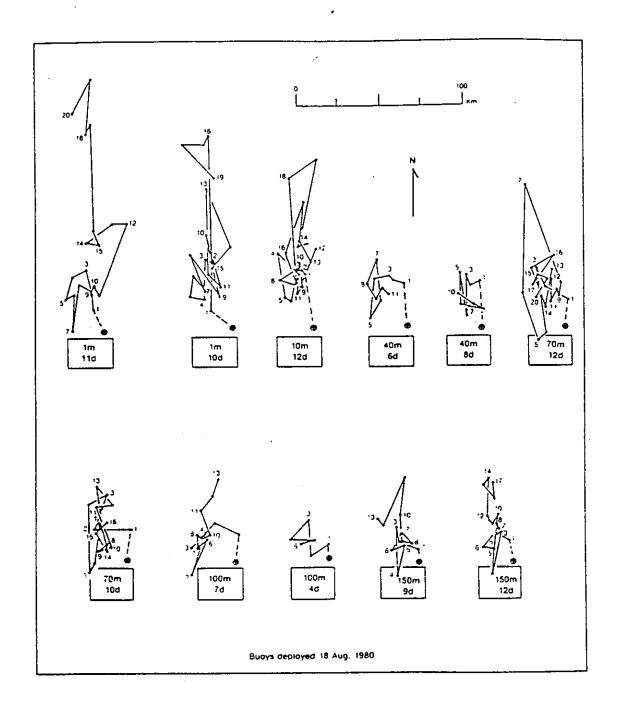


Figure 11c

The buoys deployed in October 1979 described a gyre-like path which was consistent with the geostrophically derived current pattern (compare Figures 10 and 11a). In March 1980, on the other hand, the buoys behaved as one would expect under the influence of an Antilles Current. They migrated westward. A third mode of translation was evident in August 1980 when the buoys moved north of the dumpsite and described a series of north-to-south and south-to-north migrations.

The spatial scales covered by the October 1979 and November 1980 geostrophic calculations are small because of the station spacing. The time scale for such calculations is only that of a single snapshot. While eddy-like flow was observed in one case and westward flow in the other, no information was gained about the percentage of time either or another flow regime applies. The radio-tracked buoys provided time scales up to 15 days. The space scales were relatively small. In October 1979 and August 1980, the buoys remained within about 50 to 100 km, respectively, of the dumpsite because they did not move continuously in one direction. In March 1980, the buoys appeared to be on a steady westward course away from the dumpsite but could be followed for only 6 days or less.

Figure 12 is long-term, large-scale flow, data obtained from a satellite-track buoy which was drogued at 10m and deployed at the dumpsite on October 2, 1980 (Williams, 1981). Briefly, the buoy initially migrated southwestward toward the Mona Passage (between Puerto Rico and Hispaniola), then, after 5 days, and within 25 km of shore, it turned onto an easterly course. After parelleling the entire north coast of Puerto Rico, it turned northward at about 65°W and moved approximately 500 km seaward. A shorter easterly drift of 100 km then preceded a southward migration to about the latitude of the dumpsite where the buoy headed westward. On January 20, 1981, 110 days after initial deployment, the buoy was within a few km of its starting point. As, at the time of deployment, the buoy again moved southwestward

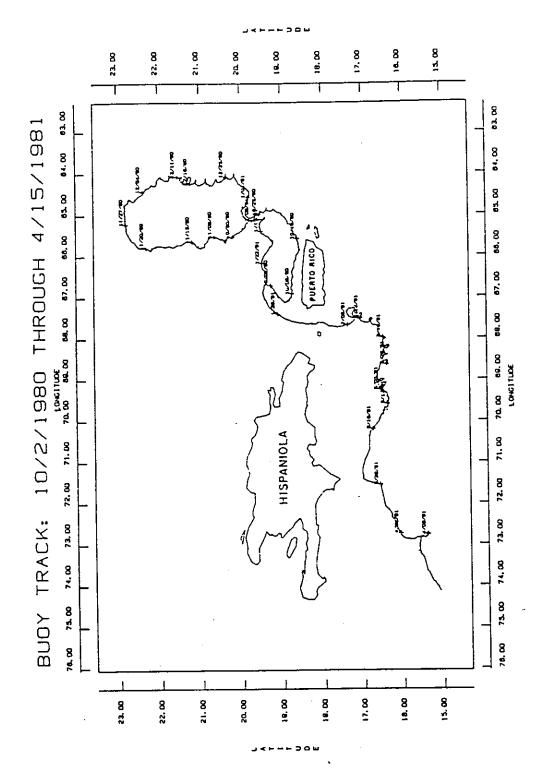


Figure 12. Path described by a satellite-tracked buoy, drogued at 10 m, deployed at the dumpsite on October 2, 1980. Locations were determined by satellite at about a 12-hour frequency. Dates corresponding to buoy's position at selected points are indicated (Williams, 1981).

from the dumpsite, but on this occasion it passed through the Mona Passage. Within the Caribbean it appeared to become entrained within an eddy which moved to the west forcing the buoy to describe a trochoidal track. Later, the trochoid motion disappeared; the buoy continued westward to 71.5° longitude, a point south of the midpoint of Hispaniola. The remainder of the track was toward the southwest. On April 13, 1981, the drogue broke off the buoy (as indicated by a signal to the satellite), and the buoy increased its translational velocity.

The long- and short-term data indicate that the Puerto Rico dumpsite does not lie within a steady westerly current. Atlases showing such a current (e.g., USNAVOCEANO, 1970) are based on ship drift data which are probably biased by the trade winds which are from the east and are constant in the Puerto Rico region. This wind will tend to push a ship westward.

The critical information needed to define the capacity of a dumpsite for waste dilution is the flow rate through it of water not previously contaminated by ocean dumping. That definition could be made rather easily if flow were unidirectional. One could conservatively limit the flux of water to that flowing between the north and south boundaries of the site, about 20 km, at an average velocity of 25 cms<sup>-1</sup>. Limiting the vertical extent of wastes to 20 m would yield a water flux of about  $10^{10}$  m<sup>3</sup> d.<sup>-1</sup>. The flux of pharmaceutical wastes to the site in 1980 (Table 1) averaged to about  $10^3$  m<sup>3</sup> d<sup>-1</sup>. Conservatively, the water flux would achieve waste dilutions by a factor of  $10^7$  (corresponding to waste concentrations of 0.1 ppm).

That simple approach cannot be used for the Puerto Rico Dumpsite. The water flux available for dilution is the product of the volume into which wastes can mix times the rate at which the volume is replaced. For example, if at a given time the dumpsite was on the western side of a westward migrating eddy, the eddy was 100 km in dimater, and wastes mixed only within the upper 20 m,

the volume available for dilution would be  $1.6 \times 10^{11} \, \mathrm{m}^3$ . If the eddy moved westward at  $5 \, \mathrm{cm}^{-1}$ , it would move  $100 \, \mathrm{km}$  and be beyond the dumpsite in 23 days. The flux of water would therefore be  $6.8 \times 10^9 \, \mathrm{m}^3 \, \mathrm{d}^{-1}$ , and, with a waste input of  $1 \times 10^3 \, \mathrm{m}^3 \, \mathrm{d}^{-1}$ , the maximum dilution factor would be  $6 \times 10^6$ . Coincidentally, this is similar to the result just obtained with the unidirectional flow assumption. However, that former calculation constrained the meridional dispersion of wastes to the 20 km north-south dimension of the site and is unrealistically conservative. The point of this latter calculation is to emphasize the importance of determining the size and residence time of discrete mixing volumes surrounding the dumpsite. The choices of a  $100 \, \mathrm{km}$  diameter eddy progressing at  $5 \, \mathrm{cm s}^{-1}$  are arbitrary.

Ideally, space and time scales of contamination due to pharmaceutical waste dumping could have been established through chemical analysis. Sampling in October 1979, November 1980, February 1981, and May 1981 (Figures 7b through 7e) was designed to find spatial limits. However, as discussed earlier, the October 1979 sampling found wastes over an area somewhat larger than 2 x  $10^4$  m $^2$  but not the limits to its distribution. The last three sample sets were not deemed indicative of any contamination.

If areas of contamination could be delineated, concentrations of wastes could, in principle, be integrated to obtain the total waste mass. Comparisons of that mass with inputs would then yield the residence time of wastes and therefore water in the area. Unfortunately, this mass balance approach requires a constancy of waste composition and that was not the case. For example, Hatcher and Harvey (1978) reported wastes to contain N,N-dimethy aniline at a concentration of 52 g kg<sup>-1</sup>. (The only source of this compound was the waste from Bristol Inc. [Atlas et al., 1981; Brooks et al. 1983a]. During the first 5 days of February 1978, loads of Bristol wastes to the Arecibo holding tank represented 6 percent of total loadings [Pollution Control Inc. logs]. Thus, Bristol must have been discarding material containing N, N-dimethyl

aniline at a concentration of  $880~{\rm g~kg}^{-1}$  which seems uneconomic and probably not a common practice.) Brooks et al. (1983a) reported two waste samples collected in February 1978 to differ in N,N-dimethyl aniline concentration by a factor of four. That compound did not appear in mixed waste samples collected in October 1979 or later, while it did show up at a concentration of 5 mg kg<sup>-1</sup> in a 1980 analysis of Bristol waste (Brooks et al., 1983a). A second example of waste variability is the data of Brooks et al. (1983a) for the wastes analyzed in October 1979 compared to the compounds used to identify the wide spread distribution of wastes. Chromatograms of volatile organics in raw wastes were similar to those (except in concentration) obtained from seawater analysis, but in the wastes toluene was more concentrated than xylenes while the ocean samples displayed a dominance of xylenes. Because of differential vapor pressures and degradabilities, the spectrum of compounds in raw wastes need not remain stable in the ocean. However, that fact only complicates the variability of the wastes themselves and increases the difficulty of associating compound concentrations with waste inputs.

Direct physical oceanographic measurements appear to be the only avenue for defining the flushing capacity of the dumpsite. Given the complexity of flow in the region, measurements have not been sufficient to quantify mixing volumes or residence times. However, in his discussion of the long-term buoy experiments Williams (1981) has used the only other long-term trajectory and recent hydrographic information to put some tentative limits on those critical parameters.

Figure 13 (Hansen, 1974) is the track described by a buoy drogued at 30 m and followed by satellite for 212 days. The area containing the entire tract, 21° to 25°N and 66° to 74°W, is well to the northwest of the dumpsite but is in an oceanic region nominally considered to be within the Antilles Current. The track appears to describe an eddy in which the buoy was entrained for

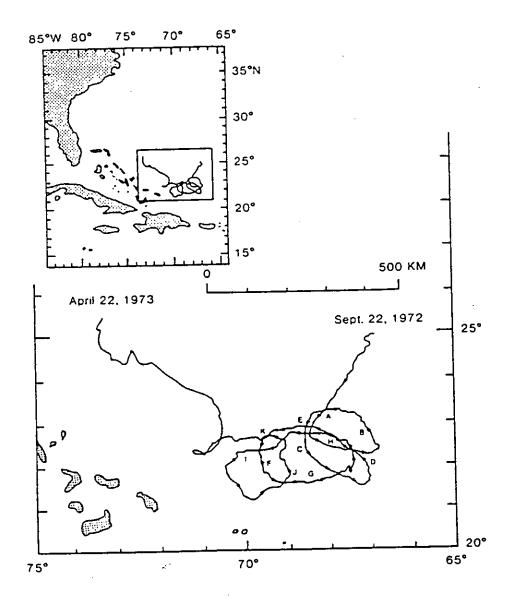


Figure 13. Track of buoy drogued at 30 m and followed by satellite over the period September 22, 1972, to April 22, 1973 (Hansen, 1974). Sequential letters and arrows which aid in following path have been added using detailed information supplied by Hansen (personal communication, 1980).

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112 days (the sequential letters and arrows in Figure 13 have been added from detailed information supplied by Hansen; 112 days cover the period from points A to K). Assuming the buoy revolved around the eddy center, the eddy moved 350 km westward in that time for an average translational velocity of 4 cms<sup>-1</sup>. Assuming that the buoy was situated near the edge of the eddy, the eddy was more or less circular with a diameter of 150 to 250 km.

Figure 14 (Williams, 1981) shows the surface temperature structure over a large oceanic area, again northwest of Puerto Rico, obtained over the period November 2 to 15, 1980 (F. Schott, personal communication), a period encompassed by the Williams buoy The synoptic surface temperature structure is experiment. augmented in the figure by temperature data at 1 m reported from the buoy. Temperatures were higher as the buoy moved northward along approximately 66°W than on its southward migration along Figure 14 illustrates a northward about 64°W (Figure 12). intrusion of warm water from the island arc to 25°N, and, with less definition, corresponding southward tongues of colder water from that latitude. Geostrophic calculations relative to a measured 500-m depth of no motion yielded currents corresponding to that temperature structure which are southwards towards the islands and possibly eastward north of Puerto Rico (Figure 15). Williams (1981) has interpreted the buoy track of October 1980 to April 1981 (Figure 12) as being consistent with, not proving, a series of alternatively warm and cold tongues between the island arc and the subtropical convergence. The meridional and zonal scales of those tongues could be as large as 600 and 300 km, respectively. Evidence for the meridional temperature variation is also found by Williams (1981) in the data of Carnes et al. (1980) for small-scale surveys in October 1978 and October 1979. Williams (1981) further indicates that Voorhis et al. (1976) have reported surface temperature features of 40 km wide and 400 km long to be generated by eddies at the MODE site (Mid-Ocean Dynamics Experiment centered at 25°00'N and 67°25'W).

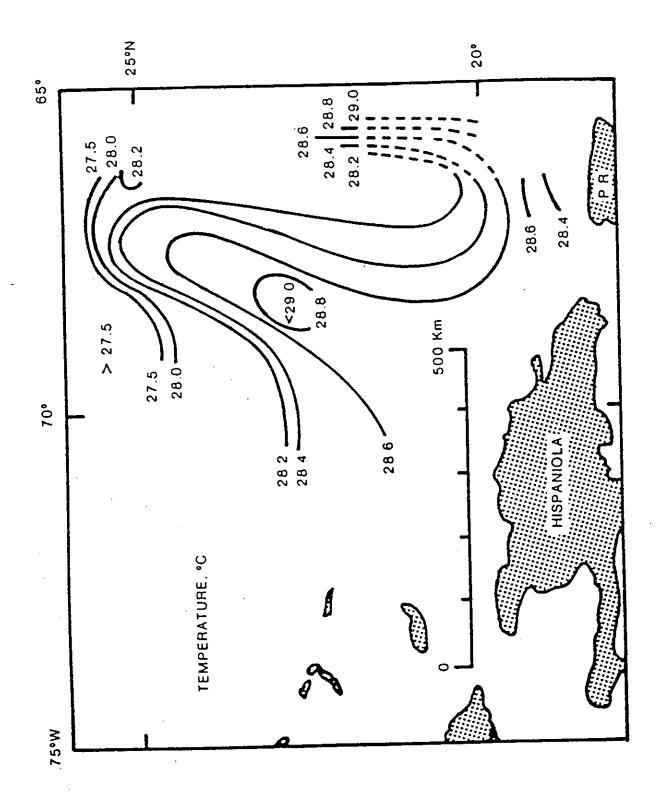


Figure 14. Surface mixed-layer temperature, November 2 to 15, 1980, from Williams (1981) using data supplied by Schott (personal communication, 1981). Isotherms extended from buoy temperature data are indicated with dashed lines.

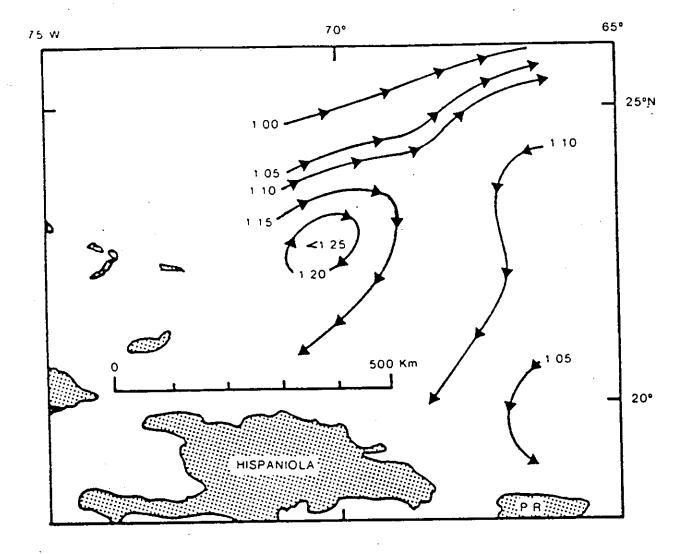


Figure 15. Dynamic heights relative to 500 m and corresponding surface current structure for the period, November 2 to 15, 1981, as communicated to Williams (1981) by Schott (personal communication, 1981).

A very tentative picture emerges from this analysis of some data which are specific to the dumpsite region and some which are in a similar oceanographic setting. Waters nominally within the Antilles Current are periodically occupied by eddies that have the effect of creating tongues of cold water from the north and warm water from the south. The size, lifetime, and/or translational velocity of these eddies and the tongues of water they create are the physical oceanographic parameters determining the diluting capacity of the Puerto Rico Dumpsite. Ideally, they could be measured by satellite imagery of the sea surface. The utility of that technique is well demonstrated, for example, by The Ring Group (1981) in their study of Gulf stream rings off the east coast of the United States. Conversion of satellite information to detailed sea surface temperature structure is routinely done and issued as "Oceanographic Analysis" charts by NOAA's National However, that analysis does Earth Satellite Service. presently differentiate between waters which differ by less than 1° in temperature (Clark, personal communication, 1982). indicated in Figure 14, the temperature differences between "cold" and "warm" tongues in the Antilles region are less than that. sea surface temperature structure similar to that proposed here has been observed in the satellite imagery (Clark, personal communication, 1982).

Some time and space limits can be placed on mixing volumes available for diluting wastes dumped at the Puerto Rico Dumpsite. First, the largest spacial scale known to contain contamination due to dumping is larger than 2 x  $10^4$  km² (Figure 7b). The eddy described by the buoy of Hansen (1974) (Figure 13) was of the order of 3 x  $10^4$  km². The loop traversed by William's buoy (Figure 12) was about 5 x  $10^4$  km². A time scale over which a given locale is within an eddy could be of the order of 4 months. This is the time over which Williams' buoy was deployed and returned to near the dumpsite. On the other hand, the translational speed of the loops traversed by Hansen's buoy of

4  ${\rm cms}^{-1}$  implies that a 200-km-wide eddy would pass over a fixed location in 2 months.

Since the volatile organic compounds in pharmaceutical wastes were usually in the concentration range of 10 to 100 mg kg $^{-1}$ , and since they could be detected in seawater at concentrations of the order of 1 to 10 ng kg $^{-1}$ , wastes were detectable at dilutions of the order of  $10^7$ . This detection places some limits on time scales.

Wastes constrained to an area of 5 x  $10^4$  km<sup>2</sup>, and a depth of 50 m, and well mixed in that volume at a dilution of  $10^7$ require  $2.5 \times 10^5 \text{ m}^3$  of wastes. It was dumped at a rate (though not dumped daily) of  $1 \times 10^3$  m<sup>3</sup> d<sup>-1</sup>. Thus, wastes would be detectable through that volume if wastes were mixed only into that volume for 8 months. If the wastes had a shorter residence time they could be diluted within the mixing volume to below Eight months is probably an overestimate. detectability. Detecting wastes does not mean they are uniformly distributed (Brooks et al. [1983a] found xylene concentrations to increase towards the northeast in October 1979), nor is it established that the whole mixing volume has been used. This estimate could be reduced to 4 months by decreasing the area to 2.5  $\times$   $10^4$  km $^2$ , but that would approximate the area over which wastes have been detected without establishing spatial limits to its occurrence.

It does seem evident that the important time and space scales are of the order of 100 days and  $10^4~\rm km^2$ . Although in 100 days waste constituents can descend below the pycnocline as part of biological debris (e.g., Elder and Fowler, 1977) and although Brooks et al. (1983) report qualitative chemical evidence of waste below 200m, it is reasonable to consider wastes to be primarily within the upper mixed layer of 30 to 70 m (Figure 4). Using a depth of 50 m and an area of only 2 x  $10^4~\rm km^2$ , for a mixing volume and allowing the dumpsite to remain within that volume for 100

days yields a maximum dilution factor of  $10^7$  for wastes dumped at an average rate of  $10^3 \ \mathrm{m}^3 \ \mathrm{d}^{-1}$ .

In terms of assessing the biological consequences of a pharmaceutical waste dumping, the critical concentrations and scales range from 200 ppm and 1.4 km $^2$  directly behind a discharging barge to 4 ppm and 125 km $^2$  within 1 day for a given dump to 0.1 ppm and 2 x  $10^4$  km $^2$  for the resultant of all dumping into discrete mixing volumes. In the absence of limits to horizontal mixing imposed by eddy-like boundaries, individual plumes should be diluted well beyond the  $10^7$  limit.

## Biological Response

In a global sense, the fishery resources of Puerto Rico are very small. Reported landings of fish and shellfish in Puerto Rico for 1973, for example, were  $1.9 \times 10^3$  metric tons (mt) (Weiler and Suarez-Caabro, 1980). In that same year, 1.3 x 10<sup>6</sup> mt of fish, exclusive of shellfish, were taken from a major fishing area, off the east coast of the United States from Cape Hatteras to the Canadian border (NOAA, 1982). A very rough straight-line estimate of coastal length in these two areas (500 km surrounding Puerto Rico, 1500 km along east coast north of Cape Hatteras) can be used to normalize those landings but still leaves the Puerto Rican resource more than 300 times smaller. The difference would increase if landings of lobster, crab, quahogs, oysters, scallops, and other shellfish were included in the east coast total. More recent data (Weiler and Suarez-Caabro, 1980; NOAA, 1982) show landings for Puerto Rico versus the east coast to be 2.8 x  $10^3$  mt versus  $4.5 \times 10^5$  mt in 1978. These data reflect increased fishing off Puerto Rico and restrictions on fishing off the east coast but the utilized Puerto Rico resource remains small in comparison.

On a local scale, the north coast is the least productive of the four Puerto Rican coasts. In 1977 and 1978, for example, landings at piers along that coast accounted for 9.8 percent and 10.2 percent of total landings (Weiler and Suarez-Caabro, 1980). The north coast resource is relatively small because of the narrow shelf (distance to 200 m isobath, Figure 1) and the direct exposure to high seas off the Atlantic during winter. The high sea physically precludes small craft fishing, and, in conjunction with the narrow shelf, limits the number and size of coral reefs. The Puerto Rican fishing fleet is an assemblage of small boats (90 percent of the 1073 boats used in 1978 were 7 m or less in length). The exploited fishes are primarily reef fishes. In total, fishes from three main groups, grunt, snapper and grouper, constituted 49 percent and 51 percent of the 1977 and 1978 Puerto Rico landings (Weiler and Suarez-Caabro, 1980).

The fishing which does occur off the north coast, as with all coasts, is restricted primarily to shallow waters. Only recreational fishing for billfish such as marlin occurs in the open-ocean deep waters. The paucity of landings from the deep ocean north of the island is not likely due to only a lack of fishing effort. Because the great depth precludes a nutrient supply from the seafloor, open-ocean waters, except in areas of major upwelling of deep water, are generally of low resource value (Ryther, 1969).

Some relative measure of the biological activity of waters north of Puerto Rico is available by comparing data on zooplankton abundances. In July of 1976 and 1977, George (1981) took samples at stations within an area bordered by 18°50' to 20°00'N and 66°05' to 66°35'W (10 to 160 km north of Puerto Rico). At the six sampled stations copepod abundances were 33, 61, 62, 76, 269 and 513 individuals per m³ for a mean of 69 individuals per m³. Grice and Hart (1962) used a collection net twice as coarse as that of George (0.24 mm versus 0.11 mm) at 55 stations extending from Montauk Point, New York, to Bermuda over the period of September 1959 to August 1960. Copepod abundances ranged from more that 1000 individuals per m³ over the continental shelf to less than 100 individuals per m³ in the Sargasso Sea. The abundances

reported by George (1981) are indicative of open-ocean waters and imply that the absence of an exploited fishery resource is inherent in the region's oceanography rather than a lack of fishing effort.

The low resource value of the open ocean in the region of the dumpsite is a reason for choosing such a waste disposal location. It does not preclude assessing the biological response to dumping. Assessing the response defines the environmental cost of the specific disposal operation and adds to a growing knowledge on use of the ocean for waste disposal. Not assessing the response would be tantamount to writing off the open ocean as valueless except for disposal and to ignoring an opportunity to gain important information for waste management.

Two major concerns in the context of ocean-waste disposal which did not apply when the dumpsite was used for pharmaceutical waste disposal are creation of direct public health hazards and contamination of seafood. As noted, the wastes were a source of bacteria. Pathogenic bacteria were not specifically identified in waste samples, but even if present they would have been dumped too far from shore to affect water quality in recreational areas. Accumulation of bacteria by fish, if it did occur, would not have been a public health hazard since uncooked fish are not eaten. Shellfishing beds are closed along U.S. coasts when coliform bacteria concentrations in water, sediment or tissue exceed established standards since shellfish are often eaten raw. Again, as with beachwater quality, the distance of the site from shore precludes shellfish contamination. The stations nearest to shore which displayed chemical evidence of pharmaceutical wastes (Figure 7) were about 10 km seaward. As seen in Figure 1, the depth at that distance exceeds 200 m and is inaccessible for practical shellfishing. Moreover, possibly because bacteria from wastes have relatively short lifetimes in seawater, bacterial evidence of wastes were not as widespread as chemical evidence (Figures 8 and 9) and did not extend to within 10 km of land. The

highest concentration of colony-forming units was observed near the discharge of the Barceloneta treatment plant, and, on that occasion, it decreased seaward.

Chemical contamination of seafood was not of concern in this situation. If pharmaceutical wastes had contained compounds with a strong tendency towards being partitioned into fish tissue from seawater it would have been necessary to relate the distribution and concentrations of those compounds with the distribution of The objective would have been to establish the level of fish exposure. However, the compounds identified in pharmaceutical wastes do not have that tendency to a strong degree. Bioaccumulation of organic compounds is predictable on the basis of equilibrium partitioning of compounds between water and the organic solvent octanol (e.g., Chiou et al., 1977). In effect, fish tissue, primarily its lipid content, is an organic matrix which competes with seawater for those compounds. partitioning between water and octanol or water and fish is, inversely related to a compound's solubility in water. Chiou et al. (1977), and more recently, Mackay (1982) have directly related bioaccumulation factors to solubility.

The compounds listed in Table 4 as characteristic of pharmaceutical wastes are listed again in Table 16 along with their solubilities and calculated or measured bioconcentration factors. It is evident that some compounds are so water soluble that they should equilibrate to lower concentrations in fish than in seawater. The maximum bioconcentration factor is less than  $10^3$ . Using that factor and assuming that wastes, when diluted by  $10^7$  contain compounds at concentrations of 100 ng kg $^{-1}$  (this is a high concentration since, in waste the concentration would have to be 1 g kg $^{-1}$ ) yield an equilibrium concentration in fish tissue of 0.1 ppm. Comparatively, the existing limit for acceptability of seafood containing polychlorinated biphenyls is 5 ppm.

Table 16. Solubilities (S, mol  $1^{-1}$ ), octanol-water partition coefficients (K $_{\rm OW}$ ) and bioconcentration factors (K $_{\rm B}$ ) for compounds listed in Table 4.

	log S	log K <sub>ow</sub>	log K <sub>B</sub>
Chloroform	-1.19	1.95 (b)	
Benzene	-0.64 (a)	2.13 (a)	1.10 (c)
Carbon tetrachloride	-2.28	2.64 (b)	1.24 (c)
Tetrahydroforan		•	
Trichlorethylene			1.56 (d, tetrachloroethylene)
Toluene	-2.25 (a)	2.69 (a)	1.37 (d)
Ethyl benzene	-2.84 (a)	3.15 (a)	1.83 (d)
m-xylene	-2.73 (a)	3.20 (a)	1.88 (d)
o-xylene	-2.72 (a)	2.77 (a)	1.45 (d)
Propyl benzene	-3.30 (a)	3.68 (a)	2.36 (d)
Cumene			
Mesitylene			
Butyl benzene	-3.60 (a)	4.11 (a)	2.79 (d)
Dimethyl pyridine			
N,N-dimethylaniline	-2.04 (a)	2.31 (a)	0.99 (d)
Naphthalene	(-3.08)(a)	3.36 (a)	2.63 (c)

<sup>(</sup>a) Chiou et al. (1982).

<sup>(</sup>b) MacKay (1982).

<sup>(</sup>c) Experimental data included in MacKay (1982).

<sup>(</sup>d) Calculated by equation:  $\log K_B = \log K_{ow} -1.32$  (MacKay, 1982).

The dumpsite location and characteristics of pharmaceutical wastes eliminated concern for lessening recreational or food value of marine resources. The remaining concern centered on the integrity of the open-ocean ecosystem for its own sake and as it supports the type and abundance of valued fisheries. The ecosystem in question is primarily planktonic so this concern was addressed through studies of marine bacteria, phytoplankton, and zooplankton. The responses sought were changes in the species composition of bacteria and phytoplankton communities and decreases in the respiration rate of zooplankton.

As discussed earlier, laboratory tests of pharmaceutical waste toxicity to phytoplankton showed a wide range of sensitivities among species and within clones of single species. Thus, a change in open-ocean phytoplankton communities was possible, whereby the more sensitive organisms would grow slowly or not at all, while the resistant ones grew faster. It has been demonstrated in large enclosures that contamination can alter the composition of phytoplankton communities (Thomas and Seibert, 1977). Capuzzo and Lancaster (1983, in press) have shown that rates of oxygen consumption by zooplankton, a relatively easy measurement, correlate well with decreases in egg production, a difficult measurement. Studies of respiration rate in the field could reveal responses to contamination which have consequences at the population level.

Planktonic responses which occur only within newly created and, therefore, small scale and relatively concentrated plumes are transient and of no serious consequence. Because the reproductive cycles of bacteria, phytoplankton, and zooplankton are of the orders of minutes, hours, and days, respectively, changes in planktonic communities due to waste dumping can be obliterated so long as wastes are dispersed into water containing unaffected communities. As plumes are diluted by being entrained into surrounding water, affected phytoplankton communities become an increasingly diminutive fraction of an otherwise unaffected

community. Temporary shifts in species abundance due to varying sensitivities to wastes should be erased as normal relative growth rates among species dominate community structure. Losses of zooplankton egg production should be effectively cancelled if individual fecundity returns to normal upon waste dispersion or, even if exposed organisms are permanently changed, by reproduction of unexposed zooplankton.

On the other hand, if wastes are dumped into an already altered ecosystem, their effect can persist. As estimated at the end of the previous section, the cumulative contamination due to pharmacuetical waste dumping could be a 2 x  $10^4 \, \mathrm{km}^2$  area containing surface waters with wastes diluted to a concentration of 0.1 If this concentration were to alter planktonic ecology, there could be subsequent effects on fish stocks. That consequence would require that altered planktonic species composition and abundance not be supportive of the natural fish population. Such an effect has been observed within contaminated embayments receiving excess nutrients which caused changes in the phytoplankton populations (Curl et al., 1979). It has not occurred in the open-ocean. If plankton were affected over a 2 x  $10^4$  km<sup>2</sup> area it is not certain that fish populations would suffer. The scales over which fish migrate may be much larger than that. However, large scale changes at the plankton level should be sought and, if found, their consequences to fisheries addressed.

The most widespread ecological change thought to be observed in the context of pharmaceutical waste dumping was a shift in the species composition of marine bacterial communities. All bacterial analyses of waters near Puerto Rico made during the years 1979 through 1981 showed culturable marine bacteria to be almost exclusively of the <u>Vibrio</u> genus with some <u>Acinetobacter</u> spp. and almost devoid of <u>Pseudomonas</u> spp. (Grimes et al., 1983). It had been considered axiomatic that the culturable bacterial community in the open-ocean was dominated by <u>Pseudomonas</u> spp. A

series of surface water samples taken by Sieburth (1971) north of Puerto Rico have shown nearly all of the culturable bacteria to be Pseudomonas spp. Similarly, Pfister and Burkholder (1965) reported 66 percent of the bacteria isolated from seawater near Puerto Rico to be Pseudomonas spp. Furthermore, Grimes et al. (1983) demonstrated that when laboratory microcosms containing Vibrio spp. and Pseudomonas spp. initially at a 50/50 ratio were amended with phamaceutical wastes at concentrations of 100 ppm (v/v) the Vibrio spp. usually attained dominance.

be considered these observations cannot However. dumping induced demonstration that pharmaceutical waste wide-range ecological response at the bacterial level. systems containing no wastes also evolved to a Vibrio dominance. The differences in the extent of species shift between controls and the lowest tested waste concentration of 100 ppm were small (Table 17). The field observations were too geographically widespread to attribute them to waste disposal at the Puerto Rico Dumpsite. Figure 9 shows stations extending more than 1000 km eastward and northward of the dumpsite and hundreds of kilometers southward into the Caribbean. Wastes were not chemically evident at all these stations, but all samples showed a dominance of Vibrio spp. and a paucity of Pseudomonas spp. (Sampling along the November 1981 track, Figure 9a, was accompanied by onboard chemical analysis. Samples were collected for later analysis on the June 1981 track, Figure 9b. Toluene at low levels was detected in some samples in both cases but that is not considered evidence in this report for the presence of pharmaceutical wastes). The area encompassed by this sampling exceeds  $10^6 \text{ km}^2$ . If all the pharmaceutical wastes ever dumped,  $2.5 \times 10^6$  m<sup>3</sup>, were contained in the upper 50 m over an area of  $10^6\ \mathrm{km}^2$ , the average concentration would be less than 0.05 ppm. This is an absolute upper limit because it excludes mixing of wastes by physical or biological means into deeper water and losses of wastes by volatilization to the atmosphere, and allows for no biological degradation of wastes. The lack of chemical evidence for wastes

Table 17. Changes in the ratio of <u>Vibrio</u> to <u>Pseudomonas</u> spp. in microcosms amended with pharmaceutical waste.

	% <u>Vibrio</u> /% <u>Pseudomonas</u> <u>Hours</u> b				
Waste Concentration	48	72	96	120	144
O ppm <sup>C</sup>		45/55		30/70	
100 ppm after 72h <sup>C</sup>		35/65		22/78	
O ppm <sup>d</sup>	93/7		89/11		89/11
100 ppm after 48h, 200 ppm after 96 h	91/9		98/2		96/4

a Grimes et al. (1983).

b Ratio 50/50 at 0 hours.

C <u>Vibrio</u> strain PR-110, <u>Pseudomonas</u> strain PR-211.

d <u>Vibrio</u> strain PR-110, <u>Pseudomonas</u> strain AO-66.

on this scale is consistent with extensive dilution since dilutions by more than a factor of  $10^7$  probably render the wastes undetectable. The laboratory evidence for effects of wastes on bacteria do not indicate any response at so great a dilution but do not preclude the possibility that extremely low concentrations for long times induce a <u>Vibrio</u> dominance. However, the simple fact that in every case, without exception, <u>Vibrio</u> spp. dominated the culturable marine bacteria could mean that older data showing a different species distribution are the result of improvements in bacterial identification methods. As Grimes et al. (1983) discuss, some bacteria isolated a decade ago and identified as Pseudomonas would today be classified as <u>Vibrio</u>.

Changes in phytoplankton communities were observed during cruises of May and October, 1979. Results of analyses of preserved samples from those cruises (Murphy et al., 1983) are given in Table 18, along with an indication of whether samples were taken in plumes, and, if so, at which time interval since the plume was created. The only apparent differences among those percentage those underlined showing the samples are dinoflagellates at 30 percent or less of the total identified cells. The remaining cells were classified as microalgae for the May samples with pennate diatoms having been significant contributors along with dinoflagellates and microalgae in October The fact that samples with less than 30 percent dinoflagellates appeared within only 3 to 9 hours of a dumping event suggests that wastes at the concentrations characteristic of fresh plumes did induce species shifts in the natural community.

A decrease in dinoflagellates is consistent with laboratory observations (Table 8) indicating sensitivity towards pharmaceutical wastes of dinoflagelates, pennate diatoms, and green algae. The microalgal category in Table 18 includes small cells which would include chlorophytes (green algae). Tested chlorophytes, Chlorella autotrophica (Table 7) and Dunaliella tertiolecta (Table 8) were the least sensitive of all tested

Table 18. Numbers of identifiable phytoplankton cells per liter and their distribution among groups in samples taken prior to and after dumping events.

% Dinoflagellates/% Microalgae
(Total cells $1^{-1} \times 10^3$ )

May 1979	<u>1 m</u>	<u>10 m</u>	<u>25 m</u>
Before dump Before dump Before dump Before dump 3.0h post-dump 9.5h post-dump 16.5h post-dump 24.5h post-dump 32.5h post-dump 40.0h post-dump 48.5h post-dump 56.0h post-dump	40/60 (10) 40/60 (6) 60/40 (4) 45/55 (3) 20/80 (5) 60/40 (5) 50/50 (5) 60/40 (5) 65/35 (7) 60/40 (6) 65/35 (5)	60/40 (7) 60/25 (4) 60/40 (4) 60/40 (6) 10/90 (5) 30/60 (5) 65/35 (5) 40/60 (7) 65/35 (7) 65/35 (9) 65/35 (4) 65/35 (8)	60/40 (5) 40/60 (6) 40/60 (5) 70/30 (7) 55/45 (7) 10/90 (5) 70/30 (8) 80/20 (7) 80/20 (7) 85/15 (5) 90/10 (5) 95/5 (10)

% Dinoflagellates/% Pennate diatoms/% Microalgae (Total cells  $l^{-1} \times 10^3$ )

October 1979	5 m	<u>25-30 m</u>
Before dump Before dump 2.5h post-dump 6.4h post-dump 9.5h post-dump 16.0h post-dump 22.5h post-dump 30.5h post-dump 36.0h post-dump	45/25/30 (4) 45/25/30 (4) 30/20/50 (3) 40/40/20 (4) 20/60/20 (5) 50/30/30 (9) 40/30/30 (4) 40/30/30 (9)	60/20/20 (5) 50/20/30 (5) 50/15/35 (5) 25/10/65 (8) 55/15/30 (7) 45/15/40 (10) 65/15/20 (5) 65/15/20 (6) no data

Murphy et al. (1983). Hours rounded to nearest 0.5 hours, percentages estimated to nearest 5 percent, total cells to nearest 1.0  $\times$  10<sup>3</sup> cells l<sup>-1</sup>.

phytoplankton. If the observed shift in species composition was due to wastes, it would have been necessary that cell division occur at a relatively rapid rate. A result of changes among those rates could have appeared in 3 hours if the phytoplankton divison rate of 3 hours for tropical waters reported by Sheldon and Sutcliffe (1978) was representative of the natural community. Alternatively, since copepods responded to wastes within plumes (as noted below), changes in composition of phytoplankton communities could have been due to altered predation pressure upon them.

The results in Table 18 indicate an effect of pharmaceutical waste dumping only for short times and within plumes. Samples taken 16 or more hours after dumping events could not be considered to contain different communities from those obtained prior to dumps. In general, dinoflagellates dominated or were about half of the total community. However, since chemical sampling during May and October of 1979 showed wastes to be present away from the dumpsite and prior to studied dumping events (Figures 7a and 7b), the possibility remained that all phytoplankton analyses in Table 18 were indicative of waste effects at low concentrations.

Chemical sampling during a cruise in November 1980 did not reveal the presence of wastes except in a specific plume (Figure 7c). Phytoplankton communities were different in two major respects from those collected in 1979. First, the numbers of total cells were 5 to 10 times higher. In May and October of 1979, total cell concentrations (Table 18) ranged from (3 to 10) x  $10^3$  cells  $1^{-1}$ . In November 1980 (Table 19), the range was (50 to 120) x  $10^3$  cells  $1^{-1}$  (Murphy, in preparation). Second, microalgae were the dominant group among identified cells. There were no significant differences in either the concentration or species composition of identified cells among stations within the dumpsite before and after a dump event and those as far as 125 km west of the site.

During the November cruise two phytoplankton types not previously included in these analyses were quantified, and coastal outfall were Barceloneta near the Coccolithophores were preserved and counted, amounting to less identified cells at all stations. 10 percent of than Cyanobacteria, very small (less than 20 um) procaryotic (no chlorophyll-containing cells, were cell nucleus) distinct quantified aboard ship by fluorescence microscopy. In terms of phytoplankton. Relative the thev dominated concentrations of eucaryotic cells (Table 19) the cyanobacteria were, on an average, 75 times more concentrated in the open-ocean samples and 600 times more concentrated in samples taken near the outfall. The ecological significance of cyanobacteria is unknown. While their numbers are high, they may not be major components of phytoplankton communities in either biomass or productivity, and it is not known if they are important sources of food to secondary No variation in their numbers could be attributed to producers. Their concentrations and those of identifiable waste dumping. cells were higher near the Barceloneta outfall than elsewhere. This may have been a response to the outfall but could also have simple manifestation of coastal waters being more productive than the open-ocean.

The November 1980 results contradict the conclusion from the 1979 samples (Table 18) where decreases of dinoflagellates to less than 30 percent of the community were attributed to waste dumping. By that criterion one would conclude that all but one of the November 1980 samples was influenced by pharmaceutical wastes. Yet, no wastes were detected. Unless samples can be stratified on the basis of wastes being present or absent no differences between those samples can be attributed to wastes. In the November 1980, there were no differences between those samples taken in a fresh plume and those taken elsewhere. The differences between the 1979 and 1980 phytoplankton samples in terms of cell concentrations and species composition must be attributed to natural variations. Historical data from this oceanographic region (Murphy, in

Table 19. Numbers of identifiable phytoplankton cells and their distribution among groups in 10 m samples taken during November 1980 along station track shown in Figure 7c.<sup>a</sup>

%	Dinoflage	ellates	5/%	Mic	roalg	ae <sup>b</sup>
	(Total	cells	٦-:	l x	10 <sup>3</sup> )	

Charles and				Time Since
Station !			)	•
Lat.(°N)	Long. (°W)	west or l	Jumpsite	- Dump
19°10.0'	68°00.4'	31/66	(110)	
19°10.5'	67°58.3'	31/66	(85)	
19°10.5'	67°58.3'	37/60	(52)	
19°36.8'	67°18.3'	38/41	(70)	
19°41.8'	67°18.9'	34/54	(50)	
20°00.0'	67°19.0'	50/44	(50)	
		Within D	umpsite	
19°14.8'	66°42.7'	26/56	(120)	
19°17.0'	66°39.0'	35/45	(80)	0.25 h
19°17.4'	66°40.3'	28/57	(120)	2.0 h
19°16.9'	66°39.4'	30/58	(110)	4.0 h
•				·
	Nea	ar Barcelon	eta Outf	all
•				
18°31.0'	66°32.9'	25/50	(140)	
18°32.8'	66°30.4'	25/57	(190)	
18°29.8'	66°32.8'	28/53	(150)	
	66°33.7°	27/55	(150)	<b></b>

66°34.51

18°31.4'

24/64 (230)

<sup>&</sup>lt;sup>a</sup> Murphy (Bigelow Laboratory for Marine Science, in preparation).

Remaining identified cells generally equally divided between pennate diatoms and coccolithophorids.

Except for three stations all sampling was prior to a specific dump.

preparation) include a range of cell concentrations and types which incorporates all the observations in Tables 18 and 19.

The conclusion, therefore, from the available information is that phytoplankton communities unless already dominated by microalgae are altered in favor of microalgae within fresh waste plumes. Ten hours after a dumping event evidence for that change is lost through plume dispersion. At the level of input used for pharmaceutical wastes no longer-term, wide-scale effects of phytoplankton could be established.

The results relative to zooplankton are similar. Capuzzo (1982) found the dominant copepod in waters north of Puerto Rico to be a <u>Labidocera</u> spp. in November 1980. Individuals collected within 1 hour of a dumping event and within a plume showed sluggish swimming behavior and a 50 percent reduction in respiration rate relative to those collected prior to dumping. Those collected 6 hours after dumping showed a 25 percent reduction in respiration rate. Affected organisms did not recover when transferred to clean seawater. It must be concluded that damage suffered by exposure to wastes at concentrations of 10 to 50 ppm is permanent. Laboratory tests with L. aestiva showed egg production to decrease in parallel with decreases in respiration rate and for both to decrease by about 50 percent upon exposure to pharmaceutical wastes at 10 ppm. Therefore, the consequence of waste dumping may have been to periodically decrease the rate of growth of zooplankton populations over the scale of fresh plumes (50 km<sup>2</sup> after 10 hours, Table 15). There is no evidence for zooplankton populations north of Puerto Rico to have been depleted by waste dumping. The copepod populations reported by George (1981) and discussed above were consistent with those observed in surface waters over the deep ocean. Combining the conservative estimates that wastes were dumped into a mixing volume with a  $2 \times 10^4 \text{ km}^2$  area and 4-month residence time with the dumping frequency indicates that 48 separate plumes of 50 km<sup>2</sup> could have been created over the  $2 \times 10^4 \text{ km}^2$ . The total cumulative plume area would have been  $2.4 \times 10^3 \ km^2$ . Assuming that egg production was decreased by 50 percent in those plumes and was not at all compensated by increased production by unexposed zooplankton, total egg production over the  $2 \times 10^4 \ km^2$  mixing area would have decreased by about 5 percent. So small a change could not be detected among a series of measurements of zooplankton abundance.

In addition to seeking possible effects of wastes on species composition of bacteria and phytoplankton populations and on respiration rates of zooplankton, examinations of planktonic animals were made for evidence of disease. There was no a priori reason to suspect that pharmaceutical waste disposal would cause disease, but, as with ocean dumping studies related to the 106-Mile Site, it seemed prudent to observe the health of animals in waters receiving wastes.

pathological repeatable and single outstanding observation at the 106-Mile Site was a high frequency of gill melanization in euphausids (small, shrimp-like crustacea). Over five cruises a total of 5712 individuals were examined and 16 percent were found to display this gill blackening condition. Through study of euphausids over wide ocean areas, it was subsequently determined, that the high frequency of gill melanization observed in the 106-Mile Site area was a reflection of certain open-ocean north Atlantic species being naturally susceptible to this condition and was not related to waste disposal (MacLean, 1981). In the course of that study 1525 euphausids were collected in the Puerto Rico Dumpsite region during May 1979. Only 4 (0.2 percent) of those animals showed evidence of gill melanization (MacLean, 1979). A similarly low incidence of parasitism was found in the branchial chambers of planktonic shrimp where 11 of 1531 (0.7 percent) individuals were parasitized. No pathology was associated with copepods. While 34 percent of examined mysids had swollen carapaces filled with coagulated hemolymph, it was deemed to be a consequence of the organisms' premolt, non-feeding, protein-laden condition at the time of fixation.

One histological observation seemed to have a possible pharmaceutical waste dumping. Gram-positive connection bacterial infections were observed in the hepatopancreas of 13 percent of the histologically examined euphausids. pharmaceutical wastes were a source of Gram-positive bacteria (Colwell, 1981), it could have been the source of the infections. discussed earlier, gram-positive bacteria are However, as naturally present in the ocean in low numbers, and the observed histology could have been indicative of a common condition independent of waste disposal. The infection was most likely unrelated to waste dumping because it had previously been observed in the vicinity of the 106-Mile Site. Gram-positive bactérial infections were evident in 16 percent of the euphausids and 12 percent of the isopods collected in mid-November 1978 (MacLean, 1979). The 106-Mile Site receives primarily industrial wastes which are generated by purely chemical processes and not likely to be a significant source of bacteria. During 1978, it also received sewage sludge from Camden, New Jersey, and wastes obtained upon cleaning out sewage sludge digestors. These were sources of bacteria, but sewage sludge dumping ceased in June 1978, and no digestor cleanout disposal occurred in November 1978. (Anderson, personal communication, 1982). The 106-Mile Site is in a well-flushed area with an average residence time for wastes in the site of less than 1 week (O'Connor and Park, 1982). The site is periodically within warm-core Gulf Stream eddies which will limit the translation of waste plumes, but it was not so situated until late in November 1978 (Celone and Chamberlin, 1979). The bacterial infections observed in the November samples were therefore not caused by sewage-derived bacteria. concluded that the infections observed north of Puerto Rico need not have been related to wastes.

There are no indications that pharmaceutical waste dumping exerted any biological responses except over small scales for short times. Nevertheless, this report should include mention of a major fish kill which occurred in the Caribbean during late summer of 1980. Dead fish, sometimes amounting to tons of biomass, were found along the shores of Puerto Rico, Hispaniola (Dominican Republic and Haiti), Jamaica, Mexico, Belize, Honduras, Panama, Venezuela, Netherlands Antilles, Cuba, and the Cayman Islands (Juhl and Weidner, 1981). Reports of the fish kill began in mid-August in the western Caribbean (Mexico and Belize) and extended through early to mid-September in the southern (Venezuela and Panama) and eastern regions (Puerto Rico and Hispaniola). The oceanic area surrounded by these countries is about 2 x 10<sup>6</sup> km<sup>2</sup>.

The physical scale and temporal sequence of kill reports--the west first--both preclude pharmaceutical waste disposal as a cause for the kill. Nevertheless, since initial reports were sporadic, it was believed that the kill was restricted to the Dominican Republic and the west coast of Puerto Rico (i.e., the Mona Passage Arrangements were made through the University of area). Puerto Rico and the Environmental Protection Agency to have four moribund or recently dead fish put on ice and sent for bacterial and histological analysis. Decaying fish would have been of no value in attempting to discern the cause of death through such The deaths could not be attributed to bacterial infections. While one fish showed signs of decay and was probably dead for some time prior to collection, the others appeared normal and bacteria were not consistently isolated within or on the examined internal organs (Colwell et al., 1981). Examination of gill tissue was similarly unrevealing. While there were reports that some fish collected in the context of this kill showed extensive protozoan infestations of gill tissue, no such condition was noted on the fishes which had also been subjected to bacteriological examination (Newman, personal communication, 1981).

In his summary of a symposium on this fish kill, Atwood (1981) listed the various speculations proposed to explain its occurrence. None were proven or can be proven now, since whatever unique conditions prevailed during the kill no longer prevail. Hurricane Allen, the most intense storm to traverse the Caribbean in this century, did so between August 4 and 8, 1980, just prior to initial reports of fish kills. The most likely proposed cause of the fish kill is that this storm induced water column changes either through coastal runoff or upwelling which stimulated growth of blue-green or dinoflagellate algal species which are toxic to The large scale, episodic, and unique occurrence of the fish. kill implies a similarly large, episodic, and unique cause which the hurricane provided. The continuous use of the Puerto Rico Dumpsite for pharmaceutical waste disposal from 1973 through 1981 cannot be implicated as the causal agent.

## Present Situation

Because it is less expensive to discharge wastes through an ocean outfall than to barge them out to sea (Black and Veatch, 1975), the wastes which were formerly ocean dumped began being discharged through sewer lines to the Barceloneta Regional Waste Treatment Plant (Figures 16 and 17) in September 1981. It was not until then that the plant was equipped to provide secondary treatment of wastes as required (Anderson, personal communication, 1982) prior to ocean discharge. Table 20 lists inputs to the plant and compares those flows with daily volumes of ocean-dumped wastes in 1980.

Six formerly ocean-dumped wastes are only part of the flow to the treatment plant. (Squibb, the seventh source of ocean-dumped wastes, is located in Humacao, well away from Barceloneta. Wastes for off-site disposal stopped being produced in 1981.) Of the total 1.33 x  $10^4$  m $^3$  d $^{-1}$  (3.5 million gallons per day) flow through the plant, 7 percent is municipal wastes, 26 percent is

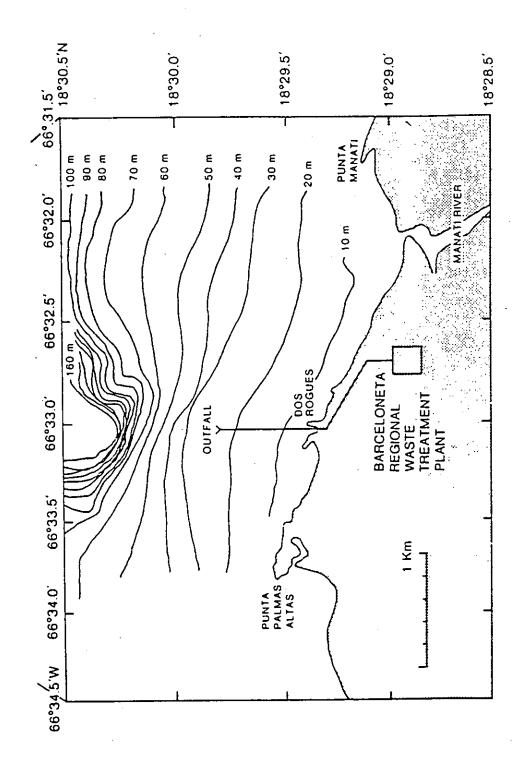


Figure 16. Expanded scale of area surrounding outfall from Carceloneta Regional Waste Treatment Plan (adapted from Black and Veatch, 1975).

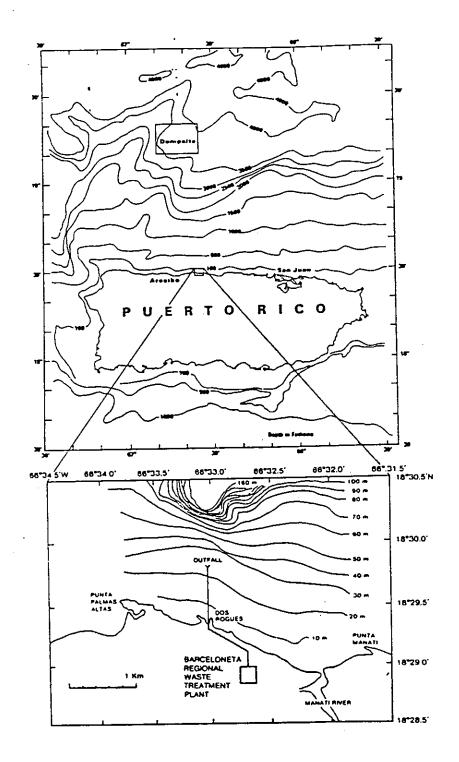


Figure 17. Figure 16 in relation to north coast of Puerto Rico and ocean dumping site (Figure 1).

Table 20. Waste volumes discharged through the Barceloneta Regional Treatment Plant or, formerly, ocean dumped by individual waste generators.

Source	( <u>Product</u> )	To Treatment Plant <sup>a</sup>	Ocean Dumped <sup>b</sup> $10^{3} \text{m}^{3} \text{d}^{-1}$
Upjohn	(pharmaceuticals)	1.02	0.52
Merck	(pharmaceuticals)	1.01	0.12
Shering	(pharmaceuticals)	0.13	0.14
American Cyanamid	(pharmaceuticals)	0.09	0.04
Pfizer	(pharmaceuticals)	0.04	0.05
Bristol	(pharmaceuticals)	1.52	0.01
Union Carbide	(sausage casings) <sup>C</sup>	2.28	
Abbott	(pharmaceuticals)	1.90	
Casera	(food cannery)	0.37	
Caribe Biochemical		0.41	
Winthrop	(pharmaceuticals)	0.05	
Indal		0.02	
Barceloneta (Town)	1	0.75	
Septic tank cleaning trucks		0.23	
Infiltrations and		3.42	
	Total	13.3	0.87

As reported by Puerto Rico Aqueducts and Sewers Authority for first 2 weeks of February 1982 (a period coinciding with a NOAA study of the region) (O'Neal, personal communication, 1982).

<sup>&</sup>lt;sup>b</sup> 1980 total volumes (EPA, Region II, 1982) divided by 365.

<sup>&</sup>lt;sup>C</sup> Black and Veatch (1975).

unaccounted for infiltration, and 67 percent is industrial wastes. Of the industrial wastes, 43 percent comes from sources which had generated ocean-dumped wastes. The remainder is wastes which have been discharged through the plant since the outfall pipe was completed in 1978. These industrial wastes have always been secondarily treated at their respective sources with the effluent going to the Barceloneta Plant or, prior to the pipeline's availability, into the Manati River (Figure 16).

The total waste flux from the six pharmaceutical plants which formerly ocean dumped wastes is about 4 times greater to the treatment plant than it was to the Arecibo holding tank. Most of this increase is due to Bristol and Merck (Table 20). Merck had always treated wastes on site to remove the more toxic fraction for ocean dumping, with the remainder going to the Barceloneta Plant. That fraction is no longer removed. The waste water flow from Bristol is more than 100 times its ocean-dumped flow. flow to the Barceloneta Plant now includes wash water which was not included with ocean-dumped wastes (Clevinger, personal communication, 1982). The Upjohn and American Cyanamid waste volumes appear to have about doubled. This, presumably, is due to incorporation of process waters which were not added to oceandumped wastes. A comparison of bulk chemical characteristics measured in both treatment plant effluent and ocean-dumped wastes (Table 21) shows the effluent to be of the order of 10 times less concentrated in suspended solids, organic carbon, and nitrogen. Also, while only about a third of the nitrogen in ocean-dumped wastes was in the form of ammonia, essentially all the effluent nitrogen is ammonia.

When wastes are discarded in the ocean, there is often a choice between discharging through an outfall or dumping from a barge. While discharging is the less expensive alternative, environmental costs can be higher simply because the coastal ocean is used. In terms of the three categories of environmental costs (direct public health hazards, seafood contamination, and

Table 21. Bulk characteristics of effluent from Barceloneta Regional Treatment Plant and ocean-dumped wastes.

## Concentration (percent by weight)

· .	Effluent <sup>a</sup> Av. (Range)	Barged Wastes <sup>b</sup> Av. (Range)
Total suspended solids	0.03 (0.01 to 0.05)	0.6 (0.1 to 1.7)
Total organic carbon	0.04 (0.03 to 0.05)	1.5 (0.7 to 2.9)
Ammonia nitrogen	0.02 (0.02 to 0.02)	0.09 (0.002 to 0.5)
Total nitrogen	0.02 (0.02 to 0.02)	0.3 (0.004 to 1.5)
рН	6.9 (7.6 to 8.2)	6.4 (5.6 to 7.0)

Data submitted to EPA as required for analyses of effluent over period of September 1 to 30, 1981. Concentrations originally in mg  $l^{-1}$ .

b Summary of ocean dumped waste characteristics for 1981 (Table 3).

ecological alteration), risks of coastal discharge exceed those of ocean dumping. The waters are used for recreation. They are the source of seafood, and, while the ecological system may be more resistant to contamination than its oceanic counterpart, it is a If the present method of discarding more productive system. pharmaceutical wastes were simply a replacement of a barge with a pipe, comparing the consequences of the two methods would be a useful endeavor in the overall context of developing waste management strategies. However, the discharged wastes are different wastes; whatever environmental cost is associated with discharging them cannot be attributed solely to formerly ocean-dumped wastes. Given that a clearcut comparison between two ocean-disposal techniques cannot be made, a study of the Barceloneta outfall would be a study of one of more than 200 coastal discharges in U.S. waters (Basta et al., 1982). NOAA cannot become the agency responsible for assessing the consequences of using each of these outfalls and cannot, therefore, examine the Barceloneta situation in detail. However, one cruise was conducted in February 1982 which included intense sampling in the outfall area. Results from it (while incomplete as of this writing) suggest that as existing data implied, the coastal region is not readily flushed of discharged wastes, and contamination does extend to the shoreline.

Prior to construction of the outfall from the Barceloneta Plant an environmental study of the discharge area was conducted by Black and Veatch (1975). Two current meters were deployed for a 30-day period in October to November of 1974 at the point where the pipeline would terminate with a diffuser, 0.8 km offshore at a depth of 25 m (Figure 16). One meter was set at a depth of 9 m, the other at 21 m. Continuous vector diagrams for the meter records described areas of about 5 x  $10^3 \ \mathrm{km}^2$  (170 km east-west, 30 km north-south) for the shallow meter and 4 x  $10^3 \ \mathrm{km}^2$  (140 km east-west, 30 km north-south) for the deep meter. Flow was essentially eastward for the first 5 days and westward for the remaining time, with offshore or onshore migrations interspersed

with the generally meridional flow. The closest shoreward points on the continuous vectors were 6 km offshore for the shallow meter (it progressed to 28 km offshore in a northeast direction over the first 5 days and moved, generally southwestward thereafter) and 0.5 km offshore for the deep meter (it progressed about 21 km northeastward over the first 5 days and southeastward thereafter). Segments of the continuous vectors do display significant periods of shoreward migration. For example, the shallow record for the period of October 26 to 31 yields a vector to the southeast with a shoreward movement of 22 km. If the total record had begun on October 26 instead of October 21, the continuous vector would have run well up on the island. Similarly, the deep record for the period of November 10 to 19 had about a 20 km shoreward component. Basically, the bulk of the seaward and westward extent of the total current records was achieved in the first 5 days.

Continuous vector diagrams are extrapolations which assume that summing velocities and directions measured at one point over a segment of time describes the trajectory of a water parcel which at the meter at the beginning of that time segment. Alternatively, records can be analyzed to summarize the statistics of flow for the continuum of water parcels which are at the meter. Just as with the continuous vector, there were shoreward components in such an analysis. Black and Veatch (1975) showed tidal currents to be eastward on the flood, westward on the ebb, and stronger at 21 m that at 9 m. Non-tidal currents were again generally eastward or westward and usually the dominant influence at 9 m but often masked by tidal currents at 21 m. Eastward tidal currents had a shoreward component with a mean direction of 100° and 111° at the shallow and deep meters, respectively. Combined currents, when towards the east, were mostly in the directions of  $95^{\circ}$  to  $125^{\circ}$  at the shallow meter and  $95^{\circ}$  to  $110^{\circ}$  at the deep As a point of reference (not a prediction), it can be noted that a passive tracer released at the end of pipeline and moving in a direction of 110° would intersect the shoreline near Punta Manati (Figure 16) after a distance of about 2.5 km. The times to traverse this distance would be 3.5 hours and 2.6 hours at the most frequently observed velocities at the deep and shallow meters, respectively. As summarized by Black and Veatch (1975), the currents in the discharge area were generally parallel to the shore in either direction with an overall net offshore migration. However, with a waste source only 0.8 km from shore only small variations around the average can result in contamination of recreational waters.

The same conclusions, that nearshore waters can move shoreward, were reached by Smith and Stuart (1975) after a current study near Los Negritos, about 9 km west of the Barceloneta outfall, which was done in the context of siting cooling water intake and discharge pipes for a proposed nuclear power plant at Barrio Islote. They deployed current meters at five stations, three along the 20-m isobath and one each at 40 and 12 m, for periods of 3 to 27 days in January, February, May, June, September, October, and November, 1974. As with the Black and Veatch (1975) record, tidal currents were to the east as tide rose and to the west on the ebb. Net flow was generally parallel to the coastline with long-term net flow to the east during summer and to the west in winter. Smith and Stuart (1975) noted that shoreward movement was more prevalent than offshore movement, and, in some cases, was stronger than the east-west current. Short-term drogue or dye-drop tracking (time scales for such observations were hours) did occasionally reveal shoreward movement from the remaining long-term current The stations. meter current observation for the north coast of Puerto Rico (Bogert-Spectrum, 1972) did not indicate an onshore flow. A current meter array was deployed for 34 days in May to June 1972 in 24-m deep water off Arecibo. Continuous vector diagrams for meters at 3, 13, and 20  $\rm m$ were to the east primarily with periods of western, northward, and northeastern or northwestern flow.

Given some evidence that wastes discharged through the Barceloneta outfall could migrate towards shore, intensive

sampling near the discharge was done in February 1982. measures of wastes were attempted. First, since the Barceloneta Plant receives municipal wastes (Table 20), and the effluent is not chlorinated or otherwise sterilized, bacteria are a possible indicator of its presence. (The plant monitoring data for the month of September used to construct Table 21 indicated an average total coliform bacteria concentration in the effluent of 82 x  $10^6\,$ Second, a volatile organic chemical signal was per 100 ml). sought. This would allow continued use of the technique employed for studying the distribution of ocean-dumped wastes. separate effluent samples were analyzed. One sample collected in December 1981 (actually two subsamples on each of 2 consecutive days for a total of four separate liters) contained, in general, five volatile organic compounds. Of those, methylene chloride and ethyl mercaptan which elute almost together generated the major GC peak. The other compounds were tetrahydrofuran, toluene, and an unknown hydroxylated compound (Kennicutt et al, 1983). A sample collected on February 5, 1982, contained no volatile organic compounds. A sample collected on February 10, 1982 contained a distinctive array of volatilizable high-molecular weight (more than 14 carbon atoms) alkylated compounds. The GC spectrum due to these compounds was also found in ocean samples during the February cruise.

Concentrations of bacteria and volatile organic compounds observed over the station array shown in Figure 18 are listed in Table 22. Most samples were taken 1 km or more offshore because rough seas prevailed throughout the cruise, making it unsafe to bring a large oceanographic vessel close to shore. On one occasion, near the end of the cruise, seas had subsided enough to allow deployment of launches from the ship for occupation of the 10- and 20-m deep stations closer to shore than the outfall in Figure 17. Samples were collected at the water's edge by hand.

There was no clearly defined distribution of chemical or bacterial contamination, which could be described by a series of

Table 22. Concentrations of total coliform (TC), fecal coliform (FC), fecal streptococci (FS), bacteria and volatile organic compounds (VOC) observed north of Puerto Rico in deepwater, nearshore, and near Barceloneta outfall over February 6-12, 1982. a,b

Station <sup>C</sup>	TC <sup>d</sup> ,e	FC <sup>d</sup>	FS	d voc <sup>f</sup>
1	1(10)	1(10)	1(10)	38(15), 10(15)
2		<b></b>		0.2(10), 0.2(20)
3				0.1(10), 0.2(10)
4				1.3(10), 0.3(10),0.2(20)
5				0.1(10)
6	<del>,,</del>			0.1(10), 0.1(10)
7				0.1(10), 0.1(10), N.D.(10)
8				0.1(10), 0.1(10), 0.7(10)
9	18(10)	78(10)	< 1(10)	0.1(10), 0.1(10), N.D.(10)
10	3(20)	146(20)	< 1(20)	< 0.1(10)
11	523(40	483(40	290(40)	0.6(10)
12	43(15)	36(15)	< 1(15)	97(10), 26(10)
13	88(40)	1(40)	< 1(40)	11(10), 32(50)
14	115(40)	174(40)	35(40)	4.2(10)
15·	17(45)	8(45)	3(45)	0.4(10),6.6(45)
16 -	46(45)	8(45)	-2(45)	4.0(10), 8.7(40)
17	22(50), 29(100)	146(50), 99(100), 3(50	) <1(100)	0.2(10), 5.6(40)
18	1(40)	5(40)	< 1(40)	11.1(10)
19	5(40)	5(40)	2(40)	2.8(10)
20	3(40)	7(40)	1(40)	3.0(10)
B1	95	388	<1	2.7
B2	5	264	<1	
В3	3	430	<1	0.1
<sub>B4</sub> g	42	12500	14	3.9
B5	98	357	<1	3.9
в6 <sup>ћ</sup>	15	109	< 1	

(10) (10)
(10)
9(10)
9(35)
(150)
2(10)
.1(5)
.2(5)
.1(5)
9 ( 2

Bacteria data from Grimes (personal communication, 1982).

b Chemical data from Kennicutt et al. (1983).

Station numbers are consecutive in order of their occupation, locations are shown on Figure 18.

d Bacteria concentrations in units of colonies per 100 ml.

Depths (m) of samples indicated in parenthases beside concentrations except for stations B1 through B6 where samples were taken at shoreline.

 $<sup>^{\</sup>mathsf{f}}$  VOC concentrations in units of ug kg $^{\mathsf{-1}}$ .

<sup>9</sup> Station at mouth of Manati River not shown on Figure 18.

h Station at point on Figure 18 below which outfall pipe enters the ocean.

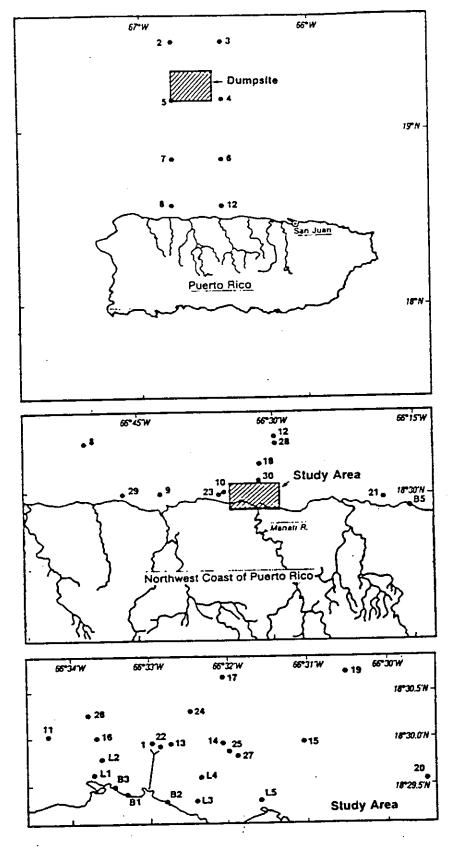


Figure 18. Locations of stations occupied over the period February 6-12, 1982. Numbers are in consecutive order of station occupation.

contours. Since the flow into which effluent is discharged is not steady such a clear distribution would not be expected even if the chemical and bacterial composition of the effluent were constant. However, while the higher chemical concentrations were offshore, the beach and nearshore samples showed evidence of contamination. Fecal coliform bacteria concentrations were generally as high for the nearshore and beach samples as at the offshore stations near the outfall.

These data are consistent with outfall's being a source of contamination to recreational waters. There may be other sources of bacterial and chemical contamination. The samples taken at the shoreline near the mouth of the Manati River showed the highest fecal coliform concentrations of all samples. However, while river flow data have not been obtained, and the timing of all samples relative to tidal cycle has not been tabulated, it would appear from salinity data that the river influence on all but river mouth samples was trivial. Salinity at the river mouth sampling station was 2.2 o/oo at all other stations the salinity was in the range of 35.5 to 35.8 o/oo. The Black and Veatch (1975) study concluded that only salinities of less than 34 parts per thousand would indicate some river influence. The chemical signal was also generated by samples taken as far west as Arecibo and as far east as Dorado and at Dorado Beach (Figure 18). Conceivably this was due to the Barceloneta outfall, but it would be necessary to exclude all other possible sources (other sewage treatment plants and coastal runoff) before being confident of such a conclusion.

Water quality measurements taken by Black and Veatch (1975) prior to the existence of the outfall can be compared with those taken in February 1982. Measures of fecal coliform bacteria were made in both cases, but in February 1982, the culturing technique was slightly modified to enhance detection (Grimes, personal communication, 1982). Total coliform counts were done by conventional techniques in both cases. The Black and Veatch

(1975) results for over 500 analyses of samples in the same general vicinity as the "Study Area" in Figure 18 indicated concentrations to be less than their detection limit of 3 per 100 ml in 75 percent of the samples. Except for one 200 per 100 ml concentration, all positive indications of total coliform bacteria were in water of low salinity and within a turbid plume from the river. At the shoreline, total coliform bacteria were detected in 37 of 76 samples (49 percent); however, excluding their river mouth station, only 32 percent (12 out of 37) of the samples exhibited 3 or more total coliforms per 100 ml. The concentrations and distributions of total coliform bacteria in Table 22 and Figure 18 are consistent with outfall effluent's being a contaminant source.

More study should be done by local authorities on the possibility of coastal (including beach) contamination being generated by the Barceloneta outfall. Existing data indicate that it may be. Chemical and bacterial sampling, however, was only over a 5-day period and did not observe contamination necessarily unique to plant effluent. Water flow data exists for only a 30-day interval and is solely Eulerian (speed and direction at a single point). Effluent specific compounds, if found, could be unique chemical tracers. Lagrangian flow data (trajectories of droques or other moving indicators), if obtained on a long-term routine basis could define the residence time of effluent in the coastal zone and its probability of reaching the shore. The need to better define the effluent distribution is now evident. becomes more pressing with the realization that effluent flow is scheduled to increase by a factor of 10 to 114,000  $m^3$   $d^{-1}$  by the year 2000 (Black and Veatch, 1975) and with the possibility that a present sludge disposal problem of the Barceloneta Plant may be solved by discharging it through the pipeline.

If it is determined that the existing outfall is a source of nearshore contamination, two solutions, excluding resumption of ocean dumping, appear possible. (1) Remove viable bacteria by

This would raise the potential of forming chlorination. chlorinated analogs of organic compounds in the effluent. would also decrease their biodegradability and increase both their toxicity and bioaccumulation tendency. (2) Lengthen the pipeline: increased distance would decrease the potential for shoreline contamination. If the discharge were 1.6 km offshore (twice its present distance), it would be at a depth of 80 m. This would appear to put it below pycnocline depth. Black and Veatch (1975) reported pycnoclines in the discharge area to begin at 40 to 50 m over the July to December 1974 period. The temperature and salinity profiles obtained during the February 1982 cruise indicated a pycnocline that began at 75 m. The advantage of subpycnocline discharge of effluent has been demonstrated in the case of pipelines (3 to 11 km long discharging at 50 to 60 m) off southern California (Bascom et al., 1979). Just as relatively light ocean-dumped wastes are limited in their vertical mixing by a pycnocline below, discharged effluent can be excluded from surface waters by a pycnocline above. If this possible extension of the pipeline is to be entertained, it will be necessary to consider the oceanic distribution of effluent and its possible effects on seafood, fisheries, and ecological systems, but risk of nearshore and beach contamination could be diminished.

## Discussion

The NOAA investigation of waste dumping north of Puerto Rico began 5 years after dumping began. The overall objective was to identify environmental changes associated with that dumping. That was completed, and in the process conclusions were drawn that will be useful in assessing other ocean disposal operations and in judging the acceptability of ocean-disposal proposals. The investigation consisted of several interdependent parts. Toxicity testing and chemical characterization would have yielded the same results regardless of where (in the ocean) and how the pharmaceutical wastes were discarded. Plume dispersion studies would have yielded similar results regardless of where the wastes

were dumped if dumping was done in the same way, and dispersion was not limited by solid boundaries (i.e., shorelines Waste dispersion beyond the plume stage was site specific since the controlling process is oceanic circulation. Field measures of biological responses to dumping could be site specific. If the input rate of wastes relative to the flushing rate of the dumpsite area is low enough to create high enough steady-state levels of contamination to affect local organisms, that effect would be site specific primarily because of local hydrography. The numbers and kinds of organisms exposed to wastes are site specific; benthic creatures are more likely to be exposed when dumpsites are shallow than when they are deep; coral reef communities can be exposed only when wastes are discarded nearby, and coastal fish populations are not exposed when wastes are The significance of biological dumped over the deep sea. responses is site specific. While judgments of significance are subjective, all marine life is not of equal commercial or aesthetic value, and individual organisms are not valued equally with populations of a species.

These considerations lead to a sequence of information which ideally should be gained if waste disposal already occurs or is proposed at a given site. The steady-state distribution of contaminant concentrations should be measured on the basis of chemical or bacteriological signals or estimated from hydrographic data. Biological responses to those concentrations should be measured or estimated from toxicity tests and, if possible, from knowledge of biological responses to specific waste constituents. The significance of those responses should be judged in terms of effects on populations, resource value of those populations, and possible human health hazards. The consequences of dumping can then be accepted or lessened. To decrease consequences requires using another disposal location or disposal method or, when possible, decreasing waste toxicity.

This series of information was obtained in the case of pharmaceutical waste dumping north of Puerto Rico. The only biological responses found were among planktonic organisms within waste plumes. This was consistent with observed ranges of waste toxicity in laboratory studies and with rough, conservative estimates of circulation in the dumpsite area. With effects having been limited to small spacial scales and short times with quickly regenerated organisms, there was no environmental reason to have ceased the dumping operation. Gaining the information was a learning process. Toxicity testing was overemphasized, while physical oceanography was not pursued sufficiently.

Predicting actual effects of waste disposal from laboratory toxicity studies is fraught with difficulties. As evidenced by phytoplankton responses to pharmaceutical wastes, the effect on growth of a given concentration is very dependent on the particular isolate of organism used. When the same organism is subjected to a variety of wastes, a valid relative order of waste toxicities evolves. The toxicities, are characteristics of the wastes; they are not predictions of actual responses in the ocean. When the measured response was survival of animals rather than growth of phytoplankton, the range in effective concentrations was not wide. With animals, the toxic concentrations were much lower when the tested response was survival of young as opposed to adult organisms or especially when reproductive capacity was measured.

If other wastes were to be dumped at the Puerto Rico Dumpsite, it would not be worthwhile to run a large battery of toxicity tests. It would be more efficient to repeat one of the tests used for pharmaceutical wastes. This would yield an estimate of whether the new wastes are more or less toxic than those whose effect in the ocean have already been investigated. It would probably be most beneficial to repeat measures of the effect of wastes on copepod egg production since decreases in its rate were elicited by lower concentrations than those found to

affect any other life process of any other organism tested against pharmaceutical wastes.

Predicting the environmental consequences of dumping these new wastes would be simple if their physical properties were similar to those of pharmaceutical wastes; they were dumped from barges at a rate of about  $80~\text{m}^3~\text{km}^{-1}$ , were not dumped in daily amounts in excess of  $10^3~\text{m}^3~\text{d}^{-1}$ ; and they were not more toxic relative to copepod reproduction than pharmaceutical wastes. The effect of these wastes would, like pharmaceutical wastes, be limited to short-term, small-scale planktonic responses within plumes. If, unlike pharmaceutical wastes, they contained organic compounds with a strong tendency toward bioaccumulation (high octanol/water coefficients, low solubility), some attention would have to be given to contamination of living tissue.

However, such a predictive ability is of limited use since other wastes may very well not be of similar physical properties, generated in similar amounts or be less toxic than pharmaceutical wastes. If the new wastes have a higher bulk density or contain large amounts of particles which would settle through the water column, it would be necessary to consider its distribution in more than the upper mixed layer. If they were more toxic, efforts over larger scales than only within-plumes would have to be hypothesized and tested. If they were to be discarded in larger amounts than pharmaceutical wastes it would be necessary to have better estimates of the flushing capacity of the dumpsite.

Two of these three outstanding needs are independent of dumping at a particular site. Knowledge on particle settling and coagulation is needed to predict distributions of particulate wastes (e.g., sewage sludge) regardless of dumpsite location. Methods for testing hypotheses on biological responses to water column contamination need refinement regardless of where they are applied. The Puerto Rico investigation included novel approaches in which phytoplankton community structure and copepod respiration

were employed as indicators of effects in the ocean. These approaches suffer from community determinations being tedious and time consuming and from respiration measurements requiring delicate handling of samples to avoid having respiration rates altered by sample collection. It would be more efficient if biochemical indices could be developed which relate to phytoplankton growth or to animal reproduction and which vary in response to contamination and do not require live samples or detailed enumeration of species within a sample.

The outstanding need which is unique to Puerto Rico is quantification of circulation rates north of the island. investigation found that flow was not as simple as assumed on the basis of an Antilles Current. The drogue studies, measures of density distributions and waste distributions, did not yield definitive information on what the flow structure actually is. It was concluded that wastes dumped at the site can horizontally disperse into eddies or tongues of water of about  $10^4\ \mathrm{km}^2$  in surface area and that the dumpsite could lie within an individual eddy or tongue for a 100-day period. However, considerably more information is required to establish the diluting capacity of the dumpsite with confidence. It would seem that observations of sea surface temperature structure would yield the most useful information in this regard, if satellite sensors can discern the small temperature differences that apply in the area. More application of the long-term drogue tracking technique would also be beneficial.

Future use of the deep ocean north of Puerto Rico for waste disposal should be preceded by more circulation studies. Coastal circulation north of the island, while not investigated in detail, also appears to need of quantification. Waste discharges in this area could be sources of shoreline contamination.

## References

- Atlas. E. G. Martinez, and C. S. Giam. (1981). Chemical characterization of ocean dumped waste materials. In: Ocean Dumping of Industrial Wastes (eds. B. H. Ketchum, D. R. Kester, and P. K. Park) Plenum Press, New York. pp. 233-246.
- Atwood, D. K. (1981). Executive summary and recommendations. In:

  Report of Symposium on 1980 Caribbean Fish Kill (ed. D. K. Atwood) Symposium sponsored by Gulf and Caribbean Fisheries Institute. Report prepared by NOAA/Atlantic Oceanographic and Meteorological Laboratories, Miami. pp. iii-ix.
- Bascom, W., N. Brooks, R. Eppley, T. Hendricks, G. Knauer, D. Pritchard, M. Sherwood, and J. Word. (1979). Southern California Bight. In: Assimilative Capacity of U.S. Coastal Waters for Pollutants (ed. E. D. Goldberg) Proceedings of a Workshop at Crystal Mountain, WA, July 1979, NOAA/Environmental Research Laboratories. pp. 179-242.
- Basta, D. J., B. P. Chambers, C. H. Ehler, and T. F. LaPointe. (1982). Identifying and evaluating alternative ocean dump sites. NOAA Office of Ocean Resources Coordination and Assessments, Washington, D.C. 17 pp.
- Batterton, J., K. Winters, and C. Van Baalen. (1978). Anilines: selective toxicity to blue-green algae. <u>Science</u> 199:1068-1070.
- Black and Veatch. (1975). Final Report: Oceanographic Baseline
  Study prepared by Black and Veatch, Rafael A. Domenech, and
  Associates for Puerto Rico Aqueduct and Sewer Authority. Vol. 1.
  183 pp., Vol. 2., 416 pp.
- Bogert-Spectrum. (1972). Arecibo: Oceanographic Study prepared by Bogert-Spectrum Associates, Fort Lee, NJ, for Puerto Rico Aqueduct and Sewer Authority. 28 pp with appendices.
- Brooks, J. M., and M. C. Kennicutt II. (1982). Analysis of Puerto Rico waste samples. Report to NOAA/OMPA, Rockville, MD. 8 pp.
- Brooks, J. M., D. A. Wiesenberg, G. Bodennec and T. C. Sauer. (1983a). Volatile pharmaceutical organics at the Puerto Rico Dumpsite. In: Wastes in the Ocean Vol. 1: Industrial and Sewage Wastes in the Ocean (eds. I. W. Duedall, B. H. Ketchum, P. K. Park, and D.R. Kester) Wiley-Interscience, New York. pp. 171-200.
- Brooks, J. M., D. A. Wiesenberg and T. Ichiye (1983b) Use of volatile organic compounds in analysis of waste dispersion (in preparation).

- Capuzzo, J. M. (1982). Responses of zooplankton populations to pharmaceutical wastes discharged at the Puerto Rico Dumpsite. Report to NOAA/OMPA, Rockville, MD. 13 pp.
- Capuzzo, J. M., and B. A. Lancaster. (1983). Response of zooplankton populations to industrial wastes discharged at Deepwater Dumpsite 106 and their usefulness in estimating assimilative capacity. In: Wastes in the Ocean Vol. 5 Deep-Sea Waste Disposal (eds. D. R. Kester, W. V. Bort, P. K. Park, I. W. Duedall, and J. M. Capuzzo). Wiley-Interscience, New York (in press).
- Carnes, M., M. Inoue, and T. Ichiye. (1980). Hydrographic Data from the Puerto Rico Waste Dumping Study Cruises of 1978 and 1979. Texas A&M Technical Report 80-9-T, College Station, TX. 332 pp.
- Celone, P. J., and J. L. Chamberlin. (1979). Anticyclonic warm-core Gulf Stream eddies off the northeastern United States in 1978. Annals Biologiques 35:50-55.
- Chiou, C. T., V. H. Freed, D. W. Schmedding, and R. L. Kohnert. (1977). Partition coefficient and bioaccumulation of selected organic chemicals. Envir. Sci. Tech. 11:475-478.
- Chiou, C. T., D. W. Schmedding, and M. Manes. (1982). Partitioning of organic compounds in octanol-water systems. Envir. Sci. Tech. 16:4-10.
- Colwell, R. R. (1980). Microbial indicators of environmental impact at deep ocean dumping sites. Report to NOAA/OMPA, Rockville, MD. 66 pp.
- Colwell, R. R., F. L. Singleton, and E. L. Elliot. (1981). Bacteriological analysis of fish collected during 1980 fish-kill near Puerto Rico. Report to NOAA/OMPA, Rockville, MD. 12 pp.
- Csanady, G. T. (1973). <u>Turbulent Diffusion in the Environment</u>, D. Reidel, Dordrecht, The Netherlands, 248 pp.
- Csanady, G. T. (1981). An analysis of dumpsite diffusion experiments. In: Ocean Dumping of Industrial Wastes (eds. B. H. Ketchum, D. R. Kester, and P. K. Park) Plenum Press. New York, pp. 109-130.
- Curl, H. Jr., R. Dugdale, E. Jenne, D. P. Larsen, R. Lasker, J. M. De Manche, C. Officer, and J. Ryther. (1979). Biostimulants. In: Scientific Problems Relating to Ocean Pollution (ed. E. D. Goldberg) Proceedings of a Workshop at Estes Park, CO, July 1978. NOAA/Environmental Research Laboratories. pp. 153-177.

- Defant, F. (1961). Physical Oceanography Vols. I and II, Pergamon Press, London.
- Elder, D. L., and S. W. Fowler. (1977). Polychlorinated biphenyls: penetration into the deep ocean by zooplankton fecal pellet transport. Science 197:459-461
- Faisst, W. K. (1981). Characterization of particles in digested sewage sludge. In: <u>Particles in Water</u> (eds. M. C. Kavanaugh and J. O. Leckie) ACS Advances in Chemistry Series No. 189, American Chemical Society, Washington, D.C. pp. 259-282.
- George, R. Y. (1981). Zooplankton copepod community in the Puerto Rico Trench pharmaceutical dumpsite. Final Report to NOAA/OMPA, Rockville, MD. 33 pp. with appendix.
- Grice, G. D., and A. D. Hart. (1962). The abundance, seasonal occurrence and distribution of epizooplankton between New York and Bermuda. <u>Ecol. Monographs</u> 32:287-309
- Grimes, D. J., F. L. Singleton, H-S. Xu, and R. R. Colwell. (1983). Effect of ocean dumping on microbial communities of surface waters of the Puerto Rico Trench. Appl. Environ. Microbiol (submitted).
- Gschwend, P. M., O. C. Zafiriou, R. Fauzi, C. Mantoura, R. P. Schwarzenbach, and R. B. Gagosian. (1982). Volatile organic compounds at a coastal site. <u>1</u>. Seasonal variations. <u>Environ. Sci. Tech.</u> 16:31-37.
- Hansen, D. (1974). A lagrangian buoy experiment in the Sargasso Sea. In: <u>Drift Buoy Symposium</u>. American Institute of Aeronautics, and Astronautics Technical Committee on Marine Systems and Technologies, Hampton, VA. pp. 175-192.
- Hatcher, P. G., and G. R. Harvey. (1978). Trace organic studies at the Puerto Rico pharmaceutical waste dumpsite. Final Report to NOAA/OMPA, Rockville, MD. 11 pp.
- Ichiye, T., M. Inoue, and M. Carnes. (1981). Horizontal diffusion in ocean dumping experiments. In: Ocean Dumping of Industrial Wastes (eds. B. H. Ketchum, D. R. Kester, and P. K. Park) Plenum Press, New York. pp. 131-160.
- Juhl, R. T., and D. Weidner. (1981). Summary of information on mass fish mortalities in the Caribbean/Gulf of Mexico collected by the U.S. NOAA/National Marine Fisheries Service and U.S. Department of State. In: Report of Symposium on 1980 Caribbean Fish-Kill (ed. D. K. Atwood) Symposium sponsored by Gulf and Caribbean Fisheries Institute. Report prepared by NOAA/Atlantic Oceanographic and Meteorological Laboratories, Miami, FL. pp.1-8.

- Kennicutt, M. C. II, J. M. Brooks, and T. J. McDonald. (1983). Volatile organic inputs from an ocean outfall near Barceloneta, Puerto Rico. Envir. Sci. Tech. (submitted).
- Lavelle, J. W., and E. Ozturgut. (1981). Dispersion of deep-sea mining particulates and their effect on light in ocean surface layers. Marine Mining 3:185-212.
- Lee, W. Y., and J. A. C. Nicol. (1981). Toxicity of biosludge and pharmaceutical wastes to marine invertebrates. In: Ocean Dumping of Industrial Wastes (eds. B. H. Ketchum, D. R. Kester, and P. K. Park) Plenum Press, New York. pp. 439-454.
- Lee, W. Y., and J. Bird. (1983). Puerto Rico Ocean-Dumped Industrial Wastes: Sublethal Effects on Feeding, Growth and Fecundity of a Marine Planktonic Copepod, Temora Turbinata. In:

  Wastes in the Ocean Vol. 5 Deep-Sea Waste Disposal (eds. D. R. Kester, W. V. Burt, P. K. Park, I.W. Duedall, and J. M. Capuzzo). Wiley-Interscience, New York. (in press).
- Lee, W. Y. (1983). Copepods and Ichthyoplankton: laboratory studies of pharmaceutical waste toxicity. In: <u>Wastes in the Ocean Vol. 1: Industrial and Sewage Wastes in the Ocean (eds. I. W. Duedall, B. H. Ketchum, P. K. Park and D. R. Kester) Wiley-Interscience, New York. pp. 235-250.</u>
- Mackay, D. (1982). Correlation of bioconcentration factors. Environ. Sci. Tech. 16:274-278.
- MacLean, S. A. (1979). Report of May 1979 Puerto Rico Dumpsite cruise; planktonic crustacea. Report to NOAA/OMPA, Rockville, MD. 15 pp.
- MacLean, S. A. (1981). Focal gill melanization in euphausids: summarization of field studies. Report to NOAA/OMPA, Rockville, MD. 11 pp.
- Murphy, L. S., and R. A. Belastock. (1980). The effect of environmental origin on the response of marine diatoms to chemical stress. <u>Limnol. Oceanogr.</u> 25:160-165.
- Murphy, L. S., R. R. L. Guillard, and J. Garvis. (1982). Evolution of resistant phytoplankton strains through exposure to marine pollutants. In: Ecological Stress and the New York Bight: Science and Management (ed. G. F. Mayer), Estuarine Research Foundation, Columbia, SC. pp. 401-412.
- Murphy, L. S., E. M. Haugen, and J. F. Brown. (1983). Effects of industrial wastes on marine phytoplankton: a comparison of bioassay and dumpsite results. In: Wastes in the Ocean Vol. 1: Industrial and Sewage Wastes in the Ocean (eds. I. W. Duedall, B. H. Ketchum, P. K. Park, and D. R. Kester) Wiley-Interscience, New York. pp. 219-234.

- Nicol, J. A. C., W. Y. Lee, and N. Hannebum. (1980). Toxicity of Puerto Rican organic waste materials on marine invertebrates. In: Final Report: Biological Process Effects of Organic Wastes at Puerto Rican Ocean Dumping Site (ed. D. E. Wohlschlag). Report to NOAA/OMPA, Rockville, MD. pp. 65-102.
- NOAA. (1982). Status of Fishery Resources off the Northeastern United States for 1981. NOAA/National Marine Fisheries Service/Northeast Fisheries Center Technical Memorandum. NOAA/NMFS-F/NEC-12. 114 pp.
- Okubo, A. (1971). Oceanic diffusion diagrams. <u>Deep-Sea Res.</u> 18:789-802.
- O'Connor, T. P., and P. K. Park. (1982). Consequences of industrial waste disposal at the 106-mile ocean waste disposal site In: Ecological Stess and the New York Bight: Science and Management (ed. G. F. Mayer), Estuarine Research Foundation, Columbia, SC. pp. 675-697.
- Orr, M. H., and L. Baxter III. (1983). Dispersion of particles after disposal of industrial and sewage wastes. In: Wastes in the Ocean. Vol 1. Industrial and sewage wastes in the ocean. (eds. I. W. Duedall, B. H. Ketchum, P. K. Park, and D. R. Kester). Wiley-Interscience, New York. pp. 117-140.
- Peele, E. R., F. L. Singleton, J. W. Deming, B. Cauari, and R. R. Colwell. (1981). Effects of pharmaceutical wastes on microbial populations in surface waters at the Puerto Rico Dumpsite in the Atlantic Ocean. <a href="https://example.com/appl.environ.microbiol">Appl. Environ. Microbiol</a>. 41:873-879.
- Pfister, R. M., and P. R. Burkholder. (1965). Numerical taxonomy of some bacteria isolated from Antarctic and tropical seawaters. J. Bacteriol. 90:863-872.
- Presley, B. J., J. S. Schofield, and J. Trefry. (1981). Waste material behavior and inorganic geochemistry at the Puerto Rico Waste Dumpsite. In: Ocean Dumping of Industrial Wastes (eds. B. H. Ketchum, D. R. Kester, and P. K. Park) Plenum Press, New York. pp. 233-246.
- Pritchard, D. W., and A. Okubo. (1969). Summary of our present knowledge of physical processes of mixing in the ocean and coastal waters and a set of practical guidelines for the application of existing diffusion equations in the preparation of nuclear safety evaluations of the use of nuclear power sources in the sea. Report No. NYO-3109-40 (U.S. Atomic Energy Commission) Reference 69-1 Chesapeake Bay Institute, The Johns Hopkins University, Baltimore, MD.

- Proni, J. R., and D. V. Hansen. (1981). Dispersion of particulates in the ocean studies acoustically: the importance of gradient surfaces in the ocean. In: Ocean Dumping of Industrial Wastes (eds. B. H. Ketchum, D. R. Kester, and P. K. Park) Plenum Press, New York. pp. 161-174.
- Raytheon. (1977). Final Report. Ocean Monitoring Study Puerto Rico Chemical Waste Dump Site. Prepared for Bristol-Alpha Corp. Inc., Merck Sharp and Dohme Quimica de Puerto Rico, Inc., Pfizer Pharmaceuticals, Inc., Puerto Rico Olefins Company, Shering Corp. (Puerto Rico), Squibb Manufacturing, Inc., and Upjohn Manufacturing Company under Contract IWR-26 by Raytheon Company, Oceanographic and Environmental Services. 72 pp. with appendices.
- Ryther, J. H. (1969). Photosynthesis and fish production in the sea. Science. 166:76-76.
- Sauer, T. C., Jr. (1981). Volatile organic compounds in open ocean and coastal surface waters. Organic Geochem. 3:91-101.
- Schwab, C. R., T. C. Sauer, Jr., G. F. Hubbard, H. Abdel-Reheim, and J. M. Brooks. (1981). Chemical and biological aspects of ocean dumping at the Puerto Rico Dumpsite. In: Ocean Dumping of Industrial Wastes (eds. B. H. Ketchum, D. R. Kester, and P. K. Park) Plenum Press, New New York. pp. 247-274.
- Sheldon, R. W., and W. H. Sutcliff, Jr. (1978). Generation times of 3 hr for Sargasso Sea microplankton determined by ATP analysis. Limnol. Oceanogr. 23:1051-1055.
- Sieburth, J. McN. (1971). Distribution and activity of oceanic bacteria. Deep-Sea Res. 18:1111-1121.
- Singleton, F. L., J. W. Deming, E. R. Peele, B. Cavari, B. Gunn, D. Popkin, and R. R. Colwell. (1983). Microbial communities in surface waters at the Puerto Rico Dumpsite. In: Wastes in the Ocean Vol. 1: Industrial and Sewage Wastes in the Ocean (eds. I. W. Duedall, B. H. Ketchum, P. K. Park, and D. R. Kester) Wiley-Interscience, New York. pp. 201-218.
- Smith, T., and J. W. Stuart. (1975). Hydrology. In: Environmental Studies of the Proposed North Coast Nuclear Plant Unit No.

  1 Site: Final Report prepared by Puerto Rico Nuclear Center of the University of Puerto Rico for Puerto Rico Water Resources Authority. pp. 5-24 in Vol. 1 and Appendices 1, 2, 3 in Vol. II.
- The Ring Group. (1981). Gulf Stream cold-core rings: their physics, chemistry and biology. <u>Science</u> 212:1091-1100.
- Thomas, W. H., and D. L. R. Seibert. (1977). Effects of copper on the dominance and the diversity of algae: controlled ecosystem pollution experiment. <u>Bull. Mar. Sci.</u> 27:23-33.

- USNAVOCEANO. (1970). Oceanographic Atlas of North Atlantic Ocean U.S. Naval Oceanographic Office Publication 700, Washington, D.C.
- Van Baalen, C., and J. C. Batterton. (1979). Effects of pharmaceutical wastes on growth of microalgae. In: Final Report:
  Biological Process Effects of Organic Wastes at Puerto Rican Ocean Dumping Site (ed. D. E. Wohlschlag) Report to NOAA/OMPA, Rockville, MD. pp. 103-112.
- Van Baalen, C. (1980). Final Report: NOAA Puerto Rico pharmaceutical wastes. Report to NOAA/OMPA, Rockville, MD. 8 pp.
- Van Baalen, C. (1981). Final Report: NOAA Puerto Rico pharmaceutical wastes: Report to NOAA/OMPA, Rockville, MD. 17 pp.
- Voorhis, A. D., E. H. Schroeder, and A. Leetma. (1976). The influence of deep mesoscale eddies on surface temperature in the North Atlantic subtropical convergence. <u>J. Phys. Oceanogr.</u> 6:953-961.
- Weiler, D., and J. A. Suarez-Caabro. (1980). Overview of Puerto Rico's Small-Scale Fisheries Statistics; 1972-1978. Corporation for the Development and Administration of the Marine, Lacustrine and Fluvial Resources of Puerto Rico (Fisheries Research Laboratory). 27 pp.
- Williams, W. G. (1981). Lagrangian measurements in the fall and winter of mesoscale circulation north of Puerto Rico and transport through Mona Passage. Final Report from Clearwater Consultants, Inc. to NOAA/OMPA, Rockville, MD. 34 pp. with appendices.
- Wohlschlag, D. E., and F. R. Parker. (1983). Fish: response to ocean dumped pharmaceutical wastes. In: Wastes in the Ocean Vol. 1: Industrial and Sewage Wastes in the Ocean (eds. I. W. Duedall, B. H. Ketchum, P. K. Park, D. R. Kester) Wiley-Interscience, New York, pp. 251-270.