

# **Contaminants in the Crescent Wetland, Orcas Island, and Comparison Sites**

Report to the San Juan County Land Bank



**Russel Barsh, Jack Bell, and Sam Barr**

Kwiáht (Center for the Historical Ecology of the Salish Sea), Lopez, WA

February 25, 2007

# **Contaminants in the Crescent Wetland, Orcas Island, and Comparison Sites: Report to the San Juan County Land Bank**

Russel Barsh, Jack Bell, and Sam Barr

## SUMMARY

A preliminary assessment of inorganic, bacterial and organic contaminants (PBTs or Persistent Bioaccumulative Toxics) was conducted on surface water in wetlands on the San Juan County Land Bank's Buck property at Crescent Beach, Eastsound, Orcas Island using standard colorimetric methods for the inorganic targets, and liquid chromatography (HPLC=High Performance Liquid Chromatography) for the organic targets.

The study area consists of two compartmentalized wetlands, one bearing surface runoff from Buck Mountain by way of the OPALCO office and maintenance facility and the other mainly influenced by surface runoff and storm sewer effluent from Orcas public school complex. Both wetlands originally terminated in a salt marsh protected by a long sand spit on East Sound, but are now impounded by Crescent Beach Road.

Following scoping exercises in April 2006 (14 surface water specimens from six upstream and downstream sampling sites) and July 2006 (12 surface water and sediment specimens from five sites), we made carefully controlled collections of water, sediments and sedge from four sites in the wetlands.

At least 270 ppb cadmium and 290 ppb copper were found at the upstream end of the east wetland, near the OPALCO facility, and at least 150 ppb cadmium and 120 ppb lead were found at the downstream end of the west wetland. Sources of metals could not be identified with any certainty. However, relatively acidic conditions in the upper east wetland suggest reduction of metal cations in surface water. Cadmium, copper and lead at these levels could adversely affect plants and animals—some species being much more sensitive than others, and some species actually tolerating and hyperaccumulating metals. Data from the Land Bank's Weeks Wetland property included for comparison purposes.

Inorganic nutrients (nitrates and phosphates) and fecal coliform bacteria, usually associated with human or animal waste, fertilizers and cleaning fluids, were only found in modest concentrations. Their distribution suggested the school, and homes along Terrill Beach Road as sources, but this cannot be confirmed. Further residential development in the area could eventually overwhelm the capacity of the wetlands to process nutrients.

We found no evidence of five priority organic contaminants (PBTs): PCBs, PCP, 2,4-D, chlordane, or creosote (=naphthalene, acenaphthene, phenanthrene). However, two as-yet unidentified organic compounds were found in specimens from the upstream side of Crescent Beach Road—perhaps oils used by the county to consolidate gravel roads.

A more precise survey of toxic metals in the wetlands is recommended, as well as seasonal monitoring of inorganic nutrients, and positive identification of the suspected road-sealant compounds. Crescent Beach is proposed for long-term monitoring of PAHs derived from creosote, which persist in sediments after treated wood has been removed.

# Contaminants in the Crescent Wetland, Orcas Island, and Comparison Sites: Report to the San Juan County Land Bank

Russel Barsh, Jack Bell, and Sam Barr

## TABLE OF CONTENTS

INTRODUCTION.....	1
SITE HISTORY AND HYDROLOGY.....	2
SAMPLING STRATEGY.....	3
COLORIMETRIC METHODS.....	4
COLORIMETRIC RESULTS.....	5
LIQUID CHROMATOGRAPHY METHODS.....	6
PREPARATION OF HPLC STANDARDS.....	6
PREPARATION OF HPLC SAMPLES.....	9
HPLC RESULTS.....	10
IMPLICATIONS.....	13
RECOMMENDATIONS.....	17
ANNEX	
MAP 1: CRESCENT WETLAND HYDROLOGY	
MAP 2: CRESCENT WETLAND SEEPS	
MAP 3: CRESCENT WETLAND SAMPLING SITES	
MAP 4: CRESCENT WETLAND CHEMISTRY	
TABLE A: NOVEMBER COLORIMETRIC DATA	
TABLE B: NOVEMBER MEAN/ADJUSTED DATA	
TABLE C: MEAN ERROR OF MEASUREMENT	
TABLE D: LIQUID CHROMATOGRAPHY DATA	
TABLE E: HPLC SPECIMEN INVENTORY	
TABLE F: WEEKS WETLAND COLORIMETRIC DATA	

# **Contaminants in the Crescent Wetland, Orcas Island, and Comparison Sites: Report to the San Juan County Land Bank**

Russel Barsh, Jack Bell, and Sam Barr

## INTRODUCTION

The San Juan Archipelago, comprising one-third of Puget Sound's total shoreline, is often perceived to be in a relatively pristine state. Little visual evidence remains of the canneries, mills and quarries that once thrived in San Juan County. Old fruit orchards are not associated in the public mind with the use of lead arsenate or chlordane as pesticides, commonplace until a generation ago. Nor are contemporary docks and roads appreciated as potential sources of PAHs or other highly toxic compounds in the county's freshwater and marine environments. There has been relatively little actual testing for contaminants in surface waters of San Juan County, other than for contaminants associated with septic system failure (nitrates, phosphate, fecal coliform bacteria).

Although the county requires broad-spectrum testing of new wells, contaminants in surface waters may also affect human health by entering the food system—for example through local fish and shellfish, and garden crops. It is not safe to assume that well water testing will disclose problems with surface water, since all surface waters do not recharge aquifers, and the process of infiltration removes some contaminants. This is particularly in the San Juan Islands where many wells draw on bedrock fissures and recharge rates are low. Under these circumstances, surface waters can be considerably more contaminated than well water.

At the same time, the county's wetlands have been promoted as crucial biofilters, removing contaminants from surface waters before they can adversely affect streams and marine habitats. This is an important consideration but it is also untested. While wetland plants may metabolize inorganic nutrients such as nitrates and phosphates, toxic metals and persistent bioaccumulative toxics (PBTs) are at best sequestered in sediments or plant tissues, from which they are eventually released back into the environment through plant decay and herbivory. Even in the case of nutrients, furthermore, a wetland's capacity can be overwhelmed.

The San Juan County Land Bank owns wetlands on the outskirts of urban areas on San Juan, Orcas, and Lopez Islands. Stewardship of the county's surface waters includes conserving urban wetlands, but also ensuring that wetlands are not contaminated in ways that may adversely affect wildlife or human health. As the uplands surrounding wetlands are developed, septic system effluent and road surface runoff will increase. Even if there were no historical sources of wetland contamination to consider, it is prudent to monitor wetland chemistry for possible toxic accumulation, and determine whether contaminants already sequestered in wetlands should be removed or left undisturbed.

The San Juan County Land Bank retained us to ascertain what contaminants may exist on the “Buck property” at Crescent Beach, Orcas, and to identify their likely origin. This site is significant because it borders a major population growth center (Eastsound), has some industrial history (OPALCO transformer yard), and drains directly into a very rich marine environment of eelgrass, sand dollars, and commercial oyster cultivation.

#### SITE HISTORY AND HYDROLOGY

The study site consists of two small wetlands divided by a low north-south ridge (Map 1). The west wetland receives surface runoff as well as storm sewer effluent from the Eastsound public school complex; and (through a storm sewer culvert under Market Drive) some of the town’s retail stores and parking lots. The east wetland receives runoff from Buck Mountain by way of the OPALCO maintenance yard and homes along Terrill Beach Road. Crescent Beach Road acts as a dam, blocking both drainages, so that during the winter water backs up on the north side of the road, and there may be some exchange of water between the east and west drainages.

The area immediately north of the road was historically a salt marsh—a brackish, tidally influenced mixing zone, protected by a low lying sand spit. Most of what remains today of the sand spit is covered with charcoal and bivalve shells from pre-Contact Coast Salish processing of shellfish from East Sound.

The west wetland includes (on San Juan Preservation Trust property) a bulrush-dominated marsh with standing water much of the year. This marsh drains to East Sound through a ditch on the west side of the kayak rental shop, where we have observed spring flows of 1-2 cubic feet per second. Water in the ditch is sometimes brackish in the range of 2-7 ppt, and it is likely that storm surges periodically throw salt water across Crescent Beach Road into the wetlands.

By comparison, the east wetland is seasonally a long, shallow sedge-filled slough that persists until early summer, and seeps out under Crescent Beach Road and the beach (Map 2); there is no channel or culvert.

The ridge was farmed, which implicates pesticides, herbicides, fertilizers, and the disposal of vehicles including motor oils and fuels, electrical equipment and batteries on the property over a period of more than 75 years. OPALCO has yarded transformers and other electrical equipment on the east wetland since 1938, implicating PCBs and battery metals such as copper and lead. Motor oils, motor fuels, and asphalt components may be introduced into both wetlands from parking lots and paved; whereas creosote constituents may wash into the wetlands on storm surges. On-site septic systems and household waste were not expected to be major inputs to the wetlands. The school grounds were predicted to be a potential source of nitrates, phosphates and lawn chemicals, however.

We initially installed piezometers at roughly 1m depth for comparison of surface and groundwater, but found very little infiltration below 25 cm: the Crescent wetlands are

shallow, consisting of very thin accumulations of clay-rich silts on old beach terraces. At the same time, the seasonal pools that form on the north side of Crescent Beach Road are likely to trap most waterborne sediment and those contaminants—metals and PBTs—that tend to adhere to fine particles of silt and clay.

## SAMPLING STRATEGY

Upstream and downstream sampling stations were identified in each wetland with a view to comparing inputs and outputs (Map 3). A storm sewer that drains much of the west portion of the town of Eastsound was included for comparison purposes (site 9, Map 3), and a saltwater sampling site (site 8, Map 3) was included specifically for monitoring creosote. Two sampling sites on the west wetland (sites 4 and 6) were wet in February 2006, but were unproductive when we collected specimens in April, July and November. There was little surface water in the upper west wetland (site 3) in November, so only the lower part of this wetland was sampled at that time.

Specimens collected in April were tested colorimetrically for a broad spectrum of possible inorganic contaminants, as well as fecal coliform bacteria, as a scoping exercise. The results, set out in our July 18 progress report, suggested a focus on metals rather than septic system byproducts such as inorganic nutrients and bacteria. Similarly, specimens collected in July were analyzed by HPLC (liquid chromatography) to explore the kinds of PBTs that might be present, so that we could purchase the standards necessary for further analysis.

November specimens were collected with particular care to avoid any possibility of bias or contamination. Specimens were collected in randomly numbered containers, and two separate samples were collected at each station. Sample identification numbers were not reconciled with station location information until all testing had been completed and recorded. The comparison of paired samples provided a basis for estimating errors of measurement. Two samples of distilled water were also randomly included in the testing queue as reagent blanks.

Water specimens for colorimetric analysis were collected in precleaned 250 ml glass jars with Nalgene lids. Each jar was washed three times in the waters to be sampled before the specimen was collected by immersion of the jar; except at site 2 where surface water was shallow and silty, and a disposable glass bulb pipette was used to draw water from the surface with a minimum of silt. Jars were immediately refrigerated to minimize biological or chemical activity.

Water, sediment and sedge specimens for HPLC analysis were collected in EPA certified contaminant-free 125 ml glass tubes with Nalgene caps. Water specimens were collected by immersion. Sediment was scooped from the top 1 m of the substrate with an aluminum spoon that was washed between uses. Sedge roots were pulled by hand.

## COLORIMETRIC METHODS

Colorimetry is the simplest and least expensive method of identifying metals and inorganic ions (*e.g.* phosphates, nitrates, sulfides) in water. A standard chemical reaction is used to produce a complex with the target that has a distinctive color. The colorimeter is a specially programmed spectrophotometer that measures the intensity of the resulting color and compares it with a pre-recorded standard absorption curve.

The relationship between absorption and concentration is logarithmic, not simply linear (Beer-Lambert's Law) and it breaks down at high concentrations; hence the analyst must use a standard reaction appropriate to the suspected range of concentrations of the samples to be analyzed. Some colorimetric tests are subject to interference effects from high concentrations of non-target ions, moreover. If cadmium and manganese are in the same sample, for instance, the result of the cadmium test will be somewhat inflated. The effect is not simply additive, however. This means that the analyst must measure all ions in the sample that may interfere with each other, before being able to determine, with any accuracy, the concentration of any of them.

For all of these reasons, it is important to establish the lower limit of detection and the range of potential instrument error (or precision) for each kind of colorimetric test by testing a number of reagent blank (double distilled water) and standard solutions (known concentrations) of the target analytes.

For this project we used a factory calibrated LaMotte Smart2 colorimeter and test solutions prepared and certified by LaMotte. The LaMotte Smart2 Colorimeter contains an LED emitter with filters at 430, 520, 570 and 620 nanometers (nm), and a photodiode detector with a nominal accuracy of 1 percent. Most contaminants surveyed here become health concerns in the range of 10 ppb (parts per billion) to 10 ppm (parts per million), all within the limits of reliability of colorimetry. Confirmation of results using spectroscopy, GC (gas chromatography) or for metals ICP (inductively coupled plasma spectroscopy) is advisable when precision of 0.01 ppm or greater is required. Standardized reactions used were as follows:

- Nitrate nitrogen: Cadmium reduction
- Phosphate: Ascorbic acid reduction
- Iron: 1,10-Phenanthroline
- Copper: Diethyldithiocarbamate
- Mercury: Thio-Mikler's ketone
- Lead: 4-[2'-Pyridylazo]-Resorcinol (PAR)
- Cadmium: 1-[2-Pyridylazo]-2-Naphthol (PAN)
- Manganese: 1-[2-Pyridylazo]-2-Naphthol (PAN)
- Chlorine: DPD Diethyl-p-phenylene diamine

Cuvettes and all other glassware coming into contact with samples was washed in RO water, 10 percent hydrochloric acid (to de-plate metals) and Milli-Q water before re-use to prevent cross-contamination. Pre-cleaned Nalgene transfer pipettes were disposed after each use.

Fecal coliform bacteria were counted by 24-hour culturing at 37° C on Coliscan dye-tagged growth medium, which distinguishes *Escheria coli* colonies (typical of human and animal fecal matter) from other bacteria. An Oakton electronic pH meter was used to measure acidity, and a simple refractometer to measure salinity.

## COLORIMETRIC RESULTS

Colorimetric results for November 2007 specimens are set out in Annex Table A. Mean results of paired specimens are show in Annex Table B(1), and adjusted minimum results in Annex Table B(2). Adjusted minimum results take account of measured limits of detection and variance between tests conducted on the same sample (instrument error or precision); they are conservative estimates of actual contaminant concentrations. Data used to compute error ranges for each kind of colorimetric test appear in Annex Table C.

Results can best be understood in geographical context (see Map 4):

West wetland: Both downstream stations (sites 1 and 7) showed some phosphate, iron, copper and lead. The ditch that drains the marsh was more acidic, however, and had significant levels of nitrate and cadmium. Since upstream source waters are the same for both sampling sites, differences presumably reflect conditions in the marsh, which could become a sink for metals and nutrients. Surplus nitrate suggests that nitrate inputs may have exceeded the capacity of the marsh to metabolize this nutrient; while cadmium may indicate oxygen poor conditions in the marsh substrate.

East wetland: The upstream samples (site 5) were very acidic and enriched with iron, copper and cadmium, suggesting low-oxygen conditions in the sedge slough. Some nitrate was found in the downstream samples (site 2), which were also somewhat alkaline and accordingly comparatively low in metals. Downstream nitrate may have downstream sources: residences along Terrill Beach Road. Organic inputs could explain the alkalinity of downstream water. This was the only sampling site where we observed any significant fecal coliform bacteria in April. Septic contamination of the downstream end of the east wetland may, by raising pH, reduce its accumulation of toxic metals.<sup>1</sup>

Water from two stations (sites 1 and 5) had a yellowish green hue, reflecting algal growth; all other samples were colorless. Otherwise, the water chemistry at these stations would seem quite different. The distribution of algae, especially diatoms, in the wetlands was not investigated, but insofar as algae are bioindicators, it would be worthy of study.

---

<sup>1</sup> J. Maloney. 1996. Influence of organic enrichment on the partitioning and bioavailability of cadmium in a microcosm study. *Marine Ecology Progress Series* 144: 147-161.

## LIQUID CHROMATOGRAPHY METHODS

High Performance Liquid Chromatography (HPLC) instrumentation was available for our use at the University of Washington's Friday Harbor Laboratories (FHL) although gas chromatography with mass spectrometry (GC/MS) is the preferred method for PCBs and other organics and is recommended for further studies. For the polynuclear aromatic hydrocarbons (PAHs), EPA methods 610 (2 and 3) and 8310 (4) specify use of an HPLC with an ultraviolet-visible (UV-Vis) light absorbance detector in series with a highly sensitive fluorescence detector. The HPLC at FHL has a UV-Vis detector appropriate for a survey of only those organics that absorb light in that range of the light spectrum. For a comprehensive survey and unambiguous identification of all PAHs, both fluorescence and mass spectrometry detectors are required.

The HPLC at FHL is an ISCO 2360 ternary gradient programmer, 2350 pump, V4 UV-Vis variable wavelength detector and built-in strip chart recorder. The Rheodyne 7725i injector, with 1 mL sample loop, is back-filled with 10 uL of sample using a 100-uL syringe. The reverse phase HPLC column was manufactured by Varian model Micro-Pak SP C18-5. Its dimensions are 4 mm internal diameter by 150 mm in length. The column packing is a standard C-18 phase covalently bonded to 5-micron spherical silica gel particles. The column was operated at ambient temperature. The HPLC mobile phase solvents were deionized, organic-free water from the Milli-Q filter system at FHL and HPLC grade acetonitrile from Baker, Inc. The isocratic (constant strength) mobile phase is composed of 30% water and 70% acetonitrile pumped at a flow rate of 1mL/minute, generating a back pressure of up to 3000 psi. Because the solvents are not degassed before use, a backpressure regulator is used to prevent bubbles in the detector flow cell. The detector's wavelength is set at a UV wavelength of 254 nm and maximum sensitivity of 0.002 absorbance units full scale (aufs) for detection of organics in samples.

The principles behind HPLC are actually quite simple. Organic compounds vary greatly in size and weight. When forced through a silica gel column under pressure, the smaller and lighter molecules travel faster than the heavier molecules. Retention time in the column is therefore a relative measure of molecular size; and UV-Vis absorbance tells us something about the chemical structure and concentration of each kind of molecule as it emerges from the column and passes the detector. By comparison, a mass spectrometer takes molecules already sorted by weight, and weighs their constituent atoms, producing a precise molecular formula.

## PREPARATION OF HPLC STANDARDS

HPLC analysis proceeds by comparing the retention-time and absorbance profile of the sample with "standards" acquired from a reliable source. HPLC standards must be pure—or as close to pure as can be manufactured. We identified a set of standards most likely to be useful in view of the local history of farming and transformer storage, and the proximity of roads, docks, and creosote pilings:

- Naphthalene, acenaphthene and phenanthrene: Of the 13 polynuclear aromatic hydrocarbons (PAHs) assessed by the EPA as “priority pollutants” in creosotes, these three were chosen as more volatile and soluble early markers.<sup>2</sup>
- Pentachlorophenol (PCP): Fungicide and persistent endocrine disrupting chemical restricted in the US to preserving utility poles, railroad ties, and wharf pilings.
- 2,4-dichlorophenoxyacetic acid (2,4-D): A systemic herbicide and plant growth regulator, 2,4-D is in Ace Lawn Food with Weed Control, for example. 2,4-D is a suspected endocrine disruptor.
- Alpha-chlordane: Unregulated but widely banned termite pesticide, cholinesterase inhibitor (nerve poison), probable carcinogen, and suspected endocrine disruptor.
- Polychlorinated biphenyls (PCBs): Banned in 1977 as suspected carcinogens and endocrine disruptors, but may still be found in insulating oils in capacitors and transformers. We used Arochlor 1260, one of several Arochlor mixtures, each of them a dozen or more congeners amounting to hundreds of individual chemicals contaminating the environment.

All chemical standards were obtained from Supelco, Inc, except for naphthalene, acenaphthene and phenanthrene, which were from the stockroom at FHL. The standards are used as a reference point for calculations and for quality control of the HPLC process. If a chromatographic peak in a sample has the same elution retention time (co-elution) as a peak in a standard solution, then the sample may provisionally be considered to contain that analyte, until confirmed by mass spectrometry. If a sample peak does not match the retention times of the available standards, or the sample does not display any of the peaks of the standard, those analytes can be eliminated from consideration with a high level of certainty, at or above the limit of detection (LOD) of the method. Use of a method with a lower LOD may detect these analytes. We determined if a peak was significant by using the lower limit of detection (LOD) definition of three times baseline noise, which is three times the size of the baseline. If a peak is equal to or greater than this, then it represents the analyte. Short-term baseline noise is typically a chart distance of 1 mm peak-to-peak at full sensitivity 0.002 aufs. Therefore, peaks greater than 3 mm in height are considered significant and above the instrumental LOD for our method.

The procedures used for preparing standard solutions and using them to calibrate the instrument are illustrated for our three PAHs:

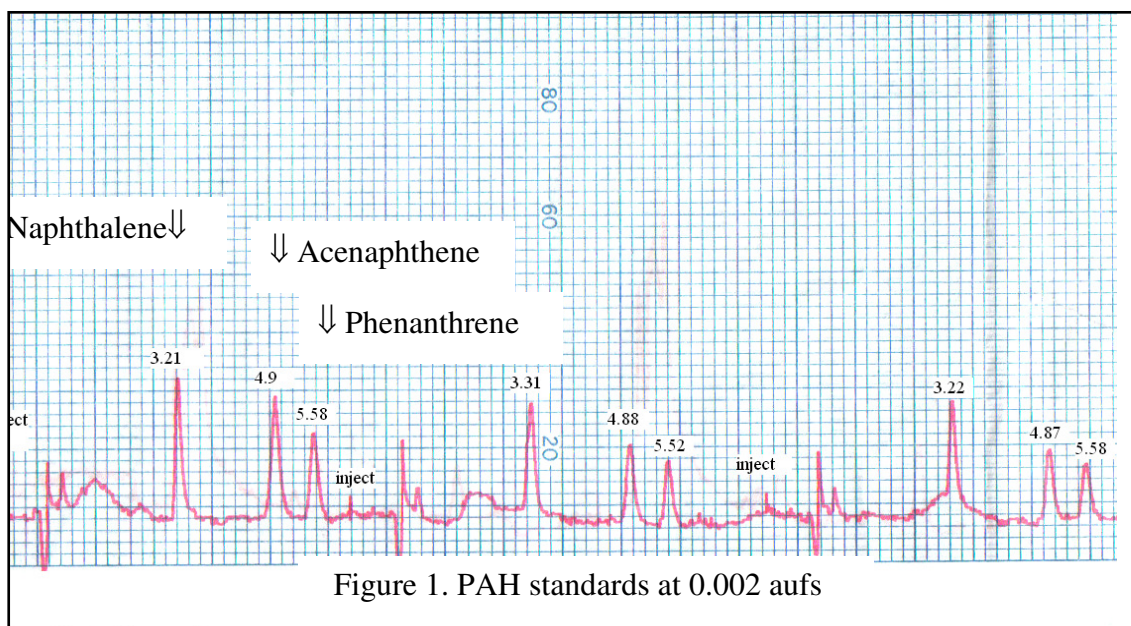
- Naphthalene stock: 0.01 M molar naphthalene (12.8 mg of naphthalene dissolved in 10 mL of methanol).
- Acenaphthene stock: 0.01 M of acenaphthene (15.4 mg of acenaphthene dissolved in 10 mL of methanol).

---

<sup>2</sup> "Method 610 - Polynuclear Aromatic Hydrocarbons," in Appendix A to Part 136, "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater," EPA 600/4-82-025, National Technical Information Service, PB82-258799, Springfield, Virginia 22161, June 1982; "EPA Method Validation Study 20, Method 610 - PNA's," EPA 600/S4-84-063, National Technical Information Service, PB84-211614, Springfield, Virginia, 22161, August 1984.

- Phenanthrene stock: 0.01 M of phenanthrene (17.8 mg of phenanthrene dissolved in 10 mL of methanol).

Two serial dilutions in acetonitrile were made to afford a working standard of the three PAHs at final concentrations of  $5 \times 10^{-6}$  M naphthalene,  $5 \times 10^{-6}$  M acenaphthene, and  $5 \times 10^{-7}$  M phenanthrene, respectively. The phenanthrene standard was adjusted to a lower concentration so that its peak height is similar to the others. Figure 1 shows three replicate chromatography runs of the standard mixture at the highest sensitivity.



The Response Factor (RF) is the ratio of peak height to nanograms of standard injected. We use the average of three calibration runs to calculate RFs using naphthalene as an example. A 10- $\mu$ L injection of  $5 \times 10^{-6}$  M naphthalene produces a peak height of 18 mm as measured on the chromatogram (above). The mass of naphthalene injected “on column” is calculated from its molarity as follows:  $5 \times 10^{-6}$   $\mu$ moles/ $\mu$ L  $\times$  10 $\mu$ L =  $5 \times 10^{-5}$   $\mu$ moles of naphthalene, and  $5 \times 10^{-5}$   $\mu$ moles  $\times$  128.2  $\mu$ grams/ $\mu$ moles = 0.00641  $\mu$ grams or 6.41 ng of naphthalene on-column. Naphthalene’s peak height RF is 18 mm/6.41 ng or 2.8 mm/ng. The instrumental LOD for naphthalene is 3mm  $\div$  2.8 mm/ng = 1.1 ng on column. These results are summarized in Figure 2, rounded to an appropriate number of significant figures:

Figure 2. Summary of calibration results for the three PAH's

PAH	Response Factor (RF) Peak height/mass	Instrumental Limit of Detection (instrument LOD)
Naphthalene	2.8 mm/ng	1.1 ng on column
Acenaphthene	1.2 mm/ng	2.6 ng on column
Phenanthrene	7.9 mm/ng	0.4 ng on column

## PREPARATION OF HPLC SAMPLES

Sediments, surface water suspensions and plant materials were extracted with acetonitrile, a solvent in which the standards are known to be highly soluble. Nine mL of acetonitrile is added to one gram of sample in a 20 mL glass vial, sealed with a screw cap lined with an acetonitrile-resistant plastic. This constitutes a 1/10 dilution of the sample. The vial is vigorously shaken and intermittently heated for 20-30 minutes in a water bath at 50-55 °C. The warm suspension is filtered through an HPLC grade, PTFE 0.2-micron filter (Acrodisc, 25 mm diameter) fitted on a 10 mL glass syringe and pre-wetted with acetonitrile. Surface water samples are filtered without dilution. Filtrates are stored at 4 °C in the same type of 20 mL vials as used in the extraction.

The following protocols were observed to avoid cross contamination of standards and samples: All vials and their caps are clearly labeled. A separate injector syringe was used for the standard solution to avoid any false positives from standard solution residues left in the syringe when injecting the sample. The syringe used for injecting samples was thoroughly flushed with acetonitrile between injections. Any glassware in contact with samples and standards, such as vials, pipettes and beakers, was first scrubbed in detergent and hot water if surface residues or grease are apparent, then rinsed three times each with 90% acetone, Milli Q grade water and HPLC grade acetonitrile, respectively, and allowed to drain and dry on fresh paper towels. To minimize contamination of stock solvents and solutions, small amounts are used in 20 mL glass vials, and they are routinely checked for contaminants by HPLC analysis. For example, at the highest sensitivity of 0.002 aufs, no peaks are observed at the retention times of our three target PAHs, as shown in Figure 3. An acetonitrile blank from the working vial was injected before and after each sample to ensure a “clean baseline”.

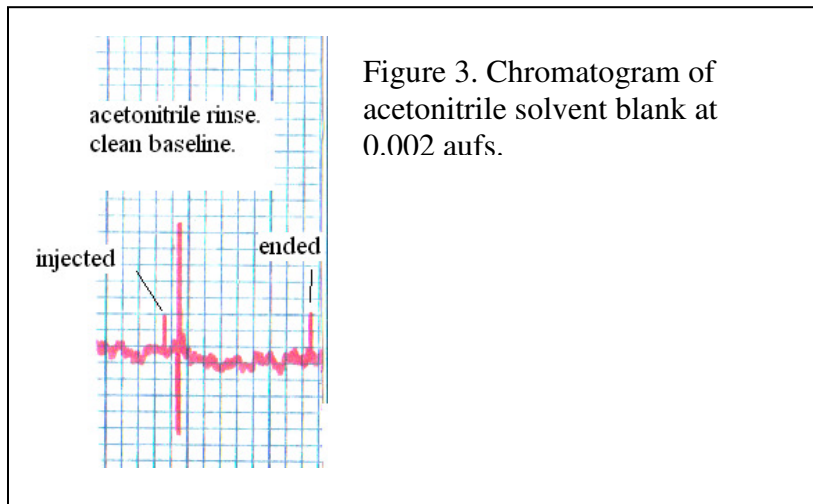
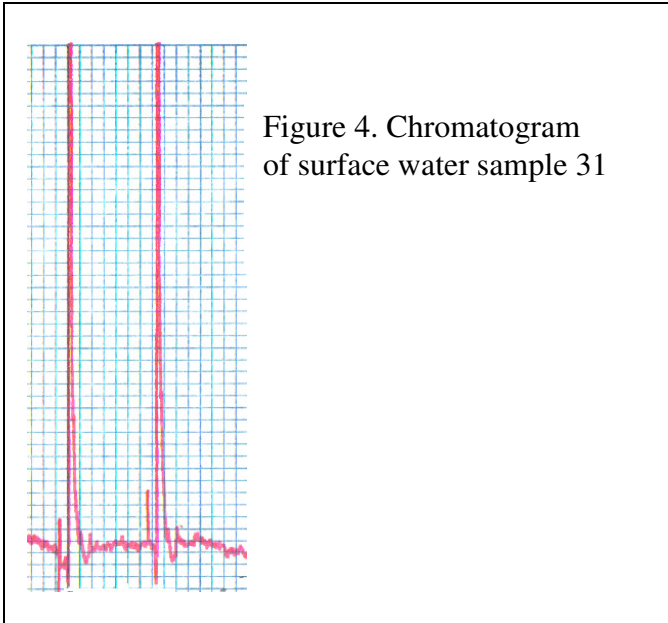


Figure 3. Chromatogram of acetonitrile solvent blank at 0.002 aufs.

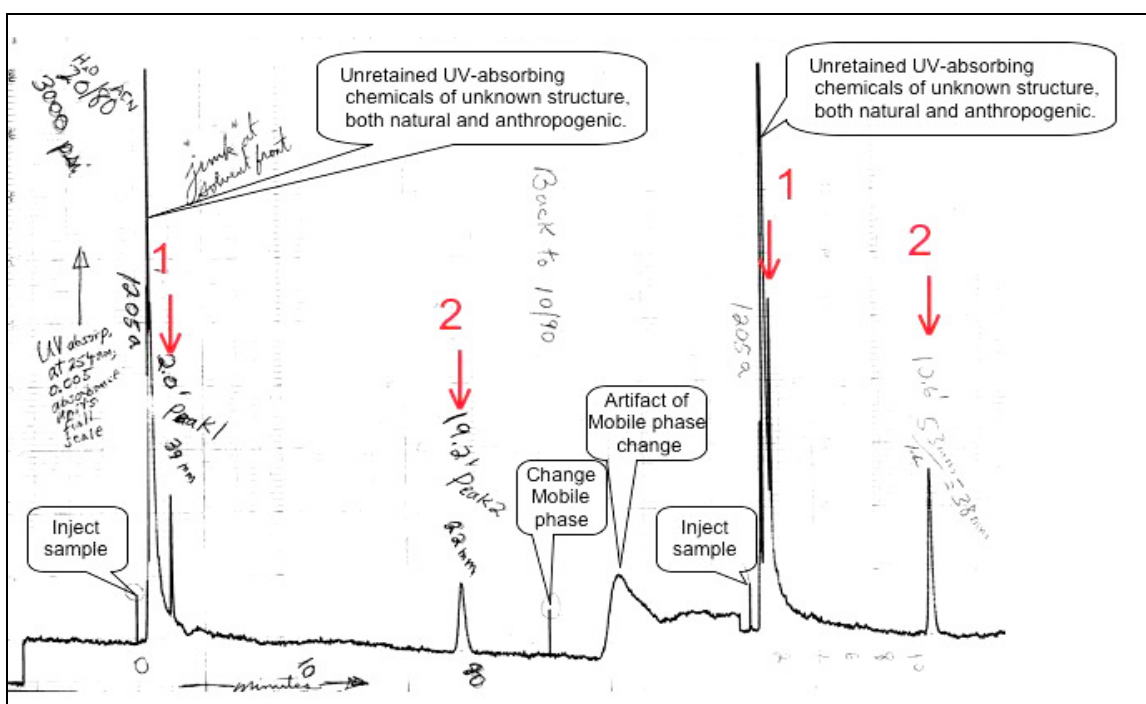
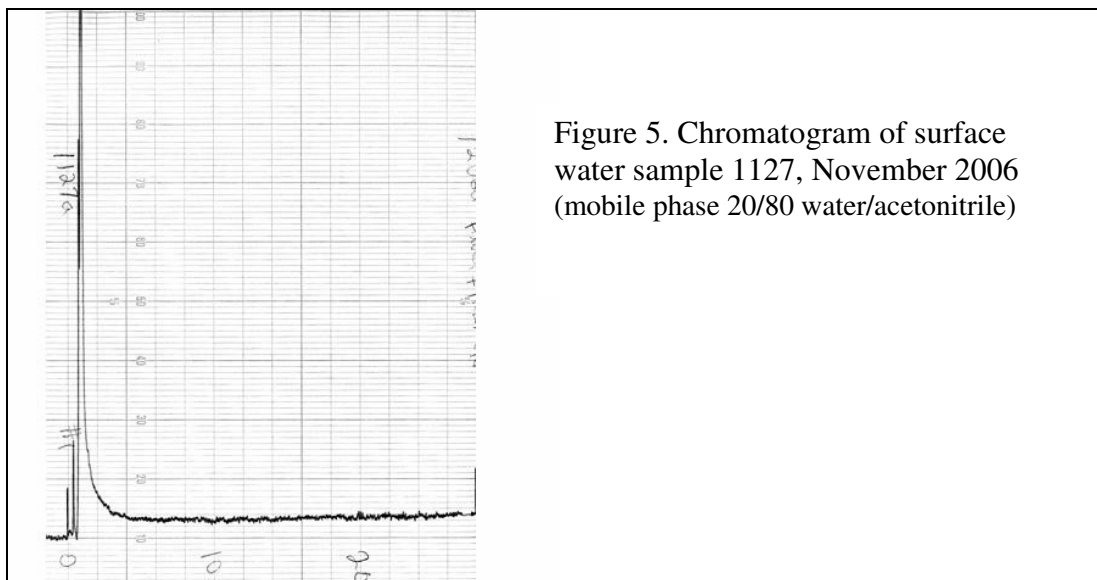
## HPLC RESULTS

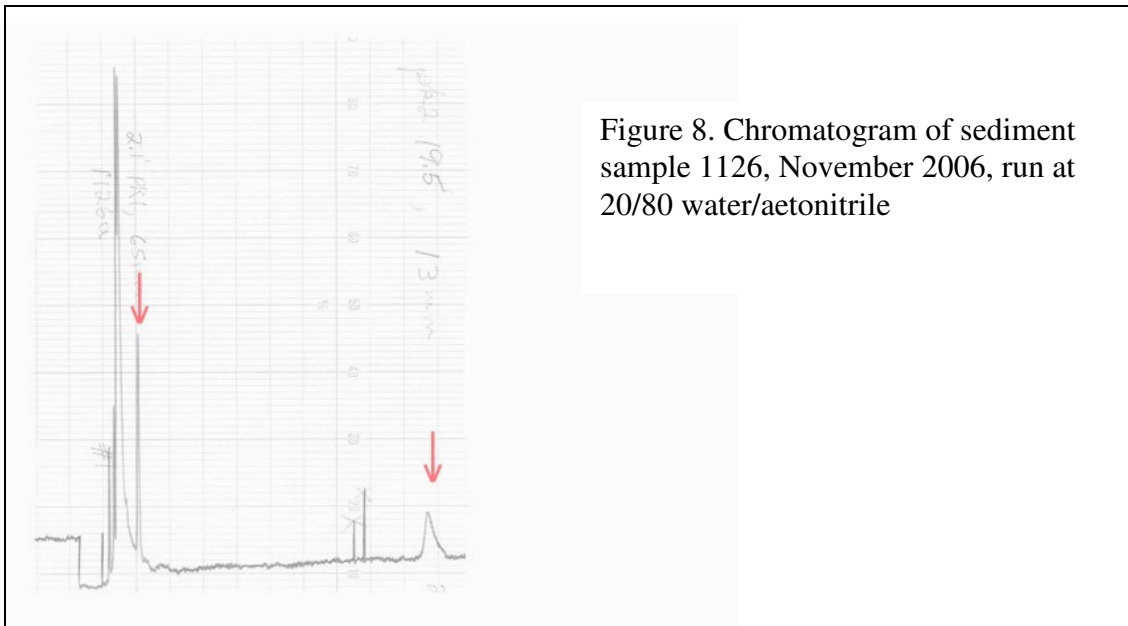
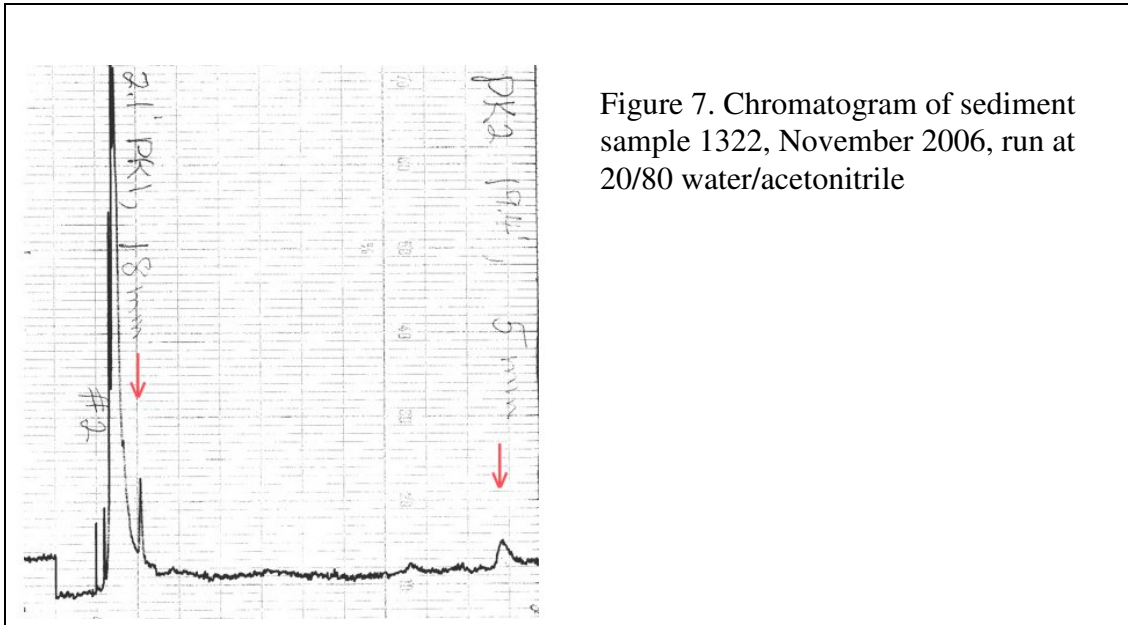
Chromatograms of two HPLC runs of surface water sample 31 (site 8) are shown in Figure 4 to illustrate what we find for all of the Crescent Beach wetland samples: there are no discernable peaks where the three PAHs elute, only the random noise of a clean baseline and the ubiquitous, early eluting peak of unknown UV-absorbing compounds. Based on our instrument's limit of detection and the 10-fold dilution of sediment extracts, we conservatively suggest at this time that we do not detect the three PAHs down to a level of approximately 1 µg/g of sediment, and 0.1 µg/mL of surface water (0.1 ppm). State-of-the-art methods developed by the EPA and NOAA can detect PAHs well below these levels. However, in comparing our results to those in an NOAA report of PAH levels found in various locations in central Puget Sound,<sup>3</sup> our initial survey suggests that the Crescent Beach wetlands are not contaminated with the three creosote-related PAHs that we studied.



We collected a second set of samples in November from the same sites. Again, we did not find the three target PAHs at our instrument's limit of detection in the samples tested: sediment and surface water from site 1 (lower west wetland, samples 1126, 1127), and sediments and surface water from site 2 (lower east wetland, samples 1205, 1322 and 1206). However, we detected two chromatographic peaks in the sediments not matching any of the standards we had prepared (Peaks 1 and 2 in Figures 6, 7, and 8; Annex Table D). They are in trace amounts, but of unknown structure and amount until appropriate standards are found and mass spectra of collected peaks are obtained.

<sup>3</sup> "Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound." In NOAA Technical Memorandum OMPA-2 1556 .E87, 1982.





The two unknown peaks 1 and 2 may well be components of oils/tars applied to Crescent Beach Road to bind the constituent gravels. They appear consistently in waters and sediments adjacent to the road.

## IMPLICATIONS

Despite the exploratory nature and limited sampling period of the present study, it has a number of implications for protection of the Buck property, and the aquatic wildlife within the wetlands, and immediately downstream of the property in East Sound.

### Nutrients

Meaningful assessment of nutrient loads is difficult without very frequent testing. Inputs can be sporadic: application of fertilizer to a large lawn; overflow of a septic tank; a flock of geese feeding in a meadow for several days. Persistent high nutrient loads are generally only observed around large animal populations lacking waste management e.g. feed lots or similar sedentary livestock operations, and human residential clusters without effective sewage treatment or on-site septic systems. In other environments there may be significant pulses of nutrients from various sources, but dilution and uptake by plants will extinguish the signal within days to weeks.

Preliminary sampling and testing carried out in April 2006 found modest levels of nitrates and phosphates in the wetlands and the comparison site near the Outlook Inn (site 9). A large spike in nitrates was observed a few days after the school mowed and treated the playfields; it persisted for a week.

Lower results for nitrates and phosphates in November may result from dilution—April was relatively dry but there was heavy rainfall preceding the November sampling—or because of reduced lawn maintenance activity at the school, which was the most likely source of the nutrient loads observed in April. In any event, the nutrient levels observed in the Crescent wetlands were low compared to well-fertilized residential lawns, farms, or pastures, and well below levels of concern. It is not possible to estimate, from our data, how much this is due to low inputs of nutrients, and how much is due to the metabolism of nutrients by wetland plants.

Changes in grounds maintenance practices at the school complex could increase nutrient inputs to the west wetland. Growth in high-maintenance residential lawns along the surrounding roads could also increase nutrient loads significantly.

### Fecal bacteria and chlorine

Fecal coliform bacteria (FECs) such as *Escheria coli* are common human gut flora and are generally not dangerous themselves, but are widely used as an indicator of septic system leakage. FECs can survive for days to weeks in fresh water, but die within hours of introduction to saltwater. Standardized culture-plate tests for FECs cannot completely distinguish between the species that inhabit human, bovine, ovine or avian gut, therefore depending upon local land use patterns, high FEC results may represent livestock or bird flocks as well as failing septic systems.

No significant FECs were found in the April samples and we did not test again for FECs in November. The highest result (5/ml) came from site 2, at the downstream end of the east wetland, where it could conceivably represent some septic leakage from the older homes along Terrill Beach Road. Unless a large number of septic systems are installed in future around the wetlands, FECs are unlikely to reach levels of concern, and monitoring FECs should be unnecessary.

Free chlorine is almost always anthropogenic i.e. from water purification systems. Chlorine evaporates quickly from chlorinated water released into the environment. Only high levels of chlorination in large quantities of effluent result in measurable chlorine and environmental impacts. Low but reliably measurable levels of chlorine were found in the east and west wetlands in April, but chlorine was barely measurable in November. These results may reflect dilution, November having seen considerably more precipitation than April. It may also reflect heavier use of chlorine in residential water systems during the warmer months when bacteria and algae grow faster.

The main input of chlorinated water to the wetlands would appear to be the public school complex, which maintains extensive landscaped playfields. We did not determine whether chlorinated water is used to water the school grounds, but this would be a matter the Land Bank may wish to discuss with school officials. Chlorinated water is ordinarily inappropriate for discharge into wetlands, because it can be lethal to the native algae and protists that form the base of wetland food webs—and process most of the nutrients that enter the wetland. Chlorine interferes with wetlands' role as biofilters.

#### Potentially toxic metals

Preliminary sampling and testing in April 2006 suggested that metals were a more serious concern than nutrients. More careful, multiple sampling and testing in November and December confirmed relatively high levels of iron, copper and cadmium just south of OPALCO in the east wetland (site 5, Map 3), and measurable levels of lead and cadmium in the drainage ditch at the bottom of the west wetland (site 7, Map 3).

High iron concentrations may be expected in wetlands as a function of acidity. In November, surface water from all but one of our sampling stations was somewhat (Annex Table C). The OPALCO sampling site was the most acidic, with a mean pH of 5.26, and that is where the highest levels of iron were found.

Acidity is a dynamic process in wetlands. Precipitation is slightly acidic, more or less depending on atmospheric chemistry. Even “pure” rainfall is acidic due to dissolved carbon dioxide, forming carbonic acid. As rainwater infiltrates soils, biological processes and dissolved minerals tend to increase its pH towards neutrality (pH=7.0) or even to the point of becoming moderately alkaline (pH=7.1-7.8). The buffering capacity of wetlands is considerable, but not inexhaustible.

In deep standing water and waterlogged soils, lack of oxygen (anoxic conditions) can result in a *reducing* environment in which ferrous iron, manganese, copper, cadmium,

and other metals tend to leave solution and accumulate in the substrate. The reduction of these metals results in acidification. Persistent acidity in a wetland may promote an acid-tolerant plant community such as sphagnum moss. More often, it reduces plant diversity and overall primary productivity.

Moderate acidity in the range we observed at Crescent is not, by itself, a concern. Rather, it is indicative of a redox environment in which sediments are likely to continue to be enriched with whatever metals are present as cations in surface waters. Local metal sources may include exposed bedrock, minerals in glacial drift deposits, and metal waste, such as abandoned automobiles and farm machinery.

Animals and plants can tolerate relatively high concentrations of iron, and the iron results reported here fall below the levels at which there would be a concern for human or animal health—although they are great enough to affect the taste of water. Cadmium, by comparison, is highly toxic and bioaccumulative.<sup>4</sup> The L<sub>50</sub> level for cadmium in shiner perch is 1100 ppb; for purple sea urchins 500 ppb, and for copepods, an important prey item for juvenile salmon and other fish, as little as 50 ppb,<sup>5</sup> which is less than the cadmium concentration reported here for the OPALCO site. Current EPA National Primary Drinking Water Regulations recommend no more than 5 ppb cadmium in potable water supplies.<sup>6</sup>

Modest concentrations of copper were also observed near the OPALCO facilities. Copper is highly toxic to aquatic organisms. EPA recommends action at 1.3 ppm, about four times the level we observed.<sup>7</sup>

Traces of lead were found in the drainage ditch at the downstream end of the west wetland (site 7). Lead is highly toxic but generally not bioaccumulative. Recommended level zero, action level 15 ppb.<sup>8</sup> We observed 120 ppb at Kayak. Lead-based paints and discarded automobile batteries are common sources of lead in the environment; lead also enters the environment from motor fuels. Its source can be geological, but the absence of detectable lead in samples from other parts of the study area suggests a localized source.

Some potentially toxic metals are removed periodically from water and sediments by plants or fungi (sequestration). Copper is a constituent of chlorophyll, although more than trace levels of copper are toxic to many aquatic and terrestrial plants. Some species

---

<sup>4</sup> For current knowledge and references relating to toxic metals see U.S. Environmental Protection Agency, Ecological Risk Assessment, <http://www.epa.gov/region5/superfund/ecology/html/toxprofiles.htm#cd>.

<sup>5</sup> L<sub>50</sub> refers to the dose that is lethal to 50 percent of the target organism in experimental studies, and is a common means of expressing toxicity in environmental health research. For L<sub>50</sub> data on cadmium, see INCHEM, International Programme on Chemical Safety, Environmental Health Criteria 135: Cadmium-Environmental Aspects, <http://www.inchem.org/documents/ehc/ehc/ehc135.htm#SubSectionNumber:6.2.1>.

<sup>6</sup> Current standards may be found at U.S. Environmental Protection Agency, Ground Water and Drinking Water, [http://www.epa.gov/safewater/contaminants/dw\\_contamfs/cadmium.html](http://www.epa.gov/safewater/contaminants/dw_contamfs/cadmium.html).

<sup>7</sup> Ibid. <http://www.epa.gov/safewater/dwh/c-ioc/copper.html>.

<sup>8</sup> Ibid. <http://www.epa.gov/safewater/dwh/c-ioc/lead.html>.

of plants and fungi actively accumulate cadmium. We did not observe any known hyper-accumulators in the study area, but only careful analysis of cadmium levels in local plant communities can rule out the possibility of previously undocumented hyper-accumulator species in our area. When hyper-accumulators die and decay, they return metals to water and substrates; or if consumed by animals, they facilitate bioaccumulation in the trophic web. It can be useful to identify hyper-accumulators and develop a plan for periodically harvesting and safely disposing of them.

It is tempting to attribute the toxic metals at site 5 to the OPALCO maintenance yard, just a short distance upstream. It may indeed be a source. However, we have found comparable concentrations of cadmium in other San Juan County wetlands, including the Beaverton Valley marsh on San Juan Island and Weeks Wetland on Lopez. This suggests a geological source. Carbon-rich shales (mudstones) deposited in reducing environments have been shown to be enriched in cadmium,<sup>9</sup> and such rocks do form part of the exposed bedrock geology of the San Juan Islands.<sup>10</sup> A recent U.S. Geological Survey study found very high concentrations of cadmium (1-2 ppm) in some San Juan County bays,<sup>11</sup> which is consistent with widespread cadmium concentrations of c.200 ppb in surface waters of the county. The possibility of pervasive bedrock-derived cadmium in San Juan County fresh water systems deserves further investigation. Continued monitoring of cadmium on Land Bank property would contribute to this effort.

### Organic contaminants (PBTs)

This study focused on a small fraction of the manufactured chemicals that could be present in the Crescent wetland. The reason for this is economy; testing for hundreds of compounds would be prohibitively time-consuming and expensive. Priorities were set by (1) determining from historical records which compounds are most likely to be found in detectable concentrations at the study site; (2) selecting a representative cross-section of “likely” compounds that are also especially toxic, persistent, and bioaccumulative.

Organic contaminants vary greatly in their volatility, solubility and stability in the environment. Some, like the phenolic constituents of creosote, are volatile and evaporate quickly, which dilutes them but disperses them widely. Others are relatively stable and insoluble, and tend to adsorb to silt and clay particles; they may eventually be entombed in sediments. Most are at least weakly soluble, however. The various PAHs in creosote vary greatly in solubility, from smaller molecules that completely dissolve in seawater in a matter of weeks to months, to larger molecules that leave residues in pilings and around them for years.<sup>12</sup> Others decompose rapidly. Soil bacteria quickly metabolize glyphosate

---

<sup>9</sup> H.-J. Brumsack. 2005. The trace metal content of recent organic carbon-rich sediments: Implications for Cretaceous black shale formation. *Palaeogeography, Palaeoclimatology, Palaeoecology* 232: 344-361.

<sup>10</sup> M.T. Brandon, D.S. Cowan, and J.A. Vance. 1988. *The Late Cretaceous San Juan Thrust System, San Juan Islands, Washington*. Geological Society of America, Special Paper No. 221. Boulder, CO.

<sup>11</sup> R.K. Takesui, E.E. Grossman, S. Wyllie-Echeverria, and J.K. Elliott. 2006. High cadmium may contribute to eelgrass (*Zostera marina*) habitat loss in Westcott Bay, San Juan Island. ASLO, Victoria, BC, June 2006. Also R. Takesui, personal communication, January 2007.

(Roundup), for example, while dioxins such as 2,3,7,8-TDD can still be identified in lake sediments a century after their discharge by wood-processing mills.

We found none of our five target PBTs in surface waters or sediments of the Buck property. However, we found evidence of two as-yet unidentified organic compounds in samples taken along the north (upstream) side of Crescent Beach Road, which we suspect are related to the tars/oils used by the county to seal gravel roads. Until these compounds are identified, we cannot say whether they pose any threat to aquatic plants or wildlife. It would be prudent for the Land Bank to obtain complete specifications of the road sealant currently in use by the county. It would also seem prudent to characterize the two peaks in our chromatograms by running the relevant specimens on GC/MS, and comparing the results with the reported composition of the road sealant.

It would also be prudent to ascertain whether beach sediments contain creosote-related PAHs of higher molecular mass and lower volatility than the three PAHs that we targeted for the present study; if not a complete analysis of all 13 PAH priority pollutants as required by EPA methods 610 and 8310. It is unknown whether creosote constituents are accumulating or dissipating in any San Juan County beaches. Such data will become increasingly germane as more creosote-treated driftwood is removed from beaches. How much of a reduction can be expected in toxic exposure of marine organisms such as oysters and crustaceans? To what extent are creosote pilings continuing to add toxic loads to the beaches from which drift logs have been removed? At present, no beaches are monitored for trends in actual creosote concentrations or toxicity.

## RECOMMENDATIONS

Elevated levels of cadmium, copper and lead, while they may be due to geological sources, are a concern for ecosystem structure and health. If we are correct in attributing observed concentrations of these metals to low-oxygen reducing environments in parts of the wetlands, it is likely that other toxic metals are present that we did not test for, such as chromium, cobalt, nickel, and zinc; or that we tested at relatively high levels of detection, such as mercury and arsenic.

1. We recommend a survey of surface water and sediment from the two wetlands for a broader range of metal cations using a higher-sensitivity method (Atomic Absorption Spectrophotometry, or AA): twelve paired samples should suffice.
2. If elevated toxic metal loads are confirmed, further sampling of plants, fungi, and animals in the two wetlands should be considered to identify accumulator species, and ascertain if metals are likely to enter the human food system.

Although nutrient levels and FECs were low, suggesting a combination of low inputs and healthy wetland functioning, it should be borne in mind that East Sound is a

---

<sup>12</sup> Most bioaccumulative compounds are at least somewhat lipophilic (fat-soluble) and well as hydrophilic (water-soluble), and are most concentrated in the fatty tissues and livers of animals that consume them.

very shallow basin with strong summer stratification (poor vertical mixing of the water column).<sup>13</sup> Nutrient inputs from the Land Bank property to the bay will consequently tend to remain close to the shore—and the oyster farm—during the warmest months, an important reason for continuing to monitor nutrient levels and intervening if significant new inputs of nutrients are detected. Elevated nutrient levels can be good for oysters—but at very high levels, nutrients promote flushes of algae that reduce dissolved oxygen as well as toxic algae (dinoflagellates).

3. We recommend seasonal monitoring of nutrient levels in the lower wetlands (spring, summer, and fall) as well as monitoring of surfactants and caffeine as more reliable indicators of household/septic inputs than coliform bacteria.<sup>14</sup>

There remains much to be learned about PBTs in San Juan County wetlands, and the Crescent Beach wetlands in particular. County roads follow shorelines and cut across wetlands throughout the islands, thus the possibility of contamination by road sealants is of broad significance. We are not aware of local research on this issue. Similarly, we are unable to find any relevant local research on the residence time of different creosote PAH constituents in beaches and nearshore sediments—a question that could be addressed by establishing a long-term monitoring site such as Crescent Beach

4. It would be prudent to identify the organic compounds that we found in lower wetlands, to determine if they are indeed associated with county road sealants, and to ascertain whether they pose any threat to wetland ecosystems.
5. Crescent Beach offers an exceptional opportunity for long-term monitoring of the accumulation and dissipation of toxic creosote components, at a time when creosote-treated drift logs are being removed from island beaches.

Although this preliminary study found no unequivocal threats to human, animal or environmental health in surface waters of the Buck property at Crescent Beach, we could not test and exclude all possibilities, particularly with respect to PBTs. At the same time, our study points to potential issues with metals that could bear on future commercial and recreational use of Crescent Beach tidelands, and recommends further study to assess the nature and extent of elevated metal loads to a higher degree of precision and reliability—and explore remedial options as appropriate. We recommend that the Land Bank take no public position on the environmental quality of the wetlands pending the results of further research; but engage businesses and landowners surrounding the wetlands with a view to sharing responsibility for future monitoring and management of local surface waters.

---

<sup>13</sup> Bradford Jensen, Western Washington University, personal communication. Jensen monitored marine nutrients, salinity and temperatures off Madrona Point throughout 2005.

<sup>14</sup> Coliforms are less persistent than surfactants or caffeine in the environment: they are preyed on by other microorganisms, require nutrients, can be filtered out of chemically contaminated effluent (they are vastly larger than molecules), and die quickly if exposed to salt water.