ASSESSING THE POTENTIAL IMPACT OF THE ANTISAPSTAIN CHEMICALS, DDAC AND IPBC, IN THE FRASER RIVER

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ABSTRACT

Canadian National Water Quality Guidelines were developed for the antisapstain chemicals, didecyl dimethyl ammonium chloride (DDAC) and 3-iodo-2-propynyl-butyl carbamate (IPBC). Based on toxicity studies, the draft interim guideline for the protection of freshwater life is set at 1.5 μg/L for DDAC and 1.9 μg/L for IPBC. These proposed guidelines must undergo a review process through the CCME and obtain approval before being established as official Water Quality Guidelines.

A survey of DDAC and IBPC concentrations in the Fraser River downstream of mill discharge points found that dissolved DDAC concentrations in river waters appeared to be affected by adsorption and complexation processes. Analytical recovery from river water was greatly reduced, possibly due to the presence of suspended solids. Recovery results suggested the adsorption with particulate matter or complexation with anionic substances was irreversible. IPBC in Fraser River water remained in the dissolved phase and appeared to be unaffected by suspended solids. It was present in the stormwater runoff from lumber mills but levels in the river water downstream of the discharge point were below detection limits.

Overall, zones of potential biological impact of DDAC and IPBC in the water near outfalls appeared to be quite restricted due to physical chemical processes and relatively low concentrations of DDAC/IPBC in discharges coupled with high suspended solids encountered during the summer sampling. However, sediments surveyed near lumber mills in the Fraser River contained levels of both DDAC and IPBC to concentrations of 1.26 and 0.49 μg/g, respectively.

Toxicity bioassays with *Hyalella azteca* and *Daphnia magna* were conducted using Fraser River sediments to evaluate the potential for toxic effects from sediments contaminated with DDAC. The acute toxicity was significantly reduced in the presence of sediment, as expected. The results confirmed that adsorption of DDAC onto particulate matter reduced acute toxicity. However, DDAC in the sediment remained bioavailable to both organisms, as well as Microtox® bacteria.

RÉSUMÉ

On a établi des recommandations nationales pour la qualité des eaux au Canada relatives aux produits chimiques anti-tache colorée de l'aubier que sont le chlorure de didécyldiméthylammonium (CDDA) et le 3-iodo-2-propynyl-butylcarbamate (IPBC). D'après les études toxicologiques, les concentrations recommandées provisoires pour la protection de la vie dulcicole sont de 1,5 µg/L pour le CDDA et de 1,9 µg/L pour l'IPBC. Ces recommandations proposées doivent être examinées par le CCME et être approuvées avant d'obtenir le statut de recommandations officielles pour la qualité des eaux.

Dans le cadre d'un relevé des concentrations de CDDA et d'IPBC dans le Fraser en aval de points de rejet d'usines, on a observé que les concentrations de CDDA dissous dans les eaux du fleuve semblaient être fonction de processus d'adsorption et de complexation. L'extraction analytique de cette substance dans l'eau du fleuve était grandement réduite, peut-être à cause de la présence de solides en suspension. Les résultats de l'extraction laissent penser que l'adsorption avec les matières particulaires ou la complexation avec des substances anioniques étaient irréversibles. L'IPBC dans les eaux du Fraser demeurait dissous et semblait ne pas être affecté par les solides en suspension. Il était présent dans les eaux pluviales de ruissellement issues de scieries, mais les niveaux dans le fleuve en aval du point de rejet étaient sous les seuils de détection.

Globablement, les zones où le CDDA et l'IPBC pouvaient avoir un impact biologique dans les eaux près des émissaires ont semblé assez restreintes en raison des processus physico-chimiques et des concentrations relativement faibles de CDDA et d'IPBC dans les rejets, associées à de fortes concentrations de solides en suspension dans les échantillons recueillis durant l'été. Cependant, les sédiments recueillis près des scieries dans le Fraser renfermaient des concentrations de CDDA et d'IPBC atteignant 1,26 et 0,49 µg/g, respectivement.

On a effectué des bio-essais de toxicité avec *Hyalella azteca* et *Daphnia magna* utilisant les sédiments du Fraser pour évaluer les effets toxiques potentiels des sédiments contaminés par le CDDA. La toxicité aiguë était significativement réduite en présence de sédiments, comme prévu. Les résultats confirment que l'adsorption du CDDA sur la matière particulaire réduit la toxicité aiguë. Cependant, le CDDA dans les sédiments demeurait biodisponible pour les deux organismes, de même que pour des bactéries utilisées avec le système Microtox.

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1.0 INTRODUCTION

Didecyl dimethyl ammonium chloride (DDAC) and 3-iodo-2-propynyl-butyl carbamate (IPBC) are antisapstain fungicides which are chemicals used to prevent fungal growth on softwood lumber during shipment, particularly from Canadian coastal mills. Sapstain fungi do not damage the structural integrity of the wood, however, a bluish-black stain is produced that is aesthetically unacceptable to customers and reduces the marketability of the lumber. The presence of well-established colonies of mould and sapstain fungi may be followed by decay fungi, which reduce the strength of the timbers. Antisapstain chemicals are used globally to produce sapstain-free lumber.

Historically, the primary antisapstains were sodium pentachlorophenate (PCP) and sodium tetrachlorophenate (NaTCP). During the 1980's, controversy over the safety of these chemicals (both environmental and worker health) forced the industry to look for alternatives. The initial alternatives were products containing the active ingredients, copper 8-quinolate (Copper-8), 2-(thiocyanomethylthio)benzothiazole (TCMTB), borates ("borax" - disodium tetraborate decahydrate or disodium octaborate tetrahydrate) and sodium carbonate (Na_2CO_3). Two of these products (Copper-8 and TCMTB) were withdrawn after environmental and human health concerns which were similar to those with chlorophenates. The second generation of alternative chemicals are currently the most common antisapstain fungicides in use at Canadian lumber mills. These are DDAC (Bardac 2280®), IPBC (Troysan Polyphase P-100®) and to a lesser extent, azaconazole (sold as Rodewod®). Borates and Na_2CO_3 (sold as Ecobrite®) are also used by mills in British Columbia, most frequently as a co-active ingredient to DDAC. One mill in the province also continues to use TCMTB (Busan 1030®) (Leiss, 1992; Szenasy and Bailey, 1996; Redenbach, 1997).

Antisapstain chemical use is concentrated in the coastal regions where rainfall is high and the wood is very wet - ideal conditions for fungal growth. Lumber mills in Quebec, Nova Scotia and New Brunswick also use DDAC as an antisapstain chemical, however, the amount of chemical used per year is greatest in British Columbia. As of 1996, there are 52 lumber mills in BC using

antisapstain chemical formulations, all of which are located in the Lower Mainland, Vancouver Island, the Prince Rupert area, with one mill in the Southern Interior. The quantity of antisapstain chemical formulations used by mills along the lower Fraser River in the Lower Mainland was 680,475 kg in 1996, the majority of which contained DDAC. In 1996, the amounts of DDAC and IPBC used were 155,179 kg and 10,965 kg, respectively. The quantity of borates and azaconazole used by Fraser River mills the same year were 108,411 kg and 3860 kg, respectively. The majority of BC coastal mills use the formulation, NP1, a mixture of DDAC and IPBC. The second most common formulation is F2, containing DDAC and a borate salt (disodium octaborate tetrahydrate) as active ingredients (Redenbach, 1997).

DDAC is one of the most heavily used pesticides in the province, ranking third behind creosote and CCA, which are wood preservative products. Currently, over 90% of BC coastal mills use antisapstain formulations containing DDAC as the active ingredient. Most frequently IPBC is used as the co-active ingredient. Although much less IPBC is used than DDAC, it's toxicity to aquatic organisms is similar to DDAC and the interaction of the two chemicals may produce synergistic effects in some organisms (Farrell et al., 1998b). While 108 metric tonnes of borates were used, they are roughly 850 times less toxic to fish than DDAC and are not considered to be of concern in the Fraser Basin (Cavanagh, 1995).

DDAC is a cationic surfactant that belongs to a group of chemicals known as quaternary ammonium compounds (QACs) (Figure 1). QACs are commonly used industrially as disinfectants and are part of many household items such as fabric softeners and anti-static agents. More recently, DDAC has been used in Ontario as a molluscicide to control zebra mussels (TRS, 1997; Schoenig, pers. comm. 1997). The mode of action of DDAC is cellular membrane disruption, causing damage to exposed areas in animals (such as gills and digestive tracts) (Wood et al., 1996b; Henderson, 1992a). It is not surprising then, that DDAC is toxic to aquatic organisms, both fish and invertebrates (Farrell et al., 1998a). In general however, the aquatic toxicity of DDAC is much less than the chlorophenates and TCMTB which were previously used. However, the toxic effects of DDAC are moderated by its bioavailability to the organisms. Physical chemical data from the manufacturer and studies on other QACs suggest that bioavailability in the water

column is likely limited, due to the high affinity of DDAC to any solid material (TRS, 1997; Boethling and Lynch, 1992).

IPBC is a carbamate compound (Figure 1). Carbamates are commonly used as pesticides for a variety of purposes. The mode of action in animals is typically acetylcholinesterase inhibition (Ecobichon, 1991), however, the specific behaviour of IPBC is unknown. In fungi, the mode of action is associated with iodine toxicity (Ward, pers. comm., 1997). Similarly to DDAC, IBPC is also toxic to aquatic invertebrates and fish (Farrell et al., 1998a,b). However, long term toxicity is not expected to be an issue due to the rapid biodegradation rate of IPBC (i.e., half-life of 2 hours). Although a major degradation product, propynyl butyl carbamate (PBC) forms, it too degrades after 4 days (Szenasy and Bailey, 1996; Henderson, 1992b). Most concern for IPBC toxicity is immediately downstream of discharge sites and the potential for synergistic toxicity with DDAC.

These chemicals are released to the environment during stormwater events when precipitation washes them off treated lumber stored in the open yard or from equipment used to move the treated lumber around the site. Levels of DDAC and IPBC in the runoff effluent are regulated by the BC Ministry of Environment, Lands and Parks (BCMELP). The current effluent criteria in BC for DDAC and IPBC levels are 700 μg/L and 120 μg/L, respectively (Government of British Columbia, 1990). In 1994, BCMELP revised the stormwater discharge criteria derivations and proposed new limits, reducing the levels to 395 μg/L for DDAC and 67 μg/L for IPBC (Mason, 1994). However, the revised criteria are currently not enforced. Generally, BCMELP assumes a mixing zone of 100 meters from a discharge point. Beyond the realm of a mixing zone, it is further assumed that the chemical concentrations are such that no biological effects will occur (Szenasy and Bailey, 1996; Henderson, 1992a,b; Government of British Columbia, 1990). A technical review of antisapstain chemicals suggested that the algorithm used for the development of discharge criteria for DDAC and IPBC was likely conservative. The algorithm has no provision for bioavailability factors such as adsorption and biodegradation. However, there was no ambient water quality information to evaluate the adequacy of the algorithm (Szenasy and Bailey, 1996).

The identification of DDAC and IPBC as chemicals of concern in the Fraser River Basin prioritised them for the development of national Water Quality Guidelines (WQGs) by Environment Canada. These guidelines are designed to protect freshwater organisms in the ambient receiving environment. They do not, however, apply to levels in the sediment. A separate set of guidelines must be developed for that compartment. The toxicological information requirements for the WQGs were fulfilled by a separate study with researchers at Simon Fraser University in Burnaby, BC (Farrell et al., 1998a,b). The guideline values will be used to aid in the interpretation of additional studies with DDAC and IPBC.

To better understand the behaviour and fate of DDAC and IPBC in the Fraser River, concentrations in receiving waters downstream of lumber mill stormwater discharge sites were assessed. This study also assessed the interaction of these chemicals with suspended sediments present in the river water, an important factor since particulate matter is expected to effect bioavailability of the chemicals to organisms hence altering toxicity (TRS, 1997). This is especially relevant for DDAC, based on its chemical properties as a cationic surfactant.

DDAC is known to adsorb (bind) to organic matter such as soil and sediments, even glass. This property is especially relevant to the Fraser River, which is a turbid river with a great deal of organic matter present (McLaren and Ren, 1995). When DDAC enters the river, it passes from the water column onto the suspended sediment particles which eventually deposit into bed sediments. These depositional areas are high in organic matter and consequently should have high productivity. To compliment the new toxicity information developed for representative fish and invertebrate species from the Fraser River (Farrell et al., 1998a), toxicity bioassays were conducted with a benthic amphipod exposed to Fraser River basin sediment spiked with DDAC. In addition, depositional zones in the Fraser River downstream of stormwater discharge from lumber mills were sampled for DDAC and IPBC. This information is especially relevant since long term exposure to DDAC will most likely be from bed sediments in depositional zones.

This report puts the more formal toxicity evaluation used for setting national guidelines into a practical context that may be used to develop site specific objectives for the Fraser River Basin and other areas of heavy antisapstain usage.

2.0 DEVELOPMENT OF CANADIAN WATER QUALITY GUIDELINES FOR DDAC AND IPBC

Once an effluent reaches the receiving environment, ambient Water Quality Guidelines and criteria are used to assess the risks to aquatic species. Canadian Water Quality Guidelines (WQGs) are developed by the federal government (Guidelines and Standards Division, Environment Canada) under the auspices of the Canadian Council of Ministers of the Environment (CCME). Although these recommended benchmarks are not enforceable by law, they are used by other levels of government as the scientific basis for site-specific objectives that, in turn, are used to develop standards or discharge limits, which can be legally enforceable.

Initially, WQGs are subject to a peer review prior to being considered for national approval by the federal-provincial CCME Water Quality Guidelines Task Group. Pending adoption or modification of the guidelines, these reference values will serve as our effects-based benchmarks to interpret the relevance of ambient concentration data collected under FRAP.

In order to develop WQGs, a toxicological and environmental fate database on each chemical is compiled from all sources including the peer-reviewed literature and in some cases, voluntary submissions from the chemical manufacturer.

Toxicological and environmental fate information was gathered from all available sources. Standard test organisms using standardised protocols (e.g., Environment Canada, USEPA, ASTM) are preferred for guideline development, however novel test methods using ecologically relevant species with experimental protocols are also considered. Main sources of data for DDAC and IPBC were FRAP sponsored toxicological research (Farrell et al., 1998a,b) and industry data from the manufacturers DDAC (Lonza, Inc.) and IPBC (Troy Corporation).

In May 1998, Environment Canada released a draft document “Water Quality Guideline for the Protection of Aquatic Life for Didecyl dimethyl ammonium chloride (DDAC).” A similar document pertaining to IPBC is expected to follow in the near future.

2.1 DDAC toxicology and guideline value

The draft interim guideline value derived according to CCME protocol (CCME, 1991), was calculated by multiplying the most sensitive endpoint value by a safety factor of 0.05 (Table 2). The 48-hour LC_{50} value for *Daphnia magna* was selected as the most defensible sensitive endpoint value. The safety factor value assumed non-persistence. It is based on acute toxicity responses, and it is lower than would be the case if chronic endpoint data were available. The recommended draft interim guideline value is 1.5 µg/L (Table 2).

The water quality guideline (WQG) value for DDAC also takes into consideration its persistence in the aquatic environment. Environmental fate data are used to determine the safety factor. The persistence of DDAC remains a disputed issue and is currently being assessed. The half life may be as short as 11.2 days, or as long as 23 years (TRS, 1997; Henderson, 1992a), however, studies on other QACs indicate that this class of chemical is not persistent and the half life is on the order of days, rather than years (Boethling and Lynch, 1992).

Invertebrate toxicity varies widely, from a 48-hour LC_{50} of 29.5 µg/L for the water flea, *Daphnia magna* (Farrell et al., 1998a) to a 48-hour LC_{50} of 6.12 mg/L of active ingredient for the mussel, *Obliquaria refexa* (Waller *et al.*, 1993; Table 2).

Fish toxicity data ranged up to a 96-hour LC_{50} of 2.81 mg/L for *O. mykiss* (Liu, 1990 in Henderson, 1992; Table 2). Sturgeon fry at 40 to 60 days old were reported to be much more sensitive to DDAC than any other species tested. A 96-hour LC_{50} (lethal concentration at which 50% of organisms die) between 1.0 and 10 $\mu g \cdot L^{-1}$ was reported for fry (Bennett, 1996). This is one to two orders of magnitude lower than the next lowest observed effect level (LOEL) for fish, a 24-hour LOEL of 100 µg/L for the swimming performance of *Oncorhynchus mykiss* (rainbow trout) (Wood et al., 1996). In white sturgeon (*Acipenser transmontanus*), toxicity generally decreased with increasing age and size of the fish (Bennett, 1996). A study with 80 day old fry found toxicity decreased to 400 µg/L (TRS, 1997).

The sturgeon larval/fry study (Bennett and Farrell, 1998; Bennett, 1996) was found to be unacceptable for the purpose of guideline derivation. The study was exploratory in nature and was

not conducted according to a standardised toxicological test method. Furthermore, the data is outside the range of data collected for other fish species; outlier data estimated using novel approaches are not used for guideline development. However, the study has raised potential concerns regarding sturgeon larval/fry sensitivity to DDAC.

Two other ecologically relevant species which occur in the Fraser estuary, mysid shrimp (*Neomysis*) and starry flounder (*Plathicthys stellatus*), were also tested. In general, these two species were less sensitive to DDAC and IPBC than the freshwater organisms (Farrell et al., 1998a).

2.2 IPBC toxicology and guideline value

The draft interim guideline was derived by multiplying the 35-day LOEL for fathead minnow (*Pimephales promelas*) with a safety factor of 0.1, assuming non-persistence and based on chronic toxicity, in accordance with the protocol (CCME, 1991). The protocol yielded a recommended draft interim guideline value of 1.9 μg/L (Table 2).

IPBC is not considered a persistent substance because soil studies have found that degradation is rapid under aerobic conditions. Although there are no studies available for biodegradation in water, its behaviour is expected to be similar. Its half-life in soil is 2 hours, producing the major degradation product, propargyl butyl carbamate (PBC), which in turn, has a half-life of 4.3 days. Carbamates are not generally considered persistent in water (Menzer, 1991). In addition, toxicity of PBC to *O. mykiss* is 10,000 times less toxic (85 mg/L) than IPBC (6.7 μg/L) and 1,000 times less toxic to *Daphnia magna* (60 mg/L) when compared to IPBC (40 μg/L) (Springborn Laboratories, 1992a in Szenasy and Bailey, 1996). The toxicological database is summarised in Table 1. The distribution of toxicity data in relation to the critical value and the proposed water quality guideline value is illustrated in Figure 3.

The most sensitive endpoint for fish was a 35-day LOEL of 19 μg/L for reduced weight and length of larval fathead minnows exposed to IPBC as embryos (Springborn Laboratories, 1992). Toxicity levels ranged up to a 96-hour LC_{50} of 1.90 mg/L in Coho salmon embryo (Wood et al.,

1996a). Invertebrate toxicity ranged from a 48-hour LC_{50} for 40 µg/L for adult *Daphnia magna* (Farrell et al., 1998b) to a 24-hour LC_{50} of 1.419 mg/L for juveniles <24 h old of the same species (Inversek Research International, 1989).

To establish full guidelines for IPBC, some additional primary studies are required. These studies are: one primary chronic fish study on any species resident in North America, other than *O. mykiss* or *Pimephales promelas*; one primary chronic invertebrate study on a species resident in North America and from a class other than Crustacea and at least one primary study on a freshwater vascular plant or algal species resident in North America.

2.3 Potential application for setting site-specific objectives

Ambient WQGs can be used to develop site-specific water quality objectives for the Fraser River Basin. There are several factors that may affect the application of guideline values. These include: (1) physical, chemical and biological characteristics of the water bodies; (2) effects of local environmental conditions on water quality; (3) processes affecting the concentration of the chemical in water; and (4) factors that modify toxicity to aquatic organisms (CCME, 1991).

The local environmental conditions of this area may exert a major influence on the local objective. In particular, the high suspended sediment content of the river can affect the biological availability of the chemical, especially during freshet. DDAC readily adsorbs to particulate matter in the Fraser River and has been shown to be highly adsorptive to sediments, sand and soils (this study; TRS, 1997; Szenasy and Bailey, 1996). Studies demonstrating the amelioration of DDAC in Fraser River water and sediment were initiated by the manufacturer, the results of which are summarised in Table 3. The results of these studies show that particulate matter present in natural waters reduce the bioavailability of DDAC by binding the chemical, thus reducing toxicity to aquatic organisms. Another factor which will affect its impact is the intermittent nature of the runoff events. These site specific factors may increase the value chosen for the local objective considerably.

3.0 DDAC AND IPBC CONCENTRATIONS IN FRASER RIVER WATER

The impact on organisms in the Fraser River is dependent not only on the toxic effects of these chemicals, but also on their bioavailability to the organisms. A reconnaissance of DDAC and IPBC concentrations in the Fraser River was undertaken downstream of stormwater discharges at selected sawmills using formulations of DDAC/IPBC or DDAC in 1997. The purpose of this project was to provide a preliminary assessment of DDAC/IPBC concentrations in receiving waters adjacent to outfalls of selected sawmills using formulations of DDAC/IPBC or DDAC/borates. DDAC and IPBC concentrations in Fraser River water were evaluated at various distances downgradient from stormwater discharges. The objectives of this project also included providing a preliminary assessment of DDAC and IPBC environmental fate by comparing dilutions, using a fluorescent dye, versus their concentrations in the receiving environment and providing a description of the plume dispersion patterns for the outfalls at the studied sites. In addition, concentrations of DDAC and IPBC were evaluated in suspended solid fractions present in the water column. Given the lack of information available on the environmental fate of DDAC and IPBC field sampling protocols were also assessed, particularly since a complicating factor is the difficulty in handling DDAC, which readily adsorbs to any surface.

The survey was divided into two components, the plume dispersion study and an on-site dilution study. The purpose of the dilution study was to measure DDAC and IPBC from effluent, during a rainstorm event, in a dilution series with river water to assess interactions with suspended sediments. The objective of the field study was to determine the concentrations of DDAC in the ambient environment through plume dispersion from the mill outfall into the Fraser River during a rainstorm event.

3.1 Methodology

River sampling was conducted between April and August 1997, during rainstorm events at several sawmills in the Vancouver area. Two types of mills were selected, those using the DDAC/borate formulation, F2, and mills using the DDAC/IPBC formulation, NP1. Unfortunately, several

environmental and economic factors combined to lessen application of these results to the lower Fraser River. Firstly, the number of significant rain events that could be conveniently sampled were low compared to the fall and winter. Secondly, the overseas lumber market demand declined throughout the period which meant less wood was being treated. In addition the survey results are only applicable to river conditions with high suspended sediment concentrations.

3.1.1 Sampling procedure

There were two major requirements for study sites:

- a distinct discharge plume with no interference from log booms nor river traffic; and,
- a single (or one major) discharge point to enable a reasonable assessment of dilution, without the interference of adjacent multiple discharge points.

Only four mills in the Lower Mainland had discharge points which met the above noted criteria and sampling had occurred at all four mills. The mills are not named to assure anonymity.

The following conditions were required for sampling:

- the occurrence of a reasonable rainfall to enable a continuous stormwater discharge;
- adequate concentrations of DDAC and IPBC in the stormwater effluent, such that the levels in the receiving water were above laboratory detection limits for accurate measurement; and,
- ebb tide conditions ensuring a downriver flow direction for the stormwater plume and to simplify the details of the plume.

The mills were also selected to provide an assessment of DDAC concentrations in the receiving environments of mills which use an F2 product (a mixture of DDAC and borates) and mills which use NP1 (a mixture of DDAC and IPBC).

3.1.2 Sampling at F2 mills

The first sampling at Mill #1 occurred on April 15, 1997. Rhodamine WT dye was used to define a dilution plume within the study area at distances of 10, 50, 100 and 150 metres, at a depth of 0.5 metres; however, dye readings were sporadic and unable to define a dilution plume within the

study area and all samples of DDAC were lower than the analytical detection limit. The sampling was repeated on May 27, 1997. Since the plume location was verified with the dye, and noted to be directly adjacent to the shoreline, further sampling was done from shore without the use of a boat. The distances were reduced to 1, 5 and 10 metres from the discharge point and sampled as surface grabs. Dilutions were assessed by use of boron analyses.

3.1.3 Sampling at NP1 mills

Four separate samplings had occurred at the NP1 mill sites. Based on dye placement at each discharge point, it was visibly evident that samples could be obtained from the shoreline during ebb-tide events and the use of a boat was not considered to be necessary. As well, it was in indicated in laboratory tests that IPBC would be a sufficient indicator of dilution. Effluent and river samples were obtained at one NP1 mill on two different occasions, however the concentrations of DDAC and IPBC in the effluent were too low to enable studies of the receiving environment, (i.e., the concentrations in the effluent were near the laboratory detection limits for both DDAC and IPBC). Similarly the effluent samples at two other NP1 mills were also considered to be too low to continue the studies of concentrations in the receiving environment (Table 4).

As a result, the study plan was revised to assess the impact of river water on the analytical recoveries of DDAC, IPBC and borates.

3.1.4 Laboratory dilution studies

To investigate the influence of river water on chemical recoveries, river water sampled upgradient of sawmill effluent discharge points was used to dilute effluent samples from the F2 mill and spiked effluent samples from an NP1 mill.

Mixtures with 50%, 25% and 10% effluents were prepared by addition of river water.

3.1.4.1 Sample preservation and preparation

All samples collected for DDAC/IPBC were preserved in the field with hydrochloric acid and Rexonic N25-7, a multi-component non-ionic surfactant in the chemical form of alkyl polyoxyethylene glycol ether, which was added to prevent chemical adsorption to the sample container. The samples were then stored at 4^{o}C upon receipt at the Envirochem Laboratory. All field samples were analysed within 7 days of sampling. Tetra methyl ammonium chloride (TMAC) was added to all laboratory glassware used for the collection of solvent extracts to prevent chemical adsorption.

Total DDAC/IPBC samples were prepared by shaking the sample bottle vigorously for 30 seconds. A 500 mL sample was then analysed. The decanted samples were prepared by siphoning with Teflon tubes. All samples were allowed to settle in the cold room (4^{o}C) for 24 hours after sampling. One end of a Teflon tube was placed at 10 cm from the bottom of the 2.5 L amber glass bottle and the water sample was siphoned off.

A surrogate, dilauryl dimethyl ammonium bromide (DDAB), was added to the 500 mL sample aliquot in the separatory funnel for every set of samples except the last set. For the last set of samples submitted on September 9, 1997, DDAB was added to each sample bottle upon receipt.

3.1.4.2 Analytical procedures

For each sampling point or prepared mixture, two samples were analysed:

- a total sample; and,
- a decanted sample which was obtained by allowing a separate sample to settle in a 2.5 L bottle over a 24 hour period and by decanting the resulting supernatant by use of a Teflon tube siphon.

The analytical procedures for DDAC/IPBC were conducted in accordance to the British Columbia Environmental Manual - DDACX364 and IPBCX371, and the Environment Canada procedure dated September, 1995. DDAC/IPBC was extracted by dichloromethane after DDAB was added. The extract was concentrated and made up to volume. Two performance standards, cetyl

trimethyl ammonium chloride (CTAC) and quinaldine were added to the final extract to quantify DDAC and IPBC, respectively, using a gas chromatograph equipped with a nitrogen phosphorus detector.

Boron was measured by ICP at Quanta Trace Laboratories (now Northwest laboratories), in accordance to EPA Method 3197-4B. Two hundred millilitres of solution were used to determine suspended solid concentrations as per BC Environment Laboratory Manual-0008X332.

Total suspended solids analysis was performed as per procedure outlined in the British Columbia Environmental Laboratory Manual - 0008X332. The sample was filtered through a pre-weighed glass fibre filter (Whatman 934-AH) and the residue on the filter was dried to constant weight at 103^{o}C - 105^{o}C. The increase in weight of the filter was reported as Total Suspended Solids (TSS).

3.1.4.3 Laboratory quality control

- Blanks and spikes were analysed for each batch of 10 samples or less.
- Duplicates were prepared every 10 samples.
- The surrogate, DDAB, was added to each sample prior to extraction.
- The performance standards, CTAC and quinaldine were used to quantify DDAC and IPBC, respectively.
- DDAC spike recovery was 80 to 110 %.
- IPBC spike recovery was 90 to 110 %.
- Surrogate (DDAB) recovery was 80 to 110 %.

  In general, the presence of interfering substances (such as suspended solids, hydrocarbons or leachates) might lower the surrogate recovery. Surrogate recoveries typically are:

  1. greater than 80% in laboratory reagent water.
  2. greater than 70% in field samples with minimal emulsion during the extraction procedure.
  3. greater than 60% in field samples with large amount of emulsion during the extraction procedure.
- No detectable quantities of DDAC and IPBC should be found in the method blank.
- Chemical spikes with recoveries less than expected are repeated.
- Samples with surrogate recoveries less than those noted above are repeated.

- The relative percent difference (RPD) of duplicates should be no greater than 20%.
- The relative retention time (RRT) of the peaks of interest from gas chromatography (GC) analysis should be within 0.06 minutes of the corresponding standard.

3.2 Results and Discussion

3.2.1 Plume dispersion study

The stormwater discharge plume was required to contain sufficient DDAC and IPBC for analysis and to be distinct without interference. The Mill #1 (DDAC/borates) discharge and subsequent plume met all the requirements on May 27. A single plume remained adjacent to the shoreline. The effluent contained enough DDAC to measure in the plume for up to 10 metres. The original sampling of this mill on April 15 contained higher levels of DDAC, however, the sampling dilution zone was too large to detect DDAC. In addition, the dye tests were inconclusive to evaluate dilution factors since there were difficulties in obtaining samples which were representative of actual dilution factors, i.e., localised eddies and location of the plume at the surface. In contrast, three mills were sampled for the NP1 (DDAC/IPBC) study without obtaining sufficient levels of the chemicals in the effluent. Levels of DDAC ranged from 11 to 44 µg/L for samples collected between July 1 and August 6, 1997. The plumes differed in character as well. Only Mill #4 remained a single plume adjacent to the shoreline, the others split or fingered. The effluent concentrations and plume descriptions are given in Table 4.

At the F2 mill site on May 27, the plume sampling zone was reduced to 10 metres. The effluent contained an average of 446 µg/L DDAC, of which approximately half was dissolved. At a distance of 1 metre from the discharge point, the recoverable total DDAC levels in the plume had dropped to 111.5 µg/L while the dissolved fraction was only 47 µg/L. By 5 metres distance, total recoverable DDAC was at the analytical detection limit. Boron was used as a tracer to follow the plume and to calculate DDAC recovery. Concentrations of recoverable DDAC and boron are given in Table 5 and the decrease in levels in relation to the distance from the discharge is shown in Figure 4.

Approximately 56% DDAC was adsorbed onto particulate matter in the storm drain as only 44% of the compound was present in the decanted fraction of the effluent sample. DDAC recoveries in effluent samples were generally good. At a distance of 1 metre from the outfall, only 23.5% of DDAC was recovered, by 5 metres the amount of DDAC was at the detection limit (11 µg/L) at 2.5% recovery and at 10 metre DDAC was no longer detected (<10 µg/L) (Table 6, Figure 5). In contrast, boron recovery was directly proportional to the distance from the outfall, confirming that boron was an appropriate indicator of dilution factors for an F2 sawmill discharge. This difference suggests that recoverable DDAC concentrations were reduced much more rapidly than the boron concentrations. These results show the dilution capacity of the Fraser River is very high in the summer months, during freshet.

The amount of total suspended solids (TSS) in the river and plume were very high. These levels were not unexpected since sampling occurred during freshet and the Fraser River is known to be turbid. In contrast, typical TSS levels in winter range between 10 and 20 mg/L (Sekela, 1995). The TSS was 140 to 150 mg/L, downstream of the outfall compared to over 400 mg/L outside the plume (Table 5, Figure 5). This is most likely due to turbulent re-suspension of bottom sediments created by the force of the stormwater discharge.

The timing of the NP1 plume study coincided with a market slow-down for timber products. Inventories were generally lower than average and, mills had extended shut-downs and/or operations at one-shift per day, versus two or three shifts. In four sampling events at three different mills, the DDAC and IBPC concentrations in effluent samples were only slightly above laboratory detection limits (Table 4). As well, the field observations in Table 4 indicate that plume patterns may differ significantly dependent upon local conditions. The plume study was abandoned because the concentrations of DDAC and IPBC in the effluent were too low for accurate detection, especially after discharge into the river.

3.2.2 On-site dilution study

To evaluate the partitioning of the chemicals between suspended solids and water, as well as to assess analytical recovery in both total and decanted samples, effluent containing DDAC was diluted with known volumes of river water.

Dilutions of effluent from the F2 site with Fraser River water had boron levels at the theoretically expected concentrations, i.e., a 50% solution yielded 50% of the original concentration, with no differences between dissolved and total concentrations, indicating that boron remained in the dissolved phase at all times and was an acceptable conservative tracer (Tables 5 and 6; Figures 6 and 7). In contrast, recovery of DDAC decreased as the proportion of river water increased, dropping below 50% in a 1:1 dilution (Table 6, Figure 7). There was no significant difference between the recovery of DDAC from the total and decanted fractions, suggesting that the loss of DDAC may have resulted from analytical difficulties, rather than interaction with suspended solids. Analytical recovery may have been reduced by both complexation with anionic substances in the river water (Boethling and Lynch, 1992) or possibly the negative charges of the inorganic particulates in the river enhanced the binding of the positively charged quaternary ammonium ion. Recovery of the surrogate, DDAB, was similar to DDAC in the total fraction, however, recovery from the decanted fraction was over 76% for all dilutions and the effluent. This may be an artifact of the methodology, which added DDAB to the supernatant, after decanting, thus reducing the potential interactions with suspended solids (Table 6).

The concentrations of DDAC remained higher in the total fraction than the decanted samples, the difference being the greatest in the effluent (Table 5 and Figure 6). The levels of TSS ranged from 142 to 200 mg/L with the lowest levels in the 100% river water sample, showing that the effluent contained a significant portion of the TSS, which most likely had already bound a portion of the DDAC collected from the lumber yard runoff. No correlation between DDAC recovery and suspected solids could be made during this portion of the study because the concentrations of the suspended solids in the effluent and river waters were in the same order of magnitude. However, the river water definitely had an effect on the recovery of DDAC, suggesting that the composition of the suspended solids may be significant.

The poor recovery rate for DDAC was confirmed by results for individual river waters spiked with 774 µg/L F2 (i.e., 700 µg/L DDAC) (Table 7). Recoveries of the surrogate DDAB added to the total river water samples (with suspended solids) were similar to recoveries of DDAC in the total solution. These results suggest that DDAB is a good surrogate for DDAC and that the effects of suspended solids in the river waters are similar for both compounds. DDAB recovery in the decanted sample was higher because DDAB was added after the decanted portion was siphoned from the overall mixture.

Since effluent from NP1 mills during the sampled runoff events did not contain sufficient DDAC and IPBC to detect in the mixing zone, the effluent was spiked with NP1 containing 1400 µg/L DDAC and 100 µg/L IPBC to determine dilution recoveries. River water was obtained upgradient of a sawmill site and analysed to confirm the absence of DDAC and IPBC. This water was used as dilution water to prepare various test mixtures. In this study, 500 µg/L DDAB was added to the effluent/river water mixture. Hence, DDAB was added prior to decanting, in contrast to the F2 study where DDAB was added after the fractions were separated. The river water used for this portion of the study was lower in suspended solid content than the river water used in the F2 study. The analytical results are shown in Tables 8 and 9, and in Figures 8 and 9. Less than 100% of IPBC was recovered. This is evidence for some adsorption to TSS and this may increase with time as sediments downstream have measurable amounts of IPBC. DDAC recoveries were affected to a similar degree as observed earlier in the F2 studies. However, there was no significant difference between the total and decanted fractions. Recoveries were significantly below the expected theoretical values based solely on dilution. In addition, DDAC within the stormwater effluent was not fully recoverable. The effluent spiked with 1400 µg/L DDAC yielded only an average of 1,038 µg/L or a recovery of only 72% in the total sample. The TSS content of the effluent was relatively low, at 32 mg/L, suggesting the loss was due to either complexation processes or an analytical limitation (Table 3).

Table 8 shows a possible correlation between suspended solid concentrations and decreased recovery of DDAC. As TSS increased, recovery of DDAC decreased. There could be a competitive process between TSS and anionic substances in the river water for DDAC binding. As the adsorptive properties of DDAC are well documented during laboratory procedures (BC

Research, 1991; Environment Canada, 1991), it is not surprising that adsorption to particulate matter in a river receiving environment would occur.

3.2.3 Evaluation of pH on DDAC and IPBC recoveries

A series of tests were conducted to evaluate whether an increase in the extraction pH could result in enhanced recoveries of DDAC in the presence of suspended solids.

Three samples each of deionized water, river water and effluent were pH-adjusted to be acidic, neutral or basic, at pH 2, 7 and 12, respectively. Each sample, at each pH, was spiked with NP1 solution at 1,400 µg/L DDAC and 100 µg/L IPBC concentrations. They were also spiked with 500 µg/L DDAB to evaluate the impact of pH on recovery. Table 10 indicates that there are no significant differences in recoveries of DDAC from deionized water and stormwater effluents at pH readings 2, 7 and 12. However, DDAC recoveries from river waters could be enhanced by increasing the pH of the extraction solution to 12. Recovery of the spiked DDAC was still low at approximately 32% however. IPBC recoveries at pH 12 were significantly affected due to the possible hydrolysis of the ester group or the removal of the iodide from the alkyne group.

4.0 SEDIMENT TOXICITY TESTING WITH DDAC

The majority of toxicity information on DDAC has been regarding exposure from the water column, but very limited information exists on the effects of this chemical when bound to sediments. Exposure over the long term is most likely to occur from sediments. Toxicity tests were conducted with the freshwater benthic amphipod, *Hyalella azteca*, using a bulk sediment sample collected from the upper Fraser Basin which was spiked with DDAC. The tests were conducted to assess the toxicity of DDAC from sediment to invertebrates over a 14 day period. These animals live in sediments and are ecologically relevant to the Fraser River. The toxicity of the sediment was confirmed by a solid phase Microtox® test. A concurrent bioassay was run with the freshwater crustacean, *Daphnia magna*, to determine if DDAC was being released into the water column from the sediment at toxic levels.

4.1 Methodology

4.1.1 Sediment collection and preparation

Clean sediment was collected on November 12, 1997 from a site in the Nechako River near Prince George, British Columbia. The location was downstream of Miworth at 53°57.89' and 122°54.50'. This site is part of the Fraser River Basin and was selected due to previous sampling results indicating very low contaminant levels and a composition of silts and clays with some fine sands mixed in (Sekela et al., 1995; Northwest Hydraulic Consultants, 1993). Sampling was conducted by Environment Canada staff from Prince George. The sample was held at 4°C in the dark until spiking. One kilogram of the clean sediment was weighed out and placed in a standard kitchen blender. A pre-weighed quantity of Bardac 2280® was poured from a 50 mL beaker over the sediment as evenly as possible. 75 mL of deionized water was used a little at a time to rinse the beaker as well as to increase the moisture content of the sediment. The sediment and Bardac/water mixture was blended for 60 to 120 seconds or until homogenisation was reached at a high speed setting. Sediment was spooned out of the blender and into a 1 L jar that had been cleaned and prepared according to organic chemistry standards. Aluminum foil was laid over top of the jar and capped with a plastic lid. This procedure was repeated twice for each concentration to prepare duplicates. The jars were placed in a "Rotary Extractor." This instrument is a turning mechanism whereby the jars are tumbled at a slow speed for 6 hours thereby enhancing homogenisation of the sediment. The jars were allowed to settle overnight at 4°C. The supernatant was poured off and 100 mL quantities of sediment at each concentration were placed in 300 mL high-form beakers and topped with 175 mL of laboratory well water.

A sample of the Nechako River control sediment was analysed for particle size distribution by SoilCon Laboratories Ltd. (Richmond, BC).

4.1.2 *Hyalella azteca* 14-day growth and survival bioassay

Bioassay methodology followed the procedure outlined in Report EPS 1/RM/33, "Biological Test Method: Test for Growth and Survival in Sediment Using the Freshwater Amphipod *Hyalella*

azteca." November 1997. Prior to testing, the culturing methods also followed procedures outlined in the aforementioned document. Five replicates for each DDAC concentrations and controls were run with *H. azteca*. An additional three replicates contained no organisms and were used for chemistry subsampling on Day 0, Day 7, and Day 14, respectively. Unspiked Fraser River sediment and autoclaved silica sand were used as control sediments.

4.1.3 *Daphnia magna* 14-day survival bioassay

One replicate at each concentration, was run with *Daphnia magna* added to the overlying water. No *H. azteca* were present. Ten neonates were added to each jar and monitored for survival over the 14-day test period. Visual observations of reproduction and atypical behaviour were also noted. The organisms were fed and the procedures followed the *H. azteca* bioassay protocols.

4.1.4 Solid phase Microtox®

Solid phase Microtox® testing was conducted for:

- Day 7: 0 (control), 375, 750, 1500, 3000 and 6000 μg/g on Dec. 4, 1997
- Day 14: 0 (control), 375, 750, 1500, 3000 and 6000 μg/g on Dec. 16, 1997
- Day 0: 0 (control), 500 and 1000 μg/g on Jan 22, 1998
- Day 14: 0 (control), 500 and 1000 μg/g on Jan 30, 1998

Material and methods followed Environment Canada, Biological Test Method: Toxicity Test Using Bioluminescent Bacteria, Report EPS 1/RM/24 November 1992 and standard Microbics procedures (December 1992 Updated Manual for Microtox® testing). The replicates used for chemistry subsampling were used for the solid phase Microtox® test samples. The samples were placed in 50 mL centrifuge tubes and stored in the dark at 4^{o}C prior to centrifuging. The samples were centrifuged for 30 minutes at 4^{o}C and 4000 rpm to remove the pore water. An aliquot of 0.3 g of sample was serial diluted to obtain the test concentrations. The sediments were dried for 24 hours at 100^{o}C to correct for moisture content.

4.1.5 Chemical analysis of DDAC

Sediment and overlying water was analysed for DDAC concentrations on Day 0, Day 7 and Day 14.

All solvents for DDAC analysis were pesticide grade. Concentrated hydrochloric acid, formaldehyde and ammonium chloride were all ACS Reagent grade. Bardac 2280® (80% DDAC) was provided by Lonza Inc. (Fair Lawn, New Jersey). The surrogate, DDAB, at 98% purity, was purchased from Aldrich Chemical Co. Canada. The internal standards, cetyl trimethyl ammonium chloride (CMAC) was purchased from Sigma Inc. Rexonic N25-7 was obtained from Hart Chemical, Guelph, Ontario, Canada.

Immediately after sampling, the sediment and water samples were preserved with Rexonic solution and formaldehyde, then stored in darkness at 4^{o}C until analysis.

The extraction procedure used was developed for this study by Environment Canada's Pacific Environmental Science Centre (PESC). A wet sediment sample, about 10 g, was dried overnight in thermostat at 60^{o}C to constant weight for moisture content determination. Another wet sample approximately 1.5 g, was weighed into a 100 mL screw top centrifuge bottle. A surrogate (DDAB), 5 mL of 10% Rexonic in acetone, and 50 mL of acidified methanol were added to the sample. The sample was shaken on wrist-action shaker for 2 hours and then centrifuged at 3000 rpm for 15 minutes. The supernatant was decanted into a 500 mL round bottom flask. Pellet was washed twice with 10 mL aliquots of acidified methanol, centrifuged and supernatants collected in 500 mL round bottom flask. The supernatant was rotary evaporated to approximately 10 mL and transferred into 50 mL volumetric flask with acidified methanol. A 250 mL separatory funnel, containing 200 mL of a 5% ammonium chloride solution and 5 mL of 10% Rexonic in water was prepared. Different volumes, depending on the concentration of DDAC in soil, were transferred from 50 mL volumetric flask into 250 mL separatory funnel. DDAC was back extracted into organic phase by shaking with three 25 mL aliquots of dichloromethane (DCM). Organic phases were collected through a layer of baked sodium sulphate into 150 mL round bottom flask. The combined DCM solution was rotary evaporated to about 2 mL, 10 mL of acetone was added and volume further reduced to about 2 mL again. Sample was then transferred into volumetric flask

and a final volume made up to 5 mL with acetone. One mL of sample was transferred into GC vial. An internal standard was then added and the sample was analysed by High Resolution Gas Chromatography using nitrogen-phosphorus detector (HRGC-NDP).

Water samples were extracted as per soil samples back extraction. Briefly, the water sample was put into a 250 mL separatory funnel, surrogate (DDAB) was added, 5 mL of 10% Rexonic in water was added and the procedure was continued as described above.

The recovery of DDAC from water and sediment was greater using the technique developed by PESC than previous techniques and those used in Section 3.0. The differences may be due to modifications in the extraction procedure. Specifically, the technique used by PESC extracted the DDAC with dichloromethane and reconstituted the residue with acetone, which was then analysed by HRCG-NPD. In contrast, the procedure used in Section 3.0 also extracted the DDAC with dichloromethane, however the residue was reconstituted with a 1:1 mixture of DCM and toluene, the glassware was treated with Tetra methyl ammonium chloride (TMAC), and two performance standards, cetyl trimethyl ammonium chloride (CATC) and quinaldine (QUIN), were added to the vial before analysis.

4.2 Results and Discussion

Sediment toxicity bioassays were conducted with DDAC to assess the bioavailability and toxicity to aquatic organisms. Three types of organisms were used concurrently to compare availability patterns. *Hyalella azteca* was used to assess toxicity to benthic invertebrates. *Daphnia magna* was used to determine if DDAC in the sediment was bioavailable and toxic to the overlying water. A solid phase Microtox® was done to confirm that the toxicity to *H. azteca* was due to DDAC in the sediment, rather than in the water.

Water quality conditions for the 14 day test were measured on Day 0 and Day 14. Temperature of the test vessels was 23 $\pm 1^{o}$C; pH ranged from 7.6 to 8.3; dissolved oxygen levels ranged from 6.9 to 7.9 mg/L. Hardness ranged from 80 to 100 mg/L as $CaCO_3$, which is classified as moderately hard. These conditions were representative of the Fraser River water quality, with the exception of temperature (Sekela et al., 1995).

Acute and chronic toxicity of DDAC from spiked sediment was tested with the freshwater amphipod, *Hyalella azteca*. The 14-day LC_{50} was 1,099.8 µg/g DDAC with a steep dose-response curve (Table 11 and Figure 10). The NOEL was 750 µg/g and the LOEL was 1000 µg/g. In contrast, there was no observed effect of DDAC on *H. azteca* growth (Table 11 and Figure 11), possibly as a result of mortalies occurring at many of the test concentrations. However, the LC_{50} for sediment was ten times higher than previously reported for water only acute toxicity. The 48-hour LC_{50} for *H. azteca* in water without sediment was 110 µg/L (Farrell et al., 1998a). While a direct comparison is difficult, it is clear that toxicity in the presence of particulate matter is reduced. This difference is comparable to other toxicity results based on amelioration studies with DDAC and river water containing particulate matter (Table 3). A recent 28-day chronic study with *Chironomus tentans* conducted by the manufacturer found an LC_{50} of 2,085 µg/g and a chronic LOEC (for emergence) of 1,000 µg/g (TRS, 1997). These results suggest that DDAC is slightly less toxic to *C. tentans* than to *H. azteca*, but toxicity to both organisms is considerably less than water-only studies. However, the static nature of the sediment bioassays may reduce bioavailability compared with a natural system. In a river environment, organisms may breath the sediments because of the kinetic energy of the water flow which keeps them in suspension which in turn may increase bioavailability (Farrell, pers. comm., 1998).

A concurrent 14-day bioassay was run with *Daphnia magna* neonates exposed to the same spiked sediment concentrations, to assess DDAC exposure in the overlying water. Based on sediment concentrations, the 14-day LC_{50} was 2,250 µg/g, with a NOEL value of 1,500 µg/g and a LOEL value of 3,000 µg/g. The LC_{50} based on exposure concentrations from the water was 1,033 µg/L. The NOEL was 456 µg/L and the LOEL was 1,609.5 µg/L. All mortalities occurred within 48 hours of Day 0. All observed concentrations resulted in either 0 or 100% mortality (Figure 10). At sediment DDAC concentrations of ≤1,500 µg/g, the animals appeared healthy for the duration of the 14 day test. There was no observed effect on reproduction. Table 12 summarises the response of *D. magna* to DDAC exposure from sediment. The observed LC_{50} was 10 to 20 times higher than previously determined. Other studies with daphnids found LC_{50} values based on 48-hour static exposure from laboratory water ranged from 37 to 94 µg/L (Farrell et al., 1998a; Springborn, 1990 in TRS, 1997). The corresponding NOEL from the Farrell et al. (1998b) study

is 30 µg/L (37 µg/L LC_{50}) Amelioration studies conducted with DDAC and site water found a NOEL of 375 µg/L for *Ceriodaphnia dubia* (7-day test) which is very similar to the NOEL of 456 µg/L from this study. The difference between response in laboratory dilution water and site water or laboratory water with sediment present, is most likely due to complexation or adsorption to organic matter suspended in the overlying water.

Microtox® solid phase results are expressed as an IC_{50} (the statistical concentration of sample to cause a 50% decrease in light emission from the luminescent bacteria, *Vibrio fischeri*). The results are listed in Table 13. The data interpretation guidelines for the results were developed by the Environment Canada Aquatic Toxicology Laboratories in the Atlantic and Pacific Regions. They are based on data generated from toxicity tests and chemical analyses conducted on numerous soil and sediments. A wet weight value of 1.0% or greater is considered non-toxic to the bacteria. Values of 0.1% or less are considered very toxic and values ranging between 0.1% to 1.0% are considered moderately toxic. A dry weight value of 0.5% or greater is considered practically non-toxic to the bacteria. Values of 0.1% or less are considered toxic and values ranging between 0.1% and 0.5% are considered marginally toxic. A contaminated HS-6 sediment received from the National Research Council was tested as a reference toxicant for quality control.

The Microtox® solid phase test results indicate that DDAC spiked sediment with concentrations of 1500 µg/g or greater were toxic to the bacteria. DDAC spiked sediment with concentrations of 1000 µg/g or less were non-toxic to the bacteria. The effect of DDAC concentration on IC_{50} values is also shown in Figure 10. At each concentration, comparisons between Day 0, Day 7 and Day 14 test results indicate minimal differences. The HS-6 reference toxicant had an IC_{50} of 0.0213% which is an acceptable result and within the laboratory control chart warning limits.

Concentrations in the sediment and overlying water were verified on Day 0, Day 7 and Day 14. Percent recoveries from sediment and verifications of DDAC concentrations in the overlying water are summarised in Table 14. Details of the analytical results are provided in Appendix 2. Analysis results show that DDAC is stable for the duration of the study with minimal degradation in the sediment. The concentration range was 375 to 6000 µg/g. Average recoveries from sediment ranged from 72 to 110% for all concentrations. The recoveries indicated that the

overwhelming majority of DDAC was bound to the sediment particles rather than being present in the pore water. While it is possible that DDAC in the pore water accounted for a portion of the toxicity observed with *Hyalella azteca,* the solid phase Microtox® results also indicated that toxicity was observed with sediment-bound DDAC.

Levels of DDAC in the water were highest on Day 0 and lowest on Day 14. Concentrations ranged from 261 μg/L (Day 0, sediment exposure concentration 750 μg/g) to 2,959 μg/L (Day 0, sediment exposure concentration 6,000 μg/g). DDAC was below the detection limit in the water at exposure concentrations of 375 and 500 μg/g. In general, the amount of DDAC released into the water column from the spiked sediment did not exceed 0.05%, relative to sediment levels.

The sediment available for testing consisted of 77.1% sand, 16.3% silt and 6.4% clay. The predominance of sand as an unexpected result. This composition increases the bioavailability and recovery of DDAC since clays are known to bind DDAC more strongly (TRS, 1997). The composition of bed sediments in Lower Fraser River depositional zones is predominantly sand and silts in areas with stronger current, however calm water sloughs contain a higher ratio of silts and clays (Brewer et al., 1998; McLaren and Ren, 1995).

This study shows that even when adsorbed to sediment particles containing sand and silts, DDAC is bioavailable and toxic to benthic organisms at concentrations in excess of 1,500 μg/g. In confirmation of the amelioration studies conducted by the manufacturer, toxicity of DDAC in the presence of organic matter is reduced approximately 10-fold. A more important factor becomes the issue of persistence, which has been disputed in the past and remains unresolved. The half life may be as short as 11 days or as long as 23 years. This sediment test found no degradation after 14 days at 23^{o}C. Consequently, since biodegradation is a temperature dependent process, it may be assumed that DDAC in the Fraser River sediments will likely persist longer than the 14 day duration of the bioassay as river temperatures are often well below 23^{o}C.

5.0 DDAC AND IPBC IN FRASER RIVER SEDIMENTS - A PRELIMINARY SURVEY

A preliminary survey of sediments in depositional zones along the Fraser River was conducted on March 19, 1998. Four sites were selected based on their proximity to lumber mills using DDAC and IBPC, as NP1. The purpose of this study was to determine if DDAC and IPBC were present in sediments downstream of potential sources and assess if depositional areas could be considered zones of potential biological impact.

5.1 Methodology

5.1.1 Study Design

Four sites in the lower Fraser River were selected for sampling. The locations were chosen based on their proximity to lumber mills using both DDAC and IPBC. All samples were collected on Thursday, March 19, 1998. The weather was fair with some high cloud; there was dead calm. The weather was dry for the two days prior to sampling.

No reference site was sampled that day, however, the sediment sample collected from the Nechako River for the sediment toxicity bioassays (Section 4) may be considered a reference site as it is part of the Fraser River Basin. No DDAC was detected in that sample and IPBC was not tested.

Site # 1

Site #1 was downstream of S&R Sawmills in Parsons Channel, around Barnson Island, in Surrey, BC. Location co-ordinates were 49^{o}10.904' N and 122^{o}42.520' W. Samples were collected at a depth of 3 metres approximately 100 metres downstream of the mill, along the left bank, about 15 metres from the shore. There was a surface runoff drainage pipe about 40 metres upstream of the sampling location.

Samples were collected at 10:15 am (PST). The tide was just beginning to ebb.

Site # 2

Site #2 was downstream of Teal Cedar Products Stag Timber Mill in Parsons Channel, around Barnson Island, in Surrey, BC. Location co-ordinates were 49°11.508' N and 122°43.626' W. Samples were collected at a depth of 9.1 metres. The location was approximately 20 metres downstream of a loading pier, about 20 metres upstream of a ferry terminal, and 8 to 10 metres from the shore.

Samples were collected at 10:55 am (PST).

Site # 3

Site #3 was downstream of Interfor-Fraser Mills in the Sapperton Channel near Queen's Reach, upstream of the Brunette River in Coquitlam, BC. Location co-ordinates were 49°13.466' N and 122°51.481' W. Samples were collected along the right bank, approximately 50 metres from the shore at about 50 metres from both a barge and the filling cranes, at a depth of 2.6 metres.

Samples were collected at 1:30 pm (PST).

Site # 4

Site #4 was downstream of Canfor-Eburne Sawmills in the North Arm of the Fraser River, across from Sea Island, in Vancouver, BC. Location co-ordinates were 49°12.159' N and 123°08.551' W. Samples were collected in the slough, not the river channel, along the right bank, approximately 7 metres from the shore at a depth of 2.8 metres.

Samples were collected at 3:40 pm (PST).

5.1.2 Sample Collection

Samples were collected by Environment Canada staff following standard bed sediment sampling procedures (Brewer et al., 1998). All field equipment was made of stainless steel. All sample containers were made of glass with aluminum foil under the lids. Prior to being in contact with sediment samples, the containers were washed with tap water and laboratory detergent, then

rinsed with tap water, then deionized water, rinsed with pesticide-grade acetone followed by a hexane rinse, then air dried.

Sites were sampled by boat using an Eckman dredge (15 cm X 15 cm X 15 cm). Five bed sediment samples were collected from each site. The top 2 to 3 cm layer of each grab was collected with a stainless steel spoon while the outer 2 cm rim of the grab that contacted the dredge was discarded. All five samples were placed on a stainless steel tray and homogenised by hand. The composite sample was then placed into the glass jar and kept chilled until delivery to the laboratory.

5.1.3 Laboratory Analysis

Samples were stored at 4^{o}C until analysis. Samples were analysed for DDAC and IPBC at the Pacific Environmental Science Centre (PESC). The particle size distribution of the sediment was determined by SoilCon Laboratories, Ltd. (Richmond, BC) and validated by PESC QA/QC procedures. Extraction procedures and analysis techniques are described in Section 4.1.5. Both DDAC and IPBC were analysed using the same technique with DDAB as the surrogate for extraction efficiency determination.

5.2 Results and Discussion

Sediment samples were analysed for DDAC and IPBC in duplicate. The concentrations of DDAC in the samples ranged from 0.52 to 1.26 μg/g with a mean of 0.91 ±0.29 μg/g dry weight (n=8). The concentrations of IPBC in the same samples ranged from 0.19 to 0.57 μg/g with a mean of 0.35 ±0.14 μg/g dry weight (n=8). DDAC and IPBC levels at the four sites are given in Table 15. The sediment samples from Sites #2 and #4 were spiked with DDAC and IPBC to determine extraction efficiencies. Extraction efficiency data is provided in Table A6 (Appendix 3). Recoveries ranged between 69% to 95% for DDAC and 38% to 89% for IPBC. The recovery for IPBC was relatively low at Site #4, possibly due to the higher moisture content of the sediment which resulted in a dry weight of only 6 g. Generally a sample's dry weight should be over 10 g

for recovery analysis. Most samples were approximately 8 g, which may have also reduced extraction efficiencies for DDAC and IPBC. Values are shown in Table 15.

The sediment composition was predominantly silt (over 60%) at three sites and sand (over 50%) at Site #2. The clay content ranged from 9% to 30% for the four sites. Sediment compositions are shown in Table 16. The predominance of silt and sand suggests that DDAC, and probably IPBC, increases the potential for bioavailability. The K_{ow} of DDAC is estimated to be between 6.03 and 6.65 (MacKay et al., 1993; Lyman and Loreti, 1987 in Lyman, 1995) which suggests a potential for bioaccumulation, however DDAC and other QACs are not known to bioaccumulate (Boethling and Linch, 1992; TRS, 1997). Previous studies have focused on DDAC binding to bentonite clays, which is thought to reduce bioavailability through strong adsorption of DDAC (TRS, 1997; Bargar, 1991). However, depositional zones in the lower Fraser River are unlikely to contain such fine particulates in significant quantities.

The sediment levels were higher than anticipated, particularly for IPBC, which should have a half life in aerobic soil of only 2 hours (Szenasy and Bailey, 1996). In addition, the amount of DDAC used by mills is 93% higher than IPBC, however, the difference of the two chemicals in the sediment is only approximately 60% (based on the mean values), suggesting that IPBC is much more persistent than expected.

The levels of both chemicals were orders of magnitude higher than other pesticides measured in the Fraser River sediments. By comparison, bed sediment levels of lindane in the North and Main arms of the Fraser River had a maximum of only 0.84 ng/g dry weight (Brewer et al., 1998), which exceeded federal sediment quality guidelines. No sediment guidelines exist for DDAC or IPBC.

5.0 CONCLUSIONS

DDAC and IPBC criteria have been proposed for ambient waters based on information on acute toxicity to aquatic organisms. There is limited information available on chronic toxicity, possibly

due to the mode of action of these chemicals. In particular, DDAC typically produces a very sharp dose-response curve with aquatic organisms. Information from FRAP funded studies with Simon Fraser University researchers and the chemical suppliers was used to develop Canadian National WQG. The draft interim guideline for the protection of freshwater life is set at 1.5 μg/L for DDAC and 1.9 μg/L for IPBC. The draft guidelines must undergo a review process through the CCME and obtain approval before being established as official national (CCME) WQG.

Dissolved DDAC concentrations in river waters appear to be affected by adsorption and complexation processes. Analytical recovery from river water was greatly reduced, possibly due to the presence of suspended solids. Recovery results for the total and dissolved fractions of DDAC suggest the adsorption with particulate matter or complexation with anionic substances is irreversible, at least with the extraction method commonly used. Data indicate that the bioavailability of DDAC from stormwaters to fish is also significantly reduced upon mixture with Fraser River water.

IPBC in Fraser River water remains in the dissolved phase and appears to be unaffected by suspended solids. It was present in the stormwater runoff from lumber mills and would be present downstream of the outfalls where dilution would eventually dissipate it.

Overall, the zone of potential biological impact of DDAC and IPBC in the aquatic phase appears to be quite restricted due to physical chemical processes and due to low concentrations of DDAC/IPBC in discharges coupled with high suspended solids encountered during the summer sampling. However, there may be potential for impact to organisms in depositional zones downstream of discharge sites. The sediments used for toxicity bioassays in this study were typical of Fraser River bed sediments in depositional sites downstream of lumber mills, with the exception of some sloughs (Brewer et al., 1998; McLaren and Ren, 1995).

The results of the sediment toxicity testing confirmed that amelioration with suspended solids reduces acute toxicity, however, this study found that DDAC in sediment remained bioavailable to benthic organisms and invertebrates in the water column, as well as the Microtox® bacteria. The acute toxicity was much lower than water-only tests, as previously studies have shown (TRS, 1997). Generally, bound particles are not considered to produce acute toxicity to fish, however

the effects of ingestion of these DDAC contaminated particulates is unknown. A recent study by Qiao and Farrell (1996) found that organic chemicals adsorbed on suspended sediments from the Fraser River transferred onto the gills of *O. mykiss* and bioaccumulated, under laboratory conditions. It is possible that the DDAC had adsorbed onto the sediment particles and transferred onto the gills of the benthic amphipod, *Hyalella azteca*, resulting in the observed acute toxicity discussed in this report.

The preliminary survey of bed sediments near lumber mill discharge sites found that both DDAC and IPBC were present at levels that are in the parts per million range. These levels of DDAC were orders of magnitude (1000 times) lower than levels at which acute toxicity was observed. While IPBC sediment toxicity has not been studied, it is also likely that IPBC, at the levels observed, would not be acutely toxic. However the possibility of additive or synergistic effects from DDAC and IPBC in the sediment have not been assessed. For instance, in water-only tests, the combination of DDAC and IPBC have synergistic effects on *Hyallela azteca* (Farrell et al., 1998b). On the other hand, a recent study reported the two chemicals may be antagonistic to other species (EVS, 1998) which makes conclusions about synergism speculative at this time.

While this study suggests that the DDAC which settles into the Fraser River sediments is not acutely toxic, the persistence of DDAC remains a disputed issue. DDAC in the Fraser River sediments would be stable for even longer than observed in the sediment bioassays, particularly since the temperature, a factor in degradation, is generally much lower in the river. Accordingly, the possibility of long term chronic toxicity cannot be dismissed.

The confirmed presence of these antisapstains in Fraser River bed sediments along with their heavy usage in a concentrated area of the Fraser River and coastal BC, suggest a potential for exposure to aquatic organisms. The combined hazard and exposure indicates that there may be a risk to both fish and invertebrates. Until further tests are available, both DDAC and IPBC must be considered chemicals of concern in the Fraser River Basin (as well as the Georgia Basin), and potentially in other areas of Canada where they are being released into aquatic systems.

6.0 RECOMMENDATIONS

- The present effluent guidelines (700 μg/L for DDAC and 120 μg/L for IPBC) were set in 1988 in the absence of the newer toxicity information used to propose the interim ambient guidelines. With the proposed effluent criteria, dilutions of 466:1 and 63:1 would be needed for DDAC and IPBC, respectively to meet the proposed guideline in the absence of any discharges upstream of a particular stormwater outfall. Based on the current information, a re-evaluation of the current effluent limits is recommended to determine if they are compatible with the proposed WQG (1.5 μg/L for DDAC and 1.9 μg/L for IPBC).

- Another independent study assessing sensitivity of white sturgeon to DDAC should be undertaken. As well, the potential toxicity of IPBC to this species should be investigated.

- Site-specific objectives for the Fraser River should be developed. While it is likely that somewhat higher site specific objectives than the proposed guidelines could be chosen for DDAC, this may not be the case for IPBC which isn't adsorbed by sediments nor is it as quickly degraded as previously thought. This step would address the concerns of industry about the relevance of the national WQG to conditions in the Fraser River; an important consideration, given the current economic conditions in the British Columbia lumber industry and the lack of an economical alternative for DDAC.

- The toxicity of DDAC and IPBC in a marine receiving environment should also be evaluated. While it is argued that ionic complexation in seawater would lessen toxicity, suspended sediment adsorption and possible inactivation may not be a factor in many coastal mill sites that use the chemicals.

- To define further the potential for exposure to DDAC from sediments, additional sediment toxicity bioassays should be conducted to validate the results from this study. These future studies could be used to develop national sediment quality guidelines, which require at least two organisms and two different testing laboratories for guideline development (CCME, 1991).

- Future studies should include more thorough assessments of the amount and availability of both DDAC and IPBC in deposition zones in the Fraser River and Georgia Basins, including the marine environment and local reference sites. Such studies would allow the evaluation of the ecological relevance of the current toxicological studies and assessment of the risks associated with exposure to these chemicals.

- The receiving environment study of DDAC and IPBC from stormwater runoff should be repeated during the winter months when rainstorm events are more frequent and consequently usage of antisapstains is much higher. This would enable a more accurate characterisation of the discharge plume and dilution zone.

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TABLES

Table 1. Summary of toxicological database for DDAC and IPBC.

Parameter	DDAC	IPBC
toxicity range for fish	0.00074 - 2.81 mg/L	0.019 - 1.90 mg/L
toxicity range for invertebrates	0.0295 - 6.12 mg/L	0.04 - 1.419 mg/L
most sensitive fish	juvenile *Acipenser transmontanus* (white sturgeon)	*Pimephales promelas* (fathead minnow)
most sensitive invertebrate	*Daphnia magna* (water flea)	*Daphnia magna* (water flea)
most sensitive species	juvenile *A. Transmontanus* (white sturgeon)	*Pimephales promelas* (fathead minnow)
least sensitive species	*Obliquaria refexa* (threehorn wartyback mussel)	*Oncorhynchus tshawytscha* (Chinook salmon)

(Sources: Farrell et al., 1998a,b; Bennett, 1996; Springborn Laboratories, 1992; TRS, 1997; Inveresk Research International, 1989; Henderson, 1992a,b; Bargar, 1991)

Table 2. Recommended draft interim Canadian Water Quality Guidelines values for DDAC and IPBC.

Parameter	draft interim Guideline Value (µg/L)	Critical Value (µg/L)	Safety Factor	Test	Organism
DDAC	1.5	29.5	0.05	48-h EC_{50}	*Daphnia magna* (water flea)
IPBC	1.9	19	0.1	35-d LOEL	*Pimephales promelas* (fathead minnow)

Table 3. DDAC amelioration studies conducted with site water or sediment (from TRS, 1997). Toxicity is reduced in the presence of particulate matter by lowered bioavailability of DDAC to organisms.

Study	Test Conditions - DDAC exposure in different dilution waters	Results
96-h *Acipenser transmontanus*	laboratory water* laboratory water* with Fraser River sediment	LC_{50} = 416 µg/L LC_{50} = 6500 µg/L
96-h *Pimephales promelas*	laboratory water* Fraser River sediment 100 mg/L TSS** 200 mg/L TSS** 400 mg/L TSS** Fraser River water	LC_{50} = >300<1000 µg/L LC_{50} = >1000<3000 µg/L LC_{50} = >1000<3000 µg/L LC_{50} = >1000<3000 µg/L LC_{50} = >1000<3000 µg/L
7-d *Pimephales promelas*	laboratory water* site water	NOEL = 190 µg/L NOEL = 2500 µg/L
7-d *Ceriodaphnia dubia*	laboratory water* site water	NOEL = 37.5 µg/L NOEL = 375 µg/L

* standard laboratory dilution water

** TSS = total suspended solids

Table 4. Concentrations of DDAC and IPBC in stormwater effluent and description of plume dispersion patterns from sawmill outfalls.

Site	total DDAC (µg/L)	total IPBC (µg/L)	Plume Description
Mill #1 (F2 - April 15)	692 (±240)*	n/a	single plume adjacent to shoreline.
Mill #1 (F2 - May 27)	446 (443-449)**	n/a	single plume adjacent to shoreline.
Mill #2 (NP1 - July 1)	11	<5	split into two parts - one near shore and the other perpendicular to shoreline.
Mill #2 (NP1 - July 5)	23	5	split with a portion along the shoreline.
Mill #3 (NP1 - August 6)	35	11	fingered due to discharge of effluent on rip-rap.
Mill #4 (NP1 - August 6)	44	<5	adjacent to shoreline.

* mean value (n=4) with standard deviation in brackets.

** average value (n=2) with range in brackets.

Table 5. Levels of DDAC, boron and total suspended solids (TSS) in stormwater effluent and in samples diluted with Fraser River water.

F2 Mill Site	Sample ID	DDAC Concentrations (µg/L)		Boron Concentrations (µg/L)		TSS (mg/L)
		Total	Dissolved	Total	Dissolved	
Distance from Discharge	100% effluent (0 m)	446 (443-449)*	198	1150	1120	148
	1 m	111.5 (104-119)*	47	610	670	165
	5 m	11	<10	200	170	431
	10 m	<10	<10	90	90	389
Dilutions	50:50**	102 (93-111)*	24	580	560	187
	25:75	31 (25-37)*	15	300	290	180
	10:90	<10	<10	130	120	200
	river water	<10	n/a	<10	<10	142

* Average value (n=2) with range in brackets.

** percent effluent:percent river water

Table 6. Recovery of DDAC and surrogates from samples diluted with Fraser River water.

F2 Mill Site	Sample ID	DDAC % original concentration		Boron % original concentration		DDAB % recovery	
		Total	Dissolved	Total	Dissolved	Total	Dissolved
Distance from Discharge	100% effluent (0 m)	100[a]	100[a]	100	100	71	76
	1 m	25.0 (23.5-26.5)*	23.7	53.0	59.8	60 (55-65)*	81
	5 m	2.5	<5	17.4	15.2	28	72
	10 m	<2	<5	7.8	8.0	32	61
		% recovery		% recovery			
Dilutions	50:50**	45.8 (41.4-50.2)*	31.8 (24.2-39.4)*	100.8	100.0	54.5 (49-60)*	82.5 (81-84)*
	25:75	28.0 (22.4-33.6)*	29.2 (28.0-30.4)*	104.0	104.0	43.5 (43-44)*	78.5 (77-80)*
	10:90	<25	50	113.0	107.0	27 (24-30)*	77.0 (71-83)*
	river water	-	-	-	-	9	-

* Average value (n=2) with range in brackets.

** percent effluent:percent river water

[a] assumed value.

Table 7. Concentrations and recovery of DDAC, boron and the surrogate, DDAB, from spiked samples.

Sample	DDAC Measured concentration (µg/L)		Boron % original concentration		DDAB % recovery	
	total	dissolved	total	dissolved	total	dissolved
Bardac & river water** (700 µg/L)	37 (31-43)*	73	5.2 (4.4-6.1)*	10.4	7 (6-8)*	41
F2 & river water** (774 µg/L)	91 (89-93)*	39	11.8 (11.5-12.0)*	5.0	17 (15-19)*	71
Bardac & deionized water (700 µg/L)	572.5 (558-587)*	-	81.8 (79.7-83.9)*	-	82 (80-84)*	-
Bardac & deionized water (50 µg/L)	46	-	92.0	-	101	-
Blank	<10	-	-	-	102.5 (101-104)*	-

* Average value (n=2) with range in brackets.

** river water was sampled on May 27, 1997.

Table 8. Results of DDAC/IPBC monitoring at NP1 mill sites and laboratory dilution study with spiked effluent.

Site	Sample	DDAC Concentrations		IPBC Concentrations		TSS
		Total (µg/L)	Dissolved (µg/L)	Total (µg/L)	Dissolved (µg/L)	(mg/L)
Mill sampled Aug. 6, 1997	effluent	35	n/a	11	n/a	n/a
NP1 dilutions	effluent**	1038.5 (937-1140)*	1002.5 (975-1030)*	96.5 (94-99)*	101.5 (98-105)*	32
	50:50	230.5 (215-246)*	272	49.5 (49-50)*	45	52
	25:75	61	70	24	24	93
	10:90	13	7.5 (7-8)*	10	9 (8-10)*	108
	river water	<10	n/a	<5	n/a	126

* Average value (n=2) with range in brackets.

** Effluent collected on August 6, 1997, was spiked with NP1 solution containing 1400 µg/L DDAC and 100 µg/L IPBC.

Table 9. Recoveries of DDAC and IPBC from effluent/river water mixtures sampled using effluent.

Sample	DDAC % recovery		IPBC % recovery		DDAB % recovery	
	total	dissolve	total	dissolve	total	dissolve
effluent**	72.5 (67-78)*	72 (70-74)*	87 (85-89)*	91 (88-95)*	70.5 (68-73)*	52 (51-53)*
50:50	33.0 (31-35)*	39	89 (88-90)*	81	33 (31-35)*	25
25:75	17	20	86	86	14	11
10:90	9	5.5 (5-6)*	90	81 (72-90)*	10	3.5 (3-4)*
river water	<10	-	<5	-	9	-
method blank	<10	-	<5	-	90	-
QA/QC spike	98	-	93	-	97	-

* Average value (n=2) with range in brackets.

** Effluent collected on August 6, 1997, was spiked with NP1 solution containing 1400 µg/L DDAC and 100 µg/L IPBC.

Table 9. Effects of pH on DDAC and IPBC recoveries.

Sample	DDAC (% total)	IPBC (% total)	DDAB (% total)
deionized water pH 2	99 % 1390 µg/L	105	90
deionized water pH 7	97 % 1360 µg/L	96	71
deionized water pH 12	94% 1310 µg/L	27	68
river water pH 2	20.5 (20-21)%* 290 (280-300) µg/L*	91 (90-92)*	24
river water pH 7	18.5 (18-19)%* 256 (250-262) µg/L*	82 (76-88)*	20.5 (20-21)*
river water pH 12	31.5 (31-32)%* 441 (440-442) µg/L*	7.2 (<5-12)*	31.5 (30-33)*
effluent pH 2	95 % 1330 µg/L	97	84
effluent pH 7	74 % 1040 µg/L	96	68
effluent pH 12	81 % 1130 µg/L	18	70

* Average value (n=2) with range in brackets.

Table 10. Data summary of *Hyalella azteca* 14-day growth and survival bioassay with DDAC spiked sediment.

Sample #	Survival (%)	Mortality (%)	Significant* ($p<0.05$)	Mean Weight/ Animal (mg)	% of Control Sediment	Significant* ($p<0.05$)
Silica Sand Control	94	6	-	0.22	-	-
Sediment Control	95	5	-	0.18	100	-
375 µg/g DDAC	80	20	Yes	0.22	120	No
500 µg/g DDAC	92	8	No	0.19	102	No
750 µg/g DDAC	92	8	No	0.14	76	No
1000 µg/g DDAC	62	38	Yes	0.19	102	No
1500 µg/g DDAC	0	100	Yes	0.00	-	-
3000 µg/g DDAC	0	100	Yes	0.00	-	-
6000 µg/g DDAC	0	100	Yes	0.00	-	-

* based on a 1-tailed t-test.

Table 11. Data summary of *Daphnia magna* 14-day survival bioassay with DDAC spiked sediment.

DDAC (In Sediment) Nominal (µg/g)	DDAC (In Water) Verified (µg/L)	Total	Live	Dead	Average Mortality	Growth and Reproduction	Notes
Lab Control (Silica Sand)	Lab Control (Silica Sand)	10	10	0	0%	Good	healthy
Sediment Control	Sediment Control	10	10	0	0%	Good	healthy
375	< 50	10	10	0	0%	Good	healthy
750	261	10	10	0	0%	Good	healthy
1500	456	10	10	0	0%	Good	healthy
3000	1609.5	10	0	10	100%	n/a	dead within 48 hours
6000	2956	10	0	10	100%	n/a	dead within 12 hours

Table 12. Data summary of solid phase Microtox® using the luminescent bacteria, *Vibrio fischeri* with DDAC spiked sediment.

DDAC concentration (µg/g)	IC_{50} wet[a] (%)			IC_{50} dry[b] (%)		
	day 0	day 7	day 14	day 0	day 7	day 14
control	2.83	3.20	3.30/2.92*	2.23	2.47	2.59/2.26*
375	-	2.35	1.89	-	1.83	1.46
500	1.80	-	1.90	1.41	-	1.49
750	-	2.00	2.17	-	1.55	1.68
1000	1.40	-	2.00	1.09	-	1.57
1500	-	0.124	0.183	-	0.100	0.140
3000	-	0.029	0.022	-	0.023	0.017
6000	-	0.011	0.011	-	0.0086	0.0084

* first value obtained from test with 500 and 1000 µg/g concentrations; second value obtained from original concentration range.

"-" means not tested

[a] not moisture corrected

[b] moisture corrected

Wet weight key for IC_{50} values:

> 1.0% is non-toxic
>0.1% but < 1.0 % is moderately toxic
<0.1 % is very toxic

Dry weight key for IC_{50} values:

> 0.5 % is practically non-toxic
>0.1 % but < 0.5 % is marginally toxic
< 0.1 % is toxic

Table 13. Summary of DDAC recovery from sediment and verification of concentrations in water samples from a 14-day spiked sediment bioassay with *Hyalella azteca*.

DDAC nominal concentration (µg/g)	Sediment DDAC % recovery*			Water DDAC verified concentrations (µg/L)		
	day 0	day 7	day 14	day 0	day 7	day 14
control	-	-	-	<50	<50	<50
375	79	84	72	<50	<50	<50
500	106	104	92	<50	-	<50
750	84	88	81	261	<50	<50
1000	110	-	90	53	-	<50
1500	92	89	99	456	105	<50
3000	93	87	86	1610	698	<50
6000	84	90	94	2959	644	82

* recovery on dry weight basis

Table 14. DDAC and IPBC concentrations in Fraser River sediments.

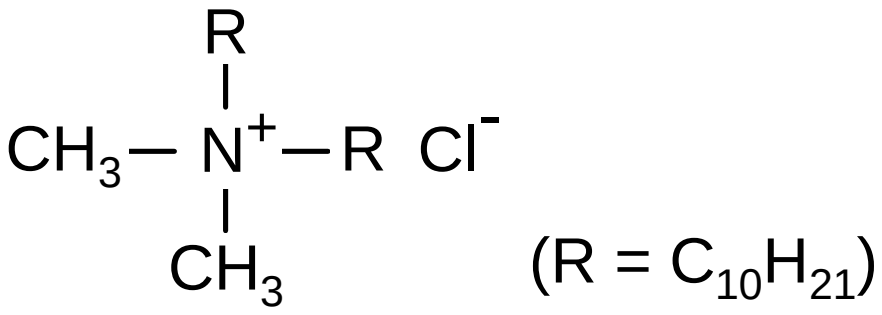
Site #	Sample* #	wet weight (g)	dry weight (g)	% moisture	surrogate recovery	DDAC (µg/g DW)	IPBC (µg/g DW)
1	1	14.7	7.8	47	58	1.21	0.22
1	2	14.7	7.8	47	68	1.26	0.25
2	1	15.2	8.5	44	73	1.04	0.26
2	2	15.2	8.5	44	95	1.14	0.57
3	1	15.1	8.5	44	76	0.56	0.19
3	2	15.4	8.6	44	82	0.52	0.36
4	1	15.7	6.0	62	67	0.80	0.47
4	2	15.3	5.8	62	69	0.76	0.49
average		15.2	7.7	49	74	0.91	0.35

* sub-samples of a single grab per site.

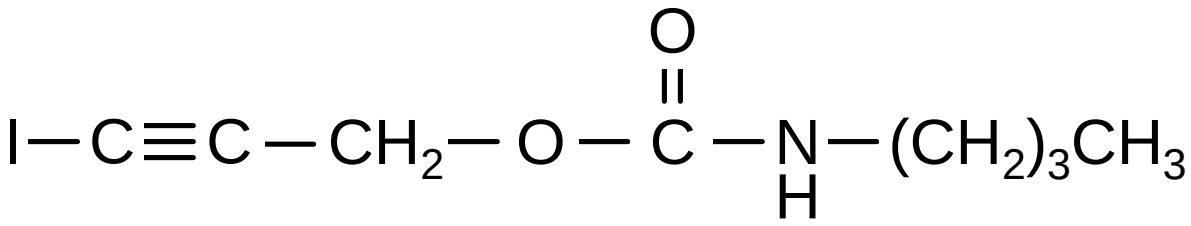
Table 15. Particle size distribution of sediment samples collected from the lower Fraser River.

Site #	Gravel (> 2mm)	Sand (2 - 0.063 mm)	Silt (0.063 - 0.004 mm)	Clay (<0.004 mm)
1	0.11 %	16.30 %	68.31 %	15.28 %
2	0.23 %	50.49 %	40.00 %	9.27 %
3	0.00 %	24.56 %	62.82 %	12.62 %
4	0.00 %	1.24 %	68.89 %	29.87 %

FIGURES



didecyl dimethyl ammonium chloride (DDAC)



3-iodo-2-propynyl-butyl carbamate (IPBC)

Figure 1. Chemical structures of didecyl dimethyl ammonium chloride (DDAC) and 3-iodo-2-propynyl butyl carbamate (IPBC).

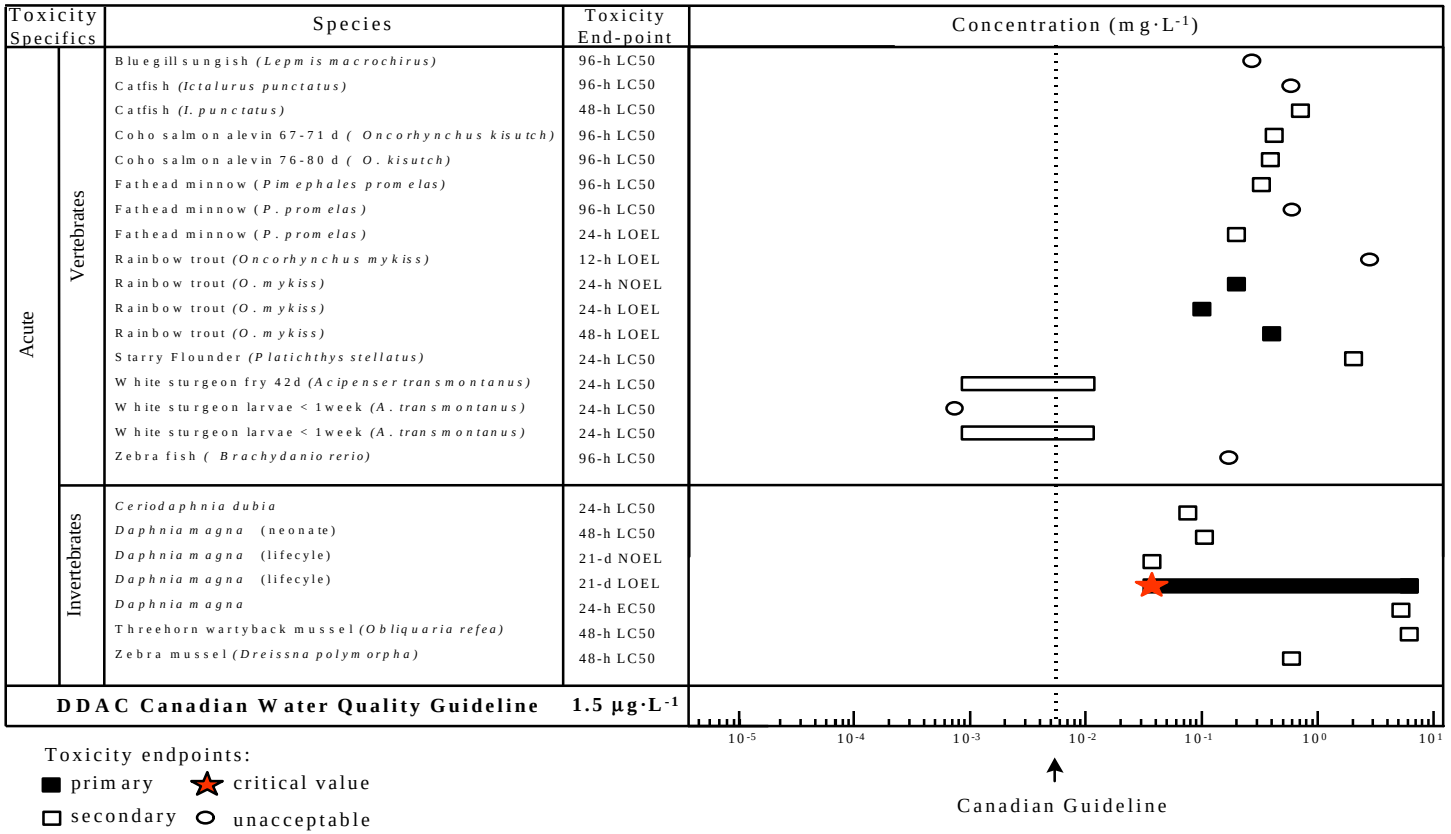


Figure 2. **Chart indicating the draft interim Canadian Water Quality Guideline value in relation to the critical toxicity endpoint value and spread of toxicity data for DDAC.**

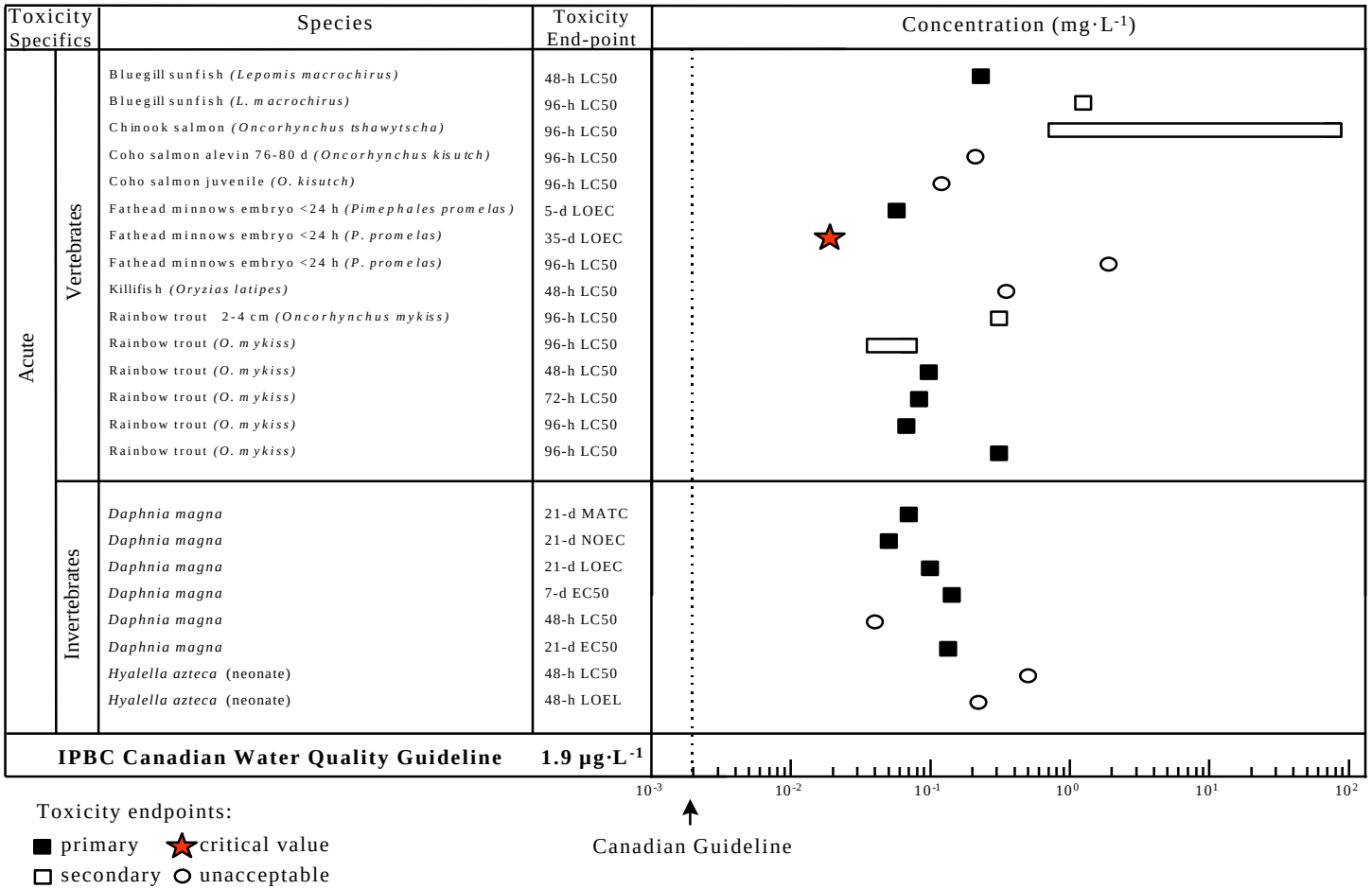


Figure 3. Chart indicating the draft interim Canadian Water Quality Guideline value in relation to the critical toxicity endpoint value and spread of toxicity data for IPBC.

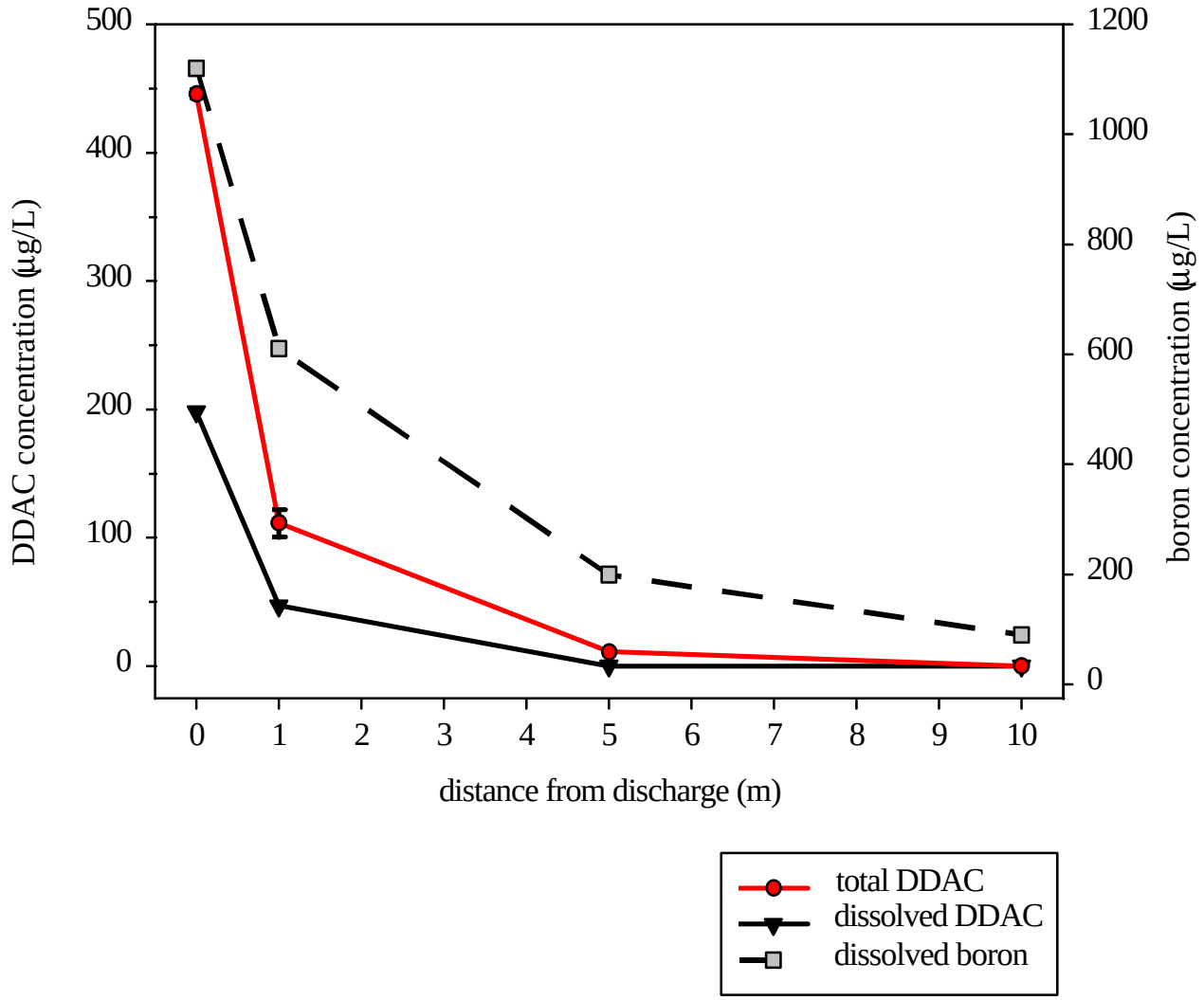


Figure 4. **F2 mill site results. Concentrations of DDAC and boron in the Fraser River at distances downstream of the stormwater discharge.**

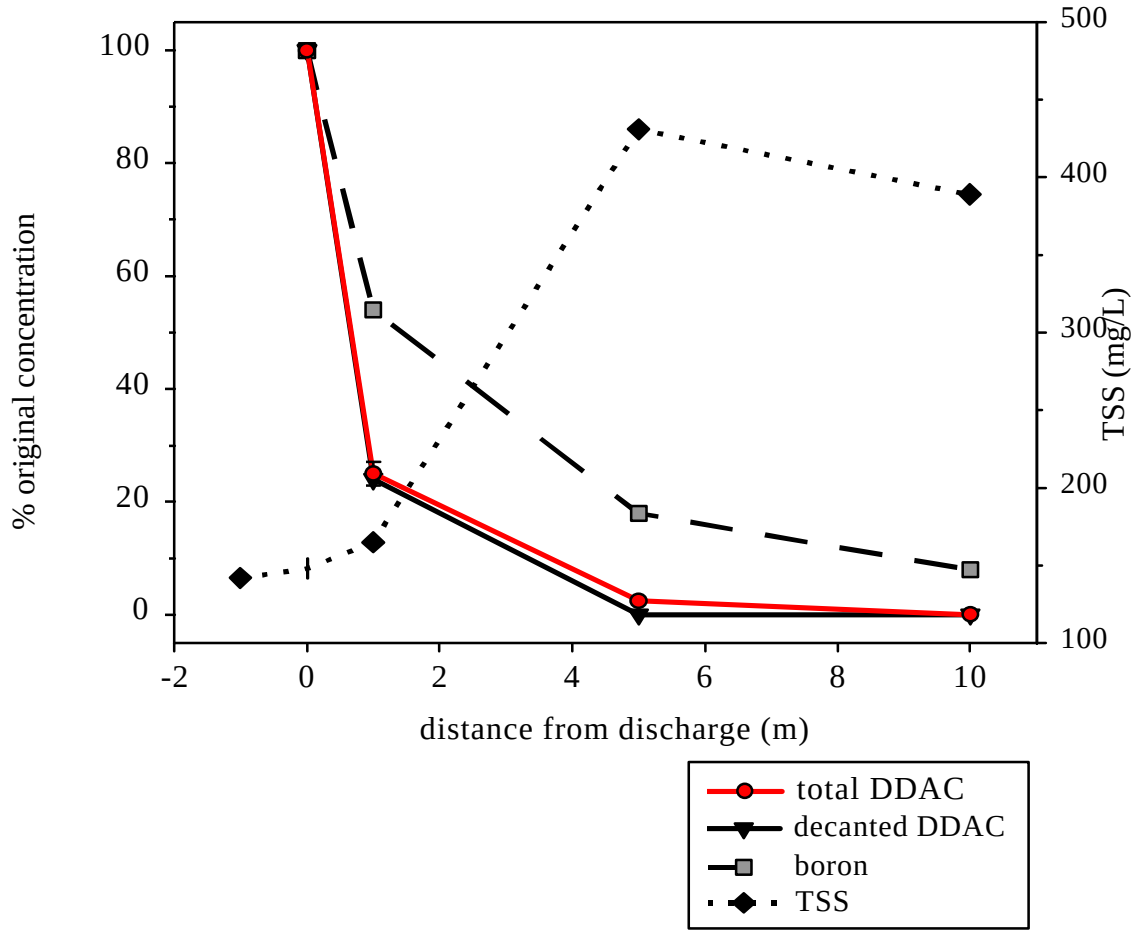


Figure 5. **F2 mill site results. Recoveries of DDAC and boron relative to effluent concentrations and levels of total suspended solids (TSS).**

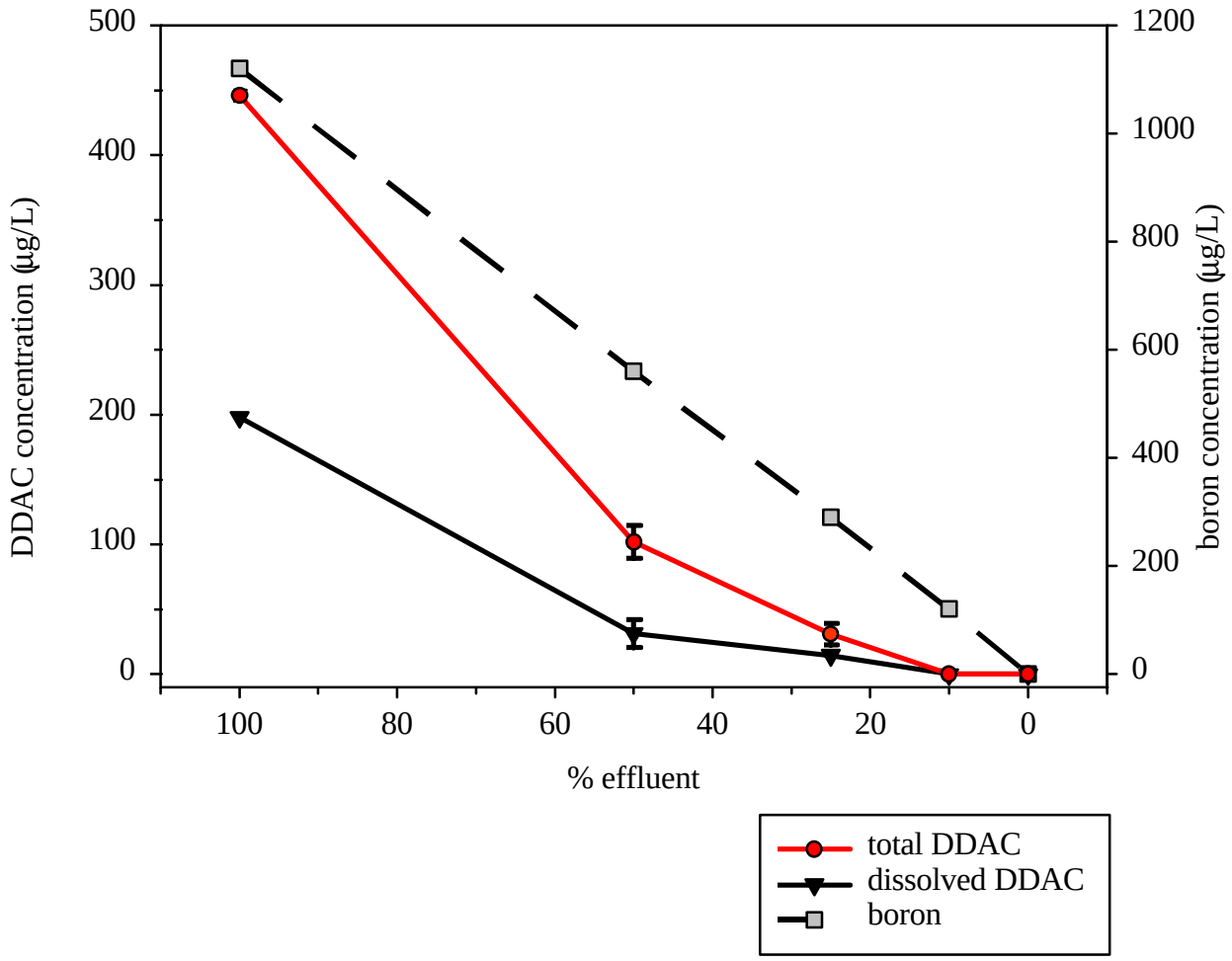


Figure 6. F2 laboratory studies. Concentrations of DDAC and boron in stormwater effluent diluted with Fraser River water.

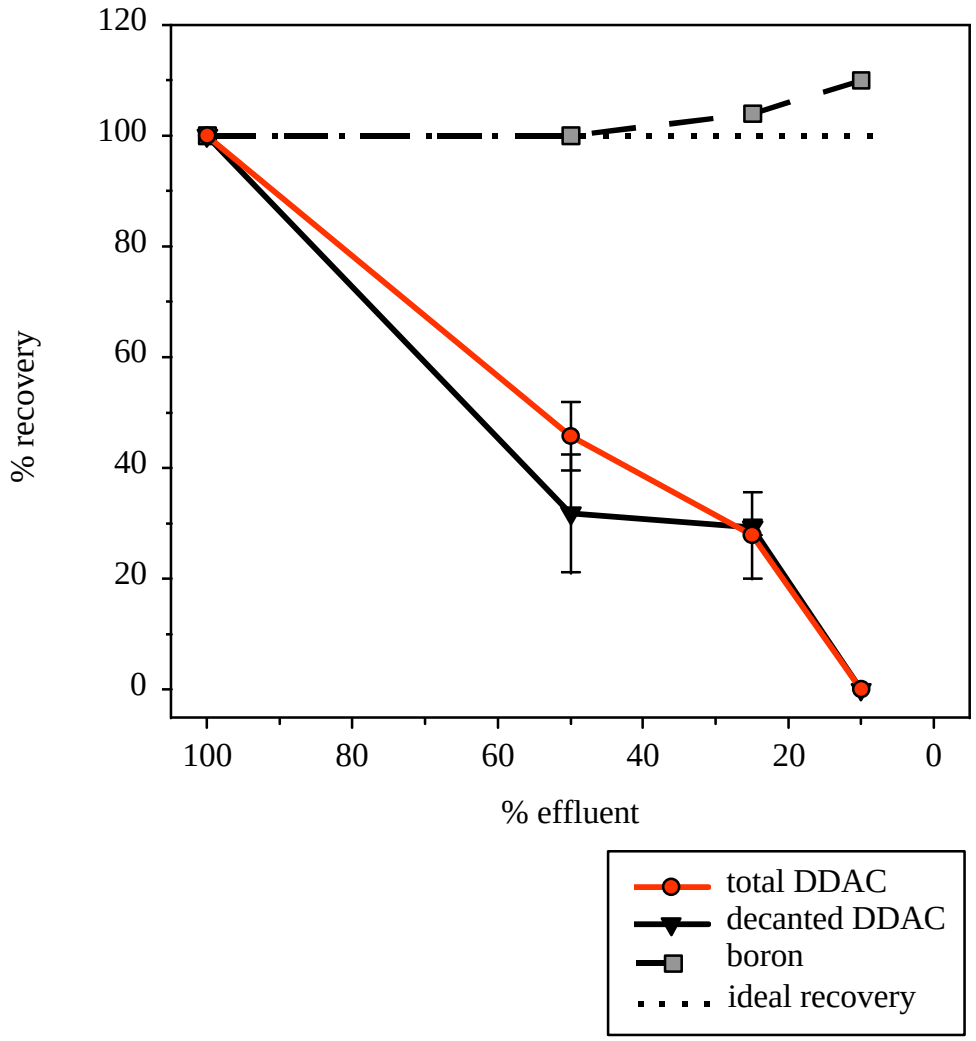


Figure 7. F2 laboratory studies. The effect of river water on DDAC and boron recovery.

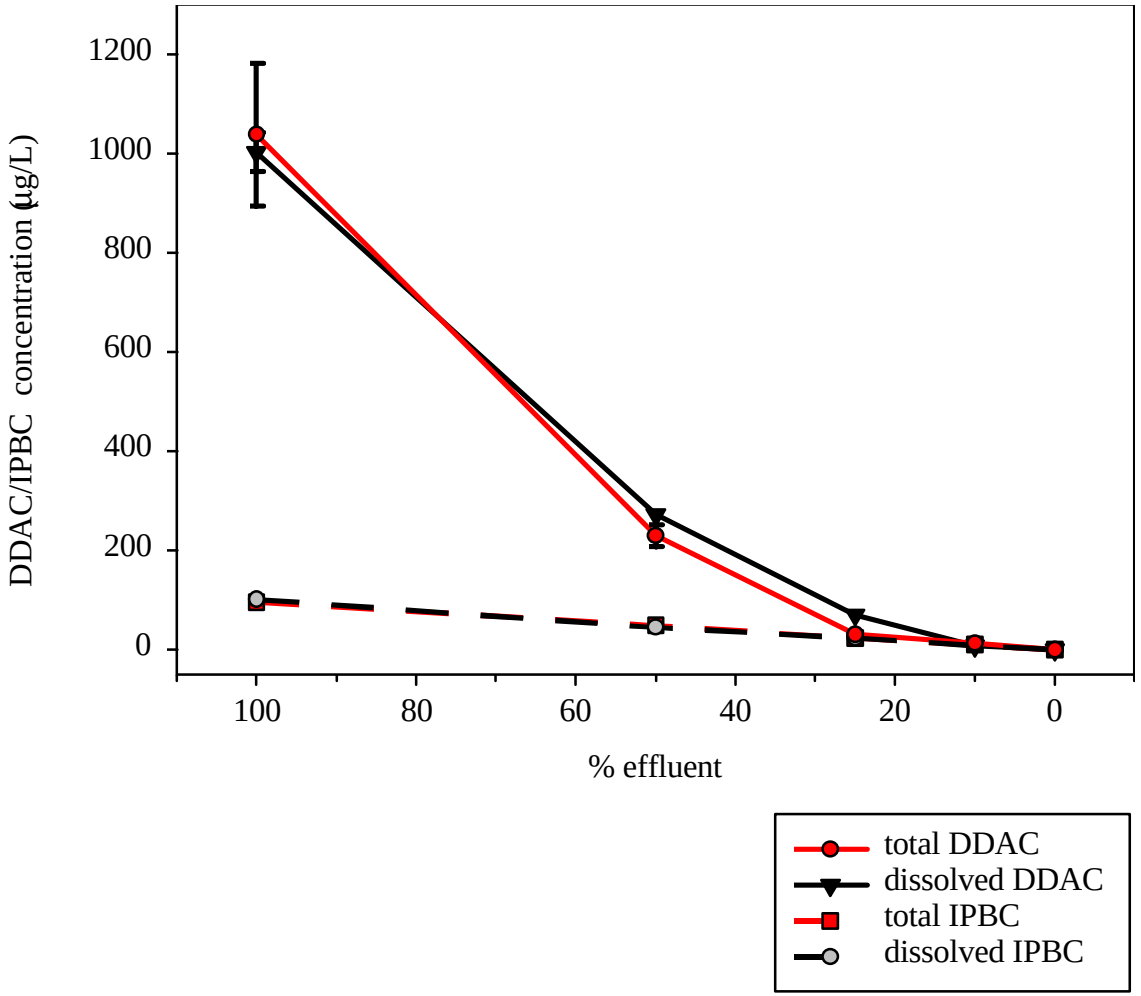


Figure 8. NP1 laboratory studies. Concentrations of DDAC and IPBC in effluent diluted with Fraser River water. Effluent was spiked with 1400 µg/L DDAC and 100 µg/L IPBC.

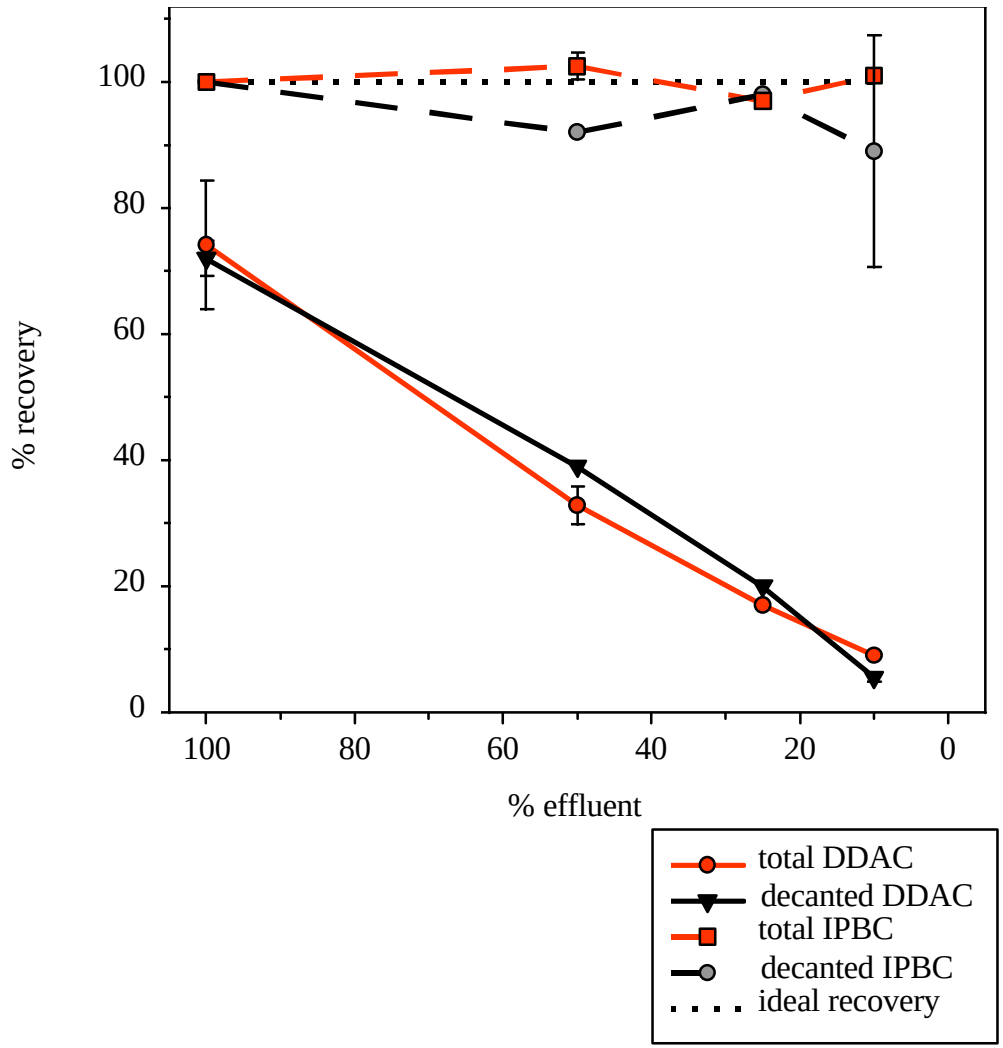


Figure 9. **NP1 laboratory studies. The effect of river water on DDAC and IPBC recovery from effluent spiked with NP1 containing 1400 µg/L DDAC and 100 µg/L IPBC.**

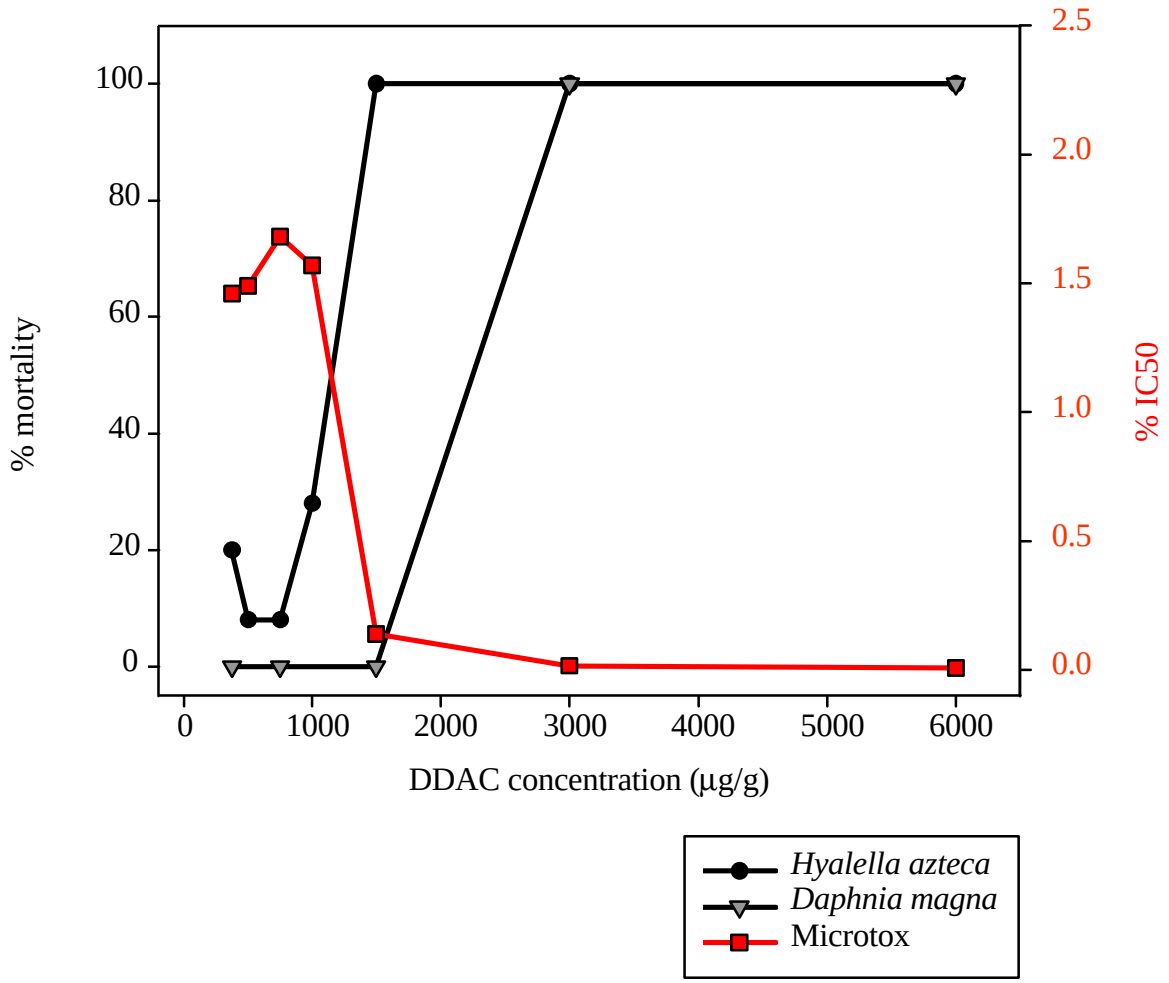


Figure 10. **Dose-response curves of the benthic amphipod, *Hyalella azteca*, the crustacean, *Daphnia magna* and the luminescent bacteria, *Vibrio fisheri* (solid phase Microtox®) to Fraser Basin sediments spiked with DDAC from a 14-day sediment toxicity bioassay.**

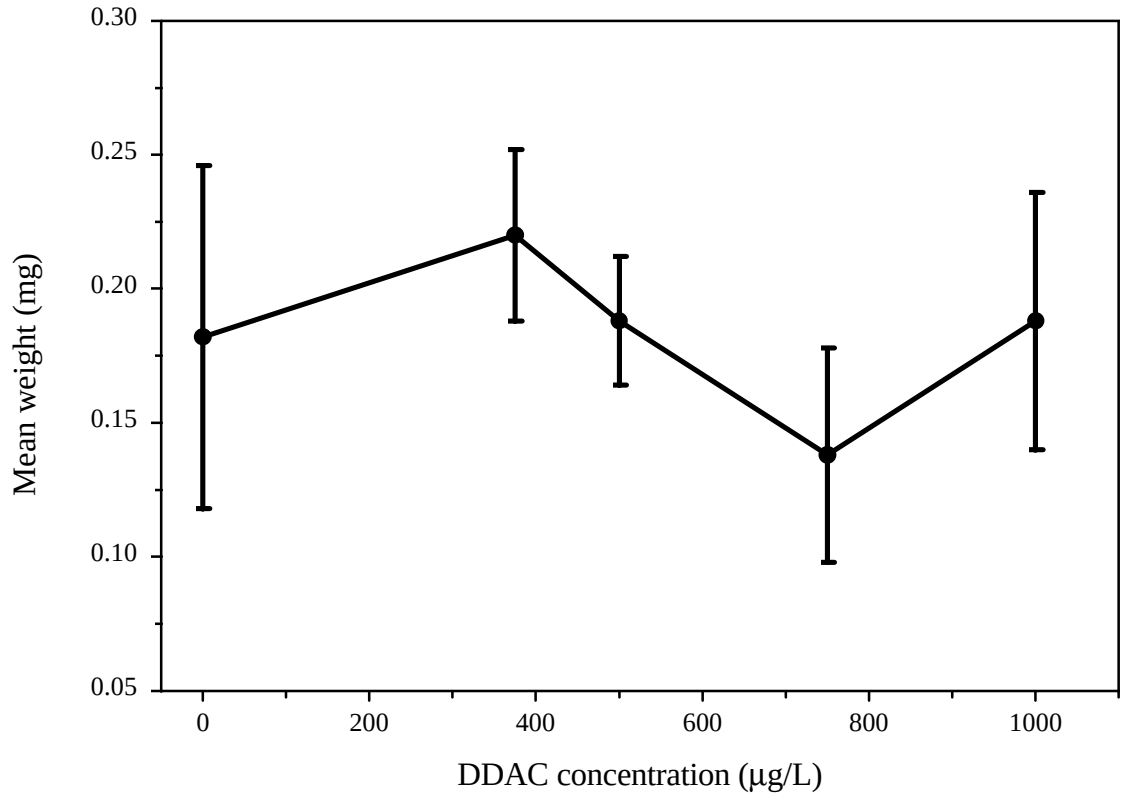


Figure 11. The effect of DDAC on growth of the benthic amphipod, *Hyalella azteca*, during a 14-day sediment toxicity bioassay.

APPENDIX 1

Summary of field sampling information from a survey of DDAC and IPBC concentrations in the lower Fraser River.

Table A1. Summary of field sampling information.

Date	Samples Collected	Tidal Conditions	Analyses	Notes
April 15, 1997 F2 Mill #1	• two sets effluent; 10, 50, 100 and 150 m downstream • upgradient sample	• ebb tide from 11:25 to 18:15 at which low tide was 1.8 m	• DDAC • suspended solids • dye	• raining • effluent estimated at 0.5 L/sec (first set) and 4 L/sec (second set) • dye adjacent to shore
May 27, 1997 F2 Mill #1	• effluent; 1, 5 and 10 m downstream • upgradient sample	• ebb tide from 08:15 to 15:20 to which low tide was 3.0 m	• DDAC • borates • suspended solids	• heavy shower • effluent estimated at 3 L/sec • dye adjacent to shore
July 1, 1997 NP1 Mill #2	• effluent; 1, 5 and 10 m downstream • upgradient sample	• ebb tide from 01:55 to 09:20 at which low tide was 3.1 m	• DDAC in effluent • IPBC in effluent • downstream samples not analysed	• effluent estimated at 2.0 L/sec • dye split with a portion along shore
July 5, 1997 NP1 Mill #2	• effluent 1, 5 and 10 m downstream • upgradient sample	• ebb tide from 04:55 to 12:10 at which low tide was 2.2 m	• DDAC in effluent • IPBC in effluent • downstream samples not analysed	• effluent estimated at 2 L/sec • dye split with a portion along shore
August 6, 1997 NP1 Mill #3	• effluent 1, 5 and 10 m downstream • upgradient sample	• ebb tide from 06:55 to 13:25 at which low tide was 4.7 m	• DDAC in effluent • IPBC in effluent • downstream samples not analysed	• downpour • effluent release high-not estimated • dye fingered
August 6, 1997 NP1 Mill #4	• effluent 1,5 and 10 m downstream • upgradient sample	• ebb tide from 06:55 to 13:25 at which low tide was 4.7 m	• DDAC in effluent • IPBC in effluent • downstream samples not analysed	• rainfall high • effluent volume not estimated • dye along shore

APPENDIX 2

Raw data from sediment toxicity bioassays with DDAC

Table A2. ***Hyalella azteca*** **14-day DDAC-spiked sediment bioassay data sheet.**

Start Date: November 27, 1997
End Date: December 11, 1997
Test Volume: 100 mL sediment; 175 mL dilution water
Aeration: yes
Temperature of test vessels: 23 ±1°C

Rep #	Description	Initial D.O.	Initial pH	Total	Live	Dead	Final D.O.	Final pH	Comments
a	Lab Control	7.9	7.7	10	9	1	7.6	7.9	
b	(Silica)			10	10	0			
c	Trial #1			10	9	1			
d				10	10	0			
e				10	9	1			
a	Lab Control	7.9	7.8	10	10	0	7.8	7.8	
b	(Silica)			10	10	0			
c	Trial #2			10	10	0			
d				10	7	3			
e				10	10	0			
a	Sediment	7.9	7.9	10	10	0	7.4	8.1	Good mobility
b	Control			10	10	0			
c	Trial #1			10	10	0			
d				10	10	0			
e				10	10	0			
a	Sediment	7.8	7.8	10	8	2	7.8	8.0	
b	Control			10	10	0			
c	Trial #2			10	8	2			

Table A2 continued

Rep #	Description	Initial D.O.	Initial pH	Total	Live	Dead	Final D.O.	Final pH	Comments
d				10	10	0			
e				10	9	1			
a	375 µg/g	7.7	7.7	10	8	2	7.5	8.1	Good mobility
b				10	9	1			
c				10	7	3			
d				10	8	2			
e				10	8	2			
a	500 µg/g	7.9	8.1	10	10	0	7.9	8.1	
b				10	10	0			
c				10	9	1			
d				10	9	1			
e				10	8	2			
a	750 µg/g	7.7	7.6	10	10	0	6.9	8.0	Good mobility
b				10	9	1			
c				10	8	2			
d				10	9	1			
e				10	10	0			
a	1000 µg/g	7.4	7.7	10	7	3	7.8	8.1	
b				10	4	6			
c				10	7	3			
d				10	8	2			
e				10	5	5			

Table A2 continued

Rep #	Description	Initial D.O.	Initial pH	Total	Live	Dead	Final D.O.	Final pH	Comments
a	1500 µg/g	7.6	7.8	10	0	10	7.5	8.2	Grass growth
b				10	0	10			
c				10	0	10			
d				10	0	10			
e				10	0	10			
a	3000 µg/g	7.1	7.7	10	0	10	7.3	8.3	
b				10	0	10			
c				10	0	10			
d				10	0	10			
e				10	0	10			
a	6000 µg/g	7.5	7.8	10	0	10	7.8	8.0	
b				10	0	10			
c				10	0	10			
d				10	0	10			
e				10	0	10			

Table A3. ***Hyalella azteca*** **14-day DDAC-spiked sediment bioassay animal weights data sheet.**

SITE	REP #	BOAT #	WT. OF BOAT	WT. ANIMALS & BOAT	WT. ANIMALS (mg)	# ANIMALS (mg)	MEAN WT. /ANIMAL (mg)	MEAN WT. /SITE (mg)	% OF CONTROL
Silica Sand	a	H1	1.0035	1.004	0.5	9	0.06	0.22	
Control	b	H2	1.0066	1.009	2.4	10	0.24		
	c	H3	1.0102	1.0121	1.9	9	0.21		
	d	H4	1.0159	1.0198	3.9	10	0.39		
	e	H5	1.004	1.0055	1.5	9	0.17		
	a'	H6	0.97839	0.98252	4.13	10	0.41		
	b'	H7	0.98567	0.98715	1.48	10	0.15		
	c'	H8	0.98397	0.98559	1.62	10	0.16		
	d'	H9	0.9814	0.98395	2.55	7	0.36		
	e'	H10	0.98178	0.98236	0.58	10	0.06		
Sediment	a	H11	1.0132	1.0144	1.2	10	0.12	0.18	100%
Control	b	H12	1.0064	1.0078	1.4	10	0.14		
	c	H13	1.0149	1.0162	1.3	10	0.13		
	d	H14	1.0186	1.02	1.4	10	0.14		
	e	H15	1.016	1.0172	1.2	10	0.12		
	a'	H16	0.97872	0.98046	1.74	8	0.22		
	b'	H17	0.98164	0.98375	2.11	10	0.21		
	c'	H18	0.9805	0.98206	1.56	8	0.20		
	d'	H19	0.9822	0.98444	2.24	10	0.22		
	e'	H20	0.98196	0.98487	2.91	9	0.32		
375 µg/g	a	H21	1.0221	1.0237	1.6	8	0.20	0.22	120%
	b	H22	1.0119	1.0136	1.7	9	0.19		
	c	H23	1.0225	1.0243	1.8	7	0.26		
	d	H24	1.0185	1.0205	2	8	0.25		
	e	H25	1.0201	1.0217	1.6	8	0.20		

Table A3 continued

SITE	REP #	BOAT #	WT. OF BOAT	WT. ANIMALS & BOAT	WT. ANIMALS (mg)	# ANIMALS (mg)	MEAN WT. /ANIMAL (mg)	MEAN WT. /SITE (mg)	% OF CONTROL
500 µg/g	a	H26	0.98591	0.98787	1.96	10	0.20	0.19	102%
	b	H27	0.98308	0.98508	2	10	0.20		
	c	H28	0.98401	0.9859	1.89	9	0.21		
	d	H29	0.98306	0.98465	1.59	9	0.18		
	e	H30	0.98234	0.98354	1.2	8	0.15		
750 µg/g	a	H31	1.0307	1.0317	1	10	0.10	0.14	76%
	b	H32	1.0301	1.0318	1.7	9	0.19		
	c	H33	1.0215	1.0224	0.9	8	0.11		
	d	H34	1.0291	1.0302	1.1	9	0.12		
	e	H35	1.0349	1.0366	1.7	10	0.17		
1000 µg/g	a	H36	0.9802	0.98169	1.49	7	0.21	0.19	102%
	b	H37	0.98149	0.982	0.51	4	0.13		
	c	H38	0.98236	0.98338	1.02	7	0.15		
	d	H39	0.97929	0.98086	1.57	8	0.20		
	e	H40	0.98213	0.98337	1.24	5	0.25		
1500 µg/g	a	H41	1.0326	No survival					
	b	H42	1.0302						
	c	H43	1.021						
	d	H44	1.021						
	e	H45	1.0109						
3000 µg/g	a	H46	1.0326	No survival					
	b	H47	1.022						
	c	H48	1.0307						
	d	H49	1.0233						
	e	H50	1.0273						

Table A3 continued.

SITE	REP #	BOAT #	WT. OF BOAT	WT. ANIMALS & BOAT	WT. ANIMALS (mg)	# ANIMALS (mg)	MEAN WT. /ANIMAL (mg)	MEAN WT. /SITE (mg)	% OF CONTROL
6000 µg/g	a	H51	1.0235	No survival					
	b	H52	1.0248						
	c	H53	1.0268						
	d	H54	1.0242						
	e	H55	1.0333						

Table A4. Chemical analysis results of DDAC extraction from spiked sediment from the Fraser River Basin used for *Hyalella azteca* bioassay.

Parameter	day 0		day 7		day 14		average recovery	standard deviation
DDAC exposure concentration	control	control	control	control	control	control		
wet weight (g)	1.337	-	1.208	-	1.664	1.563		
% moisture	31	-	27	-	28	33		
surrogate recovery	88%	-	92%	-	80%	118%	94%	16%
DDAC recovery*	-	-	-	-	-	-	-	-
DDAC exposure concentration	375 µg/g	375 µg/g	375 µg/g	375 µg/g	375 µg/g	375 µg/g		
wet weight (g)	1.304	-	1.405	1.450	1.468	-		
% moisture	30	-	27	27	27	-		
surrogate recovery	65%	-	92%	80%	70%	-	77%	12%
DDAC recovery*	79%	-	87%	82%	72%	-	80%	6%
DDAC exposure concentration	500 µg/g	500 µg/g	500 µg/g	500 µg/g	500 µg/g	500 µg/g		
wet weight (g)	1.601	1.565	-	-	1.582	-		
% moisture	32	33	-	-	33	-		
surrogate recovery	73%	62%	-	-	111%	-	82%	26%
DDAC recovery*	106%	104%	-	-	92%	-	100%	8%
DDAC exposure concentration	750 µg/g	750 µg/g	750 µg/g	750 µg/g	750 µg/g	750 µg/g		
wet weight (g)	1.474	1.46	1.406	-	1.304	-		
% moisture	29	29	26	-	26	-		
surrogate recovery	82%	84%	84%	-	69%	-	80%	7%
DDAC recovery*	84%	88%	81%	-	74%	-	82%	6%

Table A4 continued

Parameter	day 0		day 7		day 14		average recovery	standard deviation
DDAC exposure concentration	1000 µg/g	1000 µg/g	1000 µg/g	1000 µg/g	1000 µg/g	1000 µg/g		
wet weight (g)	1.534	-	-	-	1.525	1.620		
% moisture	33	-	-	-	33	33		
surrogate recovery	76%	-	-	-	114%	116%	102%	22%
DDAC recovery*	110%	-	-	-	87%	92%	97%	12%
DDAC exposure concentration	1500 µg/g	1500 µg/g	1500 µg/g	1500 µg/g	1500 µg/g	1500 µg/g		
wet weight (g)	1.220	-	1.150	-	1.273	-		
% moisture	32	-	29	-	28	-		
surrogate recovery	97%	-	101%	-	105%	-	101%	4%
DDAC recovery*	92%	-	89%	-	99%	-	93%	5%
DDAC exposure concentration	3000 µg/g	3000 µg/g	3000 µg/g	3000 µg/g	3000 µg/g	3000 µg/g		
wet weight (g)	1.350	-	1.359	-	1.376	1.288		
% moisture	31	-	28	-	28	28		
surrogate recovery	96%	-	101%	-	102%	84%	96%	8%
DDAC recovery*	93%	-	87%	-	91%	81%	88%	5%
DDAC exposure concentration	6000 µg/g	6000 µg/g	6000 µg/g	6000 µg/g	6000 µg/g	6000 µg/g		
wet weight (g)	1.287	-	1.297	-	1.230	-		
% moisture	29	-	26	-	27	-		
surrogate recovery	99%	-	121%	-	108%	-	109%	11%
DDAC recovery*	84%	-	90%	-	94%	-	89%	5%

* based on dry weight
"-" not tested

Table A5. Chemical analysis results of DDAC concentrations in water overlying spiked sediment collected from the Fraser River Basin used for *Hyalella azteca* bioassay.

Time	day 0			day 7		day 14	
date analysed	16/12/97	4/02/98	6/02/98	17/12/97	6/02/98	21/10/98	4/02/98
DDAC sediment concentration	control	control	control	control	control	control	control
sample used (mL)	50	155	138	50	140	165	169
surrogate recovery	91%	85%	88%	76%	92%	63%	80%
DDAC concentration (µg/L)	<50	<50	<50	<50	<50	<50	<50
Time	day 0			day 7		day 14	
date analysed	16/12/97			17/12/97		21/01/98	
DDAC sediment concentration	375 µg/g	375 µg/g	375 µg/g	375 µg/g	375 µg/g	375 µg/g	375 µg/g
sample used (mL)	150	-	-	100	-	177	-
surrogate recovery	95%	-	-	79%	-	66%	-
DDAC concentration (µg/L)	<50	-	-	<50	-	<50	-
Time	day 0			day 7		day 14	
date analysed	4/02/98					4/02/98	
DDAC sediment concentration	500 µg/g	500 µg/g	500 µg/g	500 µg/g	500 µg/g	500 µg/g	500 µg/g
sample used (mL)	165	-	-	-	-	165	-
surrogate recovery	84%	-	-	-	-	74%	-
DDAC concentration (µg/L)	<50	-	-	-	-	<50	-
Time	day 0			day 7		day 14	
date analysed	16/12/97			17/12/97		21/01/98	
DDAC sediment concentration	750 µg/g	750 µg/g	750 µg/g	750 µg/g	750 µg/g	750 µg/g	750 µg/g
sample used (mL)	150	-	-	100	-	175	-
surrogate recovery	92%	-	-	89%	-	72%	-
DDAC concentration (µg/L)	261	-	-	<50	-	<50	-

Table A5 continued

Time	day 0			day 7		day 14	
date analysed	4/02/98					4/02/98	
DDAC sediment concentration	1000 µg/g	1000 µg/g	1000 µg/g	1000 µg/g	1000 µg/g	1000 µg/g	1000 µg/g
sample used (mL)	169	-	-	-	-	159	-
surrogate recovery	74%	-	-	-	-	67%	-
DDAC concentration (µg/L)	53	-	-	-	-	<50	-
Time	day 0			day 7		day 14	
date analysed	16/12/97			17/12/97	6/02/98	21/01/98	
DDAC sediment concentration	1500 µg/g	1500 µg/g	1500 µg/g	1500 µg/g	1500 µg/g	1500 µg/g	1500 µg/g
sample used (mL)	100	-	-	50	110	153	-
surrogate recovery	102%	-	-	76%	106%	60%	-
DDAC concentration (µg/L)	456	-	-	74	136	<50	-
Time	day 0			day 7		day 14	
date analysed	16/12/97	6/02/98		17/12/97	6/02/98	21/01/98	
DDAC sediment concentration	3000 µg/g	3000 µg/g	3000 µg/g	3000 µg/g	3000 µg/g	3000 µg/g	3000 µg/g
sample used (mL)	50	88	-	25	25	175	-
surrogate recovery	87%	79%	-	77%	83%	63%	-
DDAC concentration (µg/L)	1838	1381	-	722	675	<50	-
Time	day 0			day 7		day 14	
date analysed	16/12/97	16/12/97	4/02/98	17/12/97	6/02/98	21/01/98	
DDAC sediment concentration	6000 µg/g	6000 µg/g	6000 µg/g	6000 µg/g	6000 µg/g	6000 µg/g	6000 µg/g
sample used (mL)	50	50	82	25	134	151	-
surrogate recovery	90%	117%	87%	66%	90%	62%	-
DDAC concentration (µg/L)	2972	3675	2229	644	645	82	-

"-" not tested

APPENDIX 3

Extraction efficiencies of DDAC and IPBC from Fraser River sediments

Table A6. Recoveries of DDAC and IPBC from spiked sediments for assessing extraction efficiency.

Site #	Sample #	wet weight (g)	dry weight (g)	% moisture	surrogate* recovery	DDAC (ppm)	DDAC recovery	IPBC (ppm)	IPBC recovery
2	1	15.8	8.8	44	88	18.9	95%	17.8	89%
2	2	15.2	8.5	44	82	18.0	90%	14.4	72%
4	1	15.9	6.0	62	56	13.7	69%	7.5	38%
4	2	15.7	6.0	62	65	14.8	74%	8.1	41%
average		15.6	7.3	53	73	16.4	82%	12.0	60%

* surrogate was DDAB (didodecyl dimethyl ammonium bromide) for both DDAC and IPBC.