STATE OF WASHINGTON

Dixy Lee Ray
Governor

DEPARTMENT OF ECOLOGY

7272 Cleanwater Lane, Olympia, Washington 98504 206/753-2353

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MEMORANDUM
April 19, 1979

To: Rick Pierce

From: Greg Cloud

Subject: ASARCO Class II Survey

On September 20, 1978 Mike Morhous and Greg Cloud visited the ASARCO copper refinery in Tacoma to perform a Class II industrial survey on the industrial effluents to Commencement Bay. Composite samplers were installed on the north, middle, and south outfalls. Field grab samples were obtained at each outfall during composite sampler installations (see Table I). All analyses on the composite samples and flows for the 24-hour period are presented in Table II.

ASARCO has no NPDES permit limitations on trace metals in its effluent. The permit does require monthly reports for trace metal concentrations. The data presented (Table II) can be used for laboratory comparison. Most of the analysis correlate well except for the south outfall composite (DOE) and south outfall grab (DOE). These data sets seem to be reversed, either by the DOE laboratory or ASARCO. In either case, the values for arsenic in these two samples do not compare well.

With permission from Charles Randt, assistant plant manager, biological specimens were obtained near the north outfall. A map of the ASARCO refinery with an insert of the north outfall will be found on Figure 1. The biological specimens collected included copper rockfish (*Sebastes caurinus*), pile perch (*Rhacochilus vacca*), and edible mussels (*Mytilus edilus*). Enough specimens were taken to split samples for analysis by ASARCO and DOE. The purpose of this sampling was to assess, if possible, the assimilation of trace metals discharged from ASARCO by some of the biota living in the slag fill and piling habitat. These specimens were collected between the surface and 10 meters by scuba equipment and pole spear. The edible mussels are intratidal and were removed from dock pilings.

Habitat

The ASARCO copper smelter is built, for the most part, on slag waste. The slag was dumped hot into the salt water. This forms vitreous ellipsoidal masses with large cracks and gas pockets. This substance offers maximum protection for shrimps and small fishes. It also provides a good substrate for algal growth. The slag has been studied for trace

Class II Field Review and Sample Collection
24 Hour Composite Sampler Installations

Sampler	Date and Time Installed	Location
1. North outfall aliquot - 250 ml/30 min.	9/19/78 - 1010 hrs.	North outfall (last grate before discharge)
2. Middle outfall aliquot - 250 ml/30 min.	9/19/78 - 1030 hrs.	Middle outfall (last grate before discharge)
3. South outfall aliquot - 250 ml/30 min.	9/19/78	South outfall (last channel before seep pond)

Grab Samples

	Date and Time		Analysis	Sample Location
1.	9/20/78	1010 hrs.	Temp., pH, Cond.	North Outfall
2.	9/20/78	1040 hrs.	Temp., pH, Cond.	Middle Outfall
3.	9/20/78	1100 hrs.	Temp., pH, Cond.	South Outfall
4.				
5.				
6.				

Flow Measuring Device

1. Type - Bubble head gages, weir types unknown, inaccessible.
2. Dimensions -

   a. Meets standard criteria /__/ Yes

   /__/ No Explain:

   b. Accuracy check not accessible

	Actual Instan. Flow	Recorder Reading	Recorder Accuracy (% of inst. flow)
1.			
2.			
3.			

/__/ is within accepted 15% error limitations

/__/ is in need of calibration

Field Data

Parameter	Date and Time		Sample Location	Result
Temperature	9/20/78	1010 hrs.	North Outfall	>30.0°C
pH	9/20/78	1010 hrs.	North Outfall	7.0
Conductivity	9/20/78	1010 hrs.	North Outfall	210 μmhos/cm
Temperature	9/20/78	1040 hrs.	Middle Outfall	18.3°C
pH	9/20/78	1040 hrs.	Middle Outfall	7.3
Conductivity	9/20/78	1040 hrs.	Middle Outfall	135 μmhos/cm
Temperature	9/20/78	1100 hrs.	South Outfall	19.9°C
pH	9/20/78	1100 hrs.	South Outfall	7.1
Conductivity	9/20/78	1100 hrs.	South Outfall	>20,000 μmhos/cm

Table II
ASARCO Effluent Data
(mg/l)

Discharge Point	Analysis by DOE							Analysis by ASARCO						
	Pb	Cu	Zn	Cd	Cr	Ni	As	Pb	Cu	Zn	Cd	Cr	Ni	As
North Outfall 24-hr. DOE Composite	<.05	.04	.02	<.01	<.02	<.05	.008	0.1	0.12	0.0	0.0	--	--	0.0
Middle Outfall 24-hr. DOE Composite	<.05	2.1	1.4	.05	<.02	<.05	2.7	0.1	1.96	1.15	0.04	--	--	3.0
South Outfall 24-hr. DOE Composite	<.05	2.8	1.6	.03	<.02	<.05	.81	0.3	1.05	1.06	0.15	--	--	10.0
South Outfall DOE Grab	~.02	.95	1.4	.16	<.02	.2	5.98	0.2	3.07	1.24	0.03	--	--	2.0
South Outfall 24-hr. ASARCO Composite	~.02	.92	1.3	.14	<.07	.2	4.90	0.2	0.53	0.91	0.11	--	--	6.0

Discharge Point	Outfall Flows (24-hour Composite Sampling)	
	Total Flow Each Outfall	Total Combined Flow
North Outfall 24-hr. DOE Composite	630,320 gpd	3,427,320 gpd (3.43 mgd)
Middle Outfall 24-hr. DOE Composite	1,346,000 gpd	
South Outfall 24-hr. DOE Composite	1,451,000 gpd	

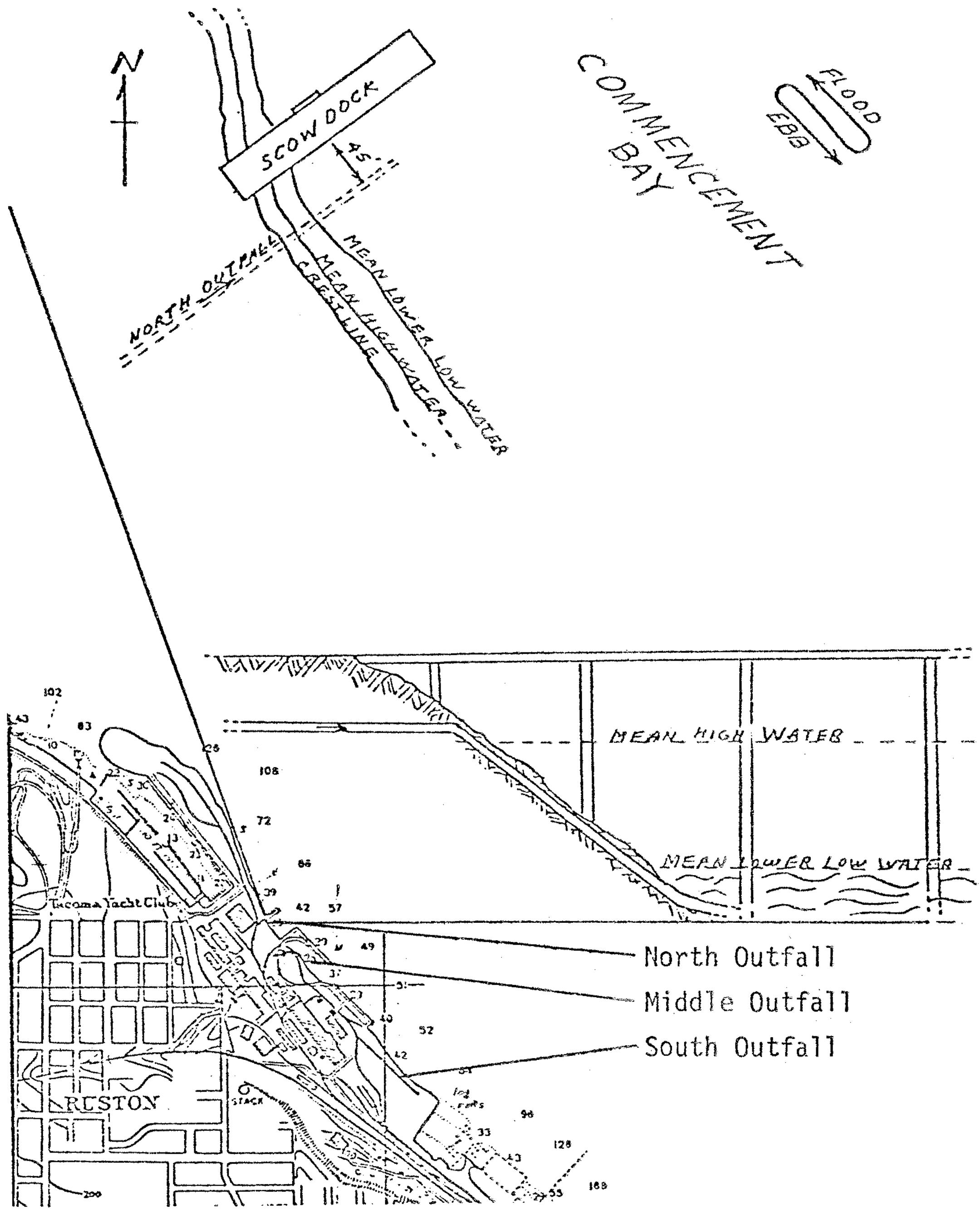

Figure 1. ASARCO Study Area and Receiving Waters

Inset: North Outfall - Biological Study Area and Plan View metal leachate and results indicate it is very stable in sea water (Carpenter, University of Washington, personal communication). The slag slopes at about 20 degrees to a depth of 3 to 4 meters. It then increases to 45 to 55 degrees to 10 to 12 meters depth at the base of the slag. The natural sea floor slopes quickly away to reach depths of 30 meters within 150 meters of the shoreline. Three large loading piers are located on the shoreline with pilings in the sea floor and in the slag. Assorted industrial debris is scattered subtidally along the slag and dock areas. Refined copper sheeting scraps were observed in various stages of corrosion.

Analysis

In sampling the organisms, enough were taken to split samples with ASARCO for comparison analysis. Unfortunately, a misunderstanding on ASARCO's part led to their analyzing the wrong tissue. This report, therefore, makes no attempt to compare ASARCO's data with DOE's data. It was clearly explained to ASARCO personnel that analyses were to be done on muscle fiber, gill tissue, and liver tissue on both the copper rockfish and pile perch. They reported whole fish values and made no distinction as to which species or whether both species were used for analysis. They mention in their letter of November 7, 1978 that "shellfish are notorious for accumulating metals and some very high values are found in the literature". The results of ASARCO's shellfish analysis are included at the bottom of Table III. The total of all ASARCO tissue analysis are summarized in Table VI.

The samples to be analyzed by the DOE laboratory were dissected by the author and Mike Morhous in the DOE laboratory within 1 hour after collection. Stainless steel dissection instruments were used in the process. The tissue samples were placed in sterile "whirlpack" plastic bags and frozen at 0°C for future analysis. One month later the samples were thawed slowly, dried, dessicated, ashed at 350°C for 1 hour, weighed, and boiled in HNO_3 until clear. The individual samples were brought to volume and the supernatant removed for analysis. Each element was determined by atomic absorbtion flame spectrophotometer (Perkins Elmer Model No. 360). All results in Tables III and IV are reported as mg/kg wet weight.

Discussion

The three effluents from ASARCO are discharged at relatively shallow depths. The southern effluent seeps through slag from a pond and enters the sea water at the shoreline. The middle and north outfalls are between 10 to 15 meters in depth from Mean Lower Low Water. All three of these effluents have elevated trace metal concentrations. The south outfall generally carries higher concentrations of arsenic as it drains the old arsenic operations of the smelter. These effluents move laterally along the shoreline as the tides ebb and flood.

Table III

DOE Tissue Samples
(mg/kg wet weight)

Organism	Pb	Cu	Zn	Cd	Cr	Ni	As	Mn
Copper Rockfish (Muscle)	2.5	3.4	51.0	0.8	<1.0	<5.0	1.1	11.6
Copper Rockfish (Liver)	<2.5	9.3	26.0	0.5	<1.0	<5.0	0.43	1.0
Copper Rockfish (Gills)	6.6	7.5	22.0	0.4	<1.0	<5.0	1.2	<0.5
Copper Rockfish (Gut Contents)	3.0	2.4	20.0	0.3	<1.0	<5.0	0.66	3.7
Pile Perch (Muscle)	<2.0	3.7	8.8	0.1	<1.0	<5.0	0.81	<0.4
Pile Perch (Liver)	3.8	24.0	48.0	1.4	<1.0	<5.0	0.55	1.0
Pile Perch (Gills)	4.5	8.5	26.0	0.8	<1.0	<5.0	1.8	4.0
Pile Perch (Gut Contents)	5.8	54.0	80.0	1.3	<1.0	<5.0	1.1	11.6
Edible Mussels (*Mytilus edulis*)	5.8	49.0	78.0	1.3	<1.0	<5.0	0.76	6.4
Edible Mussels* (Tissue from 4 specimens)	4.9	67.3	67.3	0.76	--	--	2.6	--

*Analysis by ASARCO.

Table IV

Edible Mussel Tissue Sample
(Michael Price, 1977)
(mg/kg Wet Weight)

Edible Mussels	Pb	Cu	Zn	Cd	Cr	Ni	As	Mn
Site* #22	1.61 ±.03	1.56 ±.06	61 ±2	2.11 ±.05	-- --	-- --	6.0 ±.2	-- --
Site* #23	1.27 ±.08	1.01 ±.07	31 ±3	0.56 ±.05	-- --	-- --	5.5 ±.1	-- --
Site* #24	2.05 ±.06	1.77 ±.05	62 ±4	1.5 ±.1	-- --	-- --	7.2 ±.4	-- --
Site* #25	0.9 ±.1	0.79 ±.09	26 ±1	0.76 ±.07	-- --	-- --	3.1 ±.3	-- --
4 Sta. Median*	1.44	1.39	46	1.13	--	--	5.75	--
22 Sta. Median**	3.0	1.6	51	1.6	--	--	7.2	

*Sites in Vicinity of ASARCO Discharges.
**Sites Throughout Southern Puget Sound.

Table V

Provisional Weekly Intake (lbs. of Flesh)
Required to Reach Ingestion Limits of 3 mg Pb and 0.4 mg Cd

Food Source	Pb lbs/wk	Cd lbs/wk
Edible Mussels	1.14	.68
Copper Rockfish (Muscle)	2.64	1.1
Pile Perch (Muscle)	3.3	8.8

Table VI

Analysis by ASARCO
(mg/kg Wet Weight)

Specimen	Pb	Cd	Cu	Sb	Zn	As
Fish Fin	4.9	.060	13.4	<2.0	46.4	1.1
Fish Entrails	1.4	.36	25.4	<1.0	23.1	1.1
Fish Head	.79	.027	3.2	<1.0	23.3	.46
Fish Bones	.49	.033	2.8	<1.0	17.9	.20
Fish Flesh	.01	.001	.15	<1.0	6.4	<.006
Fish Skin	1.1	.033	5.5	<1.0	39.1	.41
Whole Fish	.46	.037	3.0	<1.0	14.8	.22
Tissue from 4 Shellfish	4.9	.76	67.3	<4.0	67.3	2.6

In Table III, all DOE tissue analyses are presented. The arsenic values in all samples are lower than expected considering the proximity of the discharge. The data presented in Table IV was compiled by Michael Price, Evergreen State College. Price's data on stations 22, 23, 24, and 25 (ASARCO area) show markedly higher arsenic values than those determined by DOE. Price's total of 22 stations scattered throughout Puget Sound show a median value for arsenic even higher than the median value of these four stations within the smelter area. The cause of this anomally is not known.

At the time of collection of the biota, the effluent grab sample from the south outfall contained 5.98 mg/l As. (see Table II).

Copper was much higher in the DOE mussel samples than those reported by Price (see Tables III and IV). Sources of copper for which ASARCO is responsible include effluent concentrations of (0.4 - 2.8 mg/l) and corrosion of metallic copper scraps on the subtidal habitat. The National Academy of Science's *Monograph on Copper (1977)* notes "Copper is an effective molluscide. Copper concentrations of 0.1 ppm are acutely toxic to Nereis [pile worms]." (National Academy of Science, 1977.)

One problem associated with arsenic, copper, or any other trace metal is an accurate interpretation and comparison of data. The problem is aggravated because: 1. Different species assimilate and eliminate trace metals at different rates; and, 2. Individuals within a given species assimilate trace metals at different rates according to size, sex, habitat, and time of year. Background data for comparison of the ASARCO tissue samples is difficult to interpret due in part to an incomplete understanding of trace metal flux in marine ecosystems. Therefore, conclusions which can be based on present tissue analyses are limited. Edible mussels, (*Mytilus edilus*), are filter feeders and mussel tissue is often analyzed to reveal toxins or pathogens. Concentrations of copper, cadmium, zinc, and lead in mussel tissue were among the highest recorded in this study. The sea perch, (*Rhacochilus vacca*), feed mainly on edible mussels and barnacles. The gut contents of the sea perch collected consisted mainly of barnacles and mussels. As one would expect, there appears to be a close relationship between trace metal concentrations in mussels and sea perch gut contents (Table II).

The copper rockfish had herring remains in its stomach. These herring could be residents and/or transients. In addition to herring, the rockfish are probably feeding on both the smaller sea perch and/or other small resident fishes in the area. In addition, numerous shrimp were noted in the collection area and are commonly eaten by copper rockfish. Shrimp are nonselective feeders and feed on any detritis available. Trace metal concentrations in rockfish gut contents were generally lower than those in pile perch gut contents and may reflect decreased metal concentrations in higher trophic levels.

The World Health Organization (Tech. Report No. 505, 1972) recommends a provisional weekly limit of 3 mg lead per person. The cadmium limit is 400 to 500 μg (0.4 - 0.5 mg) per individual per week. This information has been applied to the lead and cadmium values for edible mussels, copper rockfish muscle, and pile perch muscle. The results, listed in Table V, are reported as the amount of ingested tissue needed to reach the provisional tolerable limit.

Summary

General conclusions which can be made regarding the impact of trace metals in ASARCO effluents and slag on aquatic organisms are limited. It appears, however, that copper concentrations in mussels collected during this investigation were substantially elevated. Fowler and Oregioni (1976) report copper concentrations in mussels collected along the California coast averaged approximately 1.4 mg Cu/kg wet wt. (7 mg/kg dry wt.). This agrees well with Price's average of 1.6 mg Cu/kg wet wt. By contrast, copper concentrations in this study revealed concentrations of 49 to 68 mg Cu/kg wet wt.

Lack of adequate baseline data makes further conclusions difficult. The data presented here should, however, provide good baseline information for future studies in the ASARCO area. It is recommended that control sites be established to collect duplicate species to correspond with future biological sampling at ASARCO. Sediments and algae should also be collected for trace metal determination.

GC:cp

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