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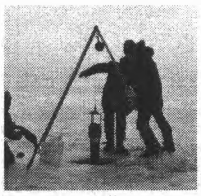
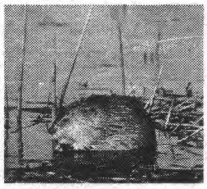


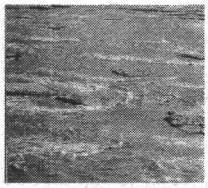


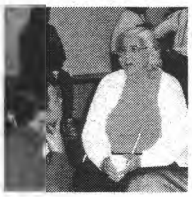





NORTHERN RIVER BASINS STUDY PROJECT REPORT NO. 137

A BIOENERGETIC MODEL OF FOOD CHAIN UPTAKE AND ACCUMULATION OF ORGANIC CHEMICALS, ATHABASCA RIVER



Prepared for the
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under Project 2381-D1

by

Mary Ellen Starodub and Glenn Ferguson
CanTox Inc.

NORTHERN RIVER BASINS STUDY PROJECT REPORT NO. 137

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PREFACE:

The Northern River Basins Study was initiated through the "Canada-Alberta-Northwest Territories Agreement Respecting the Peace-Athabasca-Slave River Basin Study, Phase II - Technical Studies" which was signed September 27, 1991. The purpose of the Study is to understand and characterize the cumulative effects of development on the water and aquatic environment of the Study Area by coordinating with existing programs and undertaking appropriate new technical studies.

This publication reports the method and findings of particular work conducted as part of the Northern River Basins Study. As such, the work was governed by a specific terms of reference and is expected to contribute information about the Study Area within the context of the overall study as described by the Study Final Report. This report has been reviewed by the Study Science Advisory Committee in regards to scientific content and has been approved by the Study Board of Directors for public release.

It is explicit in the objectives of the Study to report the results of technical work regularly to the public. This objective is served by distributing project reports to an extensive network of libraries, agencies, organizations and interested individuals and by granting universal permission to reproduce the material.

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Whereas the above publication is the result of a project conducted under the Northern River Basins Study and the terms of reference for that project are deemed to be fulfilled,
IT IS THEREFORE REQUESTED BY THE STUDY OFFICE THAT;
this publication be subjected to proper and responsible review and be considered for release to the public.

F. J. Wrona — 14 May 96
(Dr. Fred J. Wrona, Science Director) (Date)

Whereas it is an explicit term of reference of the Science Advisory Committee "to review, for scientific content, material for publication by the Board",
IT IS HERE ADVISED BY THE SCIENCE ADVISORY COMMITTEE THAT;
this publication has been reviewed for scientific content and that the scientific practices represented in the report are acceptable given the specific purposes of the project and subject to the field conditions encountered.
SUPPLEMENTAL COMMENTARY HAS BEEN ADDED TO THIS PUBLICATION: [ ] Yes [ ] No

P. A. Larkin — 24 May/96
(Dr. P. A. Larkin, Ph.D., Chair) (Date)

Whereas the Study Board is satisfied that this publication has been reviewed for scientific content and for immediate health implications,
IT IS HERE APPROVED BY THE BOARD OF DIRECTORS THAT;
this publication be released to the public, and that this publication be designated for: **[ ] STANDARD AVAILABILITY [ ] EXPANDED AVAILABILITY**

Lucille Partington — May 29/96
(Lucille Partington, Co-chair) (Date)

Robert McLeod — May 21/96
(Robert McLeod, Co-chair) (Date)

A BIOENERGETIC MODEL OF FOOD CHAIN UPTAKE AND ACCUMULATION OF ORGANIC CHEMICALS, ATHABASCA RIVER

STUDY PERSPECTIVE

That the aquatic environments contained within the Northern River Basins Study area (NRBS) were being changed as a result of development was not challenged. To describe and predict the change likely to arise from one or more developments continued to be a challenge at the onset of the Study. Even though the aquatic environment of the basin was being described and monitored prior to the onset of the Study there existed disparate information bases and information gaps that made it difficult to understand what was happening to the surface waters and their associated habitats as a result of development activities.

Related Study Questions

13a) *What predictive tools are required to determine the cumulative effects of man made discharges on the water and aquatic habitat?*

14) *What long term monitoring programs and predictive models are required to provide an ongoing assessment of the state of the aquatic ecosystems. These programs must ensure that all stakeholders have the opportunity for input.*

The aquatic ecosystems of the Peace, Athabasca and Slave rivers are large, complex and subject to significant seasonal variation. The use of models to assess the consequence of changing one or many parameters presents researchers and managers with the capability of being better able to understand and predict changes arising from development in such a large ecosystem. The NRBS undertook to investigate the potential use of models. A decision was made to utilize WASP IV, Thomann/Connolly and Gobas food chain models, to assess the fate and bioaccumulation of point-source contaminants entering the Athabasca River.

The modelling effort by NRBS was a multi-faceted initiative involving review and interpretation of sediment transport dynamics, contaminant distribution and concentration in sediment, water and biota and the refinement of existing models. This report describes the results of adapting existing food chain-water quality-sediment transport models to describe the movement of contaminants within the aquatic environment of the Athabasca River.

Seasonal fluctuations of flow rate, suspended solids, variability in effluent quantity and quality, combined with the seasonal mobility of fish stocks challenged the modellers ability to reliably predict change. While progress was made with the contaminant fate and food chain models, deficiencies were existent, albeit more the calibration that with formulation. The food chain model requires further work with the selection of chemical-specific parameters, testing and calibration.

Complementary work is reported in Northern River Basins Study Project Reports No. 136 (*Contaminant Fate Modelling for the Athabasca River: Implementation of New Sediment Flux Routines*), No. 113 (*A Bioenergetic Model of Food Chain Uptake and Accumulation of Organic Chemicals, Athabasca River, Stochastic and Time Variable Version*), No. 129 (*Environmental Contaminants in Fish: Spatial and Temporal Trends of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans, Peace, Athabasca and Slave River Basins, 1992 to 1994*), and No. 101 (*Environmental Contaminants in Fish: Polychlorinated Biphenyls, Organochlorine Pesticides and Chlorinated Phenols, Peace and Athabasca Rivers, 1992 to 1994*).

REPORT SUMMARY

Objective

The objective of this study is to construct and calibrate a steady-state food chain model to simulate the uptake and bioaccumulation of selected organic chemicals, with different physical-chemical properties, in the mountain whitefish, longnose sucker and northern pike food web of the Athabasca River. For each chemical modelled, to identify the primary exposure pathway through a sensitivity analysis.

Model Selection

A bioenergetic model based on Thomann and Connolly (1984) was selected to simulate the uptake and accumulation of selected chemicals in the Athabasca food web. This model was selected since observed trends in chemical concentrations in three different species of fish collected within one km downstream of a BKM could not be explained solely on the basis of equilibrium-lipid partitioning,

Model Configuration

Gut contents analysis of mountain whitefish, longnose sucker and northern pike provide the basis for the food web configuration. Predator-prey relationships which resulted in distinct exposure pathways for fish inhabiting the river are described by the model. The model distinguishes between exposure to water column dissolved, porewater dissolved, suspended-sediment adsorbed and detritus adsorbed chemical. Concentrations of selected organic chemicals in abiotic media (*i.e.*, water column dissolved, suspended sediment sorbed, porewater dissolved, and detritus) were entered into the model to predict corresponding chemical concentrations in biota at various locations on the Athabasca River at locations upstream and downstream of Weldwood Haul. Two distinct exposure pathways are considered by including bottom-feeding invertebrate (BFI) and filter-feeding invertebrate (FFI) at the lower trophic level.

Chemical Selection

Organic chemicals selected for food chain modelling are:

2,3,7,8-Tetrachlorodibenzofuran (TCDF);
Dehydroabietic acid (DHA);
12,14-Dichlorodehydroabietic acid (DCDHA);
3,4,5-Trichlorocatechol (TCC);
3,4,5-Trichloroguaiacol (TCG); and,
3,4,5-Trichloroveratrole (TCV).

Model Calibration

Chemical parameters describing the octanol-water partition coefficient (K_{ow}), the gill membrane permeability ratio (PRATIO), the dietary chemical assimilation efficiency (E), and the chemical excretion rate (k_2) of each chemical are entered into the model. Initially, values were selected on the basis of published peer-reviewed laboratory studies. For chemical parameters lacking data the sensitivity of the model to a range of assumed values was tested. The purpose of the sensitivity analysis is to identify the chemical-specific and species-specific value of the kinetic parameter(s) that provided the best fit to the monitoring data.

2,3,7,8-Tetrachlorodibenzofuran, which has a longer half-life than the resin acids or chlorinated phenolics and is relatively non-reactive due to its non-polar chemistry, would be expected to result in the most predictable behaviour and consistent concentrations in the aquatic environment. Consequently, TCDF was selected for food chain model calibration with respect to predator-prey relationships.

Biological parameters describing the growth rate, respiration rate, lipid content, weight, fraction dry weight, food assimilation efficiency of each species modelled were determined using site-specific field data and allometric equations.

Concentrations of 2,3,7,8-tetrachlorodibenzofuran (TCDF) measured in abiotic and biotic samples collected in 1992 at various locations on the Athabasca River downstream of Weldwood Haul were used in the food chain model calibration. Biological data included fillet concentrations in two species of bottom feeding fish, mountain whitefish (*Prosopium williamsoni*) and longnose sucker (*Catostomus catostomus*), and one species of piscivorous fish, northern pike (*Esox lucius*), as well as pooled samples of three different orders of invertebrates (NRBS, 1992). A sensitivity analysis identified the model parameters on a chemical-specific basis which had the greatest influence on predicted chemical concentrations in mountain whitefish, longnose sucker, northern pike and bottom-feeding and filter-feeding invertebrates.

Results

TCDF

2,3,7,8-Tetrachlorodibenzofuran is a hydrophobic chemical which when introduced to aquatic systems readily adsorbs to organic carbon of suspended solids and accumulates in biological tissues. Predicted tissue concentrations of TCDF were directly proportional to the percent diet comprised of filter-feeding invertebrates. These modelling results support the theory that consumption of filter-feeding invertebrates and suspended solids represent the primary exposure pathway for mountain whitefish to TCDF and likely to other chlorinated dioxins and furans downstream of pulp mills. The model was able to simulate the trend in TCDF contamination of whitefish > longnose sucker > northern pike, observed within 1 km downstream of the BKM at Weldwood Haul.

The percent diet comprised of filter-feeding invertebrates *versus* bottom-feeding invertebrates, the dietary chemical assimilation efficiency and the excretion rate are the model parameters having the greatest influence on predicted tissue concentrations of TCDF.

Predicted tissue concentrations were within 2.5-fold of observed concentrations, assuming TCDF assimilation efficiencies of 0.54 and 0.15, and excretion rates of 0.003 and 0.015 d^{-1} for fish and invertebrates, respectively. These values were selected from a review of the relevant literature.

Predicted tissue concentration equalled observed values when excretion rates were adjusted accordingly:

BFI0.003 d^{-1}
FFI0.052 d^{-1}
MWF0.0025 d^{-1}
LNS0.025 d^{-1}
and NP0.0075 d^{-1}.

DHA and DCDHA

These resin acids with log K_{ow} values of 6.1 and 6.4, respectively, would be expected to adsorb to suspended and bed sediments, and accumulate in biological tissues. However, bioassay data indicate BCFs of about 100 in fish. In contrast, BCFs estimated from the percent lipid * K_{ow} relationship are approximately three-orders of magnitude greater than measured values. The Athabasca field data indicate that DHA and DCDHA are not appreciably accumulated in aquatic species. Fish and invertebrate samples collected from the Athabasca R. 1992, generally, had non-detectable concentrations, < 0.001 μg/g, of DHA and DCDHA.

Kinetic data are limited for DHA and DCDHA. Bioconcentration factors of 96 and 92 were input directly into the food chain model for DHA and DCDHA, respectively. No dietary chemical assimilation efficiency data was identified for the resin acids for fish or invertebrate species. Thus a range of E values from 0.001 to 0.25 were tested. The best fit was obtained using an input BCF value of 96 and an E of 0.001 for DHA, and a BCF of 92 and an E of 0.001 for DCDHA.

Due to their hydrophobic nature, the primary exposure pathway to these resin acids would be through consumption of suspended solids and contaminated prey. A sensitivity analysis of predicted tissue concentrations to variations in the concentration of dissolved DHA and DCDHA in the water column and pore water revealed that direct uptake from water is insignificant.

TCC, TGC, and TCV

Trichlorocatechol, trichloroguaiacol, and trichloroveratrole have log K_{ow} values ranging from 3.7 to 4.6, indicating their greater solubility in the aqueous phase than the organic phase. Hence these

chlorinated phenolics remain in the dissolved fraction of the water column compared to the hydrophobic resin acids and chlorinated dibenzofurans. A laboratory study conducted in rainbow trout exposed to various chlorinated phenolics reported a BCF of 268 and a half-life of 2 days for trichloroguaiacol. This value is similar to that calculated from the percent lipid * K_{ow} relationship. The laboratory measured BCF of 268 was input to the model for all fish species. BCF values of 268 and 34 based on the value reported for fish and that reported for bivalves exposed to trichloroguaiacol were input for invertebrate species.

Only one study was identified that determined the dietary chemical assimilation efficiency of the chlorinated phenolics selected for assessment. In the absence of other data this chemical assimilation efficiency of 0.03 for TCG in rainbow trout was assigned to all fish and invertebrate species for TCC, TCG and TCV..

Model-predicted concentrations in bottom-feeding and filter-feeding invertebrates best simulated observed concentrations when a BCF of 268 was used for all species modelled. Predicted concentrations in invertebrates were generally within 2-fold of observed concentrations. However, the model generally overestimated observed concentrations in fish by at least 10-fold (the majority of observed concentrations were <0.0004 μg/g), with the exception of concentrations of trichloroveratrole in mountain whitefish at Windfall for which predicted concentrations (0.0011μg/g) equalled observed (0.0012 μg/g).

Conclusions

1. The Athabasca R. is characterized by seasonal variations in flowrate and total suspended solids, subject to variations in loadings of selected chemicals related to mill operations. Thus, non-equilibrium conditions would be expected to prevail.

2. Predicted chemical concentrations were about 2.5-fold to 10-fold greater than observed concentrations. These results were considered reasonable since resident fish would not be expected to reach steady-state tissue concentrations due to fluctuations in environmental concentrations, fish migration and variety in diet. These factors would result in continually changing exposures. Other factors affecting model predictions included the high detection limit for DHA, DCDHA, TCC, TCG and TCV for which many samples had non-detectable concentrations of these chemicals. Input of concentrations equal to the detection limit for water and sediment concentrations also explains why predicted tissue concentrations were greater than observed.

3. The bioenergetic based food chain model simulating exposure *via* BFI and FFI as two distinct exposure pathways was able to simulate observed differences in uptake and accumulation of three classes of chemicals with different physical-chemical and pharmacokinetic characteristics.

4. Phase II will address the observed variation in tissue concentrations within and among species of fish through the development of a stochastic version of the bioenergetic model using Monte Carlo techniques.

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1.0 INTRODUCTION

This report discusses the methodology and results of a site-specific food chain model simulation of the uptake and accumulation of organic chemicals in the Athabasca River ecosystem. CanTox was contracted by the Contaminants Working Group of the Northern Rivers Basin to construct and calibrate a site-specific steady-state food chain model for the Athabasca River ecosystem, downstream of Weldwood Haul using NRBS field data. To supplement the Athabasca R. database, field data for the Smoky/Wapiti river system was identified to fill data gaps describing food web relationships.

The impetus for the food chain modelling component stemmed partially from observations downstream of BKM of greater concentrations of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF) in mountain whitefish (*Prosopium williamsoui*) compared to longnose sucker (Mah *et al.*, 1989; Whittle *et al.*, 1990; Owens *et al.*, 1994), including NRBS data that reported significantly greater concentrations of TCDF in fillets of mountain whitefish than longnose sucker and northern pike (*Esox lucius*), sampled 1 km downstream of a BKM (Pastershank and Muir, 1995). These differences could not be attributed solely to lipid-partitioning (Owens *et al.*, 1994; Pastershank and Muir, 1995).

It has been hypothesized that observed differences in tissue concentrations may be attributed to differences in feeding habits of mountain whitefish and longnose sucker (Owens *et al.*, 1994). Longnose sucker (*Catostomus catostomus*) and white sucker (*C. commersoni*), characteristically bottom feeders (Scott and Crossman, 1973; Bond and Berry, 1980), have been commonly selected as sentinel species of PCDD/PCDF contamination in the Canadian aquatic environment (Mah *et al.*, 1989; Whittle *et al.*, 1990; Servos *et al.*, 1989a; Hodson *et al.*, 1992). Mountain whitefish, although classified as bottom-feeders, have been observed to feed on drifting organisms but not directly off the bottom (Thompson and Davies, 1976). Indeed, mountain whitefish of the Smokey-Wapiti river were reported to selectively consume Trichoptera, caddisfly larvae, despite the fact that these were not the most abundant invertebrates (Swanson, S., personal communication). Northern pike, top predatory fish, are classified as omnivorous carnivores, consuming an optimum prey-size of between one-third and one-half the size of the pike (Scott and Crossman, 1973).

Another major incentive for conducting the food chain modelling study is the need for proactive watershed management tools to assess the potential environmental impacts of chemical loadings to the Northern River Basins. Environmental impacts include the potential accumulation of organic chemicals in aquatic species and potential health risks to piscivorous wildlife and humans.

2.0 OBJECTIVE

The objective of this study is to construct and calibrate a steady-state food chain model to simulate the uptake and bioaccumulation of selected organic chemicals with different physical-chemical properties in the mountain whitefish, longnose sucker and northern pike food web of the Athabasca River. For each chemical modelled, to identify the primary exposure pathway through a sensitivity analysis.

3.0 METHODS

3.1 CHEMICAL SELECTION

Organic chemicals selected for food chain modelling are:

2,3,7,8-Tetrachlorodibenzofuran (TCDF);
Dehydroabietic acid (DHA);
12,14-Dichlorodehydroabietic acid (DCDHA);
3,4,5-Trichlorocatechol (TCC);
3,4,5-Trichloroguaiacol (TCG); and,
3,4,5-Trichloroveratrole (TCV).

These chemicals encompass a wide range in physical-chemical and pharmacokinetic characteristics.

3.1.1 TCDF

For example, 2,3,7,8-tetrachlorodibenzofuran (TCDF) along with 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) belongs to a class of chemicals termed the polychlorinated dibenzofurans (PCDFs). Considerable efforts have targeted bleached kraft mills (BKM) using molecular chlorine as major sources of TCDF, TCDD and other PCDDs/PCDFs in the aquatic environment (Rappe *et al.*, 1989; Mah *et al.*, 1989; Sherman *et al.*, 1990; Whittle *et al.*, 1990; Hodson *et al.*, 1992; Servos *et al.*, 1989a). 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin is toxic to fish at part-per-trillion levels in tissues (Cook *et al.*, 1991; Spitsbergen *et al.*, 1991; Walker *et al.*, 1991). These chemicals are non-polar hydrophobic organic chemicals, which upon release to the aquatic environment accumulate in sediments and biological tissues (Yockim *et al.*, 1978; Tsushimoto *et al.*, 1982; Adams *et al.*, 1986; Servos *et al.*, 1989b; Muir *et al.*, 1985; Corbet *et al.*, 1983).

2,3,7,8-Tetrachlorodibenzofuran is relatively persistent in the aquatic environment and is slowly metabolized and excreted by aquatic species (Muir *et al.* 1992b). The predominant route of uptake of 2,3,7,8-TCDD and 2,3,7,8-TCDF in aquatic species is through the consumption of contaminated food and sediments (EPA, 1993; Muir *et al.* 1992a). Therefore, ecological assessments of 2,3,7,8-TCDF and 2,3,7,8-TCDD in the aquatic environment require consideration of feeding interactions of aquatic species and their predators using a food chain approach (Starodub and Willes, 1991; Starodub *et al.*, 1995, in Press; Expert Panel, 1994).

3.1.2 DHA AND DCHA

Dehydroabietic acid and DCDHA belong to a class of chemicals termed the resin acids which have been identified as a major contributors to the toxicity of pulp and paper mill effluents (Rogers and Mahood, 1974; Leach and Thakore, 1975; McLeay and Brown, 1979; Pearson, 1980; Kovacs, 1986; Priha and Talka, 1986; Taylor and Yeager, 1987). The octanol-water partitioning coefficient

(K_{ow}) of these resin acids is of the same order of magnitude as TCDF, although the chlorinated dehydroabietic acids are less persistent and are amenable to microbial attack (Kutney *et al.*, 1982, 1983a,b; Servizi *et al.*, 1986). Limited data on the BCF of DHA and DCDHA in fish indicate that these chemicals do not appreciably accumulate in aquatic species (Niimi and Lee, 1992; Oikari and Kunnamo-Ojala, 1987; Oikari *et al.*, 1982).

3.1.3 TCC, TCG and TCV

The chlorinated phenolics, TCC, TCG and TCV have also been identified as contributors to the toxicity of bleached kraft mill effluents (McKague, 1981). These chlorinated phenolics are water soluble and upon release to the aquatic environment remain predominantly in the dissolved phase. These chemicals do not have a high bioaccumulative potential (Passivirta *et al.*, 1985; Renberg *et al.*, 1980; Landner *et al.*, 1977). Chlorinated guaiacols and chlorinated catechols do not persist in the environment (Expert Panel, 1994). In the aquatic environment these chemicals are subject to acid hydrolysis, photolysis and biodegradation; the rates of chemical loss *via* these mechanisms being determined by the characteristics of the aquatic system (Carey, 1994). Chlorinated guaiacols and chlorinated catechols are readily biotransformed under aerobic conditions *via O*-methylation into chloroveratroles (Neilson *et al.*, 1983, 1984; Allard *et al.*, 1985, 1988; Remberger *et al.*, 1986). 3,4,5-Trichlorguaiacol was metabolized to 3,4,5-trichloroveratrole, 3,4,5-trichlorocatechol and 3,4,5-trichlorosyringol by bacterial strains isolated from areas receiving pulpmill effluents (Neilson *et al.*, 1983). Anaerobic *O*-demethylation of chlorinated guaiacols to form the corresponding chlorocatechols has been detected in sediments (Neilson *et al.*, 1983, 1984; Allard *et al.*, 1985, 1988, 1991; Rosemarin *et al.*, 1990). Microbially mediated dechlorination is the primary metabolic pathway of chlorocatechols (Allard *et al.*, 1991; Neilson *et al.*, 1987; Pieper *et al.*, 1991).

3.2 MODEL THEORY

A major consideration in the selection of an appropriate food chain model for the Athabasca R. ecosystem was the flexibility of the mathematical relationships to simulate the various exposure pathways of concern, including differences in lower trophic levels and differences in the pharmacokinetics of the selected chemicals. Since the field data could not be readily explained on the basis of simple lipid-equilibrium partitioning the model chosen for study needed to consider other relationships.

3.2.1 Thomann and Connolly Model

The steady-state food chain model developed for the Athabasca River ecosystem is based on the theory of Thomann and Connolly, (1984). The general equation for the model is:

$$dv_i / dt = K_{ui}c + \Sigma\, a_{ij}C_{ij}v_j - K'_i v_i \qquad (1)$$

where,

K'_i	=	loss due to excretion and dilution due to growth
	=	$K_i + (dw_i/dt)/w_i$
K_i	=	excretion rate of the organism i (d^{-1})
w_i	=	weight of organism i (g)
t	=	time (d)
K_{ui}	=	uptake of organism i (L/d/g)
a_{ij}	=	chemical assimilation efficiency of organism i on organism j
C_{ij}	=	consumption rate of organism i on organism j [g(prey)/g (pred)/d]
v	=	concentration of chemical in a given organism i or j (μg/g)
c	=	dissolved chemical concentration
n	=	total number of organisms preyed on by organism i

Chemical uptake from the water column was calculated using the respiration rate for a given species and gill membrane permeability ratio of chemical contaminant to oxygen in a temperature dependent manner. For each species the respiration rate (R) was calculated according to the following equation (Thomann, 1981):

$$R = 0.036w^{-0.2} \quad (2)$$

Food consumption rate was computed as the daily food intake required to sustain a specified growth rate and respiration rate of the organism relative to a specified food assimilation efficiency. The general equation used to calculate the food consumption rate was:

$$C = R + G / a \quad (3)$$

where,

C	=	food consumption rate [g (prey)/g(pred)/d]
G	=	growth rate
a	=	food assimilation efficiency

Finally, the excretion rate constant was calculated as a function of the bioconcentration factor (BCF) and the uptake rate constant from water, K_{ui}, according to the following equation.

$$BCF = K_{ui} / k_2 \quad (4)$$

where,

BCF	=	bioconcentration factor = fraction lipid * K_{ow}
k_2	=	the excretion rate for organism i.

Alternatively, the chemical excretion rate (k_2) and rate of uptake across the gill membrane (k_{ui}) may be used to calculate the BCF.

At steady-state, the rate of change in tissue concentration is assumed to be negligible,

$$i.e., \; dv_i/dt = 0$$

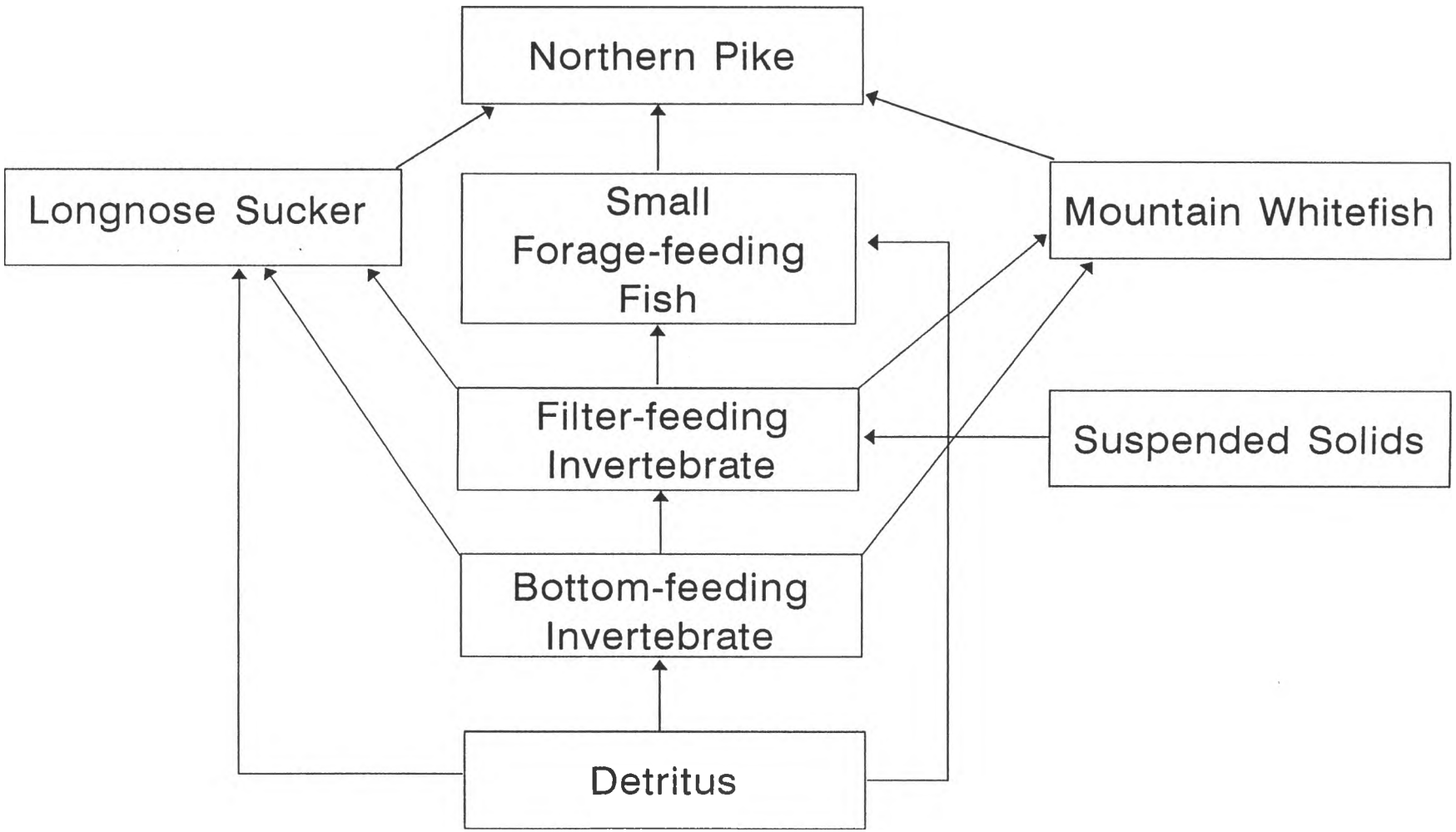
A detailed discussion of the model theory is provided in **"APPENDIX D: FOOD CHAIN MODELLING - MODEL THEORY AND APPLICATION FOR THE NRBs."**

3.3 FOOD CHAIN MODEL CONFIGURATION

3.3.1 Delineation of Food Web and Predator-Prey Preference

Three fish species, mountain whitefish, longnose sucker and northern pike were selected for the food chain simulation. Food webs were identified for the Athabasca River ecosystem and the Smoky-Wapiti rivers ecosystem on the basis of NRBS 1992 monitoring data and data from the Smoky/Wapiti Ecosystem Study (Swanson, 1992). Feeding interactions selected to simulate the Athabasca River and Smoky/Wapiti food webs are illustrated in **Figure 1: Feeding Interaction Modelled for Athabasca River Ecosystem**. These feeding interactions are based on the frequency of occurrence of various prey items identified through stomach contents analysis for fish collected from the Athabasca R. and Smoky/Wapiti rivers, respectively.

Figure 1 Feeding Interactions Modelled for Athabasca River Ecosystem



3.3.1.1 **Athabasca River food web.** The prey preference was determined through an analysis of stomach contents conducted by R.L. & L. Environmental Services (1993) of mountain whitefish, and northern pike (**Table 1: Relative Frequency of Prey Items (Wet Weight) for Ten Mountain Whitefish**). Prey preference for longnose sucker was based on gut analysis of fish from the Smoky/Wapiti (Swanson, 1992). On a mass basis, the frequency of occurrence of the different prey was determined for each species as depicted in **Figures 2a: Observed Frequency of Prey Items in Mountain Whitefish, 2b: Observed Frequency of Prey Items in Northern Pike,** and **2c: Observed Frequency of Prey Items in Longnose Sucker,** respectively. To complete the diet of northern pike a small forage-feeding fish was also included.

Table 1: Relative Frequency of Prey Items (Wet Weight) for Ten Mountain Whitefish

Order	Total Weight (g)	Relative Frequency
Trichoptera	1.02	60.2
Ephemeroptera	0.171	10.0
Plecoptera	0.466	27.4
Diptera	0.0352	2.07
Other	0.00459	0.270
Gastropoda	0.000330	0.0194
Total	1.70	99.9

The taxonomical identification of macroinvertebrates in the stomach content analyses to the level of Order does not provide sufficient information to fully characterize the dietary habits of these invertebrates. Instead, the relative dietary composition of different macroinvertebrates was based on broad ecological classifications of bottom-feeding invertebrates, namely scrapers and detritivores, and of filter-feeding invertebrates consuming suspended solids. This classification as either bottom-feeding invertebrates (BFI) or filter-feeding invertebrates (FFI) enabled the simulation of two distinct exposure pathways to fish. In addition, this dual-exposure pathway methodology allowed the investigation of incremental effects of variations in the dietary composition of bottom-feeding *versus* filter-feeding invertebrates on the uptake and accumulation of 2,3,7,8-TCDF in different species of fish within the same ecosystem.

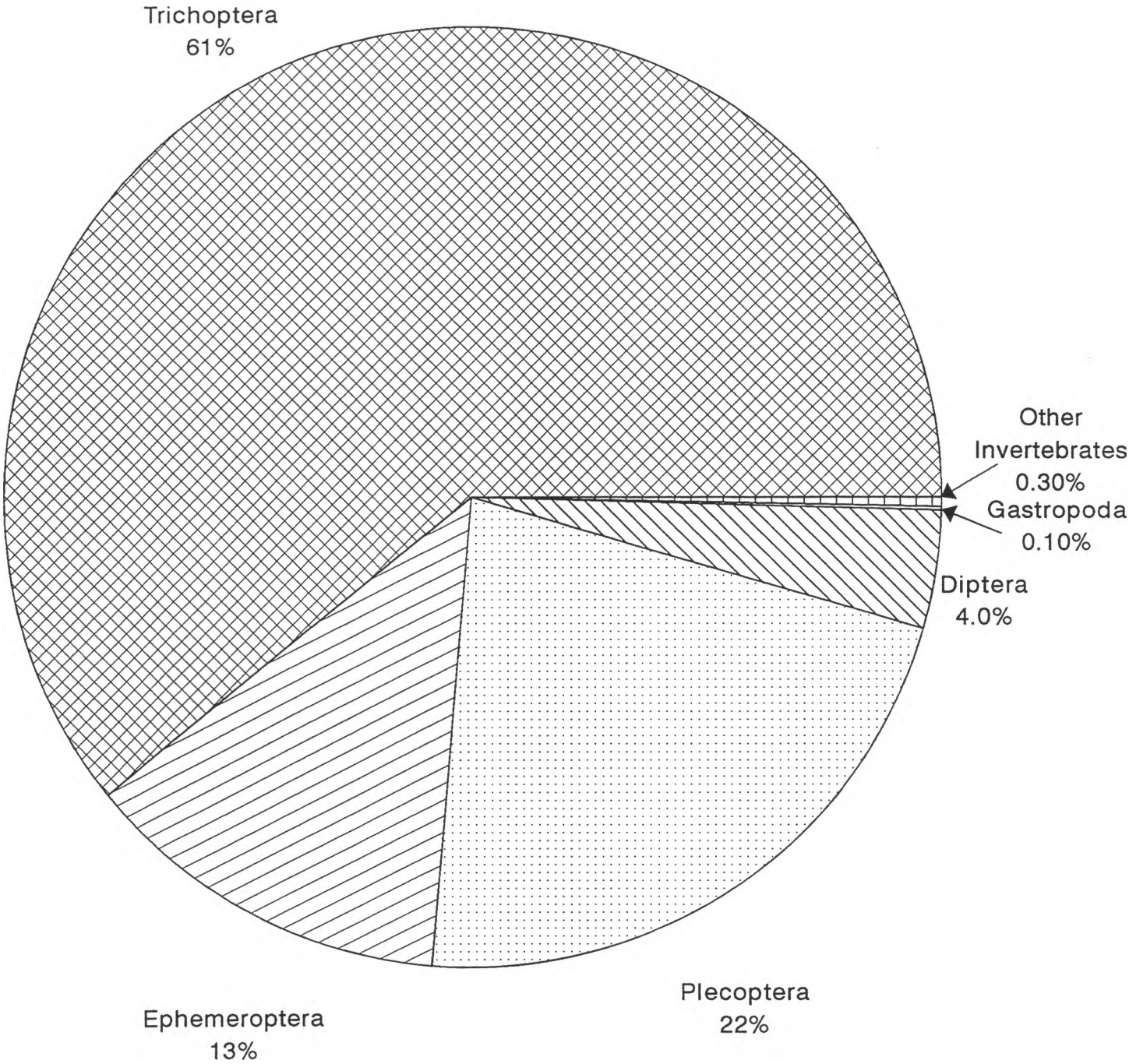


Figure 2a **Observed Frequency of Prey Items in Mountain Whitefish (Athabasca R., Spring, 1992; n=10) (Source: R.L. & L. Environmental Services Ltd., 1993)**

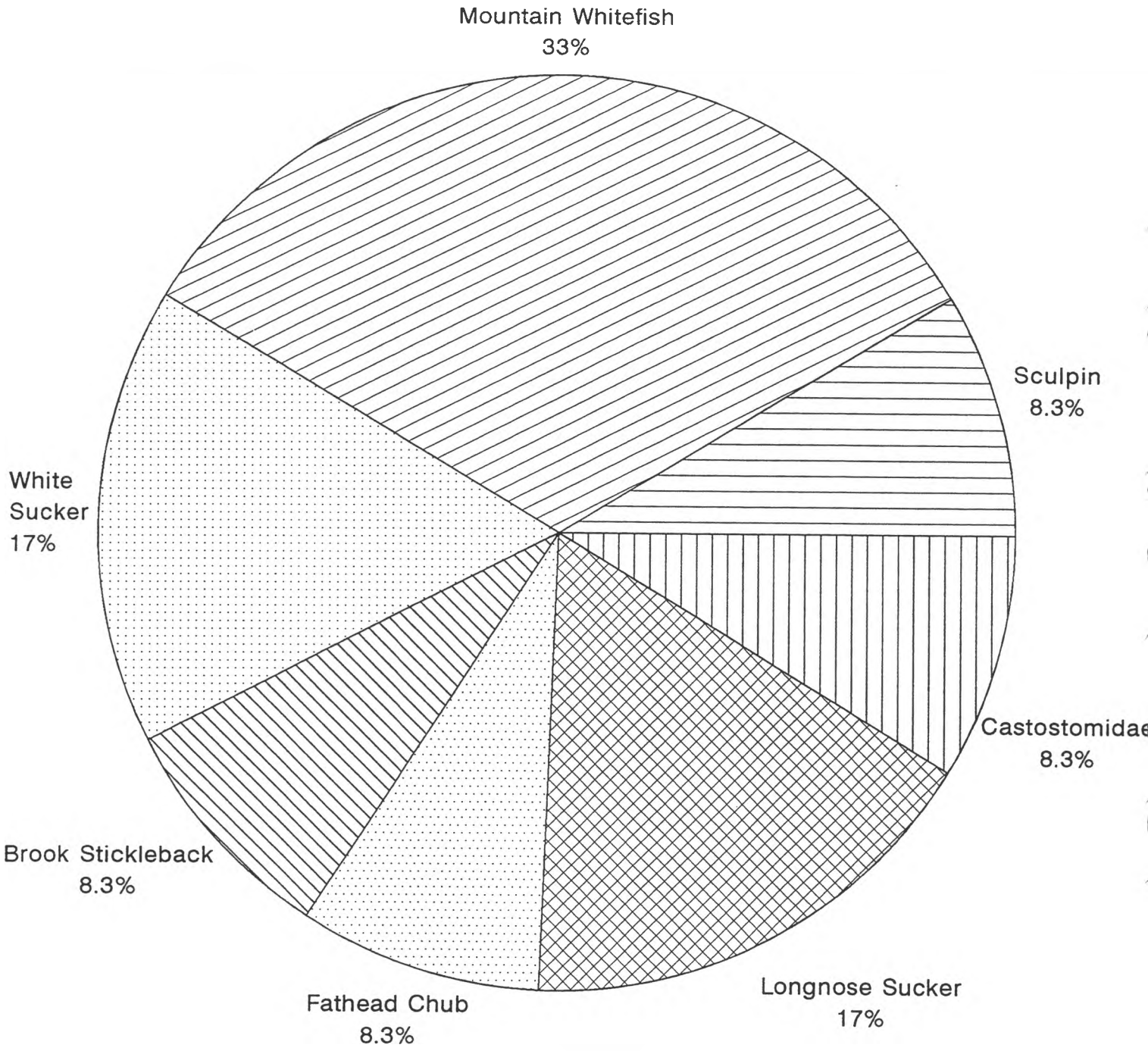


Figure 2b **Observed Frequency of Prey Items in Northern Pike (Athabasca River Spring, 1992; n=9) (Source: R.L. & L. Environmental Services, 1993)**

For each species the relative dietary compositions of food items for each species modelled are listed in **Table 2: Dietary Composition of Athabasca R. Food Web Model**.

Table 2: Dietary Composition of Athabasca R. Food Web Model

	Consumer[a]					
Food item	BI	FFI	MWF	NP	LNS	SFF
Bottom substrate[b]	100%				45%	
Suspended solids[c]		100%				
Bottom-feeding invertebrate (BI)			39%		49%	95%
Filter-feeding invertebrate (FFI)			61%		6%	5%
Mountain whitefish (MWF)				31%		
Longnose sucker (LNS)				39%		
Small forage-feeding fish (SFF)				30%		

[a] BFI= bottom-feeding invertebrate; FFI= filter-feeding invertebrate; MWF= mountain whitefish; LNS=longnose sucker; SFF= small foraging fish.

[b] Bottom substrate consists of detritus (*e.g.*, includes biofilm and depositional sediments).

[c] Suspended solids consists of all suspended particulate material (*e.g.*, may include phytoplankton, microinvertebrates, organic/inorganic solids).

3.3.1.2 Smoky/Wapiti River food web. A food web for the Smoky/Wapiti River ecosystem was constructed based on the predator-prey interactions identified for longnose sucker (**Figure 2c: Observed Frequency of Prey Items in Longnose Sucker**) and mountain whitefish (**Figure 2d: Observed Frequency of Prey Items in Mountain Whitefish**) (Swanson,1992). Gut contents analyses for northern pike of the Athabasca R. were used *in lieu* of site-specific data. In keeping with the food web of the Athabsca R. the lower trophic level was characterized by bottom-feeding invertebrates (BFI) and filter-feeding invertebrates (FFI), each representing a distinct exposure pathway to fish (**Table 3: Dietary Composition of Smoky/Wapiti R. Food Web Model**).

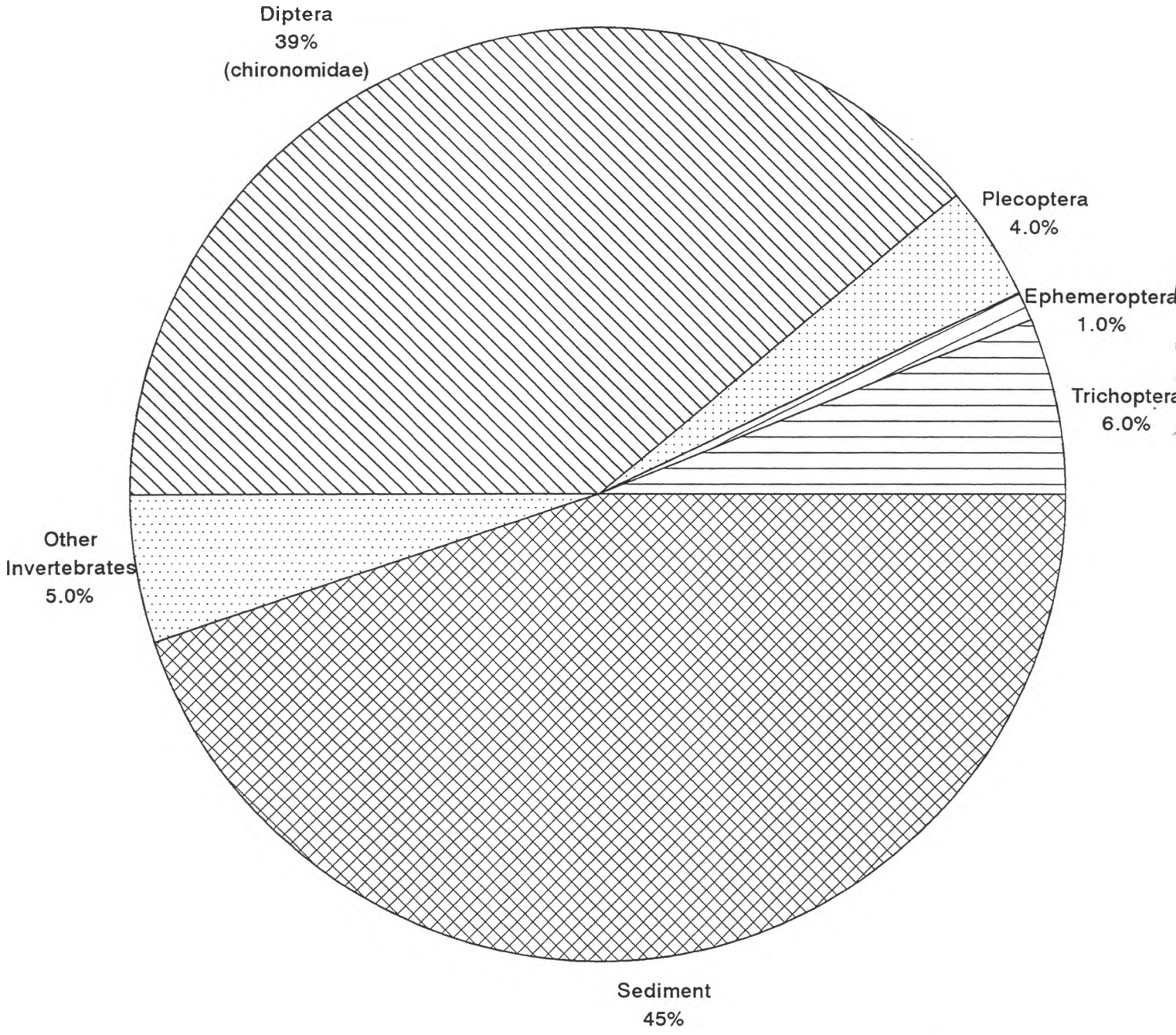


Figure 2c **Observed Frequency of Prey Items in Longnose Sucker (Smoky Wapiti River System; n=23) (Source: Swanson *et al.*, 1992)**

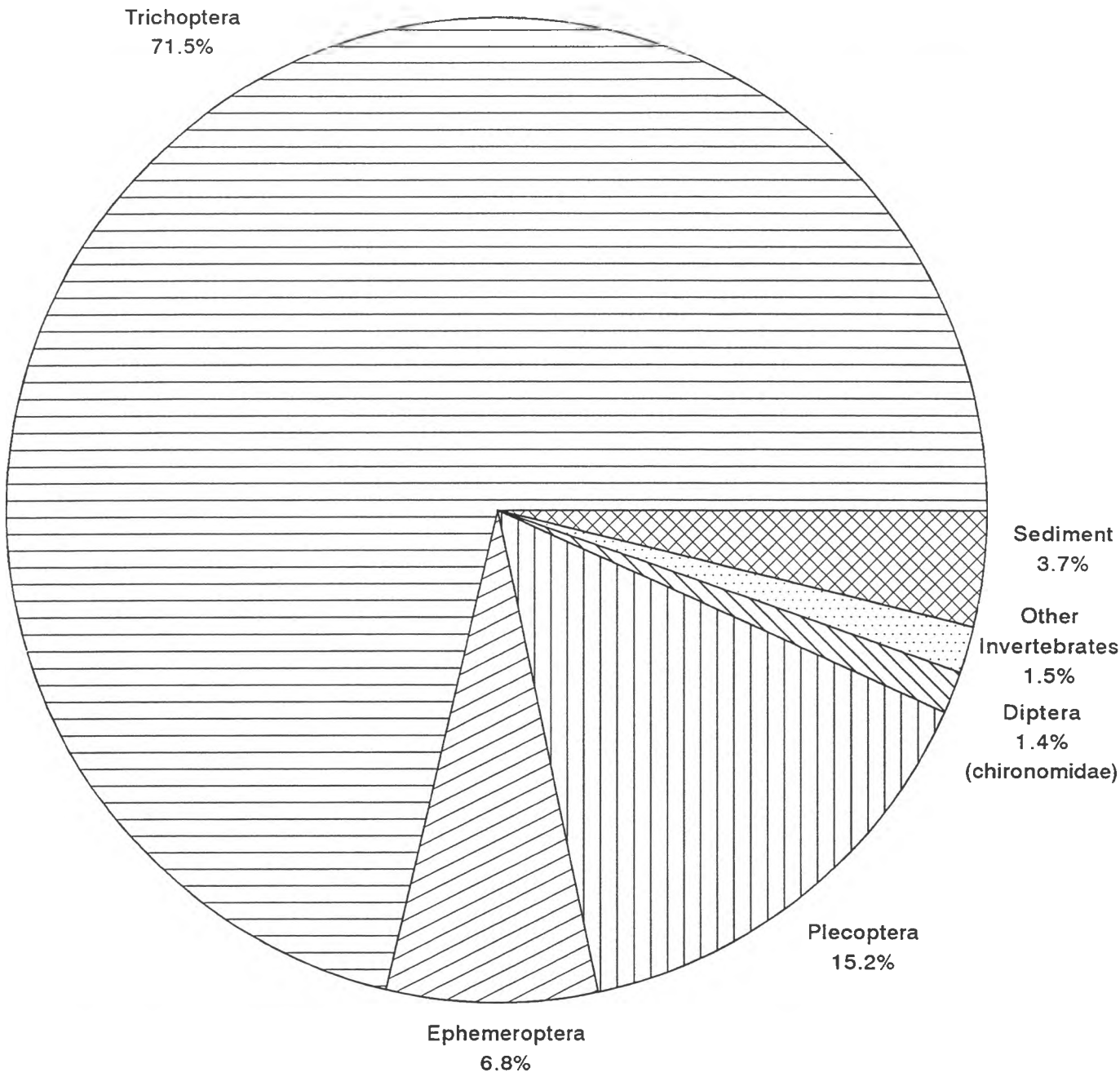


Figure 2d **Observed Frequency of Prey Items in Mountain Whitefish (Smoky Wapiti River System; n=35) (Source: Swanson *et al.*, 1992)**

Table 3: Dietary Composition of Smoky/Wapiti R. Food Web Model

	Consumer[a]					
Food item	BI	FFI	MWF	NP	LNS	SFF
Bottom substrate[b]	100%		3.7%		45%	
Suspended solids[c]		100%				
Bottom-feeding invertebrate (BI)			24.8%		49%	95%
Filter-feeding invertebrate (FFI)			71.5%		6%	5%
Mountain whitefish (MWF)				31%		
Longnose sucker (LNS)				39%		
Small forage-feeding fish (SFF)				30%		

a BFI= bottom-feeding invertebrate; FFI= filter-feeding invertebrate; MWF= mountain whitefish; LNS=longnose sucker; SFF= small foraging fish.

b Bottom substrate consists of detritus (*e.g.*, includes biofilm and depositional sediments).

c Suspended solids consists of all suspended particulate material (*e.g.*, may include phytoplankton, microinvertebrates, organic/inorganic solids).

3.3.2 Biological Parameters

In addition to the configuration of feeding interactions, several biological parameters characterizing each species modelled were assembled for model input (**Table 4: Biological Parameters for Food Chain Model**). Note that for the Athabasca R. the % lipid for bottom-feeding invertebrate and filter-feeding invertebrate were identical, and the % lipid of mountain whitefish was less than 1% greater than that of longnose sucker.. However, for the Smoky/Wapiti all invertebrates were assumed to have the same %lipid, and tissues of LNS had 2-fold less lipid than MWF.

For all fish species, growth rates were determined by linear regression of the *ln* weight *vs* age using field data of fish collected from the Athabasca River. Respiration rates were calculated according to equation (2) using Athabasca River field data. Values for biological parameters describing bottom-feeding and filter-feeding invertebrates were based on data for Chironomidae and Trichoptera, respectively. Mean weights of these invertebrates were estimated from mean lengths of each Order of invertebrates reported in the mountain whitefish gut content analyses, according to the length:weight relationship of Hynes and Coleman (Hamilton, 1968). These weights were then translated into growth rates (G) using the relationship of Thomann (1981):

$$G=0.01w^{-0.22} \quad (6)$$

Respiration rates for invertebrates were calculated using equation (2). These and other biological parameters are listed in **Table 4: Biological Parameters for Food Chain Model**.

Table 4: Biological Parameters for Food Chain Model

Biological Parameter	BFI[a]	FFI[b]	MWF	LNS	NP	SFF[c]
Respiration rate (g/g/d)	0.108	0.07	0.00388	0.0038	0.0032	0.0126
Growth rate	0.033	0.021	0.00026	0.000093	0.00099	0.00343
Food assimilation efficiency	0.06	0.06	0.82	0.82	0.82	0.82
Fraction dry weight	0.19	0.19	0.24	0.28	0.22	0.162
Percent lipid (mean) - Athabasca R.[d]	50%	5.0%	5.2%	4.6%	1.0%	3.0%
- Smoky/Wapiti[e]	12.9%	12.9%	6.2%	2.1%	1.0%	3.0%

[a] Based on Trichoptera data from Athabasca, River study.
[b] Based on Chironamidae data from Athabasca River study.
[c] Based on data for brook stickleback and percent lipid of yellow perch.
[d] Based on data from Athabasca River study.
[e] Based on data from Smoky/Wapiti River (Swanson, 1992).

3.4 CHEMICAL DATA

3.4.1 TCDF

Chemical dependent parameters used in the calculation of the rate of uptake of TCDF through respiration and food consumption, and of the rate of loss of TCDF due to excretion are presented in **Table 5: Chemical Dependent Parameters used in Food Chain Model**. Reported chemical assimilation efficiencies (E) for TCDF in fish ranged from 0.49 to 0.62 (Muir *et al.*, 1992b). Reported chemical assimilation efficiencies of TCDD in fish range from 0.34 to 0.50 (Expert Panel, 1994). Little information is available on the assimilation efficiency of TCDF and TCDD in aquatic invertebrates. Assimilation efficiencies of TCDF of 0.15 in chironomidae and emerging insects, and of 0.05 in Hexagenia were determined by Muir *et al.* (1992c). Assimilation efficiencies of 0.017 to 0.092 and k_2 values of 0.025 to 0.070 d^{-1} were determined for filter-feeding caddisfly larvae consuming particulate bound TCDF in a lab study (Pastershank, 1994). Several studies have reported excretion rates for TCDF in fish (Muir *et al.*, 1992b; Kuehl *et al.*, 1986; Opperhuizen and Sijm, 1990; Merhle *et al.*, 1988; Cook *et al.*, 1991).

3.4.2 DHA and DCDHA

Limited data was identified on the pharmacokinetics of the resin acids, DHA and DCDHA. Bioconcentrations factors of DHA in fish have been reported to range from 92 to 1,460 (Oikari and Kunnamo-Ojala, 1987; Oikari *et al.*, 1982; Niimi and Lee, 1992). However, these values were determined under laboratory conditions and do not necessarily represent BCFs at chemical equilibrium. Resin acids are metabolized into glucuronide and sulfate conjugates (Oikari and Anas,

1985; Oikari *et al.*, 1984). In a study of the kinetics of free and conjugated resin acids (abietic, dehydroabietic, chlorodehydroabietic, dichlorodehydroabietic, neoabietic, pimaric, isopimaric, sandaracopimaric and palustric acids) in rainbow trout BCFs ranged from <25 to 130 in fish exposed to waterborne concentrations of 0.7 to 3.6 μg/L for 20 d (Niimi and Lee, 1992). No detectable levels of free and conjugated acids in fish were found 4 to 10 days after exposure had ceased. The authors concluded that that the half-lives of these free and conjugated resin acids would be <4d in trout.

The mean BCFs reported for DHA was 96 +/- 35 and for DCDHA was 92 +/- 29 (Niimi and Lee, 1992). These measured values are several orders of magnitude less than the calculated BCFs based on a K_{ow} * %lipid relationship. Consequently, measured BCF values were input directly into the model since it was apparent from the field data that BCFs calculated based on K_{ow} * % lipid would grossly overestimate observed concentrations of DHA and DCDHA.

No data was identified on the dietary chemical assimilation efficiency of the resin acids. Therefore, the sensitivity of the model to a range in values was tested. Chemical assimilation efficiencies assumed are listed in **Table 5: Chemical Dependent Parameters used in Food Chain Model**. The gill membrane permeability was estimated from the ratio of the diffusitivity of the resin acid in water to that of O_2 according to a molecular weight relationship (Mills *et al.*, 1982). No data was identified on the kinetics of resin acids in invertebrates.

3.4.3 TCC, TCG, and TCV

The kinetics of these chlorinated phenolics in fish and invertebrates have not been well characterized (Niimi *et al.*, 1990). Generally, the chlorinated guaiacols and chlorinated catechols are readily metabolized and excreted by fish, with a half-life of 1 to 2 days for trichloroguaiacol and tetrachloroguaiacol in bleak (*Alburnus alburnus*) (Renberg *et al.*, 1980) and of <10d for tetrachloroguaiacol in trout liver (Landner *et al.*, 1977). Equilibrium BCFs for waterborne exposed rainbow trout ranged from 1 to 270 among the chloroguaiacols tested, <5 for the chlorovanillins and 125 for trichlorosyringol (Niimi *et al.*, 1990). A BCF of 268 was reported for trichloroguaiacol-exposed fish. In the absence of data for TCC and TCV, a BCF of 268 was selected to represent the BCFs in fish for the chlorinated phenolics. A BCF in mussels of 34 was reported (Makela and Oikari, 1990), this value was input to the model to represent the BCF in invertebrates of the chlorinated phenolics. It should be noted that reported measured BCFs for these chemicals are similar to the calculated BCF values based on K_{ow} * %lipid relationships. A dietary absorption efficiency of 3% for TCG and a 2d half-life in rainbow trout was reported by Niimi *et al.* (1990).

Table 5: Chemical Dependent Parameters used in Food Chain Model

Chemical	Parameter					
	log Kow	PRatio	E_{invert}	E_{fish}	k_2 invert (d^{-1})	k_2 fish (d^{-1})
2,3,7,8-TCDF	6.1[a]	0.20[b]	0.15[c]	0.54[d]	0.015[c]	0.003[e]
DHA	6.1	0.57	0.25	0.25	-	-
12, 14-DCDHA	6.4	0.54	0.25	0.25	-	-
3,4,5-TCC	3.7	0.62	0.03	0.03	-	-
3,4,5-TCG	4.2	0.61	0.03	0.03	-	-
3,4,5-TCV	4.6	0.60	0.03	0.03	-	-

[a] Mackay *et al.* 1992.
[b] McKim *et al.*, 1989.
[c] Muir *et al.*, 1992c.
[d] Muir *et al.*, 1992b.
[e] Data estimated from a study by Kuehl *et al.*, 1986.

4.0 MODEL CALIBRATION AND SENSITIVITY ANALYSIS

4.1 ATHABASCA FOOD WEB MODEL

The food chain model was calibrated to the field data through the use of site-specific data to characterize feeding interactions and to estimate values for biological parameters. Concentrations of TCDF, DHA, DCDHA, TCC, TCG and TCV in samples of water column, suspended sediments and depositional sediments at various reaches upstream and downstream of the BKM at Weldwood Haul, Athabasca River (NRBS 1992 data) were used in the model calibration to hindcast relative concentrations in mountain whitefish, longnose sucker and northern pike sampled from these sites. These data are summarized in **Table 6: Environmental Chemical Concentrations and Speicies Data from NRBs Data Set**.

Table 6: Environmental Chemical Concentrations and Species Data from NRBs Data Set

Site	n	TCDF	DHA	12, 14-DHA	Tric-C	Tri-G	Tri-V	% Lipid	Wet Wt (g)	Age (yr)	Dry Wt Fraction
Water Column - Centrifugate (μg/L)											
U/S Control	1	(4E-7)	(0.063)	(0.036)	(0.05)	(0.05)	(0.05)				
Weldwood	1	1.0E-7	0.125	0.0034	(0.05)	0.42	(0.05)				
Obed	1	(4E-7)	(0.16)	(0.069)	0.035	0.18	0.0157				
Emerson	1	9.0E-8	0.046	0.0035	(0.05)	0.19	(0.05)				
Knight	1	(2E-8)	0.076	(0.0025)	0.0093	0.03	0.005				
Windfall	1	(4E-7)	(0.087) n=2	(0.055) n=2	0.0092	0.023	0.0041				
Water Column - Freely Dissolved (μg/L) (calculated*)											
U/S Control	1										
Weldwood	1	3.5E-08									
Obed	1	2.58E-07									
Emerson	1	2.5E-08									
Knight	1	2E-09									

Table 6: Environmental Chemical Concentrations and Species Data from NRBs Data Set

Site	n	TCDF	DHA	12, 14-DHA	Tric-C	Tri-G	Tri-V	% Lipid	Wet Wt (g)	Age (yr)	Dry Wt Fraction
Windfall	1	2.35E-07									
Water Column - Susp. Sed. (pg/g)											
U/S Control	1	0.3	140,000	20	(1,100)	5,900	(1,650)				
Weldwood	1	2.2	1,400,000	140,000	45,300	(7,000)	(1,650)				
Obed	1	2.6	1,200,000	140,000	(1,100)	56,000	(1,650)				
Emerson	1	3.2	1,300,000	260,000	41,600	(14,000)	(3,300)				
Knight	1	2.8	1,200,000	190,000	40,500	(21,000)	(4,950)				
Windfall	1	2.3	980,000	97,000	(1,100)	46,000	(1,650)				
River Bed - Bed Sediment (pg/g) depositional											
U/S Control	1	(0.1)	60,000	(100)	(1,100)	ND	(1,650)				
Weldwood	1	0.4									
Obed	1	0.9	410,000	81,000	6,110	1,120	2,010				
Emerson	1	1.9									
Knight	1										
Windfall	1		390,000	29,000							

Table 6: Environmental Chemical Concentrations and Species Data from NRBs Data Set

Site	n	TCDF	DHA	12, 14-DHA	Tric-C	Tri-G	Tri-V	% Lipid	Wet Wt (g)	Age (yr)	Dry Wt Fraction
Fish (calculated BCF) (x 10E6) - Mountain Whitefish											
U/S Control	10										
Weldwood	12	6.53									
Obed	10	0.906									
Emerson	10	8.26									
Knight	10	54.2									
Windfall	10	0.717									
Fish (calculated BCF) (x 10E6) - Northern Pike											
U/S Control	6										
Weldwood	2	2.48									
Obed	-										
Emerson	1	17.5									
Knight	10	375									
Windfall	10	1.58									

Table 6: Environmental Chemical Concentrations and Species Data from NRBs Data Set

Site	n	TCDF	DHA	12, 14-DHA	Tric-C	Tri-G	Tri-V	% Lipid	Wet Wt (g)	Age (yr)	Dry Wt Fraction
Fish (pg/g) (wet wt) - Mountain Whitefish											
U/S Control	10	0.86	(1,000) N=6	(1,000) N=6	650	(400)	(400)	4.2	473	8.4	0.23
Weldwood	12	13			(400)	(400)	(400)	5.8	573	8.6	0.27
Obed	10	12	(1,000)	(1,000)	512	412	575	5.6	726	7.9	0.26
Emerson	10	14			(400)	(400)	(400)	6.5	617	8.6	0.22
Knight	10	3.7			(400)	(400)	(400)	4.1	715	8.1	0.21
Windfall	10	8.6	(1,000) N=5	(1,000) N=5	(400)	(400)	1,200	5.1	566	9.6	0.26
Fish (pg/g) - Northern Pike											
U/S Control	6	0.49	(1,000)	(1,000)	1,900	(400)	680	0.67	1038	3.7	0.21
Weldwood	2	0.6			(400)	(400)	(400)	0.68	598	3	0.22
Obed	-										
Emerson	1	7.9			(400)	(400)	(400)	1.8	2,596	6	0.22
Knight	10	6.2			(400)	(400)	(400)	0.97	1,902	4.8	0.22
Windfall	10	2.6	(1,000)	(1,000)	(400)	(400)	(400)	0.71	1,353	4.7	0.21
Fish - Longnosed Suckers											
Weldwood	10	2.42			(400)	680	(400)	3.47	623.8	9.4	0.24

Table 6: Environmental Chemical Concentrations and Species Data from NRBs Data Set

Site	n	TCDF	DHA	12, 14-DHA	Tric-C	Tri-G	Tri-V	% Lipid	Wet Wt (g)	Age (yr)	Dry Wt Fraction
Fish - Mountain Whitefish											
Weldwood	10	14.7			(400)	1,030	(400)	5.77	716.5	7.6	0.31
Invertebrates (pg/g) - O. Plecoptera											
U/S Control	1	(0.5)	(1,000)	(1,000)	(400)	(400)	(400)	2.4			0.13
Weldwood	1	6			4,700	18,000	(400)	6.4			0.21
Obed	1	1.4	(1,000)	(1,000)	1,500	3,000	(400)	3.7			0.18
Emerson	1	(8.0)			(400)	2,500	(400)	4			0.23
Knight	1	(1.8)			(400)	(400)	(400)	3.5			0.2
Windfall	1	(0.4)	(1,000)	(1,000)	4,600	4,100	(400)	2.8			0.19
Invert. - O. Emphemeroptera											
U/S Control	1	(0.5)	(1,000)	(1,000)				2.4			0.13
Weldwood	1	6.8			3,300	2,700	(400)	2.4			0.15
Obed	1	3.6						6.2			0.21
Emerson	1	13						6.7			0.19
Knight	1	(9.5)						4.7			0.21
Windfall	1	1.4	(1,000)	(1,000)	3,100	(400)	6,300	6			0.18

Table 6: Environmental Chemical Concentrations and Species Data from NRBs Data Set

Site	n	TCDF	DHA	12, 14-DHA	Tric-C	Tri-G	Tri-V	% Lipid	Wet Wt (g)	Age (yr)	Dry Wt Fraction
Invert. - O. Trichoptera											
U/S Control	1										
Weldwood	1	13						4.2			0.15
Obed	1	(0.9)						6.7			0.22
Emerson	1	4.8			14,000	15,000	(400)	4.2			0.19
Knight	1	9			3,200	2,700	(400)	4.8			0.18
Windfall	1	(0.4)			6,300	2,500	2,700	3.1			0.15
Biofilm - (pg/g)											
U/S Control	1	(0.1)	(1,000)	(1,000)	(400)	(400)	(400)	0.056			0.52
Weldwood		(0.9)			5,000	3,500	(400)	0.02			0.17
Obed	2	0.38	(1,000)	(1,000)	9,900	(400)	(400)	0.13			0.27
Emerson		(1.9)			16,000	2,100	(400)	0.16			0.13
Knight		(3.2)			(400)	(400)	(400)	0.1			0.11
Windfall	1	(0.1)	(1,000)	(1,000)	4,900	2,800	(400)	0.14			0.38

Values in brackets are less than detection limit.

Freely dissolved concentrations of TCDF in the water column were estimated assuming equilibrium-partitioning (Pastershank and Muir, 1995). Environmental concentrations of TCDF at various sites of the Athabasca River sampled in 1992 are presented in **Figure 3: 2,3,7,8-Concentrations from Various Locations along the Athabasca River**.

It is important to recognize that ecosystem models consist of a series of mathematical equations that describe numerous complex interactions and reactions that may occur simultaneously and/or sequentially in the real environment. The predicted outcome of the mathematical models are influenced by the current understanding of the physical-chemical, biological and time-dependent processes governing fate, transport and pharmacokinetics in the aquatic environment. On a site-specific basis the outcome of the model is dependent on the user's understanding of the various physical and ecological components of the ecosystem of study. Uncertainties in the data characterizing chemical and biological parameters are therefore investigated through a sensitivity analysis to determine the critical input parameters with respect to the best fit or agreement between the predicted tissue concentrations and the observed based on current scientific understanding of exposure pathways and pharmacokinetics.

The sensitivity of the model to the following input parameters was tested:

1) variations in diet, such as % diet comprised of BFI *vs* FFI and the addition of a predacious invertebrate was explored for the mountain whitefish, longnose sucker and northern pike;

2) water column dissolved and porewater dissolved concentrations;

3) bed sediment and biofilm concentrations;

4) direct input of excretion rate vs calculated BCF vs direct input of lab derived BCF; and

5) chemical assimilation efficiency for resin acids (no chemical-specific data identified).

A final model calibration step was undertaken for TCDF by adjusting the entered excretion rate for invertebrate and fish species until the predicted value equalled the observed. The adjusted excretion rates were compared with those determined from laboratory bioassays identified from a review of the literature (see section 3.4).

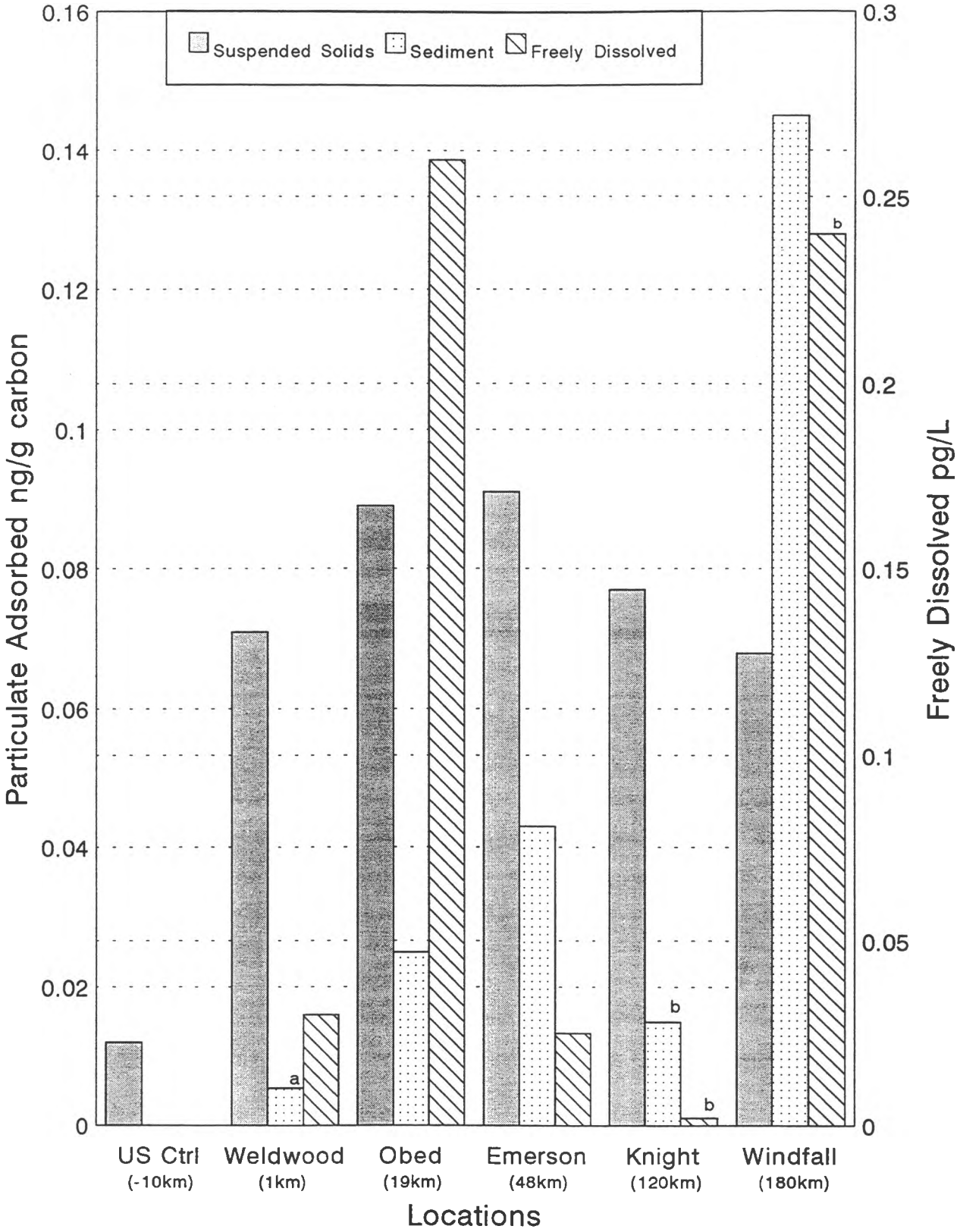


Figure 3 2,3,7,8-TCDF in Water and Sediment of the Athabasca River (Source: Pastershank and Muir, 1994)

[a] $\bar{x}$; n = 2

[b] Assumed to equal d.l.

5.0 MODEL RESULTS AND DISCUSSION

5.1 TCDF

Predicted concentrations in fish were directly related to the dietary contribution of filter-feeding invertebrates. This was determined through an initial sensitivity analysis of the model to variations in the relative percentages that bottom-feeding invertebrates *versus* filter-feeding invertebrates comprise of the total diet of mountain whitefish and longnose sucker (**Table 7: NRBs Food Chain Model Predator-Prey Relationships** and **Figures 4a: Influence of Diet on Predicted 2,3,7,8-T_4CDF Concentrations (pg/g) in Mountain Whitefish for Weldwood Haul, 4b: Influence of Diet on Predicted 2,3,7,8-T_4CDF Concentration (pg/g) in Northern Pike for Weldwood Haul**, and **4c: Influence of Diet on Predicted 2,3,7,8-T_4CDF Concentrations (pg/g) in the Longnose Sucker for Weldwood Haul**). Based on the comparison of predicted TCDF concentrations to observed concentrations, the predator-prey preferences for the Athabsca R. and the Smoky/Wapiti food webs used in model simulations of the other selected chemicals were fixed as delineated in Section 3.3.1 (**Table 2: Dietary Composition of Athabasca R. Food Web Model** and **Table 3: Dietary Composition of Snoky/Wapiti R. Food Web Model**).

Table 7: NRBs Food Chain Model Predator-Prey Relationships[a,b]

	Prey % of Diet based on Frequency of Occurrence									
	Detritus	Sus.Sed	Filter Feeding In. O.Trich.	Bottom Feeding In.			Mountain Whitefish	Longnose Sucker	Northern Pike	Small Foraging Fish
				O.Chiron.	O.Ephem.	O.Plecop.				
Version 1a,b										
Bottom Feeding In	100									
Filter Feeding In		100								
Mountain Whitefish			61	39						
Longnose Sucker	45		6	49						
Northern Pike							34	42		24
Small Foraging Fish			5	95						
Version 2a,b										
Bottom Feeding In.	100									
Filter Feeding In.		100								
Mountain Whitefish			75	25						

Table 7: NRBs Food Chain Model Predator-Prey Relationships[a,b]

	Prey % of Diet based on Frequency of Occurrence									
	Detritus	Sus.Sed	Filter Feeding In. O.Trich.	Bottom Feeding In.			Mountain Whitefish	Longnose Sucker	Northern Pike	Small Foraging Fish
				O.Chiron.	O.Ephem.	O.Plecop.				
Longnose Sucker	45		6	49						
Northern Pike							34	42		24
Small Foraging Fish			5	95						
Version 3a,b										
Bottom Feeding In.	100									
Filter Feeding In.		100								
Mountain Whitefish			100							
Longnose Sucker				100						
Northern Pike							34	42		24
Small Foraging Fish			5	95						
Version 4a,b										
O.Chironomid	80				20					
O. Ephemeroptera	100									
O. Plecoptera			30	40	30					
O. Trichoptera		100								
Mountain Whitefish			61		17	22				
Longnose Sucker	45		6	49						
Northern Pike							34	42		24
Brook Stickleback			5	95						

a Thomann and Connolly food chain model using BCF = log K_{ow} * %lipid.
b Thomann and Connolly food chain model entering excretion rate.

Figure 4a **Influence of Diet on Predicted 2,3,7,8-T_4CDF Concentrations (pg/g) in the Mountain Whitefish for Weldwood Haul**

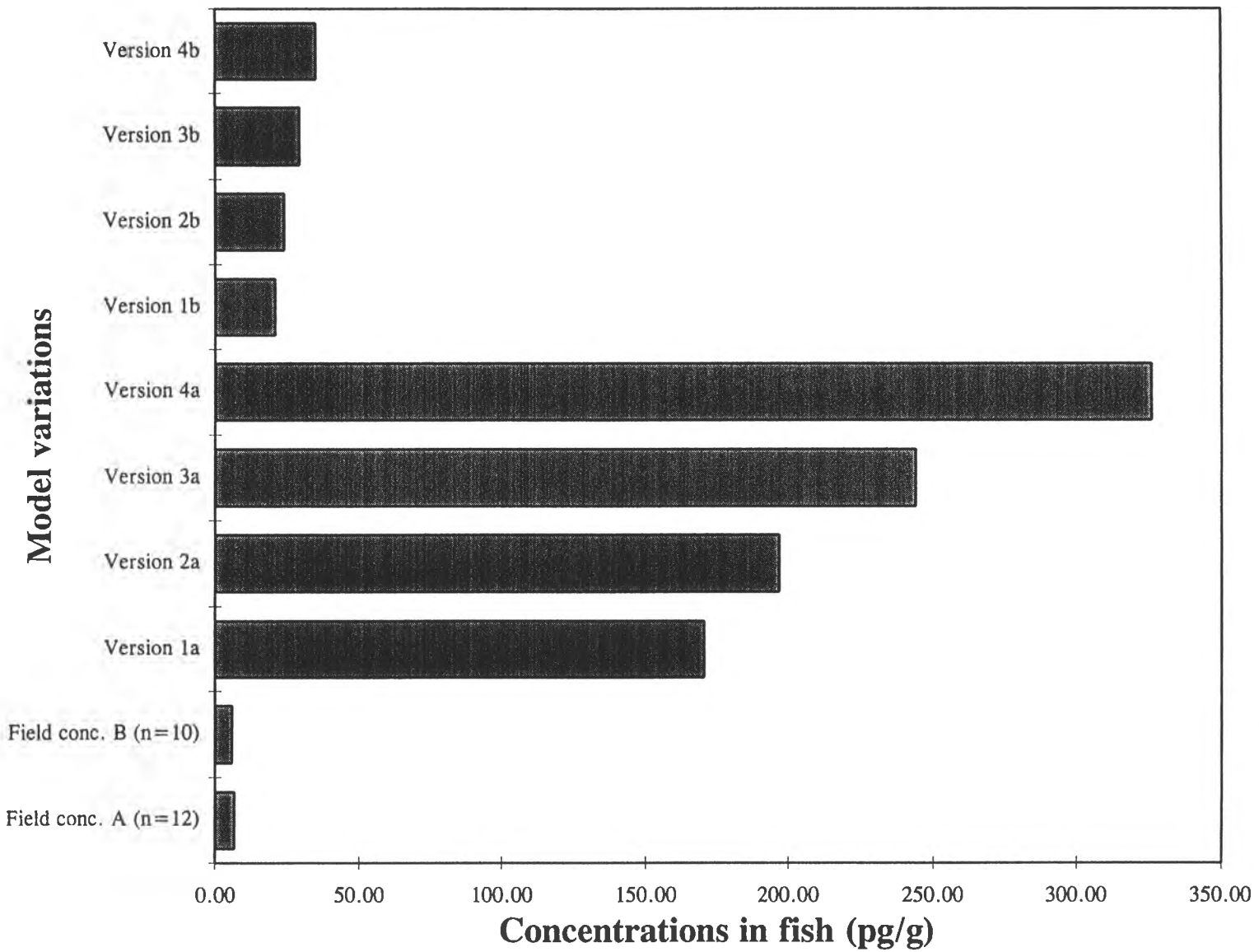


Figure 4b Influence of Diet on Predicted 2,3,7,8-T_4CDF Concentrations (pg/g) in Northern Pike for Weldwood Haul

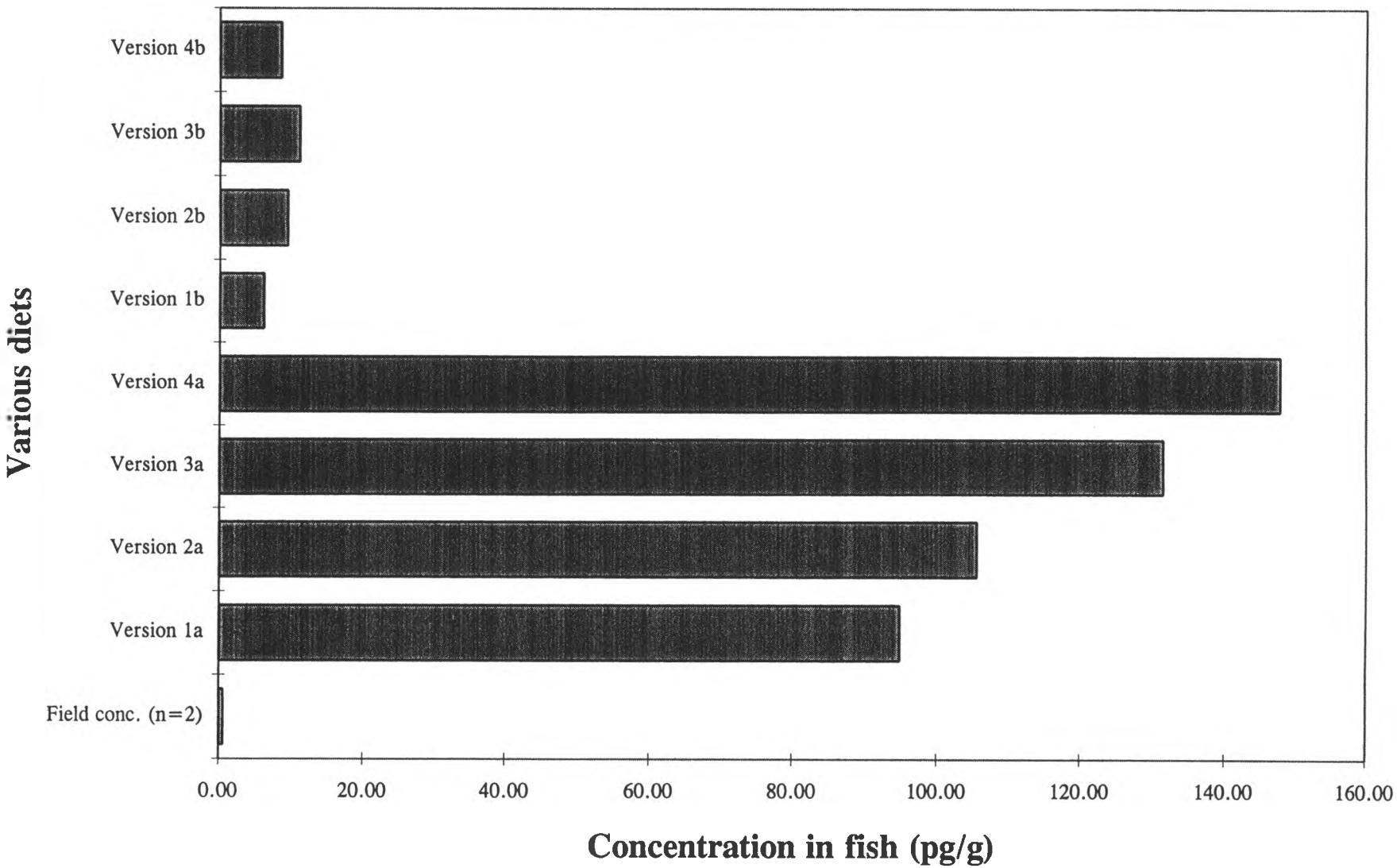
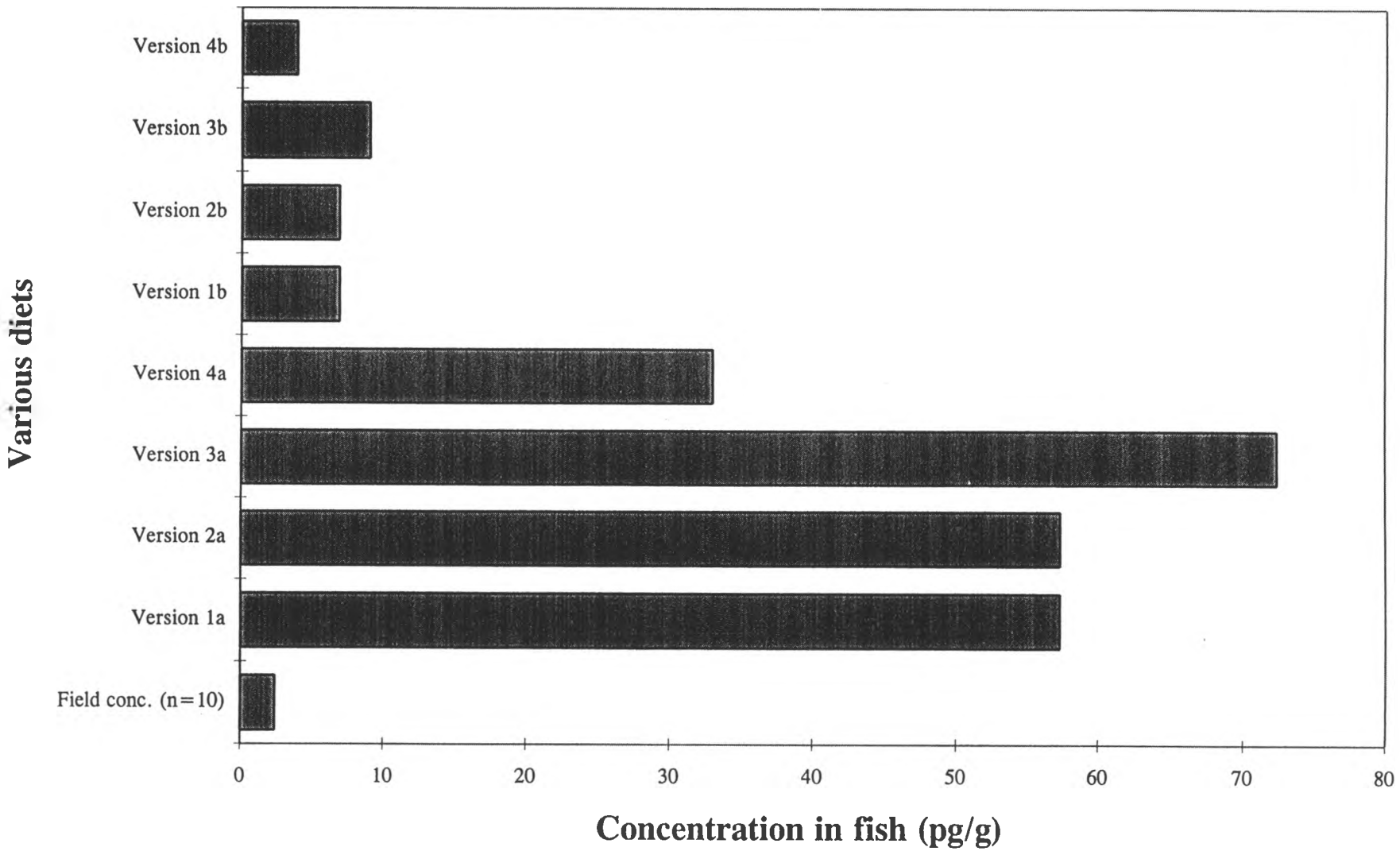


Figure 4c

Influence of Diet on Predicted 2,3,7,8-T_4CDF Concentrations (pg/g) in the Longnose Sucker for Weldwood Haul



Results of a sensitivity analysis of the model to calculation of the BCF on the basis of K_{ui}/k_2 *versus* %lipid * K_{ow} are presented in [**Figures 4a: Influence of Diet on Predicted 2,3,7,8-T_4CDF Concentrations (pg/g) in Mountain Whitefish for Weldwood Haul, 4b: Influence of Diet on Predicted 2,3,7,8-T_4CDF Concentration (pg/g) in Northern Pike for Weldwood Haul**, and **4c: Influence of Diet on Predicted 2,3,7,8-T_4CDF Concentrations (pg/g) in the Longnose Sucker for WWeldwood Haul,**(version a *vs* b)]. The input of excretion rates to calculate respective BCFs for each species resulted in a better agreement with the field data. Predicted tissue concentrations using the default K_{ow}*%lipid to estimate the BCF were 10-fold greater than observed concentrations. However, when the model was run entering an excretion rate of 0.003 d^{-1} for fish species and 0.014 d^{-1} for invertebrate species the predicted concentrations were within 2.5-fold of the observed concentrations. Therefore, the calibrated model used the relationship K_{ui}/k_2 = BCF, assuming literature reported excretion rates for all fish and invertebrates of 0.003 d^{-1} (Kuehl *et al.*, 1986) and 0.015 d^{-1} (Muir *et al.*, 1992c), respectively.

Results of the literature calibrated model simulation for TCDF using an excretion rate of 0.003d^{-1} in fish and 0.014d^{-1} in invertebrates are presented in **Figure 5: Predicted 2,3,7,8-TCDF (pg/g) *vs* Observed. Athabasca River 1992 Field Data**. **Figure 5: Predicted 2,3,7,8-TCDF (pg/g) *vs* Observed. Athabasca River 1992 Field Data** provides a comparison of the predicted tissue concentrations in biota *vs* the average tissue concentration observed in biota collected in 1992 at various locations in the Athabasca River downstream of Weldwood Haul, not considering biofilm.

The river bed of the Athabasca downstream of Hinton consists of large cobble (80 to 90%) with few areas of depositional sediment (10 to 20%) (Leigh Noton, Albert Environment, personal communication). This cobble bottom provides surface area for biofilm growth. The influence of biofilm on predicted tissue concentrations in bottom-feeding invertebrates and their consumers was addressed by calculating the concentration of TCDF in detritus based on the observed concentration in depositional sediments, apportioned by a factor of 10% and the concentration in biofilm, apportioned by a factor of 90%. Since observed concentrations of TCDF in biofilm samples were typically non-detectable, the concentration in the biofilm was assumed to equal the detection limit of the corresponding samples.

Predicted tissue concentrations *vs* observed concentrations taking into consideration biofilm contributions are presented in **Figure 6: 2,3,7,8-TCDF in Biota, Predicted *vs* Observed Using Biofilm, All Locations**. As expected the contribution of biofilm resulted in lower concentrations in BFI and LNS for which the predominant exposure pathway is detritus. Predicted concentrations in FFI were unaffected and those in MWF were slightly less than those predicted excluding biofilm. Similarly, predicted concentrations in northern pike, the diet of which was assumed to consist of 39% LNS were also lower when biofilm contributions were included in the model input.

Figure 5 Predicted 2,3,7,8-TCDF (pg/g) *vs* Observed. Athabasca River 1992 Field Data

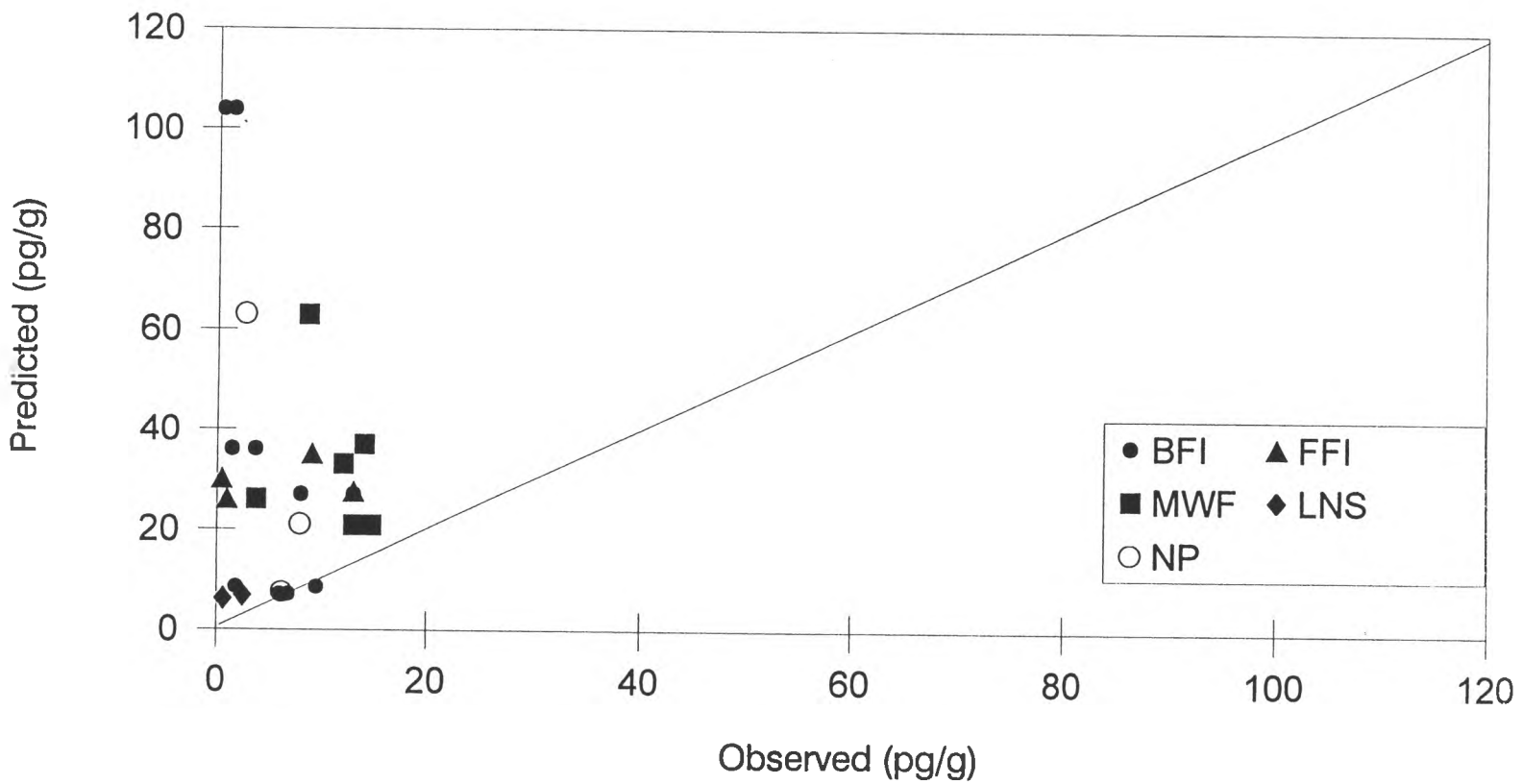
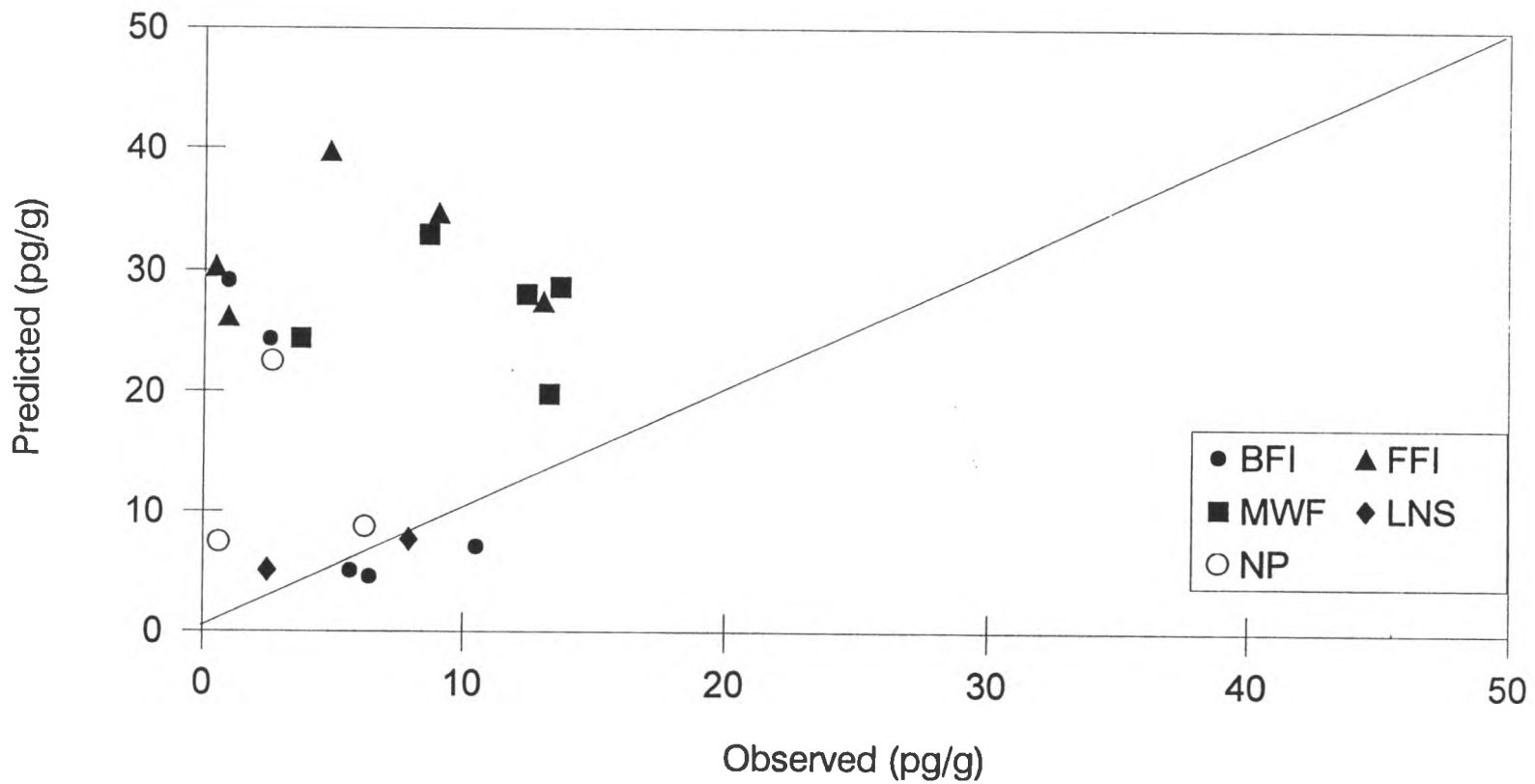


Figure 6 2,3,7,8-TCDF in Biota, Predicted *vs* Observed Using Biofilm, All Locations



Presentation of the model results for each location downstream of Weldwood Haul are provided in **"APPENDIX B: MODEL RESULTS - ATHABASCA RIVER PER LOCATION."**

Predicted TCDF concentrations *vs* observed concentrations in biota from the Smoky/Wapiti river system computed using the Smoky/Wapiti food web model are compared in **Figure 7: Comparison of Observed TCDF Concentrations Smoky/Wapiti Site 1, 2 and 4 in 1990 *vs* Predicted** and **Figure 8: Comparison of Observed TCDF Concentrations Smoky/Wapiti Site 1 and 2 in 1991 *vs* Predicted**, for three different sites based on data collected in the fall of 1990 and 1991 (Swanson, 1992). The less accurate predictions of the Smoky/Wapiti food web model may be attributed to the use maximum concentrations in suspended solids and of non-site-specific data to characterize the biological parameters of the species modelled, with the exception of lipid. Consequently, input of environmental concentrations and respiration rates and growth rates of BFI, FFI, LNS and MWF based on Athabasca R. data appeared to overestimate tissue concentrations in these species. Thus, emphasizing the importance of calibrating models with site-specific data and the range in environmental concentrations, as data permits.

In the field, fish would not be expected to reach steady-state equilibrium with the environmental concentrations due to potential variations in exposure related to movement upstream and downstream as well as variations in diet and concentration in food items. Therefore, it is not unreasonable that the steady-state model used in this study tended to over-estimate concentrations of TCDF in fish.

Generally, the best agreement was obtained for the BFI, which being relatively sedentary and in direct contact with the substrate, are better represented than fish by steady-state equilibrium partitioning. Exposure of FFI would be more dynamic than that of BFI, reflecting variations in concentrations of TCDF on suspended solids, dependent on the characteristics of mill effluents and changes in water column chemistry.

Reflected in the monitoring data are decreases in TCDF loadings by the mills related to bleaching process technology changes directed at elimination of the production of chlorinated dioxins and furans. Most notable is the switch from molecular chlorine (Cl_2) bleaching to chlorine dioxide (ClO_2) substitution. The fact that biofilm samples had non-detectable concentrations of TCDF provides an element of uncertainty in the monitoring data. It is possible that dietary exposures of BFI and LNS may have been over estimated by assuming that the biofilm contribution to detritus was equal to the detection limit. How representative are these biofilm samples of the TCDF concentration in detritus available for consumption by BFI and LNS is unknown. In consideration of these uncertainties the literature calibrated kinetic model appears to predict tissue concentrations of TCDF in BFI, FFI, MWF, LNS and NP of the Athabasca R. reasonably well.

Figure 7 Comparison of Observed TCDF Concentrations Smoky/Wapiti Site 1 and 4 in 1990 *vs* Predicted

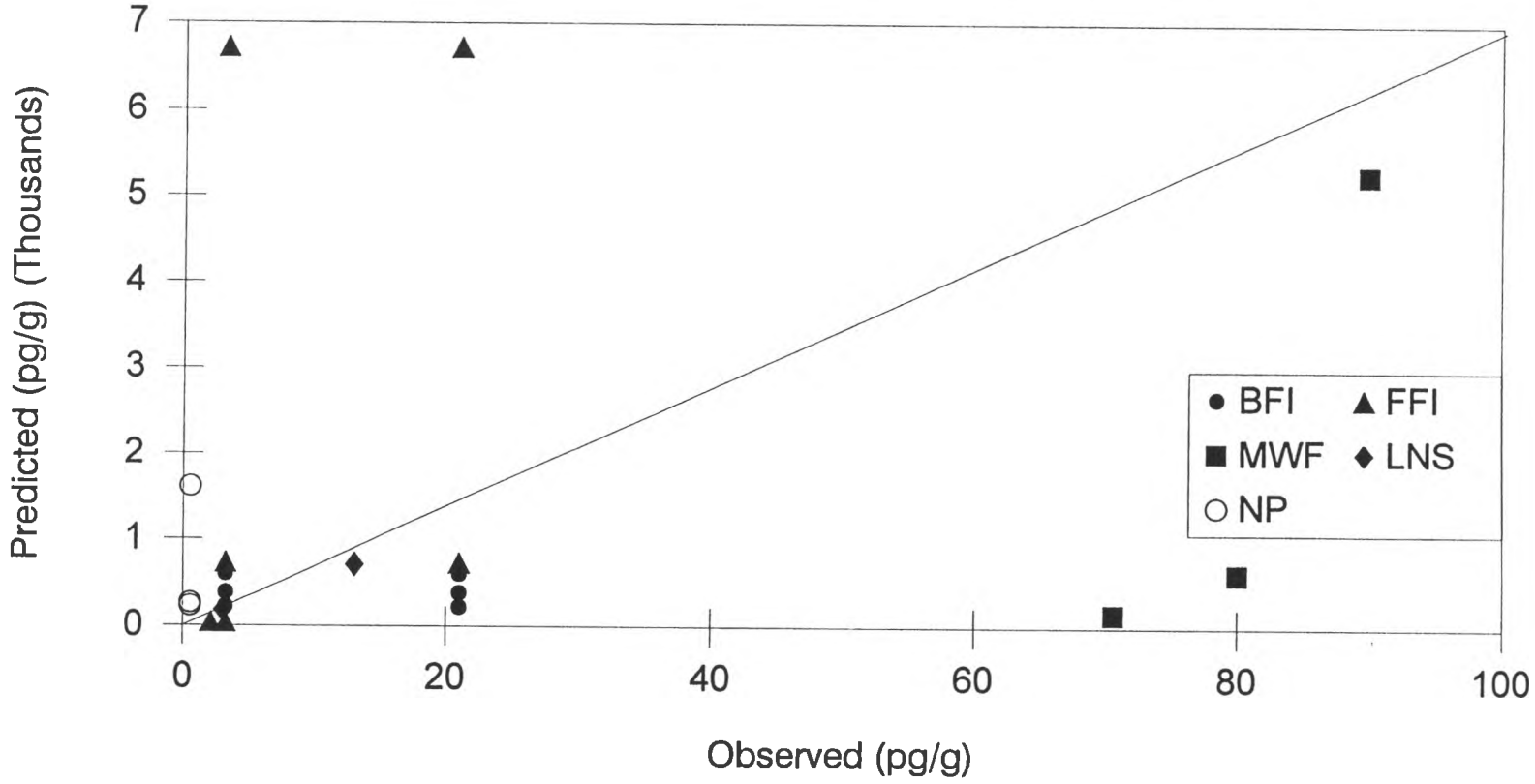
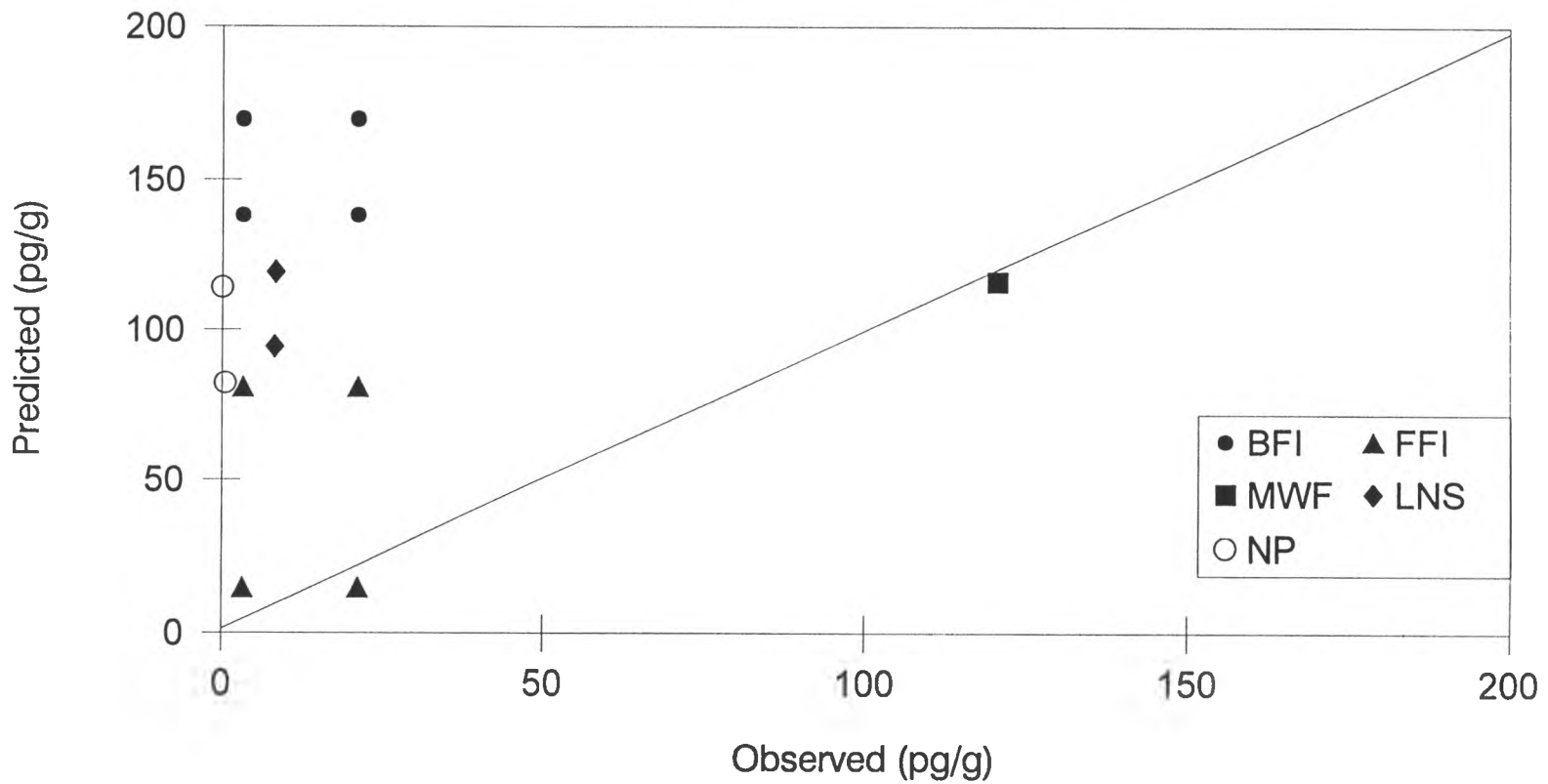


Figure 8 Comparison of Observed TCDF Concentrations Smoky/Wapiti Site 1 and 2 in 1991 *vs* Predicted



As a final calibration step, the excretion rate input for each species modelled was adjusted until the respective predicted concentration in each species matched the observed data. A comparison of the adjusted excretion rates to those identified in the literature through bioassays is provided in **Table 8: Comparison of Literature based Excretion Rates *vs* Adjusted Excretion Rates**. The greatest difference between adjusted and literature values was for the FFI, BFI and LNS. These observations may be attributed to the following:

1) Exposure of FFI was overestimated by assuming a constant concentration on suspended solids; the dietary assimilation efficiency in invertebrates of TCDF sorbed to suspended solids is less than 0.15.

2) Exposure of BFI and LNS was overestimated by the assumption that the concentration in detritus was attributed to 90% biofilm and 10% depositional sediments; and the assumption that TCDF concentration in biofilm equalled the detection limit overestimated the actual concentration in biofilm.

3) The dietary assimilation efficiency of TCDF sorbed to detritus is less than 0.54 for LNS.

Further research is required to address whether or not species related differences in dietary assimilation efficiency and excretion of TCDF exist. And to determine the influence of the food matrix on dietary assimilation efficiency of TCDF.

Table 8: Comparison of Literature based Excretion Rates *vs* Adjusted Excretion Rates

Species	Literature based Excretion Rate (d^{-1})	Adjusted Excretion Rate (d^{-1})
Bottom feeding invertebrate	0.014	0.003
Filter feeding invertebrate	0.014	0.052
Mountain whitefish	0.003	0.0025
Longnose sucker	0.003	0.025
Northern pike	0.003	0.0075
Brook stickleback	0.003	0.003

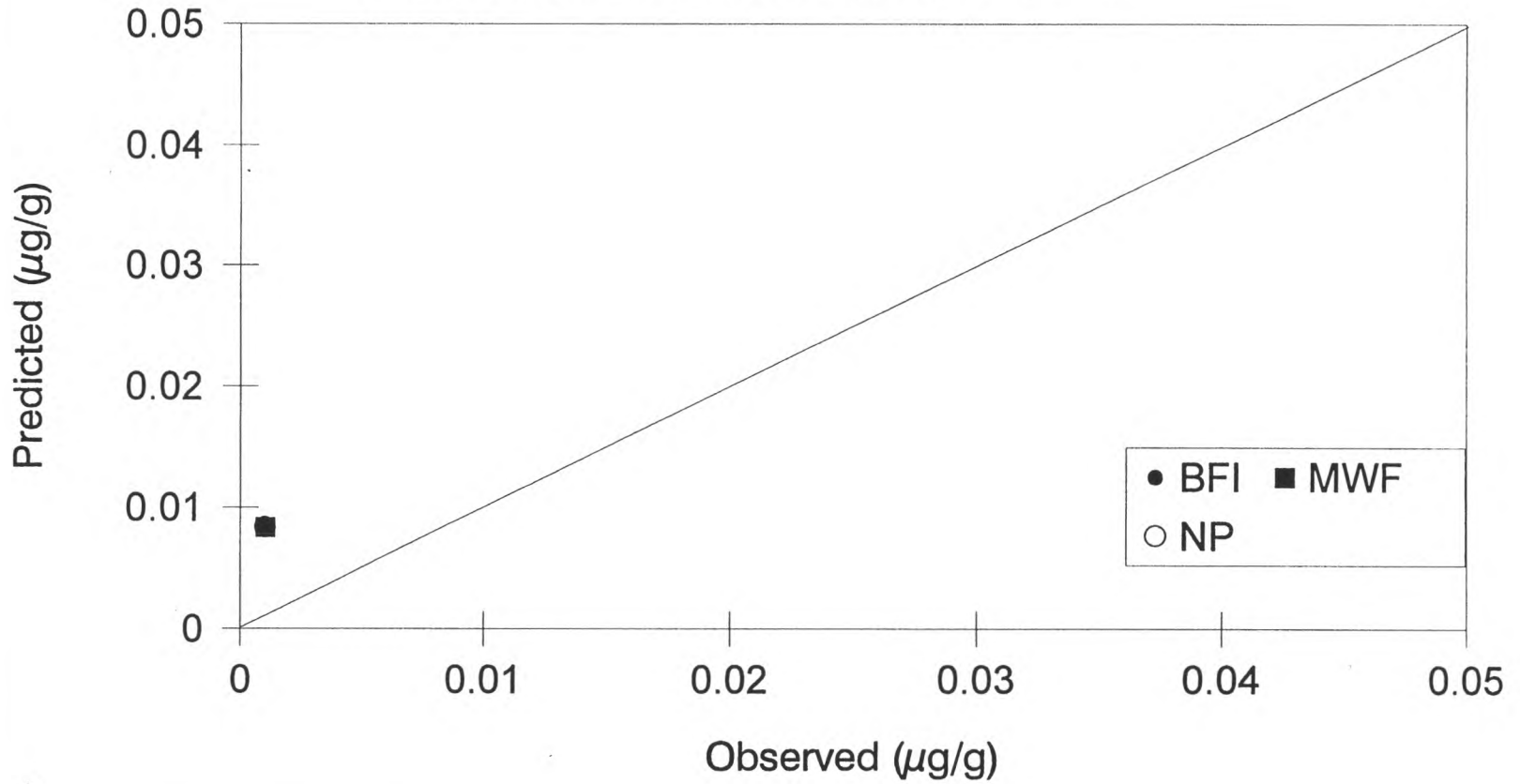
5.2 DHA AND DCDHA

Since no dietary chemical assimilation efficiency data was identified for the resin acids for fish or invertebrate species, a range of E values from 0.001 to 0.25 were tested. The best fit was obtained using an input BCF value of 96 and an E of 0.001 for DHA, and a BCF of 92 and an E of 0.001 for DCDHA. Model results for DHA and DCDHA are compared to the observed concentrations in biota of the Athabasca R. in **Figure 9: Comparison of Observed DHA Concentrations at the**

Windfall Site, Predicted *vs* Observed and **Figure 10: Comparison of Observed DCDHA Concentrations at the Windfall Site, Predicted *vs* Observed**, respectively.

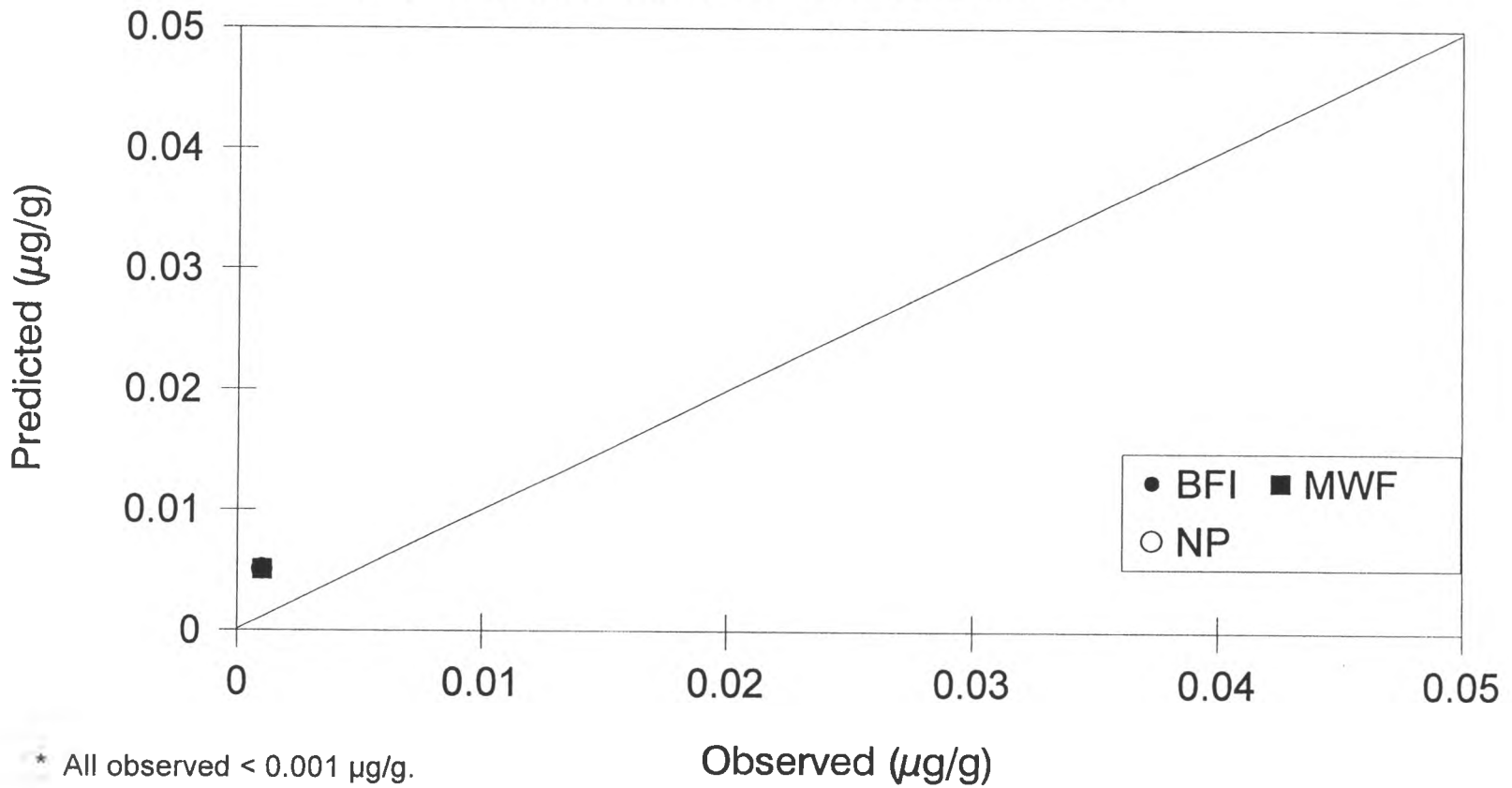
Due to their hydrophobic nature the primary exposure pathway to these resin acids would be through consumption of suspended solids and contaminated prey. However, on the basis of their molecular weights permeability ratios of $>50\%$ were entered into the model, simulating uptake across the gills. A sensitivity analysis of the food chain model to variations in the concentration of DHA and DCDHA to the dissolved concentration in the water column and pore water revealed that for these model parameters direct uptake from water was also a significant pathway (**Figure 11: Influence of Porewater Concentration on Predicted Tissue Concentrations of Dehydroabietic Acid** and **Figure 12: Influence of Porewater Concentration on Predicted Tissue Concentrations of 12, 14-Dichlorodehydroabietic Acid**). Limitations of the monitoring data precluded the value of further sensitivity analysis. Should additional monitoring data be available, with lower detections limits sensitivity analyses to dietary assimilation efficiency, gill permeability ratio, BCF and excretion would be recommended. Predictions of the model would then provide a hypothesis for further research on kinetics of resin acids.

Figure 9 Comparison of Observed DHA Concentrations at the Windfall Site, Predicted *vs* Observed



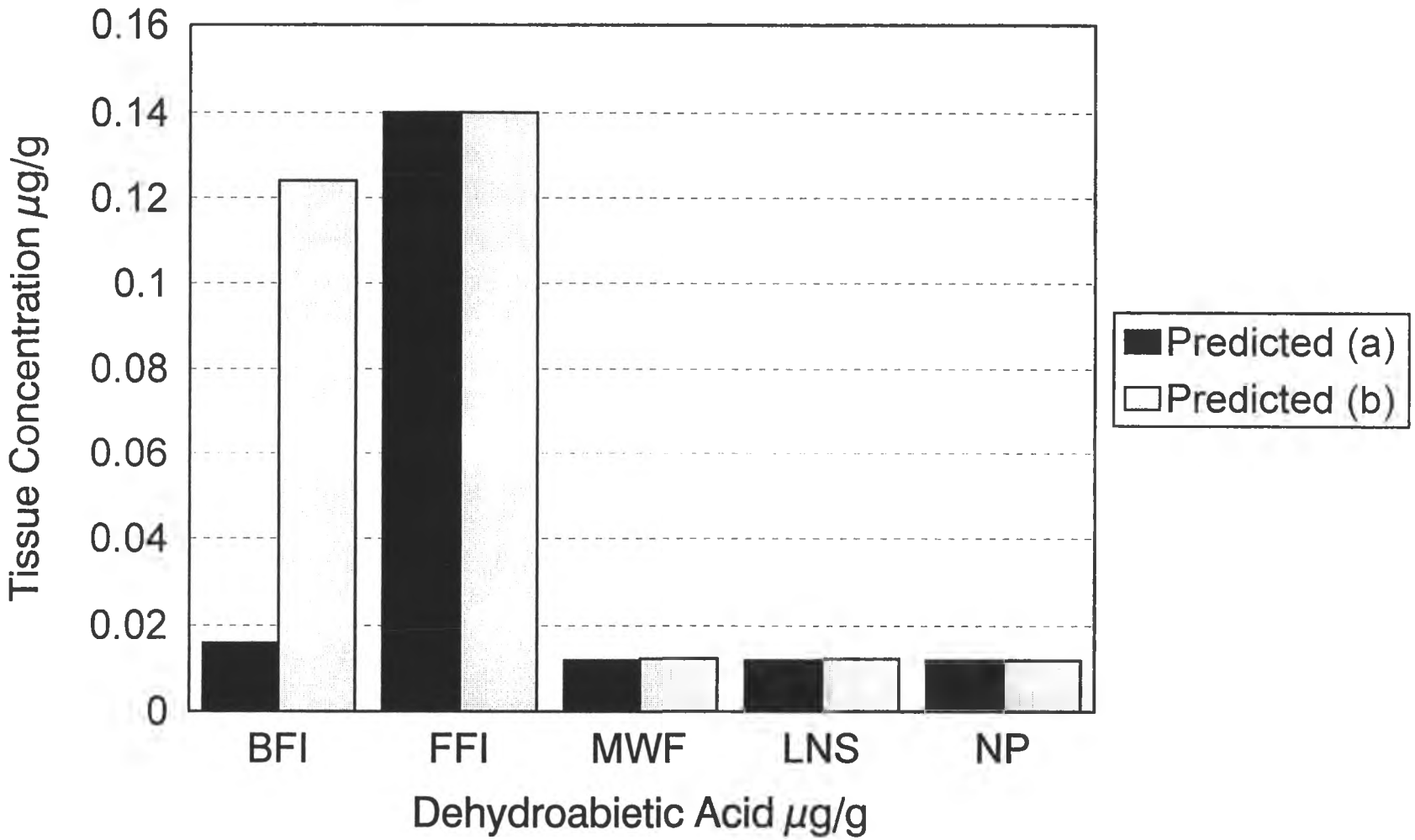
* All observed < 0.001 µg/g.

Figure 10 Comparison of Observed DCDHA Concentrations at the Windfall Site, Predicted *vs* Observed



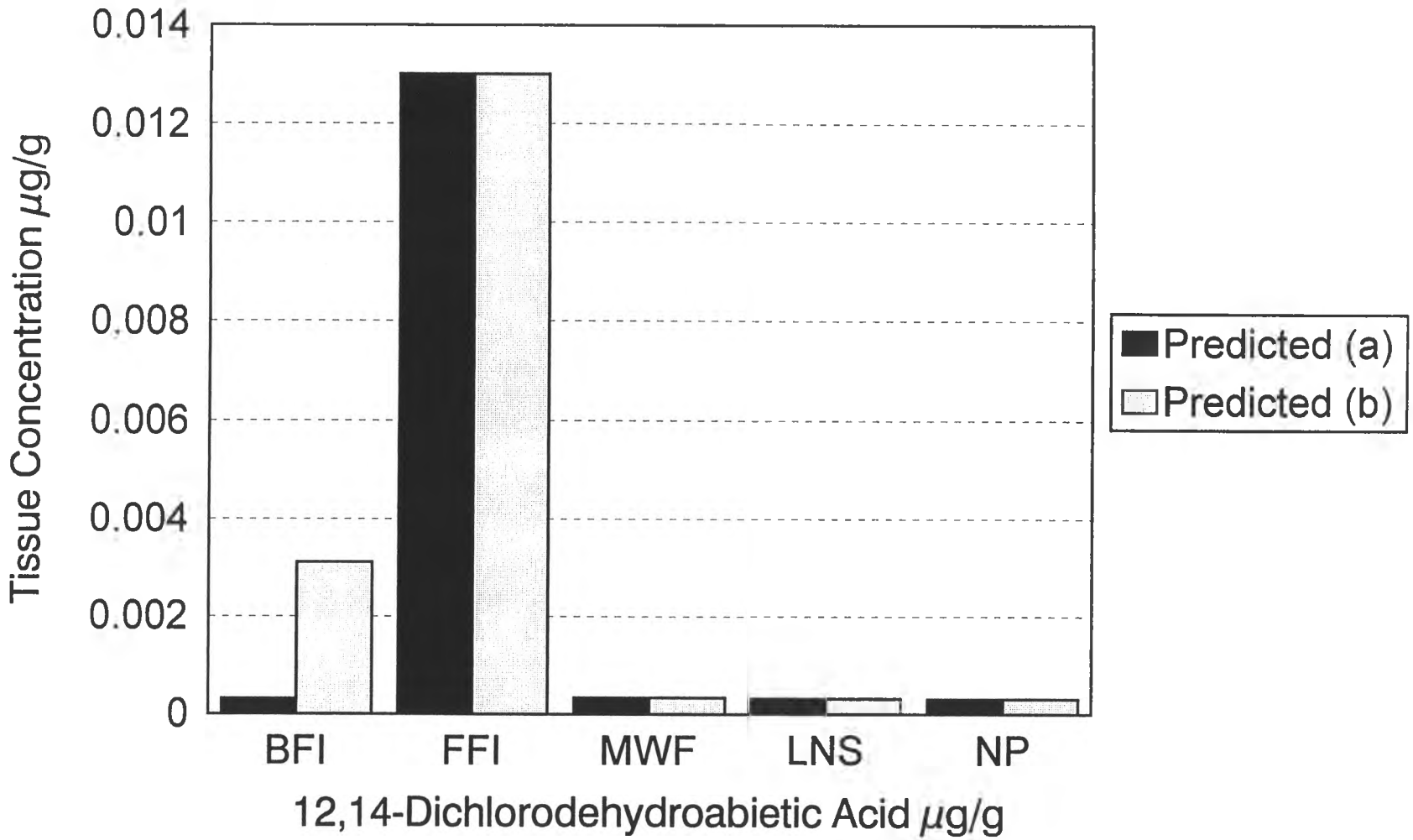
* All observed < 0.001 µg/g.

Figure 11 Influence of Porewater Concentration on Predicted Tissue Concentrations of Dehydroabietic Acid



Predicted (a): Porewater = w.c. dissolved
Predicted (b): Porewater = 10 x w.c. dissolved

Figure 12 Influence of Porewater Concentration on Predicted Tissue Concentrations of 12,14-Dichlorodehydroabietic Acid



Predicted (a): Porewater = w.c. dissolved
Predicted (b): Porewater = 10 x w.c. dissolved

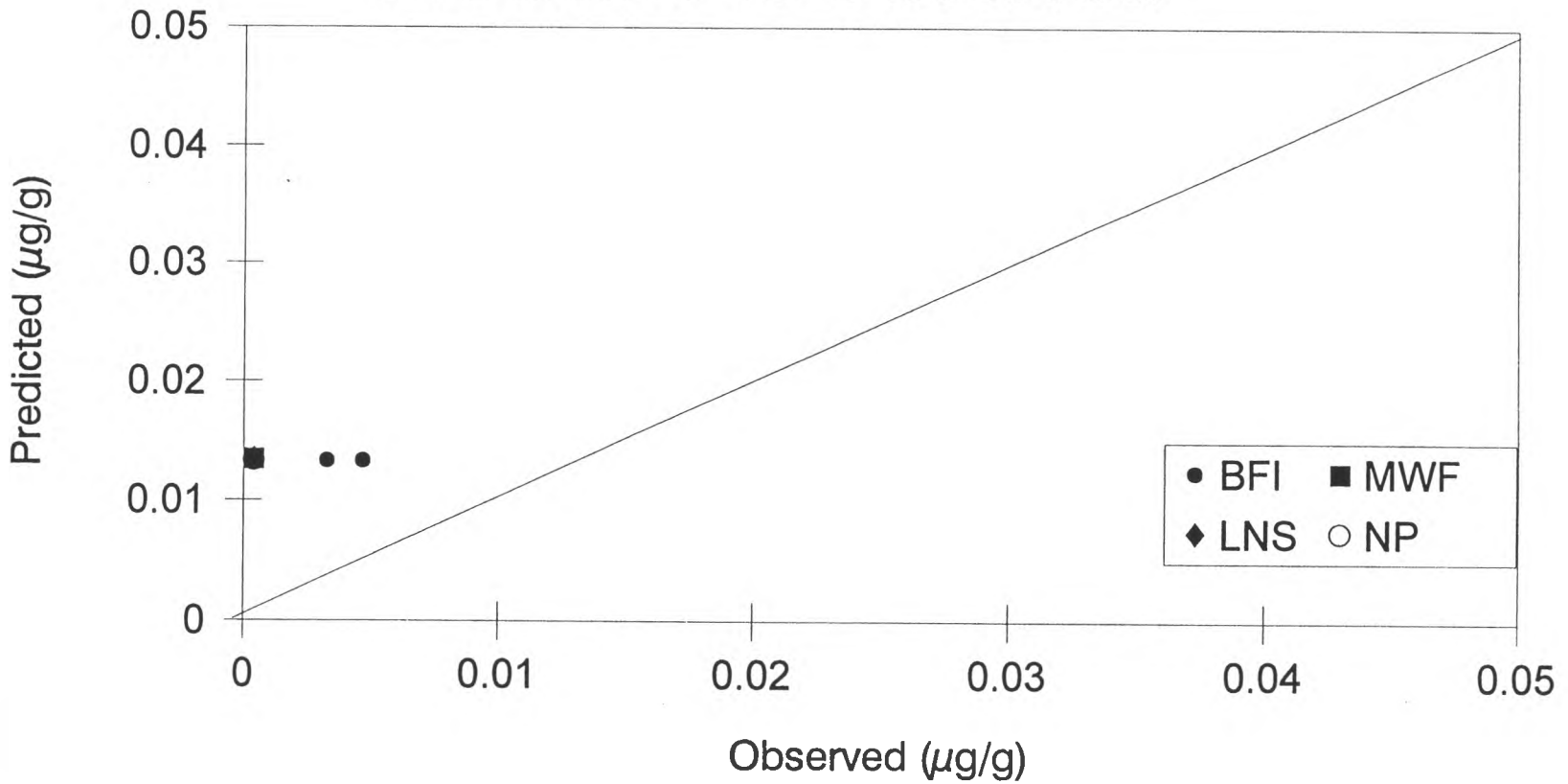
5.3 TCC, TGC, AND TCV

The BCF of 268 input for TCC, TCG and TCV based on a laboratory measured value for TCG is about 2-fold less than that calculated from the % lipid * K_{ow} relationship for the species modelled. This value was input to the model for all fish species. Initially, a BCF of 34 was entered for all invertebrate species; however, this underestimated observed concentrations in invertebrates. Therefore a BCF of 268 was entered for all invertebrate species, as well as fish. This had the effect of increasing the predicted concentrations in BFI and FFI by about 10-fold The results of the model predicted concentrations are presented in **Figure 13: Comparison of TCC Concentrations at the Weldwood Site, Predicted *vs* Observed, Figure 14: Comparison of TCG Concentrations at the Weldwood Site, Predicted *vs* Observed**, and **Figure 15: Comparison of TCV Concentrations at the Weldwood Site, Predicted *vs* Observed**.

Model predicted concentrations in bottom-feeding and filter-feeding invertebrates best matched observed concentrations when a BCF of 268 was used for all species modelled. Predicted concentrations in invertebrates were generally within 2-fold of observed concentrations. However, predicted concentrations of chlorinated phenolics in fish generally overestimated observed concentrations by at least 10-fold (the majority of observed concentrations were non-detectable *i.e.*, < 0.0004 μg/g). With the exception of concentrations of trichloroveratrole in mountain whitefish at Windfall for which predicted concentrations (0.0011 μg/g) equalled observed (0.0012 μg/g).

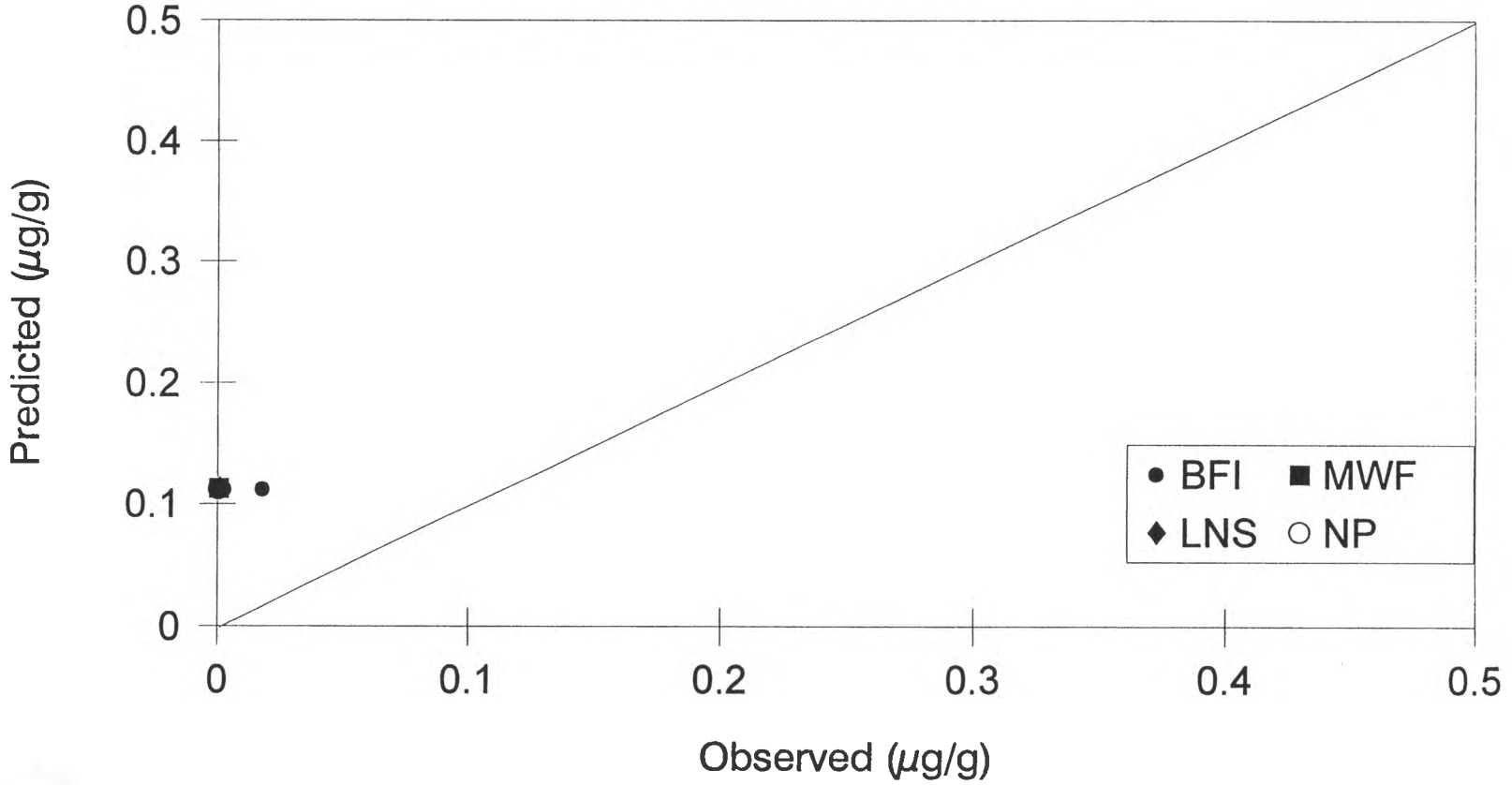
The sensitivity of the model to dissolved concentrations of these chlorinated phenolics in the water column and porewater is presented in **Figure 16: Influence of Porewater Concentrations on Predicted Tissue Concentrations of 3,4,5-Trichlorocatechol, Figure 17: Influence of Porewater Concentrations on Predicted Tissue Concentrations of 3,4,5-Trichloroguaiacol**, and **Figure 18: Influence of Porewater Concentration on Predicted Tissue Concentrations of 3,4,5-Trichloroveratrole**. As would be expected on the basis of their physical-chemical properties, dissolved concentrations in the water column had a significant effect on the predicted tissue concentration. The model supports that the primary exposure pathway for TCC, TCG and TCV is uptake from the water column, as determined from laboratory studies. The critical model input parameters for TCC, TCG and TCV are the gill permeability ratio, the dissolved water concentration, and either the BCF or excretion rate. Dietary uptake and dietary assimilation efficiency of these chemicals had no discernable effect on predicted concentrations in biota. Limitations of the monitoring data precluded further sensitivity analysis, since many of the samples were less than detection limits. Should additional monitoring data become available with lower detection limits a more rigorous sensitivity analysis is recommended for the parameters noted above.

Figure 13 Comparison of TCC Concentrations at the Weldwood Site, Predicted *vs* Observed



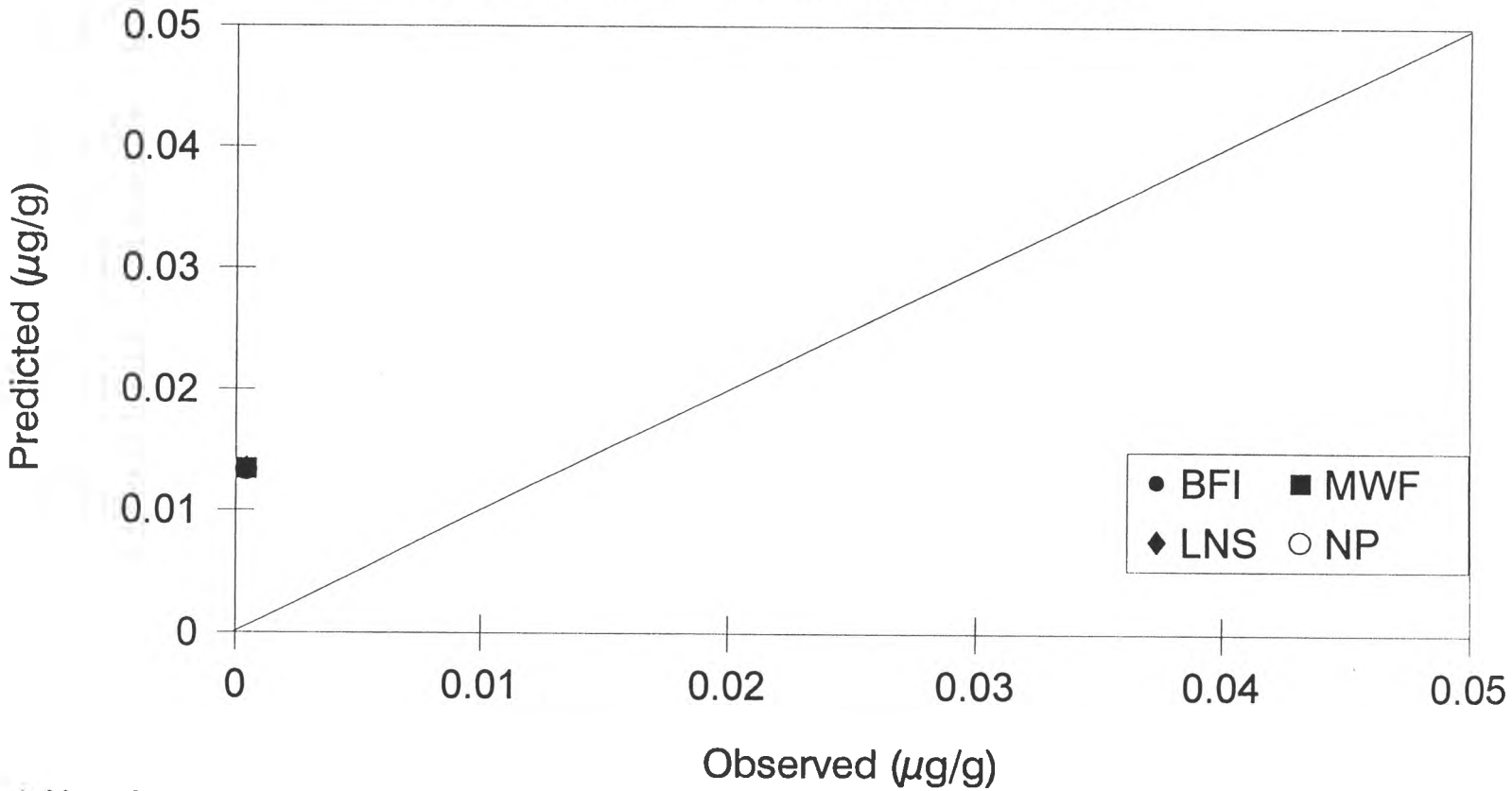
* Mean for all fish < 0.0004 µg/g; except MWF collected at control site and OBED, and NP collected at control site.

Figure 14 Comparison of TCG Concentrations at the Weldwood Site, Predicted *vs* Observed



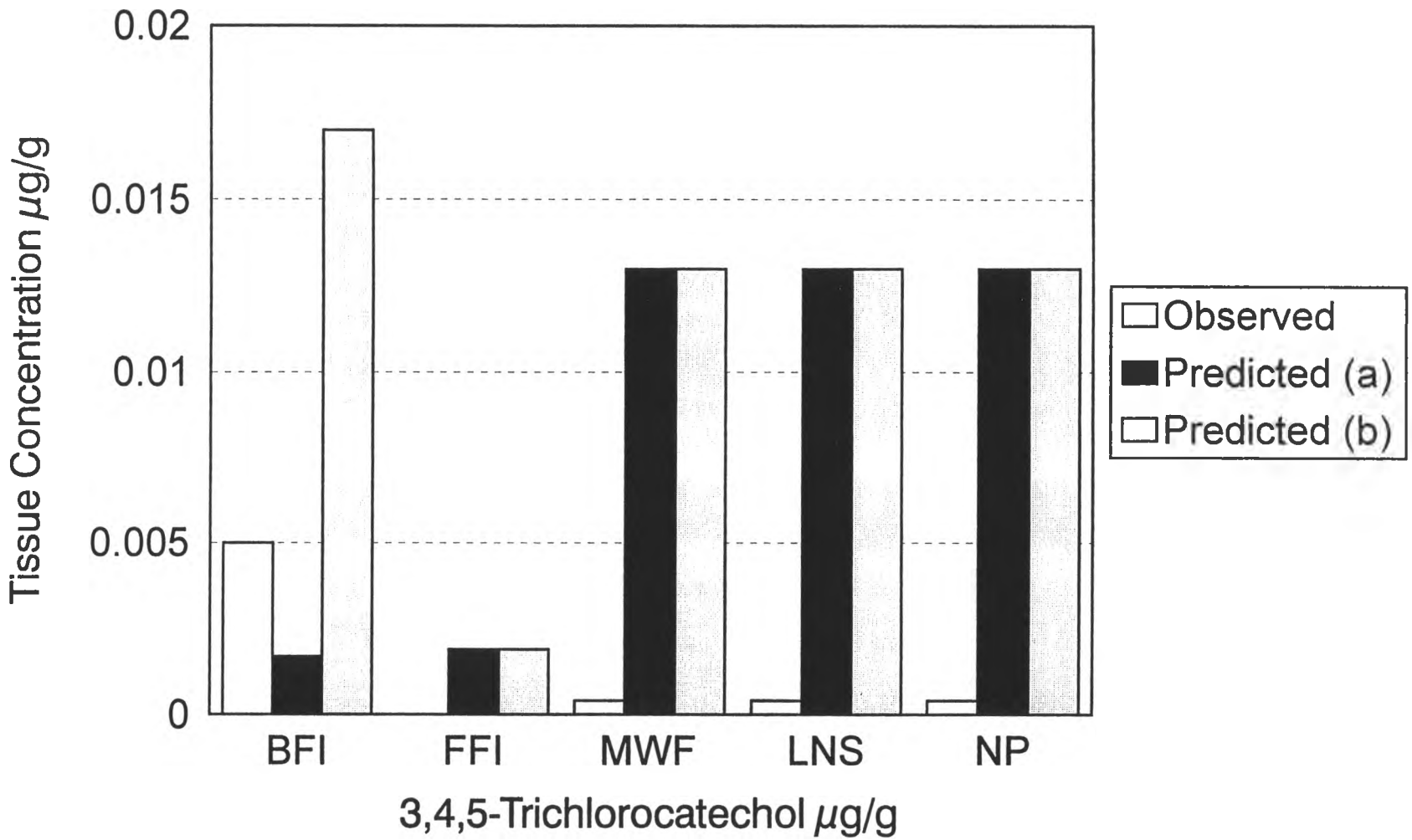
* Mean for all fish < 0.004 µg/g; except MWF collected at OBED.

Figure 15 Comparison of TCV Concentrations at the Weldwood Site, Predicted *vs* Observed



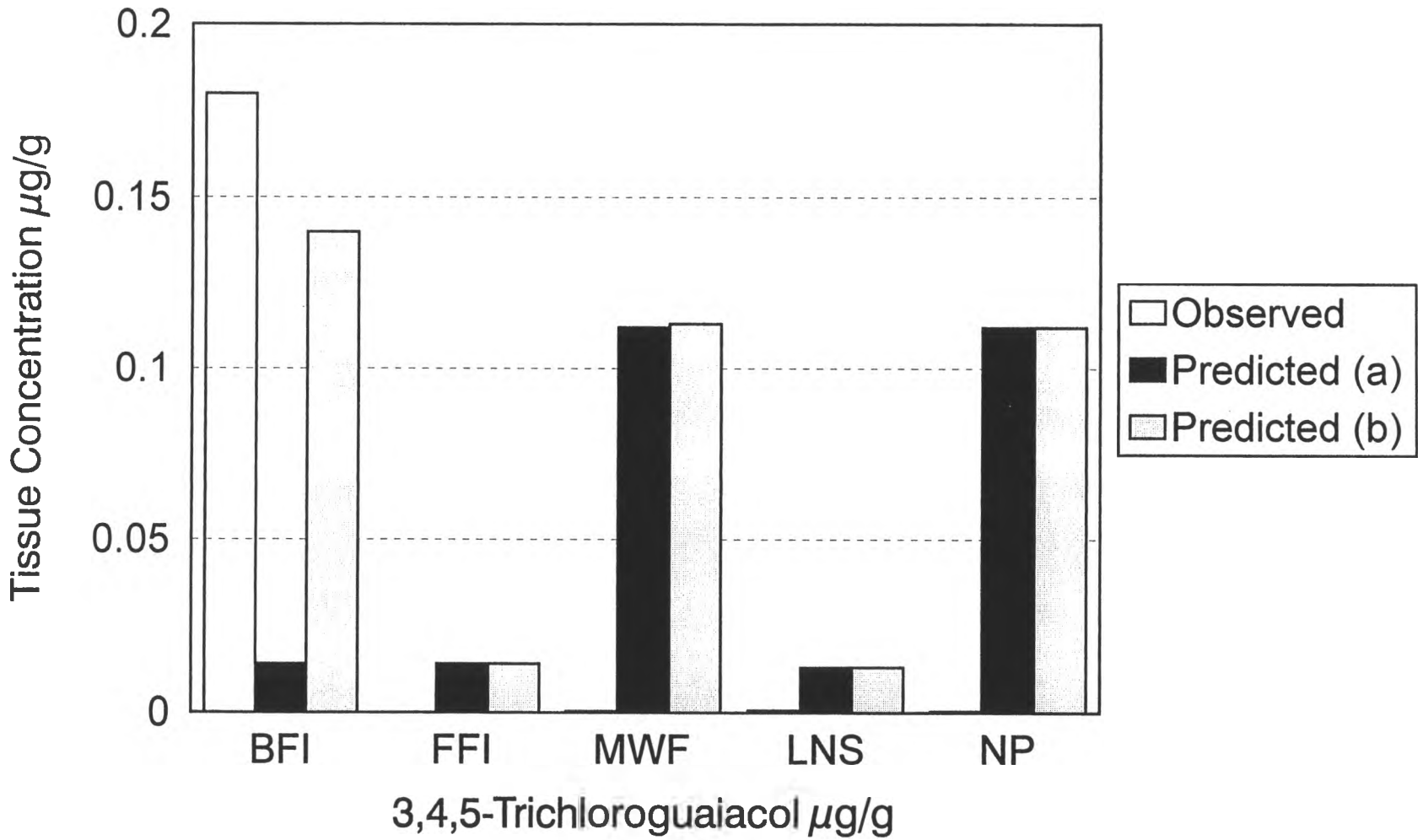
* Mean for all fish < 0.004 µg/g; except MWF collected at OBED and Windfall and NP collected at control site.

Figure 16 Influence of Porewater Concentration on Predicted Tissue Concentrations of 3,4,5-Trichlorocatechol



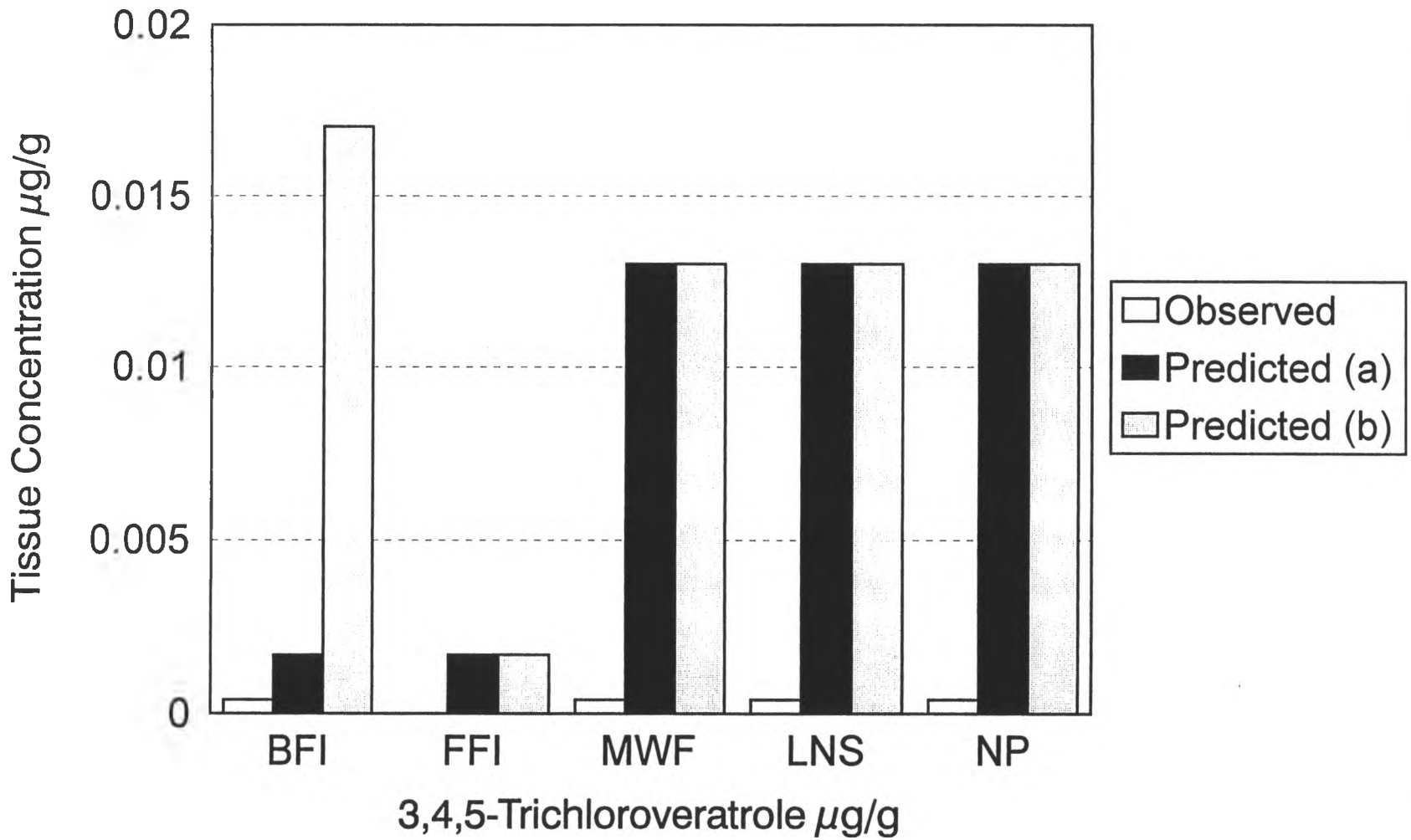
Predicted (a): Porewater = w.c. dissolved
Predicted (b): Porewater = 10 x w.c. dissolved

Figure 17 Influence of Porewater Concentration on Predicted Tissue Concentrations of 3,4,5-Trichloroguaiacol



Predicted (a): Porewater = w.c. dissolved
Predicted (b): Porewater = 10 x w.c. dissolved

Figure 18 Influence of Porewater Concentration on Predicted Tissue Concentrations of 3,4,5-Trichloroveratrole



Predicted (a): Porewater = w.c. dissolved
Predicted (b): Porewater = 10 x w.c. dissolved

6.0 CONCLUSIONS

Differences between predicted and observed concentrations of chemicals in mountain whitefish, longnose sucker, northern pike, bottom-feeding and filter-feeding invertebrates may be related to variability in environmental concentrations. Water column, suspended sediments, depositional sediments and biofilm samples collected in 1992 represent a snapshot analysis of actual environmental concentrations. The Athabasca River is a dynamic system characterized by seasonally variable flowrates and levels of suspended solids, subject to variations in chemical loading rates depending on mill operations. Environmental concentrations of selected chemicals would be expected to mimic these variations resulting in a range in concentrations, both temporally and spatially.

A comparison of TCDF concentrations in abiotic media from various reaches downstream of Weldwood Haul indicates the system is in disequilibrium. Chemical concentrations in biota also exhibit variation among samples collected at one location and among locations, reflecting differences in waterborne, sediment and dietary mediated exposures of fish related to migratory movement and differences in chemical-specific and species-specific rates of metabolism. These factors would result in continually changing tissue concentrations not characteristic of steady-state conditions.

Thus, in the Athabasca R. non-equilibrium conditions would prevail which would explain lower observed tissue concentrations than predicted concentrations assuming steady-state conditions. Therefore, while predicted tissue concentrations tended to be about 3- to 10-fold greater than observed concentrations these results were not unreasonable. Furthermore, from a resource management perspective it is preferable to over-estimate tissue concentrations, within reason, in order to assess potential risks to ecosystem and human health rather than under-estimate tissue concentrations and corresponding health risks.

The bioenergetics Athabasca Food Chain Model was flexible allowing the user to input chemical specific data for a variety of chemicals with different physical-chemical and pharmacokinetic characteristics to predict concentrations in aquatic species. Through the consideration of chemical exposure and accumulation related to respiration, food consumption and excretion, rather than simple lipid-based equilibrium partitioning, the model was able to simulate observed trends in chemical contamination among different fish and invertebrate species.

Specifically, the model predicted concentrations of TCDF in the order of greatest to least for mountain whitefish > longnose sucker > northern pike within 1km downstream of the BKM at Weldwood Haul. The results of the food chain modelling support the theory that preferential consumption of filter-feeding invertebrates feeding on suspended solids represents the primary exposure pathway of mountain whitefish to TCDF. The primary exposure pathway of longnose sucker to TCDF is through the consumption of bottom-feeding invertebrates and detritus (*i.e.*, biofilm and bed sediments).

Food chain model predictions of TCDF concentrations in fish were best achieved when excretion rates and site-specific feeding interactions were considered. To conduct meaningful ecological

assessments of TCDF and presumably other PCDDs/PCDFs, feeding interactions of aquatic species and their predators must be delineated to identify species with the greatest potential for exposure and estimate respective exposures through food chain interactions.

Bioaccumulation models that do not to consider interactions of lower trophic levels with suspended solids and bottom sediments would not adequately simulate the exposure pathways of primary concern for hydrophobic chemicals such as TCDF in aquatic-based ecosystems with high suspended solids concentrations or receiving effluents containing contaminated suspended solids. On the basis of these findings it is likely that a decrease in discharge of suspended solids containing TCDF would result in a measurable decrease in TCDF concentrations in mountain whitefish resident downstream of the BKM outfall.

Less well characterized is the exposure and pharmokinetics of the resin acids, DHA and DCDHA. These chemicals are either less bioavailable for uptake or are metabolized faster than TCDF resulting in smaller BCFs for DHA and DCDHA than TCDF. Exposure to DHA and DCHA was *via* dietary and respiratory pathways. However, given the limitations of the field data (majority of samples were non-detects) and the laboratory data, a 10-fold difference between predicted and observed concentrations was the best achievable fit. Potential improvements to the data set include lower detection limits for DHA and DCDHA and additional laboratory studies of the waterborne, and chemical dietary uptake and excretion of these chemicals in aquatic species.

A paucity of pharmokinetic data was identified for trichlorocatechol, trichloroguiaicol, and trichloroveratrole in aquatic species. These chemicals are water soluble and hence the primary exposure pathway is uptake across the gills. Calculation of chemical uptake from water from the species-specific respiration rate and chemical-specific permeability ratio and subsequent loss due to excretion (calculated from the BCF/K_{ui} , where BCF =268) and growth resulted in good agreement between predicted and observed tissue concentrations of these chlorinated phenolics.

In conclusion the Athabasca River ecosystem bioenergetics-based steady-state food chain model has the predictive capability to simulate chemical uptake and accumulation of a variety of chemicals with a wide range in physical-chemical and pharmokinetic characteristics. The bioenergetic based model is able to simulate multiple exposure pathways simultaneously. Phase II will address the variation in observed tissue concentrations in mountain whitefish, longnose sucker and northern pike through the development of a stochastic version of the bioenergetics model and application of the Monte Carlo based exposure model to simulate the 1992 NRBS data for the Athabasca River.

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APPENDIX A: TERMS OF REFERENCE

Project 2381-D1: Contaminant Fate and Food Chain Model Development and Implementation

A.1 Background and Objectives

One of the major objectives of the Northern River Basins Study (NRBS) is to develop predictive tools to determine the cumulative effects of man-made discharges on the aquatic environment (Study Board Question 13a) and predictive models to provide an ongoing assessment of the state of the aquatic ecosystem (Study Board Question 14). The Contaminants Component of the NRBS assumed the task of modelling the fate, accumulation and effects of contaminants released into the aquatic environment. A modelling sub-committee was formed and, in April 1993, the sub-committee hosted a contaminant fate and food chain modelling workshop (NRBS Projects 2381-C1-C4) to provide direction for future modelling initiatives (Brownlee and Muir 1994). The workshop was attended by government representatives, members of the academic community, environmental consultants, representative from resource-based industries in the northern river basins and NRBS-affiliated research scientists. Based on presentations and discussions at the workshop, the sub-committee decided to utilize the WASP IV model, developed by the U.S. Environmental Protection Agency, and the Thomann/Connolly and Gobas food chain models to model the fate and bioaccumulation of point-source contaminants entering the Athabasca River system.

Late in 1993, a consultant was selected to review existing Northern River Basins Study data and to meet with the modelling sub-committee to develop a strategy for modelling the fate and bioaccumulation of specific organic compounds associated with point source releases during fiscal 1994/95 (Project 2381-C6). A six point plan was formulated at the meeting for the implementation and development of contaminant fate and food chain modelling for the Athabasca River. The plan calls for the involvement of members of the modelling sub-committee and other NRBS-affiliated research scientists at all decision points related to model development. The plan also calls for the development of user-friendly interfaces for the model so that it can be handed off to NRBS researchers and government agencies for future use.

Contaminant fate and food chain model development is to be based on previous contaminant fate modelling carried out in the Athabasca River Basin (Macdonald and Radermacher 1992) and Wapiti-Smoky rivers (HydroQual 1990). These models will also incorporate historic contaminants data collected by Alberta Environmental Protection, Environment Canada and industry in the Athabasca River and Wapiti-Smoky rivers, and recent data collected by the NRBS. Results from the 1992 and 1993 NRBS Reach Specific Study and the February/March 1993 NRBS/Alberta Environmental Protection winter synoptic survey will be of particular significance for contaminant fate and food chain modelling. The Hydrology/Hydraulics Component of the NRBS will also be supplying the contractor with algorithms for the WASP model that deal with the shear stress and erodibility of flocculated sediments (Project 1332-D1) and will identify sediment depositional areas in the Athabasca River and Wapiti-Smoky rivers.

This project has been established to develop and implement the contaminant fate and food chain modelling of the six-point plan during fiscal 1994/95. The results of the modelling exercise will be used to direct the collection of additional data for model refinement in the last year of the Study. If modelling is successful, it will represent a major initiative to determine the cumulative effects of point source discharges on the aquatic environment of the Northern River Basins.

A.2. General Requirements

The objective of this project is to set-up and calibrate a set of models that will enable the NRBS to describe linkages between contaminant sources and:

1) contaminant exposure concentrations in the water column;
2) contaminant exposure concentrations on suspended sediments;
3) contaminant exposure concentrations in bottom sediments;
4) contaminant tissue concentrations in biofilm;
5) contaminant tissue concentrations in invertebrates; and
6) contaminant tissue concentrations in fish.

All available, relevant information collected by the NRBS, Alberta Environmental Protection, Environment Canada and industry sources within the basins are to be used in the development of the models. The models are to be developed in association with NRBS scientists who will assist in defining pathways, reviewing and compiling data and who will be the end users of the model. All aspects of the calibrations are to be open to external scientific review. Results of the review may be used to focus future modelling activities.

Contaminant fate and food chain modelling is to consider (1) the Athabasca River, from Hinton to, but not including, the Peace-Athabasca Delta, and (2) the Wapiti and Smoky rivers from Grande Prairie to the confluence with the Peace River.

A.3 Specific Requirements

A.3.1 Task 1 - Information Review and Compilation

This task is to develop the information base required for the model calibration and will include the following:

1) Dr. Brian Brownlee will lead the review of the Northern River Basins Study data and will supply an electronically compiled dataset, including sample date, location (in UTMs), and medium sampled, in addition to the chemical, physical or biological values measured for each sample. The specific data formats will be determined by the contractor in consultation with Dr. Brownlee. Particular emphasis will be placed on Reach Specific Survey data collected by the NRBS for the Athabasca River. Included in the review/compilation will be all source data (effluent) collected and/or compiled by Alberta Environmental Protection (including the winter synoptic surveys)

and identified in the NORTHDAT database (McCubbin 1993), and municipal and non-pulp mill industry database (Project 2112-B1/C1) prepared for the NRBS. The contractor should be aware that the McCubbin database on pulp mill effluents is currently being updated with data to December 1993 and with all historic data before 1990. This information will be provided to the contractor when available (probably August/September 1994). All data collected or compiled by the NRBS will be supplied to the contractor by the Study Office.

2) As appropriate, the contractor will review and synthesize multi-media chemical data prepared by industries located on the Athabasca River and the Wapiti-Smoky rivers. In particular, Alberta Pacific and Weyerhaeuser have receiving environment data that is to be reviewed with the intent of incorporating it into the fate models. **However, before they can be used all industry data sets must be reviewed by the modelling sub-committee and/or NRBS affiliated scientists to determine the validity of the data.**

A.3.2 Task 2 - Model Configuration

1) If necessary, modify the reach structure of the existing WASP configuration (Macdonald and Radermacher 1992) to ensure comparability with chemical monitoring data.

2) Set-up the models to simulate river hydrology for 1992 and 1993 as a daily time-series using Water Survey of Canada stream gauge data and, where relevant, Alberta Environmental Protection, Hydrology Branch data.

3) Confirm the mass balance calibration of the models using conservative parameters such as sodium, chloride and zinc derived from water column and effluent monitoring data from Alberta Environmental Protection and summarized in NORTHDAT.

4) Calibrate water column concentrations of TSS using Alberta Environmental Protection and NORTHDAT data. The objective of the calibration will be to create a reasonably accurate time-series of water column TSS concentrations as well as sediment loss to and gain from the river bottom.

5) The proposed equations governing contaminant processes intended for exposure modelling are also to be defined so as to enable review by the modelling sub-committee and other scientists affiliated with the Northern River Basins Study.

6) Define the critical receptors and predator-prey relationships. Based on the information reviewed and compiled in Task 1 for the reaches, respective environmental concentrations and the representative food chain to be modelled will be coordinated by Derek Muir in consultation with CanTox and other NRBS Groups. For this study the food chain will be modelled for steady-state species, and will be

restricted to four (4) trophic levels and no more than three (3) species of fish. CanTox will prepare an initial list of information requirements and will specify the format of the data required for input to the models. Derek Muir will ensure that the data are provide to CanTox in the required format.

A.3.3 Task 3 - Rate Coefficient Compilation

Compile a table of published physical and chemical rate coefficients and constants for use in the WASP IV and food chain models. Necessary coefficients and constants will depend on the definition for the controlling processes identified under Task 2. The contractor and CanTox will begin the task by compiling a list of coefficient and constant information requirements from in-office available sources (CanTox for the food chain models and Golder for the WASP model). Upon completion, the tables will be circulated to Dr. Brian Brownlee, Dr. Derek Muir and any other scientist who may have information in their personal library and that they would be willing to contribute. All values added to the tables must include a valid reference. The end objective will be to describe each rate constant as a range and a most probable value. Final coefficient selection and editing of the tables will be directed by Dr. Brian Brownlee.

A.3.4 Task 4 - Simulation and Calibration of Contaminant Fate

1) Using only effluent and background concentration data, the calibrated physical model structure defined in Task 2, and the most probable rate coefficients and constants defined in Task 3, run WASP IV to simulate contaminant concentrations in the water column (dissolved and associated with particulates), and in the sediments. The contaminants to be modelled include:

   i) 2,3,7,8-tetrachlorodibenzofuran (2378 TCDF);
   ii) dehydroabietic acid (DHA);
   iii) chlorinated dehydroabietic acid (12/14-monochloro and/or 12, 14-dichloro);
   iv) phenanthrene;
   v) 3,4,5-tetrachlorocatechol (345TCC);
   vi) 3,4,5-tetrachloroguaiacol (345TCG); and
   vii) 3,4,5-tetrachloroveratole (345TCV).

2) Graphically compare these results to measured concentrations (as outlined under Task 1). This information will be circulated to the modelling sub-committee and CanTox as preliminary results.

3) Based upon the results from 4b, above, proceed to make modifications to the modelling assumptions if a better match between observed and simulated conditions is required. All modifications will be recorded along with the rationale for the changes. Results for the "best" calibration as compared with observed will then be graphed and circulated for review with the modelling sub-committee and CanTox.

4) CanTox will conduct an initial simulation of the food chain using the feeding structure and biological information determined in Task 2, and the constants and coefficients determined in Task 3. The first model simulations will be based upon the most probable coefficients derived in Task 3 and the field measured chemical-specific dissolved concentration in the water column (Task 1). Simulation results will then be graphically compared with field measured tissue concentrations from Task 1; results will be circulated within the modelling sub-committee. In the event that data are lacking for certain chemical-specific parameters, the comparison of model predictions with field measured data will be used to determine the most representative values.

   CanTox will run both the Thomann and Connolly model, and Gobas model simultaneously. This will determine whether there are any significant differences between the models, and will link these observations with the data requirements and theory of the two models.

5) The contractor will provide CanTox with model output from the best calibration of the exposure models (WASP) (Task 4c) for input into the best calibration of the food chain models (Task 4d). Results from both the contaminant fate models and food chain models will be integrated and presented graphically against measured concentrations in all mediums. By way of comparison, CanTox will also run Frank Gobas' food chain model for both the Athabasca and Wapiti-Smoky river systems. Results from the two river systems will be graphically compared and circulated to members of the modelling sub-committee for review.

6) Sensitivity analysis is to be carried out on the final configuration of the models to identify key process rates.

A.3.5 Task 5 - Technical Review Meeting

The contractor, in conjunction with CanTox and members of the modelling sub-committee, will identify and contact a few key individuals, external to the NRBS, who may be willing to provide expert review of the modelling efforts. Once confirmed, these external reviewers will be sent copies of the Task 4 document for review. They will also be requested to attend a two-day review meeting in late January 1994 where the modelling will be critically reviewed, alternative calibrations tested using the models in real-time, and details regarding potential improvements to the model and the information base discussed. Prior to the meeting, external reviewers will be asked to provide the contractor, CanTox and the modelling sub-committee with review comments. At the meeting, external reviewers will be asked to make a brief presentation which is to include direction for future model development. Costs for external reviewers and meeting facilities are not included in this contract.

A.3.6 Task 6 - User Interface and User Training

1) The contractor will expand upon the WASP interface currently being developed for Alberta Environmental Protection, to accommodate the Athabasca River configuration and the needs of the NRBS. This is to include the ability of the models to:

   i) handle time series data;
   ii) change key input values, such as source rates, rate coefficients, etc.;
   iii) graphically compare model results to measured values;
   iv) provide easy output of results for use in the food chain models.

2) The contractor, in association with CanTox Inc. will provide a two-day user training course for key NRBS scientists. The focus of the course will be using the calibrated models to predict chemical concentrations in all mediums (water, sediment, biota).

A.4 Reporting Requirements

A.4.1 General

1) The Contractor is to provide draft and final reports in the style and format outlined in the NRBS document, "A Guide for the Preparation of Reports," which will be supplied upon execution of the contract.

   The final report is to include the following: an acknowledgement section that indicates any local involvement in the project, Report Summary, Table of Contents, List of Tables, List of Figures and an Appendix with the Terms of Reference for this project.

   Text for the report should be set up in the following format:

   i) Times Roman 12 point (Pro) or Times New Roman (WPWIN60) font.
   ii) Margins; are 1" at top and bottom, 7/8" on left and right.
   iii) Headings; in the report body are labelled with hierarchical decimal Arabic numbers.
   iv) Text; is presented with full justification; that is, the text aligns on both left and right margins.
   v) Page numbers; are Arabic numerals for the body of the report, centred at the bottom of each page and bold.

   - If photographs are to be included in the report text they should be high contrast black and white.
   - All tables and figures in the report should be clearly reproducible by a black and white photocopier.
   - Along with copies of the final report, the Contractor is to supply an electronic

version of the report in Word Perfect 5.1 or Word Perfect for Windows Version 6.0 format.

Electronic copies of tables, figures and data appendices in the report are also to be submitted to the Project Liaison Officer along with the final report. These should be submitted in a spreadsheet (Quattro Pro preferred, but also Excel or Lotus) or database (dBase IV) format. Where appropriate, data in tables, figures and appendices should be geo-referenced.

2) All figures and maps are to be delivered in both hard copy (paper) and digital formats. Acceptable formats include: DXF, uncompressed EØØ, VEC/VEH, Atlas and ISIF. All digital maps must be properly geo-referenced.

3) All sampling locations presented in report and electronic format should be geo-referenced. This is to include decimal latitudes and longitudes (to six decimal places) and UTM coordinates. The first field for decimal latitudes / longitudes should be latitudes (10 spaces wide). The second field should be longitude (11 spaces wide).

4) Six to ten 35 mm slides that can be used at public meetings to summarize the project, methods and key findings. The package of slides is to be comprised of one original and four duplicates of each slide.

A.4.1.1 Task 1 - Information Review and Compilation

Prepare a summary report indicating locations, mediums, chemical parameters, ranges of values, number of samples, etc. of the chemical information to be used for the modelling. This report is to be completed and submitted to the component coordinator by September 30, 1994.

A.4.1.2 Task 2 - Model Configuration

A summary report describing the work done under Task 2 is to be prepared and submitted to the component coordinator by October 30, 1994. The summary report is to include:

1) an outline of the reach structure to be used in the WASP IV models, including the rationale for selecting each reach in the Athabasca River and Wapiti-Smoky rivers;
2) a graphical representation of daily time-series hydrology for selected reaches of the Athabasca River and Wapiti-Smoky rivers for 1992 and 1993;
3) a discussion, and, as appropriate, graphical presentation confirming the mass balance of each model using sodium, chloride and zinc in the water column and effluent as derived from existing water quality data;
4) a discussion, and, as appropriate, graphical presentation of attempts to calibrate water column concentrations of TSS using existing water quality data; and
5) tables outlining the proposed equations governing contaminant processes intended for use in the WASP IV models.
6) description of the defined aquatic food chain for the Athabasca and Wapiti River.

The report will also provide estimates of the percent time each species spends in each river reach, as well as the rationale behind each of the estimates.

A.4.1.3 Task 3 - Rate Coefficient Compilation

Compile tables of published physical and chemical rate coefficients and constants for use in each of the WASP IV model, Thomann/Connolly food chain model, and the Gobas food chain model. These tables are to be submitted to the component coordinator by September 15, 1994.

A.4.1.4 Task 4 - Simulation and Calibration of Contaminant Fate

In coordination with CanTox, prepare and submit a draft report detailing the results, methods, data sources, assumptions and modifications made to the WASP and Food Chain Modelling calibrations (Tasks 1-4 inclusive). The report is to be submitted to the component coordinator by January 15, 1994.

A.4.1.5 Task 5 - Technical Review Meeting

In conjunction with CanTox., the contractor is to prepare a workshop proceedings document incorporating reviewer comments and meeting conclusions. A draft of the workshop proceedings is to be submitted to the component coordinator by February 20, 1994. Three weeks after the receipt of review comments on the draft workshop proceedings, the contractor is to submit ten (10) cerlox bound copies, two unbound, camera ready copies and an electronic copy (in Word Perfect 6.0 format) to the component coordinator. The style and format of the final report is to follow that outlined in the NRBS style manual. A copy of the NRBS style manual will be supplied to the contractor by the NRBS.

A.4.1.6 Task 6 - User Interface and User Training

In conjunction with CanTox., the contractor is to prepare an electronic interface program for the WASP model. The contractor is also to prepare written instructions on how to install the WASP program and models on personal computers, and comprehensive WASP and food chain model users manuals. This material is to be submitted to the component coordinator by February 28, 1995.

Final Project Report

In conjunction with CanTox Inc., the contractor is to prepare a final project report outlining the work carried out under Tasks 1-4 and making reference to the work and documents and computer programs prepared under Task 5 and 6. Ten cerlox bound copies of the draft project report are to be submitted to the component coordinator by March 31, 1995. Three weeks after receipt of review comments, the contractor is to submit ten cerlox bound copies, two unbound camera ready copies and an electronic copy (in Word Perfect 6.0 format) of the final project report to the component coordinator. The style and format of the final project report are to conform to that outlined in the NRBS style manual.

A.5 Deliverables

The following is a summary of the deliverables to be submitted to the Study Office in accordance with the requirements and dates specified in section IV above.

1) A summary report of the chemical information base to be used for the modelling.
2) A summary report describing the contaminant fate and food chain model configurations.
3) Tables of published rate coefficients and constants to be used in each model.
4) A draft report detailing the simulations and calibrations of the WASP IV and Food Chain models.
5) A workshop proceedings document resulting from the technical review meeting.
6) An electronic interface program for the WASP model, and installation instructions and users manuals for the WASP and Food Chain models.
7) A final project report.
8) A package of 35 mm slides (originals plus four duplicate copies) for presentations.

A.6 Contract Administration

This project is being coordinated by the modelling sub-committee of the Contaminants Component of the Northern River Basins Study. The Scientific Authorities for this project are:

Dr. Brian Brownlee
National Water Research Institute
867 Lakeshore Road,
P.O. Box 5050
Burlington, Ontario
L7R 4A6
phone: (905) 336-4706
fax: (905) 336-4972.

Questions of a scientific nature related to the contaminant fate model should be directed to him.

Dr. Derek Muir
Fisheries and Oceans Canada
Fresh Water Institute
501 University Crescent
Winnipeg, Manitoba
R3T 2N6
phone: (204) 983-5168
fax: (204) 984-2403

Questions of a scientific nature related to the food chain model should be directed to him.

Members of the modelling sub-committee include:

Dr. Brian Brownlee, National Water Research Institute, Burlington - Contaminant fate
Dr. Anne-Marie Anderson, Alberta Environmental Protection, Edmonton - Benthos
Bob Crosley, Environment Canada, Calgary - Water and sediment
Dr. Mike MacKinnon, Syncrude Research, Edmonton - Oil sands
Dr. Derek Muir, Fisheries and Oceans Canada, Winnipeg - Food chain
Leigh Noton, Alberta Environmental Protection, Edmonton - Pulp mills

They will have direct input with the contractor in the development of the model. The leaders of other Northern River Basins Study components will also have direct input into the development of the model. These include: Dr. Terry Prowse - Hydrology/Hydraulics Component; Dr. Patricia Chambers - Nutrients Component; Mr. Tom Mill - Food Chain Component (interim leader, with Dr. Ray Hesslein as Scientific Advisor).

The Component Coordinator for this project is:

Richard Chabaylo
Northern River Basins Study
690 Standard Life Centre
10405 Jasper Avenue
Edmonton, Alberta
T5J 3M4
phone: (403) 427-1742
fax: (403) 422-3055

Questions of an administrative nature should be directed to him.

A.7 Literature Cited

Brownlee, B. and D. Muir. 1994. Proceedings of the Contaminants Fate and Food Chain Modelling Workshop. Draft report submitted to the Northern River Basins Study.

HydroQual Canada Limited. 1990. Implementation of Water Quality Models for the Wapiti-Smoky and Peace River Systems. Report prepared for Alberta Environment, Standards and Approvals Division, Edmonton.

Macdonald, G. and A. Radermacher. 1992 (May). Athabasca River Water Quality Modelling - 1990 Update. Prepared for: Standards and Approvals Division, Alberta Environment, Edmonton. Prepared by: Environmental Management Associates, Calgary.

McCubbin, N. 1993. NORTHDAT: An Effluent Database Management System, Application Description. Northern River Basins Study Project Report No. 16. Prepared by: N. McCubbin Consultants Inc., Hull, Quebec.

APPENDIX A: TERMS OF REFERENCE

Project 2381-E1: Contaminant Fate Model - Sediment Routine Development

A.1 Background and Objectives

One of the major objectives of the Northern River Basins Study (NRBS) is to develop predictive tools to determine the cumulative effects of man-made discharges on the aquatic environment (Study Board Question 13a) and predictive models to provide an ongoing assessment of the state of the aquatic ecosystem (Study Board Question 14). The Contaminants Component of the NRBS assumed the task of modelling the fate, accumulation and effects of contaminants released into the aquatic environment. A modelling sub-committee was formed and, in April 1993, the sub-committee hosted a contaminant fate and food chain modelling workshop (NRBS Projects 2381-C1-C4) to provide direction for future modelling initiatives (Brownlee and Muir 1994). The workshop was attended by government representatives, members of the academic community, environmental consultants, representative from resource-based industries in the northern river basins and NRBS-affiliated research scientists. Based on presentations and discussions at the workshop, the sub-committee decided to utilize the *WASP IV* model, developed by the U.S. Environmental Protection Agency, and the Thomann/Connolly and Gobas food chain models to model the fate and bioaccumulation of point-source contaminants entering the Athabasca River system.

Contaminant fate and food chain model development is to be based on previous contaminant fate modelling carried out in the Athabasca River Basin (Macdonald and Radermacher 1992) and Wapiti-Smoky rivers (HydroQual 1990). These models will also incorporate historic contaminants data collected by Alberta Environmental Protection, Environment Canada and industry in the Athabasca River and Wapiti-Smoky rivers, and recent data collected by the NRBS. Results from the 1992 and 1993 NRBS Reach Specific Study and the February/March 1993 NRBS/Alberta Environmental Protection winter synoptic survey will be of particular significance for contaminant fate and food chain modelling.

To date, the contractor has completed the following tasks:

1) Information review and compilation - summary report including locations, mediums, chemical parameters, ranges of values, number of samples, etc, of the chemical information to be used in the model;
2) Model configuration - modify reach structure of existing *WASP* configuration, simulate river hydrology, confirm mass balance calibration, calibrate water column concentrations of TSS;
3) Rate coefficient compilation - a table of published physical and chemical rate coefficients and constants for use in the WASP and food chain models;
4) Simulation and calibration of contaminant fate;
5) Technical review meeting - meeting with members of the modelling sub-committee and the Contaminants Component Leader; and
6) User interface and user training.

The existing *WASP IV* requires some adjustments to develop a more appropriate sediment transport routine. *WASP IV* handles sedimentation processes through a net flux. Sediment flows are input as velocities and areas. Sediment velocities are allowed to vary in time and may represent the net settling, sedimentation deposition and scour. Only solids and sorbed chemicals are transported by the *WASP IV* flow fields. Up to three sediment size fractions may be incorporated into the WASP model using all of the three principal constituent solid fields. Using *WASP* to model sediment processes requires formulating the velocity time function for each sedimentation zone in the river, prior to running the *WASP* simulation. However, if the sedimentation is a function of flocculation influenced by effluent concentrations, then the formulation of this pre-processed input deck is a function of the post-processed water column concentrations.

Based on the inadequacy of the *WASP IV* model discussed above, the objective of this project will develop a sediment flux routine and incorporate that routine into the model. The incorporated sediment flux routine will be based on a current study of critical sheer stresses for erosion and deposition of fine sediment (Krishnappan and Stephens 1995). The *WASP IV* model will then be able to calculate automatically the sediment flux velocities based on the input values for river reach hydraulics. The sediment routines will do this by estimating reach averaged shear velocities and predicting settling rates, scour rates and these will then be converted to a net settling velocity for internal use in *WASP IV* by taking into account the flocculation mechanism.

A.2 General Requirements

The contractor will proceed with the sediment development project in three phases, with input from B. Krishnappan, NWRI.

A.2.1 Model Development

1) Development of the empirical/theoretical sedimentation processes will be conducted by B. Krishnappan, based on his work to date (NRBS Project 1332-D1). He will supply the contractor with a sedimentation model suitable for coding into computer programs. This model will be an explicit formulation of mathematical expressions for estimating settling rates, scour rate and flocculation as a function of river shear stress, river sediment composition and effluent quality affecting flocculation.. The basis for estimating the reach averaged river shear stress using available hydraulic information used in *WASP IV* will also be required from B. Krishnappan based on his current knowledge of sedimentation in the Athabasca River and river hydraulics in general.

   Development of new computer codes for sedimentation flux will be developed by the contractor, based on the expressions developed by B. Krishnappan. The new routines will use as input the reach averaged velocity, effluent load, river background sedimentation concentration, and fixed inputs describing the bed slope and roughness which would be required to estimate bed shear stress. These routines will be developed as stand-alone routines for testing and QA/QC. Additionally, the

contractor will include hydraulic calibration of the existing Athabasca River information to estimate reach averaged shear velocities as a function of the flow information available.

2) Incorporate the new sediment routines into *WASP IV* and provide documentation limited to the technical basis and practical use of the new sediment routines. The new sediment velocity calculation routines will be merged into *WASP IV* by intercepting the sedimentation velocity in the appropriate routines. At this point in the *WASP IV* program, either the current time-step or the past time-step contaminant water column and effluent concentration, will be visible and available for use in calculation flocculation processes as specified by B. Krishnappan.

3) Re-simulation of the existing NRBS contaminant fate model for the Athabasca River. The re-simulation will include minor changes to the existing calibration as necessary. The re-simulation will include simulation of suspended solids and each of the chemicals considered in the existing model under the current contract (NRBS #95-F-G-98-3)

A.3 Reporting Requirements

1) Ten bound copies of a Draft Report which incorporates the new sedimentation flux routines into a re-calibrated *WASP IV* contaminant fate model will be submitted to the Component Coordinator, including an electronic disk version, by **October 15, 1995**.

Five copies of the computer software and User's Manual to be distributed as follows:

i) National Water Research Institute - B. Brownlee/B. G. Krishnappan
ii) Freshwater Institute - D. Muir
iii) Alberta Environmental Protection - L. Noton
iv) Environment Canada - R. Crosley
v) Northern River Basins Study

2) Three weeks after receipt of review comments, the contractor is to submit ten cerlox bound copies, two unbound camera ready copies, and an electronic disk version of the final project report to the Component Coordinator.

3) The Contractor is to provide draft and final reports in the style and format outlined in the NRBS document, "A Guide for the Preparation of Reports," which will be supplied upon execution of the contract.

The final report is to include the following: an acknowledgement section that indicates any local involvement in the project, Report Summary, Table of Contents, List of Tables, List of Figures and an Appendix with the Terms of Reference for this project.

Text for the report should be set up in the following format:

i) Times Roman 12 point (Pro) or Times New Roman (WPWIN60) font.
ii) Margins; are 1" at top and bottom, 7/8" on left and right.
iii) Headings; in the report body are labelled with hierarchical decimal Arabic numbers.
iv) Text; is presented with full justification; that is, the text aligns on both left and right margins.
v) Page numbers; are Arabic numerals for the body of the report, centred at the bottom of each page and bold.

- If photographs are to be included in the report text they should be high contrast black and white.
- All tables and figures in the report should be clearly reproducible by a black and white photocopier.
- Along with copies of the final report, the Contractor is to supply an electronic version of the report in Word Perfect 5.1 or Word Perfect for Windows Version 6.0 format.
- Electronic copies of tables, figures and data appendices in the report are also to be submitted to the Project Liaison Officer along with the final report. These should be submitted in a spreadsheet (Quattro Pro preferred, but also Excel or Lotus) or database (dBase IV) format. Where appropriate, data in tables, figures and appendices should be geo-referenced.

4) All figures and maps are to be delivered in both hard copy (paper) and digital formats. Acceptable formats include: DXF, uncompressed E∅∅, VEC/VEH, Atlas and ISIF. All digital maps must be properly geo-referenced.

5) All sampling locations presented in report and electronic format should be geo-referenced. This is to include decimal latitudes and longitudes (to six decimal places) and UTM coordinates. The first field for decimal latitudes / longitudes should be latitudes (10 spaces wide). The second field should be longitude (11 spaces wide).

6) Ten to twenty-five 35 mm slides that can be used at public meetings to summarize the project, methods and key findings. The package of slides is to be comprised of one original and four duplicates of each slide.

A.4 Deliverables

1) A draft report submitted to the Study Office by October 15, 1995.
2) An electronic interface program for the re-simulated and re-calibrated *WASP IV* model, and installation instructions and users manual for the model.
3) A final project report.
4) A package of 35 mm slides (originals plus four duplicate copies) for presentations public presentations .

A.5 Contract Administration

This project is being coordinated by the modelling sub-committee of the Contaminants Component of the Northern River Basins Study (Component Leader - Dr. John Carey, NWRI, Burlington). The Scientific Authority for this project is:

Dr. Brian Brownlee
National Water Research Institute
867 Lakeshore Road,
P.O. Box 5050
Burlington, Ontario
L7R 4A6
phone: (905) 336-4706
fax: (905) 336-4972.

Questions of a technical nature should be directed to him.

Members of the modelling sub-committee include:
Dr. Brian Brownlee, National Water Research Institute, Burlington - Contaminant fate
Dr. Anne-Marie Anderson, Alberta Environmental Protection, Edmonton - Benthos
Bob Crosley, Environment Canada, Calgary - Water and sediment
Dr. Mike MacKinnon, Syncrude Research, Edmonton - Oil sands
Dr. Derek Muir, Fisheries and Oceans Canada, Winnipeg - Food chain
Leigh Noton, Alberta Environmental Protection, Edmonton - Pulp mills

They will have direct input with the contractor in the development of the model. The leaders of other Northern River Basins Study components will also have direct input into the development of the model. These include: Dr. Terry Prowse - Hydrology/Hydraulics Component; Dr. Patricia Chambers - Nutrients Component; Mr. Tom Mill - Food Chain Component.

The Component Coordinator for this project is:

Richard Chabaylo
Northern River Basins Study
690 Standard Life Centre
10405 Jasper Avenue
Edmonton, Alberta
T5J 3M4
phone: (403) 427-1742
fax: (403) 422-3055

Questions of an administrative nature should be directed to him.

A.6 Literature Cited

Brownlee, B. and D. Muir. 1994. Proceedings of the Contaminants Fate and Food Chain Modelling Workshop. Draft report submitted to the Northern River Basins Study.

HydroQual Canada Limited. 1990. Implementation of Water Quality Models for the Wapiti-Smoky and Peace River Systems. Report prepared for Alberta Environment, Standards and Approvals Division, Edmonton.

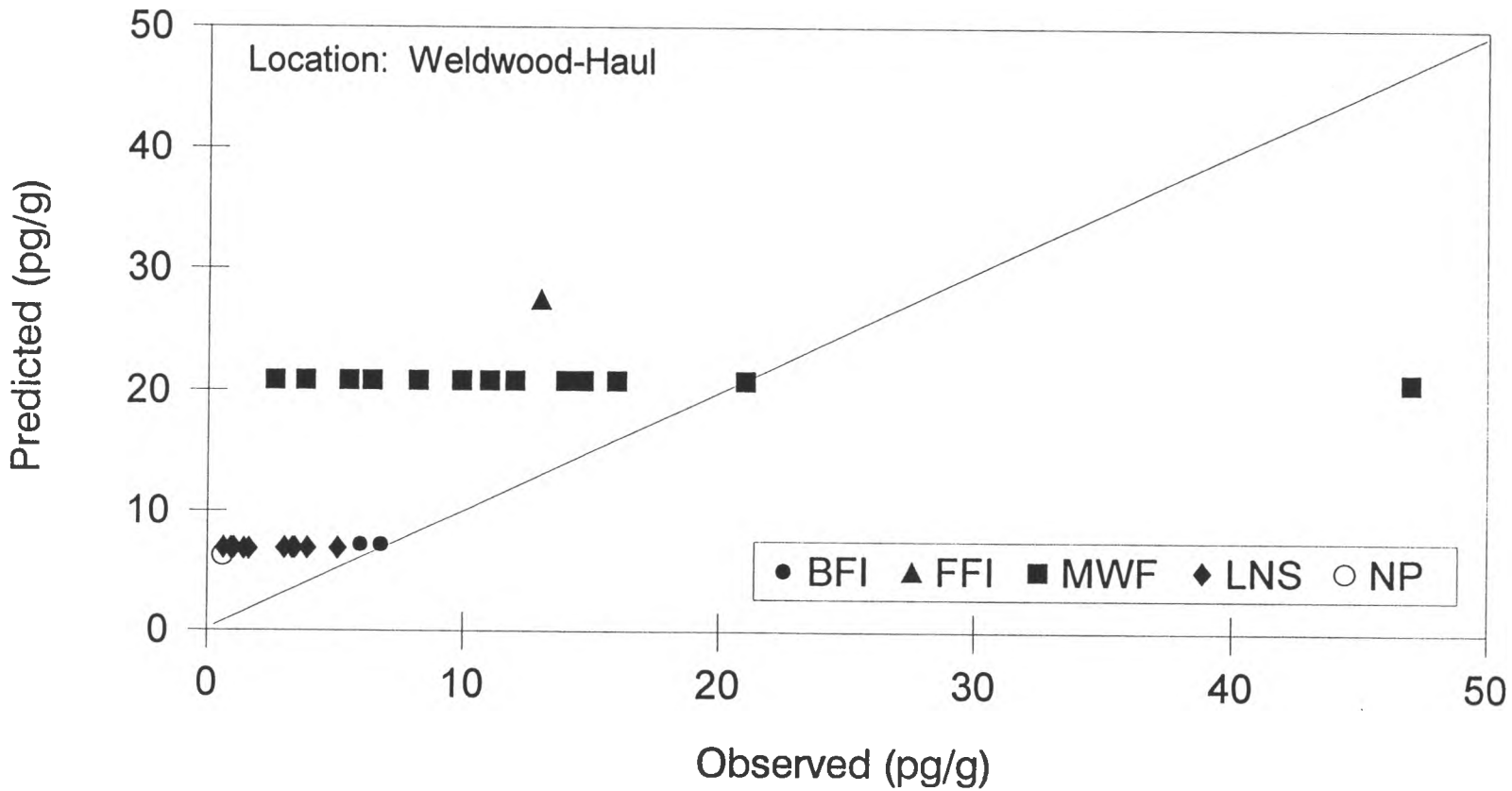
Krishnappan, B.G. and R. Stephens. 1995. Critical sheer stresses for erosion and deposition of fine suspended sediment from the Athabasca River. Draft Report prepared for the Northern River Basins Study, Edmonton. 17 pp.

Macdonald, G. and A. Radermacher. 1992 (May). Athabasca River Water Quality Modelling - 1990 Update. Prepared for: Standards and Approvals Division, Alberta Environment, Edmonton. Prepared by: Environmental Management Associates, Calgary.

MODEL RESULTS - ATHABASCA RIVER PER LOCATION

APPENDIX B

2,3,7,8-TCDF in Biota, Predicted *vs* Observed



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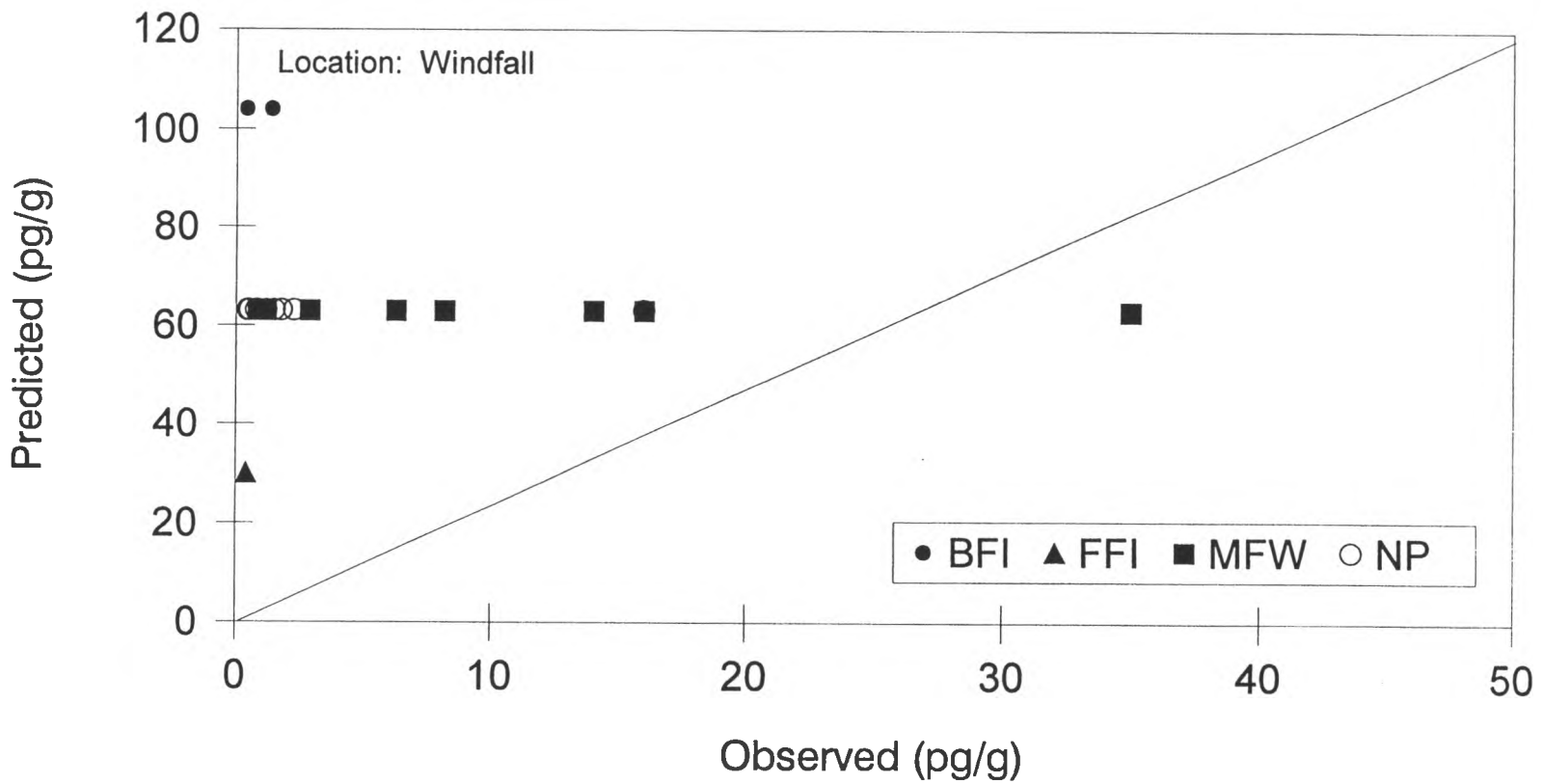

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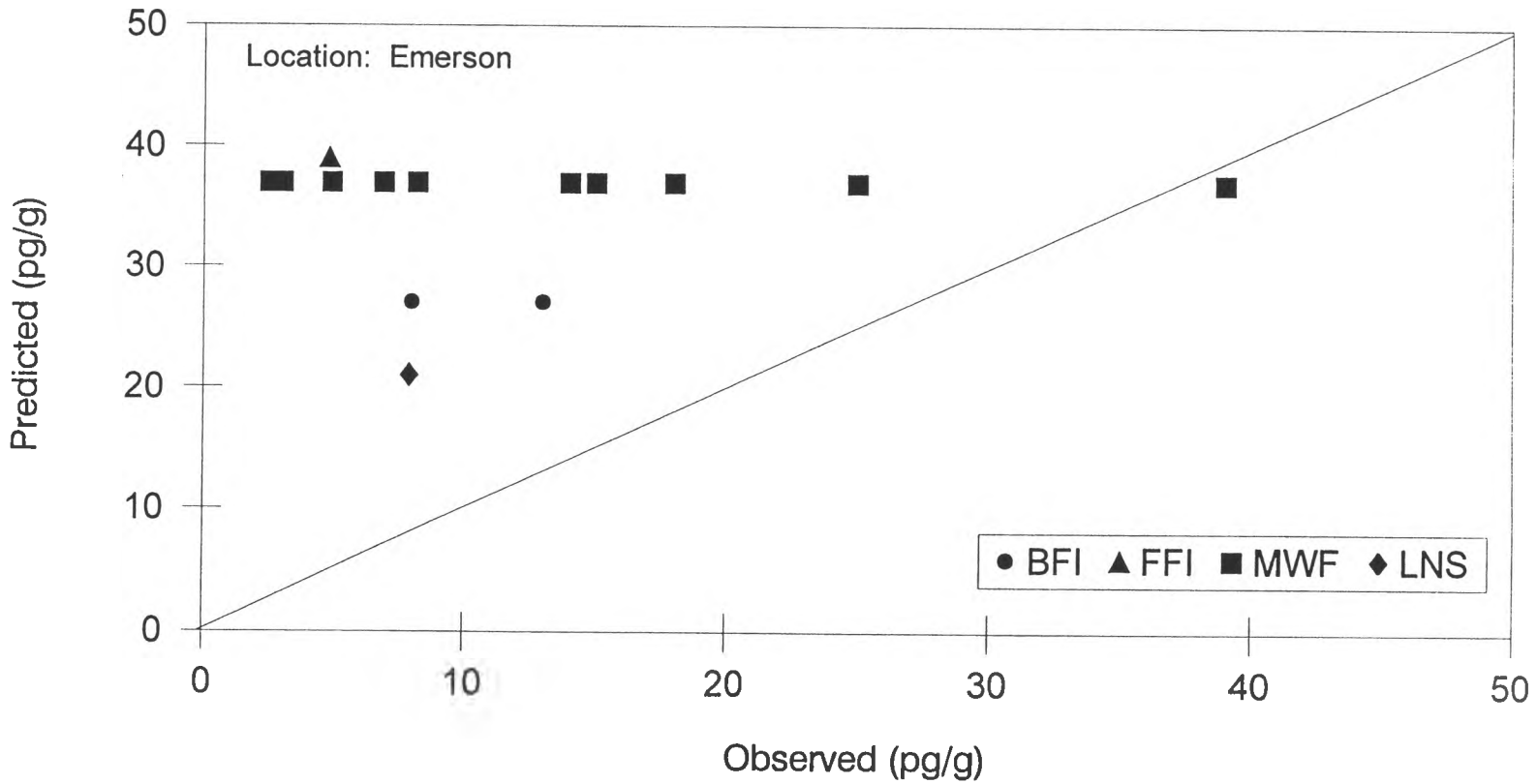

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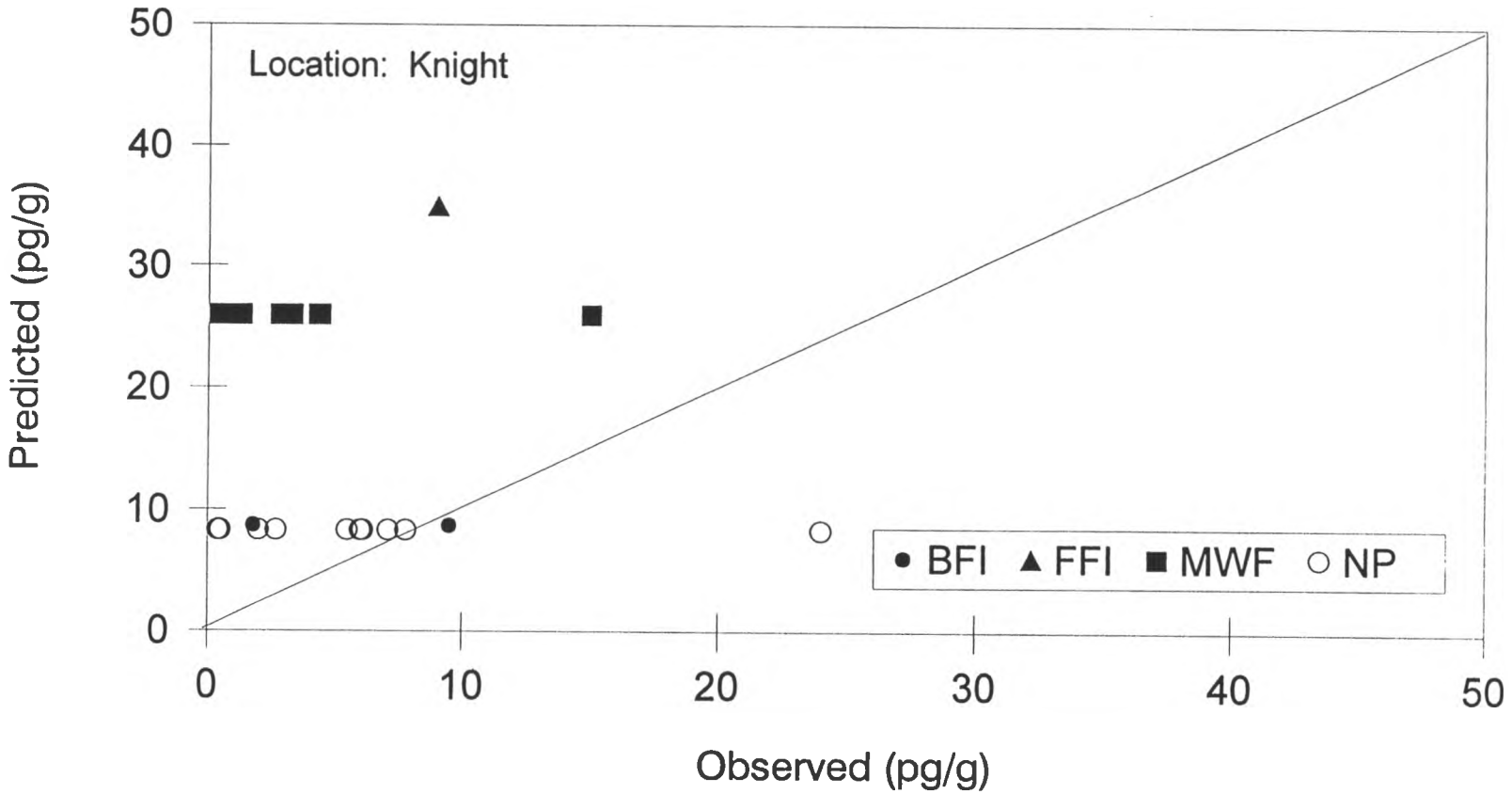

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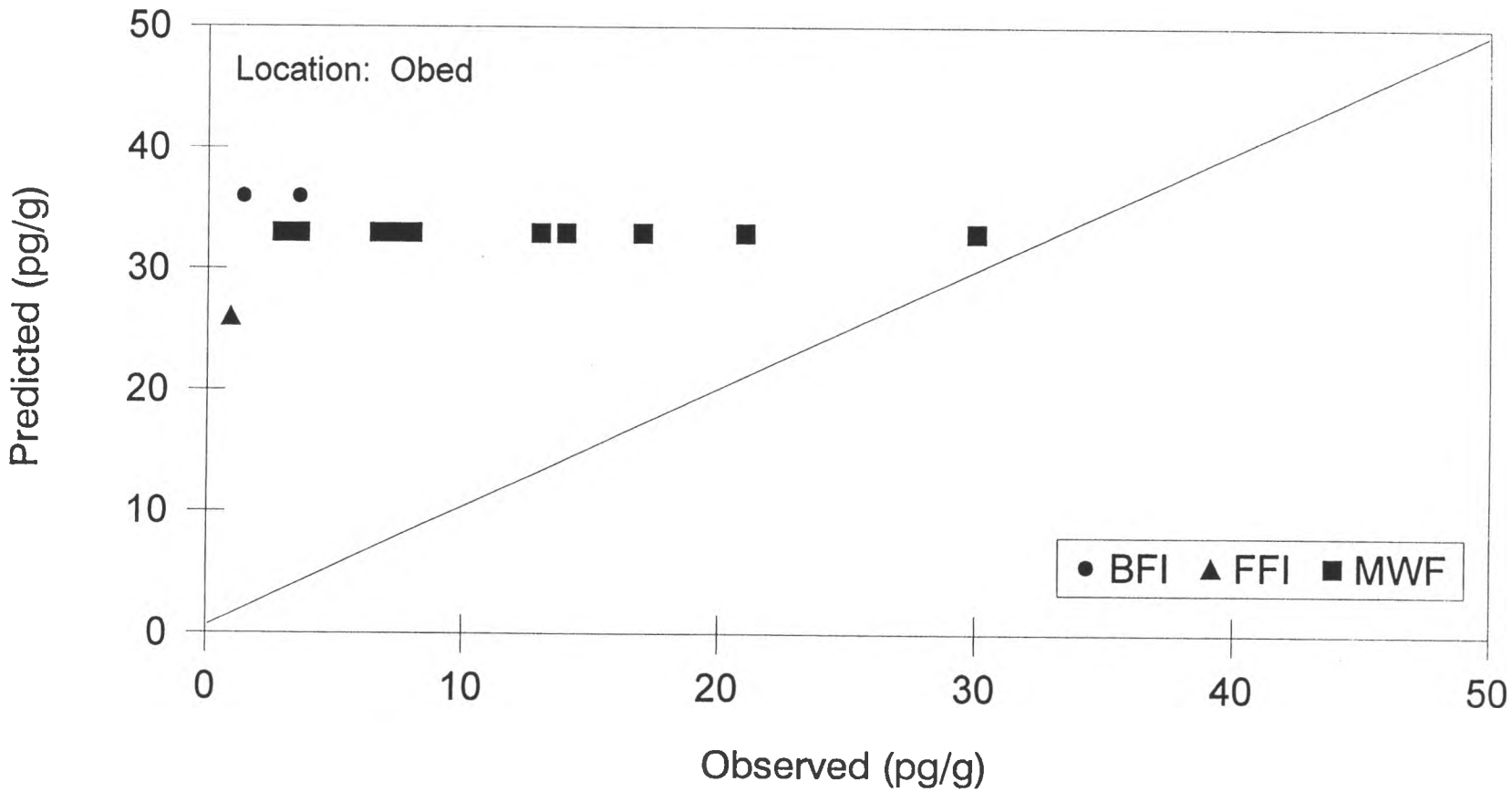
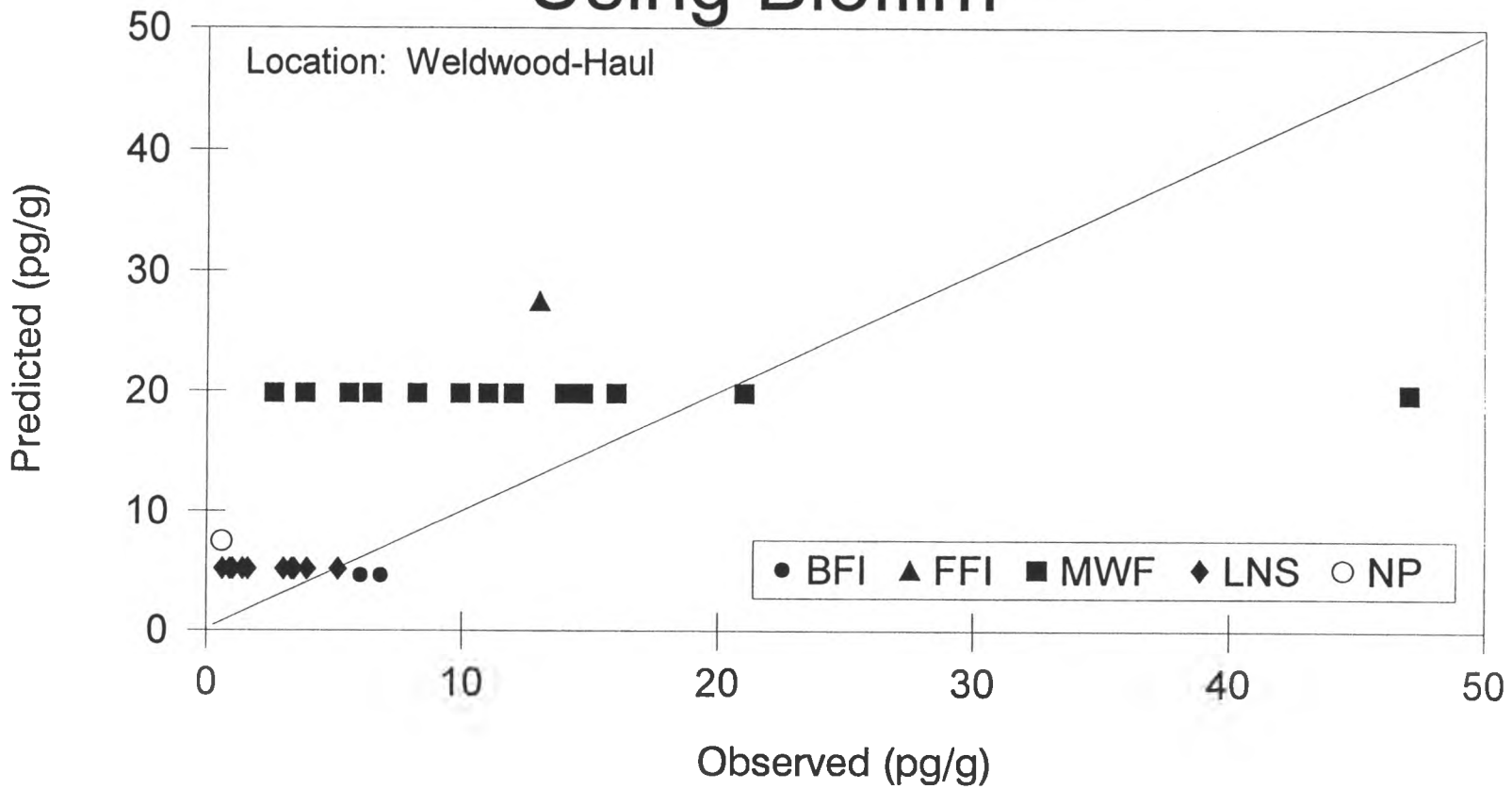


2,3,7,8-TCDF in Biota, Predicted *vs* Observed Using Biofilm



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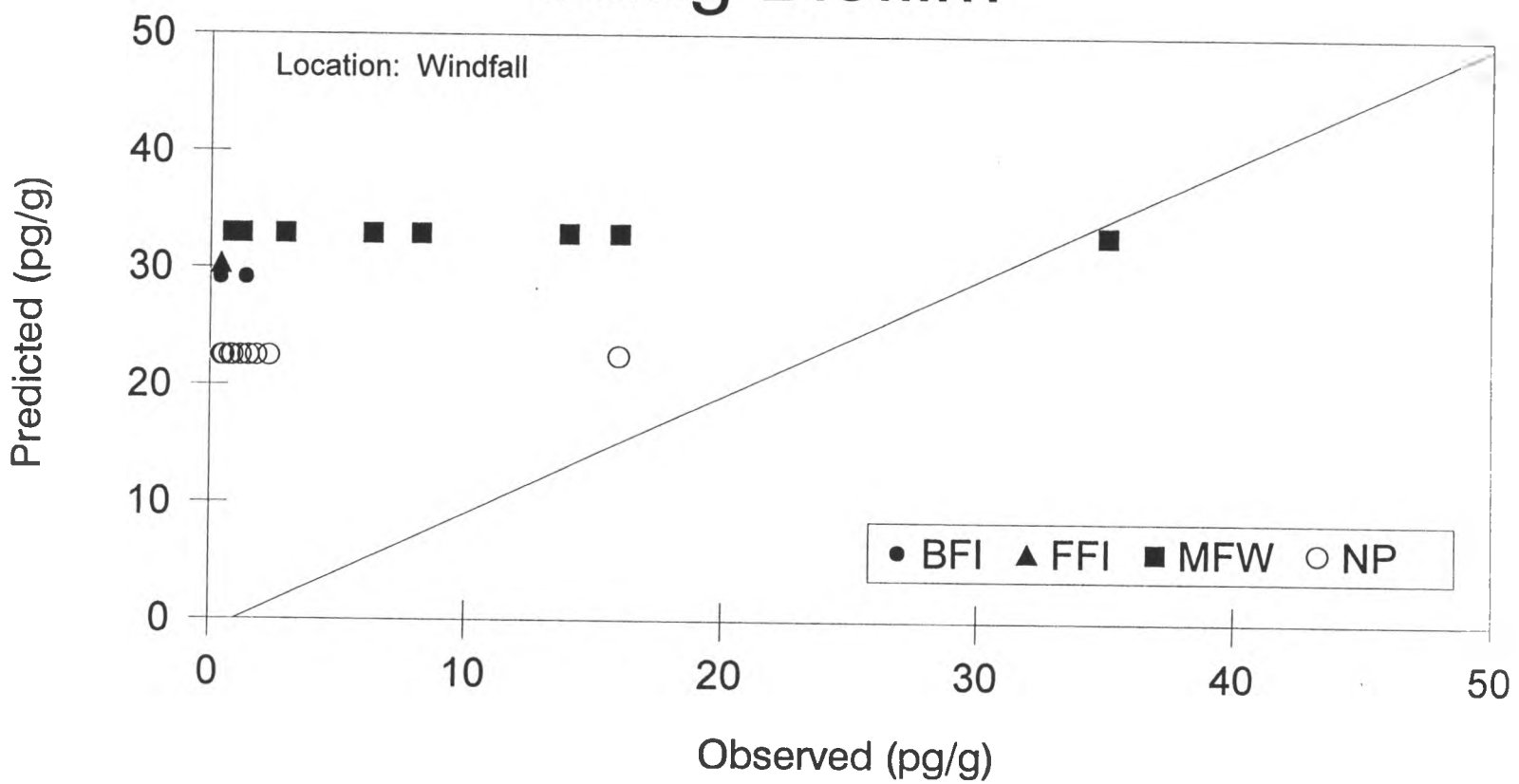

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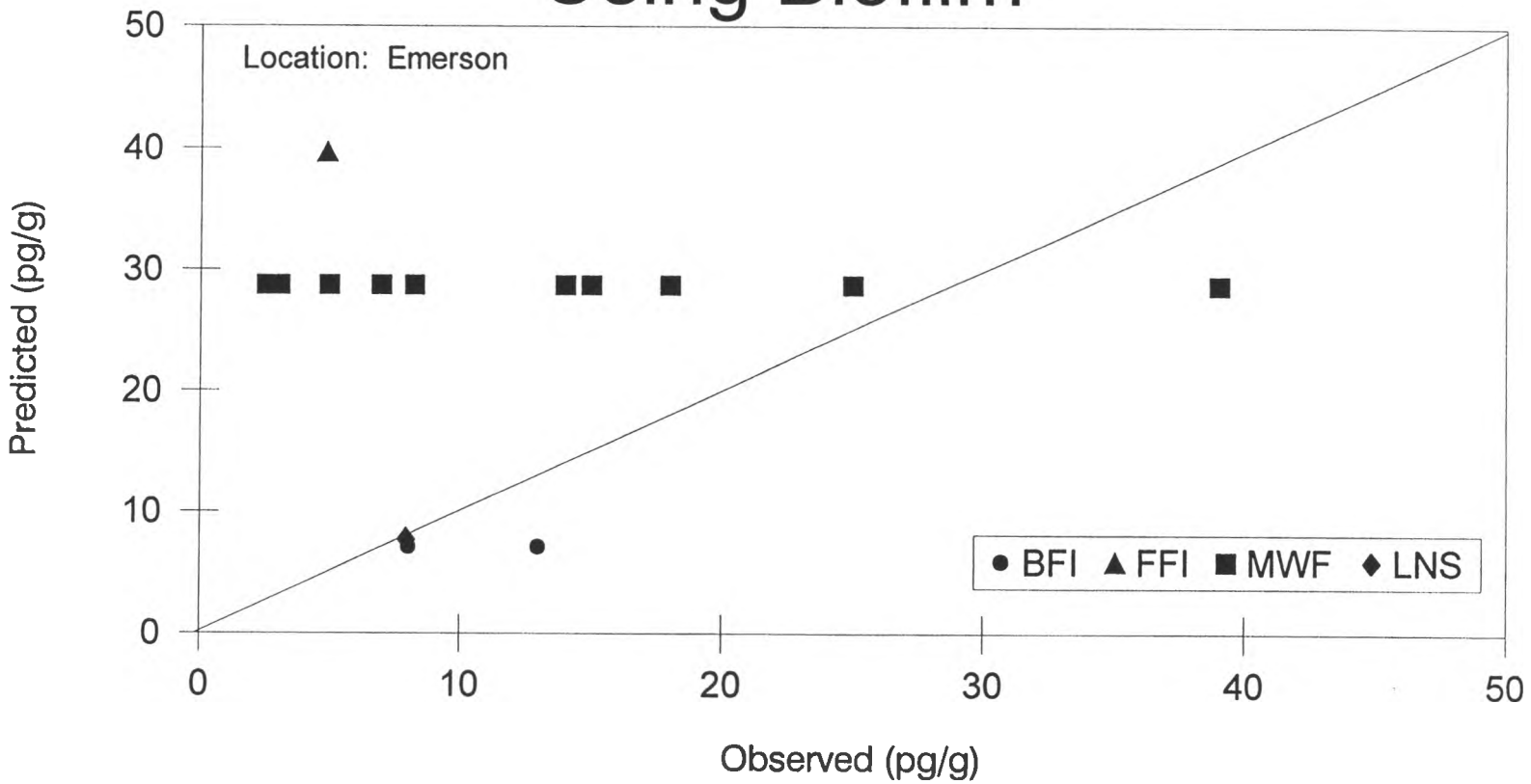
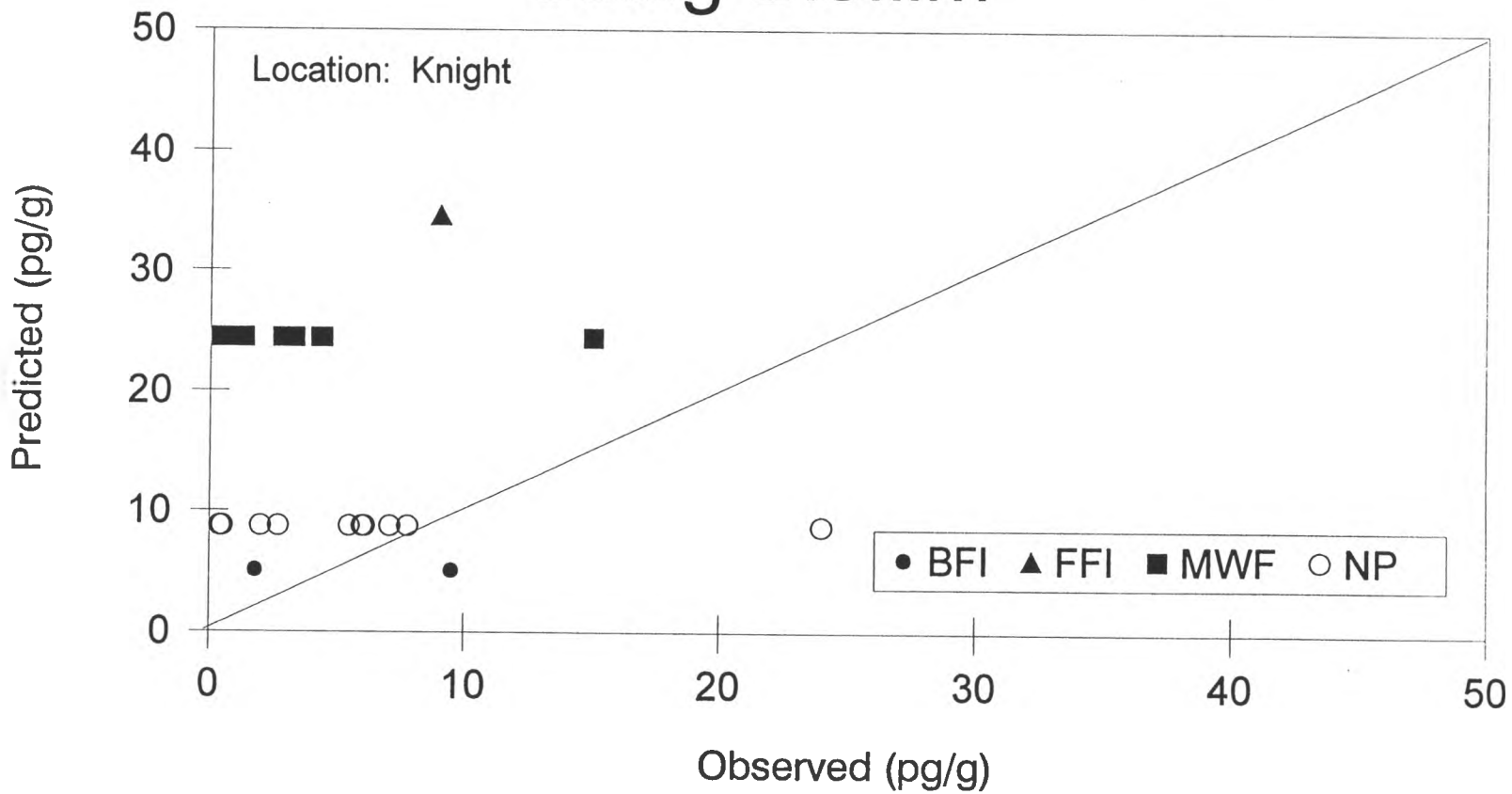
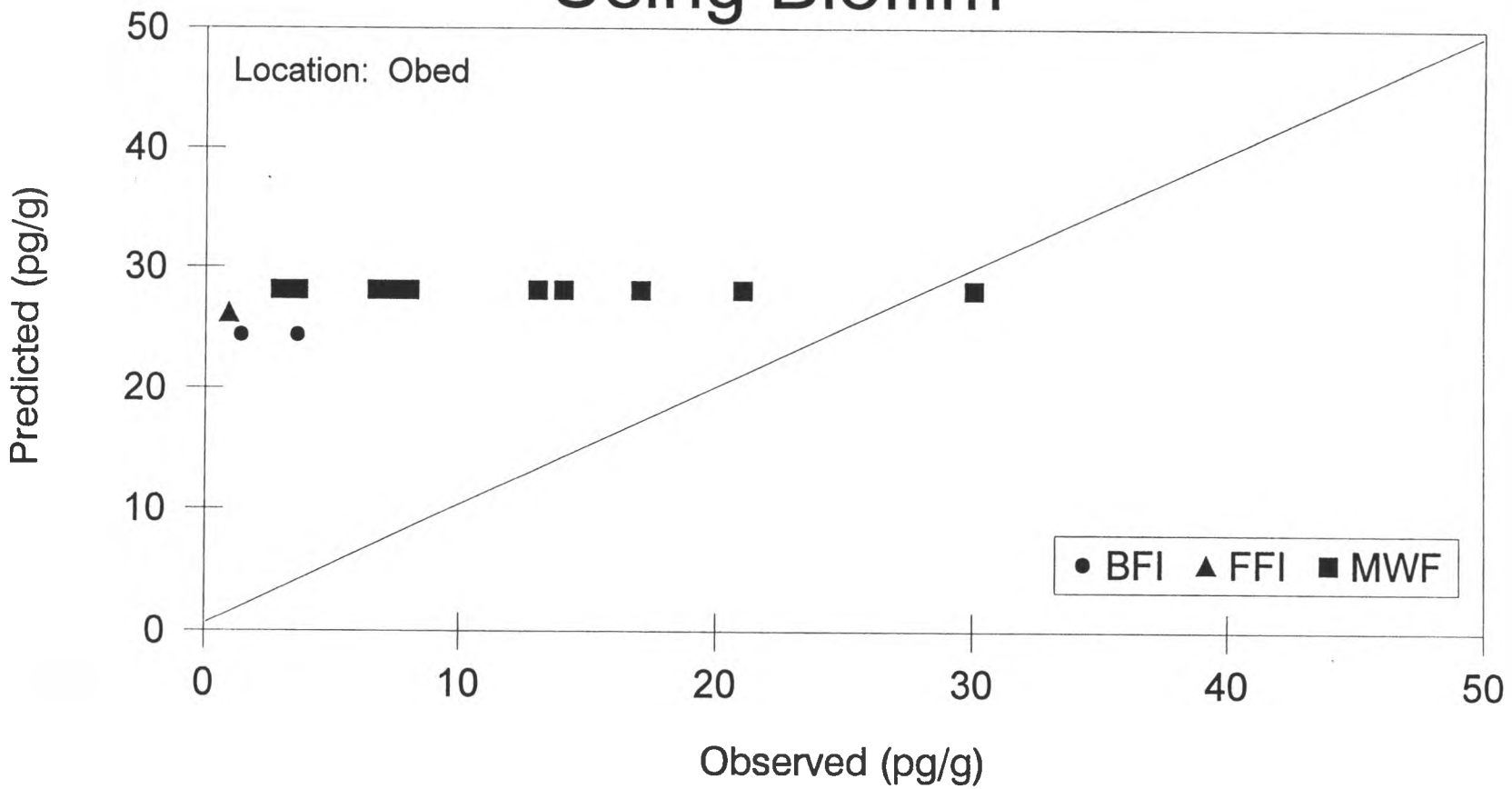


2,3,7,8-TCDF in Biota, Predicted *vs* Observed Using Biofilm



2,3,7,8-TCDF in Biota, Predicted *vs* Observed Using Biofilm



APPENDIX C: ANALYSIS OF ATHABASCA FOOD CHAIN MODELLING ASSESSMENT USING GOBAS FOOD CHAIN MODEL

C.1 Assumptions

1) all assessments were conducted based on Weldwood Haul site from the NRBS data set;

2) models runs were conducted with log K_{ow} values of 6.5 and 6.1, for comparative purposes;

3) suspended sediment T_4CDF concentrations ($\mu g/g$) and corresponding organic carbon content of sediments were input to simulate dietary exposures of mountain whitefish through consumption of filter-feeding invertebrates; and

4) bed sediment T_4CDF concentrations and corresponding organic carbon content were input to simulate dietary exposures of longnose sucker through consumption of benthic invertebrates.

Table 1: Measured T_4CDF Concentrations at the Weldwood Haul (NRBS, 1992)

	Centrifugate in water column (ng/L)	Suspended sediment (ng/kg)	Bed sediment (ng/kg)	Mountain whitefish (ng/kg)	Longnose sucker	Northern Pike
T_4CDF concentration	0.0001	2.2	0.4	13.0 (n=10) 14.7 (n=10)	2.42 (n=10)	0.6 (n=2)

Table 2: Fraction of Organic Carbon Content (FOC) in Modelled Media

	Suspended Sediment	Bed Sediment
Fraction of organic carbon	0.031	0.055

Table 3: Biological Data for Aquatic Species Modelled

Species	Individual weights (kg)		Growth Rate Constants (1/d)	% Lipid[a]
	Mean	Standard Deviation		
Phytoplankton	NA	NA	NA	0.5[c]
Zooplankton	NA	NA	NA	5.0
Filter-feeding Invertebrate	NA	NA	NA	5.0
Benthic Invertebrate	NA	NA	NA	5.0
Small foraging fish	0.00172	0	0.007144	3.0 [b]
Mountain whitefish	0.5732	0.2893	0.002235	5.22
Longnose sucker	0.7165	0.5367	0.002138	4.62
Northern pike	0.598	0.2588	0.002217	1.0

[a] Based on NRBS 1992 data.
[b] Assumed based on % lipid of yellow perch.
[c] Default Gobas model.
NA Data not required by Gobas model system.

Table 4: Feeding Interactions Simulated for Each Species

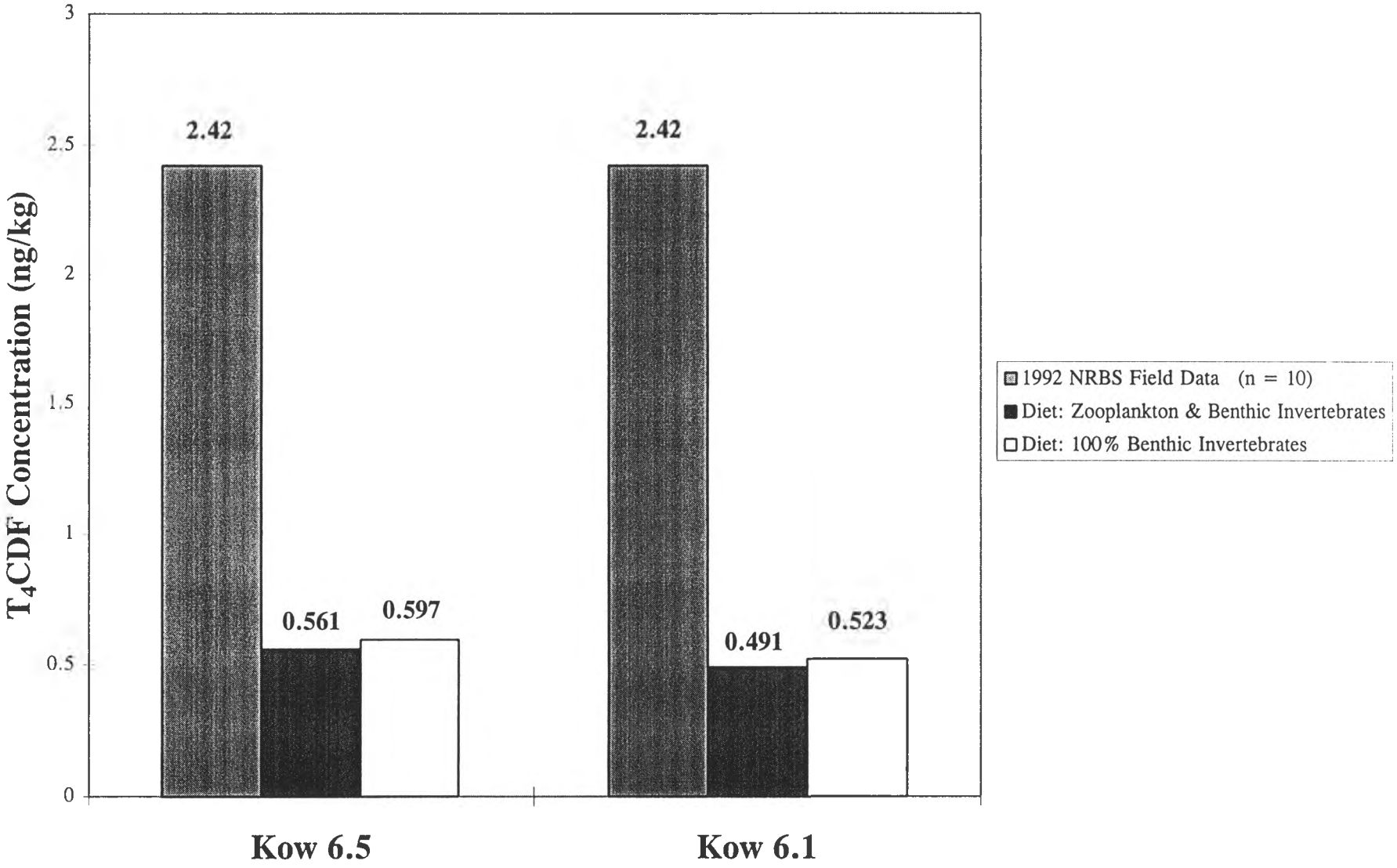
Predator Species	Prey Species						
	Benthic invertebrate	Zooplankton	Filter-feeding invertebrate	Small filter-feeding fish	Mountain Whitefish	Longnose sucker	Northern pike
Small filter-feeding Fish							
(Benthic diet)	95%	5%	-	-	-	-	-
(Filter-feeding diet)	-	5%	95%	-	-	-	-
Mountain whitefish							
(Normal diet)	39%	61%	-	-	-	-	-
(100% Benthic)	100%	0%	0%	-	-	-	-
(100% Filter-feeding)	-	0%	100%	-	-	-	-
Longnose sucker							
(Normal diet)	94%	6%	-	-	-	-	-
(100% Benthic)	100%	0%	-	-	-	-	-

Table 4: Feeding Interactions Simulated for Each Species

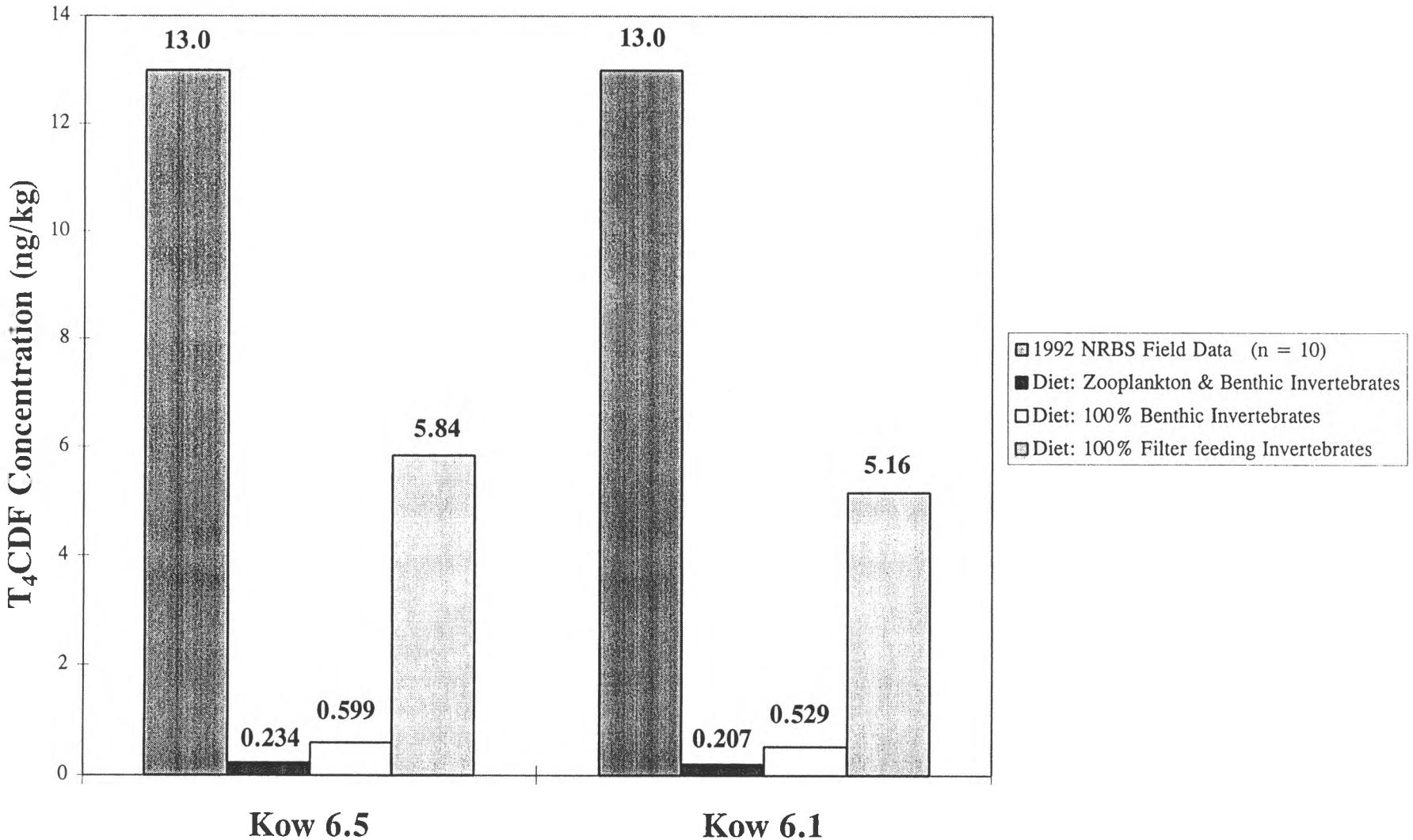
Predator Species	Prey Species						
	Benthic invertebrate	Zooplankton	Filter-feeding invertebrate	Small filter-feeding fish	Mountain Whitefish	Longnose sucker	Northern pike
Northern pike	-	-	-	30%	31%	39%	-

Note: No dietary interactions for benthic invertebrates, filter-feeding invertebrates, or zooplankton are required by the Gobas model.

Predicted T_4CDF Concentrations in the Longnose Sucker at Weldwood Haul using the Gobas Food Chain Model *vs* Observed



Predicted T_4CDF Concentrations in the Mountain Whitefish at Weldwood Haul using the Gobas Food Chain Model *vs* Observed



APPPENDIX D: FOOD CHAIN MODELLING: MODEL THEORY AND APPLICATION FOR THE NRBS

D.1 Introduction

The uptake of chemicals by aquatic organisms through the food chain can occur through several processes, including direct uptake from the water column, adsorption to the exterior surfaces of the organism, and uptake from contaminated food sources. When the uptake exceeds the ability of the animal to excrete the chemical from its body, the tissue concentrations in the animal become higher than the chemical concentrations in the surrounding environment in a process known as bioaccumulation. Some chlorinated organics (*i.e.*, PCB and dioxins) are eliminated or excreted from the body very slowly, and therefore tend to accumulate in a variety of species. Bioaccumulation reported in higher organisms has been largely attributed to ingestion of contaminated food (Muir, 1988), although uptake from water also occurs in aquatic species.

Food chain models may be used to predict concentrations of various chemicals in aquatic species of surface water receiving chemical emissions from point sources and non-point sources (*e.g.*, industrial effluents, atmospheric deposition, surface runoff and groundwater entry from agricultural, urban and other contaminated sites). Such models can be used to provide an indication of the potential and extent of bioaccumulation of various chemicals in aquatic ecosystems and to assist in the development of field monitoring studies by targeting key determinants of bioaccumulation, critical species of concern and predator-prey interactions leading to elevated levels in top predators. Model predicted fish tissue concentrations may be used in an exposure analysis when field data are unavailable to assess the potential impact of contaminants in fish on the health of fish-eating wildlife or humans from releases of chemicals to the aquatic environment. Aquatic food chain models can be used to predict the ecological impact of contaminated sediments on aquatic based ecosystems and are a tool to be used in determining the effect that rehabilitation of surface waters may have on indigenous species, re-introduced species (*e.g.*, fish stocking, biological control agents), and foreign species may have on the cycling and transport of chemical contaminants *via* the food web. Food chain models may be integrated with environmental fate models to simulate the ecosystem response to various loading rates of chemicals and to provide an indication of the assimilative capacity of aquatic systems that would not result in adverse effects on human health and the environment.

D.2 Model Conceptualization

The first step in selecting a food chain model is to determine what are the basic objectives of the modelling exercise and how the data will be used in the final analysis. This requires that the receptors of concern (*i.e.*, aquatic species, wildlife, humans) are characterized with respect to their dietary habits including species preferences and relative dietary proportions. Questions relevant to the assessment of human health include: Is the area used for sport or commercial fishing? If so, what are the major species harvested? Cultural or socio-economic consumption habits that may influence chemical exposure, such as consumption of crab or lobster hepatopancreas, eels, or certain fish species, and must be considered at this time in order that the representative aquatic species are included in the drafting of the food chain to be modelled. For wildlife and aquatic receptors

prevalent to the ecosystem in question consideration must be given to the characteristic ecology of each species including seasonal and developmental differences in dietary habits. Information from biological monitoring surveys can be used to identify aquatic species to be included in the model.

Next a simplified food chain, consisting of the major fish and other aquatic species identified in step one and their respective dietary interactions is drafted. This involves a review of the existing site-specific biological sampling data and identification of representative feeding structures for the predominant species of concern. The final model configuration will best simulate the interactions of the food web and pathways governing the transfer of chemicals from the dissolved and particulate phase to various trophic levels for the ecosystem in question. Biological analyses of gut contents of fish, stable isotope analysis, biological/ecological surveys and radiotelemetry studies are potential sources of information for construction of a representative food web.

Several food chain models have been and are continuing to be developed to predict the uptake and accumulation of chemicals in aquatic species. The majority of these models have been developed to simulate the accumulation of PCBs in aquatic food webs of the Great Lakes. The theoretical basis of the food chain models is relatively new and is continuing to be developed.

Two food chain models that have been peer reviewed and will be used to simulate the uptake and accumulation of chemical contaminants in the Northern Rivers Basin are: i) Version 4.1 of the steady-state/age-dependent food chain model developed from Thomann and Connolly (1984b); and ii) the steady-state food chain model developed by Gobas (1993). It is essential that the user be familiar with the theories on which these models are based, and be aware of the merits and shortcomings of each model prior to conducting a food chain model analysis. A major consideration is whether or not the model is able to reasonably simulate the major exposure pathways for concern. For example, hydrophobic chemicals the prodominant pathways are: i) consumption of contaminated prey; ii) consumption of contaminated particulate materials (suspended and bottom sediments); iii) uptake from water across the gills; and iv) dermal adsorption. The flexibility of the model to address the site-specific species of concern is also critical model selection. If the model does not simulate all exposure pathways the user needs to be aware of which exposure pathways are not addressed. The user must determine whether this omission is critical to the exposure assessment? To answer this question, consideration is given to the ecosystem characteristics, site-specific food chain interactions of predators and prey at all trophic levels, and whether or not organically rich particulates or dissolved organic material are a major food source for preferred prey species.

Consideration also given to whether or not effluents entering the receiving waters would be expected to influence the bioavailability of chemicals at the base of food chain, which could either enhance or reduce chemical accumulation in species at higher trophic levels. These comments are substantiated by results of a comprehensive field study conducted on pulp mill receiving waters which found that concentrations of PCDDs and PCDFs were greater in rocky mountain whitefish than any other species in the same receiving environment (Birkholz *et al.*, 1992; Kloepper-Sams and Benton, 1992). These observations could only be explained by food chain interactions of rocky mountain whitefish which prey on filter-feeding caddisfly larvae which consume suspended organic particulates concentrating adsorbed PCDDs and PCDFs. Consequently, considerable attention must

be given to the structure of food chain interactions being simulated. Furthermore, depending on the chemicals of concern, the model selected must be flexible enough to address different and potentially significant routes of exposure of aquatic species.

D.3 Food Chain Model Theory

Aquatic organisms are exposed to chemicals in the environment through a number of routes, including exposure from the dissolved water column concentration and exposure from consumption of contaminated prey or sediment particulates. However, the ability of an organism to accumulate chemicals from water and diet is not a simple direct relationship. Numerous biological, physical and chemical characteristics (*i.e.*, growth rate, metabolism, lipid content, feeding structure, molecular structure, K_{ow}, DOC, foc,) of the organism, chemical and the environment act together to determine chemical bioavailability, uptake, elimination and accumulation of chemicals in the aquatic organism.

Chemical exposure through the consumption of contaminated prey is believed to be the major exposure pathway for hydrophobic chemicals. Dietary chemical exposure is dependent on the concentration of chemical in its prey, the prey-specific consumption rate of the predator and the degree to which the chemical is absorbed from the food into the tissues of the predator (*i.e.*, the chemical assimilation efficiency). The secondary exposure pathway is direct chemical uptake from water across the gills. Chemical exposure from water is dependent on the solubility of the chemical, the respiration rate of the organism, and the water to gill membrane transfer efficiency of the chemical which may be related to the chemical diffusivity in water.

Organisms at the base of the food chain or at lower trophic levels, such as plankton and benthic invertebrates, usually reach steady-state relatively rapidly in the natural environment. Adult stages of these species often do not differ significantly in concentration from the earlier life stages. Therefore, it is reasonable to assume that a steady-state calculation would adequately represent their concentrations. Organisms at higher trophic levels are continually growing, may change their dietary habits with age and may even migrate within a given ecosystem. Thus, chemical concentrations in tissues of higher trophic species may vary depending on environmental concentrations, life-stage and seasonal migration. Although a simple steady-state food chain model is a good start in understanding the flow of chemical contaminants within the food web such a calculation may not adequately predict chemical body burdens in higher organisms, for which a dynamic age-dependent model would be more realistic.

D.3.1 Thomann and Connolly Food Chain Model

The age-dependent food chain model of Thomann and Connolly (1984b) was developed from an earlier steady-state version (Thomann, 1981). Chemical concentrations in aquatic organisms are computed by the model from user-specified chemical concentrations in the water column (dissolved, μg/L ; adsorbed to suspended solids, μg/g carbon) and the sediment (dissolved μg/L; adsorbed, μg/g carbon). The model calculates chemical uptake from the water column *via* respiration and through consumption of contaminated food. It is well established that the respiration rate of aquatic species

is temperature dependent, therefore the respiration rate and hence chemical uptake is corrected for environmental temperature by the model. Chemical loss due to excretion and dilution from growth is also calculated. The model simulates the total chemical uptake and accumulation for both steady-state species (organisms for which the chemical body burden remains relatively constant) and age-dependent species (organisms for which the chemical body burden changes with the age, growth rate and dietary habits of each age-class). Species are designated as either steady-state or age-dependent by the user. The following discussion focuses on the theory for steady-state species which will be used for the Northern Rivers Basin.

The food chain model developed by Thomann and Connolly addresses the complexities of food chain accumulation of chemicals in an aquatic environment from the lowest trophic level (*e.g.*, phytoplankton and detritus) to top predatory fish. Version 4.1 of the model simulates chemical exposures through the consumption of suspended particles or sediments by either fish or benthic species, dietary exposure through the consumption of contaminated prey, and chemical exposure from pore water and water column (**Figure 1: Simplified Food Chain Model**). This version of the Thomann and Connolly model allows steady-state benthic species (*i.e.*, animals breathing interstitial water) to consume any designated organism or particulate material, a feature that provides the user with maximum flexibility in assigning feeding interactions and simulating the transfer of chemicals in the natural environment. The model also allows the user to specify initial chemical concentrations rather than begin model simulations assuming a pristine environment. This feature enables one to investigate how changes in chemical loadings might affect future chemical concentrations in aquatic food chains and allows implementation of recovery scenarios. Other enhancements include the ability to model up to five chemicals simultaneously and to simulate species migration between environmental compartments.

The general equation of the food chain model is:

$$dv_i/dt = K_{ui}c + (\text{sum of}) a_{ij}p_{ij}C_iv_j - K'_iv_i$$

where,

K_{ui}	=	uptake rate from water
c	=	dissolved water concentration (μg/L)
a	=	chemical assimilation efficiency of i on j
p	=	fraction of consumption of i on j
C	=	weight-specific consumption of i
v	=	chemical concentration of j or i
K'	=	loss rate due
i	=	predator species
j	=	prey species.

A steady-state model based on four trophic levels (*i.e.*, phytoplankton or detritus serving as the base of the food chain, benthic and pelagic invertebrates, small fish , and large fish) will be delineated for the Athabasca, Wapiti and Smoky rivers.

The base of the food chain model, phytoplankton or detritus, is assumed to be in steady-state equilibrium with chemicals in the surrounding aquatic environment. Chemical accumulation at this level of the food chain is generally considered to be a function of surface adsorption and subsequent cellular incorporation of the chemical (Thomann and Mueller, 1987). Therefore, the mass balance equation used to describe the accumulation of chemical in this trophic level is:

$$dv_o/dt = k_{uo}c - K_o v_o \quad (1)$$

where, v_o = the concentration of chemical in phytoplankton (μg/g wet weight)
k_{uo} = sorption of chemical from water (L/day/g (wet weight))
K_o = desorption rate (d^{-1})
c = concentration of dissolved chemical (μg/L)

Uptake and elimination of chemicals (or sorption/desorption) at this low level of the food chain was considered to occur rapidly, compared to uptake and elimination rates at higher levels in the food chain. Therefore, equilibrium is assumed to occur instantaneously (*i.e.*, $dv_o/dt = 0$), and the equation above reduces to:

$$v_o = N_o * c; \quad (2)$$

where N_o equals the bioconcentration factor (uptake rate/elimination rate). This calculation yields the concentration of the chemical (μg/g wet weight) for organisms at the base of the food chain.

The Thomann and Connolly model either accepts direct input of the phytoplankton bioconcentration factor (BCF) if specific data are available or computes the phytoplankton BCF from the K_{ow} converted to K_{oc} for the chemical and the fraction organic carbon of the phytoplankton. However, the above relationship appears to describe the phytoplankton bioconcentration of only organic chemicals with a log K_{ow} less than about 6 (Thomann, 1989). The phytoplankton BCF for chemicals with a log K_{ow} in the range of 5 to 8 tends to be independent of K_{ow} (Connolly, 1990). This conclusion is based on the field data for PCB accumulation in Lake Ontario phytoplankton (Oliver and Niimi, 1988) and laboratory phytoplankton BCF data for PCB (Wang *et al.*, 1982; Lederman and Rhee, 1982).

For trophic levels above the base of the food chain, accumulation of the chemical is assumed to occur from the dissolved fraction of the chemical present in water and from that present in contaminated food.

The body burden of the chemical in the upper trophic levels of the food chain (*i.e.*, zooplankton, small fish and large fish) is calculated in the model by considering the contributions in each species from both ambient water exposure and food ingestion as follows:

$$dv_i'/dt = k_{ui}w_i c + (\text{sum of}) a_{ij}p_{ij}C_{ij}v_j w_i - K_i v_i' \quad i = 1...m \quad (3)$$

where food chain level i preys upon lower food chain levels indexed as j and

v_i' = chemical body burden (μg)
k_{ui} = uptake rate from water {L/[d * g (w)]}
w_i = weight of the organism or average individual (g (w))
c = dissolved water concentration (μg/L)
a = chemical assimilation efficiency of i on j (μg chemical absorbed/μg chemical ingested)
p = the fraction of the consumption of i that is on j
C_{ij} = weight-specific consumption of i on j (g prey/g predator/day)
v_j = chemical concentration of j
K_i = loss of chemical due to excretion or desorption (1/d)

Equation 3 is therefore divided into three parts; the first dealing with uptake occurring directly from the water, the second dealing with the flux of the chemical into the body via feeding activities and the third dealing with elimination, loss or reduction of the chemical due to desorption, excretion or dilution due to growth (Thomann and Connolly, 1984b). Each of these components will be discussed separately below.

D.3.1.1 Calculation of Respiration Rate

The respiration rate [g (wet) respired/g body weight/day] of steady-state species is calculated by the model from equation (4) below, which considers the effect of temperature on respiration:

$$R' = RESP * e^{rho*T} \quad (4)$$

where,
RESP = respiration rate per day (data entered into model)
rho = temperature coefficient ($^oC^{-1}$)
T = temperature (^oC)

Respiration rate is inversely related to body weight, body weight is important in estimating the quantity of chemical eliminated due to natural metabolic processes.

The model converts the respiration rate from units of g (wet)/g (wet)/day to units of g (O_2)/g (wet)/day, assuming a stoichiometric conversion of carbon to oxygen and a carbon to dry weight ratio of 0.4 g carbon/g (day). The respiration rate, R, is equal to :

$$R = 2.7\ a_c\ n\ R' \quad (5)$$

where,
2.7 = g oxygen utilized/g carbon body weight
a_c = carbon to dry weight ratio (g carbon/g day) = 0.4
n = dry weight to wet weight ratio for the organism (g (dry)/g (wet))
R' = respiration rate [g (wet)/g (wet)/day]

D.3.1.2 Calculation of Uptake Rate from Water

Uptake of a chemical from the dissolved fraction in the water column or pure water is assumed to occur in the same manner as oxygen uptake at the gill (Thomann and Connolly, 1984b). The uptake of oxygen at the gill, or the mass transport, was assumed to be dependent upon a number of parameters, including the diffusivity of oxygen, the surface area of the gill, and the gill thickness (Thomann and Connolly, 1984b):

$$M = (DA/t)\, c \qquad (6)$$

where,
- M = mass transport (μg/d)
- D = diffusivity (cm^2/d)
- A = gill surface area (cm^2)
- t = thickness of gill (cm)
- c = concentration in water (μg/L)

Consequently, the mass transport of chemicals is directly related, by the permeability ratio of chemical:oxygen, to the mass transport of oxygen across the gills.

The rate of chemical uptake is thus described by the equation:

$$k_u' = B\, Mo_2/Co_2 \qquad (7)$$

where, k_u' = the rate of chemical uptake for the whole organism (*i.e.*, L of chemical/d),

and the mass transport of chemical across the gill surface (M_{chem}), is equal to:

$$M_{tox} = k_u' * C_{chem} \qquad (8)$$

From the Ku' the rate of chemical uptake per unit weight (Ku) is obtained by dividing by weight (w):

$$Ku = k_u'/w = B\, [(Mo_2/w)/Co_2] \qquad (9)$$

The gill permeability ratio (PRATIO) is input to the model .

The model calculates the oxygen concentration in water by assuming saturation that is temperature dependent.

$$Co_2 = (14.45 - 0.413*T + 0.00556*(T^2)) * 1E\text{-}03 \qquad (10)$$

The rate of direct chemical uptake from water is calculated by multiplying Ku by the water column concentration (μg/L).

$$WATER = Ku * CHEM \quad (11)$$

where, CHEM = water column concentration

D.3.1.3 Calculation of Food Consumption

The model is highly flexible and is capable of simulating a complicated feeding structure within the food chain. Each steady-state species modelled may be assigned up to four different prey items. The actual feeding structure for a given organism will be determined from the available scientific data. Each prey item is described as a fraction of the total diet of the predators.

The influx due to feeding is calculated by determining the chemical uptake for each contaminated prey based on the amount of food consumed, chemical concentration in the prey, assimilation of prey by predator and food preference of predator. The weight specific consumption (C) is calculated by the model using a relationship for growth and respiration.

The chemical uptake from feeding on contaminated prey is calculated using the following equation and may be integrated over time ascending to the general equation:

The biomass assimilation efficiency represents the fraction of food ingested that is actually assimilated into the body and therefore does not appear in the faeces. The model calculates the biomass assimilation efficiency as follows:

$$PRYASM_{ij} = ASIM * FDRY_j/FDRY_i \quad (12)$$

where, ASIM = food assimilation efficiency
$FDRY_j$ = fraction dry weight of prey
$FDRY_i$ = fraction dry weight of predator

D.3.1.4 Calculation of Chemical Elimination

The rate of chemical loss from the body of an organism is considered to be a function of both elimination via excretion or desorption and dilution due to growth. This parameter may be calculated by the model using the following equation:

$$DECAY = EXC + G \quad (13)$$

where, EXC = desorption or elimination rate (1/d)
G = growth rate (1/d)

Alternatively, the excretion rate may be entered directly or may be calculated from the bioconcentration factor (BCF):

$$EXC = k_u / BCF \quad (14)$$

where, k_u = uptake rate (day^{-1})
BCF = bioconcentration factor ($\mu g/g$ (wet)/$\mu g/L$)

The BCF may be entered directly if specific data are available or may be computed from the K_{ow} for the chemical and the fraction lipid (f_L) for each species of each trophic level according to the equation:

$$BCF = f_L * K_{ow} * 1E\text{-}03 \quad (15)$$

D.3.1.5 Calculation of Chemical Concentration

The chemical concentration (CFC) for any steady-state species is the sum of the chemical influx due to feeding and water intake divided by the rate of decay:

$$CFC = (FOOD + WATER)/DECAY \quad (16)$$

Figure 1

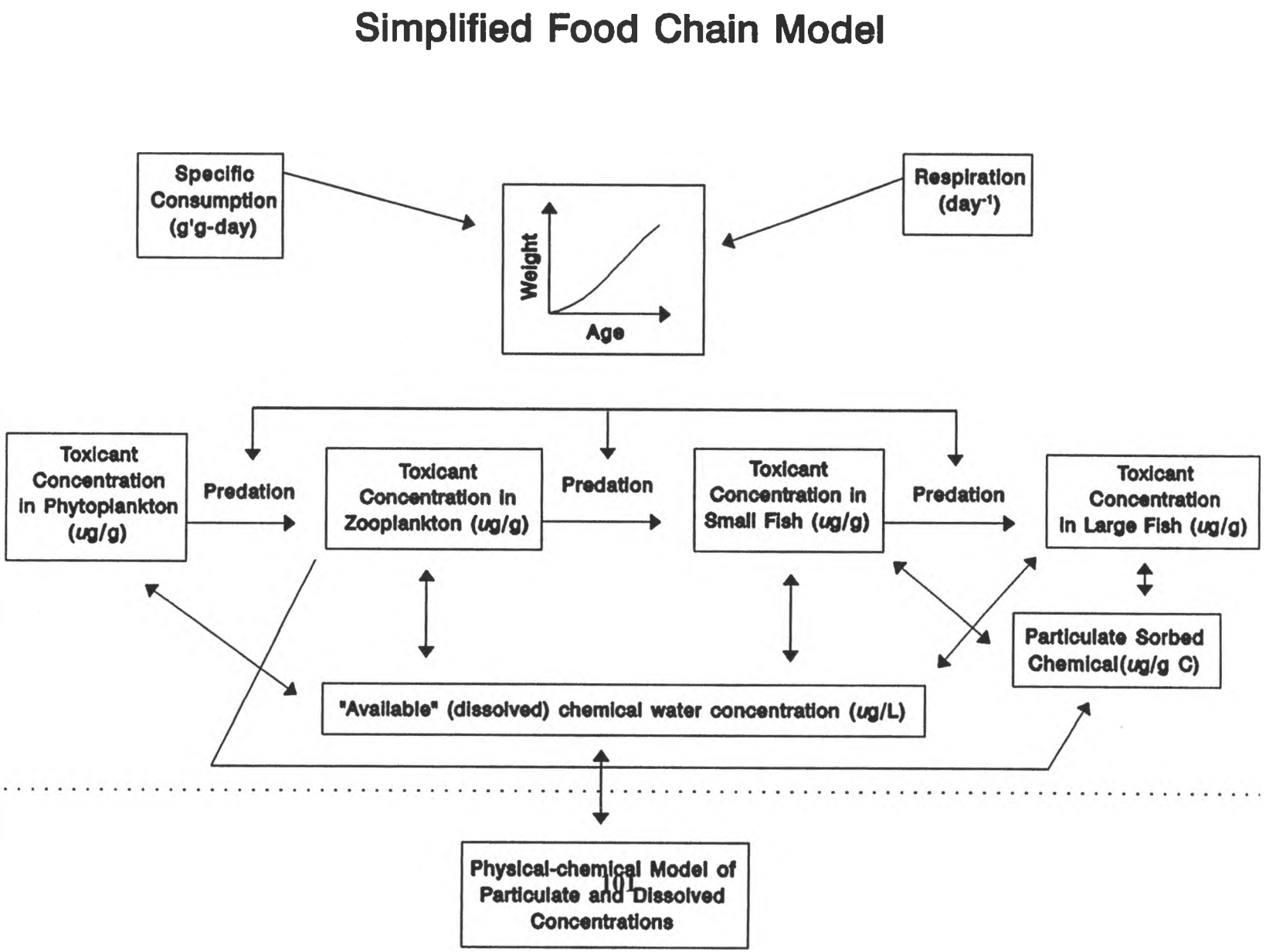
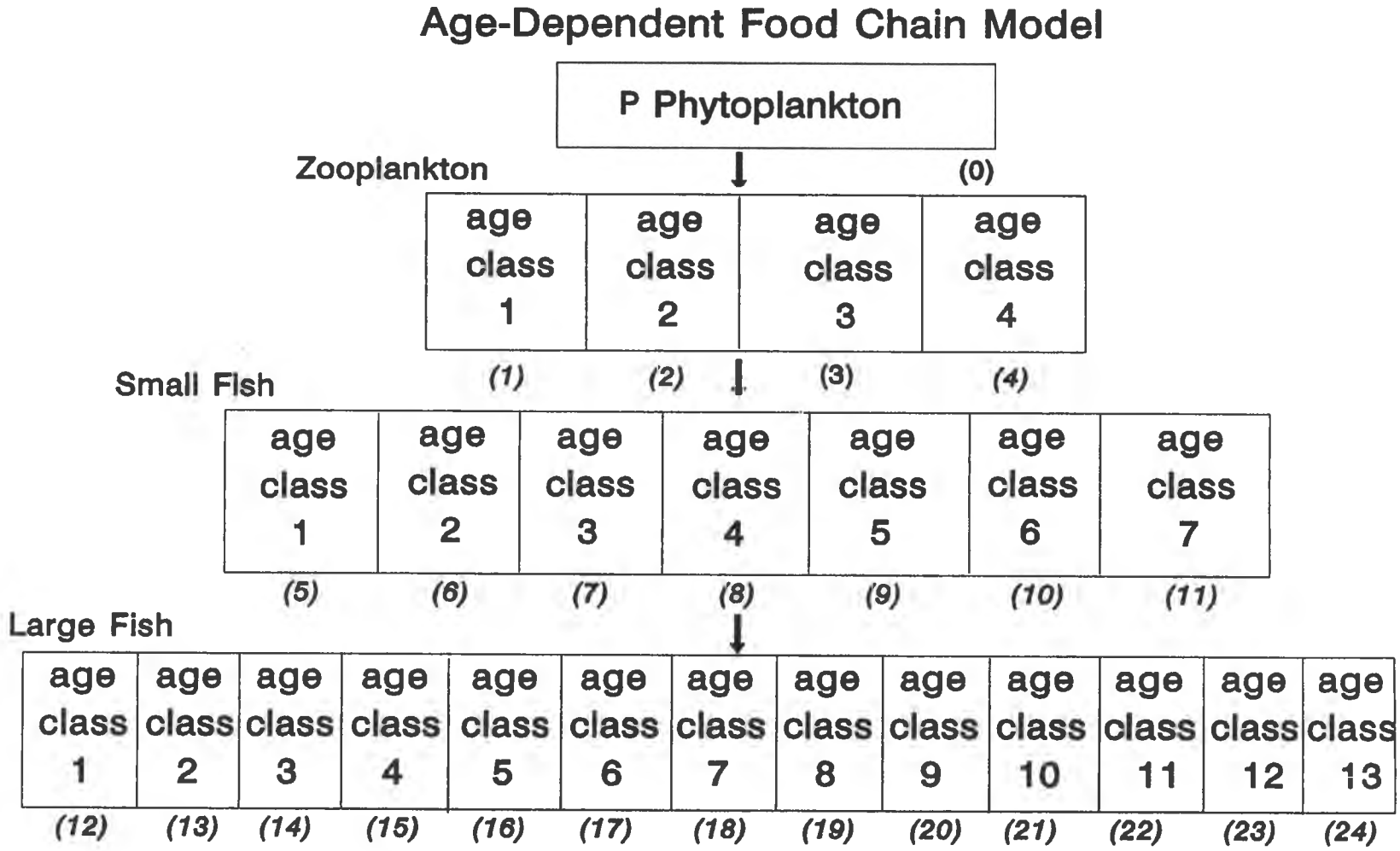

Simplified Food Chain Model
Specific Consumption (g'g-day)
Respiration (day-1)
Weight
Age
Toxicant Concentration in Phytoplankton (ug/g)
Predation
Toxicant Concentration in Zooplankton (ug/g)
Predation
Toxicant Concentration in Small Fish (ug/g)
Predation
Toxicant Concentration in Large Fish (ug/g)
Particulate Sorbed Chemical(ug/g C)
"Available" (dissolved) chemical water concentration (ug/L)
Physical-chemical Model of Particulate and Dissolved Concentrations

Figure 2


Age-Dependent Food Chain Model
P Phytoplankton
Zooplankton
(0)
age class 1
age class 2
age class 3
age class 4
(1)
(2)
(3)
(4)
Small Fish
age class 1
age class 2
age class 3
age class 4
age class 5
age class 6
age class 7
(5)
(6)
(7)
(8)
(9)
(10)
(11)
Large Fish
age class 1
age class 2
age class 3
age class 4
age class 5
age class 6
age class 7
age class 8
age class 9
age class 10
age class 11
age class 12
age class 13
(12)
(13)
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(22)
(23)
(24)

D.3.2 Gobas Food Chain Model

A simple steady-state food chain model for predicting the bioaccumulation of hydrophobic organic chemicals has recently been developed by Gobas (1993). The model has been applied to simulate the accumulation of organic chemicals in Lake Ontario. This model requires basic data describing the environmental conditions, characteristics of the aquatic organisms of the food web and physical-chemical properties of the chemical. Monte Carlo uncertainty analysis is a novel feature of this model, which integrates sample distributions in fish weight, and chemical concentrations in water and sediment as input into the model. Chemical uptake from water across the gills and through consumption of contaminated prey, elimination across the gills, chemical loss due to metabolic transformation, fecal egestion and dilution due to growth are considered by the model. These processes are described by equilibrium partitioning equations which relate the distribution of chemical between the water and the biological lipid phase to the K_{ow} and lipid content of the organism. Equilibrium partitioning relationships described by the K_{ow} and lipid content essentially drive the model.

Chemical uptake at the base of the food chain and lower trophic levels is assumed to occur only from the truly dissolved water phase; no chemical uptake through food consumption is considered for these species. The same steady-state equation is used to calculate chemical accumulation in phytoplankton, aquatic macrophytes and zooplankton. The general form of this equation is:

$$BCF = C_A / C_{WD} = k_1 / (k_2 + k_G) \quad (1)$$

where,
- C_A = chemical concentration in the organism (μg/kg)
- C_{WD} = the "truly" dissolved or bioavailable chemical concentration in water (μg/L)
- k_1 = uptake rate of chemical from water (L/kg * day)
- k_2 = elimination rate of chemical to water (L/kg * day)
- k_G = first order growth rate constant (1/d).

In the Gobas model the phytoplankton, zooplankton and macrophyte BCF are approximated from the K_{ow} and the lipid content (kg/kg) by $L_A * K_{ow}$ where L_A = fraction lipid.

Equilibrium partitioning of the chemical between the lipid content of the organism, the organic carbon fraction (OC) of the sediment and the interstitial or pore water is the basis for the calculation of chemical accumulation in benthic invertebrates. The model does not consider chemical uptake from water and consumption of food separately for invertebrates. Thus, the user is unable to address chemical transfer in these organisms as a function of diet or respiration rate. The general equation used in the Gobas model is:

$$C_B \, d_L / L_B = C_S * d_{OC} / OC = K_{LW} * C_P \quad (2)$$

where,
- C_B = chemical concentration in the benthic invertebrate (μg/kg wet weight)
- C_S = chemical concentration in the sediments (μg/kg dry weight),

C_P = "truly" dissolved chemical concentration in the pore water (μg/L)
L_B = lipid fraction of the benthos (kg/kg)
d_L = density of the lipids (kg/L)
OC = organic carbon fraction of the sediment
d_{OC} = density of the organic carbon fraction of the sediment (kg/L)
K_{LW} = dimensionless lipid water partition coefficient.

The steady-state mass balance equation for bioaccumulation of chemical in fish is:

$$C_F = (k_1 * C_{WD} + k_D * C_D) / (k_2 + k_E + k_M + k_G) \quad (3)$$

where, $k_1/(k_2 + k_E + k_M + k_G)$ is usually referred to as the bioconcentration factor (BCF) and $k_D/(k_2 + k_E + k_M + k_G)$ is the biomagnification factor (BMF).

The rate of chemical uptake from water, k_1, via gill ventilation and the fraction actually absorbed is expressed as the gill uptake efficiency, $k_1 * E_W$. For chemicals with a low log K_{ow} (< 4.5 to 5) k_1 and E_W increase with K_{ow}, for chemicals with a log K_{ow} between 5 and 7,k_1 and E_W are constant, and for chemicals with a log K_{ow} > 7,k_1 and E_W decrease with increasing K_{ow} (McKim *et al.*, 1985; Gobas *et al.*, 1986; Gobas and Mackay, 1987). Based on these observations a two-phase resistance transport model has been proposed and is used in the Gobas model to estimate k_1 from K_{ow} and weight of the fish according to the equations:

$$1/k_1 = (V_F / Q_W) + (V_F / Q_L) / K_{ow} \quad (4)$$

and

$$Q_W = 88.3 * V_F^{0.6(\pm 0.2)} \quad (5)$$

where, Q_W and Q_L are the transport rates (L/day) in the water and lipid phases of the fish, respectively, and V_F is the weight of the fish (in kg).

Chemical elimination across the gills is similarly calculated from the K_{ow}, lipid weight V_L, Q_W and Q_L. Chemical loss due to metabolism may be estimated by the user or assumed to be zero provided k_M is sufficiently small compared to k_2 or k_E.

Chemical uptake from diet is also calculated based on equilibrium partitioning according to the equation:

$$k_D = E_D * F_D / V_F \quad (6)$$

where,
k_D = the rate of chemical uptake from food (kg food/kg fish/day)
E_D = dietary uptake efficiency (bioavailability)
F_D = food ingestion rate (kg food/day)

For chemical uptake across the gills, a two-phase resistance model for dietary uptake involving transport of chemical in aqueous and lipid phases is used.

$$1/E_D = A * K_{ow} + B \quad (7)$$

where, A and B are transport rate constants of chemical in the aqueous and lipid phases, respectively. From non-linear regression of experimental data A was determined to be 5.3(± 1.5) * 10^{-8} and B was 2.3(± 0.3).

The Gobas model also calculates chemical loss due to egestion based on the general observation that k_E is approximately 0.25 k_D and calculates loss due to growth using the equation for growth derived by Thomann *et al.* (1992). A detailed discussion of the Gobas model is presented in Gobas (1993).

D.3.3 Model Comparison

From a comparison of the theory behind the two models there are several similarities in the Thomann and Connolly, and Gobas models. The major differences between the models is in their handling of chemical accumulation in phytoplankton and lower trophic levels. The Gobas model requires the less species specific-data and is based solely on lipid and K_{ow} relationships. The present version of the Gobas model does not allow the user to address interactions between organisms and particulates. Consequently, the model may oversimplify the processes governing chemical transfer and accumulation at the base of the food chain. These limitations restrict the simulation of chemical exposure and food chain transfer arising from the consumption of organic particles by filter feeders. In addition, the scientific basis for treatment of chemical accumulation in phytoplankton, aquatic macrophytes and zooplankton by the same partitioning relationships based on lipid and K_{ow} is debatable. While the mechanisms regarding chemical accumulation and food chain transfer at these lower trophic levels are still unresolved by the scientific community, the Gobas model does not offer the user the same flexibility at the base of the food chain as the Thomann and Connolly model to address these issues. Consequently, the model may be limited in its actual ability to simulate the accumulation and transfer of chemicals in ecosystems receiving organically rich particulates or in which complexities at the base of the food chain dominate the transfer of chemicals between trophic levels.

D.4.0 Food Chain Model Data Requirements

The next step in food chain model development is to gather the required data for input to the model. Both food chain models require input of environmental concentrations of chemical(s) and receive data for chemical concentrations in the water column, suspended sediments, porewater and bed sediments. In the initial calibration step for NRBS these values will be entered into the model based on site-specific measured data. Sediment data must be entered on an organic carbon dry weight basis.

Data describing the dietary habits, biological parameters of selected aquatic species and chemical dependent parameters may be found in the published scientific literature. Site-specific information should be used whenever available; however, these data may be supplemented with relevant data from the literature. Species-appropriate chemical assimilation efficiencies, chemical uptake and elimination rates for each chemical selected for fate and bioaccumulation simulation may be

identified from the literature and input to the model. The calibration process generally involves a sensitivity analysis to demonstrate which parameters have the greatest effect on the predicted chemical concentrations in aquatic species. In addition, an uncertainty analysis of the modelled outcome is recommended to determine the influence of the variability in measurements of growth rates, food assimilation efficiencies, chemical assimilation efficiencies, lipid content on predicted whole fish chemical concentrations. It can not be overstated that the confidence in the model predictions is dependent on the validity and veracity of the data input and used to calibrate the models.

Dietary interactions of aquatic species will vary depending on the ecosystem, the general abundance and availability of a potential food source, competition, seasonal changes in water temperature and other factors. Since dietary habits are known to influence chemical uptake and accumulation, the reliability of food chain model results on a site-specific basis would be increased by using site-specific survey data of the aquatic biota and the dietary interactions of selected species through the examination of gut contents stable isotape data.

Data requirements of the Thomann and Connolly and Gobas food chain models are presented in **Table 1: Data Requirements: Thomann and Connolly Food Chain Model Gobas Steady-State Food Chain**. Fraction lipid values are those reported for whole fish. For each age-class the model requires data for initial weights and growth rates.

Table 1: Data Requirements: Thomann and Connolly Food Chain Model and Gobas Steady-State Food Chain

Thomann and Connolly Food Chain Model		Gobas Steady-State Food Chain Model
Steady-State Species	Age-Dependent Species	
log K_{ow}	log K_{ow}	K_{ow}
phytoplankton BCF		
permeability ratio of chemical	permeability ratio of chemical	
chemical assimilation efficiency	chemical assimilation efficiency	
food assimilation efficiency	food assimilation efficiency	
respiration rate	respiration coefficients	
fraction dry weight	fraction dry weight	
growth rate	growth rate for each age class	
	initial weight for each age class	weight of fish species
fraction lipid	fraction lipid for each age class	fraction lipid
chemical BCF (optional)	chemical BCF for each age class (optional)	
predator-prey relations	predator-prey relations for each age class	predator-prey relations
chemical concentration dissolved in water column (μg/L)	chemical concentration dissolved in water column (μg/L)	total chemical concentration in water column (ng/L)

Table 1: Data Requirements: Thomann and Connolly Food Chain Model and Gobas Steady-State Food Chain

Thomann and Connolly Food Chain Model		Gobas Steady-State Food Chain Model
Steady-State Species	Age-Dependent Species	
chemical concentration adsorbed in water column (μg/g carbon)	chemical concentration adsorbed in water column (μg/g carbon)	
chemical concentration dissolved in pore water (μg/L)	chemical concentration dissolved in pore water (μg/L)	
chemical concentration adsorbed in sediment (μg/g carbon)	chemical concentration adsorbed in sediment (μg/g carbon)	chemical concentration in the sediment (ng/g dry weight)
mean water temperature	mean water temperature	mean water temperature
		organic content of water (kg/L); organic carbon content of sediments (%)
		density of lipids (kg/L); density of organic carbon (kg/L)
		metabolic transformation rate constant (assumed negligible compared to loss via elimination and egestion)

D.5 Important Considerations in Food Chain Modelling

The user should be aware that BCF values from field and lab studies may be inappropriate for input to the model due to the extreme variability reportedly due to variation in analytical methodology for determining the dissolved concentration, and variable exposure periods (Servos et al., 1989; Opperhuizen and Sijm, 1990). For example, BCF values calculated using water concentrations that included the dissolved organic carbon fraction and/or that sorbed to suspended particulate material would have overestimated the truly dissolved water concentration (*i.e.*, bioavailable fraction), and hence, underestimated the BCF. As well, field study BCF values are actually bioaccumulation factors (BAF) since chemical concentrations in fish would be the result of combined water column and dietary uptake. The Thomann and Connolly model will accept input bioconcentration factors (BCF) for each species; however, these may also be calculated by the model from the lipid content and log K_{ow}. Based on the quality of the available data, the user must decide whether or not to use a BCF or lipid * log K_{ow} approach to best represent the uptake of chemicals from the aqueous phase.

Both models assume phytoplankton, at the base of the food chain, to be at steady-state and to reach equilibrium rapidly with the truly dissolved water column concentration. As discussed previously, the Gobas model estimates chemical accumulation in phytoplankton based on the lipid content and K_{ow} of the chemical, while the Thomann and Connolly model estimates chemical accumulation by phytoplankton as a relationship to the organic carbon fraction or lipid fraction or directly from a user-specified BCF. It should be noted that a linear relationship between chemical uptake from water and the lipid * K_{ow} often does not apply for chemicals with a log K_{ow} in the range of 5 to 8

(Thomann, 1989; Connolly, 1990, McKim *et al.*, 1985; Gobas *et al.*, 1986; Gobas and Mackay, 1987). This observation is especially true for phytoplankton (Oliver and Niimi, 1988; Wang *et al.*, 1982; Lederman and Rhee, 1982). Consequently, the simple equilibrium partitioning equation used in the Gobas model to estimate chemical accumulation in phytoplankton, macrophytes and zooplankton may not reasonably predict chemical uptake and food chain transfer for hydrophobic chemicals such as PCDDs. This phenomenon may be circumvented as in the Thomann and Connolly model by the direct input of a phytoplankton BCF measured for the "truly" dissolved and hence bioavailable chemical fraction in the dissolved phase. The primary mechanisms that control the transfer and accumulation of chemicals at the base of the food chain are still unresolved. It is conceivable that these may be a combined function of the site-specific characteristics of the receiving water and the nature of the effluents. Together, these properties would be expected to influence nutrient levels and concentrations and composition of suspended materials which may in turn modify phytoplankton growth and provide alternative food sources for invertebrates. These complex processes occurring at the base of the food chain would be expected to influence substantially the uptake and accumulation of chemicals between various trophic levels.

It is a well established fact that chemical uptake from the water column is directly related to gill respiration. The rate of respiration of all animals has been correlated to body size; smaller organisms having higher rates of respiration. The rate of respiration is also influenced by temperature and other forms of stress; under conditions of higher temperature (*i.e.*, lower oxygen concentration in the water) respirations rates increase thereby increasing the potential for chemical exposure. The transport equations used in the Gobas model do not directly compensate for changes in chemical uptake as a function of changes in respiration rate due to fluctuations in environmental temperature, whereas the Thomann and Connolly model does. As stated previously the Gobas model is driven by lipid and K_{ow} relationships. However a recent study of the uptake of hydrophobic chemicals across fish gills noted that chemical diffusion and ventilation flow were the dominant chemical uptake limitations with blood flow being less important (Sijm, 1993). Furthermore, these results demonstrated that gill uptake rate constants are independent of chemical hydrophobicity, except for organotin compounds. Chemical uptake across the perfused isolated gills was studied at 5° C, 12° C and 18° C at a constant ventilation rate; it was concluded that temperature which caused changes in membrane fluidity determined the rate of chemical uptake.

Chemical assimilation efficiency may be measured in the laboratory under controlled conditions. Until recently, unlike fish, very little data have been published on the chemical assimilation efficiencies of invertebrates. When faced with similar data gaps it is recommended that a range of values be tested based on bioavailability data for the same or similar chemicals in similar environmental media to other species.

When selecting physical-chemical data, consideration should be given to the date of publication and the analytical method, selecting the value from the most recent study based on the assumption that the most recent analytical technique would be the most reliable (Mackay *et al.*, 1992). Furthermore, water solubilities and octanol-water partition coefficients reported for superhydrophobic chemicals such as PCDD/PCDF have been erroneously reported in the past, thus it has been advised that any

log K_{ow} values greater than 8 be considered with caution (D. Mackay, 1992 personal communication).

As mentioned previously, both of the selected food chain models were developed based on and applied to the Great Lakes. The validity of using these models for ecosystems such as rivers has not yet been firmly established. The importance of advection in terms of reductions in residence time of water- and particulate-borne chemicals, and the impact that this would have on the accuracy of the modelling should be assessed. However, the Thomann and Connolly model has been successfully calibrated and applied to several ecosystems. Thomann and Connolly (1984a;b) successfully calibrated the accumulation of PCB in a Lake Michigan food chain. The model was also calibrated for kepone accumulation in striped bass from the James River estuary (Connolly and Tonelli, 1985) and for PCB accumulation in lobster and winter flounder in New Bedford Harbour (Connolly, 1990).

Extensive field data is required for each chemical and aquatic species modelled to calibrate the model for a ecosystem.

D.6 Conclusions

In the absence of field-measured data for chemical concentrations in environmental media such as surface waters, sediments and aquatic organisms, ecosystem models based on mathematical theories and principles of the processes governing chemical fate and accumulation in aquatic environments are a useful tool for risk assessment. Environmental concentrations of chemicals can be predicted using these models and further used to estimated chemical exposure of fish-eating wildlife and human receptors. Reliable predictions of environmental concentrations of chemicals and confidence in model simulations require rigorous calibration of model input with sound scientific data and validation of model results with comprehensive field data. The user must be ever vigilant that the data input to the models are scientifically valid. Furthermore, it should not be forgotten that ecosystem models are simplified mathematical representations of complex interactions and processes the occur in the natural environment. As such the theory on which they are based is continually evolving, and therefore, existing models will be updated as information becomes available. The onus is on the user to ensure that the ecosystem model used most accurately reflects the most recent scientific consensus regarding fate and accumulation of chemicals in the aquatic environment.

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