Skagit County Marine Resources Committee Contamination Project

in cooperation

with the

Samish Indian Nation

for:

Fidalgo Bay

June 2007

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Erica Pickett

Dixon Elder

Project Abstract
The Samish Indian Nation Department of Natural Resources has concluded a one year study to collect and analyze water quality data to help characterize the existing conditions of surface waters and to identify and/or quantify existing and/or potential pollutant sources in Fidalgo Bay storm outfalls and small creeks.

This project funded through the Northwest Straights Commission, involved testing at 17 sample sites in Fidalgo Bay, with supplemental Marine Resource Commission funds in the amount of $10,948.00. Metals and nutrients were collected a total of 4 times, once per month, March thru May including one rain event in addition to the existing sampling plan, for a total of 68 samples for nutrients and 68 samples for metals. Pesticide sampling occurred at 3 selected sites once a month, starting in March ending in May, and included one rain event for a total of 12 samples for the pesticides.

This report is a summary of the data collected by the Samish Indian Nation Department of Natural Resources and volunteers. All volunteers were trained by the tribal staff prior to sample collection.

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Project Introduction

One of the major water-quality issues in Washington is protecting the quality of Puget Sound and its contributing waterways from the effects of non-point source contamination. Nitrate is one of the most prevalent concerns in the State, but pesticide/herbicide contamination of water supplies and surface waters is becoming a major concern with the advent of the use of these chemicals in small communities on lawns and gardens. Agriculture, a major industry in some areas of Washington has also had a wide effect on water quality. Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted.

Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into surface water and groundwater. Point source contamination from industrial and commercial activities is present in a number of locations, but as the Puget Sound region continues to grow, the non-point-source effects of urbanization on water quality will increase. For both the protection of drinking water supplies, stream ecosystems and Puget Sound (Fidalgo Bay) the effects of development and other human activities on water quality need to be better understood.

What this project addressed is a small but critical part of a much bigger picture. The information gathered in this study will help to address problems and to fill in some of the data gaps with baseline information on Fidalgo Bay.

The Samish Indian Nation Department of Natural Resources (Samish DNR) conducted a chemical analysis of 17 stormwater outfalls along the Fidalgo Bay Shoreline for metals (copper, zinc, cadmium and lead) and nutrients (nitrate, soluble potassium, ortho-phosphorous and ammonia). Out of the 17 outfalls, 3 of those were also analyzed for Synthetic Organic Compounds using Method 525.2. This included a screening for PCB's (Total Aroclors) and specifically for Aroclors 1221, 1231, 1242, 1248, 1254, 1260, 1016. Screening for Toxaphene, PAH's, Phthalates, EPA Regulated Pesticides, EPA unregulated Pesticides and State Unregulated-Other. Along with the chemical analyses, all sites are tested for Dissolved Oxygen, Temperature, Salinity/Conductivity and pH.

The contamination project is built upon a study that the Samish DNR started in 2005 with funding from the Bureau of Reclamation collecting fecal coliform samples, pH, dissolved oxygen and temperature at 46 outfalls, 3 freshwater seep sites and 5 deep water sites in Fidalgo Bay. As a result of this study, the outfalls were already mapped and had been added to the tribal GIS database.

The project area includes the western, southern and eastern shores of Fidalgo Bay from 32nd street in Anacortes, to the southeastern corner of the Bay and continues to the March point Shell RV Park.(see map: page13).

Water quality measurements of metals, nutrients and pesticides, according to the

documentation for this area that has been reviewed, were limited at best. A comprehensive literature search for any water quality data for Fidalgo Bay Data was conducted by contacting Dan Doty (Washington State Department of Ecology, WDOE-he is in charge of the Restoration Plan and Environmental Assessment for the Texaco Oil Spill into Fidalgo Bay in 1991 and 1992) also contacted were Environmental Protection Agency (EPA) Region 10, Washington State Department of Health, Skagit County and the City of Anacortes.

There has been some chemical analysis collected by WDOE on sediments in 1999 and toxins analysis as it relates to shellfish health in 2000. The Swinomish Tribe analyzed sediment and shellfish for metals, PCB's PBDE's in 2002 and 2004. Battelle Marine Sciences Laboratory did a comprehensive report on Habitat Protection, Restoration and Enhancement in 2000. Since there is no commercial harvesting of shellfish in Fidalgo Bay and only recreational harvesting occurs, the Washington State Department of Health (WDOH) has not been required to complete a Sanitary Survey of the Bay. The WDOH has analyzed municipal and industrial wastewater discharge for fecal coliform only and has permanent restrictions for harvest of shellfish near the wastewater discharges none of which occur in Fidalgo Bay.

Project Goals:
No major rivers enter Fidalgo Bay. Runoff into the Bay is predominantly from non-point sources, small creeks/seeps and outfalls. The goal of this project was to collect and analyze data to characterize the existing conditions of the surface waters and to identify and quantify existing sources of potential pollution to Fidalgo Bay, and in conjunction with that, establish a database for the pesticides, metals and nutrients and start to typify the waters that enter Fidalgo Bay from the outfalls.

This project work plan includes the following:

- Quality Assurance Protection Plan (QAPP) for the project
- baseline data collection for metals, nutrients, pesticides, dissolved oxygen, pH, temperature, salinity of the 17 stormwater outfalls
- map of 17 stormwater outfalls
- data sharing with all relative agencies and organizations

Methods:
Samish DNR sampled at selected sites 3 times and one storm event with the help of volunteers Erica Pickett, Dixon Elder and Dian Jahn. Samples were collected from the 17 outfalls using guidelines provided by Edge Analytical Laboratory and using EPA protocol. Purple nitrile gloves were used and changed at each site. Pre-cleaned Nalgene sample bottles for the metals and nutrients were used at low flow sites. After use, we discarded them, but at medium and high flow sites samples were taken from direct stream flow.

Figure 1: Amber Glass 1 Liter
Pesticide Sampling Bottle

Figure 2: Site FB3

Duplicate samples were taken three of the four sampling rounds and an equipment blank was taken for the fourth sample round. All duplicates passed for Quality Control. Tap water was used for the equipment blank and there were low level hits of copper and nitrate-n. No other analytes were detected. The copper most likely came from the pipes in the building or from the water itself. We will re-run the equipment blank using De-ionized water from Edge Analytical for the next grant cycle.

Pesticides:
The pesticide sampling, showed a hit on only one out of the 3 sample sites (MP7) for Pentachlorophenol and Bromocil. There were hits at all four sampling events at this site including the duplicate. The numbers ranged from 0.51ppm to 1.55ppm
Site MP7 is a ditch that runs between a farm and the railroad tracks on March Point. It eventually enters a culvert, goes under the March Point road and empties into Fidalgo Bay. The contamination could be from the treated railroad ties.

Pentachlorophenol C6Cl5OH CAS # 87-86-5 was widely used as a pesticide and wood preservative. Since 1984, the purchase and use of pentachlorophenol has been restricted to certified applicators. It is no longer available to the general public and is used industrially as a wood preservative for utility poles, railroad ties, and wharf pilings. Exposure to high levels of pentachlorophenol can cause increase in body temperature, liver effects, damage to the immune system, reproductive effects, and developmental effects. This substance has been found in at least 313 of the 1,585 National Priorities List sites identified by the EPA.

Pentachlorophenol is a manufactured chemical that does not occur naturally. Pure pentachlorophenol exists as colorless crystals. Impure pentachlorophenol (the form usually found at hazardous waste sites) is dark gray to brown and exists as dust, beads, or flakes. Humans are usually exposed to impure pentachlorophenol (also called technical PCP) has been detected in surface waters and sediments, rainwater, drinking water, aquatic organisms, soil, and food, as well as in human milk, adipose tissue, and urine.

Currently, releases to the environment are more limited as a result of decreasing volumes used and changing use methods. However PCP is still released, to surface waters from the atmosphere by wet deposition, from soil by run off and leaching, manufacturing and processes facilities. PCP is also released directly into the atmosphere via volatilization from treated woods products and during production. Finally, releases to the soil can be by leaching from treated wood products, atmospheric deposition in precipitation (such as rain and snow), spills at industrial facilities and at hazardous waste sites.

- Pentachlorophenol can be found in the air, water, and soil. It enters the environment through evaporation from treated wood surfaces, industrial spills, and disposal at uncontrolled hazardous waste sites.
- Pentachlorophenol is broken down by sunlight, other chemicals, and microorganisms to other chemicals within a couple of days to months.
- Pentachlorophenol is found in fish and other foods, but tissue levels are usually low.
- The general populations can be exposed to very low levels of pentachlorophenol in contaminated indoor and outdoor air, food, drinking water and soil.
- People who work or live near a wood treatment facility or in the production of utility poles, railroad ties, or wharf pilings may be exposed to pentachlorophenol in the air or by coming in contact with the treated wood.
- People living near hazardous waste sites may also be exposed to higher than usual levels of pentachlorophenol.

The EPA has set a limit for drinking water of 1 part of pentachlorophenol per billion parts of water (1 ppb).

Bromacil was also found at sample site MP7 in concentrations ranging from 0.6 ppm to 1.4ppm. The source of the herbicide is undetermined at this point.

Bromacil $C_9H_{13}BrN_2O_2$ CAS #314-40-9 is a broad spectrum herbicide used to control weeds in the agricultural food crops citrus and pineapple. In addition, both bromacil and its lithium salt are used to control weeds and brush in nonagricultural areas including utility right-of-ways, railroads, electrical switching stations, and industrial yards.

Use practice limitations include prohibitions on direct application to water, areas where surface water is present or intertidal areas below the mean high water mark. They also prohibit application through any type of irrigation system. Bromacil may not be applied directly to water or wetlands, and should be kept out of lakes, streams, and ponds.
Bromacil was first registered as a pesticide in the U.S. in 1961. EPA issued a Registration Standard for bromacil in September 1982 (PB87-110276). A Data Call-In (DCI) was issued in September of 1991 requiring additional chemistry, toxicology, ecological, and environmental fate data. As of April of 1996, 95 products were registered. In addition to federal regulation, the states of Florida and California have imposed more stringent regulations on the use of bromacil because of its occurrence in groundwater.

On August 3, 1996, the Food Quality Protection Act of 1996 (FQPA) was signed into law. FQPA amends both the Federal Food, Drug, and Cosmetic Act (FFDCA), and the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). The FQPA amendments went into effect immediately and were considered during this reregistration decision.

Bromacil generally is of low acute toxicity, but demonstrates thyroid, adrenal, eye, and thymus effects in animal studies and has been classified as a Group C, possible human carcinogen.

Parent bromacil is persistent and highly mobile, and has been detected in groundwater. Bromacil is stable to hydrolysis under normal environmental conditions. The primary routes of dissipation appear to be photolysis in water under alkaline conditions and microbial degradation in anaerobic soil. Bromacil's persistence is demonstrated by half-lives of 124 to 155 days in the field dissipation studies.

EPA is requiring the following additional generic studies for bromacil to confirm its regulatory assessments and conclusions:
Avian Reproduction Quail [71-4 (a)]
Avian Reproduction Duck [71-4 (b)]
Early Life-Stage Fish [72-4(a)]
Life-Cycle Aquatic Invertebrate [72-4(b)]
Dermal toxicity study [82-2]
Groundwater monitoring studies [166-1]
The Agency also is requiring product-specific data including product chemistry and acute toxicity studies, revised Confidential Statements of Formula (CSFs) and revised labeling for reregistration.

Nutrients:

Table 1: Nutrient Sampling Results

	Nutrients			
Sample #	Ammonia	Nitrate-N	Potassium	Ortho-Phosphate
P2	4 out of 4	4 out of 4	4 out of 4	4 out of 4
P4	4 out of 4	0 out of 4	4 out of 4	4 out of 4
P5	4 out of 4	4 out of 4	4 out of 4	4 out of 4
P6	4 out of 4	4 out of 4	4 out of 4	4 out of 4
FB2	2out of 4	4 out of 4	3 out of 4	4 out of 4
FB3	4 out of 4	4 out of 4	2out of 4	4 out of 4
HWY2	4 out of 4	4 out of 4	4 out of 4	4 out of 4
HWY3	4 out of 4	4 out of 4	4 out of 4	4 out of 4
HWY4	4 out of 4	4 out of 4	4 out of 4	4 out of 4
MP1A	3 out of 3	3 out of 3	3 out of 3	3 out of 3
MP3	4 out of 4	4 out of 4	4 out of 4	4 out of 4
MP5	4 out of 4	4 out of 4	4 out of 4	4 out of 4

MP7	4 out of 4	4 out of 4	4 out of 4	4 out of 4
NMP1	3 out of 3	3 out of 3	3 out of 3	3 out of 3
NMP3	4 out of 4	4 out of 4	4 out of 4	4 out of 4
NMP5	1 out of 1	1 out of 1	1 out of 1	1 out of 1
NMP6	3 out of 3	3 out of 3	3 out of 3	3 out of 3

4 out of 4 means that the parameter was detected 4 out of 4 sample rounds for that site. 3 out of 4 means the parameter was detected 3 times out of four sample rounds for the site etc...
The red highlight means that the parameter was only detected in some but not all sample rounds.

The nutrient samples were consistently high in potassium ranging from 0.61 ppm to 129 ppm. However, the sites that had somewhat high salinity values (HWY2, HWY3, HWY4 and MP1A) being removed from the equation, this drops the potassium numbers down to a range of 0.61ppm to 11 ppm.
P4 had a non-detected for nitrate-n. All the other sites had a range from .01 to 3.24ppm for nitrate-n.

All of the sites had ortho-phosphate in the sample ranging from 0.02ppm to 1.25ppm
All site had Ammonia hits ranging from .02ppm to 1.3ppm
Except for FB2 on the 2nd and 4th sample round had non- detected for NH3.

Phosphorus is an essential nutrient for aquatic plants and algae. It occurs naturally in water and is, in fact, usually the limiting nutrient in most aquatic systems. In other words, plant growth is restricted by the availability of phosphorus in the system. Excessive phosphorus inputs stimulate the growth of algae and diatoms on rocks in a stream and cause periodic algal blooms in reservoirs downstream. Slippery green mats of algae in a stream, or blooms of algae in a lake are usually the result of an introduction of excessive phosphorus into the system that has caused algae or aquatic plants to grow at abnormally high rates. Eutrophication is the term used to describe this growth of algae due to an over abundance of a limiting nutrient. Sources of phosphorus include soil, disturbed land, wastewater treatment plants, failing septic systems, runoff from fertilized crops and lawns, and livestock waste storage areas. Phosphates have an attraction for soil particles and phosphorus concentrations can increase greatly during rains where surface runoff is a problem.

Orthophosphate: This is a measure of the dissolved phosphorus which is immediately available to plants or algae. Orthophosphate is also referred to as phosphorus in solution.

Ammonia and Nitrate/Nitrite Nitrogen: Nitrogen is contained in the remains of decaying wastes of plants and animals. Some species of bacteria and fungi decompose these wastes and ammonia (NH3) is formed. The most probable sources of ammonia nitrogen are agricultural runoff, livestock farming, septic drainage and sewage treatment plant discharges. Waters with low oxygen concentrations that are polluted with nitrogen-rich organic matter may show high ammonia levels and low nitrate levels. Where waters are more oxygen-rich, ammonia will more quickly oxidize to nitrites and nitrates. Most

mountain streams are oxygen-rich and are more likely to show higher nitrogen concentrations in the form of nitrate/nitrite.

Like phosphorus, nitrate (NO3) serves as an algal nutrient contributing to excessive stream and reservoir algal growth. In addition, nitrate is highly toxic to infants and the unborn causing inhibition of oxygen transfer in the blood stream at high doses. Sources of nitrates include wastewater treatment plants, failing septic systems, runoff from fertilized lawns and agricultural crops, runoff from livestock waste storage areas, and industrial discharges.

Nitrates from land sources end up in streams more quickly than other nutrients such as phosphorus because they dissolve in water more readily and can travel with ground water into streams. Consequently, nitrates are a good indicator of the possibility of sources of pollution from sewage or animal waste during dry weather.

Metals:

Table 2: Metals Sampling Results

	Metals			
Sample #	Copper	Zinc	Cadmium	Lead
P2	ND	2out of 4	ND	2out of 4
P4	ND	ND	ND	ND
P5	ND	3 out of 4	ND	3 out of 4
P6	ND	2out of 4	ND	2out of 4
FB2	ND	ND	ND	ND
FB3	ND	ND	ND	ND
HWY2	ND	2out of 4	ND	ND
HWY3	ND	1out of 4	ND	ND
HWY4	ND	1out of 4	ND	1out of 4
MP1A	ND	3 out of 3	ND	ND
MP3	ND	2out of 4	ND	2out of 4
MP5	ND	1out of 4	ND	ND
MP7	ND	3 out of 4	ND	2out of 4
NMP1	ND	ND	ND	ND
NMP3	ND	ND	ND	ND
NMP5	ND	1 out of 1	ND	1 out of 1
NMP6	ND	1 out of 3	ND	ND

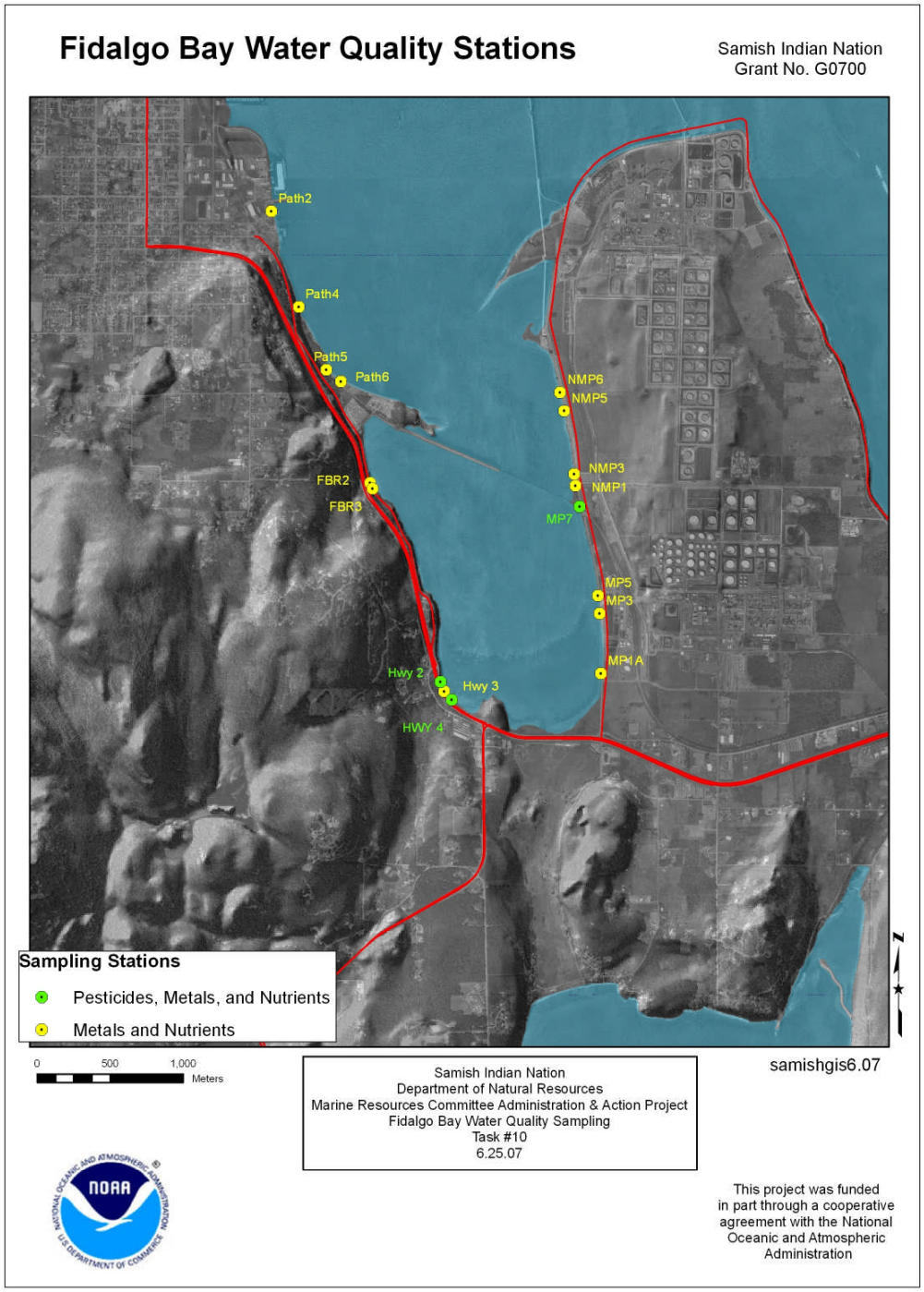
There was no detection in any of the sampling of copper or cadmium.
Zinc was detected the most frequent and in higher numbers than lead.

Metals are found naturally occurring in surface waters in minute quantities as a result of chemical weathering and soil leaching. However, concentrations greater than those occurring naturally can be toxic to human and aquatic organisms. Elevated levels are often indicative of industrial pollution, wastewater discharge, and urban runoff, especially from areas with high concentrations of automobiles. Because metals absorb readily to many sediment types, they may easily enter streams in areas with high

sediment runoff. Another source of heavy metals can be runoff from agricultural fields using sewage sludges as fertilizer**.**

Conclusion:
Thanks to funding from the Northwest Straights Commission, this ongoing project will hopefully be funded for two more years. At the conclusion of the entire three year project, there should be a better understanding about what is flowing into Fidalgo Bay through the outfalls as it relates to pesticides, nutrients and metals.

Figure 3 : Map of Sample Sites



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