CAPPING OF CREOSOTE CONTAMINATED SEDIMENT PROTECTS AQUATIC HABITAT IN THE FRASER RIVER, VANCOUVER, BC.

Reidar Zapf-Gilje, University of British Columbia and Golder Associates Ltd., Vancouver, BC, Canada
Gerry O'Hara, Golder Associates Ltd., Vancouver, BC, Canada
Mike Rankin, Golder Associates Ltd., Vancouver, BC, Canada

ABSTRACT
Historical use of coal tar and creosote on waterfront sites has led to widespread contamination of adjacent waterbodies and sediment. A site which used coal tar for manufacturing of roofing tiles and tar paper has been the subject of several phases of investigation and remediation design and implementation over a four year period. Leaks and spills from site activities had resulted in significant soil contamination. Dissolved and free-phase creosote (DNAPL) had migrated from the source to the adjacent Fraser River causing sediment contamination. Upland and foreshore remediation included removal of near surface soil and sediment resulting in a contamination mass reduction of 60%; and hydraulic control of dissolved and free-phase creosote contamination from the remaining deep contamination through pumping from on-site wells. Contaminated subtidal sediment was covered with a permeable riprap cap, based on the results of an aquatic risk assessment, which involved a physiologically based toxicokinetic (PBTK) model for estimation of uptake and depuration of PAH by starry flounder, and several bioassays. Semi-permeable membrane devices (SPMDs) were used to assess the performance of the remedial measures.

RESUME
L'utilisation historique du créosote et des composés bitumineux dans des sites côtiers a résulté dans la contamination des cours d'eau adjacents et des sédiments. Un site industriel utilisant des composés bitumineux pour la production des tuiles a été le sujet de recherches réalisées en plusieurs étapes dont la restauration implantée sur un période de quatre ans. Des fuites et des déversements ont contaminé significativement les sols. Du créosote dissout et en phase libre (DNAPL) a migré de la source vers la rivière Fraser adjacente au site causant la contamination des sédiments. La restauration des terrains en rive ont inclut l'extraction des sols superficiels diminuant ainsi la contamination de 60%. Un contrôle hydraulique du créosote dissout et en phase libre a été pompé par l'installation de puits sur le site. Basés sur les résultats d'une évaluation du risque aquatique – qui a inclus l'utilisation d'un modèle physiologique toxico-cinétique (PBTK), des sédiments sous-tidales contaminés ont été recouverts par une couche du type riprap. Une membrane semi-perméable (SPMDS) a été utilisée afin d'évaluer la performance de la mesure de restauration.

1. INTRODUCTION

The 9250 Oak Street, Vancouver, BC site (Figures 1 and 2) has soil and groundwater containing polycyclic aromatic hydrocarbons (PAHs), resulting from decades of roofing product manufacturing. The manufacturing involved processing of coal tar into suitable pitch-based roofing shingles and tar paper. This process produced a number of byproducts including creosote. Leaks and spills at the site resulted in release of a black, viscous pitch which was confined to the fill layer above the silt; and reddish dark brown creosote with viscosity of 0.94 poise at 14.7 °C (average groundwater temperature), which is roughly equivalent to that of a crude oil. The creosote had a density of 1.047 kg/L, a surface tension of 7 dynes/cm, and consisted of approximately 50 % napthalene. The dense non-aqueous phase liquid (DNAPL) creosote had migrated through the overbank silt layer into the underlying sand and gravel aquifer. The downward migration of DNAPL was confined at a depth of approximately 15 m by a compact fine sand layer which sloped towards the river (slope ~10%). Dissolved and free-phase creosote (DNAPL) had migrated from the source to an adjacent estuarine section of the Fraser River causing sediment contamination.

Figure 1 – Site Location

The Site was remediated under provincial Remediation Order, and the upland portion of the remediation was completed in 1999 (Golder, 2001). The remediation of contaminated sediment was subsequently completed by

2001. The sediment remedial planning process involved identifying preferred, feasible remedial options for the river sediments, and to support the adequacy of such options to protect the aquatic environment with a dedicated and appropriately scaled risk assessment study. The subtidal sediment remediation addressed in this paper is estimated to constitute 1% or less of the original total PAH mass.

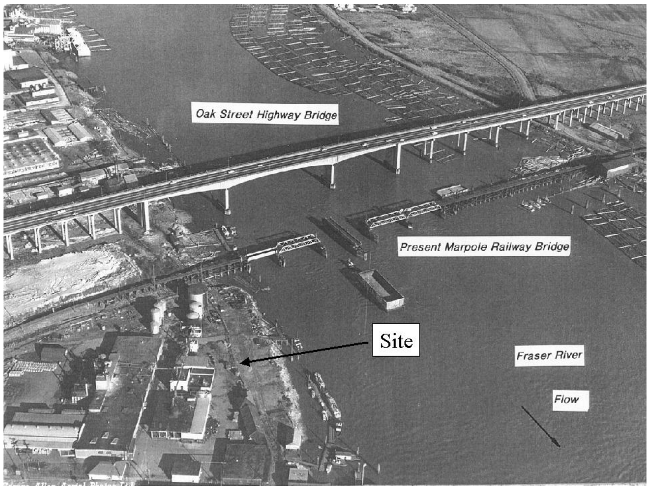

Figure 2 – Historical View of the Site (ca. 1950)

1.1 Upland Site Remediation

Upland remedial activities resulted in removal of approximately 60% of the PAH mass through excavations of contamination along the intertidal beach, foreshore, and uplands fill soils, and through recovery of DNAPL and dissolved-phase PAH. Additional PAH mass (DNAPL and dissolved-phase PAH) continues to be removed by operation of the DNAPL recovery and hydraulic containment systems. This system effectively controls further migration of PAH contamination into Fraser River sediments (Figure 3).

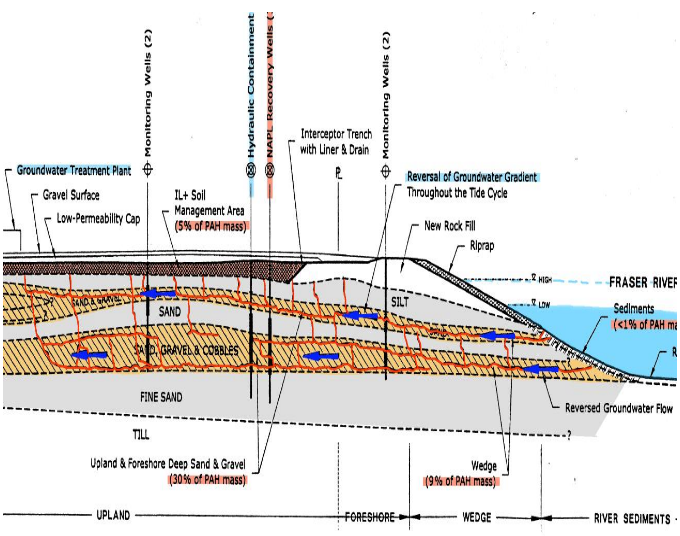

Figure 3 – Conceptual Cross Section

1.2 Site Constrants for Sediment Removal

Remedial options for the contaminated sediments were selected based on proven technologies that were feasible for the Site, given the site conditions and constraints. The main constraints include the mobility of river sediments, river slope stability (if disturbed), and an increase in PAH contamination with depth in the primary impacted zone. Other constraints include the presence of logs and concrete debris, the CP Rail trestle bridge which bisects the contaminated sediment area, and the Site's proximity to the navigational shipping channel.

Sediments along the riverbed are eroded during large flow events and are replaced with sediment eroded from upstream areas as the flow event wanes. PAH contaminated sediments may be transported away from the Site during the large flow events leaving behind freshly exposed contaminated sediments which will be subsequently reburied by newly arriving uncontaminated material from upstream. Fine sediments such as silts may accumulate over the Site during the low flow periods. These fine sediments form a surficial layer that may be remobilized during the next large flow event. The long-term trend of the riverbed in this reach of the Fraser River, given this successional erosion and infilling process, is overall one of aggradation. The riverbed has experienced average net accretion of 1.2 m between 1976 and 1999 and has been remobilized within the past few years to an estimated depth of 0.3 m.

1.3 Aquatic Habitat Conditions

Habitat conditions at the Site are limited for aquatic biota. The riverbed along the foreshore of the Site is dominated by silt and sand, and little overhanging or instream cover (e.g., riparian vegetation, boulders) exists. Spawning and rearing habitat is, therefore, limited. Although this section of the river is used as a migration corridor for salmonids, it provides only a very small percentage (~4% of the river bed width of the North Arm) of the migration route within the Fraser River. Additionally, species such as starry flounder and peamouth chub may use the area for rearing and migration. Common benthic invertebrates found in these sediments include: oligochaetes, chironomids, nematodes and copepods. Fraser River Estuary Management Plan (FREMP) habitat classification has designated the foreshore along the Site as having low productivity and diversity (FREMP, 1996).

2. SEDIMENT CHARACTERIZATION

Surficial sediments at the Site were categorized into three different zones based on mean PAH concentrations. The "primary" zone shown of Figure 4 had contamination exceeding 20 µg/g total PAH and represents the zone of highest surficial PAH contamination. The "secondary" zone includes the area outside of the primary zone where PAH concentrations generally fell below 20 µg/g, but exceed background levels The outermost zone is referred to as the "background zone" and represents an area where PAH concentrations fell within the typical background concentrations for Fraser River sediments. Most surficial cores collected within the primary zone exhibited creosote odour and sheen with OVM (Organic Vapour Monitor) readings ranging from 15 to 50 ppmv (REF). Surficial sediments in the secondary zone and the background zone did not have noticeable odours or sheens.

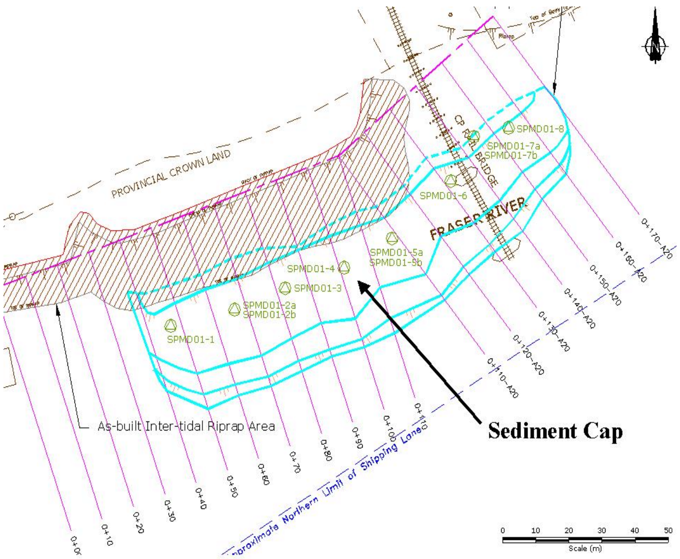

Figure 4 – Site Plan Showing Foreshore and Sediment Cap

Deep sediments were contaminated in the primary zone only. Moderate to strong coal tar odour and sheen were observed in distinct narrow layers in all cores to a maximum depth of approximately 5.0 m. Wood debris was observed randomly throughout these deep cores, indicating a net burial of riverbed material over time.

The contamination in the deep and surficial sediments in the primary zone consisted predominantly of low molecular weight (LMW) PAHs. However, the LMW PAHs in the deep sediments comprised a larger percentage of the total PAHs than in surficial sediments (i.e., ~85% in deep vs ~60% in surficial). The LMW PAHs in deep sediments are almost entirely made up of naphthalene (~50%) and 2-methylnaphthalene (~15%). By comparison, proportions of LMW PAHs and naphthalene were lower in the surficial sediments, indicating changes in PAH composition likely attributable to natural attenuation.

In contrast, high molecular weight (HMW) PAHs dominated the composition of PAHs in surficial sediments in both the secondary and the background zones as compared with surficial sediments in the primary zone (Figure 5). The PAHs in the secondary zone have a balance of light and medium molecular weight PAHs, and relatively lower proportions of the heaviest compounds such as benzo(a)pyrene (~3%); whereas the proportion of benzo(a)pyrene (10%) is higher in the background zone. These results likely reflect different source(s) of PAH, most likely anthropogenic, from storm water and other discharges to the Fraser River.

- Primary Zone: Total PAH concentrations in surficial sediments ranged from 36.5 to 256.6 µg/g, with a mean concentration of 139 µg/g and a standard deviation of 87.3 µg/g. Total PAH concentrations in deep sediment in the primary zone ranged from 0.349 to 1067 µg/g with a mean concentration of 579 µg/g and a standard deviation of 2760 µg/g.

- Secondary Zone: Total PAH concentrations ranged from 1.698 to 23.25 µg/g with an mean concentration of 11.2 µg/g and a standard deviation of 7.1 µg/g

- Background Zone: Mean total PAH concentrations ranged from <0.005 to 1.82 µg/g. Concentrations of HMW PAHs were approximately three-fold higher than concentrations of LMW PAHs.

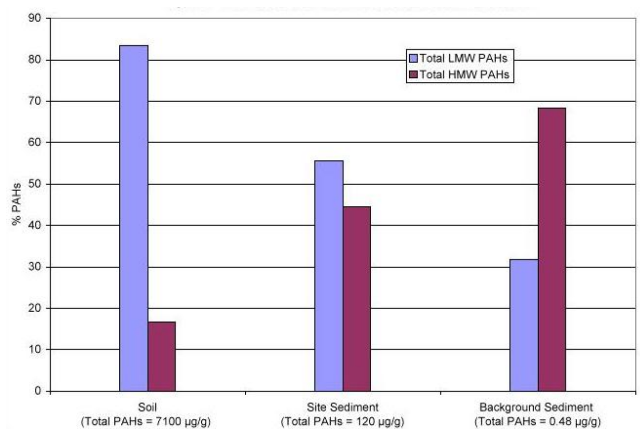

Figure 5 –LMW/HMW Ratio of Mean PAH Concentrations

3. MODELLING OF PERMEABLE CAP

3.1 Basal Layer Mixing

Dissolved groundwater PAH concentrations ranged as high as 10 mg/L total PAH (average concentration in pumped groundwater) in the uplands portion of the Site where the majority of the contamination is located. The maximum measured concentration in groundwater below the surface sediments (2 to 4 m depth) was 1.36 mg/L (six other samples had 1 to 2 orders of magnitude lower concentrations). The PAH concentrations that might enter the river are further reduced by attenuation due to tidal dispersion, sorption and biodegradation within the surface sediment.

In order to predict the dissolved PAH concentrations that benthic fish could potentially be exposed to, a simple mixing-box-model was developed. The model involved mixing of PAH-contaminated groundwater discharged from the Site with river water in the basal flow layer immediately above the sediments. This model was based on several key factors such as: Groundwater flux, near-bed velocities under low flows, river gradient, thickness of the basal flow layer near the bed (which is a function of the riverbed roughness), flux of river water per unit meter of bed width and advection/dispersion conditions of the proposed capping layer.

Components of the mixing-box model are illustrated in Figure 6. It involves the mixing of river flow (low flow conditions) with the groundwater over the primary zone of PAH contamination (130 m long by 20 m wide). The thickness of the basal layer is determined by the roughness of the bottom surface, which result in turbulence and a high degree of mixing. Near-bed velocities were estimated from mean river velocities by using a logarithmic decay profile. River flow velocities were determined from the discharge records for the river: Low flow near bed velocity = 0.04 m/s; Mean flow near bed velocity = 0.12 m/s; and High flow near bed velocity = 0.24 m/s. The calculated near bed velocities were cross-checked against sediment transport. A modified Shields parameter was used along with grain size data collected from the Site to determine if transport occurs. The flow velocity for low flow resulted in no sediment motion and the high flow velocity resulted in sediment motion. These calculations provided confidence that the calculated near-bed velocities are realistic. The river gradient was estimated based on Matthews and Sheppard (1962) who report a river gradient of 0.5 foot per mile (gradient of $9x10^{-5}$), and Public Works Canada bathymetric charts (gradient of $7x10^{-5}$). River gradient is highly variable depending on tidal level and discharge in the river. A range of gradients from $5x10^{-5}$ (low flow, high tide) to $1x10^{-4}$ (high flow, low tide) was considered representative.

The basal mixing layer thickness is proportional to the roughness of the bed. Work by Kostaschuk and Church (1993) indicates that the level of mixing associated with the bed is approximately twice the bed roughness height or the height of the mean bedform height. Mean bedform height is 0.5 m. Thus the mixing layer in the river was estimated to be approximately 1 m thick. The flux into a 1 m wide mixing layer on the river bed was calculated by multiplying the thickness of the mixing layer by the mean velocity.

The total groundwater flux over the 130 m long primary sediment contamination zone was estimated to be 3 x 10^{-4} m^3/s. (Golder 1999). The estimated concentration reduction factor, therefore, is approximately 3000 fold. It is recognized that this is only an approximate estimate of the concentration reduction that is likely to occur in the basal flow layer. The assumption of complete mixing within this layer is believed to be reasonable, as the river bottom roughness is large at the Site. However, any lack of conservatism in these assumptions are countered by the relative conservative selection of other river conditions, such as the use of the mean low flow condition.

3.2 Retardation and Mixing Within Cap

In order to predict the concentration of PAH at the surface of the proposed rock armour cap, a hydrogeological evaluation

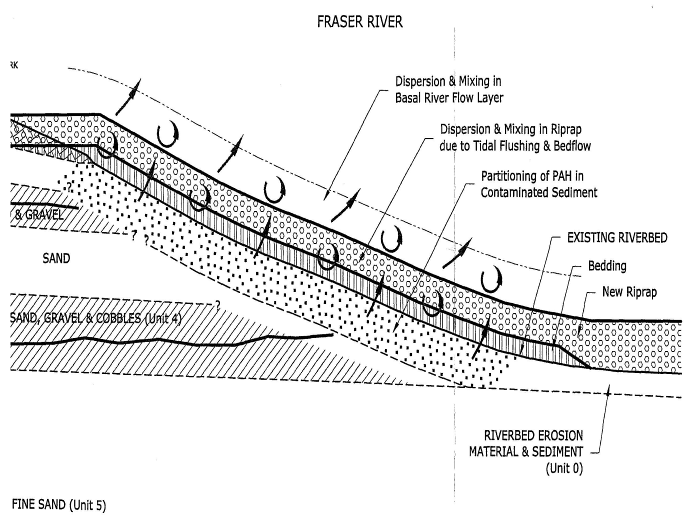

Figure 6 – Conceptual Mixing Model

Table 1 – Estimated River Flux into Mixing Layer

Flow Condition	Near bed Velocity (m/s)	Velocity at top of mixing layer (m/s)	Mean Velocity (m/s)	Mean Flux into 1 m wide by 1 m deep box (m^3/s)
Low	0.04	0.07	0.05	0.05
Mean	0.12	0.22	0.17	0.17
High	0.24	0.44	0.34	0.34

For a one metre thick mixing zone, the river flux into the 20-m wide mixing-box is 1 m^3/s during low flow conditions.

of groundwater flow and transport of dissolved chemicals was conducted. It was assumed that the riprap layer would be about 1 m thick, and the riprap would be infilled with silt. One-dimensional model of groundwater flow and transport was developed using the FEFLOW modelling code (Diersch, 1998). FEFLOW is a finite element code capable of simulating density- and viscosity-coupled groundwater flow, transport of solutes, and heat flow in three-dimensional porous media under a variety of boundary conditions.

It was assumed in this one-dimensional model that advection, longitudinal dispersion, and retardation due to sorption are the only transport processes that influence movement of dissolved chemicals. The effects of transverse dispersion, which under tidal influence may significantly reduce chemical concentrations, and river flow through the riprap were not included in this model. Furthermore, the impact of attenuation resulting from biological and/or chemical degradation of dissolved chemicals was not directly included. Biodegradation of LMW PAH compounds is likely to be an important process in the river sediment and/or rock riprap where these compounds will encounter oxygenated river water.

In light of the simplifications noted above, the one-dimensional model is considered conservative in that it accounts only for the reduction of concentration of dissolved chemicals due to longitudinal dispersion enhanced by tidal fluctuations and due to retardation. In reality the reduction or attenuation in the concentration of dissolved chemicals is likely to be much greater than that predicted by the model.
Two modelling cases were considered. In both cases it was assumed that the hydraulic containment system for arresting DNAPL at the Site (this system is described in 6.1) would not be operating:

- Case I, where it was assumed that the movement of chemicals dissolved in groundwater is not retarded due to sorption. The model was run for a period of 10 days. This time-frame was considered sufficient because the advective front would move through the riprap in approximately 1.7 days. A constant time step of 0.48 hour was used throughout the simulation, which resulted in 26 time steps per one tidal cycle. The time-step length was selected to provide sufficient resolution for tidal fluctuations at the model boundaries, and to satisfy Courant stability criteria for the numerical solution of transport equation (Zheng and Bennett, 1995).

- Case II, where it was assumed that retardation reduces transport velocities of dissolved chemicals. Breakthrough concentrations were predicted for naphthalene, a compound which is usually more mobile than other polyaromatic hydrocarbons (PAH). The retardation factor for naphthalene was estimated at 96 based on an organic carbon partition coefficient (*K_{oc}*) of 1,300 mL/g (Fetter, 1993) and fraction of organic carbon of 1% (measured in river sediments). The model was run for a period of 260 days as the advective front would move through riprap in approximately 170 days. The constant time step of 1.56 hour (8 time steps per tidal cycle) was used in the simulation to provide sufficient resolution for tidal fluctuations and to satisfy stability criteria for the numerical solution.

In Case I the model predicts that for the constant-concentration source located below the riprap, the effects of the tidal fluctuations on chemical concentrations extend up to 0.5 m below the river bottom. At the boundary representing the river/riprap contact, the maximum concentration is predicted to be 78% of source concentration, and the 25 hour average concentration is 20% of source concentration.

In Case II the model predicts that, for the retarded species like naphthalene, the maximum concentration at the river/riprap boundary does not exceed 13% of source concentration and the 25 hour average concentration is approximately 6%. The reduction of concentration for less mobile chemicals like pyrene and benzo(a)pyrene is estimated to be much greater then the reduction simulated for naphthalene.

Table 2 – Estimated Concentration Reduction Factors

Modeling Case	K_{oc} (mg/l)	Concentration Reduction Factor*
Cases I – Retardation	-	5
Case II – Assuming Retardation		
Naphthalene	1,300	17
Pyrene	38,000	>>17**
Benzo(a)pyrene	5,500,000	>>>17*

* Concentration reduction was calculated as the Ratio of source concentration to predicted concentration.
** Concentration reduction for pyrene and benzo(a)pyrene was estimated from the results simulated for naphthalene and by comparing the K_{oc} values.

4. TOXICOLOGICAL AND AQUATIC RISK EVALUATION

The toxicological and aquatic risk evaluation focussed on benthic invertebrates and fish, and included assessment of four main components: bioassays, benthic survey, literature survey and PBTK modelling. The risk evaluation framework is shown in Figure 7.

The Fraser River watershed harbours the most varied landscape in North America and includes nine of British Columbia's twelve biogeoclimatic zones (Bocking 1997). The River provides spawning and rearing habitat, and a migratory route for millions of fish, including the five species of salmon (i.e., coho, chinook, pink, sockeye and chum salmon) which are most important to humans and wildlife. It was found that several studies have been conducted on potential impacts of contaminants on fish from the lower Fraser River, and have concluded that demonstrating cause-effect relationships between a particular contaminant source and fish species in the Fraser River is difficult, if not impossible. This conclusion was based on the facts that: i) even non-migratory fish travel significant distances within the river, ii) there are numerous contaminant sources, iii) there are numerous contaminants, and iv) there has been difficulty in catching sufficient numbers of fish to determine a cause-effect relationship.

The review also revealed that limited PAH tissue monitoring has been conducted and the data indicate that fish species in the North Arm, and the remainder of the lower Fraser River are exposed to these chemicals. However, when interpreted against critical PAH body residues reported in the toxicity literature, the observed tissue levels of PAHs in Fraser River fish do not appear to compromise fish health. It was also found that the starry flounder, an indigenous benthic fish, would be among the more suitable species to monitor for effects from contaminated Fraser River sediments. This provided a strong basis to undertake toxicokinetic studies and modelling of PAHs in this species to provide additional insight for purposes of risk management at the Site. This is described further in the following section.

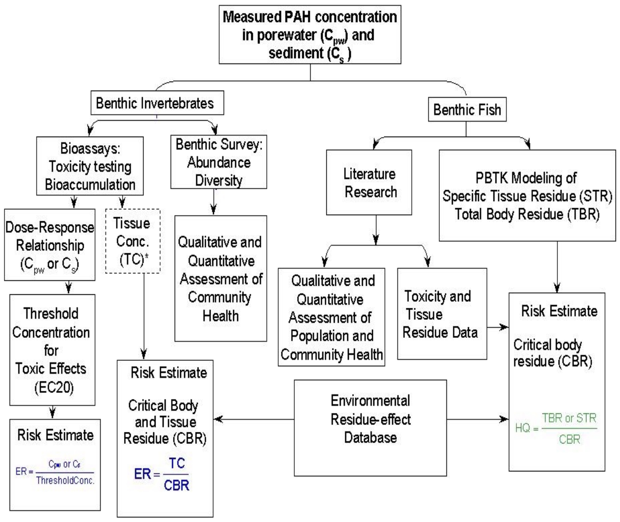

Figure 7 – Aquatic Risk Evaluation Framework

5. PHYSIOLOGICALLY BASED TOXICOKINETIC MODELING OF PAHS IN BENTHIC FISH

A physiologically based toxicokinetic (PBTK) model was used to describe PAH levels in the tissues of starry flounder based on laboratory exposure studies using Site sediment samples, and extrapolation to the field situation. The basic objective was to evaluate whether current or future sediment conditions pose unacceptable risks from PAHs to benthic fish, which may frequent the Site. Starry flounder, *Platichthys stellatus*, was used as a representative benthic fish species.

A PBTK model defines an organism in terms of its anatomic spaces, physiology, and biochemistry. It provides a good understanding of the disposition of a chemical in the tissues of an organism and facilitates extrapolation over a wide range of conditions including different exposure routes, dosing regiment and environmental conditions. The PBTK model employed in this assessment was based on a previous model which was developed to predict the time course of pyrene in the tissues of starry flounder following exposure to waterborne pyrene (Namdari 1998). Pyrene was selected as a model PAH due to its physico-chemical properties and the fact that previous studies have shown a relatively high concentration of pyrene in sediments and the fish of PAH-contaminated waters. However, in addition to pyrene, the present model was expanded to address naphthalene (Naph) and benzo(a)pyrene (BaP) uptake and tissue concentrations as well. These three compounds were then used as surrogates for both toxicokinetics and mixture toxicity to describe risks arising from other PAHs with similar structure and/or physico-chemical characteristics.

The PBTK modelling was designed to answer the following questions: (i) *Without the hydraulic control and containment system, would contaminated sediments at the site, if not remediated and left unarmored, present an unacceptable long term risk to benthic fish such as Starry flounder?; and (ii) If some form of engineered cap is employed to prevent direct exposure of benthic fish to contaminated sediment, what level of risk reduction across the cap is required to offer acceptable risks to organisms interacting with this zone?*

This was examined by exploring whether or not the predicted accumulation via gill-uptake (i.e., from groundwater/porewater discharge), dietary absorption (i.e., consumption of benthic invertebrates) and dermal absorption (i.e., contact with sediments) of *individual PAHs, grouped or total PAHs* result in unacceptable tissue levels.

Figure 8 is a schematic diagram of the PBTK model used to simulate the disposition of PAHs in starry flounder. The model consists of eight compartments representing major organs or tissues such as liver, kidney, muscle, gill, gut, skin, blood and carcass of starry flounder. The compartments are connected by the cardiovascular system; blood flow rates and tissue-to-blood partitioning govern the transfer of chemical between compartments. The model allows for PAH uptake by flounder *via* the branchial (gill), dermal and dietary routes.

The existing PBTK for PAHs in starry flounder was first optimized to more effectively address sediment-mediated exposure to a mixture of PAHs, as would be expected in the field situation. This was accomplished by exposing flounder to site sediment samples in the lab, measuring the tissue PAH residues at various times, and then calibrating the model to the observed results. Subsequently, input parameters were adjusted to reflect exposure concentrations at the Site in sediment, porewater, and benthic invertebrates.

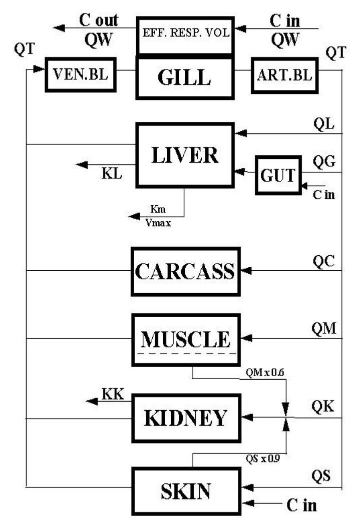

Figure 8 – PBTK Model

It was assumed that as a result of migratory behaviour (described previously in Fraser River Fish Health literature review) a flounder would spend 20% of its time in the primary contaminated zone of the Site. We further assumed that the subject fish would have local presence near the Site for 10 days, after which no encounter with the Site would occur for several weeks. The exposure was further examined by creating three exposure regiments for simulation by the PBTK model. The results of the worst case are shown in Table 3 (Flounder is present at the site for two consecutive days within the 10 day time period).

The predicted PAH tissue residues (in particular for whole body residues) in starry flounder were then compared to critical body residues (CBR) reported in the literature and expressed as a series of exposure ratios. The exposure ratio (also known as hazard quotient and hazard index) is the predicted whole body PAH residue expressed as a fraction of the reference dose (i.e. CBR). Conventionally, a hazard index of one is considered the upper bound of acceptable risk.

The effect endpoints associated with the CBR (taken as the lowest observed effect dose, LOED) were induction of mixed function oxidase enzymes for pyrene-like and BaP-like compounds, and alteration of neurotransmitter levels for Naph-like compounds. Extrapolation of LOEDs from literature values (i.e., for salmonids and catfish) to flounder was achieved by incorporating an uncertainty factor ranging from 1 to 5. The effect end points are considered conservative, and likely to preserve a reproduicing population of flounder.

We also addressed the potential for an effect from unmeasured PAHs and related heterocyclic hydrocarbons by allowing for a "risk adjustment factor". This was conducted by multiplying the predicted hazard index by a factor ranging from 1 (i.e., no effect) to 10 (i.e., potential 10-fold increase due to unmeasured PAHs and derivatives). The latter adjustment infers that the exposure concentrations, pharmacokinetics and toxicity of unmeasured PAHs and derivatives are distributed similarly to the three categories of PAHs considered above (i.e., Naph-like, pyrene-like and BaP-like PAHs).

The vast majority of the predicted risk (about 98%) was determined by the contribution from the BaP-like compounds. This in turn was derived primarily from the dietary pathway where PAH intake was mediated through intake of contaminated benthic invertebrates. Figure 9 provides a summary of the estimated risk contributions from the different contaminant groups and exposure pathways.

The conventional risk estimates which address the three key PAH groups (i.e., Pyrene-like, Naph-like and BaP-like) suggest the level of risk is quite marginal, which is consistent with the findings of Fraser River Fish Health Review. This result is based on the conservative toxicity extrapolation assumption that flounder may be 5-times more sensitive than the reference test species, which may not apply. As well, the effect of the 1 m thick water mixing layer along the sediment interface was conservatively assumed to result in a 1000-fold dilution rather than the modelled value

Table 3 – Estimated Hazard Quotients

PAH	PWB, ug/g	LOED µg/g	IUF	CBR, µg/g	HQ
Pyrene-like	0.039	30	1-5	6-30	0.001 to 0.007
Naph-like	0.563	100	1-5	20-100	0.006 to 0.03
BaP-like	0.036	0.1	1-5	0.02-0.1	0.4 to 1.8
Hazard Index[2]					0.4 to 1.84 (18.4)

1) Based on river dilution factors of 1000.
2) Sum of HQs (Parenthetic values are the upper range using 10-fold "risk adjustment factor" for unmeasured PAHs.)
3) LOED = Lowest observed effect dose.
4) HQ = hazard quotient
5) CBR = Critical Body Residue
6) PWB = Predicted Whole Body concentration
7) Interspecies uncertainty factor

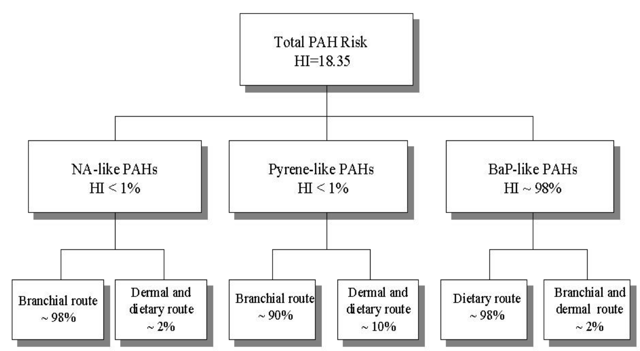

Figure 9 – Risk Estimates by Exposure Routes

of 3000. If these collective conservative assumptions were not employed, the resultant risk would be within acceptable levels. After allowing for uncertainties associated with unmeasured PAHs and related heterocyclic hydrocarbons, the hazard index for the collective contribution from Naph-like, pyrene-like and BaP-like PAHs suggests some individual fish might be marginally affected with regard to the effect endpoints previously noted. Other individuals, however, may experience less risk to health due to lower or no exposure. The likelihood for an effect at the population level was not assessed, due to lack of a fish population model for this species.

Under the conservative conditions described above the calculated HI for fish health was about 18 times higher than the conventionally accepted value of one. The corresponding value was approximately halved under less conservative conditions where the flounder would be present at the site for non-consecutive time periods for a total of two days over a 10 day period. These data suggest that some means of protection is desirable at the Site and that such protection should provide about a 10-20-fold risk reduction factor. Note however, that conservative assumptions inherent in these results would suggest the risks are lower than identified here.

It is also important to note from the modelling analysis that the vast majority of risk (approximately 98%) is driven by BaP-like compounds, and further, the most relevant pathway is through dietary exposure (Figure 9). In this regard, the PBTK approach is an improvement over basic environmental contaminant partitioning, because it addresses the well-developed capacity of fish to metabolize PAHs and accounts for physiological changes that may affect the toxicokinetics of PAHs derived from different exposure pathways. Since BaP-like compounds have low solubility and are more likely to remain in the sediment bound state (rather than the dissolved mobile state), the concept of contaminant transport and attenuation across the riprap interface takes on less importance than i) protection of aquatic organisms from direct contact with contaminated sediments (surface or deep sediments); and ii) proximity to DNAPL, which is the more effective transport medium of heavy (BaP-like) PAHs. This suggests that elimination of the dietary contribution of risk to benthic fish (as predicted in the baseline scenario herein) would be an effective risk reduction option.

If Site sediments are not remediated or are left unarmoured, the foregoing analysis suggests the sediments in the primary contaminated zone may present a marginal risk to benthic fish like the starry flounder. It is important to recognize, however, that while some individual bottom fish may experience the risks predicted here, a large proportion of the local Fraser River fish population are likely to experience less risk from the site, simply because of their semi-migratory behaviour and the probability of infrequent episodic exposure to the sediment in question.

Based on the PBTK data, a 10-20-fold risk reduction was identified as reasonable from the baseline scenario. As shown, the permeable riprap cap provides an effective means to achieve this, as it would eliminate exposure of benthic fish to the existing contaminated sediments and food items (98% of risk) and prevent the recurrence of such an exposure scenario.

5.1 Bioassay Program

The purpose of the toxicity program was not to support a conventional aquatic risk assessment, rather, it was conducted to collect toxicity data that would specifically assist in developing remedial options such as sediment capping for the Site. The toxicity program was intended to address the following key questions: (i) *Do Site sediments with the total PAH levels exceeding 20 µg/g exhibit acute or chronic toxicity to benthic invertebrates?; and (ii) In the event an engineered cap is created along the groundwater discharge zone to armour the bottom sediments and to modify the exposure scenario by creating a "benthic mixing zone", will the resulting dispersion and attenuation sufficiently reduce potential waterborne toxicity from PAHs dissolved in the discharged groundwater?*

The approach for this component of the program was to employ bioassays, which focussed on both the contaminant transport medium (i.e., groundwater), as well as the receiving environmental medium (i.e., sediment). The bioassays included sensitive invertebrates that represent both the benthic habitat (i.e., *Hyalella,* and bacteria), as well as the water column (i.e., *Ceriodaphnia dubia*).

Hyalella is not frequently found within this reach of the Fraser River, however, since it is a sensitive species it was selected to address improvement in environmental conditions in the lower Fraser River. The test was conducted following Environment Canada Test Method (EPS 1/RM/33). Bioassays were conducted either as pass/fail screening tests (three in total), or as a dilution series to characterize the dose-response relationship (two in total). Briefly, the test involves placing the sediment in a test chamber and adding 10 amphipods. The organisms are allowed to burrow into the sediment, which forms the basis of the exposure scenario. After 14 days, the exposure is terminated and the sediment is inspected for surviving amphipods, which are counted and weighed. Inhibition of growth and survival, relative to controls, are the effects endpoints. Two sets of controls were used; laboratory control and grain size control.

The growth data in the *Hyalella* bioassay is highly subjective due to several factors including: organisms are weighed as a group rather than individually, weight is only collected after exposure and not before the exposure, water attached to organisms can cause potentially large error in weights, and loss of organisms from acute mortality may bias the recorded weight of some of the samples. Therefore, no meaningful remediation levels could be derived from this data.

The survival data produced variable results. One of the dilution series exhibited no dose response and suggested high levels of PAHs (i.e., on the order of 100 µg/g total PAHs) were not acutely toxic. A second dilution series exhibited a dose-response effect with acute toxicity exhibited at about 20 µg/g, total PAHs. Three screening tests conducted resulted in no significant acute mortality at total PAH concentrations of 66 to 100 µg/g.

While the *Hyalella* bioassays suggested elevated levels of PAHs could be tolerated by benthic invertebrates, remedial cleanup goals could not be derived because of data limitations including: (i) questionable health status of test organisms in the initial suite of bioassays; ii) variability in sediment exposure concentrations (due to inherent variability in sediment concentrations in spite of sample homogenization); and iii) possible sediment contaminant attenuation and/or decreased bioavailability caused by the elapsed time between sample collection and bioassays. The data suggests that moderately high levels of total PAHs (i.e., 66 to 100 µg/g) were without significant effect. Thus *Hyalella* bioassays did not provide a firm basis to define a target remedial sediment concentration respecting PAH.

Potential effects of dissolved PAH in groundwater was assessed by bioassays using the freshwater microcrustacean, *Ceriodaphnia dubia.* The groundwater used in these tests was collected from wells in the upland area, which had higher dissolved concentrations than those measured in the sediment; and the results are therefore conservative. The toxicity test was conducted following Environment Canada Test Method (EPS 1/RM/33). This is a 7-day test in which neonate daphnids are exposed to contaminated groundwater. Inhibition of growth and reproduction, relative to controls, are the effect endpoints. The objective was to conduct assays using a dilution series to characterize the dose-response relationship and then derive the requisite dilution factor required to guard against these effect endpoints.

The results would suggest that dissolved PAH contaminant levels in groundwater do not require containment or reduction through dispersion, mixing and attenuation before entering the biologically active zone (i.e., absence of groundwater containment pumping). The results suggest that a reduction factor of 2-3-fold would be sufficient to allow for a margin of safety beyond the current no-effect level associated with “Pre-treatment” groundwater. Modelling of concentration reduction across the riprap capping layer suggests this level of reduction and margin of safety would be achievable.

6. SEDIMENT CONTAINMENT FACILITY

The sediment containment system consisted of: (i) the permeable riprap cap; and (ii) and the hydraulic control and containment system (HCCS). The riprap cap prevents erosion and downstream transport of contaminated sediments, provides a barrier between the contaminated sediments and the aquatic community, and allows for an attenuation zone for groundwater that may come into contact with the sediments. The HCCS provides for collection of DNAPL and dissolved groundwater PAH, and prevents future releases to the river.

The sediment containment facility was designed for: (i) Future conditions with groundwater pumping: Under this scenario the placement of a rock riprap cap over the primary zone sediments will eliminate exposure due to direct contact with the sediments; and due to sediment erosion; and (ii) Future conditions with <u>no</u> groundwater pumping: The second scenario addresses the potential for turning off the groundwater containment and control system, once DNAPL recovery is complete.

6.1 Hydraulic Containment and Control System

The hydraulic containment and control system (HCCS) installed at the Site provides a reversal of groundwater gradients for recovery of dissolved PAH, arresting DNAPL flow and inducing DNAPL recovery in the uplands portion of the deep sand and gravel aquifer. Control of the groundwater gradient is effected by pumping from six containment wells (five operational, one backup) strategically placed around the inferred DNAPL zone so that the desired magnitude and direction of the opposing gradient is achieved and maintained throughout tidal and seasonal variations. The optimum total pumping rate required to arrest DNAPL movement is greater than that required to capture groundwater containing the dissolved components and therefore total capture of the dissolved phase plume is effected by normal operation of the HCCS.

The HCCS includes on-site water treatment (discharge under permit to sanitary sewer), integrated monitoring system and telemetry. Supplementary to the HCCS is a dedicated DNAPL recovery system comprising three wells with automated pumps.

Direct measurement of DNAPL movement cannot be undertaken. Instead, the effectiveness of the HCCS is assessed by measurement of the induced groundwater gradients and comparison of these gradients to the required gradients determined from analytical solutions for DNAPL restraint. This analytical solution incorporates DNAPL density, groundwater density, planar geometry and groundwater gradients. In addition, three-dimensional groundwater gradient assessment is undertaken at intervals by placing pressure transducers and dataloggers temporarily in monitoring wells peripheral to the primary gradient field and at different elevations within the aquifer. The ongoing monitoring and numerical modelling has demonstrated that the HCCS is performing as expected with the desired groundwater gradient being applied to arrest DNAPL migration towards the Fraser River and to capture the entire dissolved phase PAH groundwater plume.

6.2 Design of Rock Riprap Cap

The design criteria for the subtidal permeable riprap cap were based on a maximum mean flow velocity of 1.8 m/sec and a bed material with a D_{50} of 0.06 mm. The design mean flow velocity was estimated for a 1 in 200 year flood flow event for this reach of the lower Fraser River (Hay & Company, 1995). Additional design criteria for the proposed capping layer have been necessitated by the proximity of tug boats working close to the bank and giving rise to propeller-induced scour. This consideration is particularly important in shallow conditions when the depth of water below the propeller shaft is relatively small when compared to the diameter of the propeller, as is present at the Oak Street Site. For tugboat traffic which will remain at least 10 m from the shore, the propeller jet thrust on the bed is estimates at 3,500 kg corresponding to a velocity of 3 m/sec. This near bed velocity is ten times greater than the near bed velocity estimated for a 1 in 200 year flood.

The original design concept for the proposed capping blanket comprised three key elements: a bedding layer, a riprap layer and a self-launching toe. The function and description of each of these components is provided in the following sections and Figure 10.

The riprap layer provides two functions: firstly, primary scour protection and secondly an active attenuation zone for reduction in PAH concentrations due to tidal dispersion/mixing and retardation/biodegradation. An 800 mm thick riprap layer having a D_{50} of 450 mm and maximum and minimum sizes of 600 and 250 mm respectively has been used.

The function of toe protection to the riprap is to mitigate undermining of the riverbed immediately beyond the downslope extent of the riprap and any resultant disturbance of the riprap and underlying bedding layer. Launchable rock was used to protect the toe of the riprap cap. This involved placement of rock in a blanket of increased thickness along expected erosion areas at an elevation above the zone of scour. As the scour and resulting erosion occur below the rock, the rock is undermined and rolls/slides down the slope, stopping the erosion. By adjusting the riprap grading, the final design of the cap resulted in a single layer design.

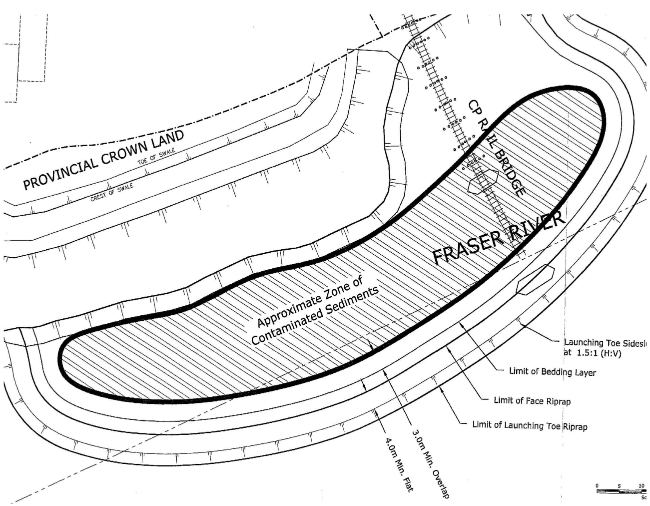

Figure 10 – Permeable Riprap Cap Layout

7. IMPLEMENTATION

7.1 Cap Construction

The majority of the coarse rock fill for the sub-tidal rip rap blanket was placed below low tide level using cable controlled, spud-barge supported equipment in October and November, 2001. The nominal 1.1 metre thick layer of rock fill was placed on an irregular and sloping river bed surface in a pre-configured overlapping grid pattern over substrates comprising soft or loose silt and sand sediments. Pre and post-construction bathymetric surveys were carried out using electronic multi-beam scanning equipment to provide quality assurance of the finished product.

The bathymetry results indicate that the sub-tidal rip rap blanket was completed in accordance with the design approved by the Regulator. The thickness plan information indicates that the rock fill material was placed within the designated area and to adequate thickness for the sub-tidal rip rap blanket. It should be noted that the pre and post-construction bathymetry surveys identified areas outside of the placement area where some change in vertical elevation of the river bed may have either naturally occurred or resulted in finer material transported from the completed work area.

It is expected that the irregular rip rap blanket surface may fill in with river sediments over a period of time, which may contribute favourably to the coverage and protection of the underlying contaminated sediments. Monitoring the integrity of the rip rap blanket surface, by conducting a bathymetry survey, was undertaken in 2002 and confirmed that the cover was in good condition.

7.2 Performance Monitoring

Semi-permeable membrane devices (SPMD's) were placed at 11 locations on the surface of the completed cap approximately 20m apart together with a number of control locations upstream, cross-stream and downstream of the Site. These instruments provide integrated measurement of PAH concentrations in the river/cap interface zone over an approximate one month period and allow comparison to conditions measured using a similar array deployed prior to installation of the cap. SPMD monitoring is scheduled to be conducted twice a year for the first two years after construction. The SPMD's consist of a thin film of triolene sealed in a low-density semi-permeable polyethylene layflat tube suspended in perforated stainless steel canisters. Monitoring using the SPMD's to date (one year) indicates that PAH levels detected above the cap (with the HCCS in operation) are comparable to background levels in the river measured upstream, cross-stream and downstream of the Site.

8. CONCLUSIONS

The aquatic risk assessment and sediment remediation assessment has demonstrated the following:

- Conservative modelling predicts that the primary zone sediments could have presented a marginal risk to benthic fish and invertebrates resulting from direct contact with the PAH-contaminated sediments, if left uncapped.
- Operation of the hydraulic containment and control system is sufficient alone to reduce the risks to aquatic life (from mobile DNAPL and dissolved groundwater PAH) to acceptable levels.
- If uncontrolled, natural hydraulic river processes could result in erosion and migration of the PAH-contaminated sediments from the primary zone

causing some release of PAHs to the river environment.

- Therefore placement of the permeable riprap cap over the primary zone sediments has eliminated erosion and subsequent PAH release to the river environment, prevents direct contact of benthic fauna with any surficial PAH-contaminated sediments; and would provide attenuation of dissolved-phase PAH contamination when the pumping to capture the dissolved-phase PAH plume is **not** functioning).

- Once DNAPL recovery operations at the Site are completed, the riprap capping system alone will provide the necessary level of risk management to aquatic life within the Fraser River at the site.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the valuable and significant contribution to this project by Mr. Brian Conlin (Project Advisor), Dr. Rostam Namdari (PBTK model and aquatic risk assessment), Mr. Willy Zawadzki (groundwater modeling and design), Mr. Don Chorley (groundwater modeling and design), Mr. Michael Z'Graggen (aquatic risk assessment), Ms. Bettina Sander (aquatic habitat and risk assessment), Mr. Peter Morgan (river hydraulics and cap design), Mr. Neil Wedge (geotechnical aspects related to cap design), and Mr. Rowland Atkins (river geomorphology).

REFERENCES

Diersch, H.G. 1998. *FEFLOW Interactive, Graphics-Based Finite-Element Simulation System for Modeling Groundwater Flow, Contaminant Mass and Heat Transport Processes*. WASY Institute for Water Resources Planning and System Research Ltd., Berlin, Germany.

FREMP Habitat Inventory Index Map: Fraser River North and Middle Arms. Prepared for the North Fraser Harbour Commission and the Department of Fisheries and Oceans, Vancouver, BC, 1996

Hay & Co. "Study of Mitchell Island Bank Erosion", October 1995.

Kostaschuk R.A. and Church M.A. 1993. Macroturbulence generated by dunes: Fraser River, Canada. Sedimentary Geology, 85, 25-37.

Matthews W.H. and Shepard F.P. 1962. Sedimentation of Fraser River Delta, British Columbia. Bul. Amer. Assoc. Pet. Geol. Vol. 46, No 8, pp 1416-1443.

Namdari, R. (1998) A physiologically based toxicokinetic model of pyrene and its major metabolites in starry flounder (*Platichthys stellatus*). Ph.D. Thesis. Simon Fraser University, B.C. Canada.

Zapf-Gilje, Reidar, Patrick G.C. and McLenehan, R. Overview of the Remediation Process at Sites with Creosote Related Contamination in Soil, Groundwater and River Sediment, Can. J. Civil Eng., Vol. 28, (Suppl. 1), 2001.

Zheng, C. and G.D. Bennett. 1995. *Applied Contaminant Transport Modeling: Theory and Practice*. Van Nostrand Reinhold Co., NY. 440 p.