## CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD NORTH COAST REGION Preliminary Report

September 25, 1989

To: BDK, JRH, File

From: WER

Subject: Mussel Collections and Analyses for Dioxins and Furans along the North Coast from the Mouth of San Francisco Bay to Crescent City

In 1987, dioxins and furans were discovered in the effluent of the pulp mills (Louisiana Pacific Corporation's Samoa Pulpmill and Simpson Paper Company's Fairhaven Pulpmill) located on the North Spit of Humboldt Bay. Additional sampling as part of the receiving water monitoring program in the mills' National Pollutant Discharge Elimination System (NPDES) Permit and Waste Discharge Requirements adopted by the Regional Board show that dioxins and furans have bioaccumulated in Dungeness Crab.

A health risk assessment for dioxins and furans was prepared for Dr. Erik Rifkin on behalf of the mills by the Radian Corporation. The study showed that dioxins and furans were found in Dungeness Crab and Pacific Tomcod at the diffusers and at two control stations located about 5 miles and 26 miles north of the outfalls. The levels found in Tomcod muscle at the three sampling locations were essentially the same. Generally, the crab data showed lower levels at the two control stations then at the near diffuser locations. This data suggested that a background level of dioxins and furans exist in coastal waters.

In an effort to investigate background levels, Regional Board staff obtained laboratory funding from the State Board. The funds were limited and did not provide any money for collection of samples. Because of the limited funding a program was designed that would allow Regional Board Staff to perform the sample collection. The California Mussel, Mytilus californianus was selected as the test organism because it is ubiquitous along the California Coast and is sessile. The Bay Mussel, M. edulus was collected in Humboldt Bay as this species is endemic to the bay. One oyster sample was collected in the bay.

Thirteen Stations were identified along the North Coast for collection of samples. Sampling methodology was simple. A minimum of 20 mussels were collected at each site. The mussels collected were in a size range of 55 to 65 mm in length. They were pried from the rocks using a spring steel abalone bar which was cleaned by thoroughly rinsing in ocean water at each station. Following collection the mussels were wrapped in two layers of aluminum foil and placed in a ZIPLOCKR polyethylene bag of 4 mm thickness. The bags were wrapped with time tape and clearly labeled. The information included station name, and date and time of collection. The bagged mussels were placed in an ice chest for transport to the laboratory. By necessity the mussels were collected over a period of almost a month. The constraints on collection included weather, tides, and conflicting work schedules. Collection began on May 10, 1989 and was completed on June As the samples were collected they were delivered to the Regional Boards contract laboratory, NET Pacific, for storage in a freezer. The samples were shipped under "chain of Custody" procedures by NET Pacific to Enseco-CRL Ventura for dissection. Following dissection the mussels were transferred to Enseco's West Sacramento

laboratory for analysis. No project specific quality control spikes or duplicates were requested because of funding constraints.

The sample locations (see attached maps), date and times of collection were:

	STATION LOCATION	TIME	DATE
1	Anchor Bay Campground Rocks 100 yards northwest of		May 5, 1989 ing ramp
2	Estero Americano Rocks 100 yards northwest of		May 11, 1989 ish Growers outfall
3	Bodega Head Rocks just south of main part	1030 king lot	May 11, 1989
4	<u>Kirby Beach</u> (Tennessee Pt.) Rocks at point west of Rodeo		May 22, 1989
5	Goat Rock South side of Goat Rock	0730	May 23, 1989
6	Mad River Oyster Bed # 1 Humboldt bay oyster (bottom o		June 5, 1989
7	Bird Island West Side Bay Mussel (bottom dweller)	0930	June 5, 1989
8	Crescent City Control Rocks, west end of Presto States mussel watch program a	on Island,	This is the same station used in the
9	Trinidad Head Large rock directly west Marine Laboratory. This northern reference station.	0830 of the Hum site is al	June 6, 1989 boldt State University's Telonicher so the State mussel watch program
10	<u>Humboldt Bay</u> , North Jetty Inside jetty at interface bet	0930 tween dolos a	June 6, 1989 nd rock
11.	<u>Humboldt Bay</u> , Eureka Channel Samoa Bridge pier, southeast		June 7, 1989

13 Fort Bragg 0930 June 8, 1989
Rocks off Georgia Pacific haul road immediately west of Fort Bragg airport

June 7, 1989

1430

Rocks at Abalone Point, south of sewage treatment plant

The results of the sampling and analysis show that furans are ubiquitous along the coast. 2,3,7,8 TCDF was found at every station. The concentrations in mussel tissue ranged from 0.41 parts per trillion (PPT) to 7.8 parts per trillion. 2,3,7,8-TCDD was detected only in Humboldt Bay at two stations where the samples were collected from the bay bottom. The oysters collected at Humboldt Bay Mad River # 1 showed 2.4 PPT dioxin. 2,3,7,8-TCDF levels were 7.8 PPT. Mussels collected from the bay bottom at the west side

12 <u>Shelter</u> Cove

of Bird Island had 2,3,7,8-TCDD levels of 3.9 PPT. 2,3,7,8-TCDF levels were 2.8 PPT. Total Octachlorodibenzo-p-dioxin (OCDD) was reported at all stations except Anchor Bay and Estero Americano. The range was 44 to 150 PPT. OCDDs are believed to have low toxicity and according to some references appear to be a common trace environmental contaminant. The only station that showed the full range of dioxin isomer groups was Humboldt Bay Mad River # 1 which consisted of an oyster sample.

The Anchor Bay station and Estero Americano station were reported on a "Wet Weight Basis" due to an error during extraction. All other stations are reported as "Dry Weight". Wet weights can be back calculated and should be used when making comparisons to standards and criteria that are expressed in wet or fresh weights. Fish and shellfish are caught, cooked and consumed with body moisture essentially intact so the standards and criteria are expressed on a wet weight basis.

The Humboldt Bay Eureka Channel station results were similar to the northern open water stations. Those mussels living in the water column and not in contact with or in close proximity to fine grained sediments showed non-detectable levels of dioxin except OCDD which appeared at all stations except Anchor Bay and the Estero Americano.

The Humboldt pulpmills are the only known active dischargers of dioxins and furans in the area. There have been other sources of dioxins and furans in the past in the Humboldt Bay. Pentachlorophenol (PCP) was a widely used wood preservative fungicide throughout the Humboldt Bay area for decades. PCP is known to contain contaminants including dioxins and furans produced during its manufacture. Sloppy treatment and storage practices at many sawmills around the bay resulted in discharges of PCP along with the contaminants dioxin and furan. Because of their environmental persistence these compounds can be present for many years after the use of PCP has stopped. None of the mills around the bay currently use PCP. The Regional Board is currently involved in PCP cleanup activities at several mills.

Study data from the State Board's Report No. 88-5WQ "CHLORINATED DIBENZO-P-DIOXIN AND DIBENZOFURAN CONTAMINATION IN CALIFORNIA FROM CHLOROPHENOL WOOD PRESERVATIVE USE" shows that the following 2,3,7,8-chlorinated CDD and CDF compounds are most likely to occur as the result of pentachlorophenol use at treatment plants and wood treatment plants.

1,2,3,6,8-hexaCDD

2,3,7,8-tetraCDF

1,2,3,7,8-pentaCDF

2,3,4,7,8-pentaCDF

1,2,3,6,7,8-hexaCDF

Further sample collection and analysis is needed to develop data on 2,3,7,8-chlorinated CDD and CDF compounds in Humboldt Bay.

Chlorophenoxy herbicides used within the watershed of Humboldt Bay may have also contained dioxin and furan contaminants.

Mussels should be a useful indicator organism for detecting dioxin provided one recognizes their limits. As shown by comparing the Humboldt Bay stations Dioxins were detected only in those organisms that live and feed on the bottom. The water column samples within the bay showed non-detect levels of dioxin. 2,3,7,8- TCDF was detected at all stations. The solubility of individual compounds of CDD's and CDF's appears to vary widely. The solubility variable and other factors may explain the reasons for detecting furans and not dioxins. Additional work is necessary to clarify this.

synthetic organic concentrations in organisms vary with the lipid content of the tissues analyzed. Chlorinated hydrocarbons are much more soluble in lipids than water. They tend to partition into lipid rich tissues of aquatic organisms. Animals with higher lipid levels usually have higher concentrations of chlorinated hydrocarbon pollutants. Percent lipids for each sample station is attached.

Future work efforts both in Humboldt Bay and off shore should focus on sediments and bottom dwelling organisms. As a start, on September 19, 1989, Regional Board staff collected sediment samples in Humboldt Bay. Sample locations were selected to reflect potential historic discharges of PCP to the Bay. In all 13 samples were collected. One sample was collected in a drainage, tributary to McDaniel Slough, on Beaver Lumber Company property.

In cooperation with the Department of Fish And Game arrangements have been made to collect samples of English Sole, Petrale Sole, and Dover Sole. The samples are to be collected from commercial boats fishing immediately off the Humboldt Coast.

Both the sediment and fish samples will be analyzed at a laboratory contracted to the Environmental Protection Agency, Region 9, San Francisco.

Attached are maps showing the mussel sampling stations and sediment sampling stations. Copies of the Enseco Laboratory results and a summary of the mussel data is also included.

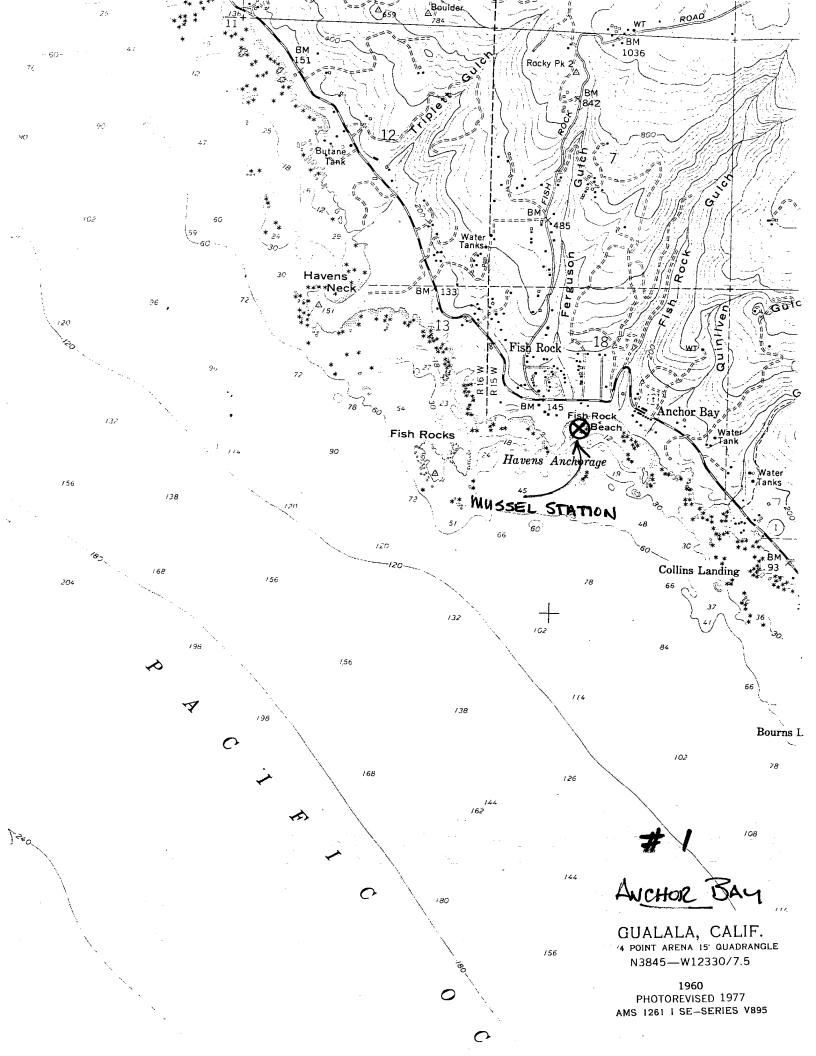
DATA #MARY
MUSSEL COLLECTIONS ALONG THE CALIFORNIA COAST FROM SAN FRANCISCO BAY TO CRESCENT CITY
May 5th through June 8, 1989

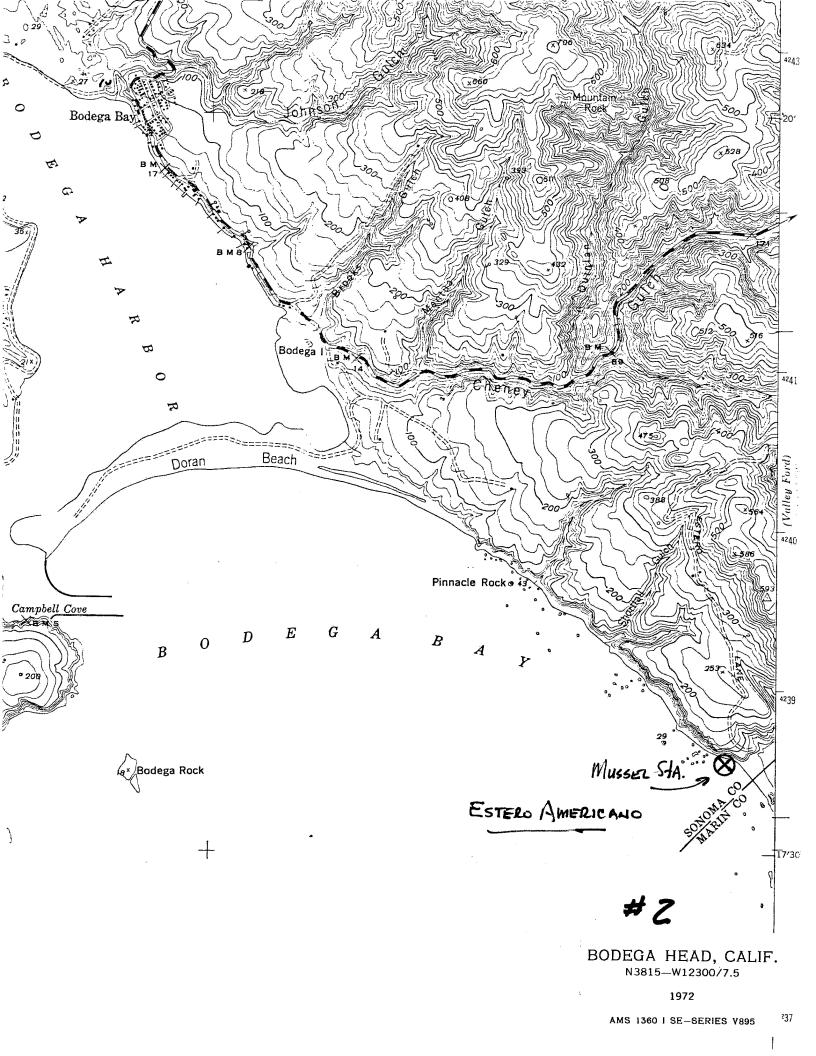
Results reported as pg/g dry weight

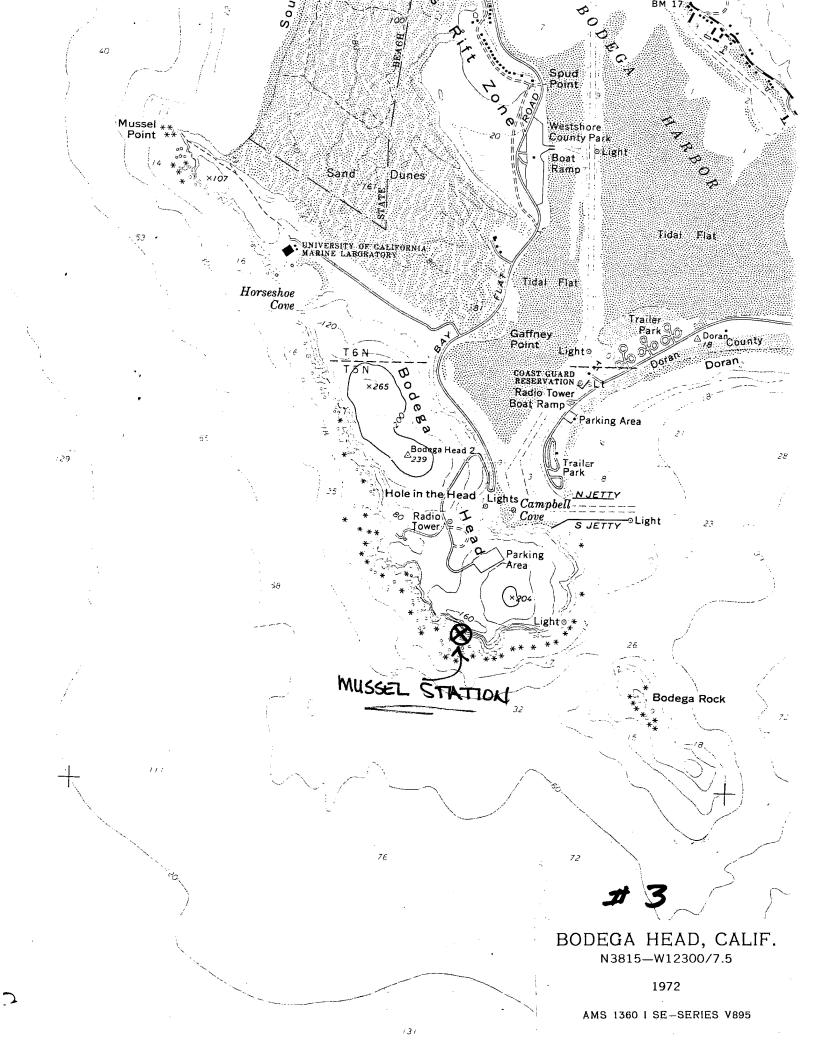
TRINIDAD CRESCENT HEAD CITY		5.3 5.2	pu pu	pu pu	pu pu	pu pu	1.5 2.1		nd nd	nd nd	pu pu	5.7 nd	61 88	pu pu	0.27 0.30
HUMB BAY T		8.8	pu	pu	ри	ри	2.0		pu	pu	4.9	31	150	pu pu	1.15
BIRD IS WEST		20	pu	Ē	pu	þ	2.8		3.9	pu	pu	рu	81	3.9	4.26
HUMB BAY MAD R # 1		33	6.0	ъ	멸	멸	7.8		6.9	7.3	6.9	8.6	23	2.4	10.9
HUMB BAY NORTHJETTY		1.6	ри	pu	pu	멸	0.61		pu	рu	рц	рu	44	pu	0.11
SHEL TER Cove		3.7	pu	pu	pu	pu	0.72		pu	pu	pu	7.4	75	pu	0.22
FORT BRAGG		2.0	pu	рц	힏	ם	0.84		힏	ם	ъ	ш	99	ם	0.15
ANCHOR BAY		0.49	nđ	рц	рu	pu	0.48		рц	рц	pu	pu	þu	pu	0.048
GOAT ROCK		1.5	pu	pu	ш	ы	0.59		멑	ы	뒫	ри	22	ם	0.12
BODEGA HEAD		5.8	pu	pu	pu	nd	0.50		nđ	ы	ы	7.0	99	рц	0.19
ESTERO <sup>1</sup> AMERICANO		0.41	<u>p</u>	ш	pu	pu	0.41		pu	pu	pu	pu	nd	pu	0.041
KIRBY <sup>1</sup> BEACH		7.7	pu	pu	pu	pu	2.4		pu	pu	pu	19	36	pu	0.52
	FURANS	TCDF(T)	PeCDF(T)	HxCDF(T)	HpCDF(T)	OCDF	2,3,7,8-TCDF	DIOXINS	TCDD(T)	PeCDD(T)	HxCDD(T)	HpCDD(T)	aaso	2,3,7,8-TCDD	Equivalent concentration of 2,3,7,8-TCDD <sup>2</sup>

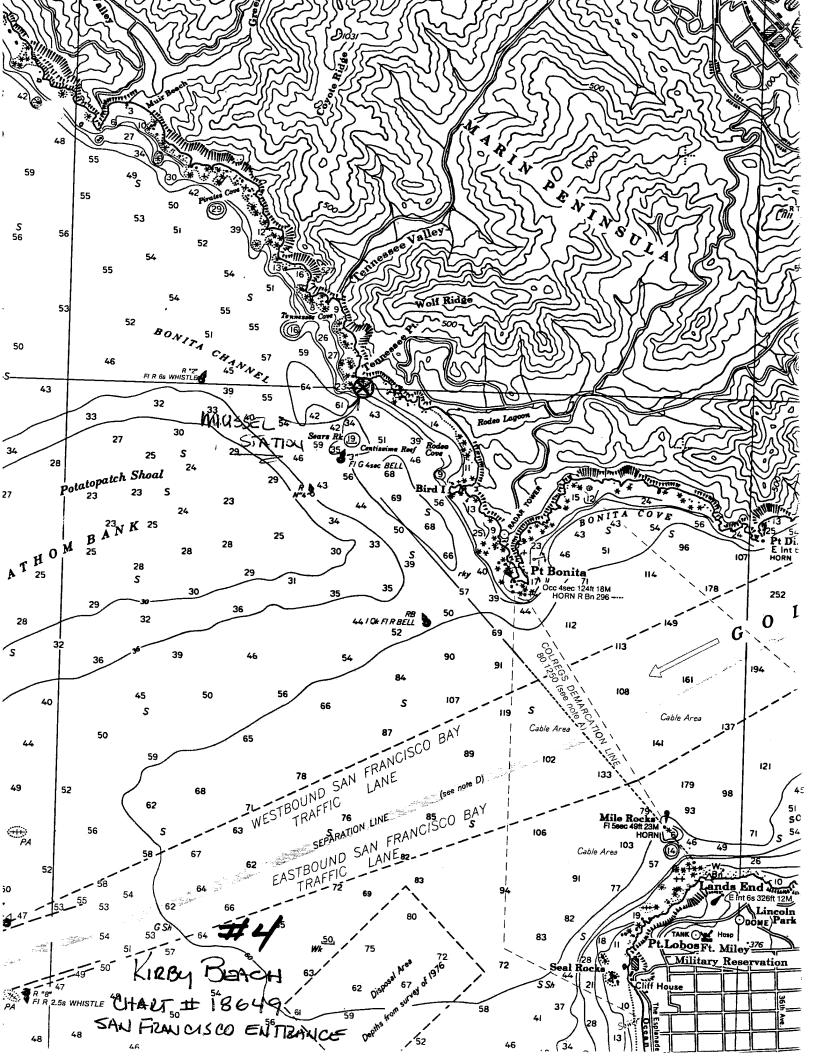
 $<sup>^{</sup>m 1}$ Wet Weight

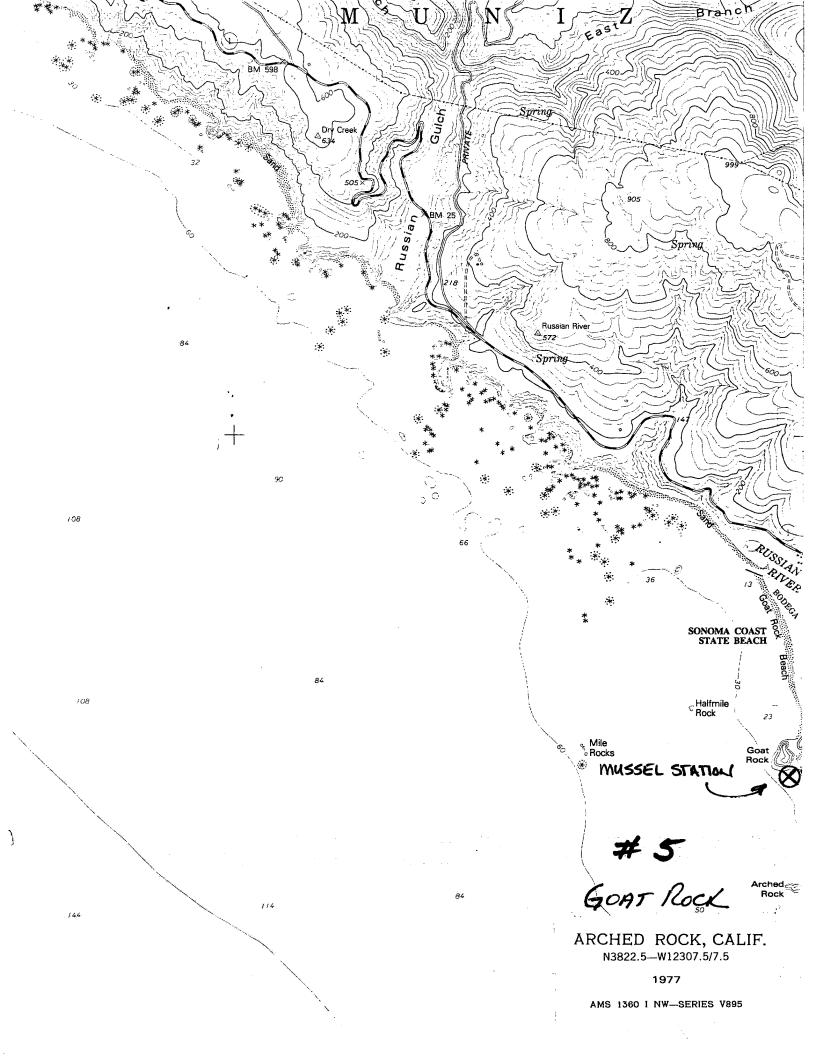
<sup>&</sup>lt;sup>2</sup>TEQ calculated using I-TEFs/89, EPA document no. EPA/625/3-89/016, with the assumption that all tetra through heptaCDDs and CDFs are chlorinated at positions 2,3,7, and 8. This procedure may overestimate the 2,3,7,8 compounds

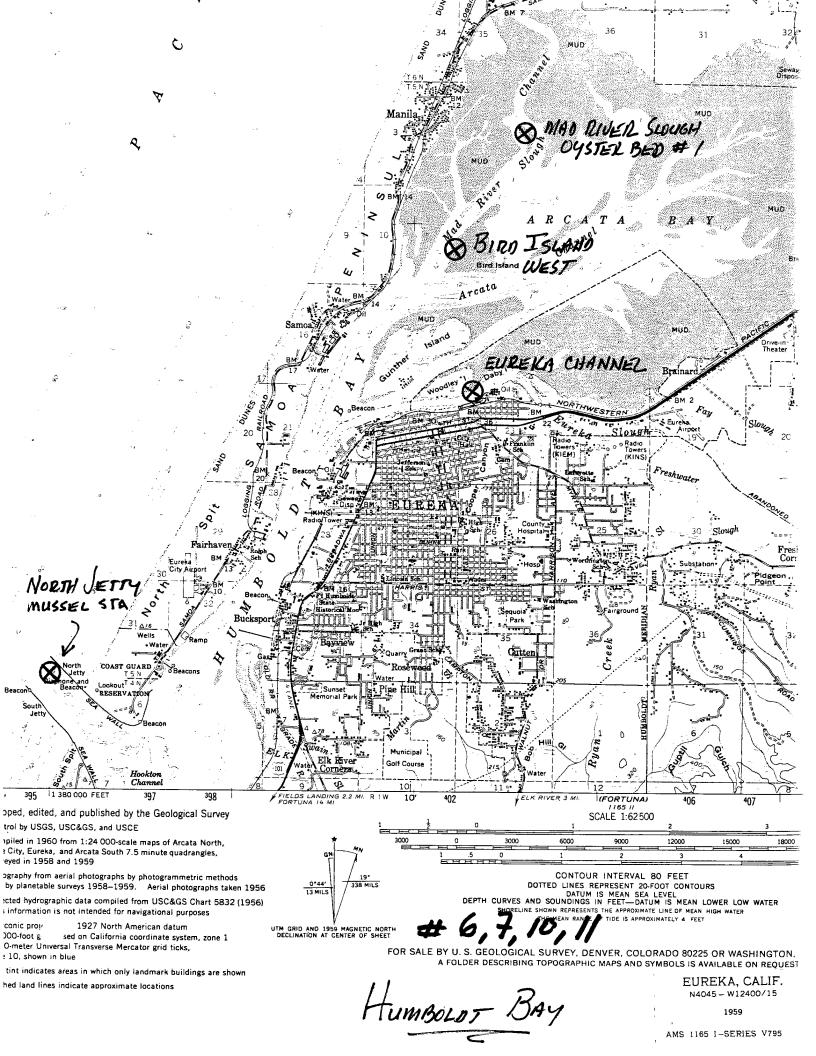


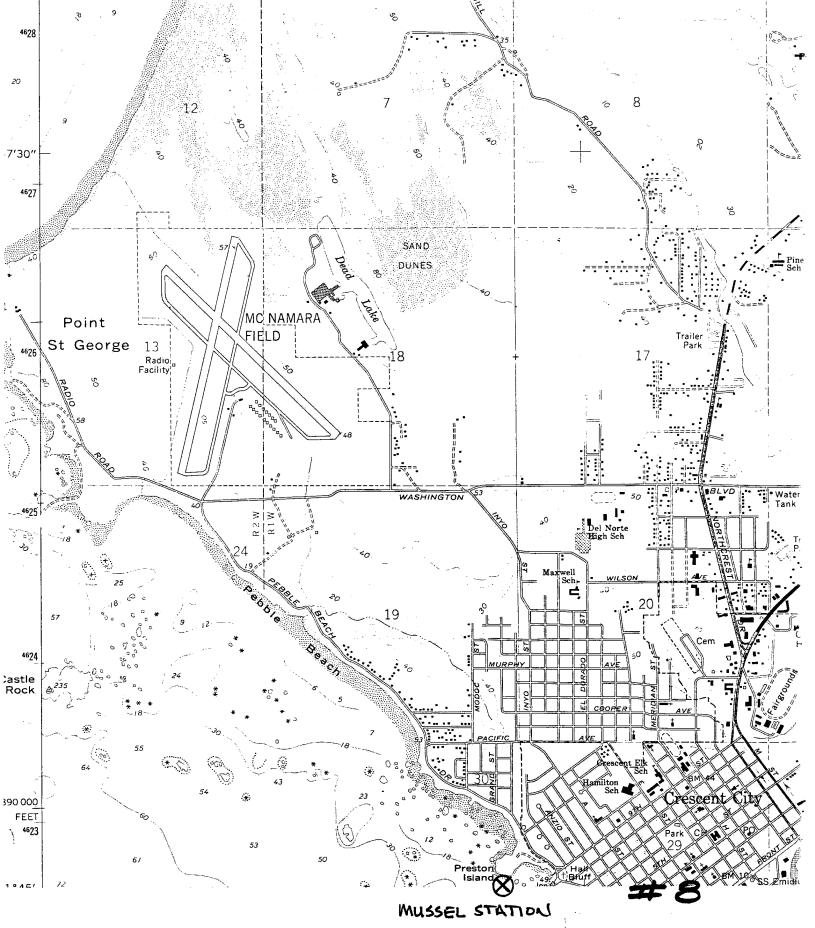












CRESCENT CITY, CALIF.
sw/4 crescent city 15' QUADRANGLE
N4145—W12407.5/7.5

1966 PHOTOREVISED 1978 AMS 1167 I SW-SERIES V895

